Guest Editors: M. Salomé Rodríguez-Morgade and Nagao Kobayashi

This issue of JPP is dedicated to Professor Tomás Torres on the occasion of his 65th birthday. The cover picture represents his colorful life. It shows a selection of palette colors obtained in the group of Professor Torres, which illustrate just a small part of the assorted colored structures designed and prepared in Madrid. The background picture is The Plaza de Cibeles square, an emblematic landmark of Madrid, the city where Torres was born and is developing his scientific career.

Reviews

pp. 843-854
Synthesis of low melting point porphyrins: A quest for new materials
César A. Henriques, Sara M.A. Pinto*, João Canotilho, M. Ermelinda S. Eusébio and Mário J.F. Calvete*

Preparation of porphyrins which do not aggregate, possessing low melting points is an endearing challenge for several applications in materials science. In this contribution a viewpoint regarding the synthesis of low melting point porphyrins is presented, along with some new results on the spectroscopic and thermal characterization of some low melting point meso-tetrasubstituted porphyrins.

pp. 855-888
What's in a name? The MacDonald condensation
Timothy D. Lash*

First reported by MacDonald and coworkers in 1960, the condensation of dipyrrylmethanes with dipyrrylmethane dialdehydes has proven to be an amazingly versatile approach for the synthesis of diverse porphyrin structures. In addition, a "3 + 1" variation on this strategy has been particularly effective in preparing remarkably disparate porphyrinoid macrocycles, and other combinations of reactants have been utilized in the construction of expanded porphyrin systems. Unfortunately, some confusion has arisen in the literature concerning what is meant by a MacDonald condensation and guidelines for identifying this valuable methodology are provided.
Multisensor systems based on phthalocyanines for monitoring the quality of grapes

Maria Luz Rodriguez-Mendez*, Celia García-Hernandez, Cristina Medina-Plaza, Cristina García-Cabezón and José Antonio de Saja

Arrays of phthalocyanine-based sensors with complementary activity have been developed and successfully used to analyze complex liquids such as grape juices.

Phosphorus complexes of porphyrinoid macrocycles

Ritambhara Sharma and Mangalampalli Ravikanth*

The synthesis, structure and properties of P(V) complexes of various porphyrinoids are described.

The copper-catalyzed alkyne-azide cycloaddition for the construction of fullerene–porphyrin conjugates

Uwe Hahn and Jean-François Nierengarten*

Among the click chemistry approaches known to date, it is undoubted that the copper–catalyzed alkyne-azide 1,3-dipolar cycloaddition (CuAAC) has played a key role. Such reactions in general offer virtually unlimited possibilities to prepare new molecules for e.g. materials science applications. As such, the synthesis of porphyrin–fullerene conjugates obtained via CuAAC are summarized.

Catalytic reduction of proton, oxygen and carbon dioxide with cobalt macrocyclic complexes

Kentaro Mase, Shoko Aoi, Kei Ohkubo* and Shunichi Fukuzumi*

The catalysis of cobalt(II) macrocycle complexes for the selective two-electron reduction of O₂ to hydrogen peroxide has been highlighted together with that for the selective reduction of CO₂ to CO in competition with the reduction of proton to hydrogen. The catalytic mechanisms are discussed based on detailed kinetic study under homogeneous conditions.
Synthesis and anion binding properties of porphyrins and related compounds

Flávio Figueira, João M.M. Rodrigues, Andreia A.S. Farinha, José A.S. Cavaleiro and João P.C. Tomé*

Over the last two decades the preparation of pyrrole-based receptors for anion recognition has attracted considerable attention. In this regard macrocyclic porphyrins, phthalocyanines and expanded porphyrins have been used as strong and selective receptors. In this review, we summarize the most recent developments in anion binding studies, outlining the strategies that may be used to synthesize and functionalize these type of compounds.

Tomás Torres’ research in a nutshell

Giovanni Bottari*, Andres de la Escosura*, David González-Rodríguez* and Gema de la Torre*

This review offers an overview of the main achievements of Prof. Tomás Torres in his research career, which has been devoted to the development of synthetic methods and applications of novel functional systems based on phthalocyanines and other porphyrinoid analogs.

Synthesis and photochemical studies of a tris(4-iodophenoxy) subphthalocyaninato boron(III)-fulleropyrrolidine dyad

Robert Cantu, Habtom B. Gobeze and Francis D’Souza*

A subphthalocyanine-fullerene dyad, Subpc-C$_{60}$ has newly synthesized through axial functionalization via central boron of subphthalocyanine, and the effect of 4-iodophenoxy substituents on the subphthalocyanines in modulating photochemical events has been studied in organic solvents of different polarity. Femtosecond transient absorption studies revealed photoinduced electron transfer to be the main quenching mechanism resulting in SubPc$^•+$-C$_{60}$•- radical ion-pair formation. The radical ion-pair populated the low-laying SubPc$^•+$ prior returning to the ground state, as revealed by nanosecond flash-photolysis studies.

A bis-Au(III) [28]hexaphyrin triphenylphosphine adduct

Koji Naoda and Atsuhiro Osuka*

Nucleophilic addition of triphenylphosphine to a bis-Au(III) [26] hexaphyrin smoothly proceeded to furnish a [28]hexaphyrin triphenylphosphine adduct. The product was fully characterized by NMR, UV-vis absorption, and MS spectroscopies as well as X-ray diffraction analysis. The hexaphyrin displayed Hückel antiaromaticity due to the 28 electrons in its conjugated circuit. X-ray analysis revealed that a phosphorane form is more important contribution in solid state than a phosphorus ylide form.
Non-linear optical, electrochemical and spectro-electrochemical properties of amphiphilic inner salt porphyrinic systems
Claude P. Gros*, Clément Michelin, Griet Depoter, Nicolas Desbois, Koen Clays, Yan Cui, Lihan Zeng, Yuanyuan Fang, Hoang Minh Ngo, Colin Lopez, Isabelle Ledoux, Jean-François Nicoud, Frédéric Bolze* and Karl M. Kadish*

A new series of inner salt donor acceptor meso-substituted porphyrin derivatives were synthesized and characterized by the linear and nonlinear optics, electrochemistry and spectroelectrochemistry in non-aqueous media.

Synthesis and photophysicochemical properties of BODIPY dye functionalized gold nanorods for use in antimicrobial photodynamic therapy
Gugu Kubheka, Imran Uddin, Edith Amuhaya, John Mack* and Tebello Nyokong

A series of boron dipyrromethene (BODIPY) dyes have been prepared with properties that are ideal for a good photosensitizer. Functionalization with bromine atoms and attachment to gold nanoparticles through a meso-aniline group results in high singlet oxygen quantum yields and low fluorescent quantum yields. Molecular modelling was used to analyze trends in the MO energies of various brominated aniline BODIPY dyes.

Catching metallic nitride endohedral fullerenes in organic and aqueous media
Volker Strauss, Shankara Gayathri Radhakrishnan, Jenny Malig, Norbert Jux and Dirk M. Guldi*

The association of two bis-tetraphenylporphyrin tweezers-like conjugates, as excited state electron donors, with Sc,N@C₆₀, as ground state electron acceptors, was tested in organic and aqueous media.

A hindered subphthalocyanine that forms crystals with included aromatic solvent but will not play ball with C₆₀

A novel subphthalocyanine containing bulky substituents placed at its peripheral sites was assessed for supramolecular binding with C₆₀ through crystallization and fluorescence studies. Three different crystal polymorphs of the subphthalocyanine were obtained that showed inclusion of a single aromatic solvent molecule within the well-defined cavity of the molecule but complete exclusion of C₆₀.
**pp. 1041-1048**

**Water-soluble porphyrinoids as G-quadruplex binders and telomerase inhibitors**

Yoshiya Ikawa, Sho Katsumata, Ryuichi Sakashita, Shinobu Sato, Shigeori Takenaka and Hiroyuki Furuta*

Water-soluble derivatives of three kinds of expanded porphyrins (N-fused pentaphyrin, hexaphyrin, and heptaphyrin) were synthesized and their binding ability to G-quadruplex (G4-) DNA and the inhibitory effects on enzymatic telomere extension were investigated. While expanded porphyrins increased the melting temperature of G4-DNA more effectively than the regular porphyrins, a porphyrin isomer (N-confused porphyrin) showed the highest inhibitory effect on telomerase activity.

**pp. 1049-1054**

**A novel isoindole-containing polyaromatic hydrocarbon unexpectedly formed during the synthesis of meso-2,6-dichlorophenyl-substituted tribenzosubporphyrin**

Yuta Shiina, Hideaki Karasaki, Shigeki Mori, Nagao Kobayashi, Hiroyuki Furuta* and Soji Shimizu*

A novel isoindole-containing polyaromatic hydrocarbon was unexpectedly formed during the synthesis of meso-2,6-dichlorophenyl-substituted tribenzosubporphyrin from a reaction of phthalimide and 2,6-dichlorophenylacetic acid in the presence of boric acid. In this manuscript, synthesis and properties of this polyaromatic hydrocarbon and meso-2,6-dichlorophenyl-substituted tribenzosubporphyrin are reported.

**pp. 1055-1059**

**A new synthesis of isoamethyrins: A 4+2 route**

Gonzalo Anguera, Salvador Borrós, José I. Borrell and David Sánchez-García*

A concise and versatile strategy for the preparation of isoamethyrin is presented. The novel procedure is predicated on the acid catalyzed condensation of a quaterpyrrole and a bipyrrole dialdehyde. As application of this procedure an aryl substituted isoamethyrin has been synthetized and characterized.

**pp. 1060-1064**

**Designing liquid-crystalline gold nanoparticles via the olefin cross-metathesis reaction**

Thanh Tung Nguyen, Thi Le Anh Nguyen* and Robert Deschenaux*

Grafting mesomorphic α,β-unsaturated carbonyl olefins onto the organic shell of gold nanoparticles containing terminal olefin ligands by applying the olefin cross-metathesis reaction gave liquid-crystalline gold nanoparticles. The title materials gave rise to the formation of smectic A phases in agreement with the structure and nature of the liquid-crystalline promoters. The olefin cross-metathesis proved to be an elegant reaction for the design of liquid-crystalline nanoparticles.
Highly soluble tetrasubstituted lanthanide bis-phthalocyanines; synthesis, characterization, electrical properties and aggregation studies
Ahmet T. Bilgiçli, Armağan Günsel, Mehmet Kandaz*, Ahmet Altindal and Hüseyin Cömert

The synthesis and characterization of soft-metal ionophore lanthanide bis-phthalocyanines bearing 1-hydroxyhexan-3-ylthio groups. Also, elucidation of M- or J-type aggregation studies of functional lanthanide bis phthalocyanines in the presence of soft metal ion in THF/MeOH solution. In addition, electrical properties of ionophore double-decker lanthanide bis-phthalocyanines.

Synthesis of meta-methoxyphenyl substituted tetraazaporphyrin and corrolazine phosphorus(V) complexes
Taniyuki Furuyama, Yusuke Sugiya, Takuya Yoshida and Nagao Kobayashi*

Octa-(meta-methoxyphenyl) substituted tetraazaporphyrin (TAP) and corrolazine (Cor) phosphorus(V) complexes have been synthesized and characterized. meta-methoxyphenyl substituted PTAP has a blue-shifted, small charge transfer (CT) band while para-methoxyphenyl substituted PTAP has a red-shifted, intense CT band. The difference could be interpreted as an inductive effect of the meta-methoxy groups.

Synthesis and spectroscopic properties of photochromic dithienylethene-functionalized subphthalocyanine conjugate
Maohu Shi, Jingzhi Chen and Zhen Shen*

A novel subphthalocyanaine-dithienylethene dyad has been synthesized. Closed form → open form is photoinduced upon subphthalocyanaine moiety as a light-harvesting unit and the fluorescence emission of hybrid dyad could be modulated by the isomerization state of the dithienylethene moiety.

Synthesis and photophysical studies of a low-symmetry tribenzoisothiazoleporphyrine
Desiré Molina, Mohamed E. El-Khouly*, Savvas Ioannou, Andreas S. Kalogirou, Panayiotis A. Koutentis and Angela Sastre-Santos*

A new low-symmetry tribenzoisothiazoleporphyrine has been synthesized and its photophysical behavior has been examined and compared with that of the symmetrical tert-octyloxy zinc phthalocyanine by using steady-state absorption and fluorescence, cyclic voltammetry, molecular orbital calculation, and femtosecond transient absorption techniques.
Organometallic pyrene-containing porphyrins: Synthesis, characterization, and non-covalent interactions with C_{60} fullerenes
Yang Li, Hannah M. Rhoda, Anthony M. Wertish and Victor N. Nemykin*

Several pyrene-porphyrin and ferrocene-pyrene-porphyrin systems were prepared and characterized by spectroscopy, X-ray crystallography, DFT and TDDFT calculations. Formation of non-covalent complex between pyrene-porphyrin and C_{60} fullerene was confirmed by steady-state fluorescence spectra.

Subphthalocyanine derivatives as donor for solution-processed small molecule organic solar cells
Fatma Aslıhan Sari, Abdulcelil Yuzer, Werther Cambarau and Mine Ince*

A series of symmetrically substituted Subphthalocyanine derivatives with diverse substituent such as electron-donating or electron-withdrawing moieties at the peripheral position have been synthesized and their photophysical and electrochemical properties have been investigated. Solution-processed bulk heterojunction (BHJ) organic solar cells using SubPc derivatives as electron donor and fullerene derivative PCBM as an electron acceptor in the active layer were fabricated and characterized to evaluate the photovoltaic behaviour of these molecules.

Predominant effect of connecting atom and position of substituents on azomethine nitrogens’ basicity in phthalocyanines
Antonin Cidlina, Jan Svec, Lucie Ludvová, Jiří Kuneš, Petr Zimcik and Veronika Novakova*

Extraordinary high differences in the basicity were observed in the series of α- and β- substituted phthalocyanines bearing alkylxylo, alkylsulfanyl or alkyl group with log K values from 2.6 up to more than 7. Whereas log K values in β-series correlated with electronic effects of substituents, weak bonding interactions in α-series led to substantial increase of basicity of α-alkylxoylo and α-alkylsulfanyl derivatives.

A novel hybrid blend based on phenoxy-substituted boron subphthalocyanine for organic photodetectors
Sergey S. Maklakov*, Tatiana V. Dubinina, Marina M. Osipova, Elizaveta F. Petrucevich, Alexey D. Mishin and Larisa G. Tomilova

A phenoxy-substituted boron subphthalocyanine blended with MEH-PPV produces a photorestive material for the visible region. Micro-inhomogeneity drops photorestive properties of the blend ten-fold. Photorestive properties are discussed in terms of impedance spectroscopy.
Synthesis and self-assembly properties of fullerene/porphyrin-phthalocyanine and fullerene/bis-phthalocyanine triads

Khanh Hy Le Ho, Bruno Jousselme and Stéphane Campidelli*

In this work, we report on the synthesis and characterization of two fulleropyrrolidines bearing porphyrin/phthalocyanine and bis-phthalocyanine tweezers. The self-assembly properties in different solvents have been investigated by AFM and SEM. When deposited on surface from dichloromethane solutions, the fullerene derivatives formed aggregates of ca. 4–8 nm in height while hollow nanospheres with diameters of ca. 300–1000 nm are obtained from crystallization attempts.

Light harvesting subphthalocyanine–ferrocene dyads: Fast electron transfer process studied by femtosecond laser photolysis

Mohamed E. El-Khouly*, Maged A. El-Kemary, Ahmed El-Refaey, Kwang-Yol Kay and Shunichi Fukuzumi*

Fast and efficient electron-transfer processes of novel light harvesting ferrocene-subphthalocyanine dyads, where ferrocene is linked with subphthalocyanine at its axial position with the B–O band through the para and meta positions, have been confirmed in this study by utilizing the femtosecond laser photolysis technique.

Synthesis and catalytic activity of µ-oxo ruthenium(IV) porphyrin species to promote amination reactions

Paolo Zardi, Daniela Intrieri, Daniela Maria Carminati, Francesco Ferretti, Piero Macchi and Emma Gallo*

This work describes the synthesis of new ruthenium(IV) µ-oxo porphyrin complexes of general formula [RuIV(TPP)(X)]2O which reacted with organic azides in both stoichiometric and catalytic amination reactions. The reaction of [RuIV(TPP)(OCH3)]2O with Ph3CN3 or (CH3)3SiN3 yielded the new compound [RuIV(TPP)(N3)]2O which was fully characterised.

Polymeric phthalocyanine sheets as electrocatalytic electrodes for water-oxidation

Clemens Geis, Simon P. Schneider and Derck Schlettwein*

Polymeric copper and cobalt phthalocyanine (Cu-pPc and Co-pPc) thin films were prepared via a CVD process. In particular Co-pPc showed remarkable efficiency and stability in the oxygen-evolution-reaction (OER). Different oxidation states of the metal atoms were detected by photoelectron spectroscopy. (Spectro-) electrochemical experiments served to analyze details of the reversible electrochromic reduction, in particular of Cu-pPc.
Optical, electrochemical and third-order nonlinear optical studies of triphenylamine substituted zinc phthalocyanine
Narra Vamsi Krishna, Puliparambil Thilakan Anusha, S. Venugopal Rao* and L. Giribabu*

Zinc phthalocyanine substituted with triphenylamine group at peripheral positions have been synthesized and characterized using absorption, fluorescence and electrochemical techniques. Finally, NLO properties of TPA-ZnPc have been investigated using Z-scan technique with ps and fs pulses.

Subtle variations of the behavior of a silylated tetraethylene glycol-substituted Zn phthalocyanine towards acids
Emel Önal, Sevinc Z. Topal, Mohamed Tarhouni, Ümit Işıç, Jamoussi Bassem, Vefa Ahsen* and Fabienne Dumoulin*

An organosoluble phthalocyanine substituted by four silylated tetraethylene-glycol chains becomes water-soluble after acid-promoted removal of the TBDMS moieties. This a naked-eye observation system of acid aqueous media.

Photocatalytic degradation of persistent organic pollutants under visible irradiation by TiO₂ catalysts sensitized with Zn(II) and Co(II) tetracarboxyphthalocyanines
Yaghub Mahmiani, Altuğ Mert Sevim and Ahmet Gül*

In order to realize photocatalytic reactions under visible light more efficiently, new heterogeneous photocatalysts were prepared by anchoring carboxylic acid substituted Zn(II) and Co(II) phthalocyanines onto polycrystalline TiO₂ surface and their photocatalytic activities were investigated. New heterogeneous composites were characterized by using X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FT-IR), and ultraviolet-visible diffuse reflectance spectroscopy. The optimum loading value of the dyes on TiO₂ were 0.98 µmol/g TiO₂ for CoPc and 0.86 µmol/g TiO₂ for ZnPc. The photocatalysts showed excellent activities by irradiation with visible-light in the photocatalytic degradation of 4-chlorophenol, chlorobenzene and 1,2,4-trichlorobenzene. During two hours of irradiation with visible light, nearly 99% of the organic pollutants were decomposed.

Photocatalytic hydrogen production based on a water-soluble porphyrin derivative as sensitizer and a series of Wilkinson type complexes as catalysts
Athanassios A. Panagiotopoulos, Efthymios G. Fasoulakis, Eleftheria E. Vardalachaki and Athanassios G. Coutsolelos*

New photochemical hydrogen evolution systems consisting of various rhodium based catalysts with Wilkinson type structures, Zn metalated porphyrins and fluorescein as photosensitizers and triethanolamine as a sacrificial electron donor in acetonitrile/H₂O (1:1) solution, is reported.
pp. 1207–1216
Modifications of an unsymmetrical phthalocyanine: Towards stable blue dyes for dye-sensitized solar cells
Gloria Zanotti*, Nicola Angelini, Giuseppe Mattioli, Sara Notarantonio, Anna Maria Paoletti, Giovanna Pennesi, Gentilina Rossi, Daniela Caschera, Luisa De Marco and Giuseppe Gigli

A new copper phthalocyanine, namely 9(10),16(17),23(24)-tri-tert-butyl-2-[acetynyl-(4-carboxy)phenyl]phthalocyaninato-copper, and its corresponding free base have been synthesized and tested as potential stable blue dyes for dye sensitized solar cells. Chemical and optical characterization have been performed parallel to ab initio simulations, useful to clarify the frontier orbital behavior of our target compounds. The obtained results have been compared with their analogous blue-greenish zinc derivative whose maximum efficiency value has been raised from a reported 0.75% to 2.10%.

pp. 1217–1223
Aminophenyl/carboxyphenylporphyrins as sensitizers for dye sensitized solar cells
Alexander B. Rudine, Nicholas U. Day, Xisen Tian, Chang Lee, Keith E. James and Carl C. Wamser*

Tetraphenylporphyrins with all combinations of p-amino or p-carboxy substituents are effective dyes for dye-sensitized solar cells (DSSCs). The porphyrins with greater numbers of amino groups generally show greater efficiency, attributed to the well known push–pull effect in porphyrin-sensitized DSSCs. The most efficient sensitizer was the trans disubstituted zinc porphyrin, with an overall solar energy conversion efficiency of 5.66%, slightly higher than the triamino zinc porphyrin at 5.18%.

pp. 1224–1232
Study of the coordination of quinuclidine to a chiral zinc phthalocyanine dimer
Nelson Giménez-Agulló, Gemma Aragay, José Ramón Galán-Mascarós* and Pablo Ballester*

The dimerization process of a chiral Zn-phthalocyanine was found to be favored at high temperatures and entropy-driven. Studies of the coordination process of enantiopure and racemic Zn-phthalocyanine with quinuclidine were performed using two very different monomer concentrations, in order to dissect the coordination processes of the monomeric and dimeric states of the phthalocyanine. When coordinated to quinuclidine the thermodynamic stability of the coordinated dimer is reduced compared to that of the non-coordinated counterpart.

pp. 1233–1243
Electronic and magnetic interactions in diporphyrinylamines
Khalissa Merahi, Ana M.V.M. Pereira, Christophe Jeandon, Laurent Ruhlmann, J osé A.S. Cavaleiro, Maria G.P.M.S. Neves, Maylis Orio, Philippe Turek, Sylvie Choua* and Romain Ruppert*

The synthesis of new metalated diporphyrinylamines is described. The electronic properties of these compounds and the magnetic interactions between copper(II) centers and/or between one copper(II) center and an organic radical generated by oxidation were studied.
pp. 1244–1255
Stable, low-melting trans-A2B-corroles
Agnieszka Nowak-Król, Eleanor Fourie, Chris C. Joubert, Dorota Gryko*, Daniel T. Gryko* and Jannie C. Swarts*

The role of electron-withdrawing substituents and the length of alkyl chains on physicochemical properties of meso-substituted corroles has been investigated. The studies indicate that the presence of eight fluorine atoms has profound effect on the stability via affecting first oxidation potential of free-base corroles. The presence of three C18H37O substituents makes corrole capable of having two melting points (27.6 °C and 63.7 °C) depending on crystal packing.

pp. 1256–1263
Synthesis and characterization of a β-fused tetraporphyrin-phthalocyanine star-shaped array
Federica Mandoj, Giuseppe Pomarico, Frank R. Fronczek, Kevin M. Smith and Roberto Paolesse*

The condensation reaction of a β-fused dicyanoquinolazine tetraphenylporphyrin affords a star-shaped array where four porphyrin subunits are annulated to a central phthalocyanine ring. The visible spectrum of the array shows the features of the individual subunits. The synthetic pathway could allow the preparation of a wide range of chromophores, where porphyrin and phthalocyanine rings are fused together at their peripheral positions.

pp. 1264–1271
Formation and stability of porphyrin and phthalocyanine self-assembled monolayers on ZnO surfaces
Hanna Hakola*, Essi Sariola-Leikas, Paavo Jäntti, Thomas Mokus, Kati Stranius, Alexander Efimov and Nikolai V. Tkachenko*

Formation and stability of self-assembled monolayers (SAMs) of three porphyrin and one phthalocyanine derivatives on thin ZnO films was studied by monitoring absorption spectra of the samples. As a result of this study a simple monitoring procedure for routine and reliable deposition of porphyrinoid compounds with different anchor groups was established.

pp. 1272–1276
Spectroscopic characterization of water soluble phosphonato corrole: The effect of H-bounds on the self-assembled species
Rosalba Randazzo, Andrea Savoldelli, D. Andrea Cristaldi, Alessandra Cunsolo, Massimiliano Gaeta, M. Elena Fragalà, Sara Nardis, Alessandro D’Urso*, Roberto Paolesse* and Roberto Purrello*

The role of hydrogen bonds in the formation of aggregate of porphyrinoids was investigated by the comparison between the aggregation pathway of the porphyrin H2TPPP and the analogue corrole H2TPPC. The lack of one hydrogen bond in the aggregated species make the corrole aggregate more labile in strong acidic conditions.
Deep-cavity subporphyrazines with extended π-perimeters

Roman Münnich, Patricia Löser, Andreas Winzenburg and Rüdiger Faust*

Polyphenylated/perfluorinated quinoxalino subporphyrazines with an extended π-perimeter and deep cone-shaped topology have an excellent solubility that makes them attractive for a variety of applications. Wavelength dependent singlet oxygen measurements uncovered their potential acting as efficient photosensitizers.

Synthesis and electrochemistry of A₂B type mono- and bis-cobalt triarylcorroles and their electrocatalytic properties for reduction of dioxygen in acid media

Yue Wang, Zhongping Ou*, Yuan yuan Fang, Rui Guo, Ji jun Tang, Yang Song and Karl M. Kadish*

Two A₂B mono-cobalt corroles and the corresponding bis-cobalt derivatives linked by a xanthene acyl group were synthesized and characterized as to their electrochemistry and catalytic properties for reduction of dioxygen.

Improvement of nonlinear optical properties of phthalocyanine bearing diethyleneglycole chains: Influence of symmetry lowering vs. heavy atom effect


This paper reports the synthesis of the low symmetry phthalocyanines: metal-free 2,3-bis[2′-(2′′-hydroxyethoxy)ethoxy]j-9,10,16,17,23,24-hexa-π-butoxyphthalocyanine 1H₂ and its zinc complex 1Zn along with their nonlinear optical behavior in solution and in polycarbonate polymeric matrix together with CdSe@CdS-TOPO quantum dots. In such composite the value of Im[χ(3)]/α was almost three times higher in comparison with 1H₂ solution in chloroform.

Poly-(D,L-lactide-co-glycolide) nanoparticles with covalently-bound porphyrins for efficient singlet oxygen photosensitization

Ester Boix-Garriga, Francesca Bryden, Huguette Savoie, M. Llúisa Sagristá, Margarita Mora, Ross W. Boyle* and Santi Nonell*

The chemical nature of the photosensitizer influences its localization and singlet oxygen production ability in PLGA nanoparticles.
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pp. 1319–1333
Novel 4,4’-{(diphenylmethylene) bis(4,1-phenylene)bis(oxy)}-bridged ball-type phthalocyanines: Electrochemical, electrocatalytic oxygen reducing and heavy metals ions sensing properties
Elvan Doğan, Metin Özer*, Ahmet Altindal, Ali Rıza Özkaya, Bekir Salih and Özer Bekaroğlu*

Novel 4,4’-{(diphenylmethylene) bis(4,1-phenylene)bis(oxy)}-bridged ball-type metal-free, zinc(II), cobalt(II) and iron(II) ball-type metallophthalocyanines were synthesized by the reaction of the bisphthalonitrile derivative in 2-dimethylaminoethanol. Dinuclear ball-type metallophthalocyanines, cobalt(II) and especially iron(II) displayed high catalytic activity towards dioxygen reduction. In addition, by using these compounds as sensing materials, in particular iron(II) complex, a flow type quartz crystal microbalance sensor was developed for the detection of small concentrations of heavy metal ions.

pp. 1334–1341
Controlled preparation of ZnS nanoparticle arrays in Langmuir monolayer of an unsymmetrical phthalocyaninato zinc complex: Synthesis, organization, and semiconducting properties
Kai Chen, Yanling Wu, Xia Kong, Pingshun Zhang, Feifei Sun, Yanli Chen* and Jianzhuang Jiang*

Organic-inorganic hybrid Zn[Pc(C8H17)3(OPhOH)2]/ZnS nanocomposite films fabricated using the Langmuir–Shäfer (LS) method with Langmuir monolayer of the amphiphilic phthalocyanine complex as an organic template were revealed to exhibit a significantly enhanced conductivity over the single component ones.

pp. 1342–1349
Synthesis of porphyrin-steroid conjugates
Hasrat Ali, Samira Osati, Ehtsham H. Khan, Shafiullah and Johan E. van Lier*

A number of porphyrin derivatives substituted with one or two steroid moieties coupled via a 17α-ethyl group of estradiol, testosterone and 19-nortestosterone were synthesized using Pd(II) as a catalyst.

pp. 1350–1360
Porphycene dimer-based non-fullerene acceptor for organic solar cell
Takuya Okabe, Daiki Kuzuhara*, Mitsuharu Suzuki, Naoki Aratani and Hiroko Yamada*

The porphycene dimers with meta-phenylene and 2,5-thienylene linkages have been synthesized. The blended films of porphycene dimers and P3HT formed amorphous films with smooth and low-roughness surfaces, whereas the blended film of porphycene monomer and P3HT created the highly crystalline film with huge domain structures. The power conversion efficiencies of organic solar cells composed of porphycene dimers and P3HT was twice as high as that of monomer-based OSC.

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**pp. 1361-1367**

*Introducing rigid π-conjugated peripheral substituents in phthalocyanines for DSSCs*

Lara Tejerina, Esmeralda Caballero, M. Victoria Martínez-Díaz*, Mohammad Khaja Nazeeruddin*, Michael Grätzel and Tomas Torres*

The introduction of bulky and rigid 2,6-diarylphenyl substituents, linked to three peripheral positions of a carboxy-Zn(II)phthalocyanine through π-conjugated alkyloyn spacers, accounts for a remarkable red shift of the phthalocyanine Q-band until ca. 700 nm. However, aggregation phenomena may explain the moderate overall efficiencies achieved with these DSSC devices.

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**pp. 1368-1376**

*Selective recognition of cyanide ions by amphiphilic porphyrins in aqueous medium*

Albish K. Paul, Suneesh C. Karunakaran, Dhanya T. Jayaram, Nagappanpillai Adarsh, Joshy Joseph* and Danaboyina Ramaiah*

We synthesized two amphiphilic porphyrins and have investigated their anion recognition properties. These studies have confirmed 1,4-addition of CN\(^-\) ions to the pyridinium moiety of the porphyrin chromophore, which led to the aggregation induced self-assembly resulting in the sensitive detection of CN\(^-\) ions in aqueous medium through changes in their absorbance and fluorescence intensity.

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**pp. 1377-1389**

*Synthesis under high hydrostatic pressure — a new method to prepare 5,10,15,20-tetrakis[4-(substituted amino)-2,3,5,6-tetrafluorophenyl]porphyrins*

Ana T.P.C. Gomes, Patrícia C. Freire, Catarina R.M. Domingos, Maria G.P.M.S. Neves, José A.S. Cavaleiro, Filipe A. Almeida Paz, Jorge A. Saraiva and Augusto C. Tomé*

High pressure increases significantly the rate of the reaction of H\(_2\)(TF,PP) with amines. Tetrasubstituted porphyrin derivatives are obtained in good to excellent yields, under mild temperature conditions, when primary or heterocyclic amines are used. Remarkably, secondary amines having long alkyl groups also react with H\(_2\)(TF,PP) yielding mono(dialkylamino)-substituted porphyrins.

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*Non-covalent incorporation of some substituted metal phthalocyanines into different gel networks and the effects on the gel properties*

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The use of metallo-phthalocyanines (MPc) in many technological applications requires the development of specific methods for flexible thin film fabrication. An interesting and simple strategy is the physical encapsulation of MPcs within viscoelastic gel scaffolds. However, non-covalent incorporation of large external molecules into gel networks is challenge because the balance between dissolution and crystallization in metastable gel phases is likely to be altered changing the properties and/or stability of the material and, therefore, threatening its functionality. In this work, we report preliminary results regarding non-covalent inclusion of MPcs into different gel networks and the effects on their thermal, morphological and mechanical properties.
Group III perfluoroalkyl perfluoro phthalocyanines

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We report the synthesis, redox and photo-physical properties, and reactivity of the first representative Group III metal perfluoroalkyl perfluoro phthalocyanines (F₆₄PcMCl, M = Ga, In). The materials exhibit π-type behavior, high thermal and chemical stability while photoactivating O₂ to produce hydroperoxides.