3. 1 Introduction

Porphyran arrays are useful in many research areas encompassing biomimetic photosynthesis, molecular electronics, molecular catalysis etc. Most of the porphyrin arrays reported so far have been synthesized via typical organic reaction sequences carried out at the porphyrin peripheral (i.e. β- pyrrole or meso) position/s. In recent years, 'inorganic' reactions that can be conducted at the axial sites of porphyrin-bound metal ions are also being employed for the construction of metalloporphyrin arrays. Adapting this latter 'axial-bonding' strategy and utilizing the well-known oxophilicity of metalloid ions, a series of trimers based on phosphorus(V), tin(IV) or germanium(IV) porphyrin scaffolds have been reported recently. During the course of the present investigations, it was realized that it should be possible to synthesize more elaborate hybrid-type porphyrin arrays having diverse structures and functions by utilizing the reactivities at both the peripheral and axial sites of a metalloid porphyrin species. Continued research efforts in this direction showed that the above concepts are readily achievable. Accordingly, a nonameric array - the structure of which is illustrated in the Fig 3. 1, was constructed. As seen in this figure, while a typical organic reaction {ether
[H$_2$(p-OH)$_2$DiTP] + [H$_2$(p-O-(CH$_2$)$_2$Br)TriTP] → (H$_3$)$_3$ SnCl$_2$, Pyridine
aq. Ammonia
Fig. 3.1 Scheme leading to the synthesis of $(H_2)_6(Sn)_3$
formation) involving the porphyrin peripheral hydroxy group/s is employed for the propagation of this array in the lateral direction, oxophilic nature of the tin center has been advantageously utilized for its expansion in the axial direction. This Chapter provides details of design, construction, spectral characterization and redox as well as singlet state properties of this new nonameric array.

3.2 Experimental details

3.2.1 Synthesis of 5-(4-hydroxyphenyl)10,15,20-tri(4-methylphenyl)porphryin ([H$_2$(p-OH)TriTP])$^{36}$

4-hydroxybenzaldehyde (6.1 g, 50 mmol) dissolved in 350 ml of propanoic acid was stirred at 120 °C for 10 min. To the resulting solution, 12.0 g (100 mmol) of p-toluualdehyde followed by 10.5 g (157 mmol) of pyrrole were added. The mixture was refluxed for 45 min., left overnight at 10 °C and then filtered. The black-violet residue obtained was washed several times with hot water, followed by methanol and purified by chromatography on a basic alumina column. Elution with CHCl$_3$ - CH$_3$OH (97 : 3, v/v) gave the desired product. Yield: 1.25 g (5%).

3.2.2 Synthesis of 5-(4-methylphenyl)dipyrromethane $^{37}$

A solution of 4-methylbenzaldehyde (0.5 g, 4.15 mmol) and pyrrole (2.8 ml, 40 mmol) was degassed by bubbling nitrogen for 10 min. Trifluoroacetic acid (0.08 ml, 0.1 mmol) was then added to this deaerated solution and it was
stirred for 15 min. at room temperature, at which point no starting aldehyde was seen to be present (TLC analysis). The mixture was diluted with CH$_2$Cl$_2$ (50 ml), washed with 0.1 M aqueous NaOH and then with water and finally, dried over anhydrous Na$_2$SO$_4$. The unreacted pyrrole was removed by vacuum distillation at room temperature. The resulting yellow amorphous solid was dissolved in minimal quantity of the CH$_2$Cl$_2$ and loaded onto a silica gel column. Elution with hexane - ethylacetate - triethylamine (80: 20: 1, v/v) gave pure sample of 5-(4-methylphenyl)dipyrromethane. Yield: 0.75 g (76%).

3.2.3 Synthesis of 5,15-bis(4-hydroxyphenyl)10, 20-bis(4-methylphenyl)porphyrin ([H$_2$(p-OH)$_2$DiTP])

This compound was synthesized according to a reported procedure. A solution containing 4-hydroxybenzaldehyde (0.24 g, 2 mmol) and 5-(4-methylphenyl)dipyrromethane (0.51 g, 2 mmol) in 250 ml of CHCl$_3$ was purged with nitrogen for 10 min. and then a catalytic amount of BF$_3$.O(Et)$_2$ was added. The resulting solution was stirred for 1 h. at room temperature and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.02 g, 4.5 mmol) was added. The mixture was stirred at room temperature for an additional hour and then the solvent was removed. The crude product was loaded onto a silica gel column. Elution with CHCl$_3$ - CH$_3$OH (98 : 2, v/v) gave pure sample of [H$_2$(p-OH)$_2$DiTP]. Yield: 0.12 g (13%).
3. 2. 4 Synthesis of 5-(4-(3-bromo-1-propoxy)phenyl)-10,15,20-tri-(4-methylphenyl)porphyrin ([H$_2$(p-O-(CH$_2$)$_3$Br)TriTP])$^{38}$

A mixture of [H$_2$(p-OH)TriTP] (2.0 g, 3 mmol), 1, 3-dibromopropane (4.1 g, 22 mmol) and 3.0 g of anhydrous K$_2$CO$_3$ was stirred magnetically in 50 ml of dimethylformamide for 48 h. at room temperature under the nitrogen atmosphere. The reaction mixture was then poured onto a solvent mixture containing 170 ml water and 30 ml methanol. The precipitated porphyrin was filtered off, washed successively with water and methanol and dried under vacuum. It was loaded onto a neutral alumina column. Elution with CHCl$_3$ gave [H$_2$(p-O-(CH$_2$)$_3$Br)TriTP]. Yield: 2.43 g (95%).

3. 2. 5 Synthesis of free-base trimer (H$_2$)$_3$

A mixture containing [H$_2$(p-OH)$_2$DiTP] (0.20 g, 0.30 mmol), [H$_2$(p-O-(CH$_2$)$_3$Br)TriTP] (2.38 g, 3 mmol) and 0.5 g of anhydrous K$_2$CO$_3$ in 50 ml of dimethylformamide was stirred magnetically for 72 h. at room temperature under the nitrogen atmosphere. The product was precipitated by pouring the reaction mixture onto 100 ml of 10% aqueous methanolic solution. The precipitate obtained was filtered off and dried under vacuum. The solid was chromatographed on a neutral alumina column. Elution with CHCl$_3$ - hexane (1 : 1, v/v) gave unreacted [H$_2$(p-O-(CH$_2$)$_3$Br)TriTP], subsequent to which free-base trimer (H$_2$)$_3$ was eluted out. It was recrystallized from CH$_2$Cl$_2$ - hexane. Yield: 0.29 g (46%).
3. 2. 6 Synthesis of tri-tin(IV) trimer Sn₃

A mixture containing (H₂)₃ (0.21 g, 0.10 mmol) and SnCl₂ (0.50 g, 2.23 mmol) in pyridine (20 ml) was refluxed for 2 h., after which 10 ml aq. ammonia (25%, v/v) was added to it. The resulting solution was stirred for 1 h. at 50 °C. Solvent pyridine was removed under the reduced pressure. The solid obtained was taken up in CHCl₃ and washed several times with water. The organic layer was dried by passing through anhydrous Na₂SO₄ and chromatographed over basic alumina. Elution with CHCl₃- CH₃OH (98 : 2, v/v) gave Sn₃. The compound was recrystallized from CH₂Cl₂ - hexane. Yield: 0.22 g (88%).

3. 2. 7 Synthesis of *(free-base porphyrin)₆ - (Sn (IV) porphyrin)₃*’

Nonamer (H₂)₆Sn₃

Trimer Sn₃ (0.05 g, 0.02 mmol) and monomer [H₂(p-OH)TriTP] (0.20 g, 0.30 mmol) were dissolved in dry C₆H₆ (20 ml) and the contents were refluxed for 12 h. under the nitrogen atmosphere. Evaporation of the solvent and purification of the residue by preparative TLC on neutral alumina (solvent: CHCl₃) afforded (H₂)₆Sn₃. It was recrystallized from CH₂Cl₂ - hexane. Yield: 0.04 g (33%). Anal: Cald. for: C₄₂₈H₃₁₈O₁₀N₃₆Sn₃: C, 79.31; H, 4.94; N, 7.78. Found: C, 78.71; H, 5.06, N, 7.34. Mass (MALDI-TOF): calcd: 6482, found: 6482.
Each investigated porphyrin was purified on a short alumina column before the spectral measurements were inadequate. All the spectroscopic and electrochemical experiments have been carried out as described in Chapter 2.

3.3 Results and discussion

3.3.1 Design and Synthesis

The majority of established methods that are available for the construction of porphyrin arrays involve either manipulation at the porphyrin peripheral position/s or axial ligation at the central metal/metalloid ion. In the present study, relying on a 'building block' approach, synthesis of \((\text{H}_2\text{Sn})_6\) has been achieved by employing sequential 'organic' and 'inorganic' reactions. Indeed, from a retrosynthetic view point, whereas propagation of these 'branched-chain' type arrays in the lateral direction involves typical ether bond formation reaction, construction of the perpendicular 'branches' employs the 'axial-bonding' capability of the central oxophilic tin(IV) ion. The precursor porphyrin building blocks necessary for the construction of nonamer \((\text{H}_2\text{Sn})_n\) (i.e. \([\text{H}_2\text{(p-OH)}_2\text{DiTP}]\) and \([\text{H}_2\text{(p-O-(CH}_2)_3\text{Br)TriTP}]\)) were prepared by closely following the corresponding methods reported in the literature. The nonamer was constructed in a step-wise manner starting from the trans-dihydroxy porphyrin \([\text{H}_2\text{(p-OH)}_2\text{DiTP}]\) as the basic building block, Fig. 3. 1. Reaction of \([\text{H}_2\text{(p-OH)}_2\text{DiTP}]\) with bromide \([\text{H}_2\text{(p-O-(CH}_2)_3\text{Br)TriTP}]\) in \(\text{K}_2\text{CO}_3/\text{DMF}\) milieu and purification afforded trimer \((\text{H}_2)_3\). The tri-tin(IV) trimer \(\text{Sn}_3\) was
synthesized in high yield by reacting \((\text{H}_2)\text{Sn}_3\) with \(\text{SnCl}_2\) in refluxing pyridine for 2 h. followed by treatment with aq. ammonia. This trimer, with the two axial hydroxy ligands amenable for further reaction on each of its tin(TV) centers, reacted smoothly with excess \([\text{H}_2(p-OH)\text{TriTP}]\) in refluxing dry \(\text{C}_6\text{H}_6\) to afford the 'axial-bonding' type nonameric array \((\text{H}_2)\text{Sn}_3\) in good yield.

3.3.2 Ground state properties

Preliminary characterization of \((\text{H}_2)\text{Sn}_3\) was carried out by mass (MALDI-TOF) and UV-visible spectroscopic methods. MALDI-TOF spectra showed a peak at 6482 consistent with the calculated value. UV-visible data of \((\text{H}_2)\text{Sn}_3\) as well as those of the corresponding monomers \([\text{H}_2(p-OH)\text{TriTP}], 5,10,15,20\text{-tetra(4-methylphenyl)} \text{porphyrinato tin(IV)} \text{dihydroxide ([(TTP)Sn}_4^{\text{IV}}(\text{OH})_2])}\) and trimers \((\text{H}_2)_3\) and \(\text{Sn}_3\) are summarized in Table 3.1. UV-visible spectrum of \((\text{H}_2)\text{Sn}_3\) is illustrated in Fig. 3.2. A comparison of the data for \((\text{H}_2)\text{Sn}_3\) and that obtained for the spectrum of a solution containing 1:2 (mole/mole) equivalents of \([\text{H}_2(p-OH)\text{TriTP}]\) and \([(\text{TTP})\text{Sn}_4^{\text{IV}}(\text{OH})_2]\) reveals that, within the experimental error, the peak maxima \((\lambda_{\text{max}})\) and also the molar absorptivities at the peak maxima \((\log e)\) of this physical mixture and that of the nonamer are close to each other. This observation clearly indicates that there is minimal perturbation of the electronic structures of the individual macrocyclic \(n\)-systems in this array. Specifically, there exists no indication of the presence of
exciton coupling between the porphyrin rings (i.e. axial-axial, axial-basal or basal-basal).

Fig. 3. 3 illustrates the \( ^1H \) NMR spectrum of \((H_2)_6Sn_3\) along with the proton assignments, which are made on the basis of \( ^1H \) NMR data of the corresponding trimeric\(^{35}\) and hexameric\(^{40}\) arrays as well as on examination of the \( ^1H - ^1H \) COSY spectral features. Table 3. 2 summarizes the \( ^1H \)NMR data of \((H_2)_6Sn_3\) along with that of relevant reference porphyrins. All the twenty four \( \beta \)-pyrrole protons present on the three tin(TV) porphyrins of the nonamer (protons of the type a, see Fig. 3. 3) resonate at 9. 35 \((m, 24H)\) ppm. On the

### Table 3. 1 UV-visible data in CH\(_2\)Cl\(_2\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}}, \text{nm (log} \varepsilon) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>********</td>
<td>Soret band</td>
</tr>
<tr>
<td>([H_2(p-OH)TriTP])</td>
<td>418 (5. 30)</td>
</tr>
<tr>
<td>([H_2(p-OH)_2DiTP])</td>
<td>420 (5. 16)</td>
</tr>
<tr>
<td>([H_2(p-O-(CH_2)_3Br)TriTP])</td>
<td>420 (5. 37)</td>
</tr>
<tr>
<td>((TTP)Sn^{IV}(OH)_2)</td>
<td>428 (5. 56)</td>
</tr>
<tr>
<td>((H_2)_{3})</td>
<td>420 (5. 76)</td>
</tr>
<tr>
<td>Sn_3</td>
<td>430 (5. 70)</td>
</tr>
<tr>
<td>((H_2)_6Sn_3)</td>
<td>422 (5. 99)</td>
</tr>
</tbody>
</table>

a) Error limits: \( \lambda_{\text{max}} \pm 1 \) nm; log \( \varepsilon \), \( \pm 10\% \)
Fig. 3. 2 UV-visible spectrum of $(\text{H}_2)_6\text{Sn}_3$ in CH$_2$Cl$_2$. 
Fig. 3. $^1$H NMR spectrum of (CDCl$_3$, TMS) of (H$_2$)$_6$Sn$_3$. 
Table 3. $^1$H NMR data (CDCl$_3$, TMS)$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>P$_2$ pyrrole (central) (a)</th>
<th>P$_2$ pyrrole (axial) (d, e &amp; f)</th>
<th>Axial Phenyl (c, g)</th>
<th>-NH (k)</th>
<th>Meso-tolyl (e, h, i)</th>
<th>Spacer -OCH$_2$</th>
<th>-CH$_3$ (m, n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H$_2$(p-OH)TriTP]</td>
<td>8.88 (s, 8H)</td>
<td>-</td>
<td>-</td>
<td>-2.73  (s, 2H)</td>
<td>8.18 (d, 8H) [8.4]</td>
<td>-</td>
<td>2.78 (s, 9H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.45 (d, 6H) [8.4]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>7.22 (d, 2H) [8.4]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[H$_2$(p-OH)$_2$DiTP]</td>
<td>8.87 (s, 8H)</td>
<td>-</td>
<td></td>
<td>-2.72  (s, 2H)</td>
<td>8.15 (d, 8H) [8.6]</td>
<td>-</td>
<td>2.79 (s, 9H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.48 (d, 4H) [8.6]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>7.21 (d, 4H) [8.6]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[H$_2$(p-O-(CH$_2$)$_3$-Br)TriTP]</td>
<td>8.88 (s, 8H)</td>
<td>-</td>
<td></td>
<td>-2.73  (s, 2H)</td>
<td>8.18 (d, 8H) [8.2]</td>
<td>4.48, 436 (t, 4H)</td>
<td>2.78 (s, 9H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.51 (d, 6H) [8.2]</td>
<td>2.79 (m, 2H)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>7.31 (d, 2H) [8.2]</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th></th>
<th>(H₂)₃</th>
<th>Sn₃</th>
<th>(H₂)₆Sn₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.89 ppm</td>
<td>9.15 ppm</td>
<td>9.35 ppm</td>
<td>8.89 ppm</td>
</tr>
<tr>
<td>(m, 24H)</td>
<td>(m, 24H)</td>
<td>(m, 24H)</td>
<td>(m, 24H)</td>
</tr>
<tr>
<td>-2.72 ppm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(s, 6H)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8.12 ppm</td>
<td>8.23 ppm</td>
<td>8.30 ppm</td>
<td>8.12 ppm</td>
</tr>
<tr>
<td>(m, 24H)</td>
<td>(m, 24H)</td>
<td>(d, 24H)</td>
<td>(m, 24H)</td>
</tr>
<tr>
<td>4.63 ppm</td>
<td>4.65 ppm</td>
<td>4.28 ppm</td>
<td>4.63 ppm</td>
</tr>
<tr>
<td>(t, 8H)</td>
<td>(t, 8H)</td>
<td>(m, 8H)</td>
<td>(t, 8H)</td>
</tr>
<tr>
<td>2.78 ppm</td>
<td>2.69 ppm</td>
<td>2.62 ppm</td>
<td>2.78 ppm</td>
</tr>
<tr>
<td>(m, 28H)</td>
<td>(m, 28H)</td>
<td>(m, 82H)</td>
<td>(m, 28H)</td>
</tr>
</tbody>
</table>

a) Error limits: 8, ± 0.01 ppm; J, ± 1 Hz

other hand, P-pyrrole proton signals of the axial free-base porphyrins are seen to be shifted to the upfield region (compared to those of [H₂(p-OH)TriTP]) and are also split into a multiplet (8. 75, m 24H) and a pair of doublets at 8. 51(d, 12H) and 8. 15 ppm (d, 12H). The resonances centered at 8. 75, 8. 51 and 8. 15 ppm are assigned to protons of the type d, c and b respectively, that are differently affected by the ring current of the central metalloid porphyrin. On the other hand, protons meta- (type e) and ortho- (type f) to the phenoxy groups of the free-base porphyrins, being affected by both the inherent deshielding
effect of the axial free-base porphyrin and the shielding effect of the basal porphyrin, resonate at 6.55 (d, 12H) and 2.40 ppm (d, 12H) respectively, as detected by the proton connectivity pattern in the corresponding $^1$H - $^1$H COSY spectrum. The inner imino protons of the axial free-base porphyrins (type k) of $(H_2)_6Sn_3$ are seen to experience the 'long range' shielding effect due to ring current of the basal tin(IV) porphyrin and resonate at -2.90 ppm (s, 12H) as against the corresponding -NH protons of $[H_2(p-OH)TriTP]$ that appear at -2.73 ppm. The ortho- and meta- phenyl protons of the meso-tolyl groups (g and h, see: Fig. 3.3) on the basal tin(IV)porphyrins, being located in a deshielding zone of each porphyrin ring current, resonate at 8.30 and 7.43 ppm, respectively. The corresponding protons of the axial free-base porphyrins (protons i and j) resonate as multiplets centered at 7.98 and 7.43 ppm, respectively (Table 3.2). The terminal methylene protons of the spacer -O-CH$_2$-CH$_2$-CH$_2$-O- (protons 1) of the Sn$_3$ backbone in $(H_2)_6Sn_3$ resonate as a multiplet at 4.28 ppm, whereas the central methylene protons (m) resonate at 2.62 ppm - a region in which all the methyl protons (protons n) also resonate.

An additional concern with this class of octahedral tin(IV) complexes is lability of the axial bonds and, has indeed been investigated earlier by the NMR method for tin(IV) porphyrins having 'inorganic' or 'organic' ligands.$^{42-44}$ Specifically, $^1$H NMR studies carried out earlier on $\{(P)Sn^IV(OC(O)A)_2\}$ (where P is a tetraryl porphyrin and OC(O)A is the axially ligated anthracene 9-carboxylate subunit), have revealed presence of the ligand on-off equilibrium, in
addition to the \(n-n\) interaction between the porphyrin and anthracene rings.\(^{44}\) In contrast, neither the \(n-n\) interaction nor the ligand on-off equilibrium was discernable from the NMR data of \((H^2)_6Sn_3\), as is the case with its trimeric and hexameric predecessors.\(^{35,40}\) This observation indicates that, under the present set of experimental conditions, the two trans free-bases are strongly bound in a symmetric manner at each tin(IV) center in these tin(IV) porphyrin based arrays. In addition, the fact that resonance positions of the various protons of the axial free-base ligands present in \((H^2)_6Sn_3\) are close to those of the corresponding protons of the trimer/hexamer suggests that the interaction between the axial rings bound at different tin(IV) centers are minimal in this higher array. However, it should be noted that free rotations about the axial Sn-O bonds can not be altogether neglected in this 'axial-bonding' type array. The issues concerning the axial bond rotation and the conformational equilibria that are possible in \((H^2)_6Sn_3\) can be addressed with the help of variable temperature NMR data, but such experiments have not been carried out during the present study.

The electrochemical redox potentials, as measured from the cyclic- and differential pulse voltammetric measurements, also reveal the absence of electronic interaction between the various porphyrin rings in \((H^2)_6Sn_3\). Fig. 3. 4 illustrates the differential pulse voltammograms obtained during the cathodic scan and Table 3. 3 provides redox potential data of \((H^2)_6Sn_3\) and the corresponding reference porphyrins. The nonameric array undergoes up to four
Fig. 3. 4 Differential pulse voltammogram of (H₂)₆Sn₃ in CH₂Cl₂, 0.1 M TBAP (scan rate 10 mV s⁻¹).
Table 3.3 Redox potential data in CH$_2$Cl$_2$, 0.1 M TBAP

<table>
<thead>
<tr>
<th>Compound</th>
<th>Potential, V vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reduction</td>
</tr>
<tr>
<td>[H$_2$(p-OH)TriTP]</td>
<td>-1.24, -1.64</td>
</tr>
<tr>
<td>[H$_2$(p-OH)$_2$DiTP]</td>
<td>-1.20,-1.60</td>
</tr>
<tr>
<td>[H$_2$(p-O-(CH$_2$)$_3$Br)TriTP]</td>
<td>-1.12, -1.44</td>
</tr>
<tr>
<td>[(TTP)Sn$^{IV}$(OH)$_2$]</td>
<td>-0.88,-1.02</td>
</tr>
<tr>
<td>(H$_2$)$_3$</td>
<td>-1.14,-1.45</td>
</tr>
<tr>
<td>Sn$_3$</td>
<td>-0.89,-1.27</td>
</tr>
<tr>
<td>(H$_2$)$_6$Sn$_3$</td>
<td>-0.96,-1.28,-1.47b,-1.68</td>
</tr>
</tbody>
</table>

a) Error limits: $E_{1/2} \pm 0.03$ V
b) Quasi-reversible/irreversible

reduction steps (Fig. 3.4) and up to two oxidation steps in CH$_2$Cl$_2$, 0.1 M TBAP. Wave-analysis of the corresponding cyclic voltammetric responses suggested that, in general, the first oxidation and also the first two reduction steps are reversible ($i/i_p = 0.9 - 1.0$ where $i$ is the peak current) and diffusion controlled ($i/i_v = constant$ in the scan rate ($v$) range 50 - 500 mV s$^{-1}$) one-electron transfer ($AE_p = 60 - 70$ mV where $AE_p$ is the peak-to-peak potential difference; $AE = 65 \pm 3$ mV for Fc/Fc couple) reactions.$^{45}$ The subsequent
steps are either quasi-reversible (ΔE_p = 90 - 200 mV and i/i_0 = 0.5 - 0.8 in the scan rate 100 - 500 mV s^{-1}) or totally irreversible. Based on redox potential data of the individual monomers (i.e. [H_2(p-OH)TriTP] and [(TTP)Sn^{IV}(OH)_2]) and also that of [(TTP)Sn^{IV}(OPh)_2] (where OPh is the axially ligated phenoxy group), the various midpoint potentials have been assigned to either the basal- or the axial porphyrins. Analysis of the data reveals that the redox potentials of the hybrid array are in the same range as those of the corresponding monomeric analogues or the precursor trimeric porphyrins.

Collectively, UV-visible, ^1H NMR and redox potential data indicate that there exists a symmetric disposition of the two axial free-base porphyrins with respect to plane of the corresponding basal tin(IV) porphyrin in (H_2)_6Sn_3. These data also indicate that there is no specific interaction between the neighboring axial free-base porphyrins in this array. Notwithstanding this analysis, it needs to be emphasized that the structural drawing of (H_2)_6Sn_3 shown in Fig. 3.1 does not necessarily convey the actual arrangement of the porphyrin rings. Specifically, the Sn-O-C angles are not equal to 180°; instead, it is likely that the free-base porphyrins might be somewhat diagonally disposed towards the tin(IV) porphyrins in this array as reported for [(P)Sn^{IV}(ONap)_2] (where Nap is the axially ligated napthyl subunit). To date, attempts to grow single crystals of this large array for the possible determination of its structure by the X-ray crystallographic method have been unsuccessful.
3.3.3 Singlet State Properties

When excited at 445 nm, the tri-tin(IV)trimer $\text{Sn}_3$ showed a typical two-banded fluorescence spectrum in $\text{CH}_2\text{Cl}_2$ with the emission maxima centered at 615 (band I) and 667 nm (band II). The quantum yield of fluorescence ($\phi$) of this tin(IV) porphyrin precursor is found to be close to that of the reference porphyrin $[(\text{TTP})\text{Sn}^{\text{IV}}(\text{OH})_2]$ ($\phi = 0.05$) as measured in the band I region. Excitation ($\lambda_{\text{exc}} = 405$ nm) of the precursor free-base porphyrins, $[\text{H}_2(\text{p-OH})\text{TriTP}]$ and $(\text{H}_2)_3$ also resulted in a two-banded spectra; the emission maximum of the major band is located in the band II region (655 nm) mentioned above and the minor band is centered at ~720 nm (band III) in each case. The fluorescence quantum yield of $(\text{H}_2)_3$ is found to be nearly equal to that of $[\text{H}_2(\text{p-OH})\text{TriTP}]$ ($\phi = 0.12$). These data of the monomeric and trimeric porphyrin precursors (Table 3.4) indicate that it is possible to individually address the singlet state properties of the axial and basal porphyrins in $(\text{H}_2)_6\text{Sn}_3$. Thus, irradiation of this nonameric hybrid array at 405 nm should result in a predominant absorption by the axial free-base porphyrins and that at 445 nm excites the central tin(IV) porphyrins. Moreover, fluorescence due to the tin(IV) and free-base components of the array can be exclusively monitored at bands I and III respectively, with the band II being common to both. Armed with this information, fluorescence studies were carried out for $(\text{H}_2)_6\text{Sn}_3$ and the results reveal that, unlike the case with the ground state properties, the singlet state activity of this array is quite different from the
corresponding activities of its precursor reference compounds, as described below.

3. 3. 3. 1 Excitation at 445 nm

Excitation of toluene, CH2Cl2 or dimethylformamide solutions of (H2)6Sn3 at 445 nm was seen to result in strong quenching of its fluorescence with respect to fluorescence of [((TTP)SnIV(OH)2]. In fact, the % quenching (%Q1, eqn. 3. 1) is close to 100 in each investigated solvent, with the band I that is characteristic of the tin(IV) porphyrin emission being totally absent in the spectrum of this array (see: Fig. 3. 5 and Table 3. 4).

\[ Q_1 = \frac{\phi((TTP)Sn^{IV}(OH)_2) - \phi((H_2)_6Sn_3))}{\phi((TTP)Sn^{IV}(OH)_2))} \] (3.1)

This total quenching of emission observed for (H2)6Sn3 is in contrast with the partial quenching observed when the trimer (H2)2Sn was excited under the similar set of experimental conditions of excitation wavelength and solvent, Fig. 3. 5. Inspection of this figure reveals that while spectrum of the trimer shows the presence of band I along with bands II and III, that of (H2)6Sn3 is characterized by only bands II and III. It should be noted here that appearance of the bands II and III that are ascribable to the free-base porphyrin emission in the spectra of
Fig. 3. 5 Fluorescence spectra of equi-absorbing (O. D. = 0.16) solutions of 
$\text{(H}_2\text{)}_6\text{Sn}_3$ (——), $\text{(H}_2\text{)}_4\text{Sn}_2$ (——) and $\text{(H}_2\text{)}_2\text{Sn}$ (……) in toluene ($\lambda_{\text{exc}}$ = 445 ran)
Table 3. 4 Fluorescence data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Toluene</th>
<th>CH$_2$Cl$_2$</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{em}$ nm ($\phi$, % Q)</td>
<td>$\lambda_{em}$ nm ($\phi$, % Q)</td>
<td>$\lambda_{em}$ nm ($\phi$, % Q)</td>
</tr>
<tr>
<td>[H$_2$(p-OH)TriTP]</td>
<td>$\lambda_{em}$ = 405 nm</td>
<td>$\lambda_{em}$ = 445 nm</td>
<td>$\lambda_{em}$ = 405 nm</td>
</tr>
<tr>
<td></td>
<td>656.721 (0.11)</td>
<td>655.717 (0.12)</td>
<td>655.718 (0.11)</td>
</tr>
<tr>
<td>[H$_2$(p-OH)$_2$DiTP]</td>
<td>655.716 (0.10)</td>
<td>656.719 (0.10)</td>
<td>658.719 (0.11)</td>
</tr>
<tr>
<td>[H$_2$(p-O)(CH$_2$)$_2$Br)TriTP]</td>
<td>656.718 (0.11)</td>
<td>658.719 (0.10)</td>
<td>657.720 (0.11)</td>
</tr>
<tr>
<td>[TTP]Sn$^\nu$(OH)$_2$</td>
<td>-</td>
<td>614.660 (0.06)</td>
<td>614.667 (0.05)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>658.719 (0.11)</td>
<td>-</td>
</tr>
<tr>
<td>(H$_2$)$_2$Sn$_3$</td>
<td>-</td>
<td>655.720 (0.12)</td>
<td>655.718 (0.11)</td>
</tr>
<tr>
<td></td>
<td>616.667 (0.05)</td>
<td>615.665 (0.11)</td>
<td>616.666 (0.03)</td>
</tr>
<tr>
<td>(H$_2$)$_6$Sn$_3$</td>
<td>657.720 (0.010, 97)</td>
<td>657.719 (0.006, 94)</td>
<td>658.719 (0.004, 94)</td>
</tr>
<tr>
<td></td>
<td>(0.001, 100)</td>
<td>(0.001, 100)</td>
<td>(0.001, 100)</td>
</tr>
</tbody>
</table>

a) Error limits: $\lambda_{em}$, ± 2 nm; $\phi$, ± 10%

this nonamer when $\lambda_{exc}$ = 445 nm is not due to the direct excitation of its axial free-base components (Note, in this regard, that absorbance due to the free-base components of both (H$_2$)$_6$Sn$_3$ and (H$_2$)$_2$Sn is minimum (<5%) at 445 nm) Rather, it is a consequence of the excitation energy transfer (EET) from the central metalloid porphyrin to the axial free-base porphyrin, as represented in equn. 3.2.
In eqn. 3.2, Sn(IV)P and H₂P are the tin(IV)- and free-base porphyrin components present in the nonameric array, respectively and * represents the electronically excited singlet state. Such an intramolecular EET is a thermodynamically favored process in this array; singlet state energy of the tin(IV) porphyrin is higher (2.04±0.03 eV) than that of the free-base analogue (1.94±0.04 eV). Additionally, there is a considerable overlap of absorption by the free-base porphyrin and emission by the tin(IV) porphyrin in the 580 - 640 nm region. Indeed, estimation of the Forster overlap integral, \( J_{\text{Forster}} \), by utilizing the emission spectrum of \([(TTP)Sn^{IV}(OH)_2]\) and absorption spectrum of \(H_2TTP\) gave a value that is as high as \(1.40 \pm 0.2 \times 10^{-14} \text{ cm}^6 \text{mmol}^{-1}\) (eqn. 3.3)\(^4\)
where $F(\nu)$ is fluorescence intensity of [(TTP)Sn$^{IV}$(OH)$_2$] at wavenumber $\nu$ (cm$^{-1}$), and $e$ is the molar extinction coefficient (mmol$^{-1}$ cm$^{-1}$) of H2TTP. Further support for the intramolecular energy transfer being the quenching mechanism comes from the excitation spectral measurements. Overlap of the normalized excitation spectrum (emission collected at 720 nm - where the emission is exclusively due to the free-base porphyrins) with the corresponding absorption spectrum of (H$_2$)$_6$Sn$_3$ revealed that efficiency of the intramolecular EET from the basal tin(IV) porphyrin to the axial free-base porphyrins in (H$_2$)$_6$Sn$_3$ is $\sim 85\pm10\%$ - a value close to that observed for the corresponding hexamer (H$_2$)$_4$Sn$_2$. On the other hand, the reported EET efficiency for the lower homologue (H$_2$)$_2$Sn is only $68\pm10\%$. Interestingly, the higher fluorescence intensities observed for (H$_2$)$_6$Sn$_3$ compared to the trimer, under the similar set of experimental conditions (see Fig. 3. 5), is consistent with this variation of EET efficiency. The reason/s for the efficient EET observed for the higher homologues compared to the trimer in this class of 'axial-bonding' type hybrid arrays is still unclear. However, it should be noted that the number of acceptors (i. e. free-base porphyrins) in the neighborhood of a given donor (i. e. tin(IV) porphyrin) increases as one moves from the lower homologue to the
higher D-A ensembles in this series. Thus, unlike the case with the **trimer** where EET is from the basal tin(IV) porphyrin to its (own) two axial free-base acceptors, additional energy transfer from a given tin(IV) porphyrin to the free-bases ligated at the neighboring tin(IV) centers (i.e. 'trans-axial' energy transfer) is likely to occur in the higher arrays leading to more efficient quenching. Interestingly, the high efficiency of energy transfer from the basal tin(IV) porphyrin to the axial free-base acceptors observed here for the 'axial-bonding' type D-A array \((H_2)_6Sn_3\) is in contrast with an inefficient flow of energy from a zinc(II) porphyrin to the axially ligated free-base porphyrin both of which are a part of an elegantly assembled 'wheel-and-spoke' array reported by Lindsey and co-workers.\(^{33}\)

As the quenching efficiency is **100%** but, the EET efficiency is ~ 85% for these arrays, it was found necessary to examine pathways other than the EET to explain the observed quantitative quenching. Among the various other mechanisms considered, a photoinduced electron transfer (PET) from the ground state free-base porphyrin to the singlet tin(IV) porphyrin seems to be more probable. This PET reaction in \((H_2)_6Sn_3\) leads to a charge transfer state of the type Sn(IV)P\(^{-}\) - H\(_2\)P\(^{+}\), and involves free-energy change \(\Delta G_1(\text{PET})\) of \(-0.25\pm0.04\) eV (equn. 3.4).

\[
\Delta G_1(\text{PET}) = E_{ox}(H_2P) - E_{\text{red}}(\text{Sn(IV)P}) - E_{\text{o,0}}(\text{Sn(IV)P})
\]  
  \((3. 4)\)
Where $E^\text{ox}(H_2P)$ and $E^\text{red}(\text{Sn(IV)P})$ are the oxidation potential of the axial free-base porphyrin and the reduction potential of the basal tin(IV) porphyrin respectively, and $E_{0-0}(\text{Sn(IV)P})$ is singlet state energy of the tin(IV) porphyrin. Thus, the co-occurrence of an efficient EET and less prominent PET reactions as illustrated in equn. 3. 2 can rationalize the 100% fluorescence quenching observed for the tin(IV) porphyrins of this array.

3. 3. 3. 2 Excitation at 405 nm

Excitation of toluene, CH$_2$Cl$_2$ or dimethylformamide solutions containing (H$_2$)$_6$Sn$_3$ at 405 nm resulted in a typical two-banded fluorescence spectrum in each case with emission maxima appearing at ~ 656 (band II) and ~ 718 (band III) nm. The quantum yields of fluorescence were measured based on the uncorrected fluorescence intensities in the band III region of the corresponding deconvoluted spectra using H$_2$TPP as the standard, and were found to be much lower than those due to monomer [H$_2$(p-OH)TriTP] or trimer (H$_2$)$_3$. The $\%Q$ values ($\%Q_2$, equn. 3. 5) for this array vary between 94 - 97.

$$Q_2 = (\phi([H_2(p-OH)\text{TriTP}]) - \phi((H_2)_6\text{Sn}_3)) / \phi([H_2(p-OH)\text{TriTP}]) \quad (3. 5)$$

The $Q_2$ values thus evaluated for (H$_2$)$_6$Sn$_3$ (see Table 3. 4) are quite close to the corresponding values of (H$_2$)$_4$Sn$_2$ but are marginally higher than those reported for the trimeric homologue (H$_2$)$_2$Sn.$^{35,40}$ As noted above, singlet state of the free-
base porphyrin lies at a lower energy than that of the tin(IV) derivative in these arrays and hence, an EET from the axial-free-base porphyrins to the basal tin(IV) porphyrins can be safely ruled out as a quenching mechanism. On the other hand, a PET from singlet state of the axial free-base porphyrins to the tin(IV) macrocycle seems to be probable pathway of the observed quenching (see equn. 3.6).

\[ \Delta G_2(\text{PET}) = E^{\text{ox}}(\text{H}_2\text{P}) - E^{\text{red}}(\text{Sn(IV)P}) - E_{0,0}(\text{H}_2\text{P}) \]  

\[ (3.6) \]

Indeed, free-energy change for this PET (\( \Delta G_2(\text{PET}) \)) is exoergic by 0.15±0.03 eV for \((\text{H}_2)_6\text{Sn}_3\) (equn. 3.7).

\[ \Delta G_2(\text{PET}) = E^{\text{ox}}(\text{H}_2\text{P}) - E^{\text{red}}(\text{Sn(IV)P}) - E_{0,0}(\text{H}_2\text{P}) \]  

where \( E_{0,0}(\text{H}_2\text{P}) \) is singlet state energy of the free-base porphyrin. This interpretation is consistent with the similar interpretation made earlier for the trimeric and hexmeric species.\(^{35,40}\)

Overall, the above analysis reveals that singlet state dynamics of this nonamer involves: (i) EET from the basal tin(IV) porphyrin to the axial free-base porphyrin and PET from ground state of the free-base porphyrin to singlet state of the tin(IV) porphyrin (excitation at 445 nm) and (ii) PET from the singlet free-base porphyrin to the tin(IV) porphyrin (excitation at 405 nm), as illustrated...
in Fig. 3. 6. While it was possible to experimentally verify the occurrence of EET reaction, PET has only been inferred based on the thermodynamic arguments.

3. 4 Summary

In summary, a new higher order array, \((\text{H}_2)_6\text{Sn}_3\), has been synthesized by adopting a hybrid 'organic - inorganic' protocol that involves synthetic manipulation at both the peripheral and axial sites of tin(IV) porphyrin scaffold. The array is highly soluble in various organic solvents and does not aggregate in solution as revealed by its spectral data. The structural features as probed, mainly, by the NMR method indicate unique 'axial-bonding' type architectural identity for this system. While the ground state properties of \((\text{H}_2)_6\text{Sn}_3\) are close to those of the corresponding reference compounds, the singlet state properties of it are quite different from those of the constituent monomers. Fluorescence quenching observed for the tin(IV)- and free-base porphyrin components of this bichromophoric system has been rationalized in terms of intra-array electron- and energy transfer reactions.
Fig. 3. 6 A generalized energy level diagram illustrating the singlet state dynamics of $(H_2)_6Sn_3$. The various energy levels were obtained by the absorption, emission, and redox data. EET = Excitation Energy Transfer and PET = Photoinduced Electron Transfer. $H_2$ and Sn represent free-base and tin(IV) porphyrin components, respectively.
3. 5 References


