CONTENTS

About the Cover

See Evgeny A. Lukyanets and Victor N. Nemykin pp 1–40
Phthalocyanines and their structural analogs are well-known for their traditional and contemporary high-tech applications and schematically shown on the background of the illustration. The typical UV-vis spectra and colors of tetraazaporphyrins, phthalocyanines, and naphthalocyanines as well as their core structures are also shown.

Review

pp. 1–40
The key role of peripheral substituents in the chemistry of phthalocyanines and their analogs
Evgeny A. Lukyanets† and Victor N. Nemykin

General strategies for the preparation of peripherally substituted phthalocyanines, naphthalocyanines, anthracyanines, aza-analogs of phthalocyanines, and tetraazaporphyrins have been discussed. An influence of the types and positions of the substituents attached to the macrocyclic core on the optical properties of these compounds has been generalized. In many cases, poorly known methodologies, published in mostly unavailable Russian journals, were highlighted throughout this review.

Articles

pp. 41–46
Syntheses and structural studies of \( \eta^5 \)-pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes of a Schiiff-base expanded porphyrin
Luciano Cuesta, Vincent M. Lynch and Jonathan L. Sessler*

The synthesis of new binuclear rhodium(III) and iridium(III) semi-sandwich complexes of a Schiiff-base expanded porphyrin is reported here. Single crystal X-ray diffraction analyses and complementary NMR studies provide evidence for the existence of strong intramolecular hydrogen-bonding interactions between the pyrrolic NH protons and the chloride ligand both in dichloromethane solution and in the solid state.
pp. 47–54
Synthesis of near-infrared absorbed metal phthalocyanine with S-aryl groups at non-peripheral positions
Keiichi Sakamoto*, Eiko Ohno-Okumura, Taku Kato and Hisashi Soga

The target compounds were synthesized: 15 phthalocyanines from 2,3-dicyanohydroquinone in 3 steps via 1,2-dicyanobenzene-3,6-bis-(trifluorate) and 1,2-dicyanobenzene-3,6-thiophenols. The Q bands of obtained compounds appeared in the near-infrared region. In particular, 1,4,8,11,15,18,22,25-octakis(thiophenylmethyl)phthalocyaninate lead shows a Q band at 857 nm. Furthermore, non-colored transparent films in the visible region can be produced.

pp. 55–63
Through space singlet energy transfers in light-harvesting systems and cofacial bisporphyrin dyads
Pierre D. Harvey*, Christine Stern, Claude P. Gros and Roger Guilard*

This review focuses on the photophysical processes and dynamics in the light harvesting devices, notably LH II, in the heavily investigated purple photosynthetic bacteria, and compares these parameters with our cofacial bisporphyrin dyads build upon octa-etoio-porphyrin chromophores and rigid and semi-rigid spacers.

pp. 64–68
Photooxidation of phenol derivatives using μ-(dihydroxo)dipalladium(II) bisporphyrin complex
Yuko Takao*, Toshinobu Ohno, Kazuyuki Moriwaki, Fukashi Matsumoto and Jun-ichiro Setsune*

μ-(dihydroxo)dipalladium(II) complex with N1,N2-etheno bridged tetr phenylporphyrin ligand was employed in the catalytic photooxidation of phenol derivatives in aerated homogeneous solution with visible light irradiation. The Pd complex promoted degradation of p-tert-butylphenol and selective photooxidation of some phenol derivatives to afford the corresponding quinones. This Pd complex showed higher light durability compared with ordinary porphyrin free base and its Pd complex.

pp. 69–80
Morphology and radical reactions of Cu(II) and Co(II) sulfonated phthalocyanines covalently linked to poly(ethylene-amide)
Gustavo T. Ruiz, Alexander G. Lappin and Guillermo Ferraudi*

The tetrasulfonated CuII(tspc)4-, tspc = 4,4′,4″,4‴-phthalocyaninetrastilbene-1,2,3,4-tetrathione and the trisulfonated CoII(tspc)3-, tspc = n,n′,n″-phthalocyanine-trisulfonate where n, n' and n″ indicate the sulfonated positions of the various isomers, were covalently linked to a poly(ethyleneamine). The redox reactions of the phthalocyanine pendants with pulse radiolytically generated radicals (e.g., CH3OH, (CH3)2COHC•H2, CO2•-, N3• and SO4•-) produce phthalocyanine radicals, Cu(I) and CoIII-hydroxyalkyl reaction intermediates.
pp. 81–88  
**Porphyrin self-assembled monolayers and photodynamic oxidation of tryptophan**
Isabelle Chambrier, David A. Russell, Derek E. Brundish, William G. Love, Giulio Jori*, M. Magaraggia and Michael J. Cook*

Self-assembled monolayer (SAM) films of purposely synthesized zinc and magnesium diporphyrin derivatives, 1b and 1c, have been deposited on the surface of gold-coated glass substrates. The SAM films were characterized by RAIR and fluorescence spectroscopy. The potential for the films to promote the oxidation of tryptophan within human serum albumin upon irradiation with white light has been demonstrated and attributed to the porphyrins acting as photosensitizers of oxygen to form oxidizing species.

pp. 89–100  
**Efficient synthesis of an A-B-C-tricycle fragment for a structural model of tolyporphin**
Bing C. Hu*, Wei Y. Zhou, Zu L. Liu, Chao J. Cai and Shi C. Xu

An efficient stereocontrolled synthesis of an A-B-C-tricycle fragment for a structural model of tolyporphin is described. One of the two key steps is a selective ring-opening reaction of the lactone cycle which introduces the chirality into synthetic compounds. The other key step is the combination of A ring with B-C-bicycle via a two-time Eschenmoser sulfoxide contraction.

pp. 101–107  
**Synthesis and self-assembly of a novel cobalt(II) porphyrin lipoic acid derivative on gold**
Christoph S. Eberle, Ana S. Viana, Franz-Peter Montforts and Luisa Maria Abrantes*

A novel cobalt(II) porphyrin lipoic acid derivative was synthesized starting from deuteroporphyrin(IX)bis-alcohol and enantiomerically enriched lipoic acid. The two disulfide functionalities of the lipoic acid moieties allowed its immobilization on gold by a self-assembly method. It was found that the Co(II) porphyrin self-assembled monolayer is electroactive and exhibits catalytic activity towards reduction of oxygen.

pp. 108–114  
**Synthesis, characterization and electrochemistry of the novel metalloporphyrazines annulated with tetraethiafulvalene having pentoxycarbonyl substituents**
Fengshou Leng, Ruibin Hou, Longyi Jin, Bingzhu Yin* and Ren-Gen Xiong*

Three novel tetraethiafulvalene-annulated metalloporphyrazines with electron-withdrawing pentoxycarbonyl groups at the periphery were synthesized via the cyclotetramerization of dipentyl 6,7-dicyanotetraethiafulvalen-2,3-dicarboxylate in the presence of corresponding metal salts (Zn(OAc)2·2H2O, Cu(OAc)2·2H2O and NiCl2) and in pentanol. Solution electrochemical data showed one reductive and three oxidative processes within a -2000 mV to +2200 mV potential window.
Inter-ring interactions in [Fe(alkylP)(Cl)] (alkyl = ethyl, n-propyl, n-hexyl) complexes: control by meso-substituted groups

Ming Li, Teresa J. Neal, Noelle Ehlinger, Charles E. Schulz* and W. Robert Scheidt*

We report syntheses, molecular structures and magnetic susceptibilities of three meso-substituted high-spin iron(III) porphyrinate complexes ([Fe(TEtP)(Cl)], [Fe(TPrP)(Cl)], and [Fe(THexP)(Cl)]). It was determined that the inter-ring interactions within each dimeric unit change upon alteration of the alkyl groups at the meso positions. Magnetic exchange couplings between iron centers of the dimers are in accord with the trends in structural inter-ring geometries.