About the cover

This special issue of the Journal of Porphyrins & Phthalocyanines celebrates the outstanding contributions of Prof. T. K. Chandrashekar in the field of porphyrinoids on the occasion of his 65th birthday. The contributions from his former students, colleagues, friends and well-wishers are brought together in this special issue.

Thanks to Rima Sengupta, a student of Prof. Ravikanth, for the cover design.

Reviews

pp. 359–381
Bactericidal efficiency of porphyrin systems
B. Habermeyer, T. Chilingaryan and R. Guilard*

Porphyrin-based fluorophores are shown to be remarkable dye candidates for photodynamic inactivation (PDI). The porphyrin-based antimicrobial materials and their potentialities for industrial applications are described. The failings and perspectives of PDI are also analyzed.

pp. 382–395
Porphyrin-based supramolecular assemblies and their applications in NLO and PDT
Madoori Mrinalini, Madarapu Naresh, Seelam Prasanthkumar* and Lingamallu Giribabu*

Self-assembly in tetrapyrrolic systems are investigated via supramolecular interactions leading to well-defined nanoarchitectures. Furthermore, the importance of tetrapyrrolic based derivatives utilized in non-linear optics and chemotherapeutic applications are reviewed.
pp. 396–399
Synthesis of unsymmetrically substituted expanded hemiporphyrazines: A monoiodo functionalized hemihexaphyrazine
Yana E. Philippova, Mikhail K. Islyaikin* and Tomás Torres*
A new expanded hemiporphyrazine — an unsymmetrically iodo substituted hemihexaphyrazine of ABAB’AB’-type was obtained by statistical condensation of 4-iodophthalonitrile, 4-tert-butylyphthalonitrile and 2,5-diamino-1,3,4-thiadiazole (molar ratio 1:2:3).

pp. 400–406
[38] Octaphyrin bis-Sn(IV) complexes with unique coordination geometries
Mondo Izawa, Akito Nakai, Taisuke Suito, Takayuki Tanaka* and Atsuhiro Osuka*
Two new [38]octaphyrin bis-Sn(IV) complexes were isolated and characterized as weakly aromatic molecules. One had a similar characteristic to octaphyrin bis-Si(IV) and bis-Ge(IV) complexes reported previously, and the other showed a different coordination mode that was fixed by intramolecular hydrogen bondings between pyrrolic NH and axially ligated OH on the tin ion.

pp. 407–417
Effect of auxiliary acceptor on D-π-A based porphyrin sensitizers for dye sensitized solar cells
Koteswar Devulapally, Govind Reddy, Seelam Prasanthkumar, Anooja Jagadeesh, Suraj Soman* and Lingamallu Giribabu*
Dye sensitized solar cells were fabricated using new dyes LG22 and LG23 as sensitizers. This work highlights the effect of a spacer on the device performance.

pp. 418–427
Synthesis and studies of covalently linked pyrrolyl bridged fluorescent dimers
Avisikta Sinha, Booruga Umasekhar and Mangalampalli Ravikanth*
Pyrrolyl bridged bis-(dipyrromethene) was used as a key precursor to prepare pyrrolyl bridged bis-(BODIPY) and bis-(22-oxacorrole) dimers.
**pp. 428–435**

**Thioether linked meso functionalized BODIPY DYEmers**  
Bhausaheb Dhokale, Indresh Singh Yadav, Shaikh M. Mobin and Rajneesh Misra*

Thioether linked meso functionalized BODIPY DYEmers 3 was synthesized using two different routes and characterized by $^1$H, $^{13}$C, $^{11}$B, $^{19}$F NMR, HRMS, and single crystal X-ray crystallography.

**pp. 436–446**

**Fluoride ion promoted NH deprotonation of dioxaphlorin with NIR absorption vs. acid induced facile conversion to aromatic dioxasapphyrin: Synthesis, spectroscopic and theoretical characterization**  
Buddhadeb Chakraborty, Maheshwari Horalavadi Mahadavaiah, Dandamudi Usharani* and Harapriya Rath*

The first ever structural isolation and characterization of nonaromatic expanded dioxaphlorin with NIR absorption being benefitted by fluoride ion triggered deprotonation of pyrrole rings NHs is reported.

**pp. 447–455**

**Metal complexes of 5,10,15-tris(pentafluorophenyl)-20-pyrrolyl N-confused porphyrin and its meso-pyrrolyl-bridged dimers: Synthesis and optical properties**  
Kazuhisa Yamasumi, Shigeki Mori, Takayuki Tanaka, Masatoshi Ishida* and Hiroyuki Furuta*

N-confused porphyrin derivatives possessing a meso-pyrrolyl-substituent at the C20 position offers unique inner and outer coordination spheres to form π-extended heteroleptic complexes. The peripheral coordination leads to remarkable bathochromic shifts of their absorption bands up to $\lambda \sim 1300$ nm.

**pp. 456–468**

**Fluorinated aluminum(III) porphyrins: Synthesis, spectroscopy, electrochemistry and photochemistry**  
Niloofar Zarrabi, Noah Holzer, Brandon J. Bayard, Sairaman Seetharaman, Benjamin G. Boe, Francis D'Souza and Prashanth K. Poddutoori*

A series of fluorinated free-base porphyrins (H$_2$TPPF$_n$) and the corresponding aluminum(III) porphyrin (AlTPPF$_n$-Ph) derivatives, where $n$ = 0, 8, 12, 20, 24, were synthesized and their spectroscopic, redox and optical properties investigated. The studies show that the structural, optical and redox absorption properties are sensitive to the degree of fluorination on the meso-phenyl units.
Light-induced energy transfer followed by electron transfer in axially coordinated benzothiazole tethered zinc porphyrin-fullerene[C_{60}/C_{70}]pyrrolidine triads

Raghu Chitta*, Deepak Badgurjar, Govind Reddy, Kanika Jain, Vijender Reddy Karla, Anjaiah Boligorla and Lingamallu Giribabu*

When rationally designed benzothiazole-zinc porphyrin dyads were assembled with imidazole-appended fullerene[C_{60}/C_{70}]pyrrolidines via axial co-ordination to the zinc center of the dyads, supramolecular triads that behave as artificial photosynthetic models of the photosynthetic antenna-reaction center complex were obtained. Photoexcitation of the BTZ moiety resulted in the singlet-singlet energy transfer (PEnT) from '1BTZ*' to ZnP forming singlet excited ZnP followed by the electron transfer (PET) from '1ZnP*' to fullerene mimicking the synergic energy-electron events in antenna-reaction center complexes of natural photosynthesis.

Hexathianonaphyrin(1.0.0.1.0.0.1.0.0): Synthesis, optical, redox and protonation induced antiaromaticity

Jayaprakash Ajay, Thondikkal Sulfikarali, Kakarlamudi Akhil Chakravarthy, Vennapusa Sivaranjana Reddy and Sabapathi Gokulnath*

A simple non-rigid precursor termed as a “triheterole” was prepared and allowed to undergo acid catalyzed condensation in the presence of Lewis acid (BF_3·Et_2O) to produce the [3+3+3] cyclotrimer 1. Electronic absorption and NMR studies suggest a (4n)π-conjugated circuit. The expected C_3 symmetry of 1 in solution could not be seen from its unsymmetric NMR features due to its large conformational flexibility. Theoretical assessments, e.g. nucleus-independent chemical shift (NICS) revealed a weak antiaromatic character attributed to the large fluxional behavior of 1 in solution as inferred from the 'H NMR chemical shifts.

An AIE active BODIPY based fluorescent probe for selective sensing of Hg^{2+} via dual mechanism PET and CHEF

Vishwa Deepak Singh, Rajendra Prasad Paitandi, Yogesh Kumar and Daya Shankar Pandey*

The BODIPY based ligand (L) was synthesized and its photophysical and aggregation behavior was established with the help of various spectroscopic studies (UV-vis, fluorescence and SEM). L was employed for the detection of mercury ion (Hg^{2+}) based on dual mechanism (PET and CHEF).
Effect of solvent on the electronic absorption spectral properties of mixed β-octasubstituted free base tetraphenylporphyrins

P. Bhyrappa* and U.K. Sarangi

Optical absorption spectra of a family of mixed β-octasubstituted free base mesotetraphenylporphyrins with varying degrees of orthogonal dipole moment were examined in different solvents. The red-shift in their absorption bands was recorded as high as 75 nm in Q(0,0) and about 30 nm in the B band. This has been ascribed to solvation and solvent...N4H2 (porphyrin core) interactions in polar solvents.

Electronic structure and reactivity of heme bound insulin

Madhuparna Roy, Ishita Pal, Chinmay Dey, Abhishek Dey* and Somdatta Ghosh Dey*

When heme is incubated with insulin in a 1:1 stoichiometric ratio, heme binds insulin to form a six-coordinate high spin species as the major component with a possible mono-His coordination and a weakly bound water derived ligand in the distal site. In presence of excess insulin, the six-coordinate low spin species, with a probable bis-His coordination, predominates. When the heme-amylin complex is treated with two equivalents of insulin, the latter sequesters heme from the former, forming heme-insulin (with the six-coordinate low spin species as major component) thereby significantly reducing the PROS formation.

Fluoro-bridged dimanganese(III) porphyrin dimer: Effect of intermacrocyclic interactions in modulating metal spin state

Debangsu Sil, Sayantani Banerjee, Sudip Kumar Ghosh and Sankar Prasad Rath*

A remarkably bent dimanganese(III)-μ-fluoro porphyrin dimer is reported. Unlike its diiron analog, two equivalent high-spin manganese(III) centers with equally distorted porphyrin rings are observed in the complex.

Donor–acceptor conjugates derived from cobalt porphyrin and fullerene via metal-ligand axial coordination: Formation and excited state charge separation

Dili R. Subedi, Youngwoo Jang, Ashwin Ganesan, Sydney Schoellhorn, Ryan Reid, Guido F. Verbeck IV and Francis D’Souza*

The occurrence of photoinduced energy and electron transfer events in newly assembled cobalt porphyrin-fulleropyrrolidine assembled via metal-ligand axial coordination, probed by spectroscopic, electrochemical and ultrafast spectroscopic techniques is reported.
β-Disubstituted silver(III) corroles: Facile synthesis, photophysical and electrochemical redox properties
Inderpal Yadav, Divyansh Dhiman and Muniappan Sankar*

A series of β-disubstituted Ag(III) tritolylcorroles (2–5) were synthesized via Pd-catalyzed reactions. Methyl acrylate appended Ag(III) corrole (4) exhibited high ground state dipole moment (10.31 D) which could be the potential candidate for nonlinear optical (NLO) applications.

Electrochemical characterization of β,β'-butanoporphyrrins containing sterically hindered meso-2,6-dihalogenophenyl substituents and first-row transition metal ions in nonaqueous media
Yueping Hou, Yuanyuan Fang*, Zhongping Ou, Liping Wang, Weijie Xu and Karl M. Kadish*

The β,β'-butano substituted tetra(dihalogenophenyl)porphyrins containing first row transition metal ions were synthesized and characterized as to their electrochemical properties. The effect of butano and meso-sterically hindered substituents on redox potentials and mechanism is discussed.

meso-Carbazole substituted palladium porphyrins: Efficient catalysts for visible light induced oxidation of aldehydes
Anu Janaagal, Vijayalakshmi Pandey, Sudhir Sabharwal and Iti Gupta*

Pd(II) porphyrins having N-butylcarbazole and p-cyanophenyl groups on their meso-positions were synthesized and characterized. These porphyrins showed triplet emission ~670 nm and significant amounts of singlet oxygen generation upon light exposure. The photo-catalytic application of Pd(II) porphyrins for aerobic oxidation of aromatic aldehydes is demonstrated.