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About the Cover

Guest Editors: Martin Bröring and Norbert Jux

This commemorial issue of the *Journal of Porphyrins and Phthalocyanines* is devoted to the late Emanuel Vogel. Coming from the chemistry of the annulenes, his interpretation of porphyrin chemistry has triggered tremendous interest in non-natural porphyrin variants as functional dyes with many potential applications. Beside science, the art of presentation was always a characteristic of Emanuel Vogel. In his eyes, art and science should meet in the ideal presentation of chemical structures. The title page shows examples from his research in porphyrinoid chemistry in form of a collection of his famous Christmas cards.

Reviews

**pp. 423–433**

*Carbaporphyrins, porphyrin isomers and the legacy of Emanuel Vogel*

Timothy D. Lash*

The influence of Vogel’s studies into bridged annulenes, constitutional porphyrin isomers and related macrocycles on the author’s investigations into carbaporphyrinoid systems is discussed. Further support for the concept that porphyrins are bridged [18]annulenes has been obtained by synthesizing a dideazaporphyrin that retains porphyrin-like characteristics. Furthermore, a new class of porphyrin isomers has been synthesized that complements previous studies into N-confused porphyrins and Vogel’s constitutional isomers.

**pp. 434–463**

*Synthesis of glycosylated metal phthalocyanines and naphthalocyanines*

Alexey Lyubimtsev, Zafar Iqbal, Göran Crucius, Sergey Syrbu, Thomas Ziegler and Michael Hanack*

The preparation of symmetrically and unsymmetrically zinc phthalocyanines and naphthalocyanines in which the sugar is attached either anomerically or via another one of its OH-groups to the macrocycles are reviewed.
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pp. 464–748
Synthesis of extended porphyrins by connection of meso-aryl groups with β-pyrrolic positions
Ana M.V.M. Pereira, Sébastien Richeter, Christophe Jeandon, Jean-Paul Gisselbrecht, Jennifer Wytko and Romain Ruppert*

This review focuses on synthetic strategies leading to extended porphyrins, but is limited to examples in which at least one β-pyrrolic carbon is linked to a meso-aryl substituent. The highly extended aromatic structures obtained in this way are promising for molecular materials or photochemical applications in biology.

Articles

pp. 479–487
π-Metal complexes of i-propyldinaphthoporphycene
Gabriela I. Vargas-Zúñiga, Vladimir V. Roznyatovskiy, Alexander Nepomnyaschii, Vincent M. Lynch and Jonathan L. Sessler*

The synthesis and characterization of four metalloporphycenes containing a $[\text{MCp}^*]^+$ (Cp* = pentamethylcyclopentadiene; M = Rh, Ir, and Ru) fragment directly bonded to the π-framework of the macrocycle were obtained. The electrochemical and optical properties of these complexes revealed that the electron acceptor properties of the macrocycle can be enhanced by the coordination of an organometallic fragment to the π-electron face.

pp. 488–498
DNA-porphyrin hybrids as reaction centers for photosensitized ene reactions with singlet oxygen
Rüdiger Haug, Helmut Griesser, Thomas Sabirov and Clemens Richert*

A solid-phase synthesis of tetrakis(p-hydroxyphenyl)porphyrin-oligonucleotide hybrids with up to four DNA chains per porphyrin is described. The diastereo- and enantioselectivity of the photosensitized ene reaction of singlet oxygen with mesitylhol was measured by NMR and gas chromatography. Porphyrin-DNA hybrids may form nanostructured reaction media.

pp. 499–507
Photophysics of novel 22π porphyrinoids
Daniel O. Mártire, Sigrid Russell, Hans-Jürgen Dietrich, Carlos J. Cobos and Silvia E. Braslavsky*

The 22π porphyrinoids do not produce singlet molecular oxygen, but have a high fluorescence yield in the red spectral region.
pp. 508–517
Synthesis and structure of expanded pyriporphyrins containing a dipyrrylpyridine unit
Jun-ichiro Setsune* and Keigo Watanabe

 Expanded pyriporphyrin with four pyroles and one pyridine was prepared in good yield by using 2,6-bis(2-pyrryl)pyridine and bis(azafulvene) under neutral conditions. This olive green colored macrocycle 3 and its TFA adduct, 3-(TFA)₂, have highly distorted ring structure with alternate up and down tilting of the four pyrrole rings, but Ni, Cu, Yb, and Lu complexes of 3 were obtained in good yields. The double sized pyriporphyrin 4 with ten nitrogens was also obtained and characterized by X-ray crystallography.

pp. 518–529
Formation and characterization of five- and six-coordinate iron(III) corrolazine complexes
Satoshi Kurahashi, Takahisa Ikeue*, Tamotsu Sugimori, Masashi Takahashi, Masahiro Mikuriya, Makoto Handa, Akira Ikezaki and Mikio Nakamura*

 Spin states and electron configurations of five- and six-coordinate corrolazine (H₃Cz) complexes, [Fe(III)(TBP₂Cz)L]⁺ and [Fe(III)Cz(TBP₂Cz) L₂]⁺ (L = CN, HIm, 1-MeIm, DMAP, Py, 4-CNPy, and tBuNC), have been determined by means of ¹H NMR, ¹³C NMR, EPR, Mössbauer spectroscopy as well as SQUID magnetometry.

pp. 530–536
Synthesis and photosensitizing properties of porphycene with imidazolium tag
Hisashi Shimakoshi, Kenichi Sasaki, Yusuke Iseki and Yoshio Hisaeda*

 Porphycene having an imidazolium cation tag was synthesized and characterized by elemental analysis, UV-vis, NMR and ESI-mass spectroscopies. Photosensitizing reactions using this new porphycene for the oxidation of 1,5-dihydroxynaphthalene in ionic liquids were investigated and found to form 5-hydroxy-1,4-naphthoquinone. The recycled use of the porphycene was efficiently achieved in ionic liquids.

pp. 537–544
The overhanging carboxylic acid strategy: an alternative route to the porphyrin core expansion/modification for the coordination of large metal ions
Stéphane Le Gac and Bernard Boitrel*

 Overhanging carboxylic acid strapped porphyrins are shown to be efficient ligands for the fast and stable complexation of large cations, with possibly unexpected nuclearities.
pp. 556–563
Corroles programmed for regioselective cycloaddition chemistry — synthesis of a bisadduct with C₆₀-fullerene
Chengjie Li, Martin Fechtel, Yaqing Feng and Bernhard Kräutler*

Tetra-β,β'-sulfoleno-corroles are programmed for regioselective cycloaddition chemistry. Their directly connected β,β'-sulfoleno-pyrroles loose SO₂ with ease, providing an efficient and broadly useful synthetic entry to specific functionalized corroles. Selective vicinal addition of two C₆₀-fullerenes gives a difullereno-corrole. Its two remaining sulfolene groups in the other half are “caged dienes,” useful for further cycloaddition reactions.

pp. 564–575
Fused π-extended discotic triangular porphyrinoids
Lena Arnold, Sreenivasa Reddy Puniredd, Christian von Malotki, Wojciech Pisula, Nobuyoshi Koshino, Hideyuki Higashimura, Martin Baumgarten, Manfred Wagner and Klaus Müllen*

Novel fused π-extended porphyrinoids have been designed in a triangular fashion including three coordination cavities. These coordination sites are in unprecedented vicinity to each other and thus provide maximum density of active sites inplane for applications as catalyst. A series of trinuclear derivatives have been synthesized and their optical and electrochemical properties as well as their supramolecular organization have been investigated. The network forming of the triangle is useful for the development of highly active catalyst for the reduction of oxygen (ORR) e.g. in fuel cell applications.

pp. 576–588
meso-Tetraphenylporphyrin-derived oxypyriporphyrin, oxy-pyrichlorin, and thiomorpholinochlorin, as their Ni(II) complexes
Subhadeep Banerjee, Matthias Zeller and Christian Brückner*

The tertiary diol functionality in [meso-tetraphenyl-trans-diolklorinato]Ni was cleaved to generate a meso-tetraphenylsecoclorin bismethylketone. This was cyclized to provide a meso-tetraphenylloxipyriporphyrin that could be reduced to an oxypyrchlorin. Reaction of the bismethylketone with Lawesson’s reagent generated a thiomorpholinochlorin.

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pp. 589–602
The long and winding road to new porphycenes
Igor Czerski, Arkadiusz Listkowski, Jan Nawrocki, Natalia Urbańska, Hubert Piworski, Adam Sokolowski, Oksana Pietraszkiewicz, Marek Pietraszkiewicz* and Jacek Waluk*

New porphycenes are reported, some of them custom-designed for tautomerization studies. Structure and energy computations of possible tautomeric forms lead to predictions regarding the kinetics and mechanisms of intramolecular double hydrogen transfer. The occurrence of tautomerization in single molecules of tert-butyl-substituted porphycenes is demonstrated by using fluorescence polarization techniques.

pp. 603–615
Synthesis and cellular studies of PPIX-homing peptide conjugates
Martha Sibrian-Vazquez, Xiaoke Hu, Timothy J. Jensen and M. Graça H. Vicente*

Five protoporphyrin IX-peptide conjugates were synthesized and investigated in human HEp2 and HL-60 cell lines. All conjugates showed low toxicities, their cellular uptake depended on the peptide sequence, and the main sites of subcellular localization were the lysosomes (HEp2 cells) or mitochondria (HL-60 cells).

pp. 616–625
Reaction of cobalt porphycene with hydride reagents: spectroscopic detection of Co–H porphycene species and formation of Co–SnR₃ porphycene species
Takashi Matsuo*, Kunihiko Komatsuzaki, Takanori Tsuji and Takashi Hayashi*

Tetrapropylporphycenatocobalt(III) is able to stabilize a cobalt-hydride species, relative to the corresponding cobalt porphyrin. This is mainly caused by the lower LUMO energy level in the porphycene ring as a result of decreased symmetry, compared with that of the porphyrin. Furthermore, stable cobalt-trialkyltin complexes are also formed by the porphycene ligand. These complexes were characterized and their formation pathways are discussed.

pp. 626–632
Synthesis of a cofacial chlorin dimer of defined symmetry
Nguyen Thi Viet Thanh, Thorsten Könekamp, Daniela Hanke, Franziska Löwer, Tobias Borrmann and Franz-Peter Montforts*

Special pair chlorophylls arranged in a cofacial dimeric structure play an important role in the initial step of light induced electron transfer of photosynthetic reaction centers of bacteria and plants. For mimicking the natural photosynthetic reaction center we aimed on synthesis of an artificial special pair 13 constructed from two chlorin subunits 5a,b and a rigid biphenylene spacer moiety 11. Due to the reduced C₂ᵥ symmetry of the chlorin units compared with so far used D₄h porphyrins and due to the rigid spacer a cofacial dimer of defined symmetry and distance was obtained.

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pp. 633–640  
**Tautomerism and dual fluorescence in 9-substituted n-propyl- and methoxyethyl-porphycenes**  
Oriol Planas, Roger Tejedor-Estrada and Santi Nonell*

Tautomerism coupled to selective stabilization of one of the tautomers is the basis for dual fluorescence observed in 9-substituted porphycenes.

pp. 641–650  
**Pseudohalogenido complexes of iron-2,2′-bidi-pyrins**  
Martin Bröring*, Silke Köhler and Clemens Pietzonka

The ligand exchange of the iron bilin analog chloroiron-2,2′-bidipyrrin with pseudohalides leads to new pseudohalogenido complexes of this linear tetrapyrole and to the formation of 10-oxacorrole and 10-thiacorrole complexes with the ferric iron ion in a nonadmixed intermediate spin state.

pp. 651–662  
**Synthesis and physico-chemical properties of porphycenes**  
Wolfgang Brenner, Jenny Malig, Christian Oelsner, Dirk M. Guldi* and Norbert Jux*

A new and improved synthesis for porphycenes is presented. The synthetic part of this project is followed by a global analysis of the physicochemical properties of three exemplary 2,7,12,17-substituted porphycenes, including absorption, emission, and electrochemistry. In-situ UV/vis/nIR spectroelectrochemistry was used to determine the spectral signatures of the radical anion and cation species. Temperature-dependent fluorescence lifetimes were determined under air as well as under inert atmosphere.

pp. 663–673  
**Iron complexes of tris(4-nitrophenyl)corrole, with emphasis on the (nitrosyl)iron complex**  
Pinky Singh, Irena Saltsman, Atif Mahammed, Israel Goldberg, Boris Tumanskii and Zeev Gross*

The (nitrosyl)iron complex of 5,10,15-tris(4-nitrophenyl)corrole has been prepared with $^{57}$Fe and $^{15}$N labelling. The X-ray structure reveals a linear Fe-N-O moiety and spectroscopic studies of the reduced species confirms that reduction occurs at the FeNO centre.
pp. 674–684
Electrochemistry of mono- and bis-porphyrins containing a β,β'-fused tetraazaanthracene group
Zhongping Ou*, Weihua Zhu, Paul J. Sintic, Yuanyuan Fang, Maxwell J. Crossley* and Karl M. Kadish*
Electrochemical and thin-layer spectroelectrochemical properties of three mono-porphyrins and five bis-porphyrins containing a β,β'-fused tetraazaanthracene group were examined in non-aqueous media. The effect of the fused TA group on the redox potentials and UV-visible spectra of the mono- and bis-porphyrins is discussed.

pp. 685–694
Decoupling the artificial special pair to slow down the rate of singlet energy transfer
Pierre D. Harvey*, Adam Langlois, Mikhail Filatov, Daniel Fortin, Kei Ohkubo, Shunichi Fukuzumi* and Roger Guilard*
A trimer composed of a cofacial heterobismacrocycle, octamethylporphyrin zinc(II) (donor 1) and bisarylporphyrin zinc(II) (donor 2) held by an anthracenyl spacer, and a flanking acceptor, bisarylporphyrin free base (acceptor; Ar = -3,5-(tBu)2C6H3), exhibits a singlet energy transfer (donor 1 → donor 2/acceptor) of ~90 fs and a relaxation of the donor 2/acceptor moiety of ~1.5 ns (by fs transient absorption spectroscopy).

pp. 695–704
Electronic absorption spectra of copper corroles: unexpected substituent effects in trans-meso-A2B-triarylcorrole complexes
Abraham Alemayehu, Marrigje M. Conradie and Abhik Ghosh*
The electrochemistry and electronic absorption spectra of a series of copper trans-A,B-triarylcorrole complexes show that although both 5,15- and 10-substituents appear to influence the oxidation and reduction potentials of the copper corroles in a simple, additive manner, they affect the Soret maxima very differently.