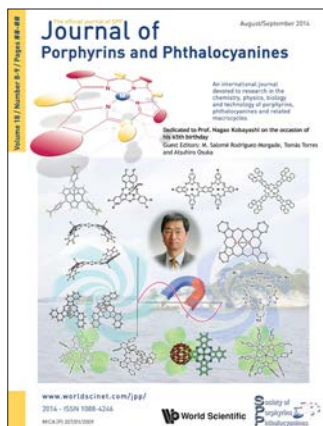


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About the Cover



Guest Editors: M. Salomé Rodríguez-Morgade, Tomás Torres and Atsuhiko Osuka

This issue of JPP is the first of two special issues dedicated to Professor Nagao Kobayashi on the occasion of his 65th birthday. They consist of 51 review and original research papers presented by his colleagues and friends, covering general topics on porphyrins, phthalocyanines and related macrocycles. Professor Kobayashi is a very ingenious scientist. His continual creativity has brought about a number of porphyrin variants with original structures and unusual properties. The cover picture shows the structures of some selected macrocycles that were designed and characterized by Professor Kobayashi. These architectures display an assortment of shapes and sizes, as it can be found in edifices of Sendai, the city where he has developed his scientific career. Professor Kobayashi has also studied in depth properties such as chirality, absorption profiles and electronic structure of porphyrinoids. The cover background represents the magnetic circular dichroism spectroscopy (MCD), which is one of his areas of expertise.

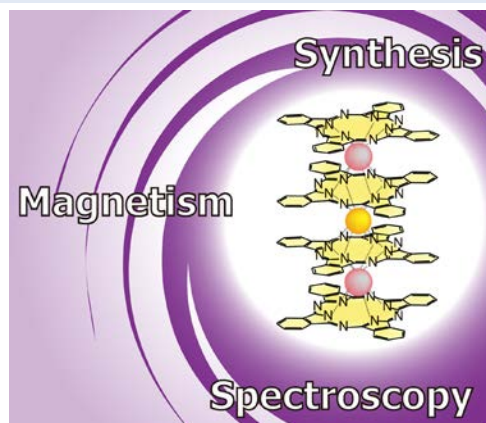
Reviews

pp. 615–629

Quadruple-decker phthalocyanines — one additional layer for a molecule, one giant leap for phthalocyanine chemistry

Takamitsu Fukuda* and Naoto Ishikawa*

Recent synthetic and physicochemical developments of quadruple-decker phthalocyanines have been reviewed. The effects of stacked π -electronic structures, and weak f–f interactions on the spectroscopic properties and dynamic magnetic relaxation processes, respectively, are discussed.

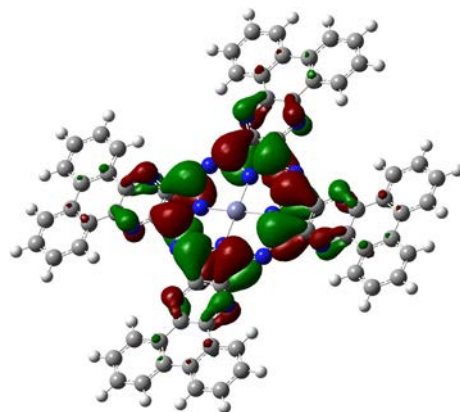


pp. 630–641

Trends in the TD-DFT calculations of porphyrin and phthalocyanine analogs

John Mack*, Justin Stone and Tebello Nyokong

In recent years, it has become increasingly clear that TD-DFT calculations with the commonly used hybrid B3LYP exchange-correlation functional of the Gaussian software package are problematic in the B-band region of porphyrinoid spectra, since the degree of configurational interaction between the B and higher energy $\pi\pi^*$ state appears to be significantly overestimated. The use of the CAM-B3LYP functional to address this issue is analyzed by calculating the optical spectra of a series of the Zn(II) complexes of 19 fused-ring-expanded porphyrins and tetraazaporphyrinoids.



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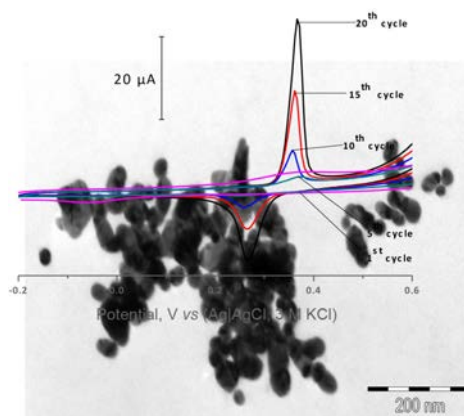
Articles

pp. 642–651

The influence of gold nanoparticles on the electroactivity of nickel tetrasulfonated phthalocyanine

Audacity Maringa and Tebello Nyokong*

The electrodeposition of gold nanoparticles (AuNPs) followed by electropolymerization of nickel tetrasulfonated phthalocyanine (NiTSPc) on the glassy carbon electrode results in improved electrocatalytic activity compared to individual components.

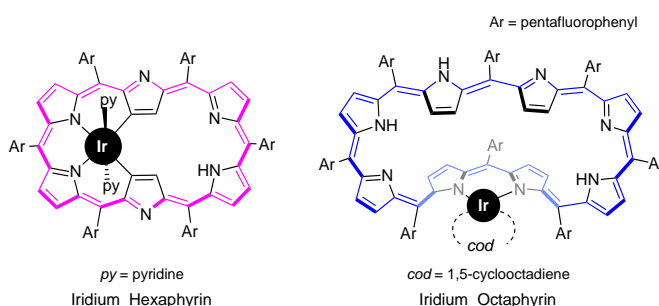


pp. 652–658

Iridium complexes of [26]hexaphyrin(1.1.1.1.1.1) and [36]octaphyrin(1.1.1.1.1.1.1.1)

Koji Naoda and Atsuhiko Osuka*

Iridium metalation of [26]hexaphyrin and [36]octaphyrin gave Ir(III) complex of [26]hexaphyrin and Ir(I) complex of [36]octaphyrin, respectively. The former complex is an aromatic molecule displaying considerably electron-rich nature, while the latter complex shows weak antiaromatic nature with a small HOMO–LUMO gap of 0.82 eV.

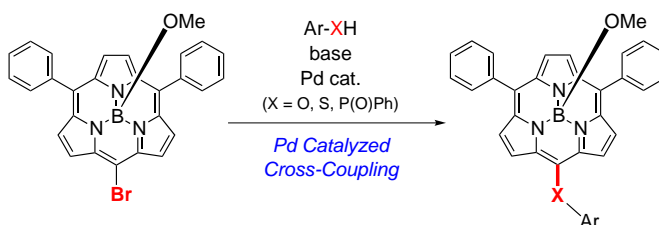


pp. 659–665

Synthesis of *meso*-heteroatom-substituted subporphyrins

Masaaki Kitano, Daiki Shimizu, Takayuki Tanaka, Hideki Yorimitsu and Atsuhiko Osuka*

Meso-aryloxy-, *meso*-alkoxy-, *meso*-arylsulfanyl-, *meso*-alkylsulfanyl-, and *meso*-phosphoryl-substituted subporphyrins were effectively synthesized by Pd-catalyzed substitution reactions of *meso*-bromosubporphyrin. Efficient fluorescence quenching was observed with both electron rich and electron deficient substituents probably originating in the intramolecular electron transfer. X-ray crystallographic analysis are also discussed.

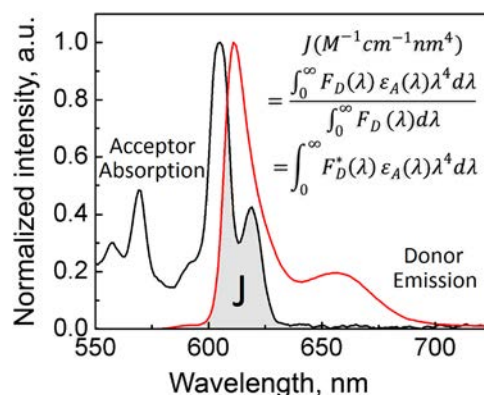


pp. 666–674

Maple™-assisted calculations of the J-integral: a key parameter for the understanding of excited state energy transfer in porphyrins and other chromophores

Adam Langlois and Pierre D. Harvey*

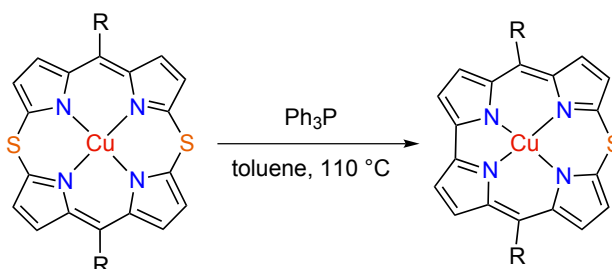
The spectral overlap between the emission of a donor molecule and the absorption of an acceptor molecule is a parameter of extreme importance when studying the excited state energy transfer by either the Förster or Dexter mechanism. Despite its extreme importance it is often misinterpreted, approximated or incorrectly calculated. A detailed description for the correct calculation of the J-integral is herein reported and presents a Maple™ assisted template that is capable of performing this calculation.



pp. 675–678**Synthesis, reactivity and property of 5,15-dithiaporphyrin copper(II) complex**

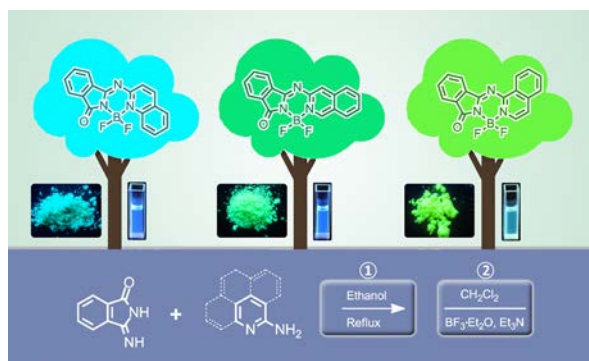
Naruhiko Wachi, Takeshi Kondo, Satoru Ito, Satoru Hiroto, Ji-Young Shin and Hiroshi Shinokubo*

5,15-Dithiaporphyrin copper(II) complex was prepared. X-ray diffraction analysis elucidated its dimeric structure in the solid state, in which the *meso*-sulfur atom served as an axial ligand to each pentacoordinated Cu(II) center. 5,15-Dithiaporphyrin Cu(II) complex was converted into 10-thiacorrole Cu(II) complex in good yield upon heating with triphenylphosphine in refluxing toluene.

**pp. 679–685****Aza boron-pyridyl-isoindoline isomers: synthesis and photophysical properties**

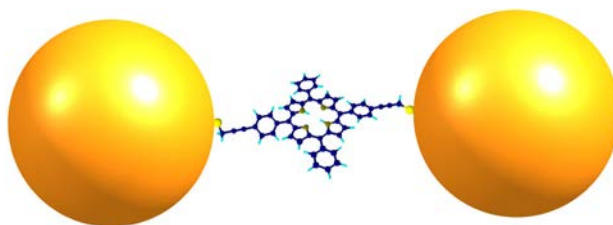
Hui Liu, Yanping Wu, Zhifang Li and Hua Lu*

Three aza boron-pyridyl-isoindoline isomers have been synthesized through a facile and scale-up two step reaction. These isomers show broad envelopes of intense vibrational bands in the absorption and emission spectra with moderate fluorescence quantum yields in solution and the solid-state.

**pp. 686–697****Synthesis, spectroscopy, and photophysics of porphyrins attached to gold nanoparticles *via* one or two linkers**

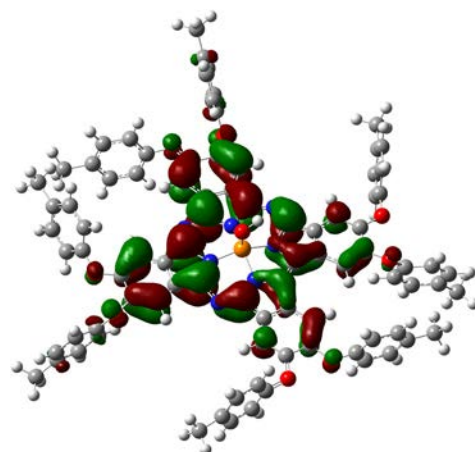
Jakub Ostapko, Joanna Buczyńska, Maria Pszona, Patrycja Kowalska and Jacek Waluk*

Gold nanoparticles were prepared, functionalized with *meso*-tetraphenylporphyrin, singly and doubly substituted with thiocarbamate and thioacetate groups. The porphyrins with one linker attach to single nanoparticles, whereas the dual linker derivatives induce formation of aggregates, providing a “hot-spot” type structure.

**pp. 698–707****Synthesis, characterization and photodynamic therapy properties of an octa-4-*tert*-butylphenoxy-substituted phosphorus(V) triazatetrabenzcorrole**

Maohu Shi, Jiangwei Tian, Colin Mkhize, Gugu Kubheka, Jinfeng Zhou, John Mack*, Tebello Nyokong and Zhen Shen*

A novel octa-4-*tert*-butylphenoxy-substituted phosphorus(V) triazatetrabenzcorrole (P^VTBC), has been synthesized and characterized by MALDI-TOF MS and NMR, FT-IR and MCD spectroscopy. The fluorescence emission spectrum was used to determine the fluorescence quantum yield and the quantum yield for singlet oxygen generation was calculated by using 1,3-diphenylisobenzofuran as a scavenger. The photocytotoxicity against U87MG cells was measured. The results indicated that P^VTBC is potentially useful as an NIR region photosensitizer for photodynamic therapy (PDT).

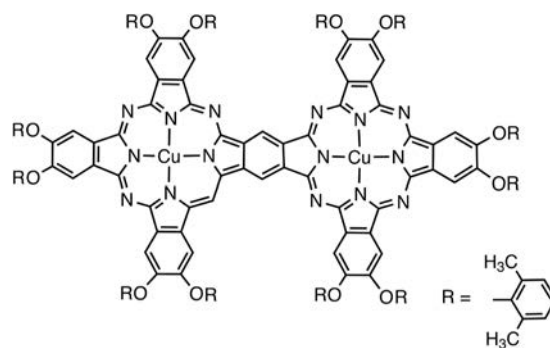


pp. 708–714

Synthesis and magnetic properties of an annulated dinuclear copper(II) phthalocyanine peripherally having 2,6-dimethylphenoxy substituents

Takahisa Ikeue*, Naoko Sawada, Naomi Matsumoto, Ayaka Miyazaki, Tamotsu Sugimori, Masayuki Koikawa, Ichiro Hiromitsu, Katsumi Yoshino, Masahiro Mikuriya, Yusuke Kataoka and Makoto Handa*

A dinuclear copper(II) phthalocyanine complex with 12 2,6-dimethylphenoxy groups at the peripheral positions of the [CuPc]₂ framework, where [CuPc] units are linked by a common annulated benzene ring to give the planar dinuclear structure, was prepared and characterized. An appreciably large antiferromagnetic interaction ($J = -1.8 \text{ cm}^{-1}$) was observed between the copper(II) ions through the common benzene ring, which was confirmed by the DFT calculation.

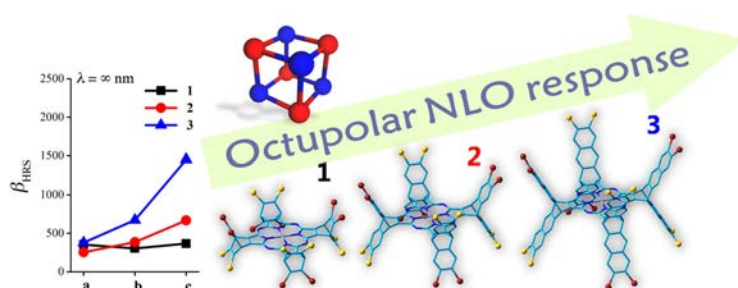


pp. 715–720

Density functional theory study of pure octupolar porphyrazines with second-order nonlinear optical activity

Luyang Zhao, Chao Chen, Zimeng Li, Dongdong Qi* and Jianzhuang Jiang*

Pure octupolar tetra(triptycene)porphyrazine molecules were theoretically designed. The octupole contribution with better isotropy to the second-order NLO response are revealed in detail on the basis of density functional theory.

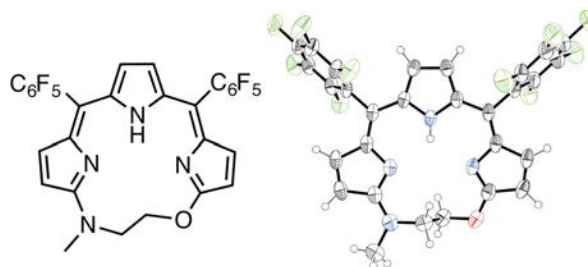


pp. 721–726

Unexpected formation of a triphyrin in the reaction of dibromodipyrromethene and *N,N*-dimethylaminoethanol

Soji Shimizu*, Shoma Hirokawa and Nagao Kobayashi*

A novel triphyrin was unexpectedly formed in the synthesis of *meso*-aryl-substituted dibenzo-5,10,15-triazaporphyrin from 1,9-dibromodipyrromethene and 1,3-diiminoisoindoline in the presence of *N,N*-dimethylaminoethanol. Its unique properties, such as conformational flexibility of the bridging moiety and broad absorption in the visible region, were also revealed by ¹H NMR and UV-vis absorption spectroscopies.

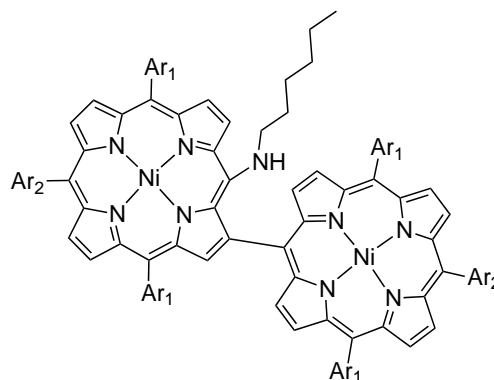


pp. 727–734

A new porphyrin dimer as an unexpected side-product

Ana M.V.M. Pereira, Christophe Jeandon, José A.S. Cavaleiro, Maria G.P.M.S. Neves and Romain Ruppert*

The synthesis of a new diporphyrinylamine is described. In particular, the possibility to use the Buchwald or Ullmann amination reactions to obtain these compounds is detailed. Attempts to obtain symmetrical diporphyrinyl amines linked by a tertiary amine are exposed and the obtention as side-product of an unexpected unsymmetrical porphyrin dimer with a *meso*-β linkage is described.

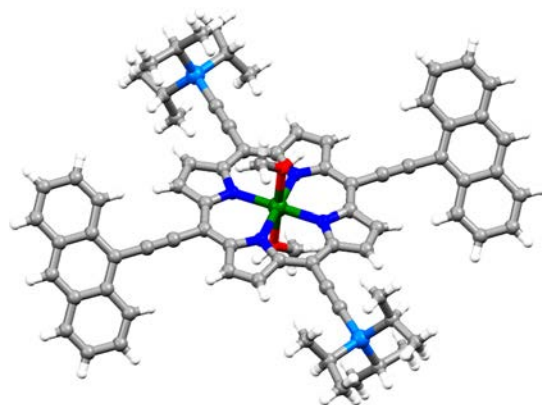


pp. 735–740

Influence of additives in bulk heterojunction solar cells using magnesium tetraethynylporphyrin with triisopropylsilyl and anthryl substituents

Takafumi Nakagawa, Junichi Hatano and Yutaka Matsuo*

Magnesium tetraethynylporphyrin bearing two triisopropyl groups and anthryl groups in a trans fashion was synthesized and applied for solution-processed organic solar cells. The effect of various additives including coordinating molecules on photovoltaic performance was investigated.

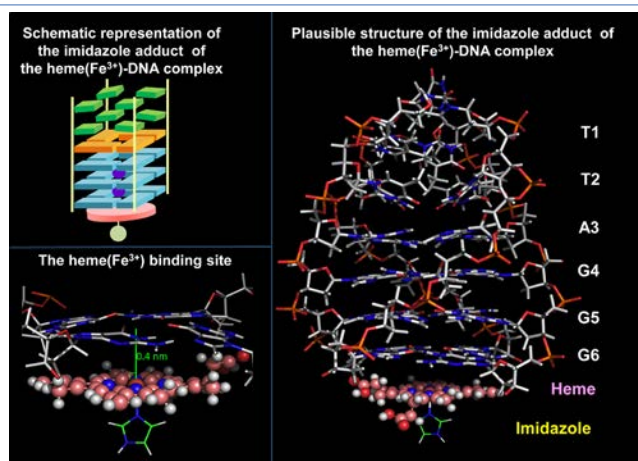


pp. 741–751

Structural characterization of imidazole adducts of heme-DNA complexes

Yasuhito Suzuki, Hulin Tai, Kaori Saito, Tomokazu Shibata, Masashi Kinoshita, Akihiro Suzuki and Yasuhiko Yamamoto*

The structural characterization of a ternary complex composed of heme, a parallel G-quadruplex DNA formed from d(TTAGGG), and imidazole revealed that the heme stacks onto the 3'-terminal G-quartet of the DNA and imidazole is coordinated to the heme Fe atom on the side of the heme opposite to the G-quartet in the complex.

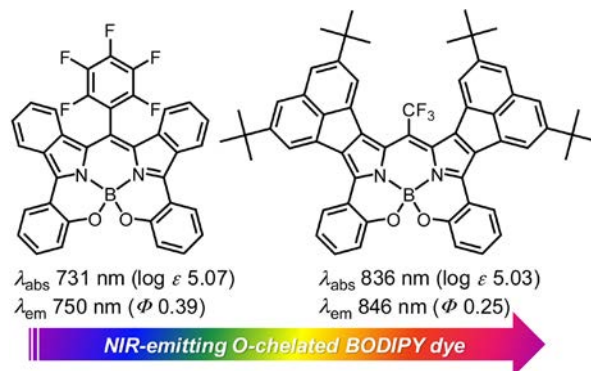


pp. 752–761

Synthesis of NIR-emitting O-chelated BODIPYs fused with benzene and acenaphthylene

Tetsuo Okujima*, Yoichi Shida, Keishi Ohara, Yuya Tomimori, Motoyoshi Nishioka, Shigeki Mori, Takahiro Nakae and Hidemitsu Uno*

A series of O-chelated BODIPYs fused with aromatic rings such as benzene and acenaphthylene at β,β -positions was synthesized as a near-infrared dye. The photophysical properties were examined by UV-vis-NIR absorption and fluorescence measurement. Acenaphthylene-fused O-BODIPYs showed an intense absorption at 750–840 nm with the ϵ of $10^5 \text{ M}^{-1}\text{cm}^{-1}$, and a fluorescence emission at 770–850 nm with the high Φ value of 0.25–0.43.

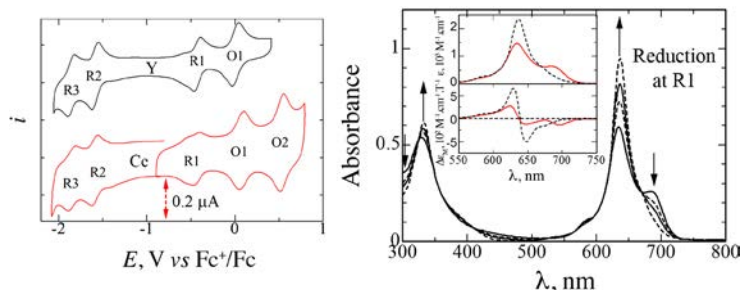


pp. 762–770

Anomaly of double-decker bis(phthalocyaninato)cerium(IV) in its electrochemical properties amongst rare-earth analogs

Hiroaki Isago*

The quasi-reversible metal-centered reduction in the title complex has been investigated and spectral properties of the initial and reduced species are reported.



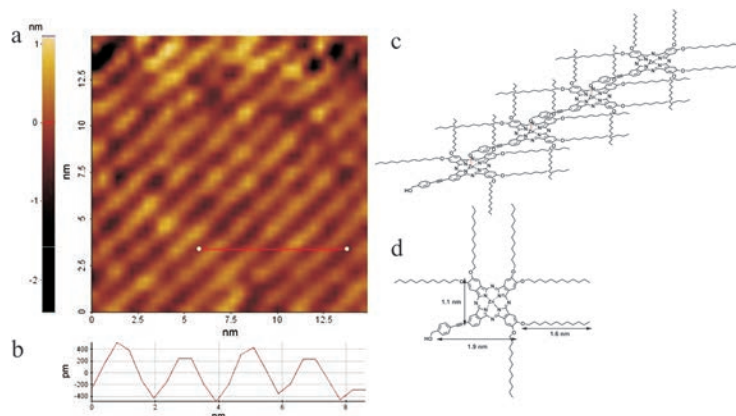
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pp. 771–777

Self-assembled phthalocyanine derivatives on highly ordered pyrolytic graphite

S. Gokhan Colak and Mine Ince*

A novel unsymmetrically substituted hydroxy-functionalized Pc 1 bearing long aliphatic dodecyloxy chains has been synthesized as the building block for the construction of multipurpose materials for potential optoelectronic applications. AFM studies of unsymmetrical substituted Pcs 1 on the graphitic surface revealed the formation of wire-like structures in different lengths from nanometer to micrometer scale.

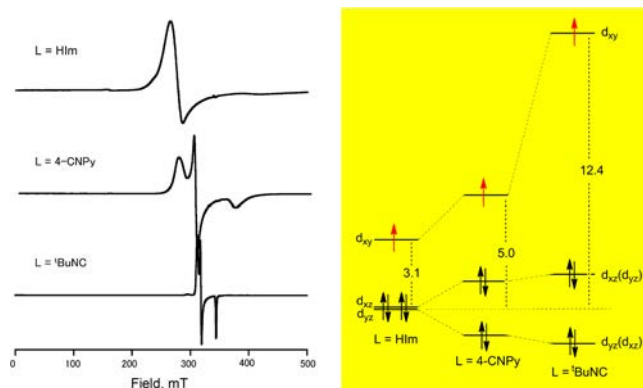


pp. 778–791

Electronic structure of low-spin six-coordinate iron(III) meso-tetrapropylchlorin complexes

Akira Ikezaki, Jyunpei Ono, Yoshiaki Ohgo, Mari Fukagawa, Takahisa Ikeue and Mikio Nakamura*

On the basis of the ^1H NMR, ^{13}C NMR and EPR spectra of $[\text{Fe}(\text{T}^{\text{h}}\text{PrC})(\text{BuNC})_2]^+$, we have concluded that the complex adopts the quite pure $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state at 4.2 K where the EPR spectra were measured, while it should rather be expressed as low-spin Fe(II) chlorin π -radical cation $[\text{Fe}^{\text{II}}(\text{T}^{\text{h}}\text{PrC})(\text{BuNC})_2]^+$ at ambient temperature where the NMR spectra were examined.

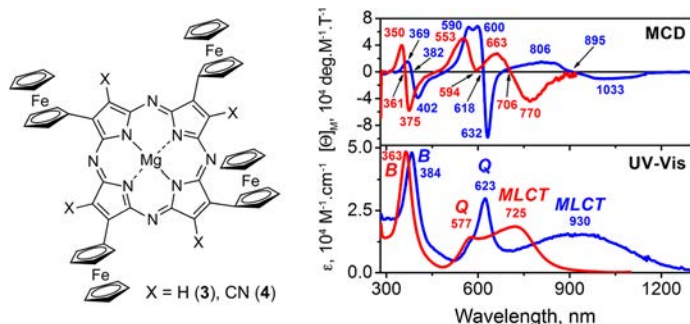


pp. 792–803

Tuning the near-IR band energy and redox potentials of magnesium tetra(ferrocenyl)tetraazaporphyrins

Victor N. Nemykin*, Elena A. Makarova, Jeffrey O. Grosland, Semyon V. Dudkin, Richard Dennison and Anatolii A. Purchel

Two ferrocene-substituted magnesium tetraazaporphyrins with direct ferrocene-tetraazaporphyrin bond were prepared and characterized using UV-vis, MCD, NMR, and mass spectrometries. Redox and unusual optical properties of new compounds were investigated using UV-vis, MCD, electro-, and spectroelectrochemical methods and correlated with DFT and TDDFT calculations.

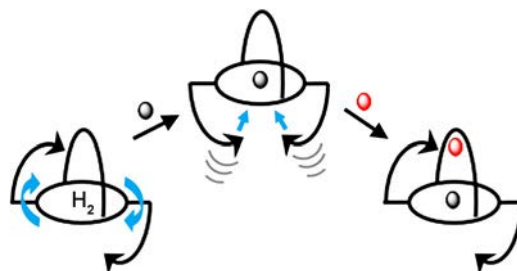


pp. 804–813

Coordination controlled atropoisomerism in phenanthroline-strapped porphyrins: A swinging affair

Pauline Vorburger, Jennifer A. Wytko and Jean Weiss*

Atropoisomerism can be controlled *a posteriori* in heme protein models bearing a predefined distal coordination site by the stepwise introduction of metals in the structure.

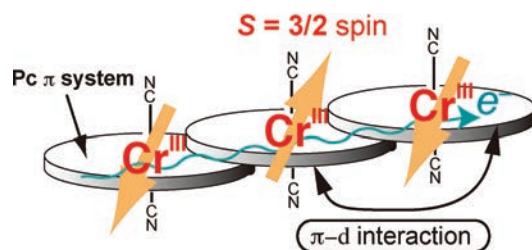


pp. 814–823

One-dimensional phthalocyanine-based conductor with $S = 3/2$ isotropic magnetic centers

Yusuke Takita, Hiroyuki Hasegawa, Yukihiro Takahashi, Jun Harada, Akinori Kanda, Noriaki Hanasaki and Tamotsu Inabe*

The axially ligated phthalocyanine conductor with d^3 ($S = 3/2$) metal Cr^{III} has been successfully prepared. The crystal is composed of slipped-stacked one-dimensional π - π networks of the Pc rings. Temperature dependence of the electrical conductivity is semiconducting and reveals the development of charge disproportionation. The resistance decreases when magnetic fields are applied, indicating π - d interactions in the Cr system.

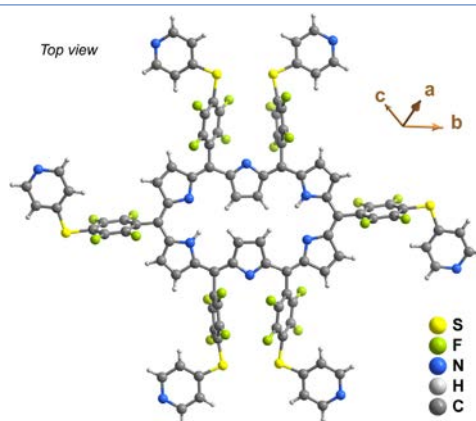


pp. 824–831

Synthesis of hexaphyrins and *N*-fused pentaphyrins bearing pyridin-4-ylsulfanyl groups

Flávio Figueira, Andreia S. F. Farinha, Augusto C. Tomé, José A. S. Cavaleiro, Filipe A. Almeida Paz and João P. C. Tomé*

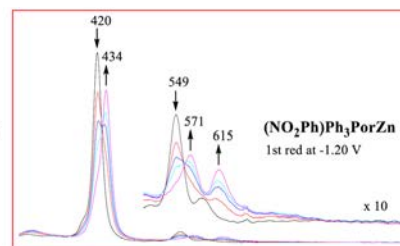
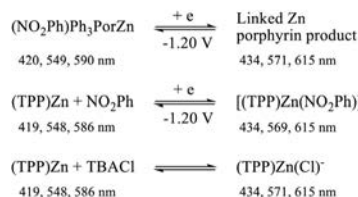
The nucleophilic aromatic substitution reaction of fluorine atoms by 4-mercaptopyridine in *meso*-hexakis(pentafluorophenyl) [26]hexaphyrin **1** and *meso*-pentakis(pentafluorophenyl)*N*-fused [22]pentaphyrins **3** provided the corresponding hexaphyrin **5** and *N*-fused pentaphyrin **6** bearing pyridin-4-ylsulfanyl groups.



pp. 832–841

Redox properties of nitrophenylporphyrins and electrosynthesis of nitrophenyl-linked Zn porphyrin dimers or arrays

Yuanyuan Fang, Xiaoqin Jiang, Zhongping Ou, Clément Michelin, Nicolas Desbois, Claude P. Gros* and Karl M. Kadish*



Five nitrophenylporphyrins were investigated as to their electrochemical properties in CH_2Cl_2 containing 0.1 M TBAP and the products of the first reduction examined by UV-visible spectroelectrochemistry.