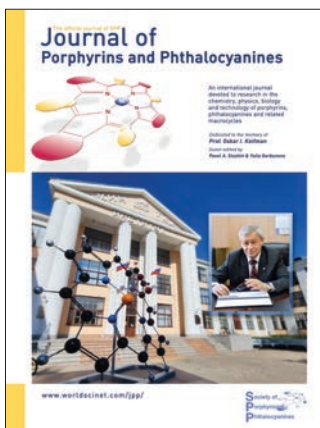


## About the Cover



This special memorial JPP issue is dedicated to Professor Oskar Iosifovich Koifman on the occasion of his 80<sup>th</sup> Anniversary. It contains 17 original research and review articles written by colleagues and friends commemorating Professor Oskar Koifman, his contribution to the chemistry of porphyrins and phthalocyanines and the development of their research in Russia. On the cover, one can see the main entrance of Ivanovo State University of Chemistry and Technology where he was Rector and President and founded the Research Institute of Macrocyclic Compounds.

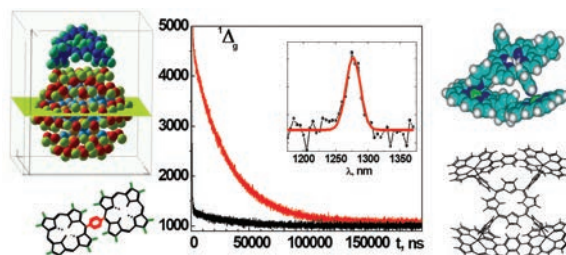
## Review

549–570

### Singlet oxygen generation by nanoassemblies containing porphyrin macrocycles: Steric and screening effects, energy transfer and competing processes

Eduard I. Zenkevich\*, Marina V. Parkhats, Boris M. Dzhagarov and Christian von Borczyskowski

Competing processes (steric hindrance interactions, screening effects, energy transfer and electron tunneling) should be taken into account upon a quantitative description of the singlet oxygen  $^1\Delta_g$  generation by various photosensitizers. These include tetrapyrrolic compounds: monomers, porphyrin chemical dimers, self-assembled triads and pentads as well heterogeneous nanoassemblies based on semiconductor quantum dots and porphyrins. It is shown that direct experimental measurements of  $^1\Delta_g$  IR-emission should be adjusted for solvent influence on the rate constant of the radiative transition  $^1\Delta_g \rightarrow ^3\Sigma_g^-$ .

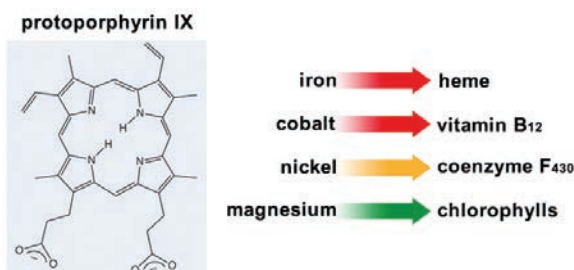


571–583

### Naturally occurring porphyrins: The colored molecules of life

Karl M. Kadish and Roger Guilard\*

This mini-review focuses on biosynthesis pathways leading to naturally occurring porphyrins. ALA, protoporphyrin IX, chlorophylls and their derivatives are more and more used in applications such as medicine, sensing, or chemical biology. A knowledge of their biosynthesis and unique functions in living organisms is a prerequisite before involving these molecules in drugs or processes.



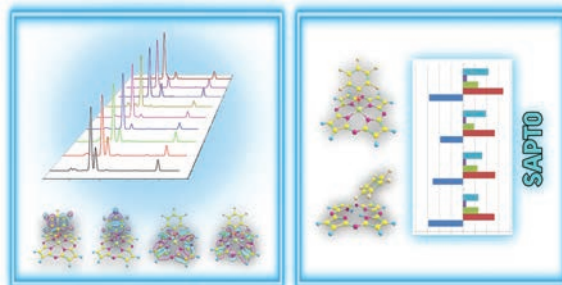
## Articles

584–590

**DFT and TDDFT study of Al(III), Ga(III), In(III) porphyrazines and their perhalogenated derivatives**

Dmitriy A. Vyalkin, Alexey V. Eroshin, Arseniy A. Otylotov, Yury Minenkov, Daniil N. Finogenov, Yuriy A. Zhabanov\* and Pavel A. Stuzhin

The effect of perhalogenation (F, Cl) of the porphyrazine macrocycle on the molecular structure, electronic and spectral properties of Al<sup>III</sup>, Ga<sup>III</sup> and In<sup>III</sup> complexes bearing an axial pentafluorophenoxy (OC<sub>6</sub>F<sub>5</sub>) group was investigated by DFT and TDDFT methods. Analysis of the simulated spectra showed a bathochromic shift of the Q-band for the perchlorinated complexes which correlates with a narrowing of the HOMO-LUMO gap.



591–600

**No more doubts about four NH-tautomers formation: 5,10-diaryl-corroles case theoretical study**

Mikalai M. Kruk\*, Lev L. Gladkov and Dmitry V. Klenitsky

The individual features of four NH-tautomers of the 5,10-di-aryl-corroles are reported in the manuscript.

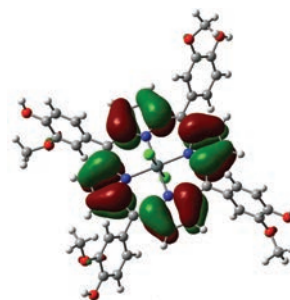


601–617

**Photodynamic anticancer and antibacterial properties of a series of Sn(IV) tetraarylporphyrins**

Rodah C. Soy, Balaji Babu, John Mack\* and Tebello Nyokong

A series of Sn(IV) porphyrins with 4-methoxy-, 3-methoxy-, 4-hydroxy- and 3-methoxy-4-hydroxyphenyl *meso*-aryl rings have been synthesized and characterized. Their potential utility as photosensitizer dyes in photodynamic therapy and photodynamic antimicrobial chemotherapy is investigated *in vitro* against MCF-7 breast cancer cells and planktonic and biofilm cells of *S. aureus* and *E. coli*.

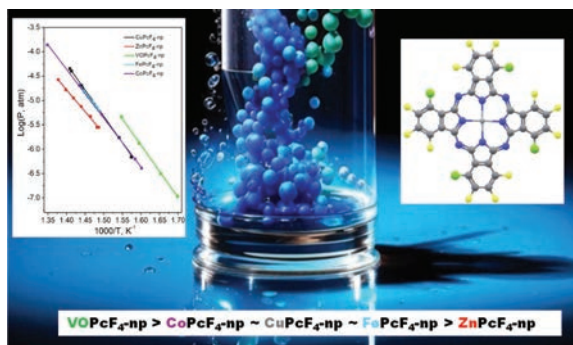


618–625

**Vapor pressure of tetrasubstituted metal phthalocyanines bearing fluorine substituents in non-peripheral positions**

Dmitry V. Bonegardt, Sergei V. Trubin, Aleksandr S. Sukhikh, Darya D. Klyamer and Tamara V. Basova\*

The temperature dependence of the saturated vapor pressure of fluorosubstituted phthalocyanines with substituents in non-peripheral positions of the macro ring of MPcF<sub>4</sub>-np where M=Cu, Fe, Co, or VO, was investigated. The volatility decreased in the order: VOPcF<sub>4</sub>-np > CoPcF<sub>4</sub>-np ~ CuPcF<sub>4</sub>-np ~ FePcF<sub>4</sub>-np > ZnPcF<sub>4</sub>-np, and correlated in the same order with the increase in their crystal lattice energy. The volatilities of most MPcF<sub>4</sub>-np derivatives (M = Cu, Zn, Co, VO) was lower than that of MPcF<sub>4</sub>-p.



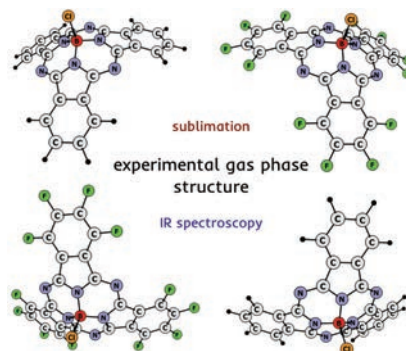
Articles

626–638

**Molecular structure, thermodynamic and spectral characteristics of chloroboron(III) subphthalocyanine and its dodecafluorinated derivative**

Ivan Yu. Kurochkin\*, Alexander E. Pogonin, Alexey V. Eroshin, Yuriy A. Zhabanov, Olga G. Krasnova, Ivan A. Skvortsov, Pavel A. Stuzhin, Nina I. Giricheva and Georgy V. Girichev\*

A comprehensive study of the structural, spectral and energetic properties of chloroboron(III) complexes of subphthalocyanine and dodecafluorinated subphthalocyanine was performed by mass spectrometry, gas-phase electron diffraction, IR spectroscopy and quantum chemical calculations.

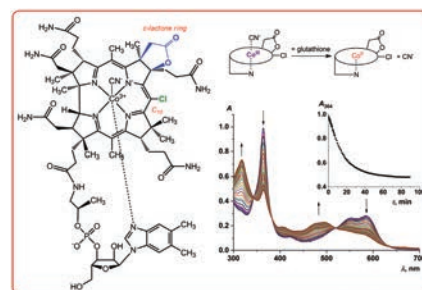


639–646

**c-Lactone ring increases the reactivity of cyanocobalamins toward glutathione**

Vladimir S. Osokin, Darya O. Fugina, Ilya A. Dereven'kov\*, Ilya A. Khodov and Sergei V. Makarov

Introducing a *c*-lactone ring to cyanocobalamin or its halogenated versions substantially accelerates their reduction by glutathione to Co(II)-species. The highest rate of the reaction was observed in the reduction of *meso*-chlorinated cyanocobalamin *c*-lactone.

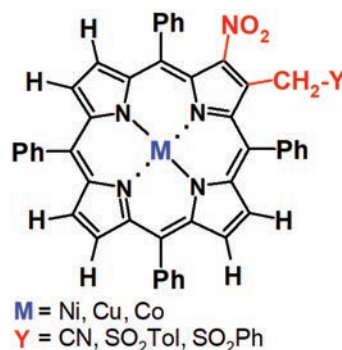


647–653

**Vicarious nucleophilic substitution of hydrogen and synthesis of nickel-, copper-, and cobalt-porphyrates — double functionalized at the β-positions of the same pyrrole unit**

Agnieszka Mikus\* and Stanisław Ostrowski\*

2-Nitro-5,10,15,20-tetraphenylporphyrin nickel(II), copper(II), and cobalt(II) complexes were reacted with carbanion precursors of the type XCH<sub>2</sub>Y, where X and Y are leaving and stabilizing groups, respectively according to the *vicarious nucleophilic substitution* scheme (VNS). This led to derivatives which are β,β-disubstituted on the same pyrrole ring with satisfactory yields of up to 95%. These types of products are essentially unavailable by alternate synthetic methods.

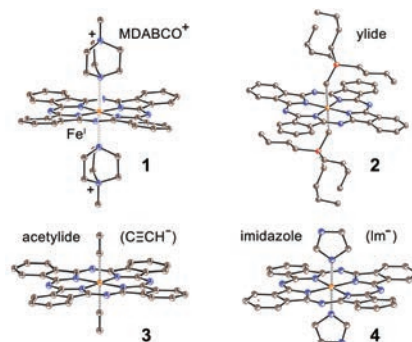


654–664

**Coordination complexes of iron(II) phthalocyanine with cationic, anionic and neutral ligands**

Nikita R. Romanenko, Maxim A. Faraonov, Alexey V. Kuzmin, Salavat S. Khasanov and Dmitri V. Konarev\*

A series of coordination complexes of iron(II) phthalocyanine (Fe<sup>II</sup>Pc) with cationic (MDABCO<sup>+</sup>) ligands in **1**, neutral Bu<sub>3</sub>PCH<sub>2</sub> ylide ligands in **2** and anionic acetylide (C≡CH<sup>-</sup>), or imidazole (Im<sup>-</sup>) ligands in **3** and **4**, respectively, were obtained in crystalline form. Metal-centered reduction of Fe<sup>II</sup>Pc<sup>2-</sup> has been shown to form the [Fe<sup>I</sup>Pc<sup>2-</sup>]<sup>-</sup> anions in **1**, weak charge transfer to Fe<sup>II</sup> in **2** and **3**, and the formation of unmodified [Fe<sup>II</sup>(Pc<sup>2-</sup>)] species in **4**.



Articles

665–674

**Photophysical properties of hybrid porphyrin-erythrosine B fluorophore in aqueous media and PVA films**

G.M. Mamardashvili, E.Yu. Kaigorodova, K.S. Nikitin and N.Z. Mamardashvili\*

A hybrid porphyrin, erythrosine photoactive fluorophore was synthesized. The material demonstrates high fluorescent sensitivity to local viscosity in a binary water-glycerol solvent when immobilized in a PVA film material and retains fluorescent molecular rotors properties in non-aqueous media.

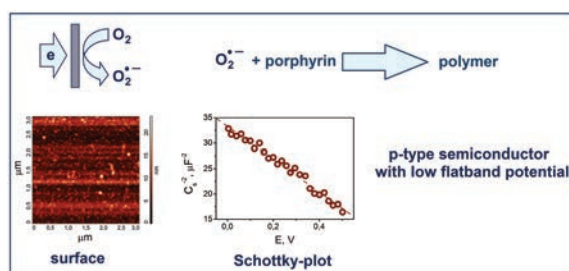


675–682

**Electrophysical characteristics of a film based on 2H-5,10,15,20-tetrakis(para-aminophenyl)porphyrin**

Vladimir I. Parfenyuk, Svetlana A. Chulovskaya\* and Sergey M. Kuzmin

The potentials for 2H-5,10,15,20-tetrakis (para-aminophenyl) porphyrin film formation, as well as the efficiency and dynamics of their deposition were determined. The obtained film has a continuous and smooth coating, with a thickness of about 100 nm and roughness of 2.4 nm. It possesses p-type conductivity, a donor density of  $8.7 \times 10^{19} \text{ cm}^{-3}$  and a flatband potential of about 1.01 V.

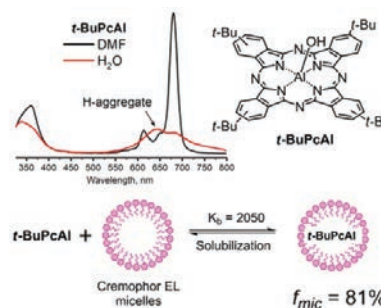


683–690

**Solubilization of tetra-tert-butylphthalocyanine aluminum(III) in micellar surfactant solutions**

Mikhail S. Belousov, Margarita A. Gradova, Lyubov A. Wasserman and Tatiana V. Dubinina\*

A comparative study for the aggregation behavior of tetra-tert-butylphthalocyanine aluminum(III) in micellar aqueous solutions of different surfactants was carried out. The results indicate an effective stabilization of the photoactive monomolecular form of t-BuPcAl in Cremophor EL micelles, allowing for consideration of this formulation as a promising dosage form for further *in vitro* studies.

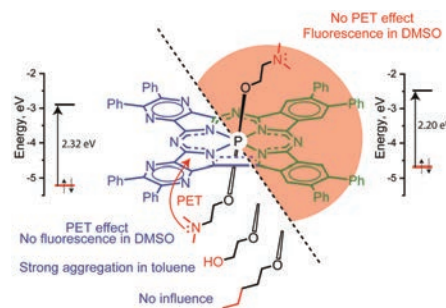


691–700

**Spectral-luminescence properties of P<sup>V</sup> corrolazines with axial alkoxide ligands**

Dmitriy A. Lazovskiy, Anton A. Danilenko and Pavel A. Stuzhin\*

A series of axial bis-alkoxido substituted P<sup>V</sup> corrolazines were synthesized with terminal hydroxy- and dimethylamino-groups. Quenching of the excited state and fluorescence due to a photoinduced electron transfer effect from the NMe<sub>2</sub> group was observed in DMSO only for the pyrazine fused P<sup>V</sup> corrolazine and is absent for the benzo annulated corrolazine macrocycle having a higher energy LUMO.



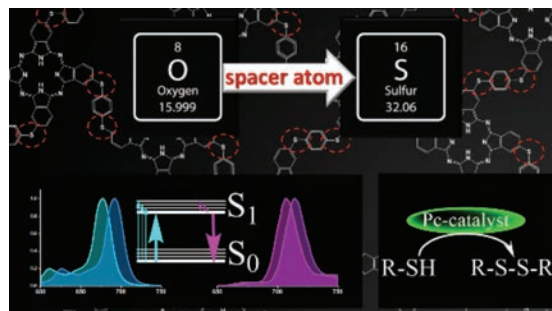
Articles

701–709

**The role of spacer heteroatomic fragment in spectroscopic and luminescent behavior of phenyl-substituted phthalocyanine complexes**

D. Erzunov, A. Alekseeva, I. Sarvin, S. Tonkova and A. Vashurin\*

Peripheral phenyl-substituted metal phthalocyanines were obtained with thio or oxa substitution in the spacer bridge fragment. It was revealed that the presence of a spacer fragment is one of the key factors that strongly influence both the solubility of phthalocyanine complexes and their aggregation behavior in various solvents.

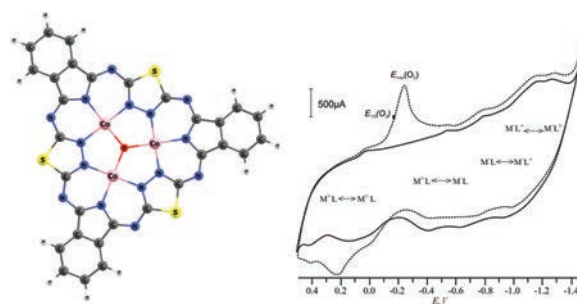


710–715

**Electrochemical and electrocatalytic properties of hemihexaphyrazine and its trinuclear cobalt complex**

Evgenii N. Ivanov, Nadezhda M. Berezina, Anton A. Belyaev, Yana E. Kibireva, Mikhail I. Bazanov\* and Mikhail K. Islyaikin\*

Electrochemical and electrocatalytic properties of hemihexaphyrazine ( $H_3Hhp$ ) and its trinuclear cobalt complex ( $Co_3OHhp^+$ ) have been studied by cyclic voltammetry. The possibility of detecting cationic and anionic forms of compounds during polarization of electrodes at potentials between 0.5 and -1.5 V was established. It was shown that the cobalt complex exhibits a sufficiently high catalytic activity for the oxygen reduction reaction in an alkaline solution.



716–727

**Dicationic salt of  $\beta$ -alkyl substituted sapphyrin-type porphyrinoid: Acid-basic properties, thermal stability and quantum-chemical calculations**

Anastasia E. Likhonina, Mikhail A. Krest'yaninov, Dar'ya V. Petrova, Alexander S. Semeikin and Dmitry B. Berezin\*

The state of the dicationic salt of  $\beta$ -alkylsubstituted sapphyrin in solutions with different polarities and acid-basic properties was determined. Anionic forms of sapphyrin are not obtained in diethylamine (DEA), 1,8-diazabicyclo[5.4.0] undecene (DBU) or tetramethylammonium hydroxide ( $NMe_4OH$ ) solutions up to 3.7 M of the base. The low acidity of NH bonds in the sapphyrin molecule was confirmed using thermogravimetric data and quantum-chemical calculations.

