

# Near IR absorbing planar aromatic [34]octaphyrins(1.1.0.1.1.0.0.0) containing a quaterthiophene subunit†‡

Rajeev Kumar,<sup>a</sup> Rajneesh Misra,<sup>a</sup> Tavarekere K. Chandrashekar<sup>\*ab</sup> and Eringathodi Suresh<sup>c</sup>

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The synthesis and structural characterization of the first examples of planar aromatic core modified [34]octaphyrins(1.1.0.1.1.0.0.0) with three different heteroatoms containing a quaterthiophene subunit are reported.

Expanded porphyrins continue to attract the attention of chemists and material scientists because of their diverse applications such as PDT, MRI contrasting agents, neutral substrate binding, anion recognition, and as NLO materials.<sup>1,2,9</sup> Octaphyrins are a class of expanded porphyrins in which eight pyrrole/heterocyclic rings are connected to each other through *meso* carbon bridges as in **1–5**,<sup>3–7</sup> or through direct pyrrole–pyrrole link as in **6** (Fig. 1).<sup>8</sup> Octaphyrins exhibit different conformations such as figure-eight, twisted or planar depending on the nature of linkage, number of *meso* carbon bridges as well as the steric bulk of the *meso* aryl substituents. Adaptation of twisted or figure eight conformations leads to loss of aromaticity. Thus development of methods to synthesize planar, aromatic octaphyrin is still a synthetic challenge. Recently we were successful in synthesizing aromatic, planar octaphyrins<sup>6</sup> by: (a) replacing the few pyrrole rings by heavier heterocyclic rings such as thiophene or selenophene in the core; and (b) by increasing steric bulk on the *meso* aryl substituents to avoid the twisting of the macrocycle. These core modified octaphyrins exhibit ring inversions, where one or more pyrrole/heterocyclic rings are inverted and this ring inversion depends on the nature of the *meso* substituents and nature of heteroatom. In continuation of this strategy of synthesizing aromatic, planar octaphyrins, in this communication we wish to examine the effect of changes in the steric bulk of the *meso* substituents and the increase in the number of heteroatoms on the ring inversions and the conformation of the octaphyrins.

Our synthetic strategy involved preparation of a novel quaterthiophene fragment; 5,5''-bis(mesitylhydroxymethyl)-2,5' : 2',2'' : 5'',2'''-quaterthiophene, **7** as one of the precursors and the modified tetrapyranes (**8–11**) in which *meso* substituents were varied from bulkier mesityl group to less bulkier anisal and phenyl groups, as the other precursor. Further, X can be either S or Se, leading to increase in the number of the heteroatoms. Thus,

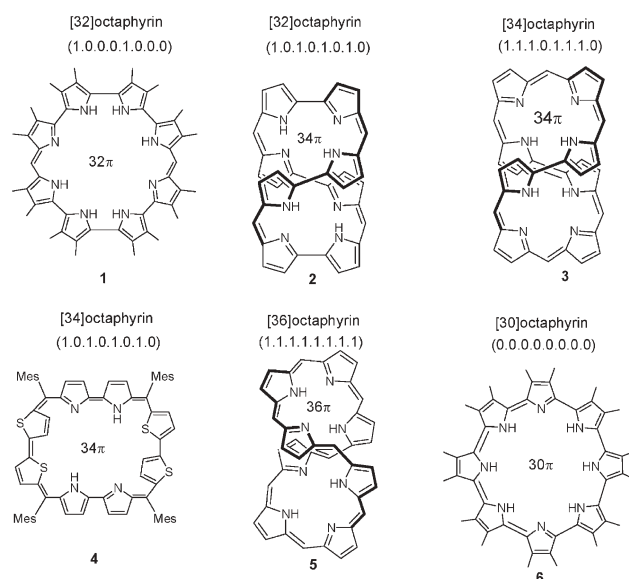


Fig. 1 Octaphyrins known in literature.

reaction of **7** with **8–11**, under acid-catalyzed condensation with *p*-toluenesulfonic acid (PTSA) as catalyst, followed by chloranil oxidation leads to formation of the desired octaphyrins **12–15** (Scheme 1). Reduction in the steric bulk in the precursor **8–11**, from mesityl to anisal and phenyl did not change the conformation of the octaphyrins, suggesting the two *meso* mesityl substituents are good enough to prevent twisting at the *meso* position, therefore avoiding the formation of figure-eight conformation. The advantage of this methodology is the formation of a single product in good yields (18–20%), thus, avoiding tedious chromatographic separations.

The proposed structure of the macrocycle comes from the various spectroscopic analysis and the single-crystal X-ray structure obtained for **12** (see ESI†). The FAB mass spectra show peak at  $m/z = 1238.70$  for **12**, and  $m/z = 1144.25$  for **13**, confirming the free base composition of these macrocycles. The UV/Vis absorption spectrum of **12** in dry methylene chloride is characterized by the presence of an intense Soret-band [578 nm ( $\log \epsilon = 4.98$ )] and Q-bands [766 nm (4.44) and 842 nm (4.70)] into the near IR region and interesting results were obtained on careful protonation with TFA. At less acid concentration (1 eq.), there were three distinct bands at 650 nm ( $\log \epsilon = 4.02$ ), 757 nm (2.35), and 1090 nm (2.13). This absorption spectrum represents the diprotonated form of **12** (Fig. 2). Further addition of TFA results in gradual increase in absorption at 650 and 1090 nm at the expense of absorption at 757 nm. This changes are typical of

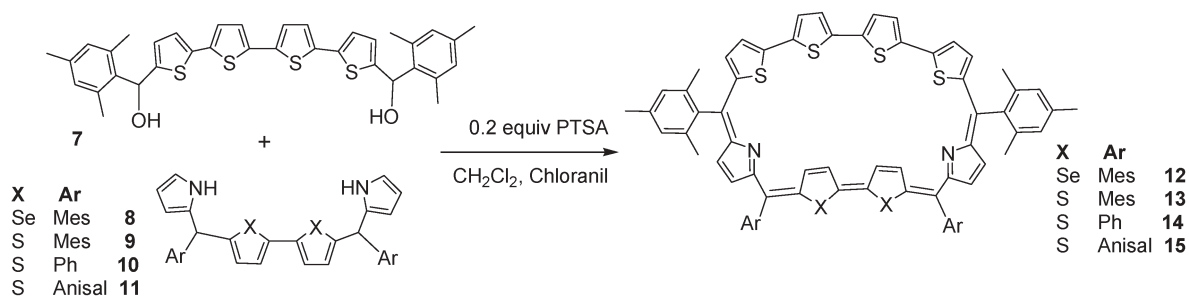
<sup>a</sup>Department of Chemistry, Indian Institute of Technology, Kanpur, 208016, India. E-mail: tkc@iitk.ac.in

<sup>b</sup>Director, Regional Research Laboratory, Trivandrum, 695019, Kerala, India

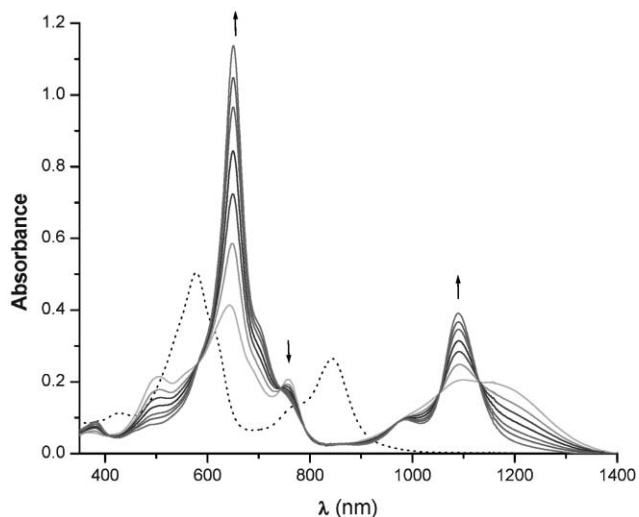
<sup>c</sup>Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat -, 364 002, India

† The HTML version of this article has been additionally enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Details of experimental procedures, characterization of compounds **7** and **12–15**. See DOI: 10.1039/b614290g



**Scheme 1** Synthesis of octaphyrins by [4 + 4] acid catalyzed condensation.



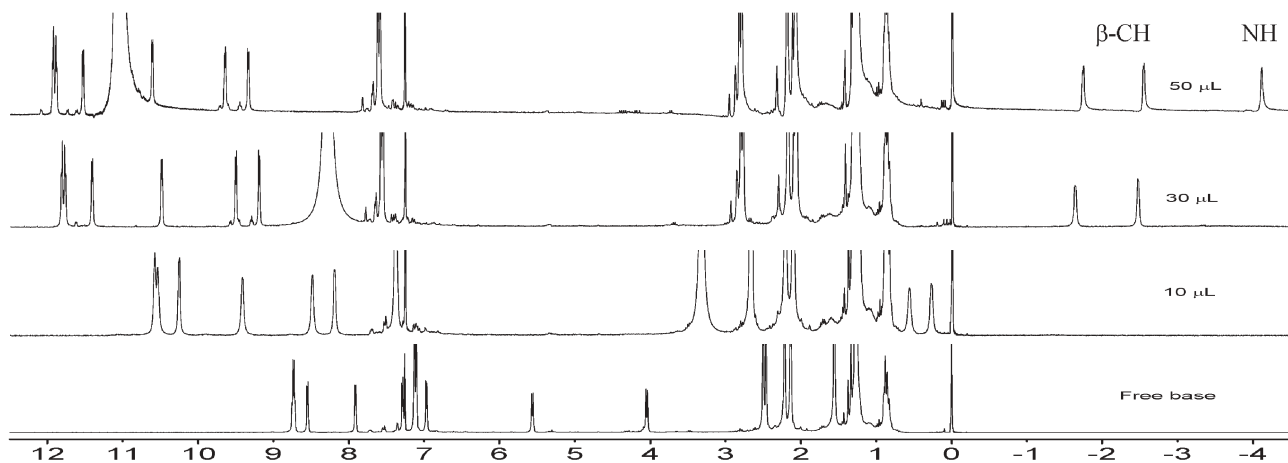
**Fig. 2** UV/Vis- near IR absorption spectra of **12** (---) [ $7.73 \times 10^{-6}$ ] and the protonated derivative (—) in  $\text{CH}_2\text{Cl}_2$ .

binding of anion to the macrocycle. A similar behaviour was observed for octaphyrins **12–15**, suggesting that these macrocycles bind trifluoroacetate anion in the diprotonated state.

Detailed  $^1\text{H}$  and 2D NMR studies provide important information about the conformation and aromaticity of these octaphyrins. Specifically, the  $^1\text{H}$  NMR spectrum of **12** (Fig. 3) taken in  $\text{CDCl}_3$  revealed eight sets of doublets between 8.75 and 4.05 ppm, integrating to two protons each, observed for  $\beta$ -CH protons,

which suggests it has a  $C_2$  symmetric conformation in  $\text{CDCl}_3$ . Both the selenophene rings opposite to the tetrathiophene unit are inverted in free base as well as in protonated forms. Very interesting results were obtained when trifluoroacetic acid (TFA) was added stepwise to a solution of free base octaphyrin **12** in  $\text{CDCl}_3$ . The degree of inversion of the selenophene rings was found to be dependent on TFA concentration. In the freebase form the  $\beta$ -CH protons of these inverted rings resonate at 5.57 and 4.05 ppm. On addition of 10  $\mu\text{L}$  TFA solution, (10% TFA in  $\text{CDCl}_3$ ) these  $\beta$ -CH protons resonate at 0.56 and 0.28 ppm and this upfield shift increases further as more TFA was added. Finally at excess TFA concentration (50  $\mu\text{L}$ ) these  $\beta$ -CH protons resonate at  $-1.73$  and  $-2.54$  ppm and the NH protons resonate at  $-4.11$  ppm (Fig. 3). These observations suggest that after adding TFA, biselenophene unit comes into plane of the macrocycle and macrocycle becomes more planar.  $\Delta\delta$  value of 16.10 ppm supports a strong diatropic ring current, inferring their aromatic nature.

Additional evidence for the aromatic character comes from the cyclic voltammetric studies. Octaphyrins **12–15** exhibit two reversible reductions and two reversible oxidations (see ESI†). An estimated HOMO–LUMO gap of 1.09 V for **14** indicates a significant reduction relative to *meso* aryl sapphyrin (1.88 V), rubyrin (1.64 V), and heptaphyrin (1.38 V), thus explaining large red shifts observed in the electronic spectrum. A linear correlation obtained (Fig. 4) when the energy of the Soret maximum and HOMO–LUMO gap ( $\Delta_{\text{redox}}$ ) were plotted *versus* increase in  $\pi$  electrons in the delocalization pathway, gives a strong evidence of the aromatic nature of **12–15**.



**Fig. 3** TFA concentration dependent  $^1\text{H}$  NMR spectra of **12** in  $\text{CDCl}_3$ . Amounts of TFA added, are shown in spectra.

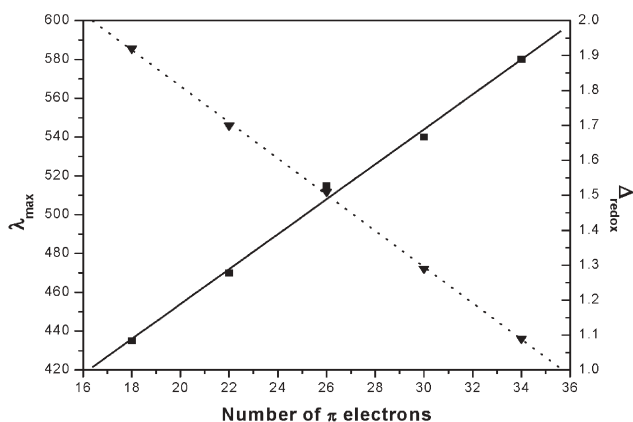


Fig. 4 Variation of energy of the Soret band (■) and HOMO–LUMO gap (▼) with increasing number of  $\pi$  electrons.

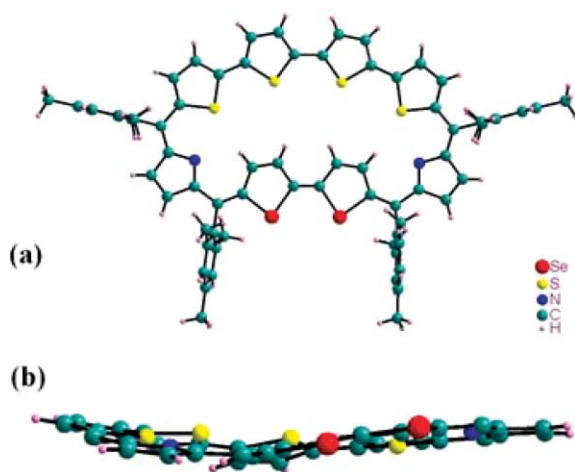


Fig. 5 Single crystal X-ray structure of **12**, top view (a) and its side view (b). *Meso* substituents in side view are removed for clarity and only one of the two independent molecules in the asymmetric unit of **12** is shown.

The confirmation of planar structure for **12** came from the single-crystal X-ray analysis<sup>10</sup>§ (CCDC-622228). The structure shown in Fig. 5 confirms the inversion of both the selenophene rings. There are two independent molecules in the asymmetric unit and the inverted biselenophene unit, having different dihedral angles (9.52 and 22.6°) with respect to the mean plane defined by four *meso* carbon atoms. The molecules deviate slightly from planarity as seen in side view (Fig. 5b). NMR studies also support such an observation where the degree of inversion of the biselenophene unit depends on the amount of TFA added and at excess TFA concentration, the biselenophene unit comes into the plane as defined by the four *meso* carbons. And the macrocycle adopts a planar conformation.

In summary, it has been shown that: (a) use of rigid quaterthiophene subunit as one of the precursors restricts the ring inversion only on the tetrapyrrole subunit unlike in **4**, where both the subunits are involved in ring inversions; (b) variation of X in the tetrapyrrole moiety has no bearing on the ring inversions; (c) reduction in the steric bulk of the *meso* substituents in the tetrapyrrole moiety did not result in the twisting of the

macrocycle. These subtle variations in the structure can play a major role in the resulting conformation of the octaphyrin leading to change in the electronic structure and aromaticity. Systematic studies of these variations on the structure property correlations are underway.

## Notes and references

§ *Crystallographic summary* for **12**:  $C_{72}H_{60}N_2S_4Se_2$ ,  $M = 1239.42$ . Crystals were grown by slowly diffusing dry n-hexane over a chloroform solution of **12**. Blue rectangular, triclinic,  $P-1$ ,  $\mu = 1.134 \text{ mm}^{-1}$ ,  $Z = 4$  in a cell of dimensions:  $a = 20.276(4) \text{ \AA}$ ,  $b = 21.240(4) \text{ \AA}$ ,  $c = 21.313(4) \text{ \AA}$ ;  $\alpha = 81.06(3)^\circ$ ,  $\beta = 62.88(3)^\circ$ ,  $\gamma = 66.62(3)^\circ$ ,  $V = 7495(3) \text{ \AA}^3$ ,  $\rho_{\text{cal}} = 1.098 \text{ Mg m}^{-3}$ ,  $F(000) = 2552$ . A total of 26051 independent reflections were measured on a CCD area detector using graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $-173^\circ \text{C}$ . The structure was refined on  $F^2$  to an  $R_w = 0.1411$ , with a conventional  $R = 0.0614$ , and a goodness of fit = 0.920 for 1465 parameters using the SHELXTL<sup>10</sup> package. CCDC 622228. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614290g.

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