About the Cover

See Fabienne Dumoulin, Derya Topkaya, Songül Yaşar, Vefa Ahsen* and Ümit İşci* pp. 571–661

A comprehensive review of the covalent and supramolecular combinations of two major groups of molecules, resorcinarenes and porphyrinoids, is presented and highlights the bright future of such combos.

Review

pp. 571–581
Covalent or supramolecular combinations of resorcinarenes and porphyrinoids
Fabienne Dumoulin, Derya Topkaya, Songül Yaşar, Vefa Ahsen* and Ümit İşci*

A review detailing the different combinations of resorcinarenes, an intriguing type of cavitands, with porphyrinoids.

Articles

pp. 582–589
N-methylated 25-oxasmaragdyrins: Synthesis, structure and properties
Tejinder Kaur, Way-Zen Lee and Mangalampalli Ravikanth*

The N-methylation was carried out in 25-oxasmaragdyrins to understand the effect of macrocyclic distortions on electronic and structural properties of expanded porphyrins.
Synthesis and characterization of chlorophyll a enol derivatives: Chlorophyll a tert-butyldimethylsilyl-enol ether and 13'-deoxo-13',13''-didehydro-chlorophyll a
Paavo H. Hynninen* and Markku Mesilaakso

The use of 1,8-diazabicyclo[5.4.0]undec-7-ene as a sterically hindered base for enolization and tert-butyldimethylsilyl-trifluoromethanesulfonate for silylation, produced Chl a tert-butyldimethylsilyl-enol ether (3) in a yield of 77%. The yield in the synthesis of 13'-deoxo-13',13''-didehydro-Chl a (4) was only modest (23%). In that synthesis, the elimination of water (dehydration) was found to be a delicate reaction, which probably depended sensitively on temperature, timing and the strengths of the bonds connecting the 13'-hydroxyl group and 13',13''-hydrogens in the isocyclic ring of 13'(R/S)HO-pheophytin a. The 1H and 13C NMR chemical shifts of the Chl a enol derivatives 3 and 4 indicated that these molecules are still diamagnetic and aromatic, but possessed a weaker ring-current than that of Chl a. The possible functional role of Chl a enol derivatives in photosynthetic reaction centers is briefly discussed.

Influence of N atom number and form on the photodynamic activities of zinc phthalocyanines
Wei W. Jin, Yue Wang, Ao Wang, Lin Zhou*, Yun Lin and Shao H. Wei*

Two polyamine modified Pcs (1-(4-methoxyphenyl)-N, N-dimethylmethanamine and N1,N1-diethyl-N2-(4-methoxybenzyl)-ethane-1, 2-diamine) and their water soluble derivatives, hydrochloride and quaternizing derivatives were synthesized. They were divided into three groups according to their structural characteristics. With increasing the number on N atom, the ROSs generation ability, cancer cell uptaken ability and photoinduced anticancer activity were all increased in all formulations of Pc derivatives.

Electrochemical behavior of a number of bispyridyl-substituted porphyrins and their electrocatalytic activity in molecular oxygen reduction reaction
Minh N. Do, Nadezhda M. Berezina*, Mikhail I. Bazanov, Sabir S. Gyseinov, Mikhail M. Berezin and Oscar I. Koifman

A free bispyridyl-substituted porphyrin and some cobalt complexes were synthesized and investigated as to their electrochemical and electrocatalytic properties in KOH. The redox-processes related to the transformation of the porphyrin macrocycle, the pyridyl substituents and the central metal ion have been established. The voltammetric analysis has showed that all studied compounds exhibit the catalytic activity in oxygen reduction reaction.

The magnetic properties, DNA/HSA binding and nuclease activity of manganese N-confused porphyrin

The oxidative cleavage of DNA by manganese N-confused porphyrin [chloro(2-aza-2-methyl-5,10,15,20-tetrakis(p-chlorophenyl)-21-carbaporphyrin)manganese(III), I] using H2O2 oxidant and its magnetic, DNA and HSA binding properties were investigated. I binds to ct-DNA via an outside groove binding mode, and it may also selectively bind the hydrophobic cavity located in subdomain IIA of HSA. I could cleave the supercoiled plasmid DNA efficiently in the presence of hydrogen peroxide. Hydroxyl radical (·OH) was found to be the reactive oxygen species for oxidative damage of DNA.
pp. 639–646
Reduction of (chloro)-µ-nitrido-bis[(tetra-tert-butyl-phthalocyaninato)iron(IV)] with organic N-bases
Svetlana V. Zaitseva, Sergei A. Zdanovich, Elena Y. Tyulyaeva*, Ekaterina S. Grishina and Oskar I. Koifman

The one-electron reduction of (chloro)-µ-nitrido-bis[(tetra-tert-butyl-phthalocyaninato)iron(IV)] Cl(FeIVPc)N under the action of axially attached organic N-bases L as electron-donors (L = diethylamine, imidazole, 1-methylimidazole, 2-methylimidazole) with the formation of (L)PcFeII–N–FeIVPc(L) was investigated in benzene at 298 K by UV-visible, IR, ESI-MS and EPR technique. The reaction kinetics was studied, the pre-equilibrium constants $K_{eq}$ and rate constants $k$ were obtained.

pp. 647–655
Spectroscopic investigations and theoretical calculations of DABCO induced xanthene bridged self-assembled zinc(II) porphyrin dimer
Li Xu, Tingting Huang, Xu Liang*, John Mack*, Jessica Harris, Tebello Nyokong, Minzhi Li and Weihua Zhu*

An in-depth study of the electronic structure of a 1,4-diazabicyclo[2.2.2]octane (DABCO) induced molecular self-assembled xanthene-bridged and amide-bonded porphyrin dimer is reported. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are used to identify trends in the optical spectroscopic properties. B3LYP geometry optimization predicts the formation of an almost perfectly eclipsed structure with respect to the two porphyrin rings with the analogous pyrrole nitrogens separated by 7.7–8.1 Å.

pp. 656–661
Synthesis of Ag(II) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin and its facile demetalation to 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin
Sasitha Vidyarini Ravindran, Anuj Krishnasundar Pennathur, G. Nandhini Devi* and Gautam Pennathur*

A novel one-step strategy for the synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin using AgIIOBP. Bromination of AgII TPP was carried out in a one-step reaction by varying the time interval and stoichiometric addition of Br₂ subsequently demetalation of AgIIOBP using H₂S.