

## Supramolecular assemblies for molecular scale information transport processes\*

V. KRISHNAN

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, and Chemical Biology Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), IISc Campus, Bangalore 560 012, India.

### Abstract

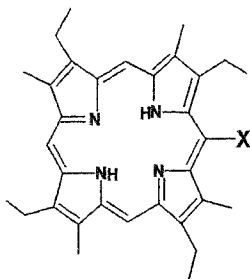
The increasing interest in miniaturization of electronic components has stimulated research on supramolecular assemblies with device-like functionalities. This article explores some of the interesting aspects of porphyrin assemblies beginning with the desirable attributes of basic porphyrin core such as its response to photons of different frequencies and its reactivity at the electrode surface. The careful design and synthesis of covalently linked nanoscopic molecular assemblies consisting of three or four porphyrin units are described. The critical choice of the different porphyrin units in the assembly depend on the desired functionality, viz. molecular wire, charge-storage device or optoelectronic device. The presence of redox distinct porphyrin units in the assemblies confers wire- or charge-storage-like functionalities and of spectrally distinct porphyrin units in the assembly leads to optoelectronic devices. It is shown that a judicious combination of both these features can be incorporated into the molecular assembly that displays optoelectronic device-like functionalities. These studies provide insight into the creation of molecular systems of nanoscopic dimensions with properties and functions determined by their electronic structures.

**Keywords:** Porphyrin assemblies, excitation energy transfer, electron transfer, device-like functionalities.

### 1. Introduction

In recent years there has been a tremendous interest in the design and synthesis of large molecular systems of nanometric size endowed with certain functionalities. The main strategy for these endeavours is to ultimately employ molecules as integral components in electronic devices. This has resulted in the new area of research 'molecular electronics.' The syntheses of these molecules are either carefully designed and executed or the basic molecular unit is tailored in a manner to induce self-assembling of the units resulting in supramolecular systems. The design criteria include induction of functionalities such as redox, magnetic, photochemical and photophysical, catalytic and other properties. The introduction of required functionality into the molecular systems is to individually manipulate or address for reading or writing of information to a molecular bit. Two conditions have to be met by the designer molecule to qualify as a component in an electronic device, the first being to respond to photons (optical) at different frequencies and the second to external electric field and applied voltage (electronic). Hence, if a molecular assembly responds to both photons and applied electric field

\*Text of lecture delivered at the Annual Faculty Meeting of the Jawaharlal Nehru Centre for Advanced Scientific Research at Bangalore on November 13, 1998.



**X = NH<sub>2</sub>, H, CH<sub>2</sub>OH, CHO, Cl, NO<sub>2</sub>**

FIG. 1. Chemical structure of aetioporphine is shown here with different substituents. The basic porphine core is without the substituents.

then it satisfies the condition as a component for optoelectronic devices. The essential components for molecular scale information transport process consists of wires, logic switches and gates and memory devices. In chemical language, one can define the components as follows. Molecular wires are those systems which are endowed with extensive  $\pi$  conjugation capable of mediating electronic delocalisation or electron transfer between the ends. The molecular switch is simply a system which interrupts the flow of electrons across an external stimulus. On the other hand, a molecular assembly can be designed in such a way that it interconverts to different states reversibly. This essentially implies that these systems can be utilized as energy storage devices. Recent literature<sup>1,2</sup> is abundant with examples of molecular systems that can be used as components in electronic devices.

## 2. The basic building block: Porphyrins

This paper essentially outlines recent advances made in the author's laboratory employing basic molecular systems, porphyrins and related cyclic conjugated tetrapyrrole entities. These units are present extensively in biological systems performing diverse functions starting from light harvesting and electron transfer in photosynthesis to catalytic oxidations and electron transfer in cytochromes, cytochrome-oxidase and others. These functions are related to the structures of these systems. The basic unit porphine (Fig. 1) is a 22-electron cyclic  $\pi$  system<sup>3</sup> and the electronic structure is described in terms of four-orbital model of Goutermann<sup>4</sup> (Fig. 2). Optical transitions in this unit are classified as  $Q_x$  and  $Q_y$  bands (in the visible regions) and  $B_1$  and  $B_2$  correspond to Soret bands. These arise from a linear combination of the molecular orbitals,  $b_1$  and  $b_2$  (two nearly degenerate highest occupied molecular orbitals, HOMO) and  $c_1$  and  $c_2$  (two degenerate lowest unoccupied molecular orbitals, LUMO) in a  $D_{4h}$  symmetry.

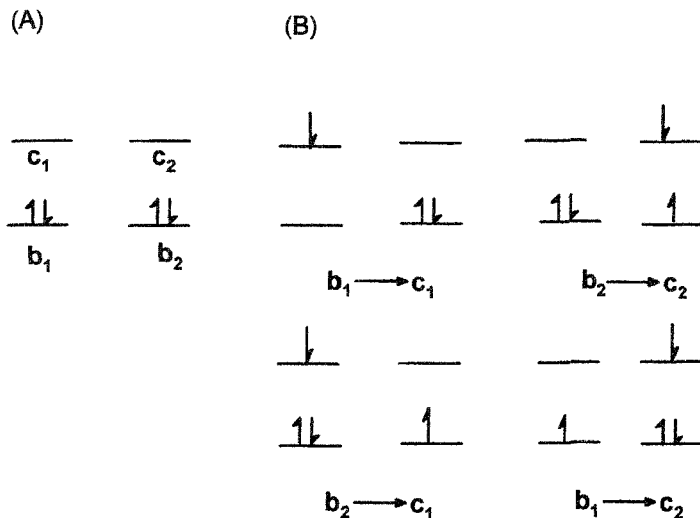
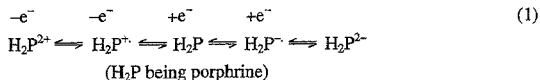
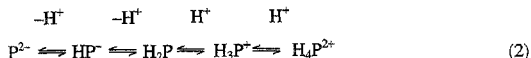


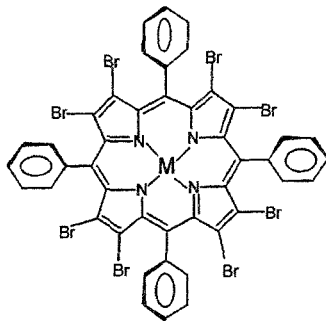
Fig. 2. Four-orbital model of porphyrin. (A) Ground and (B) excited states.

These systems also display sharp singlet and triplet emission features. In view of the unique electronic structure of these systems, they undergo reversible one-electron redox reactions at the electrode surface.



The potentials at which these reactions occur are in the convenient range to perform chemical reactions. The difference between the first one-electron reversible oxidation and reduction electrochemical potentials of the porphyrins is directly related to HOMO/LUMO difference. This immediately implies that a measure of the redox potentials of the porphyrins leads to a quantitative estimate of the energy of the molecular band gap,  $E_m$ , akin to band gap in semiconductors. The design of molecules with different  $E_m$  is then possible through purely chemical routes. In addition, the free-base porphine (with two inner imino nitrogens in tact) undergo protonation and deprotonation reactions resulting in the highly charged cations and anions with characteristic absorption and emission spectra.





M = 2H, VO(IV), Co(II), Ni(II), Cu(II),

Ag(II), Zn(II), Pd(II), Pt(II)

FIG. 3. Chemical structure of octabromo tetraphenylporphyrin and its metal (II) derivatives.

The interesting optical and electrochemical properties of the porphine confer important features for these systems to be ideally suited as components in electronic devices (optoelectronic devices). In what follows now, we shall describe a few interesting representative systems that have been developed in the course of our research efforts.

### 3. Variation of molecular band gaps of the basic core

It is recognized that the optical transition energies and electrochemical redox potentials of the planar porphyrin molecule can be altered in different ways either by changing the molecular symmetry or through electronic effects. The distortion of the planar core can be accomplished either by substitution at the porphyrin periphery with different nature of the substituents or through introduction of metal ions of appropriate size into the porphyrin core. The modification of the planar core results in the change of electronic structure and hence the energies of HOMO/LUMO levels. Octabromo tetraphenylporphyrin (Fig. 3) is one of the excellent examples.<sup>5,6</sup> The eight bromine atoms at the porphyrin periphery due to mutual bromine-bromine van der Waals repulsion result in the perturbation of the planar core. The distortion of the porphyrin core brought about by octa substitution of alkyl, phenyl, halogen and other substituents is documented in literature. It is known that substitution at the  $\beta$ -positions of the tetraphenylporphyrins produces dramatic changes in the structural parameters compared to that of the substitution at the *meso* aryl groups. The basic feature as to the number of minimum substituents that cause the distortion of the porphyrin has been addressed. A representative example of the extent of distortion of the porphyrin core in a few bromo- and nitro-substituted porphyrins is shown in Fig. 4. Optical parameters and redox data of these porphyrins are

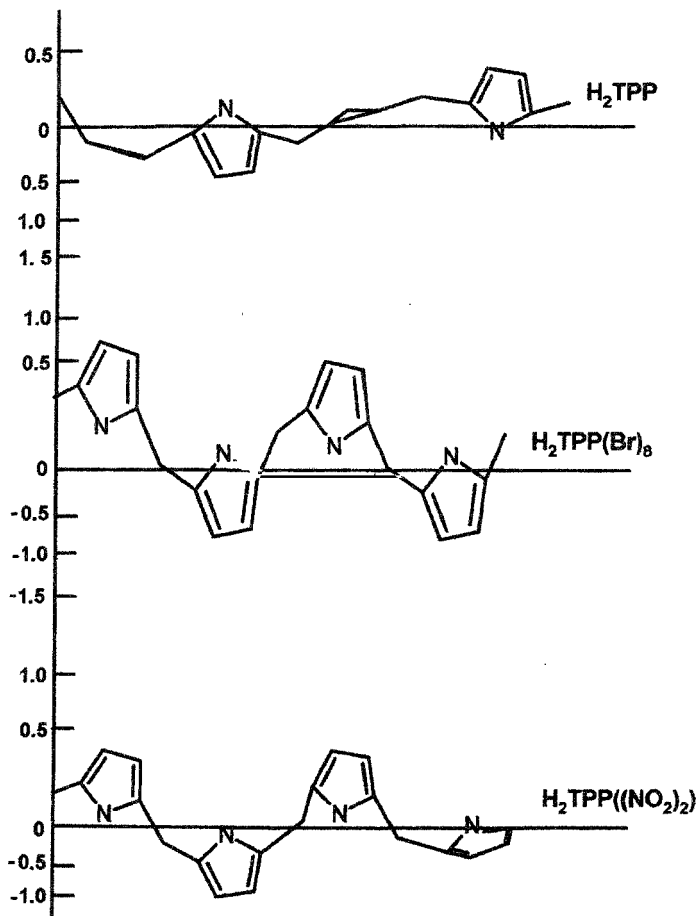


FIG. 4. The extent of distortion of the porphyrin core in different porphyrins is derived from single crystal diffraction studies. The pyrrole-substituted free-base porphyrins are shown: unsubstituted tetraphenylporphyrin ( $H_2TPP$ ), octabromo tetraphenylporphyrin,  $H_2OBP$  and 3,12-dinitrotetraphenylporphyrin,  $H_2TPP.2NO_2$ . The distortion of the pyrrole ring away from the planarity is shown in the y scale.

**Table I**  
Optical and electrochemical redox properties of a few representative tetraphenylporphyrins<sup>a</sup>

Compound	Optical data (nm)		$E_m^d$ (eV)
	Absorption	Emission	
H <sub>2</sub> TPP	418, 514, 548, 590, 647	652, 710 <sup>b</sup> (11.0)	2.09
H <sub>2</sub> TPP Br <sub>8</sub>	469, 569, 626, 743	762, 790, 825 <sup>c</sup> (113)	1.64
H <sub>2</sub> TPP2NO <sub>2</sub>	438, 538, 628, 687	766 <sup>b</sup> (1.05, 3.22)	1.84
ZnTPP	420, 549, 589	597, 645 <sup>c</sup> (2.10)	2.16
ZnTPPBr <sub>8</sub>	466, 598, 656	725, 765, 825 <sup>c</sup> (230)	1.89
ZnTPP2NO <sub>2</sub>	437, 567, 613	708 <sup>b</sup> (2.56, 1.06)	1.90

<sup>a</sup>The data in CH<sub>2</sub>Cl<sub>2</sub> solvent at room temperature 298 K; <sup>b</sup>: singlet emission with lifetime in ns in parenthesis; <sup>c</sup>: triplet emission with lifetime in ns in parenthesis; <sup>d</sup>:  $E_m = E_{1/2}(\text{ox}) - E_{1/2}(\text{red})$ ,  $E_{1/2}$  (one-electron ring redox potentials).

shown in Table I. Distortion of the porphyrin core results in large changes in optical and electrochemical redox properties. The puckering of the porphyrin nucleus leads to relative ease of one-electron ring reduction potentials followed by difficult one-electron ring oxidation potentials. This feature has been exploited for the catalytic photooxidation of organic substrates by bromo-substituted porphyrins. Optical absorption and emission bands of the highly distorted porphyrins are found to shift to the red region of the electromagnetic spectrum followed by reduced singlet and triplet lifetimes. These features have been analysed using theoretical calculations. It is found that electronic factors induced by nitro and bromo substituents contribute only 20–30% to changes in optical and redox properties. Hence, these studies bring forth clearly the desirable effects of distortion of porphyrin in altering the energy of the molecular band gap and also photophysical properties.

The electronic effects of the substituents at the porphyrin periphery have been analysed in a few cases. It is found in the course of our work that it may be necessary to have porphyrins with small changes in the one-electron ring redox potentials and slightly varying optical absorption and emission bands. This is essential for the design of a supramolecular assembly consisting of porphyrin arrays with differing optical and redox properties. These porphyrin arrays would then be ideal candidates for the transfer of electronic excitation energy within and between molecules. Such studies are important to the understanding of light harvesting systems in natural photosynthetic process. These molecular systems can also function as light conversion molecular devices (Fig. 5) operating on a three-step mode: absorption → energy transfer → emission. An additional feature of these porphyrin arrays is the presence of redox porphyrin units constituting the assemblies. Multiple redox sites in porphyrin array provide the possibility of electron transfer from one porphyrin to another in a successive manner due to gradient in the one-electron redox energies of the individual porphyrin units in the assembly.

A series of tetraphenylporphyrin with different substituents in the *meso* aryl groups and also in  $\beta$ -pyrrole carbons have been synthesised and their electrochemical, optical and magnetic resonance properties studied (Fig. 6). The presence of electron-donating and withdrawing substituents in the porphyrin periphery results in interesting changes of the physical

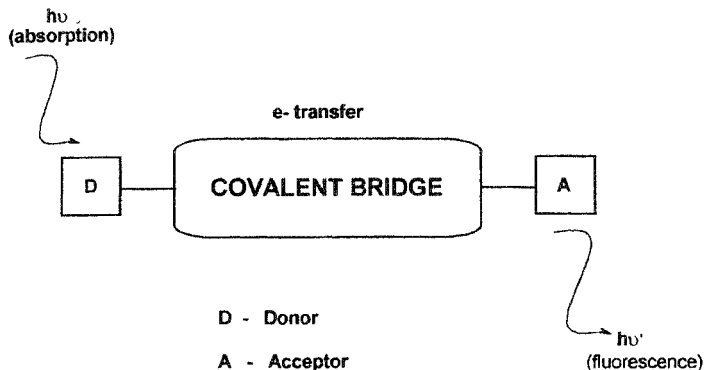
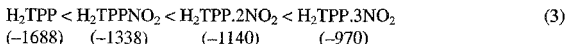


Fig. 5. Schematic illustration of the light-conversion molecular device.

properties. The presence of  $\text{NO}_2$  group in one of the  $\beta$ -pyrrole carbons diminish the magnitude of the one-electron ring reduction potential by  $\sim 300\text{mV}$  relative to that observed for the unsubstituted tetraphenylporphyrin.<sup>7,8</sup> The introduction of more than one nitro group at the pyrrole carbons successively reduces the magnitude of one-electron reduction potentials as indicated below. The reversible one-electron ring reduction potentials in mV referenced against SCE are given in parenthesis.



In a related study, a series of porphyrins have been synthesised endowed with a nitro group in one of the pyrrole carbons and varying substituents in the *meso* aryl groups. The motivation behind this study is to investigate the effect of substituents in the *meso* aryl groups on the ring redox potentials of the mononitrotetraphenyl porphyrin. The manner in which the one-electron ring reduction potentials of the mono  $\beta$ -nitro tetraphenylporphyrin is modulated is given in a series of representative porphyrins:<sup>9</sup> mononitrotetramesityl porphyrin > mononitrotetra (2, 5-difluoro phenyl) porphyrin. The gradual variation of one-electron ring oxidation and reduction potentials in these porphyrins and their optical properties suggest that these units can be assembled together in the construction of molecular porphyrin assembly. The earlier studies on distorted porphyrins (vide infra) provide additional basic units to couple the excitation energy transfer with electron-transfer systems.

It is worthy to mention here that the variation in the molecular band gap,  $E_m$  of the porphyrins can be accomplished by using different metal ions in the porphyrin core. This provides an additional method to induce changes in the optical and electrochemical redox properties of porphyrin without going through substitution reactions at the porphyrin periphery. It is of interest to note that metal ions such as  $\text{Co(II)}$ ,  $\text{Ag(II)}$  and  $\text{Ni(II)}$  in the porphyrin core undergo

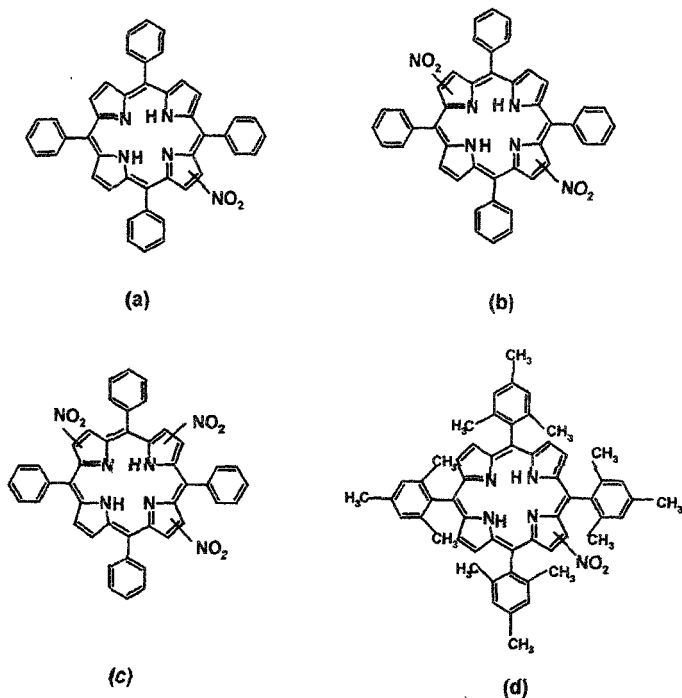


FIG. 6. Chemical structures of (a) mono nitro, (b) dinitro, and (c) trinitro tetraphenylporphyrins. The structure of one of the aryl-substituted porphyrin and (d) mononitrotetramesityl porphyrin is shown.

reversible one-electron reduction and oxidation of the metal ions within the potential range of one-electron ring redox potentials of the porphyrins. Thus, the presence of oxidized [Co(III), Ag(III) and Ni(III)] and reduced [[Co(I), Ag(I) and Ni(I)] porphyrins have pronounced effect in shifting the one-electron ring redox potentials. This additional feature furnishes an important aspect in the design of the porphyrin arrays with different metal ions.

#### 4. Tri- and tetrameric assemblies

Attempts have been made to design and synthesise large macrocyclic porphyrins that fold or assemble to form large well-defined structures.<sup>10,11</sup> A critical element which is often difficult to



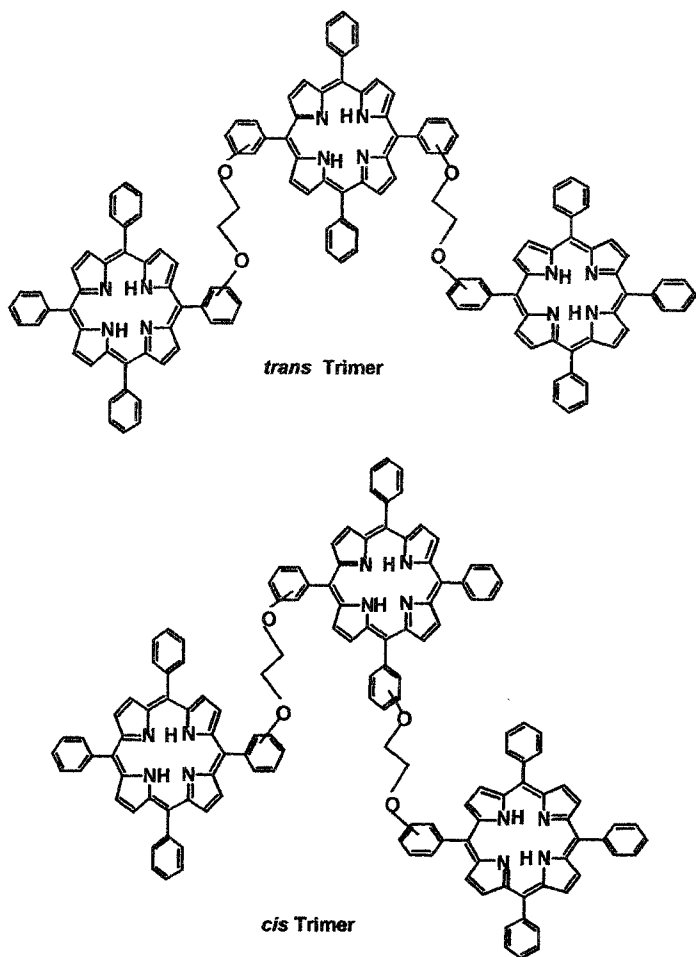
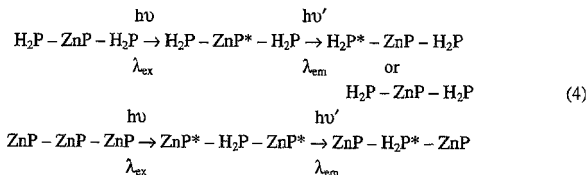


Fig. 7. Structure of *trans* and *cis* tetraphenylporphyrin trimers.

control in synthetic models is the geometry and distance that separates the donor and acceptor. Covalently linked trimeric and tetrameric porphyrin assemblies are known to display charge separation and electron-transfer reactions. Here we present tri- and tetrameric porphyrin assemblies endowed with identical porphyrin units<sup>12</sup> (Figs 7 and 8). The spectral distinction of these units has been brought about by incorporating specific metal ions paving ways to demonstrate excitation migration in these systems akin to that depicted below.



The steady-state and time-resolved studies on these porphyrins revealed efficient excitation energy transfer from ZnP unit to the H<sub>2</sub>P unit. The mechanism of energy transfer in these systems

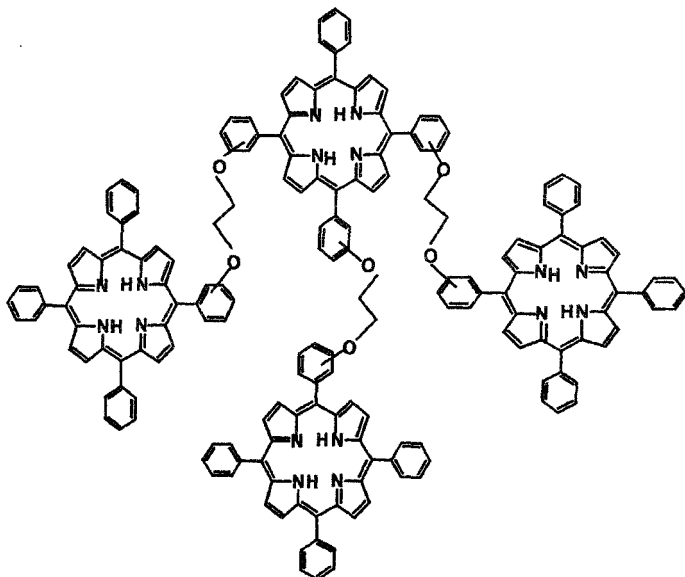


Fig. 8. Structure of the tetrameric tetraphenylporphyrin unit.

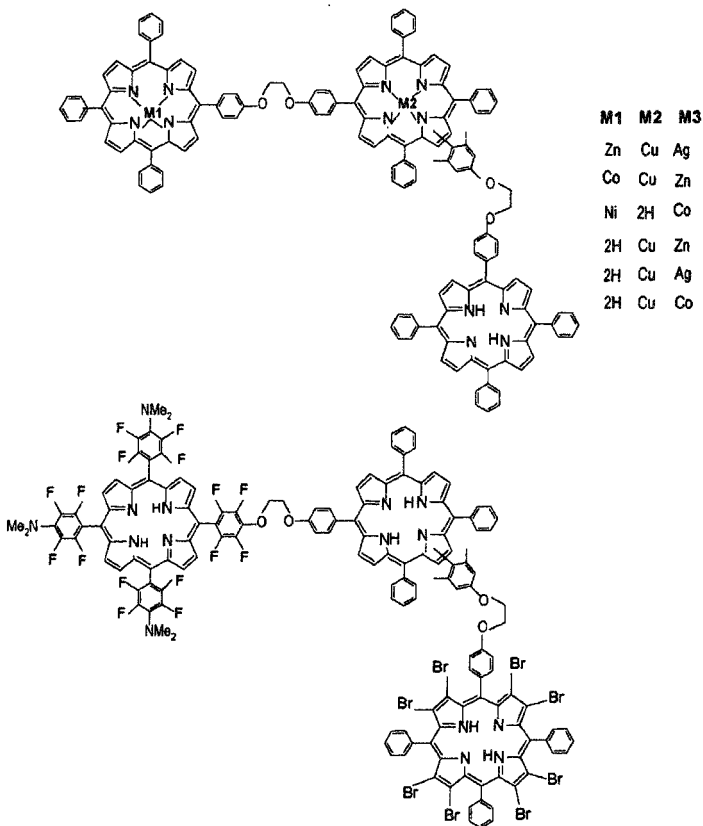


FIG. 9. Structure of the porphyrin trimers containing different metal ions and also trimers consisting of differently substituted porphyrins.

tems is essentially of Förster type and proceeds through space with a critical Förster distance ( $R_0$ ) of  $\sim 25\text{\AA}$ . The efficiency and rate of energy transfer are dependent on the number of free-base units in the hetero-oligomers and the geometrical position of the units. A possible reason for this lies in the presence of conformationally mobile ethylene oxide covalent bridges

in these trimers. Molecular modelling studies revealed the folding of only one of the porphyrin units towards central unit with the other porphyrin ring positioned perpendicular to the cofacial

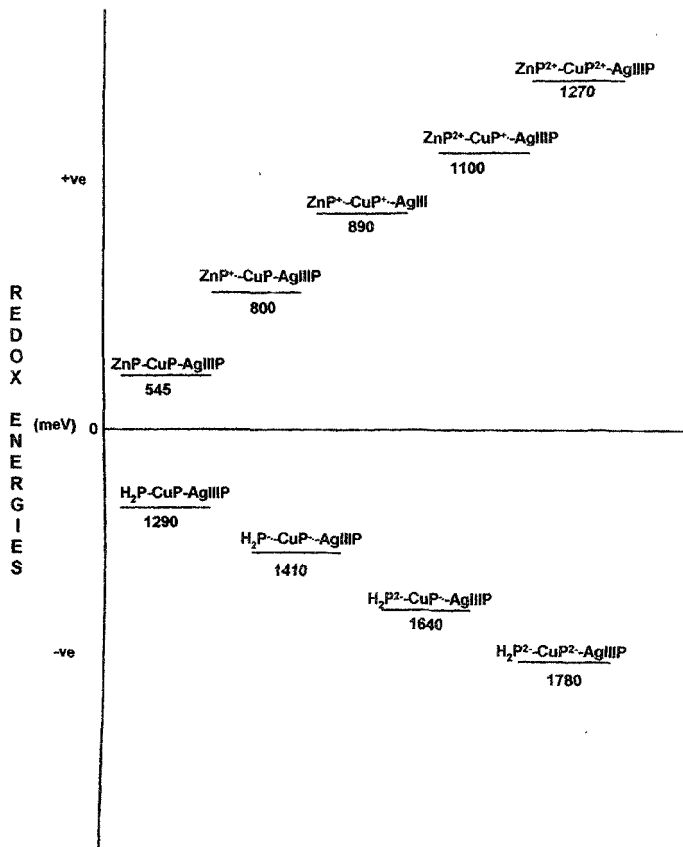


FIG. 10. The one-electron oxidation (positive) and reduction (negative) energies respectively of  $\text{ZnP-CuP-AgP}$  and  $\text{H}_2\text{P-CuP-AgP}$  trimeric systems are pictorially represented along with the corresponding states. The potentials are referenced against SCE and arbitrarily depicted as zero energy. The  $\text{Ag(II)}$ -centered oxidation at 545 mV results in  $\text{ZnP-CuP-Ag}^{\text{III}}\text{P}$ . The other redox reactions are porphyrin ring centered.

unit in the case of *m/p cis* trimers. The time-averaged geometries of the tri- and tetrameric porphyrin assemblies indicate that the optical excitation at one end of the porphyrin unit permits efficient energy migration resulting in the emission of light at longer wavelength. In addition to the demonstrated efficient energy transfer in these heterometalloporphyrins these supramolecular porphyrin assemblies provide interesting redox systems.

A few novel porphyrin trimeric assemblies either consisting of different porphyrin units or those bearing dissimilar metal ions have been reported<sup>13, 14</sup> (Fig. 9). Importantly, the trimers consisting of monomeric porphyrins with large differences in the ground state absorption spectrum cover a wide range of solar spectrum with intense bands at different regions and each moiety could be selectively excited for a specific photochemistry. The electrochemical redox behaviour of these trimers displays both ring- and metal-centered redox reactions. It is of interest to note that these metal-centered oxidation/reduction reactions can be rationalized in terms of involvement of *d*-orbitals (not easily accessible) in the case of metal ions while the delocalized  $\pi$ -systems are easily available for oxidation/reduction reactions. The appearance of metal-centered oxidation/reductions is clearly seen in  $H_2P-CuP-CoP$ ;  $H_2P-CuP-AgP$  and  $ZnP-CuP-AgP$  systems. The five reversible oxidations of one of the trimers,  $ZnP-CuP-AgP$ , are shown in Fig. 10 along with four reductions of  $H_2P-CuP-AgP$ . In other words, the molecular band gaps of different porphyrin units in the supramolecular trimer depicted in Fig. 10 clearly signify that these molecular entities are potential molecular wires. The graded energies of the band gaps furnish an easier path for the electron from one end to the other. Interestingly, these trimers can be used as storage for large number of electrons and hence have utility as storage devices.

## 5. Conclusion

The supramolecular porphyrin assemblies discussed above are a few among the other similar systems described in literature. The importance of having porphyrin as a basic unit in the design and construction of supramolecular assemblies is well illustrated. Interesting features such as photoinduced reactions in these assemblies are not discussed apart from gradient in ground-state electrochemical redox potentials. The excited singlet states of the porphyrin units are highly oxidative in nature and thus open an entirely new way of looking at the systems. Typically, the energy and electron transfer pathways in the trimers and tetramers can easily be modulated with careful design of positioning an appropriate porphyrin unit. These studies are not discussed here. Another point of interest is the deliberate choice of ethylene oxide spacer groups in these assemblies in contrast to the  $\pi$ -bonded bridging groups. Ethylene oxide groups predominantly exist in *gauche* form and this provides proximity to the porphyrin units. The presence of these groups also furnishes good binding site of monovalent alkali cations which in principle organize the supramolecular entities in an ordered fashion. Efforts in this direction are being pursued. A combinatory library of large number of porphyrin units with different substituents and their photophysical and electrochemical redox properties has been built up in our research group to accomplish molecular devices with optoelectronic functionalities.

### Acknowledgement

The author thanks all his co-workers whose names appear in the reference list for their untiring work that enabled to present a cogent theme. The author is grateful to them. Thanks are also due to the Department of Science and Technology, Government of India, New Delhi, for financial support. In all these endeavors, JNCASR has been rendering crucial support and the author owes his thanks to the Centre.

### References

1. OLENYUK, B., FECHTENROTTER, A. AND STANG, P. J. *J. Chem. Soc. Dalton Trans.*, 1998, 1707–1725.
2. WARD, M. D. *Chem. Ind.*, 1996, 568–571.
3. SHEELA RAO AND KRISHNAN, V. *J. Mol. Struct.*, 1994, **327**, 279–284.
4. GOUTERMANN, M. *J. Mol. Spectrosc.*, 1961, **6**, 138–143.
5. BHYRAPPA, P. AND KRISHNAN, V. *Inorg. Chem.*, 1991, **30**, 239–245.
6. BHYRAPPA, P. AND KRISHNAN, V. *Chem. Lett.*, 1993, 869–871.
7. SANJAY DAHAL AND KRISHNAN, V. *J. Photochem. Photobiol.*, 1995, **89**, 105–110.
8. SANJAY DAHAL AND KRISHNAN, V. *Chem. Phys. Lett.*, 1997, **274**, 390–394.
9. SEN, A., ANANDHI, U., KIRUBA SEBASTIAN MARY, G. AND KRISHNAN, V. Unpublished results.
10. LEHN, J. M. *Supramolecular chemistry*, V.L.H. Weinheim, 1995.
11. ANDERSON, H. L. AND SANDERS, J. K. M. *Angew. Chem. Int. Edn.* 1990, 1400–1405.
12. VAIJAYANTHIMALA, G. AND KRISHNAN, V. *J. Porphyrins Phthalocyanines*, 1997, **1**, 17–28.
13. SEN, A. AND KRISHNAN, V. *Tetrahedron Lett.*, 1996, **37**, 5421–5423.
14. SEN, A., ANANDHI, U. AND KRISHNAN, V. *Tetrahedron Lett.*, 1998, **39**, 6539–6541.