About the Cover

Guest Editors: Tomás Torres and M. Salomé Rodriguez Morgade

This issue of JPP is the second of three issues dedicated to Professor Karl M. Kadish on the occasion of his 65th birthday. The cover is taken in part from Prof. Kadish’s website and graphically illustrates his most important service and research activities in recent years, service being represented by JPP, SPP and ICPP and research being represented by his many publications in the area of porphyrins (Por), phthalocyanines (Pc) and corroles (Cor). The current issue of JPP contains 31 manuscripts and selected structures of compounds being characterized by authors in this issue are also shown on the cover.

Reviews

pp. 757–779
Modifying the porphyrin core — a chemist’s jigsaw
Lena Arnold and Klaus Müllen*

Modifications of the porphyrin core results in porphyrinoids with novel and unique physical and electronic properties. Recent improvements in synthetic protocols allow the easy replacement of pyrrolic units in the porphyrin core — just like puzzle pieces in a jigsaw. In this review, the various possible core modified porphyrins and their syntheses along with their electronic and spectroscopic properties are summarized.

pp. 780–790
Covalent phthalocyanine-fullerene dyads: synthesis, electron transfer in solutions and molecular films
Nikolai V. Tkachenko*, Alexander Efimov and Helge Lemmetyinen

This micro review focuses on covalently linked phthalocyanine-fullerene conjugates in solutions and solid nanostructures. The covalent bonding enables sufficient degree of control over mutual organization of the donor and acceptor parts, and makes possible to investigate the relationships between molecular structure and functioning of single molecules and molecular assemblies.
### Contents

#### pp. 791–808
**Conjugated di- and trinuclear phthalocyanines and their analogs**  
Sergey G. Makarov*, Olga N. Suvorova and Dieter Wöhrle*

Structural features, synthesis and properties of conjugated di- and trinuclear phthalocyanines and their analogs are described. Annulated systems sharing a common benzene ring, condensed ones of fused phthalocyanine ligands and examples of di- and trinuclear phthalocyanines linked via one or two carbon atoms of each macrocycle are discussed.

#### pp. 809–834
**The synthesis, reactivity, and peripheral functionalization of corroles**  
Christopher M. Lemon and Penelope J. Brothers*

This review provides an overview of methods for the synthesis of corroles, and a comprehensive description of the chemical reactivity and functionalization of corroles, focusing especially on reactions at the periphery of the macrocycle.

#### pp. 835–847
**Diazo compounds in the functionalization of porphyrin macrocycles**  
Ana T.P.C. Gomes, Maria G.P.M.S. Neves and José A.S. Cavaleiro*

This highlight presents a synopsis of the reported studies on the functionalization of porphyrins using diazo compounds as reagents.

#### pp. 848–857
**Templated synthesis of catenanes incorporating Zn(II) or Rh(III)-complexed porphyrins: the coordination chemistry-only approach**  
Maryline Beyler, Valérie Heitz*, Julien Taesch and Jean-Pierre Sauvage*

Porphyric [2]catenanes were synthesized by using Cu(I)–N interactions to assemble acyclic complexes and the central porphyric metal and pyridyl groups to generate rings. The metal can be a substitution-labile metal center such as Zn^{2+} thus favoring reactions performed under thermodynamic control, or substitution inert metals carried out with kinetic control.

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*J. Porphyrins Phthalocyanines 2011, 15: 757–1092*
Articles

pp. 858–864
Comparative photophysics of sapphyrin derivatives: effects of confused and fused pyrrole rings
Jong Min Lim, Iti Gupta, Hiroyuki Furuta* and Dongho Kim*

The photophysical properties of [22]π-conjugated pentapyrrolic systems, sapphyrin, N-confused and N-fused sapphyrins were investigated. The absorption spectra of N-confused and N-fused sapphyrins was found to exhibit relatively red-shifted features compared to sapphyrin.

pp. 865–870
Aryl nitroporphycenes and derivatives: first regioselective synthesis of dinitroporphycenes
Gonzalo Anguera, Maria C. Llinás, Xavier Batllori and David Sánchez-Garcia*

The mono nitration of 2,7,12,17-tetraphenylporphycene (TPPo) has been optimized. The resulting 9-nitro-2,7,12,17-tetraphenylporphycene is a versatile derivative useful to prepare TPPo conjugates. With this aim, 9-(glutaric methylsteramide)-2,7,12,17-tetraphenylporphycene was synthesized. Extending the reaction time of the nitration, the dinitration of TPPo can be achieved providing 9,20-dinitro and 9,19-dinitro-2,7,12,17-tetraphenylporphycenes in a ratio of 3 to 1.

pp. 871–882
Polyoligopeptides functionalized zinc(II)porphyrins. Step towards artificial hemes
Shawkat M. Aly, Hannah Guernon, Brigitte Guérin* and Pierre D. Harvey*

Two zinc(II)porphyrin oligopeptide conjugates (zinc(II)-5,10,15,20-bis[4-(peptide)phenyl]porphyrin and -tetrakis[3,5-di(peptide)phenyl]porphyrin (peptide = -CH2(CO)Gly-Phe-Ala-CNH2) were prepared, their photophysical properties examined, and their structures addressed by modeling.

pp. 883–889
β-tetabromo-meso-tetrakis(4′-substituted phenyl)porphyrins: synthesis and electrochemical redox properties
P. Bhryappa* and V. Velkannan

Synthesis, characterization and electrochemical redox properties of free-base β-tetabromo-meso-tetrakis(4′-substituted phenyl)porphyrins and their metal complexes are reported. These derivatives revealed fairly linear trend in the redox potentials with the increase in Hammett parameter of the substituents.
pp. 890–897
Characterization, liquid crystallinity and spin-coated films of some metalated 1,4,8,11,15,18,22,25-octaalkyl tetrabenzo[b,g,l,q][5,10,15]triazaporphyrin derivatives
Andrew N. Cammidge*, Isabelle Chambrier, Michael J. Cook*, Ernie H. G. Langner, Munibar Rahman and Jannie C. Swarts

The preparation and characterisation of a number of metallated derivatives of 1,4,8,11,15,18,22,25-octaalkyltetrabenzotriazaporphyrins (TBTAPs) are reported. The mesophase behavior exhibited by compounds has been characterised by differential scanning calorimetry (DSC) and polarized light optical microscopy. A parallel was drawn with molecular reorganizations detected in spin coated films of examples of the compounds using variable temperature UV-vis spectroscopy.

pp. 898–907
The trisubstituted-triazole approach to extended functional naphthalocyanines
Michal Juríček, Kathleen Stout, Paul H.J. Kouwer and Alan E. Rowan*

A novel approach towards extended phthalocyanines was developed and applied in the synthesis of an octaatriazole-fused naphthalocyanine. This method employs the fusion of an ortho-bis(iodotriazole) system by using the intramolecular homocoupling procedure (orange). Due to the extended core size (by four benzene and eight triazole rings compared with phthalocyanines), this class of materials is predicted to possess strong aggregation properties, which can be modified upon doping of four functional cavities (purple) with metals or guest molecules.

pp. 908–917
Development of lutetium bisphthalocyanine/carbon nanotube Langmuir-Blodgett films. Sensing properties
Constantin Apetrei, Marina Nieto, Maria Luz Rodríguez-Méndez* and José Antonio de Saja

A novel class of sensors based on Langmuir-Blodgett (LB) films a composite lutetium bisphthalocyaninate/carbon nanotube is reported. The influence of the carbon nanotube in the structure of the LB films and in their spectroscopic, chemical, electrochromic and gas sensing properties has been evaluated.

pp. 918–929
Syntheses, properties and cellular studies of metallo-isoporphyrins
Sandra C. Mwakwari, Haijun Wang, Timothy J. Jensen, M. Graça H. Vicente and Kevin M. Smith*

b-Bilene hydrochlorides give zinc(II) and copper(II) isoporphyrin salts upon macrocyclization with a carbonyl-containing linker. Metal-free isoporphyrins were also isolated. In vitro studies using human carcinoma HEp2 cells show that all metallo-isoporphyrins accumulate within cells and localize partially in the mitochondria. The zinc-isoporphyrins were found to be moderately phototoxic while the copper complex showed the lowest phototoxicity.
Synthesis, structures and properties of benzoporphycenes and naphthoporphycenes
Daiki Kuzuhara, Hiroko Yamada*, Shigeki Mori, Tetsuo Okujima and Hidemitsu Uno

Benzoporphycenes and naphthoporphycenes were prepared by retro-Diels-Alder reaction of bicyclo[2.2.2]octadiene-fused precursors. The crystal structures of free-base tetrabenzoporphycene showed a herringbone structure, while zinc tetrabenzoporphycene showed a hexagonal box-structure with six pyridine ligands inside. Tetrabenzo-, dibenzo-, and dinaphthoporphycenes showed fluorescence with quantum yields of 0.32, 0.42, and 0.31, respectively, although their precursors were non-fluorescent.

Synthesis and characterization of silicon phthalocyanines bearing axial phenoxyl groups for attachment to semiconducting metal oxides
Jesse J. Bergkamp, Benjamin D. Sherman, Ernesto Mariño-Ochoa, Rodrigo E. Palacios, Gonzalo Cosa, Thomas A. Moore*, Devens Gust* and Ana L. Moore*

A series of octabutoxy axial phenoxy silicon phthalocyanines have been prepared from the corresponding phenols. The phenols bear either carboxylic ester or phosphonate groups which, upon deprotection, can serve as anchoring groups for attaching the phthalocyanines to semiconducting metal oxides used in dye sensitized solar cells (DSSCs). All the phthalocyanines of the series absorb in the near infra-red region, 758–776 nm. Based on the first oxidation potential for each phenoxy derivative, these dyes should be able to photosensitize TiO₂.

Porphyrin molecular tweezers for fullerenes
Hidemitsu Uno*, Mina Furukawa, Akiko Fujimoto, Hiroki Uoyama, Hajime Watanabe, Tetsuo Okujima, Hiroko Yamada, Shigeki Mori, Makoto Kuramoto, Tatsunori Iwamura, Noriyuki Hatae, Fumito Tani and Naoki Komatsu

Facing zinc bisporphyrins connected with diethanoanthracene and diethano naphthacene contain large clefts with different sizes capable for complexation with fullerenes such as C₆₀ and C₇₀. These designed syn-oriented bisporphyrins serve as effective and selective molecular tweezers for C₇₀.

Charge transfer properties of phthalocyaninato zinc complexes for organic field-effect transistors: tuning semiconductor nature via peripheral substituents
Ronghua Guo, Lijuan Zhang, Yuexing Zhang*, Yongzhong Bian and Jianzhuang Jiang

DFT calculations revealed the effect of peripheral substituents on tuning the nature of phthalocyaninato zinc semiconductor: introduction of eight weak electron-donating methoxy groups onto the peripheral positions of ZnPc induces a better p-type semiconductor material while peripheral methoxy carbonyl substitution changes the semiconductor nature from p-type to n-type.
CONTENTS

pp. 973–983
Synthesis and toxicity of cobaltabisdicarbollide-containing porphyrins of high boron content
N.V.S. Dinesh K. Bhupathiraju, Vijay Gottumukkala, Erhong Hao, Xiaoke Hu, Frank R. Fronczek, David G. Baker, Nobuko Wakamatsu and M. Graça H. Vicente*

Two porphyrins of high boron content were synthesized in high yields. Both were found to have low cytotoxicity toward HEp2 cells, and to localize mainly in the cell lysosomes. Animal toxicity studies revealed maximum tolerated doses for these porphyrins of 160 mg/kg and 320 mg/kg, respectively.

pp. 984–994
Tetra-2,3-pyrazinoporphyrazines with externally appended pyridine rings. 11. Photoactivity of a new Pt(II) pentanuclear macrocycle bearing four cisplatin-like functionalities and its related monometalated species
Maria Pia Donzello*, Elisa Viola, Luisa Mannina, Mario Barteri, Zhen Fu and Claudio Ercolani

Synthesis, IR/UV-visible spectral properties and photoactivity for the generation of singlet oxygen, \(^1\text{O}_2\), were investigated for three related platinated compounds — [\((\text{PtCl}_2)_4\text{L}\text{Pt}\)], [\text{L}\text{Pt}\] (L = tetrakis-2,3-[5,6-di-(2-pyridyl)pyrazino]porphyrazino dianion) and [\text{L’}\text{Pt}\]|\text{I}\) (L’ = octamethylated L).

pp. 995–1003
Central metal ion determined self-assembly of intrinsically chiral porphyrins
Lise N. Feldborg, Wojciech J. Saletra, Patrizia Iavicoli and David B. Amabilino*

The incorporation of metal ions into the chelating tetrapyrrolic ring of a chiral porphyrin of molecular weight around 2000 Daltons makes dramatic changes on both the stability and type of aggregate, even in the absence of very specific non-covalent interactions. The changes can influence both the optical activity, the gelling ability — which is a direct reflection of the capacity for forming linear aggregates — as well as the morphology of the gel-derived materials.

pp. 1004–1010
Dye sensitized solar cells using non-aggregated silicon phthalocyanines
Luis Martín-Gomis, Eva. M. Barea*, Fernando Fernández-Lázaro, Juan Bisquert and Ángela Sastre-Santos*

Two new silicon phthalocyanines (SiPcs 1 and 2) axially substituted with carboxylic acid appends have been synthesized and chemically characterized. DSC devices using SiPcs as sensitizers have been prepared for the first time. Although similar HOMO–LUMO values were obtained for both SiPcs, the device prepared with the SiPc 2 gives both higher open circuit voltage (\(V_{oc}\)) and also higher injection (\(J_{sc}\)), so the overall conversion efficiency is longer than for the one where SiPc 1 is used as a dye.
**pp. 1011–1023**

Corroles bearing diverse coumarin units — synthesis and optical properties
Mariusz Tasior, Roman Voloshchuk, Yevgen M. Poronik, Tomasz Rowicki and Daniel T. Gryko*

Diverse set of coumarin-corroles has been synthesized via both direct condensation of formyl-coumarins with dipyrranes and post-functionalization of simple trans-A,B-corroles. Second approach was proved to be overall more effective. The optical properties of synthesized bichromophoric systems were evaluated and suggest that the linked components are weakly electronically coupled.

**pp. 1024–1032**

Synthesis and characterization of nanosized poly-carboranyl-porphyrine conjugates
Daniela Pietrangeli, Angela Rosa and Giampaolo Ricciardi*

This paper reports on the synthesis and characterization of the 2,3,7,8,12,13,17,18-octakis-[6-(2′-(1-methyl-1′,2′-dicarba-closo-dodecaboran-2′-yl)-hexyl)-1,2-dicarba-closo-dodecaboran-1-yl(hexylthio)] 5,10,15,20 (21H, 23H) porphyrine, (H4(MCHE)CHESPz), a nanosized molecule bearing height dicarboranyl-substituted carbonarod-like alkyl pendants.

**pp. 1033–1043**

Formation and photoinduced properties of zinc porphyrin-SWCNT and zinc phthalocyanine-SWCNT nanohybrids using diameter sorted nanotubes assembled via metal-ligand coordination and π–π stacking
Sushanta K. Das, Navaneetha K. Subbaiyan, Francis D’Souza*, Atula S.D. Sandanayaka, Takatsugu Wakahara and Osamu Ito*

Self-assembly, photoinduced electron transfer, photocatalysis to accumulate one-electron reduced product, and photoelectrochemical behavior of nanohybrids comprised of zinc porphyrin (ZnP) or zinc phthalocyanine (ZnPc) with semiconducting (7,6)- and (6,5)-enriched SWCNTs are described.

**pp. 1044–1051**

The influence of molecular structure and π-system extent on nano- and microstructure of Langmuir layers of copper azaporphyrins
Larissa A. Valkova*, Victor V. Erokhin, Alexandr S. Gilbin and Oscar I. Koifman

It is shown that both the lack of one meso-atom and the increase of the extent of the π-system cause the balance between intermolecular interactions (AP-AP) — (AP-water) to shift to the latter and lead to formation of stable monolayers with the most open face-on structure of nanoaggregates instead of the edge-on one, all other factors being equal, in Langmuir layers prepared from solutions in aromatic solvents. The micro-level structural difference of copper tetra-tert-butyl-substituted porphyrin (CuPazBu4) and phthalocyanine (CuPctBu4) resulted from the structural difference of two-dimensional nanoaggregates forming the layers was shown using Brewster angle microscopy.
 Synthesis and aggregation behavior of a novel watersoluble porphyrin platinum(II) terpyridine complex
Maria Rosaria Plutino, Maria Angela Castriciano*, Antonino Mazzaglia, Maria Saporita, Andrea Romeo and Luigi Monsù Scolaro*

The cationic water soluble complex \([\text{Pt(terpy})]_n(\text{TpyP})^{+}\) has been synthesized and fully characterized. The introduction of the Pt(II) terpy molecular fragments allows to extend the aromatic surface promoting aggregation in solutions, as well as on glass surface. Kinetics of Cu(II) insertion have been carried out on anionic (SDS) micellar phase.

Photodynamically active phthalocyanine building blocks for click chemistry
Veronika Novakova*, Kamil Kopecky, Miroslav Miletin, Jana Ivincova and Petr Zimcik*

Zinc phthalocyanines bearing different number of quinoxaline units containing terminal azide were prepared and fully characterized. Adjacent and opposite isomers were also separated. All compounds showed singlet oxygen quantum yields over 0.60 and fluorescence quantum yield in a range 0.03–0.06. All compounds absorbed strongly over 700 nm.

Synthesis of novel porphyrin and chlorin phosphonic acids and their immobilization on metal oxides
Martin Erbacher and Franz-Peter Montforts*

In this study an easy and flexible synthetic access to porphyrin and chlorin phosphonic acids starting from the red blood pigment hemin chloride is presented. Phosphonic acid functions were linked to the porphyrinoids via appropriate spacer moieties. Self-assembled monolayers of the phosphonic acid terminated porphyrins and chlorins on mesoporous TiO₂ electrodes of 3 μm thickness were formed as indicated by change in color. Surface concentrations range from 1 to 4 × 10⁻⁸ mol.cm⁻².

Photo-catalytic activity of cationic zinc(II) complexes of phthalocyanine and porphyrazine derivatives loaded on the surface of silica gel
Kuninobu Kasuga*, Hiroyuki Irie, Hidekazu Tanaka, Takahisa Iketue, Tamotsu Sugimori and Makoto Handa*

Complexes 1 and 2 were loaded on the surface of silica gel by use of an electrostatic interaction with deprotonated silanol groups of silica gel. While complex 1 formed its dimer species with increase in the amount of the complex in the composite, complex 2 hardly formed the dimer in the composite due to the steric hindrance of its peripheral substituents. 1,3-Diphenylisobenzofuran was more effectively photo-oxidized using the composite of complex 2 in aerated methanol. Bilirubinditaurate was also photo-oxidized using the composites in an aerated aqueous solution.
Synthetic protocols for the nitration of corroles
Giuseppe Pomarico, Frank R. Fronczek, Sara Nardis, Kevin M. Smith and Roberto Paolesse*

Nitration of free base meso-triphenylcorrole was investigated using two different nitrating systems, based on NaNO₂, in acidic medium. These protocols led to the formation of corrole derivatives nitrated at their β-pyrrolic positions, characterized as their Co triphenylphosphino complexes.