meso-Substituted Aromatic 34π Core-Modified Octaphyrins: Syntheses, Characterization and Anion Binding Properties

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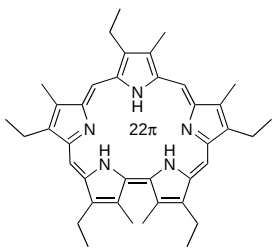
Abstract: Modified octaphyrins with 34π electrons have been synthesized and characterized following a simple synthetic methodology. An acid-catalyzed α,α coupling of tetrapyrranes containing furan, thiophene and selenophene rings resulted in the formation of the respective octaphyrins in relatively good yield. Solution studies by ^{1}H NMR and 2D NMR methods and single crystal X-ray structural characterization reveal an almost flat structure with two heterocyclic rings inverted. Specifically, in **14** two selenophene rings (one on each biselenophene unit) are inverted while in **15** two furan rings (one on each bifuran unit) are inverted when the meso substituent are mesityl groups. On changing the mesityl substituent to *m*-xylyl group as in **19**, the location of ring inversion shifts to pyrrole rings (one on each bipyrrole unit) indicating the dependence of structure on the *meso* substituents. UV/Vis studies, both in freebase and protonated forms reveal typical porphyrinic character and the aromatic nature of the octaphyrins. The $\Delta\delta$ values evaluated by ^{1}H NMR spectroscopy also support their aromatic nature. The protonated forms of octaphyrins bind TFA anion in a 1:2 ratio. The TFA anions are located one above and below the plane of the octaphyrin macrocycle and they are held by weak electrostatic N-H-O interactions similar to that observed for protonated rubyrins. However, in the present case, there is an additional non-electrostatic C-H-O interaction involving β-CH of the inverted heterocyclic ring and the carbonyl oxygen of the TFA. Furthermore, inter molecular interactions between the C–H of the *meso*-mesityl group and the fluorine of CF_3 group of bound TFA leads to the formation of one-dimensional supramolecular arrays with interplanar distance of 13 Å between two octaphyrins.

Keywords: anion binding · aromaticity · porphirinoids · supramolecular array · 34π electrons

Introduction

Expanded porphyrins continue to attract attention of synthetic chemists due to their diverse applications.[1] Apart from host of diverse applications[2–6] they can also be used as a tool for accessing higher aromatic systems[7–10] unknown to date. Expanded porphyrins have more than 18π electrons in the conjugated pathway either due to increased number of heterocyclic rings or due to multiple meso carbon bridges. Sapphyrin (22π), **1**, and rubyrin (26π),[11] **2**, are examples of expanded porphyrins, which display physical properties similar to that of the parent 18π porphyrin. Replacement of the nitrogens by other chalcogens such as O, S or Se yield core modified expanded porphyrins.[12] *meso*-Aryl substitutions on expanded porphyrins revealed structural diversities such as mono-[12a] and bis-[13] ring inversions leading to inverted expanded porphyrins[14] **3**–**7** (see below). These molecules have been synthesized by efficient synthetic methods and characterized through various spectroscopic methods. The higher analogues of expanded porphyrins were found to be non-aromatic,[15–18] until we reported the first aromatic 30π modified heptaphyrins,[19] **6** and **7**, bearing seven heterocyclic



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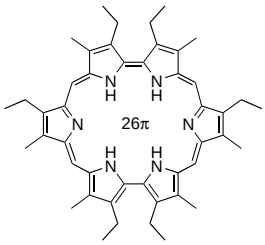

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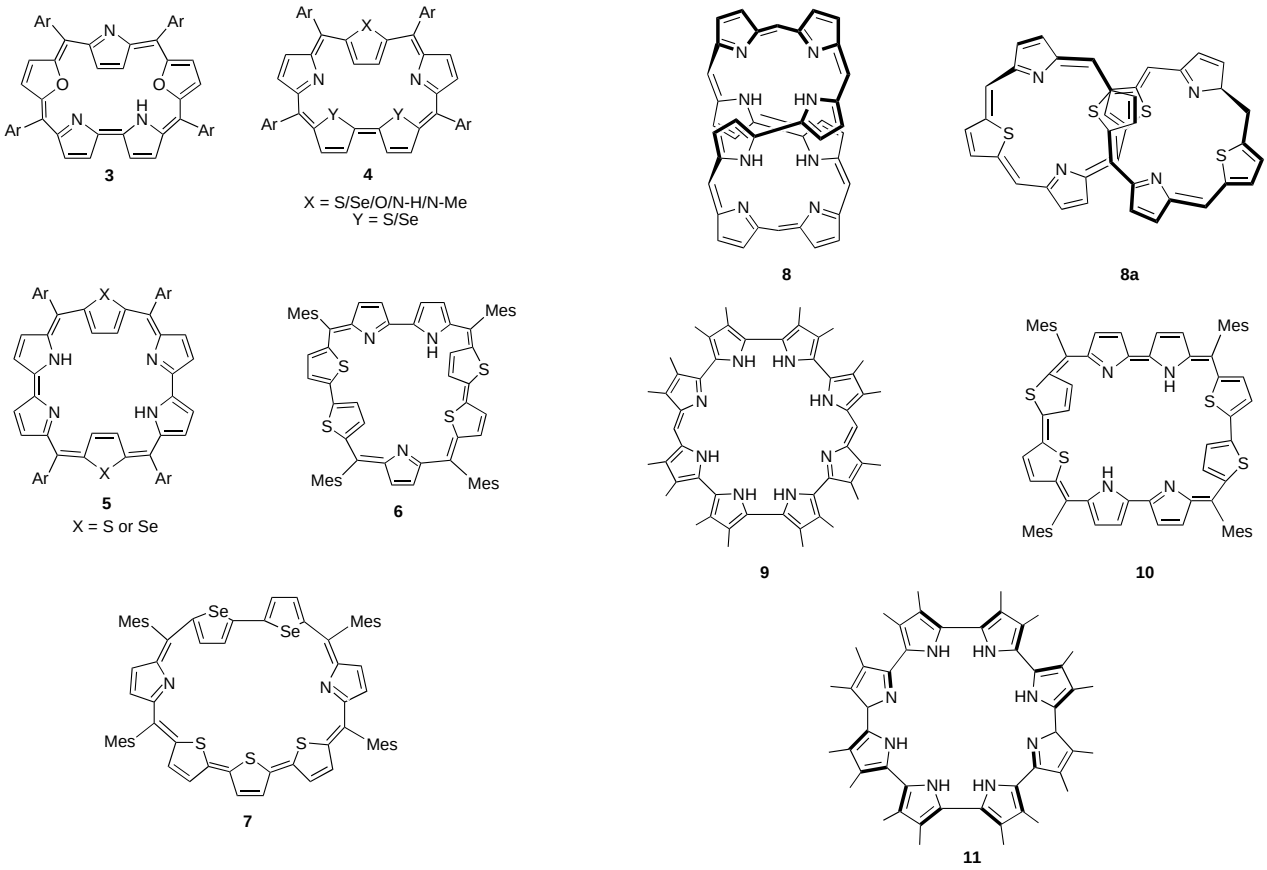


units. Isomers of heptaphyrins are synthesized by either through an acid-catalyzed condensation or oxidative coupling reaction of appropriate precursors.[20] Later, Sessler and co-workers reported an all aza isomer of 30π heptaphyrin[21] that exhibits a flat structure in solution, while a figure eight conformation in the solid state.

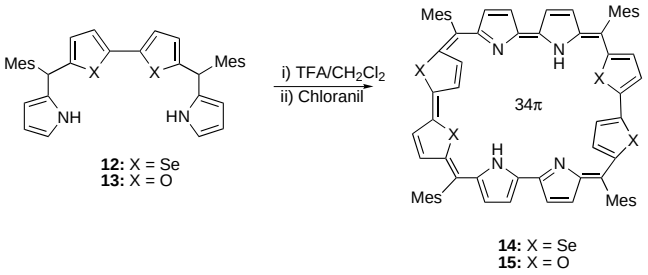
Octaphyrins, expanded porphyrins with eight heterocyclic units, with 32π,[15] 34π,[18] 36π[17] and 38π[22] (see above) reported in literature were found to exhibit both planar and twisted figure eight conformations, but are non-aromatic in nature. In a recent preliminary communication,[23] we have devised a one-pot synthesis for aromatic 34π tetrathia octaphyrin, **10**, through acid catalyzed oxidative coupling reaction of modified tetrapyrranes. This molecule exhibits an absolute flat structure as analyzed by X-ray analysis, in sharp contrast to the figure eight conformations of other octaphyrins known so far. Further confirmation for the aromatic nature came from the observation of the signals in the high field region for the β-CH protons of the inverted heterocyclic rings and the NH protons of the pyrrole rings. Even though Franck and co-workers[9] have reported a 34π vinylogous porphyrin, only solution-state studies proved the aromatic behavior. In a recent report,[24] Sessler and co-workers have reported a cyclo[8]pyrrole, **11**, which has eight pyrrole rings linked to each other without any *meso* carbon bridges. This molecule was also found to be flat as analyzed in solid state, but was accounted to have only 30π electrons in its conjugated pathway. The cavity of octapyrrole was found very compatible to bind a sulphate ion in the protonated form. In this paper we wish to report syntheses, characterization and anion binding properties of oxa and selena octaphyrins. These octaphyrins also exhibit ring inversions where the heterocyclic rings experience a 180° ring flipping both in solution and solid state. Furthermore, the change of *meso* mesityl substituent to *m*-xylyl group results in the inversion of pyrrole rings rather than the selenophene or furan rings. The X-ray structural studies on the TFA bound octaphyrins reveal formation of 1:2 anion complex, with different binding modes. The details of these studies are reported in this contribution.

Results and Discussion

Syntheses: Octaphyrin syntheses have been achieved by various methods involving appropriate precursors.[17, 18, 22, 25] Cyclisation of simple molecules to huge macrocycles either through acid-catalyzed condensation or oxidative coupling is an attractive methodology to access novel higher order aromatic expanded porphyrins. But all such methods have been fruitful only in the syntheses of nonaromatic and nonplanar octaphyrins.[15] Generally it has been observed that polycyclopyrroles undergo a twisting, which is responsible for the loss of planarity and hence aromaticity. Due to such curling, the molecule inspite of following the Hückel's $(4n+2)\ \pi$ rule does not exhibit aromatic features. Therefore, arresting the twist in the molecule is a key step in sustaining the planar form. Also an observation of the previous syntheses on octaphyrins, revealed steric hindrance due to bulky substituents on the β-positions of the pyrrole rings.[26]

Such a strain can be minimized if the steric strain is shifted to the *meso* carbons, thereby making the *meso* substituents more orthogonal to the porphyrin plane. Also the presence of bigger atoms in the core of the macrocycle should be an added advantage in further affecting the desired modifications. This idea stimulated from the retrosynthetic analysis (Scheme 1) for designing the planar octaphyrin. The 34π system is twisted to form the non-aromatic molecule. The planar form can be envisaged by hindering the molecule from the twist. The untwisted octaphyrin could be split into two equal halves, which will contain a quarter pyrrole unit with two *meso* carbons. Theoretically, bridging the two tetrapyrranes directly by oxidative coupling reaction should yield the desired octaphyrin. Based on this, one can expect that the linear tetrapyrrole could be coupled to get the all aza non-twisted octaphyrin. But according to a recent report,[26] the bipyrrole diol dissociates to bipyrrole and benzaldehyde under acidic conditions. Hence the above approach could not be applied for the synthesis of all aza isomer of octaphyrin. On the other hand, these quarter pyrroles can be modified into the requirements as mentioned above by incorporating the requisite bulky *meso* substituents. In the process the required precursor turns out to be the known modified tetrapyrrane,[27] which has been, used extensively in the synthesis of various expanded porphyrins. The modified tetrapyrranes can be synthesized from the modified diols, which can be obtained from the corresponding biselenophene/bifuran.

A similar process, as reported earlier for the synthesis of tetrathia octaphyrin,[23] has been employed for the synthesis of tetraselena and tetraoxa octaphyrins. When the same reaction was attempted with *meso* phenyl derivative, the formation of octaphyrin was restricted, indicating the necessity of bulkier groups on the *meso* carbons. The modified tetrapyrranes, **12** and **13** on treatment with trifluoroacetic acid (TFA) and further oxidation by chloranil under reflux conditions yielded the planar octaphyrins, **14** and **15** in 9.6 and 4% yield, respectively (Scheme 2). The variation of acid concentration within the range of one equivalent did not affect the reaction, while acid concentration of two equivalents yielded more of corresponding rubyrin probably due to the acidolysis of the tetrapyrromethanes.[20]

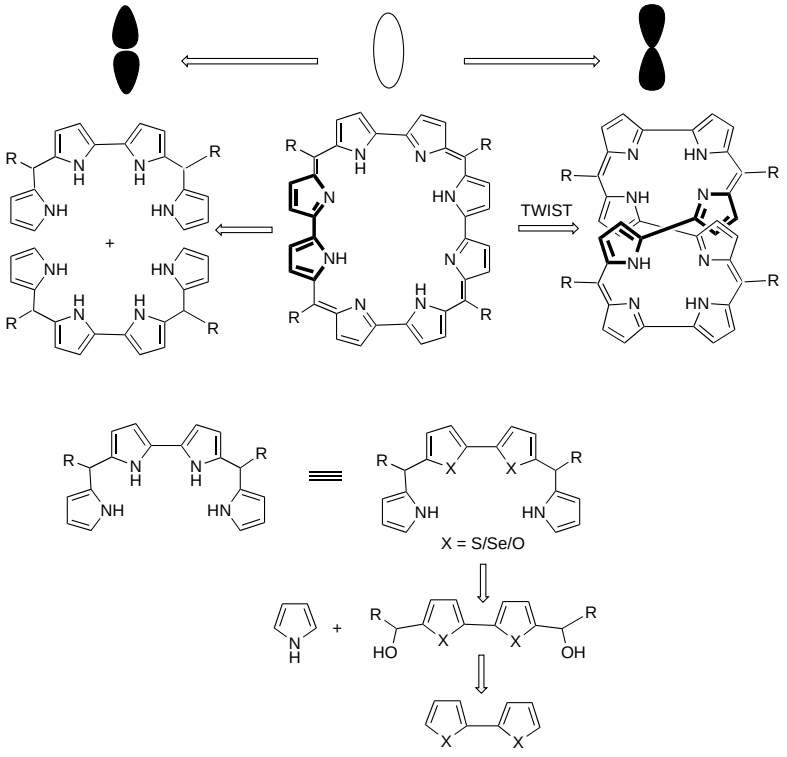


Scheme 2. Synthesis of octaphyrins.

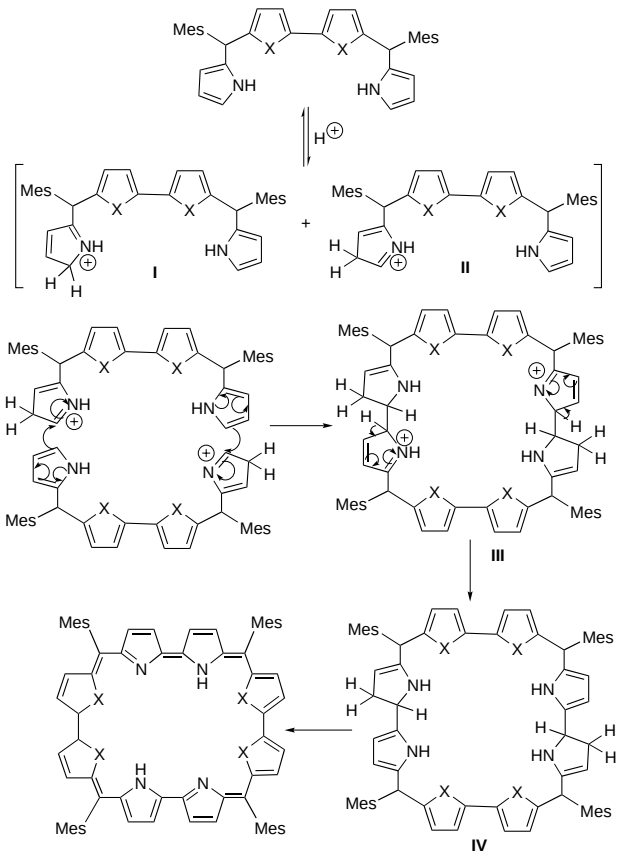
The formation of octaphyrin at very less concentrations of TFA indicates the α,α coupling[13] of tetrapyrrane with the formation of two direct pyrrole–pyrrole links to form an octaphyrinogen intermediate, which on subsequent oxidation with chloranil yielded the 34π octaphyrin. The probable mechanism is shown in Scheme 3.

The protonation of tetrapyrrane leads to two intermediates **I** and **II** in which the protonation occurs at α and β positions, respectively. Based on the product formed, intermediate **II** is preferred to form intermediate **III** through an intermolecular electrophilic attack. Further rearrangement of **III** followed by oxidation with chloranil results in the formation of octaphyrin. The inability to isolate the intermediate **III** before oxidation reveals the unstable nature of the octaphyrinogen relative to the corresponding aromatic congener.

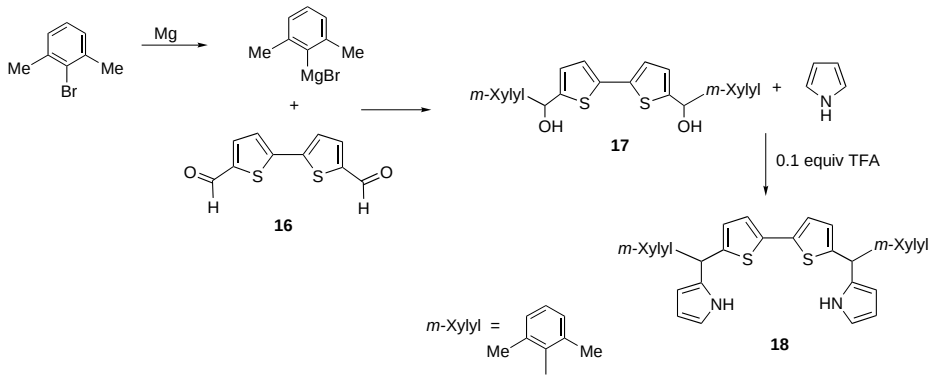
The understanding that the presence of bulkier groups on the second and sixth positions of the *meso* phenyl rings facilitates the formation of the planar octaphyrins further prompted us to check such validity. Instead of the mesityl substituent, a *m*-xylyl group was chosen, since it also has methyl groups on the *ortho* positions. The required precursor was synthesized in a modified way from bithiophene dialdehyde, **16**. The dialdehyde was further reduced to the corresponding diol **17** by Grignard reagent prepared from bromoxylene (Scheme 4).



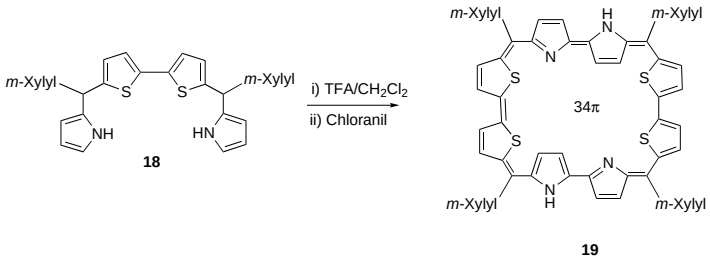
Scheme 1. Retrosynthetic analysis.



Scheme 3. Mechanistic scheme for the α,α coupling of tetrapyrranes under acidic conditions.



Scheme 4. Synthesis of *m*-xylyl substituted bithiophene diol and tetrapyrrane.



Scheme 5. Synthesis of *m*-xylyl substituted tetrathiaoctaphyrin **19.**

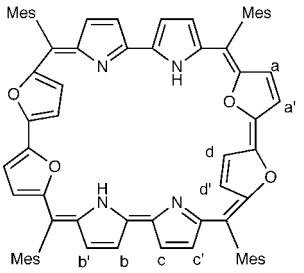
COSY correlations are marked in the spectrum. There are five signals in the region 9.8–11.3 ppm, which are assigned to the protons of bipyrrolic and bifuran protons. The multiplet at 10.8 ppm is correlated to two doublets at 10.05 and 9.83 ppm confirming the assignment of those to bipyrrolic protons [b, c and b′, c′]. The other two doublets at 11.3 and 10.2 ppm are correlating among themselves and hence assigned to β-CH proton of non-inverted furan rings [a, a′]. The conformation for the ring inversion came from the COSY analysis of the signals in the upfield region. In the upfield region, two doublets at -4.8 and -5.1 ppm were found along with two broad signals at -2.6 and -3.15 ppm. The doublets were found to be correlated amongst themselves indicating their origin from the same heterocyclic ring, which are inverted. The signals at -3.1 and -2.6 ppm did not show any correlations and hence were assigned to the NH of the pyrrole rings. The $\Delta\delta$ value of 16.4 ppm justifies the aromatic character of the octaphyrin.

Tetraselena derivative **14** exhibited only broad signals in the up-field and low-field region. Temperature variation from 333 to 210 K went futile in resolving the ^{1}H NMR spectrum. At room temperature, two signals at 10.41 and 9.85 ppm corresponding to the protons of the biselenophene unit and two signals at 9.52 and 8.77 ppm corresponding to pyrrole protons were observed. A broad signal for the protons of inverted selenophene rings was observed at -2.06 ppm, clearly indicating the ring current effect on the protons present inside the cavity of the macrocycle. These are expected due to ring inversions of one of the heterocyclic ring in the biselenophene unit as observed in the case of tetra thia octaphyrin.[23]

m-Xylyl substituted octaphyrin **19** also exhibits aromaticity as observed by spectroscopic analysis. Based on ^{1}H NMR spectrum, **19** also exhibit ring inversions due to the observation of the signals in the upfield region. In the upfield region, two broad signals are observed at -3.2 and -4.2 ppm for the β-CH of the inverted heterocyclic rings. In the low field region (Figure 2), two sets of doublets and a broad singlet at 14.1 ppm are observed. Two doublets at 11.9 and 11.0 ppm

Compound **17** on subsequent reaction with pyrrole in presence of acid yielded the required tetrapyrrane **18**. Oxidation of **18** under acidic conditions yielded the desired planar and aromatic octaphyrin, **19** in 5% yield (Scheme 5). This reaction clearly indicates the necessity of bulkier groups on the *ortho* positions of the *meso* phenyl rings in stabilizing the planarity of the molecule.

^{1}H NMR spectroscopy: The ^{1}H NMR spectrum of tetraoxa octaphyrin **15** was well resolved in free base form. A typical spectrum observed for free base of **15** shown in the Figure 1 and the corresponding assignments which is based on ^{1}H,^{1}H



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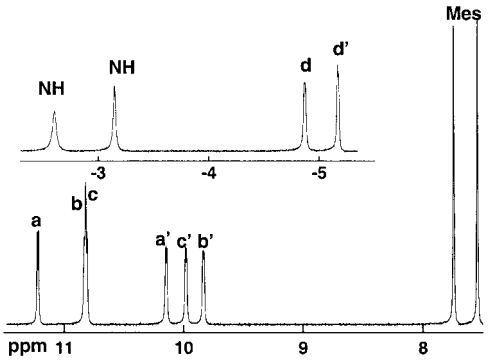
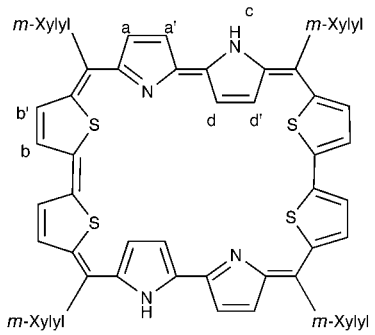


Figure 1. ^{1}H NMR spectrum of **15** in $CDCl_3$ at 298 K. The assignments are marked based on the ^{1}H,^{1}H COSY spectrum.



19

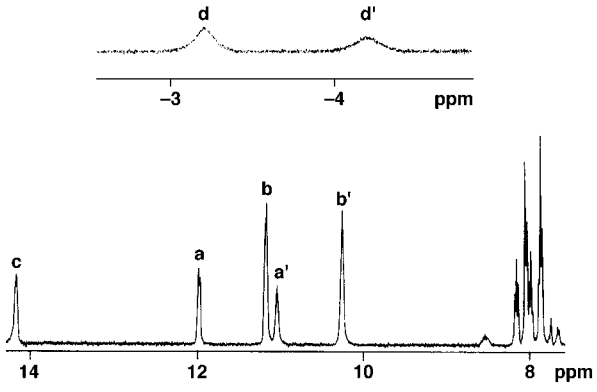


Figure 2. ^{1}H NMR spectrum of **19** in $CDCl_3$ at 298 K in the low field region. The assignments are marked based on the ^{1}H,^{1}H COSY spectrum. The inset shows the up field region.

corresponding to one proton each and other two doublets at 11.1 and 10.2 ppm corresponding to two protons each show correlations amongst themselves in the ^{1}H,^{1}H COSY spectrum. While the broad singlet at 14.1 ppm does not show any correlation with any other signal in the spectrum. These results lead to the understanding that pyrrole ring of the bipyrrole is inverted rather than the thiophene rings. Such inversion of pyrrole from the bipyrrolic units has been observed earlier in di-oxa rubyrins.[12c]

The protonated derivatives of [**14**$\cdot$**(TFA)$_2$**, **15**$\cdot$**(TFA)$_2$**, **19**$\cdot$**(TFA)$_2$**] showed only broad resonances in the temperature 333 to 210 K and hence no attempt was made to analyze the spectra in detail.

Spectral characterization: Electronic absorption spectra of octaphyrins **14** and **15** display typical porphyrinoid characteristics. Compound **14** exhibits an intense Soret-like absorption at 645 nm ($\varepsilon = 2.8 \times 10^5$) and weak (Q-band like) absorptions in the region 745 – 910 nm (Figure 3). Upon protonation, the

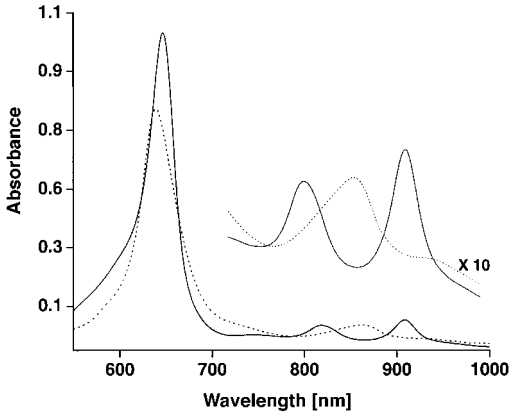


Figure 3. Electronic absorption spectra of 1.35×10^{-5} M of **14** (6.75×10^{-6} M for protonated) in CH_2Cl_2. The diprotonated species was generated by addition of a dilute solution of TFA in CH_2Cl_2.

Soret-like absorption is shifted to 639 nm ($\varepsilon = 2.1 \times 10^5$), while a lone Q-band like absorption is observed at 862 nm. In case of **15**, a strong split Soret-like absorptions at 600 nm ($\varepsilon = 17.8 \times 10^4$) and 633 nm ($\varepsilon = 14.4 \times 10^4$) along with Q-band like absorptions in the region 790 – 885 nm were observed. On protonation the Soret-like absorption is shifted to 636 nm ($\varepsilon = 27.98 \times 10^4$) while the Q-band like absorptions are further red shifted to lower energy region (855 – 933 nm). The electronic absorption spectrum of **19** does not vary much from that of the tetrathiophene congener **10**. Both in the freebase form and in the protonated form, they resemble very much with each other. These observations reveal that octaphyrins have the electronic properties similar to that of the parent porphyrin.

Crystallographic characterization: Octaphyrin **10**, displays a planar geometry even in solid state. Also two different tautomers were identified in the solid state based on the position of the NH protons.[23] It was observed that the location of NH adjacent to the non-inverted thiophene helped the formation of weak N-H-S hydrogen bonds, while, the β-CH of the inverted thiophene ring formed weak C-H-N hydrogen bonds with the adjacent pyrrole nitrogens. This helped the molecule to sustain a flat structure. In the case of

the other tautomer, the presence of β-CH and the pyrrole NH created a minor steric hindrance leading to the tilt of the thiophene ring away from planarity.

A similar structure has been observed even for the octaphyrins **14** and **15** and also it was found that these octaphyrins are able to bind anions when they are crystallized in acidic conditions (Table 1). Since the octaphyrins have been crystallized under acidic conditions, there is no possibility of isolating two tautomers. In acidic conditions both the octaphyrins bind two TFA molecules in 1:2 ratio, one above and below the plane of the macrocycle. These octaphyrins revealed for the first time novel interactions between the host and guest apart from the usual electrostatic interactions. The TFA anion complex of **14**·$(TFA)_2$ displays a fairly flat structure of the macrocycle similar to that as observed for tetrathia octaphyrin (Figure 4). The planarity of the macrocycle is slightly disrupted probably due to the binding of the anions. Four hydrogen bonding interactions were found to be responsible for the binding of each TFA to the macrocycle. They are i) N2-H-O1 (2.232 Å, 143.67°), ii) N2-H-O1 (2.139 Å, 146.64°), iii) C11-H-O1 (2.444 Å, 171.04°) and iv) C34-H-F2 (2.323 Å, 146.22°). Of the above four interactions, the first two are typical electrostatic interactions. The protonation of the imino type nitrogens creates a positive charge, which attracts the counter anion (CF_3COO^-). The other two interactions are induced probably due to the geometric features of the interaction between the anion and the host macrocycle. The β-CH of the inverted selenophene ring forms a strong hydrogen bond with the oxygen of the -OH group in TFA. The proximity for the interaction is clearly evident from the near linear bond angle, which is one of the strong reasons for the existence of this hydrogen bond. Such an interaction could be comprehended only due to the complete inversion of the selenophene ring. Due to such geometry, the β-CH of the inverted ring comes in plane with the -CO of the TFA as supported by the bond angle of 171.04°.

Table 1. Crystal data for TFA complexes of **14** and **15**.

	Se4N4·$(TFA)_2$	O4N4·$(TFA)_2$
solvent of crystallization	CH_2Cl_2/TFA/hexane	CH_2Cl_2/TFA/hexane
empirical formula	$C_{72}H_{62}N_4Se_4$	$C_{72}H_{62}N_4O_4$
T [K]	88(2)	86(2)
crystal System	orthorhombic	monoclinic
space group	*Pbca*	*P*2(1)/*c*
V [Å^3]	8176.5(8)	3610.4(3)
a [Å]	23.6220(14)	9.8383(5)
b [Å]	13.4931(8)	24.1836(13)
c [Å]	25.6532(15)	15.3442(8)
α [°]	90.00	90.00
β [°]	90.00	98.5330(10)
β [°]	90.00	98.5330(10)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.241	1552
refls coll./unique	7189/5567	6349/4604
F(000)	3080	1552
limit. indicies	$-28 \le h \le 28$	$-11 \le h \le 11$
	$-16 \le k \le 16$	$-28 \le k \le 28$
	$-30 \le l \le 30$	$-18 \le l \le 18$
GoF (F^2)	1.105	1.030
inal R indicies $\{I > 2\sigma(I)\}$	$R1 = 0.0651$	$R1 = 0.0692$
	$wR2 = 0.1492$	$wR2 = 0.1822$

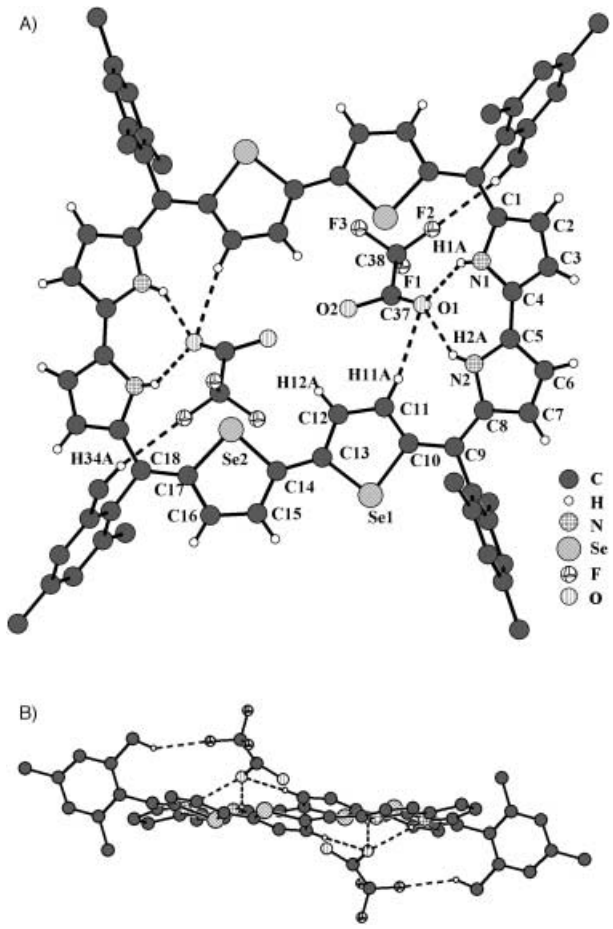


Figure 4. A) Top view of the TFA bound complex of octaphyrin, **14.** B) Side view; the *meso*-mesityl rings and noninteracting hydrogens which are not involved in the hydrogen bonding are omitted for clarity.

Even though, expanded porphyrins with inverted heterocyclic rings are known to bind anions, this is the first report of the solid-state evidence for the involvement of the β-CH in binding a guest molecule to the macrocycle. The carbonyl group oxygen of TFA was disordered and has 50% probability, hence it was considered for any type of interactions with the octaphyrin. Another important interaction observed was between the fluorine of the TFA and the hydrogen of the methyl group on the *meso*-mesityl ring between the non-inverted heterocyclic rings. Two such interactions are observed due to the binding of two anions to the macrocycle. Such type of intramolecular hydrogen bonding between the *meso*-substituent of the macrocycle and the guest molecule defines novel binding modes between the host and the guest in expanded porphyrins. (For relevant bond angles and the important bond lengths refer Tables S1 and S2 in the Supporting Information.)

Further analysis on hydrogen bonding revealed that octaphyrins form one-dimensional supramolecular array (Figure 5) through intermolecular C-H-F hydrogen bonds (C-H-F: 2.55 Å; 149.43°). This array is formed through the involvement of the aromatic CH from the *meso*-mesityl rings adjacent to the inverted selenophene rings and one of the fluorine from the TFA. As described schematically, two TFA molecules are sandwiched between two octaphyrins, which

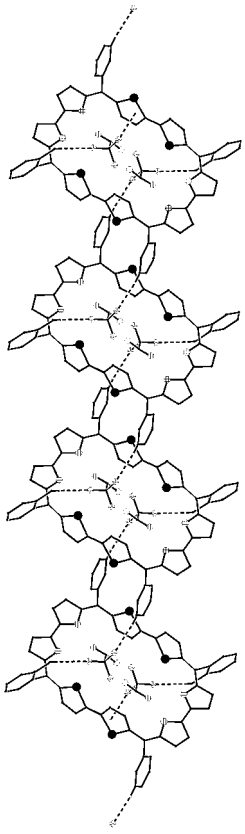


Figure 5. A view of the one-dimensional array formed by **14**·$(TFA)_2$. The hydrogen bonding interactions are shown in the dotted lines.

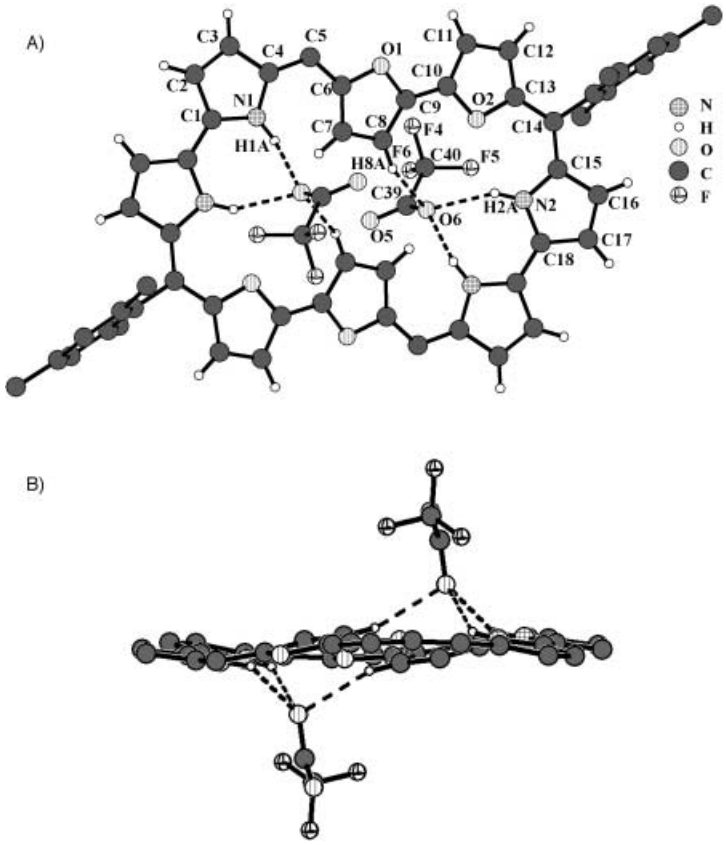
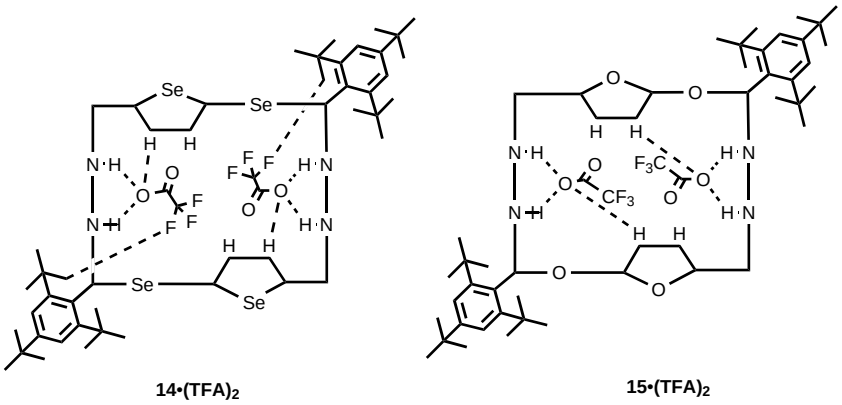


Figure 6. A) Top view of the TFA bound complex of octaphyrin, **15**. The disordered mesityl rings are omitted for clarity. B) Side view; the *meso*-mesityl rings and non-interacting hydrogens which are not involved in the hydrogen bonding are omitted for clarity.

are separated by a distance of 13 Å approximately. To the first octaphyrin, the TFA is bound to pyrrolic nitrogens, inverted ring proton and the methyl group of the mesityl ring. At the other end it has two fluorine atoms free. One of them forms a weak hydrogen bond with the aromatic CH of the mesityl ring from the second octaphyrin. A complementary interaction between the TFA from the second octaphyrin to the first one makes the interaction stronger. Such interactions continue to add up over each octaphyrin molecule, thus forming the supramolecular array in one dimension.

Tetraoxaoctaphyrin, **15**, also binds two TFA molecules, one above and below the plane of the molecule (Figure 6). The distortion to the octaphyrin plane was found to be very minimal in comparison to **14** and the macrocycle exhibits a planar structure. In this case, the TFA and one of the mesityl rings are disordered and hence those groups have been excluded while considering the intra- and intermolecular interactions. Both the TFA molecules are bound to the macrocycle by three hydrogen bonding interactions. They are i) N-H-O (2.142 Å, 142.43°), ii) N-H-O (2.057 Å, 139.66°), iii) C-H-O (2.335 Å, 149.3°). The first two are electrostatic interactions, while the C-H-O is a nonelectrostatic interaction due to the β-CH of the inverted furan ring. The mode of TFA binding to **14** and **15** differs in the way the β-CH of the inverted ring interacts with the guest molecule (Scheme 6). In case of **14**, the β-CH of the inverted ring binds the TFA bound to the bipyrrolic unit adjacent to it. On the other hand, in **15**, the β-CH of the inverted ring binds to TFA bound to the non-adjacent bipyrrol unit. The difference observed is credited to the modifications observed in the bifuran unit. The non-inverted ring is slightly pushed away from the center of the cavity, while the inverted ring is pushed more inside and



Scheme 6. Different modes of TFA binding to octaphyrins **14** and **15**.

towards the adjacent furan unit. This makes the β-CH of the inverted furan unit to come in close proximity with the TFA bound to the nonadjacent bipyrrol unit. This could be probably due to the short size of the oxygen in furan unit, which experiences more strain on cyclisation and probably more in the protonated form.

Conclusion

The syntheses of *meso* aryl aromatic octaphyrins with different heteroatoms have been achieved by a simple synthetic methodology. These molecules are aromatic in nature and are largest aromatic molecules to be characterized in solid state to date. Oxidative coupling of appropriate precursors under acidic conditions has become an attractive strategy for the synthesis of higher order aromatic expanded porphyrins. These flat molecules bind anions in acidic conditions in 1:2 ratio. It is expected that by having appropriate *meso* substituents it is possible to stack long arrays of planar molecules, which lead to the formation of channels of varied dimensions.

Experimental Section

Instrumentation: Electronic spectra were recorded on a Perkin–Elmer Lambda 20 UV/Vis spectrophotometer. Proton NMR spectra were obtained on a 400 MHz JEOL spectrometer in $CDCl_3$. FAB-MS spectra were obtained on a JEOL-SX-120/DA6000 spectrometer.

X-ray crystallographic studies: X-ray quality crystals for all compounds were grown as described in the experimental section. The crystals were removed from the tube and covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets for all compounds were collected using a Siemens SMART system, complete with 3-circle goniometer and CCD detector operating at −54 °C. The data sets for compounds **14**·$(TFA)_2$, and **15**·$(TFA)_2$ were collected at 88 K and 86 K, respectively, using a custom build low temperature device from Professor H. Hope (UC Davis). In all cases graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was employed. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different Φ angle, and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied for all compounds utilizing the program SADABS.[29] The crystal structures of all compounds were solved by Direct Methods, as included in the SHELXTL-Plus program package.[30] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F^2 (SHELX-93).[31] Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C–C bonds for methyl groups with U_{iso} constrained at 1.2 for non-methyl groups, and 1.5 for methyl groups times U_{eq} of the carrier carbon atom. The crystallographic programs used for structure refinement and solution was installed on a Silicon Graphics Indigo^2 R10000 Solid Impact or a PC clone. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms were refined anisotropically. Disorder was typically handled by including split positions for the affected groups, and included in the refinement of the respective occupancies. Complex **14**·$(TFA)_2$ contains a particularly disordered TFA unit situated in holes in the crystalline network. The TFA molecules have been removed from the structure so that a better refinement could be obtained using the Squeeze program, as implemented in Platon.[32] The electron density and hole size agree well with the solvent being TFA. Further details about the refinements are outlined in the Supporting Information.

CCDC-196155 (**14**) and 196156 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223–336033; or deposit@ccdc.cam.ac.uk).

Chemicals: All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran and *n*-hexane were purified and distilled by standard procedures. Bifuran and biselenophene diols and tetrapyrranes were synthesized according to the published procedure and stored under inert atmosphere.[27]

Syntheses

5,5′-Bis-(xylylhydroxymethyl)-2,2′-bithiophene (17): To Magnesium turnings (0.35 g, 14.4 mmol) in dry tetrahydrofuran (THF) (5 mL) under nitrogen was added *m*-bromoxylene (1.8 mL, 14.4 mmol) in dry THF (2 mL). The mixture was stirred overnight for the formation of the Grignard reagent. Then bithiophene dialdehyde **16** (1 g, 4.5 mmol) in dry THF (10 mL) was added over a period of 30 minutes at 0 °C. The reaction was further stirred for 4 h and later quenched with dilute hydrochloric acid (10 mL). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine (0.1N) and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to obtain a brown semi solid. This was taken directly for the preparation of tetrapyrrane **18**.

5,14-Dixylyl-20,21-dithiatetrapyrrane (18): A known procedure for the synthesis of tetrapyrrane **18** was followed using diol **17** (0.4 g, 0.92 mmol) and pyrrole (2.6 mL, 36.8 mmol). Purification by column chromatography (silica gel, 100–200 mesh, petroleum ether/ethyl acetate 98:2 gave a light brown colored solid identified as **18** (0.32 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81$ (br s, 2NH), 7.06–6.96 (m, 6H), 6.85 (d, $J = 3.8$ Hz, 2H), 6.64 (d, $J = 3.6$ Hz, 2H), 6.61, (m, 2H), 6.11(m, 2H), 6.02 (s, 2H), 5.99 (s, 2H), 1.5 (s, 12H); FAB MS: *m/z* (%): 532 (100) [M^+].

General synthesis of octaphyrins

5,14,23,32-Tetramesityl-35, 36, 39, 40-tetraselenaoctaphyrin (14): Tetrapyrrane **12** (0.25 g, 0.4 mmol) was dissolved in dry CH_2Cl_2 and stirred under nitrogen atmosphere in absence of light for 15 minutes. TFA (0.03 mL, 0.4 mmol) in dry CH_2Cl_2 was added and stirring continued for another one hour. Reaction mixture was opened to air. chloranil (0.1 g, 0.4 mmol) was added, and the reation mixture was heated under reflux for one hour on a preheated oil bath. The solvent was removed under reduced pressure. The residue obtained was purified by chromatography on a basic alumina column. A blue color band eluted with petroleum ether/CH_2Cl_2 (3:2) gave a brownish metallic solid identified as **14** (0.05 g, 9.6%). Recrystallization from CH_2Cl_2/*n*-hexane afforded gold colored crystals. M.p. 225 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 10.42$ (s, 2H), 9.85 (s, 2H), 9.58–9.48 (br, 4H), 8.77–8.72 (br, 4H), 7.57 (s, 4H), 7.42 (s, 4H), 2.75 (s, 6H), 2.66 (s, 6H), 2.23 (s, 12H), 2.08 (s, 12H), −2.1 (br s, 4H); FAB MS: *m/z* (%): 1300 (30) [M^++2]; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}): 646 (28), 745 (1.3), 818 (2.07), 908 nm (3.1); (CH_2Cl_2/TFA): λ_{max} ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}): 638 (21), 862 nm (2.07); elemental analysis calcd (%) for $C_{72}H_{62}N_4Se_4$: C 66.56, H 4.81, N 4.30; found: C 66.89, H 4.70, N 4.19.

5,14,23,32-Tetramesityl-35,36,39,40-tetraoxaoctaphyrin (15): A procedure similar as described above was followed by using tetrapyrrane **13** (0.25 g, 0.47 mmol), TFA (0.03 mL, 0.4 mmol) and chloranil (0.116 g, 0.47 mmol). Upon chromatographic separation with basic alumina, a blue colored band eluted with petroleum ether/CH_2Cl_2 (1:1) gave a brownish metallic solid identified as **15** (0.02 g, 4%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 11.28$ (d, $J = 3.6$ Hz, 2H), 10.88 (m, 4H), 10.21 (d, $J = 3.6$ Hz, 2H), 10.04 (d, $J = 3.6$ Hz, 2H), 9.9 (d, $J = 4$ Hz, 2H), 7.8 (s, 4H), 7.6 (s, 4H), 2.99 (s, 6H), 2.84 (s, 6H), 2.25 (s, 12H), 2.18 (s, 12H), −2.54 (br s, NH), −3.08 (br s, NH), −4.8 (d, $J = 4$ Hz, 2H), −5.1 (d, $J = 4$ Hz, 2H); FAB MS: *m/z* (%): 1046 (100) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}): 600 (16.12), 633 (14.38), 792 (1), 885 nm (4.8); (CH_2Cl_2/TFA) λ_{max} ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}): 636 (28), 784 (0.5), 855 (0.9), 965 nm (3.4); elemental analysis calcd (%) for $C_{72}H_{62}N_4O_4$: C 82.57 H 4.95, N 5.34; found: C 82.88, H 6.12, N 5.25.

***5,14,23,32-Tetraxylyl-35,36,39,40-tetrathiaoctaphyrin (19)*:** A similar procedure as mentioned above was employed using tetrapyrrane **18**,

(0.25 g, 0.47 mmol) and TFA (0.04 mL, 0.47 mol) and chloranil (0.115 g, 0.47 mmol). Upon chromatographic purification with basic alumina, a blue colored band eluted with petroleum ether/CH_2Cl_2 (7:3) gave a brownish metallic solid identified as **19** (0.025 g, 5%). Recrystallization from CH_2Cl_2/*n*-hexane afforded gold colored crystals. M.p. 250°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 14.15$ (brs, 2NH), 11.98 (d, $J = 4$ Hz, 2H), 11.17 (m, 4H), 11.04 (brs, 2H), 10.25 (brs, 4H), 8.54–8.17 (m, 4H), 8.15–8.05 (m, 4H), 8.02 (m, 4H), 2.24 (s, 12H), 2.1 (s, 12H), −3.2 (brs, 2H), −4.2(brs, 2H); FAB MS: *m/z* (%): 1055 (30%) [M^++H]; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$ M^{-1}cm^{-1}): 596 (6.28), 750 (0.7), 833 (1.10), 907 nm (0.6); (CH_2Cl_2/TFA): λ_{max} ($\varepsilon \times 10^{-4}$ M^{-1}cm^{-1}): 645 (17.53), 792 (0.5), 868 (0.7), 981 nm (2.36).

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