DOI: 10.1002/asia.200700202

Axial-Bonding Heterotrimers Based on Tetrapyrrolic Rings: Synthesis, Characterization, and Redox and Photophysical Properties

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Abstract: We prepared two heterooligomeric arrays based on free base/metalloporphyrins at axial positions and a metalloid phthalocyanine as a basal scaffolding unit by using the axial-bonding capabilities as well as the known oxophilicity of dihydroxytin(IV) phthalocyanine. Both heterotrimers were completely characterized by elemental analysis, MALDI-TOF MS, and ^{1}H NMR (one- and two-dimensional), UV/Vis, and fluorescence spectroscopy as well as cyclic voltammetry. The ground-state properties indicate that there is minimal π–π interaction between the macrocyclic units. The excited-state properties show that there is electronic energy transfer competing with photoinduced electron transfer from the singlet state of the axial porphyrin to the central metalloid phthalocyanine and a photoinduced electron transfer from the ground state of the axial porphyrin to the singlet state of the central metalloid phthalocyanine.

Keywords: fluorescence spectroscopy · oligomers · photoinduced electron transfer · phthalocyanines · porphyrins

Introduction

Among the many interesting light-induced reactions, those inspired by natural photosynthesis have attracted special attention. As a result of extensive spectroscopic studies and detailed structural determinations, the photoinduced charge separation that takes place at the reaction center and the antenna effect carried out by light-harvesting units are now understood in great detail.[1] Artificial systems that mimic natural photoinduced processes are the subject of continuous research activity, fostered by the problem of solar-energy conversion.[2] In many of these artificial systems, oligomers based on porphyrins (and/or metalloporphyrins) and closely related compounds such as phthalocyanines (and/or metallophthalocyanines) play a major role as active chromophores.[3] Porphyrins and phthalocyanines display harmonizing optical transitions. In particular, porphyrins absorb radiation very strongly at around 420 nm (Soret band) and with medium strength in the range 500–650 nm (Q bands), and emit strongly at 650–700 nm (fluorescence quantum yield of 5,10,15,20-tetraphenylporphyrin (H_2TPP) = 0.11). On the other hand, the absorption bands of phthalocyanines and metallophthalocyanines occur at around 350 nm (Soret band) and in the range 600–750 nm (Q bands). The absorption wavelength of phthalocyanine mostly overlaps with the emission wavelength of porphyrins; an efficient electronic energy transfer (EET) is expected from porphyrin to phthalocyanine. Moreover, phthalocyanines are easier to reduce than porphyrins, which implies that an efficient photoinduced electron transfer (PET) is possible between the two. Thus, oligomeric arrays that contain porphyrin and phthalocyanine in the same molecular framework are expected to be effective in capturing a wide range of visible light efficiently. Such systems are particularly useful for mimicking natural photosynthesis, dye-sensitized solar cells, organic light-emitting diodes, and nonlinear optics.

Oligomers based on either porphyrins (and/or metalloporphyrins) or phthalocyanines (and/or metallophthalocyanines) are widely reported in the literature; they are constructed by using covalent, noncovalent, and metal-mediated interactions.[4] On the other hand, a few heterooligomers based on porphyrin–phthalocyanine systems were reported to contain various spacers such as imidazole, ethynyl, phenylethynyl, piperazinyl, alkoxy, spirocyclic, and ether groups.[5] Furthermore, heterooligomers were also reported to use metal–ligand interactions.[6] A heterodimer of phthalocyanine–subphthalocyanine was reported to be formed by

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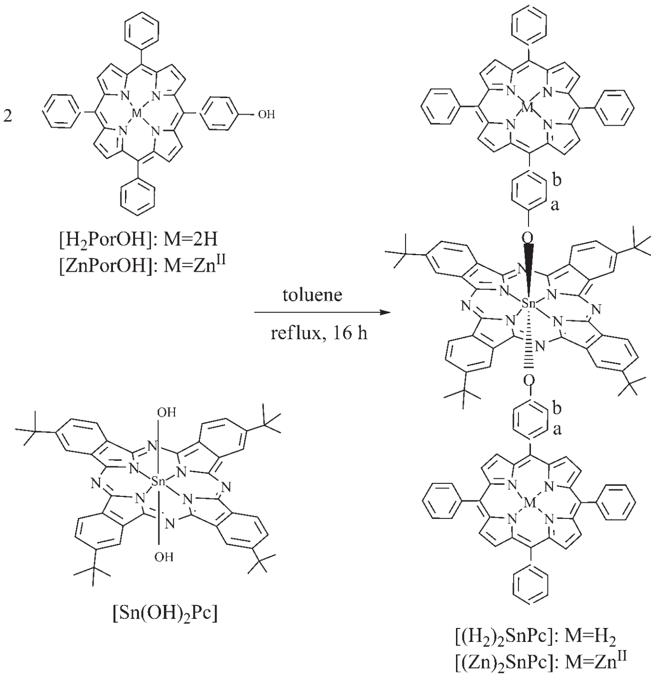
an ethynyl bridge.[7] The majority of these hitherto (hetero or otherwise)-reported oligomers were obtained by multistep and often cumbersome organic reaction sequences carried out at the peripheral positions of the porphyrin (either pyrrole-β- or -*meso*) and phthalocyanine. In contrast, utilization of "inorganic" reactions, which can be readily conducted, either at the phthalocyanine central cavity (e.g., metal/nonmetal ion insertion) or on the resident metalloid ion (e.g., metal–metal interaction, metal–ligand coordination, covalent-bond formation, etc.) appears to be an attractive and viable alternative approach for the facile construction of hetero-type macrocyclic arrays.

Maiya and co-workers reported homooligomers of metallo/metalloid porphyrin based branched arrays by using the "axial-bonding" concept; they studied EET and PET reactions in these oligomers.[8] Herein, we constructed heteroarrays for the first time by using the axial-bonding strategy as well as the oxophilicity of dihydroxytin(IV) phthalocyanine as a basal scaffolding unit and either a free-base porphyrin or metalloporphyrin as the axial donor subunits for the fabrication of these oligomers. Notably, reports of tin(IV) phthalocyanines have so far been limited to only their dichloro and dihydroxy compounds.[9]



Scheme 1. Synthesis of heterotrimers. Pc = phthalocyanine, Por = porphyrin.

Results and Discussion

Both the heterotrimers [$(H_2)_2$SnPc] and [$(Zn)_2$SnPc] were prepared by condensation of [$Sn(OH)_2$Pc] with an excess of [H_2PorOH] and [ZnPorOH], respectively, in toluene heated under reflux for 16 h (Scheme 1). The desired compound was obtained in 60 % yield in both cases after purification with column chromatography and recrystallization. Preliminary characterization of these new heteroarrays was carried out by MALDI-TOF MS and UV/Vis spectroscopic methods. The mass spectrum of [$(H_2)_2$SnPc] showed a peak at $m/z = 2120$ ($[M]^+$, $C_{136}H_{106}N_{16}O_2Sn$) ascribable to the molecular-ion peak. Subsequent peaks at $m/z = 1490$ and 856 can be ascribed to the detachment of one ($[M-C_{44}H_{29}N_4O]^+$) and two ($[M-2C_{44}H_{29}N_4O]^+$) axial free-base subunits from the basal Sn^{IV} phthalocyanine, respectively. A similar type of fragmentation was also observed in the case of [$(Zn)_2$SnPc]. The UV/Vis spectra of the heterotrimers and their corresponding precursor units were recorded in CH_2Cl_2, and the λ_{max} and ε values are presented in Experimental Section. Figure 1 shows the absorption spectrum of [$(H_2)_2$SnPc]. A comparison of the UV/Vis spectrum of the heterotrimer with the spectra of the corresponding precur-

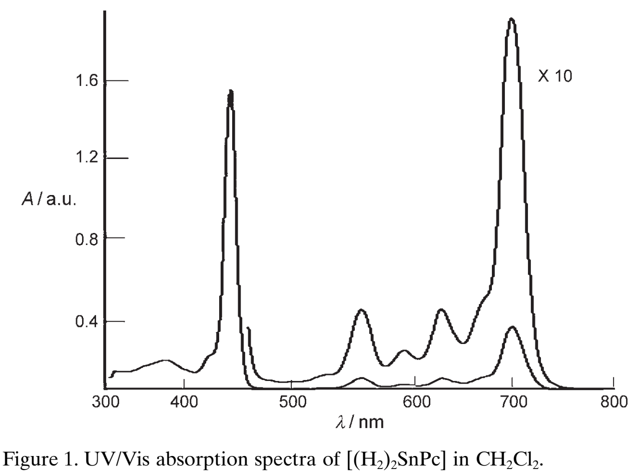


Figure 1. UV/Vis absorption spectra of [$(H_2)_2$SnPc] in CH_2Cl_2.

Abstract in Telugu:

హెటరో ఒలిగోమేరు బారుల. పోర్ఫైరిన్స్ పై భాగమున మరియు టిన్ (IV) తలోసయనిన్ మధ్య భాగమున. పై భాగపు బంధన సామర్థ్యము మరియు తెలిసిన ఒక్సోఫిలిసిటీ యొక్క టిన్ (IV) తలోసయనిన్ ను ఆధారము చేసికొని మేము మా పరిశోధన ఫలితాలను ప్రకటిస్తున్నాము. రెండు హెటరో త్రిభాగీయులు , CHN, MALDI-TOF, ^{1}H NMR (1D – మరియు – 2D – కొలత), UV/Vis మరియు flnoresceuce spectroscopy మరియు cyclic voltammetry ను ఆధారము చేసికొని సంపూర్ణముగా పరిశీలన చేసినము. ఈ హెటరో ఒలిగమర్స్ లో అత్యల్ప π - π సంఘర్షణ మ్యాక్రోసైక్లిక్ యూనిట్స్ లో ఉన్నావని గ్రౌండ్ స్థితి ధర్మములు తెలుపుచున్నవి . ప్రేరేపించే స్థితి ధర్మముల లో , శక్తి బాధలి మరియు ఎలెక్ట్రాన్ ల బాధలి పైన పోర్ఫిరిన్ ల సింగలెట్ స్థితి ఉంది గ్రౌండ్ స్థితి మధ్య తలోసయనిన్ కు మరియు ఎలెక్ట్రాన్ ల బాధలి గ్రౌండ్ స్థితి పైన పోర్ఫిరిన్ ల నుండి సింగలెట్ స్థితి మధ్య తలోసయనిన్ కు జరుగు చున్నవి .

sor units suggests that the λ_{max} values of both heterotrimers are found in the same range as those of the reference compounds. Furthermore, the ε values of the bands of the heterotrimers are nearly equal to sum of the ε values of the corresponding bands of the constituent monomers. Thus, the spectrum of each heterotrimer is more or less similar to the spectrum resulting from a combination (1:2 mol/mol) of the corresponding individual precursors [$Sn(OH)_2Pc$] and [H_2Por] or [ZnPor]. The features seen in the UV/Vis spectra of these heteroarrays, while establishing, to a certain extent, their structural integrities, reflect the lack of any exciton-coupling interactions between the individual macrocyclic units.[10] Exciton coupling is known to occur when there is complete delocalization of the excitation over the entire supermolecule and excitation of any particular component of the molecule is not possible. For example, various types of covalently or noncovalently linked porphyrin dimers, phthalocyanine dimers (e.g. face-to-face, slipped, etc.), and aggregates, which are characterized by π–π interactions between the constituent chromophoric units in them, were reported to show UV/Vis spectra distinct to those of the corresponding monomeric analogues.[4e,11] In particular, the λ_{max} and ε values of the Q bands and, more importantly, the Soret bands of these dimers/aggregates were reported to be sensitive to the strength of interaction between the monomeric π planes and the geometry of the ensembles. In contrast, the UV/Vis spectra of the heterotrimeric systems reported herein are quite similar to those of their monomeric constituents. Thus, the UV/Vis data reveal that there exists minimum interaction between the individual macrocyclic units in these arrays.

On the other hand, ^1H NMR spectroscopic investigations revealed that certain specific spectral features observed for the signals of the protons on the axial free-base porphyrins/metalloporphyrins are quite different from those observed for the same protons in the spectra of [H_2PorOH] and [ZnPorOH]. Figure 2 shows the 2D NMR spectrum of [$(H_2)_2SnPc$]; a similar spectrum was observed in the case of [$(Zn)_2SnPc$]. The structures of these new heterotrimers were determined on the basis of the resonance positions and integrated intensity data as well as the proton-to-proton connectivity information revealed in the COSY spectra. Thus, in the free-base heterotrimer [$(H_2)_2SnPc$], the signals for the phthalocyanine macrocyclic aromatic protons appeared at low field: multiplets at 9.83 and 9.74 ppm and a doublet at 8.45 ppm; these signals are similar to those of the isolated dihydroxytin(IV) phthalocyanine [$Sn(OH)_2Pc$]. The signals for the *tert*-butyl protons of phthalocyanine appeared at 1.30–1.90 ppm. On the other hand, the signal for all 16 β-pyrrole protons of porphyrin appeared at 8.80 ppm, as is the case with the isolated porphyrin [H_2PorOH]. The two doublets at 8.20 and 7.77 ppm belong to the phenyl protons of the porphyrins. On the other hand, the signals for the protons of the axial aryloxy group and the inner imino protons appeared differently for [$(H_2)_2SnPc$] than for the isolated [H_2PorOH]. The two doublets at 6.48 (d, 4H; Figure 2, b) and 3.17 ppm (d, 4H; Figure 2, a) belong to the protons *meta* and *ortho* to the oxo group ($J_{H,H} = 8.0$ Hz), respectively. This was also confirmed by the proton-connectivity pattern in the ^1H–^1H COSY spectrum. The signal for the inner imino protons of the axial free-base porphyrins appeared at −2.96 ppm, as opposed to that for the corresponding protons of [H_2PorOH], which appeared at −2.71 ppm. The protons on the aryloxy bridges of this heterotrimer experience the shielding effect of the central phthalocyanine and the deshielding effect of the axial porphyrins simultaneously.[12] Similar shielding and deshielding effects were also observed in the case of [$(Zn)_2SnPc$]; the only difference is the absence of inner imino protons here. This shielding and deshielding effect of these heteroarrays suggests that the orientation between the π planes is of the "vertical" type and certainly not of the face-to-face (parallel) type, in which additive shielding effects, as reported for the axial protons of the "wheel-and-axle"-type porphyrins and face-to-face phthalocyanines, would be expected.[11] A similar shielding effect was also observed in aryloxysilicon(IV) phthalocyanines as well as Ru^{II} phthalocyanine based heterooligomers.[6,13] All these ground-state properties suggest that there exists minimal π–π interactions between the macrocyclic units of these heterotrimers.

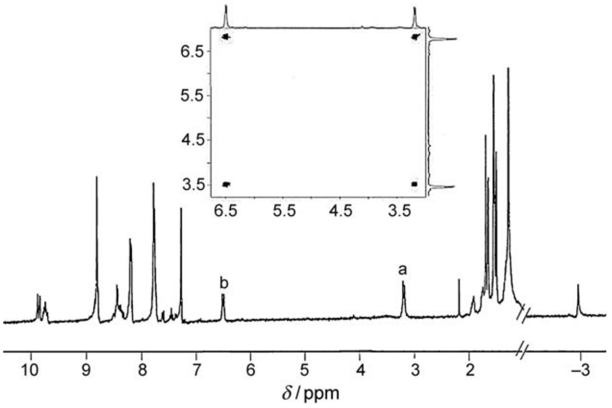


Figure 2. ^1H NMR spectrum of [$(H_2)_2SnPc$] ($CDCl_3$, tetramethylsilane (TMS)). Inset: ^1H–^1H COSY spectrum of [$(H_2)_2SnPc$], clearly showing cross-peaks resulting from coupling of the spacer *meta* and *ortho* protons.

With a view to evaluating the energies of the charge-transfer states (E_{CT}), which, as will be discussed later, are useful quantities for analyzing the photochemical properties of these heterotrimers, we carried out an electrochemical investigation. Figure 3 shows the cyclic voltammograms of both heterotrimers, and Table 1 summarizes the redox-potential data along with that of the relevant monomeric analogues. Each heterotrimer undergoes up to four reduction steps and up to four oxidation steps in CH_2Cl_2 and 0.1 M tetrabutylammonium perchlorate (TBAP). Wave analysis suggested that, in general, whereas the first three reduction steps and the first two oxidation steps are reversible ($i_{pc}/i_{pa} = 0.9$–1.0), diffusion-controlled ($i_{pc}/\nu^{1/2} =$ constant for scan rate $\nu = 50$–500 mV s^{-1}) one-electron transfer ($\Delta E_p = 60$–70 mV; $\Delta E_p = (65 \pm 3)$ mV for ferrocenium/ferrocene couple) reactions, the subsequent steps are, in general, either quasirever-

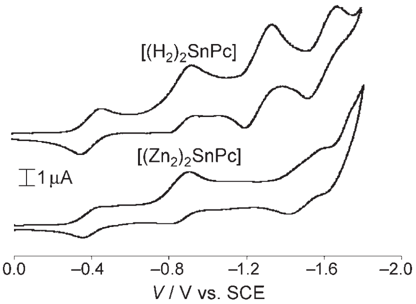


Figure 3. Cyclic voltammograms of $[(H_2)_2SnPc]$ and $[(Zn)_2SnPc]$ in CH_2Cl_2 and 0.1 M TBAP (scan rate $100\,mV\,s^{-1}$). SCE = saturated calomel electrode.

Table 1. Redox-potential data.[a]

Compound	Potential [V] vs. Ag/AgCl Reduction	Oxidation	$E_{CT}(Pc^{-}P^{+})$	$E_{CT}(Pc^{+}P^{-})$
$[H_2Por]$	−1.21, −1.51	1.01, 1.39	–	–
$[ZnPor]$	−1.40, −1.71	0.74, 1.09	–	–
$[Sn(OH)_2Pc]$	−0.44, −0.80, −1.33, −1.62	0.92,[b] 1.33	–	–
$[(H_2)_2SnPc]$	−0.38, −0.81, −1.22, −1.60	0.92,[b] 1.15, 1.35, 1.46	1.30	2.14
$[(Zn)_2SnPc]$	−0.38, −0.82, −1.40, −1.71	0.74, 0.97,[b] 1.09, 1.34	1.12	2.37

[a] CH_2Cl_2, 0.1 M TBAP, glassy carbon working electrode, Pt auxillary electrode. Error limits for $E_{1/2}$ ±0.03 V. [b] Quasireversible or irreversible.

sible ($E_{pa}-E_{pc}=90$–200 mV, $i_{pc}/i_{pa}=0.5$–0.8 for $\nu=100$–$500\,mV\,s^{-1}$) or totally irreversible. Nonetheless, on the basis of the redox data of the individual monomers, we attempted to assign the peaks to the basal phthalocyanine and axial porphyrins separately. Analysis of the data in Table 1 revealed that the electrochemical redox potentials of the heterotrimers are in the same range as those of their corresponding monomeric analogues. Indeed, the energies of the possible charge-transfer states (i.e., $E_{CT}(M^{+}Sn^{-})$ and $E_{CT}(M^{-}Sn^{+})$, in which $M=H_2$ or Zn) of these heterotrimers, as evaluated from the redox-potential data, testify to this conjecture.

Unlike the ground-state properties, major differences were noticed between the singlet-state activities of the heterotrimers and their corresponding individual constituents. From the absorption data (see Experimental Section and Figure 1), it is clear that these heterotrimers can be exclusively excited at either the porphyrin or the phthalocyanine absorption maximum. Figure 4 shows the emission spectra of $[(H_2)_2SnPc]$ and $[(Zn)_2SnPc]$ and their individual constituents, and the corresponding singlet-state data are presented in Table 2. With excitation at 420 nm, that is, the λ_{max} of porphyrin absorption, quenched emission peaks were observed for both $[(H_2)_2SnPc]$ and $[(Zn)_2SnPc]$ relative to their individual constituents $[H_2Por]$ and $[ZnPor]$. The same emission quenching was also observed with excitation at 700 nm, that is, the λ_{max} of phthalocyanine absorption, for both heterotrimers relative to $[Sn(OH)_2Pc]$ (Figure 4). We carried out the fluorescence experiments in three different solvents, and the data are presented in Table 2. The spectral shapes and wavelengths of maximum emission for individual chromophores of these trimers remain close to those for the corresponding monomeric entities. Thus, the E_{0-0} (i.e., singlet-state energy) values of the individual components of these trimers are assumed to be essentially similar to those of the

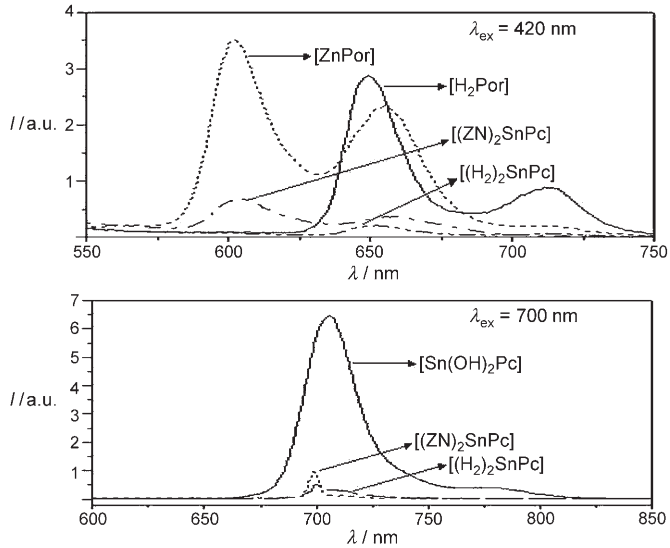


Figure 4. Fluorescence spectra of equiabsorbing solutions (optical density (λ_{ex}) = 0.11) of trimers along with those of the corresponding monomers in CH_2Cl_2.

Table 2. Fluorescence data.[a]

Compound	λ_{em} [nm] (ϕ, Q[b] [%]) Hexane $\lambda_{ex}=420$ nm	$\lambda_{ex}=700$ nm	CH_2Cl_2 $\lambda_{ex}=420$ nm	$\lambda_{ex}=700$ nm	CH_3CN $\lambda_{ex}=420$ nm	$\lambda_{ex}=700$ nm
$[H_2Por]$	652, 716 (0.110)	–	651, 714 (0.110)	–	653, 715 (0.120)	–
$[ZnPor]$	590, 637 (0.032)	–	604, 650 (0.036)	–	602, 655 (0.033)	–
$[Sn(OH)_2Pc]$	–	703, 780 (0.410)	–	706, 782 (0.440)	–	705, 783 (0.450)
$[(H_2)_2SnPc]$	652, 715 (0.006, 94)	703, 781 (0.050, 88)	651, 714 (0.005, 95)	705, 782 (0.004, 91)	652, 715 (0.005, 95)	706, 785 (0.005, 99)
$[(Zn)_2SnPc]$	592, 639 (0.002, 94)	704, 780 (0.045, 89)	599, 647 (0.004, 89)	706, 784 (0.005, 92)	604, 657 (0.002, 93)	705, 785 (0.006, 98)

[a] Error limits: λ_{ex} ±2 nm, ϕ ±10%. [b] Q is defined in Equation (1) (see text).

constituent monomers.[14] Quenching efficiencies (Q) were evaluated by using the quantum-yield data [Eq. (1)]:

$$Q = (\phi(\mathrm{ref}) - \phi(\mathrm{trimer}))/\phi(\mathrm{ref}) \qquad (1)$$

in which ϕ(trimer) and ϕ(ref) refer to the quantum yield of a given trimer and appropriative reference compound, respectively. It was found that Q for these hybrid trimers is in the range 90–95 %.

Various radiative and nonradiative intramolecular processes can be conceived to participate in the excited-state decay of these novel, hybrid-type donor–acceptor (D–A; in actual fact, D_2–A or D–A_2) systems. Among these, EET from the excited axial H_2/Zn to the central metalloid phthalocyanine and PET from the ground state of the axial H_2/Zn to the excited state of the central metalloid phthalocyanine seem to be most probable as revealed by the thermodynamic considerations based on the singlet-state energy (E_{0-0}) redox-potential (E_{CT}) data (Table 1 and Figure 5).

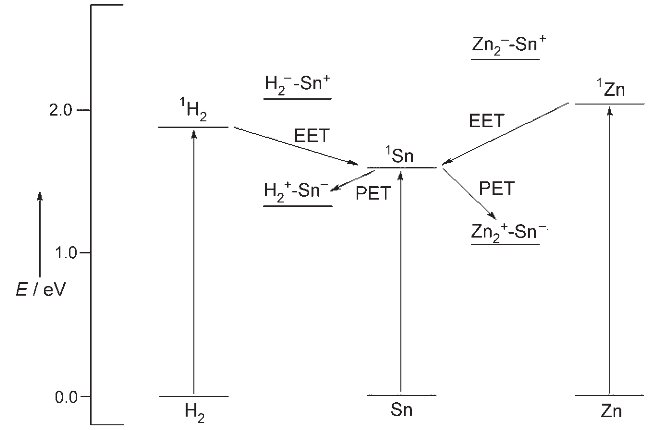


Figure 5. Energies of the singlet and charge-transfer states of the heteroarrays investigated in this study.

There exists a strong overlap between the emission of porphyrin and the absorption of phthalocyanine in these triads; this suggests that fluorescence quenching of these triads is due to an intramolecular EET from the singlet state of the axial porphyrin to the central metalloid phthalocyanine. Furthermore, overlap of the corrected and normalized excitation spectra (emission collected at the phthalocyanine emission maximum, 780 nm) with the corresponding absorption spectra (Figure 6) reveals that the fluorescence quenching is due to the intramolecular energy transfer in these hybrid trimers from the axial H_2/Zn to the central metalloid phthalocyanine with excitation at 420 nm. The efficiency of energy transfer was found to be 90 and 82 % (±10 %) in $[(H_2)_2SnPc]$ and $[(Zn)_2SnPc]$, respectively. However, the PET reaction from the singlet state of the axial H_2/Zn to the central metalloid phthalocyanine cannot be ruled out based on thermodynamic considerations with excitation at 420 nm. The change in free energy when PET occurs from the singlet state of the axial H_2/Zn porphyrin to the central metalloid phthalocyanine is calculated by Equation (2):

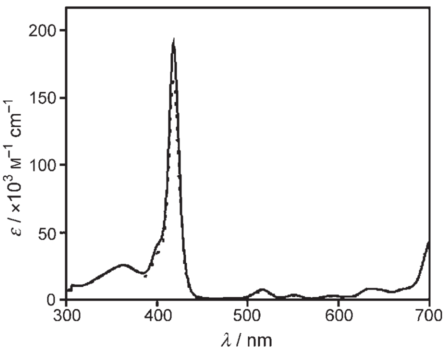


Figure 6. Overlay of excitation (-----) and absorption (——) spectra of $[(H_2)_2SnPc]$ in CH_2Cl_2 (λ_{em} = 780 nm). The excitation spectrum was corrected for the instrument response function and was normalized with respect to the absorption spectrum as described in reference [19].

$$\Delta G(^1\mathrm{Por} \rightarrow \mathrm{SnPc}) = E_{\mathrm{CT}}(\mathrm{Por}^+\mathrm{SnPc}^-) - E_{0-0}(\mathrm{H_2/Zn}) \qquad (2)$$

ΔG was found to be −0.60 and −0.95 eV for $[(H_2)_2SnPc]$ and $[(Zn)_2SnPc]$, respectively. Thus, the low ϕ values observed upon excitation of these systems at 420 nm can be rationalized in terms of intramolecular EET competing with PET from the singlet state of the axial H_2/Zn to the ground state of the central metalloid phthalocyanine.

In contrast, the emission quenching observed with excitation at 700 nm is purely due to intramolecular PET from the ground state of the axial H_2/Zn to the singlet manifold of the central metalloid phthalocyanine. This is because energy transfer from the central metalloid phthalocyanine is not thermodynamically feasible; neither was it experimentally detected in this study. The free-energy change for this electron-transfer process, $\Delta G(\mathrm{Por} \rightarrow {}^1\mathrm{SnPc})$, is calculated by Equation (3):

$$\Delta G(\mathrm{Por} \rightarrow {}^1\mathrm{SnPc}) = E_{\mathrm{CT}}(\mathrm{Por}^+\mathrm{SnPc}^-) - E_{0-0}(\mathrm{SnPc}) \qquad (3)$$

ΔG was found −0.24 and −0.65 eV for $[(H_2)_2SnPc]$ and $[(Zn)_2SnPc]$, respectively. Thus, the low ϕ values observed upon excitation of these systems at 700 nm can be rationalized in terms of PET from the ground state of the axial H_2/Zn to the singlet state of the Sn^{IV} phthalocyanine. The general dependence of ϕ on solvent polarity with excitation at 700 nm (Table 2) suggests that this process may indeed be the case, whereas the low ϕ values obtained with excitation at 420 nm is due to intramolecular EET competing with PET from the excited state of the axial porphyrins to the central metalloid phthalocyanine.

Conclusions

We have constructed heterooligomeric arrays by utilizing the axial-bonding capabilities of a tin(IV) phthalocyanine.

The approach is modular in nature and involves a simple inorganic reaction. The ground-state properties indicate that there is minimal π–π interaction between the macrocyclic units. The quenching of fluorescence intensity with excitation at 420 nm is due to intramolecular electronic energy transfer competing with photoinduced electron transfer from the singlet state of the axial porphyrin to the central metalloid phthalocyanine. A similar emission quenching observed with excitation at 700 nm is due to photoinduced electron transfer from the ground state of the axial porphyrin to the excited state of the central metalloid phthalocyanine. The excited-state properties can be tuned by changing the central metal atom. Currently, we are engaged in tuning the excited-state properties by changing the central metal atom.

Experimental Section

Materials

Chemicals and solvents utilized in this study were purchased from either Aldrich Chemical Co. (USA) or Spectrochem (India). Solvents utilized for spectroscopic and electrochemical experiments were further purified by using standard procedures.[15]

Methods

UV/Vis spectra were recorded on a Shimadzu model 170 spectrophotometer for 1×10^{-6} M (porphyrin Soret band) and 5×10^{-5} M (phthalocyanine and porphyrin Q bands, phthalocyanine Soret band) solutions. Steady-state fluorescence spectra were recorded on a Spex model Fluoromax-3 spectrofluorometer for solutions with optical density at the wavelength of excitation (λ_{ex})≈0.11. Fluorescence quantum yields (ϕ) were estimated by integrating the fluorescence bands and by using either [H_2Por] (ϕ= 0.13 in CH_2Cl_2), [ZnPor] (ϕ=0.036 in CH_2Cl_2), or zinc *tert*-butyl phthalocyanine (ϕ=0.37 in benzene).[17] MALDI-TOF MS spectra were recorded on a TO-4X KOMPACT SEQ (KARTOS, UK) mass spectrometer. Major fragmentations are given as percentages relative to the intensity of the base peak. ^{1}H NMR spectra were obtained at 300 MHz on a Bruker 300 Avance NMR spectrometer with X-WIN NMR software. Chemical shifts are given relative to TMS. FTIR spectra of all the samples were obtained on a Thermo Nicolet Nexus 670 spectrometer.

Cyclic and differential-pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI620C electrochemical analyzer. Cyclic voltammetric experiments were performed with 1 mM concentration of compounds in dichloromethane at a scan rate of 100 mV s^{-1} with TBAP as supporting electrolyte as detailed in our previous studies.[18]

Syntheses

meso-5,10,15,20-(Tetraphenyl)porphyrin ([H_2Por]), *meso*-5,10,15,20-(tetraphenyl)porphyrinatozinc(II) ([ZnPor]), *meso*-5-(4-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin ([H_2PorOH]), and *meso*-5-(4-hydroxyphenyl)-10,15,20-(triphenyl)porphyrinatozinc(II) ([ZnPorOH]) were synthesized and purified according to the reported procedure.[16]

[Sn$(OH)_2$Pc]: [Sn$(OH)_2$Pc] was synthesized by a modified procedure reported in the literature.[9] Free-base tetra-*tert*-butyl phthalocyanine (150 mg, 0.2 mmol) and $SnCl_4$ (262 mg, 1 mmol) were dissolved in 1-chloronaphthalene (10 mL). The reaction mixture was heated at reflux under argon atmosphere until the Q bands of the UV/Vis spectrum changed. The solvent was removed under reduced pressure. The resultant solid material was subjected to alumina column chromatography ($CHCl_3$/CH_3OH=95:5 *v*/*v*) to give dichlorotin(IV) tetra-*tert*-butyl phthalocyanine. The dichloro complex was dissolved in chloroform, and aqueous NaOH (10%, ≈50 mL) was added. The resulting reaction mixture was stirred magnetically at room temperature for 4 h. The organic layer was separated, washed twice with water, and dried over anhydrous Na_2SO_4. The organic layer was evaporated under reduced pressure and recrystallized from $CHCl_3$/hexane to give [Sn$(OH)_2$Pc] (150 mg, 84%). UV/Vis (CH_2Cl_2): λ_{max} (ε)=700 (5.20), 632 (4.21), 366 nm (4.75 M^{-1}cm^{-1}); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.40–9.80 (m, 8H), 8.42 (d, *J*=6.0 Hz, 4H), 1.50 ppm (d, *J*=6.2 Hz, 36H); MS (MALDI-TOF): *m*/*z* (%)=874 $[M-OH]^+$ (90); elemental analysis: calcd (%) for $C_{48}H_{50}N_8O_2Sn$: C 64.80, H 5.66, N 12.65; found: C 64.70, H 5.60, N 12.65.

[$(H_2)_2$SnPc]: [H_2Por] (300 mg, 0.5 mmol) and [Sn$(OH)_2$Pc] (100 mg, 0.11 mmol) were dissolved in toluene (40 mL). The reaction mixture was heated at reflux under argon atmosphere for 16 h. The solvent was removed under reduced pressure. The solid obtained was subjected to alumina column chromatography eluted with $CHCl_3$. The band that was bluish in color was collected and evaporated under reduced pressure to give [$(H_2)_2$SnPc] (142 mg, 61%). UV/Vis (CH_2Cl_2): λ_{max} (ε)=702 (5.11), 633 (4.40) 592 (4.00), 552 (4.04), 517, 4.32), 418 (5.76), 361 nm (4.83 M^{-1}cm^{-1}); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.90–9.70 (m, 8H), 8.80 (s, 16H), 8.45 (d, *J*=5.6 Hz, 4H), 8.20 (d, *J*=6.0 Hz, 12H), 7.77 (d, *J*= 6.0 Hz, 18H), 6.48 (d, *J*=8.0 Hz, 3.17 (d, *J*=8.0 Hz, 4H) 1.30–1.90 (m, 36H), −2.96 (s, 4H); MS (MALDI-TOF): *m*/*z*=1490 $[M-C_{44}H_{29}ON_4]^+$ (40); elemental analysis: calcd (%) for $C_{136}H_{106}N_{16}O_2Sn$: C 77.23, H 5.05, N 10.59; found: C 77.20, H 5.08, N 10.61.

[$(Zn)_2$SnPc]: This compound was synthesized by an analogous manner to the above compound by the condensation of [ZnPor] and [Sn$(OH)_2$Pc] (117 mg, 60%). UV/Vis (CH_2Cl_2) λ_{max} (ε)=701 (4.43), 632 (3.76), 595 (3.46), 553 (3.76), 423 (5.33), 358 nm (4.16 M^{-1}cm^{-1}); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.95–9.75 (m, 8H), 8.83 (s, 16H), 8.45 (d, *J*=4.8 Hz, 4H), 8.20 (d, *J*=5.0 Hz, 12H), 7.85 (d, *J*=6.0 Hz, 18H), 6.38 (d, *J*=7.8 Hz, 4H), 3.17 (d, *J*=7.8 Hz, 4H) 1.90–1.30 (m, 36H); MS (MALDI-TOF): *m*/*z*=2241 $[M]^+$ (35); elemental analysis: calcd (%) for $C_{136}H_{102}N_{16}O_2Zn_2Sn$: C 72.86, H 4.59, N 10.00; found: C 72.80, H 4.61, N=9.99.

Acknowledgements

We are grateful to Dr. V. J. Rao for providing the fluorometer facility and to Dr. B. Jagadeesh for the acquisition of 2D NMR spectra. We also thank Mr. G. Sanjay for help in translating the abstract into Telugu.

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Received: June 21, 2007
Revised: August 29, 2007