Guest Editor: Nagao Kobayashi

This issue of JPP is dedicated to Professor Kazuchika Ohta on the occasion of his retirement in the end of March 2018. It consists of 28 original research papers presented by his colleagues and friends. Professor Ohta is a very ingenious scientist. He developed a new field of metal-containing liquid crystals, namely metallomesogens in 1978. His continual creativity has brought about a number of phthalocyanine-based liquid crystals with original molecular and phase structures showing unique properties. The cover picture shows the spiranthes-like supramolecular structure of some selected phthalocyanine-fullerene dyads that were designed and characterized by Professor Ohta. From precise analysis of the SAXS and CD spectra, he established the helical structure of fullerenes in the Col₂ mesophase. Fullerenes pile up in left-handed and right-handed helicity in a ratio of 50:50. This helical structure resembles spiranthes flower. The helical stacking of C₆₀ moieties is very favorable as an electron carrier path.

Articles

**pp. 1-9**
Photophysical properties of a novel styryl-BODIPY with a fused crown ether moiety
Justin Stone, John Mack*, Tebello Nyokong, Mutsumi Kimura and Nagao Kobayashi*

The synthesis and characterization of a crown-ether-substituted 3-styrylBODIPY dye with a 4-isopropylphenyl group at the meso-position is reported.

**pp. 10-24**
A novel of PEG-conjugated phthalocyanine and evaluation of its photocytotoxicity and antibacterial properties for photodynamic therapy
Canan Uslan, Naciye Durmuş İşleyen, Yetkin Öztürk, Burcu Turanlı Yıldız, Z. Petek Çakar, Meltem Göksel, Mahmut Durmuş, Yeşim Hepuzer Gürsel and B. Şebnem Sesalan*

A new PEG-conjugated silicon(IV) phthalocyanine axially substituted with poly(ethylene glycol) (PEG 1000) chains was synthesized and characterized. Its photophysical, photochemical properties and its photocytotoxicity were also investigated by applying it on HeLa and HuH-7 tumor cells. The antibacterial activity against Gram-negative (*Escherichia coli*) bacterium was also tested.
pp. 25–31
Pyridone substituted phthalocyanines: Photophysico-chemical properties and TD-DFT calculations
Şaziye Abdurrahmanoğlu*, Mehmet Canlica, John Mack and Tebello Nyokong*

A 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy)phthalonitrile has been used to prepare a novel Zn(II) phthalocyanine with four peripheral pyridone substituents and the photophysicochemical properties of the product were analyzed.

pp. 32–45
Discotic liquid crystals of transition metal complexes, 55: Novel chlorine-substituted phthalocyanine derivatives showing mesomorphism and low HOMO energy level
Masashi Yatabe, Akio Kajitani, Mikio Yasutake and Kazuchika Ohta*

Two series of PcCu compounds, (α-C₃H₄)₈PcCu (1a–1d) and (α-C₃H₄)₈(β-Cl)₈PcCu (4a–4d) [n = 6 (a), 8 (b), 10 (c) and 12 (d)], were successfully synthesized. Among them, the derivatives 4c–4d exhibit a Col nostalg phase. The derivatives 4a–4d showed a Q band in the near-infrared region and lower HOMO levels than conventional PcCu derivatives.

pp. 46–55
Photophysical and photochemical properties of fluorooether-substituted zinc(II) and titanium(IV) phthalocyanines
İlke Gürol*, Gülay Gümüş, Deniz Kutlu Tarakci, Ömer Güngör, Mahmut Durmuş and Vefa Ahsen

The synthesis and characterization of novel zinc(II) (1a–4a) and oxotitanium(IV) (1b–4b) phthalocyanine derivatives bearing 1H,1H-nonafluoroo-3,6-dioxaheptan-1-ol groups were described for the first time. The influence of the number of the substituted groups (tetra or octa), position of the substituents (peripheral or non-peripheral) and the nature of the central metal atom (zinc or titanium) on the photophysical and photochemical properties of these phthalocyanines were investigated.

pp. 56–63
Pyrene containing liquid crystalline asymmetric phthalocyanines and their composite materials with single-walled carbon nanotubes
Esra Nur Kaya, Maxim S. Polyakov, Tamara V. Basova*, Mahmut Durmuş and Aseel Hassan

Liquid crystalline asymmetrically substituted phthalocyanines MPC (M=Cu, Co, 2H) bearing one pyrene and six polyoxy groups and their composite materials with single-walled carbon nanotubes was investigated. The incorporation of small amount of SWCNT (0.1–1 wt.%) does not alter the MPC mesophases significantly. The structural features and the sensor response of MPC/SWCNT composite thin films to ammonia vapor (10–50 ppm) was studied and compared with those of the films of pure MPC derivatives.
**pp. 64-76**  
**Structural, spectroscopic and passivation properties of a novel binuclear clamshell-type zinc(II) phthalocyanine as gate dielectric for OFET**  
Sebile Işık Büyükekşi, Ahmet Altındal, Nursel Açar and Abdurrahman Şengül*

A new clamshell-type binuclear zinc phthalocyanine (2) was synthesized and characterized by microanalysis, $^1$H NMR, $^{13}$C DEPT NMR, $^1$H–$^1$H COSY NMR, HR MALDI TOF MS, UV-vis and fluorescence spectrophotometers. The electronic structure and the nature of the excited states in 2 were correlated with the results obtained by DFT and TDDFT calculations. The performance of 2 as gate dielectric in an organic field effect transistor was investigated and a field effect mobility value of $6.4 \times 10^{-3}$ cm$^2$/V s was obtained.

**pp. 77-87**  
**Synthesis, characterization, photophysicochemical properties and theoretical study of novel zinc phthalocyanine containing four tetrathia macrocycles**  
Mohamad Albakour, Gülenay Tunç, Büşra Akyol, Sinem Tuncel Kostakoğlu, Savaş Berber, Özer Bekaroğlu and Ayşe Gül Gürek*

In this study, Zn(II) phthalocyanine bearing 13-membered tetrathia macrocycles was synthesized; the photophysical, photochemical and electrochemical properties were investigated.

**pp. 88-94**  
**Changes of phthalocyanine visible color caused by near-IR solvatochromism**  
Taniyuki Furuyama*, Shiori Uchiyama, Takayuki Iwamoto, Hajime Maeda and Masahito Segi

We show that the Zn complex of 1,4,8,11,15,18,22,28-octakis(butoxy)phthalocyanine exhibits solvatochromism and characterize the corresponding visible color changes. Although the variation of the solvent-dependent position of the $Q$ band is relatively small ($\sim$100 nm), the solution colors change from red to yellow and green depending on the composition of the solvent mixture. Substituents on oxygen atoms were shown to influence phthalocyanine aggregation and thus affect near-IR absorption, with the observed near-IR solvatochromism.

**pp. 95-101**  
**Synthesis and properties of a trinuclear copper(II) complex of a ligand with phthalocyanine and Schiff-base coordination sites**  
Makoto Handa*, Kenichi Kanagawa, Natsumi Yano, Haruki Yairi, Airi Okuno, Minoru Mitsumi and Yusuke Kataoka

A trinuclear copper(II) phthalocyanine complex was synthesized by chelate coordination of the peripherally introduced Schiff-base nitrogen and phenoxide oxygen on the Cu(pc) core to a copper(II) ion. The magnetic, spectral and electrochemical properties were investigated for the trinuclear complex.
pp. 102–111
Solvent effects on molecular aggregation of highly water-soluble phthalocyanines
Hiroaki Isago* and Harumi Fujita

Solvent effects on molecular aggregation behaviors of highly water-soluble phthalocyanines have been investigated by concentration studies on optical absorption and magnetic circular dichroism spectra in water, ethanol, and their mixed solvent systems.

pp. 112–120
Synthesis, photophysical and electrochemical properties of novel unsymmetrical phthalocyanines with a Sudan IV moiety
İbrahim Özçeşmeci, Pınar Büyük, Ilgın Nar and Ahmet Gül*

The synthesis of novel, A,B type unsymmetrical metal-free and metallo phthalocyanines bearing one aza dye group Sudan IV and three nitro terminal moieties was achieved by cyclotetramerization of novel 4-((1-((E)-(2-methyl-4-((E)-o-tolyl)diazenyl)phenyl)diazenyl) naphthalen-2-yl)oxy)phthalonitrile and 4-nitrophthalonitrile. The aggregation properties of the compounds were investigated. General trends were also studied for fluorescence quantum yields and lifetimes of these phthalocyanine compounds. In-depth investigation of the electrochemical properties showed that nitro groups extended the reduction potentials.

pp. 121–136
Electrical and gas sensing properties of novel cobalt(II), copper(II), manganese(III) phthalocyanines carrying ethyl 7-oxy-4,8-dimethylcoumarin-3-propanoate moieties
Baybars Köksoy, Meryem Aygün, Aylin Çapkin, Fatih Dumludağ* and Mustafa Bulut*

Co(II), Cu(II), Mn(III)OAc phthalocyanines bearing four ethyl 7-oxy-4,8-dimethylcoumarin-3-propanoate moieties were prepared and characterized. DC and AC (40–10^5 Hz) electrical properties of the films of metallophthalocyanines were investigated in the temperature range of 295–523 K. Impedance spectroscopy measurements revealed that bulk resistance decreases with increasing temperature indicating semiconductor property. Their gas sensing properties were also investigated for the vapors of VOCs, n-butyl acetate (200–3200 ppm) and ammonia (7000–56000 ppm) between temperatures 25–100 °C.

pp. 137–148
Photophysics and NLO properties of Ga(III) and In(III) phthalocyaninates bearing diethyleneglycol chains

This paper reports the synthesis, photophysical and nonlinear optical properties of Ga(III) and In(III) complexes with low symmetry phthalocyanine bearing diethyleneglycol chains. The NLO parameters of In(III) complex exhibited the strongest nonlinear optical behavior in comparison with Ga(III) in solution and reverse tendency when embedded in poly(bisphenol A carbonate) thin films. DFT calculations were used to rationalize these results.
Synthesis, characterization and OFET property of four
diaminouracil bridged novel ball-type phthalocyanines
Ayşegül Yazıcı, Ayşe Avci, Ahmet Altindal, Bekir Salih and
Özer Bekaroğlu*

OFET devices with top gate structure were fabricated using the new ball-type
detto phosphalocyanines as the active material. The devices characterized by
means of their output and transfer characteristics and it was found that OFET
devices exhibit p-type behavior.

Preparation, structure, and electrochemistry of porphy-
rinato titanium (IV) benzenedithiolates with a trithiole ring,
a dithin ring, and two 2-cyanoethylthio groups
Takeshi Kimura*, Yusuke Muraoka, Kaori Amano, Toshiyuki Fujio,
Takao Nishikawa, Tsukasa Nakahodo and Hisashi Fujihara

The reaction of tetra(p-tolyl)porphyrinato titanium (IV) oxide with dimercapo-
benzo[1,2,3]trithiole, dimercaptobenzo[1,4]dithin, and dimercapto-1,2-bis(2-cyano-
ethylthio)benzene produced the corresponding titanium (IV) complexes bearing a
trithiole ring, a dithin ring, and two 2-cyanoethylthio groups, respectively.

Distribution of the unpaired electron in neutral
bis(phthalocyaninato) yttrium double-deckers: An
experimental and theoretical combinative investigation
Xin Chen, Yuxiang Chen, Ming Bai*, Chiming Wang,
Dongdong Qi*, Qingyun Liu, Meixing Xu and Jianzhuang Jiang

The distribution of the unpaired electron is affected by the peripheral
substituents. The electron-donating substituents attract the unpaired electrons
concentrated on the substituted side.

Synthesis and characterization of a new meso-
tetra-di-hydrobenzocyclobutacenaphthylene free-base
porphyrin
Ümit İsci, Sevinc Zehra Topal, Emel Önal, Ismail Fidan, Savaş Berber,
Vefa Ahsen, Concepción Parejo, Ángela Sastre-Santos* and Fabienne
Dumoulin*

A meso-tetra-6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene-free base por-
phyrin was synthesized. It retains the same photophysical, photochemical and
electrochemical properties than free base meso-tetraphenylporphyrin.
pp. 181–188
Five-nuclear phthalocyanine complex bearing terpyridine zinc complex: Synthesis, and photophysicochemical studies
Pınar Sen*, S. Zeki Yıldız, Göknur Yasa Atmaca and Ali Erdoğan*  

New terpyridine-Zn(II) complexes substituted Zinc-Pc was synthesized as new functionalized materials and characterized by using different spectroscopic methods such as FT-IR, UV-vis, and 1H-NMR, 13C-NMR, elemental analysis and mass. Spectral, photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen production and photodegradation under light irradiation) properties of newly synthesized phthalocyanine (3) as five nuclear phthalocyanine were investigated in DMSO solutions.

pp. 189–197
Toluene vapor sensing characteristics of novel copper(II), indium(III), mono-lutetium(III) and tin(IV) phthalocyanines substituted with 2,6-dimethoxyphenoxy bioactive moieties
Mehmet Pişkin, Nursel Can, Zafer Odabaš* and Ahmet Altındal*  
The effects of the substituent’s positions on the toluene vapor detection capabilities of copper(II), indium(OAc), mono-lutetium(OAc) and tin(IV) phthalocyanines substituted with 2,6-dimethoxyphenol bioactive groups were investigated. Adsorption data were analysed by using first order and Elovich equations in order to investigate the adsorption kinetics. It was found that the kinetics of the toluene adsorption strongly depends on the position of the substituent groups.

pp. 198–206
Novel phthalocyanines containing azo chromophores; synthesis, characterization, photophysical, and electrochemical properties
Ebru Özkan Garip, Mukaddes Özçeşmeci, İlgın Nar, İbrahim Özçeşmeci and Esin Hamuryudan*  
A series of novel metal-free and zinc (II), copper (II), cobalt (II), and manganese (III) phthalocyanine complexes bearing peripheral 2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy units have been synthesized. The structures of these new compounds were characterized by using elemental analyses, proton and carbon nuclear magnetic resonance, fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy and mass spectrometry. The photophysical properties of metal-free and zinc(II) phthalocyanines were studied in tetrahydrofuran. The electrochemical properties of the phthalocyanine complexes were investigated by cyclic and square wave voltammetry.

pp. 207–220
Synthesis, characterization and computational investigation of novel metalloporphyrazines containing 15-membered O,S2-donor macrocyclic moieties
Yasemin Baygür, Burak Yıldız, İzzet Kara, Hakan Dal and Yaşar Gök*  
Synthesis, crystal structure and computational investigation of metalloporphyrazines containing 15-membered O,S2 macrocyclic moieties are presented.
**pp. 221–232**

Mesogenic complementary absorbing dyads based on porphyrin and perylene units

Xiangfei Kong, Hongkang Gong, Shengping Dai, Wei Yao, Linping Mu*, Shufen Zhang and Guixia Wang*

Donor–accepter dyads consisting of a porphyrin unit, which is linked to a perylene unit by a flexible aliphatic bridge, have been synthesized and characterized. These dyads have broad optical absorption in the ultraviolet and visible regions. Due to photo-induced electronic transfer, the charge-separated states of the dyad molecules formed when photo-excited. In addition, they have columnar liquid-crystal phase and tend to form the face-on alignment on the glass substrates when cooled from the isotropic liquid.

**pp. 233–242**

Antioxidant activities of the new tetrasubstituted metal-free, Zn(II) and Co(II) monophthalocyanines

Nazlı Söylemez, Ebru Yabaş*, Serap Şahin Bölükbaşı and Mustafa Süli

New tetrasubstituted metal-free, zinc(II) and cobalt(II) phthalocyanines have been synthesized and characterized. Antioxidant activities and aggregation behaviors of these compounds have been investigated.

**pp. 243–249**

Synthesis, characterization and electrochemical properties of novel pyridine phthalocyanine derivatives

Büşra Mızrak, Efe Baturhan Orman, Şaziye Abdurrahmanoğlu* and Ali Rıza Özkaya*

In this study, the novel Zn(II), metal-free and sandwich-type Lu(Pc)2 phthalocyanines containing tetra pyridine substituted at peripheral position were synthesized. All the new compounds have been characterized by FT-IR and UV-vis spectroscopies, 1H-NMR, MALDI-MS and elemental analysis. The electrochemical and spectroelectrochemical properties of all novel metallo and metal free phthalocyanine compounds were also investigated by voltammetric and in situ spectroelectrochemical measurements on Pt in dimethylsulfoxide/tetrabutylammonium perchlorate.

**pp. 250–265**

Synthesis, characterization of new phthalocyanines and investigation of photophysical, photochemical properties and theoretical studies

Ömer Tayfuroğlu, Fatma Aytan Kılıçarslan, Göknnur Yasa Atmaca and Ali Erdoğmuş*

Phthalocyanine derivatives comprise the second generation of photosensitizer molecules employed in photodynamic therapy.
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Zinc(II) and chloroindium(III) phthalocyanines bearing ethyl 7-oxy-6-chloro-4-methylcoumarin-3-propanoate groups: Synthesis, characterization and investigation of their photophysicochemical properties
Halid Kuruca, Baybars Köksöy, Begümhan Karapınar, Mahmut Durmuş and Mustafa Bulut*

The novel ethyl 7-oxy-6-chloro-4-methylcoumarin-3-propanoate substituted zinc(II) and chloroindium(III) phthalocyanines were synthesized and characterized by using different spectroscopic methods such as ^1H NMR, FT-IR, UV-vis, mass spectroscopy. The photophysical and photochemical properties as fluorescence lifetime, fluorescence, singlet oxygen and photodegradation quantum yields were investigated. The fluorescence quenching behavior of these phthalocyanines were also investigated using 1,4-benzoquinone as a quencher.

pp. 279–290
Novel peripherally and non-peripherally 6-oxyflavone substituted metal-free, zinc(II) and cobalt(II) phthalocyanines: Electrochemical and in situ spectroelectrochemical properties
Ahmet Arıbal, Efe Baturhan Orman, Ümit Salan*, Ali Rıza Özkaya* and Mustafa Bulut

Novel peripheral and non-peripheral tetra substituted 6-hydroxyflavonoxy zinc(II), cobalt(II) and metal free phthalocyanines were synthesized. Electron transfer properties of the compounds were investigated by voltammetric and in situ spectroelectrochemical measurements in nonaqueous solution medium.
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Preface — Special Issue in Honor of Professor Kazuchika Ohta

This Special Issue of the Journal of Porphyrins and Phthalocyanines is dedicated to Kazuchika Ohta of Shinshu University, Ueda, Japan on the occasion of his retirement at the end of March 2018.

Kazuchika first begun working in a new field of metal-containing liquid crystals, namely metallomesogens, in 1978 when he studied physical organic chemistry as part of his Ph.D. in Osaka University. At that time people strongly believed that liquid crystals were pure organic compounds, and only two other researchers in the world were studying metal-containing liquid crystals. After graduating in 1981, Kazuchika entered the Department of Chemical Materials, Toshiba, as an industrial researcher. During his two-year stay in Toshiba, he was encouraged by Prof. Sadao Yoshikawa, The University of Tokyo, to continue this new field of metallomesogens and to move to an academic position at Shinshu University, where Professor Ohta expanded the scope of his metallomesogen chemistry studies from β-diketonato metal complexes to phthalocyaninato-metal complexes on the occasion of his postdoctoral research with Prof. Jacques Simon at ESPCI in Paris from 1986 to 1987. He also worked in the field of electroconductivities of discotic liquid crystals based on bis(phthalocyanato)-lutetium(III) with Prof. John M. Warman at Delft Technial University, The Netherlands, from 1995 to 1996. Throughout his career, Kazuchika’s research has covered syntheses and properties of a great variety of discotic metallomesogens based on many kinds of ligands, β-diketone, dihiolene, glyoxime, phthalocyanines, porphyrins and more.

Kazuchika is my good friend. I met him for the first time in 1988 after his return to Japan from France. His unique research on phthalocyanine-based liquid crystals fascinated me. In this preface, because of limited space I would like to introduce only his metallomesogen studies based on phthalocyanines.

Professor Ohta revealed for the first time the effect of \( d \) and \( f \) electrons of transition metal ions in phthalocyanine-based metallomesogens on interlayered forces. People had long believed that liquid crystalline phases are formed only by the intermolecular forces of van der Waals force and \( \pi-\pi \) interactions. Kazuchika found a parity effect of \( d \)-electron numbers on the intercolumnar stacking distances of columnar mesophases in octakis(m-alkoxyphnenoxyphthaloxyaninato)metal(II) (abbreviated as \( (m-C_nOPhO)_{8}PcM \) (\( M = \text{Co, Ni, Cu, Zn and H}_2 \), \( n = 8-20 \)). The stacking distances are shorter for odd numbers but longer for even numbers of \( d \)-electrons. This suggests the metal complexes having odd numbers of \( d \)-electrons have an additional magnetic Coulomb force to fasten the disks, showing a shorter distance. Moreover, he found an effect of \( f \)-electron numbers on clearing points in phthalocyanine rare earth metal sandwich complexes, \( \text{bis}[2,3,9,10,16,17,23,24-octakis(3,4-didodecycloxyphenoxy)phthalocyaninato]lanthanoid(III) \) (abbreviated as \( ((C_nO)_{2}PhO)_{8}Pc)_{2}M, M = \text{La, Ce, Eu, Gd, Tb, Yb, Lu} \)). He revealed for the first time that their clearing points depend on the total spin quantum number of the rare earth metal ion. This means that an additional magnetic Coulomb force clearly enhances the liquid crystallinity.

Recently, Kazuchika found perfect homeotropic alignment between two glass plates and a Spiranthes-like Supramolecular Structure in columnar liquid crystalline phthalocyanine-fullerene (Pc–C\textsubscript{60}) dyads towards thin film organic solar cells. To date, he has successfully synthesized five series of liquid crystalline Pc–C\textsubscript{60} dyads: \( \text{C}_{12}((\text{OMalC})_{8}Pc)_{2}M, (n, m)PcCu–C_{60}, (C_{n}S)_{6}PcCu–C_{12}–C_{60} \) and \( (C_{11}S)_{6}PcCu–\text{VAN–C}_{60} \), exhibiting perfect homeotropic alignment between the two glass plates. The \( \text{C}_{12}((\text{OMalC})_{8}Pc)_{2}M \) dyad is the first example of a liquid crystalline Pc–C\textsubscript{60} dyad. From precise analysis of the small angle X-ray scattering (SAXS) data, he established the helical structure of fullerenes in the \( \text{C}_{60} \) mesophase. CD spectral data shows that fullerenes pile up in left-handed and right-handed helicity in a ratio of 50:50. This helical structure resembles a spiranthes flower. Therefore, he named this unique structure the “Spiranthes-like Supramolecular Structure.” The helical stacking of \( \text{C}_{60} \) moieties is very favorable as an electron carrier path. This structure is the same as the 1D nanoarray very suitable for organic thin film solar cells.

As described above, Professor Ohta has pioneered a new field called metallomesogens, which are self-assembled and highly functionalized. His research work has been highly appreciated both at home and abroad, and has contributed greatly to the development of chemistry in interdisciplinary fields.

Kazuchika also developed an unprecedented temperature-dependent small angle X-ray diffractometer, which
enables us to measure only 1 mg of sample in a very wide angle region from $2\Theta = 0.8$ to 33 degree (spacing from $d = 110$ to $3 \text{ Å}$) over a very wide temperature range from room temperature to $375^\circ \text{C}$ within 2 or 3 mins. This SAXS architecture has been generously shared in the supplementary data in his papers. Kazuchika and his students have also developed an original theory and technique to analyze discotic liquid crystalline phase structures. He has published the theory and technique in a book in 2000. This book is widely read as the only textbook of discotic liquid crystalline structure analysis by liquid crystal researchers and students in Japan. Thus, Professor Ohta’s ability in the analysis of liquid crystalline phase structures is outstanding, and has led to his discovery of many new liquid crystalline phases. It is noteworthy that his creative research work on discotic metallomesogens has originated from his unique ingenuity regarding the theory, method and apparatus for excellent X-ray liquid crystalline phase structure analysis.

We are grateful to all of the contributors and reviewers for making this special issue a great success. The 28 contributions that we are presenting would not have been possible without their effort. On behalf of the Editors, the Editorial Board and the contributing authors, this Special Issue is presented to Kazuchika Ohta in recognition of his scientific legacy. Thank you, Kazuchika.

JPP Guest Editor

Nagao Kobayashi
Shinshu University
Ueda, Japan
January, 2018
Photophysical properties of a novel styryl-BODIPY with a fused crown ether moiety

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This paper is dedicated to Professor Kazuchika Ohta on the occasion of his retirement.

Received 22 July 2017
Accepted 11 November 2017

ABSTRACT: The synthesis and characterization of a crown-ether-substituted 3-styrylBODIPY dye with a 4-isopropylphenyl group at the meso-position is reported. The effect that the incorporation of Na+ ions into the crown ether moiety has on the photophysical properties is investigated.

KEYWORDS: BODIPYs, Knoevenagel condensation, crown ethers, singlet oxygen, photophysics.

INTRODUCTION

Boron dipyrromethene (BODIPY) dyes have been studied for use in a wide range of applications, due to their facile synthesis and structural modification, high photostability and intense spectral bands in the visible region [1, 2]. Unsubstituted BODIPYs lack affinity for cations in solution and require ion chelating substituents to be introduced in order for them to be used as sensors or molecular switches. Crown ethers have long been known to be effective at chelating various metal cations [3], and have found use in a number of different applications, including use as ion selective electrodes, anti-microbial agents, on nanotubes, and in organic light emitting diodes [4]. Crown ethers have also been used in chromatography to successfully separate mixtures of enantiomers, drugs, and amino acids. A highly attractive property is their low toxicity in the human body, as some simple crown ether structures have been shown to be less toxic than aspirin [4]. There has been comparatively little research on the photophysical effects of attaching crown ether moieties onto BODIPY dyes. Most of the research on BODIPY-crown complexes has involved substituting a formyl crown ether unit at the 3- and/or 5-positions by introducing crown-ether-substituted styryl groups through Knoevenagel condensation-type reactions on the periphery of the pyrrole rings [5] or at the meso-position, through direct incorporation onto a benzal-dehyde during the dipyrromethane synthesis step [6]. Chelation of a cation by a meso-crown ether causes almost no change to be observed in the absorption spectra of BODIPY dyes in this context since the phenyl crown lies out of the BODIPY plane [7], but significant effects are observed in the fluorescence emission spectra [8]. Crown-ether-substituted styryl groups introduced at the 3,5-positions can affect both the absorption and emission spectra of the BODIPY [9]. As with other styryl groups, crown-ether-substituted styryls generally cause a red-shift of the main BODIPY spectral bands [10].

Significantly, crown ether moieties can transform BODIPYs into powerful molecular platforms for detecting a number of environmentally significant cations by taking advantage of competing photoelectron transfer (PET) and intermolecular charge transfer (ICT) processes [11]. To this end a number ofaza (nitrogen containing) [9] and thia (sulfur containing) [11] crown ethers have been appended to various BODIPYs [5, 12]. Although several “off-on” fluorescent switches have been developed by appending a crown ether moiety onto a BODIPY dye, there have

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been few reports on the photophysical properties of the crown ether-BODIPY dyes, especially with regard to their singlet oxygen generating ability. Ozlem and Akkaya synthesized a BODIPY that contained a 3,5-di-styryl amino groups, a meso-benzo-crown ether, and iodine atoms at the 2,6-positions [7]. They were able to demonstrate that this dye behaved as a molecular and logic gate that was able to produce a signal only when the two specific analytes (Na+ and H+) were present in solution. This was used to control the singlet oxygen generated by BODIPY by using crown ethers, however, they did not explore the fluorescence properties of this multi-functional dye. In this study, the 4’-formyl-15-crown-5 was selected for attachment onto the 3-position of the BODIPY core, since this benzaldehyde can also be used to carry out conventional styryl BODIPY syntheses using a modified version of the Knoevenagel condensation reaction [13, 14]. A novel crown-ether-substituted styrylBODIPY dye was synthesized from the 2,6-dibrominated analogue of a meso-4-isopropylphenylBODIPY. The ability of the crown-ether-substituted BODIPY dye to chelate sodium ions and the effect that this has on the photophysical properties are investigated.

EXPERIMENTAL

Materials

2,4-Dimethylpyrrole, cuminaldehyde, trifluoroacetic acid (TFA), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), p-chloranil, BF3·Et2O, triethylamine (TEA), rhodamine-6-G and 1,3-diphenylisobenzofuran (DBPF) were purchased from Sigma Aldrich. Benzene, (DMSO), tetrahydrofuran (THF), dichloromethane (DCM), acetic acid, -bromosuccinimide (NBS) and sodium hydroxide were obtained from Fluka. 3,4-Dihydroxybenzaldehyde, diethylene glycol bis (2-chloroethyl) ether, piperidine, glacial acetic acid, N-bromosuccinimide (NBS) and sodium hydroxide were obtained from Tokyo Chemical Industry Co. Ltd. Dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), dichloromethane (DCM), and ethanol were obtained from local suppliers. Benzene, n-butanol, n-heptane and methanol were purchased from the Tokyo Chemical Industry. Solvents were dried and stored over 4 Å molecular sieves as needed.

Instrumentation

UV-visible absorption spectra were recorded using a JASCO V-650 or a Shimadzu UV-2550 spectrophotometer. Fluorescence emission and excitation spectra were obtained using a Varian Cary Eclipse spectrophotometer. Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). A LDH-P-C-485 laser head driven by PDL 800-B single channel driver and a 10 MHz repetition rate was employed. All fluorescence decay curves were measured at the emission peak maxima. The decay curves were analyzed with the FluoFit program (Picoquant GmbH). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer using a Platinum ATR accessory. 1H NMR spectra were obtained using a Bruker AMX 400 MHz spectrometer in CHCl3-d1 with TMS as the standard. Mass spectrometry data were collected on a Bruker AutoFLEX III Smartbeam MALDI-TOF spectrometer using an α-cyano-4-hydroxycinnamic acid matrix and positive mode of operation when an m/z value of greater than 500 amu was anticipated for the parent peak. Otherwise an Expressions CMS Advion ESI-MS was used with a CAMAG TLC-MS interface.

Photophysics

Rhodamine-6-G (Φ F = 0.94 in ethanol) [15] was used to determine the fluorescence quantum yields of BODIYPYs 1–3 by using a comparative method [16], and Rose Bengal (Φ F = 0.86 in ethanol) [17] was employed in a similar manner to determine the singlet oxygen quantum yields by using DPBF as a singlet oxygen scavenger. An Ekspla NT 342B-20-AW laser (20 mJ/5 ns, 20 Hz) laser was used at various cross-over wavelengths for the absorption spectra of the sample and standard. The degradation of DPBF due to singlet oxygen generation was monitored by UV-visible absorption spectroscopy.

Synthesis

4’-Formylbenzo-15-crown-5 was synthesized according to a method outlined by Castro et al. [18]. Yield: (255 mg, 6.62%). 1H-NMR: ((CHCl3-d1); δ, ppm 9.83 (1H, s), 7.39–7.45 (2H, m), 6.93–6.95 (1H, m), 4.20 (4H, m), 3.93 (4H, m), 3.76–3.77 (8H, m). ESI-MS m/z calc: 296.32; Found: 296.3 amu.

1: Cuminaldehyde (0.5 g, 1.0 mole eq.) and 2,4-dimethylpyrrole (2.0 eq.) was added to a DCM (48.4 mL) under Ar/N2 with stirring. TFA (2–3 drops) was slowly added to the solution. The reaction was carried out at room temperature for 3 h under Ar/N2 with vigorous stirring. Thin layer chromatography (TLC) confirmed the absence of the aldehyde and the formation of the appropriate dipyromethene. The mixture was cooled to 0°C after which a solution of p-chloranil (1.2 mole eq.) dissolved in DCM (10 mL) was added dropwise. The solution was allowed to warm up to room temperature and the reaction mixture allowed to proceed for 30 min under Ar/N2 with stirring. A deep purple color was observed and TLC confirmed the formation of the appropriate dipyromethene. The mixture was again cooled to 0°C, TEA (7 mole eq.) and BF3·Et2O (11 mole eq.) were cooled to 0°C and added dropwise into the dipyromethene solution. The mixture was left to stir for 12 h. The resulting mixture was filtered through a silica plug using DCM (30 mL) and then extracted with 0.1 M HCl. The organic phase was dried over Na2SO4 and separated via flash...
column chromatography with ethyl acetate and hexane (1:14) as the eluent and target compound 1 was obtained as an orange crystalline powder. Yield: (102 mg, 8.2%). FT-IR (cm⁻¹): 2957 (C–H), 2922 (C–H), 2861 (C–H), 1541 (C–C), 1301 (C–N), 1154 (C–N), 1058 (C–N), 970 (C–H) 809, 711, 581, 475. 1H-NMR: (CHCl₃-d₃): δ ppm 7.32–7.34 (2H, m), 7.16–7.18 (2H, m), 5.97(2H, s), 2.96–3.00 (1H, m), 2.55 (6H, s), 1.36 (6H, s), 1.28–1.30 (6H, d). ESI-MS m/z calc for C₂₂H₂₅BF₂N₂: 366.26 amu; Found: 366.2 amu [M⁺].

2: 1 (50 mg) and NBS (2.2 mole eq.) were dissolved in DCM (10 mL). The mixture was left to stir under Ar/N₂ at room temperature for 4 h. The reaction was quenched with sodium thiocyanate and the organic phase was dried over Na₂SO₄ and separated via flash column chromatography with CHCl₃ and hexane (1:14) as the eluent. 2 was obtained as a deep red crystalline powder. Yield: (60 mg, 83.3%). FT-IR (cm⁻¹): 2959 (C–H), 2920 (C–H), 2851 (C–H), 1529 (C–C), 1462 (C–H), 1309 (C–N), 1174 (C–N), 1085 (C–N), 995 (C–H), 711, 591, 530 (C–Br). 1H-NMR: (CHCl₃-d₃): δ ppm 7.36–7.40 (2H, m, Ar-H), 7.13–7.17 (2H, m, Ar-H), 2.99–3.04 (1H, m, C–H), 2.60–2.66 (6H, s), 1.37 (6H, s), 1.30–1.31 (6H, d). MALDI TOF-MS m/z calc for C₂₂H₂₃BF₂Br₂N₂: 524.05 m/z. Found: 525.7 m/z [M⁺H⁺].

3: 2 (0.1 mmol, 1 mole eq.), 4′-formylbenzo-15-crown-5 (0.13 mmol, 1.4 mole eq.) and glacial acetic acid (0.4 mL) were dissolved in dry benzene (20 mL) under Ar with stirring. Piperidine was added slowly and the solution was heated to reflux for 48 h under Ar. A Dean-Stark trap was deployed for the azeotropic removal of water formed during the condensation reaction. The reaction was quenched with water and the organic phase was dried over Na₂SO₄. The desired products were obtained by column and flash chromatography. A blue fraction was separated with CHCl₃ and hexane (2:3) as the eluent. 3 was obtained as a deep blue ink color powder. Yield: (8 mg, 10.5%). FT-IR (cm⁻¹): 2934 (C–H), 2855 (C–H), 1719 (C–H), 1709, 1619, 1592 (C–C), 1441 (C–H), 1256 (C–O), 1034 (C–N), 987 (C–H), 854, 717, 591, 541 (C–Br). 1H-NMR: (CHCl₃-d₃): δ ppm 8.00–8.04 (1H, m), 7.48–7.52 (1H, m), 7.35–7.37 (2H, m), 7.13–7.17 (4H, m), 6.84–6.88 (1H, m), 4.15–4.25 (4H, m), 3.95–3.90 (4H, m), 3.73–3.79 (8H, m), 2.96–3.00 (1H, m), 2.63 (3H, s), 1.34–1.40 (12H, m). MALDI TOF-MS m/z calc. for C₃₇H₄₁BF₂Br₂N₂O₅: 802.36 m/z. Found: 825.3 m/z [M⁺Na⁺].

Theoretical calculations

Optimized geometries were calculated for 1–3 by using the B3LYP functional of the Gaussian software package with 6-31G(d) basis sets [19]. TD-DFT calculations were calculated in a similar manner by using the CAM-B3LYP functional, since it contains a long-range correction that provides more accurate predictions for transitions that contain significant charge transfer character [20, 21].

RESULTS AND DISCUSSION

Synthesis and characterization

BODIPY 1 was synthesized using cuminaldehyde to address a gap in the existing BODIPY literature and was achieved via the classic one-pot 3-step method [22]. Scheme 1 highlights the synthetic method employed for the synthesis of BODIPYs 1 and 2 and the Knoevenagel condensation with 4′-formylbenzo-15-crown-5 that results in the synthesis of crown-ether-substituted styrylBODIPY 3.
One of the simplest methods for fine-tuning the spectroscopic properties of the BODIPY core is by halogenation. It has long been known that the 2,6-position of a 1,3,5,7-tetramethylBODIPY dye is the most vulnerable to nucleophilic attack [23]. To this end 1 was brominated using NBS to yield 2 (Scheme 1). The disappearance of the $^1$H NMR signal for the 2,6-position protons (Fig. 1) and the appearance of a C–Br stretch in the IR spectrum (Fig. 2) demonstrated that this procedure was successful.

Crown ether macrocycles that contain as few as nine and as many as 60 carbon atoms have been reported in the literature, and by some estimates crown ether variants number well into the thousands [24]. Benzo derivatives are among the most versatile because their aromatic ring is susceptible to electrophilic aromatic substitution. Formylbenzo crown ethers can be synthesized either by ring closure of substituted catechols with glycol derivatives, or by direct substitution onto the aromatic ring (Scheme 2) [24]. These crown ethers possess cavity sizes between 1.7 and 2.2 Å which are ideal for complexing the small Na$^+$ ion [25]. A drawback associated with benzo crown ethers is that the carbon bond that is formed where the benzene ring and the crown ether moiety are fused is unusually long and this causes the binding constant for the crown ether to be lower than it otherwise would be [24], but the key advantage from the standpoint of this study is that this type of structure can be readily incorporated into BODIPY dyes by using the conventional synthetic approaches. 3 was synthesized using a modified Knoevenagel condensation reaction [13, 14] (Scheme 1) and a blue fraction was isolated and purified by column chromatography. MS data, the additional peaks that are observed in the aromatic region of the $^1$H NMR spectrum (Fig. 1) and the extra intense crown ether C–C and C–O stretch bands that are observed in the IR spectrum (Fig. 2) are consistent with the formation of 3.

Optical spectroscopy

The electronic absorption spectrum for 1 is typical for a meso-substituted BODIPY with an absorbance maximum at 503 nm in CHCl$_3$ (Fig. 3). Table 1 summarizes the absorption, excitation and emission band maxima values of BODIPY (1) in three different solvents. 1 is soluble in a wide range of solvents, and only a slight blue-shift (ca. 4 nm) is observed when the polarity of the solvent is increased. It has been suggested that this arises from the polarizability of the solvent as a similar effect has been reported for cyanine-based dyes [26]. No sign of aggregation could be observed in any of the solvents as would be expected, given the high solubility of BODIPYs in organic solvents. 1 is highly fluorescent ($\Phi_F = 0.91$) with an emission spectrum (Fig. 3) that is typical for a tetra-methyl BODIPY [27]. There are relatively small Stokes shift values of ca. 10 nm (Table 1) due to the rigidity of the BODIPY core structure. A slight blue-shift of the emission maxima is observed with...
increasing solvent polarity in a similar manner to the trend observed in the absorption spectra.

The electronic absorption and emission spectra for 2 are typical for a 2,6-dibrominated BODIPY dye (Fig. 3). The attachment of bromine atoms at the 2,6-positions causes a destabilization of the HOMO orbital relative to the LUMO orbital (Fig. 4), since there are significantly smaller MO coefficients on the styryl substituents in the LUMO (Fig. 5) [28, 29]. This results in a decrease in the HOMO–LUMO band gap (Fig. 3) and a red shift of the main spectral band (Fig. 6). Table 1 summarizes differences observed in the absorption spectrum data of BODIPY 2 in three different solvents. The absorption maximum is red shifted by ca. 30 nm when compared to that of the parent BODIPY dye 1 (Fig. 3). 2 is highly soluble in all of the solvents used and no signs of aggregation were observed. The attachment of bromine atoms at the 2,6-positions causes a relative destabilization of the HOMO orbital relative to the LUMO orbital (Fig. 4) due to the mesomeric interaction between the lone pairs on the bromine atoms and the π-system of the BODIPY core (Fig. 4) [28, 29], which decreases the HOMO–LUMO band gap and results in the observed red shift (Fig. 6 and Table 2). Relatively small Stokes shifts of ca. 10 nm are observed [1, 2], and there is a slight blue shift of the main spectral band as the solvent polarity is increased. The electronic absorption and emission spectra for 2 are typical for a 2,6-dibrominated BODIPY dye (Fig. 3). The most noteworthy effect of the bromine atoms is the relaxation of the spin-selection rule due to the heavy atom effect, which causes a sharp decrease in the fluorescence quantum yield and an increase in singlet oxygen production (Table 1). This allows for the synthesis of BODIPYs that could be used for photocatalysis applications or in PDT [30]. A comparative method was used to determine the Φ_f value for 2 (Table 1), which was found to be comparable to that of the Rose Bengal standard (Fig. 7). Ethanol was used as the solvent for the Φ_f measurements because significant photodegradation of the BODIPY dyes was observed during measurements in CHCl_3, in marked contrast with what is observed in Fig. 7.

The electronic absorption spectrum of 3 (Fig. 3) is similar to those obtained previously for monostyryl BODIPYs [1]. Adding a styryl group with a fused crown ether moiety to the 3-position of 2 causes the main BODIPY spectral band to shift to the red by ca. 70 nm relative to that of 1 to 597 nm as has typically been observed when an electron donating styryl moiety is added at this position [1]. This red-shift is caused by a destabilization of the HOMO relative to that of the LUMO in such a way as to narrow the HOMO–LUMO band gap (Figs. 4–6) [1]. A similar red-shift was also noted in the fluorescence emission maximum at 617 nm (Table 1), and a Stokes shift of 20 nm is observed. 3 possesses a relatively high molar extinction coefficient making it well suited to sensor applications (Table 1), since a relatively high fluorescence quantum yield of 0.28 was obtained in CHCl_3 despite the presence of heavy bromine atoms and a styryl substituent on the BODIPY’s core. TD-DFT calculations predict that the main spectral band continues to be dominated by
the HOMO→LUMO transition (Table 2), and hence there is only limited intramolecular charge transfer character in the S1 state, which has previously been found to significantly quench the fluorescence intensity [31]. When 2 and 3 are dissolved in ethanol solutions containing a large excess of sodium perchlorate, several observations can be made. Firstly, there is a blue-shift (5 nm) and a slight increase in the intensity of the absorption band of 3 at 588 nm (Fig. 8), and secondly there is a 14 nm blue-shift of the emission band to 608 nm along with a significant increase in the intensity (Fig. 9). Thirdly, no changes are observed in either spectrum when 2 is dissolved, so it is reasonable to assume that the effects observed for 3 are caused by the

Table 1. Photophysical data for BODIPYs 1–3

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
<th>Excitation (nm)</th>
<th>Log ε (M⁻¹ cm⁻¹)</th>
<th>ΦF</th>
<th>τF (ns)</th>
<th>Stokes shift (nm)</th>
<th>ΦΔ</th>
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<td>1 CHCl3</td>
<td>503</td>
<td>512</td>
<td>501</td>
<td>5.03</td>
<td>0.91</td>
<td>3.5</td>
<td>9</td>
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<tr>
<td>DMSO</td>
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<td>512</td>
<td>500</td>
<td>5.04</td>
<td>—</td>
<td>—</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>Ethanol</td>
<td>500</td>
<td>508</td>
<td>498</td>
<td>5.00</td>
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<td>—</td>
<td>8</td>
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<td>2 CHCl3</td>
<td>530</td>
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<td>528</td>
<td>4.98</td>
<td>0.21</td>
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<td>5.07</td>
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<td>—</td>
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<td>538</td>
<td>524</td>
<td>5.06</td>
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<td>—</td>
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<td>622</td>
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<td>Ethanol (with Na⁺)</td>
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<td>608</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>20</td>
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</table>

*Value so low to be nondetectable.

Fig. 4. MO energies of 1–3 at the CAM-B3LYP/6-31G(d) level of theory. The HOMO–LUMO gap values are plotted against a secondary axis and are denoted with large gray diamonds. Small black squares are used to highlight occupied MOs.

Fig. 5. Angular nodal patterns and MO energies for the HOMO and LUMO of 1–3 at an isosurface value of 0.02 a.u.
PHOTOPHYSICAL PROPERTIES OF A STYRYL-BODIPY WITH A FUSED CROWN ETHER

The spectral changes can be attributed to a relative stabilization of the HOMO orbital due to a change in the electron donating properties of the styryl moiety and/or the more rigid structure of the dye structure after chelation with a Na\(^+\) ion. In proof of principle terms, the observed changes demonstrate that 3 and other dyes with benzo-fused crown ether moieties incorporated onto styryl substituents could be useful as ion sensors due to the colorimetric and fluorometric changes that are observed. The singlet oxygen quantum yield of 3 was determined to be 0.35 in ethanol, which is significantly lower than that of 2, and there is an increase in the \(\Phi_\lambda\) value to 0.42 when Na\(^+\) ions are present in solution (Fig. 10). No significant degradation of 3 was observed during the course of the measurements. Given the potential combined utility of 3 for fluorescence sensor and singlet oxygen generation applications (Table 1), the introduction of different meso-aryl groups that can be further modified to enable water solubility would make dyes of this type potentially suitable for use in theranostics [32–36].

Table 2. The TD-DFT calculations at the CAM-B3LYP/6-31G(d) basis sets for the B3LYP optimized structures of 1–3

<table>
<thead>
<tr>
<th>#(^a)</th>
<th>(\nu/\text{cm}^{-1})</th>
<th>(\lambda/\text{nm})</th>
<th>(f)</th>
<th>(\nu/\text{cm}^{-1})</th>
<th>(\lambda/\text{nm})</th>
<th>Wave function(^d)</th>
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</thead>
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<td>503</td>
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<td>94% H (\rightarrow) L; …</td>
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</tbody>
</table>

\(^a\)The number of the state assigned in terms of ascending energy within the TD-DFT calculation. \(^b\)Calculated band energies (10\(^3\) cm\(^{-1}\)), wavelengths (nm) and oscillator strengths (c) in parentheses. \(^c\)Observed energies (10\(^3\) cm\(^{-1}\)) and wavelengths (nm) in DMSO. \(^d\)The wave functions based on the eigenvectors predicted by TD-DFT. H and L are used to denote the HOMO and LUMO.

Fig. 6. Calculated TD-DFT spectra at the CAM-B3LYP/6-31G(d) level of theory for 1–3. Black diamonds are used to highlight the main spectral bands that are associated primarily with the HOMO \(\rightarrow\) LUMO transition (Table 2). Simulated spectra were calculated using the Chemcraft program by using bandwidths of 30 nm. The consistent over-estimation of the energies of the main spectral bands (Table 2) is consistent with the trends that have been reported previously for structurally modified BODIPY dyes [1].

Fig. 7. Photocatalytic degradation of DPBF (\(\lambda_{\text{max}} = 410\) nm) in ethanol by BODIPY 2 (\(\lambda_{\text{max}} = 525\) nm) at 30 s intervals is indicative of singlet oxygen generation (a). The \(\Phi_\lambda\) value for 2 was determined by using a comparative method with Rose Bengal (\(\Phi_\lambda = 0.86\)) as the standard (b).
Fig. 8. UV-visible absorption spectra for BODIPY 3 in the presence and absence of Na\(^+\) in ethanol. Sodium perchlorate was present in large excess as the source of Na\(^+\) ions. BODIPY 2 was used to provide a control experiment.

Fig. 9. Fluorescence emission spectra for BODIPY 3a in the presence and absence of Na\(^+\) ions in ethanol. Sodium perchlorate was present in large excess as the source of Na\(^+\). BODIPY 2 was also studied in a similar manner to provide a control experiment.

Fig. 10. Photocatalytic degradation of DPBF during irradiation at 568 nm generated by the Rose Bengal standard, 3, and 3 in the presence of Na\(^+\) in ethanol monitored at intervals of 30 s by using the maximum of the main DPBF absorption band (a). No significant degradation of 3 was observed (b).

CONCLUSIONS

A novel 2,6-dibrominated styrylBODIPY dye with a fused crown ether moiety and a meso-4-isopropylphenyl substituent was synthesized by using 4′-formylbenzo-15-crown-5 as a precursor in a modified version of the Knoevenagel condensation reaction. The crown ether moiety was attached via a styryl bond at the 3-position of the BODIPY core and has a significant effect on the photophysical properties to suggest that the colorimetric and fluorometric changes that are observed with benzofused crown ether BODIPYs are potentially useful for ion sensor applications. The singlet oxygen quantum yield of the crown-ether-substituted styrylBODIPY is significantly lower than that of the dibrominated BODIPY core, but are found to be enhanced when the crown ether moiety complexes a sodium ion. This strategy could prove useful for improving singlet oxygen generation in high sodium environments, such as in polluted river water or cancerous tissue. The relatively high fluorescence quantum yield for the monostyryl BODIPY suggests that dyes of this type may be suitable for use in theranostics. Further studies are in progress to identify structural modifications that further enhance the photophysical properties of styrylated BODIPY dyes in a manner that makes them suitable for use in biomedical applications.
Acknowledgements

This work was partially supported by a bilateral program between the Japan Society for the Promotion of Science (JSPS) and National Research Foundation (NRF) of South Africa (uid: 92425), JSPS KAKENHI grant numbers JP15H02172 & JP15H0091, an NRF of South Africa CSUR grant (uid: 93627). Photophysical measurements were made possible by the Laser Rental Pool Programme of the Council for Scientific and Industrial Research (CSIR) of South Africa. Calculations were carried out at the Centre for High Performance Computing in Cape Town.

REFERENCES

A novel of PEG-conjugated phthalocyanine and evaluation of its photocytotoxicity and antibacterial properties for photodynamic therapy

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement.

Received 28 September 2017
Accepted 7 November 2017

ABSTRACT: A poly(ethylene glycol) (PEG)-conjugated silicon(IV) phthalocyanine axially substituted with (PEG1000) chains (SiPc-PEG) was synthesized, and this novel phthalocyanine was characterized by 'H-NMR, FT-IR and UV-Vis spectrophotometric methods. Elemental analysis data were beneficial for the evaluation of the chemical structure of the new compound. The total number of (O–CH\textsubscript{2}–CH\textsubscript{2}) units was calculated as 44 and the structure of the new PEG-conjugated silicon phthalocyanine was determined by the use of integral areas in 'H-NMR spectrum and the ratio of SiPc:PEG1000 was found as 1:2. The photophysical and photochemical properties were determined in both DMSO and aqueous solutions. In addition, the photocytotoxicity of the novel PEG-conjugated silicon(IV) phthalocyanine was also examined by testing against human cervical-carcinoma (HeLa) and hepato-carcinoma cells (HuH-7). The IC\textsubscript{50} value for the SiPc-PEG compound was determined as 0.28 μM for HeLa cells and 0.4 μM for HuH-7 cells. These results imply that HeLa cells are apparently more responsive to photodynamic therapy (PDT) treatment by SiPc-PEG than HuH-7 cells at low concentrations (up to 0.5 μM) of the studied photosensitizer. Additionally, SiPc-PEG showed antibacterial activity against \textit{Escherichia coli} at 48 h of incubation, the viabilities of \textit{E.coli} cultures exposed to 1000 μg/mL and 2500 μg/mL SiPc-PEG concentration were reduced by about 90%, and the additional growth inhibitory effect of photoactivation was also observed clearly at these efficient concentrations. To conclude, the novel compound may have a high potential for photodynamic therapy.

KEYWORDS: PEG-conjugated silicon phthalocyanine, antibacterial effect, photocytotoxicity, antitumoral activity, photodynamic therapy.

INTRODUCTION

Phthalocyanines (Pcs) have come into view as outstanding functional materials over the past few years in many fields by virtue of their biomedical, technological...
and industrial applications. They possess unique structural features such as bearing extended π-conjugated systems with large planar macrocycles, having the ability to form coordination complexes with a great number of metal atoms and having strong chemical resistance. They have been mostly used as active compounds for photocatalysts [1], nonlinear optics, optical sensors [2–5], and dye-sensitized solar cells [6].

To date, the majority of studies related to phthalocyanines have focused on biomedical applications because of their favorable photophysical properties such as high molar extinction coefficients, optical absorption in red or near-infrared regions, low dark toxicity and good excited state dynamics with high quantum yields, making them attractive agents for photodynamic therapy (PDT). Antitumor applications in medicine have gained great attention on different types of macromolecules such as positively charged Pcs [7–12]. Aggregation is a specific property of Pcs which reduces the efficiency of PDT. Our previous work included bis[1-methylpyrrolidin-2-yl]methoxy] phthalocyaninato silicon, bis[2-azepan-1-yl]ethoxy] phthalocyaninato silicon and bis[2,4,6-tris(N,N-dimethylaminomethyl) phenoxy] phthalocyaninato) silicon compounds which reduced aggregation and showed singlet oxygen generation [13].

In the photodynamic therapeutic modality, apart from DNA, other cellular components including plasma membrane, mitochondria, Golgi apparatus and lysosomes have been counted as targets for photosensitizers [14]. Maftoum-Costa et al. found that chloroaluminum phthalocyanine caused damage of HeLa cells after PDT [15]. Rello-Varona et al. revealed that Zn(II)-phthalocyanine penetrated into HeLa cells and accumulated in the Golgi complex. After the subcellular localization of Zn(II)Pc in the cells, they described a cell death mechanism [16]. The most important limiting factor for the cell death process in PDT is the poor water solubility of compounds used as photosensitizers [14]. Fukushima et al. reported the characterization of amphiphilic water soluble zinc(II) phthalocyanines and their photodynamic activity against the HeLa cell lines. They found that the most hydrophilic compound showed a significantly high intracellular concentration in HeLa cells [17].

Studies also showed that Pcs can also be used to inactivate bacteria in PDT [18]. Some metal-free and metallalatrophalocyanines were tested against various bacteria and photooinactivation properties were observed for these phthalocyanines [19, 20]. Among these, positive inactivation results were obtained with cationic, water-soluble Pcs as compared to anionic and neutral derivatives [21, 22]. The relationship between activity and structural properties of cationic Pcs was explained based on the electrostatic interaction caused by the positive charge on the Pc molecule and the negative charge on Escherichia coli [23].

Aggregation behavior and solubility problems in water are the main drawbacks that limit biomedical applications of Pcs [5, 24]. In order to deal with aggregation in organic solvents and aqueous media, along with increasing the solubility, ionic substituents were attached to Pc macrocycle on peripheral and/or non peripheral positions. Furthermore, the synthesis of axially-substituted Pcs was explained based on the electrostatic interaction caused by the positive charge on the Pc molecule and the negative charge on Escherichia coli [23].

Antitumor applications in medicine have gained great attention on different types of macromolecules such as positively charged Pcs [7–12]. Aggregation is a specific property of Pcs which reduces the efficiency of PDT. Our previous work included bis[1-methylpyrrolidin-2-yl]methoxy] phthalocyaninato silicon, bis[2-azepan-1-yl]ethoxy] phthalocyaninato silicon and bis[2,4,6-tris(N,N-dimethylaminomethyl) phenoxy] phthalocyaninato) silicon compounds which reduced aggregation and showed singlet oxygen generation [13].

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Thus, based on the literature especially on the work of Huang et al. [26], silicon Pcs substituted with longer than PEG-750 chains remain scarce in literature. We eleteded to synthesize a water-soluble silicon(IV) Pc axially substituted with PEG 1000. The photophysical properties of the studied phthalocyanine were investigated in both DMSO and water to determine its potential usefulness for PDT applications. Furthermore,
photocytotoxicity tests against HeLa and HuH-7 tumor cells were performed to determine the photosensitizer activity of the target phthalocyanine. Additionally, the antibacterial activity of this novel macromolecule was also determined.

**EXPERIMENTAL**

**Materials**

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Dichloro [phthalocyaninato] silicon(IV) was purchased from Aldrich. Toluene was distilled from sodium prior to use. Column chromatography was performed on silica gel 60 P 254. All reactions were monitored by thin layer chromatography (TLC) using 0.25 mm silica gel plates containing a UV indicator (60F254). All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Dichloro [phthalocyaninato] silicon(IV) was purchased from Aldrich. Toluene was distilled from sodium prior to use. Column chromatography was performed on silica gel 60 P 254. All reactions were monitored by thin layer chromatography (TLC) using 0.25 mm silica gel plates containing a UV indicator (60F254). All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Dichloro [phthalocyaninato] silicon(IV) was purchased from Aldrich. Toluene was distilled from sodium prior to use. Column chromatography was performed on silica gel 60 P 254. All reactions were monitored by thin layer chromatography (TLC) using 0.25 mm silica gel plates containing a UV indicator (60F254).

**Equipment**

1H-NMR spectrum was recorded on a Varian Mercury 200 MHz spectrometer in deuterated dimethyl sulfoxide (DMSO-d6). Chemical shifts were reported (δ) relative to Me4Si as an internal standard. FT-IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer. UV-visible electronic spectra were measured on Scinco Neosys 2000 double beam UV/Vis and Shimadzu UV-vis-2101 spectrophotometers with 1 cm path length quartz cuvettes in the spectral range of 300–800 nm. Fluorescence lifetimes were determined with a time-correlated single photon counting setup (TCSPC) (Horiba Fluorolog 3 equipment).

Photo-irradiations were done with a 300 W halogen lamp. A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiation. Interference filters (Intor, 670 nm with a band width of 40 nm) were placed in the light path in front of the sample. Light intensities were measured with a THORLABS powermeter [10].

**Synthesis of SiPc-PEG**

A mixture of silicon(IV) phthalocyanine dichloride (50 mg, 0.0817 mmol), PEG 1000 (163.4 mg, 0.1634 mmol) and sodium hydride (11.7 mg, 0.49 mmol) in dry toluene (25 mL) was refluxed for 22 h. After cooling to 25 °C, the reaction mixture was centrifuged at 2500 g and decanted. The solvent was evaporated in vacuo, then the residue was treated with 15 mL of ethyl acetate at room temperature. The mixture was filtered and the precipitate washed with THF. The filtrate was evaporated until dryness. The residue was purified by column chromatography on silica gel using dichloromethane: methanol (10:1) solvent system as an eluent. Yield: 32 mg (15.40%). 0.28–0.34 ppm (4H, t, Si–O–CH2–CH2), 0.71–0.88 ppm (4H, t, Si–O–CH2–CH2), 1.11–1.33 ppm (8H, t, Si–O–(CH2)2–CH2), 1.53–1.60 ppm (4H, t, Si–O–(CH2)3–CH2), 2.24–2.33 ppm (4H, t, Si–O–(CH2)2–CH2), 2.75–2.85 ppm (4H, t, Si–O–(CH2)3–CH2), 3.04–3.13 ppm (4H, t, Si–O–(CH2)3–CH2), 4.61–4.65 ppm (2H, br s, OH), 8.45–8.51 ppm (8H, m, H0), 9.61–9.67 ppm (8H, m, H0). Elemental analysis: calculated (%) for C120H194N8O46Si: C: 57.35; H: 7.78; N:4.45. Found (%): C: 57.04; H: 7.69; N: 4.05. IR νmax/cm−1: 3497 (OH); 2866 (CH–CH); 1638 (C=C); 1520 (C=C); 1453 (C=C); 1348; 1335; 1291 (C–O); 1081 (Si–O); 945; 843. UV-vis (DMSO): λmax nm (log ε): 357 (4.63), 608 (4.34), 677 (5.14). UV-vis (water): λmax nm (log ε): 357 (4.78), 616 (4.21), 682 (5.15).

**Photophysical and photochemical parameters**

Fluorescence (ΦF) and singlet oxygen (ΦO2) quantum yield calculations were carried out using the experimental setup giving in the literature [31]. The given formulas in the literature were used for these calculations [31].

**Cell culture**

Human HeLa cervical-carcinoma cells, and HuH-7 hepa-tocarcinoma cells were seeded in Dulbecco’s modified Eagle medium (DMEM) (PAN-Biotech). The medium was supplemented with 10% FBS and %1 antibiotics (pen/strep). Cell lines were incubated at 37 °C in an incubator humidified with 5% CO2. Stock solution of the studied silicon(IV) phthalocyanine (1 mM) was prepared in DMSO solvent and stored at 4°C in the dark. The solution was diluted with DMEM for desired concentrations.

**Measurement of photocytotoxicity**

Tumor cells (HeLa or HuH-7) were harvested and cultured in DMEM medium at a density of 4000 cells/well in 96 well plates (triplicates) and incubated for 24 h for cell growth. After overnight incubation, the SiPc-PEG photosensitizer was added to each well with various concentrations (0, 0.25, 0.5, 1, 2, 3, 4, 5, and 10 μM). Ninety-six well plates were incubated in dark at 37 °C in a humidified CO2 incubator for 24 h. Before irradiation, the medium was refreshed with fresh DMEM medium for each well. A Lumacare Model LC-122 light source equipped 690 ± 10 nm activation wavelength fiber-optic probe (FOP) system was used for the irradiation of the cells. The distance between the FOP tip and the cell plate surface was arranged as 20 cm. Power of FOP systems’ light on the 96 well plate surface was determined with a power meter (Ophir). The light dose was approximately 2 J.cm−2. Dark control plates were kept in dark. After illumination, the cells were incubated for 24 h and cell viability was then measured by colorimetric tetrazolium compound (MTS; Promega: (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2Htetrazolium) [32]. The MTS solution (20 μL)
was added to each well and incubated for 4 h. MTS compound is metabolized by metabolically active cells into a colored formazan. The color of the samples was measured by reading the absorbance at 490 nm by a microplate reader. The triplicate wells were calculated for the average values.

**Antibacterial assay**

Antibacterial activity of SiPc-PEG was studied against *E. coli* K12 through the viable cell count method: first, 100 μL of the -80°C frozen stock culture of *E. coli* was inoculated into 10 mL of Luria Bertani (LB) medium in a 50 mL flask, and incubated overnight at 37°C and 180 rpm. The optical density of the culture at 600 nm (OD₆₀₀) was then adjusted to 0.25 in 10 mL fresh LB media in 50 mL flasks. The flasks were incubated under control conditions (0 μg/mL SiPc-PEG), 1000 μg/mL and 2500 μg/mL SiPc-PEG at 37°C and 180 rpm, for 48 h in dark. After 48th h of incubation, cultures were diluted by 10⁶-fold. Fifty μL of the diluted cultures were spread on solid LB plates in triplicate, and incubated at 37°C for 48 h. The grown colonies were then examined for viable cell count determination, and average counts of three plates were calculated for each sample. The same method was repeated using a photo-activated SiPc-PEG. As described above, cultures at an OD₆₀₀ of 0.25 were incubated under control conditions (0 μg/mL SiPc-PEG), 1000 μg/mL and 2500 μg/mL photo-activated SiPc-PEG, and viable cell counts were determined. Photoactivation protocol was applied as described previously [10]. Briefly, a 300 W quartz lamp equipped with a bandpass filter at 670 nm was used. It was placed at 10 cm distance from the SiPc-PEG stock solution and a continuous exposure was applied for 5 min. The illumination power was measured as 0.1 mW, using a Thorlabs powermeter [10].

**RESULTS AND DISCUSSION**

**Synthesis**

In the present study, a novel PEG-conjugated silicon (IV) phthalocyanine axially substituted with PEG 1000 chains (SiPc-PEG) was synthesized by the condensation reaction between PEG 1000 bearing hydroxyl functional groups at both ends and unsubstituted silicon(IV) phthalocyanine containing chloride atoms as axially ligands (Scheme 1). The chemical structure of the synthesized compound was characterized by UV-Vis, FT-IR and ¹H NMR spectra. According to the ¹H NMR spectrum of SiPc-PEG (Fig. 1), the peaks observed between 8.45 and 9.67 ppm are assignable to the peripheral hydrogen atoms on the Pc ring (Fig. 1). Signals belonging to the CH₂ protons were observed at a high field between 0.28–0.34 ppm for Si–O–CH₂ due to magnetic anisotropy of the delocalized 18 π electrons on the phthalocyanine ring as described for SiPcs in the literature [33]. Together with elemental analysis data, the expected structure of PEG-conjugated SiPc-PEG compound was evidenced by using integrals of PEG protons as axialScheme 1. The synthetic pathway of SiPc-PEG derivative...
ligands. Incorporation of PEG 1000 blocks into Pc rings enhanced water solubility owing to the hydrophilicity of the terminal OH groups on the poly(ethylene) chain. The electronic absorption behavior of the sensitized novel SiPc substituted with PEG1000 was determined by UV-Vis spectroscopy, and the obtained spectra for this phthalocyanine in both DMSO and water are shown in Fig. 2. In a DMSO solution of SiPc-PEG, intense and sharp absorption bands at 681 nm for the Q band and 359 nm for the B band were observed and supported...
Table 1. Electronic absorption, excitation and emission spectral data for unsubstituted (SiPc) and PEG-1000 substituted (SiPc-PEG) silicon(IV) phthalocyanines in DMSO

<table>
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<th>Comp.</th>
<th>Solvent</th>
<th>Q-band $\lambda_{\text{max}}$, (nm)</th>
<th>Excitation $\lambda_{\text{Ex}}$, (nm)</th>
<th>Emission $\lambda_{\text{Em}}$, (nm)</th>
<th>Stokes shift $\Delta_{\text{Stokes}}$, (nm)</th>
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<td>DMSO</td>
<td>672$^a$</td>
<td>672$^b$</td>
<td>678$^a$</td>
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</tbody>
</table>

$^a$Data from Ref. [36].

$^b$Data from Ref. [44].

Figure 3. Electronic absorbance changes of SiPc-PEG (a) in DMSO and (b) in water at different concentrations: $1.2 \times 10^{-5}$, $1.0 \times 10^{-5}$, $8 \times 10^{-6}$, $6 \times 10^{-6}$, $4 \times 10^{-6}$, $2 \times 10^{-6}$ M (inset: plot of absorbance vs. concentration)
the formation of a non-aggregated state of the studied silicon(IV) phthalocyanine conjugated with PEG 1000 blocks. This phthalocyanine compound was present as a monomer in water, according to the narrow Q band absorption of this phthalocyanine (Fig. 2).

**Ground state electronic absorption spectra**

Ground state electronic absorption spectroscopy is the most frequently used method for definition of phthalocyanines. Two major bands, named as Q and B bands are observed for phthalocyanine derivatives in their electronic absorption spectra. While the Q band represents a $\pi \rightarrow \pi^*$ transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the B band is responsible for the transition from deeper level $\pi$ orbitals to LUMO. While the metallophthalocyanines exhibit a single narrow Q-band because of their $D_{4h}$ symmetry, the metal free phthalocyanines exhibit two split Q-bands due to their $D_{2h}$ symmetry [35].

In this study, the electronic spectrum of SiPc-PEG showed monomeric Q-band absorption bands which are characteristic of non-aggregated metallophthalocyanines [35] in both DMSO and water solutions, Table 1. The Q-band absorption for SiPc-PEG in DMSO (Table 1) was observed at 677 nm and the B-band absorption was observed at 356 nm, while in water the Q-band absorption was observed at 682 nm and the B-band absorption was observed at 357 nm. The observed sharp absorption bands are an evidence for the formation of non-aggregated phthalocyanine species at the studied concentration in both DMSO and water. The PEG-1000 substituted silicon(IV) phthalocyanine (SiPc-PEG) exhibited 6 nm red-shifted Q band compared to the unsubstituted SiPc(OH)$_2$ [36].

The electronic absorption spectrum of the studied SiPc-PEG was also measured at various concentrations in both DMSO and water for the determination of the aggregation tendency of this compound at different concentration because the aggregation of phthalocyanine compound depends on the concentration [37]. It was observed that the increase of absorbance with phthalocyanine concentration ranging from $1.2 \times 10^{-5}$ to $2 \times 10^{-6}$ M was linear in both DMSO and water (Fig. 3). This behavior implies that, at least within this concentration range ($1.2 \times 10^{-5}$ to $2 \times 10^{-6}$ M), this phthalocyanine is in the monomeric state, in agreement with the Beer–Lambert law. This is advantageous for using SiPc-PEG in photodynamic therapy applications, because the photoactivity of phthalocyanine photosensitizers is known to be reduced due to aggregation in solution.

The electronic absorption spectrum of studied SiPc-PEG compound was also recorded in different solvents (Fig. 4), to determine the most suitable solvent for photophysical and photochemical measurements. SiPc-PEG compound exhibited non-aggregated solutions in DMSO, water, dimethyl formamide (DMF), chloroform and toluene, as evidenced by a narrow Q-band absorption of this compound for studied solvents.

**Fluorescence spectra**

The fluorescence emission spectra, absorption spectra, and excitation spectra of SiPc-PEG compound were measured in both DMSO and water solutions. The obtained spectra is shown in Fig. 5. The fluorescence emission and fluorescence excitation peaks of the
Figure 5. Electronic absorption, fluorescence emission and excitation spectra for SiPc-PEG (a) in DMSO (Concentration = 1.2 × 10^{-5}) and (b) in water (Concentration = 1.00 × 10^{-5}). Excitation wavelength = 640 nm

PEG-substituted silicon(IV) phthalocyanine are listed in Table 1. The observed Stokes shift values of the SiPc-PEG compound was found to be 7 and 13 nm in DMSO and water, respectively. This value obtained in DMSO is similar to that of unsubstituted silicon(IV) phthalocyanine. The obtained excitation spectrum was similar to the absorption spectrum of the SiPc-PEG compound. Thus, they are mirror images of the fluorescence emission spectrum. The similarity between the absorption spectrum and the excitation spectra implies that the SiPc-PEG compound did not degrade in either DMSO or water during the fluorescence process.

Fluorescence quantum yield (Φ_F) of the SiPc-PEG was determined in both DMSO and in water solutions, and these values were found to be 0.10 and 0.23, respectively. The Φ_F value of SiPc-PEG was found to be lower than that of the unsubstituted silicon(IV) phthalocyanine (SiPc(OH)_{12}) (Φ_F = 0.21 in DMSO [36]) in DMSO, suggesting that the substitution of the PEG-1000 groups on the axial positions of the silicon(IV)
phthalocyanine increased fluorescence quenching. The $\Phi_F$ value of SiPc-PEG was found to be slightly higher than that of the unsubstituted silicon(IV) phthalocyanine (SiPc(OH)$_2$) in water.

Fluorescence lifetime values ($\tau_F$) of the studied phthalocyanine were determined using the time-correlated single photon counting (TCSPC) method. Time-resolved fluorescence was measured in both DMSO and water for the PEG-1000 substituted silicon(IV) phthalocyanine. The fluorescence decay curves of the studied SiPc-PEG compound are shown in Fig. 6. Fluorescence curves were obtained as mono-exponential decay in both studied solvents. This was possible since the SiPc-PEG molecules did not aggregate in either DMSO or water. The $\tau_F$ value of the SiPc-PEG was found as 3.02 ns in DMSO and 5.07 ns in water (Table 2), and this value was lower than that of the unsubstituted silicon(IV) phthalocyanine (SiPc(OH)$_2$) ($\tau_F = 4.90$ ns) [36] in DMSO. The $\tau_F$ value of SiPc-PEG was found to be higher than that of the unsubstituted silicon(IV)

Figure 6. Time correlated single photon counting (TCSPC) fluorescence decay curve of SiPc-PEG (Concentrations = 1.2 $\times$ 10$^{-5}$) (a) in DMSO and (b) in water

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J. Porphyrins Phthalocyanines 2018; 22: 18–24
Table 2. Photophysical and photochemical data for unsubstituted (SiPc) and PEG-1000 substituted (SiPc-PEG) silicon(IV) phthalocyanines in DMSO

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\Phi_t)</th>
<th>(\tau_s) (ns)</th>
<th>(\Phi_d) (10^3)</th>
<th>(\Phi_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiPc-PEG</td>
<td>DMSO</td>
<td>0.10</td>
<td>3.02</td>
<td>1.04</td>
<td>0.49</td>
</tr>
<tr>
<td>SiPc-PEG</td>
<td>Water</td>
<td>0.23</td>
<td>5.07</td>
<td>1.09</td>
<td>0.19</td>
</tr>
<tr>
<td>SiPc(OH)_2</td>
<td>DMSO</td>
<td>0.21*</td>
<td>4.90*</td>
<td>—</td>
<td>0.28*</td>
</tr>
</tbody>
</table>

*Data from Ref. [45].
*Data from Ref. [36].

Singlet oxygen quantum yields

Singlet oxygen (\(^1\)O₂) is formed when energy transfer occurs between the triplet state of photosensitizers and the ground state of molecular oxygen during light irradiation. Increasing the energy transfer produces higher amounts of singlet oxygen. The generated singlet oxygen is quantified as singlet oxygen quantum yield (\(\Phi_s\)). The singlet oxygen quantum yield (\(\Phi_s\)) correlates with the number of singlet oxygen molecules generated by one photon absorbed by a photosensitizer [38].

The singlet oxygen quantum yield (\(\Phi_s\)) values of the axially PEG-1000 substituted silicon(IV) phthalocyanine were determined in both DMSO and water solutions using an experimental method described in the literature [31]. 1,3-Diphenylisobenzofuran (DPBF) and 9,10-antracenediy1-bis(methylene)dimalonic acid (ADMA) were used as chemical quenchers for the determination of singlet oxygen generation in DMSO and in water, respectively. Unsubstituted zinc(II) phthalocyanine (\(\Phi_{sd}^d\) = 0.67 in DMSO [39]) and sulfonated zinc(II) phthalocyanine (\(\Phi_{sd}^d\) = 0.45 in DMSO [31]) were used as standards for determination of the singlet oxygen of SiPc-PEG in DMSO and water, respectively. The disappearance of DPBF absorbance at 417 nm and ADMA absorbance at 380 nm for SiPc-PEG were monitored using UV-vis spectrophotometry. SiPc-PEG solutions (C = 1 × 10⁻⁷ M) in both DMSO and in water were prepared including quencher in dark and light irradiated in the Q-band area of the samples. The quencher absorbances (at 417 nm for DPBF, 380 nm for ADMA) decrease during the irradiation, as recorded by UV-vis spectrophotometry. The \(\Phi_s\) measurement was performed using light, which has 6.63 × 10⁵ photons s⁻¹ cm⁻² intensity. Figure 7 shows the electronic absorption spectra during the singlet oxygen generation experiment.

No changes were observed in the Q-band intensity of the SiPc-PEG compound, confirming that this phthalocyanine did not show any degradation by the light irradiation used during the singlet oxygen determination period (Fig. 7). The \(\Phi_a\) value of SiPc-PEG compound was found as 0.49 which is higher than that of the unsubstituted silicon(IV) phthalocyanine (SiPc(OH)_2) in DMSO, suggesting that the addition of PEG-1000 groups as axial ligand on the silicon(IV) phthalocyanine increased the singlet oxygen generation. The \(\Phi_a\) value of SiPc-PEG was also calculated as 0.19 in water (Table 2).

Photodegradation studies

An oxidative decomposition via light is called photodegradation, and this measurement is useful to determine the stability of the compounds. Photodegradation is quantified as the photodegradation quantum yield (\(\Phi_d\)). Photodegradation of studied molecules is related to their structure, concentration, solvent used and the intensity of the light [40]. Thus, to determine the stability of the SiPc-PEG compound, photodegradation quantum yields (\(\Phi_d\)) were determined in both DMSO and water using the experimental method described in the literature [31]. The \(\Phi_d\) determinations were measured using 2.21 × 10ⁱ⁰ photons s⁻¹ cm⁻² light intensity. The spectral change of the SiPc-PEG compound with light irradiation supported that photodegradation occurred without any phototransformation because a decrease was only observed in the intensities of the Q and B bands. The formation of any new band or any shift to the wavelength of the Q or B bands was not observed during the photodegradation study (Fig. 8). The \(\Phi_d\) value was found to be similar in DMSO and water (\(\Phi_d = 1.04 × 10^3\) in DMSO and 1.09 × 10³ in water) (Table 2). These values were similar for phthalocyanine derivatives having different central metal atom and substituents on the phthalocyanine macrocycle [38].

Photocytotoxicity studies

The HeLa and HuH-7 tumor cells were incubated with the SiPc-PEG compound at different concentrations (0, 0.25, 0.50, 1, 2 and 3 μM) for 24 h and then irradiated with 2 J.cm⁻² light irradiation. The survival of cells was determined by MTS upon 24 h irradiation. The cytotoxicity of SiPc-PEG against the HeLa and HuH-7 cells in the presence or absence of irradiation is shown in Fig. 9. The results indicate that the SiPc-PEG compound is non-toxic without light, but exhibits high levels of photo-toxicity upon irradiation, when the applied concentration is higher than 0.5 μM.

The survival of the cells after PDT was reduced by less than 50% at 0.5 μM, for both cell types (Fig. 9). Half maximal effective concentration (IC₅₀) value is defined as the drug concentration required to kill 50% of the cells. The IC₅₀ value for SiPc-PEG compound was determined as 0.28 μM for HeLa cells and 0.4 μM for HuH-7 cells (data not shown). These results imply that HeLa cells seem to be more responsive to PDT treatment by SiPc-PEG than HuH-7 cells at low concentrations (up to 0.5 μM) of the studied photosensitizer.
Antibacterial activity

The addition of PEG is known to increase the hydrophilicity of compounds, thus improving their interactions with microorganisms [41]. Consequently, the SiPc-PEG compound synthesized in this study was also tested for its antibacterial activity against *E. coli*, in the presence and absence of irradiation. For this purpose, viable cell count method based on colony counts on plates with dilutions of shake flask cultures was applied. The results revealed that the SiPc-PEG showed antibacterial activity against *E. coli* at 48 h of incubation, the viabilities of *E. coli* cultures exposed to 1000 μg/mL and 2500 μg/mL SiPc-PEG concentration was reduced by about 90%, and the additional growth inhibitory effect of photoactivation was also observed clearly at these efficient concentrations (Fig. 10).

In the literature, there are many reports that include the antibacterial effect of cationic Pcs. However, studies of the bactericidal activity of PEG derivatives, even without substitution of any compounds such as Pcs, remain scarce. For instance, Nalawade *et al.* studied the bactericidal activity of propylene glycol, glycerine, PEG 400, and PEG 1000 against selected microorganisms *in vitro*. In this work, it was indicated that PEG 1000 was effective against *S. mutans* and *E. coli* at 25%. PEG 1000 was shown to be bactericidal at a lower concentration but was effective on only two organisms [42]. Based on this data,
the antibacterial effect of the newly synthesized SiPc-PEG compound was tested against the Gram-negative bacterium *E. coli*. SiPc-PEG showed antibacterial activity against *Escherichia coli* at 48 h of incubation. The viabilities of *E. coli* cultures exposed to 1000 μg/mL and 2500 μg/mL SiPc-PEG concentration were reduced by about 90%, and the additional growth inhibitory effect of photoactivation was also observed clearly at these efficient concentrations. This result was important because not only silicon Pcs but also the antibacterial effect of PEG was tested. This inhibitory effect on *E. coli* may be resulting from the passage of SiPc-PEG through the porins in the outer membrane of *E. coli*, as it has been previously reported that PEG1000 can partition into a major outer membrane protein of *E. coli* [43].

Future studies are planned to determine the subcellular localization of SiPc-PEG. As only cationic compounds have been shown to efficiently kill Gram-negative
bacteria [21], it is not surprising to have a moderate level of antibacterial activity for this non-cationic novel compound. In photodynamic inactivation assays, it has been shown that the increase in the antibacterial activity of the photoactive materials was a function of the initial bacterial cell concentration: the lower the initial bacterial cell concentration, the higher the antibacterial activity [23]. Considering also the fact that a significantly high initial bacterial concentration was used in our study, it is promising to still observe a moderate level of antibacterial activity in SiPc-PEG against \textit{E. coli}, even in the absence of a cationic charge and at significantly high initial bacterial concentrations, which are not favorable for antibacterial testing. After observation of some antibacterial activity under these conditions, other antibacterial tests are also planned using Gram-positive bacteria and yeast species, which, unlike Gram-negative bacteria, do not require a cation charge and are thus expected to be more sensitive in antibacterial tests with SiPc-PEG.

CONCLUSIONS

Axially PEG-1000 bearing silicon(IV) phthalocyanine was synthesized in this study and was characterized by spectroscopic methods (UV-Vis, FT-IR, GPC and $^1$H-NMR). These types of silicon(IV) phthalocyanines are generally obtained by the reaction of PEG (PEG 350, 550 or 700) methyl ethers that have “only one OH” functional group reacted with silicon(IV) phthalocyanine dichloride. Thus, they are “smaller” polymeric molecules which are easily detected by known spectral analyses and can be

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**Figure 9.** Photocytotoxicity of SiPc-PEG compound against HeLa and HuH-7 tumor cells incubated at 0, 0.25, 0.50, 1, 2, and 3 µM photosensitizers for 24 h after irradiation with 2 J/cm$^2$

**Figure 10.** \textit{E. coli} viable cell counts (cfu/mL) at 48 h
considered as “small polymers” by polymer scientists. The novel PEG-conjugated silicon (IV) phthalocyanine synthesized in this study is to our knowledge the first example of PEG-conjugated phthalocyanines which are axially substituted with PEG moieties that are longer than the ones reported in the literature (PEG1000 instead of PEG350-700). Additionally, unlike existing silicon (IV) phthalocyanines, the novel PEG-conjugated silicon phthalocyanine synthesized in this study has free OH functional groups on both ends.

Photophysical and photochemical properties such as fluorescence quantum yields, fluorescence lifetimes, singlet oxygen quantum yields and photodegradation quantum yields of the studied SiPc-PEG were investigated in both DMSO and water solutions. When compared with Pcs peripherally substituted with PEG blocks [44], the SiPc-PEG compound exhibited higher singlet oxygen quantum yields both in water and in DMSO. Additionally, due to the formation of aggregates, dendrimeric silicon Pcs nanoparticles [45] showed lower singlet oxygen and higher fluorescence quantum yields. The new compound presented here was another proof for high singlet oxygen efficiency with long PEG chains which reduced aggregation quite a lot compared to the small PEG blocks reported previously [26].

According to Huang et al. [26], halogen substitution on the peripheral positions does not increase the PDT efficiency of the phthalocyanine core even though halogenated phthalocyanines have a higher singlet oxygen quantum yield. Photocytotoxicity tests of SiPc-PEG were performed against HeLa and HuH-7 tumor cells, and the results indicated that PEG bearing-SiPc displayed significant levels of photocytotoxicity on the aforementioned tumor cells.

Antibacterial activity assays indicated that after 48 h incubation of E. coli bacteria with SiPc-PEG, the viability of E. coli cultures was reduced by about 90%, (Fig. 10). Addressing the need for new drugs to treat cancer, this novel SiPc-PEG compound could be an efficient applicant as a photosensitizer in PDT. To conclude, the results obtained in this study suggest that the newly synthesized PEG-attached silicon(IV) phthalocyanine compound may have a high potential for medical applications.

Acknowledgment

This work is supported by Istanbul Technical University (BAP: 39556).

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Pyridone substituted phthalocyanines: Photophysico-chemical properties and TD-DFT calculations

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This paper is dedicated to Professor Kazuchika Ohta on the occasion of his retirement.

Received 13 October 2017
Accepted 13 November 2017

ABSTRACT: A 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy)phthalonitrile has been used to prepare a novel Zn(II) phthalocyanines with four peripheral pyridone substituents. The compound has been characterized by UV-visible absorption, FT-IR and 1H-NMR spectroscopy, elemental analysis and MALDI-TOF mass spectroscopy. The fluorescence, triplet quantum and singlet oxygen quantum yields have been determined and TD-DFT calculations have been used to identify trends in the electronic structure.

KEYWORDS: phthalocyanines, pyridones, TD-DFT calculations, singlet oxygen, photophysics.

INTRODUCTION

Phthalocyanines are an important class of dyes and pigments that have been the focus of ongoing intense research since their first synthesis at the beginning of the last century. Because of their unique spectroscopic and electrochemical properties, metallophthalocyanines (MPcs) have found applications as semiconductors, nonlinear optical and optical limiting materials, chemosensors, organic photovoltaics, catalysis and photosensitizers for photodynamic therapy and photodynamic inactivation [1–13]. Pyridone derivatives are heterocyclic intermediates used for the synthesis of arylazo dyes. Azo pyridone dyes display bright hues and are used as dye colorings for polyester fabrics [14]. Recently, the synthesis and quartz crystal microbalance (QCM) based ion sensors properties of free base and cobalt Pcs with four 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy) substituents at the peripheral positions have been reported [15]. The aim of this study was to synthesize a Zn(II) phthalocyanine with a similar set of peripheral pyridone substituents (Scheme 1) and investigate their photophysicochemical properties to assess their possible utility as photosensitizers in singlet oxygen applications such as photodynamic therapy (PDT). ZnPcs are particularly important in this regard since generally they have high singlet oxygen quantum yield values due to the heavy atom effect, making these compounds suitable for use as photosensitizers in photodynamic therapy [16].

EXPERIMENTAL

Materials

All chemicals were reagent grade. Solvents were dried, purified and stored over molecular sieves.

Instrumentation

Electronic absorption spectra were obtained on a Shimadzu UV-2450 UV–visible spectrophotometer. Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Center. The 1H-NMR
Spectrum was recorded on a Varian Unity Inova 500 MHz NMR spectrometer. Mass spectra were performed on a Bruker Microflex LT MALDI-TOF spectrometer. Excitation and emission spectra were recorded on a Varian Eclipse spectrophotometer. A laser flash photolysis system was used for the determination of triplet decay kinetics.

**Synthesis**

Synthesis of the 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy)phthalonitrile precursor has been reported previously [15] and was used to prepare Zn(II) complex (1) through a metal insertion reaction. 1: A mixture of 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy)phthalonitrile (0.20 g, 1.076 mmol) and Zn(OAc)\(_2\).2H\(_2\)O (0.236 g, 1.076 mmol) was transferred to a reaction tube and the reaction mixture was heated in amyl alcohol (2 mL) by using a heat gun set at 320°C for 10 min. The reaction mixture was precipitated by adding acetic acid and methanol and the precipitate was washed with acetone. Yield 0.26 g (20%), mp >300°C. FT-IR ν (cm\(^{-1}\)): 3135, 3060, 2954, 2909, 2867, 1652, 1566, 1519, 1457, 1414, 1393, 1371, 1317, 1242, 1208, 1092, 1016, 936, 884, 821, 746. UV-vis (DMF, λ\(_{max}\) (nm) (log ε): 676 (4.97), 609 (4.29), 344 (4.71). MS (MALDI-TOF), Calc: 1250.4 m/z; Found: 1250.0 [M]⁺. Anal. Calc. for C\(_{56}\)H\(_{32}\)N\(_{16}\)O\(_{16}\)Zn: C, 53.99; H, 2.61; N, 18.06; Found: C, 53.92; H, 2.59; N, 18.20%. \(^1H\) NMR (DMSO-\(d_6\), 500 MHz) δ, ppm 7.80–7.03 (m, 12H), 5.11 (br s, 4H), 1.88 (s, 12H), 1.18 (br s, 4H).

**Theoretical calculations**

Optimized geometries were calculated for 1 by using the B3LYP functional of the Gaussian software package with 6-31G(d) basis sets [17]. A TD-DFT calculation was carried out in a similar manner by using the CAM-B3LYP functional, since it contains a long-range correction that provides more accurate predictions for transitions that contain significant charge transfer character [18, 19].

**RESULTS AND DISCUSSION**

**Synthesis and characterization**

1 was prepared in a reaction tube by reacting 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy)phthalonitrile [15] with Zn(OAc)\(_2\).2H\(_2\)O in dry amyl alcohol by using a heat gun set at 320°C for 10 min, and was found to be soluble in tetrahydrofuran, dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The structure of 1 was confirmed through elemental analysis, UV-visible absorption, FT-IR, and \(^1H\)-NMR spectroscopy and MALDI-TOF mass spectrometry.

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**Scheme 1.** Synthesis of 1, reagents and conditions. Zn(OAc)\(_2\).2H\(_2\)O, amyl alcohol, 10 min, 320°C
Optical spectroscopy

An analysis of calculated TD-DFT spectra for 1 and the unsubstituted parent ZnPc complex (Fig. 1 and Table 1), which are very similar to those observed experimentally (Fig. 2), makes it clear that the main spectral bands in the UV-visible absorption spectrum of 1, which lie at 678 and 341 nm, can be readily assigned to the Q and B bands of Gouterman’s 4-orbital model [20]. The simulated spectrum for the fourfold symmetric positional isomer of 1 is dominated by transitions (Fig. 3) between MOs derived from the HOMO and LUMO of a 16 atom 18 π-electron system associated with the inner cavity of the Pc ligand, which have $M_L = \pm 4$ and $\pm 5$ nodal patterns (Fig. 4). The Q and B bands of 1 are slightly red shifted relative to those of the parent unsubstituted ZnPc complex. An analysis of the MO energies predicted for 1 and the parent unsubstituted ZnPc complex makes it clear that the pyridone substituents have a strong electron-withdrawing inductive effect and that the narrowing of the HOMO–LUMO gap of 1 is due to a relative destabilization of the HOMO. This is probably related to the mesomeric effect that is associated with the interaction between the lone pairs on the peripheral oxygen atoms and the phthalocyanine π-system. Although there is scope for positional isomerism at the peripheral positions of the fused benzene rings, this is known to have a very limited effect on the optical spectroscopy [21], since the frontier π-MOs have relatively small MO coefficients at these positions (Fig. 3). It is noteworthy that in the context of the B band of 1, a much greater level of configurational interaction is predicted between the $1a_{1u} \rightarrow L$ ($1e_{gx}^*$); … Q

ZnPc

2, 3 16.5 607 0.48 14.9 672 93% H ($1a_{1u}$) → L/L+1 ($1e_{y}^*$); … Q

13, 14 33.9 295 1.08 29.1 344 75% H→1 ($1a_{1u}$) → L/L+1 ($1e_{y}^*$); … B

The number of the state assigned in terms of ascending energy within the TD-DFT calculation. *Calculated band energies (10³ cm⁻¹), wavelengths (nm) and oscillator strengths (c) in parentheses. †Observed energies (10³ cm⁻¹) and wavelengths (nm) in DMSO. ‡The wave functions based on the eigenvectors predicted by TD-DFT. H and L are used to denote the HOMO and LUMO with the symmetry of the MO provided in parentheses assuming $D_{4h}$ symmetry (Fig. 4), if it is one of the four frontier π-MOs of Gouterman 4-orbital model [20]. Only eigenvectors of 10% or higher are consistently reported. §The band assignment is described in the text.
one-electron transition of Gouterman’s 4-orbital model and those associated with other close-lying ππ* excited states (Table 1).

Additional weaker absorbance can be observed in the UV-vis absorption spectrum of I between the main Q and B bands when a comparison is made with the spectrum of the unsubstituted ZnPc complex (Fig. 2), and significant intensity is predicted in this region of the spectrum in the TD-DFT calculation (Fig. 1). This is likely to be primarily related to transitions into the LUMO from MOs that lie between the 1a2u and 1a1u Gouterman 4-orbital model MOs that are associated with the Q and B transitions (Fig. 3). An analysis of trends in the MO energies predicted in the TD-DFT calculations for I and unsubstituted ZnPc suggests that the occupied MOs of I that lie immediately above the 1a2u MO are either localized on the peripheral 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-ylxy) substituents (Fig. 3), or are π-MOs that are destabilized by mesomeric effects associated with the introduction of the peripheral substituents. Michl has described how a consideration of the inductive and mesomeric effects of peripheral substituents can be used to rationalize trends observed in the optical spectra of aromatic cyclic polyenes [22], and the application of this approach has been reviewed in the context of porphyrins [23] and phthalocyanines [21]. The relative destabilizations of the π-MOs that lie immediately above the 1a2u MO of I are significantly smaller than those that were reported previously for phthalocyanines with electron donating alkoxy and thioalkyl groups [24], which have more pronounced shoulders of absorbance to the red of the B band [25]. It is noteworthy that the introduction of the 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-ylxy) substituents is predicted to have a strongly electron withdrawing inductive effect on the entire stack of π-MOs of I (Fig. 3), since there is a consistent stabilization relative to those of the parent unsubstituted ZnPc, in addition to the destabilizing mesomeric effect that is associated with the lone pairs of electrons on the oxygen atoms at the point of attachment, which results in relative destabilizations of π-MOs that have large MO coefficients at the peripheral β-positions of the fused benzo rings.

**Photophysical measurements**

As would normally be anticipated for phthalocyanines, the emission spectrum is a near mirror image of the absorption spectrum in the Q band region (Fig. 5). Fluorescence quantum yields (ΦF) are used to give a measure of the efficiency of the emission process and can be determined by a comparative method using a standard [26, 27], whereby the unknown ΦF value of a newly synthesized compound is related to that of a standard with a known ΦF value (Table 2). The absorbance values of the sample and the unsubstituted ZnPc standard (ΦF = 0.20 in DMSO) were adjusted to ca. 0.05 at the excitation wavelength [16]. The ΦF value for I was...
found to be significantly lower than that of the standard (Table 2). Solutions for triplet quantum yield and lifetime determinations were de-aerated using argon for 20 min, and measurements were made by using a cross-over wavelength in the Q band region between 1 and ZnPc standard. The triplet lifetimes were determined by exponential fitting of the kinetic curves. The triplet state quantum yield value of 1 (Table 2) was determined by the triplet absorption method [28], using ZnPc as a standard ($\Phi_T = 0.65$ in DMSO) [29]. Quantum yields for internal conversion ($\Phi_{IC}$) can be obtained by assuming that only three processes (fluorescence, intersystem crossing and internal conversion) deactivate the $S_1$ state of 1 and the unsubstituted ZnPc parent complex. The $\Phi_{IC}$ value is significantly higher in the context of 1 (Table 2). One possible explanation is that the enhanced conformational flexibility introduced by the 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yloxy) substituents results in a greater rate of non-radiative decay. Since there are many examples of ZnPc complexes with bulky peripheral substituents having relatively large $\Phi_D$ values [30], however, a more likely explanation is that the strong electron-withdrawing properties of the pyridine substituents have an influence on this by introducing intramolecular charge transfer character into the $S_1$ state. The triplet decay curve for 1 was found to obey second order kinetics and the lifetime was determined to be 250 $\mu$s, which is essentially unchanged with respect to the unsubstituted ZnPc standard.

**Photochemistry**

Singlet oxygen quantum yield ($\Phi_A$) values were determined [31–33] in air using the comparative method with ZnPc ($\Phi_A = 0.67$ in DMSO) as the standard and diphenylisobenzofuran (DPBF) as a chemical quencher (Fig. 6 and Table 2). To avoid chain reactions induced by DPBF in the presence of singlet oxygen [34], the concentration of DPBF was ca. $3 \times 10^{-5}$ mol.L$^{-1}$. The $\Phi_A$ value for 1 was found to be much lower than that of the ZnPc standard as would be anticipated based on the low $\Phi_A$ value. The $S_A$ value, which is defined as $\Phi_A/\Phi_T$ and gives a measure of the efficiency of excitation energy transfer from the triplet state photosensitizer to ground state molecular oxygen, remains relatively high, however.

**Table 2. Photophysical properties of 1 and the unsubstituted ZnPc parent complex**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Abs (nm)</th>
<th>Em (nm)</th>
<th>Ex (nm)</th>
<th>Log $\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\Phi_F$</th>
<th>$\Phi_T$</th>
<th>$\Phi_S$</th>
<th>$S_A$</th>
<th>$\Phi_{IC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>678</td>
<td>688</td>
<td>678</td>
<td>4.97</td>
<td>0.10</td>
<td>0.16</td>
<td>0.14</td>
<td>0.88</td>
</tr>
<tr>
<td>ZnPc</td>
<td>DMSO</td>
<td>672</td>
<td>679</td>
<td>672</td>
<td>5.38</td>
<td>0.20</td>
<td>0.65</td>
<td>0.67</td>
<td>1.03</td>
</tr>
</tbody>
</table>

* The values for unsubstituted ZnPc are taken from Refs. 16 and 26.
CONCLUSIONS

A pyridone substituted zinc phthalocyanine has been synthesized by using 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yl)oxy)phthalonitrile. Relatively low fluorescence and triplet quantum yield values were obtained in DMSO. Although there is a slight red shift of the Q band of I towards the therapeutic window, the low singlet oxygen quantum yield value of 0.14 suggests that pyridone substituted phthalocyanines of this type are unlikely to provide useful for singlet oxygen photensitizer applications and that the structure of the 4-(6-methyl-3-nitro-2-oxo-1,2-dihydropyridin-4-yl)oxy) substituents will have to be modified in a manner that does not enhance the \( \Phi_s \) values for further studies on compounds of this type to be merited.

Acknowledgements

This work was partially supported by The Foundation of Marmara University, The Commission of Scientific Research (BAPKO) (Project No: FEN-A-101013-0397), the DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology (uid: 62620), and a NRF of South Africa CSUR grant (uid: 93627). Photophysical measurements were made possible by the Laser Rental Pool Programme of the Council for Scientific and Industrial Research (CSIR) of South Africa. Calculations were carried out at the Centre for High Performance Computing in Cape Town.

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INTRODUCTION

In past two decades, phthalocyanine (Pc) derivatives have attracted our attention as a donor material (electron-donating material) in organic thin film solar cells and organic semiconductors. This is because Pc has strong absorption bands in a visible region and excellent light fastness [1–7]. However, Pc is so strongly aggregated that it hardly dissolves in any organic solvents, and that the molecular orientation cannot be controlled. In order to solve these problems, attempts have been made in recent years to synthesize Pc-based discotic liquid crystals showing excellent solubility and molecular orientation. In general, discotic liquid crystals have a molecular structure with a rigid disk-like aromatic core in the center and flexible alkyl chains in the periphery. Because of the flexible alkyl chains in the periphery, Pc-based discotic liquid crystals become soluble in organic solvents. Also, when the discotic liquid crystal is heated, the peripheral alkyl chains melt at first, but the

Discotic liquid crystals of transition metal complexes, 55†: Novel chlorine-substituted phthalocyanine derivatives showing mesomorphism and low HOMO energy level

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†Part 54: Reference 37 in this paper.
central cores remain to stack face to face without melting to form one-dimensional columns due to the strong π–π interaction. Accordingly, they show columnar liquid crystalline phases. In the columnar liquid crystalline phase, charge carriers move so easily in the column that excellent one-dimensional charge transport can be obtained. Thus, the Pc-based discotic liquid crystals show excellent molecular orientation properties. Previously, we succeeded in synthesizing Pc-based discotic liquid crystal compounds showing very high carrier mobility comparable to amorphous silicon [8]. From these compounds with excellent solubility and molecular orientation, Pc-based discotic liquid crystals have been studied for application to organic semiconductors [9–16].

However, there are still two further problems for the application to solar cells. One of them is the absorption wavelength problem. Until now, Pc derivatives could absorb light with a wide wavelength in the ultraviolet-visible range up to about 700 nm, but could not absorb light in the near-infrared region around 1000 nm. The sunlight shining on the ground contains extremely wide range of wavelengths of light from ultraviolet, visible to near infrared. Therefore, we need a novel Pc-based discotic liquid crystal compound absorbing near infrared light longer than 700 nm as well. Another problem is the energy level problem. Conventional Pc derivatives are used as donor materials in organic thin film solar cells. However, the HOMO level is somewhat high with respect to the LUMO level of the acceptor material. Hence, an efficient open circuit voltage has not been achieved. In order to solve this problem, it is necessary to raise the LUMO level of the acceptor material or lower the HOMO level of the Pc derivative of the donor material. However, there have been very few examples of acceptor materials [14–16] due to the difficulty of molecular design. On the other hand, many donor materials have been developed due to the easiness of molecular design [17, 18]. Therefore, it may be a better strategy that the HOMO level of the novel donor Pc derivatives would be lowered.

Accordingly, in order to solve these two problems, a novel Pc-based discotic liquid crystal is designed as follows. As a solution to the first problem, electron-donating substituents are introduced to the α-positions of the Pc ring (Fig. 1). This is because it has been reported that the absorption band shifts to a longer wavelength (= red-shift) by introducing electron-donating substituents such as alkoxy groups at the α positions on the Pc ring [19–23]. In this study, we also introduce alkoxy groups as the electron-donating substituent at the α positions. As a solution to the second problem, an electron-withdrawing substituent is introduced to the β positions of the Pc ring (Fig. 1). This is because it has been reported that lowering energy levels could be achieved by substituting sixteen fluorine atoms at both the α and β positions of the Pc ring or by substituting eight alkylsulfonyl groups at the β positions of the Pc ring [24–26]. In this work, we substitute eight chlorine atoms having electron-withdrawing property slightly weaker than both fluorine atoms and alkylsulfonyl groups at the β-positions, avoiding the HOMO level becoming too low.

According to the above-mentioned molecular design, we have synthesized a series of novel PcCu compounds, (α-CnO)8(β-Cl)2PcCu (4a–4d) (n = 6 (a), 8 (b), 10 (c) and 12 (d)), in this study. For comparison, we have also synthesized another series of PcCu compounds, (α-CnO)8PcCu (1a–1d) (n = 6 (a), 8 (b), 10 (c) and 12 (d)), substituted by the alkoxy groups only at the α-positions of the Pc ring. Furthermore, we have clarified the influence of chlorine atoms substituted at the β positions of Pc ring on mesomorphism, spectroscopic and electronic properties for these two series of PcCu derivatives.

RESULTS AND DISCUSSION

Synthesis

Synthesis of (α-CnO)8PcCu (1a–1d) (n = 6 (a), 8 (b), 10 (c) and 12 (d)). The synthesis of 1a–1d was carried out according to Scheme 1. As can be seen from this scheme, phthalonitrile derivatives 3a–3d were obtained in high yields (about 90%) by a Williamson etherification reaction from the starting material of 2,3-dicyanohydroquinone 2. The target compounds of (α-CnO)8PcCu (1a–1d) (n = 6 (a), 8 (b), 10 (c) and 12 (d)) could not be synthesized by the typical synthetic method for phthalocyanine metal complexes using metal salt and DBU. Therefore, the synthesis was carried out by another route of two steps: synthesis of a metal-free phthalocyanine derivative using the lithium method and then metallation of the metal-free phthalocyanine by a metal salt. In the first step using this lithium method, we noticed that the choice of solvent was very important. This is because the alkyl group (R2) in the alcohol R2-OH employed as the reaction solvent undergoes an unexpected substitution reaction on the alkoxy group (R1) at the α position of Pc ring. When synthesis of the (α–C10H13O)8PcCu derivative (1c) having decyloxy (C10H21O) groups at the α positions was carried
Scheme 1. Synthetic route for 1,4,8,11,15,18,22,25-octakisalkoxyphthalocyaninato copper(II) [abbreviated as (α-C₈O)₈PcCu (1a–1d)]. When the same length of long alkyl alcohol (R₂ = R₁) was adopted as the reaction solvent, only one target derivative, (α-C₈O)₈PcCu (1a–1d) could be successfully synthesized.

Fig 2. MALDI-TOF mass spectrum of a mixture of the multiproducts for the synthesis of the derivative (α-C₈O)₈PcCu (1c)

out by using pentanol (C₅H₁₁OH) as the reaction solvent, a mixture of the products were unexpectedly obtained. Figure 2 shows the MALDI-TOF mass spectrum for these mixed products. As can be seen from the spectrum, the molecular weight (1826) of the target PcCu compound (α-C₈O)₈PcCu (1c) could not be observed, whereas five different products were obtained. Their molecular weights were 1758, 1688, 1618, 1548 and 1478. The
highest molecular weight of 1758 was consistent with the molecular weight of the compound \((\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) substituted by seven decyloxy chains and one pentoxy chain. The other molecular weights of 1688, 1618, 1548 and 1478 correspond to the products having the ratios of \(R_1 : R_2 = 6 : 2, 5 : 3, 4 : 4\) and \(3 : 5\), respectively. The difference among these molecular weights is 70 each. This value 70 is equal to the difference between the molecular weights of the decyloxy group \((C_{10}H_{20}O = 157)\) and the pentoxy group \((C_5H_{10}O = 87)\). A similar example was reported in 2004 [24]. Therefore, in order to prepare only one desirable target compound by the lithium method while avoiding such undesirable mixed products, the alkyl alcohol \((R_2-OH)\) and the alkoxy substituent in the phthalonitrile derivative should have the same length \((R_2 = R_1)\). When the same length of long alkyl alcohol \((R_2 = R_1)\) was adopted as the reaction solvent, we have successfully synthesized only one target derivative, \((\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) Cu \((1a–1d)\) \((n = 6 (a), 8 (b), 10 (c) and 12 (d))\).

**2-1-2 Synthesis of \((\alpha-C_6O_3)_{(\beta-Cl)}\) PCu \((4a–4d)\)** \((n = 6 (a), 8 (b), 10 (c) and 12 (d))\). Synthesis of \((\alpha-C_6O_3)_{(\beta-Cl)}\) PCu \((4a–4d)\) was carried out according to Scheme 2. As can be seen from this scheme, 2,3-dichloro-5,6-dicyano-1,4-hydroquinone \((6)\) was obtained by reduction of 2,3-dichloro-5,6-dicyano-p-benzoquinone \((5)\) with sodium hydrosulphite. The yield was as high as 80.6%. Since 4,5-dichloro-3,6-dialkoxyphthalonitrile \((7a–7d)\) could not be synthesized by Williamson etherification reaction, it was synthesized using Mitsunobu reaction. The target Pc compounds \((\alpha-C_6O_3)_{(\beta-Cl)}\) PCu \((4a–4d)\) could be synthesized in around 20% yields by the DBU method, unlike the previous Pc compounds \((\alpha-C_6O_3)_{(\beta-Cl)}\) PCu \((1a–1d)\).

Table 1 summarizes the elemental analysis data, MALDI-TOF mass spectral data and yields of \((\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) PCu \((1a–1d)\) and \((\alpha-C_6O_3)_{(\beta-Cl)}\) PCu \((4a–4d)\). Table 2 lists up the UV-Vis spectral data of \(1a–1d, 4a–4d\) and \((\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) PCu in chloroform. From Tables 1 and 2, it was confirmed that these Pc derivatives were successfully synthesized.

**Phase transition behavior**

Table 3 summarizes the phase transition temperatures and enthalpy changes of the present PcCu derivatives, \((\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) Cu \((1a–1d)\) and \((\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((4a–4d)\). As can be seen from this table, each of the derivatives \((\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) Cu \((1a–1d)\) is crystalline \((K)\) at rt, and the \(K\) phase directly melts into isotropic liquid \((IL)\) without showing mesomorphism. On the other hand, each of the chlorine-substituted PcCu derivatives \((\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((4a–4d)\) shows plural phase transitions up to \(IL\), and the longer chain-substituted derivatives \(4c–4d\) \((10 (c) and 12 (d))\) show a rectangular ordered columnar \((Col_{sac}(P2m))\) mesophase. For both series of PcCu derivatives, the transition temperature to \(IL\) \((i.e., mp\) or \(cp)\) of the PcCu derivatives \(4a–4d\) substituted by chlorine atoms are much higher than those of the PcCu derivatives \(1a–1d\) as follows:

\[(\alpha-C_6O_3)_{(\alpha-C_6O_5)}\) Cu \((1a)\): \(mp = 112.1\ °C \rightarrow (\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((4a)\): \(mp = 269.6\ °C\).

\[(\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((1b)\): \(mp = 79.8\ °C \rightarrow (\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((4b)\): \(mp = 192.7\ °C\).

\[(\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((1c)\): \(mp = 66.1\ °C \rightarrow (\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((4c)\): \(cp = 134.3\ °C\).

\[(\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((1d)\): \(mp = 53.1\ °C \rightarrow (\alpha-C_6O_3)_{(\beta-Cl)}\) Cu \((4d)\): \(cp = 79.8\ °C\).

Since the large chlorine atoms substituted at the \(\beta\) positions may act as a steric hindrance, the transition temperatures to \(IL\) of the derivatives \(4a–4d\) are expected to lower in comparison with those of the derivatives \(1a–1d\), but contrary to our expectation the temperatures rise significantly. It may be attributed to additional forces of halogen–hydrogen bond, halogen–oxygen bond, halogen–halogen bond, etc. between the upper and lower Pc disks [27–29].
### Table 1. Elemental analysis data, MALDI-TOF mass spectral data and yields of (1a–1d) and (4a–4d)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. formula (Mol.wt)</th>
<th>Elemental analysis: Found (Calcd.) (%)</th>
<th>Exact mass calculated</th>
<th>Exact mass observed</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>1a: (α-C₈O)₈PcCu</td>
<td>C₈₀H₁₁₂CuN₈O₈ (1377.37)</td>
<td>69.66 (69.76)</td>
<td>8.14 (8.20)</td>
<td>8.31 (8.14)</td>
<td>1376.80 (M+H)</td>
</tr>
<tr>
<td>1b: (α-C₁₀O)₈PcCu</td>
<td>C₉₆H₁₄₄CuN₈O₈ (1601.80)</td>
<td>71.77 (71.98)</td>
<td>9.00 (9.06)</td>
<td>7.13 (7.00)</td>
<td>1601.05 (M+H)</td>
</tr>
<tr>
<td>1c: (α-C₁₀O)₈PcCu</td>
<td>C₁₁₂H₁₇₆CuN₈O₈ (1826.23)</td>
<td>73.69 (73.66)</td>
<td>9.75 (9.71)</td>
<td>5.82 (6.14)</td>
<td>1825.34 (M+H)</td>
</tr>
<tr>
<td>1d: (α-C₁₂O)₈PcCu</td>
<td>C₁₂₈H₂₀₈CuN₈O₈ (2050.67)</td>
<td>74.59 (74.97)</td>
<td>10.45 (10.22)</td>
<td>5.33 (5.46)</td>
<td>2048.54 (M+H)</td>
</tr>
<tr>
<td>4a: (α-C₈O)₈(β-Cl)₈PcCu</td>
<td>C₈₀H₁₀₄Cl₈CuN₈O₈ (1652.91)</td>
<td>58.29 (58.13)</td>
<td>6.58 (6.34)</td>
<td>7.03 (6.78)</td>
<td>1648.49 (M+H)</td>
</tr>
<tr>
<td>4b: (α-C₁₀O)₈(β-Cl)₈PcCu</td>
<td>C₉₆H₁₃₆Cl₈CuN₈O₈ (1877.34)</td>
<td>61.79 (61.42)</td>
<td>7.49 (7.30)</td>
<td>5.91 (5.97)</td>
<td>1873.74 (M+H)</td>
</tr>
<tr>
<td>4c: (α-C₁₀O)₈(β-Cl)₈PcCu</td>
<td>C₁₁₂H₁₆₈Cl₈CuN₈O₈ (2101.77)</td>
<td>64.33 (64.00)</td>
<td>7.69 (8.06)</td>
<td>5.53 (5.33)</td>
<td>2096.99 (M+H)</td>
</tr>
<tr>
<td>4d: (α-C₁₂O)₈(β-Cl)₈PcCu</td>
<td>C₁₂₈H₂₀₀Cl₈CuN₈O₈ (2326.17)</td>
<td>66.46 (66.09)</td>
<td>8.84 (8.67)</td>
<td>4.47 (4.82)</td>
<td>2321.24 (M+H)</td>
</tr>
</tbody>
</table>
Table 2. UV-Vis spectral data of 1a–1d, 4a–4d and (β-C₈O)₈PcCu in chloroform

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration*¹ (×10⁻⁶ mol L⁻¹)</th>
<th>λₘₐₓ(nm) (log ε)</th>
<th>Q₀–₁-Band</th>
<th>Aggregation band*²</th>
<th>Q₀–₀-Band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Solet-Band</td>
<td>Q₀–₀-Band</td>
<td>Aggregation band*²</td>
<td>Q₀–₁-Band</td>
</tr>
<tr>
<td>1a: (α-C₆O)₈PcCu</td>
<td>3.96</td>
<td>330.3 nm (4.80)</td>
<td>—</td>
<td>458.7 nm (4.12)*⁴</td>
<td>672.5 nm (4.64)</td>
</tr>
<tr>
<td>1b: (α-C₈O)₈PcCu</td>
<td>4.00</td>
<td>329.6 nm (4.80)</td>
<td>—</td>
<td>459.3 nm (4.10)*⁴</td>
<td>673.0 nm (4.64)</td>
</tr>
<tr>
<td>1c: (α-C₁₀O)₈PcCu</td>
<td>4.03</td>
<td>329.7 nm (4.80)</td>
<td>—</td>
<td>458.5 nm (4.11)*⁴</td>
<td>672.7 nm (4.63)</td>
</tr>
<tr>
<td>1d: (α-C₁₂O)₈PcCu</td>
<td>4.01</td>
<td>330.4 nm (4.81)</td>
<td>—</td>
<td>458.5 nm (4.15)*⁴</td>
<td>673.4 nm (4.65)</td>
</tr>
<tr>
<td>4a: (α-C₆O)₈(β-Cl)₈PcCu</td>
<td>4.01</td>
<td>323.9 nm (4.73)</td>
<td>351.0 nm (4.73)*³</td>
<td>420.2 nm (4.26)*³</td>
<td>662.0 nm (4.68)</td>
</tr>
<tr>
<td>4b: (α-C₈O)₈(β-Cl)₈PcCu</td>
<td>4.03</td>
<td>323.6 nm (4.73)</td>
<td>351.1 nm (4.72)*³</td>
<td>420.4 nm (4.23)*³</td>
<td>662.2 nm (4.68)</td>
</tr>
<tr>
<td>4c: (α-C₁₀O)₈(β-Cl)₈PcCu</td>
<td>3.99</td>
<td>324.0 nm (4.72)</td>
<td>350.7 nm (4.72)*³</td>
<td>420.2 nm (4.23)*³</td>
<td>661.7 nm (4.67)</td>
</tr>
<tr>
<td>4d: (α-C₁₂O)₈(β-Cl)₈PcCu</td>
<td>4.01</td>
<td>324.1 nm (4.73)</td>
<td>351.2 nm (4.73)*³</td>
<td>420.3 nm (4.27)*³</td>
<td>662.0 nm (4.67)</td>
</tr>
<tr>
<td>(β-C₁₈O)₈PcCu</td>
<td>3.93</td>
<td>340.3 nm (4.88)</td>
<td>—</td>
<td>418.9 nm (4.51)*³</td>
<td>612.0 nm (4.61)</td>
</tr>
</tbody>
</table>

Polarized optical microscopic observations

Figure 3(a) shows a natural texture of \((\alpha\text{-}C_{10}O)_{8}(\beta\text{-}Cl)_{8}Cu\) \((4c)\) obtained at 131 °C by cooling from IL at a very slow cooling rate 1 °C/min. When the cover glass was pressed, it smoothly spread to show viscosity with birefringence. Therefore, this phase can be liquid crystalline, although the natural texture appears to be crystalline. Similarly, Fig. 3(b) shows a natural texture of \((\alpha\text{-}C_{12}O)_{8}(\beta\text{-}Cl)_{8}Cu\) \((4d)\) obtained at 70 °C by cooling from IL at the very slow cooling rate 1 °C/min. When the cover glass was pressed, it also smoothly spread to show viscosity with birefringence. Therefore, this phase can be also liquid crystalline.

Temperature-variable small angle X-ray diffraction measurements

To identify these liquid crystalline phases, we carried out temperature-variable small angle X-ray diffraction measurements. Figure 4 shows the X-ray diffraction patterns of (a) \((\alpha\text{-}C_{10}O)_{8}(\beta\text{-}Cl)_{8}Cu\) \((4c)\) at 123 °C and (b) \((\alpha\text{-}C_{12}O)_{8}(\beta\text{-}Cl)_{8}Cu\) \((4d)\) at 70 °C. The X-ray data are summarized in Table 4.

As can be seen from this table, \((\alpha\text{-}C_{10}O)_{8}(\beta\text{-}Cl)_{8}Cu\) \((4c)\) shows 11 reflections which coincide closely to the reflection values calculated from a two-dimensional rectangular lattice having lattice constants \(a = 23.3\ \text{Å},\ b = 20.6\ \text{Å}\) with P2m symmetry, except for the reflection at 13.5 Å identified as a stacking distance between dimers (2h). The stacking distance between monomers (1h) may be overlapped with the (2 3 0) reflection at 5.99 Å. This is because the stacking distance (1h) between the monomers

---

**Table 3. Phase transition temperatures and enthalpy changes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>(T^\circ\text{C} \ [\Delta H (\text{kJ mol}^{-1})])</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a : ((\alpha\text{-}C_{6}O)_{8}\text{PcCu})</td>
<td>K</td>
<td>112.1 [43.2]</td>
<td>I.L.</td>
</tr>
<tr>
<td>1b : ((\alpha\text{-}C_{6}O)_{8}\text{PcCu})</td>
<td>K</td>
<td>79.8 [59.5]</td>
<td>I.L.</td>
</tr>
<tr>
<td>1c : ((\alpha\text{-}C_{10}O)_{8}\text{PcCu})</td>
<td>K</td>
<td>66.1 [90.6]</td>
<td>I.L.</td>
</tr>
<tr>
<td>1a : ((\alpha\text{-}C_{12}O)_{8}\text{PcCu})</td>
<td>K</td>
<td>53.1 [72.6]</td>
<td>I.L.</td>
</tr>
<tr>
<td>4a : ((\alpha\text{-}C_{6}O)<em>{8}(\beta\text{-}Cl)</em>{8}\text{PcCu})</td>
<td>(K_1)</td>
<td>245.7 [7.2]</td>
<td>(K_2)</td>
</tr>
<tr>
<td>4b : ((\alpha\text{-}C_{6}O)<em>{8}(\beta\text{-}Cl)</em>{8}\text{PcCu})</td>
<td>(K_1)</td>
<td>54.2 [6.4]</td>
<td>(K_2)</td>
</tr>
<tr>
<td>4c : ((\alpha\text{-}C_{10}O)<em>{8}(\beta\text{-}Cl)</em>{8}\text{PcCu})</td>
<td>K</td>
<td>111.9 [2.3]</td>
<td>(\text{Col}_2(P2m))</td>
</tr>
<tr>
<td>4c : ((\alpha\text{-}C_{12}O)<em>{8}(\beta\text{-}Cl)</em>{8}\text{PcCu})</td>
<td>(K_1)</td>
<td>44.66 [22.2]</td>
<td>(K_2)</td>
</tr>
</tbody>
</table>

Phase nomenclature: Phase nomenclature: K = crystal, I.L. = isotropic liquid. Col\(_2\) = rectangular ordered columnar mesophase.

---

**Fig 3.** Photomicrographs of the Col\(_2\) (P2m) mesophases of (a) \((\alpha\text{-}C_{10}O)_{8}(\beta\text{-}Cl)_{8}\text{PcCu}\) \((4c)\) at 131 °C and (b) \((\alpha\text{-}C_{12}O)_{8}(\beta\text{-}Cl)_{8}\text{PcCu}\) \((4d)\) at 70 °C between cross polarizers. Left: natural textures obtained by slow cooling (1 °C/min) from IL. Right: showing viscosity with birefringence after pressing the cover glass.
in (α-C₁₀O)₈(β-Cl)₈Cu (4d) could be observed alone at 5.82 Å as described below. From these facts, it can be deduced that there is an equilibrium between monomers and dimers in the column. Thus, this liquid crystalline phase in 4c could be identified as a rectangular ordered columnar (Col₉(P2m) phase.

As can be seen from this table, another liquid crystalline phase in (α-C₁₀O)₈(β-Cl)₈Cu (4d) could also be identified as a Col₉(P2m) phase. In this phase, the stacking distance between the monomers (1h) could be observed alone at 5.82 Å. On the other hand, the stacking distance between dimers (2h) may be overlapped with the (1 1 0) reflection at 11.4 Å.

In these Col₉(P2m) phases of 4c and 4d, the stacking distance between the monomers (1h) appears at 5.99 Å and 5.82 Å, respectively. These values are somewhat longer than the stacking distance of a Col₉ phase generally observed in a region from 4 to 5 Å. It may be attributed to the bulky chlorine atoms at the β positions of Pc ring.

### Optical properties in solution

In order to investigate the aggregation behavior in a solvent, THF solutions were prepared for each of the derivatives 1a–1d and 4a–4d in four different concentrations (C) of 4.0 × 10⁻⁶ M, 6.0 × 10⁻⁶ M, 8.0 × 10⁻⁶ M and 10.0 × 10⁻⁶ M. Fig. 5 shows UV-Vis spectra of the representative derivatives 1a and 4a. As can be seen from this figure, each of the derivatives, 1a and 4a, shows sharp a Q-band located at 738 nm and 730 nm, respectively. The absorption maximum wavelength λ_max did not shift to be constant for all the concentrations. On the other hand, the absorbance (A) increased with

### Table 4. X-ray data of mesophases in 4c and 4d

<table>
<thead>
<tr>
<th>Compound (mesophase)</th>
<th>Lattice constants/Å</th>
<th>Spacing/Å</th>
<th>Miller indices (h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td></td>
</tr>
<tr>
<td>4c: (α-C₁₀O)₈(β-Cl)₈PcCu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Col₉ (P2m) at 123°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 23.3</td>
<td>23.3</td>
<td>23.3</td>
<td>(1 0 0)</td>
</tr>
<tr>
<td>b = 20.6</td>
<td>20.6</td>
<td>20.6</td>
<td>(0 1 0)</td>
</tr>
<tr>
<td>h = 5.99</td>
<td>15.9</td>
<td>15.4</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>Z = 0.99 for ρ = 1.20</td>
<td>13.5</td>
<td>—</td>
<td>(0 0 1)²</td>
</tr>
<tr>
<td>2h = 13.5</td>
<td>11.4</td>
<td>11.7</td>
<td>(2 0 0)</td>
</tr>
<tr>
<td>Z = 2.0 for ρ = 1.10</td>
<td>10.6</td>
<td>10.3</td>
<td>(0 2 0)</td>
</tr>
<tr>
<td></td>
<td>5.99</td>
<td>5.92</td>
<td>(2 3 0) + (0 0 1)³</td>
</tr>
<tr>
<td></td>
<td>4.39</td>
<td>4.44</td>
<td>(4 3 0)</td>
</tr>
<tr>
<td></td>
<td>4.06</td>
<td>4.06</td>
<td>(1 5 0)</td>
</tr>
<tr>
<td></td>
<td>3.62</td>
<td>3.64</td>
<td>(6 2 0)</td>
</tr>
<tr>
<td>4d: (α-C₁₂O)₈(β-Cl)₈PcCu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Col₉ (P2m) at 70°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 26.2</td>
<td>26.2</td>
<td>26.2</td>
<td>(1 0 0)</td>
</tr>
<tr>
<td>b = 20.6</td>
<td>20.6</td>
<td>20.6</td>
<td>(0 1 0)</td>
</tr>
<tr>
<td>h = 5.82</td>
<td>16.1</td>
<td>16.2</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>Z = 1.0 for ρ = 1.25</td>
<td>11.4</td>
<td>11.1</td>
<td>(2 1 0) + (0 0 1)²</td>
</tr>
<tr>
<td>2h = 11.4</td>
<td>8.69</td>
<td>8.74</td>
<td>(3 0 0)</td>
</tr>
<tr>
<td>Z = 2.0 for ρ = 1.25</td>
<td>5.82</td>
<td>—</td>
<td>(0 0 1)³</td>
</tr>
<tr>
<td></td>
<td>4.28</td>
<td>4.27</td>
<td>(4 3 0)</td>
</tr>
<tr>
<td></td>
<td>4.03</td>
<td>4.02</td>
<td>(6 2 0)</td>
</tr>
<tr>
<td></td>
<td>3.56</td>
<td>3.52</td>
<td>(7 2 0)</td>
</tr>
</tbody>
</table>
increasing concentration (C) and followed the Lambert–Beer’s rule \( (A = eCd; \text{ when } d = 1 \text{ cm}, A = eC; e:\text{ absorption coefficient}) \) showing an excellent linearity. Therefore, the absorption coefficients \( (e) \) were constant irrespective of the concentration. The other derivatives 1b–1d and 4b–4d also showed the same spectroscopic properties. From these results, it was revealed that neither series of the PcCu compounds, 1a–1d and 4a–4d, aggregates in THF and exists in the pure monomer form in the concentration range from \( 4.0 \times 10^{-6} \text{ M} \) to \( 10.0 \times 10^{-6} \text{ M} \) [22].

On the left side of Table 5, the absorption maximum wavelength \( \lambda_{\text{max}} \) (nm) and the absorption coefficient \( \log e \) of the Q-bands in the THF solutions of 1a–1d and 4a–4d at a concentration of \( 10.0 \times 10^{-6} \text{ M} \) are summarized. Comparing the Q-bands of 1a–1d, neither \( \lambda_{\text{max}} \) nor \( \log e \) changed with the alkoxy chain length. Similarly, no change was observed in 4a–4d. This means that the alkoxy chain length does not affect the absorption spectral properties in the non-aggregated solutions.

Next, we investigated the influence of chlorine atoms substituted at the \( \beta \)-positions of Pc ring substituted at the \( \beta \)-positions of the Pc ring causes a slight blue-shift by 8 nm. The \( e_{\text{max}} \) values of 1a and 4a are 185,000 and 225,000, respectively. The absorption coefficient \( e_{\text{max}} \) value of 4a was about 1.2 times higher than that of 1a. Thus, chlorine atoms substituted at the \( \beta \)-positions enhanced the absorption coefficient. Therefore, the phthalocyanine derivative 4a substituted by chlorine atoms at the \( \beta \)-positions can absorb light more efficiently.

1a and 4a in THF do not aggregate, as mentioned above. Therefore, the change of \( \lambda_{\text{max}} \) and \( e_{\text{max}} \) is attributable to the electronic state of the Pc ring substituted at the \( \beta \)-positions directly by electron-withdrawing chlorine atoms. The Q-band absorption edges in THF were estimated as 785 nm and 775 nm for 1a–1d and 4a–4d, respectively. From these estimated values, the bandgaps (\( E_g \)) of 1a–1d and 4a–4d could be calculated to be 1.57 eV and 1.59 eV, respectively, as listed in the middle part of Table 5.

It was of interest to compare the spectra of the THF solutions of the \((\alpha{-C}_6\text{O})_8\text{PcCu} \text{ (1a)}, (\beta{-C}_18\text{O})_8\text{PcCu} \text{ and} (\alpha{-C}_6\text{O})_8(\beta{-Cl})_8\text{PcCu} \text{ (4a). However, the THF solution of} (\beta{-C}_18\text{O})_8\text{PcCu could not be prepared because the} (\beta{-C}_18\text{O})_8\text{PcCu derivative was insoluble in THF. Since each of the derivatives is soluble in chloroform, we decided to compare the spectra of their chloroform solutions. Figure 7 summarizes the UV-vis spectra of these three chloroform solutions of} (\beta{-C}_18\text{O})_8\text{PcCu, 1a and} 4a.}

---

**Figure 5.** UV-vis spectra of the representative derivatives, (a) \((\alpha{-C}_6\text{O})_8\text{PcCu} \text{(1a)}\) and (b) \((\alpha{-C}_6\text{O})_8(\beta{-Cl})_8\text{PcCu} \text{(4a)}\), in THF at various concentrations.

---

**Figure 6.** UV-Vis absorption spectra of THF solution (10.0 \times 10^{-6} \text{ M}) for the representative derivatives, \((\alpha{-C}_6\text{O})_8\text{PcCu} \text{ (1a)}\) and \((\alpha{-C}_6\text{O})_8(\beta{-Cl})_8\text{PcCu} \text{ (4a). As can be seen from this figure, the} \lambda_{\text{max}} \text{ of the Q bands of} 1a \text{ and} 4a \text{ are located at} 738 \text{ nm and} 730 \text{ nm, respectively.}

---

**Figure 7.** Summary of the UV-vis spectra of the three chloroform solutions of \((\beta{-C}_18\text{O})_8\text{PcCu, 1a and} 4a.**
and 4a. As can be seen from this figure, the \( l_{\text{max}} \) (nm) of the Q-band of \((\alpha\text{-C}_18\text{O})_8\text{PcCu}\) was 680 nm. On the other hand, \( l_{\text{max}} \) (nm) of the Q-band of 4a and 1a were 741 nm and 756 nm, respectively. The Q-bands of 4a and 1a red-shifted greatly by 61 nm and 76 nm, respectively, compared with that of \((\alpha\text{-C}_18\text{O})_8\text{PcCu}\).

**Electrochemical measurements**

Figure 8 shows the cyclic voltammograms of the representative \((\alpha\text{-C}_6\text{O})_8\text{PcCu}\) (1a) and \((\alpha\text{-C}_6\text{O})(\beta\text{-Cl})_8\text{PcCu}\) (4a) in dichloromethane. Measurements were carried out using ferrocene as the reference compound. However, since the reduced wave could not be obtained, only the oxidized waves are shown in this figure.

As can be seen from Table 5, the derivatives 1a–1d and 4a–4d gave the half wave potential of the first oxidation \( E_{1/2} \) at -0.01 V and 0.38 V (vs. Fc*/Fc), respectively. Thus, the oxidation potentials of two series of the PcCu derivatives, 1a–1d and 4a–4d, are constant irrespective of the alkoxy chain length. It is compatible with our previous work [30] that the oxidation-reduction potentials of the dithiolene nickel complexes are constant irrespective of the chain length in the periphery.

Based on these first oxidation potential \( E_{1/2} \) obtained here, each of the HOMO levels was estimated. These values are summarized on the right side of Table 5. As can be seen from this table, the HOMO levels of \((\alpha\text{-C}_6\text{O})_8\text{PcCu}\) (1a–1d) and \((\alpha\text{-C}_6\text{O})(\beta\text{-Cl})_8\text{PcCu}\) (4a–4d) were -3.22 eV and -3.59 eV, respectively.

![Figure 6](image6.png)

**Fig. 6.** UV-vis spectra of \((\alpha\text{-C}_6\text{O})_8\text{PcCu}\) (1a) and \((\alpha\text{-C}_6\text{O})(\beta\text{-Cl})_8\text{PcCu}\) (4a) in THF at 10.0 × 10⁻⁶ M

![Figure 7](image7.png)

**Fig. 7.** UV-vis spectra of \((\alpha\text{-C}_6\text{O})_8\text{PcCu}\) (1a) (4.0 × 10⁻⁶ M), \((\alpha\text{-C}_6\text{O})(\beta\text{-Cl})_8\text{PcCu}\) (4a) (4.0 × 10⁻⁶ M) and \((\beta\text{-C}_18\text{O})_8\text{PcCu}\) (3.9 × 10⁻⁶ M) in chloroform

---

**Table 5. Optical and electrochemical properties of 1a–1d and 4a–4d**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optical properties*1</th>
<th>Electrochemical properties*3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption ( l_{\text{max}} ) (nm)</td>
<td>( \log \varepsilon )</td>
</tr>
<tr>
<td>1a: ((\alpha\text{-C}_6\text{O})_8\text{PcCu})</td>
<td>738 nm</td>
<td>5.28</td>
</tr>
<tr>
<td>1b: ((\alpha\text{-C}_8\text{O})_8\text{PcCu})</td>
<td>738 nm</td>
<td>5.28</td>
</tr>
<tr>
<td>1c: ((\alpha\text{-C}_{10}\text{O})_8\text{PcCu})</td>
<td>738 nm</td>
<td>5.28</td>
</tr>
<tr>
<td>1d: ((\alpha\text{-C}_{12}\text{O})_8\text{PcCu})</td>
<td>739 nm</td>
<td>5.24</td>
</tr>
<tr>
<td>4a: ((\alpha\text{-C}_6\text{O})(\beta\text{-Cl})_8\text{PcCu})</td>
<td>730 nm</td>
<td>5.37</td>
</tr>
<tr>
<td>4b: ((\alpha\text{-C}_8\text{O})(\beta\text{-Cl})_8\text{PcCu})</td>
<td>730 nm</td>
<td>5.37</td>
</tr>
<tr>
<td>4c: ((\alpha\text{-C}_{10}\text{O})(\beta\text{-Cl})_8\text{PcCu})</td>
<td>730 nm</td>
<td>5.37</td>
</tr>
<tr>
<td>4d: ((\alpha\text{-C}_{12}\text{O})(\beta\text{-Cl})_8\text{PcCu})</td>
<td>730 nm</td>
<td>5.37</td>
</tr>
</tbody>
</table>

*1 Determined in THF solution (concentration = 10 × 10⁻⁶ M). *2 \( E_g = h\nu/l_{\text{onset}} \).
*3 Determined in dichloromethane solution using a glassy carbon electrode. Concentration = 2 × 10⁻⁵ M containing 0.1 mol L⁻¹ NBu₄BF₄ as a supporting electrolyte. Oxidation voltammogram; scan rate = 0.05 V s⁻¹; T = 25°C.
*4 = vs. Fc*/Fc.
*5 LUMO = HOMO + \( E_g \).
*6 HOMO = -(4.80 + \( E_{1/2} \)).
Figure 9 illustrates the electronic properties of these two series of PcCu derivatives, 1a–1d and 4a–4d. As can be seen from this figure, when chlorine atoms are introduced to the β positions of the Pc ring, the LUMO and HOMO levels are lowered by 0.37 eV and 0.39 eV, respectively. Thus, we succeeded in stabilizing the HOMO level by introduction of chlorine atoms to the β position of the Pc ring.

CONCLUSION

We have synthesized a series of novel PcCu compounds, (α-CnO)8(β-Cl)8PcCu (4a–4d) (n = 6 (a), 8 (b), 10 (c) and 12 (d)) and, for comparison, another series of Pc compounds, (α-CnO)8PcCu (1a–1d) (n = 6 (a), 8 (b), 10 (c) and 12 (d)). The (α-CnO)8PcCu (1a–1d) derivatives are substituted by alkoxy chains only at the α positions. On the other hand, the (α-CnO)8(β-Cl)8PcCu (4a–4d) derivatives are substituted by alkoxy chains at the α positions and chlorine atoms at the β positions.

Very interestingly, 1a–1d having only alkoxy chains at the α positions of Pc ring show only one crystalline phase without showing a liquid crystalline phase. On the other hand, 4a–4d having chlorine atoms at the β positions show multiple phases, and the longer chain-substituted derivatives 4c–4d show a rectangular ordered columnar Colro(P2m) mesophase. When chlorine atoms were additionally substituted at the β positions of 1a–1d, the transition temperatures to IL of the (α-CnO)8(β-Cl)8PcCu derivatives 4a–4d significantly elevated, in comparison with the mother compounds (α-CnO)8PcCu 1a–1d. The Q-band of (β-C18O)8PcCu in THF was 680 nm, whereas the Q-bands of 4a and 1a were 741 nm and 756 nm, respectively. Thus, the Q-bands of 4a and 1a significantly red-shifted by 61 nm and 76 nm, respectively, compared

![Figure 8. CV plots of the representative derivatives in dichloromethane: (a) (α-C6O)8PcCu (1a); HOMO = -(4.8 + E1/2^oxi) = -4.79 eV and (b) (α-C6O)8(β-Cl)8PcCu (4a); HOMO = -(4.8 + E1/2^oxi) = -5.18 eV](image)

![Figure 9. Molecular structures and energy levels of 1 and 4](image)
with that of (β-C,20)PcCu. Moreover, from the UV-vis spectra and cyclic voltamograms, it was confirmed that the LUMO and HOMO levels of 4a–4d were significantly lowered by 0.37 eV and 0.39 eV, respectively, in comparison with those of 1a–1d. Thus, we successfully synthesized phthalocyanine derivatives 4a–4d showing an absorption band in the near-infrared region and lower HOMO levels than conventional phthalocyanine derivatives, according to our expectation.

**EXPERIMENTAL**

**Synthesis**

Two series of phthalocyanine copper (PcCu) complexes, (α-C,20)PcCu (1a–1d) and (α-C,20)β-(Cl)2Cu (4a–4d) \( (n = 6 \text{ a}, 8 \text{ b}, 10 \text{ c} \) and 12 \text{ d}) have been synthesized according to Schemes 1 and 2, respectively. These synthetic methods were referred to from previously reported literatures \[21, 22, 31–35\]. The starting materials of 2,3-dicyanohydroquinone (2) and 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (5) were purchased from Tokyo Chemical Industry or Wako Pure Chemical Industries. All the reactions were carried out under nitrogen atmosphere. The detailed manners are described below only for the representative compounds, 3c, 6, 7c, 1c and 4c.

**3,6-Didecyloxyphthalonitrile (Scheme 1: 3c).** Into a three-necked flask, 2,3-dicyanohydroquinone (2: 600 mg, 3.75 mmol), K2CO3 (2.10 g, 15.2 mmol) and DMF (6 ml) were placed and heated with stirring at 100°C. After 10 min, 1-bromomdecane (2.15 g, 19.74 mmol) was added and stirred at 100°C for 4 h. The reaction mixture was cooled down to rt and then extracted with a mixture solution of ethyl acetate and n-hexane \( (v/v = 1/1) \) and washed with water. The organic layer was dried over Na2SO4 overnight, filtered, and evaporated the solvents under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane, RF = 0.83) and then recrystallization from a mixture solvent of ethyl acetate and n-hexane twice to afford 1.55 g of white crystals. Yield: 93.8%. mp: 141.5°C/lit. 142°C [36]. 1H NMR (CDCl3, TMS): δ [ppm]: 7.15 (2H, s, Ar-H), 4.07 (4H, t, J = 6.6 Hz, -OCH2), 1.84 (4H, q, J = 7.0 Hz, -CH2), 1.50 (4H, q, J = 7.3 Hz, -CH2), 1.18–1.38 (24H, m, -CH2), 0.91 (6H, t, J = 6.8 Hz, -CH3).

(α-C,20)PcCu (Scheme 1: 1c). The reaction setup was shielded from light. Into a three-necked flask, an excessive amount of finely chopped lithium was placed and then C5H12OH (2.5 mL) was added thereto. The mixture was heated and stirred at 100°C. After confirming that the lithium was dissolved, 3,6-didecyloxyphthalonitrile (3c: 400 mg, 908 µmol) was added and heated up to 150°C. Immediately, the reaction solution turned green. The reaction mixture was held at 150°C for 30 min and then cooled down to rt. To the reaction solution, acetic acid (20 mL) and glacial acetic acid (1 mL) were added and stirred. The solution turned purple to give precipitations. After stirring for more 20 min, the resulting purple crystals were collected by filtration. The crystals prepared above, Cu(OAc)2·H2O (181 mg, 908 µmol) and THF (10 mL) were placed in a three-necked flask, and the mixture was heated with stirring at 50°C for 3 h. After cooling to rt, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (alumina; chloroform: n-hexane = 2: 1, RF = 0.78) to afford dark green crystals (55.1 mg). Yield: 13.8%. Elemental analysis and MALDI-TOF mass data: See Table 1. UV-Vis spectral data: See Table 2. Phase transition behavior: See Table 3.

**2,3-Dichloro-5,6-dicyano-1,4-hydroquinone (Scheme 2: 6).** Into a three-necked flask, 2,3-dichloro-5,6-dicyano-p-benzoquinone (5: 2.50 g, 11.0 mmol) and toluene (30 mL) were placed and stirred at rt. Subsequently, Na2S2O3 (3.38 g, 19.4 mmol) was added and stirred at rt for 30 min. The resulted precipitates were collected by suction filtration and washed with water and n-hexane to afford gray powder (2.03 g). Yield: 80.6%. IR: (KBr)/cm–1: 3237, 2253, 1574, 1360, 1276, 1191, 1075, 887, 776, 746, 689.

**4,5-Dichloro-3,6-didecyloxyphthalonitrile (Scheme 2: 7c).** Into a three-necked flask, 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (6: 500 mg, 2.18 mmol) and 1-decanol (1.26 g, 7.96 mmol), triphenylphosphine (1.92 g, 7.32 mmol) and dry THF (20 mL) were placed. The mixture was stirred at rt. After the reaction vessel was immersed in an ice bath to cool the solution, a solution of disopropyl azodicarboxylate (1.67 g, 8.26 mmol) in dry THF (10 mL) was added dropwise taking over 30 min. After completion of the dropping, it was warmed to rt without the ice bath and stirred at rt for 20 h. When the solvent was evaporated from the reaction solution under reduced pressure, a reddish brown viscous liquid was obtained. When diethyl ether was added to this viscous liquid, triphenylphosphine oxide was precipitated. The precipitates were removed by filtration. The filtrate was evaporated to remove the solvent under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane, RF = 0.75) and dried in vacuo to give white crystals (855 mg). Yield: 77.1%. mp: 32.0°C.1H NMR (CDCl3, SO2, TMS): δ [ppm]: 4.20 (4H, t, J = 6.6 Hz, -OCH2), 1.79 (4H, q, J = 7.0 Hz, -CH2), 1.47 (4H, q, J = 7.2 Hz, -CH2), 1.26–1.35 (24H, m, -CH2), 0.87 (6H, t, J = 7.0 Hz, -CH3).

(C,10O)β-(Cl)2Cu (Scheme 1: 1c). Into a three-necked flask, 4,5-dichloro-3,6-didecyloxyphthalonitrile (7c: 150 mg, 0.294 mmol), CuCl2 (25.1 mg, 0.186 mmol) and 1-hexanol (5 mL) were placed and refluxed with stirring. When the raw materials were completely dissolved, three drops of DBU were added. After about 10 min, the reaction solution turned green. It was refluxed for an additional 6 h. After cooling to rt, methanol was added to the reaction solution to precipitate. The resulted precipitates were collected by filtration and...
washed in an order of methanol and ethanol. The crude product was purified by column chromatography (silica gel, dichloromethane: n-hexane = 1:7, Rf = 0.63) to give green solid (31.2 mg). Yield: 20.0%. Elemental analysis and MALDI-TOF mass data: See Table 1. UV-Vis spectral data: See Table 2. Phase transition behavior: See Table 3.

**Measurements**

The 1H-NMR measurements were carried out by using a Bruker Ultrashield 400 MHz. The MALDI-TOF mass spectral measurements were carried out by using a Bruker Daltonics Autoflex III spectrometer (matrix: dithranol and 9-nitroanthracene). The elemental analyses were performed by using a Perkin–Elmer Elemental Analyzer 2400. The elemental analysis data and MALDI-TOF mass spectral data are listed in Table 1. Electronic absorption (UV-vis) spectra were recorded by using a Hitachi U-4100 spectrophotometer. The UV-Vis spectral data are summarized in Table 2. Phase transition behavior of the present compounds was observed with a polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage and a Mettler FP-90 Central Processor, and a Shimadzu DSC-50 differential scanning calorimeter. The phase transition temperatures and enthalpy changes are listed in Table 3.

The mesophases were identified by using a small angle X-ray diffractometer (Bruker Mac SAXS System) equipped with our developed temperature-variable sample holder adopted a Mettler FP82HT hot stage. The setups of the SAXS system and the temperature-variable sample holder are illustrated in Figs S1 and S2, respectively. As can be seen from Fig. S1, the generated X-ray is bent by two convergence monochrometers to produce a point X-ray beam (diameter = 1.0 mm). The point beam runs through holes in the temperature-variable sample holder. As illustrated in Fig. S2, into the temperature-variable sample holder of the Mettler FP82HT hot stage, a glass plate (76 mm × 19 mm × 1.0 mm) with a hole (diameter = 1.5 mm) is inserted. The hole can be charged with a powder sample (ca. 1 mg). The measurable range is from 3.0 Å to 110 Å and the temperature range is from rt to 375 °C. This SAXS system is available for all condensed phases including fluid nematic phase and isotropic liquid. The X-ray data are listed in Table 4.

Cyclic voltammograms were recorded using an ALS/CH Instruments Model 600A electrochemical analyzer. Cyclic voltammetry was carried out for a 2 × 10^{-5} M solution of the PcCu derivative (1a–1d and 4a–4d) in dichloromethane, containing 0.1 M NBu4BF4 as supporting electrolyte. The reference electrode was Fe/Fe^{2+} and the working electrode was a glassy carbon. These optical and electrochemical data are summarized in Table 5.

**Supplementary information**

Figures S1 and S2 are given in the supplementary material. This material is available free of charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml

**REFERENCES**

Photophysical and photochemical properties of fluoroether-substituted zinc(II) and titanium(IV) phthalocyanines

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This paper is dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 27 November 2017
Accepted 18 December 2017

ABSTRACT: The synthesis and characterization of novel zinc(II) (1a–4a) and oxo-titanium(IV) (1b–4b) phthalocyanine derivatives bearing 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol groups are described for the first time. These phthalocyanines (1a–4a and 1b–4b) were characterized by elemental analysis and different spectroscopic techniques such as UV-vis, 1H NMR, FTIR and mass. Furthermore, the photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation) properties of these phthalocyanines were investigated in tetrahydrofuran (THF) solution. The influence of the number of the substituted groups (tetra or octa), position of the substituents (peripheral or non-peripheral) and central metal atom (zinc or titanium) on the photophysical and photochemical properties of these phthalocyanines were evaluated.

KEYWORDS: zinc phthalocyanine, titanium phthalocyanine, singlet oxygen, fluorescence, photodegradation.

INTRODUCTION

Phthalocyanines (Pcs) are one of the most important compounds in dyes and pigments industries due to their bright blue color. However current research is primarily concerned with the application of these compounds in optical recording [1], solar cells [2], chemical sensors [3], biosensors [4], non-linear optics [5], liquid crystal [6, 7] and photodynamic therapy (PDT) [8, 9]. Metallo-phthalocyanine (MPC) derivatives are photoactive and may be employed in photosensitization when a diamagnetic or non-transition metal is used as a central metal in the phthalocyanine cavity [10]. Nowadays, researchers are focused on the unique photophysical and photochemical properties of these compounds [11]. Although all transition metals can coordinate to Pc ligands, only a few of them can form highly photoactive complexes, such as titanium(IV) and zinc(II), owing to the closed shell nature of the electronic configuration of Ti(IV) or Zn(II) metal ions, similar to that of main group metal ions. The Pc complexes containing other transition metals usually show very short lifetime for their S1 and T1 states and they show very low fluorescence emission efficiency [12]. Oxo-titanium phthalocyanine [Ti(IV)OPc] complexes show rich spectroscopic and photophysical properties. For example, they are known to absorb light at longer wavelengths (>700 nm) compared to other MPC complexes [13].

Unsubstituted phthalocyanines are generally insoluble in organic solvents and this behavior limits their applications in different areas. The introduction of different types of substituents such as alkyl, alkoxy, phenoxy and macrocyclic groups into the peripheral or non-peripheral positions of the Pc ring enhances solubility [14]. Recently, MPCs substituted with fluorinated groups
are receiving a great deal of attention [15]. These phthalocyanines have been reported to show improved photosensitizer activity for PDT, and their properties have been compared to non-fluorinated derivatives [16, 17]. However, the study on the photochemical and photophysical properties of fluorinated MPC complexes is still very limited. Our previous papers focused on the synthesis and photophysical and photochemical properties of zinc phthalocyanines carrying various substituents [18, 19]. Although zinc(II) metal has been studied extensively as a central metal for PDT applications of phthalocyanine derivatives, less attention has been paid to phthalocyanine complexes containing titanium(IV) as a central metal. The effects of the zinc(II) and titanium(IV) central metals on the photophysical and photochemical properties of the phthalocyanines were evaluated in dimethylsulfoxide (DMSO), dimethylformamide (DMF) and tetrahydrofuran (THF) by Nyokong and co-workers [20]. Therefore, we reported the synthesis of ZnPc derivatives substituted with polyoxyethylene and benzyloxophenoxy groups on the peripheral and non-peripheral positions of the phthalocyanine ring for investigation of their PDT properties due to their interesting photophysical and photochemical properties [21, 22].

In this work, some novel zinc(II) and titanium(IV) phthalocyanines bearing four or eight fluoroether groups in peripheral and non-peripheral positions of the phthalocyanine ring were synthesized and characterized. The photophysical (fluorescence lifetimes and quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties of these phthalocyanines were determined in THF. The effects of the nature of the central metal (zinc or titanium), the number of the substituted groups (tetra or octa) and the position of the substituents (peripheral or non peripheral) on the photophysical and photochemical properties were also investigated.

RESULTS AND DISCUSSION

Synthesis and characterization

The phthalonitrile compound 1 was prepared by nucleophilic substitution of the nitro group in 3-nitrophthalonitrile with 1H,1H-nonafluoro-3,6-dioxahexan-1-ol. Other phthalonitrile compounds bearing fluoroether groups (2–4) (Scheme 1) were synthesized and purified

<table>
<thead>
<tr>
<th>Comp.</th>
<th>M</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
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<td>H</td>
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<td>H</td>
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<tr>
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<td>Zn(II)</td>
<td>H</td>
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<tr>
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<td>H</td>
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<td>H</td>
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<tr>
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<td>OCH3,CF3,OCF3,CF3,OCF3</td>
<td>H</td>
</tr>
</tbody>
</table>

Scheme 1. The synthesis route of the zinc(II) (1a–4a) and titanium(IV) (1b–4b) phthalocyanines

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according to the literature procedures [23]. The zinc(II) phthalocyanines 2a, 3a and 4a were also prepared and characterized according to previously reported procedures [23]. The novel zinc(II) phthalocyanine 1a and titanium(IV) phthalocyanines 1b, 2b, 3b and 4b were synthesized according to the reported methods [24]. All titanium(IV) phthalocyanines (1b, 2b, 3b and 4b) were prepared by the reaction of the fluoroether substituted phthalonitrile derivatives (1, 2, 3 and 4) in the presence of titanium(IV)n-butoxide and urea in 1-octanol at 155 °C for 7 h in a Schlenk tube.

The synthesized novel compounds were characterized by elemental analysis and different spectroscopic methods. While 1H NMR, FTIR, UV-vis and mass spectroscopic techniques were used for characterization of the compounds 1 and 1a, the titanium(IV) phthalocyanines (1b–4b) were only characterized by FTIR, UV-vis and mass spectroscopic methods because these phthalocyanines did not show enough solubility in deuterated solvents.

In the IR spectrum of the compound 1, the presence of an intense stretching peak at 2235 cm⁻¹ for C≡N group clearly indicates the formation of this compound. On the other hand, observation of the characteristic C–F peaks at 1184 and 1141 cm⁻¹ is a proof for substitution of the 1H,1H-nonfluoro-3,6-dioxahaheptan-1-ol groups to phthalonitrile. In addition, the strong peak belonging to O–C–O ether groups appeared at 1100 cm⁻¹. The observed C≡N stretching peak was completely disappeared after formation of the phthalocyanine ring.

The 1H NMR spectra of compounds 1 and 1a were recorded in acetone-d₆. The aromatic protons on the phthalonitrile benzene were observed at 7.98–9.95, 7.83 and 7.75–7.73 ppm for compound 1. The aliphatic CH₂ protons have resonances at a lower field (5.11 ppm) due to the highly electronegative behavior of the fluorine atoms on the neighboring carbon atoms. These protons were observed as triplet bands due to the interaction of these protons with neighboring fluorine atoms. The aromatic protons were shifted to 8.82, 8.13 and 7.92 ppm after formation of the phthalocyanine macrocycle. The aliphatic CH₂ protons were also observed at 5.14 ppm.

In the mass spectra of all compounds, the presence of the characteristic molecular ion peaks such as m/z: 408.01 for 1, 1698.08 for 1a, 1696.58 for 1b, 1696.84 for 2b, 1835.84 for 3b and 2816.48 for 4b as [M]+ confirmed the proposed structures of the synthesized compounds.

![Fig. 1. Electronic absorption spectra of (a) 1a–4a, (b) 1b–4b in THF. Concentration = 1.2 × 10⁻⁵ M](image)
Table 1. Absorption, excitation and emission spectral data for the studied phthalocyanines in THF

<table>
<thead>
<tr>
<th>Compound</th>
<th>Q band $\lambda_{\text{max}}$, (nm)</th>
<th>Log $\varepsilon$</th>
<th>Excitation $\lambda_{\text{Exc}}$, (nm)</th>
<th>Emission $\lambda_{\text{Em}}$, (nm)</th>
<th>Stokes shift $\Delta_{\text{Stokes}}$, (nm)</th>
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<td>695</td>
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<tr>
<td>2a</td>
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<td>5.21</td>
<td>670</td>
<td>680</td>
<td>10</td>
</tr>
<tr>
<td>3a</td>
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<tr>
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<td>710</td>
<td>718</td>
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</tr>
<tr>
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<td>695</td>
<td>706</td>
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<td>666</td>
<td>673</td>
<td>7</td>
</tr>
</tbody>
</table>

*Data from Ref. [29].

The elemental analysis results of the newly synthesized compounds also confirmed the structures of target compounds.

**Ground state electronic absorption and fluorescence spectra**

The electronic absorption spectra of the studied zinc(II) (1a–4a) and titanium(IV) (1b–4b) phthalocyanine complexes showed intense Q band absorptions (Fig. 1) in THF which is typical for non-aggregated metallophthalocyanine complexes [25]. The Q band absorption maxima of the studied phthalocyanines (1a–4a and 1b–4b) in THF are supplied in Table 1. Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, variety of the substituents, complexed metal ions and temperature [26]. In the aggregation state, the electronic structures of the complexed phthalocyanine rings are perturbed, resulting in alternation of the ground and excited state electronic structures [27].

In this study, the aggregation behavior of the zinc(II) and titanium(IV) phthalocyanine derivatives (1a–4a and 1b–4b) were investigated at different concentrations in THF. The Beer–Lambert law was followed for all of studied phthalocyanines at concentration ranging from $1.2 \times 10^{-5}$ to $2.0 \times 10^{-6}$ M. As the concentration increased, the intensity of absorption of the Q-band also increased and there were no new bands related to the aggregated species [28]. (Figs S1–S4 for 1a–4a and Figs S5–S8 for 1b–4b).

**Fluorescence quantum yields and lifetimes**

All studied zinc(II) (1a–4a) and titanium(IV) (1b–4b) phthalocyanines showed similar fluorescence behavior in THF. The absorption, fluorescence emission and excitation spectra were given in Fig. 2 for phthalocyanines 1a and 1b. These spectra for the rest of the phthalocyanines are given in supporting information (Figs S9–S11 for 2a–4a and Figs S12–S14 for 2b–4b). The similarity of the Q-band absorption and the fluorescence excitation spectra for all studied phthalocyanines suggests that the nuclear configurations of the ground and excited states were similar. This means these phthalocyanines did not decompose by excitation in THF. The peak maxima of the fluorescence emission and excitation spectra of the studied compounds (1a–4a and 1b–4b) are listed in Table 1. While the fluorescence emission peaks were observed between 668 and 686 nm for zinc(II) phthalocyanines, these peaks were observed at longer wavelengths between 690 and 716 nm for titanium(IV) phthalocyanine derivatives (Table 1). The observed Stokes shifts of all these phthalocyanines were typical of metallophthalocyanine complexes in THF. All corresponding 1H,1H-nonafluoro-3,6-dioxahexatann-1-ol substituted phthalocyanines showed longer emission wavelengths compared to unsubstituted zinc(II) phthalocyanine which used as a standard.

The fluorescence quantum yields ($\Phi_F$) of the studied phthalocyanines (1a–4a and 1b–4b) were determined in THF, and the obtained values are given in Table 2. The $\Phi_F$ values of all these phthalocyanines were lower than the standard unsubstituted zinc(IV) phthalocyanine in THF ($\Phi_F = 0.25$ in THF [29]). The newly synthesized zinc(II) phthalocyanine derivatives showed higher fluorescence quantum yield values ($\Phi_F = 0.21–0.23$) than titanium(IV) phthalocyanine derivatives ($\Phi_F = 0.10–0.18$), due to the variety of the central metal atom in the phthalocyanine cavity. The substitution of the 1H,1H-nonafluoro-3,6-dioxahexatann-1-ol groups on the non-peripheral position of the phthalocyanine ring gave higher $\Phi_F$ values ($\Phi_F = 0.23$ for 1a and 0.18 for 1b) than peripheral substitution of this group ($\Phi_F = 0.21$ for 2a and 0.12 for 2b). The number of the substituents slightly affects the fluorescence behavior of the studied phthalocyanines.
Fluorescence lifetime \( (\tau_F) \) refers to the average time a molecule stays in its excited state before it returns to its ground state by emitting. Many factors such as internal conversion, intersystem crossing, aggregation and the utilized solvent affect fluorescence lifetime of a photosensitizer [11]. The fluorescence lifetime values \( (\tau_F) \) of the synthesized phthalocyanine complexes \( (1a-4a \text{ and } 1b-4b) \) were measured by a time correlated single photon counting (TCSPC) method in THF solutions. Fluorescence lifetime spectra are given in Fig. 3 for compound \( 1a \) and \( 1b \) as an example in THF solution (the TCSPC spectra of the other phthalocyanines are supplied in Figs S15–S16). Table 2 shows the fluorescence lifetime values \( (\tau_F) \) of the studied zinc(II) \( (1a-4a) \) and titanium(IV) \( (1b-4b) \) phthalocyanines. While the \( \tau_F \) values of the substituted zinc(II) phthalocyanines \( (1a-4a) \) were lower than unsubstituted zinc(II) phthalocyanine \( (\text{Std-ZnPc}) \), these values were higher for titanium(IV) phthalocyanine.

Table 2. Photophysical and photochemical data for the studied phthalocyanines in THF

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Phi )</th>
<th>( \tau_F ) (ns)</th>
<th>( \Phi_d (\times 10^{-4}) )</th>
<th>( \Phi_s )</th>
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<td>2.95</td>
<td>3.90</td>
<td>0.46</td>
</tr>
<tr>
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<tr>
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<td>1.68</td>
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<tr>
<td>4a</td>
<td>0.22</td>
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<td>1b</td>
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<td>3.46</td>
<td>0.02\textsuperscript{a}</td>
<td>0.53\textsuperscript{b}</td>
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\textsuperscript{a}Data from Ref. [29].
\textsuperscript{b}Data from Ref. [32].
photophysics (1b–4b) than Std-ZnPc. The insertion of the titanium metal in the phthalocyanine cavity produced longer fluorescence lifetimes than complexation of the phthalocyanine macrocycle with zinc metal. The tetra-substitution of the 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol groups on the non-peripheral position of the phthalocyanine ring showed lower $t_F$ values ($t_F = 2.95$ ns for 1a and 3.85 ns for 1b) than substitution of this group on the peripheral position ($t_F = 3.23$ ns for 2a and 3.97 ns for 2b). Increasing of the number substituents increased the $t_F$ values from 3.23 ns to 3.35 ns for zinc(II) phthalocyanines and from 3.97 ns to 4.65 ns for titanium(IV) phthalocyanines.

**Singlet oxygen quantum yields**

Singlet oxygen is generated as a result of a bimolecular interaction between the triplet state of a photosensitizer and ground state (triplet) molecular oxygen and quantify as singlet oxygen quantum yield ($\Phi_\Delta$). The high efficiency of energy transfer between the excited triplet state of a photosensitizer and the ground state of oxygen generates large amounts of singlet oxygen.

In this study, the singlet oxygen quantum yields of the 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol substituted zinc(II) and titanium(IV) phthalocyanines were determined in THF by chemical methods using 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen quencher. The absorbance change of this quencher was monitored at 417 nm using a UV-vis spectrophotometer during the light which was irradiated by a photochemical set-up [30, 31]. Any change was observed in the Q band intensities of the studied phthalocyanines (1a–4a and 1b–4b) during the $\Phi_\Delta$ determinations, indicating that the used light irradiation (30 V) did not degrade the studied phthalocyanines (Fig. 4 for phthalocyanines 1a–1b and Figs S17–S22 for other studied phthalocyanines).

The $\Phi_\Delta$ values of the studied phthalocyanines (1a–4a and 1b–4b) and standard unsubstituted zinc (II) phthalocyanine are given in Table 2. All studied zinc(II) and titanium(IV) phthalocyanines showed lower $\Phi_\Delta$ values than standard zinc(II) phthalocyanine in THF. The zinc(II) phthalocyanines (1a–4a) produced higher singlet oxygen than titanium(IV) derivatives (1b–4b) due to the closed shell $d^{10}$ configuration of the zinc(II) metal. The $\Phi_\Delta$ values of the non-peripherally tetra-substituted phthalocyanines (1a and 1b) were found higher than the peripheral substituted derivatives (2a and 2b) in THF. The octa-substituted phthalocyanines (4a and 4b) showed slightly higher singlet oxygen generation than tetra-substituted counterparts (2a and 2b).

**Photodegradation studies**

Degradation of the molecules under light irradiation is determined their stability and this is especially important for those molecules intended for use in photocatalytical applications. The collapse of the absorption spectra without any distortion on the shape confirms formation of photodegradation instead of phototransformation of the phthalocyanine derivatives. Generally, phthalocyanine compounds exhibit optimal stability under the light irradiation.

The electronic absorption spectral changes for all studied phthalocyanines during light irradiation for determination of photodegradation are given in Fig. 5 for 1a–1b and Figs S23–S28 for other studied phthalocyanines. The shapes of the spectra were not deteriorated under light irradiation, only a reduction in the intensities of the B and Q bands were observed. It is confirmed that only degradation occurred under light irradiation during the photodegradation studies and no photo transformation was observed. The photodegradation quantum yield ($\Phi_d$) values of the
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phthalocyanine compounds in THF are presented in Table 2. The $\Phi_\alpha$ values of all studied compounds were found in the range of $10^{-4}$ and these values are higher than standard unsubstituted zinc(II) phthalocyanine. This means that all studied phthalocyanines (1a–4a and 1b–4b) showed less stability to degradation compared to unsubstituted zinc(II) phthalocyanine (ZnPc) due to addition of 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol groups on the phthalocyanine framework.

EXPERIMENTAL

Materials and equipment

The used materials, equipment, photophysical and photochemical parameters are given as Supplementary information. The phthalonitrile compounds 2, 3, 4 and the zinc(II) phthalocyanines 2a, 3a and 4a were also prepared and characterized according to the previously reported procedure [23].

Synthesis

3-{(2,2-Difluoro-2-[1,1,2,2-tetrafluoro-2(trifluoro-methoxy)ethoxy]ethoxy}phthalonitrile (1). 1H,1H-nonafluoro-3,6-dioxaheptan-1-ol (2.0 g, 7.1 mmol) was dissolved in absolute DMF (5 mL) under argon atmosphere and 3-nitrophthalonitrile (1.2 g, 7.1 mmol) was added to this solution. After stirring for 10 min, finely ground anhydrous potassium carbonate (1.77 g, 13.0 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at $60^\circ$C for 72 h. The solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with dichloromethane (3 $\times$ 10 mL). The combined extracts were treated first with sodium carbonate solution (5%),

Fig. 4. Electronic absorption spectral changes during singlet oxygen quantum yield determination in THF at a concentration of $1 \times 10^{-5}$ M (a) for phthalocyanine 1a and (b) for phthalocyanine 1b (Inset: DPBF absorbance vs. time)
then with water and dried over anhydrous sodium sulfate. Dichloromethane was removed under reduced pressure. The product was soluble in CH$_2$Cl$_2$, CHCl$_3$, acetone, MeOH and DMSO. Yield: 1.6 g (55%). FTIR (cm$^{-1}$): 3086 (aromatic CH), 2964 (aliphatic CH), 2235 (C≡N), 1588, 1474, 1457, 1397, 1285, 1230, 1184 (aliphatic CF), 1141, 1108 (O–C–O), 964, 903, 796. 1H-NMR (500 MHz, acetone-d$_6$) $d$, ppm: 7.98–7.95 (1H, d, $J_o = 7$ Hz, ArCH), 7.83 (1H, d, $J_o = 7$ Hz, ArCH). MS m/z (%): 408.01 [M]+. Calc. for C$_{13}$H$_5$F$_9$N$_2$O$_3$ (408.17): C 38.25; H 1.23; N 6.86%; Found: C 38.21; H 1.22; N 6.80%.

1(4),8(11),15(18),22(25)-Tetrakis{2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy}phthalocyaninato zinc(II) (1a). Compound 1 (0.5 g, 1.22 mmol), anhydrous Zn(CH$_3$COO)$_2$ (0.058 g, 0.30 mmol) and 0.24 mL DBU in 5 mL n-amyl alcohol were heated to 140°C for 7 h under an argon atmosphere in a round bottomed flask. After this time, the resulting green mixture was cooled to room temperature and the formed solid was filtered off. The crude product was purified by passing through a silica gel column using acetone and then THF as eluents. Yield: 0.174 g (33%), m.p. > 220°C. FTIR (cm$^{-1}$): 3075 (aromatic CH), 2961 (aliphatic CH), 1608 (C=O), 1587, 1489, 1402, 1337, 1278, 1223, 1177 (aliphatic CF), 1136, 1106 (O–C–O), 1074, 969. 1H-NMR (500 MHz, acetone-d$_6$) $d$, ppm: 8.82 (4H, b, ArCH), 8.13 (4H, b, ArCH), 7.92 (4H, b, ArCH), 5.14 (8H, t, CH$_2$). UV-vis (THF) $\lambda_{max}$ nm (log $\varepsilon$): 686 (5.36), 658 (4.61), 621 (4.58), 366 (4.72). MS (MALDI): m/z (%): 1698.08 [M]+. Calc. for C$_{52}$H$_{20}$F$_{36}$N$_8$O$_{12}$Zn (1698.15): C 36.78; H 1.19; N 6.60%; Found: C 36.70; H 1.16; N 6.58%.

1(4),8(11),15(18),22(25)-Tetrakis[2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy]phthalocyaninato oxo-titanium(IV) (1b). Compound 1 (0.5 g, 1.22 mmol), titanium(IV)n-butoxide (0.12 g, 0.35 mmol), urea (0.037 g, 0.61 mmol) and 0.3 mL
1-octanol were heated to 155°C for 7 h in a Schlenk tube. After this time, the resulting green suspension was cooled to room temperature, and the solid was filtered off and the product washed with n-hexane. The green crude product was purified by passing through a silica gel column using CH2Cl2:MeOH (100:1) mixed solvent as an eluent. Yield: 294 mg (57%). m.p. > 220°C. FTIR (cm⁻¹): 3071 (aromatic CH), 2957 (aliphatic CH), 1609, 1489, 1397, 1277, 1227, 1140 (aliphatic CF), 1110 (O–C–O), 1079, 970. UV-vis (THF) λmax nm (log ε): 716 (5.09), 684 (4.34), 645 (4.35), 356 (4.55). MS (MALDI): m/z (%): 1696.84 [M]+. Calc. for C52H20F36N8O13Ti (2816.83): C 36.79; H 1.16; N 6.57%. Found: C 36.78; H 1.19; N 6.60%. N 6.58%.

2(3),9(10),16(17)23(24)-Tetrakis[2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy]phthalocyaninato o xo-titanium(IV) (2b). Compound 2 (0.5 g, 1.23 mmol), titanium(IV) n-butoxide (0.12 g, 0.35 mol), urea (0.037 g, 0.61 mol) and 0.3 mL 1-octanol were heated to 155°C for 7 h in a Schlenk tube. After this time, the resulting green suspension was cooled to room temperature, the solid was filtered off and the product washed with n-hexane. The green crude product was purified by passing through a silica gel column using CH2Cl2:MeOH (100:1) mixed solvent as an eluent. Yield: 100 mg (19%). m.p. > 220°C. FTIR (cm⁻¹): 3060 (aromatic CH), 2896 (aliphatic CH), 1609 (C=N), 1483, 1397, 1283, 1227, 1181, 1140 (aliphatic CF), 1113 (O–C–O), 1083, 969. UV-vis (THF) λmax nm (log ε): 716 (5.07), 683 (4.35), 645 (4.35), 355 (4.54). MS (MALDI): m/z (%): 1696.84 [M]+. Calc. for C52H20F36N8O13Ti (2816.83): C 36.78; H 1.19; N 6.60%. Found: C 36.79; H 1.16; N 6.58%.

Octakis-2,9,16,23-chloro-3,10,17,24-[2,2-di fluoro-2-[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy]ethoxy]phthalocyaninato o xo-titanium(IV) (3b). Compound 3 (0.5 g, 1.13 mmol), titanium(IV) n-butoxide (0.11 g, 0.32 mmol), urea (0.037 g, 0.61 mol) and 0.3 mL 1-octanol were heated to 155°C for 7 h in a Schlenk tube. After this time, the resulting green suspension was cooled to room temperature, the solid was filtered off and the product washed with n-hexane. The green crude product was purified by passing through a silica gel column using CH2Cl2:MeOH (100:1) mixed solvent as an eluent. Yield: 285 mg (55%). m.p. > 220°C. FTIR (cm⁻¹): 3042 (aromatic CH), 2971 (aliphatic CH), 1607 (C=N), 1479, 1441, 1390, 1222, 1179, 1138 (aliphatic CF), 1110 (O–C–O), 1079, 963. UV-vis (THF) λmax nm (log ε): 694 (5.07), 668 (4.65), 627 (4.39), 350 (4.76). MS (MALDI): m/z (%): 1835.84 [M + H]+. Calc. for C72H26F72N8O25Ti (2816.83): C 30.70; H 0.93; N 3.98%. Found: C 30.65; H 0.90; N 3.97%.

CONCLUSIONS

In the present work, the syntheses of the peripherally tetra-(2a and 2b), non-peripherally tetra-(1a and 1b), peripherally chloro-octa-(3a and 3b) and octa-(4a and 4b) zinc(II) and o xo-titanium(IV) phthalocyanines substituted with 1H,1H-nonafluoro-3,6-dioxahexan-1-ol groups were described. The zinc(II) phthalocyanine derivatives (1a–4a) were characterized using different spectroscopic techniques such as UV-vis, 1H NMR, FTIR, mass and elemental analysis as well. However, the titanium(IV) phthalocyanines were only characterized by FTIR, mass and elemental analysis due to insufficient solubility of the titanium(IV) phthalocyanines for NMR measurements. Photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation) properties of all studied phthalocyanine derivatives were determined in THF and the results were compared with standard unsubstituted zinc(II) phthalocyanine. The effects of the variety of the central metal ion (zinc or titanium), the position of the substituents (peripheral or non-peripheral) and the number of the substituents (tetra or octa) on the photophysical and photochemical behavior were determined. Although the zinc(II) phthalocyanines (1a–4a) showed higher fluorescence (ΦF) and singlet oxygen quantum yields (ΦIO) and titanium(IV) phthalocyanines (1b–4b) showed longer fluorescence lifetimes in THF. The position of the substituents also affected the photophysical and photochemical properties of the studied phthalocyanines. The non-peripheral substitution of the 1H,1H-nonafluoro-3,6-dioxahexan-1-ol groups showed higher fluorescence quantum yield and they produced more singlet oxygen than peripheral substitution of these groups on the phthalocyanine macrocycle. Longer fluorescence lifetime values were obtained for the peripherally substituted phthalocyanines than non-peripheral derivatives. Increasing the number of the substituents also increased the photoactivity of the studied phthalocyanines. The octa-peripherally substituted phthalocyanines (4a and 4b) showed higher
fluorescence quantum yields, fluorescence lifetimes and singlet oxygen generation than their tetra-peripherally substituted counterparts (2a and 2b). It is suggested that the studied zinc(II) phthalocyanine derivatives (1a–4a) are more suitable photosensitzers for PDT applications because they showed approximately four times higher singlet oxygen than titanium(IV) counterparts (1b–4b).

Supplementary information

Additional information, including Figs S1–S23 are given in the supplementary material. This material is available free of charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml

Acknowledgments

The work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK).

REFERENCES


Pyrene containing liquid crystalline asymmetric phthalocyanines and their composite materials with single-walled carbon nanotubes

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 20 November 2017
Accepted 6 December 2017

ABSTRACT: In the present work we have studied the dispersion of single-walled carbon nanotubes in liquid crystalline asymmetrically substituted phthalocyanines (MPc, where M = Cu, Co, and 2H) bearing one pyrene and six polyoxy groups as side chains. The influence of single-walled carbon nanotubes on the phase behavior of MPcs was investigated using X-ray diffraction, polarized optical microscopy and differential scanning calorimetry. It was demonstrated that the incorporation of small amounts of single-walled carbon nanotubes (≤1 wt.%) does not alter the MPc mesophases. The structural features and the sensor response of composite thin films of MPc with single-walled carbon nanotubes to ammonia vapor (10–50 ppm) was studied and compared with those of the films of pure MPc derivatives.

KEYWORDS: liquid crystals, phthalocyanines, composite materials, carbon nanotubes, sensors.

INTRODUCTION

Metal phthalocyanines (MPc) and porphyrins coupled with different carbon nanomaterials are of great interest due to their ability to form long-lived charge separated states, which makes them useful for application in photonics and solar energy harvesting [1–4]. A combination of such important properties of carbon nanomaterials as their electrical conductivity and large surface area, together with the sensitivity and selectivity of phthalocyanines to different chemical analytes, provides an effective use of hybrids of these materials as active layers of chemical sensors [5, 6]. Among various metal phthalocyanines, liquid crystalline (LC) phthalocyanines with long alkyl substituents play significant role as active layers in different electronic devices including chemical sensors [7–9]. LC phthalocyanines form films with controllable alignment and ordering and the efficient overlap of π electron orbitals of neighboring phthalocyanine macrocycles in stacks provides anisotropic electronic transport channels along columnar axis [10, 11].

Hybrids and composites of carbon nanomaterials with phthalocyanines are known to be obtained in three different ways, namely by covalent and noncovalent functionalization [12–14] of carbon nanotubes (CNT) or graphene with phthalocyanine derivatives and by preparation of blends containing various ratios of these two components [15]. In the literature, hybrids are referred to as materials where the main component is a carbon nanomaterial (carbon nanotubes, graphene, etc.).
PYRENE CONTAINING LIQUID CRYSTALLINE ASYMMETRIC PHTHALOCYANINES AND THEIR COMPOSITE MATERIALS

while phthalocyanines are attached to them via π–π interaction or covalent bondings. Composites are said to be materials consisting of a phthalocyanine derivative as the main matrix, in which a small amount of a carbon nanomaterial is dispersed. Hybrids of carbon nanotubes and graphene with covalently and noncovalently attached to the metal phthalocyanine derivatives have been studied in the literature from different points of view [1, 13, 16, 17]. The use of hybrids of these materials for the development of chemiresistive sensors has been extensively studied in recent years [18–23]. In our recent publications, we studied sensor properties of hybrids of single walled carbon nanotubes (SWCNT) and reduced graphene oxide with symmetrically polyoxyethylene octasubstituted MPc (M = 2H, Zn, Cu, Co) and similar asymmetrically substituted ZnPc [5, 23]. Those hybrids were obtained by covalent and noncovalent attachment of the phthalocyanines to the carbon nanomaterials. At the same time, the studies of composite materials obtained by dispersion of small amounts of carbon nanomaterials in the MPc matrix, including distribution and alignment of CNTs in the matrix of liquid crystalline phthalocyanines, are rather scarce and were published in only a few papers using only one ZnPc derivative [15]. A blend of ZnPc bearing 16 long alkane moieties with fullerene C60 was produced to promote self-organization on a substrate surface [24]. In our recent work we studied the distribution of SWCNT in the ordered matrix of polyoxyethylene symmetrically substituted (B4 type) and pyrene containing asymmetrically substituted (AB3 type) zinc(II) phthalocyanine derivatives [15]. Pyrene groups were demonstrated to enhance the interaction of the phthalocyanine molecules with CNTs via π-stacking interactions. It was shown that the nature of the mesophases was not altered in these composites and the lateral conductivity of the films tends to increase with the increase of SWCNT concentration as additives. However, the sensing properties of such composites obtained by dispersion of small amounts of single-walled carbon nanotubes in liquid crystalline phthalocyanines were not studied at all.

In this work, we study the dispersion of single-walled carbon nanotubes in liquid crystalline asymmetrically substituted MPc (M = Cu, Co, 2H) phthalocyanines bearing one pyrene and six polyoxy groups as side chains (Fig. 1). The synthesis of MPc (M = Cu, Co, 2H) has been published in our previous work [6], however their liquid crystalline properties have not been described so far. LC properties of MPc (M = Cu, Co, 2H) and the influence of SWCNT on phase behavior of these MPc are investigated. The structural features and the sensor response of MPc/SWCNT composite thin films to ammonia vapor (10–50 ppm) are studied here for the first time and compared with those of the films of pure MPc derivatives.

EXPERIMENTAL

Synthesis

The synthesis of 2,3,9,10,16,17-hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) metal-free phthalocyanine (H2Pc), 2,3,9,10,16,17-hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyaninato copper(II) (CuPc) and 2,3,9,10,16,17-hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyaninato cobalt(II) (CoPc) has already been described elsewhere [6]. MPc/SWCNT dispersion was prepared by adding small amount (1 wt.%) of SWCNT (Sigma–Aldrich) to the phthalocyanine solutions in dichloromethane (Merck) and subjected to sonification for up to 2 h to enhance the nanotubes’ solubility. Thin films of the obtained composites were deposited by spin coating of their dispersion in dichloromethane onto the substrates for their further investigation.

Equipment

The phase transition behavior of MPcs was observed using a polarizing optical microscope (POM) (Leitz Wetzler Orthoplan-pol.) equipped with a hot stage (Linkam TMS 93) and a temperature controller (Linkam LNP). Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo Stare Thermal Analysis System heated at a rate of 10°C min⁻¹ in a nitrogen flow (50 mL·min⁻¹). Transition temperatures were determined at a scan rate of 10°C·min⁻¹ using a Mettler Toledo Star Thermal
Analysis System/DSC 822. The differential scanning calorimeter (DSC) system was calibrated with 3 mg indium samples under a nitrogen atmosphere. X-ray diffraction measurements (XRD) (Cu-Kα-radiation) were performed using a Bruker Advanced D8 diffractometer.

Optical absorption spectra in the UV-visible region were recorded with Shimadzu UV-vis-2101 spectrometer. Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with CCD detector in back-scattering geometry. The 488 nm, 40 mW line of an Ar-laser was used for the spectral excitation.

Scanning electron microscopy (SEM) images were obtained using a FEI-nova nanosem 200. Spectroscopic ellipsometry was used to determine the thickness of the films using a Woolam M-2000VTM rotating analyser spectroscopic ellipsometer in the spectral range of 400–800 nm.

Sensor properties study

The sensor response to low-concentrations of NH3 in the range 10–50 ppm was studied. Pure commercial NH3 gas was used as the NH3 source, while air was used for dilution and purging of NH3 gas. The injection of NH3 was carried out at the constant flow of air of 200 mL/min and the exposure time was fixed at 30 s for all films. MPcs and MPc/SWCNT composites were deposited as films by spin casting of their solutions in dichloromethane onto interdigitated Pt electrodes (DropSens, G-IDEPT10). The dimension of gaps is 10 μm; the number of digits is 125 × 2 with a digit length equal to 6760 μm; cell constant is 0.0118 cm−1. Electrical characterization of the films was carried out using a Keithley 236 electrometer by applying a constant dc voltage of 10 V. The thickness of the films as determined by spectral ellipsometry was about 20 nm.

RESULTS AND DISCUSSION

Liquid crystalline properties of MPc derivatives and MPc/SWCNT composites

The LC properties of MPcs and their binary mixtures with SWCNT (0.1–1 wt.%) were investigated by POM, thermal gravimetric analysis, DSC, and XRD at room temperature, and all these phthalocyanines displayed thermotropic columnar mesomorphism. Liquid crystalline textures typical for columnar discotic mesophases were observed both for MPcs and their composites with SWCNT (1 wt.%) (Fig. 2).

No changes of the texture were observed in the temperature range from room temperatures to the temperature of their decomposition. Decomposition temperatures were independently determined by TGA to be 250°C for all studied derivatives.

Figs 2a, 2c and 2e show typical mosaic textures of pure phthalocyanine derivatives. The textures of the MPc/SWCNT composites (Figs 2b, 2d, 2f) are noticeably different; inclusion of carbon nanotubes into the columnar matrix leads to an increase of the domains size. It is possible to suggest that SWCNTs dispersed in LC matrix can act as seeds for oriented domain growth as it was observed in the case of nematic liquid crystals [25–27].

In differential scanning calorimeter (DSC) measurements, CoPc, CuPc and H2Pc show transitions at about 55°C, 50°C and 49°C for all cooling cycles, respectively. However, no changes in the optical texture are observed on cooling the mesophase between two glass slides under POM. This can be attributed to the columnar structure being “frozen” in a glassy state [28, 29]. In addition, if the samples were prepared by evaporating a dichloromethane solution of these compounds on one glass slide, a mosaic texture typical for planar alignment was obtained at room temperature without annealing. It can be concluded that CoPc, CuPc and H2Pc show columnar structure at room temperature. POM measurements showed that these phthalocyanines transfer to the isotropic liquid state at around 250°C with partial decomposition. DSC measurements of the composites with SWCNT (1 wt.%) did not show any significant peak corresponding to any phase transition or to any glassy transition.

Identification of mesophases was performed by XRD measurements and the lattice constant (a) was calculated with d-spacing and Miller indices, hkl (1/d² = 4/(h² + k² + l²a²)); results are summarised in Table 1. Dichloromethane solutions of CoPc, CuPc, H2Pc and their composites were dropped onto glass slides and left for the solvent evaporation at room temperature. The XRD patterns of the studied samples contained reflections typical of a Col mesophase of substituted phthalocyanines [30]. The four Bragg reflections having reciprocal spacings of 1/√3:1/√4:1/√7, which are characteristics of a two-dimensional hexagonal lattice in the columnar mesophase, were observed. According to the low angle region of the XRD pattern, the mesophase could be established as a discotic hexagonal columnar (Colh) mesophase. In the wide angle region the compounds show diffused halos at 4.06 Å for CoPc, 4.10 Å for CuPc, 4.13 Å for H2Pc and at 4.12 Å, 4.13 Å, 4.18 Å (20 ~ 20°) for their composites, respectively, which are compatible with the disorder of paraffinic tails in the side chains [31–33].

Films characterization

The electronic absorption spectra of the solutions and films of H2Pc, CoPc and CuPc derivatives before and after heating are given in Fig. 3. Films of the MPc derivatives exhibit optical absorption spectra typical for most phthalocyanines [34]. The maxima of Q-bands attributed to the electron transitions from the HOMO a6 to LUMO...
Fig. 2. Polarized optical microscopy images of phthalocyanines (CoPc (a), CuPc (c) and H$_2$Pc (e) and their composites (CoPc/SWCNT-1% (b), CuPc/SWCNT-1% (d) and H$_2$Pc/SWCNT-1% (f))

Fig. 3. Optical absorption spectra of solutions (a, black curves) and films of H$_2$Pc, CoPc and CuPc derivatives (b, blue lines) as well as their hybrids containing 1% (c, red lines) of SWCNT

The Q-bands in the spectra of the H$_2$Pc, CoPc and CuPc films and their composites with SWCNT are blue shifted relative to the spectra of the corresponding solutions. Such shift of the Q-bands is indicative of the cofacial (face-to-face) arrangement of MPc molecules in the films, which is typical for many phthalocyanines forming Col mesophases [35, 36].

The SEM images of the composites (Fig. 4 shows CuPc/SWCNT as an example) demonstrate that their films have a layered structure consisting of SWCNT
nanotube bundles of 10–30 nm in diameter, wrapped by layers of liquid crystalline MPc molecules.

The orientation of MPc molecules in the films of MPc derivatives and their composites were studied by polarized Raman spectroscopy. The principles of this method for the investigation of molecular film orientation were described in details in our previous publications [37, 38]. This technique resides in estimation of the angle of molecule inclination relative to the substrate surface based on the measurements of the ratio of intensities of the bands for each symmetry type of vibrations in the Raman spectra measured in the parallel (Iii) and cross (Iij) polarizations of incident and scattering light. The phthalocyanine macrocycle is characterized by D4h group symmetry where A1g, B1g, B2g, Eg modes are Raman active. In contrast to the MPcs, the metal-free phthalocyanine (H2Pc) molecule is of D 2h symmetry. Therefore, in the present case the tilt angle should be estimated using the polarizability tensor for the D2h point group. However, this would introduce a third tensor element due to the additional twist between the benzene rings. Thus, we assumed that the polarizabilities of the H2Pc in x and y directions are the same. In other words, to simplify the calculations of the tilt angles, we treated the H2Pc as a molecule of D4h symmetry.

The nonpolarized Raman spectra of MPc films are given in Fig. 5a. The Raman spectra of films of the CuPc derivative and its composite deposited on glass substrates in parallel (ii) and cross (ij) polarizations are shown in Fig. 5b as an example. The intensities of the strongest lines with known symmetry types were measured (Fig. 5b). It has already been shown that there are no intensive bands belonging to organic substituents in the range from 300 to 1650 cm⁻¹ in the Raman spectra of substituted phthalocyanines due to the resonance character of the Raman spectra excited by the lasers of visible region [39].

The average values of Ii/Ij were 3.7, 3.6 and 1.4 for A1g, B1g and B2g modes in the Raman spectra of CuPc films, while in the case of the films of CuPc/SWCNT-1% composite these values were 3.9, 3.2 and 1.4. The angles of inclination of molecules relative to the substrate surface in the films of CuPc and CuPc/SWCNT-1% were calculated to be 85° and 82°, respectively. Similar data were also obtained for H2Pc, CoPc and their composites. Therefore, inclusion of carbon nanotubes into the columnar matrix of the MPcs does not lead to the change of LC properties of the investigated materials and the orientation of their films. As most of LC phthalocyanines the films of H2Pc, CoPc, CuPc and their composites with SWCNT have planar alignment [10].

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Sensor response of MPc and MPc/SWCNT composite films to ammonia

The sensor properties of thin films of MPc and MPc/SWCNT composites containing different amounts of SWCNT toward NH₃ (10–50 ppm) were studied using the chemiresistive method. The typical sensor responses $R_n$ ($R_n = (R - R_o)/R_o$, where $R_o$ is the resistance value at the beginning of an exposure/recovery cycle and $R$ is the resistance of the film at a certain NH₃ concentration) of the MPc films are shown in Fig. 6. All three derivatives exhibit strong and reversible sensor response to ammonia (10–50 ppm).

The sensor response value increases in the order H₂Pc < CuPc < CoPc. This order is in good agreement with the results obtained by Liang et al. [40] showing by the first-principle density functional theory that the central metals play a critical role in the sensitivity towards NH₃. To study the effect of incorporation of SWCNT into phthalocyanine matrix, the sensor response of the composites containing different amounts of carbon nanotubes was measured. $R_n$ of CoPc/SWCNT containing 0.1, 0.5, 0.75 and 1 wt.% SWCNT is given in Fig. 7 as an example. The dependence of the $R_n$ on ammonia concentration for MPc/SWCNT-1% (M = 2H, Cu, Co) is given in Fig. 8 in order to compare the effect of the central metal in the phthalocyanine macrocycle on the sensor response.

The sensor response value increases in the order H₂Pc/SWCNT < CuPc/SWCNT < CoPc/SWCNT which is similar to the case of pure MPc films.

It is worth mentioning that the film resistance decreases from $10^7$–$10^8$ Ω·m to about $10^5$ Ω·m with the addition of 1 wt.% of SWCNT. The increase of film conductivity makes it possible to use simple equipment for the conductivity measurements and does not require the employment of expensive electrometers for precision high resistance and low current measurements. However it is necessary to mention that the addition of SWCNT leads to the decrease of the relative sensor response of the composites compared to that of pure phthalocyanine films. Figure 7 shows that the more amount of SWCNT incorporated into the matrix of LC phthalocyanine the less relative sensor response to ammonia is observed.

![Fig. 4. SEM image (edge view) of CuPc/SWCNT-1% film](image)

![Fig. 5. Raman spectra of H₂Pc, CuPc and CoPc derivatives (a); polarized Raman spectra of CuPc and CuPc/SWCNT-1% films, measured in parallel (ii) and cross (ij) polarizations of incident and scattering light (b). The Raman bands labelled with an asterisk correspond to those overlapped with SWCNT modes](image)
CONCLUSIONS

The dispersion of single-walled carbon nanotubes in liquid crystalline asymmetrically substituted phthalocyanines MPc (M = Cu, Co, 2H) bearing one pyrene and six polyoxy groups as side chains was studied and their composite films were examined for ammonia detection. The influence of SWCNT on phase behavior of MPcs was investigated by XRD, polarized optical microscopy and differential scanning calorimetry. It was demonstrated that the incorporation of small amounts of SWCNT (0.1–1 wt.%) does not alter the MPc mesophases, nor does it change the orientation of their films. Both MPc derivatives and their composites with carbon nanotubes form Coli mesophases at room temperature. The chemiresistive sensor response of MPc/SWCNT composite thin films to ammonia vapor (10–50 ppm) was studied and compared with those of the films of pure MPc derivatives. The sensor response to ammonia of both MPc films and composite films increases in the order H2Pc < CuPc < CoPc. On the one hand, the film resistance decreases from $10^7$–$10^8$ Ω·m to about $10^5$ Ω·m with the addition of 1 wt.% of SWCNT, which makes it easier for the measurements without the need of expensive electrometers for precision high resistance measurements. On the other hand, the addition of SWCNT leads to a decrease of the relative sensor response of the composites compared to that of pure phthalocyanine films.

Acknowledgments

This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK, Project number: 111M699) and the basic project of the Nikolaev Institute of Inorganic Chemistry SB RAS.

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Structural, spectroscopic and passivation properties of a novel binuclear clamshell-type zinc(II) phthalocyanine as gate dielectric for OFET

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Dedicated to Prof. Kazuchika Ohta on the occasion of his retirement.

Received 21 November 2017
Accepted 8 December 2017

ABSTRACT: A novel clamshell-type binuclear zinc(II) phthalocyanine (2) was synthesized by cross condensation of the bisphthalonitrile (1) with 4-tert-butylphthalonitrile and zinc acetate in 1:10:4 ratio. The structure of the novel compound was characterized by elemental analysis, UV-vis, FT-IR (ATR), HR MALDI-TOF mass, 1H NMR, 13C DEPT NMR and 1H–1H COSY NMR methods. Applying electronic absorption spectroscopy and density functional theory (DFT) revealed that in THF the geometry of 2 is twisted to adopt an intermediate clamshell conformation in which the spacing between the Zn centers is about 8.1 Å, providing a very good account of the observed spectrum exhibiting the characteristic B (Soret) band at 347 nm and the Q band at 673 nm. In solution, 2 was found to exist in non-aggregated form. The calculated fluorescence quantum yields (ΦF = 0.23 in THF and 0.10 in DMF) were relatively reduced in comparison to that of std ZnPc. In particular, understanding of leakage current conduction mechanisms in gate dielectrics is crucial for the development of field effect transistors with improved device performance. Analysis of the reverse bias current–voltage data indicated that the origin of leakage current conduction mechanisms in clamshell-type zinc(II) phthalocyanine is Poole-Frenkel emission. The capacitance density of 12.7 nF cm⁻² at 5 Hz and 12.1 nF cm⁻² at 13 MHz was obtained with the FTO/Pc/Au sandwich structure.

KEYWORDS: clamshell, OFET, leakage current, capacitance density, DFT, phthalocyanine.

INTRODUCTION

Phthalocyanines (Pcs) as planar macrocyclic compounds with extended 18 π-electron conjugated systems are very appealing and versatile compounds for use in photodynamic therapy (PDT) of cancer [1], near-IR imaging agents [2], organic-based solar cells [3–6] and organic light emitting diodes (OLEDs) [7] because of their outstanding photophysical properties and remarkable chemical and thermal stability [8]. Their intense light absorption in the visible region with very high extinction coefficients and also their rich redox features make them very promising component for an artificial photosynthetic apparatus [9]. Their chemical flexibility allows the preparation of a large variety of related structures and, consequently, tailoring of physical, electronic, and optical properties, as well as improvement of their processability [3]. Multinuclear Pcs, like their monomeric symmetrical and unsymmetrical substituted Pc counterparts, have recently gained much attention because of their different and intriguing electrical, electrochemical, electrocatalytic, gas sensing and optical properties.
As a special class of phthalocyanine, binuclear phthalocyanine tweezers [12] which are linked by a covalent bridge can have specific electro- and photocatalytic properties [13]. The chemical and physical characteristic of these compounds vary with the nature of the bridging groups, which also determine the distance between the face to face Pc molecules, and the central metals [14, 15]. Therefore, many Pc dimers having various kinds of linkages have been reported to date. Among them, closed clamshell-type or cofacial binuclear Pcs usually show spectroscopic, electrochemical and electrical properties which differ significantly from the parent monomers [16, 17].

We have previously reported that the key precursor (I) readily forms ball-type binuclear MPcs (Fig. 1) [5]. These symmetrical binuclear ball-type Co(II), Cu(II) and Zn(II) complexes showed remarkable interactions between two Pc rings and metal centers. They also showed higher catalytic activity towards oxygen reduction in comparison to mononuclear Pcs. The electronic spectra of these MPcs, which show broad Q bands with low intensity, were attributed to molecular distortion (the Pc rings adopts a domed-shaped) of the Pc rings and were also due to aggregation in polar solvents [5]. It is worthy to note that the UV-vis spectra of clamshell-type Pcs are dependent on the polarity of the solvent and the distance between the macrocycles which adopt either an opened-clamshell, synonymously "anti" or a closed-clamshell conformations, synonymously "syn" cofacial configurations [18]. Because of unique spectroscopic, electrocatalytic and photocatalytic properties, and especially non-linear optical properties of covalently linked binuclear Pcs [19–21], and also because very little information is available about their applications we wish to report the synthesis and characterization of a novel slipped-cofacial zinc(II) phthalocyanine dimer. For the purpose of comparative study, we also performed DFT and TDDFT studies on 2 to shed light on the structural and spectroscopic properties of this compound, a ball-type binuclear symmetrical analog Zn₂Pc₂ having the same bridging moieties between the two Pc rings. Analyses and comparisons were performed on total electronic energies, relative stability energies, excitation wavelengths and HOMO–LUMO energy gaps of 2 in gas phase and in THF. The present study will be useful for understanding the relationship between the molecular structures and properties of covalently linked cofacial unsymmetrical and symmetrical binuclear phthalocyanine derivatives.

Although considerable improvements in some performance parameters (such as high carrier mobility and low operating voltage) of organic-based field effect transistors (OFETs), a lot of improvement is still needed for the production of commercially available OFETs. One of the most important parameters for an OFET is leakage current, which can be considered as an indicator of the density of charge traps at the dielectric-semiconductor interface. Thus far, various organic and inorganic materials such polyimides and cross-linked poly-4-vinyl phenols [22], strontium titanate [23, 24], HfO₂ [25], Al₂O₃ [26] aluminized Mylar® films covered by ultrathin SiO₂ layer [27], cross-linkable polymers based on blending of poly(methylmethacrylate) with 1,6-bis(trichlorosilyl)hexane [28], bilayers of PMMA–Ta₂O₅ [29] and conventional polymeric materials [30, 31], have been proposed and reported as promising gate dielectric materials for achieving significant OFET performance. In this work, the performance of the compound 2 as a gate dielectric in an organic field effect transistor was investigated and a field effect mobility value of 6.4 × 10⁻³ cm²/V·s was obtained.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of the clamshell-type binuclear Pc 2 is shown in Scheme 1. The preparation of the precursor 1 and the corresponding ball-type MPcs were reported by us earlier [5]. The clamshell dimer 2 was synthesized in a good yield by cross condensation of 1 with 4-tert-butylphthalonitrile and zinc acetate in the ratio of 1:10:4 under dry argon atmosphere.

The formation of 2 is evident by the disappearance of the characteristic sharp C≡N stretching band at 2232 cm⁻¹ which is present in both phthalonitriles. The
aromatic and aliphatic CH vibrations appear at 3061, 2952 and 2863 cm\(^{-1}\), respectively (Fig. S1). In the mass spectrum (HR MALDI-TOF) of 2, the observed major peak at \(m/z = 1808.601\) [M]\(^+\) (Fig. S2) clearly proves the predicted structure as depicted in Fig. 2.

The \(^1\)H NMR spectrum of 2 (Fig. S3) is consistent with the optimized structure. The Pc core protons \(H_1, H_2, H_3\) at the tert-butylbenzene sides, \(H_4, H_5, H_6\) at the linkage-benzene sides and \(H_7\) and \(H_8\) on the linker phenyl units were identified by the \(^1\)H–\(^1\)H COSY spectrum (Fig. 3). The doublets; \(H_1, H_2, H_4, H_5\) are observed in the aromatic region at 9.59–9.28 ppm, and \(H_3\) at 8.38 ppm. The \(H_6\) and \(H_7\) have very close chemical shifts and appear together at 7.94–7.83 ppm. The \(H_8\) is observed at 8.38 ppm as a multiplet. The \(\text{tert}-\)butyl protons labeled as \(H_9\) at 1.95 ppm together with the protons belonging to the linker \(H_{10}, H_{11}, H_{12}\) at 2.56–2.45 ppm, \(H_{14}\) at 1.49–1.40 ppm and \(H_{13}\) at 1.22 ppm are observed in the aliphatic region, comparable to those of the ball-type binuclear Zn.

Fig. 2. The optimized structure of 2 in THF. The hydrogen atoms were omitted for clarity.

Scheme 1. Synthesis of an unsymmetrical binuclear clamshell-type zinc(II)-phthalocyanine (2)
phthalocyanine [5]. The proton integral ratio and values are in good agreement with the proposed structure. The cross peaks of the $^1$H–$^1$H COSY spectrum shows the correlation between Pc core protons $H_{1,2} \leftrightarrow H_3$, $H_{4,5} \leftrightarrow H_6$, and the linker phenyl protons $H_7 \leftrightarrow H_{10,11}$, $H_{10,11,12} \leftrightarrow H_{10,11,12}$, $H_{10,11,12} \leftrightarrow H_{14}$ and $H_{10,11,12} \leftrightarrow H_{13}$. The $^{13}$C DEPT NMR spectrum of $2$ (Fig. 4) unambiguously confirms the molecular integrity and the purity of the compound. The tert-butyl methyl carbon atoms, labeled as $C_9$ are observed at 33.35 ppm. Five CH$_2$ carbon atoms on the linker are observed at 45.38–23.84 ppm and labeled as $C_{10}$, $C_{11}$ and $C_{14}$. The observed eight aromatic CH carbons between 131.31–120.65 ppm are attributed to the Pc core and the linker phenyl carbon atoms. The aliphatic CH carbon atoms attributable to the linker $C_{12}$ and $C_{13}$ are observed at 51.49–33.34 ppm. The quaternary carbon atoms of the Pc core ($C_a$, $C_b$, $C_c$, $C_d$, $C_e$ and $C_f$) and the linker phenyl units ($C_i$ and $C_j$) providing total number of six carbon atoms with different chemical environments are observed at 154.38–138.30 ppm. The aliphatic quaternary carbon atoms on the butyl carbon atom ($C_q$) and the carbon atom of the linker ($C_h$) are observed at 37.43 and 65.83 ppm, respectively.

Electronic absorption and fluorescence emission studies

The electronic absorption spectrum of $2$ is typical for metal phthalocyanine complexes with characteristic B and Q bands (Fig. 5). The electronic transitions for the main absorption bands are summarized in Table 1 to clarify the interactions between the two Pc cores and the linkages in $2$. The clamshell $2$ shows typical B and Q bands at 347 nm and 673 nm, respectively. Comparing to that of symmetrical ball-type binuclear zinc phthalocyanine (Fig. 1), the intensity of the Q band at 673 nm for $2$ is greatly enhanced, which indicates that it has comparatively less coupling than the ball-type one and almost no intermetallic interactions (Fig. 5). The pattern of the electronic spectrum of $2$ is similar to that of the
corresponding mononuclear analog and so-called “angled shell” binuclear phthalocyanines [32] or slipped-cofacial Pc dimers [15]. This provides a very good account of the optimized structure which shows that the most stable conformer in THF (Fig. S4) is a twisted closed-clamshell conformation. It should be pointed out that the observed spectrum may also indicate an equilibrium between the opened and closed conformations in solution [19, 32], since the relative energies of the conformers in THF are very close as listed in Table S1. When the polarity of the solvent was increased, in the present case by using DMF, the spectrum was not altered significantly but showed a
very small decrease in the intensity of the Q band which is very common to clamshell Pc dimers (Fig. S5).

The aggregation behavior of \(2\) was also investigated at different concentrations in THF (Fig. 5). As the concentration increases, the intensity of the absorption also increases and no new bands appear due to aggregation. Beer–Lambert’s law was obeyed for the entire compound in concentrations ranging from \(1.0 \times 10^{-5}\) to \(2 \times 10^{-6}\) M. These suggested that the coupling is intramolecular in nature [19]. The UV-vis absorption and fluorescence emission spectra of \(2\) were measured in THF, DMF, THF with 1% pyridine and DMF with 1% pyridine (\(C = 0.4 \times 10^{-5}\) M) as shown in Fig. 6 for THF, and Fig. S6 for DMF, respectively. The absorption and emission data are listed together with the Stokes’ shifts in Table 1. Upon addition of pyridine, the Q band was slightly red-shifted, confirming the axial bonding of the pyridine as a coordinating solvent to the metal center.

To calculate the fluorescence quantum yields, the fluorescence area integration of the molecules vs. absorbance was plotted in THF and DMF (Fig. 7). The fluorescence quantum yields (\(\Phi_F\)) of compound \(2\) in THF and DMF are 0.23 and 0.10, respectively. It is well-known that the fluorescence quantum yield decreases with increases of the polarity of the solvent. The \(\Phi_F\) values of \(2\) are comparatively lower than that of the std ZnPc. This usual effect is due to the decrease of the HOMO–LUMO gap and a more extended vibrational level structure of the larger molecules, thus increasing the probability of nonradiative decay (charge transfer) [33].

**Table 1.** Absorption and emission data of \(2\) in THF and DMF (Maximum absorption wavelengths (\(\lambda_{\text{max}}\)), logarithmic value of extinction coefficients (\(\epsilon\)), \(\lambda_{\text{ex}}\): excitation wavelength, \(\lambda_{\text{em}}\): maximum emission wavelength, \(\Delta\lambda_{\text{ST}}\): Stoke’s shift and \(\Phi_F\): fluorescence quantum yield)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\log \epsilon)</th>
<th>(\lambda_{\text{ex}}) (nm)</th>
<th>(\lambda_{\text{em}}) (nm)</th>
<th>(\Delta\lambda_{\text{ST}}) (nm)</th>
<th>(\Phi_F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>THF</td>
<td>673</td>
<td>5.49</td>
<td>644</td>
<td>679</td>
<td>6</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>THF + 1% pyridine</td>
<td>676</td>
<td>5.53</td>
<td>647</td>
<td>687</td>
<td>11</td>
<td>0.10</td>
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<tr>
<td></td>
<td>DMF</td>
<td>677</td>
<td>5.40</td>
<td>644</td>
<td>687</td>
<td>10</td>
<td>0.10</td>
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<tr>
<td></td>
<td>DMF + 1% pyridine</td>
<td>678</td>
<td>5.38</td>
<td>644</td>
<td>688</td>
<td>10</td>
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</tr>
<tr>
<td>std ZnPc</td>
<td>THF</td>
<td>666</td>
<td>5.19</td>
<td>638</td>
<td>668</td>
<td>2</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>669</td>
<td>5.43</td>
<td>637</td>
<td>672</td>
<td>3</td>
<td>0.17</td>
</tr>
</tbody>
</table>

\(^{a}\)Data from Ref. [47].

\(^{b}\)Data from Ref. [60].

\(^{c}\)Data from Ref. [48].

**Fig. 7.** Fluorescence integrated area vs. absorbance of \(2\) and std ZnPc in THF and in DMF
The observed quenching of the fluorescence should also suggest a predominant closed clamshell conformation in DMF more than in THF [34].

**Geometrical optimization**

The optimized molecular structures of the conformers are given in Fig. S7. Table S1 summarizes the calculated dipole moments (μ, Debye), total electronic energies including zero-point correction energies (E_{ZPE}, Hartree) and relative energy values (ΔE_{rel}, kcal/mol) for the conformers in the gas phase and in THF calculated at CAM-B3LYP/LANL2DZ level. Among all conformers, 2C1 (Fig. S7, Table S1) is found to be the most stable in the gas phase and in THF. This conformer has π-stacked conformations in Pc sides. The calculated interatomic distances (Fig. S7) indicate that the most stable conformer was formed by hydrogen bonds between nitrogen of Pc and van der Waals interactions between Pcs. Intramolecular distances between Pc pairs increase in THF and the Pcs are twisted compared to the gas phase. The Pc planes are inclined at 44.51° where the spacing between the two Zn centers is about 8.1 Å based on the calculation on 2C1, the most stable conformer in THF. The phenyl units on the linkers are inclined at about 80.81°, again reflecting the deviation of the structure from the closed-clamshell to so-called “angled shell” conformation [32]. Hence, it is very difficult to experimentally observe an intramolecular interactions between the Pc units as revealed by the UV-vis spectrum of 2 (Fig. 5).

**Electronic transitions**

First, the 50 lowest singlet excited states were calculated for the molecule. Some selected S_0 → S_n (n = 1–47) electronic transitions (λ_{ex}) corresponding to vertical excitation energies (ΔE), transition dipole moments (μ_{tr}), oscillator strengths (f), excitation characters, molecular orbitals and their % contributions for the molecule in THF are summarized in Table S2. The most dominant transition is given where there are more than one transition of the same character. Fig. 8 displays the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) transitions for the molecule in the gas phase and in THF, respectively. HOMO–LUMO energy levels and energy differences, ΔE_{H,L} are also given for comparison. Although HOMO and LUMO orbital energies decreased in THF, the energy gap (ΔE_{H,L}) did not change (2.15 eV). The HOMO–LUMO transition implies a locally excited (LE) Pcs in the gas phase (Fig. 8).

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**Fig. 8.** Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for 2 in gas phase and in THF.
In contrast, it can be seen that HOMO can be found completely on the lower Pc ring and LUMO is located mostly on the upper Pc in THF (Fig. 8 and Fig. S7). This explains a significant degree of intramolecular charge transfer by $\pi-\pi^*$ and $n-\pi^*$ transitions. Consequently, the HOMO–LUMO transition implies a charge transfer between Pc units. As shown in Fig. S7, the transitions H-2 and H-7 can be found completely on the linkage. Intramolecular charge transfers (ICT) from linkage to Pcs around 463, 450 and 442 nm from H-2 to L + 1, L + 2 and L + 3 orbitals, respectively were observed. Additionally, ICT from H-7 to L (376 nm), L + 2 (368 nm and 359 nm) and L + 3 (358 nm) were also observed. Experimental and calculated UV-vis absorption spectra in THF are shown in Fig. 9, demonstrating that the experimental and the calculated results are in good agreement.

**OFET studies**

FTO/Pc/Au structures with an active area of 0.785 mm$^2$ were fabricated and characterized by means of capacitance–frequency (C–f) and current–voltage (I–V) measurements in order to investigate the dielectric behavior of the compound. It is well-known from the basics of an OFET that high capacitance density is required in order to obtain high-performance OFET. For this reason, prior to carrying out the study on the leakage current in the FTO/Pc/Au structure, we first examined the dependence of capacitive behavior of the device on the frequency. The room temperature C–f characteristics of the FTO/Pc/Au structures with the 260 nm thick Pc layer is presented in Fig. 10. The C–f characteristics of the device exhibited two different regions with different...
frequency dependency, strong frequency dispersion at low frequencies and a nearly frequency independent behavior in high-frequency region. The capacitance density of the FTO/Pc/Au sandwich structure was found to be 12.7 nF cm\(^{-2}\) at 5 Hz and 12.1 nF cm\(^{-2}\) at 13 MHz. From the obtained C–f measurements, the value of the relative dielectric constant was estimated and was found to be 3.8 at 5 Hz and 3.6 at 13 MHz.

When compared with the reported values of capacitance density of some other solution processed nanocomposites [35] and inorganic dielectrics [36], it was found that 2 had relatively high capacitance density. The performance of 2 as passivation layer was also investigated with respect to leakage current which is another indicator for high-performance OFET devices. Using a semi-logarithmic scale, the obtained J–V curve for the FTO/Pc/Au sandwich structure is presented in the inset of Fig. 10. It is clear that the device exhibits rectification behavior with a rectification ratio of 14 at ± 6 V. A leakage current value of 2.75 nA cm\(^{-2}\) at 6 V achieved with the FTO/Pc/Au device at room temperature, which is significantly lower when compared with widely-used gate dielectrics such as PVA [37] and PMMA [38], indicating that the compound has great potential for use as a gate dielectric in OFETs. Leakage current flows through the dielectric layer may originate from various mechanisms such as direct tunneling and Poole–Frenkel emission [39, 40]. The experimental data under reverse bias conditions were analyzed in terms Poole–Frenkel emission to obtain more information about the leakage current mechanism in the FTO/Pc/Au structure. The relation between the measured current density and the applied voltage for the Poole–Frenkel effect is given by [41]

\[
J = J_0 \exp \left( \frac{\beta_{PF} V^{1/2} - \varphi_{PF}}{kT} \right)
\]

where \(J_0\) is the low field current density, \(\varphi_{PF}\) is the barrier height, \(\beta_{PF}\) is the Poole–Frenkel emission coefficient, \(k\) is Boltzmann’s constant and \(T\) is the temperature. According to Equation 1, the plot of \(\ln (J)\) vs. \(V^{1/2}\) should be linear if the charge transport takes place through Poole–Frenkel emission. The variation of the \(\ln (J)\) with \(V^{1/2}\) is shown in Fig. 11. As can be seen from the Fig. 11, the experimental J–V data deviates considerably from linearity for forward bias conditions. On the other hand, under reverse bias, good correlation coefficients (\(R^2\)) obtained from the \(\ln (J)\) vs. \(V^{1/2}\) plots reveal that the mechanism responsible for conduction in FTO/Pc/Au structure under reverse bias condition can be described by the Poole–Frenkel emission. The analysis of the forward bias J–V data is out of scope of this study and it is underway.

In general, an OFET device is characterized by its output and transfer characteristics. The dependence of drain current (\(I_d\)) on the drain-source voltage (\(V_{ds}\)) and output characteristic for various gate-source voltages (\(V_{gs}\)) between 0 and -60 V is presented in Fig. 12. The output characteristic of the device can be characterized by the modulation of the \(I_d\) current by \(V_{gs}\) voltages and the presence of two different operating regions, linear and saturation regions. A possible explanation for the observed output characteristics can be given as follows: until the \(V_{ds}\) voltage exceeds a certain value, the effect of the \(V_{ds}\) voltage on the resistance of the channel region is negligible and the device behaves as a voltage controlled resistor. When the value of the applied \(V_{ds}\) voltage reaches a critical value, the channel region takes the tempered form because of the variation of voltage drops between source and drain ends measured relative to source along the channel region. With further increase in \(V_{ds}\), the channel becomes more tempered and the output characteristic does not continue as a straight line because of the increase in the resistance of the channel region.
V\textsubscript{P3HT/Au} OFET device is shown in Fig. 13 for a constant for use in OFET devices as gate dielectric. That the clamshell type Pc compound has a great potential dielectric, was about $6.4 \times 10^2$ based OFET device, in which compound voltage. On the other hand, the relation between the current and $V_{gs}$ voltage for saturation region is expressed as

$$I_d = \frac{W}{2L} C \mu_{te} (V_{gs} - V_{th})^2.$$  

For low values of the $V_{ds}$ voltages, the relationship between the drain current and the drain-source voltage is given by Equation 2 [42, 43]

$$I_d = \frac{W}{L} C \mu_{te} (V_{ds} - V_{th}) - \frac{1}{2} V_{ds}^2$$  

where $W$ and $L$ are the channel width and length respectively, $\mu_{te}$ is the field-effect mobility, $C$ is the insulator capacitance per unit area, and $V_{th}$ is the threshold voltage. On the other hand, the relation between the $I_d$ current and $V_{gs}$ voltage for saturation region is expressed as [44]

$$I_d = \frac{W}{2L} C \mu_{te} (V_{gs} - V_{th})^2.$$  

With regard to application, field effect mobility is one of the most important parameter for an OFET’s performance. The slope of the plot of $(I_d)^{1/2}$ vs. $V_{gs}$ can be used to extract the $\mu_{te}$. The obtained transfer characteristic (variation of the $I_d$ current with $V_{gs}$ voltage) for FTO/Pc/P3HT/Au OFET device is shown in Fig. 13 for a constant $V_{ds}$ voltage of -30 V. With the aid of the Equation 3, the value of $\mu_{te}$ was estimated from the slope of the $(I_d)^{1/2}$ vs. $V_{gs}$ plot. The obtained mobility values for the P3HT based OFET device, in which compound 2 used as gate dielectric, was about $6.4 \times 10^{-3}$ cm$^2$/V.s.

An overall evaluation of the experimental data reveals that the clamshell type Pc compound has a great potential for use in OFET devices as gate dielectric.

EXPERIMENTAL

Materials

All chemicals were purchased from commercial sources and used without further purification. 2-(dimethylamino) ethanol (DMAE) was supplied from ABCR, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was supplied from Aldrich, zinc acetate was supplied from Merck, 4-tert-butylphthalonitrile was supplied from TCI.

The synthesis and characterization of the key precursor 4,4'-octahydro-4,7-methano-5H-inden-5-ylidene bis(phenoxyphthalonitrile) (I) was previously reported by us [5]. The purity of the products was tested in each step by TLC (SiO$_2$). Chromatography was performed on silica gel 60. Solvents and reagents were dried and/or distilled by the usual methods and typically used under an inert gas atmosphere.

Equipment

FT-IR (ATR) spectra were recorded with a Perkin Elmer FT-IR Spectra 100 Spectrophotometer at room temperature. The $^1$H NMR, $^{13}$C DEPT NMR and $^1$H–$^1$H COSY NMR in THF-$_d_8$ with an Agilent 600 MHz Premium Compact NMR spectrometer at room temperature. Chemical shifts were given in parts per million with reference to TMS. Mass spectra were acquired on a Rapiflex MALDI-TOF MS (Bruker Daltonics, Bremen-GERMANY) equipped with a Smartbeam 3D 10kHz 355 nm Nd: YAG laser with 1000 shots per each sample spot using a single shot laser configuration. The UV-vis spectral measurements were carried out with a CARY 100 Bio UV-visible spectrophotometer. Fluorescence spectra were measured on a Perkin Elmer LS55 Fluorescence Spectrometer. All solutions for all absorption and emission measurements of the compounds were prepared freshly.

Synthesis

Preparation of binuclear clamshell zinc phthalocyanine (2)

A mixture of 1 (0.20 g, 0.35 mmol), 4-tert-butylphthalonitrile (0.64 g, 3.47 mmol) and Zn(OAc)$_2$·2H$_2$O (0.27 g, 1.47 mmol) was dissolved in DMAE (30 mL). After addition of DBU (3 drops), the mixture was set to reflux with vigorous stirring under an argon atmosphere for 16 h. The cooled reaction mixture was treated with distilled methanol (30 mL) and stirred for a further 15 min. After filtration, the crude product was washed successively with methanol. The blue precipitate was purified by column chromatography on silica gel using CH$_2$Cl$_2$/THF (100:1) as eluent. Yield 0.15 g (23%). IR (ATR) ν, cm$^{-1}$: 3061, 3037, 2952, 2901, 2863, 1613, 1600, 1487, 1472, 1392, 1363, 1331, 1282, 1256, 1169, 1145, 1087, 1045, 1012, 963, 938, 921, 893, 872, 828, 762, 746, 691, 672. $^1$H NMR (600 MHz; THF-$_d_8$; Me$_4$Si): δ$_H$, ppm 9.59–9.28 (16H, m, H$_1$, H$_2$, H$_3$, H$_4$), 8.38 (6H, m, H$_5$), 7.94–7.83 (6H, m, H$_6$, H$_7$), 7.63–7.57 (4H, m, H$_8$), 2.56–2.45 (6H, m, H$_{10}$, H$_{11}$, H$_{12}$), 1.95 (54H, s, H$_8$), 1.49–1.40 (6H, m, H$_{14}$), 1.22 (2H, m, H$_{13}$). $^{13}$C-NMR (DEPT; 600 MHz; THF-$_d_8$): δ$_C$, ppm (C) 154.38, 149.64, 148.71, 141.80, 140.49, 138.30, 134.71, 133.1, 128.2, 125.6, 116.9, 114.5, 108.7, 104.5, 101.2, 96.3, 93.8, 92.1, 89.3, 87.2, 82.8, 76.2, 74.6, 69.1, 67.2. J. Porphyrins Phthalocyanines 2018; 22: 73–76
Fluorescence quantum yield determination

Fluorescence quantum yield values ($\Phi_F$) were determined by the comparative Williams’ method [45, 46]. Accordingly, the UV-vis absorbance and corrected emission spectra of the reference standard (std ZnPc) and sample were measured under identical conditions. The absorbance value at the excitation wavelength was used. Integrated fluorescence intensities vs. absorbance for std ZnPc ($\Phi_F = 0.25$ in THF [47] and $\Phi_F = 0.17$ in DMF [48]) and samples were plotted. Quantum yield ($\Phi_F$) values were calculated according to Equation 4, where Grad represents the gradient of the plot, and the gradients of the plots are proportional to the quantum yield of the samples.

$$\Phi_F = \frac{\text{intensity}}{\text{absorbance}} \times \frac{\text{Grad}}{1.0} \times \frac{1}{\text{Grad(ref)}} \times \text{quantum efficiency}$$

Computational details

Gaussian09 [49], Gaussianview5.0 [50] and Spartan08 [51] programs were used in calculations. Initial monomer structures were obtained by Spartan 08. Ground state optimizations were carried out with density functional theory (DFT) [52]. In order to take into account the long-range interactions, we employed the hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP) in conjunction with the LANL2DZ basis set due to the presence of metal ions and the size of the system [53]. All optimized geometries have been verified as minima by frequency analysis.

Time-dependent density functional theory (TDDFT) calculations were carried out with the hybrid DFT Becke’s three-parameter nonlocal exchange functional [54, 55], with a correlation function similar to Lee–Yang–Parr (B3LYP) [56] with the same basis set. Additional TDDFT calculations were performed with CAM-B3LYP [53] using the same basis set for comparison. The 50 lowest singlet excited states were calculated for the molecule. Molecular orbital energies and the UV-vis spectra were displayed by the Gaussian program. Investigations in solution were performed using the Polarizable Continuum Model (PCM) [57, 58] to evaluate the solvation effect on the electronic transitions in THF. The molecular visualization was performed as described by Macrae et al. [59].

Fabrication and characterization of OFET

Fluorine-doped tin oxide (FTO) coated glasses were used as gate electrodes for bottom gate top drain-source contact OFET fabrication. After applying the standard cleaning procedure to FTO substrates (ultrasonic treatment in isopropyl alcohol, acetone, and de-ionized water, respectively) a thin film of 2 was formed on FTO substrates by the spin coating method. $4 \times 10^{-3}$ M DMSO solution of the compound was prepared and then 50 microliters of the solution was spun onto FTO substrates at 1400 rpm for 100 s. Then the film was dried at 120°C for 10 min in a vacuum oven to remove the remaining solvent in the film. After the spinning of the gate dielectric onto the FTO substrate, a solution of active layer poly (3-hexylthiophene) (P3HT) in toluene with a concentration of $8 \times 10^{-3}$ M was spun onto the gate dielectrics. Then the P3HT coated substrates were immediately placed in a vacuum system for the deposition of source-drain contacts. 300 nm gold source-drain electrodes were then deposited onto the active layer through a shadow mask with a channel length (L) of 80 µm and a width (W) of 4 mm. The transfer and output characteristics of the fabricated devices were measured in air using a Keithley 617 programmable electrometer and a Keithley 2400 source-meter.

CONCLUSION

A new clamshell-type binuclear zinc phthalocyanine 2 was prepared and characterized by elemental analysis, high-resolution MALDI TOF mass spectrometry and comprehensively by NMR spectrometry. The structural and spectroscopic properties were also studied by UV-vis and fluorescence spectrophotometers.

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were carried out to simulate the molecular and electronic structures together with the electronic absorption spectrum of 2. The optimized conformers showed that the molecule adopts a twisted clamshell conformation as the most stable conformer in THF but a closed-clamshell conformation in the gas phase. The intramolecular distances of between the Pc units increased in THF compared to the gas phase. Analyses of the first excited singlet states have indicated locally-excited Pcs in the gas phase and charge transfers transitions between Pcs through $\pi-\pi$ stacking in THF at 651 nm and 675 nm, respectively. 2Cl also has charge transfer from linkage to Pc in THF at 463, 450 and 442 nm in THF. A simple visual comparison of the Q-bands calculated for the three most probable conformers with the experimentally obtained spectrum of 2 in THF allows us to believe that the spatial arrangement could be tuned by the size and the nature of the peripheral substituents and their orientations, as presented here by the spacer-linked clamshell-type binuclear Pc dimer 2 which adopts a twisted clamshell conformation as the most favorable conformation in
THF but a closed-clamshell in gas phase. The TDDFT calculations and UV-vis spectrum strongly support that 2 exists in a non-aggregated form in THF. The calculated fluorescence quantum yield is comparatively lower than that of std ZnPc, as commonly observed phenomenon in clamshell binuclear Pcs which are well-known to be self-quenched between the coupled halves of the binuclear species due to nonradiative decay. In addition, as expected, the FQY decreases upon increasing the polarity of the solvent.

In particular, the dielectric performance of the clamshell-type phthalocyanine as gate dielectric for OFET was investigated by means of capacitance density and leakage current. This work has demonstrated the possibility of using clamshell-type phthalocyanine as a gate dielectric for OFET with a low leakage current density of 2.75 nA·cm⁻² at 6 V and a high low-frequency capacitance density of 12.7 nF·cm⁻².

Acknowledgments

The authors are grateful to the Bülent Ecevit University for financial support under the project [BAP Project No: 2015-72118496-05]. Some of the calculations were performed on Fencluster (Ege University, Faculty of Science) and TUBITAK-ULAKBIM Truba resources.

Supporting information

Additional information include including FT-IR, MALDI TOF MS, ¹H NMR, absorption, emission spectra, optimized molecular structures, dipole moments (μ, Debye), sum of electronic energies and zero point energies (Eelec+ZPE, Hartree) and relative energies (ΔEref, kcal/mol), electronic transitions (ΔE), transition dipole moments (μtr), oscillator strengths (f), excitation character, molecular orbitals and their % contributions and molecular orbitals (MOs) of the 2 associated with this article is provided as supplementary material. This information is available free of charge via the internet at http://www.worldscinet.com/jpp/jpp.shtml.

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Synthesis, characterization, photophysicochemical properties and theoretical study of novel zinc phthalocyanine containing four tetrathia macrocycles

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This paper is dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 26 November 2017
Accepted 18 December 2017

**ABSTRACT:** In this work, Zn(II) phthalocyanine derivative (TTU-Pc) bearing 13-membered tetrathia macrocycles was synthesized, and the novel Zn(II) phthalocyanine derivative was fully characterized by elemental analysis and general spectroscopic methods such as MALDI-TOF mass, FT-IR, UV-vis and \(^1\)H-NMR. The synthesized phthalocyanine derivative has quite limited solubility in most of the common organic solvents. Fluorescence measurement was conducted for this Zn(II) phthalocyanine to estimate its fluorescence quantum yields. The singlet oxygen generation ability was also examined to investigate its photosensitizer properties. General trends were described for quantum yields of fluorescence, photodegradation and singlet oxygen quantum yields of this compound. The electrochemical properties of the molecule were investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV). In addition, the lowest energy structure, the electronic structure and frontier molecular orbitals were calculated in DFT and the excitation spectrum was obtained by TDDFT calculations. We found that our computational and experimental results were in agreement.

**KEYWORDS:** zinc phthalocyanine, photochemistry, singlet oxygen, fluorescence, photodegradation, tetrathia, macrocyclic compound, TDDFT, cyclic voltametry.

**INTRODUCTION**

Phthalocyanines (Pcs) are the most studied compounds in supramolecular chemistry [1]. The functions of these compounds arise mainly from their conjugated 18\(^\pi\) electron system having rich electron transfer ability, which depends on the kind and number of metal centers and substituents [2, 3]. Just like many other scientists all over the world, we have been closely dealing with phthalocyanines and their derivatives because of their fascinating and fairly useful chemical features for various scientific areas. They have been employed in several “hi-tech” applications such as photoconducting material in laser printers and light absorbing layers in recordable CDs [4], and have been used in optical limiting devices [5–7], liquid crystals (LCs) [8–10], solar cells [11, 12] and batteries [13]. Due to the fact that diamagnetic central metal ions (such as Zn or Mg) enhance the phototoxicity of the phthalocyanines, the substituted phthalocyanine derivatives can also be used for photodynamic therapy (PDT) and other processes driven by visible light [14–17]. Phthalocyanines are considered to be very suitable photosensitizers for PDT due to their intense absorption in the phototherapeutic region (600–900 nm), high efficiency in generating reactive oxygen species (ROS), high phototoxicity and low dark toxicity [18–22]. In addition, Pcs have long-wavelength absorption with high
extinction coefficients and high singlet-oxygen quantum yields [23], and Pcs are suitable for combination with other additional therapeutic strategies as well [24]. Phthalocyanines bearing absorptions in the near-infrared (NIR) region are also important for applications requiring NIR absorption such as thermal imaging and optical data storage [1]. Pc absorptions can be shifted to NIR by the addition of alkythia groups (–SR) into the periphery of Pc ring [25, 26].

Macrocycle such as crown ether [27], tetraaza [28], tetraethia [29] and tetrathiadiaza [30] fused phthalocyanine derivatives were developed and their interactions with alkali and transition metals have been investigated intensively for the last decades. As far as we know, photophysical properties of macrocycle-fused phthalocyanines were only studied in our recent paper on 15-crown-5 substituted Zn(II) phthalocyanine derivative [31]. Gurek et al. [32] have reported a group of phthalocyanines fused to four 13-membered tetraphthiacyclics on the periphery as a further step of the series on macrocycle-fused phthalocyanines. However, the low solubility of these phthalocyanines is an obstacle to investigate the effects of the thia groups on the properties of phthalocyanines as in the case of their tetraoxa or tetraaza analogs. In order to solve this problem, methyl groups were integrated to the macrocycle in this study to improve the solubility. This opens up a gate to investigate photophysical and photochemical properties as well as electrochemistry of the macrocycle fused-phthalocyanines, in particular thia-macrocycles, for the first time in this study. We report herein the synthesis, spectral and electrochemical characterization of fused dimethyl substituted tetraphthia macrocycle fused zinc(II) phthalocyanine (TTU-Pc). Additionally, geometric optimizations and electronic structure calculations were performed in density functional theory (DFT) in order to better elucidate the molecular structure.

EXPERIMENTAL

Chemicals and reagents

5,5-Dimethyl-3,7-dithio-1,9-nonanediol (1) [33] and 4,5-dichlorobenzene-1,2-dicarbonitrile (3) [34] were prepared by reported procedures. All solvents and chemicals were of reagent-grade quality, purchased from Sigma–Aldrich Chemical Co. and Merck, and purified as described in Perrin and Armarego [35]. 1,3-diphenylisobenzofuran (DPBF) was purchased from Fluka. Purification by column chromatography was performed using Merck Kieselgel 60 silica gel as the stationary phase.

Equipment

Absorption spectra in the UV-vis region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Photolirradiations were done using a General Electric quartz line lamp (300W). A 600 nm glass cutoff filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiation, respectively. An interference filter (Intor, 700 nm, with a band width of 40 nm) was additionally placed in the light path in front of the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter. Fluorescence lifetime was recorded using Horiba FL3-2IHR with a Time Correlated Single Photon Counting (TCSPC) system. H and 13C nuclear magnetic resonance spectra were taken on a Bruker 200 MHz spectrophotometer. Chemical shift values (δ) are referred to tetramethylsilane (TMS), utilized as internal reference. Deuterated solvents were used in all NMR measurements. Chemical shifts (δ) are reported in parts permillion (ppm) relative to residual solvent peaks as an internal reference for 1H and 13C nuclei. Assignments were determined either on the basis of unambiguous chemical shifts or coupling patterns. Mass spectra were recorded using a VG Zab-Spec GC-MS spectrometer by electron impact technique and on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as the matrix. IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer (KBr pellet) and absorption maxima (νmax) were quoted in wavenumbers (cm⁻¹) in the range of 4000–650 cm⁻¹. Elemental Analysis was performed on a Thermo Finnigan Flash 1112 Series Elemental Analyzer operated at the Scientific and Technological Research Council of Turkey (TUBITAK), Marmara Research Center, Institute of Chemical Technology.

Photochemical parameters

**Singlet oxygen quantum yield determination.** Singlet oxygen quantum yield (Φo) was determined in air using
the relative method [40] with ZnPc (in DMSO) as the reference. DPBF (1,3-diphenylisobenzofuran) was used as chemical quencher for singlet oxygen in DMSO, using Equation 2,

$$\Phi_\text{d} = \frac{R_\text{Std} \cdot \Phi_\text{Std}}{R_\text{Std} + I_\text{abs}}$$

(2)

where $\Phi_\text{Std}$ is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\text{Std} = 0.67$ in DMSO) and $R$ and $R_\text{Std}$ are the DPBF photobleaching rates in the presence of the respective sample and standards, respectively. $I_\text{abs}$ and $I_\text{Std}$ are the rates of light absorption by the sample and standards, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [41], the concentration of quenchers (DPBF) was lowered to $\sim 3 \times 10^4$ M. Solutions of the photosensitizer containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described in the equipment section. DPBF degradation at 417 nm was monitored. The light intensity of $7.05 \times 10^1$ photons s$^{-1}$ cm$^{-2}$ was used for $\Phi_\text{d}$ determinations.

**Photodegradation quantum yield determination.** Photodegradation quantum yield ($\Phi_\text{d}$) determination was carried out using the experimental set-up described in the literature [42, 43]. $\Phi_\text{d}$ value was determined using Equation 3,

$$\Phi_\text{d} = \frac{(C_0 - C_t) \cdot V \cdot N_a}{I_{\text{abs}} \cdot S \cdot t}$$

(3)

where $C_0$ and $C_t$ are respectively the sample concentrations before and after irradiation, $V$ is the reaction volume, $N_a$ the Avogadro’s constant, $S$ the irradiated cell area and $t$ the irradiation time and $I_{\text{abs}}$ is the overlap integral of the radiation source light intensity and the absorption of the sample. A light intensity of $2.20 \times 10^{16}$ photons s$^{-1}$ cm$^{-2}$ was employed for $\Phi_\text{d}$ determinations.

**Electrochemical analyses.** Electrochemical measurements were carried out on a CH Instruments 842B model work station. The setup was a conventional three-electrode cell equipped with a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgNO$_3$ reference electrode. The glassy carbon electrode was polished routinely with 0.05 micron alumina powder/water slurry on pads before running experiments. All measurements of samples were recorded as reported analyte concentration in 0.1 M n-Bu$_4$NClO$_4$ electrolyte solutions of dimethylformamide. Solutions were deaerated by purging with argon for 5 min and kept under a blanket of argon during the experiments. All electrochemical measurements were performed at ambient temperature. Ferrocene was used as an internal reference, and all potentials were referenced to ferrocene/ferrocenium (Fc/Fc$^+$) redox couple ($E_{1/2}$: 0.480 V vs. SCE). All potentials as $E_{1/2}$ ($E_{pa} + E_{pc}$)/2 were reported vs. saturated calomel electrode (SCE). Scan rate was 100 mVs for all cyclic voltammetry (CV) experiments. The 3 mm-diameter glassy carbon working electrode (CH1104), non-aqueous Ag/Ag$^+$ reference electrode with porous teflon tip (CH1112), platinum wire counter electrode (CH1115) and electrode polishing kit (CH1120) were purchased from CH Instruments. The supporting electrolyte, n-Bu$_4$NClO$_4$ was purchased from Aldrich and dried at 40°C under vacuum for two days. Ferrocene was supplied by Fluka, AgNO$_3$ by Carlo Erba, and anhydrous dimethylformamide by Aldrich.

**Theoretical calculations.** Our structure optimization and electronic structure calculations are based on density functional theory as implemented in NWChem [44] and SIESTA [45] computer codes. The initial atomic positions for structure optimizations were taken from a flat system, and unbiased conjugate gradient total energy minimization calculations were performed in SIESTA code until all force components are less than 0.01 eV/Å on each atom. From these initial calculations, we deduced possible conformations of the 13-membered macrocycle, and prepared several initial atom coordinates using the deduced conformations. After their structure optimizations in SIESTA code, the molecular structure with the lowest energy is determined. The results presented in this work are for this ground state structure. In SIESTA calculations, Generalized Gradient Approximation (GGA) with Perdew–Burke–Ehrenzhof (PBE) parameterization [46] was used for exchange-correlation functional. The molecular structure was further optimized in NWChem code within hybrid Heyd–Scuseria–Ernzerhof (HSE) [47] and Becke, three-parameter, Lee–Yang–Parr (B3LYP) [48, 49] exchange correlation functionals to get a better description of excited states and energy gaps. The best agreement with experiments was found to be for HSE exchange correlation functional. Therefore, the energy levels and the frontier orbitals presented here are HSE results calculated with 6-311G** gaussian basis set in NWChem code. Time dependent density functional theory (TDDFT) calculations were carried in NWChem code to get oscillator strengths of excitations. In TDDFT calculations, both HSE and B3LYP produce the same main findings.

**Synthesis**

5,5-Dimethyl-3,7-dithio-1,9-nonanediol (2). 5,5-Dimethyl-3,7-dithio-1,9-nonanediol (1) (14.82 g, 66 mmol) and thiourea (10.17 g, 134 mmol) were dissolved in 36 ml of HCl (37%) and refluxed for 12 h under stirring. To the resulting solution, a solution of potassium hydroxide (22.3 g, 398 mmol) in 135 ml H$_2$O (degassed with argon) was added under argon atmosphere. This mixture was refluxed and stirred for an additional 10 h under argon. The two-phase system which resulted was cooled and separated, and the upper aqueous phase was extracted with diethyl ether (3 x 100 ml). The ether layers were combined with the oily organic layer from the reaction mixture,
and this solution was dried over Na2SO4. The dried ether solution was filtered and evaporated to give a thick liquid which was purified by column chromatography on silica gel using ethyl acetate as eluent. Yield: 10.65 g (63%).

FT-IR (KBr) (cm⁻¹) 2929, 2870 (CH₂), 2550 (SH), 1460, 1420, 1380, 1360, 1250, 1205, 1180, 1140, 970, 920, 870, 700. ¹H NMR (500 MHz, CDCl₃-d₆, δ ppm): 2.87–2.69 (m, 10H, SCH₂, SH), 2.59 (s, 4H, SCH₂), 1.04 (s, 6H, CH₃).

Elemental analysis calc. for C₉H₂₀S₄ (380.617): C, 42.14; H, 7.86, found: C, 42.01; H, 7.91.

6,6'-Dimethyl-2,3,6,7,9,10-hexahydro-5H-benzo[e][1,4,7,10]tetrathiacyclotridecine-13,14-dicarbonitrile (4). Dry DMSO (150 ml) containing NaHCO₃, (8.064 g, 96 mmol) was heated and stirred at 40 °C under Ar. To this solution, a solution of 5,5-dimethyl-3,7-dithio-1,9-nonanedithiol (2) (4.098 g, 16 mmol) and 4,5-dichlorobenzene-1,2-dicarbonitrile (3) (3.149 g, 16 mmol) in dry DMSO (200 ml) was gradually added over 6 h, and the reaction continued for over 72 h. After evaporation of DMSO at reduced pressure, H₂O (100 ml) was added to the residue, the aqueous layer extracted with CH₂Cl₂, (50 ml each) several times, the combined organic layer dried (Na₂SO₄) and evaporated, and the light-yellow oily crude product was purified by column chromatography (silica gel, eluted first by CH₂Cl₂: n-hexane/5:2 then by CH₂Cl₂): pure 4 (1.5 g, 25%). M.p. 205–207 °C. FT-IR (KBr) (cm⁻¹): 2960–2920 (CH), 2220 (C≡N), 1570, 1530, 1460, 1440, 1420, 1360, 1340, 1260, 1225, 1200, 1180, 910, 860, 830, 790, 710, 690, 530. ¹H NMR (200 MHz, CDCl₃-d₆, δ ppm): 7.70 (s, 2H, ArH), 3.29 (t, 4H, Ar-SCH), 2.86 (t, 4H, SCH₂), 2.61 (s, 4H, SCH), 0.95 (s, 6H, CH₃). ¹³C-NMR (50 MHz, CDCl₃-d₆, δ ppm): 145.59 (ArC-S), 134.51 (ArC), 125.69 (Ar-C), 43.95 (SCH₂), 36.44 (C-(CH₃)₂), 35.73 (SCH₂), 33.48 (SCH₂), 27.09 (CH₃). Elemental analysis calc. for C₁₇H₂₀N₂S₄ (380.617): C, 53.65; H, 5.30; N, 7.36, found: C, 53.17; H, 5.20; N, 7.01. EI-MS m/z (%): 380 (38, M⁺), 203 (25), 161 (35), 134 (100).

Tetra[6,6'-Dimethyl-2,3,6,7,9,10-hexahydro-5H-benzo[e][1,4,7,10]tetrathiacyclotridecine-1,11] phthalocyaninato zinc(II) (TTU-Pc). A mixture of 6,6'-dimethyl-2,3,6,7,9,10-hexahydro-5H-benzo[e][1,4,7,10]tetrathiacyclotridecine-13,14-dicarbonitrile (4) (80 mg, 0.210 mmol) and zinc (II) acetate (0.010 g, 0.53 mmol), and quinoline (0.2 ml) was heated and stirred at 185–190 °C for 5 h under Ar. After cooling to room temperature, the dark green mixture was diluted with EtOH (5 ml) and filtered off. The crude product was dissolved in pyridine (5 ml) by heating at 60 °C and precipitated by adding hot EtOH. Pure TTU-Pc (0.030 g, 36%) was obtained by washing with hot EtOH and EtO. This compound was soluble in pyridine, DMF and DMSO.

FT-IR (KBr) (cm⁻¹): 2982–2945 (CH₂), 1620, 1500, 1420, 1380, 1350, 1290, 1205, 1130, 1100, 1080, 950, 780, 750, 700. ¹H NMR (200 MHz, pyridine-d₅, δ ppm): 9.57 (s, 8H, ArH); 3.79 (t, 16H, SCH₂), 3.01 (t, 16H, SCH₂); 2.62 (t, 16H, SCH); 0.88 (s, 24H, CH₂). ¹³C-NMR (APT) (50 MHz, pyridine-d₅, δ ppm): 157.73 (ArC-S), 140.39 (ArC), 137.05 (ArC) 125.69 (Ar-C), 43.95 (SCH₂), 36.44 (C-(CH₃)₂), 35.73 (SCH₂), 33.48 (SCH₂), 27.09 (CH₃). Elemental analysis calc. for C₆₈H₸₀N₸₀S₸₁Zn (1587.858): C, 51.44; H, 5.08; N, 7.06, found: C, 51.49; H, 5.11; N, 7.17. MALDI-MS m/z :1588.87 [M+1]⁺.

Scheme 1. Synthetic route for phthalocyanine molecules TTU-Pc. (i) thiourea, HCl, reflux (ii) KOH solution, reflux.
RESULTS AND DISCUSSION

Synthesis and characterizations

We used the nucleophilic displacement reaction of 4,5-dichlorobenzene-1,2-dicarbonitrile (3) with dithiol (2) in the presence of excess NaHCO₃, a procedure reported recently for the preparation of some bis(alkylthio)- or bis(alkoxy)phthalonitrile derivatives [25, 32, 34] (Scheme 1). Of course, it was necessary to use equivalent amounts of the two reagents to promote a 1:1 condensation, but some 2:2 condensation products and other by-products were unavoidable, so the yield of the desired compound 4 was only 25% after chromatographic isolation.

The preparation of the target zinc phthalocyanine derivative (TTU-Pc) was shown in Scheme 1. The cyclo-tetramerization of phthalonitrile derivative 4 to the Zn(II) phthalocyanine TTU-Pc was accomplished in quinoline anhydrous metal salt [Zn(CH₃CO₂)₂] at 185–190°C for 5 h under an argon atmosphere. In contrast to the aza- or oxamacrocycle-fused analogs, the solubility of these phthalocyanines is very low. However, dimethyl groups on propyl unit on 13-membered tetrathia macrocycles increase the solubility of TTU-Pc slightly, according to the phthalocyanine derivative carrying only 13-membered tetra-thia macrocycle [32]. TTU-Pc is soluble, to a certain extent, in donor solvents such as pyridine, DMSO, DMF. Therefore, the insolvency of TTU-Pc in common solvents is due to the tetrathia macrocycle which does not lie in the plane of the phthalocyanine core according to DFT calculated optimized structure of the molecule, depicted in Fig. 1. The solubility of TTU-Pc in pyridine is a consequence of the binding of the solvent as axial ligands in Zn (II) complex.

The structures of novel compounds were characterized by a combination of elemental analysis and ¹H NMR, ¹³C NMR, IR, UV-vis and MS spectral data. The disappearance of the C≡N stretching vibration on the IR spectra of 4 suggested the formation of compound TTU-Pc. The signals related to aromatic protons and aliphatic protons in the macrocyclic moieties and phthalocyanine skeletons indicated significant chemical shifts characteristic of the proposed structure. In the mass spectrum of compound 4, the presence of the characteristic molecular ion peak at m/z: 380.01 as [M]+ confirmed the proposed structure of the synthesized dinitrile compound. The mass spectrum of Zn(II) phthalocyanine (TTU-Pc) was obtained by the MALDI-TOF technique using DHB as a matrix, and the molecular ion peak at m/z: 1588.87 [M + 1]+ was observed.

The elemental analysis results of the newly synthesized compounds also confirmed the structures of targeted compounds.

Ground state electronic absorption spectra

In accordance with their electronic structure, generally Pcs present two intense absorption bands in the visible region of spectrum at around 600–750 nm (Q band) due to the π–π* transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring and in the ultraviolet region of spectrum at around 300–400 nm (B or Soret band). While the Q band corresponds to transition from the highest occupied molecular orbital
to the lowest unoccupied molecular orbital $e_g$. B band corresponds to transitions from lower energy $a_{2u}$ and $b_{2u}$ molecular orbitals to the lowest unoccupied molecular orbital $e_g$ [50]. Ground-state absorption spectra of the TTU-Pc were recorded in DMF, pyridine and DMSO (Fig. 2). TTU-Pc exhibited typical electronic spectra with Q bands at 706 nm in DMF, at 712 nm in pyridine and at 709 in DMSO and with Soret (B) bands at around 372 nm with a shoulder between 634–678 nm in all three solvents. This broad shoulder is a clear evidence that TTU-Pc is aggregated in all solvents. It was shown in Fig. 2 that Q band intensity was decreased in DMSO compared to the spectra in DMF and pyridine, showing that TTU-Pc was more aggregated in DMSO. The Q band intensity in pyridine was higher than in DMSO due to the coordination of pyridine to the zinc metal breaking aggregation to some extent [32, 51]. Absorption maxima of TTU-Pc were shifted to red (6 nm) in pyridine compared to the

 absorption maxima in DMF due to the solvent effect. The Lambert–Beer law indicating linear relationship between absorbance and concentration was obeyed for TTU-Pc in DMSO in the whole concentration measurement range (Fig. 3).

Photophysics and Photochemistry

The photophysical (fluorescence quantum yield and lifetime) and photochemical (singlet oxygen generation) properties of TTU-Pc were investigated in comparison with unsubstituted zinc(II)phthalocyanine (ZnPc) in DMSO. DMSO was used as solvent for the investigation due to the nontoxic property of DMSO suitable for biological media. All of the data discussed below are summarized in Table 1.

Photophysical properties

The fluorescence quantum yield value ($\Phi_f$) of TTU-Pc phthalocyanine derivative is shown in Table 1. The fluorescence emission spectra of TTU-Pc is a mirror image of its absorption spectra, which is itself similar to the excitation spectrum (Fig. 4). The observed Stokes shift is typical for MPC complexes for TTU-Pc. The fluorescence quantum yields were calculated according to well-known methods [37]. TTU-Pc showed slightly lower $\Phi_f$ value of 0.10 compared to unsubstituted ZnPc.

Fluorescence lifetime ($\tau_f$) refers to the average time a molecule stays in its excited state before returns to its ground state by emitting. Many factors such as internal conversion, intersystem crossing, aggregation and used solvent effects the fluorescence lifetime of a photosensitizer [18]. Fluorescence lifetime was quantified by time-resolved fluorescence measurements. The fluorescence lifetime of TTU-Pc was measured in ambient conditions by a time correlated single photon counting (TCSPC) method in DMSO. The data is represented in Fig. 5. TTU-Pc exhibited single exponential decay. The fluorescence lifetime value was within the range reported for Pc complexes [26]. The fluorescence lifetime value of TTU-Pc was lower than that of unsubstituted derivative ZnPc.

Photochemical properties

Singlet oxygen plays a number of different and important roles in biological systems. Light excitation of phthalocyanine molecules causes an intermolecular triplet–triplet energy transfer that generates the highly reactive cytotoxic agent, the singlet oxygen molecule ($\text{O}_2^*$), within a targeted region and destroys the affected cells. Therefore singlet oxygen quantum yield ($\Phi_{\text{O}_2^*}$) is a determinative photochemical parameter in PDT. The efficiency of these compounds in generating singlet oxygen was measured by the steady-state method using 1,3-diphenylisobenzofuran (DPBF) as the quencher. The
The absorption of DPBF at 417 nm was monitored along with irradiation time. The curves in DMSO are presented in Fig. 6 for TTU-Pc, and the results are summarized in Table 1. Quantum yield was calculated using ZnPc as a reference (Φ = 0.67 in DMSO). Tetrathia macrocycle incorporation to Pc decreased the singlet oxygen generation (Φ = 0.25 in DMSO) compared to unsubstituted ZnPc and sulfonyl substituted examples in literature, probably due to the aggregation of TTU-Pc in DMSO [26, 52] (Table 1).

Since different ranges of photostability are needed for different applications, it is significant to determine the photodegradation of studied molecules. Lower photodegradation values of a photosensitizer show better photostability. Photodegradation measurements were performed in DMSO (Fig. 7), and the photodegradation quantum yield (Φd) is presented in Table 1. TTU-Pc exhibited high photostability in DMSO.

**Electrochemical determination**

Redox processes of zinc phthalocyanines occur only on the macrocyclic ring since the central zinc metal ion is redox-inactive [55–57]. For this reason, all observed processes are attributed to successive removal/addition of electrons from/to the ligand-based orbitals. For TTU-Pc, a one-electron exchange was involved in each of the oxidation and reduction steps.

Phthalocyanine concentration was fixed at 1 × 10⁻⁴ M to avoid aggregation. Figure 8 represents CV and SWV responses of TTU-Pc in DMF/n-Bu₄NClO₄ on a GCE working electrode. All the processes are reversible or quasi-reversible. TTU-Pc undergoes two reduction couples (Red₁ at -0.74 V and Red₂ at -1.22 V) and two oxidation couples (Ox₁ at 0.3 V and Ox₂ at 1.12 V). \( \Delta E_{1/2} \) of the complex (1.14 V) reflect the energy band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which is in harmony with earlier reports for ZnPc complexes [58, 59]. These redox couples were analyzed to identify the HOMO, LUMO energy levels. Additional oxidation, Ox₂ at 0.74 V and reduction at -0.90 V, were also observed, probably due to the aggregated species of the molecule [60].

Molecular orbital energy levels can be determined from electrochemical measurements or by theoretical calculations. The band gap energy values that define the

---

**Table 1.** Photophysical and photochemical characterization of TTU-Pc in comparison with ZnPc in DMSO. (λ\(_{Q\max}\), maximum Q-band absorption wavelength, λ\(_{ex}\), excitation wavelength, λ\(_{em}\), maximum emission wavelength, Δλ\(_{ST}\), Stoke’s shift, τ\(_F\), fluorescence lifetime, Φ\(_F\), fluorescence quantum yield, Φ\(_D\), singlet oxygen quantum yield, Φ\(_d\), photodegradation quantum yield)

<table>
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<th>log ε</th>
<th>λ(_{ex}) (nm)</th>
<th>λ(_{em}) (nm)</th>
<th>λ(_{em}) (nm)</th>
<th>Δλ(_{ST}) (nm)</th>
<th>τ(_F) (ns) (abundance)</th>
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<td>645</td>
<td>682</td>
<td>673</td>
<td>9</td>
<td>3.59 (100%)b</td>
<td>0.18</td>
<td>0.67</td>
<td>2.61</td>
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<tr>
<td>TTU-Pc</td>
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<td>717</td>
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<td>4</td>
<td>2.09 (100%)</td>
<td>0.10</td>
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a Data from Ref. [39], b Data from Ref. [52], c Data from Ref. [53], d Data from Ref. [54].

---

**Fig. 4.** Fluorescence excitation and emission spectra of TTU-Pc in DMSO

**Fig. 5.** Fluorescence decay profile of TTU-Pc
energy necessary for the transition of an electron from
the HOMO to the LUMO level can be deduced from
these data or obtained from the UV-vis absorption band
decker (\(E_{\text{edge}}\)). In the present work, the three methods
were used to estimate these values which were summarized
in Table 2. HOMO and LUMO energy levels of TTU-Pc
were calculated using the HOMO level of ferrocene at
-4.8 eV \([26, 61, 62]\) and the first oxidation and first
reduction values of TTU-Pc in DMF (Table 2). Equations
4 and 5 were used for the calculation of HOMO and
LUMO energy levels, respectively.

\[
E_{\text{HOMO}} = - \left( (E_{\text{ox}} - E_{1/2(\text{ferrocene})}) + 4.8 \right) \quad (4)
\]
\[
E_{\text{LUMO}} = - \left( (E_{\text{red}} - E_{1/2(\text{ferrocene})}) + 4.8 \right) \quad (5)
\]

**Theoretical DFT calculations**

In our theoretical calculations, the electronic structures
of the optimized molecular structures were calculated in
PBE, B3LYP, and HSE exchange correlation functionals.
We found the energy gaps to be 1.19 eV in PBE, 1.98 eV
in B3LYP, and 1.59 eV in HSE. As expected, the PBE
functional underestimates the optical energy gap.
However, the PBE values are in good agreement with
our electrochemistry results. In our PBE calculations, we
found the highest occupied molecular orbital (HOMO)
and lowest unoccupied molecular orbital (LUMO) levels
to be -4.96 eV and -3.7 eV respectively, which are in
agreement with our electrochemistry data. The HSE
calculated value of 1.59 eV for energy gap is in excellent
agreement with the optical energy gap of 1.58 eV in
our experiments, presented in Table 2. Thus, the HSE
results for the electronic structure of TTU-Pc
molecule are presented in Fig. 1, where the HOMO and LUMO
orbitals are depicted as 3D isosurfaces.

In our structure optimizations, several competing
conformations for the 13-membered macrocycle were
calculated in addition to the ground state structure.
We found that the energy gaps and TDDFT calculated
oscillator strengths do not depend on the conformation
of the 13-membered macrocycle. Although the orbitals
for the lowest total energy structure are shown in Fig. 1;
the results for other conformations, not shown here, are
essentially identical.

The HOMO and LUMO orbitals in Fig. 1 are over
layered with the ball-and-stick model of the optimized
molecular structure, which was obtained in our
conjugate gradient calculations. The different colors
on isosurfaces are to distinguish the opposite phases of
wavefunctions. The LUMO and LUMO+1 levels are
almost degenerate with eigenvalues of -3.664 eV and
-3.663 eV respectively. Practically, the system has a
twofold degenerate LUMO level, and thus both orbitals
are shown as frontier orbitals in Fig. 1. The HOMO
orbital with -5.253 eV eigenvalue is localized on the
central TTU-Pc ring as in other phthalocyanines, and
has only small contributions from S atoms. Our HOMO
and LUMO energy level values indicate an energy
gap of 1.59 eV. The LUMO and LUMO+1 orbitals in
Fig. 1 are also localized on the central TTU-Pc ring. The
degeneracy of LUMO and LUMO+1 is reflected on the
orbital shapes as they are orthogonal to each other and
are closely related. Since the 13-membered macrocycles
are not involved in HOMO and LUMO orbitals, their
different conformations result in the same energy gap.
The frontier orbitals in Fig. 1 point out that the useful
electronic and optical properties of phthalocyanines
should also exist for our molecule.

Next, the oscillator strengths of the excitations were
calculated in TDDFT, and are presented in Fig. 9.
The results in Fig. 9 were computed with the HSE
exchange-correlation functional. The computations with
the B3LYP exchange correlation functional, not shown here, give essentially identical results. We found that the transition from ground state S0 to the first excited state S1 is mainly (93%) from HOMO to LUMO. Our TDDFT calculated S0 → S1 excitation energy is 1.91 eV with oscillator strength of 0.534. Since the LUMO and LUMO+1 levels are degenerate, the second excitation is between HOMO and LUMO+1 level with an energy of 1.94 eV and oscillator strength of 0.586. There is an energy difference of 1.45 eV between LUMO+1 and LUMO+2 levels. Therefore, the lower energy excitations are always to the LUMO and LUMO+1 levels, not to any higher level. We searched for the lowest 20 excitations in TDDFT. Apparently, the B band is not within the reach of our TDDFT calculations. Note that LUMO and LUMO+1 levels are practically twofold degenerate LUMO levels. The first two oscillator strengths 0.534 and 0.586 are large. The oscillator strengths of other excitations are small with peak values of 0.11 between 2.2–2.4 eV excitation energies.

**CONCLUSION**

In this study, synthesis and spectroscopic characterization of dimethyl substituted tetraphia macrocycle fused Zn(II) phthalocyanine were reported. Photophysical and photochemical properties of the phthalocyanine derivative were investigated in DMSO. The singlet oxygen quantum yield of TTU-Pc in DMSO was determined as 0.25 which was lower than reference unsubstituted ZnPc and other sulfonyl groups bearing Pc derivatives reported in the literature, showing the lowering effect of tetraphia macrocycle incorporation. However, the tetraphia macrocycle can be easily converted into its sulfonyl derivative. In the light of this information, we plan to continue our work on sulfonyl derivative of TTU-Pc in the future. We foresee an increase that might be achieved by sulfonyl groups, which will probably enhance solubility and prevent aggregation. Experimental results and theoretical calculations of HOMO, LUMO and energy gap (E_g) values for TTU-Pc were compared. We found that the frontier orbitals are on the central ZnPc ring and the conformation of the 13-member ring did not affect the electronic and optical properties. The computational

<table>
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<th>Electrochemistry</th>
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results in the PBE functional were in good agreement with our CV data, and HSE calculated energy gap confirms the measured optical gap.

Acknowledgments

Ö. Bekaroğlu is thankful to the Turkish Academy of Sciences (TUBA) for partially supporting this work.

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INTRODUCTION

Phthalocyanines (Pcs) have attracted much interest in a variety of fields due to exhibiting bright blue-to-green colors and featuring intense absorption bands in the UV and visible regions (termed Soret and Q bands, respectively, Fig. 1a) that can be fine-tuned using appropriate peripheral modifications and central elements [1]. In this regard, some experimental and theoretical studies of Pc absorption properties have been reported [2], so that fine-tuning in the visible region can be viewed as an “established” technology. Recently, we could shift the Pc Q band to the near-IR (NIR) region beyond 1000 nm utilizing simple substitution effects [3]. The large contribution of α-carbons to the Pc HOMO allows the introduction of electron-deficient elements (such as group 15 elements) at this position to be used for destabilizing its energy. Moreover, the Pc LUMO features large contributions from pyrrole nitrogens, implying that the introduction of electron-deficient elements (such as group 15 elements) at this location should result in LUMO stabilization. Thus, the positions of Pc near-IR absorption bands can be tuned using simple synthetic procedures.

Chromic effects are extensively utilized in various fields, e.g., for detecting toxic volatile organic compounds (VOCs) and for biological imaging [4]. In particular, solvatochromic materials exhibit solvent polarity–dependent colors, typically containing electron donor and acceptor parts connected via an aromatic system and featuring main absorption band position changes of 100–300 nm in the visible region [5]. However, such significant changes impose limitations on the design of solvatochromic materials, requiring the development of novel strategies.

Herein, we realize visible color changes by utilizing the chromic effect of simple Pcs in the near-IR region (near-IR solvatochromism) [6]. Notably, Pcs with Q bands positioned in the near-IR region show unusual solution colors such as red, yellow and gray, since the corresponding spectral differences cannot be recognized by the human naked eye. Although the solvent-induced
CHANGES OF PHTHALOCYANINE VISIBLE COLOR CAUSED BY NEAR-IR SOLVATOCHROMISM

Q band shift is usually small, changes occurring at the border between the visible and near-IR regions may lead to a sizable visible color change even in the case of small shifts. For instance, Kobayashi et al. reported that 1, 4, 8, 11, 15, 18, 22, 25 (αα)-octaphenylPc metal complexes show central metal-dependent colors [7]. Since the Q bands of αα-octaphenylPcs are located at 700–800 nm, we hypothesized that the solvatochromic response in this border region should result in observable color changes, utilizing αα-octaalkoxyPc metal complexes to confirm this assumption (Fig. 1b). In particular, octabutoxyPcs are widely utilized [8], with their structural features rationalized as follows. (1) The effect of group 16 elements at the α position increases in the order of O < S < Se < Te [3b], with the presence of eight oxygen atoms at the α position being sufficient for shifting the Q band to the border region [2, 8a]. (2) Although the central metal exhibits only an insignificant direct effect on the position of the Q band (with some exceptions) [3b], it exhibits a marked indirect effect by influencing the aggregation of Pcs in solution [9], with the Q band position of aggregated Pcs being different from that of monomeric species. In view of the above, the solvent-dependent Pc aggregation behavior is expected to result in solvatochromic effects. (3) Despite the effect of substituents at the oxygen atom being relatively weak, these substituents are essential for improving Pc solubility, with small alkyl chains being particularly suitable for this purpose, whereas bulky groups prevent Pc aggregation. Moreover, Pcs with long alkyl chains have been well studied as liquid crystal materials [10].

**Fig. 1.** (a) Typical absorption spectrum a metallated Pc with $D_{4h}$ symmetry. (b) Molecular design of chromic Pcs by using the near-IR region

![Absorption Spectrum](image)

**Scheme 1.** Synthesis of Pcs. Reagents and Conditions: (i) $n$BuOLi (excess.), $n$BuOH, reflux, 2 h, 56% for 1 and 30% for 4; (ii) Zn(OAc)$_2$•2 H$_2$O (5 eq), DMF, 160°C, 1 h, 47% for 2 and 27% for 5; (iii) Co(OAc)$_2$•4 H$_2$O (5 eq), DMF, 160°C, 1 h, 68%
RESULTS AND DISCUSSION

Synthesis

All desired Pcs were obtained in moderate yields, with their preparation illustrated in Scheme 1. Free-base Pcs are precursors of complexes containing various central metals (MPcs), which were chosen to be Zn and Co in the present study. The crystallographic structures of ZnPc feature coordinating solvent molecules (pyridine, THF, DMF, etc.) at the axial position of the zinc ion [11], indicating that bulky tert-butylphenyl groups do not shift peaks [14], allowing the absorption band positions of free-base Pcs to be varied in the range of 750–850 nm by changing the aggregation state. The absorption spectrum of solid-state 3 indicated that the Pc–Pc interaction in CoPc is relatively weak.

Although oxygen-attached substituents exhibited a small effect on the spectra of diluted Pc solutions in THF, different solvent effects were observed for

Optical properties in THF solution

Figure 2 shows UV-vis-NIR absorption, fluorescence, and magnetic circular dichroism (MCD) spectra of Pcs in THF, with the Q_00 bands of all Pcs appearing in the border (700–800 nm) region, as expected. The presence of sharp and intense Q bands indicates the absence of aggregation in diluted THF solutions. Although free-base Pcs typically feature two intense Q bands, a single broad Q band was observed for 1 (762 nm with a shoulder at 738 nm), which was ascribed to a partial overlap of the corresponding Q_x and Q_y bands. The MCD spectrum of 1 reveals the existence of two excited states as two oppositely signed Faraday B terms (771 and 739 nm). The Q bands of Pc metal complexes are fairly intense, with the corresponding absorption coefficients being about twice as high as those of free-base Pcs. The intense Faraday A-term MCD spectra of 2 in the Q-band region further indicate that the practical chromophore symmetry of Pcs is close to D_{5h}. Therefore, all Pcs in this study could be regarded as regular free-base and metal complexes of Pc in dilute THF solutions. Free-base Pcs and ZnPc exhibited fluorescence in the near-IR region, while CoPc showed no fluorescence. All Pc solutions had a pale green color in THF, which implied that absorption bands at ~700 nm were recognizable by the naked eye. The absorption envelopes of benzyl-substituted Pcs 4 and 5 were close to those of 1 and 2, respectively, indicating that bulky p-tert-butylphenyl groups do not affect the optical properties of Pcs in dilute solutions in coordinating solvents (such as THF).

Chromic responses

Solvatochromic responses were examined by comparing the absorption spectra of Pcs in various solvents and in the solid state (Fig. 3), with the corresponding Q-band positions summarized in Table 1. The absorption spectra of solid-state Pcs indicated the occurrence of aggregation, with two intense absorption bands at ~800 nm observed for 1 and 2. The shorter-wavelength peaks (781 nm for 1 and 749 nm for 2) were assigned to the monomeric state, whereas the longer-wavelength ones (852 nm for 1 and 830 nm for 2) were assigned to the aggregated state. Head-to-tail arrangement (J-type) of Pc molecules in the solid state is known to result in red-shifted peaks [14], allowing the absorption band positions of 1 and 2 to be varied in the range of 750–850 nm by changing the aggregation state. The absorption spectrum of solid-state 3 indicated that the Pc–Pc interaction in CoPc is relatively weak.

Although oxygen-attached substituents exhibited a small effect on the spectra of diluted Pc solutions in THF, different solvent effects were observed for
CHANGES OF PHTHALOCYANINE VISIBLE COLOR CAUSED BY NEAR-IR SOLVATOCHROMISM

Notably, 5 exhibited only insignificant solvatochromism, with the peak at ~800 nm being relatively weak in non-coordinating solvents. This difference clearly supported the assignment of the near-IR band to Pc aggregation, which could be prevented by the introduction of bulky p-tert-butylbenzyl groups. The absorption spectrum of solid-state 4 featured a decreased intensity of the above band, indicating that the bulkiness of the benzyl group prevented aggregation.

Figure 4 presents photographs of solid 1, 2, and 5 and their representative solutions, showing that free-base Pcs and the corresponding zinc complex bearing bulky substituents featured similar green colors. On the other hand, 2, a zinc complex bearing small alkyl substituents,
showed solvent-dependent colors (from red and yellow to green), although the range of the Q band shift equaled only 100 nm (1700 cm⁻¹), being smaller than that typically observed for solvatochromic molecules [5]. The observed colors were closely correlated with aggregation properties. Thus, Pc aggregation resulted in the appearance of a new peak in the near-IR region, which was invisible to the naked eye. In the visible region, the weak band assigned to the n(O)-π⁺ transition [15] was shifted to ~500 nm, resulting in “visible” red color appearance. Figure 5a shows the absorption spectra of 2 in chloroform at various concentrations, revealing that the intensities of both monomer (764 nm) and aggregate (811 nm) peaks were well correlated with concentration and confirming that solvatochromic changes in dilute solutions are concentration-independent. The colors of solutions perceived by the human eye were retained within the concentration range of 1.0 x 10⁻⁵–2.0 x 10⁻⁶ M. Finally, we investigated the solution color change of 2 in different solvent mixtures (Fig. 5b). When the THF content of chloroformic solutions was increased, the intensity of the absorption band in the near-IR region was reduced and an intense band (typical Q band) appeared in the shorter-wavelength region, indicating that the Pc was disaggregated by the coordination of THF to the central zinc atom. Importantly, the visible color also changed from red to green with increasing THF content, supporting the conclusions drawn from spectral changes.

EXPERIMENTAL

Measurements

Unless otherwise noted, solvents and reagents were purchased from Tokyo Kasei Co. and Wako Chemicals Co. and were used after appropriate purification (distillation or recrystallization).

Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic circular dichroism (MCD) spectra were obtained on a JASCO.

Fig. 4. Photographs of solid and solutions of 1 (a), 2 (b) and 5 (c)

Fig. 5. (a) UV-vis-NIR absorption spectra of 2 at various concentrations in CHCl₃. (b) UV-vis-NIR absorption spectra of 2 in several THF-CHCl₃ mixtures ([2] = 1.0 x 10⁻⁵ M)
J-725 spectrophotometer equipped with a JASCO electromagnet capable of producing magnetic fields of up to 1.03 T (1 T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla (θ/deg·dm³·mol⁻¹·cm⁻¹·T⁻¹). Fluorescence spectra were obtained on a HITACHI F-4500 spectrofluorometer. NMR spectra were obtained on a JEOL ECA-500 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). 1H were referenced to the tetramethylsilane (Me₄Si) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet and m = multiplet.

Synthesis

3,6-Dibutoxyphthalonitrile [8b] and 3,6-di-(p-tert-butylbenzyloxy)phthalonitrile [13] were prepared according to the literature.

Preparation of αααα-OBu₈Pc free-base complex (1) [16]. 3,6-Dibutoxyphthalonitrile (200 mg, 0.73 mmol) was added to a solution of lithium (28 mg, 4.0 mmol) in 2.5 mL of butanol and heated under reflux for 2 h. After the mixture was concentrated, the residue was dissolved in chloroform and washed with 2 N HClaq, water and brine. The organic layer was dried over Na₂SO₄, filtered in vacuo, and concentrated by silica gel column chromatography (CHCl₃-methanol (500 MHz; CDCl₃; Me₄Si): δ = 7.5 Hz). UV-vis (THF): λmax, nm (10⁻⁵ε): 766 (9.3), 753 sh (8.7), 677 (2.8), 330 (5.1).

Preparation of αααα-(p-tert-butylbenzyloxy)Pc zinc complex (5). The procedure described for 2 was used with 4 to give title compound as green powder (27%). 1H NMR (500 MHz; pyridine-d₅): δppm 7.86 (d, 16H, J = 5.8 Hz), 7.58 (s, 8H), 7.34 (d, 16H, J = 5.8 Hz), 6.10 (s, 16H), 1.19 (s, 72H). UV-vis (THF): λmax, nm (10⁻⁵ε): 737 (1.6), 661 (0.35), 328 (0.47) nm.

CONCLUSIONS

Herein, we investigated the chromic responses of Pcs with eight α-oxygen atoms, showing that their electron-donating effects resulted in the appearance of a Q band above 700 nm in dilute THF solutions. The central metal was demonstrated to influence the aggregation behavior of Pcs, e.g. zinc complex 2 was aggregated in non-coordinating solvents, whereas free-base Pcs and cobalt complexes were relatively weakly aggregated. The red-shifted peak of aggregated 2 was observed in the near-IR region and thus could not be recognized by the human eye. However, aggregated 2 exhibited a red-to-yellow color due to a weak n–π* transition in the visible region. Hence, the visible color of 2 could be changed by varying solvent type and solvent mixture composition, demonstrating the existence of a small solvatochromic effect (~100 nm). Bulky substituents were shown to suppress aggregation, and no sizeable visible color change could be observed. Although traditional solvatochromic molecules utilize absorption bands in the visible region, the described Pcs employed absorption bands in the “invisible” near-IR region, achieving unique solvatochromic behavior due to featuring a carefully chosen combination of peripheral oxygen atoms, central metal, and oxygen-attached substituents. Despite a Pc skeleton being used as a core chromophore in this work, the methodological development can be expanded to other chromophores featuring near-IR absorption.

Acknowledgments

This work was partly supported by a JSPS KAKENHI Grant (No. 15K05409), the Murata Science Foundation, the Kyoto Technoscience Center Foundation, and the TOBE MAKI Scholarship Foundation.

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Synthesis and properties of a trinuclear copper(II) complex of a ligand with phthalocyanine and Schiff-base coordination sites

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 29 November 2017
Accepted 5 January 2018

ABSTRACT: A trinuclear copper(II) phthalocyanine complex was synthesized by chelate coordination of the peripherally introduced Schiff-base nitrogen and phenoxide oxygen on the Cu(pc) core to a copper(II) ion. The magnetic, spectral and electrochemical properties were compared with those of the precursor mononuclear Cu(pc) complex with the NO chelate coordination site and a mononuclear Schiff-base copper(II) complex corresponding to the central bis-chelated unit of the title trinuclear complex. A stronger aggregating nature of the trinuclear complex compared with the precursor mononuclear Cu(pc) complex was confirmed by the spectral change of the Q band feature coming from the coordination to the copper(II) ion in dichloromethane. Two successive pc-ring reduction waves were not observed for the trinuclear complex in dichloromethane containing TBP(PF\textsubscript{6}), alternatively showing an irreversible wave in the reduction side. The central bis-chelated copper(II) ion was considered to play an important role for the redox behavior of the trinuclear complex.

KEYWORDS: trinuclear copper(II) phthalocyanine, peripheral Schiff-base coordination site, spectral properties, magnetic properties, electrochemical properties.

INTRODUCTION

Much interest has been devoted to phthalocyanines and their metal complexes [(M(pc))] for their unique properties based on the extended $\pi$-system within the ligands [1–4]. The strong absorption in the near-infrared region (650–700 nm) observed for them, called the Q band, is the reason why they show remarkable blue or green colors, leading to their longtime use as dyes and pigments. Recently, they have been also applied as nonlinear optics (NLO), optical storage devices, chemical sensors, electrochromic devices, photosensitizers in photodynamic therapy (PDT), etc. [5–9]. Schiff-base complexes have attracted many chemists for their interesting electrochemical, catalytic and magnetic properties [10–19]. If metallophthalocyanine [(Mpc)] and Schiff-base complexes are combined within a molecule, new interesting properties could be produced by the combination. Based on such a concept, we have been engaged in synthesizing pc-Schiff-base conjugated complexes and reported dinuclear complexes [(M1–M2(L)]\textsuperscript{2}], \textit{M1} = Ni\textsuperscript{II}, Cu\textsuperscript{II}; \textit{M2} = Ni\textsuperscript{II}, Cu\textsuperscript{II}, V\textsuperscript{V}O) [20, 21] and tetranuclear complexes [(Cu\textsubscript{4}(L\textsuperscript{2})Cl\textsubscript{4}(µ-\textit{OH}))] [22], structures of which are shown in Scheme 1. In this study, we synthesized a trinuclear copper(II) complex...
of a fused ligand having phthalocyanine and Schiff-base coordination sites (H₃L₁). The chelate coordination of NO donor atoms of a peripherally introduced Schiff-base site onto the pc ring of a copper(II) complex [Cu(HL₁)] (1) to a copper(II) ion gave the objective trinuclear complex [Cu(L₁)₂Cu] (2), the structure of which is shown in Scheme 2. Further, we prepared a mononuclear copper(II) complex of a Schiff-base ligand N-(4-methylphenyl)salicylaldimine (HL₂), because the copper(II) complex [Cu(L₂)₂] (3) corresponds to the central part of the trinuclear copper(II) complex 2. Here, we report on the syntheses and magnetic, spectroscopic, and electrochemical properties of the complexes 1–3 as well as the crystal structure of 3.

RESULTS AND DISCUSSION

The synthetic procedure from [Cu{pc(t-Bu)₃(NH₂)}] to the title trinuclear complex [(Cu(L₁)₂Cu] (2) through the mononuclear complex [Cu(HL₁)] (1) is illustrated in Scheme 3. The peripheral amino group on the pc ring of [Cu{pc(t-Bu)₃(NH₂)}] reacts with carbonyl group of salicylaldehyde to give the coordinating site consisting of Schiff-base nitrogen (N) and phenoxide oxygen (O) atoms. The NO chelate coordination to copper(II) ion produced the trinuclear complex. In order to investigate the NO chelate coordinated copper(II) site, a mononuclear complex [Cu(L₂)₂] (3) was prepared and its crystal structure determined. The crystal structure is drawn in Fig. 1. Selected bond distances and angles are given in Table S1 (see Supporting information). The crystallographical inversion center exists at the central copper atom of the mononuclear unit, hence giving the bond angles of O₁–Cu₁–O₁’ = 180° and N₁–Cu₁–N₁’ = 180°. The coordination geometry around the copper(II) ion adopts a square planar geometry, and two NO chelate ligands (L²) coordinate to the copper(II) ion with the trans arrangement. The Cu–O and Cu–N bond distances are 1.886 (1) and 2.015 (2) Å, respectively, which are comparable to those for the copper(II) complexes with the NO type Schiff-base ligands derived from condensation of aniline and salicylaldehyde derivatives [23–36]. It seems to be usual that N₂O₂-tetra-coordinated copper(II) complexes with Schiff-base ligands adopt trans square planar, distorted square planar or tetrahedral geometry. However, a cis arrangement of the copper(II) complex with the same ligand as the present study (L²) has been reported for [Cu(L²)•DMF] [31]. In [Cu(L²)•DMF, the copper(II) ion has a distorted square planar structure with a dihedral angle of 40.5(1)° between two CuNO coordination planes, where Cu–N = 1.965 (3) Å and Cu–O = 1.903 (2) and 1.895 (2) Å. DMF exists as a crystal solvent in the crystal, showing intermolecular hydrogen bonds with the Cu-complex unit. Although there have been discussions on the trans–cis isomerism concerning the copper(II)-Schiff-base complexes obtained by NO bidentate coordination, to our knowledge, the ligand HL² is the first example to give both cis and trans isomers structurally determined by X-ray structure analysis.

Figure 2 shows temperature dependence of molar magnetic susceptibility (χ_m) and effective magnetic moment (μₑff) for the complex 2. The moment (per a trinuclear molecule; μₑff = (8χ_m•T)^1/2) is 3.43 μ_B at 300 K, which is rather close to the spin-only value (μₑff = 3.00 μ_B) for magnetically independent three unpaired electrons.
(S = 1/2 for each Cu(II) ion). The moment decreases slightly with the decrease of temperature to ca. 10 K. The decrease becomes steep below 10 K, which was considered to originate from an inter- or intra-molecular interaction between Cu(II) centers. The mononuclear Schiff base complex 3 does not show such decrease in the low temperature region, as shown for Fig. S1 (see Supporting information). A tetranuclear copper(II) complex [Cu₄(L'²)Cl₂(μ-OH)] (Scheme 1(b)) was reported to demonstrate a negligible interaction through an imino nitrogen and a benzene ring of the pc ligand between Cu(II) units. The entire temperature-dependent magnetic moment behavior of 2 is similar to a dinuclear complex [Cu₂{(pc)₂(t-Bu)₆}] (Scheme 4), which did not display any important interaction through the common benzene ring, but showed a weak interaction due to the aggregation nature due to the enlarged π-conjugate system [37].

Absorption spectra of 1 and 2 measured in dichloromethane are displayed in Figs 3 and 4, respectively. Complexes 1 and 2 show the Q band peaks both at 682 and 681 nm, respectively, where the molar extinction coefficient (ε/M⁻¹·cm⁻¹) is calculated to be the value per a Cu(pc) unit for 2. It is well-known that the Q band is blue-shifted and appears as a broad band when the phthalocyanine molecules aggregate in a face to face mode [4, 38]. Although complex 1 shows the aggregating nature because the shoulder band at the shorter wavelength region comes to be remarkable in accordance with the decrease in the Q band intensity (ε/M⁻¹·cm⁻¹) when the concentration is increased from 2.0 × 10⁻⁶ M to 2.5 × 10⁻⁵ M, the aggregating nature is stronger for 2, showing a much weaker Q band intensity with a stronger shoulder band compared with those of 1.
A similar phenomenon has been observed for the tetranuclear complex [Cu4(Lb)Cl2(m-OH)], which showed a stronger aggregating nature compared with the corresponding dinuclear complex [Cu2(HLb)]. The enlarged planarity of the complex molecule by the coordination of the Schiff-base sites to copper(II) ions was considered to be the plausible reason for the increased aggregating natures of 2 and [Cu4(Lb)Cl2(m-OH)]. Interestingly, the spectral feature of 2 changed in DMF (Fig. 5) ($\lambda_{\text{max}}$ = 680 nm for the Q band) and became much similar to that of 1, of which spectrum measured in DMF is given in Fig. S2 ($\lambda_{\text{max}}$ = 682 nm for the Q band) (see Supporting information). The geometrical change around the central copper(II) ion in DMF from dichloromethane may be related to the observed spectral change.

Figure 6 displays cyclic voltammograms (CVs) measured in dichloromethane containing TBP(PF6) (0.1 M) for 1, 2 and 3. There are redox couples ($E_{1/2} = -0.96$ and -1.35 V vs. SCE) on the reduction side for 1, which can be assigned to reduction at the pc ring because the copper(II) phthalocyanine with four t-butyl groups [Cu{pc(t-Bu)4}] showed the corresponding redox couples, similarly at $E_{1/2} = -1.42$ and -1.78 V vs. Fe+/Fe [22], when taking $E_{1/2}$ (Fe+/Fe) = ca. 0.45 V vs. SCE into account [39]. The broad wave in the oxidation side (ca. 0.7 V vs. SCE) was attributed to the oxidation of the aggregated pc rings [40, 41]. The redox behavior is nearly the same as...
SYNTHESIS AND PROPERTIES OF A TRINUCLEAR COPPER(II) COMPLEX OF A LIGAND WITH PHTHALOCYANINE

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those observed for \([\text{Cu}_4(\text{L}^3)\text{Cl}_2(\mu-\text{OH})]\) and \([\text{Cu}_2(\text{L}^2)^2]\) [22]. Complex 2 shows completely different behavior, with only an irreversible wave being found at \(E_{1/2} = -0.95\) V in the reduction side, although the mononuclear Schiff-base complex 3 shows a reversible or quasi-reversible wave at \(E_{1/2} = -0.75\) V vs. SCE. Further, 2 shows the redox couples at \(E_{1/2} = -0.82\) and -1.22 V vs. SCE similarly to 1 (\(E_{1/2} = -0.78\) and -1.14 V vs. SCE) when the CVs were measured in DMF containing TBP(PF\(_6\)) (0.1 M) (Fig. 7). The different redox behaviors of 2 observed in dichloromethane and DMF may be related to the fact that the copper(II) ion adopts different geometrical structures in dichloromethane and DMF as confirmed by their Q features in the absorption spectra. Complex 3 shows an irreversible reduction wave at \(E_{1/2} = -0.6\) V vs. SCE in DMF; the redox wave has been previously reported at a similar potential around -1.0 V vs. Ag/AgCl in DMF for the same, but \(cis\)-isomer complex [31].

EXPERIMENTAL

Syntheses of complexes

Copper(II) phthalocyanine with an amino group and three \(t\)-butyl groups ([Cu\{pc(\(t\)-Bu\(_3\))(NH\(_2\))\}] was prepared according to the method described in the literature [42]. Salicylaldehyde and \(p\)-toluidine were purchased from Wako Pure Chemical Industries, Ltd. and used as being supplied.

\([\text{Cu}(\text{L}^3)]\) (1): \([\text{Cu}\{\text{pc}(\text{t\(-Bu\)_3}(\text{NH}_2)\}] (76 mg, 0.10 mmol) and salicylaldehyde (122 mg, 1.0 mmol) were dissolved in ethanol (10 mL) and refluxed for 16 h. After the solvent was removed by evaporation, the resultant solid was chromatographed on a silica gel column with a chloroform–toluene (25:1) solvent mixture as an eluent. The first fraction was collected and evaporated to remove the solvent. The obtained green powder was recrystallized using hexane (20 mL), collected again by the filtration, and dried under vacuum. The yield was 17.2 mg (20% based on \([\text{Cu}_2(\text{L}^2)^2]\)]. Anal. calcd. for \(\text{C}_{51}\text{H}_{45}\text{CuN}_9\text{O}\): C, 70.94; H, 5.25; N, 14.60%. Found C, 70.68; H, 5.27; N, 14.35. HR-MS (ESI-TOF): \(m/z\) 863.3091 (calcd. for [M+H\(^+\)] 863.3116).

\([\text{Cu}(\text{L}^2)^2]\) (2): To an ethanolic solution (60 mL) of copper(II) acetate was added a solution of 1 (34.6 mg, 0.04 mmol) dissolved in 1,4-dioxane (20 mL). The solution was refluxed for 3 h and followed by evaporation to a small portion (ca. 10 mL) and addition of hexane (20 mL). The green precipitate was collected by suction filtration, washed with ethanol, and dried under vacuum. The yield was 33.3 mg (93.8% based on 1). Anal. calcd. for \(\text{C}_{102}\text{H}_{88}\text{Cu}_3\text{N}_{18}\text{O}_2\): C, 68.50; H, 4.96; N, 14.10%. Found C, 67.88; H, 5.15; N, 13.76. HR-MS (ESI-TOF): \(m/z\) 1810.4817 (calcd. for [M+Na\(^+\)] 1810.5126).

\([\text{Cu}(\text{L}^3)]\cdot\text{Cu}\) (3): \(p\)-Toluidine (213 mg, 2 mmol) and salicylaldehyde (244 mg, 2 mmol) were mixed and refluxed with stirring for 30 min in methanol (40 mL). To the reaction solution, copper(II) acetate monohydrate (200 mg, 1 mmol) in methanol (25 mL) was added and refluxed further for 16 h. The resultant solution was evaporated to 20 mL and stored in refrigerator (at ca. \(0^\circ\)C) to give a brown precipitate, which was collected by suction filtration, washed with a small amount of methanol, and dried under vacuum. The yield was 421 mg (87.0%). Anal. calcd. for \(\text{C}_{28}\text{H}_{24}\text{CuN}_2\text{O}_2\): C, 69.48; H, 5.00; N, 5.79%. Found C, 69.32; H, 4.75; N, 5.85. Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from methanol.

Measurements

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanako CHN CORDER MT-6. Absorption spectra were measured in dichloromethane and DMF using a JASCO V-670 spectrophotometer. ESI-TOF mass spectra were taken on a Bruker microTOF system. Cyclic voltammograms were taken in dichloromethane and DMF solutions containing tetra-n-butylammonium hexafluorophosphate [TBA(PF\(_6\))] on a BAS ALS-DY2325 Electrochemical Analyzer. A glassy carbon disk (1.5 mm radius), platinum wire, and saturated calomel electrodes were used as working, counter, and reference electrodes, respectively. Variable-temperature magnetic susceptibility measurements were...
Table 1. Crystallographic data and structure refinement of [Cu(L)2] (3)

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*Standard deviations in parentheses; a R1 = Σ||Fo|| – |Fc||Σ|Fo|; wR2 = [Σw(Fo2–Fc2)]²/Σ(Fo2)²|½.

carried out using a superconducting quantum interference device (SQUID) MPMSXL-5 from Quantum Design. The measured data were corrected for diamagnetic contributions [43].

X-ray diffraction data of complex 3 was collected at 150 K on a RIGAKU Saturn 724 CCD system equipped with Mo rotating-anode X-ray generator with Monochromated Mo Kα radiation (λ = 0.71075 Å) and were processed with using CrystalClear-SM 2.0 program (RIGAKU). The structure of complex 3 was solved by the direct method (SIR-2011) and refined using the full-matrix least-squares technique F2 with SHELXL2014 equipped in the CrystalStructure 4.2.5 software (RIGAKU). Non-hydrogen atoms were refined with anisotropic displacement, and almost all of the hydrogen atoms were located through a difference Fourier map and refined with isotropic thermal parameters. Crystal data as well as the details of data collection and refinement for complex 3 are summarized in Table 1 and can be obtained as a CIF file from Cambridge Crystallographic Data Center (CCDC). The deposition number of complex 3 is CCDC-1587713.

CONCLUSION

A trinuclear copper(II) phthalocyanine complex (2) was synthesized by chelate coordination of the peripherally introduced Schiff-base nitrogen and phenoxide oxygen on the [Cu(pc)(t-Bu3)] core to a copper(II) ion. The magnetic and spectral properties were compared with those of the precursor mononuclear Cu(pc) complex with the NO chelate coordination site (1) and the mononuclear Schiff-base copper(II) complex (3) corresponding to the central bis-chelated unit of the trinuclear complex. A stronger aggregating nature of the trinuclear complex compared with the precursor mononuclear complex was confirmed by the spectral change of the Q band feature coming from the coordination to the copper(II) ion in dichloromethane. Further, two successive pc-ring reduction waves were not found for the trinuclear complex in dichloromethane containing TBP(PF6), alternatively showing an irreversible wave in the reduction side. It was considered that the central bis-chelated copper(II) ion should play an important role for the redox behavior. However, it is still unknown why only the present trinuclear complex showed the behavior whereas the tetranuclear copper(II) complex of a pc-Schiff-base fused ligand with a hydroxide- and phenoxido-copper(II) binuclear core [Cu4(L4)Cl2[μ-OH]] did not show such a behavior. The trinuclear complex with a redox inactive metal ion at the central coordinated unit could give the useful information. Efforts to prepare the heterometal complexes such as Cu–Zn–Cu and Zn–Zn–Zn combinations are being made in our laboratory.

Acknowledgments

The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 15K17897 and 16K05722 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan). The authors are grateful to Dr. Michiko Egawa (Shimane University) for her measurements of elemental analyses and Prof. Masahiro Mikuriya (Kwansei Gakuin University) for his helpful discussion.

Supporting information

Selected bond distance and angles of 3 (Table S1), temperature dependences of magnetic susceptibility and moment of 3 (Fig. S1) and absorption spectra of 1 in DMF (Fig. S2) are given in the supplementary material. This material is available free of charge via Internet at http://www.worldscinet.com/ipp/ipp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-1587713. Copies can be obtained on request, free of charge, via the internet at http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).
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INTRODUCTION

Molecular aggregation phenomena have attracted great interest from viewpoints of aggregation-induced emission [1], light-harvesting [2], neurodegeneration in Alzheimer’s and Parkinson’s diseases [3] and so on. Phthalocyanines and related compounds are known as versatile dyestuffs and enjoy various applications in industrial and medical fields [4, 5], e.g. non-linear optics [6], optical data storage [7], solar cells [8], charge-generating materials for photocopiers and laser-printers [9], electrochromic displays [10, 11], photosensitizers for solar cells (DSC) [12] and photocatalysts [13], those for photodynamic therapy (PDT) [14] of tumors and photodynamic antimicrobial therapy (PACT) [15], chemical probes for bio-imaging (photodynamic diagnosis (PDD) of cancer) [16], semiconductors [17] and synthetic metals [18], and are also well-known to undergo this kind of phenomenon [14, 19–27]. Aggregation of dye molecules is quite an interesting subject from a viewpoint of supramolecular chemistry [28] because this gives rise to significant changes in their physical properties. Eventually aggregation of phthalocyanines produces dramatic spectral changes according to the manner of alignment of macrocycles due to exciton coupling between the chromophores [29–31]. However, this also may cause a serious problem in some of the aforementioned applications, in particular when their excited states are involved [12–16], because photo-excited dye molecules in aggregates are rapidly relaxed to their ground state and lifetimes of their excited states are significantly shortened and consequently their photochemical activities are considerably reduced [32, 33]. This problem can be fatal for phthalocyanines in aqueous media. Although a large number of water-soluble phthalocyanines have been reported so far, the
majority of them aggregate to a considerable extent in water even though they are highly soluble [34]. As those macrocyclic dyes are mostly used under aqueous conditions in such applications as DSC, PDT, PACT, PDD, where photoexcited dye molecules play a crucial role, molecular aggregation can give rise to a grave problem. Moreover, exciton coupling theory predicts that alignment of two dye molecules in a cofacial fashion (H-aggregation) will make the lowest excited state of the dimer electronically forbidden, while it will be allowed when aligned in a slipped-cofacial fashion [35]. Thus, availability of dye molecules in those applications considerably depends on presence/absence of aggregation phenomena and their manner of intermolecular alignment when present. Therefore, it is quite important to understand what dominates aggregation behaviors of dye molecules under specific conditions. A highly water-soluble phthalocyanine (tetraakis(2’,6’-dimethyl-4’-sulfonic acid)phenoxy)phthalocyanine (Fig. 1a; hereafter abbreviated as H$_2$Pc)), its copper(II) (Fig. 1b; Cu(Pc)) and antimony(V) derivatives have recently been prepared in our laboratory [22]. Of the three, only the antimony derivative is free from aggregation in water [22] while the others (copper and metal-free derivatives) strongly aggregate without surfactant or cosolvent [22, 36]. During the course of this study, it was found that the manner of alignment of Cu(Pc) molecules in their aggregate depends on the media in which the macrocyclic dyes are dissolved, while not in the case of the free base. In this work, aggregation behaviors of the macrocyclic compounds in aqueous, ethanolic, and their mixed-solvent systems are discussed by using optical absorption and magnetic circular dichroism (MCD) spectroscopies on the basis of Kasha’s exciton coupling model [35].

RESULTS AND DISCUSSION

Outline of optical absorption spectra of H$_2$Pc and Cu(Pc) in aqueous and ethanolic solutions

Figure 2 shows optical absorption spectra of Cu(Pc) and H$_2$Pc in aqueous and ethanolic solutions, which were measured at very low concentrations (ca. 10$^{-6}$ M). In ethanol, the copper derivative shows a sharp prominent

![Fig. 2. Optical absorption spectra of Cu(Pc) (red) and H$_2$Pc (black) in aqueous (solid lines) and ethanolic (broken lines) solutions (measured at ca. 10$^{-6}$ M). Note: those spectra in water are plotted assuming that the aggregated species is composed of four molecules (i.e. a tetramer) and hence these spectral intensities are multiplied 4 times](image)
absorption band with its peak at 677 nm. This spectrum is typical for metalated phthalocyanines with $C_4$ symmetry [29–31] and the prominent band is generally called a “Q band” and assigned as a degenerate HOMO–LUMO transition in the macrocyclic ligand [29]. H$_2$Pc in ethanol shows similarly sharp but twin bands in the same region (663 and 701 nm), which are characteristic of free-base phthalocyanines [29–31]. The splitting of the Q band in H$_2$Pc is attributed to the lower symmetry ($C_2$) of the macrocycle due to the presence of two hydrogen atoms in the cavity [29]. On the other hand, both of the compounds show a broad band with its peak around 615 nm in pure water. These spectra are characteristic of strongly aggregated phthalocyanines [29–31]. The significant broadening of the Q band in aqueous solutions reveals that H$_2$Pc and Cu(Pc) molecules strongly aggregate therein. It should be noted that the absorption spectra in water are shown on the assumption that the aggregated species are composed of four monomers (see below). Absorption spectra of both Cu(Pc) and H$_2$Pc are dependent of their concentration in ethanol (although quite slightly for H$_2$Pc) as described below, but little change has been observed in pure water when their concentrations are varied by 2 orders (ca. 10$^{-7}$ to 10$^{-5}$ M), indicating that they strongly aggregate even at very low concentration.

**Concentration study on absorption spectra of Cu(Pc) in water, ethanol, and their mixed solvent systems**

**Aggregation in aqueous solutions**

Some surfactants or cosolvents are known to facilitate disaggregation of aggregated phthalocyanines in water [21, 22, 26, 27, 34, 37]. Therefore, a number of research groups have monitored aggregation-disaggregation equilibrium by varying concentration/ratio of surfactant or cosolvent while the concentration of phthalocyanines of interest are kept constant [34]. However, as aggregation-disaggregation phenomena are basically equilibria involving monomer, dimer, trimer or higher aggregates, concentration study on the macrocyclic compound would be a more preferable approach to investigate such phenomena. Moreover, solvent study can give rise to misleading results due to unexpected reaction(s) with impurities contained in the solvent used [31].

Optical absorption spectra of Cu(Pc) in aqueous solutions containing various concentration of Triton X-100 with [Cu(Pc)] kept constant are shown in Fig. 3. Although Cu(Pc) shows a spectrum typical of strongly aggregated species in pure water as is shown in Fig. 2, that of the surfactant solution (10% w/v) is monomer-like and very close to that in ethanol, indicating that Cu(Pc) is present mostly as a monomer under these conditions. With decreasing surfactant concentration, the monomer Q band (687 nm) lowered, and incidentally another band appeared at 646 nm. Sharp isobestic points were observed in the Q band envelope in the range of surfactant concentration (0.02–10% w/v), indicating that the monomer and the new species are in equilibrium, which may be attributed to dimerization (i.e. dimer shows its Q band peak at 646 nm) as further discussed below. These spectral changes are reversible because aqueous Cu(Pc) solutions containing an appropriate amount of surfactant, where monomer is predominant, exhibit a dimer peak and lowering of monomer Q band upon the addition of appropriate salt, such as NaCl, probably due to salting-out effects. In a solution of lower surfactant concentration (0.01%), the observed Q band peak wavelength (629 nm) is neither that of monomer (687 nm) nor dimer (646 nm); hence aggregates composed of more than two dye molecules contribute to this spectrum (i.e. at least three molecules are involved). Moreover, in pure water, as the absorption maximum wavelength (613 nm) corresponds to not to a monomer, dimer, or (tentatively) trimer, it may be concluded to be composed of at least four molecular aggregated species as mentioned above.

It is noteworthy that the Q band blue shifts in the order of the monomer (687 nm), dimer (646 nm), trimer (629 nm; tentatively), and tetramer (613 nm; tentatively). Since a similar propensity is known for a series of monomeric, dimeric, and trimeric silicon-phthalocyanines (the macrocycles are bridged via μ-oxo axial ligand for the dimer and trimer) [38], this speculation is considered reasonable. This is easily interpreted in terms of exciton coupling between the macrocyclic chromophores [35].

It is suggested that the monomer-dimer equilibria can be monitored by varying concentration of Cu(Pc) under appropriate conditions (0.02% < Triton X-100 < 10%) as found in Fig. 3. Optical absorption spectra of Cu(Pc) at various concentrations in aqueous solutions in the presence of Triton X-100 (0.1%) are shown in Fig. 4. At the lowest concentration (2.90 × 10$^{-6}$ M), the observed spectrum is essentially that of monomer;
a sharp prominent Q band appears at around 687 nm. Hence, the Cu(Pc) species in the solution is predominated by monomeric species at this concentration. With an increase in its concentration, the apparent intensity of the monomer Q band lowers and a broad band grows around 640 nm. As sharp isosbestic points are observed in the Q band envelope, this new and monomeric species are in equilibrium: hence this new species may be assigned as a Cu(Pc) dimer. It should be noted that the dimer band appears only at the blue flank of the monomer Q band.

Kobayashi and Lever have demonstrated a blue shift of phthalocyanine Q band upon dimerization in a cofacial manner [39]. It is well known that the Q band transition for metallated phthalocyanine of C₄ symmetry is doubly degenerate and x- and y-polarized (when the molecular plane is taken as the x, y-plane) [29–31] (Fig. 5), as is exemplified below. Therefore, in this alignment, because both the x- and y-polarized excitons are also parallel, only the higher excited state is electronically allowed according to exciton coupling theory [35]. Moreover, phthalocyanine cores are basically hydrophobic even though they are surrounded by four hydrophilic substituents. Hence it is reasonable that the macrocyclic dyes are aligned in a cofacial manner to minimize the surface area of their hydrophobic moiety exposed to aqueous circumstance.

This speculation has been further supported by magnetic circular dichroism (MCD) study. The alignment shown in Fig. 5 suggests that the excited state, in which the lowest transition (Q band) is involved, should also doubly degenerate because both the x- and y-polarized excitons are parallel. Consequently, a clear Faraday A-term would be also observed in the Q band envelope of the dimeric species. Figure 6 shows optical absorption and MCD spectra of a monomer-dimer equilibrium mixture of Cu(Pc) in an aqueous solution (0.025% Triton X-100) as well as those of a monomer. At a very low concentration (3.99 × 10⁻⁶ M), the MCD spectrum around the Q band envelope is dominated by a distinctive sigmoid
curve with its center close to the monomer Q band peak wavelength (i.e., a Faraday A-term), indicating degeneracy of this transition as mentioned above. On the other hand, the spectrum at a much higher concentration \((1.40 \times 10^{-5} \text{ M})\) exhibits at least two sigmoid curves with their centers at around 645 and 684 nm, the latter of which is attributable to a monomer. As the center of the former sigmoid curve is also close to the optical absorption maximum wavelength of the dimer (645 nm), which may be assigned as a Faraday A-term, indicating degeneracy of the Q band transition in the dimer. It should be mentioned that Kobayashi and his coworker have also reported MCD spectra of water-soluble phthalocyanines and have concluded that Q band transitions in the dimers should be degenerate [26, 27].

**Aggregation in ethanolic solutions**

In ethanolic solutions, Cu(Pc) molecules are mostly in monomeric form at low concentrations but do aggregate at elevated concentrations. Figure 7 shows optical absorption spectra in ethanolic solutions containing Cu(Pc) at various concentrations. Although the spectrum at the lowest concentration is characteristic of a monomer, the apparent Q band intensity lowers with an increase in concentration and additional absorption bands grow at both red and blue flanks of the monomer Q band and some sharp isobestic points are observed in the spectral changes. This clearly indicates presence of equilibrium between monomeric species and aggregates (probably dimers). The appearance of extra bands at both flanks of the Q band clearly reveals that this compound aggregates in a “slipped-cofacial” manner (i.e., J-aggregation). It is generally accepted that the main band of J-aggregate appears at the red flank of that of the corresponding monomer according to exciton coupling theory [35]. However, in this case, as the Q band transition is doubly degenerate, it is not surprising that J-bands appear both at the blue and red flanks of the monomer Q band [21, 31, 37]. This speculation has been further supported by MCD work, because neither of \(x\)-nor \(y\)-polarized component is degenerate any longer in such alignment. Figure 8 shows MCD spectra of Cu(Pc) monomer and an equilibrail mixture of monomer and dimer in ethanol solutions as well as their absorption spectra. In a dilute solution \((2.87 \times 10^{-6} \text{ M})\), the MCD spectrum around the Q band envelope is dominated by a distinctive sigmoid curve with its center at the absorption maximum wavelength.
(i.e. a Faraday A-term, which is observed when the electronic transition is degenerate [29]) because Cu(Pc) is present mostly as monomer therein. On the other hand, at a higher concentration (4.65 \times 10^{-5} \text{ M}), apart from the Faraday A-term due to a monomer, a Gaussian type negative trough appears at around 720 nm, close to the absorption maximum wavelength (717 nm) of the dimer band of lower energy (i.e. a Faraday B-term [29]). Its higher energy counterpart (560–650 nm) has a positive signal but is rather complicated, probably because of the presence of vibronic bands of monomers and dimers. A schematic view of a slipped-cofacial dimer is presented in Fig. 9. Thus, y-polarized excitons are parallel while x-polarized ones are aligned in a head-to-tail manner, which gives rise to blue shift and red shift of the monomer band, respectively [31], according to exciton coupling theory [35].

Similar absorption and MCD spectra have been reported for an amphiphilic antimony(V)-phthalocyanine complex [21, 31]. Although the majority of phthalocyanines aggregate in a cofacial manner (i.e. H-aggregate) [23–27, 29–31, 34, 36, 39] due to strong \( \pi-\pi \) interaction between chromophores, it is understandable that the antimony-complex molecules align in a slipped-cofacial manner because of the presence of two hydrophilic and bulky axial ligands, which prevent H-aggregation of the macrocycles [21]. Thus J-aggregation is much less common for phthalocyanines unless steric hindrance occurs due to the presence of either axial ligand(s) on the metal ion [20, 21, 31, 37], or the metal ion itself protrudes from the cavity of the macrocyclic ligand [19, 40–42], or something else [43]. Nevertheless, the copper ion in Cu(Pc) has no axial ligand on the basis of its mass spectrum [22] and is quite likely to be located within the molecular plane of the macrocycle [44]. Kobuke’s group has reported rigid slipped-cofacial dimers of phthalocyanine complexes bearing an imidazolyl group as a peripheral substituent which coordinates to another metal ion in the cavity of its macrocyclic ligand [43]. Substituents of the macrocyclic ligand in this study also have sulfonic acid groups, which are capable of coordination to a metal ion in the cavity of another macrocycle. Therefore, J-aggregation in ethanol can be inhibited by addition of an appropriate ligand to block the fifth coordination site of copper in Cu(Pc). Eventually, absorption spectra of Cu(Pc) in ethanol solutions depend little on its concentration up to \( c_{\text{Cu(Pc)}} = 10^{-4} \text{ M} \) in the presence of a large excess amount of 4-phenylpyridine (PhPY). Although little spectral change is observed for Cu(Pc) monomer upon the addition of PhPY (see Figs 2 and 10), slipped-cofacial dimerization has been entirely inhibited. On the contrary, another absorption band grew at the blue flank of the monomer band above the concentration (e.g. at 4.37 \times 10^{-4} \text{ M}), which is attributable to a cofacial

**Fig. 9.** A schematic view of a slipped-cofacial dimer of Cu(Pc) (a) and coupling between x-polarized transitions and y-polarized ones (b)
dimer (Fig. 10a), as is the case for aqueous solutions. This clearly indicates that PhPY has blocked the fifth coordination site and inhibited coordination of sulfonate, furthering dimerization in a slipped-cofacial manner. As an alternative explanation, the addition of PhPY can facilitate disaggregation of Cu(Pc) dimers by electrostatic repulsion between negatively charged Cu(Pc) molecules generated owing to withdrawal of a proton from each of sulfonic acid groups by PhPY. However, this is considered much less likely for the following reason: As –SO₃H is a strong acid, negatively charged Cu(Pc) (and H₂Pc as well) molecules in pure water would be mostly in a monomeric form if electrostatic repulsion would play a predominant role in disaggregation of the macrocyclic compounds; nevertheless, they strongly aggregate in water (Fig. 2). It has been concluded in the earlier work in the comparison with aggregation-free antimony(V) derivative [22] that the presence of this peripheral group greatly contributes to their high water-solubility, but something else is needed for the macrocycles to disaggregate.

**Aggregation in aqueous solutions in water/ethanol mixed solvent systems**

It has been revealed that Cu(Pc) H-aggregates in water while J-aggregates in ethanol. The next mystery is “what will happen in water/ethanol mixed solvent systems?” Effects of ethanol on optical absorption spectra in water have briefly been studied elsewhere by varying water/ethanol ratio alone but keeping [Cu(Pc)] constant [22]. Monomer-dimer equilibria are observed when the ratios of water are less than 60% (v/v), whereas above this ratio, contribution from aggregates of higher orders can no longer be negligible (as is the case for aqueous Triton X-100 solutions of low concentration). Therefore, this work has focused its survey on the following five mixed solvent systems; water/ethanol = 40/60, 20/80, 10/90, 5/95, 1/99 (v/v). Figure 11 shows optical absorption spectra of Cu(Pc) at various concentrations in 40/60 (Fig. 11a), 10/90 (Fig. 11b), and 1/99 (Fig. 11c) mixed solvent systems (the others are shown in supporting information; Fig. S2). In water-rich systems (40/60 (Fig. 11a) and 20/80 (Fig. S2a)), the concentration-dependence is essentially the same as those in aqueous Triton X-100 solutions (Fig. 4), suggesting dimerization in a cofacial manner. On the other hand, in ethanol-rich systems (5/95 (Fig. 11c) and 1/99 (Fig. S2c)), the spectral changes are similar to those in pure ethanol, and hence dimerization in a slipped-cofacial fashion is likely to occur. These findings are not surprising because they are easily deduced from the aggregation behaviors in pure water and ethanol, respectively. Interestingly, absorption spectra of Cu(Pc) in 10/90 system depend little on its concentration, and the Q band intensity obeys Lambert–Beer’s law up to almost 10⁻⁴ M. Although it appears strange that the presence of a considerable amount of water facilitates disaggregation of phthalocyanines, this is not necessarily surprising if water is considered not only as solvent but also as a ligand at the fifth coordination site of copper ions, which competes with the peripheral sulfonic acid groups (just like PhPY). A 10/90 mixed solvent system is equal to an ethanolic solution containing ca. 5.6 M of water as extra ligand. As the affinity between water and copper ions is not so strong, such a large amount may be needed to sufficiently inhibit coordination of sulfonic acid groups.

**Concentration study on absorption spectra of H₂Pc in aqueous and ethanolic solutions**

H₂Pc has been found to strongly aggregate in pure water as is shown in Fig. 2. H₂Pc molecules are present mostly in monomeric form even in water in the presence of Triton X-100 above 1.0% (w/v). The presence of monomers and dimers in equilibrium is observed in the presence of Triton X-100 above 0.02% but contribution...
from aggregates of higher order (composed of at least three at 0.01% and four molecules in pure water) is no longer negligible below the concentration range (Fig. 12a). Concentration study on H₂Pc in the surfactant concentration range clearly shows alignment of two macrocycles in a slipped-cofacial manner (Fig. 12b) unlike its copper analog in water. This is because absorption bands attributable to a dimer appear not only at the blue flank of the monomer Q band envelope (around 650 nm) but also at the red flank (around 750 nm), as is the case for Cu(Pc) in ethanol. However, the magnitude of the slippage along the x-axis (Fig. 9) should be not as large as that in the Cu(Pc) slipped-cofacial dimer, judging from the smaller red shift of the dimer band and its weakness [35]. Hence, two macrocycles are considered to be aligned essentially in a cofacial manner but are slightly slipped against each other along the x-axis. A similar aggregation manner has been proposed for amphiphilic
metal-free phthalocyanines in aqueous media [45, 46] and for hydrophobic free-base phthalocyanines in non-aqueous media as well [23] on the basis of NMR studies. It should be noted that addition of NaCl into solutions, in which monomers are predominant, here again facilitates dimerization in a slipped-cofacial manner.

In ethanolic solutions, the absorption spectrum of H$_2$Pc depends little on its concentration up to ca. $5 \times 10^{-5}$ M; absorbance at its Q band peaks (663 and 701 nm) obeyed Lambert–Beer’s law. However, careful comparison between spectra at different H$_2$Pc concentrations has detected small but non-negligible differences: lowering of apparent Q band intensities and growth of its blue and red flank at higher concentrations, suggesting a contribution from a slipped-cofacial dimer (Fig. S2). Interestingly, H$_2$Pc is essentially free from aggregation in ethanol regardless of its similar structure with that of Cu(Pc). However, this may be reasonable because coordination chemistry involving copper ions plays a crucial role in the significant J-aggregation of Cu(Pc) as described above while H$_2$Pc has no metal ion.

**EXPERIMENTAL**

**Materials**

A highly water-soluble metal-free phthalocyanine, tetrakis{(2',6'-dimethyl-4'-sulfonic acid)phenoxy}phthalocyanine and its copper derivative, were synthesized from tetrakis{(2',6'-dimethyl)phenoxy}phthalocyanine and its copper complex, respectively, according to the previous work [22]. Synthetic procedures of the starting materials are described in the earlier work [20]. All the other chemicals were of reagent grade unless otherwise noted and used without further purification. For study on water/ethanol mixed solvent systems, solutions were prepared as follows: Ethanolic solutions of known volume containing a known amount of Cu(Pc) were mixed with water of desired volume in a volumetric flask and then the total volume was adjusted with ethanol to prepare solutions of highest concentration of Cu(Pc). The others were prepared by diluting the solutions with the same solvent system (i.e. the same water/ethanol ratio) to the desired concentrations.

**Measurements**

The measurements of optical absorption spectra were performed with a Shimadzu UV-1800 spectrophotometer. Magnetic circular dichroism (MCD) spectra were recorded on a JASCO J-720 spectropolarimeter equipped with a JASCO MCD-104 electromagnet, which is capable of generating magnetic fields of up to 0.8 T. A constant field of a magnitude of 0.65 T was applied to sample solutions during the measurements. All the measurements were done at room temperature (25 ± 1 °C). Concentration studies on optical absorption and MCD spectra were carried out using a quartz cell of mostly an optical path length of 1 cm, but with cells of a shorter path length (5 mm, 2 mm, or 1 mm) when absorption was greater than 2 (greater than one for MCD works).

**CONCLUSION**

Aggregation behaviors of a highly water-soluble H$_2$Pc and its copper complex have been investigated mainly on the basis of concentration in water, ethanol, and their mixed solvent systems. Both in aqueous and ethanolic solutions, H$_2$Pc molecules aggregate in a slipped-cofacial manner although remaining essentially free from aggregation in the latter. Nevertheless, aggregation behaviors of Cu(Pc) are significantly subject to the nature of solvent systems; in a cofacial manner in water, while in a slipped-cofacial fashion in ethanol. It has been elucidated that coordination chemistry involving copper ions greatly contributes to this mystery when the fifth coordination site on copper ions is available. A sulfonate group in a substituent of another Cu(Pc) is capable of attacking the site, generating a slipped-cofacial dimer. In aqueous solutions, the fifth site may be blocked by a water molecule, but Cu(Pc) molecules should be aligned to minimize surface area of hydrophobic π-system of the macrocyclic ligand exposed in aqueous circumstance, which should generate a cofacial dimer. It is unknown at present what makes Cu(Pc) molecules aggregate in a cofacial manner in water whereas H$_2$Pc does not aggregate in this way, regardless of their having essentially the same structure. As is the case in ethanol, coordination chemistry could play the role; two Cu(Pc) molecules sharing one water molecule as a bridging axial ligand, for example. This mystery may be the subject of future work.

**Acknowledgments**

This work was supported in part by a grant from the Japan Society for the Promotion of Science (KAKENHI No. 17K06850).

**Supplementary information**

Figures S1 and S2 are given in the supplementary material. This material is available free of charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml

**REFERENCES**

INTRODUCTION

Phthalocyanines (Pcs) are intensively investigated as advanced materials. There are similarities between Pc structures and some important macrocyclic structures such as cytochrome, hem and chlorophyll [1]. Pcs are used commercially as pigment and dye and they have numerous high-tech applications. The general aim of Pc studies is improving solubility of the Pc molecules and enabling different physical and chemical properties according to the desired usage. Pcs with different ions in the core can be synthesized for this purpose; furthermore, Pcs with different substituted groups can be synthesized to tune the electronic properties of the Pc system [1–3]. If substituted groups are bulky or their structures are hydrophobic, solubility of Pcs in organic solvents will increase. In recent years, particular attention has been paid to the development of unsymmetrical Pcs, due to their possessing a number of unique physicochemical properties and improved organization capabilities, which render these compounds valuable for applications in materials science such as non-linear optics for optical limiting applications, chemical sensors and medical applications [4].

Pcs show a tendency to aggregate through coplanar association of the Pc rings in solution. Pcs form the dimer and higher oligomer species owing to the extended π system. Aggregation can affect the solubility of phthalocyanines in organic solvents negatively [4–6]. Aggregation also dramatically affects the photophysical and photochemical properties of Pcs. This situation has led to a growing interest in designing non-aggregated Pcs. For this reason, many strategies have been explored to prevent self-association of Pc-based materials, such as

Synthesis, photophysical and electrochemical properties of novel unsymmetrical phthalocyanines with a Sudan IV moiety

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 1 December 2017
Accepted 18 December 2017

ABSTRACT: The synthesis of novel, A₂B type unsymmetrical metal-free and metallophthalocyanines bearing one aza dye group Sudan IV and three nitro terminal moieties was achieved by cyclotetramerization of novel 4-((1-((E)-(2-methyl-4-((E)-o-tolyldiazenyl)phenyl)diazenyl)naphthalen-2-yl)oxy)phthalonitrile and 4-nitrophthalonitrile. The new unsymmetrical metal-free and metallophthalocyanines have been characterized using elemental analyses, ¹H NMR, FT-IR, UV-vis and mass spectroscopic data. The aggregation properties of the compounds were investigated in a concentration range of 1.0 × 10⁻⁴ M–6.25 × 10⁻⁶ M. General trends were also studied for fluorescence quantum yields and lifetimes of these phthalocyanine compounds in tetrahydrofuran. The fluorescence of the synthesized unsymmetrical metal-free and metallophthalocyanines is effectively quenched by 1,4-benzoquinone (BQ) in THF. In-depth investigation of the electrochemical properties showed that nitro groups extended the reduction potentials.

KEYWORDS: phthalocyanine, Sudan IV, unsymmetrical, aggregation, fluorescence.

SPP Full member in good standing

◊ SPP Full member in good standing

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placing bulky substituents or aryl groups at peripheral or non-peripheral positions of the Pc core, or studying unsymmetrical Pcs [7, 8].

Azo dyes form an important class of chromophores. Azo dyes have been explored deeply for centuries. They have been shown to be important colorants between yellow and orange in industrial implementations. Nowadays, azo dyes have many applications such as chelate indicators to detect metal ions and increasing the color strength and brightening shades of synthetic fabrics [9, 10].

In this study, we report here in the synthesis of A3B type unsymmetrically substituted metal-free and metallo (Zn and Co) Pcs carrying one Sudan IV (1-((E)-(2-methyl-4-(E)-o-tolyldiazenyl)-phenyl)diazenyl)naphthalen-2-ol and three nitro substituents on the periphery. We also report spectroscopic characterization, aggregation behavior as well as photophysical (fluorescence quantum yields and lifetimes) and quenching properties and electrochemical properties of these novel unsymmetrical metal-free and metallophthalocyanines.

**RESULTS AND DISCUSSION**

**Synthesis and characterization**

There are mainly three routes for obtaining unsymmetrically substituted Pcs: a statistical cyclization reaction of two different substituted phthalonitriles [11], a solid-state reaction of two different substituted phthalonitriles on macromolecular carriers [12] and a ring-expansion treatment of subphthalocyanine with diiminoisoindoline [13]. In this study the statistical cyclization approach was used in the synthesis of unsymmetrical Pcs. Although symmetric Pc synthesis with four Sudan IV groups was also tried during this work, no appreciable product could be isolated, probably due to obstruction of cyclotetramerization by the bulky substituents.

4-Nitrophthalonitrile and 4-(1-((E)-(2-methyl-4-(E)-o-tolyldiazenyl)phenyl)diazenyl)naphthalen-2-ol (Sudan IV) and 3 nitro substituents on the periphery. We also report spectroscopic characterization, aggregation behavior as well as photophysical (fluorescence quantum yields and lifetimes) and quenching properties and electrochemical properties of these novel unsymmetrical metal-free and metallophthalocyanines.

![Scheme 1. Synthetic route of 4-((1-((E)-(2-methyl-4-((E)-o-tolyldiazenyl)phenyl)diazenyl)naphthalen-2-yl)oxy)-phthalonitrile (2)](image-url)
and 77.98% for 5) and were characterized by elemental analysis together with their spectral data (FT-IR, mass, ¹H NMR and UV-vis spectra). The data are consistent with the assigned structures. The FT-IR spectra of the Pcs 4 and 5 are very similar to that of metal-free (3), the only difference being the absence of the NH stretching band. In the IR spectra of compounds 4 and 5 the intense stretching bands of aromatic groups around 3060–3055 cm⁻¹ and aliphatic groups around at 2955–2860 cm⁻¹ clearly appear. The ¹H NMR spectrum of MPc 4 is consistent with the proposed structure. The elemental analysis and the mass spectra confirmed proposed structural assignment. The peaks for the molecular ions were found at m/z = 1090.897 [M + 1]⁺ for the MPc 4 and m/z = 1084.920 [M]⁺ for 5.

Ground state electronic absorption spectra

In substituted metal-free and MPcs, strong absorption bands are detected in the visible region between 600 and 700 nm, referred to as the Q band, and in the UV region between 300 and 350 nm, called the B (Soret) band. The electronic absorption spectra of 3 recorded in THF exhibit intense Q bands at 683 and 699 nm and the B bands in the UV region, around 350 nm (Fig. 1) [15–17]. The electronic absorption spectra of 4 and 5 recorded in THF exhibit single intense Q bands at 687 for 4 and 671 nm for 5. The B bands of MPcs (4 and 5) appeared in the UV region, around 345–350 nm (Fig. 1). When the UV spectra of MPcs (4 and 5) are compared with that of H₂Pc (3), splitting in the Q band region disappeared as a consequence of metal insertion.

Aggregation study

Weaker absorptions of Pcs on the lower wavelength side of the Q bands show the presence of aggregated species which are usually observed together with the main absorption peaks.
Q bands mainly responsible for the intense absorption associated with the monomeric species [18]. When the electronic spectra of the H$_2$Pc (3) and MPcs (4 and 5) were examined, weak peaks were observed around 620–640 nm just on the higher energy side of the strong Q band. Whether these bands are a consequence of aggregation or not was investigated by measuring absorption spectra in a concentration range. In the concentration ranges studied (10.0 $\times$ 10$^{-5}$ M–6.25 $\times$ 10$^{-6}$ M) for 3 (Fig. 2a), for 4 (Fig. 2b) and for 5 (Fig. 2c), no aggregation tendency has been discovered as the appearance of the Q-band absorption maxima remained unchanged as the concentration increases, as well as the apparent molar extinction coefficient remaining almost constant, indicating a purely monomeric form which obeyed the Beer–Lambert Law in the outlined range of concentration (Fig. 2d). By evaluating these observations, it can be clearly concluded that the unsymmetrical Pc derivatives (3–5) did not show aggregation behavior in THF at different concentrations [19].

Fluorescence spectra

The fluorescence properties of H$_2$Pc (3) and ZnPc (4) were studied in THF (Fig. 3), upon excitation at 650 nm for both 3 and 4. Fluorescence emission peaks appeared at 719 nm for 3 and 709 nm for 4 (Table 1). The observed Stokes shifts were within the region ~4.5–5.0 $\times$ 10$^5$ cm$^{-1}$ observed for studied Pcs and they were typical of Pcs [21]. The excitation spectrum of H$_2$Pc (3) (Fig. 3a) has

---

**Table 1. Absorption, excitation and emission spectral data for phthalocyanines (3–5) in THF**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Q Band $\lambda_{max}$, (nm)</th>
<th>(log $\varepsilon$)</th>
<th>Excitation $\lambda_{exc}$, (nm)</th>
<th>Emission $\lambda_{em}$, (nm)</th>
<th>Stoke shift $\Delta_{stokes}$, ($\times$10$^5$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>683, 699</td>
<td>4.16, 4.17</td>
<td>681, 708</td>
<td>719</td>
<td>5.00</td>
</tr>
<tr>
<td>4</td>
<td>687</td>
<td>4.44</td>
<td>691</td>
<td>709</td>
<td>4.54</td>
</tr>
<tr>
<td>5</td>
<td>671</td>
<td>4.35</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ZnPc</td>
<td>666$^*$</td>
<td>5.19$^*$</td>
<td>666$^*$</td>
<td>673$^*$</td>
<td>14.28$^*$</td>
</tr>
</tbody>
</table>

$^*$Reference [20].
two shoulders in the Q band region, and the emission maxima of 3 appears at lower energy than the emission maxima of ZnPc (4) (Fig. 3b). This means that H$_2$Pcs shows a red shift in emission maxima compared to MPcs because of symmetry lowering [22]. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for ZnPc (4) suggests that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF.

**Fluorescence quantum yields and lifetimes**

Fluorescence quantum yields ($\Phi_F$) of the unsymmetrical Pcs (3 and 4) were studied in THF. The fluorescence quantum yields were calculated as 0.13 for H$_2$Pc (3) and 0.21 for ZnPc (4). The measured fluorescence quantum yields for the unsymmetrical Pcs (3 and 4) were lower than that of unsubstituted ZnPc ($\Phi_F = 0.25$) in THF at room temperature (Table 2). This implies that the presence of peripheral Sudan IV and nitro substituents caused some fluorescence quenching of these Pcs. In our study, the fluorescence lifetimes ($\tau_F$) were calculated using the Strickler–Berg equation (Eq. 2). The $\tau_F$ values of the studied unsymmetrical Pcs (3 and 4) (0.39 and 1.75 ns, respectively) are lower compared to unsubstituted ZnPc in THF [23], suggesting more quenching by substitution. The natural radiative lifetime ($\tau_o$) and the rate constants for fluorescence ($k_F$) values are also given in Table 2. The $k_F$ values of studied unsymmetrical Pcs (3 and 4) are higher than unsubstituted ZnPc in THF.

**Fluorescence quenching studies by 1,4-benzoquinone (BQ)**

Fluorescence quenching of studied unsymmetrical Pcs (3 and 4) by benzoquinone (BQ) in THF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Figure 4 shows fluorescence emission spectral changes of H$_2$Pc (3) (Fig. 4a) and ZnPc (4) (Fig. 4b) on addition of different concentrations of BQ in THF. The Stern–Volmer plots of these Pcs gave straight lines depicting diffusion controlled quenching mechanisms (Figs 4c–4d). The slope of the plots shown in Fig. 4 gave $K_{SV}$ values and the bimolecular quenching constant ($k_q$) values for the BQ quenching of Pcs in THF are listed in Table 2. The $K_{SV}$ values of studied unsymmetrical Pcs (3 and 4) are higher than Std-ZnPc in THF.

**Electrochemical properties**

The electrochemical properties were studied by using cyclic and square wave voltammetry in dry DMF as solvent containing 0.1 M TBAP as supporting electrolyte. Figure 5 shows the electrochemical data for 4 and 5, and the corresponding redox potentials are summarized in Table 3.

Metal-free (3) and ZnPc (4) derivatives show one oxidation potential at 1.16 and 1.20 V, respectively, assigned to the Pc ring moiety and

![Fig. 3. Excitation and emission spectra for compound 3 (a) and 4 (b) in THF. Excitation wavelength = 650 nm for 3 and 4 in THF](image-url)
SYNTHESIS AND PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF NOVEL

three reduction potentials. Since 3 and 4 have redox inactive centers, the first and third reduction peaks can be assigned as the reduction of the Pc ring and the second peak can be assigned as the reduction of the nitro moiety on the Pc periphery [4, 24–31]. CoPc (5) shows three reduction couples at $E_{1/2} = -0.46$ V, -0.94 V and -1.47 V and two oxidation couples at $E_{1/2} = 0.85$ and 1.17 V. The first reduction peak can be assigned to the reduction of the cobalt, and the second and third reduction peaks can be assigned to the reduction of the nitro and Pc ring, respectively. It is known in the literature that in the solvent like DMF or DMSO the first oxidation can be assigned to the oxidation of the cobalt [32, 33].

**Table 3.** The electrochemical half wave potentials ($E_{1/2}$, V vs. SCE) of 3, 4 and 5

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_1$</th>
<th>Ox_1</th>
<th>Ox_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-1.50</td>
<td>-0.95</td>
<td>-0.73</td>
<td>1.16</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>-1.49</td>
<td>-0.95</td>
<td>-0.64</td>
<td>1.20</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>-1.47</td>
<td>-0.94</td>
<td>-0.46</td>
<td>0.85</td>
<td>1.17</td>
</tr>
</tbody>
</table>

R: reduction; Ox: oxidation.

**Fig. 4.** Fluorescence emission spectral changes of 3 (a) (8 × 10^{-6} M) and 4 (b) (8 × 10^{-6} M) and Stern–Volmer plots for benzoquinone (BQ) quenching of 3 (c) and 4 (d) on addition of different concentrations of BQ in THF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M

**Fig. 5.** Cyclic and square wave voltammograms of 4 and 5 in DMF containing 0.1 M TBAP at a scan rate of 25 mV·s^{-1}
EXPERIMENTAL

Materials

All chemicals and reagents were purchased from major suppliers and used without any further purification. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer; electron spectra were recorded on a Scincos LabProPlus UV/vis spectrophotometer. All reported 1H NMR spectra were recorded on an Agilent VNMR 500 MHz spectrometer using TMS as internal reference. Fluorescence spectra were recorded on a Perkin–Elmer LS55 fluorescence spectrophotometer. Mass spectra were measured on a Bruker microflex LT MALDI-TOF MS spectrometer. Electrochemical measurements were carried out using a Gamry Reference 600 galvanostat/potentiostat at 298 K with a glassy carbon working electrode and saturated calomel reference (SCE) electrodes with 0.1 M n-Bu4NClO4 in DMF under N2 atmosphere. Silica gel (Kieselgel 60, 200–400 mesh) was used in the separation and purification of compounds by column chromatography. All reactions were carried out under nitrogen atmosphere in dried solvents. The homogeneity of the products was tested in each step by TLC.

4-Nitro-phthalonitrile (1) was prepared as given in the literature [34].

Photophysical parameters

Fluorescence quantum yields and lifetimes

The comparative method was used to determine the fluorescence quantum yields (ΦF) according to the following Eq. (1) [35], utilizing unsubstituted ZnPc in DMF as the standard (ΦF = 0.17) [36]

\[
ΦF = ΦF(Std) \frac{F_{Std}}{F_{Sample}} \frac{A_{Sample}^2}{A_{Std}^2} \frac{η_{Sample}}{η_{Std}}
\]

where \( F \) and \( F_{Std} \) are the areas under the fluorescence curves of the zinc phthalocyanines and the standard, respectively. \( A \) and \( A_{Std} \) are the respective absorbances of the sample and the standard at the excitation wavelengths and \( η \) and \( η_{Std} \) are the refractive indices of solvents used for the sample and standard, respectively.

Radiative or natural lifetimes (\( τ_Φ \)) were estimated using the PhotochemCAD program which uses the Strickler–Berg equation [37]. Finally, the fluorescence lifetimes (\( τ_F \)) were calculated using the following Eq. (2):

\[
ΦF = \frac{τ_F}{τ_Φ}
\]

Fluorescence quenching by 1,4-benzoquinone

Fluorescence quenching experiments on Pcs (3 and 4) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M, respectively. The fluorescence spectra of unsymmetrical Pcs (3 and 4) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration were obtained by the Stern–Volmer (SV) Eq. (3) [38]:

\[
\frac{I_0}{I} = 1 + K_{SV} [AQ]
\]

where \( I_0 \) and \( I \) are the fluorescence intensities of fluorophore in the absence and presence of quenchers, respectively. [BQ] is the concentration of the quencher and \( K_{SV} \) is the Stern–Volmer constant which is the product of the bimolecular quenching constant (\( k_q \)) and the \( τ_F \) and is expressed in Eq. (4):

\[
K_{SV} = k_q \times τ_F
\]

The ratios of \( I_0/I \) were calculated and plotted against [BQ] according to Eq. (4) and \( K_{SV} \) is determined from the slope.

4-((1-((E)-(2-methyl-4-((E)-o-tolyldiazenyl)phenyl)diazenyl)naphthalen-2-yl)oxy)phthalonitrile (2), 4-Nitrophthalonitrile (0.865 g, 5 mmol) was dissolved in dry DMF under \( N_2 \) atmosphere and 1-((E)-2-methyl-4-((E)-o-tolyldiazenyl)phenyl)diazenyl)naphthalen-2-ol (Sudan IV) (1.9008 g, 5 mmol) was added at room temperature. After stirring for 15 min, anhydrous K2CO3 (2 g, 14.5 mmol) was added portion-wise during 2 h with efficient stirring. The reaction mixture was further stirred for 24 h. Then the mixture was poured into ice water. The resulting dark red solid was collected by filtration and washed with water until the washings were neutral. Then it was first dried in vacuo at 100°C and then crystallized from ethanol to produce the red, crystalline powder. The yield was 1.060 g (42.01%); m.p. 149.5°C; IR (ν, cm−1): 3060 (Ar-H), 2940–2850 (alkyl CH), 2231 (C=O); 1H NMR (500 MHz; CDCl3; Me4Si): 7.67–7.49 (m, Ar-H), 7.26–7.01 (m, Ar-H), 2.76 (3H, br, CH3); MALDI-TOF MS: m/z: 507.126 [M]+; For C13H10N4O Anal. calc.: C, 75.87; H, 4.38; N, 16.59%. Found: C, 75.84; H, 4.34; N, 16.61%.

2,9,16-Tris(nitro)-23-[(E)-(2-methyl-4-((E)-o-tolyldiazenyl)phenyl)diazenyl)naphthalen-2-oxo]metal-free phthalocyanine (3). A mixture of 4-nitrophthalonitrile (0.176 g, 1.02 mmol), compound (2) (0.167 g, 0.33 mmol) and lithium metal (1.5 mg, 0.5 mmol) in n-pentanol (1.5 mL) was heated at 145°C with stirring for 2 h under \( N_2 \). The resulting green suspension was cooled to ambient temperature. The reaction mass was then dissolved in dimethylformamide (DMF) (1 mL) and poured into 200 ml ice water mixture with the addition of 4 mL conc. hydrochloric acid (HCl). In this mixture, the Li3Pcs formed was converted into H2Pcs. The precipitate was filtered off and washed with cold methanol and then dried in vacuo. The purification
was carried out by column chromatography on silica gel using hexane/chloroform (CHCl₃) (1:10) as the eluent to afford 3 as a green solid. The yield was 10.53% (0.036 g).

M.p. > 200°C. IR (v, cm⁻¹): 3285 (N-H), 3055 (Ar-H), 2925–2873 (alkyl CH), 1526, 1534 (N-O), 1230 (C–O–C); ¹H NMR (500 MHz; DMSO-d₆; Me₄Si): 8H, ppm 8.64–8.58 (9H, br, Ar-H), 8.16–8.08 (3H, br, Ar-H), 8.08–7.88 (6H, br, Ar-H), 7.56–7.47 (3H, br, Ar-H), 7.34–7.17 (4H, br, Ar-H), 2.81 (3H, br, CH₃), 2.29 (3H, br, CH₃); UV-vis (THF): λₘₐₓ nm (log ε) 351 (4.22), 687 (4.44); MALDI-TOF MS: m/z: 1090.897 [M⁺].

The reaction of metal-free Pc (3) with metal salts led to the formation of desired unsymmetrical MPcs (4 and 5). The newly synthesized PCs (3–5) show very good solubility in a number of solvents such as THF, CHCl₃, DMF. The aggregation behavior, photophysical and photochemical properties of these novel A,B type metal-free and MPcs (3–5) have been also investigated. The studied PCs 3 and 4 show lower fluorescence quantum yields and shorter lifetimes when compared to unsubstituted zinc Pc in THF. The fluorescence of 3 and 4 are effectively quenched by 1,4-benzoquinone in THF. The electrochemical properties showed that while PCs 3 and 4 gave ring and nitro group based redox processes, 5 gave both cobalt, nitro group- and ring-based redox processes.

Acknowledgments

This work was supported by the Research Fund of the Technical University of Istanbul. AG thanks the Turkish Academy of Sciences (TUBA) for partial support.

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INTRODUCTION

Compounds containing a coumarin (2H-1-benzo-pyran-2-one, benzo-annulated oxygen heterocycles) component have been useful in many fields such as nonlinear optical materials [1], fluorescence materials and laser dyes [2], photo refractive materials [3], intermediates for drug synthesis [4] and luminescence materials [5]. In addition, coumarins are biologically relevant heterocyclic compounds with many interesting pharmacological properties. They are used as anticoagulants and in preparation of insecticides [6]. Antibacterial, anticancer and anti-HIV activities of coumarins are also known [7]. The type of substituents, such as long ester chains, influence the photophysical parameters of coumarin. The introduction of monohydroxycoumarin derivatives into the peripheral/nonperipheral ring of phthalocyanines increases the photophysicochemical properties of phthalocyanines [8–10]. Therefore, the combination of coumarin and Pc functional groups into a single hybrid compound via a suitable synthetic methodology is expected to produce highly functional compounds with intriguing physicochemical properties.

Electrical and gas sensing properties of novel cobalt(II), copper(II), manganese(III) phthalocyanines carrying ethyl 7-oxy-4,8-dimethylcoumarin-3-propanoate moieties

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 7 December 2017
Accepted 19 December 2017

ABSTRACT: The synthesis of metallophthalocyanines (M = Co, Cu, Mn) bearing four ethyl 7-oxy-4,8-dimethylcoumarin-3-propanoate moieties was performed. These novel compounds were characterized by elemental analysis, 1H-NMR spectroscopy, FT-IR, UV-vis and mass spectral data. DC and AC electrical properties of the films of metallophthalocyanines were investigated in the temperature range of 295–523 K. AC measurements were performed in the frequency range of 40–105 Hz. Activation energy values of the films took place between 0.55 eV–0.93 eV. Impedance spectroscopy measurements revealed that bulk resistance decreases with increasing temperature, indicating semiconductor properties. DC conductivity results also supported this result. Their gas sensing properties were also investigated for the vapors of Volatile Organic Compounds (VOCs), n-butyl acetate (200–3200 ppm) and ammonia (7000–56000 ppm) between temperatures 25–100 °C. Sensitivity and response times of the films for the tested vapors were reported. The results were found to be reversible and sensitive to the vapors of n-butyl acetate and ammonia. It was found that Mn(OAc)Pc showed better sensitivity than CoPc and CuPc for n-butyl acetate vapors at all measured vapor concentrations and temperatures. Mn(OAc)Pc also showed better sensitivity than CoPc and CuPc for ammonia vapors at 22 °C.

KEYWORDS: coumarin, metallophthalocyanine, VOC, gas sensing, conductivity, impedance spectra.
On the other hand, phthalocyanines (Pcs) form an important class of macrocyclic compounds that do not occur in nature [11]. Following their first synthesis in 1907, they have been firmly established as blue and green dyes [12] and enjoy widespread usage in diverse areas such as gas and chemical sensors [13–15], electrochemical devices [16], non-linear optics [17, 18], liquid crystals, Langmuir–Blodgett films and substituted derivatives, which can also be used for photodynamic cancer therapy and other processes driven by visible light [19–21]. A decisive disadvantage of phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased by introducing alky1, alkoxy or long ester chain groups into the periphery or non-periphery positions of the phthalocyanine framework. The preparation of phthalocyanines with monohydroxycoumarins has been reported in several papers and their different properties, such as photophysical, photochemical, electrochemical and spectroelectrochemical, have been investigated [22–29]. In this paper, the combination of ethyl 7-hydroxy-4,8-dimethylcoumarin-3-propanoate and 3-nitrophthalonitrile (1) functional groups into a single hybrid compound, ethyl 7-(2,3-dicyanophenoxy)-4,8-dimethylcoumarin-3-propanoate (2) via nucleophilic aromatic substitution reaction is performed, and this time coumarin is substituted with ethyl propanoate in the 3-position of three lactone ring, and the corresponding Co(II), Cu(II) and Mn(III) phthalocyanines bearing ethyl 7-oxy-4,8-dimethylcoumarin-3-propanoate groups were prepared. The choice of coumarino-phthalocyanine derivatives as sensing molecules is reasonable since the coumarin part of the respective PCs have good photostability, high quantum yields, a large Stokes shift and possible reactive sites in the skeleton for modification.

Metallophthalocyanines (MPC) are organic p-type semiconductors and have been extensively used as a sensitive material in gas sensors such as acetone and chloroform [30], xylene [31], NO₂ [32], and toluene sensors [30, 33]. Volatile Organic Compounds (VOCs) are found in nature as a result of industrial and home sensors [30, 33]. Volatile Organic Compounds (VOCs) and Administration (OSHA). PEL were declared as 50 ppm over 500 ppm concentration levels. Permissible Exposure Limits (PEL) were declared as 50 ppm for ammonia gas by the Occupational Safety Health and Administration (OSHA). PEL were declared as 150 ppm as an 8 h time weighted average (TWA) concentration and 200 ppm as a short term exposure limit (STEL, 15 min TWA exposure that should not be exceeding at any time during a workday) for vapors of n-butyl acetate by OSHA. N-Butyl acetate is also an irritant of the eyes, nose, respiratory tract and skin in exposed workers. Humans exposed to concentrations as high as 3300 ppm experienced larmation and conjunctival redness [35]. Hence the sensing of these gases is extremely important.

Different sensors working with different sensing mechanisms can be found commercially such as optical, spectroscopic, and conductometric sensors, but conductometric sensors have some advantages such as being cheap and mobile. According to the best of our knowledge, there is no report on coumarino-phthalocyanine applications as gas sensors except the report on optical ammonia sensors by Widmer and coworkers [36] and carbondioxide sensors by Altun and coworkers [37]. Therefore, this report will be the first for ethyl 7-oxy-4,8-dimethylcoumarin-3-propanoate bearing phthalocyanines as conductometric n-butyl acetate and ammonia sensors.

Investigation of some fundamental electrical properties such as conductivity and charge transport mechanism of synthesized compounds was also one of the aims of the present work. In order to investigate electrical properties of the films of the compounds 3–5, DC and AC and impedance spectroscopy (IS) measurements were performed as a function of temperature and frequency, in vacuum at ambient temperature and in the dark. Gas sensing properties of the films of the coumarino-phthalocyanine compounds 3–5 were investigated for n-butyl acetate and ammonia vapors depending on ambient temperatures (25–100 °C). Principle sensor parameters such as sensitivity and response times of the films for the tested vapors of VOCs were also reported. Compounds 3–5 were found to be reversible and sensitive to the vapors of n-butyl acetate and ammonia. It was also found that Compound 5 showed better sensitivity than 3 and 4 for n-butyl acetate vapors at all measured vapor concentrations and temperatures. 5 also showed better sensitivity than 3 and 4 for measured ammonia vapors at 22 °C.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis route for compounds 1, 2 and 3–5 are summarized in Scheme 1. In this study, a novel compound, ethyl 7-(2,3-dicyanophenoxy)-4,8-dimethylcoumarin-3-propanoate (2), was prepared and used as a starting material for the preparation of novel coumarino-phthalocyanines. The phthalonitrile compound 2 was synthesized from the reaction of 3-nitrophthalonitrile with ethyl 7-hydroxy-4,8-dimethylcoumarin-3-propanoate (1) using a base catalyst, anhydrous potassium carbonate, in DMF. Also; the synthesis of Co(II), Cu(II) and Mn(II)OAC coumarino-Pcs (3–5) was achieved by metal-ion mediated cyclotetramerization reaction of ethyl 7-(2,3-dicyanophenoxy)-4,8-dimethylcoumarin-3-propanoate (2) at about 370–390 °C for 5–10 min using anhydrous Co(OAc)₂, Cu(OAc)₂ or Mn(OAc)₂, respectively. Characterization of the dinitrile compound 2 and their new metallophthalocyanines 3–5 involved a combination of methods including elemental
analyses, FT-IR, UV-vis and MALDI-TOF-mass spectroscopy techniques.

In the IR spectra of 2, taken in KBr pellets, showed an intense absorption band at 2231 cm⁻¹, corresponding to the –C≡N group. Vibration bands were observed at 3096–3039 cm⁻¹ (aromatic-CH), 2994–2949 cm⁻¹ (aliphatic–CH), 1709 cm⁻¹ (lactone–C=O), 1622 (aromatic–C=C), 1247 cm⁻¹ (aromatic–O–aromatic). The FT-IR spectra of MPcs (M = Co, Cu, Mn) after conversion of the dinitrile derivative 2 into the coumarino-Pcs 3–5, the sharp peak for the –CN vibration around 2231 cm⁻¹ disappeared in all MPcs. Aromatic –CH and aliphatic –CH stretchings were observed in all MPcs at around 3084–3036 cm⁻¹ and 2983–2853 cm⁻¹, respectively. Lacton peaks (–C=O) were observed at 1701 cm⁻¹ for 3, 1703 cm⁻¹ for 4 and 1704 cm⁻¹ for 5.

¹H-NMR spectra of dinitrile 2 are recorded in d-CDCl₃ (Fig.1). The aromatic protons appeared at 7.58–6.94 ppm, the two methyl protons at the 3- and

Scheme 1. Synthetic route of phthalonitrile 2 and the corresponding metallophthalocyanines (3–5). (i) 3-Nitrophthalonitrile, K₂CO₃/DMF, 50°C, 5 days, (ii) Co(OAc)₂.H₂O (for CoPc), inert atmosphere, 370°C or Cu(OAc)₂.H₂O (for CuPc), inert atmosphere, 390°C. (iii) Mn(OAc)₂.4H₂O (for MnPc), inert atmosphere, 370°C.
8-positions of coumarin moiety were observed upfield at 2.49 and 2.33 ppm and –CH₂– protons were observed as two triplets at 3.01 and 2.64 ppm. Finally, the ethoxy protons were observed as a quartet and a triplet at 4.13 and 1.26 ppm. The MALDI-TOF spectra of 2 showed a molecular peak at 416 m/z as [M]+.

The MALDI-TOF mass spectra provided definitive characterization of the structures of all complexes 3–5. The linear mode positive ion MALDI-TOF mass spectra could be obtained in 2,5-dihydroxybenzoic acid (DHB) Maldi matrix. The protonated molecular ion peaks, [M]+ or [M + H]+ of the complexes were observed at 1724.46 for 3 (Fig. 2), 1729.82 Da for 4. In the MALDI-TOF mass spectra of the manganese phthalocyanine, a molecular ion peak was not observed. However, [M–OAc]⁺ and [M + H–OAc]⁺ peaks were observed at 1780.45 Da for 5. These mass values overlapped with the theoretical calculated mass values for the [M⁺] or [M + H⁺] of all the complexes. Elemental analyses for nitrile 2 and phthalocyanines (3–5) confirmed their proposed structure.

The UV-visible spectra of metallophthalocyanines 3–5 showed two basic bands which are Soret and Q bands. The UV-vis spectra showed Q bands at 679 nm for 3, 693 nm for 4 and 738 nm for 5 in DMF and Soret bands at 321 nm for 3 and 4 and 318 nm for 5 in DMF solvent (Fig. 3). Although manganese(II) acetate salt was used for synthesis of manganese phthalocyanines, manganese (III) phthalocyanines were obtained because of the sensitivity of Mn (II) salt to oxidation [38]. Additionally, the bands of 5 at around 500 nm are generally related to the charge transfer in MnPc complexes [39-41].

**Electrical properties**

**DC properties**

DC conductivity measurements of the thin films of 3, 4 and 5 were done in a homemade aluminum chamber at different temperatures in the range of 295–523 K in vacuum (<10⁻³ mbar) and in the dark. Current values passing through the films were recorded vs. applied voltages (between a -1 and 1 voltage sweep with 50 mV increments) during the heating process (I–V curves). DC conductivity of the deposited films on IDT was determined using Eq. 1 and the slope of the I–V curves.

$$\sigma_{dc} = \frac{1}{(\frac{I}{V})} \left(\frac{d}{(2n-1)h}\right)$$

where, \((I/V)\) is slope of the I–V graph, \(d\) is distance between the finger pair, \(n\) is number of the finger pair, \(l\) is overlap length and \(h\) is thickness of the electrodes.

DC conductivity of the thin films of the compounds 3, 4 and 5 was calculated using the slopes of I–V curves.
and Eq. 1, as $1.74 \times 10^{-10}$ S/cm, $3.47 \times 10^{-10}$ S/cm and $1.71 \times 10^{-10}$ S/cm at 295 K, respectively. The conductivity values increased to $3.55 \times 10^{-7}$ S/cm, $3.44 \times 10^{-7}$ S/cm, $7.54 \times 10^{-7}$ S/cm at 523 K, respectively. Variations of DC conductivity values of the thin films of the compounds 3, 4 and 5 between the temperatures 293 K–523 K are presented in Fig. 4. All the films of the compounds showed nearly equal conductivity values at the same temperatures, from 293 K to 378 K. The $T > 378$ K film of compound 3 exhibited the highest conductivity compared to the others. Calculated DC conductivity values in this study were found to be in the same order of magnitude as the previously reported values for different phthalocyanine compounds [23, 42]. The curves in Fig. 4 can be represented by Eq. 2, indicating that compounds 3, 4 and 5 are semiconductors. As shown in Fig. 4, the conductivity curve for 3 contains only one linear region in the measured temperature range. However, 4 and 5 contain two different linear regions. The first linear region is observed at the low temperature region ($T \leq 363$ K) and the second one at the high temperature region ($T \geq 458$ K). Each linear region corresponds to two different activation energies. The conduction in the first linear region can be interpreted as extrinsic conduction because of probably adsorbed oxygen molecules during the deposition of the compounds onto electrodes. That might cause new acceptor levels within the band gap. Similar behaviors have been reported previously for some organic molecules. This behavior was attributed to exhaustion of absorbed oxygen by the authors [42–46]. The second linear region in the Arrhenius plot shows that the compounds behave as intrinsic semiconductors.

Variations of the calculated DC conductivity with temperature, presented in Fig. 4, can be expressed by the well-known Arrhenius equation (Eq. 2)

$$\sigma_{dc} = \sigma_0 \exp \left(-\frac{E_A}{kT}\right)$$  \hspace{1cm} (2)

where $\sigma_0$ is a pre-exponent factor of DC conductivity, $E_A$ is activation energy, $k$ is Boltzmann’s constant and $T$ is temperature. Activation energy values of the films were calculated for both linear portions of the curves in the Arrhenius plot ($E_{A1}$ for the first linear region, $E_{A2}$ for the second linear region) and found to be 0.78 and 0.55 eV;
0.69 eV and 0.93 eV for the films 4 and 5, respectively. The value for the film 3 was found as 0.81 eV all over the temperature region. Activation energy values reported in this study were found in the same order of activation energy values as other reports for different phthalocyanine compounds, e.g. 0.6–0.9 eV [47, 48].

AC properties

AC conductivity measurements

AC conductivity ($\sigma_{ac}$) measurements of the films 3, 4 and 5 were performed in the frequency range of $4 \times 10^2$–100 kHz at different temperatures in the temperature range of 295–523 K at ambient temperature and in vacuum (<10^-3 mbar) in the dark. Log ($\sigma_{ac}$) vs. –Log ($f$) curves for the film 4 between the temperatures of 295 K–523 K are presented in Fig. 5. As shown in the figure, AC conductivity of the film of the compound increases as both of frequency and temperature increase. Temperature dependence of the curves can be examined in two parts as the low temperature region ($T < 458$ K) and the high temperature region ($T \geq 458$ K). In the low temperature region ($T < 458$ K), as seen from the Log–Log scaled graph, conductivity of the film strongly depends on frequency and increases with increasing frequency, especially at high frequencies.

In the high temperature region ($T \geq 458$ K), frequency dependence of AC conductivity of the film decreases in the measured frequency range except 4 and 5 in the low frequency region for $T > 458$ K. At all temperatures, frequency dependence of the measured AC conductivity of 3, 4 and 5 can be represented by the universal power law. The universal power law is given by Eq. 3 [49].

$$\sigma_{ac} = A \omega^s$$

where $\omega$ is the angular frequency and $A$ and $s$ are material-dependent constants. To predict the charge transport mechanism for the compounds, exponent $s$ in Eq. 3 was calculated at each measurement temperature for low, middle, and high frequency regions. $S$ values were calculated from the slope of the straight portions of the AC conductivity vs. frequency plot.

Temperature dependence of $s$ values of the films of the compounds for low ($f \leq 1$ kHz), middle (1 kHz < $f$ < 10 kHz), and high frequency ($f \geq 10$ kHz) regions are presented in Fig. 6. It is observed that $s$ values decreased with increasing temperature and frequencies except 4 and 5 in low frequency region for $T > 458$ K.

A number of models were suggested to explain the AC charge transport mechanism in the compounds. In the hopping model the electrons hop over the coulomb barrier. In this model, AC conductivity is proportional to frequency and exponent $s$ values take places less than 1. [50]. In the Correlated Barrier Hopping (CBH) model [50], AC conductivity (first order approximation) is given by Eq. 4:

$$\sigma_{ac} = \frac{1}{24} n \pi^3 N^2 \varepsilon e_0 R_w^6$$

where $n = 1$ for a single electron $n = 2$ for hopping of two electrons and $R_w$ is the hopping distance, $N$ is the spatial density of defect states, and $\varepsilon$ and $\varepsilon_0$ are dielectric constants of the materials and free space, respectively. In the CBH model, [50, 51], $s$ values decrease with increasing temperature and is given by Eq. 5:

$$s = 1 - \beta = 1 - \frac{6e_0 T}{W_m}$$
where \( k_B \) is Boltzmann's constant, \( W_m \) is the binding energy and \( T \) is temperature. In the small polaron quantum mechanical tunneling (SP) model, \( s \) increases with increasing temperature \([50, 51]\). Our results showed that \( s \) values tend to decrease with increasing temperature over the measured frequency and temperature range, except \( 4 \) and \( 5 \) in the low frequency region for \( T > 458 \) K. The variation of \( s \) with temperature and the variation of AC conductivity with frequency (Fig. 6) are in agreement with the prediction of the hopping model. The same type of temperature dependence for \( s \) was reported in literature for different phthalocyanine films \([52]\). However, the charge transport mechanism of the films \( 4 \) and \( 5 \) can be modeled by the SP model in the low frequency region for \( T > 458 \) K.

**Impedance measurements**

The films were also characterized by the technique of impedance spectroscopy (IS). The impedance data were represented by \(-Z''(\omega)\) vs. \( Z'(\omega)\) curves in a complex plane commonly called the Cole–Cole plot (Nyquist plot), where \( Z'(\omega) \) and \( Z''(\omega) \) components are real and imaginary components of impedance. Impedance spectra (Nyquist Plots) for film \( 5 \) are presented in Fig. 7.

The curves in Fig. 7a are observed in a semicircular shape, indicating pure capacitive behavior. This type of curve can be modeled by a resistor parallel with a capacitor in series with another resistor \([53]\). At the temperatures \( T \leq 458 \) K, film of the compounds \( 3 \) and \( 4 \) also showed similar behavior. At the temperatures \( T \geq 478 \) K, the impedance spectra for the film \( 5 \) are presented in Fig. 7b. It is observed that semicircular shaped curves in Fig. 7a transformed into full semicircles as in the Fig. 7b with increasing temperature. Impedance spectra contain curves in semicircle form with a different radius at each measured temperature, and the radius of the semicircles decreases with increasing temperature. Peak frequency of the semicircle at each measurement temperature, \( \omega_p \), satisfies \( \omega_p \tau_0 = 1 \), where \( \tau_0 \) is the time constant \([53]\). An ideal semicircle in a Nyquist plot can be observed for single-relaxation time process. For the curves, as in our case, the relaxation time in Debye dispersion relation is considered as a distribution of relaxation time values, rather than as a single relaxation time \([54]\). The depressed semicircles with different radii indicate deviations from the Debye dispersion relation. Thus, the equivalent circuit is adapted to include a constant phase element (CPE). The ohmic losses in the
experimental set-up and sheet resistance of the electrodes are represented by series resistance in the equivalent circuit. The bulk resistance of the coating material is represented by the parallel resistance. The intersection point of the semicircular arcs and real axis gives us information about the bulk resistance of the compounds. Decreasing of bulk resistance with increasing temperature is indicative of semiconductor properties (Fig. 7). A systematic decrease in bulk resistance indicates that the energy barrier for charge transport decreases with increasing temperature. At the temperatures 478, 498, and 523 K, a straight line was also observed in the low frequency region (Fig. 7b). The straight line in the low frequency region indicates the presence of a Warburg component [55]. A Warburg component was not observed for the film 3. The complex impedance spectrum for the film 4 at the temperatures \( T \geq 478 \) K was similar to those in Fig. 7b.

The plot of the imaginary parts of impedance vs. frequency (-\( Z'' \) vs \( f \)) for the films of 3 and 4 in the temperature range of 295–523 K is presented in Fig. 8. At the temperatures \( T \leq 438 \) K, the imaginary part of the impedance decreases with increasing frequency. As seen from Fig. 8a, the rate of decrease in the imaginary part of impedance with frequency is quite low as frequency approaches 100 kHz indicating that there is no current dissipation at these temperatures. At high temperatures, three different remarkable behaviors were observed. (i) A peak of the imaginary part of the film was observed for each curve. (ii) The frequencies of the peaks shifted to higher frequencies as temperature increased. This behavior may be an indication of the occurrence of different electrical relaxation times in the film. (iii) A broadening was observed for the curves with increasing temperature. This behavior also suggests the occurrence of an electrical process with a number of different relaxation times, depending on the temperature. The -\( Z'' \) vs \( f \) curves for the film 4 are presented in Fig. 8c. The curves for film 5 are similar to that of film 4 in the temperature range of 295–523 K.

**Gas sensing properties**

Gas sensing properties of the films of the compounds were investigated as a function of gas concentration and temperature (22–100°C) for target vapors n-butyl acetate and ammonia. During measurements at elevated temperatures carrier gas and target gas (n-butyl acetate and ammonia) were also heated to the measurement temperature before exposure to the sensors. Gas sensing measurements were performed after the current passed through the sensor in nitrogen atmosphere was constant (steady-state) and for 300 s cycles of tested gas and purging gas (N\(_2\)), repeatedly. In order to measure the current passing through the sensors, 2 V (DC) were applied to the electrodes of the sensors.

**n-Butyl acetate sensing properties**

In this part of the study, the effect of sensing material (3–5) and temperature on n-butyl acetate sensing properties were investigated. The n-butyl acetate vapor concentrations were 200, 400, 800, 1600, 2400 and 3200 ppm. The effects of the n-butyl acetate vapors on the DC conductivity of the films of 3–5 at 22°C are presented in Fig. 9.
By examining Fig. 9, it could be said that central metal atoms in the compounds played an important role on sensing properties. In 5 min of exposure of the vapor, the current did not reach saturation except for compound 3. We may also say that adsorption processes is reversible since the current decreased to nearly its initial value (~90%) in 5 min intervals, for each recovery process except 4. It would be said that adsorption process is also reversible for 4, but 5 min was not enough time to reach the initial current level. In order to investigate the effect of temperature on sensing properties, measurements were also performed at elevated temperatures. Figure 10 shows responses of the sensor 5 towards n-butyl acetate vapors at 22, 50, 75 and 100°C. The current values in this graph were multiplied by different factors to draw the curves in the same graph. The first observation on the curves is that base currents passing through the sensors were decreased after exposing the purging gas (N2) towards to sensor (recovery). For the recovery process, the rate of change in the initial current is greater than that of the values later. The responses of the sensors were found to be reversible.

In order to investigate the effect of temperature on ammonia sensing properties, measurements were also performed, additionally to 22°C, at elevated temperatures between 50–100°C. Figure 12 shows the response of the sensors 4 (Fig. 12a) and 5 (Fig. 12b) towards ammonia vapors at 22, 50, 75 and 100°C. To draw the curves in the same graph, the current values were multiplied by different factors. The temperature effect can be seen easily in Fig. 12. The first observation on the curves is that base currents passing through the sensors increased with increasing temperature, and the second observation was on the response and recovery processes. It was observed that the response and recovery processes were affected by temperature and that results’ response time and sensitivity values changed depending on temperature. The response characteristics can be explained as an interaction between films and VOCs vapors as in the case of the n-butyl acetate sensing mechanism. Comparisons of response time and sensitivity values for all of the sensors are discussed in detail in the following section, “Sensitivity and response time.”

Ammonia sensing properties

As in the case of n-butyl acetate sensing, in this part of the study effect of sensing material and temperature on ammonia sensing properties were also investigated. The ammonia vapor concentrations were 7000, 14000, 28000, 42000 and 56000 ppm. Fig. 11 shows the effect of the ammonia vapors on the DC conductivities of the films of 3–5 at 22 and 100°C. The current values of the curves in Fig. 11b for the sensor 5 were multiplied by 2.5 to draw the curves in the same graph.

As seen from the figure, the rate of change in current at initial exposure is high. The rate decreases with increasing time. During the exposure process, saturation was not reached. It is observed that current values passing through the sensors were decreased after exposing the purging gas (N2) towards to sensor (recovery). For the recovery process, the rate of change in the initial current is greater than that of the values later. The responses of the sensors were found to be reversible.
Sensitivity and response time

Sensitivity (S) and response time (t90) values were also investigated. The sensitivity (S) is defined using Eq. (6) [30, 37]:

\[
S = \frac{1}{C_i} \left[ \frac{\Delta I}{I_0} \right]
\]

where \(C_i\) is concentration of the VOC vapors, \(\Delta I\) is the change in current at the concentration used, \(I_0\) is the reference current value passing through the sensor in a nitrogen atmosphere at ambient temperature in steady state. The unit of sensitivity (S) is ppm\(^{-1}\), since sensitivity is defined as the relative change in current (with respect to the reference current) per unit of gas concentration (Eq. 6).

Sensitivity values of the sensors of 3–5 for the vapors of \(n\)-butyl acetate (Fig. 13a) and ammonia (Fig. 13b) are presented with the 3D graph in Fig. 13. Sensitivity behavior of the sensors for \(n\)-butyl acetate vapor can be analyzed in two parts: (i) depending on gas concentration, and (ii) depending on temperature. From Fig. 13a, in general, \(n\)-butyl-acetate sensitivity depending on gas concentration decreased with increasing gas concentration, and the same behavior was observed at each operating temperature between 22–100°C.

Sensitivity variations depending on temperature can be analyzed as follows. Sensitivity of the sensors 3, 4 and 5 showed different temperature dependence behaviors. While the sensitivity of 3 decreased with temperature, the sensitivity of 4 increased as the temperature increased from 22°C to 50°C then gradually decreased towards 100°C. However, the sensitivity of 5, first increased as the temperature increased from 22°C to 50°C, then decreased towards 75°C, then again increased towards 100°C. Even though there is a fluctuation in sensitivity values of 5 with temperature, in general, the sensitivity of sensor 5 tends to increase with increasing temperature, especially at high gas concentrations. The best sensitivities for \(n\)-butyl-acetate sensing were obtained at 22°C for 3 and at 50°C for 4 and 5. The best sensitivity values for \(n\)-butyl-acetate sensing were calculated as \(9.89 \times 10^{-3}\) ppm\(^{-1}\) for 200 ppm (22°C), \(3.76 \times 10^{-2}\) ppm\(^{-1}\) for 200 ppm (50°C), and \(6.91 \times 10^{-2}\) ppm\(^{-1}\) for 400 ppm (50°C), for 3, 4 and 5, respectively. In order to calibrate the \(n\)-butyl acetate sensing behavior of the sensors, sensitivities as a function of gas concentration (S–C) curves with slope and \(R^2\) values for 3–5 at the temperature of 50°C are presented in Fig. 14.

Ammonia sensitivity behavior of the sensors can also be analyzed in two parts: (i) depending on gas concentration, and (ii) depending on temperature. Ammonia sensitivity depending on gas concentration
tends to increase with increasing gas concentration at the temperatures of 22–75°C. However, at 100°C, sensitivity behavior becomes the opposite of that at 22–75°C. Sensitivity of the sensors showed similar temperature dependence behavior and decreased with increasing temperature (except 5 at 100°C). Sensitivity of the sensor 5 increased as the temperature increased from 75°C to 100°C. The best sensitivity values for ammonia sensing were found as $3.52 \times 10^{-7}$ ppm$^{-1}$ for 56000 ppm, $6.15 \times 10^{-5}$ ppm$^{-1}$ for 28000 ppm, and $8.50 \times 10^{-3}$ ppm$^{-1}$ for 28000 ppm, for 3, 4 and 5 at 22°C, respectively. In order to calibrate the ammonia sensing behavior of the sensors, sensitivities as a function of gas concentration (S–C) curves with slope and $R^2$ values for 3, 4 and 5 at the temperature of 22°C are presented in Fig. 14.

As an example of the sensitivity calibration is presented in Fig. 14. This figure shows that the sensitivity of the films of 3, 4 and 5 depends on vapors of $n$-butyl acetate concentration at 50°C and on vapors of ammonia concentration at 22°C, fitting lines at indicated temperatures. In order to obtain calibration functions, equations of fitting lines were determined. The slopes of fitting lines for $n$-butyl acetate sensing were calculated as $-7.91 \times 10^{-7}$, $-5.20 \times 10^{-6}$, $-1.61 \times 10^{-5}$ for the sensors of 3, 4 and 5 at 50°C, respectively. From regression analysis, $R^2$ values were calculated as 0.99, 0.67, and 0.87 for the sensors of 3, 4 and 5 respectively. The slopes and $R^2$ values of the fitting lines for ammonia sensing were calculated as $5.40 \times 10^{-8}$, $3.85 \times 10^{-8}$, $1.74 \times 10^{-9}$ and 0.73, 0.32 and 0.01 for the sensors of 3, 4 and 5 at 22°C, respectively.

Response time values ($\tau_{90}$) were defined as the time interval between the time of exposure and the time of 90% of total change in current in the measurement time interval at the indicated concentration and temperature. Longer response time ($\tau_{90}$) means slow response to the vapors tested of the sensors. Response time values of the sensors 3, 4 and 5 depending on the vapors of $n$-butyl acetate (Fig. 15a) and ammonia (Fig. 15b) at different temperatures are presented in the 3D graph in Fig. 15. From Fig. 15a, response time values of the 3 were found to be shorter than that of the other sensors. While
response time of the sensors 4 and 5 took values between 150–300 s at each temperature, it decreased from 150 s for 200 ppm to 37 s for 3200 ppm of n-butyl acetate vapor at 22 °C for 3. From Fig. 15b, ammonia response time values of 3 were also found shorter than for 4 and 5 as in the case of the n-butyl acetate sensing. While the response time of the sensors 4 and 5 took values between 200–300 s, it decreased from 162 s for 7000 ppm to
A VARIAN UNITY INOVA 500 MHz spectrometer. Deposition of the Tubitak Marmara Research Centre. Deposition according to the reported procedure [56].

EXPERIMENTAL

Synthesis of starting compounds and equipments

The starting compound, 3-nitrophthalonitrile, was prepared according to the reported procedure [56]. All solvents and metal salts were purchased from Sigma–Aldrich. All reactions were carried out under N2 atmosphere. The purity of products was tested in thin-layer-chromotography (TLC). IR spectra were recorded by the Instrumental Analysis Laboratory of the Tubitak Marmara Research Centre. Deposition of gold (Au) and chromium (Cr) metal electrodes for fabricating Interdigital Transducers (IDT) were done using an Edwards Auto 500 thermal evaporation system. Current passing through the sensors was measured using a Keithley model 6517B electrometer. Flow rate of the gases were adjusted using an MKS Instruments model 647C flow controller unit and flow meters.

Ethyl 7-hydroxy-4,8-dimethylcoumarin-3-propanoate (1). Ethyl 7-hydroxy-4,8-dimethylcoumarin-3-propanoate was synthesized according to the literature [57].

Ethyl 7-(2,3-dicyanophenoxy)-4,8-dimethylcoumarin-3-propanoate (2). Ethyl 7-hydroxy-4,8-dimethylcoumarin-3-propanoate (1) (1 g, 3.45 mmol) 3-nitrophthalonitrile (0.596 g, 3.45 mmol) and K2CO3 (0.713 g, 5.16 mmol) were stirred at 50°C. After 5 days, the reaction was completed. The mixture was poured into 50 ml ice water and the precipitate was filtered off, washed with water and dried over P2O5 and finally was purified by column chromatography with dichloromethane/methanol (100:1) as eluent. Yield: 1.04 g (73%). Anal. Calc. for [C24H20N2O5] (Mw: 416.43 g/mol): requires: C, 69.22; H, 4.84; N, 6.73%, found: C, 69.18; H, 4.80; N, 6.69%, FT-IR (KBr pellet, cm⁻¹): 3084, 3028, 2983, 2932, 2231, 1712, 1622, 1261, UV-vis (CH 2Cl2, nm): 317, 1H-NMR for phthalonitrile derivative

![Fig. 16. Calibration curves for response time values of the sensors 3, 4 and 5 at 50°C for n-butyl acetate vapors (filled symbols, left axis) and for ammonia (open symbols, right axis)](image-url)
Preparation of films of the compounds for electrical and gas sensing measurements

Interdigital transducer (IDT) was employed in order to investigate DC and AC electrical properties and gas sensing properties of the compounds. Interdigital transducers were fabricated onto glass substrate in our laboratory. The transducers used in this study contain 10 finger pairs of Cr/Au interdigitated electrodes. These IDTs were fabricated according to our reported procedures [30, 58]. Certain concentrated solutions of compounds 3–5 were prepared in eppendorf tubes by dissolving the compounds in DMF (N,N-dimethylformamide, HCON(CH₃)₂) at room temperature. After sonication in ultrasonic cleaner for five min, homogeneous solutions of 3, 4 and 5 were deposited on the IDTs by the drop coating method using micro-syringes. To prepare seemingly identical films, thin films of a sensing material were prepared using certain concentrated solutions of the compounds. Temperature of the glass substrates was kept at 22 °C during the deposition of the films. Thin films of the compounds were formed after evaporation of the solvents. The reproducibility of the films was investigated by inspecting the DC and AC conductivity values and sensitivity values depending on different transducers coated with same sensitive material. The reproducibility was found to be in the range of 5% for DC and AC conductivity values and 8% for sensitivity values during six months.

Electrical and gas sensing measurements

DC current values were recorded by applying DC voltages between -1 V and 1 V with 50 mV steps. AC conductivity and impedance spectra (IS) measurements were performed in the frequency range of 4 × 10²–100 kHz using a Keithley model 3330 LCZ meter. Electrical measurements were performed at different temperatures (295 K–253 K) in vacuum (×10⁻² mbar) and in the dark. Gas sensing measurements of the films of the compounds were done as a function of gas concentration and temperature (22–100°C) in a temperature-controllable homemade electrostatically-screened teflon measurement chamber. DC conductivity response of the films towards the vapors of n-butyl acetate (C₅H₁₂O₂) and ammonia (NH₃) were investigated. The concentrations of the VOCs vapors took place between 200–3200 ppm for n-butyl acetate, and 7000–56000 ppm for ammonia vapors (ppm = parts per million). The Antoine equation was used to calculate VOCs vapors pressure (Eq. 7):

\[
\log_{10}(P) = A - \frac{B}{(T + C)}
\]

where P is the vapor pressure in bar, T is the temperature in Kelvin, A, B, and C are Antoine coefficients depending on solvent and temperature range [59]. Test gases were diluted with dry nitrogen (N₂) (purity > 99%) using computer controlled mass flow controllers (MKS Inst). Gas sensing properties were obtained for 300 s intervals; 300 s for tested gases and 300 s for purging with nitrogen. DC voltage of 2 V was applied to the electrodes of the IDTs. Gas sensing measurements were performed after the current passing through the sensor in nitrogen atmosphere was constant (steady-state). All the data were recorded by personal computer using an IEE488 data acquisition system.

CONCLUSION

In this study, we synthesized, purified and characterized new nonperipheral coumarinophthalocyanines (3-5). All characterization methods such as FT-IR, UV-vis, Maldi-TOF and elemental analyses verified structures of either nitrile or phthalocyanine complexes.

Behavior of DC conductivity of the compounds with temperature indicates that compounds 3, 4 and 5 are semiconductors. By examining AC measurement results, charge transport mechanisms of the films can be modeled by hopping. However, charge transport mechanisms of the films 4 and 5 can be modeled by the SP model in the low frequency region for T > 458 K. From impedance spectra results, it is observed that bulk resistance of all the compounds decreases with increasing temperature indicating semiconductor properties. This result also supports the DC measurement results.

Gas sensing properties of the films of coumarinophthalocyanine compounds were studied for the vapors of n-butyl acetate and ammonia in the temperature range of 22–100°C. The films were found to be sensitive to the n-butyl-acetate and ammonia vapors. The results showed that responses of the films are reversible and depend on
central metal atoms in the compound, the kind of VOC vapors, vapor concentrations, and temperature. The best sensitivity values for ammonia were obtained at 22 °C but for n-butyl-acetate sensing at 22 °C (3) and at 50 °C (4 and 5). Sensor 5 showed the best sensitivity for ammonia only at 22 °C but for n-butyl acetate at measurement temperatures. Response time values took place between 100–290 s.

Acknowledgments

We are thankful to the Research Foundation of Marmara University (BAPKO), Commission of Scientific Research Projects. [Grant Numbers FEN-C-LYP-150513-0182 and FEN-C-DRP-140312-0050 and FEN-A-130711-0258].

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INTRODUCTION

Optical limiting (OL) materials have become of interest to research because of the need to protect sensitive optical devices, such as human eyes, against high intensity light sources such as lasers [1]. When OL materials are exposed to very intense light, they have the ability to limit the output energy of the emerging beam. The optical limiting process is a result of a highly populated excited triplet state with respect to the ground state. This phenomenon is known as reverse saturable absorption (RSA), as opposed to saturable absorption (SA) that is seen in most molecules [2–4].

Phthalocyanines (Pcs) have shown potential applications as optical limiters, optical switches and optical signal-processing devices due to their highly delocalized π-electron systems [5–8]. Advantages of Pcs include architectural flexibility, ease of processing into thin films/optical devices, ultrafast response time, high triplet state yields, and stability [9–13]. Metallo-phthalocyanines (MPcs) having heavy central metals such as indium exhibit better optical limiting due to the heavy metal effect, which enhances the intersystem crossing through spin orbit coupling, leading to a higher triplet state population [14–16]. Asymmetric MPcs are desired due to the presence of permanent dipole moment which encourages nonlinear optical (NLO) response [17–20]. Incorporation of Pcs into nanomaterials is also known to have profound effect on their NLO properties [21, 22]. For practical purposes in NLO applications, Pc complexes can be embedded in thin films of polymers.
such as poly(methylmethacrylate) (PMMA), polyacrylic acid (PAA) [23] or poly(bisphenol A carbonate) (PBC), [24] resulting in improved optical limiting behavior compared to the one in solution. These films fabricated with indium(III) and gallium(III) cations — $\text{InOAc}$ and $\text{GaOH}$ respectively (Fig. 1). NLO characteristics of these complexes were studied in DMSO solution and when embedded in poly(bisphenol A carbonate) (PBC). Due to the presence of diethyleneglycol chains with numbering of atoms for assignment of $^1\text{H}$-NMR spectra. $\text{M} = 2\text{H} - \text{InOAc}$, $\text{M} = \text{GaOH} - \text{1GaOH}$, $\text{M} = \text{InOAc} - \text{1InOAc}$

Recently, we have demonstrated that the A$_2$B-type phthalocyanine ligand $\text{1H}_2$ (Fig. 1), bearing two [2′-(2″-hydroxyethoxy)ethoxy]-substituents and six solubilizing $n$-butoxy groups reveals good OL properties, exceeding those of symmetrical octa-$n$-butoxy-phthalocyanine [29]. Moreover, this ligand was found to be a convenient platform for preparation of sandwich double- and triple-decker complexes, revealing superior OL characteristics which can be further improved by grafting them onto the surface of quantum dots modified with mercaptosuccinic acid [30]. Substitution of OH-groups in $\text{1H}_2$ with thiols afforded a molecule which could be directly grafted onto the surface of quantum dots and silver nanoparticles [31].

In the present work, we synthesized and explored photophysical properties of complexes formed by $\text{1H}_2$ with indium(III) and gallium(III) cations — $\text{InOAc}$ and $\text{GaOH}$ respectively (Fig. 1). NLO characteristics of these complexes were studied in DMSO solution and when embedded in poly(bisphenol A carbonate) (PBC). Due to the presence of diethyleneglycol chains, these molecules can be grafted on the surface of nanoparticles and quantum dots to form advanced hybrid nanomaterials [30].

**EXPERIMENTAL**

**Materials**

Poly(bisphenol A carbonate) (PBC), 1,2,4-trichlorobenzene (TCIB), 1-chloronaphthalene (CIN), phenol, gallium and indium acetylacetonates (Ga(acac)$_3$ and In(acac)$_3$) were used as received from Sigma Aldrich. Neutral alumina (Macherey Nagel) was used for chromatography. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Merck) was distilled over CaH$_2$ in vacuo and stored under argon. Isoamyl alcohol (Sigma-Aldrich) was distilled over sodium under argon. The ligand $\text{1H}_2$ was synthesized starting from 4,5-dibutoxyphthalonitrile and 1,2-dicyano-4,5-bis[2′-(2″-hydroxyethoxy)ethoxy] benzene according to previously reported procedures [29, 32].

**Equipment**

Ground state UV-vis spectra were recorded at room temperature on Thermo Evolution 210 and Shimadzu UV-2550 spectrophotometers in a 1 cm pathlength cuvette. $^1\text{H}$ NMR spectra were obtained using a Bruker ADVANCE 600 MHz NMR spectrometer in DMSO-$d_6$ or in a mixture of CDCl$_3$ with CD$_3$OD. The numbering of atoms is given in Fig. 1. MALDI TOF mass-spectra were measured on an Ultraflex spectrometer (Bruker Daltonics) with 2,5-dihydroxybenzoic acid (DHB), used as a matrix. The measurements were performed using equipment of CKP FMI IPCE RAS.

FT-IR spectra were measured on Bruker® ALPHA FT-IR spectrometer with universal attenuated total reflectance (ATR) sampling accessory. Scanning electron microscope (SEM) images were recorded using a TESCAN Vega TS 5136LM microscope. Fluorescence emission was recorded on a Varian Eclipse spectroflurometer. Fluorescence lifetimes were measured with a FluoTime 300 “EasyTau” spectrometer (PicoQuant GmbH) using a time correlated single photon counting (TCSPC) technique. The samples were excited at 670 nm with a diode laser (LDHP-670, 20 MHz repetition rate, 44 ps pulse width, PicoQuant GmbH). The detector employed was a Peltier cooled Photo-multiplier (PMA-C192-M, PicoQuant GmbH).

Laser flash photolysis experiments were performed to determine the triplet decay kinetics. The excitation pulses were produced by a tunable laser system consisting of a Nd:YAG laser (355 nm, 135 mJ/4–6 ns) pumping an optical parametric oscillator (OPO, 30 mJ/3–5 ns) with a wavelength range of 420–2300 nm (NT-342B, Ekspla). The details have been reported previously [33]. Solutions for triplet state studies were de-aerated with argon for 20 min before measurement. The absorbance of the solution at the Q band was 1.5 for these studies. Triplet lifetimes were determined by exponential fitting of the kinetic curves using Origin Pro 8 software.

All Z-scan analyses were performed using a frequency-doubled Nd:YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source. The laser was operated in a near-Gaussian transverse mode at 532 nm (second harmonic), with a pulse repetition rate of 10 Hz and energy range of 0.1 mJ–0.1 mJ, as limited by the energy detectors (Coherent J5-09). The low repetition rate of the laser prevents cumulative thermal nonlinearities. The beam was spatially filtered to remove the higher order modes and tightly focused with a 15 cm focal length lens. The Z-scan system size ($\text{L} \times \text{W} \times \text{H}$) used was...
600 mm × 300 mm × 350 mm (excluding the computer, energy meter, translation stage driver, and laser system). The liquid samples were placed in a cuvette (internal dimensions: 2 mm × 10 mm × 55 mm, 0.7 mL) and a path length of 2 mm (Starna 21-G-2). The nonlinear optical properties of phthalocyanines were evaluated using the Z-scan technique that has been previously described [34, 35]. More details about the analysis of Z-scan data are given in supplemental material.

The Gaussian 03 software package [36] running on an Intel/Linux cluster was used to perform all DFT calculations. The calculations were carried out at the B3LYP level of theory with 6-31G(d) and SDD basis sets. The B3LYP exchange-correlation density functional employs Becke’s method for using Lee–Yang–Parr’s gradient-correction, which includes a hybrid of semi-empirical Hartree–Fock and DFT exchange.

The second-order nonlinear optical response was investigated using an effective method developed by Champagne and co-workers [37]. This response is evaluated using the hyper-Rayleigh scattering (HRS) response $\beta_{\text{HRS}}$ (-2α, α, α). In this study, DFT calculations were employed to study the nonlinear optical properties. The molecules were optimized at the level of B3LYP/SDD, and based on optimized structures, the static second-order polarizabilities including the empirical Hartree–Fock and DFT exchange.

The molecules were optimized at the level of B3LYP/SDD, and based on optimized structures, the static second-order polarizabilities including the dipolar/octupolar contributions were determined with the harmonic light intensity given by the Bersohn’s expression [38, 39]. More details about DFT calculations are given in supplementary material.

**Synthesis**

*Acetatoindium(III) 2,3-bis[2’-(2’’-hydroxyethoxy)ethoxy]-9,10,16,17,23,24-hexa-n-butoxyphthalocyaninate, 1InOAc.* The ligand $\text{H}_2$ (30 mg, 26 μmol) and In(acac)$_3$ (79 mg, 189 μmol) were dissolved in CIN (3 ml). The reaction mixture was refluxed under argon. The completion of the reaction was checked using UV-vis spectra, which provided evidence for full conversion of the starting ligand into the metal complex within 40 min. The reaction mixture was cooled to room temperature and transferred onto the column, packed with neutral alumina in hexane and chloroform 3:7 (vol.) mixture. Chloroform was used to elute the target complex was eluted with the mixture of chloroform and 4 vol.% methanol. After size-exclusion chromatography on Bio-Beads S-X1 (eluion with the mixture of chloroform and 2.5 vol.% methanol). The liquid samples were placed in a cuvette (internal dimensions: 2 mm × 10 mm × 55 mm, 0.7 mL) and a path length of 2 mm (Starna 21-G-2). The nonlinear optical properties of phthalocyanines were evaluated using the Z-scan technique that has been previously described [34, 35]. More details about the analysis of Z-scan data are given in supplemental material.

**Preparation of thin films**

Thin films were prepared according to literature methods [18, 40]. Poly(bisphenol A carbonate) (110 mg) and 0.1 mg of complexes 1InOAc or 1GaOH were dissolved in dichloromethane (1.5 ml) and sonicated for 30 min until homogeneous mixtures were obtained. The solution was dropped on glass substrates, placed in a Petri dish, and the solvent was allowed to evaporate at room temperature. The average film thickness of the complexes was determined to be 53 and 58 μm for complexes 1InOAc and 1GaOH respectively using SEM.

**Fluorescence and triplet quantum yields**

Fluorescence ($\Phi_F$) and triplet ($\Phi_T$) quantum yields were determined by comparative methods reported before [41–43] using the fluorescence quantum yield of ZnPc in DMSO ($\Phi_T$ = 0.20 [42], $\Phi_T^{\text{calc}}$ = 0.65 [43]). The triplet decay ($\tau_T$) was measured using laser flash photolysis and the data was analysed using OriginPro 8.0 software.
RESULTS AND DISCUSSION

Synthesis and characterization of complexes 1InOAc and 1GaOH

Synthesis of complexes 1GaOH and 1InOAc was performed starting from the previously reported metal-free phthalocyanine 1H2 (Scheme 1), according to the procedures reported previously for the synthesis of Ga(III) and In(III) crownsphthalocyaninates [27, 44].

Gallium(III) complex 1GaOH was synthesized using gallium acetylacetonate and phenol for metalation of 1H2 in the refluxing mixture of isooamyl alcohol and 1,2,4-trichlorobenzene (TCIB). Upon elution of the complex from alumina with the mixture of chloroform and methanol the exchange of axially coordinated acetylacetonate counterion to OH-group occurred which was confirmed by MALDI TOF mass-spectrometry (Fig. 2). Indium(III) complex was prepared by reaction of 1H2 with indium acetylacetonate in refluxing 1-chloronaphthalene (ClN). The formed complex had a higher tendency to absorption on the surface of alumina which was used for chromatographic purification; therefore the elution of complex from alumina was performed by a mixture of chloroform, methanol and acetic acid. It resulted in the exchange of axially coordinated acetylacetonate counterion to OAc-group, which was also confirmed by MALDI TOF mass-spectrometry (Fig. 2).

In the UV-vis spectra in DMSO the Q band of the complex 1GaOH (693 nm) is slightly blue shifted with respect to the Q band of 1InOAc (697 nm), Fig. 3, Table 1. The broad absorption band between 400 and 500 nm, observed in both complexes, is attributed to charge transfer transition from the peripheral alkoxy-groups to the Pc macrocycle [45].

Fluorescence lifetime (tF) and quantum yield (ΦF)

Figure 4 shows the absorption, excitation and emission spectra of complexes 1InOAc and 1GaOH in DMSO. The Q band maxima of the absorption and excitation spectra were similar, and mirror images of the emission spectra for both complexes were observed. The above observation suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMSO.

The fluorescence quantum yield (ΦF) for complex 1GaOH was determined to be 0.052, which is higher than that of complex 1InOAc at 0.014 (Table 1). Complex 1InOAc contains indium, which is a heavier metal than gallium in complex 1GaOH, resulting in increased intersystem crossing for the former, resulting in reduced fluorescence.

Fluorescence lifetime (tF) values of complexes 1InOAc and 1GaOH were determined using a time correlated single photon count (TCSPC) method, following excitation at the emission maxima (Table 1).
A typical fluorescence decay profile for complex 1GaOH (as an example) is shown in Fig. 5. A mono-exponential decay profile was obtained for both compounds. The \( \tau_F \) values were determined to be 3.1 ns for both compounds. The fluorescence lifetime values are typical for Pcs [46].

**Triplet lifetimes (\( \tau_T \)) and quantum yield (\( \Phi_T \))**

The transient absorption spectra of complexes 1InOAc and 1GaOH are shown in Fig. 6, respectively. A typical triplet decay profile using complex 1GaOH as an example is shown in the insert. The spectra were recorded in an argon-degassed DMSO solution, by exciting the complexes at 680 nm and recording the spectra from 400 to 800 nm. The transient absorption spectra for complex 1GaOH shows a singlet depletion and a very weak triplet–triplet absorption peak around 500 nm as compared to complex 1InOAc showing a strong triplet–triplet absorption peak. This observation suggests that for complex 1InOAc the triplet state is more populated (as observed from the triplet quantum yield, see Table 1) with respect to complex 1GaOH. The results further suggest that indium as the central metal is more efficient in promoting intersystem crossing with respect to gallium.

The \( \tau_T \) for both complexes were determined to be 48 \( \mu \)s (Table 1), while the \( \Phi_T \) were 0.35 and 0.27 for complexes 1InOAc and 1GaOH, respectively. The \( \Phi_T \) value for complex 1InOAc is larger than for 1GaOH due to the presence of a heavier central metal in the former, which leads to improved population of the triplet state as a result of the heavy atom effect discussed above.

**Nonlinear optical (NLO) parameters**

The Z-scan plots for complexes 1InOAc and 1GaOH in solution are shown in Fig. 7. The Z-scan plots show typical nonlinear absorption behavior, with reverse saturable absorption (RSA) profiles. The \( \beta \) values were obtained by a nonlinear fit of \( q_0(Z_0) \) following literature methods [34, 35, 47–49] as a parameter that characterizes the strength of the nonlinearity in the curve depicted in Fig. 7. Equations S1–S10 (supplemental material) were used to determine the nonlinear absorption coefficient (\( \beta \)) for the two complexes, and the results are summarized in Table 2. The experimental \( \beta \) values for complexes 1InOAc and 1GaOH in DMSO were found to be \( 7.2 \times 10^9 \) m\(^2\) W\(^{-1}\) and \( 6.0 \times 10^9 \) m\(^2\) W\(^{-1}\), respectively. The results suggest that complex 1InOAc shows better \( \beta \) values compared to complex 1GaOH. The above results are consistent with the calculated triplet state quantum yield, which shows a greater triplet state population for 1InOAc with respect to 1GaOH. The magnitude of the \( \beta \) values observed are within range or better than \( \beta \) values of monomeric Pcs reported in literature [2, 50].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{Abs} ), nm</th>
<th>( \lambda_{Em} ), nm</th>
<th>( \Phi_T )</th>
<th>( \tau_T ), ( \mu )s</th>
<th>( \Phi_F )</th>
<th>( \tau_F \pm 0.01 ), ns</th>
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</thead>
<tbody>
<tr>
<td>1GaOH</td>
<td>693</td>
<td>700</td>
<td>0.27</td>
<td>48</td>
<td>0.052</td>
<td>3.1</td>
</tr>
<tr>
<td>1InOAc</td>
<td>697</td>
<td>707</td>
<td>0.35</td>
<td>48</td>
<td>0.014</td>
<td>3.1</td>
</tr>
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</table>

**Fig. 3.** UV-vis spectra of complexes 1GaOH and 1InOAc in DMSO

**Fig. 4.** Absorption, excitation and emission spectra of complexes 1GaOH and 1InOAc in DMSO
Both complexes were embedded in a PBC polymer supported on a glass substrate and their $b$ values were measured. Z scans of the films are shown in Fig. 8. Complex $\text{InOAc}$, when imbedded in PBC, gave a higher $b$ value of $6.0 \times 10^{-9}$ m·W$^{-1}$ compared to complex $\text{GaOH}$ with a $b$ value of $4.8 \times 10^{-9}$ m·W$^{-1}$. Thus similar to solutions, complex $\text{InOAc}$ gives better $b$ values compared to complex $\text{GaOH}$. The $b$ values obtained for complexes $\text{InOAc}$ and $\text{GaOH}$ in film were found to be less than the values determined in solution, as expected. A reduction in $b$ values is expected for molecules which are dipolar, due to the centrocymmetric alignment of the dipole moment in bulk material [51].

Table 2 summarizes the $\text{Im}[\chi^{(3)}]$ and $\gamma$ values of complexes $\text{InOAc}$ and $\text{GaOH}$ in solution and as films. These values were determined using Eqs. S11–S13 (supplemental material). The concentration of the complexes $\text{InOAc}$ and $\text{GaOH}$ in solution were determined to be in the order of $10^{-7}$ M. The thickness of the films were also determined to be 53 and 58 μm for complexes $\text{InOAc}$ and $\text{GaOH}$, respectively using SEM. $\text{Im}[\chi^{(3)}]$ and $\gamma$ values are larger for complex $\text{InOAc}$ compared to $\text{GaOH}$ both in solution and thin films, due to heavy atom effect of the former. Also the $\text{Im}[\chi^{(3)}]$ and $\gamma$ values are much larger in thin films compared to the corresponding solution (Table 2).

The ground state absorption cross sections ($\sigma_{0\text{G}}$) of the samples at 532 nm were calculated using Eq. 1 [52].

$$\sigma_{0\text{G}} = \frac{\ln(10)10^2\alpha}{N_A}$$

where $\alpha$ and $N_A$ are the linear absorption coefficient at 532 nm and the concentration respectively. Table 2 shows the determined absorption cross section value for complexes $\text{GaOH}$ and $\text{InOAc}$ as $4.95 \times 10^{-18}$ and $1.67 \times 10^{-18}$ cm$^2$ respectively, which are in the range of the reported absorption cross section for ZnPc [53]. The $\sigma_{0\text{G}}$ values were used to calculate the optical limiting property $I_{\text{lim}}$, which is a threshold limit intensity or fluence at which the transmittance is 50% of the linear transmittance [54]. The $I_{\text{lim}}$ value can be used to classify materials which are ideal for optical limiting applications, such as nonlinear material developed for the protection of human eyes from an intense laser beam. Table 2 shows the $I_{\text{lim}}$ values of complexes $\text{InOAc}$ and $\text{GaOH}$ to be $2.51 \times 10^4$ and $7.43 \times 10^4$ J·cm$^{-2}$ respectively. The lower the $I_{\text{lim}}$ value, the more ideal the material is as
an optical limiter. In this case $I_{\text{lim}}$ values suggest that complex $1\text{InOAc}$ is a better nonlinear optical limiter compared to complex $1\text{GaOH}$. The above conclusion is affirmed by the $\beta$ values determined for these complexes, whereby complex $1\text{InOAc}$ was expected to show better NLO properties due to its large $\beta$ value compared to complex $1\text{GaOH}$. The $I_{\text{lim}}$ could not be calculated for the films using the above solution-based calculation; hence as a rough estimate, a logarithmic plot of output vs. input intensity was used for comparison. Figure 9 shows the logarithmic plot of output vs. input intensity of complexes $1\text{InOAc}$ and $1\text{GaOH}$ in DMSO and as films. Table 2 records the $I_{\text{out}}$ percentage at 50% of the $I_{\text{in}}$ percentage. The $I_{\text{out}}$ percentage values suggest that responses to the incident laser beam are nearly identical for complexes $1\text{InOAc}$ and $1\text{GaOH}$ in DMSO (53% and 51% respectively). However, as a film complex $1\text{GaOH}$ shows a better response of 68% compared to complex $1\text{InOAc}$ (54%) embedded in film.

**DFT calculation of nonlinear optical (NLO) parameters**

In order to rationalize the experimental results observed above, dipolar and octupolar ($F_{1,1}$ and $F_{3,3}$) contribution of indium and gallium complexes were
theoretically calculated from $\beta_{\text{HRS}}$ values (see Table 3) using Eqs. S14 to S21 following the literature methods [38, 51, 55, 56] (see supplemental material). All DFT calculations were carried out using the SDD basis set at the B3LYP level of theory, with the model phthalocyanine ligand $\text{Pc}^*$ with hydroxyl groups in place of butoxy-group. DFT calculated $\beta_{\text{HRS}}$ values followed the opposite trend to the experimentally determined $\beta$ values, whereby the model complex $\text{Pc}^*\text{InOAc}$ showed a lower $\beta_{\text{HRS}}$ value with respect to complex $\text{Pc}^*\text{GaOH}$ (see Table 3). Even though theoretical $\beta_{\text{HRS}}$ and Z-scan derived $\beta$ values represents different nonlinear terms (second-order polarizability and two-photon nonlinear absorption coefficient respectively) of the studied compounds, the dipolar/octupolar ($\Phi_{\text{p-o}}$, $\Phi_{\text{o-o}}$ and $\Phi_{\text{o-o}}$) contribution to $\beta_{\text{HRS}}$ can help explain the differences observed in experimental optical limiting properties.

After excitation of an electron by absorption of light, there is a relaxation in geometry which can lead to the formation of nonlinear excitations. Differences in $\beta$ values are related to third order NLO-effects which are, in turn, related to geometry relaxation of the molecule. Geometry relaxation is known to be a much slower process with respect to the instantaneous change in $\pi$-electron distribution. The instantaneous shift in $\pi$-electron density is responsible for the large and fast polarizabilities of $\pi$-electron networks [57]. Since dipolar/octupolar contributions are characterized by their differences in charge distribution in response to an applied electric field resulting in spatial asymmetry of the electron distribution, differences in instantaneous change in $\pi$-electron distribution coupled with slower geometry relaxation could result in different $\beta$ values for different molecules. Hence differences in dipolar/ octupolar contributions could be used to understand the variation in $\beta$ values for different complexes. Large $\beta$ values are expected for molecules possessing large dipole moments; however, in films (or bulk material) the large dipole moments form centrosymmetric bulk material. Centrosymmetric films are known to show lower $\beta$ values. Hence, octupolar molecules have been preferably used as films because they can form noncentrosymmetric bulk material with a large macroscopic second-order NLO response.

$\beta_{\text{HRS}}$ values of harmonic light intensity as a function of the polarization angle $\psi$ is shown in Fig. 9, and the dipolar/octupolar ($\Phi_{\text{p-o}}$, $\Phi_{\text{o-o}}$) contribution to $\beta_{\text{HRS}}$ is shown in Table 3. For model complex $\text{P}^*\text{InOAc}$, dipolar and $\chi^{(3)}$ contributions are characterized by their differences in charge distribution in response to an applied electric field resulting in spatial asymmetry of the electron distribution, differences in instantaneous change in $\pi$-electron distribution coupled with slower geometry relaxation could result in different $\beta$ values for different molecules. Hence differences in dipolar/ octupolar contributions could be used to understand the variation in $\beta$ values for different complexes. Large $\beta$ values are expected for molecules possessing large dipole moments; however, in films (or bulk material) the large dipole moments form centrosymmetric bulk material. Centrosymmetric films are known to show lower $\beta$ values. Hence, octupolar molecules have been preferably used as films because they can form noncentrosymmetric bulk material with a large macroscopic second-order NLO response.

Table 2. Nonlinear optical properties of complexes $\text{1InOAc}$ and $\text{1GaOH}$ in DMSO and thin films at 532 nm wavelength and 10 ns pulses

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\text{1InOAc}$ in DMSO</th>
<th>$\text{1GaOH}$ in DMSO</th>
<th>$\text{1InOAc}$ in PBC</th>
<th>$\text{1GaOH}$ in PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$, mm</td>
<td>10.09</td>
<td>9.74</td>
<td>10.6</td>
<td>8.38</td>
</tr>
<tr>
<td>$z_0$, mm</td>
<td>4.84</td>
<td>4.29</td>
<td>3.8</td>
<td>3.82</td>
</tr>
<tr>
<td>$\beta \times 10^5$, m·W$^{-1}$</td>
<td>7.2</td>
<td>6</td>
<td>6</td>
<td>4.8</td>
</tr>
<tr>
<td>$C \times 10^4$, M</td>
<td>1.12</td>
<td>1.21</td>
<td>53$^a$</td>
<td>58$^a$</td>
</tr>
<tr>
<td>$\text{Im}[\chi^{(3)}] \times 10^{20}$, esu</td>
<td>2.36</td>
<td>1.97</td>
<td>6.3</td>
<td>4.77</td>
</tr>
<tr>
<td>$\gamma \times 10^{-3}$, esu</td>
<td>10.82</td>
<td>8.3</td>
<td>9.54</td>
<td>8.99</td>
</tr>
<tr>
<td>$\sigma_{\text{m}} \times 10^{-18}$, cm$^2$</td>
<td>4.95</td>
<td>1.67</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$I_{\text{in}}, \mu$J·cm$^{-2}$</td>
<td>2.51</td>
<td>7.43</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$I_{\text{out}}$, % at 50% $I_{\text{in}}$</td>
<td>53</td>
<td>51</td>
<td>54</td>
<td>68</td>
</tr>
</tbody>
</table>

$^a$Thickness of films measured by SEM.
Octupolar contributions are calculated to be 0.29 and 0.71 respectively. For complex \( \text{Pe}^*\text{GaOH} \), dipolar and octupolar contributions are calculated to be 0.68 and 0.32 respectively. Dipolar/octupolar theoretical results show that complex \( \text{Pe}^*\text{InOAc} \) has much greater octupolar contribution compared to complex \( \text{Pe}^*\text{GaOH} \), as expected due to the acetate axial group. The nonlinear anisotropy parameter values also confirm that \( \text{Pe}^*\text{InOAc} \) (\( \rho = 2.44 \)) is more octupolar in character compared to \( \text{Pe}^*\text{GaOH} \) (\( \rho = 0.46 \)), since the nonlinear anisotropy parameter values run from 0 (pure dipole) to \( \infty \) (pure octupole).

Due to the higher octupolar contribution, acetato-indium(III) phthalocyaninate is expected to show better NLO properties in films compared to hydroxogallium(III) complex, however this expectation is not corroborated with experimental optical limiting results above for \( \text{InOAc} \) and \( \text{GaOH} \) PBC films. The above suggests that there are other factors which contribute to the NLO properties of Pcs when embeded in PBC films.

\( \text{PBC} \) has been shown to enhances the NLO of \( \text{Cd 2,3-[octakis{4-tert-butylphenoxy}phthalocyanine]} \), with the enhancement attributed to factors such as film thickness and disaggregation of the Pc in the film [40].

The calculated DR values are consistent with observed dipolar/octupolar contributions. The lower the DR value, the greater the octupolarity of the molecule. Since \( \beta \) values depend on the polarization of the \( \pi \) electrons and the octupolar part represents complex electron redistribution of the \( \pi \) electrons, the observed differences
in β values (in DMSO) are attributed to the differences in dipolar/octupolar contributions. The theoretical results suggest that complexes 1InOAc and 1GaOH, are respectively predominantly octupolar and dipolar in nature as observed from the shape of the harmonic light intensity as a function of the polarization angle ψ plots (see Fig. 10).

To reveal the effect of axial ligands on NLO properties, DFT calculations were also performed for complexes Pe*InOH and Pe*GaOAc. The differences in dipolar/octupolar contribution for Pe*InOAc and Pe*InOH show that the axial ligand has an effect on NLO properties. The $\Phi_{d,1}$ and $\Phi_{d, 3}$ terms for Pe*InOH were calculated to be 0.75 and 0.25 respectively, while for Pe*GaOAc were calculated to be 0.23 and 0.77 respectively. The calculated dipolar/octupolar contributions are similar to the ones determined for the isosctructural model complexes Pe*GaOAc and Pe*InOAc. However, the hydroxogallium(III) complex has a larger value of $\beta_{RSS} = 7.2 \times 10^3$ m·W⁻¹ in comparison with the hydroxogallium(III) counterpart (6.0 $\times 10^3$ m·W⁻¹). These results are in line with the previous studies of the superior optical limiting of indium phthalocyaninates in comparison with other trivalent metal complexes [26, 58].

CONCLUSION

Asymmetrical indium(III) and gallium(III) complexes 1InOAc and 1GaOH with 2,3-bis[2',2'-hydroxyethoxy]ethoxy)-9,10,16,17,23,24-hexa-n-butoxyphthalocyanine 1H₂ were synthesized and studied. Photophysical measurements revealed that $\Phi_\gamma$ values were higher and $\Phi_\beta$ values lower for the complex containing indium(III) cation. The NLO properties of these complexes were studied in solution and when embedded in poly(bisphenol A carbonate) films. The $\ln[\gamma(\lambda)]$ and γ values were measured and found to be higher for complex 1InOAc as compared to complex 1GaOH in solution. $I_{lim}$ values and $I_{lim}$ vs. $I_{th}$ plots suggest that complex 1InOAc is a better nonlinear optical limiter compared to complex 1GaOH in DMSO, but the reverse tendency is observed when the complexes are embedded in PBC films. DFT calculations have shown that acetatoindium(III) phthalocyaninate is expected to show better NLO properties in films compared to hydroxogallium(III) complex due to predominantly octupolar nature of the former complex, hence this expectation did not corroborate with experimental optical limiting results for 1InOAc and 1GaOH PBC films. This observation suggests that further work should be done to understand the effects of PBC films on NLO properties of PCs.

The results of the DFT calculations emphasize that the effect of counterions in NLO properties of trivalent metal phthalocyaninates may also contribute to optical limiting characteristics affecting their nonlinear anisotropy. These results may be used as a further guideline for rational design of new optical limiters.

Acknowledgments

This work was supported by the Russian Science Foundation (grant #14-13-01373p), the Department of Science and Technology (DST) and National Research Foundation (NRF), South Africa through DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology (UID = 62620) as well as Rhodes University.

Supporting information

Additional information regarding nonlinear optical parameters and DFT calculations, including Eqs. S1–S21 are provided as supporting information. This material is available free of charge via the Internet at http://www.worldscientific.com/jpp/jpp.

REFERENCES


INTRODUCTION

As functional materials, phthalocyanines and many of their derivatives exhibit properties which are interesting for applications in different scientific and technological areas. The structures and properties of phthalocyanine compounds can be tuned by introducing different numbers of substituents with different electronic properties onto the peripheral or nonperipheral positions of the phthalocyanine ring [1–8].

Ball-type phthalocyanines are a new type of phthalocyanine, one of which was reported in the literature for the first time in 2002 [9, 10]. This new type of phthalocyanine has four bridged substituents on the one peripheral positions of each benzene ring of the face-to-face two phthalocyanine molecules. The distance between the two Pc-rings and the chemical and physical properties depend on the constituents of those linkers and differ significantly from the parent monomers [11]. Ball-type Pcs, either metal free or containing two homo or hetero-metal centers, have attracted much attention because of their intrinsic properties [12]. Ball-type bis metallophthalocyanine compounds show different and interesting properties, such as electrical [13–18], gas sensing [19–21], and optical properties [22]. The starting material 1 and ball-type phthalocyanines 2 and 3 were synthesized according to literature methods [23]. More recently, field effect transistors containing phthalocyanine thin films as active layers were fabricated and characterized by various groups [24–26]. In recent years, phthalocyanine based organic field effect transistors (OFETs) with various configurations have been fabricated and characterized by various groups [27–30]. One of the key parameters in an OFET is field effect mobility. OFET devices fabricated using Pc film as an active layer have been reported with field effect mobility ranging from

SYNTHESIS, CHARACTERIZATION AND OFET PROPERTY OF FOUR DIAMINOURACIL BRIDGED NOVEL BALL-TYPE PHTHALOCYANINES

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This paper is dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 8 December 2017
Accepted 22 December 2017

ABSTRACT: New ball-type metallobisphthalocyanines 2 (Co₂Pc₂) and 3 (Zn₂Pc₂) were synthesized from the corresponding 4,4′-[(5,6-diaminopyrimidine-2,4-diyl)bis(oxy)] diphytalonitril 1, which can be obtained by a nucleophilic displacement reaction of 4-nitrophthalonitrile with 5,6-diaminouracil sulfate. Characterization of novel compounds was performed by UV-vis, FT-IR, 1H-NMR, MALDI-TOF mass spectroscopy and elemental analysis. Organic field effect transistor devices (OFETs) with top gate structure were fabricated using these novel compounds as the active material. The devices were characterized by means of their output and transfer characteristics, and it was found that these OFET devices exhibit p-type behavior. When compared with the 2-based device, the OFET with 3 showed higher field effect mobility and larger on/off current ratio.

KEYWORDS: ball-type phthalocyanines, homodinuclear, field effect, threshold voltage, OFET.
10^5 to 10^2 cm² V⁻¹ s⁻¹ [9, 31]. Solution-processed films of 1,4,8,11,15,18,22,25-octakis(hexyl) copper phthalocyanine were utilized as active semiconducting layers in the fabrication of organic field-effect transistors (OFETs) in the bottom-gate configurations, and field-effect mobility (4 × 10⁻² cm² V⁻¹ s⁻¹) was reported [32]. The performance of organic transistors based on sodium salts of sulfonated metal phthalocyanines were compared to those based on their non-sulfonated counterparts by Glezos et al. [33]. It was reported that the values of the field-effect mobility of the OFET devices using sulfonated metal phthalocyanines films are much higher than the values of the respective devices using nonsulfonated metal phthalocyanines. Central metal atoms and substituents were shown to affect the OFET's performance parameters [34, 35]. In this study, new ball-type homodinuclear CoII–CoII 2 and ZnIII–ZnIII 3 Pcs were synthesized by heating compound 1 with the metal salts in the medium without solvent. The new ball-type phthalocyanines were obtained in sufficient purity after washings with different solvents and then characterized by spectroscopic methods. We also report the use of compound 2 and 3 as semiconducting active layers in OFET devices.

EXPERIMENTAL

Materials

All solvents (reagent grade) and the starting materials were acquired from Sigma–Aldrich and were used without purification. IR spectra were recorded on a Bruker 400 spectrometer at room temperature using tetramethylsilane (TMS) as the internal standard. All MALDI TOF Mass spectra were acquired on a Voyager DE-PRO MALDI TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV Laser operating at 337 nm. Spectra were recorded in linear and reflectron mode with average of 100 shots.

Synthesis

**Synthesis of [4,4’-(5,6-diaminopyrimidin-2,4-diyl)bis(oxypyridine)] diphthalonitrile (1).** To a solution of 4-nitrophthalonitrile (0.35g, 2 mmol) in dry dimethylformamide (DMF, 10 mL) 5,6-diaminouracil fluoride (0.14 g, 1 mmol) was added and the temperature was increased to 70 °C, anhydrous K₂CO₃ (0.42 g, 3 mmol) was added to the reaction mixture in six equal portions at 15 min with efficient stirring and the reaction system was stirred at the same temperature for 4 days. Then, the reaction mixture was poured into ice water (100 mL) and it was stirred for 15 min. The precipitate was filtered off and washed several times with cold water. The crude product was dried in air. The yellow solid was soluble in ethanol, acetone. Yield: 0.14 g (59%). mp 240 °C. Anal. calculated for C₈₀H₄₀N₃₂O₈: C, 60.91; H, 2.54; N, 28.43 (%); Found: C, 61.13; H, 2.24; N, 28.92. IR (KBr): ν (cm⁻¹) 3400–3300 (NH); 3100, 3074, 3039 (arom.–CH); 1589, 1483 (Ar–C=O); 1253 (Ar–O). 1H NMR (400 MHz, DMSO-d₆): δppm; 7.73 (dd, J = 2.4 Hz and J = 8.8 Hz, 2H), 8.08 (d, J = 2.4 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H), 8.34 (s, 4H). MS (MALDI-TOF) m/z: 395 [M + H]⁺.

**Synthesis of [2’,10’,16’,24’-tetrakis{4,4’-(5,6-diaminopyrimidin-2,4-diyl)bis(oxypyridine)}] diphthalocyaninedi-co (II) (2).** A well-powdered mixture of compound 1 (0.050 g, 0.127 mmol) and cobalt(II) acetate (0.016 g, 0.063 mmol) were heated in a sealed glass tube at the presence of DBU, under argon atmosphere, at 270 °C for 20 min. After cooling to room temperature, a green-colored reaction product was obtained. DMF (10 mL) was added to the residue in order to dissolve the product. The reaction mixture was precipitated by adding hexane. The precipitate was filtered, washed with hot water, chloroform and then acetone to remove the unreacted starting materials and finally dried in the room temperature. The dark green product was slightly soluble in THF, and was soluble in DMF and DMSO. Yield: 0.07 g (33%). dp > 350 °C. Anal. calculated for C₈₀H₄₀N₃₂O₈: C, 56.21; H, 2.34; N, 26.43 (%); Found: C, 56.93; H, 2.13; N, 26.62. IR (KBr): ν (cm⁻¹) 3400–3300 (NH); 3078, 3050 (arom.–CH); 1592, 1485 (Ar–C=O); 1248 (Ar–O–Ar). UV-vis (DMF), λmax nm, (log ε): 676 (4.29), 612 (4.00), 335 (4.29). MS (MALDI-TOF) m/z: 1696 [M + H]⁺.

**Synthesis of [2’,10’,16’,24’-tetrakis{4,4’-(5,6-diaminopyrimidin-2,4-diyl)bis(oxypyridine)}] diphthalocyaninedizinc (II) (3).** Compound 3 was synthesized in a similar manner to that described above for 2, using zinc acetate (0.014 g, 0.063 mmol). Yield: 0.06 g (29%). dp > 350 °C. Anal. calculated for C₈₀H₄₀Zn₄O₈: C, 56.21; H, 2.34; N, 26.23 (%); Found: C, 56.93; H, 2.13; N, 26.03. IR (KBr): ν (cm⁻¹) 3400–3300 (NH); 3080 (arom.–CH); 1599, 1522 (Ar–C=O); 1230 (Ar–O–Ar). UV-vis (DMF), λmax nm, (log ε): 681 (4.36), 611 (3.93), 340 (4.59). 1H NMR (400MHz, DMSO-d₆): δppm 8.29–6.92 (m, 40 H). MS (MALDI-TOF) m/z: 1705 [M + H]⁺.

MALDI sample preparation

MALDI matrix, 2,5-dihydroxybenzoic acid was prepared in acetonitrile-dimethyl sulfoxide (ACN-DMSO) (2:1, v/v) containing 0.2% trifluoroacetic acid at a concentration of 6 mg/mL. MALDI sample was prepared by mixing sample solutions (2.0 mg/mL in ACN-DMSO mixture (2:1, v/v) having 0.2% trifluoroacetic acid) with the matrix solution (1:10, v/v) in a 0.5 mL epipendorf micro tube. Finally 0.5 μL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.
OFET fabrication and characterization

The 2 and 3 based FET devices were fabricated with the top-gate and bottom source–drain contact geometry configuration. The detail of the fabrication procedure was as follows: first, 120 nm Au source/drain electrodes were formed on pre cleaned glass substrates using the photolithography technique. The channel in the fabricated devices had a length (L) and width (W) 500 μm and 50 μm, respectively. Thin films of 2 and 3 were formed onto the source/drain electrodes by spinning DMF solutions of the compound. The thickness of the semiconducting 2 and 3 films were determined by ellipsometric technique and was found to be 130 nm and 135 nm, respectively. The gate dielectric layer, 250 nm thick polyvinylalcohol (PVA), was deposited on top of the semiconductors by the spin coating method at 2200 rpm for 60 s. In order to be sure that the solvent in PVA film is completely evaporated, the PVA films were dried in a vacuum oven at 95°C for 75 min. After the drying process, top gate electrodes of Ag with a thickness of 150 nm were deposited onto the PVA layer by thermal evaporation of Ag wire with a purity of 99.99%. The transfer and output characteristics of the devices were measured at ambient conditions using a Keithley 617 programmable electrometer and a Keithley 2400 source-meter.

RESULTS AND DISCUSSION

In this study, a novel compound [4,4′-(5,6-diaminopyrimidine-2,4-diyl)bis(oxy)]diphytalonitril 1 was prepared and used as a starting material for the preparation of new ball-type phthalocyanines. The ball-type metallophthalocyanines 2 and 3 were synthesized from compound 1 with corresponding metal salts heating in solid phase. The synthesis routes for compounds 1, 2 and 3 are summarized in Scheme 1. Characterization of the new products involved a combination of methods including elemental analyses, FT-IR, MALDI-TOF mass, 1H-NMR.

![Chemical structure](image-url)

Scheme 1. (i) K₂CO₃, DMF, Ar, 70°C; (ii) Co(AcO₂)₂·4H₂O, DBU, Ar, 300°C, without solvent; (iii) Zn(AcO₂)₂·2H₂O, DBU, Ar, 300°C, without solvent.
The IR spectra taken with KBr pellets of 1, 2 and 3 clearly indicate the presence of NH$_2$ groups by the absorption bands at 3400–3300 cm$^{-1}$. Also, aromatic CH peaks were observed at 3100–3033 cm$^{-1}$; when compared with the IR spectrum of 4-nitrophthalonitrile, the structure of 1 is confirmed by the disappearance of the aromatic NO$_2$ bands 1530 cm$^{-1}$ and 1350 cm$^{-1}$ and also the appearance of an intense new absorption band at 1253 cm$^{-1}$ attributable to Ar-O-Ar. In addition the IR spectra of compound 1 shows a very sharp –C≡N vibration at 2232 cm$^{-1}$, which disappears on coordination to the metal ions. Additionally, the strongest peaks appearing at ca. 1248 cm$^{-1}$ for 2, and 1230 cm$^{-1}$ for 3 in the spectra of the novel synthesized compounds were attributed to the aromatic ether bands (Ar-O-Ar). Furthermore, the peaks observed at 1589, 1483 cm$^{-1}$, 1592, 1485 cm$^{-1}$ and 1599, 1522 cm$^{-1}$ were attributed to aromatic C=C double bond stretching frequencies for 1, 2 and 3 respectively.

The phthalocyanines show typical electronic spectra with two strong absorption regions, one of which is in the UV region at around 300–350 nm (B-band) and the other is in the visible region between 600–700 nm (Q-band). The typical UV-vis spectra of the phthalocyanine complexes 2 and 3 in DMF showed characteristic absorptions between 676 and 681 nm in the Q-band region (Fig. 1). These characteristic absorptions are due to the π-π* transitions of conjugated 18π electron systems. The comparison of UV-vis spectra of 2 and 3 in DMF shows that the Q-band of 2 is broader than that of 3. The B-bands of the 2 and 3 are more intense than Q bands of phthalocyanine complexes which indicate strong aggregation [36]. This is due to the mix of B-bands with the charge transfer bands of the phthalocyanine complexes. The B-bands for 2 and 3 occurred at 335 and 340 nm, respectively.

The positive ion and linear mode MALDI-TOF-MS spectrum of compound 1 was obtained and is given in Fig. 2. Only 2,5-dihydroxybenzoic acid MALDI matrix was yielded intense molecular ion signal and low fragmentations under the MALDI-TOF-MS conditions for this ligand. The protonated molecular ion signal for the ligand was only obtained in linear mode.

In the case of phthalocyanine complex 2 (Fig. 3), high resolution MALDI-TOF-MS spectrum was obtained. Isotopic mass distribution and the intensities of this complex was calculated theoretically and compared with the isotopic mass distribution and the peak intensities of the experimental results. It was observed that theoretical and experimental results matched each other in good agreement.

Similar experimental conditions were conducted to the zinc complex (Fig. 4). The isotopic mass distribution of the theoretical results of zinc complex was found to be matched with the experimental results. All these information showed that complexes were synthesized in the desired manner. It was observed that theoretical and experimental results were matched each other in good agreement.

The $^1$H NMR spectra of compounds 1 and 3 were taken in dimethylsulfoxide-d$_6$, at room temperature. In the $^1$H NMR spectrum of compound 1, the phenyl protons appeared at 7.73 ppm (dd), 8.08 ppm (d), 8.25 ppm (d), and -NH$_2$ protons at 8.34 ppm (s). The $^1$H NMR spectrum of 3 was similar to that of 1. The protons of 3 were observed as broad multiplets at 8.29–6.92 ppm in its $^1$H NMR spectrum (Fig. 5). The singlet peaks at 2.75 and 2.88 ppm in this spectrum are attributed to the –CH$_3$ protons of the solvent DMF. $^1$H NMR measurement was precluded for the compound 2 owing to the paramagnetic nature.

**OFET studies**

In an OFET, strong correlation between the drain-source current ($I_{DS}$) and gate–source voltage ($V_{GS}$) is a well-known phenomena. A comparison of the output characteristics of the 2 and 3 based OFETs using polyvinylalcohol as gate dielectric at various gate voltages from 0 to -80 V is shown in Figs 6(a) and 6(b),

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![Fig. 1. UV-vis spectra of 2 (1.05 × 10$^{-5}$ M) and 3 (1.30 × 10$^{-5}$ M) in DMF](image-url)
respectively. The effects of the molecular structure of the active layer are well reflected in the OFET characteristics, and the performance of the 3 based OFET is improved. The characteristic feature of the ¹NMR spectrum of 3 is the modulation of the $I_{DS}$ current by $V_{GS}$ voltage (as is clear from (Fig. 5), $I_{DS}$ current increases with negative $V_{GS}$ voltages for both devices). Figure 6 reveals that both devices exhibit field effects, which are operating in $p$-type accumulation mode. Two different operating regions, linear and saturation regions, can be seen clearly with the variation of drain–source voltage ($V_{DS}$) for both devices. For a given gate–source voltage, it is clear that for low values of $V_{DS}$ the $I_{DS}$ current increases linearly with increase in $V_{DS}$. Ohmic behavior for low $V_{DS}$ suggests the formation of a channel with uniform depth and charge density. With further increase in $V_{DS}$, the resistance of the channel increases because of non-uniform voltage drop along the channel. In this case, the $I_{DS}$ vs. $V_{GS}$ plots do not simply obey Ohm’s law, as observed. The observed saturation in $I_{DS}$ current at higher values of $V_{DS}$ can be attributed to the pinch-off of the channel.

From the analysis of the curves in Figs 6(a) and 6(b), it can be seen clearly that the observed maximum $I_{DS}$ current for the 3 based OFET device was about three times higher than the 2 based device for the same gate–source bias of -80 V. An $I_{DS}$ current of $1.05 \times 10^{-4}$ A at gate–source voltage of -80 V was observed for 2 based OFET device, while the maximum value of $I_{DS}$ current for 3 based device was $2.92 \times 10^{-4}$ A for the same $V_{GS}$ voltage of -80 V. It is well-known that the electronic band

Fig. 2. Positive ion and linear mode MALDI mass spectrum of compound 1

Fig. 3. Positive ion and reflectron mode MALDI mass spectrum of 2
structure and the first oxidation and reduction potential of the Pc compounds depend on several factors including the central metal ion and the position of the substituent unit. The observed high $I_{DS}$ value can be attributed to the difference between the first oxidation and first reduction potential of the compound of 2 and 3. As is clear from Fig. 6, modulated $I_{DS}$ current by negative $V_{GS}$ voltage, $I_{DS}$ current for both 2 and 3 based devices increases with the

Fig. 4. Positive ion and reflectron mode MALDI mass spectrum of 3

Fig. 5. $^1$H NMR spectrum of compound 3
increase of negative $V_{GS}$ voltage, indicating $p$-channel behavior of the devices (when a negative bias voltage applied to the gate electrodes accumulation of holes in the channel region takes place).

For linear region, the dependence of $I_{DS}$ on $V_{GS}$ is given by Eq. 1 [37]

$$I_{DS} = \frac{W}{L} C_{in} \mu_{fe} (V_{GS} - V_{th}) V_{DS} - \frac{1}{2} V_{DS}^2$$  \hspace{1cm} (1)$$

where $W$ and $L$ are the channel width and length, respectively, $\mu_{fe}$ is the field-effect mobility, $C_{in}$ is the insulator capacitance per unit area, and $V_{th}$ is the threshold voltage. For saturation region the relation between the $I_{DS}$ current and $V_{GS}$ voltage is expressed by Eq. 2 [38]:

$$I_{DS} = \frac{W}{2L} C_{in} \mu_{fe} (V_{GS} - V_{th})^2$$  \hspace{1cm} (2)$$

The parameters which characterize an OFET, field effect mobility and threshold voltage, can be obtained by various methods. In this work, the values of the mobility for all devices were extracted from a plot of the square root of the $I_{DS}$ current vs. $V_{GS}$ by fitting data to Eq. (2). For 2 and 3 based devices, these plots are shown in Fig. 7 for a constant value of $V_{DS}$ voltage of -30 V. From the transfer characteristics of the devices, with the aid of Eq. (2), the values of field effect mobility were determined. It was found that the 3 based device has a field effect mobility of 6.8 x 10^{-2} cm^2/V s which was 2 times larger than 2 based device. The obtained mobility values for 2 and 3 based OFET were higher than similar devices reported in the literature [25, 39, 40]. The obtained results reveals that the kind of the central metal ion in the Pc cavity has a strong effect on the OFET performance. For an organic semiconductor, short intermolecular distance, good matching of energy level between the organic semiconductor and electrode for efficient charge-carrier injection and large $\pi$-orbit overlapping are necessary in order to achieve a high-performance OFET.

It is also well-established that the molecular orientation of the Pc molecules in the solid state is of great interest because it is thought to strongly affect carrier mobility in electronic devices. Actually, it is not easy to decide which mechanism is responsible for the observed higher mobility value in the 3 based device. The performance of OFETs are closely related to the packing mode of organic molecules in thin solid films. Several works elucidated that $\pi-\pi$ stacking is a favored packing mode for OFET applications [41]. The $\pi-\pi$ stacking affords strong interactions between neighboring molecules. The presence and the kinds of central metal ions have many influences on the HOMO, LUMO, and energy level structure of the Pc complexes, sequentially does the charge mobility.

**CONCLUSION**

In conclusion, we have described the synthesis and spectral characterization of two new phthalocyanines with 5,6-diamino pyrimidine substituents on the periphery. The new ball-type homo-dinuclear CoII–CoII and ZnII–ZnII phthalocyanines have been applied as active layers in OFETs. The output and transfer characteristics of the resulting $p$-type OFET devices were investigated to evaluate main performance parameters such as the field effect mobility. From the analysis of the electrical characteristics of the OFETs, it was observed that compound 3 is a promising $p$-type semiconductor for the fabrication of OFETs with high mobility.

**Acknowledgments**

We are grateful to Firat University Scientific Research Project Coordination Unit, FÜBAP, for their financial support (Project No: FF.13.31), Yıldız Technical University Commission of Scientific Research Projects (2016-01-01-KAP04) and Turkish Academy of Sciences, TUBA, for the partial financial support.
REFERENCES
Preparation, structure, and electrochemistry of porphyrinato titanium (IV) benzenedithiolates with a trithiole ring, a dithiin ring, and two 2-cyanoethylthio groups

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 10 December 2017
Accepted 25 December 2017

ABSTRACT: The reaction of tetra(p-tolyl)porphyrinato titanium (IV) oxide (2) with 4,7-diethyl-5,6-dimercaptobenzo[1,2,3]trithiole (3a) produced the corresponding titanium (IV) complex, tetra(p-tolyl)porphyrinato titanium (IV) trithiolobenzenedithiolate (4a), fused with a trithiole ring. Related compounds 4b and 4c were prepared by a similar reaction of 2 with 5,8-diethyl-6,7-dimercapto[1,4]dithiin (3b) and 3,6-diethyl-4,5-dimercapto-1,2-bis(2-cyanoethylthio)benzene (3c). The structure of 4b was determined by X-ray crystallography. Compound 4c was further treated with cesium hydroxide to produce the corresponding dithiolate anion 4c<sub>2S</sub><sup>-</sup>, which was deposited on the gold electrode. The electrochemical property of the gold electrode was determined by cyclic voltammetry. The structure of simplified model compound 4b′ was optimized using the DFT method with the Gaussian 09 program. The optimized structure was utilized to calculate the NMR chemical shifts, the HOMO and LUMO energy levels, and the electronic transition in the absorption spectrum.

KEYWORDS: porphyrin, benzobistrithiole, X-ray crystallography, gold electrode, electrochemistry.

INTRODUCTION

Metalated porphyrins and related compounds with one or more axial coordinating groups have attracted much attention because of their potential application in electrochromic displays, field-effect transistors, nonlinear optical materials, and dye sensitized solar cells [1]. In addition to simple porphyrins, multi-porphyrin oligomers and porphyrin nanosheets have been artificially constructed to investigate new π-conjugation systems [2]. The self-assembly of porphyrin hybrid molecules is important to develop new functional materials; for example, electrodes deposited with porphyrin derivatives through thiol groups are an interesting topic in the field of photo-current generation [1(e), 3]. In many porphyrin complexes and related compounds, titanium (IV) derivatives can connect two ligands on one side of the porphyrin ring [4]. As porphyrin derivatives linked with a bidentate ligand, porphyrinato titanium (IV) complexes with titanium–oxygen or titanium–sulfur bonds were described by Deronzier, which are coordinated with catecholate or 1,2-benzenedithiolate on one side of the macrocycle [5]. Phthalocyaninato titanium (IV) complexes with two titanium–oxygen or titanium–sulfur bonds were reported by Hanack [6], and Kobayashi synthesized a mutually perpendicular phthalocyanine pentamer and related derivatives [7]. We also reported porphyrinato and phthalocyaninato titanium (IV) complexes linked with 1,2-benzenedithiols and 1,2-benzeneselenolate [8].

On the other hand, we reported that one of the trithiole rings of 4,8-diethylbenzo[1,2-d:4,5-d']bis[1,2,3]trithiole (1a) can be substituted with other functional groups;
RESULTS AND DISCUSSION

As starting compounds, 4,8-diethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole (1a), 4,7-diethyl-5,6-ethylenedithio-benzo[1,2,3]trithiole (1b), and tetra(p-tolyl)porphyrinato titanium (IV) oxide (2) were prepared by the method reported previously [9, 12]. 4,7-Diethyl-5,6-bis(2-cyanoethylthio)benzo[1,2,3]trithiole (1c) was prepared in 23% yield by treatment of 1a with sodium borohydride and then with 2-cyanoethyl bromide in the presence of potassium carbonate (Scheme 1). The structure of this compound can be determined by NMR and mass spectrometry.

To generate 1,2-benzenedithiols (3a–3c) as bidentate sulfur ligands, 1a–1c were treated with sodium borohydride in tetrahydrofuran/methanol and then with aqueous hydrochloric acid solution. Compounds 3a–3c were not isolated and reacted with porphyrin 2, respectively (Scheme 2).

Typically, a mixture of 2 and 3a in dichloromethane was stirred at room temperature under argon for 24 h. After workup and purification with silica gel column chromatography and Bio-beads (SX-1) column chromatography, porphyrin derivative 4a with trithiolobenzenedithiolate as the axial ligand was obtained in 23% yield. By a similar reaction of 2 with 3b and 3c, compounds 4b and 4c were produced in 18% and 30% yield, respectively.

In the 1H NMR spectrum, the signals of the p-tolyl groups and porphyrin ring of 4a–4c were observed at a similar magnetic field to those of 2. Signals for the ethyl groups of 4a–4c appeared at a higher magnetic field than those of 1a–1c (Table 1).

Recrystallization of 4b from chloroform/methanol gave dark purple needle crystals, and they are suitable for single crystal X-ray crystallography. The ORTEP drawing indicates that the two sulfur atoms on the benzene ring coordinate to the central titanium atom and form the five-membered dithiatitanole ring (Fig. 1). Although the benzenedithiolate coordinated to the central titanium atom is almost perpendicular to the porphyrin ring, it is slightly tilted to the N1 side on the porphyrin plane. The unit cell consists of four molecules of 4b in the crystal and two molecules closely located.

While the ORTEP drawing reveals that the form of the porphyrin skeleton is nearly planar, the central titanium and four nitrogen atoms construct a square pyramid structure. The two ethyl groups of 4b are oriented in a similar direction. Although the trihiole ring of 1a has an envelope structure in a neutral state, the five-membered dihthiastannole ring of 4b is almost a flat structure, which is similar to that of the dithiastannole ring [13]. The partial bond lengths and bond angles of 4b are shown in Table 2 (Obs). The line between S1 and S2 atoms is closely parallel to that of N2 and N4 atoms and perpendicular to that of N1 and N3 atoms. The structure of 4b is similar to that of simplified compound 4b' optimized by the DFT method. The bond lengths and bond angles of 4b (Obs) are similar values to those of 4b' (Calcd) as shown in Table 2.

To determine the electrochemical properties, the redox potentials of 4a–4c were measured by cyclic voltammetry using silver nitrate as a reference electrode (Table 3). As shown in Fig. 2, while compound 4a showed one reversible oxidation potential ($E_{1/2} = 0.73$ V) and two quasi reversible reduction potentials ($E_{1/2} = -0.92$ and $-1.69$ V), one reversible oxidation potential ($E_{1/2} = 0.74$ V) and two reversible reduction potentials ($E_{1/2} = -1.10$ V).
Preparation, Structure, and Electrochemistry of Porphyrinato Titan(IV) Benzenedithiolates

159

and -1.84 V) were observed for 4b. It appears that the reduction potentials of 4a show an anode shift compared to those of 4b and the oxidation potential of 4a is similar to that of 4b. While the oxidation potentials of 4a and 4b showed a cathode shift compared with those of 2 and 4c, their reduction potentials showed an anode shift compared with those of 2 and 4c.

In the UV-vis spectrum measured in CHCl₃, 2 shows strong Soret band absorption at 426 nm and weak three Q band absorption at around 550 nm (Fig. 3). In contrast, broadened Soret band absorption was observed at 432 nm for 4a, 431 nm for 4b, and 427 nm for 4c, together with weak absorption at higher energy region at 403 nm, 399 nm, and 403 nm, respectively.

Since the benzenedithiolate coordinates to the titanium atom of porphyrin on one side, the molecule has C₂ᵥ symmetry; therefore, the broadening of the Soret band would be related to the electronic transition of unsymmetric porphyrin [14]. The Soret band absorption of 4a and 4b is more broadened than that of 4c, suggesting that the aggregation property of 4c is weaker than that of 4a and 4b.

To obtain theoretical information, the structure of 4b′ (without four p-tolyl group) was optimized by the density functional theoretical (DFT) method at the B3LYP/6-31G (d, p) level for the hydrogen, carbon, nitrogen, and sulfur atoms and LANL2DZ level for the titanium atom using the Gaussian 09 program [11]. The optimized structure is similar to that determined by X-ray crystallography, except for the tilt angle of the axial ligand and the four p-tolyl groups. While the calculated structure shows that the form of the porphyrin skeleton is nearly planar, the central titanium and four nitrogen atoms construct a square pyramid form and the two ethyl groups of 4b′ are oriented in a similar direction. The ¹H NMR chemical shifts of 4b′ were calculated (Table 1), and are similar to those of 4b given by the experimental section. As shown in Table 2, the bond lengths and bond angles of the optimized structure 4b′ are well correlated to those of the structure 4b determined by X-ray crystallography.

To calculate the HOMO and LUMO energy levels and the electronic transition of the absorption spectrum, time-dependent density functional theory (TD-DFT)

Table 1. ¹H NMR chemical shifts of 4a–4c and 4c′

<table>
<thead>
<tr>
<th>Chemical shifts δ (ppm)</th>
<th>ArCH₂CH₂</th>
<th>ArCH₂CH₃</th>
<th>SC₂H₂</th>
</tr>
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<tbody>
<tr>
<td>4a</td>
<td>0.20</td>
<td>1.43</td>
<td>—</td>
</tr>
<tr>
<td>4b</td>
<td>0.17</td>
<td>1.58</td>
<td>2.60</td>
</tr>
<tr>
<td>4c</td>
<td>0.16</td>
<td>1.74</td>
<td>2.08</td>
</tr>
<tr>
<td>4c′</td>
<td>0.33</td>
<td>1.66</td>
<td>2.60</td>
</tr>
</tbody>
</table>

The chemical shifts for 4b′ were calculated using DFT method.

Fig. 1. ORTEP drawing of 4b

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Scheme 2. Preparation of porphyrin complexes (4a–4c)
1st Reading

calculated at the same level. Although the HOMO and HOMO–1 of 4b’ locate on the titanium and four sulfur atoms and the benzene ring, the HOMO–2 and HOMO–3 exist on the porphyrin ring (Fig. 4). The HOMO–2 and HOMO–3 could be the a2u and a1u orbitals, respectively, if their dithiolate ligand does not exist. While the LUMO + 1 of 4b’ lies on the titanium and two sulfur atoms, the LUMO is locating on the porphyrin ring. The LUMO + 2 (164) (-2.57 eV) exists on the porphyrin ring, and its shape is similar to the LUMO though the directions of their benzodithiatitanole ligands are perpendicular to each other; hence, the LUMO and LUMO + 2 could be the e_gx and e_gy orbitals, respectively, if their dithiolate ligand does not exist. Since the energy difference between the LUMO and LUMO + 1 and the LUMO + 1 and LUMO + 2 is small, these orbitals have almost degenerate energy in the calculated results. The LUMO + 4 (166) exists on the porphyrin ring and the titanium and two sulfur atoms of the dithiatitanole ring. Although this orbital has higher energy (-1.72 eV) than that of the LUMO + 2 orbital, the transition to LUMO + 4 shows higher weight than that of the other transition (Table 4). The energy difference between the HOMO and LUMO of 4b’ is about 2.59 eV which is larger than that of the ΔE value of (4b) (Table 2).

The calculated absorption wavelengths and oscillator strengths f are shown in Fig. 3 and Table 4. Although the HOMO–LUMO transition of 4b’ is observed at 610 nm (80%), the oscillator strength is 0.01. The absorption at 433 nm (f = 0.20) and 428 nm (f = 0.39) may be related to the broadening of the observed Soret band absorption. The largest oscillator strength (f = 0.60) is observed at 364 nm absorption. The configuration of these electronic transitions is shown in Table 4.

Finally, we tried to deposit compound 4a on the gold electrode. To a chloroform solution of 4a, the gold electrode was immersed for 24 h. The electrode was washed with chloroform. The electrode was utilized to measure oxidation and reduction potential using the dichloromethane solution of tetrabutylammonium perchlorate as an electrolyte (0.1 mol/L). As shown in Fig. 5, weak irreversible oxidation and reduction potentials were observed at 0.68 V and -1.48 V in the cyclic voltammogram (scan rate: 100 mV/s), suggesting that although the trithiole ring of 4a can adsorb on the gold electrode, it would not be appropriate to the deposition. Therefore, compound 4c was utilized and

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<tr>
<td>Ti-S1</td>
<td>2.3698 (11)</td>
<td>2.3753</td>
<td>Ti-N4</td>
<td>2.145 (3)</td>
<td>2.1651</td>
<td>S3-C59</td>
</tr>
<tr>
<td>Ti-S2</td>
<td>2.3794 (10)</td>
<td>2.3770</td>
<td>S1-C49</td>
<td>1.753 (3)</td>
<td>1.7710</td>
<td>S4-C60</td>
</tr>
<tr>
<td>Ti-N1</td>
<td>2.112 (3)</td>
<td>2.1136</td>
<td>S2-C50</td>
<td>1.758 (4)</td>
<td>1.7721</td>
<td>C49-C50</td>
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<tr>
<td>Ti-N2</td>
<td>2.160 (3)</td>
<td>2.1645</td>
<td>S3-C52</td>
<td>1.791 (4)</td>
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<tr>
<td>Ti-N3</td>
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<td>2.1149</td>
<td>S4-C53</td>
<td>1.783 (4)</td>
<td>1.7914</td>
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</tr>
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</table>

The bond lengths and bond angles of 4b and 4b’ were determined by X-ray crystallography (Obs) and those of 4b’ were obtained by DFT calculation (Calcd).

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<tr>
<td>S1-Ti-S2</td>
<td>79.37 (3)</td>
<td>79.62</td>
<td>N2-Ti-N3</td>
<td>83.10 (12)</td>
<td>83.24</td>
<td>S1-Ti-N4</td>
</tr>
<tr>
<td>Ti-S1-C49</td>
<td>112.38 (13)</td>
<td>112.65</td>
<td>N2-Ti-N4</td>
<td>135.95 (11)</td>
<td>134.34</td>
<td>S2-Ti-N1</td>
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<tr>
<td>Ti-S2-C50</td>
<td>112.19 (13)</td>
<td>112.69</td>
<td>N3-Ti-N4</td>
<td>83.23 (12)</td>
<td>83.26</td>
<td>S2-Ti-N2</td>
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<td>N1-Ti-N2</td>
<td>83.20 (12)</td>
<td>83.27</td>
<td>S1-Ti-N1</td>
<td>98.76 (9)</td>
<td>103.46</td>
<td>S2-Ti-N3</td>
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<td>N1-Ti-N3</td>
<td>142.72 (11)</td>
<td>144.80</td>
<td>S1-Ti-N2</td>
<td>72.18 (9)</td>
<td>73.02</td>
<td>S2-Ti-N4</td>
</tr>
<tr>
<td>N1-Ti-N4</td>
<td>82.93 (12)</td>
<td>83.28</td>
<td>S1-Ti-N3</td>
<td>109.65 (9)</td>
<td>103.39</td>
<td></td>
</tr>
</tbody>
</table>

All measurements were performed by cyclic voltammetry, using Ag/AgNO₃ (0.01 mol/L) as a reference electrode (scan rate: 200 mV/s).
the 2-cyanoethyl group was eliminated with cesium hydroxide in tetrahydrofuran/methanol to generate 4c2S. The gold electrode was immersed in the solution for 24 h and then washed with chloroform. The cyclic voltammogram of gold electrode modified with 4c2S showed one quasi reversible oxidation couple and one irreversible oxidation peak at $E_{1/2} = 1.38$ V and $E_p = 1.62$ V and one irreversible reduction peak at $E_p = -1.57$ V (scan rate: 50 mV/s).

EXPERIMENTAL

General

NMR spectra were measured with Bruker AVANCE-500 III and DRX-400 spectrometers. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded with a JASCO Ubest V-570 spectrometer. A Hokuto Denko Co. Model HAB-151 apparatus was employed for measuring oxidation potentials. Bio-beads (SX-1) for column chromatography were purchased from Nippon Bio-Rad Laboratories.

Oxidation and reduction potentials

All measurements were performed by cyclic voltammetry, using Ag/AgNO₃ (0.01 mol/L) as a reference electrode (scan rate: 200 mV/s). A solution of $n$-Bu₄NClO₄ in CH₂Cl₂ (0.1 mol/L) was used as an electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2} = 0.09$ V by the apparatus without any correction.

X-ray crystallographic analysis of 4b

X-ray crystallographic data were acquired with a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated MoKα radiation. Diffraction patterns were collected at -173 ± 1°C to a maximum 2θ value of 62.7°. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction). The structures were solved by a direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL Version2016/6: Monoclinic, $a = 14.8410$ (12) Å, $b = 25.7894$ (13) Å, $c = 13.2194$ (8) Å, β = 90.169 (6), $V = 5059.6$ (6) Å³, $P2_1/c$ (14), $Z = 4$, $D_{calc} = 1.317$ g/cm³, µ (MoKα) = 3.785 cm⁻¹, No. of Reflections Measured = Total: 34445, Unique: 11539 ($R_{int} = 0.0788$), Reflection/Parameter Ratio = 18.55, Residuals: $R_1 (I > 2.00σ(I)) = 0.0694$, Residuals: $R (All reflections) = 0.1123$, Residuals: $wR_2 (All reflections) = 0.1900$, $GOF = 1.037$, Maximum peak in Final Diff. Map = 1.46 e/Å³.

Materials

Compounds (1a), (1b), and (2) were prepared using a method described previously [9, 10].
4,7-Diethyl-5,6-bis(2-cyanoethylthio)benzotriathiole (1c). To a solution of 1a (349.9 mg, 1.1 mmol) and K₂CO₃ (140 mg, 1.0 mmol) in THF (150 ml)/MeOH (75 ml), NaBH₄ (44 mg, 1.2 mmol) was added under Ar, and the solution was stirred for 5 min. 3-Bromopropionitrile (0.25 ml, 3 mmol) was added to the solution. After stirring for 24 h and acidification with HCl, the solvent was evaporated. The product was extracted with CHCl₃ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-400, n-hexane : CHCl₃ = 1: 1) to produce 1c in 21% yield (90.0 mg); orange solid; 1H NMR (400 MHz, CDCl₃) δ 1.19 (t, J = 7.5 Hz, 6H), 2.62 (t, J = 7.0 Hz, 4H), 3.07 (q, J = 7.5 Hz, 4H), 3.19 (t, J = 7.0 Hz, 4H) ppm; 13C NMR (101 MHz, CDCl₃) δ 14.6, 18.2, 32.2, 33.2, 118.0, 137.7, 143.6, 143.8 ppm; IR (KBr) 2249 cm⁻¹ (CN); HRMS Calcd for C₁₆H₁₈N₂S₅: 398.0074. Found (m/z) 398.0076 (M⁺).

Table 4. Calculated transition energies, oscillator strengths f, and configurations for 4b'  

<table>
<thead>
<tr>
<th>Energy (nm)</th>
<th>f</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>433</td>
<td>0.20</td>
<td>158 → 165 (15%) 161 → 166 (70%)</td>
</tr>
<tr>
<td>428</td>
<td>0.39</td>
<td>158 → 162 (22%) 158 → 166 (32%) 159 → 164 (39%)</td>
</tr>
<tr>
<td>413</td>
<td>0.25</td>
<td>158 → 164 (36%) 159 → 162 (12%) 159 → 166 (33%) 160 → 166 (14%)</td>
</tr>
<tr>
<td>379</td>
<td>0.30</td>
<td>156 → 165 (17%) 158 → 164 (14%) 159 → 166 (46%)</td>
</tr>
<tr>
<td>364</td>
<td>0.60</td>
<td>158 → 162 (18%) 158 → 166 (60%) 159 → 164 (13%)</td>
</tr>
<tr>
<td>363</td>
<td>0.21</td>
<td>155 → 162 (37%) 156 → 165 (27%)</td>
</tr>
<tr>
<td>356</td>
<td>0.12</td>
<td>155 → 162 (43%) 156 → 165 (32%)</td>
</tr>
</tbody>
</table>

Excited states with energy less than 4.0 eV, f greater than 0.10, and contribution greater than 10% are shown.

Fig. 4. Optimized structure and molecular orbitals of 4b’

4,7-Diethyl-5,6-dimercaptobenzo[1,2,3]trithiole (3a). Compound (1a) (303 mg, 0.95 mmol) and NaBH₄ (57 mg, 1.5 mmol) were placed in a glass reactor under Ar. THF (10 mL) and MeOH (10 mL) were added to the reactor and the solution was stirred for 1 h. Aqueous HCl solution (10 mL) was added to the solution to generate the corresponding dithiol (3a). After evaporation of the solvent, 3a was utilized to the complexation reaction. 5,8-Diethyl-6,7-dimercaptobenzo[1,4]dithiin (3b) and 4,5-dimercapto-3,6-diethyl-1,2-bis(2-cyanoethylthio)benzene (3c) were prepared by the method described above.

Tetra(-p-tolyl)porphyrinato titanium (IV) trithiolobenzenedithiolate (4a). Compounds 2 (219 mg, 0.3 mmol) and 3a (generated by the procedure described above) were dissolved in CH₂Cl₂ (20 mL) and the solution was stirred at room temperature under Ar for 72 h. After evaporation of the solvent, the product was purified by...
column chromatography (silica gel, CHCl₃) to produce 4a in 17%; Purple crystal; ¹H NMR (400 MHz, CDCl₃) δ 0.20 (t, J = 7.6 Hz, 6H), 1.43 (q, J = 7.0 Hz, 4H), 2.71 (s, 12H), 7.59 (dd, J = 2.8 Hz, 8H), 8.03 (dd, J = 5.6 Hz, 4H), 8.12 (dd, J = 6.4 Hz, 4H), 9.06 (s, 8H); FAB-MS (m/z) 1083.2815 (M+).

Tetra-(p-tolyl)porphyrinato titanium (IV) ethylene-dithiobenzenedithiolate (4b). 23%; Purple crystal; ¹H NMR (500 MHz, CDCl₃) δ 0.17 (t, J = 7.3 Hz, 6H), 1.58 (q, J = 7.8 Hz, 4H), 2.60 (s, 4H), 2.71 (s, 12H), 7.57 (dd, J = 7.5 Hz, 8H), 8.03 (dd, J = 6.8 Hz, 4H), 8.12 (dd, J = 7.4 Hz, 4H), 9.05 (s, 8H); FAB-MS (m/z) 1006.2 (MH+).

Tetra-(p-tolyl)porphyrinato titanium (IV) bis(2-cyanoethylthio)benzenedithiolate (4c). 30%; Violet crystal; ¹H NMR (400 MHz, CDCl₃) δ 0.16 (t, J = 7.2 Hz, 6H), 1.74 (q, J = 7.6 Hz, 4H), 2.71 (s, 12H), 2.08 (t, J = 7.2 Hz, 4H), 2.67 (t, J = 6.4 Hz, 4H), 2.72 (s, 12H), 7.59 (m, 8H), 8.03 (dd, J = 7.2 Hz, 4H), 8.13 (dd, J = 7.2 Hz, 4H), 9.08 (s, 8H); HR FAB MS Calcd for C₉₀H₅₀N₆S₄Ti: 1083.2858. Found (m/z) 1083.2815 (M+).

Generation of dithiolate anion of tetra-(p-tolyl) porphyrinato titanium (IV) benzenedithiolate (4c2S⁻).

**Computational methods:** All calculations were performed using the Gaussian 09 program package.¹⁰ The structure was optimized by the DFT method at the B3LYP/LANL2DZ level for Ti and B3LYP/6-31G (d, p) level for C, H, N, and S atoms. The calculation was performed by the polarizable continuum model with the integral equation formalism variant (IEFPCM) using chloroform as a solvent. The ¹H NMR chemical shifts of 4b’ were calculated by the same basis set. The HOMO and LUMO energy levels and the electronic transition of the absorption spectrum were determined by the time-dependent density functional theory (TD-DFT) calculations at the same level.

**CONCLUSION**

The reaction of compound 2 with diethyldimercapto-benzene derivatives 3a, 3b, and 3c produced the corresponding titanium (IV) complexes (4a–4c). The structure of 4b was determined by X-ray crystallography. The structure of simplified model compound 4b’ optimized with the Gaussian 09 program was utilized to calculate the NMR chemical shifts, the HOMO and LUMO orbital energy levels, and the electronic transitions in the absorption spectra by the TD-DFT method. The optimized structure and the calculated NMR chemical shifts are well correlated to the experimental results. Compound 4c was further treated with cesium hydroxide to produce the corresponding dithiolate anion 4c2S⁻ which can modify the gold electrode. The electrochemical property of the gold electrode was determined by cyclic voltammetry.

**Supporting information**

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-1813481. Copies can be obtained on request, free of charge, via http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

**REFERENCES**


Distribution of the unpaired electron in neutral bis(phthalocyaninato) yttrium double-deckers: An experimental and theoretical combinative investigation

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ABSTRACT: The location of the unpaired electron in neutral bis(phthalocyaninato) yttrium double-decker complexes, with different substituents, has been studied on the basis of both experimental methods and density functional theory (DFT) calculations over the molecular structures, atomic charges, electronic absorption, infrared spectra, and electron paramagnetic resonance. The results reveal the location of the unpaired electron mainly on the carbon atoms of both tetrapyrrole chromophores with the population distribution obviously affected by the peripheral substituents.

KEYWORDS: phthalocyanine, yttrium, double-decker, unpaired electron, density functional calculations.

INTRODUCTION

Phthalocyanines have been the most common and important tetrapyrrole derivatives in dyes and pigments since their first discovery around the beginning of last century [1–3]. Coordination of this tetrapyrrole chromophore with some early transition metals, main-group metals, and rare earth metals leads to the formation of sandwich-type phthalocyaninato metal complexes with multiple-decker molecular structures [4]. These sandwich-type complexes, in particular phthalocyaninato rare earth multiple-decker compounds, have emerged as an important category of functional materials in the fields of molecular electronics, molecular information storage, nonlinear optics, and organic field-effect transistors, due to their unique electronic and optical properties [1, 2, 5, 6]. Among the sandwich family, neutral bis(phthalocyaninato) rare earth double-decker counterparts formulated as \([\text{M}^{III}\text{(Pc}^{2-})\text{(Pc}^{-})]\), composed by a trivalent metal center, a dianionic macrocycle, and a monoanionic radical ligand, represent an important species with a wide range of application potentials. As could be expected, the location of the unpaired electron in the bis(tetrapyrole) rare earth(III) double-decker complexes has attracted a great deal of research interest due to the important role of the unpaired electron in materials science [4, 5]. Unfortunately, single crystal
X-ray diffraction analysis seems to be unable to provide any effective information in this regard despite the unambiguous determination of the presence of an unpaired electron in the neutral double-decker compounds by ESR technique [7]. Fortunately, on the other hand, vibrational spectroscopy confirms the delocalization of the unpaired electron over both the two tetrapyrrole chromophores on the vibrational timescale [2, 3]. However, the distribution of the single electron in the double-deckers, in particular in heteroleptic compounds, still remains unexplored.

In this paper, heteroleptic bis(phthalocyaninato) yttrium double-decker complexes (Pc)Y[Pc(N(C₄H₉)₂)₈] (2) and (Pc)Y[Pc(OC₄H₉)₈] (4) were prepared. For the purpose of comparative study, the homoleptic analogs Y(Pc)₂ (1), Y[Pc(N(C₄H₉)₂)₈] (3), and Y[Pc(OC₄H₉)₈] (5), Scheme 1, have also been synthesized. Various spectroscopic techniques including electron paramagnetic resonance (EPR), electronic absorption spectroscopy, and IR spectroscopy reveal the presence of the unpaired electron in all these double-decker molecules. This, in combination with the theoretical calculations on the basis of density functional theory (DFT), clearly discloses the location of the unpaired electron mainly on the carbon atoms of both tetrapyrrole chromophores with the population distribution obviously affected by the peripheral substituents.

SYNTHESIS AND COMPUTATION

All the bis(phthalocyaninato) yttrium complexes Y(Pc)₂ (1), (Pc)Y[Pc(N(C₄H₉)₂)₈] (2), Y[Pc(N(C₄H₉)₂)₈] (3), (Pc)Y[Pc(OC₄H₉)₈] (4) and Y[Pc(OC₄H₉)₈] (5) were prepared and isolated following the published procedures, which have been characterized by a series of spectroscopic methods in addition to elemental analysis [8–11].

All structures were optimized at the DFT method B3LYP [12] with a hybrid basis set of SDDALL [13] for yttrium and 6-311G(d) [14, 15] for the other elements. This method was proven effective for theoretical investigation over the bis(tetrapyrrole) yttrium compounds in a previous study [16]. The optimized structures of compounds 1–5 were detected for the C₂ᵥ, C₄, C₄ᵥ, and C₄ point groups, respectively. Harmonic frequency analysis, spin density and electron absorption calculations were carried out at the same level subsequently. Charge distribution analysis (CDA) [17] was carried out using a full natural bond orbital (NBO) analysis population method based on the optimized structures. To determine the electron structures of the fragments in CDA calculations, single-point calculations were carried out in the level consistent with optimization. All these calculations above were carried out in Gaussian 09, Revision D.01 [18]. CDA and orbital interaction
DISTRIBUTION OF THE UNPAIRED ELECTRON IN NEUTRAL BIS(PHTHALOCYANINATO) YTTRIUM DOUBLE-DECKERS

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Fig. 1. Optimized molecular structures of Y(Pc)₂ (1), (Pc)Y[PC[N(C₄H₉)₂]₈] (2), Y[PC[N(C₄H₉)₂]₈] (3), (Pc)Y[PC(OC₄H₉)₈] (4) and Y[PC(OC₄H₉)₈] (5)

Table 1. Experimental electronic absorption spectroscopic data

<table>
<thead>
<tr>
<th>No.</th>
<th>λ/nm [log(ε)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>279 (4.73) 319 (4.76) 457 (4.15) 600 (4.12) 666 (4.93) 916 (3.36) 1410 (3.80) 1546 (3.71)</td>
</tr>
<tr>
<td>2</td>
<td>331 (5.06) — 657 (4.86) 694 (5.00) 933 (4.00) 1259 (3.86) 1428 (4.12) 1543 (3.93)</td>
</tr>
<tr>
<td>3</td>
<td>332 (5.14) 390 (5.03) — 631 (4.85) 715 (5.20) 950 (3.82) 1772 (4.29) —</td>
</tr>
<tr>
<td>4</td>
<td>289 (4.91) 331 (4.98) 487 (4.50) 602 (4.43) 667 (5.21) 914 (3.74) 1415 (4.10) 1541 (3.97)</td>
</tr>
<tr>
<td>5</td>
<td>292 (5.07) 369 (5.15) 484 (4.64) 609 (4.54) 673 (5.23) 914 (3.72) 4127 (4.09) 1576 (4.16)</td>
</tr>
</tbody>
</table>

As shown in Fig. 1, the optimized structures of the five double-decker compounds take $C_{2v}$, $C_4$, $C_{4v}$, $C_4$, and $C_4$ molecular symmetry, respectively. The yttrium atom is surrounded by the eight isoindole nitrogen atoms in the two Pc cycles, which are tilted 45° with each other. Due to the lack of single crystal molecular structure for compounds 2–5, their optimized structures are employed for further theoretical investigations. In addition, the simulated structures of compounds 1 and 3 correspond well with their single crystal molecular structures [9], which validates this treatment.

RESULTS AND DISCUSSION

Electronic absorption spectroscopy

The electronic absorption spectra of 1–5 were recorded in CHCl₃ and the data are summarized in Table 1. As shown in Fig. 2, compound 1 shows split Soret bands at 278 and 319 nm and Q bands at 600 and 666 nm. Observation of the π-radical-associated band at 916 nm, together with the characteristic intramolecular ring-to-ring charge transfer band peaking at 1410–1546 nm in the near-IR range, confirms the presence of an unpaired electron in this neutral double-decker compound. This is also true for compounds 2–5. It is worth noting that the Q bands of compounds 2–5 redshift by 28, 49, 1 and 7 nm, respectively, in comparison with the unsubstituted complex 1, indicating the electron-donating nature of –N(C₄H₉)₂ and OC₄H₉ groups [22].

Infrared spectroscopy

Figure 3 displays the IR spectra of 1–5. As can be found, in addition to the absorption bands contributed from the Pc macrocycle including the wagging and torsion vibrations of the C–H groups, isoindole ring stretching vibrations, and the C=N aza group stretching vibrations [23], intense absorption bands due to the C–H stretching vibrations of the –CH₃ and –CH₂ groups of...
the side chains are observed at ca. 2750–3000 cm\(^{-1}\) in the IR spectra of 2–5, which disappear in the unsubstituted double-decker complex 1. It is worth noting that in the IR spectra of all the double-deckers 1–5, a medium-to-strong band is observed in the range of 1319–1322 cm\(^{-1}\), which is a diagnostic marker band for the phthalocyanine \(\pi\)-radical anion [24], adding more evidence for the unpaired electron nature of these double-decker complexes.

**Electron paramagnetic resonance spectroscopy**

It is well known that electron paramagnetic resonance (EPR) [7] is a prevalent method for detecting and studying the radical nature of organic or metal materials with unpaired electrons. For this purpose, continuous wave EPR (cwEPR) spectra were recorded at X-band (8–10 GHz) in solid phase at the temperature of 5 K for
1–5. As can be seen in Fig. 4, all five of these double-decker compounds show a characteristic signal for an organic radical at $g = 2.0402, 2.0200, 2.1120, 2.0023$ and $2.0189$, respectively. However, at this temperature, both the heteroleptic double-deckers 2 and 4 show quite different spectra from their homoleptic analogs 1, 3 and 5, due to the observation of an asymmetrical rather than a symmetrical impulse signal in the range of 1000–2000 G, suggesting the unsymmetrical distribution of the radical over the two phthalocyanine rings in the heteroleptic double-decker molecules at low temperature. This, however, is not the case for the same compounds at room temperature [11]. Density functional theory (DFT) calculation results rationalize this conclusion.

**Theoretical investigation**

To further clarify the electronic distribution nature of the given skeleton together with the effects of peripheral electron-withdrawing/donating substituents, DFT calculations were carried out at the level of UB3LYP/SDDALL/6-311G(d). As can be found in Fig. 5, the spin electron cloud is mainly covering the inner N/C atoms of phthalocyanine rings, especially the N atoms directly linking the central Y atom. However, when the electron-withdrawing/donating substituents are unsymmetrically introduced onto the periphery of the skeleton, the spin electron cloud will be attracted/repulsed by them, leading to an unsymmetrical electronic spin distribution.

In order to quantitatively describe the unsymmetrical electron cloud in this skeleton, natural population analysis (NPA) [25] was also carried out at the same level. As can be found in Table 2, in comparison with the -0.750 e charge of each phthalocyanine macrocycle in the symmetrical 1, the unsymmetrical 2 has two different phthalocyanine macrocycles with the charge of -0.616 e for Pc[N(C₄H₉)₂]₈ and -0.874 e for the naked Pc ring, indicating the electron transfer from the electron-donating
substituent –N(C₄H₉)₂ to the inner N atoms. For compound 4, when electron-donating substituents –OC₅H₁₁ are introduced onto the periphery of this skeleton, the electron charge of the substituted Pc ring decreases to -0.589 e while the naked Pc ring increases to -0.898 e.

In addition, to achieve in-depth understanding of the distribution of spin electron distribution in this skeleton, charge decomposition analysis (CDA) was also carried out and the orbital interaction diagrams were plotted. As can be found in Figs 6 and 7, the HOMO involving the spin electron of the complex is constructed from the two HOMOs of the naked Pc ring and the substituent Pc ring. The ratio of (HOMO of naked Pc):(HOMO of substituent Pc) in the HOMO of heteroleptic double-decker with the electron-donating substituent –N(C₄H₉)₂ group is 55%: 45%. This gets increased to 60%: 40% in the heteroleptic double-decker involving the electron-donating substituent –OC₄H₉ group. In summary, the unsymmetrical introduction of peripheral electron-donating/withdrawing substituents breaks the degeneration of the HOMO energies in the two Pc rings, leading to the unsymmetrical HOMO coupling mechanism when they are composed into the HOMO orbital of the double-decker, and further inducing the unsymmetrical spin-density distribution. This in turn becomes responsible for the observation of the asymmetrical rather than symmetrical impulse signal of the two heteroleptic double-decker 2 and 4 in their EPR spectra as detailed above.

As mentioned above, Fig. 2 also gives the simulated UV-vis spectra of the five compounds. The calculated band at 932 nm for 1 is mainly due to the electron transition from 270α (alpha LUMO) to 273α (about 43.1% contribution) and 269β (beta LUMO) to 272β.

### Table 2. NPA analysis of the atoms in the tetrapyrrole of the five ligands

<table>
<thead>
<tr>
<th>No.</th>
<th>Y</th>
<th>N (upper inner ring)</th>
<th>N (upper outer ring)</th>
<th>N (under inner ring)</th>
<th>N (under outer ring)</th>
<th>C (upper inner ring)</th>
<th>C (upper outer ring)</th>
<th>C (under inner ring)</th>
<th>C (under outer ring)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.493</td>
<td>-0.665</td>
<td>-0.543</td>
<td>-0.665</td>
<td>-0.543</td>
<td>0.510</td>
<td>-0.073</td>
<td>0.510</td>
<td>-0.073</td>
</tr>
<tr>
<td>2</td>
<td>1.492</td>
<td>-0.667</td>
<td>0.549</td>
<td>-0.664</td>
<td>-0.542</td>
<td>0.518</td>
<td>-0.069</td>
<td>0.502</td>
<td>-0.072</td>
</tr>
<tr>
<td>3</td>
<td>1.496</td>
<td>-0.666</td>
<td>-0.549</td>
<td>-0.666</td>
<td>-0.549</td>
<td>0.510</td>
<td>-0.068</td>
<td>0.510</td>
<td>-0.068</td>
</tr>
<tr>
<td>4</td>
<td>1.489</td>
<td>-0.676</td>
<td>-0.552</td>
<td>-0.661</td>
<td>-0.542</td>
<td>0.519</td>
<td>-0.070</td>
<td>0.501</td>
<td>-0.072</td>
</tr>
<tr>
<td>5</td>
<td>1.487</td>
<td>-0.671</td>
<td>-0.552</td>
<td>-0.671</td>
<td>-0.552</td>
<td>0.510</td>
<td>-0.069</td>
<td>0.510</td>
<td>-0.069</td>
</tr>
</tbody>
</table>

Fig. 5. Spin density of the five compounds Y(Pc)₂ (1), Y[Pc{N(C₄H₉)₂}₈] (2), Y{Pc{N(C₄H₉)₂}₈} (3), Y[Y{Pc(OC₄H₉)₈}] (4) and Y[Y{Pc(OC₄H₉)₈}] (5). The blue shaded spheres are the positive spin density region and the green ones are negative, respectively.
The unpaired electron is localized in the upper and under tetrapyrrole rings of these complexes.

Figure 3 also shows the simulated infrared spectra of the five compounds. The simulation was carried out at the same level with optimization. As can be found, the simulated spectra are in good agreement with the experimental ones. The peaks between 1200–1300 cm$^{-1}$ for the five compounds are mainly attributed to the isoindole breathing coupled with C–H bending [19]. The IR spectra in the region of 600–1500 cm$^{-1}$ reveal the vibrations in the main Pc cycles [19]. In this band region, the difference between these compounds is caused by the different substitutions. The vibrations around 3000 cm$^{-1}$ are attributed to the stretching of C–H bending in the substituted groups since compound 1 shows no signal in this range. Moreover, compounds 2 and 3 share similar IR spectra patterns due to the same substituent being involved in these two complexes. This is also true for compound 4 and 5.

**CONCLUSION**

Based on comparative studies of both experimental and theoretical investigations, the unpaired electron in yttrium bis(phthalocyaninato) yttrium compounds is shown to delocalize in the carbon atoms in Pc cycles. Meanwhile, the substituents do significantly affect the population distribution of the unpaired electron. This effect varies with the electron-donating/withdrawing abilities of the substituents.
Acknowledgments

Financial support from the Natural Science Foundation of China (Nos. 21631003 and 21671017), Shandong Province Natural Science Foundation (No. ZR2014BM016), and University of Science and Technology Beijing is gratefully acknowledged.

REFERENCES

Synthesis and characterization of a new meso-tetra-dihydro benzocyclobutacenaphthylene free-base porphyrin

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A meso-tetra-6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene free-base porphyrin was synthesised and its photophysical, photochemical and electrochemical properties were compared with those of free-base meso-tetraphenylporphyrin. The frontier orbitals and the HOMO–LUMO energy gaps of both compounds were also determined. It was demonstrated that the meso-6b,10b-Dihydrobenzo[j]cyclobut[a]acenaphthylene porphyrin retained the same properties as the tetraphenylporphyrin.

KEYWORDS: porphyrin, 6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene, tetraphenylporphyrin.

INTRODUCTION

Free-base porphyrins are very efficient photosensitizers, and tetraphenylporphyrin (H2TPP) is known to generate singlet oxygen in extremely high quantum yields [1], which can be further increased by an appropriate substitution pattern, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. 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The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. 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The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]. The properties of the porphyrin core can then be modified depending on targeted applications, such as the presence of heavy atoms [2]
RESULTS AND DISCUSSION

Synthesis and characterisation

8(9)-Carboxaldehyde-DBCA 1 [13] presents the aldehyde function directly bound to the DCBA skeleton, leading to porphyrin (DBCA)4H2P which has the DCBA units directly on the meso positions. The synthesis of porphyrin (DBCA)4H2P was performed in classical Adler conditions [14] in 23% yield, showing that the reactivity of aldehyde 1 is similar to benzaldehyde.

Photophysics and photochemistry

The photophysical and photochemical properties of (DBCA)4H2P were determined and compared to those of H2TPP. All data are summarized in Tables 1 and 2 and discussed in the different sub-sections below. Toluene was selected as the solvent for all these measurements.

UV-vis spectroscopy. The maximum of the B band absorption for both compounds is very similar, with a small red-shift of 4 nm for porphyrin (DBCA)4H2P compared to H2TPP (Fig. 1). More noteworthy is the more intense absorption of H2TPP than (DBCA)4H2P. The maxima of each of the B bands are also overlapping, these latter being more intense for (DBCA)4H2P than for H2TPP. Porphyrin (DBCA)4H2P seems to be more prompted to promote n→π* transitions than π→π* transitions.

Steady-state fluorescence. Emission wavelengths are even more similar than UV-vis maximum absorption wavelengths (Fig. 2). In line with UV-vis observations, the first emission peak at 654 nm is more intense for H2TPP than (DBCA)4H2P, whereas the second band is higher for (DBCA)4H2P than for H2TPP. Porphyrin (DBCA)4H2P seems to be more prompted to promote n→π* transitions than π→π* transitions.

Singlet oxygen generation. The formation of singlet oxygen upon irradiation of (DBCA)4H2P and H2TPP was followed by observing its luminescence emission at 1270 nm (Fig. 3 and Table 2). The photo-induced singlet oxygen generation of porphyrin (DBCA)4H2P proved to be very similar to that of H2TPP.

Electrochemistry

Electrochemical characteristics of porphyrin (DBCA)4H2P were investigated by cyclic voltammetry (CV) and compared with those of H2TPP (Fig. 4 and Table 3). Both compounds have two oxidations and two reductions in the range of circa -2.1 V to +0.9 V. First oxidation at 0.534 V vs. Fc/Fc’ and second oxidation at 0.828 V were observed for H2TPP. Similarly, porphyrin (DBCA)4H2P showed a first oxidation peak at 0.494 V and a second one at 0.887 V. Compound (DBCA)4H2P had lower first oxidation potential (0.494 V) than H2TPP had (0.534 V), as expected. The 0.040 V potential difference was possibly due to the electron rich nature of aromatic fragments on meso-phenyls of porphyrin core. In terms of reductions, redox patterns and potentials were almost overlapped to each other with very small potential shifts. It could be concluded that electron rich aromatic fragments on porphyrin (DBCA)4H2P diminish first oxidation potential (0.040 V difference) of porphyrin macrocycle, however exhibit no significant changes on the potentials of other redox processes.

Frontier orbitals and energy gaps

The frontier HOMO–LUMO orbitals and energy gaps of H2TPP and of (DBCA)4H2P have been determined from the electrochemistry data and by calculations after optimization of their geometry. Data are summarized in Table 4.

Determination from electrochemistry data

The band gap energy values define the energy necessary for the transition of an electron from the
SYNTHESIS AND CHARACTERIZATION OF A NEW meso-TETRA-DIHYDROBENZOCYCLOBUTACENAPHTYLENE

Table 1. UV-vis data for (DBCA)₄H₂P and H₂TPP

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>B band</th>
<th>Q1 band</th>
<th>Q2 band</th>
<th>Q3 band</th>
<th>Q4 band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λmax (nm)</td>
<td>Log ε</td>
<td>λmax (nm)</td>
<td>Log ε</td>
<td>λmax (nm)</td>
</tr>
<tr>
<td>(DBCA)₄H₂P</td>
<td>424</td>
<td>5.69</td>
<td>518</td>
<td>4.70</td>
<td>552</td>
</tr>
<tr>
<td>H₂TPP</td>
<td>420</td>
<td>5.87</td>
<td>515</td>
<td>4.68</td>
<td>549</td>
</tr>
</tbody>
</table>

Table 2. Fluorescence parameters and singlet oxygen generation quantum yield

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>λex (nm)</th>
<th>λem₁ (nm)</th>
<th>λem₂ (nm)</th>
<th>Δλem (nm)</th>
<th>ΦF</th>
<th>τF (ns)</th>
<th>kF = ΦF/τF (s⁻¹)</th>
<th>ΦΔ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DBCA)₄H₂P</td>
<td>410</td>
<td>654</td>
<td>721</td>
<td>652</td>
<td>2</td>
<td>0.11</td>
<td>9.97</td>
<td>1.10 × 10⁷</td>
</tr>
<tr>
<td>H₂TPP</td>
<td>410</td>
<td>653</td>
<td>720</td>
<td>651</td>
<td>2</td>
<td>0.12¹[15]</td>
<td>11.02</td>
<td>1.08 × 10⁷</td>
</tr>
</tbody>
</table>

Fig. 1. Absorption spectra of (DBCA)₄H₂P (blue) and H₂TPP (red) in toluene in the 0.6–5.0 μM concentration range (5.00, 2.50, 1.25, 0.63 μM). Inset: Absorbance vs. concentration

HOMO to the LUMO, and band gap energy was calculated from the LUMO and the HOMO values which were obtained from electrochemical data. The HOMO and LUMO energy levels of (DBCA)₄H₂P and H₂TPP were calculated using the HOMO level of ferrocene at -4.8 eV [17], and the first oxidation and first reduction values of the dyads in o-dichlorobenzene/acetonitrile (4:1). Equations 1 and 2 were used for the calculation of the HOMO and LUMO energy levels, respectively. As can be seen from Table 4, a slightly lower band gap of (DBCA)₄H₂P was observed compared to H₂TPP, and this information is matching with the ~4 nm red shift of the absorption wavelength maxima of (DBCA)₄H₂P compared to H₂TPP.

\[ E_{\text{HOMO}} = -(E_{\text{ox}} - E_{1/2(\text{ferrocene})}) + 4.8 \]  

\[ E_{\text{LUMO}} = -(E_{\text{red}} - E_{1/2(\text{ferrocene})}) + 4.8 \]

Determination from calculations

The molecular structures were optimized before the electronic structure determination. We used PBE and HSE exchange correlation functionals, and compared our results in Table 4. As expected, the energy gaps are underestimated in PBE, and this shortcoming is corrected in the HSE exchange correlation functional. The trends are the same for both exchange correlation functionals. The calculated HOMO–LUMO gaps of 2.204 and 2.188 eV for H₂TPP and porphyrin (DBCA)₄H₂P respectively are in good agreement with our electrochemistry data. The gap of porphyrin (DBCA)₄H₂P is only slightly smaller than that of H₂TPP. The similarities between the electronic structures of H₂TPP and porphyrin (DBCA)₄H₂P may be understood through the shape and localization of their frontier orbitals.

The calculated wavefunctions for the HOMO and LUMO levels are shown as 3D contour plots in Fig. 5,
where the different colors on isosurfaces distinguish opposite phases of the wavefunctions. Although no symmetry constraints were imposed during the structure optimizations, the relaxed molecular structures, depicted in Fig. 5, have inherited certain symmetry. The HOMO and LUMO orbitals occupy the same region and have similar character. Both HOMO and LUMO levels are twofold degenerate for both $H_2TPP$ and porphyrin (DBCA)$_4H_2P$. Therefore, the HOMO-1 and LUMO+1 as well as the HOMO and LUMO are shown. The degenerate molecular orbitals in Fig. 5 are closely related and orthogonal to each other. The frontier orbitals of $H_2TPP$ and porphyrin (DBCA)$_4H_2P$ are localized on the central ring. The involvement of side groups in frontier orbitals is prevented by the rotation of these groups with respect to the plane of the central ring. The central ring dominates the highest occupied and lowest unoccupied levels for both $H_2TPP$ and porphyrin (DBCA)$_4H_2P$. As a result, similarities between the frontier orbitals of $H_2TPP$ and porphyrin (DBCA)$_4H_2P$, shown in Fig. 5, are striking. Since the main structural properties of $H_2TPP$ also exist in porphyrin (DBCA)$_4H_2P$, the energy levels are similar.

During our structure optimization attempts, we sometimes obtained configurations that had reduced...
SYNTHESIS AND CHARACTERIZATION OF A NEW \textit{meso}-TETRA-DIHYDROBENZOCYCLOBUTACENAPHTYLENE

SYNTHESIS AND CHARACTERIZATION OF A NEW \textit{meso}-TETRA-DIHYDROBENZOCYCLOBUTACENAPHTYLENE

We find this lifts the symmetry results in small splitting of the degenerate levels, but does not induce significant changes in the energy gaps.

EXPERIMENTAL

Synthesis

Materials and methods. Aldehyde 1 was prepared as previously reported [13]. All reagents and solvents were of synthetic grade and used as received. FT-IR spectra were recorded between 4000 and 650 cm\(^{-1}\) using a PerkinElmer Spectrum 100 FT-IR spectrometer. NMR spectra were recorded in deuterated solvents on a Varian 500 MHz spectrometer at 298 K. Mass spectra were recorded on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT.

Synthesis of porphyrin (DBCA)\(_4\)H\(_2\)P. A mixture of 10\(\text{mg}\) of 8(9)-(6b,10b-dihydrobenzo[j]cyclobuta[a]cenaphthylene)carbaldehyde 1 (128 mg, 0.5 mmol) and propionic acid (5 mL) were heated to reflux for 5 min and then pyrrole (0.04 mL, 0.55 mmol) was added and refluxed during 45 min. Water was added to the cooled reaction mixture and the resulting precipitate was filtered. Finally, (DBCA)\(_4\)H\(_2\)P was purified by silicagel column chromatography eluted by CH\(_2\)Cl\(_2\)-EtOH (100:1). Yield 23\% (35 mg). Purple powder. C\(_{92}\)H\(_{54}\)N\(_4\), MW: 1215.472. m.p. > 250\(^\circ\)C. 1H NMR (500 MHz, CDCl\(_3\)): \(\delta\), ppm 8.8–8.4 (m, 8 H), 7.9–7.2 (m, 24 H), 7.1–7.0 (m, 12 H), 5.67 (m, 8 H). FT-IR (\(\nu\), cm\(^{-1}\)): 3311, 2922, 2855, 1602, 1492, 1458, 1403, 1362, 1348, 1240, 1156, 1100, 1067, 1010, 973, 925, 899, 843, 786, 773, 729, 672. MALDI-TOF-MS (DHB) \(m/z\): Calcd for C\(_{92}\)H\(_{55}\)N\(_4\) 1216.480; found 1216.934 [MH\(^+\)].

Photophysics and photochemistry

Absorption and fluorescence emission measurements. Absorption spectra were recorded using a

<table>
<thead>
<tr>
<th>Method</th>
<th>Molecule</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>HOMO–LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclic voltammetry</td>
<td>H(_2)TPP</td>
<td>-5.334</td>
<td>-3.107</td>
<td>2.227</td>
</tr>
<tr>
<td></td>
<td>(DBCA)(_4)H(_2)P</td>
<td>-5.294</td>
<td>-3.102</td>
<td>2.192</td>
</tr>
<tr>
<td>Calculated with HSE</td>
<td>H(_2)TPP</td>
<td>-5.002</td>
<td>-2.798</td>
<td>2.204</td>
</tr>
<tr>
<td></td>
<td>(DBCA)(_4)H(_2)P</td>
<td>-4.931</td>
<td>-2.743</td>
<td>2.188</td>
</tr>
<tr>
<td>Calculated with PBE</td>
<td>H(_2)TPP</td>
<td>-5.004</td>
<td>-3.307</td>
<td>1.697</td>
</tr>
<tr>
<td></td>
<td>(DBCA)(_4)H(_2)P</td>
<td>-4.846</td>
<td>-3.163</td>
<td>1.683</td>
</tr>
</tbody>
</table>
Shimadzu 2101 UV-visible spectrophotometer, and fluorescence emission spectra were recorded using a Horiba FL3-21HR with a 10 mm path length quartz cell at room temperature.

**Fluorescence lifetime measurements.** Fluorescence lifetimes were recorded using a Horiba FL3-21HR with a Time Correlated Single Photon Counting (TCSPC) system. The instrument was equipped with a nanoLED 390 nm as the excitation source. During measurements, the Instrument Response Function (IRF) was obtained from a non-fluorescence suspension of a colloidal silica (LUDOX 30%, Sigma Aldrich) in water, held in 10 mm path length quartz cell.

**Fluorescence quantum yield determination.** Fluorescence quantum yield values (Φ) were calculated employing the comparative Williams’ method. For this purpose, the absorbance and fluorescence spectra of a reference standard (H$_2$TPP) and (DBCA)$_4$H$_2$P were measured at three different concentrations under identical conditions. The integrated fluorescence intensities were plotted vs. absorbance for H$_2$TPP (Φ = 0.12 in toluene [15] and (DBCA)$_4$H$_2$P. The ratio of the gradients of the plots is proportional to the quantum yield. Quantum yield (Φ) values were calculated according to Equation 3. Grad is the gradient of the plot.

\[
\Phi_f = \Phi_{f_{ST}} \left( \frac{\text{Grad}}{\text{Grad}_{ST}} \right)
\]  

**Singlet oxygen quantum yield determination.** Singlet oxygen productions were measured in toluene by optical methods which are based on comparison between singlet molecular oxygen phosphorescence in the near infrared region at ~1270 nm produced by (DBCA)$_4$H$_2$P and the reference photosensitizer H$_2$TPP (Φ = 0.63 in toluene [16]. Phosphorescence signals of O$_2^+$ were recorded by a Horiba–Jobin Yvon Fluorolog-3R spectrophotometer using a 450 W Xe arc lamp as a light source equipped with high sensitive Hamamatsu PMT cooled housing detector (300–1700 nm). In this system, a high cut filter (1250 nm) was used in order to prevent the interference light below 1250 nm. For this purpose, the absorbance and phosphorescence measurements of (DBCA)$_4$H$_2$P and H$_2$TPP were carried out at two different concentrations. The phosphorescence intensities were plotted vs. absorbance for (DBCA)$_4$H$_2$P and H$_2$TPP. Singlet oxygen quantum yields (Φ) were calculated according to the following Equation 4 using the ratio of the gradients.

\[
(\Phi_{O_2^+})_x = (\Phi_{O_2^+})_{ST} \left( \frac{\text{Grad}}{\text{Grad}_{ST}} \right)
\]  

**Electrochemistry**

Electrochemical measurements were carried out on a CH Instruments 842B model work station. The setup was a conventional three-electrode cell equipped with glassy carbon working electrode, platinum wire counter electrode, and Ag/AgNO$_3$ reference electrode. The glassy carbon electrode was polished routinely with 0.05 micron alumina powder/water slurry on pads before running experiments. All measurements of samples were recorded as reported analyte concentration in 0.1 M n-Bu$_4$NClO$_4$ electrolyte solutions of o-dichlorobenzene/acetonitrile (4:1) mixture. Analyte solutions were degassed with an Argon purge for 5 min and kept under a blanket of
Argon during the experiments. All electrochemical measurements were performed at ambient temperature. Ferrocene was used as an internal reference and all potentials were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Potentials were reported vs. ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Scan rate was 100 mV/s for all CV experiments.

3 mm-diameter glassy carbon working electrode (CHI104), non-aqueous Ag/Ag⁺ reference electrode with porous teflon tip (CHI112), platinum wire counter electrode (CHI115) and electrode polishing kit (CHI120) were purchased from CH Instruments. Supporting electrolyte, n-Bu₄NClO₄, was purchased from Aldrich and dried overnight at 50°C under vacuum. Ferrocene was supplied by Fluka, anhydrous acetonitrile by VWR and 1,2-dichlorobenzene by Merck.

Calculations

The structure optimizations and electronic structure calculations were performed in density functional theory (DFT) as implemented in NWChem [18] and SIESTA [19] computer codes. The structure optimizations were started from the initial atomic positions of a flat molecule, and no symmetry constraints were used. Conjugate gradient total energy minimization steps were continued in SIESTA code until all force components were less than 0.01 eV/Å on each atom. The only constraint was to bind H atoms to the same side of the pentagon edge so that the extremities are curled in the same direction. In SIESTA calculations, Generalized Gradient Approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) parameterization [20] was used for exchange-correlation functional, and the interactions between the core and valence electrons were handled by norm-conserving pseudopotentials. The molecular structure was further optimized in NWChem code within hybrid Heyd–Scuseria–Ernzerhof (HSE) [21] exchange correlation functional to get a better description of excited states and energy gaps. In HSE calculations, 6-311G** Gaussian basis set was employed. The calculated values in HSE exchange correlation functional were in good agreement with our measurements, while GGA underestimated the HOMO–LUMO gaps.

CONCLUSIONS

A novel porphyrin, (DBCA)₄H₂P which has 8(9)-6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene units directly on the meso positions of the porphin core, has been synthesized. Its photophysical, photochemical and electrochemical properties, as well as its frontier orbitals and the HOMO–LUMO gaps, have been determined and compared to those of tetraphenylporphyrin. (DBCA)₄H₂P is therefore an alternative to H₂TPP with the additional advantage to offer further functionalization and also polymerization opportunities.

Acknowledgments

Support from the Ministerio de Economía Industria y Competitividad of Spain (CTQ2014-55798-R) is gratefully acknowledged. The calculations were performed at TRUBA resources.

REFERENCES

INTRODUCTION

Phthalocyanine (Pc) complexes are being extensively researched owing to their diverse applications in various scientific and technological areas [1]. This family of aromatic macrocycles is important due to their delocalized 18π electron system and high thermal, chemical and photochemical stabilities. Their uses as nonlinear optical (NLO) devices [2] chemical sensors [3] liquid crystals [4], in optical data storage [5], dye-sensitized solar cell [6] have been reported. There has also been growing interest in the use of phthalocyanines as photosensitizers in photodynamic therapy of cancer (PDT) because of their stronger absorption in the red visible light region and their higher efficiency at generating singlet oxygen [7, 8].

The choice of central metal and type of the substituent strongly influences the physical, chemical and electronic properties of these macrocycles. MPC complexes containing diamagnetic and non-transitional central metals are photoactive and are often employed in photosensitization [9]. Among the metal phthalocyanines studied, zinc (II) Pc complexes have attracted much interest for PDT application because of their appreciably high triplet yields and long lifetimes [10, 11].

2,2’:6’,2’’-Terpyridine compounds are important chelating ligands in a great number of applications in the fields of supramolecular and macromolecular chemistry [12]. The terpyridine ligands act as a tridentate N3 donor with very high binding affinity towards transition metal ions [13]. Thus, they have been extensively studied as complexing agents due to their rich coordination chemistry [14–16]. Their interesting photophysical, electrochemical and magnetic properties led them to...
be used in several applications such as catalysis, nonlinear optics, solar cell devices, electrochemistry, DNA metallointercalators and anti-tumor active agents [17]. More recently, these compounds have also attracted particular interest as photosensitizers [18].

Even though a large field of applications of phthalocyanines and terpyridine complexes exists, only a few studies involve the combination of these functional groups [19], except for the studies performed by our group [20].

Electronic interaction studies in systems containing multiple redox-active centers are of fundamental importance in development of molecular-based electronic and optoelectronic devices or multielectron redox catalysts [21]. In addition, such systems can be beneficial as models for the photoinduced intramolecular electron or energy transfer studies to improve the understanding of complex but practically useful processes such as solar energy conversion and artificial photosynthesis [22]. Photoinduced electron transfer or energy transfer processes in supramolecular species (molecular dyads, triads, and tetrads) consisting of ruthenium polypyridine and metalloporphinin complexes are currently the objective of immense investigations [23, 24].

This paper describes the terpyridine-Zn(II) complexes directly linked through oxygen bridges to a zinc-Pc core as new functionalized materials. We report the synthesis and characterization of a terpyridine substituted phthalonitrile complex and its Pc derivative. The spectroscopic, photophysical and photochemical properties of these two new functional compounds were also investigated to give an indication of the potential of the complexes as photosensitizers for PDT applications.

**EXPERIMENTAL**

**Chemicals and instruments**

Deuterated dimethylsulfoxide (DMSO-d₆) for NMR spectroscopy and the following chemicals were obtained from Sigma–Aldrich: Ethanol (EtOH), diethyl ether, tetrahydrofuran (THF), n-hexane, n-pentanol, dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1,3-diphenylisobenzofuran (DPBF), NH₃ solution, P₂O₅, ZnCl₂. All solvents were stored over molecular sieves (4 Å) after they were dried and purified as described by Perrin and Armarego [25]. Oxygen-free inert atmosphere was supplied by argon through a dual-bank vacuum-gas manifold system. Thin-layer chromatography (TLC) was performed using silica gel 60-HF₂₅₄₄ as an adsorbent. Melting points (m.p.) were determined by using a Barnstead-Electrotermel 9200 apparatus and are uncorrected. Electronic spectra were recorded on a Shimadzu UV-2600 Pc-spectrophotometer with a quartz cell of 1 cm. Infrared spectra were recorded on a Perkin Elmer Spectrum two FT-IR spectrophotometer equipped with a Perkin Elmer UATR-TWO diamond ATR and corrected by applying the art-correction function of Perkin Elmer Spectrum software. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. For Maldi-TOF spectra, experiments were carried out using a Bruker microTOF (Germany) in Gebze Institute of Technology. The elemental compositions of the samples were analyzed by an element analyzer (Flash 2000, Thermo Scientific). Fluorescence spectra were measured using a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Photo-irradiations for singlet oxygen determination were measured using a General Electric quartz line lamp (300 W). A 600 nm glass cutoff filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiation respectively. An interference filter (Intor, 700 nm, with a bandwidth of 40 nm) was additionally placed in the light path in front of the sample. Light intensities were measured with a POWER MAX 5100 (Mol electron detector incorporated) power meter.

**Synthesis**

4-(2-{(2,2′:6′,2″-Terpyridine)-4′-yl(methyl)amino)ethoxy}phthalonitrile (1). The preparation of 1 was carried out as part of our earlier studies and has been reported previously [20].

4-(2-{(2,2′:6′,2″-Terpyridine)Zn(II)-4′-yl(methyl)(amino)ethoxy}phthalonitrile (2). 4-(2-{(2,2′:6′,2″-terpyridine)-4′-yl(methyl)amino)ethoxy}phthalonitrile (1) (100 mg, 0.231 mmol) was added to a stirred solution of ZnCl₂ (32 mg, 0.231 mmol) in ethanol (20 mL) and the mixture was stirred at an ambient temperature for 12 h. The progress of the reaction was monitored by TLC using THF/Hexane/NH₃(aq) (5/4/0.5) solvent system. After the complexation was completed, the resulting mixture was evaporated to 1/3 volume by a rotary-evaporator to yield the occurred precipitate. The resultant complex was collected by filtration, washed with water, ethanol, diethyl ether and dried in vacuum oven at 40°C over P₂O₅. The complex 2 was obtained as a pale-yellow solid powder in sufficient purity. Yield: 92% (0.12 g). Anal. Calc. for C₃₀H₂₅ClN₆OZn (%): C, 54.90; H, 3.54; Cl, 12.47; N, 14.78; O, 2.81; Zn, 11.50; Found (%): C, 54.52; H, 3.58; N, 14.63. UV-vis (DMSO-1 × 10⁻³ M); λmax nm (log ε): 264 (4.56), 300 (4.54). ¹H NMR (DMSO): δ ppm: 8.71 (d, 2H, ArH), 8.64 (d, 2H, ArH), 8.18 (t, 2H, ArH), 7.95 (d, 1H, ArH), 7.76 (s, 1H, ArH), 7.75–7.37 (m, 4H, ArH), 7.35–7.32 (m, 1H, ArH), 4.43 (t, 2H, AliphH), 4.11 (t, 2H, AliphH), 3.27 (s, 3H, AliphH). ¹³C NMR (DMSO): δ ppm 166.68, 158.50, 156.03, 155.08, 149.56, 145.35, 132.74, 128.24, 123.27, 122.40, 121.28, 115.58, 115.12, 105.18, 102.80, 67.27, 50.65, 41.98. MS (MALDI-TOF): m/z 649.27 (calcd. for [M + Na + 2H₂O + 1]⁺ 648,04), 591.16 [M + Na]⁺, 533 [M – Cl]⁻. FT-IR (PIKE
RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

Scheme 1 shows the synthetic route for the target macromolecular complex. Terpyridine Zn(II) complex substituted phthalocyanine (3), starting from its corresponding terpyridine Zn(II) complex (2), has been prepared as a new compound.

The preparation of 1 has been performed in five steps starting from commercially available 2-ethyl picolinate and acetone according to the literature method published by our group [20]. Complexation reactions of ligand 1 were carried out in one step by simply adding stoichiometric amounts of ligand to a solution of zinc (II) chloride in ethanol to obtain Zn(II)-terpyridine complex 2. The complex was obtained in nearly quantitative yield in sufficient purity. The tetra-terpyridine metal complex substituted ZnPc derivative 3 was prepared from the cyclotramerization reaction of phthalonitrile derivative 2 with corresponding anhydrous Zn(II) salt in the presence of DBU as a strong base at reflux temperature under argon atmosphere in DMF/n-pentanol.

Characterization of the products was carried out using a combination of methods including FT-IR, 1H-NMR, 13C-NMR, melting point, UV-vis, elemental analysis and mass spectroscopy. All the spectral data are in accordance with the proposed structures.

When the FT-IR spectra of 1 and 2, were compared, the –C≡N vibration of the pyridine ring at 1600 cm\(^{-1}\) shifted to 1614 cm\(^{-1}\) upon coordination. These upper shifts in the spectrum of complexes are due to chelate formation, which makes the complexes more stable and the ligand bonds located around the metal ions stronger. Similarly, the –C≡N band at 2235 cm\(^{-1}\) of ligand 1 shifted
to 2227 cm\(^{-1}\) for 2. In the infrared spectra of the complex 2, the typical aryl ether stretching band was observed at 1256 cm\(^{-1}\) for 2, in contrast to 1250 cm\(^{-1}\) observed for ligand 1. Formation of terpyridine complex substituted ZnPc (3) starting from corresponding phthalonitrile 2 was confirmed by the disappearance of the stressed –C≡N stretching vibration band at 2227 cm\(^{-1}\) as a proof of the cyclotetramerization reaction of dinitrile.

In the \(^1\)H-NMR spectrum of compound 2, the aromatic protons appeared at 8.71–7.32 ppm and the aliphatic protons at 4.43–3.27 ppm. The \(^1\)C NMR spectrum of compound 2 indicated carbon atoms at 166.68–41.98 ppm. In addition, nitrile carbon atoms were observed for compound 2 at 115.58, 115.12 ppm.

Since target complex (3) is insoluble in common organic solvents and just slightly soluble in DMSO, we could not obtain a satisfactory spectrum in the \(^1\)H-NMR and \(^13\)C-NMR. However, it was characterized by FT-IR spectroscopy, melting point, UV/vis, elemental analysis and mass spectroscopy. All the spectral data are in accordance with the proposed structures.

The mass spectra of 2 and 3 were recorded by the MALDI-TOF Mass spectrometer to confirm the proposed structures. 2,5-dihydroxybenzoic acid (DHB) was used as matrix for the target compounds (2 and 3). In the mass spectrum of 2, hydrated and Na-adducted peaks were observed at \(m/z\) 591.16 [M + Na]\(^+\) and \(m/z\) 649.27 [M + 2Na + 2H\(_2\)O + 1]\(^+\). One of the fragment ion peaks was observed at \(m/z\) 533 [M – Cl]\(^+\) for 2, as well. In the mass spectrum of 3, a clear molecular ion peak at \(m/z\) 2341.617 [M + H]\(^+\) and hydrated and Na-adducted peak at \(m/z\) 2452.249 [M + 4Na + H\(_2\)O + 1]\(^+\) were observed. The base peak of the spectrum at \(m/z\) 2006.009 was attributed to a fragment ion peak calculated as [M – 3ZnCl\(_2\) + 3H\(_2\)O + 1]\(^+\), and one of the fragment ion peaks at \(m/z\) 2234.853 [M – 3Cl]\(^+\) was also observed for compound 3 (Fig. 1).

![Fig. 1. MALDI-TOF MS spectra of 2 (a) and 3 (b) - P. SEN ET AL.](image-url)
The elemental analysis results for the synthesized new compounds (2 and 3) were consistent with the theoretical calculated values given in the experimental section.

The UV spectroscopic properties of the terpyridine-Zn(II) complex substituted phthalonitrile (2) was obtained in solution (DMSO). The complex (2) shows bands in the ultraviolet region centered at 290 nm and 300 nm assigned to $\pi-\pi^*$ transition. These $\pi-\pi^*$ transitions bands are typical for pyridine ligands and their complexes (Fig. 2) [26].

Phthalocyanines show typical electronic spectra with two absorption regions. One of them is in the UV region at about 300–350 nm (B-band) and the other in the visible area at 600–700 nm (Q-band). The Q-band was attributed to $\pi-\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other band, the so-called B-band, arises from the deeper $\pi$ levels to the LUMO [27].

The comparative electronic absorption spectra of 2 and 3 were examined in DMSO.

The UV-vis spectrum of the prepared phthalocyanine compound (3) showed a characteristic Q-absorption band at 678 nm and B band at 352 nm. The UV-vis spectrum of 3 showed no splitting of the Q-bands which are assigned to metallophthalocyanines with $D_{4h}$ symmetry, as expected (Fig. 2) [28].

**Photophysical and photochemical studies**

**Fluorescence spectra and quantum yields**

Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method [29] Eq. (1):

$$\Phi_F = \Phi_{F_{\text{Std}}} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2}$$  \hspace{1cm} (1)

where $F$ and $F_{\text{Std}}$ are the areas under the fluorescence curves of the MPC derivatives and the reference, respectively. $A$ and $A_{\text{Std}}$ are the absorbances of the sample and reference at the excitation wavelength, and $n^2$ and $n_{\text{Std}}^2$ are the refractive indices of solvents used for the sample and standard, respectively. The sample and the standard were excited at the same relevant wavelength. Five-nuclear phthalocyanine complex 3 exhibits a strong emission peak at 702 nm when excited at 635 nm in DMSO solution at room temperature. The emission shifted about 23 nm when compared to standard ZnPc (679 nm) [30], due to the presence of zinc complexes on the Pc ring. The excitation spectra were similar to the absorption spectra, and both were mirror images of the fluorescence spectra for complex 3. Figure 3 shows the absorption, fluorescence excitation and emission spectra for the complex 3 in DMSO [31].

The closeness of the wavelength of each component of the Q-band absorption to the Q-band maxima of the
excitation spectra for the complex suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation [31].

Complex 2 also was excited at 290 nm and gave an emission at 453 nm in DMSO (Fig. 4).

When compound 3 was excited at 290 nm (Fig. 5) where the zinc complexes absorb, then the emission occurring at about 700 nm was weakened due to absorption of the phthalocyanine core at this wavelength; the overall result was an enhancement of the emission at 702 nm for compound 3 due to a singlet–singlet energy transfer from the excited arm to the central phthalocyanine core. In the case of dyad compound 3, the fluorescence of zinc complexes was quenched and emission intensity of the phthalocyanine part of the molecule around 702 nm was increased because of the radiative energy transfer resulting from the inner filter effect of the phthalocyanine core [24]. We studied for the quantum yield determination in DMSO. The quantum yields in this solvent differ from each other; 2 in DMSO was 0.005 and 3 in DMSO was 0.22. We report that the new compound 3 has a similar fluorescence quantum yield compared to what is reported in the literature [31–34].

Singlet oxygen and photodegradation quantum yields

Quantum yields of singlet oxygen were determined in air (no oxygen bubbled) using the relative method with ZnPc (in DMSO) as a reference; DPBF as a chemical quencher for singlet oxygen, using Eq. (2):  

\[
\Phi_\Delta = \frac{\Phi_\Delta^{\text{std}} R_{\text{std}}}{R_{\text{std}} - I_{\text{abs}}} 
\]

where \(\Phi_\Delta^{\text{std}}\) is the singlet oxygen quantum yield for the standard ZnPc, \(\Phi_\Delta^{\text{std}} = 0.67\) in DMSO [35]. \(R\) and \(R_{\text{std}}\) are DPBF photo bleaching rates in the presence of the respective sample and standard, respectively. \(I_{\text{abs}}\) and \(I_{\text{std}}\) are the rates of light absorption by the sample and standard, respectively. Solutions containing DPBF were prepared in the dark and irradiated in the Q band region. The degradation of DPBF at 417 nm was monitored after each 5 s irradiation. The light intensity of \(7.05 \times 10^{15}\) photons s\(^{-1}\) cm\(^{-2}\) was used for \(\Phi_\Delta\) determinations. The absorption band of DPBF was reduced by light irradiation (Fig. 6). The compound 3 in DMSO (\(\Phi_\Delta = 0.37\)) had low singlet oxygen quantum yield compared to as a standard ZnPc (\(\Phi_\Delta^{\text{std}} = 0.67\) in DMSO).

The singlet oxygen quantum yield (\(\Phi_\Delta = 0.37\)) of the compound is normal for metal phthalocyanines [35–37]. Physical quenching of the excited singlet oxygen molecules can be caused by the peripheral substituents but is probably caused by the surrounding turbid medium [38]. Photodegradation quantum yield (\(\Phi_\Delta\))
determinations were carried out using the experimental set-up described in the literature Eq. (3) [39]:

\[
\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{abs} \cdot S \cdot t}
\]  

(3)

where \(C_0\) and \(C_t\) are the sample concentrations before and after irradiation respectively, \(V\) is the reaction volume, \(N_A\) is Avogadro’s constant, \(S\) is the irradiated cell area, \(t\) is the irradiation time, \(I_{abs}\) is the overlap integral of the radiation source light intensity and the absorption of the sample. A light intensity of \(2.42 \times 10^{16}\) photons s\(^{-1}\) cm\(^{-2}\) was employed for \(\Phi_d\) determinations.

The photodegradation quantum yield \((\Phi_d)\) value of complex 3 in DMSO is \(6.05 \times 10^{-4}\) [40, 41], and the photostability of compound 3 is similar to other known MPcs complexes which containing different substituents on the macrocycle [42, 43].

**CONCLUSION**

A pentanuclear phthalocyanine complex bearing a terpyridine zinc unit was synthesized in moderate yield and fully characterized by known spectroscopic techniques such as UV-vis, FT-IR, MS, \(^1\)H NMR, \(^{13}\)C-NMR (for precursors), and elemental analysis. The absorption spectrum of 3 showed monomeric behavior, as evidenced by a single (narrow) Q band typical for metallophthalocyanines in DMSO. The fluorescence behavior of 3 was studied in DMSO, and this compound showed similar fluorescence quantum yield \((\Phi_F)\) compared to standard zinc(II) phthalocyanine. Zinc (II) phthalocyanine revealed good singlet oxygen quantum yield (0.37) in DMSO. The obtained photophysical properties suggested the potential for photodynamic therapy studies of zinc complexes conjugated zinc (II) phthalocyanine.

**Acknowledgment**

This work was supported by the Research Fund of Sakarya University (Project No. 2014-02-04 007).

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INTRODUCTION

Because of their potential contribution to the next generation of molecular electronic devices such as electrochromic and electro-luminescent displays, nonlinear optics, photovoltaics, chemical sensors nanotechnology, and photosensitizers for photodynamic cancer therapy (PDT) of tumors, studies on the synthesis and characterization of novel phthalocyanines (Pcs) compounds are of considerable interest [1–11]. All the properties of Pcs are influenced and enhanced both by the nature of central metals and the substituent and substituent’s position (peripheral or non-peripheral) in the Pc ring. Pcs exhibit a tendency in solution to form the dimer and higher oligomeric species, which is called aggregation. However, many Pcs have been restricted in application areas owing to their lower solubility and aggregations in common organic solvents [11]. To prepare soluble Pc, the peripheral and/or non-peripheral positions of the Pc ring is attached with functional groups such as bulky or long chain alkyl and alkoxy, crown ether groups, amide or carboxylic acid groups [12–14]. In addition, to obtain non-aggregated and soluble Pcs, both axial positions of the central metal ions in the Pc cavity can be attached the various groups [15].

Recently, in situ detection of volatile organic compound (VOC) vapors such as toluene and benzene has become a serious task due to regulations in many countries [16]. In particular, toluene is a well-known health-threatening gas. Higher levels of toluene can cause permanent damage to the brain, and continuous exposure can result in death. Already established methods for toluene detection are mostly based on optical methods such as surface plasmon resonance [16] and cataluminescence [17]. Various
chemoresistive metal oxide gas sensors have been used to detect toluene, which include monodispersed Cr$_2$O$_3$ porous microspheres [18], SnO$_2$ nanofibers [19], SnO$_2$–Fe$_2$O$_3$ interconnected nanotubes [20] and SmFeO$_3$ [21]. However, metal oxide chemoresistive gas sensors have some well-known disadvantages, e.g. poor selectivity, high operating temperature and long response and recovery time of the sensor signal [22]. When compared with inorganic based sensors, molecular semiconductor based sensors have several advantages. Unique physical and chemical properties of Pcs make them ideal candidates for sensing applications [23–25]. Some physical, photophysical and photochemical of 2,6-dimethoxyphenoxy substituted metal-free and metallophthalocyanines (indium(III) and zinc(II) Pcs) were investigated by our group [26]. We wondered how copper(II), indium(III), mono-lutetium(III) and tin(IV) Pcs substituted with 2,6-dimethoxyphenoxy bioactive moieties affect the physical, electronic and toluene sensing properties. Hence, highly soluble peripherally and non-peripherally substituted Cu(II), In(III), Lu(III) and Sn(IV) Pcs with 2,6-dimethoxyphenoxy were also synthesized (Scheme 1), and the effects of the position of the substituents and the variety of central metal ions on the their spectroscopic and toluene vapors sensing properties were investigated in this study.

**EXPERIMENTAL**

**Materials and Equipment**

2,6-Dimethoxy-phenoxy substituted phthalonitriles (1 and 2) were obtained by the reaction of 2,6-dimethoxyphenol with 3-nitrophthalonitrile or 4-nitrophthalonitrile through base catalyzed nucleophilic aromatic displacement reaction [26]. All other starting materials and solvents used were obtained commercially. All reactions were carried out under dry nitrogen atmosphere. The novel Pcs (3–10) were successively cleaned by washing with hot acetic acid-water solution by volume 7/3, water, ethanol and acetonitrile in the Soxhlet apparatus. Column chromatography was performed on silica gel 60 for a proper purification of the raw compounds. The purity of the products was tested in each step by thin layer chromatography (Silicagel F-254 coated TLC plate). Melting points of the Pc compounds were found to be higher than 300°C. IR Spectra and electronic spectra were recorded on a Shimadzu FTIR-8300 (ATR) and a Shimadzu UV-1601 spectrophotometer, respectively. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK–Ankara. Mass spectra were acquired on a Microflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen UV-Laser operating at 337 nm in reflectron mode with an average of 50 shots.

**Synthesis**

*General procedure for the synthesis of metallophthalocyanines (3–10).* 0.25 g (0.89 mmol) of compound 1 or 2 and 0.46 mmol powdered metal salts [0.06 g CuCl$_2$, 0.14 g In(OAc)$_3$, 0.16 g Lu(OAc)$_3$ or 0.05 g SnCl$_2$], and 0.20 mL of N,N-dimethylformamide (DMF) were transferred in a reaction tube and heated at 360°C for 25 min under dry nitrogen atmosphere. The mixture was precipitated by adding methanol. The green products were filtered and washed with acetic acid (only for Cu(II))
Pcs 3 and 4), methanol, ethanol, acetone, acetonitrile, and n-hexane, for 15 h in the Soxhlet apparatus. The crude products were purified by column chromatography with silica gel eluting with CHCl₃.

1(4),8(11),15(18),22(25)-Tetakis-(2,6-dimethoxyphenox)phthalocyaninatoindium(II) (5). Yield: 99.06 mg (24.16%). Calculated for C₆₅H₅₈InN₈O₁₂: C, 68.54%; H, 8.56%; N, 8.82%. IR (ATR) λₘₐₓ/cm⁻¹: 742, 802, 878, 976, 1079 (C–C str.), 1104 (C–N str.), 1181 (C–N str.), 1207, 1234 (C–O str.), 1280 (C–O str.), 1333 (C–O str.), 1437 (C–H bend.), 1449 (C–H bend.), 1479 (C–H bend.), 1598 (C–S str.), 1652 (C–S str.), 1730 (C–O str.), 1770 (C–O str.), 2848 (∼CH₃ str.), 2930 (∼CH₃ str.), 3008 (∼CH₃ str.), 3083 (∼C–H str.), 3003 (∼C–H str.), 3030 (∼C–H str.), 3070 (∼C–H str.). UV-vis (DMSO, 1 × 10⁻⁵ M): λₘₐₓ (nm), (log ε): 333 (4.72), 354 (4.73), 614 (4.22), 660 (4.38), 684 (5.03). MALDI-TOF-MS: 1184.78 [M]⁺.

2(3),9(10),16(17),23(24)-Tetakis-(2,6-dimethoxyphenox)phthalocyaninatoindium(III) acetate (6). Yield: 99.06 mg (24.16%). Calculated for C₆₅H₅₈InN₈O₁₂: C, 68.54%; H, 8.56%; N, 8.82%. IR (ATR) λₘₐₓ/cm⁻¹: 742, 802, 878, 976, 1079 (C–C str.), 1104 (C–N str.), 1181 (C–N str.), 1207, 1234 (C–O str.), 1280 (C–O str.), 1333 (C–O str.), 1437 (C–H bend.), 1449 (C–H bend.), 1479 (C–H bend.), 1598 (C–S str.), 1652 (C–S str.), 1730 (C–O str.), 1770 (C–O str.), 2848 (∼CH₃ str.), 2930 (∼CH₃ str.), 3008 (∼CH₃ str.), 3083 (∼C–H str.), 3003 (∼C–H str.), 3030 (∼C–H str.), 3070 (∼C–H str.). UV-vis (DMSO, 1 × 10⁻⁵ M): λₘₐₓ (nm), (log ε): 333 (4.72), 354 (4.73), 614 (4.22), 660 (4.38), 684 (5.03). MALDI-TOF-MS: 1184.78 [M]⁺.

2(3),9(10),16(17),23(24)-Tetakis-(2,6-dimethoxyphenox)phthalocyaninatoindium(IV) chloride (9). The SnCl₃·Pe (9) is soluble in toluene, CHCl₃, DCM, THF, DMF and DMSO. Mp > 300°C. Yield: 72.86 mg (21.43%). Calculated for C₆₅H₅₈InN₈O₁₂SnCl₃: C, 58.65%; H, 3.69%; N, 8.55%; found C, 58.53%; H, 3.84%; N, 8.41%. IR (ATR) λₘₐₓ/cm⁻¹: 706, 707, 766, 801, 878, 951, 962, 1020 (C–C str.), 1070 (C–C str.), 1129 (C–N str.), 1159 (C–N str.), 1229 (C–O str.), 1303 (C–O str.), 1336 (C–O str.), 1437 (C–H bend.), 1479 (C–H bend.), 1595 (C–S str.), 1669 (C–N str.), 2837 (∼CH₃ str.), 2913 (∼CH₃ str.), 3012 (∼C–H str.), 3067 (∼C–H str.). UV-vis (DMSO, 1 × 10⁻⁵ M): λₘₐₓ (nm), (log ε): 327 (4.75), 365 (4.60), 668 (4.39), 705 (4.52), 743 (5.07). MALDI-TOF-MS: 1239.21 [M–2Cl]⁻ and 1275.88 [M+2 H₂O]⁻.
SnCl₂Pc (10) is soluble in toluene, CHCl₃, DCM, THF, DMF and DMSO. Mp > 300°C. Yield: 80.48 mg (23.67%). C₆₄H₄₈N₈O₁₂SnCl₂: C, 58.65%; H, 3.69%; N, 8.55%; found C, 58.78%; H, 3.81%; N, 8.69%. IR (ATR) λmax/cm⁻¹: 675, 724, 736, 771, 825, 869, 891, 949 (C–C str.), 1043 (C–C str.), 1106 (C–N str.), 1181 (C–N str.), 1221 (C–O str.), 1276.02 [M + 2H₂O]⁺.

**Gas sensing measurements**

10 × 10 mm² glass substrates with photolithographically patterned gold interdigitated micro electrodes were used as transducers for toluene vapor sensing experiments. Thin films of the sensing layer were deposited on the transducer surface by the spin coating method after cleaning the substrate with isopropyl alcohol, acetone, and deionized water in an ultrasonic bath. After applying the cleaning procedure, 25 μL of DMF solutions of the compounds were added with a glass pipette onto the micro electrodes held on a spinner. To avoid the formation of films with different phases, the concentration of the spreading solutions was held constant at 4 × 10⁻⁵ M for all compounds. The substrate was spun at 1250 rpm for 75 s and then dried at 70°C under vacuum for 2 h to ensure removal of the residual solvent in the films. The toluene vapor was generated by controlled evaporation of liquid toluene at low temperatures. Well-defined concentrations of toluene vapor were prepared by mixing the reference gas (dry nitrogen, in our case) with the toluene vapor. The toluene sensing experiment consisted of repeated exposure to toluene vapor and subsequent purging with dry N₂ gas. The total gas flow rate was adjusted to 100 standard cubic centimeter (sccm) during exposure and purging stages. The toluene sensing capability of the sensors was determined by measuring the sensor current as a function of toluene concentration in a temperature controlled stainless-steel chamber. During sensing experiments a constant dc bias of 1.5 V to devices and the sensor current was monitored by using an electrometer (Keithley model 617). A data acquisition system incorporated personal computer was used to record the time evaluation of the sensor current in response to various exposure to toluene vapor.

**RESULTS AND DISCUSSION**

**Syntheses and characterization**

The 2,6-dimethoxyphenoxy substituted phthalonitrides (1 and 2) were synthesized as described in the literature [26]. To synthesize non-peripherally and peripherally novel Cu(II) (3 and 4), In(OAc)₃ (5 and 6), Lu(OAc)₃ (7 and 8) and Sn(IV) (9 and 10) Pcs, a mixture of compound 1 (or 2), metal salts (CuCl₂, In(CH₃COO)₃, Lu(CH₃COO)₃, or SnCl₂) in dried DMF was heated at approximately 360°C for 25 min.

According to the literature, Sn(II)Pc can be obtained by using excess amounts of SnCl₂ [27], and stoichiometric use of SnCl₂ results in Sn(III)Pc. In this study, the Sn(IV)Pc derivative was synthesized using stoichiometric amounts of SnCl₂. Two different lutetium Pcs can be obtained depending on reaction conditions. If the phthalonitrile compound reacts with lutetium(III) acetate in DMF, mono LuPc complex can occur; bis lutetium Pc can be synthesized using pentanol or hexanol with 1,8-diazabicyclo[5.4.0]undec-7-ene (in stronger basic media). In this study, lutetium(III) acetate in DMF was used to synthesize mono LuPc complexes [28].

The proposed structure of these novel compounds was confirmed by elemental analysis, IR, UV-vis, ¹H-NMR, and the MALDI-TOF mass spectroscopic data.

In the IR spectra of the Pcs, the sharp peaks for the –C≡N vibrations of bands at 2231 cm⁻¹ for 1 and 2237 cm⁻¹ for 2 disappeared after phthalocyanine formation in the IR spectrum.

The observed single (narrow) Q bands in electronic spectra in ~1 × 10⁻⁵ mol.dm⁻³ DMSO indicate monomeric behavior of the compounds. The UV-vis spectra of Pcs showed characteristic absorptions in the Q band region with log ε (ε = molar extinction coefficient) at 702 (5.02), 719 (5.07), 702 (5.08), 743 (5.07) nm for the non-peripherally substituted Cu(II), In(OAc)₃, Lu(OAc)₃ and SnCl₂Pcs (3, 5, 7 and 9) and at 683 (5.05), 698 (4.98), 684 (5.03) and 714 (5.05) nm for the peripherally substituted metallophthalocyanines (4, 6, 8 and 10) in DMSO, respectively (Fig. 1). When compared with peripherally substituted Pcs, non-peripherally substituted metallophthalocyanines are more liable to non-planar distortion due to linear combinations of the atomic orbitals (LCAO) coefficients at the non-peripheral positions of the HOMO being greater than those at the peripheral positions. As a result, the HOMO level is more destabilized at the peripherally position. Essentially, the energy gap (ΔE) between the HOMO and LUMO becomes smaller, resulting in a bathochromic shift [29–31].

The Q band of the non-peripherally substituted Cu(II), In(OAc)₃, Lu(OAc)₃ and SnCl₂Pcs (3, 5, 7 and 9) was red-shifted by 19, 21, 18 and 29 nm when compared to the corresponding peripherally substituted Pc complexes (4, 6, 8 and 10) in DMSO, respectively. Their characteristic B1 and B2 bands (3–10) were observed at a range of 313–405 nm (Fig. 1). In this study, the aggregation behavior of the Pc complexes (3–10) was investigated in various commonly known organic solvents DMSO, chloroform and THF. The Pc complexes (3–10) did not form aggregates in these solvents. In addition, any bands
TOLUENE VAPOR SENSING CHARACTERISTICS OF NOVEL COPPER(II), INDUML, MONO-LUTETIUM(III) 193

were observed at range of 470–550 nm in the UV-vis spectra of lutetium Pcs complex 7 and 8. This result shows that these complexes are mono lutetium Pcs (not Double–Decker complexes) [28].

The MALDI-TOF mass spectra were identified easily with DHB MALDI matrix in the reflectron mode using MALDI-TOF mass spectrometry. In the spectra, peaks were observed at m/z: 1184.36, 1184.78 Da for [M]+ of Cu(II)Pcs (3 and 4), 1389.23, 1389.37, 1449.22, 1449.41 Da for [M – OAc + DHB]+ of the In(OAc)Pcs and Lu(OAc)Pcs (5–8), 1239.21, 1339.43, Da for [M–2Cl]+ of the SnCl2Pcs (9 and 10), and 1275.88, 1276.02 Da for [M + 2H2O]+ of SnCl2Pcs (9 and 10), respectively.

**Toluene sensing**

In order to examine the effects of the position of substituents and metal atoms in the cavity on toluene sensing performance and adsorption kinetics, sensing experiments were carried out on eight Pc films (Scheme 1) with the same thickness. Figure 2 shows the response of the peripherally (a) and non-peripherally (b) substituted compounds to different concentrations of toluene vapor at room temperature (298 K).
sensor response reveals that the toluene adsorption take place close to the surface of the sensing layer and the presence of a weak interaction force. It is known that toluene is a reducing gas or electron donor which causes a decrease in electrical conductivity of a \( p \)-type semiconductor material. It is believed that most of the Pc molecules exhibit \( p \)-type behavior. Phthalocyanine molecules are characterized by the aromatic nature and delocalized \( \pi \)-electron system.

Due to the weakly bound \( \pi \)-electrons to the Pc molecules, they are good electron donors. For this reason, it is expected that Pc molecules will interact effectively with electron acceptor (oxidizing) gases. On the other hand, it is well known that the strengths or weakness of the delocalization of \( \pi \)-electrons can be controlled by the position and the chemical properties of the substituent groups, which modify the interaction force between gas molecules and Pc macrocycles. In the case of substituted Pcs, substitutions have a considerable effect on the surface and the film structure. Recently, the influence of the metal atom and the nature of the substituent groups on the toluene sensing performance of the metallophthalocyanine thin films were studied by infrared spectroscopy, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques [34]. The presence of amorphous or semicrystalline forms as well as different molecular organizations into the thin films for unsubstituted and substituted Pcs was verified by XRD and SEM analysis. The actual adsorption processes is more complicated, and there is no satisfactory explanation for the origin of the interaction mechanism between the Pc films and the gas molecules. The observed unexpected increase in sensor current cannot be explained completely within the scope of this paper, but it can be attributed, at least partly, to the 2,6-dimethoxyphenoxy substituent, which may be responsible for accepting donor charges and thus increasing the observed conductivity. A speculative conclusion for the observed response-recovery behavior of the sensors can be given by creation of acceptor levels near the bad edge of the phthalocyanine molecules. When the target molecules, toluene in our case, interact with the \( \pi \)-electron network of the phthalocyanine molecule, it causes the transfer of an electron from the phthalocyanine ring to the analyte molecule. Thus, the induced positive holes on the film surface give rise to an increase in the \( p \)-type conductivity of the sensing layer. When the sensor is then exposed to dry nitrogen, desorption of adsorbed toluene molecules from the surface of the active sensing layer occurs. This decreases the acceptor concentration and thus the sensor current.

In order to discuss the role played by the position of substituent in the sensing processes, the toluene sensing performance of the compounds were compared with their sensitivity. The sensor sensitivity, \( S \), is defined as,

\[
S = \left( \frac{\Delta I}{I_0} \right)
\]  

Fig. 3. Room temperature toluene sensitivities of the compounds

where \( \Delta I \) is the change in current at a known toluene concentration and \( I_0 \) stands for the current of the sensor in the reference gas (dry nitrogen in our case). The variation of the sensor sensitivities with toluene concentration for peripheral and non-peripheral substituted Pcs are shown in Fig. 3. A close investigation of Fig. 3 indicates that the peripherally substituted compounds exhibited larger sensitivity than non-peripherally substituted film which means that the peripherally substituted compounds exhibited the biggest affinity to the toluene. This is understandable because Germain et al. [35] have already observed this type of behavior.

The sensing performance of ZnPc and its peripherally substituted derivative hexadecafluorophthalocyanine films against various reducing gases were examined by Germain et al. [35]. It was reported by these workers that the conductivity of the ZnPc film does not change any more in the presence of \( \text{NH}_3 \) gas, while film of \( \text{ZnF}_{16}\text{Pc} \) exhibits high sensitivity to this gas. Results observed in their study were related to redox potentials of the Pcs films investigated. It is also clear from the Fig. 3 that the toluene vapor sensitivity of the compounds exhibit metal ion dependence. It is well-known that the relevant factors in the vapor-metallophthalocyanine interaction are the conjugated \( \pi \)-electron system, the presence of hetero atoms and the central metal ion. It has been reported previously by Spadavecchia et al. [36] that primary interaction involves the Pc metal and the hetero atoms on the analyte molecule and a secondary interaction is determined by the substituents.

**Adsorption kinetics**

**Elovich model**

The adsorption kinetics of toluene vapor onto the surface of Pc thin films were examined using two different kinetic models. One of them is the Elovich model. This model is the earliest one developed to
understand the nature of the adsorption process onto heterogeneous solids. Zeldowitsch [37] observed that the rate of adsorption of CO gas decreases exponentially with an increase of gas adsorbed on MnO₂. In the Elovich model it is assumed that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the relation [38]:

\[ \frac{d\theta}{dt} = ae^{\alpha \theta} \]  

(2)

where \( \theta \) represents the amount of adsorption at time \( t \), \( a \) is the sorption rate and \( \alpha \) is the desorption constant. In the Elovich equation, the constant is regarded as the initial adsorption rate because \( \frac{d\theta}{dt} \) approaches \( a \) when \( \theta \) approaches 0 and it depends on the activation energy. The integrated form of Eq. (2) with the following boundary conditions; \( \theta = 0 \) at \( t = 0 \) and \( \theta = \theta \) at \( t = t \) becomes

\[ \theta = \frac{1}{\alpha} \ln(\alpha \theta + 1) \]  

(3)

By assuming that \( \alpha \theta \gg 1 \), as suggested by Chien and Clayton [39], Eq. (3) becomes:

\[ \theta = \frac{1}{\alpha} \ln(t) + \frac{1}{\alpha} \ln(\alpha \theta) \]  

(4)

When the sensor operates under constant bias voltage condition, as in our case, it is reasonable that the variation of the sensor current can be directly related to the amount of adsorption (\( \theta \)), and Eq. (4) can be rewritten as,

\[ I(t) = \frac{1}{\alpha} \ln(t) + \frac{1}{\alpha} \ln(\alpha \theta) \]  

(5)

where \( I(t) \) represents time dependence of the sensor current during toluene exposure.

The applicability of Eq. (5) to toluene adsorption data can now be checked by the plots of \( I(t) \) vs. \( \ln(t) \). According to Eq. (5), plots of \( I(t) \) vs. \( \ln(t) \) should give a straight line with slope of \( (1/\alpha) \) and intercept of \( (1/\alpha) \ln(\alpha \theta) \). The correlation coefficient \( R^2 \) was used as an indicator of the conformity between the model prediction and experimental adsorption data. Figure 4 shows Elovich plots for 300 ppm toluene adsorption onto the peripherally substituted (a) and non-peripherally substituted (b) Pc compounds. An examination of Fig. 4 shows that the Elovich equation does not give a good fit to toluene adsorption onto peripherally substituted compounds. As indicated in Fig. 4 (a), the correlation coefficients are in the range of 0.911–0.965, which indicates bad correlation. Such a deviation from linearity of the Elovich plot for the adsorption of nitrogen dioxide on iron and copper Pc thin film has been reported earlier [40, 41]. On the other hand, the fitting of the toluene vapor adsorption data on the non-peripherally substituted compounds gives correlation coefficients between 0.993 and 0.997 (Fig. 4(b)), which are indicative of a good correlation. Therefore, it can be concluded that the Elovich equation is an appropriate model to represent the toluene adsorption onto the non-peripherally substituted compounds.

The first-order model

Lagergren’s first-order model assumes that the rate of occupation of adsorption sites is directly proportional to the number of unoccupied sites, and it can be represented as follows [42]:

\[ \frac{dq}{dt} = k_a (q_e - q_t) \]  

(6)

where \( q_t \) and \( q_e \) are the amounts of analyte vapor adsorbed at equilibrium and at any time \( t \), respectively. \( k_a \) is the first-order adsorption rate constant. Integrating Eq. (6) for the boundary conditions at \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \), results to the following equation,
which may be rearranged to:

\[ \log(q_e - q_t) = \log q_e - \frac{k_a}{2.303} t \]  \hspace{1cm} (8)

By assuming that the sensor current is proportional to the amounts of adsorbed toluene, Eq. (8) can be rewritten as,

\[ \log(I_m - I(t)) = \log I_m - \frac{k_a}{2.303} t \]  \hspace{1cm} (9)

where \( I_m \) stands the maximum steady-state sensor response. It is clear that the plots of \( \log (I_m - I(t)) \) vs. \( t \) should yield straight lines, if the adsorption processes follows the pseudo first-order model. To quantify the applicability of the first-order model, the correlation coefficient was calculated from Fig. 2 (b). Figures 5(a) and 5(b) show a plot of the first-order model for the 300 ppm toluene adsorption onto the peripherally and non-peripherally substituted compounds, respectively. As can be seen from the comparison of Figs 5(a) and 5(b), much lower correlation coefficients for all peripherally substituted compounds suggest that Lagergren’s first-order equation is inappropriate to use as a model to represent toluene adsorption onto 3, 5, 7, and 9. Very good correlation coefficients for compounds 4, 6, 8, and 10, when compared with 3, 5, 7, and 9, indicate that the adsorption of toluene vapors onto the non-peripherally 2,6-dimethoxyphenol substituted Pcs was more favorable by the pseudo-second order kinetic model.

In our previous work, we studied the effect of relative humidity and bridging units on the toluene vapor detection capabilities of novel dimethoxyphenoxy phthalocyanine thin films [33]. We found that the toluene sensitivity of the films strongly depends on the bridging unit: toluene sensitivities of the azo-bridged Pcs were higher than those of the homologous oxo-bridged derivatives. Kinetics of toluene adsorption on these azo and oxo bridged phthalocyanine thin films were also investigated. Kinetic studies indicated that the toluene adsorption onto both azo and oxo bridged phthalocyanine thin films can be represented by a simple adsorption–desorption model. It reveals that the kinetics of toluene adsorption on the dimethoxyphenoxy substituted Pcs films does not depend on the kind of the bridging unit. On the other hand, results of this study clearly indicate that toluene adsorption kinetics onto dimethoxyphenoxy phthalocyanine thin films strongly depend on the position of the substituent group.

**CONCLUSION**

Highly soluble novel peripheral and non-peripheral substituted metallophthalocyanines were synthesized and characterized by elemental analysis, UV/vis, IR, and MALDI-TOF mass spectrosocopies. The effect of metals on spectroscopic properties and aggregation behavior of the novel Pcs were investigated in common organic solvents. A comparative study of the applicability of kinetic models of pseudo first-order and Elovich models to describe the experimental adsorption of toluene on non-peripheral substituted metallophthalocyanines and peripheral analogs has been carried out. Calculated regression coefficients \( R^2 \) indicate that adsorption data on peripherally substituted Pcs are best described by the pseudo first-order model, while the Elovich equation fits the experimental data well with regression coefficients larger than 0.993 for non-peripherally substituted Pcs. This result indicates that the sensing behavior and kinetics of the adsorption strongly depend on the position of the substituent groups.
Acknowledgments

We are thankful to the Foundation of Marmara University and the Commission of Scientific Research (BAPOK) (Project Nos: FEN-C-YLP-140115-0010 and FEN-C-YLP-111115-0515).

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**INTRODUCTION**

Phthalocyanines (Pcs), having been the subject of intense exploration over several decades due to their stability, architectural flexibility, diverse coordination properties, and spectroscopic characteristics [1–3], are also very promising complexes for various applications such as dyes and pigments [4], catalysts [5], medical applications [6], gas sensors [7, 8], electrochromic display devices [9], liquid crystals [10], nonlinear optical devices [11], solar cells [12], and Langmuir–Blodgett films [13]. The increasing importance and use of phthalocyanines as advanced materials have provided an attractive opportunity for chemists to explore designing variables of the central metal ion, changing substituents in the peripheral, non-peripheral or axial positions, changing the symmetry of the Pc molecule to achieve the targeted interesting properties [14–18].

Dyestuffs are generally synthesized from organic compounds and are classified by the functional groups they contain (azo, indigo, anthraquinone, triarylmethane, methylene, phthalocyanine) and by the applications they are used for.

Azo dyestuff which consists of at least a conjugated chromophore azo (–N=N–) group, are the most widely used class of dyes due to their versatile applications in various fields such as the dyeing of textile fibers and coloring of different materials, plastics, biological-medical studies, in high technology areas like lasers, liquid crystalline displays, electrooptical devices, ink-jet printers and advanced applications in organic synthesis [19–23]. Because of their conjugated structures, azo compounds usually show strong absorptions in the visible region (400–650 nm) in spite of very weak or even no absorption for the Pcs in this range [24–26].

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salts are obtained with a reaction called diazotization, and they are very important as starting materials in syntheses and also as reagents for azo dyestuffs. For the syntheses of azo compounds, there are many methods available, but the most important is to react the aromatic diazo compound and another molecule, known as the coupling reagent.

Many kinds of azo compounds and Pcs have been synthesized separately in many fields, but synthesis, photophysical, and electrochemical properties of Pcs containing azo groups are relatively rare [27–32]. In this study, the synthesis and characterization of 2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy substituted novel phthalonitrile compound and its peripherally substituted metal-free and zinc (II), copper (II), cobalt (II), and manganese (III) phthalocyanane derivatives were performed for the first time. These compounds were characterized by data obtained from general spectroscopic methods such as FT IR, $^1$H NMR, $^{13}$C NMR, UV-vis, elemental analysis, and mass characterization techniques. The photophysical properties of these phthalocyananes were investigated in THF. The electrochemical properties of phthalocyanane complexes 2–6 were also determined.

**EXPERIMENTAL**

Materials

All reported $^1$H NMR and $^{13}$C NMR spectra were recorded on an Agilent VNMR 500 MHz spectrometer. Chemical shifts (δ, ppm) were determined with TMS as the internal reference. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR capability. Electronic spectra were recorded on a Scinco SD 1000 diode array, single-beam ultraviolet-visible (UV-vis) spectrophotometer. Melting points were recorded on a Büchi Melting Point B-540. Fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. Mass spectra were performed on a Perkin-Elmer Clarus 500 GC–MS and a Bruker Microflex MALDI–TOF mass spectrometer. The homogeneity of the products was tested in each step by TLC (SiO$_2$). 2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenol was prepared according to the reported procedure [33]. Electrochemical measurements were carried out using a Gamry Reference 600 galvanostat/potentiostat at 298 K with a glassy carbon working electrode and platinum wires as counter and saturated calomel reference (SCE) electrodes with 0.1 M $n$-Bu$_4$NClO$_4$ in THF under $N_2$ atmosphere.

**Synthesis**

4-[2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy] phthalonitrile (1). 2,6-Dimethyl-4-(4-tert-butyl-phenylazo)phenol (0.815 g, 2.888 mmol) and 4-nitrophthalonitrile (0.500 g, 2.888 mmol) were dissolved in dry $N,N$-dimethylformamide (DMF) (25 mL), and anhydrous potassium carbonate (0.597 g, 4.332 mmol) was added into reaction mixture portionwise within 2 h with efficient stirring. The mixture was stirred at room temperature under nitrogen atmosphere for 72 h, then poured into ice water (400 mL). The solid product was filtered off and washed with purified water to be neutralized. The product was purified by crystallization with ethanol. Yield: 0.554 g (47%); mp: 145°C; Anal. calcd. for C$_{26}$H$_{25}$N$_4$O: C, 76.45; H, 5.92; N, 13.72%. Found: 76.41; H, 5.90; N, 13.69%; IR: $v_{\text{max}}$, cm$^{-1}$ 3075–3043 (Ar-CH), 2961–2865 (alkyl-CH), 2230 (C≡N), 1465 (N≡N); $^1$H NMR (d-acetone): δ, ppm 8.05 (d, 2H, Ar-H), 7.89 (d, H, Ar-H), 7.79 (d, H, Ar-H), 7.66 (d, 2H, Ar-H), 7.60 (s, 2H, Ar-H), 7.39 (d, H, Ar-H), 2.26 (s, 6H, CH$_3$), 1.40 (s, 9H, CH$_3$); $^{13}$C NMR (d-acetone): δ, ppm 160.70 (aromatic C), 154.88 (aromatic C), 151.56 (aromatic C), 150.50 (aromatic C), 149.80 (aromatic C), 149.80 (aromatic C), 136.23 (aromatic C-H), 131.99 (aromatic C-H), 126.20 (aromatic C-H), 126.63 (aromatic C), 122.46 (aromatic C-H), 122.46 (aromatic C-H), 120.26 (aromatic C-H), 119.98 (aromatic C-H), 119.98 (aromatic C-H), 117.73 (aromatic C), 115.53 (C≡N), 115.09 (C≡N), 108.62 (aromatic C), 30.59 (aliphatic C), 29.40 (CH$_3$), 29.40 (CH$_3$), 29.40 (CH$_3$), 15.51 (CH$_3$), 15.51 (CH$_3$); UV-vis (THF): $\lambda_{\text{max}}$, nm (log ε) 333 (5.12), 442 (3.56); MS (MALDI-TOF): m/z 408,412 [M$^+$].

**Metal free phthalocyanine** (2). Lithium (0.020 g, 2.882 mmol) was dissolved in pentanol (6 mL) by heating at 90°C, and then compound 1 (0.900 g, 2.202 mmol) was added to the reaction medium. The reaction mixture was stirred at 145°C for 5 h. After cooling to room temperature, the reaction mass was then poured into 200 mL ice water and acidified with acetic acid until the crude product precipitated. In this mixture, the lithium phthalocyanine was converted into metal-free phthalocyanine. The precipitate was filtered off and washed several times with water, ethanol and methanol. Yield: 0.486 g (54%); mp > 200°C; Anal. calcd. for C$_{26}$H$_{24}$N$_4$O: C, 76.35; H, 6.04; N, 13.70%. Found: 76.21; H, 6.02; N, 13.03%; IR: $v_{\text{max}}$, cm$^{-1}$ 3288 (N-H), 3059 (Ar-CH), 2958–2868 (alkyl-CH), 1466 (N≡N), 1210 (C-O-C); UV-vis (THF): $\lambda_{\text{max}}$, nm (log ε) 343 (5.16), 670 (4.96), 701 (4.97); MS (MALDI-TOF): m/z 408,412 [M$^+$].

**Zinc (II) phthalocyanine** (3). A mixture 0.061 mmol of compound 1 and anhydrous Zn(CH$_3$COO)$_2$ (11.19 mg, 0.061 mmol) in 2 mL 2-dimethylaminoethanol was heated and stirred at 150°C for 24 h under $N_2$ in a sealed tube. After cooling to room temperature, the reaction mixture was poured into 200 mL ice water mixture. The precipitate was filtered off, washed successively with water, hexane, hot ethanol, and methanol. Yield: 0.047 g (46%); mp > 200°C; Anal. calcd. for C$_{26}$H$_{26}$N$_4$O$_2$Zn: C, 73.51; H, 5.69; N, 13.19%. Found: 74.07; H, 5.70; N, 13.23%; IR: $v_{\text{max}}$, cm$^{-1}$ 3051 (Ar-CH), 2958–2869 (alkyl-CH), 1465 (N≡N), 1216...
General procedures for phthalocyanine derivatives (4–6)

Compound 1 (0.100 g, 0.245 mmol) and anhydrous metal salts (0.061 mmol) [CoCl₂, 7.92 mg; CuCl₂, 8.20 mg; MnCl₂, 7.68 mg] in 2 mL of 2-dimethylaminoethanol were heated and stirred at 150 °C in a glass sealed tube for 24 h under nitrogen atmosphere. After cooling to room temperature, the green reaction mixture was precipitated by pouring into ice water mixture (100 mL). The solid products were filtered off and purified by washing several times with water, hexane, ethanol, and methanol. Finally, pure products were obtained by chromatography on an aluminum oxide column using THF as an eluent.

Cobalt(II) phthalocyanine (4). Yield: 0.032 g (31%); mp > 200 °C; Anal. calcd. for C₁₀₅H₈₅N₁₆O₄Co: C, 73.78; H, 5.72; N, 13.24%. Found: C, 73.83; H, 5.69; N, 12.99%. IR: vₘₐₓ, cm⁻¹, 3063 (Ar-CH), 2960–2869 (alkyl CH), 1469 (N=N), 1220 (C-O-C). UV-vis (THF): λₘₐₓ, nm (log ε) 342 (5.16), 667 (4.38); MS (MALDI-TOF): m/z 1692.0 [M]+.

Copper(II) phthalocyanine (5). Yield: 0.036 g (35%); mp > 200 °C; Anal. calcd. for C₁₀₅H₈₅N₁₆O₄Cu: C, 73.58; H, 5.70; N, 13.20%. Found: C, 73.83; H, 5.69; N, 12.99%. IR: vₘₐₓ, cm⁻¹, 3051 (Ar-CH), 2960–2869 (alkyl CH), 1465 (N=N), 1217 (C-O-C). UV-vis (THF): λₘₐₓ, nm (log ε) 339 (5.17), 680 (4.51). MS (MALDI-TOF): m/z 1697.548 [M]+.

Manganese(III) phthalocyanine (6). Yield: 0.028 g (27%); mp > 200 °C; Anal. calcd. for C₁₀₅H₈₅N₁₆O₄Mn: C, 72.44; H, 5.61; N, 13.00%. Found: C, 71.73; H, 5.61; N, 12.86%. IR: vₘₐₓ, cm⁻¹, 3059 (Ar-CH), 2956–2869 (alkyl CH), 1401 (N=N), 1223 (C-O-C). UV-vis (THF): λₘₐₓ, nm (log ε) 344 (5.16), 498 (3.43), 723 (4.79). MS (MALDI-TOF): m/z 1724.321 [M]+.

RESULTS AND DISCUSSION

Synthesis and characterization

Peripheral tetra-substituted metal-free and metallo-phthalocyanine complexes were synthesized according to the route shown in Scheme 1. The synthesis of 4-[2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy] phthalonitrile (1) was accomplished in 47% yield through
base-catalyzed nucleophilic substitution reaction of 4-nitrophthalonitrile with 2,6-dimethyl-4-(4-tert-butylphenylazo)phenol using dry K₂CO₃ as the base in dry DMF (Scheme 1). For synthesis of compound 1, we used the diazotization reaction between 4-tert-butyl-anilin and sodium nitrite followed by azo coupling reaction with 2,6-dimethylphenol [33].

Spectral investigations of the dinitrile derivative (1) show good agreement with proposed structures. In the FT-IR spectrum of compound 1, aromatic CH, alkyl CH, azo group (N=N), and C-O-C stretching vibrations appeared at 3075–3043, 2961–2865, 1465, and 1243 cm⁻¹, respectively. In addition, the characteristic vibration of the C≡N appears at 2230 cm⁻¹ as a sharp peak. In ¹H NMR analysis of 1 in d-acetone, aromatic protons appeared at 8.05, 7.89, 7.79, 7.66, 7.60, 7.39 ppm as a doublet, doublet, doublet, doublet, singlet and doublet, respectively. The CH₃ protons were observed at 2.26 and 1.40 ppm as singlets, respectively. In ¹³C NMR spectrum of compound 1 in d-acetone showed the presence of aromatic carbons atoms at 160.70, 154.88, 151.56, 150.50, 149.80, 131.99, 126.20, 123.66, 122.46, 120.26, 119.98, 117.73 and 108.62 ppm, respectively. The nitrile carbons appeared at 115.53 and 115.09 ppm. The aliphatic carbon and CH₃ carbons were respectively. The metal-free phthalocyanine (2) showed an additional absorption band at 3288 cm⁻¹ assigned to the NH stretching vibrations.

The MALDI-TOF mass spectra showed the molecular peaks at m/z 1636.036 [M]+ for 2, m/z 1700.052 [M+1]⁺ for 3, m/z 1692.0 [M]+ for 4, m/z 1697.548 [M]+ for 5 and m/z 1724.321 [M]+ for 6.

Ground state electronic absorption spectra

Electronic absorption spectra of phthalocyanine complexes (2–6) in THF are presented in Fig. 1. In the UV-vis absorption spectra of all metallophthalocyanines (3–6), the Q-band absorptions were observed as single bands at 679, 667, 680 and 723 nm, respectively. The metal-free derivative 2 gave double Q bands at 670 and 701 nm as a result of the D₂h symmetry. A strong absorption band, seen in every spectrum at around 340 nm, was clearly indicative of azo groups of the chromophore system (Fig. 1) [29, 35]. The Soret bands (B bands) of phthalocyanines 2–6 overlapped with the strong absorption of azo groups (Fig. 1).

In the UV-vis absorption spectra, the Q-band absorptions for complexes 2–4 increased in the following order: CoPc < ZnPc < CuPc < MnPc. The different behavior of 3–4 should be attributable to the different kind of central metal. The Q-band of MnPc (6) was red shifted by 43–56 nm compared to the Q-band of the other metallophthalocyanines (3–5). The oxidation state of Mn in the complex with Pcs is +3, whereas the other metal Pcs (3–5) are in oxidation state +2. Moreover, the absorption band observed at 498 nm for 6 was interpreted as a charge transfer absorption (phthalocyanine → metal, LMCT) [36–38].

Fluorescence spectra

The fluorescence behavior of 2 and 3 were studied in THF upon excitation at the 608 nm Q-band vibrations for 2 and excitation at the 615 nm Q-band vibration for 3.

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Fig. 1. UV-vis spectra of 1–6 in THF (1 × 10⁻⁵ M)
Figure 2 shows the fluorescence emission and excitation spectra for 2 and 3. Fluorescence emission peaks were observed at 720 nm for 2 and 700 nm for 3 (Table 1). The observed Stokes shifts of 2 and 3 were about ~20 nm. The observed Stokes shifts were typical of Pcs [18]. The excitation spectrum of 2 has two shoulders in the Q band region and an emission maximum of 2 appears at lower energy than those of the corresponding MPc (3). It means that metal-free Pcs shows red shift in emission maxima compared to MPcs because of symmetry lowering [39]. The closeness of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for 3 suggest that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF.

Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method (Eq. (1)) [41]:

$$\Phi_F = \Phi_F(\text{Std}) \left(\frac{F\text{Std} \eta^2}{F\text{Std} A^2 \eta^2}\right)$$  \hspace{1cm} (1)

where $F_{\text{Std}}$ and $F$ are the areas under the fluorescence curves of standard Pc and studied Pc, respectively. $A_{\text{Std}}$ and $A$ are the respective absorbance of the standard and sample at the excitation and $\eta_{\text{Std}}$ and $\eta$ are the refractive indices of solvents used for the standard and sample, respectively. The unsubstituted ZnPc was used as a standard in DMSO ($\Phi_F = 0.20$) [40]. Both the standard and the sample were excited at the same wavelength. Natural or radiative lifetimes ($\tau_o$) were calculated using PhotochemCAD program which uses the Strickler–Berg equation [42]. Finally, the fluorescence lifetimes ($\tau_F$) were calculated using the following equation (Eq. (2)):

$$\Phi_F = \frac{\tau_F}{\tau_o}$$  \hspace{1cm} (2)

The fluorescence quantum yields ($\Phi_F$) of 2 and 3 are given in Table 2. The measured fluorescence quantum yields for 2 and 3 were lower than those for standard ZnPc [40]. This implies that the presence of peripheral 2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy substituents caused some fluorescence quenching of the parent 2 and 3. The $\tau_F$ values of 2 and 3 (1.05 and 1.17 ns, respectively) are a little lower compared to standard ZnPc [43], suggesting some quenching by substitution. The natural radiative lifetime ($\tau_o$) and the rate constants for fluorescence ($k_F$) values of 2 and 3 are also given in Table 2. The $k_F$ values of 2 and 3 are higher than standard ZnPc.

### Fluorescence quenching studies by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on studied Pcs (2 and 3) were achieved by the addition of different concentrations of BQ to a fixed concentration of the Pcs, and the sample was excited at the same wavelength. The observed Stokes shifts of 2 and 3 were about ~20 nm. The observed Stokes shifts were typical of Pcs [18]. The excitation spectrum of 2 has two shoulders in the Q band region and an emission maximum of 2 appears at lower energy than those of the corresponding MPc (3). It means that metal-free Pcs shows red shift in emission maxima compared to MPcs because of symmetry lowering [39]. The closeness of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for 3 suggest that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF.

Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method (Eq. (1)) [41]:

$$\Phi_F = \Phi_F(\text{Std}) \left(\frac{F\text{Std} \eta^2}{F\text{Std} A^2 \eta^2}\right)$$  \hspace{1cm} (1)

where $F_{\text{Std}}$ and $F$ are the areas under the fluorescence curves of standard Pc and studied Pc, respectively. $A_{\text{Std}}$ and $A$ are the respective absorbance of the standard and sample at the excitation and $\eta_{\text{Std}}$ and $\eta$ are the refractive indices of solvents used for the standard and sample, respectively. The unsubstituted ZnPc was used as a standard in DMSO ($\Phi_F = 0.20$) [40]. Both the standard and the sample were excited at the same wavelength.

Natural or radiative lifetimes ($\tau_o$) were calculated using PhotochemCAD program which uses the Strickler–Berg equation [42]. Finally, the fluorescence lifetimes ($\tau_F$) were calculated using the following equation (Eq. (2)):

$$\Phi_F = \frac{\tau_F}{\tau_o}$$  \hspace{1cm} (2)

The fluorescence quantum yields ($\Phi_F$) of 2 and 3 are given in Table 2. The measured fluorescence quantum yields for 2 and 3 were lower than those for standard ZnPc [40]. This implies that the presence of peripheral 2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy substituents caused some fluorescence quenching of the parent 2 and 3. The $\tau_F$ values of 2 and 3 (1.05 and 1.17 ns, respectively) are a little lower compared to standard ZnPc [43], suggesting some quenching by substitution. The natural radiative lifetime ($\tau_o$) and the rate constants for fluorescence ($k_F$) values of 2 and 3 are also given in Table 2. The $k_F$ values of 2 and 3 are higher than standard ZnPc.
Table 2. Photophysical and photochemical parameters data of studied Pcs (2 and 3) in THF

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$\Phi_f$</th>
<th>$\tau_f$ (ns)</th>
<th>$\tau_o$ (ns)</th>
<th>$k_F$ (s$^{-1}$) ($\times 10^8$)$^a$</th>
<th>$K_{SV}$</th>
<th>$k_q$ ($\times 10^{10}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.18</td>
<td>1.05</td>
<td>5.82</td>
<td>1.72</td>
<td>94.24</td>
<td>8.97</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>1.17</td>
<td>7.32</td>
<td>1.37</td>
<td>119.71</td>
<td>10.2</td>
</tr>
<tr>
<td>ZnPc</td>
<td>0.20$^b$</td>
<td>1.22$^b$</td>
<td>6.80$^b$</td>
<td>0.15$^b$</td>
<td>31.9</td>
<td>2.61</td>
</tr>
</tbody>
</table>

$^a k_F$ is the rate constant for fluorescence. Values calculated using $k_F = \Phi_f/\tau_F$.

$^b$ Reference [40].

and the concentrations of BQ in the resulting mixtures were $0, 0.01, 0.02, 0.03, 0.04$ and $0.05$ M, respectively. The fluorescence spectra of studied Pcs (2 and 3) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation [44]:

$$\frac{I_0}{I} = 1 + K_{SV}[BQ]$$

(3)

where $I_0$ and $I$ are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. $[BQ]$ is the concentration of the quencher and $K_{SV}$ is the Stern–Volmer constant which is the product of the bimolecular quenching constant ($k_q$) and the $\tau_f$ and is expressed in Eq. (4):

$$K_{SV} = k_q \times \tau_f$$

(4)

The ratios of $I_0/I$ were calculated and plotted against $[BQ]$ according to Eq. (4), and $K_{SV}$ is determined from the slope.

The fluorescence quenching of studied Pcs (2 and 3) by BQ in THF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions [45]. Figures 2 and 3 show fluorescence emission spectral changes of 2 and 3 on addition of different concentrations of BQ, respectively. The Stern–Volmer plots for studied Pcs (2 and 3) have straight lines; depicting diffusion controlled quenching mechanisms (Figs 3 and 4). The slope of the plots shown at inset Figs 3 and 4 gave $K_{SV}$ values, given in Table 2. The bimolecular quenching constant ($k_q$) values for the BQ quenching of studied Pcs (2 and 3) are also given in Table 2. The $K_{SV}$ values of the studied Pcs (2 and 3) are higher than unsubstituted ZnPc. These results can be derived from the steric effect of the substituents of the Pcs [46]. The observed $k_q$ values of the studied Pcs (2 and 3) are higher than unsubstituted ZnPc.

Electrochemical properties

The redox behaviors were studied by cyclic and square wave voltammetry in dried THF using 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte on a glassy carbon working electrode (GCE). Due to the poor solubility of phthalocyanines in CH$_2$Cl$_2$, DMF and DMSO, their electrochemical measurements were carried out only in THF. Figure 5 shows the cyclic and square wave voltammograms for 2, 3, 4, 5 and 6, and the corresponding redox potentials are summarized in Table 3.
Under these solution conditions, metal-free phthalocyanine 2, zinc phthalocyanine 3 and copper phthalocyanine 5 exhibit two one-electron oxidations and three reductions (Fig. 5), all of which are attributed to the removal/addition of one electron from/to the ligand-based orbitals of phthalocyanine [47–49]. Reduction potentials of 3 and 5 shift to negative regions when compared with 2 due to the effective nuclear charge differences between the free-base and metal-containing centers of the phthalocyanine ring. Cobalt phthalocyanine 4 shows two reduction couples at $E_{1/2} = -0.76$ V and $-1.35$ V and three one electron oxidation couples at $E_{1/2} = 0.64$, 1.02 and 1.16 V. The first reduction peak can be assigned to be the reduction of the cobalt and the second peak can be assigned to be the reduction of the phthalocyanine ring [50–52]. Manganese phthalocyanine 6 shows three reduction couples at $E_{1/2} = -0.03$ V, $-0.89$ V and $-1.32$ V and one oxidation at 0.63 V. The first and second reduction peaks can be assigned to be the reduction of the manganese and the third peak can be assigned to be the reduction of the phthalocyanine ring [53–57]. However, the last reductions of 2, 3, 4, 5 and 6 could be a multiple electron reduction of the phthalocyanine and four azobenzene-spacer moieties at $-1.34$, $-1.30$, $-1.35$ and $-1.42$ and $-1.32$ V, respectively [31, 49, 58, 59].

**CONCLUSION**

In the present study, azo group modified phthalocyanines bearing 2,6-dimethyl-4-(4-tert-butyl-phenylazo)phenoxy groups have been synthesized and characterized. The studied metal free and zinc phthalocyanines have lower fluorescence quantum yields and shorter lifetimes when compared to unsubstituted zinc Pc in THF. The fluorescence of metal-free and zinc phthalocyanines are effectively quenched by 1,4-benzoquinone in THF. The electrochemical properties of the complexes are also carried out. Metal-free, zinc and copper phthalocyanines give ring-based redox processes, while cobalt and manganese phthalocyanine complex give both metal- and ring-based redox processes.

**Acknowledgments**

This work was supported by the Research Fund of the Istanbul Technical University.

**REFERENCES**

NOVEL PHTHALOCYANINES CONTAINING AZO CHROMOPHORES; SYNTHESIS, CHARACTERIZATION, PHOTOPHYSICAL APPLICATIONS.
INTRODUCTION

One of the most important cornerstones in tetrapyrrolic macrocyclic system is porphyrazine [1]. Porphyrazines are similar to phthalocyanines, so they can also be used in similar applications. In contrast, the similarities among porphyraines and their derivatives such as aminoporphyraines, porphyrinols and porphyrainol thiolates have been less studied since their first synthesis, which took place almost 60 years ago [2–4]. Porphyraines have found vast applications in diverse areas such as industrial dyes and pigments, electrocatalysts, electrochromic displays, PDT applications, chemical sensors, Langmuir–Blodgett films, liquid crystals and non-linear optics, including their application in material science [5–7]. The first synthesis of crown-fused porphyraines has been accomplished by the groups of Hoffman and Nolte [8–10]. Porphyraine derivatives, which contain soft sulfur donor atoms, play an important role in affecting the solid-state interactions, and the sulfur atoms in the macrocyclic unit also give

ABSTRACT: New metalloporphyraines (MgPz, ZnPz) containing peripheral tetrasubstitutions derived from 7,8-dihydro-6H,14H,19H-dibenzo[b]j[1,12,5,8]-dioxadithiacyclopentadecine-16,17-dicarbonitrile (6) have been synthesized by a multistep reaction sequence and characterized. Compound 6 has been prepared by the reaction of 1,3-di(2-bromomethyl phenoxy) propane (3) or 1,3-di(2-iodomethylphenoxy) propane (4) which were prepared via bromination or iodination of 2-[3-(2-hydroxymethylphenoxy) propoxy]-phenyl] methanol (2) and cis-1,2-dicyano-1,2-ethylenedithiolate (5). The novel magnesium porphyraine was prepared by the cyclotetramerization reaction of 6 with magnesium butoxide. The one-step synthesis of porphyrainato zinc complex has been achieved without a reaction sequence by using dicyano compound (6) and zinc butoxide. The prediction of the geometry optimization, normal mode frequencies, 1H, 13C NMR, UV absorption spectra, chemical shifts, electronic properties and NBO analysis of the compound were examined by using B3LYP method with a 6-31G(d,p) basis set. These novel compounds were characterized by a combination of elemental analysis, 1H, 13C NMR, FT-IR, UV-vis and MS spectral data. An X-ray crystal structure of dicarbodinitrile compound (6) was also investigated.

KEYWORDS: mixed-donor macrocycle, porphyraine, template reaction, green chemistry, X-ray investigation, computational chemistry.

SYNTHESIS, CHARACTERIZATION AND COMPUTATIONAL INVESTIGATION OF NOVEL METALLOPORPHYRAZINES CONTAINING 15-MEMBERED O₃S₂-DONOR MACROCYCLIC MOieties

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 27 November 2017
Accepted 19 December 2017

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the opportunity to bind soft transition metal cations [11–13]. In addition, the electron-withdrawing effect of the maleonitrile moiety may reduce the electron–donating ability of sulfur donors in macrocyclic units, and this kind of heteroatoms strongly perturb the porphyrinate grand state transition and shifting to visible-to-near-IR region [14].

The chemistry of macrocycles containing mixed-donor multidentate ligands and their cation complexation abilities has been explored extensively over the past 49 years [15–17]. Another rapidly emerging topic of chemical interest in recent years concerns the synthesis of polynucleating ligands and the coordination chemistry of these kinds of macrocycles [18, 19]. Mixed donor crowns such as O₂S₂ type may be considered to lie between the two macrocyclic categories, and their properties also tend to span those of each class. These kinds of macrocycles form stable complexes with heavy metal cations while their complexes with main group metal cations become less stable.

Density Functional Theory methods have been widely used to predict the properties of molecules and bulk materials at an atomic scale, and the developments in the methodological innovations, and \textit{ab initio} and DFT approaches have turned into an inter-disciplinary approach combining molecular sciences and chemistry [20]. It is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or electron lone pairs. DFT methods are extensively used in order to simulate the electronic spectra of metal complexes despite the fact that the most appropriate method to describe the ground state properties of compounds seems to be the multiconfigurational self-consistent-field one including relativistic effects. The most popular among them is the time-dependent DFT (TD-DFT) approach [21].

In the present study, we synthesized and characterized a novel metalloporphyrinate having symmetrically four 15-membered dioxadithia (O₂S₂) crown ether moieties. X-ray crystal structural analyses concerning dicyano compound has also been performed. In addition to the detailed synthesis procedures, we also theoretically investigated the geometry optimization of precursor dicyano compound (5), magnesium and zinc porphyrinazines by means of the B3LYP method with a 6-31G\((d, p)\) basis set.

**EXPERIMENTAL**

**General**

All reactions were carried out under an argon atmosphere using Schlenk techniques connected vacuum line. 1.5-Bis(2’-formylphenyl)-1.5-dioxapentane [22] and \textit{cis}-1.2-dicyano-1.2-ethylene dithiolate sodium salt [23] were synthesized according to the literature procedures. All solvents were freshly purified by standard procedures before use [24]. Anhydrous CH₃CN and DMF were obtained by a 4 Å molecular sieve activated under 500°C for 5 h. \textit{¹}H and \textit{¹³}C NMR were recorded on an Agilent NMR-vnms 400 and on a Varian Mercury Plus 300-MHz spectrometer using TMS as internal standard. Infrared spectra were recorded on a Perkin Elmer UATR Two spectrometer. Mass spectra were determined on a Bruker Daltonics Microflex Mass Spectrometer equipped with a nitrogen UV-Laser operating at 337 nm and Thermo TSQ Quantum Access Max. LC-MS/MS instruments. Electronic absorption spectra were recorded using a Shimadzu UV-1601 spectrophotometer. All measurements were in made a sealed 1 ml quartz cuvette. Elemental analysis were performed on a Costech ECS 4010 instrument. All products were dried under vacuum before analysis. The transition metal content of the porphyrinate was measured on a Perkin Elmer Analyst 700 Atomic Absorption Spectrometer by using the emission method (signal type) at \(\lambda = 285.2\) nm. Melting points were determined on an electrothermal apparatus and are uncorrected.

**X-ray crystallography**

The suitable crystals of the title compound were crystallized from ethanol at room temperature. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K\(_{α}\) radiation (\(\lambda = 0.71073\) Å) at \(T = 120\) (2) K. Absorption correction by multi-scan [25] was applied. The structure was solved by direct methods and refined by full-matrix least squares against F² using all data [26]. All non-H atoms were refined anisotropically. Aromatic and methylene H atoms were positioned geometrically at distances of 0.95 (aromatic) and 0.99 (CH₃) from the parent C atoms; a riding model was used during the refinement process and the \(U_{iso}\) (H) values were constrained to be 1.2 Ueq (for aromatic and methylene carrier atoms). The crystallographic data are given in Table 3.

**Theoretical calculations**

One of the most successful quantum chemistry tools in describing the ground state properties of compounds is hybrid density functional theory (DFT). B3LYP (Becke3-Parameter method for calculating that part of the molecular energy due to overlapping orbitals plus the Lee–Yang–Parr method of accounting for correlation) is one of the most popular DFT methods [20–21, 27]. The molecular structures of compound 6, \textit{MgPz} and \textit{ZnPz} were optimized to obtain the global minima at B3LYP/6-31g\((d, p)\) level. The \textit{¹}H and \textit{¹³}C NMR chemical shielding constants were calculated by applying the GIAO-B3LYP; the electronic structure and NBO analysis in gas phase
were also calculated using the same procedure. All calculations were performed by using the Gaussian 09 Revision C1 program [28]. In addition, GaussView 5.0.9 was used for visualization of the structure and simulated vibrational spectra [29].

Tables S2–S4 (Table S2 (LP-Compound 6), Table S3 (LP-MgPz) and Table S4 (LP-ZnPz), see Tables S2, S3 and S4 in the Supplementary information) show the intramolecular, rehybridization NBO analysis of compound 6 and metalloporphyrazines. NBO analysis supplies a capable method for studying intra- and intermolecular bonding and charge transfer in molecular systems [30]. The second order Fock matrix was fulfilled to interpret the donor–acceptor interactions in the NBO analysis [29]. For each donor and acceptor (j), the stabilization energy $E(2)$ associated with the delocalization $i \rightarrow j$ is estimated using Eq. 1

$$E(2) = \Delta E_{ij} = q_{i}F(i, j)2/(\varepsilon i - \varepsilon j)$$

where $q_{i}$ is the donor orbital occupancy, $\varepsilon i$ and $\varepsilon j$ are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element [31, 32]. The hyperconjugative $\sigma \rightarrow \sigma^{*}$ interactions play a substantial role. These interactions express the weak separation from a properly localized natural Lewis structure that forms the primary “noncovalent” effect [33]. NBO analysis was performed on the molecule at the B3LYP/6-31G (d, p) level in order to clarify the intra-molecular rehybridization and delocalization of electron density within the molecule [34].

**Synthesis**

**Synthesis of 2-[3-(2-hydroxymethyl-phenoxypropyloxy)-phenyl]-methylmethanol (2).** Water (2.7 mL) was poured into silica (5.42 g (70–230 mesh) 90 mmol) which was charged in a round-bottomed flask (100 mL) and the mixture was stirred to produce wet silica at room temperature. 1.5-Bis (2’-formylphenyl)-1,5-dioxa-pentane (I) (7.7 g, 27.1 mmol) was then added to the prepared wet silica and the reaction mixture was stirred for an additional 5 min. A fine powdered NaBH₄ (1.03 g, 27.1 mmol) was added to this mixture and then the reaction mixture was stirred for an additional 1 min at room temperature while the reaction was performed in an explosive manner and monitored by a thin layer chromatography (silica gel (chloroform:methanol) (98:2)). Then dichloromethane (30 mL) was added and stirred to this reaction mixture for 30 min at room temperature. At the end of this period, the mixture was filtered off and washed with dichloromethane (3 × 8 mL) and the combined solvents were dried over anhydrous Na₂SO₄. The pure product was obtained by column chromatography on silica gel using the mixture of chloroform:methanol (98:2) as eluent to give a colorless solid. Yield: 6.19 g (79%); mp. 95–96°C. ¹H NMR (300 MHz, CDCl₃): δ 7.30–7.28 (m, 4H, Ar-H), 6.96 (t, $J = 7.24$ Hz, 2H, Ar-H), 6.92 (d, $J = 7.89$ Hz, 2H, Ar-H), 4.67 (s, 4H, CH₂-OH), 4.24 (t, $J = 5.70$ Hz, 4H, CH₂O), 2.56 (s, 2H, OH), 2.35–2.31 (m, 2H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 156.48, 129.26, 128.94, 120.99, 111.28, 65.04, 61.70, 29.34. FT-IR (ATR), $\nu_{max}/cm^{-1}$: 3293, 3062, 3043, 3008, 2947–2880, 1602, 1590, 1493, 1451, 1236, 1139, 998, 744. MS (ESI): m/z 310.71 [M + Na – H]⁺. Anal. calcd. for C₂₀H₁₈O₅: C, 70.83; H, 6.94. Found: C, 70.72; H, 7.04.

**Synthesis of 2-[3-(2-bromomethylphenoxypropyloxy)phenyl]methanol (3).** To PBr₃ (24.36 g, 90 mmol) in dry diethyl ether (20 mL) was added dropwise a solution of 1,3-di(2-hydroxy-methylphenoxo)propane (2) (5 g, 17.35 mmol) in a mixture of diethyl ether (270 mL) and ethyl acetate (30 mL) in cryostate under argon atmosphere at -3°C. The mixture was stirred under the above mentioned condition for 10 min and then stirring was continued at room temperature for 70 h. At the end of this period, the mixture was evaporated to dryness under reduced pressure and the crude product was mixed with ethanol (100 mL). The mixture was filtered off and washed several times with diethyl ether and then dried in vacuo. The fine desired product was obtained by recrystallization from ethyl acetate. Yield: 3.15 g (43.85%): mp. 101–102°C. ¹H NMR (300 MHz, CDCl₃): δ 7.30 (t, $J = 8.05$ Hz, 4H, Ar-H), 6.94–6.89 (m, 4H, Ar-H), 4.57 (s, 4H, BrCH₂), 4.33 (t, $J = 6.06$ Hz, 4H, OCH₂), 2.41–2.38 (m, 2H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 156.75, 130.78, 130.29, 126.06, 120.6, 111.81, 64.61, 29.27. FT-IR (ATR), $\nu_{max}/cm^{-1}$: 3042, 2963–2879, 1599, 1494, 1466, 1454, 1314, 1290, 1244, 1221, 1197, 1144, 1065, 1045. MS (ESI): m/z 415 [M + H]⁺, 432 [M + H₂O]⁺, 452.92 [M + K]⁺. Anal. calcd. for C₂₁H₂₀Br₂O: C, 49.27; H, 4.34. Found: C, 49.41; H, 4.46.

**Synthesis of 2-[3-(2-iodomethylphenoxypropyloxy)phenyl]methanol (4).** A round bottomed flask which contains compound 2 (1.44 g, 5 mmol) and NaI (4.475 g, 29.85 mmol) in dry acetonitrile (100 mL) and which was fitted with a condenser was evacuated refilled three times with argon and connected to the vacuum line. To a solution of the corresponding alcohol, bromomethylsilsane (4.54 g, 29.7 mmol) was added dropwise while continuously stirring. The reaction mixture was stirred at room temperature for 20 min and monitored by thin layer chromatography (silica gel (chloroform: methanol) (95:5)). A mixture of dichloromethane and water (100 mL (1:1)) was added to the reaction mixture and the organic phase was separated and then washed with water (50 mL), Na₂S₂O₃ solution (50 mL, 10%), brine and water and then dried over MgSO₄. The organic phase was evaporated to dryness under reduced pressure yielding a pale yellow solid that was purified by column chromatography on silica gel using the mixture of hexane: chloroform (3:2) as eluent to give a pale yellow solid. Yield: 2.15 g (84.64%): mp. 99–100°C. ¹H NMR (300 MHz, CDCl₃): δ 7.30 (d, $J = 7.43$ Hz, 2H, Ar-H), 6.92 (d, $J = 8.22$ Hz, 2H, Ar-H), 6.87 (t, $J = 7.43$ Hz, 2H, Ar-H), 4.67 (s, 4H, CH₂-OH), 4.24 (t, $J = 5.70$ Hz, 4H, CH₂O), 2.56 (s, 2H, OH), 2.35–2.31 (m, 2H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 156.48, 129.26, 128.94, 120.99, 111.28, 65.04, 61.70, 29.34. FT-IR (ATR), $\nu_{max}/cm^{-1}$: 3293, 3062, 3043, 3008, 2947–2880, 1602, 1590, 1493, 1451, 1236, 1139, 998, 744. MS (ESI): m/z 310.71 [M + Na – H]⁺. Anal. calcd. for C₂₀H₁₈I₂O: C, 58.62; H, 4.23. Found: C, 58.69; H, 4.26.
4H, Ar-H), 4.49 (s, 4H, ICH₃), 4.37 (t, J = 4.70, 4H, OCH₂), 2.45 (m, 2H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 156.44, 129.69, 127.30, 120.68, 111.81, 64.66, 29.45, 1.59. FT-IR (ATR), νmax/cm⁻¹: 3077, 3055, 3029, 2926–2927, 1597, 1493, 1451, 1247, 1124, 1044, 745. MS (ESI): m/z 509 [M + H⁺]. Anal. calcd. for C₁₇H₁₈O₂I₂: C, 40.15; H, 3.54. Found: C, 40.37; H, 3.38.

Synthesis of 7,8-dihydro-6H,14H,19H-dibenzo[bj][1,12,5,8]dioxadithiacyclo pentadecene-16,17-dicarboxonitrile (6).

Method A. cis-1,2-Dicyano-1,2-ethylenedithiolate sodium salt (5) (0.93 g, 5 mmol) and compound 3 (2.07 g, 5 mmol) were dissolved in dry DMF (40 mL), and these solutions were placed in two syringes. The contents of the syringes were added dropwise (a rate of 0.5 cm³ h⁻¹) as synchronized under an argon atmosphere at 45°C for 80 h by using a syringe pump. The reaction mixture was stirred at this temperature for a further 4 days and monitored by thin layer chromatography (silica gel (chlororm: methanol) (98:2)). At the end of this period, the reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue was partitioned between water and chloroform (100 mL (1:1)). The combined organic phases were dried (MgSO₄) and then the mixture was further heated at reflux temperature under argon atmosphere. The reaction mixture was refluxed and stirred for 24 h until a blue suspensions were cooled to room temperature, filtered and washed with methanol. The solution was concentrated in vacuo and the residue was purified by column chromatography over silica gel (hexane: chloroform) (2:1) to obtain a dark blue solid.

MgPz: Yield: 0.04 g (17.12%), mp > 300°C. ¹H NMR (300 MHz, CDCl₃): δ 7.33 (s, 8H, Ar-H), 7.12 (s, 10H, Ar-H), 6.95 (s, 8H, Ar-H), 6.61 (s, 6H, Ar-H), 4.40–4.29 (m, 32H, OCH₂). ¹³C NMR (75 MHz, CDCl₃): δ 157.72, 131.64, 130.23, 124.60, 123.70, 121.69, 114.50, 113.20, 67.25, 35.62, 29.93. FT-IR (ATR), νmax/cm⁻¹: 3062, 3038, 2958–2868, 2204 (C=C), 1597, 1493, 1452, 1315, 1291, 1242, 1187, 1158, 1094. MS (ESI): m/z: 395.08 [M + Na⁺]. Anal. calcd. for C₈₄H₇₂N₈O₈S₈Mg: C, 63.00; H, 4.50; N, 7.00. Found: C, 63.16; H, 4.69; N, 6.83.

ZnPz: Yield: 0.08 g (21%). Mp > 300°C. ¹H NMR (300 MHz, CDCl₃): δ 7.23 (m, 24H, Ar-H), 6.89 (m, 8H, Ar-H), 4.24–4.16 (m, 32H, OCH₂). ¹³C NMR (75 MHz, CDCl₃): δ 156.74, 144.61, 130.64, 129.27, 123.62, 120.71, 113.51, 66.26, 34.83, 29.95. FT-IR (ATR), νmax/cm⁻¹: 3062, 3031, 2952–2866, 2204 (C=C), 1598, 1490, 1452, 1315, 1291 (C=N), 1187, 1158, 1094. MS (ESI): m/z: 395.08 [M + Na⁺]. Anal. calcd. for C₈₄H₇₂N₈O₈S₈Zn: C, 61.40; H, 4.38; N, 6.82; Zn, 3.99. Found: C, 61.25; H, 4.56; N, 7.62; Zn, 4.16.

RESULTS AND DISCUSSION

Synthesis

Salicylaldehyde as a starting material underwent an etherification reaction with 1,3-di-bromopropane in high yield using a well-known synthetic route as outlined in Scheme 1. There are several reports for the synthesis of 1,5-bis(2-benzyl alcohol)-1,5-dioxapentane (2). One of
them mentions the compound being prepared by using a nucleophilic substitution reaction of 2-hydroxy benzyl alcohol and 1,3-dibromopropane. Compound 2 has been previously obtained in considerable amount yield via the reduction reaction of aldehyde groups by sodium borohydride [35]. Recently, wet silica as an inexpensive and readily available reagent has been frequently used for some organic syntheses such as cleavage of azomethine moieties or oxidation of alcohols [36]. The present reduction reaction is high-yielding compared with the above-mentioned reduction reactions and should prove to be extremely productive for synthesis. This reduction reaction, carried out in green chemistry media, has received great attention with advantages such as energy savings, avoidance of solvent waste and a short reaction period. The rate of reduction of aldehyde groups was dramatically accelerated and the reduction procedure was completed in 1 min (Fig. 1). ¹H, ¹³C NMR, FT-IR and MS spectral data (see the Supplementary information, Fig S1–S3) concerning structural characteristics of this compound are in accordance with the proposed structure and with the literature [37].

The alcohol groups of compound 2 were substituted by bromine moieties through use of boron tribromide to give [2-{(2-bromomethylphenoxy)propoxy}phenyl] methanol (3). This product has recently been prepared from compound 2 by means of a similar one-step procedure, but no experimental details and characterization have been furnished [38]. Phosphor tribromide in dry diethyl ether was added dropwise to a cooled (-3°C) dry diethyl ether/ethyl acetate solution. After stirring at this temperature for 10 min and letting stand a further 70 h at room temperature, the bromination derivative (3) was isolated as a yellow colored solid and then purified by column chromatography in 43.85% yield. The ¹H NMR spectrum of 3 showed the characteristic emerged signal at δ = 4.57 ppm related to bromide substitution. The other ¹H NMR signals of 3 closely resemble those of the starting compound (2). In the proton-decoupled ¹³C NMR spectrum of this compound, the signal for the
bromination of two hydroxy group carbons at $\delta = 29.27$ ppm indicated the substitution reaction was completed (Figs S4–S5). The resonances for the benzylic alcohol groups of precursor compound at 3293 cm$^{-1}$ in the FT-IR spectrum of 2 were not observed in compound 3. The absence of these stretching vibrations also indicate the displacement of hydroxy groups with bromines. The mass spectrum of this compound (Fig. S6) shows the molecular ion peak as $m/z = 415$ [M + H]$^+$, and the other, bigger fragments are observed together with the corresponding leaving groups such as 333.0498 [M–Br–1]$^+$ and 253.1225 [M–2Br–1]$^+$.

Compound 4 was prepared by reacting NaI with precursor benzylic alcohol (2) in the presence of bromotrimethyl silane. The iodine derivative of 2 was obtained in a good yield (84.64%) in a very convenient reaction route and period. Iodination of different types of alcohols were investigated in the presence of KI/BF$_{3}$, Et$_{3}$O [39], Ph$_{3}$/I [40] or trimethyl silyl chloride [40]. The choice of this route to obtain iodine derivative was essentially easier, giving an advantage in terms of yield, short reaction time and easy work-up. In addition, the macrocyclization reaction with cis-1,2-diethylene dithiolate sodium salt is moderately easier than other halogen derivatives of 2. The $^1$H NMR spectrum of 4, the disappearance of OH chemical shifts belonging to the precursor compound (2) and, along with the appearance of the resonance at $\delta = 4.49$ ppm corresponding to CH$_2$I moieties, support the formation of iodination reaction. A similar change of carbon resonance of $^{13}$C NMR spectrum of this compound is due to the displacement of hydroxy groups with iodides (see in the Supplementary information, Figs S7–S8). The absence of O–H resonances at 3293 cm$^{-1}$ in FT-IR spectrum of the same compound also indicate the displacement of hydroxy groups with iodine. The occurrence of the (M + H) peak at $m/z = 509$ in the ESI mass spectrum of this compound (see Fig. S9) indicated the formation of the desired compound.

Dicyano compound (6) was synthesized via two similar routes. In one of them, the target compound was prepared by a condensation reaction for macrocyclization from dibromo derivative (3) with cis-1,2-dicyano-1,2-ethylene dithiolate (5) under high dilution conditions. In the other, the reaction of diiodo derivative (4) and one equivalent of compound 5 in refluxing acetonitrile gave the product (6) in 33.6% yield as pale yellow crystals after column chromatography (silica gel (chloroform: methanol) (98:2)). In the $^1$H NMR spectrum of 6, the resonance signals for the OCH$_3$ and SCH$_3$ protons appeared at $\delta = 4.27$ and 4.23 ppm as combined signals, respectively, which indicates the formation of the expected macrocycle Fig. 2. The chemical shifts of the other protons were similar to those of the corresponding precursor. In the $^{13}$C NMR spectrum of this compound (Figs S10–S11), the signal for the C≡N carbon atoms appears at $\delta = 113.20$ ppm, which are similar to those of the known dicyano compounds [42].

![Fig. 1. The reduction process of compound 1](image)

![Fig. 2. The structure of compound 6](image)

According to the FT-IR spectrum of 6, the characteristic vibrations for the C≡N groups at 2204 cm$^{-1}$ supported the formation of the macrocycle. The ESI mass spectrum of this compound (6) also confirmed the proposed structure, with the molecular ion peak (Fig. S12) easily identified at $m/z = 395.0871$ [M + H]$^+$. This 15-membered O$_2$S$_2$-macrocycle was also characterized by single-crystal X-ray crystallography technique. Pale yellow single crystals of this compound suitable for X-ray analysis were obtained by column chromatography.

In the synthesis of metalloporphyrinazines (MgPz, ZnPz), equivalent amounts of dicyano compound (6) were reacted with Mg(OBu)$_2$ or Zn(OBu)$_2$ [43] in
n-butanol under reflux for 24 h. At the end of this period, novel solid products were obtained and purified by column chromatography using hexane/chloroform (2:1) as the eluent to afford dark blue target compounds in 380–395 nm which is known as the Soret band [45]. These characteristic bands strongly resemble those of symmetrical porphyrazine analogs [46]. Metallo-derivatives of porphyrazines have D₄h symmetry for this reason: their π₁* and π₂* orbitals are doubly degenerate. The above-mentioned single sharp bands relate to the π₁ and π₂ → π₁.2* transition [47]. The Soret transitions at known π → π* regions in porphyrazines are assigned to an a₁u → eg transition. The broad absorption at the 500–510 nm region should be assigned to the n→π* transitions of the nonbonding electrons of the peripheral sulfur atoms and meso nitrogen atoms which are associated with the porphyrazine core π system [48].

Some of the most important parameters in molecular orbital theory are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies. The electron conductivity and the spectroscopic properties of the molecules show the characteristics of the energy gap between the HOMO–LUMO orbitals.

According to Koopmans’ theorem [49], ionization potential and electron affinity of a species can be defined...
Fig. 3. The correlation graphs between the experimental and calculated $^{13}$C and $^1$H chemical shifts for compound 6 calculated by using B3LYP/6-31G($d, p$) level in gas phase and chloroform.

Fig. 4. The molecular electrostatic potential surface map calculated at B3LYP/6-31G ($d, p$) level of the compounds: (a) Compound 6, (b) MgPz and (c) ZnPz.
with respect to frontier molecular orbital energies. These are as in the following respectively: \( I = -E_{\text{HOMO}} \) and \( A = -E_{\text{LUMO}} \). Physical and/or chemical characteristics such as the global hardness \( \mu = (I-A)/2 \), the global softness \( S = 1/(2\eta) \), the electronic chemical potential \( \mu = -(I + A)/2 = -\chi \) (\( \chi \) is electronegativity) and the global electrophilicity index \( \omega = \mu^2/(2\eta) \) measuring the affinity of species to attract electrons could be commonly defined with these quantities [25].

One of the electronic characteristics reflecting the ability for electrons to jump from the highest occupied to the lowest unoccupied molecular orbital and the ability for the species to participate in the chemical reactions to some extent is the HOMO–LUMO gap. A high chemical stability is characterized by a large gap value. The electronic gap values calculated at B3LYP/6-31G \((d,p)\) level are 3.86 eV for compound 6, 2.20 eV for MgPz and 2.22 eV for ZnPz as seen in Table 2. The optic gap values for compound 6, MgPz and ZnPz are 3.79, 1.87 and 1.88 eV, respectively. At the same time, these energy gap values are indicators of the existence of charge transfer in the molecules.

The high electron density is mostly localized on the N atom as can be seen in Figs 5 and 7. Also, the calculated self-consistent field (SCF) energies of compound 6, MgPz and ZnPz are calculated to be -1867.355, -7669.8215 and -9248.8154 a.u., respectively. Associated with partial charge and electronegativity plots, the electrostatic potential map demonstrates the distribution of charge of compounds in terms of the difference between positive and negative charge [33]. The shape and electrostatic potential values are shown by the electrostatic potential map of the surface presented in molecular size. Different colors on the surfaces represent different values of electrostatic potentials. While the regions carrying the most electronegative potentials, i.e. electron rich regions are represented by the color red, regions of most positive potentials, i.e. electron-poor regions are represented by the color blue. Moreover, zero potential is represented by the color green. The following order shows the increase of the aforementioned potentials: red < orange < yellow < green < blue. The darkest blue region means the strongest attraction whereas the darkest red means the strongest repulsion. However, the negative (red) regions represent the electrophilic reactivity and the positive (blue) regions represent nucleophilic reactivity.

The electrostatic potential map of compound 6, MgPz and ZnPz changes are reported in Fig. 4. In the

![HOMO and LUMO](image)

**Fig. 5.** The HOMO and LUMO energies for compound 6 with B3LYP/6-31G \((d,p)\) basis set in gas phase

![UV-vis spectra](image)

**Fig. 6.** The UV-vis spectra of MgPz and ZnPz \((1 \times 10^{-5} \text{ M in chloroform})\)
electrostatic potential map of MgPz, the electrophilic reactivities at -4.0e-2a.u. and nucleophilic reactivities at 8.0e-2a.u. are starting to become active. Similarly, for the ZnPz is starting to become active the nucleophilic reactivities at 4.135e-2a.u. The MgPz complex is seen to be planar and more stable than ZnPz complex. The energy optic gaps of MgPz (ΔE_{LUMO-HOMO} = 1.88 eV) and ZnPz (ΔE_{LUMO-HOMO} = 1.88 eV) have been calculated to be significantly smaller than compound 6 (ΔE_{LUMO-HOMO} = 3.79 eV).

![Fig. 7. The HOMO and LUMO energies for MgPz and ZnPz with B3LYP/6-31G (d, p) basis set in gas phase](image)

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which could be attributed to the introduction of electron-donating sulfur atoms at the positions of porphyrazine. The HOMO–LUMO value could become smaller than compound 6, especially when sulfur moieties at the positions in porphyrazine destabilize the HOMO energy [50]. LUMO electrons are mostly localized on double- and triple-bonded groups like C=C and C≡N as shown in Fig. 5 for compound 6. In addition, it is seen that the HOMO electrons are mostly localized on the aromatic and thia ether groups whereas the LUMO electrons of MgPz (Fig. 7) are mostly localized on C–N moieties, but the HOMO electrons are mostly localized on carbon and sulfur atoms which are linked with pyrrole units. The other electronic properties of the molecules are also given in Table 2.

For the MgPz compound as seen from Fig. 8a, the electron–donations from LP1 (N9), LP1 (N10), LP1 (N36) and LP1 (N52) to the antibonding acceptor σ*(C8–N57), σ*(N54–C58), σ*(C5–N54), σ*(C34–N56), σ*(C35–N56), σ*(N55–C59), σ*(N55–C60) and σ*(N57–C173), respectively, have 14.79 kcal/mol and give the structure a strong stabilization. In the σ*(C8–N57), σ*(N54–C58), σ*(C5–N54), σ*(C34–N56), σ*(C35–N56), σ*(N55–C59), σ*(N55–C60) and σ*(N57–C173) bonds, hybrids of the C and N atoms and bonds, gain 23.91% in s character 76.02% in p character (with hybrid orbital sp3.18). Similarly, for the ZnPz compound (Fig. 8b), LP1 (N9), LP1 (N10), LP1 (N36) and LP1 (N52) to the antibonding acceptor σ*(C8–N56), σ*(N53–C57), σ*(C5–N53), σ*(C34–N55),

Fig. 8. NBO. (a) MgPz. (b) ZnPz

Fig. 9. ORTEP-3 [3] drawing of the title compound with the atom-numbering Scheme- (Displacement ellipsoids are drawn at the 50% probability level)
Table 3. Crystallographic data

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X-ray structure

X-ray structural determination of the title compound confirms the assignments of its structure from spectroscopic data (Table 3). The molecular structure, along with the atom-numbering scheme, is depicted in Fig. 9, and the bond lengths and angles are within normal ranges. The selected bond lengths, bond angles and torsion angles and the hydrogen-bond geometry are given in Table S5. The average C–S bond lengths and C–S–C bond angles are 1.782 (6) Å and 102.6 (3)° (Fig. S5), respectively. The ligand cavities may play important roles in the complexations and metal-ion selectivities. The intramolecular S1…O2 (5.180 (3) Å), S1…C12 (5.899 (3) Å), S1…C11 (5.712 (3) Å), S1…C13 (5.707 (3) Å), S1…C18 (5.534 (3) Å), C4…C18 (6.184 (3) Å) C9…C18 (6.161 (4) Å) and C9…C19 (6.051 (4) Å) distances may indicate the hole sizes of the rings. The planar rings A (C4–C9) and B (C13–C18) are oriented at a dihedral angle of A/B = 78.69° (22°). In the crystal structure, the molecules are stacked along the a-axis and elongated along the b-axis (Table S5, Fig. S19).

Table S1 reports for the first time the selected X-ray data and the theoretical bond lengths, bond angles and torsion angles belonging to the compound 6 and MgPz computed via B3LYP/6-31G (d, p). These computed values help to understand the molecular structure of compound 6 and MgPz. For instance, the mean bond length of the N–C is measured as 1.141 Å, while it is computed as 1.165 Å for compound 6, and 1.336 Å for MgPz at the B3LYP/6-31G (d) level. Additionally, the mean length value of the S–C is measured as 1.742 Å while it is computed as 1.84 Å for compound 6, 1.82 Å for MgPz and 1.82 Å for ZnPz at B3LYP/6-31G (d, p) level. The mean bond angle of the C–C–C is measured as 102.6°, it is 102.2° for MgPz and 105.3° for ZnPz and for ZnPz at B3LYP/6-31G (d, p) level. The mean bond angle of the C–C–C is measured to be 115.4°, while it is calculated to be 114.9° for compound 6, 105.3° for ZnPz and 105.3° for MgPz. The mean bond angle of the N–C–C is measured to be 177.7° whereas it is 177.9° for compound 6, 124.9° for pyrrolic (aromatic) in MgPz and 123.9° for pyrrolic in ZnPz. As a result, it is seen that there is compatibility between experimental and theoretical results for characterizing the compounds.

CONCLUSIONS

In summary, the substituted porphyrazine derivatives containing 15-membered dioxa-dithia macrocyclic moieties have been synthesized in good yields. 7.8-dihydro-6H.14H.19H-dibenzo[bfj] [1]12.5.8]dioxa-dithiacyclopentadeciene-16.17-dicarbonitrile was used for the cyclotetramerization reaction in the presence of M(BuO)₂ to obtain metalloporphyrazines. The porphyrazino-zinc complex has been achieved through a one-step reaction by using ZnP(BuO)₃ as template agent.
in this study. Attempts to obtain a metal-free derivative of ZnPz could not be achieved. This result could be ascribed as due to zinc(II) porphyrizine complex being more stable than its magnesium analogs. In addition, the optimized conditions for the same reaction steps such as reduction (2) and iodination (4) reactions have been significantly achieved. 15-membered dioxa-thia macrocycle (6) was synthesized, and the X-ray structure of this compound showed that it crystallizes in the monoclinic system with a P2₁ space group.

The geometry optimization of dioxa-dithia macrocycle (6), magnesium and zinc porphyrizines were also examined by means of the B3LYP method with a the 6-31G (d, p) basis set. Figure 9 demonstrates the comparison of such X-ray data as bond lengths, bond angles and structure concerning macrocyclic compounds with theoretical results. For the first time, the theoretical calculation of such X-ray examined by means of the B3LYP method with a the 6-31G (d, p) level are reported in this study. The compatibility between experimental and theoretical results was identified to characterize the compounds in question. The HOMO and LUMO orbitals of compound 6, MgPz and ZnPz were also predicted as theoretical.

Macrocyclic precursor compound 6 and metalloporphyrizines containing symmetrically four macrocyclic units provide an opportunity of these compounds for heavy metals especially soft species extractions from water media to organic phase. However some steps of the synthesized macrocycle could be inside the green chemistry area.

Acknowledgments

The numerical calculations reported in this paper were partially performed at TUBITAK ULAKBIM High Performance and Grid Computing Center (TRUBA resources).

Supplementary information

The utilized experimental, materials, equipment, X-ray crystallography, theoretical calculations, ¹H, ¹³C NMR and mass spectra, tables and figure are supplied as supplementary information. This material is available free of charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml

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INTRODUCTION

Organic solar cells (OSCs), featuring solution processing, light weight and mechanical flexibility, have attracted immense attention in the past decades [1–4]. At present, the state-of-the-art power conversion efficiency (PCE) for fullerene-based bulk heterojunction (BHJ) OSCs achieved 11–12% [5–7]. In recent years, non-fullerene acceptors have attracted much attention because of their easily tunable molecular energy levels and excellent optical absorption properties [8, 9]. Recently [10], more than 13% PCE was obtained by blending a fluorinated π-conjugated polymer with a fluorinated fullerene-free small-molecule acceptor. In spite of these remarkable performances, the realization of solution-processed BHJ solar cells still poses a number of problems related to both the nature of the active materials and the fabrication process [11]. For example, the fine-control of phase separation and achieving high charge-carrier mobility in active layers are still very difficult with BHJ solar cells [2, 12, 13].

Mesogenic complementary absorbing dyads based on porphyrin and perylene units

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 5 December 2017
Accepted 20 December 2017

ABSTRACT: Five novel dyads, consisting of a tetraphenylporphyrine unit connected to a perylene monoimide diester unit via a flexible bridge -CONH-(CH2)n- (n = 4, 6, 8, 10 and 12), have been synthesized. Their structures were characterized by 13C and 1H nuclear magnetic resonance spectroscopy, infrared spectroscopy, mass spectrometry and elemental analysis. The UV-vis absorption spectra revealed these dyads have broad optical absorption in the ultraviolet and visible regions due to the complementary absorption of the two units. The differential scanning calorimetry traces and polarized optical microscopy textures showed all these dyads have columnar liquid crystal phases. Cyclic voltammetry revealed the highest occupied molecular orbitals of the dyads located on the porphyrin units, and the lowest unoccupied molecular orbitals located on the perylene units. In addition, these results were in agreement with that of the theoretical modeling. When excited at 423 or 473 nm, the photoluminescent emission spectra showed that the degree of fluorescence quenching of porphyrin units increased as the spacers became shorter. This quenching was ascribed to intramolecular photoinduced electron transfer, which also induced the dyad molecules to form the charge-separated states. The charge-separated molecules were further confirmed by the photocurrent response curves. These behaviors of broad absorption of the ultraviolet-visible light, yielding the charge-separated states of the molecules when excited and the formation of columnar liquid crystal phase made these dyads candidates for single-component photovoltaic active materials.

KEYWORDS: porphyrin, perylene, discotic liquid crystal, dyad, photoinduced electron transfer.
As another interesting strategy, electron donor–acceptor dyad, triad, multiad and block copolymer molecules or all-in-one molecules where the electron donor (D) and acceptor (A) units are covalently linked in a single molecule have been reported for their potential as photovoltaic materials [12, 14–19]. These single-component photovoltaic materials possess multifunctions such as light harvesting, exciton dissociation and electron and hole transport. Moreover, several major advantages, such as a considerable simplification of device fabrication, stabilization of the morphology of the active material, and efficient (or fast) charge separation can be expected in the single-component OSCs [11]. At present, the PCE for single-component OSCs has surpassed 2% [12, 15, 17], which is lower than that of BHJ solar cells. This is because the design of electron donor–acceptor molecules for efficient single-component OSCs is in fact difficult. Some important prerequisites for solar cell applications, such as strong and broad optical absorption, the energy level matching of the donor and acceptor units, the prevention of charge recombination and the efficient transport of the separated charges to the electrodes, need to be considered and balanced [11].

Wasielewski proposed that the ideal functional organic materials used in solar cells should have electron donor and acceptor building blocks covalently attached in a single molecule, as well as the ordered arrangement of these building blocks in the solid state [13]. So far, the first aspect has been investigated as conventional single-component photovoltaic materials, while the second one is still a challenge and makes slow progress. However, the use of self-assembly strategy offers the opportunity to achieve the ordered structure and improved charge carrier mobility in the solid state [20, 21].

Calamitic and discotic liquid crystals (DLCs), featuring long exciton diffusion length and high charge-carrier mobility, have been considered as a new generation of organic photovoltaics [22]. The conventional DLC molecules comprise a planar rigid core and several aliphatic chains, normally through ether, thioether, or ester bonds peripherally attached to the cores [23–25]. The majority of DLCs are thermotropic liquid crystals and have a strong tendency for columnar mesophase formation. Since there are strong π–π interactions between adjacent cores within the same column, the carrier mobility is up to 1 cm²·V⁻¹·s⁻¹ along the columnar axes [26, 27]. In addition, the peripheral side chains act as insulating layers, and the charge-carrier mobility is low in the direction perpendicular to the molecular column. Thus, the DLC materials exhibiting ordered columnar phases have application potential as one-dimensional charge carrier transport systems [28]. So far, the 4–8% PCE of bilayer solar cells and BHJ solar cells using DLC materials have been achieved [22].

The dyad, triad and multiad DLCs, containing D and A units and forming columnar phases, are an emerging single-component photovoltaic material. Since the so-called p–n heterojunction exists at the molecular level, these D–A DLCs possess fast intramolecular photoinduced electron transfer and form charge separated states [29–33]. Some D–A DLCs yield dual pathways along molecular columns to transfer electrons and holes [34, 35]. At present, the discogens used in these D–A DLCs are limited in triphenylene, anthraquinone, perylene and BODIPY derivatives [36–42].

To use a wider range of the solar spectrum, dyads based on porphyrin and perylene units were designed in this work. Porphyrins have flat heterocyclic structure and a delocalized π-electron system, and are excellent light-harvesting compounds [43]. Prophyrin based compounds have attracted great interest in the fields of photodynamic therapy [44, 45], dye-sensitized [46, 47] and BHJ solar cells [48, 49]. While the perylene derivatives, possessing excellent photochemical and thermal stability, high fluorescence quantum yield, and multiple positions for chemical modification, were attractive candidate materials for OLEDs [50, 51] and OSCs [52–54], and several others. Herein,
the dyads consisting of a tetraphenylporphyrin unit (absorption in the purple and yellow regimes) which was covalently linked to a perylene monoimide diester (PIE) unit (absorption in the green regime) were synthesized. The molecular structures of the dyads are shown in Fig. 1, denoted as \( \text{TPP-C}_n\text{-PIE} \) (\( n = 4, 6, 8, 10 \) and 12). The experimental results revealed that these dyads have broad optical absorption in the ultraviolet and visible region, and columnar liquid crystal phases as well.

**RESULTS AND DISCUSSION**

**Synthesis**

The synthetic routes are shown in Scheme 1. Tetrahexyl-perylene-tetracarbonylate (2) [55] and perylene-mono-anhydride-diester 3 [56] were synthesized in excellent yields according to the reports in the literature. Long chain aromatic aldehyde 5 [57] was prepared in quantitative yield, with no previous protection of the aldehyde moiety. The preparation of the porphyrin ester (8, \( \text{TPPE} \)) [58] was the key step towards asymmetric porphyrin derivative synthesis, which was obtained via the well-known Adler–Longo methodology [59]. The primary amine derivatives 9–13 were prepared by aminolysis reaction of 8 [60]. Since compounds 9–13 in solution were sensitive to air, they, without further purification, were condensed with 3 to give these dyads. In addition, the reference compound \( N\)-hexyl-perylene monoimide dihexyl esters (\( \text{PIE3} \)) was synthesized according to the previous report [33].

More specifically, the first step was the hydrolysis of perylene-3, 4, 9, 10-tetracarboxylic dianhydride (1) in basic aqueous solution to prepare the potassium perylene-3, 4, 9, 10-tetracarboxylate, then converted to 2 via an efficient phase-transfer catalysis method with methyl-triptycyl-ammonium chloride as a catalyst. Dihexyl-perylene-3, 4-anhydride-9, 10-dicarboxylate (3) was obtained as precipitate through acidic hydrolysis of 2 at one side in the mixed solvents of \( n \)-heptane and toluene. In the second step, 5 was prepared in quantitative yield via the alkylation of 4-hydroxybenzaldehyde (4) in the presence of anhydrous potassium carbonate, in DMF at 80°C. 8 was prepared through the condensation reaction between 5, methyl 4-formylbenzoate (6) and pyrrole (7) in the mixed solvent of xylol and 3-nitrobenzoic acid at 140°C. Then 8 underwent an aminolysis reaction with excess alkane-\( N \)-diamines, which also acted as solvents, to give 9–13. The dyads were synthesized by the imidization reaction between 3 and the primary amine derivatives in imidazole at 130°C, as dark red solids. The yields of the imidization reaction were 33–40%, which were attributed to the instability of the compounds 9–13.

**Scheme 1.** Synthesis of dyads \( \text{TPP-C}_n\text{-PIE} \) (\( n = 4, 6, 8, 10 \) and 12). Reagents and conditions: (i) a. KOH, \( \text{H}_2\text{O} \), 75°C, 1.5 h, b. HCl, \( \text{pH} = 8–9 \), \( \text{C}_6\text{H}_5\text{Br} \), \( \text{methyl} \) triptycyl ammonium chloride, reflux, 6 h, 57%; (ii) toluene/heptane = 1/5, \( p \)-toluenesulfonic acid, 95°C, 5 h, 79%; (iii) \( \text{C}_6\text{H}_5\text{Br} \), \( \text{K}_2\text{CO}_3 \), DMF, 80°C, 12 h, 98%; (iv) xylol, 3-nitrobenzoic acid, 140°C, 3.5 h, 28%; (v) \( \text{NH}_3(\text{CH}_2)_3\text{NH}_2 \), (\( n = 2, 4, 6, 8, 10 \) and 12), 100°C, 22–48 h, 82–88%; (vi) imidazole, 130°C, 5 h, 33–40%
Phase behaviors and potential in self-organization

Phase behaviors of the dyads were investigated by polarized optical microscopy (POM, see Fig. 2) and the differential scanning calorimetry (DSC, see Fig. 3 and Figs S1–S5 in the supplementary information). Peak transition temperatures along with the associated enthalpy changes ($\Delta H$) are listed in Table 1. As shown in Fig. 3 and Fig. S1, $\text{TPP-C}_{12}\text{-PIE}$ showed two endothermic transitions and peaked at 68 and 114°C in the first heating cycle, and one exothermic peak at 68°C during the first cooling circle. Under microscopic observation, the birefringent waxy solid was deformed when squeezed at room temperature. When heated, the birefringent fluid started to flow at 100°C, and the birefringent phenomenon disappeared at 128°C. The optical texture observed at 117°C showed it had a columnar liquid crystal phase (see Fig. 2a). When cooled, the isotropic liquid cannot flow at 70°C, and the birefringence did not appear until room temperature. After applying mechanical stress, the birefringent phenomenon can be visualized expressly (see Fig. 2c).

In the first heating circle, $\text{TPP-C}_{10}\text{-PIE}$ showed three endothermic transitions which peaked at 78, 105 and 119°C. During the first cooling circle, one broad exothermic transition peaked at 87°C (see Table 1 and Fig. S3). Under microscopic observation, the birefringent waxy solid was deformed when pressed at room temperature. When heated the red fluid started to flow at 105°C with birefringence, which disappeared at 123°C with continued heating. Upon cooling, the isotropic liquid cannot run at 80°C, and the birefringence did not appear until room temperature. When squeezed, the birefringent phenomenon can be seen clearly (see Fig. 2d).

DSC curves showed two endothermic peaks at 78 and 111°C in the heating cycle for $\text{TPP-C}_{6}\text{-PIE}$, and one exothermic peak at 99°C during the first cooling (see Table 1 and Fig. S4). Under microscopic observation, the birefringent waxy solid was deformed when squeezed at room temperature. When heated, the red fluid started to flow at 90°C with birefringence, which was maintained until 105°C. Upon cooling, the isotropic liquid cannot flow at 70°C, and the birefringence did not restore until room temperature. After applying mechanical stress, the birefringent phenomenon can be visualized expressly (see Fig. 2c).

In the first heating circle, $\text{TPP-C}_{6}\text{-PIE}$ showed three endothermic transitions which peaked at 78, 105 and 119°C. During the first cooling circle, one broad exothermic transition peaked at 87°C (see Table 1 and Fig. S3). Under microscopic observation, the birefringent waxy solid was deformed when pressed at room temperature. When heated the red fluid started to flow at 105°C with birefringence, which disappeared at 123°C with continued heating. Upon cooling, the isotropic liquid cannot run at 80°C, and the birefringence did not appear until room temperature. When squeezed, the birefringent phenomenon can be seen clearly (see Fig. 2d).

DSC curves showed two endothermic peaks at 78 and 111°C in the heating cycle for $\text{TPP-C}_{6}\text{-PIE}$, and one exothermic peak at 99°C during the first cooling (see Table 1 and Fig. S4). Under microscopic observation, the birefringent waxy solid was deformed when squeezed at room temperature. When heated, the red fluid started to flow at 110°C with birefringence, and it disappeared at 125°C. When cooled, the isotropic liquid cannot run at 92°C and the birefringence was not present until room temperature. When pressed, the birefringent phenomenon could be readily observed (see Fig. 2e).
TPP-C₄-PIE showed two endothermic transitions and peaked at 78 and 114°C in the first heating cycle, and one exothermic peak at 104°C during the first cooling cycle (see Table 1 and Fig. S5). Under microscopic observation, the birefringent waxy solid was deformed when pressed at room temperature. When heated, the birefringent fluid cannot run until 115°C, and the birefringent phenomenon disappeared at 130°C. When cooled, the isotropic liquid cannot flow at 99°C and the birefringence did not resort until room temperature. When pushed, the birefringent phenomenon can be seen clearly (see Fig. 2f).

**Electrochemical behaviors and HOMO/LUMO energy levels**

The electrochemical behaviors of the reference compounds TPP and PIE3, and the dyads TPP-C₁₀-PIE were studied by cyclic voltammetry (CV) in dry acetonitrile with 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The experiments were performed at room temperature, using a standard three-electrode cell with a glass carbon electrode as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The scan rate was 50 mV s⁻¹. For all CV measurements, the ferrocene/ferrocinium (Fc/Fc⁺) redox couples were used for calibration [61].

The cyclic voltammograms of TPPE, PIE3 and TPP-C₁₀-PIE are shown in Fig. 4. The HOMO energy values of these compounds were obtained from the potential values corresponding to the onsets of the first oxidation waves (denoted as $E_{ox}$) (1). The $E_{ox}$ (1) of TPPE, PIE3 and TPP-C₁₀-PIE were 1.24, 1.75 and 1.15 V, respectively. In addition, the potential value of the dyad corresponding to the onset of the second oxidation wave (denoted by $E_{ox}$ (2)) was 1.59 V. Analysis of these data showed that the first and second oxidation waves of the dyads can be assigned to the oxidation reactions of the porphyrin unit and the perylene unit, respectively.

Calibrated with the Fc/Fc⁺ redox system, the HOMO energy value of each compound was estimated by the equation $\text{HOMO (eV)} = [-e \times (E_{ox} (1) - E_{\text{Fc/Fc⁺}})] + 4.8$ [30]. Thus, the HOMO values of TPPE, PIE3 and TPP-C₁₀-PIE were -5.50, -5.95 and -5.51 eV, respectively. The LUMO value of a compound can be estimated from the optical band gap (denoted as $E_{g}$) and the HOMO value by the equation $\text{LUMO} = \text{HOMO} + E_{g}$ [30]. The $E_{g}$ was inferred from the onset of the longest wavelength absorption band. The $E_{g}$ values of TPPE and PIE3, inferred from the onsets of the absorption spectra (Fig. 6), were 1.86 and 2.30 eV, respectively. Thus, the LUMO values of TPPE and PIE3 were -3.64 and -3.65 eV, respectively. As we know, the LUMO of a dyad linked by a flexible spacer is coincident with the lower one of the two units [30]. Thus, the HOMO value (-5.95 eV), corresponding to $E_{ox}$ (2), and $E_{g}$ (2.30 eV) of perylene unit should be used in the equation $\text{LUMO} = \text{HOMO} + E_{g}$ for the LUMO of TPP-C₁₀-PIE is -3.65 eV. In this way, the $E_{g}$ of TPP-C₁₀-PIE equals 1.86 eV.

The electronic structures of the cores of TPP-C₁₀-PIE were modeled using the Gaussian 16 suite of programs. Since the side chains have little effect on the HOMO and LUMO values of DLCs [62], the alkyl chains were all replaced by methyl groups in the computer simulations to reduce the computational load. Full geometry optimization of the dyad were performed at the density

**Table 1.** Phase behaviors of TPP-Cₙ-PIE (n = 4, 6, 8, 10 and 12). Phase transition temperatures (peak, °C) and associated enthalpy changes (J · g⁻¹, in parentheses) determined by DSC at the scan rate 10°C · min⁻¹, under N₂.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>First heating scan, temperatures (°C) ($\Delta H$ (J · g⁻¹))</th>
<th>First cooling scan, temperatures (°C) ($\Delta H$ (J · g⁻¹))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPP-C₄-PIE</td>
<td>Col¹ 68 (0.70) Col² 114 (15.76) I¹</td>
<td>I⁶ 68 (0.67) Col¹</td>
</tr>
<tr>
<td>TPP-C₆-PIE</td>
<td>Col 93 (6.71) I</td>
<td>1 74 (0.52) Col</td>
</tr>
<tr>
<td>TPP-C₈-PIE</td>
<td>Col 78 (0.16) Col2 105 (0.35) Col3¹ 119 (1.08) I</td>
<td>1 87 (0.38) Col</td>
</tr>
<tr>
<td>TPP-C₁₀-PIE</td>
<td>Col 78 (1.84) Col2 111 (0.38) I</td>
<td>1 99 (0.32) Col</td>
</tr>
<tr>
<td>TPP-C₁₂-PIE</td>
<td>Col 78 (0.52) Col2 114 (0.12) I</td>
<td>1 104 (0.32) Col</td>
</tr>
</tbody>
</table>

*Col1, Col2, Col3 and Col: columnar liquid crystal phase; I: isotropic liquid.*

**Fig. 3.** DSC traces of TPP-C₁₂-PIE. (The downward peaks are characteristic of endothermic events; first heating and cooling cycle, peak temperatures labeled, at the scan rate of 10°C · min⁻¹.)
functional theory (DFT) level using Becke’s three-parameter B3LYP exchange functional and the 6-31G basis set. The geometry of the dyad was optimized in dichloromethane (DCM), and its isosurfaces of the frontier molecular orbital are illustrated in Fig. 5. It can be seen that the dyad molecule tends to exist in extended conformations in dilute DCM solution, and the HOMO and LUMO orbitals of the dyad are located on the porphyrin and perylene units, respectively. The HOMO, LUMO and $E_g$ values were predicted to be -5.12, -3.35 and 1.77 eV, respectively, which matched the measured values.

**Steady-state spectroscopy**

*UV-vis absorption spectra.* UV-vis absorption spectra of the TPPE, PIE3, the mixture of TPPE and PIE3 (in the molar ratio of 1:1), and the dyads TPP-C$_n$-PIE ($n = 4, 6, 8, 10$ and 12) were studied in DCM solutions ($5 \times 10^{-6}$ mol·dm$^{-3}$) (Fig. 6). PIE3 has optical absorption from 250 to 540 nm. In the ultraviolet region, its absorption maximum is at 263 nm, and the peak optical density corresponds to an extinction coefficient ($\varepsilon$) of $4.56 \times 10^4$ L·mol$^{-1}$·cm$^{-1}$, belonging to the transition of $n-\pi^*$ of C=O groups [33]. In the visible region, it has a maximum absorption at 507 nm ($\varepsilon = 5.48 \times 10^4$ L·mol$^{-1}$·cm$^{-1}$) with two vibronic bands at 475 and 450 nm, correlated to the $\pi-\pi^*$ electron transitions. TPPE shows characteristic I–IV Q bands (652, 596, 557 and 517 nm) and one strong Soret band (422 nm, $\varepsilon = 4.88 \times 10^5$ L·mol$^{-1}$·cm$^{-1}$), belonging to the $\pi-\pi^*$ electron transitions of the porphyrin ring [63].

The absorption spectrum of the mixture of TPPE and PIE3 (in the molar ratio of 1:1), retained the Soret and I–IV Q bands of TPPE and the vibronic bands of PIE3, is a superimposition of the two monomeric spectra. This shows that there is no charge transfer between the TPPE and PIE3 molecules in the ground states in dilute DCM solution. The absorption spectra of the dyads are almost identical to that of the mixture of TPPE and PIE3 (in the molar ratio of 1:1), showing that in the ground states the electronic coupling between the two units of a dyad is
weak. In summary, the absorption spectra of the dyads cover the ultraviolet and visible regions of the solar spectrum due to the complementary absorption of the porphyrin and perylene units.

**Photoluminescent emission spectra.** Photoluminescent emission spectra of the dyads were measured in DCM solutions ($c = 5 \times 10^{-6}$ mol·dm$^{-3}$) at 423 and 473 nm, which correspond to the optical absorptions of the Soret band of the porphyrin unit and the perylene unit, respectively. As a comparison, the emission of the reference compounds TPPE and PIE3 were also measured.

Excited at 423 nm, PIE3 has characteristic fluorescence emissions between 490 and 700 nm, with one peak at 528 nm and two shoulders at 559 and 622 nm (see Fig. 7). The fluorescence emissions of TPPE is between 630 and 780 nm, with the peak at 662 nm and one shoulder at 728 nm. The peak intensity of TPPE is about one fifth of that of PIE3. Compared with TPPE, the spectra profiles of TPP-C$_n$-PIE (n = 4, 6, 8, 10 and 12) are very similar. The fluorescence emission of the perylene units of the dyads is completely quenched. This is attributed to the Förster and Dexter type energy transfer from the perylene units to the porphyrin units, since the fluorescence emission region of the perylene unit (490–700 nm) is overlapped with the Q-bands of porphyrin (480–680 nm), and the lengths of the bridges of the dyads are less than 10 anstroms. Thus, the porphyrin units acquiring energy from the perylene units should have a stronger fluorescence emission than that of TPPE. However, the emission intensity of the highest peaks of the dyads decrease as compared with that of TPPE, and a further decrease is found as the flexible spacers get shorter. This implies there are additional electron transfer processes between the prophyrrin and perylene units, which are responsible for the fluorescence quenching of the porphyrin units.

The fluorescence quenching of the porphyrin units can be explained by the photoinduced electron transfer theory [64]. The electron-rich porphyrin units and the electron-deficient perylene units act as the electron D and A, and were looked at as entities that could be studied separately. To simplify these processes, the HOMO and LUMO values of the D and A units are assumed to be fixed. In the case of TPP-C$_{10}$-PIE, the energetic positions of the HOMO and LUMO energy levels are shown schematically in Fig. 8.

When the D unit was excited, the electron transfer processes of the dyad were depicted in Fig. 8. Before excitation, the dyad molecule was in the ground state (indicated by A–D). When the D unit was excited (represented by Ex), an electron transitioned from the HOMO to the LUMO to give a molecule with the D unit in the excited state (denoted by A–D*). Since the LUMO level of the D unit was higher than that of the A unit, and the core of the A unit was deficient in electrons, the electron in the LUMO of the D transferred to A, yielding a molecule in charge transfer state (denoted by A*-D*). This was a photoinduced electron transfer process (represented by PET). In the end, the electron on the LUMO level of the A unit transferred to the HOMO level of the D unit, and then two units returned to the original ground state. This process was a charge recombination process (expressed by CR). In the above processes, the PET was a key step leading to fluorescence quenching. According to the theory of photoinduced electron transfer, the electron transfer rate constant decays exponentially with the distance between the D and A units [64]. Thus, the shorter the bridges are, the stronger the fluorescence quenching degrees of the D units are.

Excited at 473 nm, the profiles of fluorescence emission spectra of PIE3 and TPPE were similar to that when they were excited at 423 nm, respectively (Fig. 9), while the fluorescence emission of the featured dyads has the characteristics of both PIE3 and TPPE. Since there were the Förster and Dexter type energy transfer from the perylene units to the porphyrin units, the fluorescence emission of the perylene units of the dyads was quenched, and the emission of the porphyrin units was enhanced. It also can be seen that the peak intensities of the porphyrin.

![Fig. 7. Fluorescence emission spectra of TPPE, PIE3 and TPP-C$_{n}$-PIE (n = 4, 6, 8, 10 and 12) in DCM ($c = 5 \times 10^{-6}$ mol·dm$^{-3}$, $\lambda_{ex} = 423$ nm, the intensity of PIE3 plotted here was a quarter of its original value)](image)

![Fig. 8. Schematic representation of the photoinduced electron transfer of TPP-C$_{10}$-PIE ($\lambda_{ex} = 423$ nm, a dashed arrow indicates the two energy levels involving one transition or transfer of an electron)](image)
units decreased as the flexible linkers got shorter. The fluorescence quenching of the porphyrin units is also attributed to the photoinduced electron transfer, just as they were quenched at 423 nm.

**Photocurrent phenomena**

The photocurrent generation of TPP-C₁₀-PIE film, deposited on an indium tin oxide (ITO) glass electrode, was tested using a standard three-electrode cell. The film on the working electrode was fabricated by the drop-casting method. Using 63.2 mW·cm⁻² intermittent white light irradiation and applying a voltage of +0.1 V to the working electrode, a rapid anodic photocurrent response was observed (Fig. 10).

When the TPP-C₉r-PIE film was irradiated with white light, the molecules in charge-separated state, TPP⁺⁻C₉r-PIE⁻⁺, were yielded due to the intramolecular photoinduced electron transfer (see Fig. 8). The negatively charged perylene unit gave electrons to the conduction band of ITO, which resulted in the anodic photocurrent.

**EXPERIMENTAL**

**Materials**

All reagents and solvents were from Aladdin Industrial Corporation, Macklin Inc., XiLong Chemical and FuYu Chemical. All were analytically pure and used without further purification if not specified.

**Characterization and instrumentation**

IR was performed on a VECTOR 22 FT-IR spectrometer (KBr tablet). ¹H NMR spectra were recorded on a Bruker spectrometer (500 MHz). Mass spectra were obtained on an Agilent ESI 6400 mass spectrometer. EA was recorded on a Thermo Flash EA-1112 instrument. DSC experiments were carried out on a Thermal Analysis DSC-Q100 instrument. The mesomorphic properties were evaluated by a polarized optical microscopy instrument (Olympus THMS600) provided with a heating stage (Linkam THMSE 600). CV and photocurrent curves were performed on a Shanghai Chen Hua CHI760E electrochemical workstation. Geometry optimization of the dyad was performed by Gaussian 16 program package. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrometer. Fluorescence emissions were performed on a HITACHI F-4600 instrument.

**Synthesis**

**Synthesis of tetrahexyl perylene-3,4,9,10-tetracarboxylate (2).** The solution of 1 (0.95 g, 2.42 mmol) and potassium hydroxide (2.63 g, 46.9 mmol) in water (300 mL) was filtered after stirring at 70°C for 1.5 h. The filtrate was acidified with HCl (ca. 1 mol·L⁻¹) until the pH was 8–9. Then 1-bromohexane (4.2 g, 25.2 mmol) and methyl-trioctyl-ammonium chloride (1 g, 0.2 mmol) were added to the solution. The reaction mixture was then refluxed for 6 h under vigorous stirring, then cooled to room temperature, and filtered. The filter cake was washed with ethanol (35 mL) three times to give 2 as a yellow solid. Yield 1.05 g (57%). ¹H NMR (500 MHz; CDCl₃; Me₄Si): δ_H ppm 0.91 (12H, t, -CH₃), 1.37–1.35 (16H, m, -CH₂-), 1.48–1.42 (8H, m, -CH₂-), 1.83–1.78 (8H, m, -O-CH₂-CH₂-). 3.33 (8H, t, -O-CH₂-), 7.96–7.91 (4H, m, Ar-H), 8.13–8.06 (4H, m, Ar-H).

**Synthesis of dihexyl-perylene-3,4-anhydride-9,10-dicarboxylate (3).** 2 (4 g, 5.23 mmol) was added to the mixed solvent of toluene (3.0 mL) and heptane (15 mL). When heated to 80°C the mixture became clear.
A red slurry was obtained after the reaction mixture reacted with p-toluene sulfonic acid (1.04 g, 5.47 mmol) at 95°C for 5 h. After cooling to room temperature, the red solid was collected by filtration. The wet filter cake was recrystallized twice from DCM (24 mL) and methanol (40 mL), to give 3 as a red solid. Yield 2.39 g (79%)

1H NMR (500 MHz; CDCl3; MeSi): δH ppm 0.91 (6H, t, -CH3), 1.38–1.34 (8H, m, -CH2-), 1.49–1.44 (4H, m, -CH2-), 1.84–1.78 (4H, m, -O-CH2-CH2-), 4.35 (4H, t, -O-CH2-), 8.12 (2H, d, Ar-H), 8.48 (4H, t, Ar-H), 8.62 (2H, d, Ar-H).

**Synthesis of 4-(dodecyloxy)benzaldehyde (5).** 4 (2.44 g, 20 mmol), 1-bromododecane (6.72 g, 26.9 mmol) and anhydried potassium carbonate (5.52 g, 40 mmol) were added to dried DMF (20 mL). Under nitrogen, the mixture was stirred at 80°C for 12 h, then cooled to room temperature and diluted with water (100 mL). After extraction with DCM (4 × 30 mL), the combined organic layer was washed with brine (20 mL) and then dried (Na2SO4). The solvent was removed at reduced pressure, the crude product obtained was purified by column chromatography (silica gel, DCM/petroleum ether, 1/2 v/v) to give 5 as a yellow oil. Yield 5.75 g (98%).

1H NMR (500 MHz; CDCl3; MeSi): δH ppm 0.88 (3H, t, -CH3), 1.37–1.23 (16H, m, -CH-), 1.49–1.43 (2H, m, -CH2-), 1.83–1.77 (2H, m, -O-CH2-CH2-), 4.04 (2H, t, -O-CH2-), 6.99 (2H, d, Ar-H), 7.83 (2H, d, Ar-H), 9.88 (1H, s, Ar-NH-).

**Synthesis of methyl 4-(10,15,20-tris(4-(dodecyloxy)phenyl)porphyrin-5-yl)benzamide (8, TPPE).** One solution of 5 (5.88 g, 21 mmol) and 6 (1.19 g, 6.7 mmol) in the mixture of 3-nitrobenzoic acid (1.85 g, 13.5 mmol) and xylol (32 mL) was heated to 140°C. The other solution of pyrrole (1.805 g, 26.9 mmol) in xylol (32 mL) was heated to 140°C for another 3.5 h. After evaporation of the xylon, the crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 1/2–1/1 v/v) to give 8 as a purple oil. Yield 5.75 g (28%).

1H NMR (500 MHz; CDCl3; MeSi): δH ppm -2.79 (2H, s, pyrrole-NH), 0.90–0.88 (15H, m, -CH-), 1.50–1.34 (60H, m, -CH-), 1.65–1.61 (6H, m, -CH2-), 1.81–1.75 (4H, m, -CH2-), 2.04–1.91 (10H, m, -CH2-), 2.63–2.57 (2H, m, -N-CH2-), 3.79–3.75 (2H, m, -N-CH2-), 4.25–4.20 (6H, m, -O-CH2-), 4.31 (6H, t, -O-CH2- and -NH-CH2-), 7.03 (1H, t, -CO-NH-), 7.24 (4H, d, Ar-H), 7.26 (2H, s, Ar-H), 8.03 (2H, d, Ar-H), 8.07 (4H, d, Ar-H), 8.08 (2H, d, Ar-H), 8.20 (2H, d, Ar-H), 8.26 (2H, d, Ar-H), 8.32 (4H, d, Ar-H), 8.52 (2H, d, Ar-H), 8.76 (2H, d, Ar-H), 8.86 (6H, s, Ar-H).

13C NMR (125 MHz; CDCl3) δC ppm 14.0, 14.1, 17.8, 22.6, 22.7, 25.5, 25.7, 26.21, 26.24, 26.8, 28.5, 29.38, 29.47, 29.50, 29.53, 29.67, 29.71, 31.5, 31.9, 33.1, 39.6, 65.8, 68.23, 68.26, 112.7, 118.3, 120.0, 120.3, 121.0, 121.2, 122.2, 122.4, 125.4, 128.4, 128.6, 128.8, 128.9, 130.1, 130.5, 130.8, 131.27, 131.33, 131.5, 131.7, 131.8, 133.9, 134.1, 134.2, 134.6, 134.8, 135.5, 135.6, 145.4, 158.9, 159.0, 163.0, 163.2, 167.6, 168.1. MS (ESI): m/z 1865 (calcd. for [M + Na]+ 1865).
Synthesis of TPP-C<sub>P</sub>-PIE. The same procedure as for TPP-C<sub>P</sub>-PIE with 10 (0.5 g, 0.39 mmol), 3 (0.18 g, 0.32 mmol) and imidazole (5 g), to give the title compound as a red solid. Yield 0.27 g (40%). Anal. calcd. for C<sub>127</sub>H<sub>156</sub>N<sub>6</sub>O<sub>10</sub>: C, 79.17; H, 8.16; N, 4.36. Found: C, 79.07; H, 8.11; N, 4.41. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): <em>λ</em><sub>max</sub>, nm (log e) 263 (4.73), 422 (5.70), 473 (4.58), 505 (4.75), 556 (4.08), 593 (3.74), 651 (3.77). IR (KBr) <em>v</em><sub>max</sub> cm<sup>-1</sup> 3426 (N-H), 2922–2852 (aliphatic-CH), 1697, 1650, 1607, 1511, 1469, 1385, 1296, 1248, 1171, 1081, 1026, 798. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ ppm -2.92 (15H, m, -CH<sub>3</sub>.-), 1.66–1.62 (8H, m, -CH<sub>2</sub>.-), 1.82–1.76 (8H, m, -CH<sub>2</sub>.-), 2.00–1.93 (6H, m, -CH<sub>2</sub>.-), 3.66–3.62 (2H, m, -N-CH<sub>2</sub>.-), 4.17 (2H, t, -NH-C<sub>2</sub>H<sub>5</sub>.-), 4.32 (4H, t, -O-CH<sub>2</sub>.-), 6.49 (1H, t, -CO-NH.-), 7.28–7.25 (6H, m, Ar-H), 8.03–8.00 (2H, m, Ar-H), 8.09–8.07 (6H, m, Ar-H), 8.15 (2H, d, Ar-H), 8.25–8.19 (4H, m, Ar-H), 8.84–8.41 (2H, m, Ar-H), 8.75 (2H, d, Ar-H), 8.87 (6H, s, Ar-H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ ppm 14.0, 14.1, 22.6, 22.7, 25.7, 26.2, 27.0, 27.1, 28.0, 28.5, 29.2, 29.3, 29.4, 29.5, 29.7, 31.5, 31.9, 40.4, 40.5, 65.8, 68.3, 112.7, 118.2, 120.0, 120.3, 121.0, 121.8, 122.4, 125.2, 125.5, 128.7, 128.8, 129.0, 130.2, 131.0, 131.7, 131.8, 134.1, 134.2, 134.3, 134.7, 135.0, 135.6, 135.61, 145.4, 158.96, 158.98, 163.3, 167.7, 168.2. MS (ESI): <em>m/z</em> 1949 (calcld. for [M + Na]+ 1949).

Synthesis of TPP-C<sub>P</sub>-PIE. The same procedure as for TPP-C<sub>P</sub>-PIE with 13 (0.47 g, 0.34 mmol), 3 (0.16 g, 0.28 mmol) and imidazole (5 g), to give the title compound as a red solid. Yield 0.25 g (40%). Anal. calcd. for C<sub>129</sub>H<sub>160</sub>N<sub>10</sub>O<sub>10</sub>: C, 79.26; H, 8.25; N, 4.30, found: C, 79.08, H, 8.26, N, 4.34. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): <em>λ</em><sub>max</sub>, nm (log e) 263 (4.72), 422 (5.69), 474 (4.57), 506 (4.73), 556 (4.08), 594 (3.74), 651 (3.76). IR (KBr) <em>v</em><sub>max</sub> cm<sup>-1</sup> 3445 (N-H), 2926–2850 (aliphatic-CH), 1699, 1655, 1605, 1505, 1462, 1351, 1294, 1246, 1171, 1076, 966, 800, 729. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ ppm -2.90 (2H, s, pyrrole-NH), 0.92–0.88 (15H, m, -CH<sub>3</sub>.-), 1.46–1.31 (74H, m, -CH<sub>2</sub>.-), 1.65–1.60 (8H, m, -CH<sub>2</sub>.-), 1.83–1.72 (8H, m, -CH<sub>2</sub>.-), 2.00–1.95 (6H, m, -CH<sub>2</sub>.-), 3.65–3.61 (2H, m, -N-CH<sub>2</sub>.-), 4.12 (2H, t, -N-CH<sub>2</sub>.-), 4.25–4.22 (6H, m, -O-CH<sub>2</sub>.-), 4.33 (4H, t, -O-CH<sub>2</sub>.-), 6.49 (1H, t, -CO-NH.-), 7.27 (6H, m, Ar-H), 8.04–8.00 (4H, m, Ar-H), 8.12–8.07 (6H, m, Ar-H), 8.14 (2H, d, Ar-H), 8.21–8.18 (2H, m, Ar-H), 8.32–8.27 (4H, m, Ar-H), 8.75 (2H, d, Ar-H), 8.83 (4H, s, Ar-H), 8.86 (2H, d, Ar-H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ ppm 14.0, 14.1, 22.6, 22.7, 25.7, 26.2, 27.1, 27.2, 28.0, 28.5, 29.28, 29.33, 29.38, 29.47, 29.50, 29.54, 29.57, 29.68, 29.72, 31.5, 31.9, 40.4, 40.5, 65.8, 68.3, 112.69, 112.71, 118.2, 120.0, 120.3, 121.3, 121.6, 122.3, 125.2, 125.5, 128.7, 129.0, 130.2, 131.7, 131.8, 134.13, 134.18, 134.21, 134.4, 134.8, 135.0, 135.60, 135.63, 145.5, 159.0, 163.2, 167.7, 168.2. MS (ESI): <em>m/z</em> 1977 (calcld. for [M + Na]+ 1977).

CONCLUSION

Novel dyads TPP-C<sub>P</sub>-PIE (n = 4, 6, 8 and 10) were synthesized and fully characterized. The UV-vis spectra
revealed these dyads have broad optical absorption from the ultraviolet region to the visible region, due to the complementary absorption of porphyrin and perylene units. DSC traces and POM textures showed all these dyads have mesogenic properties, and they formed face-on alignment on the slide when cooled. When excited at 423 or 473 nm, the photoluminescent emission showed a Förster and Dexter type energy transfer from the perylene unit to the porphyrin unit. At the same time, the fluorescence quenching degree of porphyrin units increased as the spacers got shorter. This quenching was further confirmed by the photocurrent generation.

Supplementary information

The DSC curves, 1H- and 13C-NMR, IR and MS spectra of the dyads are supplied as supplementary information. This material is available free of charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml

Acknowledgments

We gratefully acknowledge financial support from the Natural Science Foundation of China (No. 11364013), Opening Fund of Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials (EMFM20181101), and the Special Funding for Distinguished Expert from Guangxi Zhuang Autonomous Region. We thank Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration for providing support to the POM measurements.

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INTRODUCTION

Oxygen is essential for life. Oxygen consumption during cell growth leads to the formation of reactive oxygen species (ROS). ROS are radical species such as superoxide anion radicals, hydroxyl radicals, hydrogen peroxide and singlet oxygen, which play a major role in pathological events associated with mutation, cancer, aging and many diseases. Physiologically harmful effects of these free radicals are balanced by the activities of antioxidant defenses. Antioxidants are vital in protecting biological systems against many incurable diseases [1–3]. It is well-known that most phenolic compounds [4] and compounds that include tertiary butyl groups [5, 6] are powerful antioxidants. On the other hand, phthalocyanines and their derivatives have been intensively investigated in different scientific and technological areas due to their interesting electrical, electrochemical, optic and spectral properties and their high chemical and thermal stability [7, 8]. These properties of phthalocyanine complexes are affected strongly by the metal ion species and the nature of substituents [9, 10]. The number and position of the substituents are also important in controlling some of the phthalocyanine properties [10, 11]. Amaral et al. observed that phthalocyanine derivatives have promising antioxidant potentials [12]. Also in recent years, antioxidant properties of different phthalocyanine derivatives have been extensively studied [13–20]. Aggregation behaviors of phthalocyanines are also important to determine their potential use in photodynamic therapy, because aggregation reduces the photosensitization efficiency of phthalocyanines [10, 21]. When phthalocyanines are combined with phenoxy and tertiary butyl groups, these compounds can show higher antioxidant activities. Therefore, we studied synthesis and characterization of 4-((4′-tert-butyl)phenoxy)phenoxy substituted metal-free (2), zinc(II) (3) and cobalt(II) (4) phthalocyanines. Antioxidant activities of

ABSTRACT: 4-[(4′-(Tert-butyl)phenoxy)phenoxy]phthalonitrile 1 has been prepared by the reaction of 4-(4-nitrophenoxy)phthalonitrile with 4-tertiarybutylphenol. 4-((4′-tert-butyl)phenoxy)phenoxy tetrasubstituted metal-free 2, zinc(II) 3 and cobalt(II) 4 phthalocyanines have been prepared by tetramerization of compound 1. The synthesized phthalocyanines showed high solubility in common organic solvents such as CHCl₃. All compounds were characterized by elemental analysis and ¹H-NMR, ¹³C-NMR, UV-vis, IR spectra. Aggregation behaviors of these compounds have been investigated in different solvents (CHCl₃, THF, DMF and DMSO) and different concentrations in CHCl₃. The in vitro antioxidant activities of phthalocyanine compounds 2, 3 and 4 were evaluated in a series of assays involving DPPH radicals, hydroxyl radicals, superoxide radicals, singlet oxygen and hydrogen peroxide. Antioxidant activity of compound 2 was found to be higher than that of compounds 3 and 4.

KEYWORDS: Phthalocyanine, synthesis, aggregation, antioxidant activity.

Antioxidant activities of the new tetrasubstituted metal-free, Zn(II) and Co(II) monophthalocyanines

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 29 November 2017
Accepted 9 January 2018

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phthalocyanine compounds 2, 3 and 4 were investigated as in vitro assays involving the reactive oxygen species.

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 shows the synthetic route employed for compounds 1–4. Compound 1 was synthesized by the reaction of 4-(4-nitrophenoxy)phthalonitrile and 4-tertiarybutylphenole in DMSO in the presence of K₂CO₃. The metal-free phthalocyanine 2 was synthesized by heating compound 1 in N,N-dimethylethanolamine. Zinc(II) 3 and cobalt(II) 4 phthalocyanines were synthesized by heating compound 1 with Zn(CH₃COO)₂ or CoCl₂ in DMF at the presence of DBU, respectively (Scheme 1). UV-vis, ¹H-NMR, ¹³C-NMR, IR spectra confirmed the proposed structure of all new compounds. The elemental analysis results of starting compound 1 and phthalocyanine compounds 2–4 show good agreement with the calculated values.

The characteristic vibration band of the –C≡N group appeared at 2231 cm⁻¹ in the IR spectrum of 1 and disappeared after conversion to metal-free 2, zinc 3 and cobalt 4 phthalocyanines [22].

In the ¹H-NMR spectrum of compound 1, which was taken in CDCl₃ at room temperature, the aromatic protons and tertiary butyl protons appeared at 7.73–7.01 ppm and at 1.37 ppm, respectively. ¹³C-NMR spectra were in good correlation with the structure of the compound 1. ¹H-NMR spectra of compounds 2 and 3 were taken in CDCl₃ at room temperature. The spectra of the 2 and 3 showed aromatic protons at 8.63–7.00 ppm and 8.41–6.78 ppm, respectively. Tertiary butyl protons of compounds 2 and 3 appeared at 1.52 ppm and 1.40 ppm, respectively. -NH protons of the phthalocyanine ring cavity of metal-free phthalocyanine 2 appeared as a broad singlet at -4.11 ppm which disappeared with D₂O exchange. Because of the paramagnetic nature of the metal center of cobalt phthalocyanine 4, the ¹H-NMR spectra of this compound could not be obtained [22, 23].

The UV-vis spectra of 2–4 in CHCl₃ showed typical absorptions between 600–700 nm in the Q band region.

Scheme 1. Synthesis of 4-((4′-tert-butylphenoxy)phenoxy tetrasthiosubstitute phthalocyanines, 2, 3, 4 (i) K₂CO₃, DMSO; (ii) (2) N,N-dimethylethanolamine. (3, 4) Zn(CH₃COO)₂ or CoCl₂, DBU, DMF
ANTIOXIDANT ACTIVITIES OF THE NEW TETRASUBSTITUTED METAL-FREE, ZN(II) AND CO(II) MONOPHTHALOCYANINES

The Q band of compound 2, which is quite typical for metal-free phthalocyanines, showed two intense absorptions at 705 nm and 673 nm. The UV-vis spectra of compounds 3 and 4 in CHCl₃ give characteristic Q band absorptions for metallophthalocyanines, with a peak at 681 nm and 670 nm, respectively. In addition, the B bands of compounds 2–4 appeared at around 334 nm, 350 nm and 325 nm, respectively [23].

Phthalocyanines aggregate due to electronic interactions between rings of two or more molecules. Aggregation is dependent on the concentration, metal ions, nature of the solvent, nature of the substituents and temperature. In many cases, the spectra in the Q band region show the effects of aggregation, typically a blue shift and broadening of the maximum absorbance [10, 24]. In this study, the aggregation behaviors of compounds 2–4 were investigated in CHCl₃, THF, DMF and DMSO.

Phthalocyanines 2–4 did not show an aggregation in these solvents at the concentration shown in Fig. 2. The aggregation behaviors of 2–4 were also investigated at different concentration in CHCl₃ (Fig. 3). There is no aggregation of compounds 2–4 at different concentrations in CHCl₃.

Antioxidant and free radical scavenging activity

We investigated the antioxidant and free radical scavenging activity of phthalocyanine compounds 2–4. The antioxidant activities of compounds 2, 3 and 4 were evaluated in a series of in vitro assays involving DPPH radicals, hydroxyl radicals, superoxide radicals, singlet oxygen and hydrogen peroxide. Aerobic organisms need oxygen to survive, but the most significant free radicals in biological systems arise from oxygen, and oxygen in
high concentrations has toxic effects. The toxic effects are caused by reactive species called "oxygen radicals." Some of the reactive oxygen species, including hydrogen peroxide, singlet oxygen, hydroxyl and superoxide radicals modify DNA and membranes by attacking the lipids, proteins and carbohydrates in cell membranes and tissues. Additionally, relationships have been observed between ROS and many diseases, including myocardial infarction, neurological disorders, asthma, diabetes, rheumatoid arthritis, cancer and aging. The role of antioxidants in preventing various degenerative and age-related diseases caused by oxidative stress is becoming increasingly clear through experimental, clinical and epidemiological studies; thus, antioxidants have gained more importance [25–28].

**DPPH free radical scavenging activity**

If antioxidants are present in the test environment, DPPH undergoes a characteristic color change from violet to colorless. By spectrophotometrically following the samples, which were prepared by dissolving in DMSO, bleaching of a 0.004% DPPH solution was used to determine the inhibition of DPPH radical formation [29]. According to this colorimetric assay, compound 2, which has the lowest IC$_{50}$ value, exhibits the strongest antioxidant activity against the DPPH radical. The DPPH radical scavenging activities of the compounds increased in the order of 3, 4 and 2, respectively. While the DPPH scavenging activity of complex 2 was higher than the activity of BHA and BHT, compounds 3 and 4 showed lower activity (Figs 4 and 5).

DPPH radical scavenging activity is a commonly used method for the investigation of antioxidant capacities of natural and synthesized compounds. Aydın et al. [30] synthesized tetra-phthalocyanines [M: 2H(2), Zn(II)(3), Co(II)(4)] with four peripheral 4-(methylthio)phenylthio groups and also investigated the antioxidant properties by free DPPH. According to the results of DPPH radical scavenging activities, the highest DPPH activity was from cobalt phthalocyanines, similar to our results. The results showed that at 500 μg·mL$^{-1}$, the highest antioxidant activity was obtained by cobalt phthalocyanines, causing 54.00% DPPH radical formation inhibition, whereas our synthesized cobalt phthalocyanines caused 60.00% DPPH at 500 μg·mL$^{-1}$ concentration. In another study, researchers synthesized peripherally tetra 4-(methylthio) phenoxy substituted metal-free, Zn(II), and Co(II) phthalocyanine derivatives. These compounds were also evaluated for their total antioxidant abilities by using DPPH free radical scavenging activity. Results showed that all tested compounds had radical scavenging activity and the highest radical scavenging activity was found from the cobalt phthalocyanine compound (at 100 μg·mL$^{-1}$ 60% DPPH radical formation inhibition), in accordance with our results (at 100 μg·mL$^{-1}$ 30% DPPH radical formation inhibition) [31]. Ağrıtaş et al. reported the synthesis and antioxidant properties of dimethyl 5-(phenoxy)-isophthalate substituted zinc, cobalt, copper, and nickel phthalocyanines. The DPPH
free radical scavenging ability of phthalocyanine Co(II) and Zn(II) complexes on DPPH were found at 44.8% and 40.1% at 100 mg·L\(^{-1}\) concentration, respectively [20]. The activity of Co(II) is greater than that of the Zn(II), as in our experimental results. Our results showed that Co(II) and Zn(II) complexes on DPPH were found at 40% and 30% at 100 mg·L\(^{-1}\) concentration, respectively. These results indicate that the position of substituents and metal ions plays an important role in the development of an effective antioxidant, and the Co(II) compound had high potential scavenging to eliminate the radicals compared to the other compounds.

**Hydroxyl radical scavenging activity**

Hydroxyl radicals contribute significantly to molecular and cellular damage within biological systems. In addition, their significant role as initiators of lipid peroxidation is well documented. Thus, scavenging and preventing the formation of hydroxyl radicals is of utmost importance [32]. Hydroxyl radical scavenging activity was examined by measuring the hydroxyl radicals generated from the Fe\(^{3+}\)/ascorbate/EDTA/H\(_2\)O\(_2\) system [33, 34]. According to extrapolated \(IC_{50}\) values, hydroxyl radical scavenging activity of compound 2 was slightly higher than for compounds 3 and 4. The presented \(IC_{50}\) values also demonstrate that the samples were better hydroxyl radical scavengers than BHT or BHA (Figs 6 and 7).

**Superoxide radical scavenging activity**

Superoxide anion radicals are produced from normal cellular functions and serve as catalysts for the formation of various other radical species. Inhibition of superoxide becomes more important because of its direct ties to different diseases. Compounds and positive standards were also found to scavenge superoxide anion radicals generated by a xanthine and xanthine oxidase system [35, 36]. Of all the samples tested, compound 2 exhibited the strongest antioxidant activity against superoxide radicals. The superoxide radical scavenging activities of the compounds sequentially decreased in compounds 2,
and 3, respectively. BHT, which has the highest IC₅₀ value, exhibited lower superoxide radical inhibition activity than the complexes (Figs 8 and 9).

Singlet oxygen inhibition activity

Singlet oxygen, the electronically excited state of molecular oxygen, is one of its more reactive and toxic forms. Singlet oxygen is a highly energetic molecule that induces a unique oxidation process by directly reacting with electron-rich double bonds without forming free radical intermediates in food and biological systems. The association of singlet oxygen with a number of pathological conditions is well documented [32]. It was found that all compounds had lower singlet oxygen inhibition activity than BHA and BHT. IC₅₀ values also showed that BHA had the most singlet oxygen inhibition activity. Compounds 2 and 4 possessed similar activity against singlet oxygen, and the singlet oxygen inhibition activity of compounds decreased in the order 2, 4 and 3, respectively (Figs 10 and 11).

Hydrogen peroxide scavenging activity

Hydrogen peroxide is not reactive on its own, but under appropriate conditions it can form hydroxyl radicals,
which are the most reactive oxygen radical species [37, 38]. Similar to the results seen with DPPH and hydroxyl radicals scavenging activity, compound 2 was found to have the highest hydrogen peroxide scavenging activity. The hydrogen peroxide scavenging activity of compound 4 was similar to that of BHA and greater than BHT (Figs 12 and 13).

EXPERIMENTAL

General

All reactions were carried out under argon atmosphere and all solvents were dried by molecular sieves or appropriate methods [39]. 4-(4-Nitrophenoxo)phthalonitrile [40] was prepared according to the literature. Solvents and all other chemical reagents were purchased from Sigma–Aldrich and Merck. IR spectra were recorded on a Perkin–Elmer Spectrum 100 spectrometer equipped with ATR. Characterization of compounds was recorded on a Shimadzu 1601 UV-vis spectrometer. Antioxidant activities of compounds were recorded by a Hitachi 220 UV-vis spectrometer. 1H-NMR and 13C-NMR spectra were obtained using a Bruker 300 MHz spectrometer. Elemental analysis was performed on a Thermo FlashEA 1112 Series. Melting points were recorded on an Electrothermal 9100 digital melting point apparatus.

Synthesis

Synthesis of 4-[4′-(tert-butyl)phenoxy]phenoxy]phthalonitrile (1). 4-(4-Nitrophenoxo)phthalonitrile (2.0 g, 7.54 mmol) and 4-tertiarybutylphenole (1.13 g, 7.54 mmol) were dissolved in DMSO (30 mL). Anhydrous potassium carbonate (3.10 g, 22.62 mmol) was added to the reaction solution over period of 2 h with efficient stirring. The reaction mixture was stirred at room temperature for 3 days. Then the mixture was poured into solution of salt water (1%), and the precipitate was filtered off, washed with water and dried in a vacuum etuv at 40 °C. The crude product was recrystallized in acetone (200 mL). The pale yellow solid was soluble in chloroform, EtOH, MeOH and THF. Yield 740.0 mg (27%), mp 119°C. Anal. calcd. for C24H20N2O2: C, 78.24; H, 5.47; N, 7.59%. Found: C, 78.03; H, 5.35; N, 7.49. 1H-NMR (300 MHz; CDCl3): δH, ppm 1.37 (9H, s, C-CH3), 7.01 (2H, d, Ar-H), 7.30–7.21 (6H, m, Ar-H), 7.49 (2H, d, Ar-H), 7.73 (1H, d, Ar-H). 13C-NMR (75.03 MHz, CDCl3): δ, ppm 162.09, 159.46, 159.18, 151.00, 149.37, 144.91, 135.85, 135.35, 127.49, 126.47, 123.17, 123.01, 120.04, 118.09, 117.42, 110.94, 31.35. IR (ATR): ᵅ, cm⁻¹ 2962, 2865, 2231, 1481, 762.

Synthesis of 2,9,16,23-Tetrakis[4-(4′-tert-butyl)phenoxy]phenoxy]phthalocyaninatozinc(II) (3). The mixture of 1 (100.0 mg, 0.27 mmol) in N,N-dimethylethanalamine (2 mL) was heated at 180 °C for 24 h. After cooling, the mixture was precipitated with MeOH, filtered off and dried in vacuum. The dark green compound was dissolved in THF and filtered off. The organic phase was precipitated with diethyl ether, filtered off and then dried in vacuum. The dark green solid was soluble in CHCl3, THF, DMF and DMSO. Yield 50.0 mg (43%), ᵅp: >300 °C. Anal. calcd. for C56H44N4O2Zn: C, 78.13; H, 5.60; N, 7.59%. Found: C, 77.98; H, 5.42; N, 7.40. UV-vis (CHCl3): λmax, nm (log ε) 705 (4.79), 673 (4.88), 639 (4.72), 334 (5.04). 1H-NMR (300 MHz, CDCl3): δH, ppm -4.11 (2H, br s, Pc-NH, disappeared on D2O addition), 1.52 (36H, s, C-CH3), 8.63–7.00 (44H, br m, Ar-H). IR (ATR): ᵅ, cm⁻¹ 2955, 2887, 1470, 1222, 743.

Synthesis of 2,9,16,23-Tetrakis[4-(4′-tert-butyl)phenoxy]phenoxy]phthalocyaninato cobalt(II) (4). The mixture of 1 (100.0 mg, 0.27 mmol) and CoCl2 (12.8 mg, 0.07 mmol) in DMF (3 mL) was heated in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 180 °C for 15 h. After cooling, the green product mixture was precipitated and purified using the same procedure as compound 2. The dark green solid was soluble in CHCl3, THF, DMF and DMSO. Yield 55.0 mg (51%), ᵅp: >300 °C. Anal. calcd. for C56H44N4O2Co: C, 74.92; H, 5.24; N, 7.28%. Found: C, 74.87; H, 5.10; N, 7.09. UV-vis (CHCl3): λmax, nm (log ε) 681 (5.28), 613 (4.60), 350 (5.05). 1H-NMR (300 MHz, CDCl3): δH, ppm 1.40 (36H, s, C-CH3), 8.41–6.78 (44H, br m, Ar-H). IR (ATR): ᵅ, cm⁻¹ 2960, 2891, 1471, 1223, 745.
DPPH free radical scavenging assay

The DPPH assay was measured by following the bleaching of a purple methanol solution of DPPH [29]. 100 µL various concentrations of the compounds (prepared in DMSO) were added to 500 µL of a 0.004% solution of DPPH in methanol. After 30 min incubation at room temperature, the absorbance was read against a blank at 517 nm. DPPH radical scavenging activity was calculated using the following formula (Eq. 1).

\[
\% \text{ Inhibition of DPPH} = \left( \frac{A_o - A_i}{A_o} \right) \times 100
\]

where \( A_o \) was the absorbance of the control and \( A_i \) was the absorbance of the presence of compounds. BHT and BHA were used as positive controls.

Hydroxyl (OH\(^{•}\)) radical scavenging assay

Hydroxyl radical scavenging activity of compounds was carried out by measuring the hydroxyl radicals generated from the Fe\(^{3+}\)/ascorbate/EDTA/H\(_2\)O\(_2\) system. The attack of the hydroxyl radical to deoxyribose leads to the formation of thiobarbituric acid reactive substances (TBARS) [33, 34]. Various concentrations of the compounds in DMSO were added to a reaction mixture containing 0.4 mL of compounds, 0.5 mL of H\(_2\)O\(_2\), and the total volume was made up to 1 mL. The reaction mixture was incubated at 37°C for 1 h. Then 1 mL of thiobarbituric acid (TBA, 1%) and 1.0 mL of trichloroacetic acid (TCA, 2.8%) were added to test tubes and they were incubated at 100°C for 20 min. After the mixtures cooled, absorbance was measured at 532 nm against a blank containing deoxyribose and buffer. The percentage inhibition (I) of deoxyribose degradation was calculated in the following way (Eq. 2):

\[
\% I = \left( \frac{A_o - A_i}{A_o} \right) \times 100
\]

where \( A_o \) is the absorbance of the control reaction (containing all reagents except the test compound) and \( A_i \) was the absorbance of the test compounds. BHT and BHA were used as positive controls.

Superoxide anion radical scavenging assay

For the evaluation of superoxide anion radical \( (O_2^{•−}) \) scavenging activity, the improved method by Imanari \textit{et al.} was applied [35] in which NBT reduction with \( O_2^{•−} \) was stopped by the addition of CuCl\(_2\). \( O_2^{•−} \) was supplied to the evaluating system from the xanthine–XOD reaction, as described in the literature [36]. Different concentrations of compounds (0.2 mL in DMSO) were added to a mixture solution containing 0.05 M carbonate buffer (pH 10.2, 4.8 mL), 3 mM xanthine (0.2 mL), 3 mM ethylenediaminetetraacetic acid (EDTA)-2Na (0.2 mL), 0.15% bovine serum albumin (BSA) (0.2 mL), 0.75 mM NBT (0.2 mL), and the mixture was incubated for 10 min at 25°C. After 0.1 units/mL XOD (0.2 mL) was added, the reaction mixture was further incubated for 20 min at 25°C. To stop the NBT reduction with \( O_2^{•−} \) to form formazan dye, 6 mM CuCl\(_2\) (0.2 mL) was added to the mixture. The absorbance of samples at 560 nm of formazan dye formed \( (A_2) \) was observed against the reagent blank \( (A_1) \). The reaction mixture without xanthine oxidase was used as a blank \( (A_0) \). Absorbance was measured, and the decrease in \( O_2^{•−} \) was represented by \( A_1−A_2 \). The scavenging activity on superoxide anion radical (SRSA) was calculated by the following equation (Eq. 3) [41]:

\[
\text{SRSA} \% = \left( \frac{A_2 - A_1}{A_0} \right) \times 100
\]

Singlet oxygen inhibition assay

The ability of compounds to inhibit singlet oxygen \( (O_2^*) \) was measured according to a spectrophotometric method explained by Maldonado \textit{et al.} with slight modification [42]. The chemical solutions were prepared in a 45 mM sodium phosphate buffer (pH 7.4), and compounds were prepared in DMSO. The reaction mixture consisted of 0.4 mL of compounds, 0.5 mL of DPN (200 µM), 0.2 mL of histidine (100 mM), 0.2 mL of sodium hypochlorite (100 mM), 0.2 mL of H\(_2\)O\(_2\) (100 mM), and the total volume was made up to 2 mL with sodium phosphate buffer. The absorbance of the reaction mixture was measured at 440 nm after incubation for 40 min at 30°C. Blanks were run for each sample with 0.4 mL of compounds and phosphate buffer. A control was prepared by replacing compounds with DMSO.

The percentage inhibition of singlet oxygen was calculated as follows: singlet oxygen inhibition activity (%) = \[ 1 – \left( \frac{\text{absorbance of the sample/absorbance of the control}}{\text{absorbance of the sample/absorbance of the control}} \right) \] × 100.

Hydrogen peroxide scavenging assay

The ability of compounds to scavenge hydrogen peroxide \( (H_2O_2) \) was determined according to the method explained by Ruch \textit{et al.} and Chanda and Dave [37, 38]. A solution of hydrogen peroxide (2 mM) was prepared in a phosphate buffer (pH 7.4). Compounds in different concentrations (prepared in DMSO, 100 µL) were added to the hydrogen peroxide solution (150 µL) and phosphate buffer (0.9 mL). Absorbance of hydrogen peroxide at 230 nm was determined after 10 min against a blank solution containing the phosphate buffer without hydrogen peroxide. For each concentration, a separate blank sample was used for background subtraction. The percentage scavenging activity of hydrogen peroxide by compounds was calculated using the formula in Eq. 4:

\[
\% \text{ Scavenging Activity [H}_2\text{O}_2\text{]} = \left( \frac{A_{\text{control}} - A_{\text{Std}}}{A_{\text{control}}} \right) \times 100
\]
CONCLUSION

4-(4′-Tert-butyl)phenoxy/phenoxo substituted phthalocyanines 2–4 were synthesized and characterized. The prepared compounds 2–4 are readily soluble in organic solvents such as CHCl₃ and THF. The effects of solvent and concentration on the aggregation behavior of compounds 2–4 were also investigated, and aggregation was not observed.

The antioxidant activity of the phthalocyanine compounds 2–4 against the free radicals DPPH, hydroxyl, superoxide, singlet oxygen and hydrogen peroxide were screened. Among the newly-synthesized 2, 3 and 4 compounds, phthalocyanine compound 2 had no coordinated metal ions in its molecular structure but exhibited superior activity in all the biological studies in comparison with compounds 3 and 4. Antioxidant and free radical scavenging activities of compounds were found to decrease in the order 2, 4 and 3. In addition, the results obtained in this study imply that these phthalocyanine compounds possess excellent antioxidant activities that are superior to those of standard antioxidants such as BHA and BHT. The observed lower IC₅₀ values in antioxidant assays demonstrated that these compounds (2, 3, 4) have the potential to eliminate the radicals. The information obtained from the present work should be helpful in developing new potential antioxidants and therapeutic reagents for some diseases.

REFERENCES


Synthesis, characterization and electrochemical properties of novel pyridine phthalocyanine derivatives

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This paper is dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 10 December 2017
Accepted 10 January 2018

ABSTRACT: In this study, the novel Zn(II), metal-free and sandwich-type Lu(Pc)2 phthalocyanines containing tetra pyridine substituted at peripheral position were synthesized. All the new compounds have been characterized by FT-IR and UV-vis spectroscopy, 1H-NMR, MALDI-MS and elemental analysis. The electrochemical and spectrolelectrochemical properties of all novel metallo- and metal free phthalocyanine compounds were also investigated by voltammetric and in situ spectrolelectrochemical measurements on Pt in dimethylsulfoxide/tetrabutylammonium perchlorate.

KEYWORDS: phthalocyanine, pyridine, bis-phthalocyanine, electrochemistry, spectrolelectrochemistry.

INTRODUCTION

Because of their synthetic and structural aspects, spectral properties, electrochromic behavior and electrical conductivity, metallophthalocyanines (MPCs), especially the lutetium bis-phthalocyanine (LuPc2) series, have recently received much attention [1–4]. These complexes display unique physical, spectroscopic and electrochemical properties, since the large conjugated $\pi$ systems in these complexes are held in close proximity by metal ions [1]. The importance of these complexes in many fields such as optical devices, chemical sensors, semi-conductors, catalysts, non-linear optics, Langmuir–Blodgett films and photodynamic therapy (PDT) has increased rapidly as a result of novel designed compounds [5–22].

It is well known that basic chemical and physical characteristics of MPCs are directly related with the extensive $\pi$-electron delocalization of the Pc rings. Furthermore, this delocalization, including the basic electrochemistry, can be modified by a careful selection of the redox activity of the central metal ions, and by changing the number, position and types of substituents on the Pc ring [23–25]. Among Pc derivatives, the synthesizes of lanthanide(III) Pcs, especially double-decker lanthanide Pcs, have attracted a great deal of interest due to their unique electrochemical, and electrochromic behavior and the $\pi$–$\pi$ interaction of the Pc rings in the double-decker complexes [26–29].

Recently, we synthesized cobalt Pcs with four 4-[(6-methyl-3-nitro-2-oxo-1,2-dihydropyridine-4-yloxy) substituents at the peripheral positions [30]. Therefore, in this study Zn(II), metal-free mononuclear and dinuclear type LuPc2 phthalocyanines bearing a similar set of peripheral pyridine substituents were synthesized and characterized. We have also examined the electrochemical and spectrolelectrochemical properties of the newly-synthesized compounds.

EXPERIMENTAL

Synthetic materials

All chemicals were reagent grade. Solvents were dried, purified and stored over molecular sieves. The progress of the reactions was monitored by thin layer chromatography (TLC).

Instrumentation

Electronic absorption spectra were obtained on a Shimadzu UV-2450 UV-vis spectrophotometer. Infrared
spectra (IR) were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. The $^1$H-NMR spectrum was recorded on a Varian Unity Inova 500 MHz NMR spectrometer. Mass spectra were performed on a Bruker Microflex LT MALDI-TOF spectrophotometer.

**Syntheses**

The synthesis of the 4-(4-methylpyridine-2-yl)oxy phthalonitrile precursor has been reported previously [30] and was used to prepare the Zn(II) complex (1) through a metal insertion reaction.

![Synthesis Scheme](image)

**Scheme 1.** Synthesis of compounds 1, 2 and 3, reagents and conditions. (i) Zn(OAc)$_2$·2H$_2$O, amyl alcohol, 12 h (ii) Li metal, amyl alcohol, 12 h (iii) Lu(OAc)$_3$·H$_2$O, DBU, amyl alcohol, 4 h (iv)
16.91. UV-vis (CHCl$_3$, $\lambda_{\text{max}}$ (nm) (log $\varepsilon$)): 343 (4.51), 610 (4.30), 676 (4.85). M/z: 1007.68 [M$^+$].

Tetrakis[4-methylpyridine-2-yl]oxy metal-free phthalocyanine (2). Li metal and 10 ml dry amyl alcohol were stirred at 50°C under an argon atmosphere until complete dissolution of Li. Then, 1.076 mmol (0.250 g) of 1 was added and refluxed for 12 h. The reaction mixture was cooled down to room temperature and precipitated by adding diluted acetic acid. After filtration, the product (6) was washed with methanol and acetone. This compound was soluble in CHCl$_3$, DMF (Scheme 1). Yield (120 mg, 47%); M.p. > 300°C. IR $\nu$ (cm$^{-1}$): 3287, 3069, 2923, 2851, 1656, 1579, 1479, 1421, 1370, 1098, 1010, 853, 744. Anal. Calc. For C$_{56}$H$_{38}$N$_{12}$O$_4$ C, 71.33; H, 4.06; N, 17.82; Found: C, 71.11; H, 3.94; N, 18.02. UV-vis (CHCl$_3$, $\lambda_{\text{max}}$ (nm) (log $\varepsilon$)): 338 (4.69), 603 (4.28), 640 (4.5), 659 (4.81), 697 (4.81). M/z: 944.43 [M$^+$].

Bis[tetrakis(4-methylpyridine-2-yl)phthalocyaninato]Lu(III) (3). A mixture of 0.074 mmol (0.070 g) 3, 0.074 mmol (0.026 g) Lu(OAc)$_3$ ⋅ H$_2$O and 0.148 mmol (0.023 mg) 1,8-diazabicyclo[5.4.0]jundec-7-ene (DBU) was refluxed in 3 ml o-dichlorobenzene for 3–4 h until the starting ligand disappeared completely. The course of the reaction was monitored by TLC. At the end of the reaction, the resulting mixture was cooled down to room temperature and precipitated by adding diluted acetic acid. After filtration, the product 3 was washed with methanol, acetone and purified by column chromatography (silica gel) with CHCl$_3$. This compound was soluble in CHCl$_3$, DMF and DMSO (Scheme 1). Yields 35 mg (46%). M.p. > 300°C. IR $\nu$ (cm$^{-1}$): 3052, 2923, 2856, 1660, 1580, 1530, 1487, 1323, 1273, 1137, 1083, 1054, 1022, 899, 746. Anal. Calc. C$_{22}$H$_{16}$N$_{12}$O$_4$Lu C, 65.40; H, 3.53; N, 16.34; Found: C, 65.29; H, 3.45; N, 16.52. UV-vis (CHCl$_3$, $\lambda_{\text{max}}$ (nm) (log $\varepsilon$)): 345 (4.62), 612 (4.33), 678 (4.87). M/z: 2057.88 [M$^+$].

Electrochemistry and in situ spectroelectrochemistry

The cyclic voltammetry (CV), square wave voltammetry (SWV) and controlled potential chronocoulometry (CPC) measurements were carried out using a Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three electrode configuration at 25°C. For CV and SWV measurements, the working electrode was a Pt plate with a surface area of 0.10 cm$^2$. A Pt spiral wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure DMSO were employed as the supporting electrolyte at a concentration of 0.10 mole dm$^{-3}$. High purity of N$_2$ was used for deoxygenating the solution at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements.

Electrochemical and colorimetry supporting in situ spectroelectrochemical measurements of the complexes 1–3 were made on a Pt working electrode in a de-aerated DMSO/TBAP electrolyte system. Table 1 lists the assignment of the redox couples and determined electrochemical data, which include half-wave peak potentials ($E_{1/2}$), anodic to cathodic peak potential separation ($\Delta E_{p}$), and the difference between the first oxidation and reduction potentials ($\Delta E_{1/2}$). For the reduction couples, $\Delta E_{p}$ values at 0.100 V·s$^{-1}$ scan rate usually ranged from 0.060 to 0.130 V, suggesting reversible to quasi-reversible behavior, except for the last

RESULTS AND DISCUSSION

Synthesis and characterization

Compound 1 was prepared by the reaction of 4-((4-methylpyridine-2-yloxy)phthalonitrile [30] and Zn(OAc)$_2$ ⋅ 2H$_2$O in refluxing dry amyl alcohol for 10 min. To synthesize lutetium bis-phthalocyanine (Pc-Lu) 3, a mixture of compound 2, Lu(OAc)$_3$, H$_2$O and DBU was refluxed in o-dichlorobenzene (3 ml) for 3–4 h. These complexes have high solubility in CHCl$_3$, THF, DMF and DMSO (Scheme 1). The structures of 1–3 were confirmed through elemental analysis, UV-vis absorption, FT-IR, and $^1$H-NMR spectroscopy and MALDI-TOF mass spectrometry.

In the UV/vis absorption spectra in solution, the characteristic Q bands of compound 1 and 3 were observed at 676 and 678 nm, respectively, as single bands with high intensities in the visible region. On the other hand, the Q-band absorptions were observed at 659 and 697 nm as double for 2. These bands confirmed the structure of metal-free Pc 2. These characteristic absorptions are due to the π–π* transition of the conjugated 18π electron systems. The elemental analytical results were also in good agreement with the calculated values. In the mass spectra of the Pc complexes, the presence of molecular ion peaks at m/z = 944.43 [M$^+$] for 1, m/z = 1007.68 [M$^+$] for 2 and m/z = 2057.88 [M$^+$] for 3 confirmed the proposed structures.
reduction couples at the end of negative potential window, for which peak separation was higher (ΔE_Ep of 0.080 V at 0.010 V·s⁻¹ was obtained for the ferrocene internal standard). The peak currents for the redox couples of the complexes were usually found to be directly proportional to the square root of scan rates ranging from 0.050 to 0.500 V·s⁻¹, suggesting their diffusion-controlled nature.

CPC studies at suitable constant peak potentials for 1–3 displayed that all reduction and oxidation processes involve the transfer of one electron. Mononuclear-type Pc complexes, ZnPc (1) and H₂Pc (2) displayed similar redox behavior with three reduction couples (R₁–R₃) and one oxidation couple (O₁) (Table 1). Figures 1 and 2 display cyclic and square wave voltammograms of 1 and 2, respectively. The half-wave potentials of 1 and 2 are generally similar to each other with slight changes which can be attributed to the differences in the polarizing effects of the relevant metal centers (Table 1). This similarity suggests that all redox processes of those complexes are Pc ligand-based [31]. The first reduction of the Pc ligand is associated to the position of the lowest occupied molecular orbital (LUMO) whereas the first oxidation of the ligand is associated to the position of the highest occupied molecular orbital (HOMO). For this reason, ΔE₁/₂ values related with the HOMO–LUMO gap in MPc species having redox inactive metal centers and for compounds 1 and 2, are generally consistent with the values reported in the literature (Table 1) [32, 33].

As shown in Figs 1 and 2, in general, the first reduction couple R₁ and the second reduction couple R₂ are chemically and electrochemically reversible with respect to ΔE_Ep, I_p/I.pc for oxidation processes at 0.100 V·s⁻¹ scan rate. The third reduction process, R₃, was ill-defined for both compounds and thus, could not be analyzed properly. Broadening of the R₃ couple may be due to the instability of the complex at high negative potentials and/or the presence of a chemical reaction succeeding the electron transfer reactions. In addition, the oxidation process O₁, could be identified only by SWV as shown in Figs 1 and 2. Electrochemical behaviors of ZnPc (1) and metal-free Pc (2) were highly different in comparison with those of dinuclear type Pc complex, LuPc₂ (3).

Table 1. The electrochemical data for 1–3. All electrochemical data were given vs. SCE

<table>
<thead>
<tr>
<th>Pcs</th>
<th>Label</th>
<th>ₐE₁/₂ (V)</th>
<th>ₐΔE_Ep (mV)</th>
<th>ₐI_p/I_pc (V)</th>
<th>ₐΔE₁/₂ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R₁</td>
<td>-0.71</td>
<td>60</td>
<td>0.96</td>
<td>1.45</td>
</tr>
<tr>
<td>1</td>
<td>R₂</td>
<td>-1.08</td>
<td>70</td>
<td>0.84</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>R₃</td>
<td>-1.62</td>
<td>120</td>
<td>0.70</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>O₁</td>
<td>0.70</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>R₁</td>
<td>-0.53</td>
<td>65</td>
<td>0.88</td>
<td>1.23</td>
</tr>
<tr>
<td>2</td>
<td>R₂</td>
<td>-0.85</td>
<td>65</td>
<td>0.92</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>R₃</td>
<td>-1.43</td>
<td>110</td>
<td>0.75</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>O₁</td>
<td>0.76</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>R₁</td>
<td>0.33</td>
<td>70</td>
<td>0.94</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>R₂</td>
<td>-0.78</td>
<td>75</td>
<td>0.93</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>R₃</td>
<td>-1.20</td>
<td>110</td>
<td>0.75</td>
<td>—</td>
</tr>
</tbody>
</table>

ₐE₁/₂ = (E_p + E_pc)/2 at 0.100 V·s⁻¹.
ₐΔE_Ep = E_p – E_pc at 0.100 V·s⁻¹.
ₐI_p/I_pc for reduction, I_p/I.pc for oxidation processes at 0.100 V·s⁻¹ scan rate.
ₐΔE₁/₂ = E₁/₂ (first oxidation) – E₁/₂ (first reduction). HOMO–LUMO gap for MPc having an electro inactive metal center.
ₐThese redox couples could be detected only by square wave voltammetry.
ₐThe redox processes of reduced form of LuPc₂ R-3c.
SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF NOVEL

The difference between the first reduction and the first oxidation processes, $\Delta E_{1/2}$, of LuPc$_2$ (3), is 0.28 V, being much lower than those for ZnPc (1) (1.21 V) and H$_2$Pc (2) (1.23 V) in DMSO (Table 1). The lower $\Delta E_{1/2}$ value for 3 is compatible with values in the literature [26, 27, 34]. It appears that in complex 3, one of the Pc rings has a $-2$ oxidation state, while the other one has a $-1$ oxidation state, which gives a radical structure to the LuPc$_2$ complexes. Although these redox processes are also ring-based due to the redox-inactive central metals, redox behavior of this complex is very different in comparison with those of 1 and 2. Accordingly, radical complex 3 was observed to be reduced and oxidized more easily than the mononuclear-type complexes 1 and 2 (Table 1). Furthermore, spectroelectrochemical measurements of complex 3 suggested that it is reduced instantly without applying any negative potential when the circuit of the electrochemical cell is connected to the potentiostat and the cell turned on. Thus, complex 3 transforms into the reduced form at 0.0 V bias potential at the beginning of the electrochemical measurements.

As shown in Fig. 3, the LuPc$_2$ complex 3 undergoes three one-electron reductions and one one-electron oxidation couples. $\Delta E_p$ values at 0.100 V $\cdot$ s$^{-1}$ scan rate was changed from 0.060 to 0.090 V for all processes of 3, which exhibited electrochemical reversibility or at least quasi-reversibility of the electron transfer reactions. In addition, the square wave voltammogram clearly confirmed the reversibility of the redox processes (Fig. 3b). The redox processes of this complex can be assigned accordingly as shown in Scheme 2.

It is not possible to detect the nature of the redox processes definitively by voltammetric measurements of CV and SWV alone. For this reason, the voltammetric measurements were supported by in situ spectroelectrochemical measurements. Controlled potential electrolysis of the solution of 3 at suitable peak potentials was carried out to provide additional support for the complete identification of the redox processes, determination the spectra and colors of its electrogenerated anionic and cationic forms and thus, identification of its suitability for usage as a color-changing electrochromic material. Figure 4 represents UV-vis spectral changes.
and a simultaneously recorded chromaticity diagram of 3 in the coordinating solvent, DMSO.

It is well known in contrast to a non-coordinating solvent such as DCM, double-decker lanthanide PCs exist in the reduced form in a coordinating solvent medium [26, 27]. Accordingly, compound 3 appears to be in the reduced form, not in the form of radical, in DMSO, as evidenced from the absence of a band around 500 nm in its original spectrum prior to application of any constant potential (Fig. 5a) [26]. This finding is further supported by the spectral changes observed during the oxidation process at 0.75 V. As shown in Fig. 4b, the oxidation at this potential produces a new band at 458 nm. As previously stated, this band is characteristic for the radical nature of lanthanum double-deckers and thus provides strong support for the idea that 3 occurs in the reduced form in DMSO. The color change associated with oxidation processes of the complex was also recorded with in situ electrocolorimetric measurements. The bluish-green color of the reduced form (R-3) (○: x = 0.3051 and y = 0.3412) turns to light yellow (□: x = 0.3841 and y = 0.3788), throughout the first oxidation at 0.75 V. It is reported in the literature that double-decker lanthanide phthalocyanines, especially lutetium double-deckers, give distinct color changes during their electron transfer reactions, and thus they are promising electrochromic materials [35, 36]. The results of this study also point out that compound 3 can be used as electrochromic material for green-to-yellow color transition. Unfortunately, the color changes associated with the reduction processes were not sharp.

CONCLUSIONS

Pyridine-substituted mononuclear zinc and metal-free and double-decker lutetium PCs have been synthesized by using 4-(4-methylpyridine-2-yl)oxyphthalonitrile. Electrochemical, in situ spectroelectrochemical and in situ electrocolorimetric properties of the newly-synthesized compounds were also investigated. Electrochemical investigation suggested that double-decker lutetium Pc 3 occurs in the reduced form in DMSO and shows enriched redox and electrochromic properties as compared to mononuclear phthalocyanines 1 and 2. Furthermore, in situ electrocolorimetric measurements pointed out the usability of compound 3 as electrochromic material for a green-to-yellow color transition.

Acknowledgments

We are thankful to the Research Foundation of Marmara University, Commission of Scientific Research Project (BAPKO) (Project No: FEN-A-101013-0397 and Project FEN-C-YLP-121214-0391) and The Turkish Academy of Sciences (TUBA).

REFERENCES

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INTRODUCTION

Phthalocyanines are an interesting class of materials. Phthalocyanine complexes belong to a wide class of π-conjugated metallomacrocycles, which are of great interest due to their various important applications in modern science and technology [1, 2]. Phthalocyanines have an original electronic structure based on 18 π delocalization, resulting in near infrared absorption around 700 nm and possibly up to 1000 nm by increasing the electronic delocalization [3]. Subsequent electronic, photophysical, and photochemical properties are desired for many applications [4].

Phthalocyanines are one of the most noteworthy types of tetrapyrole compounds, and they show wide ranges of applications in various areas such as gas and chemical sensors, solar cells, electrochromic and electroluminescent displays, photovoltaic and semiconductors, electronic devices, liquid crystals, non-linear optics materials, biomedicine and photodynamic therapy (PDT) [5–12]. Phthalocyanine derivatives comprise the second generation of photosensitizer molecules employed in photodynamic therapy (PDT) and have attracted much attention due to their outstanding photosensitizing performance. Most phthalocyanines are hydrophobic compounds that require association with drug delivery systems for clinical use [13].

The main problem limiting applications of phthalocyanines in many fields is still their limited solubility. Their solubility can be increased, however, by introducing electron-withdrawing (-F, -Cl, -Br) and electron-donating (-NH2, Ar-S-, OR-) bulky or long chain alkyl groups into the peripheral sites [14–18]. The formation of constitutional isomers and the higher dipole moment of the tetra-substituted phthalocyanines resulting from

ABSTRACT: This work describes the synthesis, spectral, aggregation and fluorescence properties of bis 4-[(4-tert-butylbenzyl)oxy substituted metal free (2), magnesium (3), zinc (4) and nickel (5) phthalocyanines. The syntheses of the novel compounds were confirmed by FT-IR, UV-vis, mass and NMR spectroscopy techniques, as well as elemental analysis. The effects of the nature of the central metal on the photophysical parameters of the phthalocyanine complexes are reported in this study. The photochemical properties (singlet oxygen quantum yields and photodegradation quantum yields) and photophysical properties (fluorescence behavior and fluorescence quantum yield) of the complexes were reported in different solutions (dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) and tetrahydrofuran (THF)). However, energy minimized structure, vibrational frequency, molecular orbital levels and electronic absorption spectra were obtained by DFT calculations which supported the experimental results.

KEYWORDS: phthalocyanines, fluorescence, aggregation, photochemistry, theoretical chemistry, DFT.

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the unsymmetrical arrangement of the substituents on the periphery lead to higher solubility of phthalocyanines in many organic solvents [19].

Aggregation of dye molecules plays an important role in energy and electron transfer and in light harvesting systems. The propensity of phthalocyanines to form aggregates because of the strong interactions between planar macrocycles in solution is well-known [20].

Substituted metallophthalocyanines could form two types of aggregations which affect electronic and optical properties, namely face-to-face H-aggregation and side-to-side J-aggregation [21, 22]. Typically, phthalocyanine aggregation results in a decrease in intensity of the Q band corresponding to the monomeric species; meanwhile a new, broader and blue shifted band is seen to increase in intensity. This shift to lower wavelengths indicates H-type aggregation among phthalocyanine molecules. In rare cases red-shifted bands have been observed corresponding to J-type aggregation of the phthalocyanine molecules. Generally, J-aggregates of Pcs occur by utilizing the coordination of the side substituent from one Pcs molecule to the central metal ion in a neighbor [23–27]. The substituted zinc Pcs in non-coordinated organic solvents, e.g. chloroform and dichloromethane exhibit J-aggregation [28–30]. In this paper we have prepared, characterized and reported the photophyisciochemical measurements of novel phthalocyanines with four bis 4-[(4-tert-butylbenzyl)oxy] units on the periphery. Additionally, geometry optimization, vibrational frequency and electronic properties of title compounds (2, 3, 4 and 5) were investigated using density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculation methods in order to better elucidate the molecular structure.

EXPERIMENTAL

Materials

All chemicals were reagent grade from Merck and Sigma–Aldrich. Solvents in reactions were distilled from appropriate drying agents prior to use and commercially available reagents were used without further purification unless otherwise stated. Flash column chromatography was carried out using silica gel 60 (0.04–0.063 mm) from Merck.

Equipment

FT-IR spectra were recorded on a spectrum one Perkin Elmer FT-IR spectrophotometer using ATR. 1H NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer. Absorption spectra were recorded with an Agilent 8453 UV-vis spectrophotometer. The elemental analyses and Bruker Microflex LT MALDI-TOF mass spectra were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). GC-Mass Spectra were performed on a Agilent 6890N GC-System-5973 IMSD. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. All chemicals used were of an analytical grade. Solvents were purified with conventional methods.

Photophysical and photochemical studies

Fluorescence quantum yields

Fluorescence quantum yields (ΦF) were determined by the comparative method (Eq. 1) [31],

$$\Phi_F = \frac{F \cdot A_{\text{std}}}{F_{\text{std}} \cdot A}$$

where $F$ and $F_{\text{std}}$ are the areas under the fluorescence emission curves of the samples and the standard, respectively. $A$ and $A_{\text{std}}$ are the respective absorbances of the samples and standard (Unsubstituted ZnPc) at the excitation wavelengths, respectively. $n^2$ and $n_{\text{std}}^2$ are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc in DMSO ($\Phi_F = 0.20$), in DMF ($\Phi_F = 0.17$), and in THF ($\Phi_F = 0.25$) [32] was used as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Singlet oxygen quantum yields

Singlet oxygen quantum yield (ΦS) determinations were carried out using the experimental set-up described in the literature [33]. Quantum yields of singlet oxygen photogeneration were determined in air (no oxygen bubbled) using the relative method with ZnPc as reference and DPBF as chemical quencher for singlet oxygen, using Eq. 2

$$\Phi_S = \Phi_{\text{S std}} \times \frac{R \cdot I_{\text{S std}}}{R_{\text{S std}} \cdot I_{\text{abs}}}$$

where $\Phi_{\text{S std}}$ is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_{\text{S std}} = 0.67$ in DMSO, 0.56 in DMF and 0.53 in THF [d]). $R$ and $R_{\text{S std}}$ are the DPBF photobleaching rates in the presence of the respective samples and standard, respectively. $I_{\text{abs}}$ and $I_{\text{abs}}^{\text{S std}}$ are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [34, 35], the concentration of the quencher (DPBF) was lowered to $\sim 3 \times 10^{-5}$ mol·cm$^{-3}$. Solutions of a sensitizer (containing DPBF) were prepared in the dark and irradiated in the Q band region using the set-up described above. DPBF degradation was monitored at 417 nm. The light intensity of $7.05 \times 10^{15}$ photons s$^{-1}$·cm$^{-2}$ was used for $\Phi_S$ determinations.
Photodegradation quantum yields

Photodegradation quantum yield (Φd) determinations were carried out using the experimental set-up described in the literature [36]. Photodegradation quantum yields were determined using formula 3,

\[ \Phi_d = \left( \frac{C_0 - C_t}{C_0} \right) \cdot \frac{V \cdot N_A}{I_{irr} \cdot S \cdot t} \]

where “C0” and “Ct” are the sample concentrations before and after irradiation respectively, “V” is the reaction volume, “N_A” is Avogadro’s constant, “S” is the irradiated cell area, “t” is the irradiation time, “I_irr” is the irradiation source light intensity and the absorption of the samples. A light intensity of \(2.38 \times 10^{16}\) photons s\(^{-1}\) cm\(^{-2}\) was employed for Φd determinations.

Synthesis

**Synthesis of 4-[(4-tert-butylbenzyl)oxy phthalonitrile (I).** A mixture of bis 4-[(4-tert-butylbenzyl) alcohol (1.00 g, 6.09 mmol) and 4-nitrophthalonitrile (1.05 g, 6.09 mmol) in DMF (25 mL) was stirred under argon atmosphere at room temperature. Anhydrous K\(_2\)CO\(_3\) (2.17 g, 15.80 mmol) was added in three equal portions and the reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was dropped into ice, and the precipitate was filtered off, washed with water and methanol and then dried. The crude product was recrystallized from ethanol. Finally the pure product was dried in vacuum. Yield: 1.65 g (93%). FT-IR (KBr), \(v/cm\(^{-1}\): 3106, 3076 (Ar-CH); 2963 (C-H); 1604 (C=C); 1218 (C-O-C ether); 1H NMR (CDCl\(_3\)): (ppm) 7.70–7.20 (m, 28 H, Ar-CH); 5.10 (s, 2 H, R-CH\(_2\)); 1.30 (s, 9 H, R-CH\(_3\)); (MALDI-TOF) m/z: \(C_{29}H_{32}N_8O_4\); Calc. 429.35; Found: 429 [M]+.

**Synthesis of metal-free phthalocyanine (2).** Compound I (0.10 g, 0.345 mmol) and 2 mL of dry pentanol were placed in a standard Schlenk tube in the presence of DBU (17 \(\mu\)L) under an argon atmosphere and this mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into n-hexane. Finally the pure metallophthalocyanine was chromatographed over a silica gel column using a mixture of CHCl\(_3\); THF (1/1 by volume) as eluent.

**General procedures of metallophthalocyanine derivatives (3–5)**

A mixture of bis 4-[(4-tert-butylbenzyl)oxy phthalonitrile I (0.10 g, 0.345 mmol), anhydrous metal salts [MgCl\(_2\) (0.032 g, 0.345 mmol), Zn(OAc)\(_2\) (0.079 g, 0.37 mmol) NiCl\(_2\) (0.044 g, 0.345 mmol)], and a catalytic amount of DBU (17 \(\mu\)L) in 2.5 mL of dry \(n\)-pentanol was heated and stirred at 160°C in a standard Schlenk tube for 6 h under N\(_2\). After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into n-hexane. Finally, the pure metallophthalocyanine was obtained after recrystallization and was precipitated by adding it drop-wise into n-hexane. Finally, the pure metallophthalocyanine was obtained after recrystallization and was precipitated by adding it drop-wise into n-hexane. Finally, the pure metallophthalocyanine was obtained after recrystallization.

**Synthesis of magnesium (II) phthalocyanine (3).** Yield: 0.033 g (32%). FT-IR (KBr), \(v/cm\(^{-1}\): 3078, 3059 (Ar-CH); 2961, 2864 (C-H); 1604 (C=C); 1218 (C-O-C ether); 1H NMR (CDCl\(_3\)): (ppm) 7.60–6.50 (m, 28 H, Ar-CH); 5.10 (s, 8 H, R-CH\(_2\)); 1.30 (s, 36 H, R-CH\(_3\)); UV-vis (THF) \(\lambda_{max}/nm\) (log(e/mol\(^{-1}\)-cm\(^{-1}\))): 354 (4.79), 612 (4.39) and 678 (5.11): MS (MALDI-TOF) m/z: \(C_{29}H_{32}NiN_8O_4\); Calc. 1185.74; Found: 1184.60 [M – H]+.

**Synthesis of zinc (II) phthalocyanine (4).** Yield: 0.049 g (45%). FT-IR (KBr), \(v/cm\(^{-1}\): 3075 (Ar-H); 2925, 2862 (C-H); 1605 (C=C); 1226 (C-O-C ether); 1H NMR (CDCl\(_3\)): (ppm) 7.70–6.50 (m, 28 H, Ar-H); 5.10 (s, 8 H, R-CH\(_2\)); 1.30 (s, 36 H, R-CH\(_2\)); UV-vis (THF) \(\lambda_{max}/nm\) (log(e/mol\(^{-1}\)-cm\(^{-1}\))): 350 (4.71), 610 (4.34) and 676 (5.04): MS (MALDI-TOF) m/z: \(C_{29}H_{32}ZnN_8O_4\); Calc. 1226.84; Found: 1225.06 [M – H]+.

**Synthesis of nickel (II) phthalocyanine (5).** Yield: 0.053 g (51%). FT-IR (KBr), \(v/cm\(^{-1}\): 3059 (Ar-H); 2960, 2882 (C-H); 1608 (C=C); 1258 (C-O-C ether); 1H NMR (CDCl\(_3\)): (ppm) 7.70–7.10 (m, 28 H, Ar-H); 5.00 (s, 8 H, R-CH\(_2\)); 1.50 (s, 36 H, R-CH\(_3\)); UV-vis (THF) \(\lambda_{max}/nm\) (log(e/mol\(^{-1}\)-cm\(^{-1}\))): 383 (4.23), 621 (4.40) and 671 (4.64): MS (MALDI-TOF) m/z: \(C_{29}H_{32}NiN_8O_4\); Calc. 1220.13; Found: 1218.04 [M – 2H]+.

Theoretical calculations

The ORCA quantum chemistry package was used for all calculations [37, 38]. In our DFT calculations we used the mixed (6-31G (d, p)) [39, 40] and def2-TZVP [41] basis sets. While a mixed basis sets were used in these calculations due to relatively less cost at acceptable precision (a balanced polarized triple-zeta basis set def2-TZVP for Zn, Mg and Ni atoms and 6-31G (d, p) basis set for C, H, N and O atoms). The optimized molecular structural parameters were used in the harmonic vibrational frequency calculation and then scaled by 0.9613 [42]. The geometry optimization was followed by frequency calculations, and no imaginary frequencies were found. That is to say, the structure obtained from
geometry optimization corresponds to a stationary point in the potential surfaces and is a stationary structure. Additionally, due to investigation of the molecular reactivity and the capability of electron transport of the title compound, the theoretical calculation and plotting of Frontier Molecular Orbital Energy Levels (FMOs) were obtained by using the above-mentioned DFT method. Finally, the electronic absorption spectra of the title compounds were calculated with the time dependent density functional theory (TD-DFT) using same functional and basis sets in vacuum and in THF solvent. The solvent effect was considered using the conductor-like screening model (COSMO). All visualizations were done using Avogadro 1.1.1 [43] and Chemcraft 1.8 software [44].

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 gives the synthetic route to novel phthalocyanines 1–5 discussed in this work. The syntheses of complexes 2–5 were achieved by treatment of phthalonitrile 1 with anhydrous metal salts in dry 1-pentanol at reflux temperature under argon atmosphere in the presence of 1,8-diazabicyclo (5.4.0) undec-7-ene (DBU) as a strong base. All of these new metal-free and metallophthalocyanines were purified by column chromatography. They were obtained in a moderate yield (52% for 2, 32% for 3, 45% for 4 and 51% for 5) and were characterized...
by elemental analysis together with the spectral data (1H NMR, FTIR, Mass and UV-vis spectroscopies, see Table 1). Characterization data of the new compounds are consistent with the assigned formula as shown in the experimental section.

Phthalocyanines generally have poor solubility in most organic solvents; nevertheless, all studied phthalocyanine complexes 2–5 exhibited excellent solubility in organic solvents such as CHCl3, CH2Cl2, THF, DMF and DMSO.

The characteristic vibrations corresponding to C≡N were observed at 2229 cm⁻¹ for 1. Aromatic C-H and aliphatic C-H peaks occurred at 3076 cm⁻¹ and 2963 cm⁻¹ for the phthalonitrile (1). After conversion into metal-free and metallophthalocyanines 2, 3, 4 and 5 the characteristic sharp C≡N stretch at 2230 cm⁻¹ for phthalonitrile 1 disappeared. The IR spectra of metal-free 2 and metallophthalocyanines 3, 4 and 5 are very similar. The significant difference is the presence of N-H vibrations of the inner phthalocyanine core which are assigned to a weak vibration at 3285 cm⁻¹ in the metal-free compound. The synthesized phthalocyanine complexes 2–5 showed characteristic vibrations belong to ether groups (C-O-C) at ca. 1230 cm⁻¹, aromatic CH stretching at ca. 3075 cm⁻¹ and aliphatic CH stretching at ca. 2960–2860 cm⁻¹.

The 1H NMR spectra of tetra-substituted phthalocyanine complexes 2–5 showed broad absorptions when compared with that of corresponding phthalonitrile derivative 1. It is likely that broadness is due to both chemical exchange caused by aggregation–disaggregation equilibrium in CDCl3 and the fact that the product obtained in this reaction is a mixture of four positional isomers which are expected to show chemical shifts which slightly differ from each other for tetra-substituted complexes 2–5. The tetra-substituted phthalocyanines 2 to 5 showed the phthalocyanine ring protons as unresolved multiplets (most likely due to the presence of isomers). The phthalocyanine ring protons for peripherally tetra-substituted complexes were observed in the range 8.70 to 6.50 ppm for 2 integrating for 28 protons, 7.60 to 6.70 for 3 integrating for 28 protons, 7.70 to 6.50 for 4 integrating for 28 protons and 7.70 to 7.10 ppm for 5 integrating for 28 protons as expected. The O-CH₂ protons for complexes 2–5 were observed at 5.00 ppm for 2, 5.10 ppm for 3 and 5.00 ppm for 4, integrating totally for 32 protons as expected. The O-CH₃ protons for complexes 2–5 were observed at 1.30 ppm for 2, 1.30 for 3 and 1.30 for 4, integrating for 36 protons and 1.50 ppm for 5 integrating for 36 protons for all studied phthalocyanine complexes, as expected. Although the presence of isomers as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals, the observed spectra of all studied complexes were relatively well-resolved. For metal-free derivative 2, protons in the inner core of phthalocyanine are screened by aromatic π electrons of the macrocycle, so they appeared at -1.14 ppm in the 1H NMR.

Table 1. UV-vis spectral and photophysical parameters for compounds 2, 3, 4, 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>λₐ (Abs)/nm</th>
<th>λₐ (Ems)/nm</th>
<th>λₐ (Exc)/nm</th>
<th>Δλₛₑₕₑₑₑ/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>THF</td>
<td>703 (4.88)</td>
<td>668 (4.82)</td>
<td>712</td>
<td>704</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>678 (5.15)</td>
<td>690</td>
<td>680</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>697</td>
<td>686</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>676 (5.15)</td>
<td>689</td>
<td>681</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>681 (5.09)</td>
<td>694</td>
<td>685</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>684 (5.12)</td>
<td>697</td>
<td>687</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>672 (4.87)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 1. Mass spectrum of compound 4
In addition to these verifying results for the structures, the mass spectra of compounds 1–5 gave the characteristic molecular ion peaks at m/z: 290 [M]+, 1163.94 [M]+, 1184.60 [M–H]+, 1225.06 [M–H]+, 1218.04 [M–2H]+, respectively, confirming the proposed structures respectively (see Fig. 1 using complex 4 as an example).

**Ground state electronic absorption**

The ground state electronic spectra are especially useful to identify the structure of the phthalocyanines. Generally, UV-vis spectra of phthalocyanines show typical electronic spectra with two strong absorption bands known as the Q and B bands. The Q band in the visible region at ca. 600–750 nm is attributed to the π–π* transition from HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc (–2) ring and the B band in the UV region at ca. 300–400 nm arises from the deeper π–π* transitions [45], but contains a small contribution from n–π* transitions.

The ground state electronic absorption spectra of the peripherally tetra-substituted phthalocyanine complexes 2 to 5 showed monomeric behavior evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes in CHCl₃, CH₂Cl₂, THF, DMF and DMSO. In the UV-vis spectrum of metal-free phthalocyanine 2, the characteristic split Q band was observed at 666 and 703 nm in chloroform, which can be attributed a₁u → eg transition [46]. A typical spectrum of the metal-free phthalocyanine 2 showed a B band at 343 nm in THF (Fig. 2). The UV-vis absorption spectra of metallophthalocyanines 3–5 were characterized by intense Q absorption at 678, 676 and 671 nm. In addition, intense B band absorptions were observed at 354 nm for 3, 350 nm for 4 and 383 nm for 5 in THF, respectively (Figs 3–5).

**Computational details**

**Geometry optimization and harmonic frequencies**

The geometry optimization of all compounds were calculated using the B3LYP functional and mixed basis set def2-TZVP for Zn, Mg, Ni atom and 6-31G (d, p) for others in gas phase. When we look at the optimized molecular structures of compound 2 (Fig. 6), 3, 4 and 5 (Fig. 7) that we have calculated, they are obtained the phthalocyanine rings in a planar structure as expected. Additionally, according to the results...
of the frequency calculations of the optimized geometry, absence of the imaginary frequency indicated that the structure was in a stationary point.

The harmonic frequencies of optimized title compounds were calculated with the same DFT level and were found to be larger than experimental measurements. This difference may be explained due to settling in the possible isomeric mixture of products, which have not been separated. Therefore, predicted vibration frequencies were scaled down with a scaling factor of 0.9613. The calculated aromatic/aliphatic C-H stretches of compound 2, 3, 4 and 5 appeared at 3096/2960–2891, 3089/(2993–2920), 3087/(2990–2917), 3092/(2994–2920) cm⁻¹ respectively. As result, the calculated harmonic frequencies of the title compounds compared with the experimental results, as can be seen in Fig. 8, in which the FT-IR spectrum (solid phase – KBr pellets) of the title compound along with theoretically simulated IR spectrum (gas phase) is given, it is understood that the theoretical data are in agreement with the experimental results.

Frontier molecular orbital energy levels

As known, the theoretical calculation of frontier MOs are a supplement to information about molecular reactivity and the accomplishments of electron transport, which usually occurs in the frontier of a system. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are very important quantum parameters which play a role in the electric and optical properties [47]. Also known as high \( \pi \) bond conjugation expects to have a low HOMO–LUMO energy gap in their structures of complex. In this study, energies of HOMO and LUMO orbitals calculated at same DFT level for the title compounds.

The theoretical frontier molecular orbital energy levels have been obtained and frequencies for compound 2, 3, 4, 5 and ZnPc are represented in Fig. 9, arranged in descending order according to the energy gap between the HOMO and LUMO. The compounds are shown at eight energy levels in the range of HOMO-3 to LUMO+3 in figure. The data for the energy gaps are marked at the appropriate orbital energy levels. The range of HOMO-3 to LUMO+3 and the HOMO–LUMO energy gap of compound 2, 3, 4, 5 and ZnPc, which are the main orbital energy levels of the compounds are also listed in Table 2 according to the ascending size of the energy gap. As shown Fig. 9 and

---

**Fig. 5.** Absorption spectral changes of 5 in THF at different concentrations

**Fig. 6.** Full optimized molecular structures at DFT method of calculations of compound 2 (a) and side view of (b)
In addition, as previously reported by Mizuseki et al. [49], charge transport was also related to the spatial distribution and composition of the frontier orbitals. Therefore, we calculated the spatial distribution HOMO and LUMO orbitals for 2, 3, 4 and 5. We show the results in Fig. 10, and according to this figure, there is no significant difference and variation in spatial distribution HOMO and LUMO orbitals, which is in accordance with very small differences the HOMO–LUMO energy gap results.

**Electronic absorption spectra**

Theoretical wavelengths, oscillator strengths, transition energies and molecular orbital excitation for the most relevant electron transitions of the electronic absorption of the compound 2, 3, 4, 5 and ZnPc in THF were achieved via time dependent density functional theory (TD-DFT) method. The electronic spectra are simulated by fitting to Lorentzian line shape with a half-width at a half-maximum of 20 nm. The theoretical UV-vis spectra of these phthalocyanine derivatives by our calculations are shown in Fig. 11, arranged in descending order of the absorption bands. Moreover, the theoretical absorption wavelength, oscillator strengths, and molecular orbital excitation configurations for the most relevant transitions of the electronic absorption band of title compounds are given in Table 3. The curves, as seen in Fig. 11, have very similar shapes and their position of absorption bands red shift compared to compound ZnPc. Also, as seen in Table 3, the theoretical UV-vis spectrum of ZnPc shows a Q band at 546 nm, whereas the compound 2, 3, 4 and 5 show them at 578, 574, 570, 569 nm respectively. Thus, the red shifts in Q bands of title compounds are close to each other and these values were are descending order from compound 2 to 5, which is consistent with the HOMO–LUMO energy gaps (Fig. 9) discussed above. The expected decrease in HOMO–LUMO gap occurs upon increasing the Q band to higher lambda maxima (so called red shift). From Table 3 it can be observed the Q bands of the title phthalocyanines correspond to a p–p* transition with the HOMO–LUMO transition (around 80%). In addition, the oscillator strengths of the Q band are increased compared to the ZnPc standard phthalocyanine. This indicates that the addition of a substituent (compound 1) in the phthalocyanine ring increased the oscillator strength of the Q band. Furthermore, as shown in Table 3, the absorption bands emerged in the 400–450 nm
Fig. 8. Experimental and theoretical IR Spectrum of compound (a) 2, (b) 3, (c) 4 and (d) 5
Table 2. The energies from LUMO+3 to HOMO-3 and the energy gap HOMO–LUMO of compound 2, 3, 4, 5 and ZnPc (eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>LUMO+3</th>
<th>LUMO+2</th>
<th>LUMO+1</th>
<th>LUMO</th>
<th>HOMO</th>
<th>HOMO-1</th>
<th>HOMO-2</th>
<th>HOMO-3</th>
<th>HOMO–LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-5.959</td>
<td>-5.794</td>
<td>5.743</td>
<td>-4.477</td>
<td>-2.421</td>
<td>-2.358</td>
<td>-0.649</td>
<td>-0.631</td>
<td>2.056</td>
</tr>
<tr>
<td>3</td>
<td>-5.866</td>
<td>-5.849</td>
<td>-5.804</td>
<td>-4.424</td>
<td>-2.359</td>
<td>-2.355</td>
<td>-0.620</td>
<td>-0.526</td>
<td>2.065</td>
</tr>
<tr>
<td>4</td>
<td>-5.880</td>
<td>-5.846</td>
<td>-5.825</td>
<td>-4.450</td>
<td>-2.350</td>
<td>-2.346</td>
<td>-0.634</td>
<td>-0.551</td>
<td>2.099</td>
</tr>
</tbody>
</table>

Aggregation studies

Aggregation is mostly described as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, the type of metal ions and temperature. The high aggregation tendency of phthalocyanine and
porphyrazine compounds due to the interactions between their 18 π-electron systems often cause weak solubility or insolubility in many solvents. The spectroscopic, photophysical, photochemical and electrochemical properties of the phthalocyanines and porphyrines were seriously affected by the aggregation [50–56].

In this study, the aggregation behavior of all phthalocyanine compounds was investigated in different solvents such as CHCl₃, CH₂Cl₂, DMF, THF and DMSO. None of the synthesized metallophthalocyanines 2–5 showed any aggregation in CHCl₃, CH₂Cl₂, DMF, THF and DMSO. The aggregation behavior of all phthalocyanines 2–5 (in THF) (Figs 2–5) was also studied at different concentrations to determine if the aggregation depends on the concentration. These studied phthalocyanines did not show any aggregation in concentration ranges between 2 × 10⁻⁶ M and 12 × 10⁻⁶ M. For complexes, as the concentration was increased, the intensity of absorption of the Q band also increased in parallel, and no new bands (normally blue shifted) which might be attributed to aggregated species were observed.

### Photophysical and photochemical studies

#### Fluorescence spectra and fluorescence quantum yields

The fluorescence emission, absorption and excitation spectra of newly synthesized phthalocyanines (2–5) were studied in DMF, DMSO and THF at 2 × 10⁻⁶ M and the spectra are given in (Figs 13 and 14). All substituted phthalocyanines (4–7) showed similar fluorescence behavior in the solvents. Phthalocyanine compounds

| Table 3. The calculated absorption wavelengths (λ), oscillator strengths (f) and electronic transition configurations for 2, 3, 4, 5 and ZnPc in THF |
|-----------------|-----|----------------|
| Compound       | λ (nm) | f     | MO Character |
| 2   | 578.5  | 0.59  | H-0 → L+1 (80%) |
|     | 569.9  | 0.79  | H-0 → L+0 (84%) |
|     | 400.8  | 0.17  | H-6 → L+0 (30%); H-5 → L+0 (22%); H-3→ L+1 (14%); H-4 → L+0 (12%) |
|     | 326.7  | 0.11  | H-0 → L+6 (32%); H-16 → L+0 (30%); H-14 → L+1 (20%) |
|     | 319.2  | 0.23  | H-0 → L+6 (50%); H-16 → L+0 (22%); H-15 → L+1 (17%) |
|     | 322.8  | 0.14  | H-16 → L+1 (45%); H-14 → L+1 (21%); H-14 → L+1 (10%) |
|     | 308.0  | 1.06  | H-19 → L+1 (37%); H-16 → L+0 (19%); H-14 → L+0 (17%) |
|     | 305.4  | 0.28  | H-21 → L+0 (49%); H-19 → L+0 (19%); H-16 → L+1 (10%) |
|     | 304.9  | 0.33  | H-21 → L+0 (46%); H-19 → L+0 (20%); H-16 → L+1 (12%) |
|     | 280.0  | 1.33  | H-19 → L+0 (32%) |

(Continued)
in particular showed great emission intensity in THF. Fluorescence emission and excitation maxima are listed in Table 4. The excitation spectra were similar to the absorption spectra, and both were mirror images of the fluorescence emission spectra for all studied phthalocyanines, suggesting that the molecules did not show any structural changing during excitation in the solutions [57].

The fluorescence quantum yield (\( \Phi_f \)) gives the efficiency of the fluorescence process. This value is defined as the ratio of the number of photons emitted to the number of photons absorbed. The fluorescence quantum yields (\( \Phi_f \)) were determined using an established method [23]. The \( \Phi_f \) values of the studied phthalocyanine compounds (2–5) are typical for phthalocyanine compounds (Table 4). These values ranged from 0.15 to 0.30 in the solutions. The magnesium (II) (3) phthalocyanine showed higher fluorescence quantum yields than the metal-free (2) and zinc(II) (4) phthalocyanines due to a metal effect. The effect of the central metal atom is clear in Table 4, where MgPc derivatives show a larger \( \Phi_f \) (comparing the same solvents) due to the small size of Mg [58]. Nickel Pc (5) did not show any fluorescence behavior due to the paramagnetic nature of the Ni (II) central atom in the Pc core. Phthalocyanine compounds 2 and 4 showed lower fluorescence quantum yields compared to the unsubstituted ZnPc. This could indicate that the substitution of the phthalocyanine ring with 4-tert-butylbenzyl)oxy groups decreased the fluorescence quantum yields of all studied phthalocyanines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda ) (nm)</th>
<th>( f )</th>
<th>MO Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>570.7</td>
<td>0.68</td>
<td>H-0 ( \rightarrow ) L+1 (78%)</td>
</tr>
<tr>
<td></td>
<td>569.7</td>
<td>0.73</td>
<td>H-0 ( \rightarrow ) L+0 (79%)</td>
</tr>
<tr>
<td></td>
<td>417.3</td>
<td>0.23</td>
<td>H-4 ( \rightarrow ) L+1 (22%); H-3 ( \rightarrow ) L+0 (60%)</td>
</tr>
<tr>
<td></td>
<td>424.5</td>
<td>0.13</td>
<td>H-4 ( \rightarrow ) L+0 (19%); H-3 ( \rightarrow ) L+1 (65%)</td>
</tr>
<tr>
<td></td>
<td>398.7</td>
<td>0.15</td>
<td>H-4 ( \rightarrow ) L+1 (46%); H-3 ( \rightarrow ) L+0 (20%)</td>
</tr>
<tr>
<td></td>
<td>393.4</td>
<td>0.16</td>
<td>H-4 ( \rightarrow ) L+0 (44%); H-3 ( \rightarrow ) L+1 (14%); H-2 ( \rightarrow ) L+1 (12%)</td>
</tr>
<tr>
<td></td>
<td>322.9</td>
<td>0.17</td>
<td>H-16 ( \rightarrow ) L+1 (48%); H-17 ( \rightarrow ) L+0 (104%); H-0 ( \rightarrow ) L+5 (32%)</td>
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<td></td>
<td>321.7</td>
<td>0.10</td>
<td>H-0 ( \rightarrow ) L+6 (58%); H-16 ( \rightarrow ) L+0 (16%); H-15 ( \rightarrow ) L+0 (11%);</td>
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<tr>
<td></td>
<td>307.6</td>
<td>0.39</td>
<td>H-20 ( \rightarrow ) L+1 (34%); H-20 ( \rightarrow ) L+0 (13%); H-14 ( \rightarrow ) L+0 (12%)</td>
</tr>
<tr>
<td></td>
<td>307.2</td>
<td>0.44</td>
<td>H-21 ( \rightarrow ) L+0 (42%); H-20 ( \rightarrow ) L+1 (28%); H-21 ( \rightarrow ) L+1 (10%)</td>
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<tr>
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<td>307.4</td>
<td>0.67</td>
<td>H-19 ( \rightarrow ) L+0 (34%); H-12 ( \rightarrow ) L+1 (22%); H-21 ( \rightarrow ) L+0 (10%)</td>
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<td>311.6</td>
<td>0.18</td>
<td>H-0 ( \rightarrow ) L+0 (68%)</td>
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<tr>
<td>5</td>
<td>615.6</td>
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<td>H-0 ( \rightarrow ) L+1 (52%); H-0 ( \rightarrow ) L+0 (33%)</td>
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<td>567.4</td>
<td>0.69</td>
<td>H-0 ( \rightarrow ) L+0 (52%); H-0 ( \rightarrow ) L+1 (33%)</td>
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<td>408.5</td>
<td>0.38</td>
<td>H-3 ( \rightarrow ) L+0 (49%); H-3 ( \rightarrow ) L+1 (33%)</td>
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<td>392.9</td>
<td>0.30</td>
<td>H-3 ( \rightarrow ) L+1 (29%); H-3 ( \rightarrow ) L+0 (17%); H-4 ( \rightarrow ) L+1 (13%)</td>
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<tr>
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<td>337.6</td>
<td>0.14</td>
<td>H-14 ( \rightarrow ) L+1 (35%); H-14 ( \rightarrow ) L+0 (18%); H-1 ( \rightarrow ) L+5 (15%)</td>
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<tr>
<td></td>
<td>329.3</td>
<td>0.19</td>
<td>H-17 ( \rightarrow ) L+0 (35%); H-17 ( \rightarrow ) L+1 (32%)</td>
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<tr>
<td></td>
<td>312.5</td>
<td>0.17</td>
<td>H-20 ( \rightarrow ) L+1 (42%); H-20 ( \rightarrow ) L+0 (24%); H-19 ( \rightarrow ) L+0 (12%);</td>
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<tr>
<td>ZnPc</td>
<td>546.1</td>
<td>0.60</td>
<td>H-0 ( \rightarrow ) L+1 (80%); H-4 ( \rightarrow ) L+0 (10%)</td>
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<tr>
<td></td>
<td>546.1</td>
<td>0.60</td>
<td>H-0 ( \rightarrow ) L+0 (80%); H-4 ( \rightarrow ) L+2 (10%)</td>
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<td>336.8</td>
<td>0.29</td>
<td>H-8 ( \rightarrow ) L+0 (75%)</td>
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<td>336.8</td>
<td>0.29</td>
<td>H-8 ( \rightarrow ) L+1 (75%)</td>
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<tr>
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<td>308.1</td>
<td>0.76</td>
<td>H-11 ( \rightarrow ) L+0 (33%); H-9 ( \rightarrow ) L+1 (15%); H-4 ( \rightarrow ) L+1 (15%)</td>
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<tr>
<td></td>
<td>308.1</td>
<td>0.76</td>
<td>H-11 ( \rightarrow ) L+1 (33%); H-10 ( \rightarrow ) L+0 (15%); H-4 ( \rightarrow ) L+0 (15%)</td>
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<tr>
<td></td>
<td>275.1</td>
<td>1.15</td>
<td>H-11 ( \rightarrow ) L+0 (36%); H-10 ( \rightarrow ) L+1 (13%); H-4 ( \rightarrow ) L+1 (11%)</td>
</tr>
<tr>
<td></td>
<td>275.1</td>
<td>1.15</td>
<td>H-11 ( \rightarrow ) L+1 (36%); H-9 ( \rightarrow ) L+0 (13%); H-4 ( \rightarrow ) L+0 (12%)</td>
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<tr>
<td></td>
<td>239.3</td>
<td>0.26</td>
<td>H-1 ( \rightarrow ) L+0 (33%); H-16 ( \rightarrow ) L+0 (27%); H-15 ( \rightarrow ) L+0 (26%)</td>
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<tr>
<td></td>
<td>239.3</td>
<td>0.26</td>
<td>H-3 ( \rightarrow ) L+2 (33%); H-0 ( \rightarrow ) L+10 (22%); H-2 ( \rightarrow ) L+3 (11%)</td>
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</tbody>
</table>
In this study, the singlet oxygen quantum yields of the phthalocyanines (2, 3, 4) were determined in different solvents using 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen quencher. The intensity of DPBF absorbance at 417 nm decreased with light irradiation for all the compounds (Figs 15–17). The $\Phi_d$ values of the studied metal-free phthalocyanines were lower than other phthalocyanines due to the lack of metal ion in the phthalocyanine cavity. Generally, zinc(II) phthalocyanines possess high triplet yields and they can generate high levels of singlet oxygen due to the $d^{10}$ configuration of the central Zn$^{2+}$ ion.

**Table 4. Photophysical and photochemical properties of the complexes in DMSO, DMF and THF**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Phi_d$</th>
<th>$\Phi_a$</th>
<th>$\Phi_g$</th>
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<td>DMSO</td>
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<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
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<td>0.11</td>
<td>—</td>
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<tr>
<td>DMF</td>
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<tr>
<td>THF</td>
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<td>0.27</td>
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<td>DMSO</td>
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<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.0020</td>
<td>0.13</td>
<td>0.30</td>
</tr>
<tr>
<td>DMF</td>
<td>0.0027</td>
<td>0.40</td>
<td>0.15</td>
</tr>
<tr>
<td>THF</td>
<td>0.0030</td>
<td>0.42</td>
<td>0.18</td>
</tr>
</tbody>
</table>

**Singlet oxygen quantum yields**

In this study, the singlet oxygen quantum yields of the phthalocyanines (2, 3, 4) were determined in different solvents using 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen quencher. The intensity of DPBF absorbance at 417 nm decreased with light irradiation for all the compounds (Figs 15–17). The $\Phi_d$ values of the studied metal-free phthalocyanines were lower than other phthalocyanines due to the lack of metal ion in the phthalocyanine cavity. Generally, zinc(II) phthalocyanines possess high triplet yields and they can generate high levels of singlet oxygen due to the $d^{10}$ configuration of the central Zn$^{2+}$ ion.
SYNTHESIS, CHARACTERIZATION OF NEW PHTHALOCYANINES AND INVESTIGATION OF PHOTOPHYSICAL PROPERTIES

Fig. 15. A typical spectrum for the determination of singlet oxygen quantum yield of compound 4 in THF

Fig. 16. A typical spectrum for the determination of singlet oxygen quantum yield of compound 3 in DMSO

Fig. 17. A typical spectrum for the determination of singlet oxygen quantum yield of compound 2 in DMF

Their cavities, which make them appropriate photosensitizers for PDT applications [36]. Therefore we obtained the highest yield for Zn phthalocyanine ($\Phi_d = 0.41$ in THF; $0.39$ in DMF; $0.60$ in DMSO). However, these results are lower than the standard ZnPc in DMSO (0.67), in DMF (0.56) and in THF (0.53).

The metal-free phthalocyanine compound 2 showed the lowest $\Phi_d$ value.

**Photodegradation quantum yields**

Photodegradation is a process through which a phthalocyanine ring is degraded under irradiation. $\Phi_d$ is affected by several factors, such as central metal atom and the ring substituents. We investigated compounds with the same substituent and different metal atoms. The photodegradation quantum yield ($\Phi_d$) values for the compounds are listed in Table 4. The compounds have a decrease in the $Q$ band in spectra measured following photodegradation. The spectral changes observed for 2, 3 and 4 compounds during irradiation are as shown in Figs 18 and 19. The most stable compound was ZnPc in DMSO (4) as expected ($\Phi_d = 1.10^{-4}$). Regarding the effect of the solvent, it generally showed the most stable behavior in DMSO.

**CONCLUSION**

In the present work, we have synthesized highly soluble metal-free (2), magnesium (3), zinc (4) and nickel phthalocyanines (5) carrying four hydrophilic 4-[(4-tert-butylbenzyl)oxy groups at peripheral positions. The aggregation behavior of the complexes was also investigated in different concentrations of DMSO, DMF and THF. No aggregation was observed in the solvents in the concentration range from 2–12 µM. Also, in this study, we wanted to investigate the photochemical and photophysical properties of the new complexes for application in cancer therapy. All compounds (except 5) showed similar and typical fluorescence behavior. Compound 3 had the highest fluorescence quantum yield ($\Phi_f = 0.30$ in THF) among the other compounds in the solutions studied. The $\Phi_d$ values of 4, obtained as a result of this study, are higher than Mg and metal-free phthalocyanine derivatives due to the heavy atom effect. Compound 5 did not show any photophysical and chemical properties due to nickel (II) ion the paramagnetic nature of the central nickel atom. When we compare the results, the yield of the compound 4 in DMSO ($\Phi_d = 0.60$) was the highest of all. Compound 4 has the most...
In addition, we examined spectroscopic and electronic properties of the moderate yields, all compounds (especially the complex 4) can be potential photosensitizers in PDT. In addition, we examined spectroscopic and electronic properties of compounds 2, 3, 4 and 5 by computational study using the DFT method and the results obtained from the theoretical studies are in agreement with the experimental ones. Especially in the results of the FMOs theoretical study, we obtained significant results in HOMO–LUMO gap calculation. The compound 2 (metal free) appears to have a low energy gap (2.05 eV), and it may be the case that compound 2 is the most suitable phthalocyanine in this study for solar cell application and similar purposes.

Acknowledgments

The numerical calculations reported in this paper were fully/partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources).

REFERENCES


Zinc(II) and chloroindium(III) phthalocyanines bearing ethyl 7-oxy-6-chloro-4-methylcoumarin-3-propanoate groups: Synthesis, characterization and investigation of their photophysicochemical properties

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\textsuperscript{a}Marmara University, Department of Chemistry, 34722 Kadıköy, Istanbul, Turkey
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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 9 December 2017
Accepted 14 January 2018

\textbf{ABSTRACT:} In this study, ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (1), ethyl 7-(2,3-dicyanophenoxy)-6-chloro-4-methylcoumarin-3-propanoate (2), ethyl 7-(3,4-dicyanophenoxy)-6-chloro-4-methylcoumarin-3-propanoate (3), ethyl 4-chloro-5-(7-oxy-6-chloro-4-methylcoumarin-3-propanoate)phthalonitrile (4) were synthesized. The phthalonitrile derivatives (2, 3 and 4) were converted to their peripheral tetra, non-peripheral tetra and peripheral chlorocta substituted zinc(II) and chloroindium phthalocyanine derivatives. All novel compounds were characterized by elemental analysis, FT-IR, \textsuperscript{1}H-NMR, MALDI-TOF mass spectrometry and UV-vis spectral data. Additionally, the spectral, photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of the resulting substituted phthalocyaninatozinc(II) and indium(III) chloride complexes (5–10) were investigated in DMF, and the obtained results were compared for determination of the effects of the substituents’ positions and the variety of the central metal atom on these properties. The fluorescence quenching behavior of these phthalocyanines (5–10) were also investigated using 1,4-benzoquinone as a quencher. The obtained ethyl 7-oxy-6-chloro-4-methylcoumarin-3-propanoate bearing phthalocyaninatozinc(II) (5, 7 and 9) and indium(III) chloride (6, 8 and 10) complexes showed excellent solubility in most organic solvents. They produced high singlet-oxygen and showed appropriate photodegradation which is very important for photodynamic therapy applications.

\textbf{KEYWORDS:} phthalocyanines, coumarin, zinc, indium, fluorescence, photodegradation, singlet oxygen.

\textbf{INTRODUCTION}

Phthalocyanines (Pcs) are a family of aromatic macrocycles delocalized with 18-π electrons system. They have been extensively studied in many fields such as optical data storage, chemical sensors, electrochromic agents, molecular metals, liquid crystals, solar energy conversion, photoelectronic generation and as catalysts [1, 2]. In recent decades, their usage as photosensitizers in photodynamic therapy (PDT) is the most attractive application because of their ability to generate high levels of singlet oxygen (\textsuperscript{1}O\textsubscript{2}) which is toxic for cells [3–5]. Most of the phthalocyanines are poorly soluble in polar solvents and have a strong tendency for aggregation [6]. This high tendency of aggregation can
even cause Pcs to be insoluble in many solvents and can also dramatically affect their photochemical properties. Pcs bearing hydrophilic moieties such as carboxylates, sulfonates, quaternized ammonium, polyoxyethylene, glucose and phosphonates have been reported to be highly aggregated in aqueous media [7]. Therefore, Pc aggregation is another limitation in their applications which drastically decreases their fluorescence quantum yields, shortens their triplet state lifetimes and reduces their photosensitizing efficiency, especially in aqueous media. This phenomenon is easily recognized by severe broadening of the absorption bands in their optical spectra [8]. In light of such considerations, design and synthesis of non-aggregated Pcs is very important, in terms of their potential applicability in various areas, especially for PDT. Pcs have two principal disadvantages as photosensitizers: One of them is their low solubility and the other is the tendency to aggregate. Peripheral substitution of the macrocyclic ring with halogen groups leads to phthalocyanine products which are soluble in common organic solvents [9]. Substitutions of the phthalocyanines at the more sterically-crowded non-peripheral positions results in less aggregated species than for substitutions at peripheral positions. Moreover, it is anticipated that the introduction of halogen/ester groups into a moiety of phthalocyanine compound will induce high solubility in organic solvents and improved photosensitizer activity of Pcs for PDT [10–14].

Coumarin (2H-chromen-2-one, 2H-1-benzopyran-2-one) and its derivatives, a group of lactones derived from 2-hydroxycinnamic acids, are extensively found in various bioactive natural and synthetic products and belong to an important class of fluorescent compounds having interesting photophysical properties and wide range of applications such in the areas of photosensitization [15, 16], pesticide [17], and as anticoagulant [18], antitumor [19–20], antithrombic [21], antioxidant [22] and antiviral [23] agents. Some coumarin derivatives have also been reported in clinical trials to demonstrate activity against breast cancer, prostate cancer, malignant melanoma and metastatic renal cell carcinoma [24, 25]. The bio-activity of coumarin involving compounds and its complexes appear to be based on the coumarin nucleus.

In our previous study, we demonstrated that the introduction of fluorene-bearing coumarin into the phthalocyanine ring increases solubility, photochemical and photophysical properties [26]. Therefore, the combination of ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (1) and Pc functional groups into a coumarino-phthalocyanine molecule by a suitable synthetic methodology may produce a potential candidate molecule for the application of PDT.

In this study, the preparation of novel ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (1) and its phthalonitrile derivatives (2–4) are described. The corresponding non-peripheral tetra, peripheral tetra and chloro-octa ethyl 7-oxo-6-chloro-4-methylcoumarin-3-propanoate substituted zinc(II) and chloroindium(III) phthalocyanine (5–10) derivatives (Scheme 1) were synthesized for the first time. The synthesized and purified novel phthalocyanines (5–10) were characterized by elemental analysis, 1H-NMR, UV-vis, FT-IR and matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry. The photophysical properties such as fluorescence quantum yields and lifetimes and photochemical properties such as singlet oxygen generation and photodegradation under light irradiation of novel phthalocyaninatozinc(II) and indium(III) chloride complexes (5–10) were investigated in DMF. The effects of the substituents’ positions and the variety of the central metal atom on these properties were determined. The fluorescence quenching behavior of these phthalocyanines (5–10) were also investigated using 1,4-benzoquinone as a quencher.

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 shows the synthetic route of the ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (1), its phthalonitrile (2, 3 and 4) derivatives, and their non-peripheral tetra, peripheral tetra and chloro-octa substituted phthalocyaninatozinc(II) (5, 7 and 9) and phthalocyaninatoindium(III) chloride (6, 8 and 10) derivatives. Ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (1) was prepared by Pechmann condensation of 4-chlororesorcinol with diethyl 2-acetylgluturate in concentrated sulfuric acid at 0–5°C. The phthalonitrile precursors (2, 3 and 4) were prepared from the aromatic nucleophilic substitution reaction between 3-nitrophthalonitrile (for 2), 4-nitrophthalonitrile (for 3) or 4,5-dichlorophthalonitrile (for 4) with coumarin derivative 1 in anhydrous DMF under nitrogen atmosphere. The synthesis of phthalocyaninatozinc(II) (5, 7 and 9) and phthalocyaninatoindium(III) chloride (6, 8 and 10) complexes were achieved by metal mediated cyclotramerization reaction of the corresponding phthalonitrile precursors (2, 3 and 4) in dry dimethylaminooethanol (DMAE) using anhydrous Zn(OAc)2, 2H2O or InCl3, as a metal source.

Synthesized phthalocyanine derivatives containing chlorinated coumarins (5–10) showed good solubility in most of organic solvents such as acetone, tetrahydrofuran (THF), DMF and dimethyl sulfoxide. Various characterization techniques such as UV-vis, FT-IR, 1H-NMR, MS spectroscopic data and elemental analysis were used for the characterization of the synthesized compounds. The obtained results were consistent with the proposed structures of the target compounds.

The corresponding vibrations for the aromatic -C≡N peaks in the IR spectra of phthalonitriles (2, 3
and 4) disappeared after conversion to phthalocyanines. The specific lactone-ring C=O vibration peaks were observed at 1714–1710 cm⁻¹ for 5–10. The ¹H-NMR spectra of phthalocyaninatozinc(II) and phthalocyaninatoindium(III) chloride derivatives were recorded in DMSO-d₆. The aromatic protons of phthalocyanine complexes (5–10) were observed between 8.51 and 6.79 ppm as multiplet peaks. The methyl protons at the 4-position of the lacton ring of coumarin were observed between 1.91 and 1.17 ppm as singlet peaks. The methylene protons at the 3-position of the lacton ring were observed between 2.9 and 2.38 ppm as two triplet peaks. MALDI-TOF mass spectra provided definitive characterization of the structure of all the investigated phthalocyanine complexes. The molecular ion peaks of the complexes were observed at 1813.085 for 5, 1897.378 for 6, 1813.130 for 7, 1897.360 for 8, 1951.834 for 9 as and 2104.026 for 10 (see Fig. 1. for examples of compounds 5(A), 8(B) and 9(C)). Consequently, all elemental analysis for coumarin, its phthalonitrile derivatives and the phthalocyanine complexes confirmed their proposed structure.

**Scheme 1.** Synthesis of new ethyl7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate, phthalonitriles (1, 2, 3 and 4) and their phthalocyanine derivatives (5–10). (i) der·H₂SO₄, 3 h. (ii) 3-nitrophthalonitrile, K₂CO₃, DMF, 60°C, 48 h. (iii) 4-nitrophthalonitrile, K₂CO₃, DMF, 60°C, 48 h. (iv) 4,5-dichlorophthalonitrile (1 eq mol), K₂CO₃, DMF, 60°C, 72 h. (v) Zn(OAc)₂·2H₂O, DMAE, 160–170°C. (vi) indium(III) chloride, DMAE, 160–170°C

**Ground state electronic absorption spectra**

UV-vis spectra of the phthalocyaninatozinc(II) complexes 5, 7 and 9 showed characteristic Q-band absorption at 688, 677 and 677 nm with shoulders at 620, 610 and 610 nm, respectively in DMF. The characteristic Q bands were observed at 702 for non-peripheral tetra-substituted phthalocyaninatoindium(III) chloride (6), 687 nm for peripheral tetra-substituted phthalocyaninatoindium(III) chloride (8) and 689 nm for phthalocyaninatoindium(III) chloride (10) in DMF. The spectra showed monomeric behavior evidenced by a single (narrow) Q band typical of metallophthalocyanine complexes [14]. The B band absorptions were observed at around 325 nm for all studied phthalocyaninatozinc(II) and indium(III) chloride complexes. The Q bands of non-peripheral substituted phthalocyaninatozinc(II) (5) and phthalocyaninatoindium(III) chloride (6) complexes were red shifted when compared to the corresponding peripheral tetra (7 and 8) and chloro-octa (9 and 10) substituted phthalocyanines in DMF. The observed red spectral shift is typical for non-peripherally-substituted...
phthalocyanines and can be explained due to linear combinations of the atomic orbitals (LCAO) coefficients at the non-peripheral positions of the HOMO being greater than those at the peripheral positions. As a result, the HOMO level is more destabilized at the non-peripheral position than at the peripheral position. Essentially, the energy gap (ΔE) between the HOMO and LUMO becomes smaller, resulting in a bathochromic shift. The red shift is 11 nm between non-peripheral (5) and peripheral substituted (7 and 9) phthalocyaninatozinc(II) derivatives. While the observed red shift is 15 nm between non-peripheral (6) and peripheral (8) tetra-substituted phthalocyaninatoindium(III) chloride compounds, this red shift is 13 nm between non-peripheral tetra (6) and peripheral chloro-octa substituted (10) phthalocyaninatoindium(III) chloride derivatives (Fig. 2).

Theoretical studies

For understanding of the structures and HOMO–LUMO energy levels of the synthesized phthalocyanine, the compounds (5–10) were optimized by using the DFT calculation method and the B3LYP/LANL2DZ basis set. The HOMO–LUMO energy levels for the band gaps of these compounds were determined by the TD-DFT calculation method. The optimized structures proved that the phthalocyanine core of the zinc(II) phthalocyanine derivatives (5, 7 and 9) is fully planar. However, indium atom was located the out of the center of the phthalocyanine ring in the indium(III) phthalocyanine derivatives (6, 8 and 10) (Table 1). The electron distributions of all synthesized coumarinophthalocyanine derivatives indicated that the π-electrons in the HOMO are delocalized over the entire phthalocyanine core (Table 1). The band gap values obtained via both experimental and theoretical measurements are given in Table 2. The experimental (UV-vis) HOMO–LUMO band gap values depends on peripheral/nonperipheral substitution or zinc(II)/indium(III) metal atom differences were compatible with the theoretical studies. The band gap values of zinc(II) phthalocyanine complexes (5, 7 and 9) are higher than indium(III) phthalocyanine complexes (6, 8 and 10), and the peripherally-substituted zinc(II) complex (7) showed higher band gap value than its nonperipherally-substituted counterpart (5) as shown by the bathochromic shift in the experimental results.

Aggregation studies

Aggregation is easily detected from optical absorption studies. Aggregation is usually depicted as a coplanar...
association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the substituents, central metal ions, temperature and the type of solvent [27]. In addition to being strongly related to concentration in the aggregated state, the electronic structures of the complexed phthalocyanine rings are perturbed, resulting in alternation of ground- and excited-state electronic structures [28].

In this study, the aggregation behavior of the studied phthalocyanines (5–10) was investigated in DMF at different concentrations. The Beer–Lambert law was obeyed for all of these compounds at concentrations ranging from $1 \times 10^{-5}$ to $1 \times 10^{-6}$ M. None of the phthalocyanine derivatives (5–10) showed any aggregation at these concentration ranges in DMF (see Fig. 3 for 5 as an example) in agreement with the literature [26].

**Fluorescence studies**

Fluorescence emission spectra were recorded for all studied phthalocyanines (5–10) in DMF. The phthalocyaninatoindium(III) chloride complexes (6, 8 and 10) showed no fluorescence emission due to the heavy atom effect of larger indium(III) in the cavities of these phthalocyanines. For this reason, the fluorescence properties of these phthalocyanines was not evaluated. The fluorescence emission peaks were observed at 695 nm for 5 and 683 nm for both 7 and 9 (Table 3). The excitation spectra of the phthalocyaninatozinc(II) complexes (5, 7 and 9) are similar to the absorption spectra and they are mirror images of the fluorescence emission spectra (see Fig. 4 for 9 as an example).

Fluorescence quantum yields ($\Phi_F$) of the phthalocyaninatozinc(II) complexes (5, 7 and 9) are given in Table 3. The fluorescence quantum yield ($\Phi_F$) values were found to be 0.055, 0.062 and 0.071 for these phthalocyanines, respectively. The $\Phi_F$ values of all studied phthalocyaninatozinc(II) compounds are lower than unsubstituted zinc(II) phthalocyanine which is used as a standard in DMF. These fluorescence quantum yield values are lower than the literature values of coumarinophthalocyanines due to of the 3-phenyl substitution [26].

The lifetime of fluorescence ($\tau_F$) refers to the average time when a molecule stays in its excited state before it returns to its ground state by emitting [29]. The $\tau_F$ values of the studied zinc(II) phthalocyanines were measured by a time correlated single photon counting (TCSPC) method in DMF solutions. The fluorescence decays of studied phthalocyaninatozinc(II) complexes...
resulted in mono exponential curves which means these phthalocyanines exhibited only one fluorescence lifetime value. The $\tau_F$ values were found to be 2.71 ns for 5, 3.04 ns for 7 and 3.16 ns for 9, and these values were similar to phthalocyanine compounds bearing different central metal atoms and substituents [29]. All obtained $\tau_F$ values were found to be higher compared to unsubstituted phthalocyaninatozinc(II) (1.03 ns) in DMF, and lifetime values of 5, 7 and 9 were approximately similar to their counterparts in the literature [26].

**Singlet oxygen quantum yields**

Singlet oxygen is one of the most reactive oxygen species which is obtained by the excitation of a photosensitizer such as phthalocyanine. The basic principle of

<table>
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<td><img src="image7" alt="Image" /></td>
<td><img src="image7" alt="Image" /></td>
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<tr>
<td>8</td>
<td><img src="image8" alt="Image" /></td>
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<td>9</td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
</tr>
</tbody>
</table>

*Table 1. The Optimized geometry and HOMO–LUMO orbitals of synthesized coumarino-phthalocyanines (5, 7, 8 and 9)*
The effect mechanism of singlet oxygen is: a photosensitizer is illuminated by light and excited to its singlet state, then it passes to its triplet state through intersystem crossing. Then its energy is transferred to ground state oxygen O₂ (^3Σg⁻) to generate the singlet oxygen O₂ (^1Δg) [30]. The formed reactive singlet oxygen damages cancer cells. The generated singlet oxygen amount is quantified as the singlet oxygen quantum yield (Φ₅).

Singlet oxygen quantum yields of the studied phthalocyanines were determined in DMF by a chemical method using 1,3-diphenylisobenzofuran (DPBF) as a quencher. The disappearance of DPBF absorbance at 412 nm was monitored using a UV-vis spectrophotometer. There was no change in the shape and intensity of the Q band absorption of the studied phthalocyanines (5–10) during the Φ₅ determinations, confirming that the complexes were not degraded during singlet oxygen studies (Fig. 5 for compound 6 as an example).

The non-peripherally tetra-substituted phthalocyanines (5 and 6) showed higher Φ₅ values (Φ₅ = 0.62 for 5 and Φ₅ = 0.76 for 6) than the peripherally tetra (7 and 8) and chloro-octa (9 and 10) substituted phthalocyanines (Φ₅ = 0.39 for 7, Φ₅ = 0.59 for 6, Φ₅ = 0.49 for 9 and Φ₅ = 0.71 for 10). This may be due to absorption of light at longer wavelengths by non-peripheral substitution than by peripheral substitution. Phthalocyaninatoindium(III) chloride complexes (6, 8 and 10) produced higher singlet oxygen than phthalocyaninatozinc(II) derivatives (5, 7 and 9) due to the heavy atom effect of the larger indium(III) atom in the macrocyclic cavities of phthalocyaninatoindium(III) complexes.

### Table 2. The experimental (optical) and theoretical band gap value of synthesized coumarino-phthalocyanines (5–10)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>EHOMO–ELUMO (Theoric/DFT) (eV)</th>
<th>E₅⁺ (eV)</th>
<th>E₆⁺ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-5.526 -3.385</td>
<td>1.802</td>
<td>2.140</td>
</tr>
<tr>
<td>6</td>
<td>-5.715 -3.636</td>
<td>1.766</td>
<td>2.079</td>
</tr>
<tr>
<td>7</td>
<td>-5.634 -3.468</td>
<td>1.831</td>
<td>2.166</td>
</tr>
<tr>
<td>8</td>
<td>-5.846 -3.751</td>
<td>1.804</td>
<td>2.094</td>
</tr>
<tr>
<td>9</td>
<td>-6.151 -3.976</td>
<td>1.830</td>
<td>2.174</td>
</tr>
<tr>
<td>10</td>
<td>-6.356 -4.250</td>
<td>1.799</td>
<td>2.106</td>
</tr>
</tbody>
</table>

*Calculated from EHOMO–ELUMO = 1240/λ, equation. E₅⁺.*

*Level of theory: TD-DFT/B3LYP/LANL2DZ basis set.

### Table 3. The spectral, photophysical and photochemical parameters of substituted phthalocyaninatozinc(II) and phthalocyaninatoindium(III) chloride compounds in DMF

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Q band λmax, nm</th>
<th>Log ε</th>
<th>Excitation λex, nm</th>
<th>Emission λem, nm</th>
<th>Stoke’s shift ΔλStokes, nm</th>
<th>Φ₅</th>
<th>Φ₆ (×10⁻³)</th>
<th>τₑ (ns)</th>
<th>τ₀ (ns)</th>
<th>kF (×10⁷)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>688</td>
<td>5.26</td>
<td>688</td>
<td>695</td>
<td>7</td>
<td>0.62</td>
<td>7.99</td>
<td>0.055</td>
<td>2.71</td>
<td>7.97</td>
</tr>
<tr>
<td>6</td>
<td>702</td>
<td>5.26</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.76</td>
<td>0.06</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>677</td>
<td>5.25</td>
<td>676</td>
<td>683</td>
<td>6</td>
<td>0.39</td>
<td>1.67</td>
<td>0.062</td>
<td>3.04</td>
<td>6.04</td>
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<tr>
<td>8</td>
<td>687</td>
<td>5.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.59</td>
<td>3.61</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>677</td>
<td>5.26</td>
<td>677</td>
<td>683</td>
<td>6</td>
<td>0.49</td>
<td>5.22</td>
<td>0.071</td>
<td>3.16</td>
<td>8.12</td>
</tr>
<tr>
<td>10</td>
<td>689</td>
<td>5.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.71</td>
<td>3.74</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Std-ZnPcα</td>
<td>670</td>
<td>5.37</td>
<td>670</td>
<td>676</td>
<td>6</td>
<td>0.56</td>
<td>2.30</td>
<td>0.170</td>
<td>1.03</td>
<td>6.05</td>
</tr>
<tr>
<td>Std-InClPcb</td>
<td>681</td>
<td>5.37</td>
<td>—</td>
<td>—</td>
<td>696</td>
<td>0.70</td>
<td>1.05</td>
<td>0.017</td>
<td>0.11</td>
<td>—</td>
</tr>
</tbody>
</table>

*a Data from Ref. [40].

*b Data from Ref. [41].

*kF is the rate constant for fluorescence. Values calculated using kF = ΦF/τₑ.*
ZINC(II) AND CHLOROINDIUM(III) PHTHALOCYANINES BEARING ETHYL

fluorophenyl groups on the 3 position, have higher singlet oxygen generation than the synthesized coumarin phthalocyanines in this work [26] due to the substitution of the phenyl groups at 3 position of the coumarin. The high singlet oxygen production abilities of the studied phthalocyanines (especially indium derivatives) makes them candidates as suitable photosensitizers for PDT applications.

Photodegradation studies

Photodegradation is an oxidative degradation where a photosensitizer molecule generates, over time, lower molecular weight fragments under light [31]. Photodegradation is related to the chemical structure of the molecule, its concentration, the type of solvent and the intensity of the used light. Photodegradation is a singlet oxygen-mediated process, and the formed singlet oxygen during irradiation is highly reactive and degrades to the photosensitizers [32]. Generally, phthalimide residual has been found to be the photooxidation product following degradation of phthalocyanines [33]. Phthalocyanine derivatives have optimal photodegradation quantum yield values, which makes them suitable for use as photocatalysts (such as photosensitizers).

Stable phthalocyaninatozinc molecules show $\Phi_d$ values as low as $10^{-6}$, and unstable molecules show $\Phi_d$ values on the order of $10^{-3}$ [34]. The spectral changes observed for the 7-oxy-6-chloro-4-methylcoumarin-3-propanoate-substituted phthalocyanine derivatives during irradiation are as shown in Fig. 6 (for compound 10 as an example in DMF). The $\Phi_d$ values of the studied phthalocyaninatozinc(II) (5, 7 and 9) and phthalocyaninatoindium(III) chloride (6, 8 and 10) complexes are given in Table 3. All these novel phthalocyanines showed $\Phi_d$ values on the order of $10^{-3}$. These values make them suitable candidates for use as photosensitizers. This result is also in agreement with the literature, including coumarino phthalocyanines [26].

Fluorescence quenching by 1,4-benzoquinone [BQ]

The fluorescence quenching behavior of phthalocyaninatozinc(II) complexes (5, 7 and 9) by BQ in DMF was found to obey Stern–Volmer kinetics, which is consistent with a diffusion-controlled bimolecular reaction. Figure 7 shows the quenching of phthalocyanine using 7 by BQ in DMF as an example. The fluorescence quenching behavior of the phthalocyaninatoindium(III) chloride complexes could not be studied because these phthalocyanine complexes did not show any fluorescence emission. The slope of the plots shown in Fig. 8 gave the Stern–Volmer constant ($K_q$) and values listed in Table 4.

Fig. 4. Absorption, excitation and emission spectra of chlorinated octa substituted phthalocyaninato zinc (II) compound 9 in DMF. Excitation wavelengths: 642 nm. Concentration = $1.0 \times 10^{-6}$ M.

Fig. 5. Electronic absorption spectral changes during singlet oxygen quantum yield determination. This determination is for compound 6 in DMF at a concentration of $1 \times 10^{-5}$ M (Inset: Plot of DPBF absorbance vs. time).

Fig. 6. Electronic absorption spectral changes of compound 10 in DMF under light irradiation showing disappearance of the Q-band at 10 min intervals (Inset: Plot of absorbance vs. time).
Both Stern–Volmer constant ($K_{sv}$) and bimolecular quenching rate constant ($k_q$) values of the studied zinc(II) phthalocyanine complexes were found to be lower than for unsubstituted zinc(II) phthalocyanine. The non-peripherally-substituted phthalocyaninatozinc(II) (5) showed the highest $K_{sv}$ and $k_q$ values among the studied phthalocyaninatozinc(II) complexes. In the literature, similar phthalocyanines showed higher $K_{sv}$ constant but lower $k_q$ values, owing to their different coumarin structures [26].

**EXPERIMENTAL**

**Materials and equipment**

The starting materials; 4-nitrophthalonitrile, 3-nitrophthalonitrile and 4,5-dichlorophthalonitrile were prepared according to the reported procedures [35–37]. 4-Chlororesorsinol, diethyl 2-acetylgutarate, dimethylformamide (DMF), 2-N,N-dimethylaminoethanol (DMAE), tetrahydروفuran (THF), 1,3-diphenylisobenzofuran (DPBF), unsubstituted zinc(II) phthalocyanine (Std-ZnPc), Triton X-100, zinc(II)acetate [Zn(OAc)$_2$], indium (III) chloride (InCl$_3$), potassium carbonate (K$_2$CO$_3$) and sodium acetate (NaOAc) were purchased from Aldrich. All reactions were carried out under N$_2$ atmosphere. All solvents were dried as described by Perrin and Armaeago before use [38].

The purity of the products was checked by a thin-layer-chromatography (TLC) technique. FT-IR spectra were recorded on a Schimadzu FT-IR 8300 spectrometer with ATR capability. $^1$H-NMR spectra were recorded on a Varian Unity INOVA 500 MHz spectrometer. UV-vis spectra were recorded on a Schimadzu UV-1601 UV-vis spectrometer. Fluorescence excitation and emission spectra were recorded on a Hitachi F-7000 spectrofluorometer using 1 cm path length cuvettes at room temperature. Mass spectra were recorded on a BRUKER Autoflex mass spectrometer using the MALDI-TOF technique and dithranol (DIT, 20 mg/mL in THF) was used as the matrix. MALDI samples were prepared by mixing the complex (2 mg/mL in THF) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf microtube. Finally, 1 µL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. Elemental analyses were carried out using a LEICO CHN 932 was performed by the Instrumental Analysis Laboratory of the Tubitak Marmara Research Centre. Fluorescence lifetimes were measured by a time correlated single photon counting (TCSPC) method using a FLUOROLOG-3 spectrofluorometer (Horiba JobinYvon, Edison, NJ) equipped with a NanoLED and a standard air cooled R928 PMT detector.

All theoretical calculations were performed by using the Gaussian 09 suite of programs [39]. The molecular geometries of the coumarin substituted phthalocyanine compounds were optimized at the density functional theory (DFT)-B3LYP-LanL2DZ basis set. The excited states were calculated using time-dependent density functional theory (TD-DFT calculations). The molecular orbital contours were visualized using Gauss view 5.0.9.

**Synthesis**

**Ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (1)**, 4-Chlororesorcino (2 g. 13 mmol) and diethyl 2-acetylgutarate (3.5 g, 15 mmol) were dissolved in concentrated sulfuric acid (5 mL) and stirred 3 h at 0–5°C. At the end of this time, the reaction mixture was poured into 15 mL of ice water, then filtered off
and washed with water until neutral. The crude product was purified by silica gel column chromatography using methanol/chloroform (100:1) solvent system as an eluent. Yield: 1.3 g (87%). M.p. 195°C. 1H-NMR (500 MHz, CDCl3): δ, ppm 7.77 (s, 1H, aromatic-CH), 7.63 (t, 1H, J = 8.29 and 8.21 Hz, aromatic-CH), 7.57 (s, 1H, aromatic-CH), 7.10 (s, 1H, aromatic-CH), 6.99 (s, 1H, aromatic-CH), 4.12 (q, 2H, J = 7.17 Hz, aliphatic-CH2), 2.63 (t, 2H, J = 7.51 Hz, aliphatic-CH2), 2.49 (s, 3H, CH3), 1.25 (t, 3H, J = 7.17 Hz, CH3), FT-IR (ATR): v, cm⁻¹ 3086–3033 (Aromatic-CH), 2982–2948 (Aliphatic-CH), 2232 (CN), 1732 (lactone-C=O), 1711 (ester-C=O), 1590 (Aromatic-C=O). Anal. Calc. for C23H16Cl2N2O5, C, 58.61%; H, 3.42%; N, 5.94%. Found C, 58.63%; H, 3.40%; N, 5.91%. MS (MALDI-TOF) m/z: 472.27 [M + H]+, 426.121 [M + Na]+.

4-Chloro-5-(ethyl 7-oxo-6-chloro-4-methylcoumarin-3-propanoate)phthalonitrile (4). Ethyl 7-hydroxy-6-chloro-4-methylcoumarin-3-propanoate (I) (1.57 g, 5.05 mmol) and 4,5-dichlorophthalonitrile (1 g, 5.07 mmol) were dissolved in 50 mL anhydrous DMF. Then anhydrous potassium carbonate (K2CO3) (1.04 g 7.52 mmol) was added to this solution with stirring. The reaction mixture was stirred at 60°C for 72 h under vacuum. At the end of this time, the reaction mixture was poured into 100 mL of ice water, then filtered off and washed with hot water until neutral. The crude product was dried under vacuum and purified by column chromatography on silica gel using a methanol/chloroform (100:1) solvent system as an eluent. Yield: 1.5 g (62.5%). M.p. 204°C. 1H-NMR (500 MHz, CDCl3): δ, ppm 7.94 (s, 1H, aromatic-CH), 7.80 (s, 1H, aromatic-CH), 7.11 (s, 1H, aromatic-CH), 6.99 (s, 1H, aromatic-CH), 4.14 (q, 2H, J = 7.1 Hz, aliphatic-CH2), 3.02 (t, 2H, J = 7.5 Hz, aliphatic-CH2), 2.49 (s, 3H, CH3), 1.25 (t, 3H, J = 7.17 Hz, CH3), FT-IR (ATR): v, cm⁻¹ 3111–3046 (Aromatic-CH), 2979–2936 (Aliphatic-CH), 2233 (CN), 1726 (lactone-C=O), 1707 (ester-C=O), 1586 (Aromatic-C=O). Anal. Calc. for C23H16Cl2N2O5, C, 58.61%; H, 3.42%; N, 5.94%. Found C, 58.63%; H, 3.40%; N, 5.91%. MS (MALDI-TOF) m/z: 472.27 [M + H]+, 426.124 [M + OCH2CH3]+.

General procedure for the synthesis of phthalocyaninatozinc(II) complexes (5, 7 and 9). The phthalocyaninol compounds (2, 3 and 4) (0.1 g, 0.378 mmol for compound 2, 3 and 0.335 mmol for compound 4) and 0.04 g (0.182 mmol) Zn(OAc)2·2H2O were dissolved in 2 mL DMAE. The reaction mixtures were stirred and heated at 170°C for 12 h under N2 atmosphere. After cooling to room temperature, the green mixtures were poured into 50 mL hot methanol. Then the precipitates were centrifuged and washed several times with hot water, ethyl acetate, diethyl ether, and methanol. The dried compound was purified by column chromatography on silica gel using chloroform as an eluent and final products were dried under vacuum.

1(4),8(11),15(18),22(25)-Tetrakis[ethyl-7-oxo-6-chloro-4-methylcoumarino-3-propanoate]phthalocyaninatozinc(II) (5). Yield: 65 mg (65%). M.p.: > 300°C.
1H-NMR (500 MHz, DMSO-d6): δ_H, ppm 7.67–6.85 (m, 20H, Ar-CH), 4.05 (q, 8H, J = 7.1 Hz, aliphatic-CH2), 2.90 (t, 8H, J = 7.7 Hz, aliphatic-CH2), 2.53 (t, 8H, J = 7.8 Hz, aliphatic-CH2), 2.40 (s, 12H, -CH3), 1.17 (t, 12H, J = 7.4 Hz, -CH3). FT-IR (ATR): ν, cm⁻¹ 3063 (Aromatic -CH), 2977–2929 (Aliphatic -CH), 1713 (C=O), 1595 (Aromatic- C=C), 1268 (Aromatic-O-Aromatic). UV-vis (DMF): 20H, Ar-CH), 4.06 (q, 8H, J = 7.8 Hz, aliphatic-CH2), 1.17 (t, 12H, J = 7.4 Hz, -CH3). FT-IR (ATR): ν, cm⁻¹ 3077 (Aromatic -CH), 2980–2945 (Aliphatic -CH), 1714 (C=O), 1607 (Aromatic-C=C), 1265 (Aromatic-O-Aromatic). UV-vis (DMF): λ_max, nm, log ε 324 (5.96), 620 (5.81), 688 (5.26). Anal. Calc. for C92H68Cl4N8O20Zn; C, 60.96%; H, 3.78%; N, 5.90%. Found: C, 58.13%; H, 3.53%; N, 5.84%. MS (MALDI-TOF) m/z: 1897.378 [M⁺], 1862.915 [M – Cl⁺].

2,3,9(10),16(17),23(24)-Tetrakis(ethyl-7-oxy-6-chloro-4-methylcoumarin-3-propanoate) phthalocyaninatozinc(II) (9). Yield: 67 mg (62%). M.p.: > 300°C. 1H-NMR (500 MHz, CDCl3): δ_H, ppm 7.93–7.75 (m, 12H, Ar-CH), 5.08 (s, 12H, -CH3), 1.08 (t, 12H, J = 7.3 Hz, -CH3). FT-IR (ATR): ν, cm⁻¹ 3085 (Aromatic -CH), 2980–2935 (Aliphatic -CH), 1714 (C=O), 1601 (Aromatic-C=C), 1265 (Aromatic-O-Aromatic). UV-vis (DMF): λ_max, nm, log ε 325 (5.96), 610 (5.69), 677 (5.25). Anal. Calc. for C92H68Cl4N8O20Zn; C, 60.96%; H, 3.78%; N, 5.90%. Found: C, 60.94%; H, 3.75%; N, 5.65%. MS (MALDI-TOF) m/z: 1813.130 [M + H⁺].

2,9,16,23-Tetrakis(ethyl-7-oxy-6-chloro-4-methylcoumarin-3-propanoate) phthalocyaninatozinc(II) (11). Yield: 67 mg (62%). M.p.: > 300°C. 1H-NMR (500 MHz, CDCl3): δ_H, ppm 8.11–6.79 (m, 20H, Ar-CH), 4.06 (q, 8H, J = 7.3 Hz, aliphatic-CH2), 2.86 (t, 8H, J = 7.7 Hz, aliphatic-CH2), 2.77 (t, 8H, J = 7.5 Hz, aliphatic-CH2), 2.36 (s, 12H, -CH3), 1.17 (t, 12H, J = 7.2 Hz, -CH3). FT-IR (ATR): ν, cm⁻¹ 3056 (Aromatic -CH), 2980–2935 (Aliphatic -CH), 1714 (C=O), 1601 (Aromatic-C=C), 1265 (Aromatic-O-Aromatic). UV-vis (DMF): λ_max, nm, log ε 324 (5.96), 620 (5.81), 688 (5.26). Anal. Calc. for C92H68Cl4N8O20Zn; C, 60.96%; H, 3.78%; N, 5.90%. Found: C, 60.84%; H, 3.69%; N, 5.84%. MS (MALDI-TOF) m/z: 1813.085 [M + H⁺].

General procedure for the synthesis of phthalocyaninatoindium(III) chloride complexes (6, 8 and 10). A mixture of phthalonitrile compound (2) 0.1 g (0.22 mmol), compound (3) 0.1 g (0.22 mmol) or compound (4) 0.1 g (0.21 mmol) and anhydrous indium(III) chloride 0.04 g (0.348 mmol) was stirred in 2 mL DMAE at 160°C for 12 h under N₂ atmosphere. After cooling to room temperature, the reaction mixture was added to water, then the obtained green precipitates were centrifuged and washed several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and purified by column chromatography on silica gel using chloroform as an eluent and final products were dried in vacuum.

CONCLUSIONS

In this paper, the synthesis, characterization, photophysical and photochemical properties of novel phthalocyaninatozinc(II) and phthalocyaninatoindium(III) chloride complexes substituted with 7-oxy-6-chloro-4-methylcoumarin-3-propanoate groups at non-peripheral tetra (5 and 6), peripheral tetra (7 and 8) and peripheral octa (9 and 10) positions were performed. The novel compounds were characterized by standard spectroscopic methods (1H-NMR, MALDI-TOF, FT-IR, UV-vis and fluorescence) and elemental analysis. The photophysical and photochemical properties of these zinc(II) and chlorindium(III) Pc complexes have also been
described in DMF. All the studied phthalocyanines are soluble in chloroform, THF, DMF and DMSO. These phthalocyanines (5–10) formed monomeric solutions in DMF because they exhibited single (narrow) Q band absorptions in their UV-vis spectra, which are typical of non-aggregated metallophthalocyanine complexes. The Q bands of non-peripherally tetra-substituted phthalocyanines (5 and 6) were red shifted (approximately 10 nm) when compared to their corresponding peripherally-substituted derivatives (7–10) in DMF due to linear combinations of the atomic orbitals (LCAO) coefficients at the non-peripheral positions of the HOMO being greater than those at the peripheral positions. The Q band absorptions of the phthalocyaninatoindium(III) chloride complexes (6, 8 and 10) were red shifted when compared to the corresponding phthalocyaninatozinc(II) complexes (5, 7 and 9), suggesting the non-planar effect of the bigger central indium atom. The phthalocyaninatoindium(III) chloride complexes (6, 8 and 10) did not show any fluorescence emission, due to the heavy atom effect of the larger indium(III) in the cavities of these phthalocyanines. The fluorescence quantum yield (Φ<sub>F</sub>) values of all studied phthalocyaninatozinc(II) complexes were found to be lower than unsubstituted phthalocyaninatozinc(II) in DMF. The non-peripherally tetra substituted phthalocyanines (5 and 6) showed higher Φ<sub>F</sub> values than the peripherally tetra (7 and 8) and chloroocta (9 and 10) substituted phthalocyanines due to absorption of light at longer wavelengths by non-peripheral substituted phthalocyanines. The studied phthalocyaninatoindium(III) chloride complexes (6, 8 and 10) produced higher singlet oxygen than phthalocyaninatozinc(II) derivatives (5, 7 and 9) due to the heavy atom effect of the larger indium(III) atom in the macrocyclic cavities of chloroindium(III)phthalocyanines. The high singlet oxygen production abilities of the studied phthalocyanines (especially indium derivatives) makes them candidates as suitable photosensitizers for PDT applications. All these novel phthalocyanines showed Φ<sub>D</sub> values on the order of 10<sup>-3</sup>, which is appropriate for ideal photosensitizers. The fluorescence quenching behavior of phthalocyaninatozinc(II) complexes (5, 7 and 9) by BQ in DMF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reaction.

Acknowledgment

We are thankful to the Research Foundation of Marmara University, Commission of Scientific Research Project (BAPKO): FEN-C-YP-110915-0439 and FEN-C-YP-120514-0165.

Supporting information

The used materials, equipments, photochemical and photophysical formulas are given as supplementary materials. This material is available free of charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

INTRODUCTION

Flavones are a class of organic compounds belonging to a large group of compounds called flavonoids, based on the backbone of 2-phenylchromen-4-one. Fruits, vegetables, and beverages such as tea and red wine are major sources of flavones. The chemical behavior of flavonoids depends on their structural class, degree of hydroxylation, substitutions and conjugations, and degree of polymerization [1]. Flavones have attracted great attention because of their pharmaceutical activities such as antiproliferative [2], antifungal [3], antiviral [4], anti-inflammatory [5], antioxidant [6] and cardiovascular effects [7]. On the other hand, studies reported on synthesis of phthalocyanines (Pcs) with various substituents and metal centers have importance due to their industrial and technological applications as pigments and dyes [8], chemical sensors [9], photodynamic therapy sensitizers [10, 11], optical recording and nonlinear optical materials [12], photovoltaics [13], catalysts [14] and electronic device components [15]. Their properties can be tuned by a judicious choice of metals and ring substituents with different steric and electronic properties [16]. The applicability of Pc compounds in most of these areas is strongly related to their redox activity. Therefore, the identification of the electron transfer characteristics of newly-synthesized Pc compounds also has special importance in terms of their usage in the relevant applications. Furthermore, the combination of Pc structure and flavonoids probably leads to a potential active molecule for some biological applications.

Novel peripherally and non-peripherally 6-oxyflavone substituted metal-free, zinc(II) and cobalt(II) phthalocyanines: Electrochemical and in situ spectroelectrochemical properties

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Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 8 January 2018
Accepted 14 January 2018

ABSTRACT: In this study, novel tetrasubstituted zinc(II), cobalt(II) and metal free phthalocyanines containing 6-hydroxyflavonoxy moieties at peripheral and non-peripheral positions have been prepared. The phthalonitriles were synthesized from 6-hydroxyflavone with 4-nitrophthalonitrile and 3-nitrophthalonitrile in dimethylformamide. Preparation of tetra-substituted peripheral and non-peripheral metal- and metal-free phthalocyanines was performed at 170–180 °C using the corresponding phthalonitriles in the presence of N,N-dimethylethanamine, metal acetate and lithium acetate, respectively. The structures of the newly-synthesized phthalocyanine compounds have been characterized by elemental analysis and UV-vis, FT-IR, 1H NMR and MALDI-TOF mass spectroscopies. Electron transfer properties of the phthalocyanine compounds were investigated by voltammetric and in situ spectroelectrochemical measurements on Pt in dimethylsulfoxide/tetrabutylammonium perchlorate. Zinc(II) and metal-free compounds show Pc ring-based one-electron redox processes, whereas cobalt(II) produces both Pc ring- and metal-based one-electron redox processes, associated with net color changes.

KEYWORDS: phthalocyanine, flavone, electrochemistry, spectroelectrochemistry.
Previous studies in the literature reported that peripheral/non-peripheral introduction of coumarin derivatives into Pc rings enhances their photochemical, photophysical, spectral and electrochemical properties [17–21]. In this study, the redox properties of the newly-synthesized metal free, zinc(II) and cobalt(II) Pcs bearing flavone substituents at peripheral and non-peripheral positions of the macrocycle (Scheme1) have been investigated by evaluation of the data from electrochemical and in situ spectroelectrochemical measurements. It is well known that solubility, aggregation and redox activity of Pc compounds can be modified by careful selection of the types and the binding positions of substituents [22–24]. Thus, the main purpose of this study is to investigate the effect of tetra-6-hydroxyflavonoxy substituents on these properties.

EXPERIMENTAL

Synthetic materials and methods

Our starting compounds 6-hydroxy-2-phenyl-4H-chromen-4-one 1, Zn(OAc)2 ·2H2O and Co(OAc)2 ·4H2O were purchased from Aldrich Chemical Co., and used as received. 4-Nitrophthalonitrile 2 and 3-nitrophthalonitrile 3 were prepared according to the reported procedures [20, 21]. All reactions were carried out under nitrogen atmosphere. All solvents were purified, dried and stored over molecular sieves (4Å). Pc compounds were received. 4-Nitrophthalonitrile (5) was prepared in each step by TLC (SiO2). Chromatography was performed on silica gel 60. UV-vis spectra were recorded on a Shimadzu UV-1601 UV-vis spectrometer. FT-IR spectra (KBr pellets) were recorded on a Shimadzu FT-IR-8300 spectrometer.

'H NMR (CDCl3 400 MHz): δ, ppm 6.85 (s, 1H), 7.15 (dd, J = 9.0 and 3.0 Hz, 1H), 7.35 (dd, J = 3.0 Hz, 1H), 7.45 (dd, J = 9.0 and 3.0 Hz, 1H), 7.55 (t, J = 6.0 Hz, 1H), 7.57 (t, J = 6.0 Hz, 2H), 7.72 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 3.0 Hz, 1H), 7.92 (dd, J = 9.0 and 2.0 Hz, 1H).

3-(4'-oxo-2-phenyl-4H-chromen-6-yloxy)phthalonitrile (5). The synthesis of 3-(4'-oxo-2-phenyl-4H-chromen-6-yloxy)phthalonitrile (5) with 3-nitrophthalonitrile (3) were the same as for compound 4.

Compound 5 is soluble in CHCl3, CH3OH and DMF.

A mixture of 4-(4-oxo-2-phenyl-4H-chromen-6-yloxy)phthalonitrile(4) (0.05g, 0.137 mmol) and Zn(OAc)2 ·2H2O (0.0075 g, 0.034 mmol) in N,N-dimethylaminoethanol (1 mL) was refluxed and stirred at 160–170 °C for 24 h under N2. After cooling, methanol (5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl3.

The zinc metal Pc 6 is soluble in CH2Cl2, CHCl3, and DMF.

A mixture of 4-(4-oxo-2-phenyl-4H-chromen-6-yloxy)phthalonitrile(4) (0.05g, 0.137 mmol) and Zn(OAc)2 ·2H2O (0.0075 g, 0.034 mmol) in N,N-dimethylaminoethanol (1 mL) were refluxed and stirred at 160–170 °C (bath temperature) for 24 h under N2. After cooling, methanol (5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl3.

The cigarette PC 6 is soluble in CH2Cl2, CHCl3, and DMF. The synthesis of 3-(4'-oxo-2-phenyl-4H-chromen-6-yloxy)phthalocyaninato zinc(II) (6). A mixture of 4-(4-oxo-2-phenyl-4H-chromen-6-yloxy)phthalonitrile(4) (0.05g, 0.137 mmol) and Zn(OAc)2 ·2H2O (0.0075 g, 0.034 mmol) in N,N-dimethylaminoethanol (1 mL) were refluxed and stirred at 160–170 °C (bath temperature) for 24 h under N2. After cooling, methanol (5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl3.

The zinc metal Pc 6 is soluble in CH2Cl2, CHCl3, and DMF.

A mixture of 4-(4-oxo-2-phenyl-4H-chromen-6-yloxy)phthalonitrile(4) (0.05g, 0.137 mmol) and Zn(OAc)2 ·2H2O (0.0075 g, 0.034 mmol) in N,N-dimethylaminoethanol (1 mL) was refluxed and stirred at 160–170 °C (bath temperature) for 24 h under N2. After cooling, methanol (5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl3.

The cigarette PC 6 is soluble in CH2Cl2, CHCl3, and DMF.
A mixture of 4-(4-oxo-2-phenyl-4H-chromen-6-yl oxy) phthalonitrile (4) (0.05 g, 0.137 mmol) and Co(OAc)₂ · 4H₂O (0.0085 g, 0.034 mmol) in N,N-dimethylamin ethanol (1 mL) were refluxed and stirred at 160–170°C (bath temperature) for 24 h under N₂. After cooling, methanol (=5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl₃.

The cobalt metal Pc 7 is soluble in DMF, CH₂Cl₂, CHCl₃, mp. > 300°C. Yield: 0.019 g (35%). Anal. calcd. for C₉₂H₄₈N₈O₁₂: C, 75.71%; H, 3.45%; N, 7.68%; found C, 76.03%; H, 3.74%; N, 7.90%. FT-IR (KBr pellet): vₘₐₓ cm⁻¹ 1254 (Ar-O-Ar), 1452–1568 (Ar C=C), 1639 (C=C), 1723 (C=O), 3062 (Ar–CH). UV-vis, (log ε) in CHCl₃: λₘₐₓ nm 299 (5.18), 673 (4.98). MS (MALDI-TOF): (m/z) 1516 [M⁺].

The metal-free Pc 8 is soluble in DMF and CHCl₃, mp. > 300°C. Yield: 0.011 g (21%). Anal. calcd. for C₁₁₂H₅₀N₈O₁₂: C, 76.03%; H, 3.74%; N, 7.90%. FT-IR (KBr pellet): vₘₐₓ cm⁻¹ 1254 (Ar-O-Ar), 1452 (Ar–O–Ar), 1451–1494 (Ar C=C), 1618 (C=C), 1728 (C=O), 3062 (Ar–CH). UV-vis, (log ε) in CHCl₃: λₘₐₓ nm 303 (5.05), 681 (4.72). MS (MALDI-TOF): (m/z) 1516 [M⁺].

A mixture of 4-(4-oxo-2-phenyl-4H-chromen-6-yl oxy) phthalonitrile (4) (0.05 g, 0.137 mmol) and LiOAc · 2H₂O (0.0036 g, 0.034 mmol) in N,N-dimethylamino ethanol (1 mL) was refluxed and stirred at 160–170°C (bath temperature) for 72 h under N₂. After cooling, methanol (=5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl₃.

The cobalt metal Pc 10 is soluble in DMF, CH₂Cl₂, and CHCl₃, mp. > 300°C. Yield: 0.020 g (37%). Anal. calcd. for C₉₂H₄₈N₈O₁₂Co: C, 72.87%; H, 3.19%; N, 7.39%; Co, 3.81%. FT-IR (KBr pellet): vₘₐₓ cm⁻¹ 1247 (Ar-O-Ar), 1470–1568 (Ar C=C), 1730 (C=O), 3062 (Ar–CH). UV-vis, (log ε) in CHCl₃: λₘₐₓ, nm 303 (5.16), 613 (4.63), 681 (5.27). MS (MALDI-TOF): (m/z) 1516 [M⁺].

A mixture of 3-(4-oxo-2-phenyl-4H-chromen-6-yl oxy) phthalonitrile (5) (0.05 g, 0.137 mmol) and Co(OAc)₂ · 4H₂O (0.0085 g, 0.034 mmol) in N,N-dimethylamino ethanol (1 mL) were refluxed and stirred at 160–170°C (bath temperature) for 24 h under N₂. After cooling, methanol (=5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl₃.

A mixture of 3-(4-oxo-2-phenyl-4H-chromen-6-yl oxy) phthalocyaninato cobalt (II) (11). A mixture of 3-(4-oxo-2-phenyl-4H-chromen-6-yl oxy) phthalonitrile (5) (0.05 g, 0.137 mmol) and LiOAc · 2H₂O (0.0036 g, 0.034 mmol) in N,N-dimethylamino ethanol (1 mL) was refluxed and stirred at 160–170°C (bath temperature) for 72 h under N₂. After cooling, methanol (=5 mL) was added in order to precipitate the green-blue product. The green-blue product was washed with hot acetic acid, hot methanol and water, and finally dried. This product was chromatographed by silica gel and eluted with CHCl₃.

The metal-free Pc 11 is soluble in DMF and CHCl₃, mp. > 300°C. Yield: 0.010 g (%20). Anal. calcd. for C₁₁₂H₅₀N₈O₁₂: C, 75.71%; H, 3.45%; N, 7.68% found C, 76.03%; H, 3.74%; N, 7.90%. FT-IR (KBr pellet): vₘₐₓ cm⁻¹ 1254 (Ar-O-Ar), 1452–1568 (Ar C=C), 1730 (C=O), 3062 (Ar–CH). UV-vis, (log ε) in CHCl₃: λₘₐₓ, nm 303 (4.99), 681 (5.10), 715 (5.17). MS (MALDI-TOF): (m/z) 1459 [M⁺].

**Electrochemistry and in situ spectroelectrochemistry**

Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out using a Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25°C. For CV and SWV measurements, the working electrode was a Pt plate with a surface area of 0.10 cm². A Pt spiral wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetraethylammoniumperchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a
concentration of 0.10 mole dm$^{-3}$. High purity N$_2$ was used for deoxygenating the solution at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements.

In situ spectroelectrochemical and in situ electrocolorimetric measurements were carried out by an external PC combined with an Ocean Optics HR2000 UV-vis spectrophotometer equipped with a potentiosstat/ galvanostat and utilizing an optically-transparent thin layer (OTTLE) cell with a three-electrode configuration at 25°C.

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 shows the synthetic route for novel peripheral and non-peripheral flavone-substituted metal free, zinc (II) and Co(II) Pcs (6–11), respectively. 4-(4-oxo-2-phenyl-4H-chromen-6-yl)phthalonitrile (4) and 3-(4-oxo-2-phenyl-4H-chromen-6-yl)phthalonitrile (5) were prepared by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile and 3-nitrophthalonitrile with 6-hydroxy-2-phenyl-4H-chromen-4-one (1). The reaction was carried out in DMF at room temperature under N$_2$ atmosphere, and the yields were 74% for 4 and 76% for 5. Cyclotetramerization of the phthalonitrile derivatives 4 and 5 to the Pcs were carried out in N$_2$N-dimethylaminoethanol at 160–170°C in a sealed tube. The crude green products were purified by washing with hot acetic acid and hot methanol. The products were chromatographed by silica gel using CHCl$_3$ as eluent. The purified Pcs were soluble in DMF, CHCl$_3$ and CH$_2$Cl$_2$. All the newly-synthesized compounds in this study gave satisfactory spectroscopic data (FT-IR, UV-vis, $^1$H NMR, MALDI-TOF MS) for the confirmation of the molecular structures of the target Pc compounds.

The FT-IR spectra of the synthesized compounds, recorded with KBr pellets in the range 4000–400 cm$^{-1}$, were in good agreement with the target structures. The peaks recorded around 2230 cm$^{-1}$ for compounds 4 and 5 were attributed to the CN functionality. The formation of final Pc compounds 6–11 was confirmed by the absence of the CN band in their FT-IR spectra. The FT-IR spectra of MPCs 6, 7, 9, 10 and metal-free Pcs 8 and 11 were very similar, with the exception of the inner core NH bands of compounds 8 and 11 at 3288 and 3282 cm$^{-1}$, respectively.

The UV/vis spectra of Pcs 6–8 in CHCl$_3$ showed Q-band absorptions within the range of 663–699 nm with vibronic bands between 605 and 631 nm, whereas compounds 9–11 displayed maximum absorbance at the range, 681–715 nm with vibronic bands at the range 613–664 nm (Table 1). These Q-band absorptions of the Pcs are attributed to the $\pi$-$\pi^*$ transitions from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of the conjugated macromolecules. Peripherally flavone substituted Pcs display a Soret band between 292 and 346 nm. This band is observed due to the transitions from the deeper $\pi$ levels to the LUMO. The UV-vis spectra of the Pcs are presented in Figs 1 and 2. The red shifts between the peripherally and non-peripherally substituted derivatives were about 15–18 nm. These bathochromic shifts are characteristic of Pcs with substituents at non-peripheral positions.

$^1$H NMR spectra were also in good correlation with the structures of the synthesized compounds. Vinilic protons for phthalonitrile compounds 4 and 5 were observed as diagnostic peaks at 6.85 and 6.78 ppm, respectively. In the spectra, chemical shifts of aromatic protons appeared at $\delta$ 7.30–7.92 and 7.15–7.88 ppm with expected coupling constant for compounds 4, 5 respectively, confirming the structures. All the complexes (6–11) were also analyzed using elemental analysis and mass spectroscopy. The MALDI-TOF MS spectra of compound 6 is presented in Fig. 3.

Spectral data of all the target compounds show good agreement with the proposed structures. All these spectral data show that all compounds were synthesized successfully using the synthesis route given in Scheme 1.

Electrochemistry and in situ spectroelectrochemistry

Voltammetry and in situ spectroelectrochemistry of compounds 6–11 were investigated by the techniques of CV, SWV and electrocolorimetry supported in situ spectroelectrochemistry. Table 2 lists the assignment of the redox couples and the electrochemical redox data, which included half-wave peak potentials ($E_{1/2}$), the ratio of anodic to cathodic peak currents ($I_p/I_c$), peak potential separations ($\Delta E_p$), and the difference between the first oxidation and reduction potentials ($\Delta E_{ox}$) in de-aerated DMSO/TBAP involving TBAP as supporting electrolyte on a Pt working electrode. The peak currents for the redox couples of the complexes were usually found to be directly proportional to the square root of scan rate, suggesting their diffusion-controlled nature. For the redox processes of the Pc compounds, $\Delta E_{pa}$ values at 0.100 V·s$^{-1}$ scan rate ranged 60 to 120 mV reflecting their reversible or quasi-reversible nature ($\Delta E_p$ of 0.080 V at 0.100 V·s$^{-1}$ was obtained for the ferrocene internal standard). The voltammetric behaviors of peripherally and non-peripherally 6-hydroxyflavonox substituted ZnPc, 6 and 9, and metal-free Pcs, 8 and 11 are similar in general to each other with some shifts which can be attributed to the differences in the polarizing effects of relevant metal centers (Table 2) [16, 25]. This similarity proposes that all redox processes of 6 and 9 are Pc ring-based one-electron redox processes [20, 26, 27]. The first reduction of the Pc ligand is associated to the position of the LUMO, whereas the first oxidation of the ligand is associated to the position of the HOMO. Therefore, $\Delta E_{1/2}$ values relate to the HOMO–LUMO...
Scheme 1. Summary of the synthesis of compounds 4–11
gap in MPc species having redox inactive metal centers [28]. ΔE_{1/2} values ranging from 1.42 to 1.65 V for the complexes ZnPc, 6 and 9, and metal-free Pcs, 8 and 11, point out the semi-conducting nature of these compounds. The values are also consistent with the values reported in literature [28]. As shown in Table 2, peripheral and non-peripheral complexes 6–11 show metal- and/or Pc ring-based redox processes in DMSO/TBAP. On the other hand, all the redox processes for 6–11 occur at remarkably more positive potentials than those of various unsubstituted Pcs [26]. This shifting can be attributed to the electron-withdrawing effect of coumarin substituents on the Pc ring, which leads to easier reduction and more difficult oxidation. The positions of substituents and their electron-withdrawing or releasing characters also affect aggregation behaviors of the metal Pcs compounds and thus, their redox processes.

Figure 4a shows CV and SWV of 6 in the coordinating polar solvent DMSO/TBAP electrolyte system. ZnPc 6 gives one oxidation and three one-electron reduction processes (O1, R1′, R1″ and R2). The broad or rounded reduction signals of this complex suggest the presence of aggregated and monomeric species in solution, and thus the complication of the redox processes by the intermolecular interactions. Thus, first redox reduction couple is split into two couples due to the formation of equilibrium between the aggregated and nonaggregated species, which are expected to be reduced at different potentials, and appears as a split couple of a ring-based process, labeled R1′ at -0.68 V and R1″ at -1.03 V. The peaks of the second reduction couple (R2) are also rounded. The broadness of the redox peaks, due to peripheral substitution and thus the presence of aggregated species, were also supported by SWV signals in the forward and reverse scans (Fig. 4a inset). It is not possible to detect the nature of the redox processes and also to realize possible aggregation effects on these processes definitely by voltammetric measurements alone. The combination of voltammetric measurements with in situ spectral measurements has vital importance, both in the identification of redox processes and in the effect of the aggregation phenomenon on these processes. Therefore, in situ spectroelectrochemistry of ZnPc 6 in DMSO/TBAP during the controlled potential electrolysis of the complexes was also employed to provide further information on the nature of the redox processes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ (nm) (log ε)</th>
<th>λ (nm) (log ε)</th>
<th>λ (nm) (log ε)</th>
</tr>
</thead>
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<tr>
<td>6</td>
<td>346 (4.82)</td>
<td>605′ (4.39)</td>
<td>675″ (5.11)</td>
</tr>
<tr>
<td>7</td>
<td>299 (5.18)</td>
<td>609′ (4.58)</td>
<td>673″ (4.98)</td>
</tr>
<tr>
<td>8</td>
<td>292 (4.99)</td>
<td>631′ (4.58)</td>
<td>663′ (4.74), 699″ (4.72)</td>
</tr>
<tr>
<td>9</td>
<td>302 (5.00)</td>
<td>620″ (4.60), 664′ (4.72)</td>
<td>690″ (5.43)</td>
</tr>
<tr>
<td>10</td>
<td>302 (5.16)</td>
<td>613′ (4.63)</td>
<td>681″ (5.27)</td>
</tr>
<tr>
<td>11</td>
<td>303 (4.99)</td>
<td>645′ (4.57)</td>
<td>681″ (5.10), 715″ (5.17)</td>
</tr>
</tbody>
</table>

*Vibronic.

Figure 1. UV-vis spectrum of compounds 6–8 in CHCl₃.

Figure 2. UV-vis spectrum of compounds 9–11 in CHCl₃.
observed, i.e. whether these processes are ligand-based or metal-based and aggregation effects.

Figure 4b–4d represents UV-vis spectral changes observed during the redox processes of 6 in DMSO/TBAP and a simultaneously recorded chromaticity diagram. Aggregation in MPc complexes is typified by a broadened or split Q band, with the high energy band being owing to the aggregate and the low energy band due to the monomer [28, 29]. Thus, the original spectrum with cyan color monitored before the application of any constant potential reflects clearly the presence of an equilibrium between the aggregated and monomer species in the solution at first (Fig. 4b). Upon first reduction at -0.90 V vs. SCE, corresponding to the redox process labeled R1’ in Fig. 4b, the intensity of the band at 639 nm decreases while the band at 677 nm increases. The shift in Q-band absorption is not observed during the reduction of the Pc ligand. In the meantime, the monomer-aggregate equilibrium appears to shift toward the monomer species during this process. The formation of disaggregated species is confirmed by well-defined isosbestic points which appeared at 662 and 669 nm during the first spectral changes. As shown by the chromacity diagram in Fig. 4d, the color of the solution changed from cyan (x = 0.323 and y = 0.354) to bluish green (x = 0.330 and y = 0.398). During the second group of spectral changes at -1.20 V constant potential in inset Fig. 4b, a new band forms at 577 nm, and a decrease in the Q-band absorption at 669 nm occurs without shift. The spectral changes have well-defined isosbestic points at 427, 609 and 729 nm, and lead to color changes from to bluish green (x = 0.3307 and y = 0.3987) to light green (x = 0.3866 and y = 0.4096) as represented by \textit{in situ} electro-colorimetric measurements, i.e. the chromaticity diagram in Fig. 4d. These spectral changes probably correspond to the reduction of disaggregated species [30]. The new band at 577 nm and the decrease in the Q-band absorption without shift are characteristics of Pc ring reductions, and thus for the formation of [Zn(II)Pc(-3)] species, confirming the CV assignment of the couple R1’ to Zn(II)Pc(-2)/[Zn(II)Pc(-3)] process [30]. Similar characteristic spectral changes were also observed during the second reduction of 6 at -1.60 V potential application vs. SCE. The absorption of the main continues to decrease without shift, while a new band appears at 543 nm (Fig. 4c). These spectral changes, accompanied by the formation of well-defined isosbestic points at 460 and 570 nm, correspond to the second ring reduction with the formation of [Zn(II)Pc(-4)]2 dianion species. \textit{In situ} electro-colorimetric measurements suggested that [Zn(II)Pc(-4)]2 species have orange color (x = 0.4317 and y = 0.4471) (Fig. 4d). The association of net color changes to the redox processes of 6 is important for its applicability as the color changing material in electrochromic device technologies.

Figure 5a shows cyclic and square wave voltamograms of non-peripherally substituted ZnPc 9 in DMSO/TBAP electrolyte system. Compound 9 displays three well-resolved reversible and diffusion-controlled reductions (R1 at -0.81 V, R2 at -1.31 V and R3 at -1.55 V vs. SCE) and an oxidation couple (O1 at 0.72 V vs. SCE). The redox behavior of 9 is similar to that of peripherally substituted ZnPc 6. However, the first reduction peak of 9 is not split. In addition, the voltammetric peaks of 9 are usually sharp. Thus, the redox signals of 9 are better defined than those of 6, probably due to the lack of aggregated species. The absence of aggregated species in solution of complex 9 should be due to its non-peripheral
nature, leading to its non-planarity. The chemical and electrochemical reversibility of the redox processes were also confirmed by SWVs in the forward and reverse scans (Fig. 5b). Figure 6a displays the spectral changes monitored during the first reduction of 9 at -1.00 V vs. SCE in DMSO/TBAP, corresponding to the redox process labeled R1 in Fig. 2a. In contrast to 6, the Q-band absorption of complex 9 before applying any constant

<table>
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<tr>
<th>Pcs</th>
<th>Redox processes</th>
<th>Label</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$I_{pa}/I_{pc}$ (V)</th>
<th>$\Delta E_{1/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Zn(II)Pc(-2)/[Zn(II)Pc(-1)]*</td>
<td>O1</td>
<td>0.74</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>Zn(II)Pc(-2)/[Zn(II)Pc(-3)]*</td>
<td>R1' R1'' (-0.68)</td>
<td>-1.03</td>
<td>—</td>
<td>—</td>
<td>1.42</td>
</tr>
<tr>
<td>6</td>
<td>[Zn(II)Pc(-3)]/[Zn(II)Pc(-4)]*</td>
<td>R2</td>
<td>-1.46</td>
<td>110</td>
<td>0.70</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>[Co(III)Pc(-2)]/[Co(III)Pc(-2)]*</td>
<td>O2</td>
<td>0.90</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>Co(II)Pc(-2)/[Co(III)Pc(-2)]*</td>
<td>O1</td>
<td>0.40</td>
<td>90</td>
<td>0.75</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>Co(II)Pc(-2)/[Co(I)Pc(-2)]*</td>
<td>R1</td>
<td>-0.33</td>
<td>80</td>
<td>0.84</td>
<td>0.73</td>
</tr>
<tr>
<td>7</td>
<td>[Co(I)Pc(-2)]/[Co(I)Pc(-3)]*</td>
<td>R2</td>
<td>-1.40</td>
<td>75</td>
<td>0.95</td>
<td>—</td>
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<tr>
<td>7</td>
<td>2H(I)Pc(-2)/2H(I)Pc(-1)*</td>
<td>O1</td>
<td>0.94</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>7</td>
<td>2H(I)Pc(-2)/2H(I)Pc(-3)*</td>
<td>R1</td>
<td>-0.71</td>
<td>90</td>
<td>0.76</td>
<td>1.65</td>
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<tr>
<td>8</td>
<td>[2H(I)Pc(-3)]/[2H(I)Pc(-4)]*</td>
<td>R2</td>
<td>-0.95</td>
<td>100</td>
<td>0.70</td>
<td>—</td>
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<tr>
<td>8</td>
<td>[2H(I)Pc(-4)]/[2H(I)Pc(-5)]*</td>
<td>R3</td>
<td>-1.55</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>Zn(II)Pc(-2)/Zn(II)Pc(-1)*</td>
<td>O1</td>
<td>0.72</td>
<td>120</td>
<td>0.80</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>Zn(II)Pc(-2)/Zn(II)Pc(-3)*</td>
<td>R1</td>
<td>-0.81</td>
<td>60</td>
<td>0.98</td>
<td>1.53</td>
</tr>
<tr>
<td>9</td>
<td>[Zn(II)Pc(-3)]/[Zn(II)Pc(-4)]*</td>
<td>R2</td>
<td>-1.31</td>
<td>75</td>
<td>0.90</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>[Zn(II)Pc(-4)]/[Zn(II)Pc(-5)]*</td>
<td>R3</td>
<td>-1.55</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>[Co(III)Pc(-2)]/[Co(III)Pc(-1)]*</td>
<td>O2</td>
<td>0.87</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>Co(II)Pc(-2)/Co(III)Pc(-2)*</td>
<td>O1</td>
<td>0.38</td>
<td>90</td>
<td>0.85</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>Co(II)Pc(-2)/Co(I)Pc(-2)*</td>
<td>R1</td>
<td>-0.36</td>
<td>80</td>
<td>0.80</td>
<td>0.74</td>
</tr>
<tr>
<td>10</td>
<td>[Co(I)Pc(-2)]/[Co(I)Pc(-3)]*</td>
<td>R2</td>
<td>-1.38</td>
<td>110</td>
<td>0.70</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>2H(I)Pc(-2)/2H(I)Pc(-1)*</td>
<td>O1</td>
<td>0.91</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>2H(I)Pc(-2)/2H(I)Pc(-3)*</td>
<td>R1</td>
<td>-0.67</td>
<td>80</td>
<td>0.84</td>
<td>1.58</td>
</tr>
<tr>
<td>11</td>
<td>[2H(I)Pc(-3)]/[2H(I)Pc(-4)]*</td>
<td>R2</td>
<td>-0.93</td>
<td>90</td>
<td>0.60</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>[2H(I)Pc(-4)]/[2H(I)Pc(-5)]*</td>
<td>R3</td>
<td>-1.58</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.10 V·s$^{-1}$.

$\Delta E_p = E_{pa} - E_{pc}$ at 0.10 V·s$^{-1}$.

$I_{pa}/I_{pc}$ for reduction, $I_{pc}/I_{pa}$ for oxidation processes at 0.100 V·s$^{-1}$ scan rate.

$\Delta E_{1/2} = E_{1/2}$ (first oxidation) $- E_{1/2}$ (first reduction). HOMO–LUMO gap for MPc having an electro inactive metal center.

The redox behavior of the compounds was complicated by aggregation phenomenon and thus, some redox couples were split.

These redox couples could be detected only by square wave voltammetry.
potential is rather narrow, suggesting that it is in the form of monomers. Upon the first reduction at -1.00 V vs. SCE in the DMSO/TBAP electrolyte system, the absorptions of the main Q band at 692 nm, the vibrational band at 668 nm and the Soret bands at 265 and 303 nm decrease, while a new broad band around 560 nm appears with the formation of well-specified isosbestic points (Fig. 6a).

As shown by the chromacity diagram in Fig. 6c, the color of the solution changes from light greenish blue ($x = 0.282$ and $y = 0.370$) to light pink ($x = 0.383$ and $y = 0.360$). These spectral changes, especially the formation of a new band at 560 nm and the decrease of the Q band without shift, are characteristic for Pc ligand-based reduction [28]. During further reduction at -1.40 V vs. SCE, the Q band at 692 nm decreases without a shift while a new band is observed at 547 nm (Fig. 6b) and the color changes from light pink to purple ($x = 0.374$ and $y = 0.280$) as given in the chromaticity diagram in Fig. 6c.

The redox potentials of peripherally and non-peripherally 6-hydroxyflavonoxy substituted cobalt Pcs, 7 and 10 are highly different in comparison with those of Zn and metal-free Pcs. The first reduction and the first oxidation processes of 7 and 10 occur at potentials less negative and less positive, respectively, than those of Zn(II) and metal-free Pcs (Table 2). The difference in the voltammetric behavior is due to the fact that MPcs, such as MnPc, CoPc and FePc, having a metal that possesses
energy levels lying between the HOMO and the LUMO of the Pc ligand, in general exhibit redox processes centered on the metal. The CV and SWV responses of non-peripherally substituted cobalt Pc, 10 in the DMSO/TBAP electrolyte system were considerably similar to those of peripherally substituted cobalt Pc 7 in terms of the number of redox signals. As shown in Table 2, small differences between their redox potentials were observed, probably due to different polarizing effects of peripheral and non-peripheral substituents changing the electron density of the Pc ring. Figure 7 displays cyclic and square wave voltammograms of 10 in DCM/TBAP. It displays two well-resolved reversible and diffusion controlled reductions (R1 at -0.38 V and R2 at -1.36 V) and two oxidation couples (O1 at 0.38 V and O2 at 0.87 V). The first reduction and first oxidation processes of 7 and 10 in DCM could be assigned to the Co(II)Pc(-2)/[Co(I)Pc(-2)]⁻ and Co(II)Pc(-2)/[Co(III)Pc(-1)]⁺ redox couples respectively, and the remaining processes to the Pc ring. The anodic to cathodic peak separations in the cyclic voltammograms and the symmetry of the square wave voltammograms clearly show the chemical and electrochemical reversibility of the redox processes (Fig. 7b).

Spectroelectrochemical measurements were also carried out to assign the first reduction and the second
NOVEL PERIPHERALLY AND NON-PERIPHERALLY 6-OXYFLAVONE SUBSTITUTED METAL-FREE, ZINC(II)

reduction processes of 10. Figure 8a represents in situ UV-vis spectral changes during the first reduction of 10 at -0.60 V vs. SCE, corresponding to the redox process labeled R1 in Fig. 7. The Q band at 675 nm shifts to 710 nm, while a new band at 470 nm appears (Fig. 8a). These spectral changes form well-defined isosbestic points at 392, 561, and 762 nm. The spectral changes, especially the formation of a new band within the range of 400–500 nm, indicate that the first reduction process (R1) of 10 is metal-based, and thus corresponds to the Co(II)Pc(-2)/[Co(II)Pc(-2)] couple [31]. During the second reduction at -1.50 V vs. SCE, the Q band at 710 nm decreases without shift (Fig. 8b). In the meantime, the absorption at 475 nm increases slightly in intensity, while the absorption between 500 and 600 nm increases. Clear isosbestic points are observed at 287 and 627 nm. These spectral changes at the potential of the couple R2 are characteristic of a ring-based reduction and confirm our voltammetric assignment of this process to [Co(I)Pc(-2)]/[Co(I)Pc(-3)]². The colors of the electrogenerated species 10 were also recorded with in situ spectrocolorimetric measurements. The color changes associated with the redox processes are shown in the chromaticity diagram in Fig. 8c. Without any potential application, the color of the solution of 10 is light blue (x = 0.282 and y = 0.371). When the potential is stepped -0.60 V, the blue color starts to change and electrochemically-produced species of the first reduction process, mono anionic [Co(I)Pc(-2)] species, are observed to have a light green color (x = 0.3742 and y = 0.270) (Fig. 5c). During the second reduction process of 10 at a constant potential of -1.40 V, the color changes to purple (x = 0.374 and y = 0.280).

CONCLUSION

In conclusion, tetra-substituted Zn(II) (6 and 9), Co(II) (7 and 10) and metal-free (8 and 11) Pcs bearing peripheral or non-peripheral 6-hydroxyflavonoxy groups were synthesized for the first time in this study. These compounds have been characterized by MALDI-TOF mass, FT-IR and UV-vis spectroscopies as well as by elemental analysis. The redox properties of these Pcs were determined by electrochemical, in situ spectroelectrochemical and in situ electrocolorimetric measurements. Electrochemical measurements showed that CoPc complexes display both metal and ligand-based one-electron redox processes, while ZnPc and H₂Pc compounds give ligand-based one-electron redox processes in a DMSO/TBAP electrolyte. On the other hand, in situ spectroelectrochemical and in situ electrocolorimetric measurements confirmed that in the case of peripherally substituted complexes, aggregated species of the complexes form in the solution and the relevant redox signals are affected by the formation of these species. In addition, the association of net color changes to the redox processes of the complexes suggested their usability as electrochromic materials.

Acknowledgments

We are thankful to the Research Foundation of Marmara University, Commission of Scientific
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Research Project (BAPKO) (Project No: FEN-C-DRP-080410-0087). Ali Rıza Özkaya also thanks The Turkish Academy of Sciences (TUBA).

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