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# Modified 26 and 28 $\pi$ Hexaphyrins with Five *meso*-Links: Optical, Redox, and Structural Properties

Sabapathi Gokulnath,<sup>[a]</sup> Viswanathan Prabhuraja,<sup>[a]</sup> Cherumuttathu H. Suresh,<sup>[b]</sup> and  
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*Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday*

**Abstract:** The syntheses of new aromatic 26 $\pi$  and non-aromatic 28 $\pi$  hexaphyrins through a [4+2] acid catalyzed condensation of easily available and air-stable precursors are reported. Both 26 $\pi$  and 28 $\pi$  hexaphyrins are reversibly transformed into one another by two-electron reduction with NaBH<sub>4</sub> or two-electron oxidation with dichlorodicyanobenzoquinone (DDQ) respectively. Detailed optical and NMR spectral studies suggests that the [26]hexaphyrin is aromatic and possesses a diatropic

ring current, while [28]hexaphyrin exhibits non-aromatic characteristics. The structural characterization has been done with extensive <sup>1</sup>H and 2D NMR studies. Theoretical calculations performed with various conformational possibilities tested for the unsubstituted hexaphyrin, at semiempirical level, sug-

**Keywords:** aromaticity • conformational analysis • conjugation • hexaphyrins • redox chemistry

gest that the most stable conformation takes an inverted structure with one pyrrole ring inversion. The energy optimization for the final geometry of the unsubstituted hexaphyrin, performed at the B3LYP/6-31G\* level of DFT, shows excellent agreement with the structure derived from the solution NMR data. Electrochemical data reveals HOMO destabilization with increasing  $\pi$ -electron conjugation consistent with the large red shifts of the absorption bands.

## Introduction

Expanded porphyrins continue to attract the attention of chemists because of their interesting structural diversity, optical and electrochemical properties.<sup>[1]</sup> Hexaphyrins in particular are known to exhibit fascinating structural diversity, redox behavior, and aromatic property. These properties are shown to be a function of their conformation, the number of

$\pi$ -electrons in conjugation, as well as the number of *meso* carbon bridges that link the six pyrrole/heterocyclic rings.<sup>[2]</sup> The hexaphyrins reported in literature to date are shown in Scheme 1. In hexaphyrins **1–4**, the six pyrrole rings are linked to each other in cyclic fashion through two, three, four, and five *meso* carbons respectively. Among these, **1**<sup>[3]</sup> and **2**<sup>[4]</sup> show non-aromatic behavior, while **3**<sup>[5]</sup> and **4**<sup>[17]</sup> exhibit aromatic characteristics. Hexaphyrins **5a–d**<sup>[6,7]</sup> exhibit different structural diversity even though they have six *meso* links, which depends on the nature of the heteroatoms in the core as well as the substituents on the periphery. For example, **5a**, which contains 28 $\pi$  electrons, has a twisted ‘non-planar’ structure, while **5b**, which also has 28 $\pi$  electrons, shows a ‘figure-eight’ structure, and both are non-aromatic. On the other hand, **5c** and **5d**, which have 26 $\pi$  electrons in conjugation, show aromatic behavior with planar or slightly tilted structures.<sup>[8,9]</sup> Thus, it is obvious that the substituents present on the  $\beta$ -pyrrole ring and the *meso* aryl group are usually the main deciding factors of structural diversity and aromatic behavior.

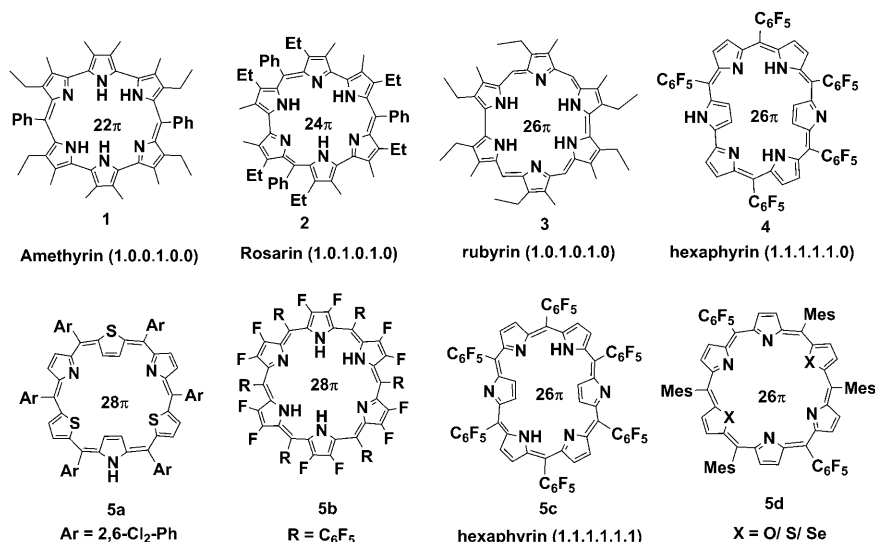
Among the series of hexaphyrins described above, hexaphyrins with four and six *meso* carbons are reasonably well studied with respect to their structural behavior and aroma-

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Scheme 1. The hexaphyrins reported in literature to date.

ticity. For example, Sessler and co-workers<sup>[10]</sup> were the first to synthesize the 26 $\pi$  rubyrin (**3**) and exploited their structural and spectroscopic behavior. Later, Chandrashekar and co-workers<sup>[11]</sup> reported a series of core-modified rubyrins and analysed their anion binding properties and aromatic behavior. On the other hand, several groups such as Gossauer and co-workers,<sup>[12]</sup> Dolphin and co-workers,<sup>[13]</sup> and Cavaleiro and co-workers<sup>[8]</sup> have synthesized and reported the properties of hexaphyrin with six *meso* links. Hexaphyrin **5c** reported by Cavaleiro and co-workers, which shows two rings with inverted structure and present in two isomeric forms, can be interconverted by a hydrogenation–dehydrogenation process. Recently, Osuka and co-workers<sup>[14,15]</sup> reported the syntheses and structural characterization of

#### Abstract in Tamil:

புதிய அரோமேட்டிக் 26 $\pi$  மற்றும் அரோமேட்டிக் அல்லாத 28 $\pi$  ஹெக்சாபைரின்கள் [4+2] அமிலதாக்க ஊக்கியின் சுருக்குவினையால் எளிதில் கிடைக்கக்கூடிய மற்றும் நிலையான முன்பொருட்கள் மூலம் தயாரிக்கப்பட்டதை அறிவிக்கப்பட்டுள்ளது. 26 மற்றும் 28 $\pi$  ஹெக்சாபைரின்கள் NaBH<sub>4</sub> மூலம் இரண்டு எலக்ட்ரான் ஆக்சிஜனோடுக்கத்தாலும் DDQவினால் இரண்டு எலக்ட்ரான் ஆக்சிஜனேற்றத்தாலும் ஒன்றோடொன்று மீளுந்தாக்குகின்றன. விரிவான ஒளிச்சூழல் மற்றும் அணுக்கரு காந்த உடனினைவு சோதனைகளினால் (NMR) 26 $\pi$  ஹெக்சாபைரின் அரோமேட்டிக் என்பதையும் 28 $\pi$  ஹெக்சாபைரின் அரோமேட்டிக் அல்லாத பண்புள்ளவை எனவும் தெரியவருகின்றன. <sup>1</sup>H மற்றும் 2D அணுக்கரு காந்த உடனினைவு (NMR) மூலம் இதன் உருவமைப்பின் சிறப்பியல்பாக்கம் விரிவாக ஆராயப்பட்டுள்ளது. அரைவிகித நிலையில் பதிலியிடப்படாத ஹெக்சாபைரின் 12aயின் பலவிதமான வெளிவடிவமைப்புகளை அறிமுகமுறை கொள்கையின் கணக்கீடுகளின் மூலம் பெரும்பான்மையான மற்றும் நிலையான வெளிவடிவ அமைப்பில் ஒரு பைரோல் மட்டும் திரும்பியுள்ளதை தெரியப்படுத்துகின்றன. ஹெக்சாபைரின் 12aயின் இறுதி வடிவத்தை DFTயின் B3LYP/6-31G\* நிலையில் வெளிப்பட்ட உருவமைப்பும் அணுக்கரு காந்த உடனினைவு (NMR) மூலமாக வரையறுக்கப்பட்ட உருவமைப்பும் மிகச்சிறப்பாக ஒத்துப்போகின்றன. மின்வேதியல் விவரத்தின் மூலம் இவைகளின் HOMOs நிலையில் ஏற்றம் பெற்றதையும் கூடுதல்  $\pi$ -எலக்ட்ரான் இனையும் அதுனுடைய உட்கவர்வு பட்டயின் அலைநீள உயர் நகர்வால் நிறுபிக்கப்பட்டுள்ளது.

[26]hexaphyrin (1.1.1.1.1.1) **5c** which also exhibits two rings inverted structure in a Rothemund type of a reaction, which employs pyrrole and an electron withdrawing aldehyde. The formation of a series of higher analogues of expanded porphyrins was also reported.

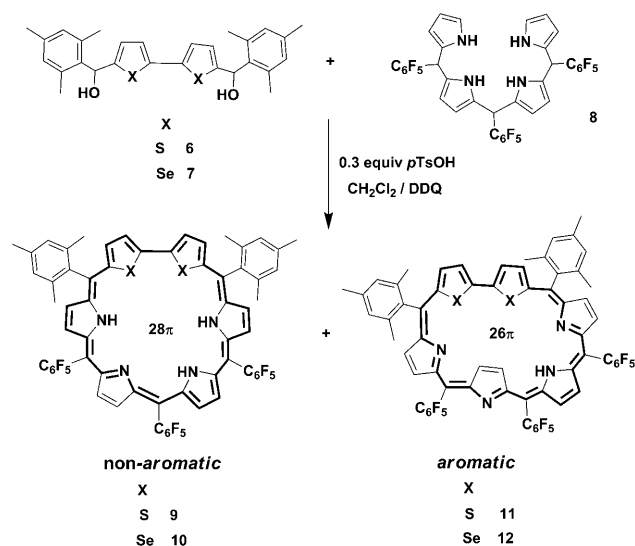
There is only one recent report on a hexaphyrin that contains five *meso* bridges. In this report, Wong and co-workers<sup>[16]</sup> described the synthesis and structural characterization of **4**. It has been shown that **4** serves as a NIR fluorescent probe for the detection of Hg<sup>2+</sup> ions. Thus, it is of interest to synthesize hexaphyrins that bear five *meso* carbons to un-

derstand their structural behavior as well as their spectroscopic properties. In this paper we wish to report a series of core-modified hexaphyrins, which are linked by five *meso* carbon bridges and the study of their structural, optical, and electrochemical properties. The hexaphyrins reported here exhibit interesting optical and electrochemical properties. For example, hexaphyrin **10** and **12** can undergo interconversion between an aromatic 26 $\pi$  system and non-aromatic 28 $\pi$  system using redox agents.

## Results and Discussion

### Syntheses

The key precursors required for the synthesis were bithiophene diol (**6**) with bulky *meso* substituents and tetrapyrane (**8**) with electron withdrawing *meso* substituents. These precursors were synthesized as reported earlier by our group as well as others.<sup>[17,18]</sup> Thus a [4+2] MacDonald type condensation of tetrapyrane **8** with bithiophene **6** or bisele-nophene diol **7** gave hexaphyrins **9–12**. In a typical synthesis, equimolar amounts of **7** and **8** were stirred for 1 h in CH<sub>2</sub>Cl<sub>2</sub> using *p*-toluenesulfonic acid as catalyst (Scheme 2). After oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), the products were purified by repeated basic alumina and silica gel column chromatography. Initially, a red fraction was eluted with CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:3. FAB-MS determined the fraction to exhibit a parent ion peak at *m/z* = 1317 (calcd. for (C<sub>65</sub>H<sub>37</sub>F<sub>15</sub>N<sub>4</sub>Se<sub>2</sub>) [*M*+1]) which was identified as hexaphyrin **10** in 5–6% yield. After this band, a violet fraction was eluted with ethylacetate/CH<sub>2</sub>Cl<sub>2</sub> = 2:98. FAB-MS determined the fraction to exhibit a parent ion peak at *m/z* = 1315 (calcd. for (C<sub>65</sub>H<sub>35</sub>F<sub>15</sub>N<sub>4</sub>Se<sub>2</sub>) [*M*+]) which was identified as **12** (yield: 11%). The important observation is that only mesityl substituents on the diols **6–7** and the electron-deficient pentafluorophenyl group on the tetra-

Scheme 2. Syntheses of *meso*-aryl hexaphyrins.

pyrrane (**8**) were well suited for the formation of hexaphyrins **9–12**. This clearly indicates that no acidolysis of the tetrapyrane **8** took place during the reaction, thereby preventing the formation of side products. The presence of bulky substituents at the *meso* position is also necessary for the formation of expanded macrocycles. A similar approach was also used in the synthesis of higher cyclooctapolyrroles, that is, octaphyrins, dodecaphyrins, and hexadecaphyrins.<sup>[19]</sup> It is assumed that the bulky groups at the *meso* positions helps the macrocyclic ring to expand rather than form smaller rings because of possible steric hindrance between the  $\beta$ -CH protons of the heterocyclic ring and the *meso* substituents. The interesting feature of the present method is the isolation of only the desired products under the reaction conditions, thus making the purification easy.

### UV/Vis Absorption Studies

In general, the electronic absorption spectra of hexaphyrins are characterized by the presence of an intense Soret-like absorption band in the region 500–560 nm and weak Q bands from 550–1000 nm. For example, the free-base form of **12** (Figure 1a) shows a Soret-type band at 558 nm ( $\epsilon = 1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) with a shoulder at 586 nm ( $\epsilon = 0.68 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) followed by a weak Q band-like absorption at 713, 776, and 887 nm. Upon protonation, the Soret-like band undergoes a 10 nm red shift with an increase in  $\epsilon$  to  $2.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  similar to the absorption spectra of other [26]hexaphyrins.<sup>[9]</sup> In contrast, [28]hexaphyrin **10**, a reduced isomer of **12**, exhibits two broad bands, namely, at 403 ( $0.38 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 561 nm ( $0.68 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) as shown in Figure 1b. On protonation, the 561 nm band undergoes a 60 nm red shift and two Q-bands are observed at 860 and 970 nm without marked increase in the  $\epsilon$  value, which is characteristic of a non-aromatic [28]hexaphyrin.

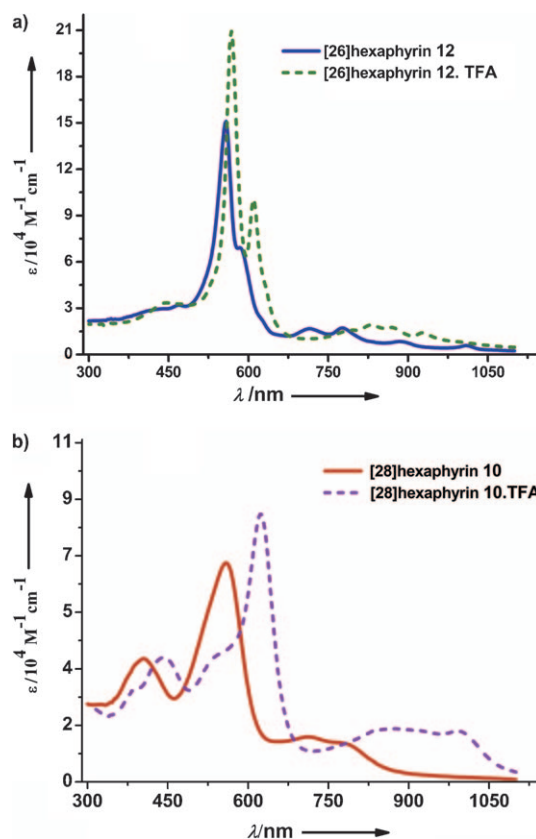


Figure 1. UV/Vis absorption spectra of a) hexaphyrin (**12**;  $1.1 \times 10^{-5} \text{ M}$ ) and its protonated form and b) hexaphyrin (**10**;  $1.14 \times 10^{-5} \text{ M}$ ) and its protonated form in  $\text{CH}_2\text{Cl}_2$ .

### Redox Inter-Conversion between Aromatic [26] and Non-Aromatic [28]Hexaphyrins

An attractive feature of conjugated expanded porphyrins is their ability to undergo two-electron oxidation and reduction reactions through facile release and uptake of two hydrogen atoms bonded to the nitrogen atoms. Recent findings from our laboratory<sup>[19]</sup> indicated that 30 and 32 $\pi$  heptaphyrins undergo facile redox inter-conversion in a reversible manner, and motivated us to investigate the redox behaviour of aromatic [26]hexaphyrin and non-aromatic [28]hexaphyrins. It was thus of interest to see if hexaphyrin **12**, a 26 $\pi$ -electron aromatic species, could be reduced to the corresponding 28 $\pi$ -electron non-aromatic species **10** simply by adding the reducing agent,  $\text{NaBH}_4$ . It is noteworthy that such an inter-conversion may lead to easy access to a wide range of expanded porphyrins with different electronic and optical properties. Thus, an increase in the concentration of  $\text{NaBH}_4$  in a mixture of methanol and dichloromethane (2:1) solution resulted in decreasing bands at 403 and 561 nm with an isobestic point at 625 nm, which suggests the presence of an equilibrium between the reduced and oxidized forms (Figure 2). In the course of our experiment, disappearance of three Q-bands at 713, 776, and 887 nm was also observed giving rise to a less intense Q-band at 785 nm. Overall, the observation of two less intense ill-defined broad

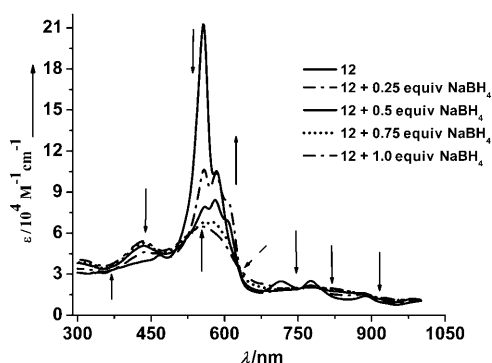


Figure 2. Redox inter-conversion between **10** and **12** in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1:2). The arrows indicate the direction of change.

bands suggest a possible conversion of aromatic [26]hexaphyrin **12** to non-aromatic [28]hexaphyrin **10** by a two-electron reduction. In order to confirm that the above transformation is reversible, the reduced form of hexaphyrin **10** was oxidized with DDQ at room temperature. The color changes observed clearly suggests rapid oxidation of **10** to **12** (see the Supporting Information). Similar reversible redox inter-conversion behavior has been reported by Cavaleiro and co-workers for 26 and 28 $\pi$  azahexaphyrins.<sup>[8]</sup>

### NMR Analysis of Hexaphyrins

The  $^1\text{H}$  NMR spectrum (Figure 3) of **12** displayed characteristic features of an aromatic macrocycle in the solution state. Signals observed both in the upfield and downfield region strongly suggests a diatropic ring current of the molecule. In the deshielded region, signals were observed from 11.56 to 8.86 ppm, while in the shielded region, resonances for the inner core  $\beta$ -pyrrolic protons were observed in the region

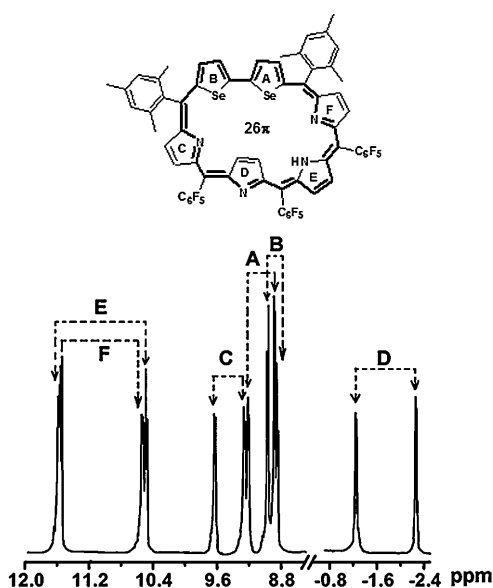


Figure 3.  $^1\text{H}$  NMR spectrum of **12** in  $\text{CD}_2\text{Cl}_2$  at 298 K. Assignments for the upfield and downfield region are shown.

from  $-1.27$  to  $-2.29$  ppm. Figure 4 shows the  $^1\text{H}$ - $^1\text{H}$  COSY spectra where six correlations for the signals both in the up-field and downfield region are observed. In the deshielded

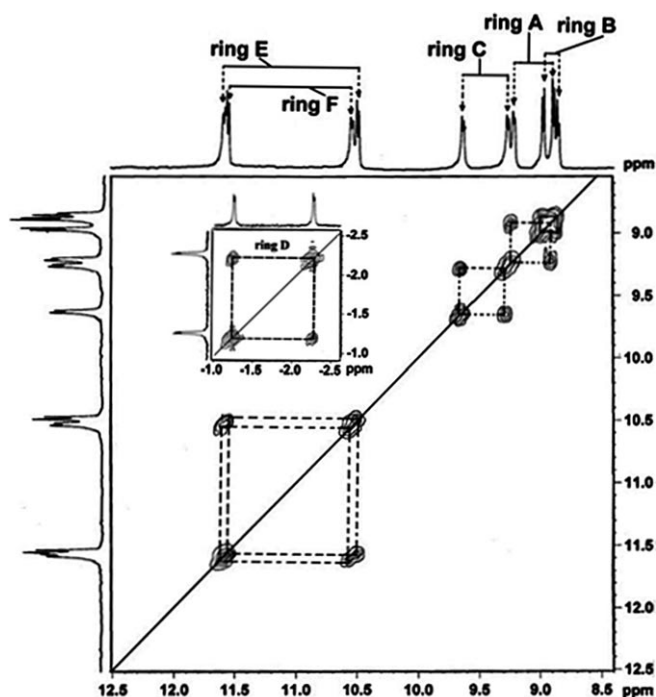


Figure 4.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **12** in  $\text{CD}_2\text{Cl}_2$  at 298 K. The dotted lines indicate the correlations observed between the signals. Inset shows the signals in the shielded region for the inverted ring.

region, a multiplet at 11.55 ppm that corresponds to two protons shows two correlations, a doublet at 10.53 ppm and a signal at 10.48 ppm corresponding to one proton each (ring E and F). Noticeably, two doublets at 8.97 and 8.86 ppm, which integrates one proton, correlates amongst themselves and hence they are assigned to the non-inverted  $\beta$ -selenophenic protons (ring A and B). Furthermore, two doublets between 9.26 and 9.62 ppm correlating with each other integrates into two protons for  $\beta$ -pyrrolic protons (ring C) and two more doublets at  $-1.27$  and  $-2.29$  ppm integrating into two protons are assigned to the inverted  $\beta$ -pyrrolic protons (ring D). The fact that the inner NH proton on the ring E was not observed in the shielded region, even at 233 K, suggests the existence of rapid tautomerism in **12**. This observation is consistent with our earlier work on core-modified smaragdyrins<sup>[20]</sup> and heptaphyrins.<sup>[21]</sup> The chemical shift difference between the most shielded and most deshielded protons ( $\Delta\delta$ ) in **12** is 14 ppm which unambiguously proves the aromatic character which arises from the 26 $\pi$ -electron pathway of hexaphyrin **12**.

Figure 5 shows the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **10** in  $\text{CD}_2\text{Cl}_2$  at 298 K. Specifically, a broad peak at 6.59 ppm which has no correlated  $^1\text{H}$  signal in the COSY spectrum integrates into two protons and is assigned to the NH's of the pyrrolic rings C and F. The two multiplets, namely at 5.23



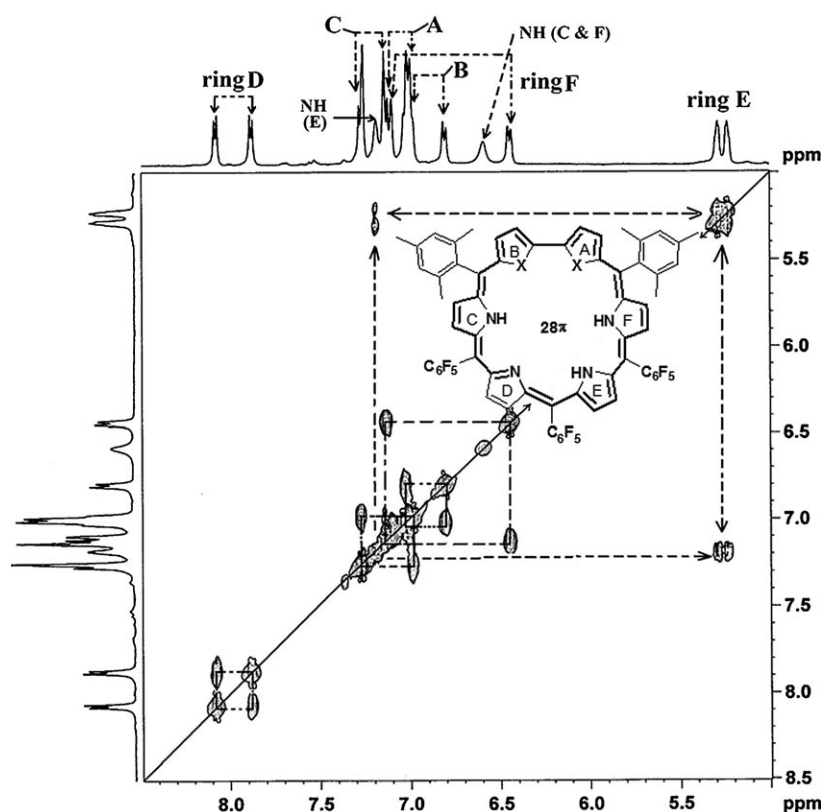


Figure 5.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **10** in  $\text{CD}_2\text{Cl}_2$  at 298 K. The dotted lines indicate the correlations observed between the signals.

and 5.28 ppm integrate into one proton which gives cross peaks with each other, and are assigned to the  $\beta$ -CH's of the pyrrole **E**. On further spatial coupling, it exhibits a larger

correlation with the proton of the pyrrolic NH (ring **E**) and appears as a broad peak at 7.2 ppm. Two closely associated doublets integrate into four protons at 7.01 ppm which shows two correlations in the COSY spectrum, one with a doublet at 7.1 ppm that integrates into one proton for ring **A**, and other with the doublet at 6.8 ppm that integrates into one proton assigned to ring **B**. In addition, the signals for the protons on the *meso*-methyl rings that resonate between 7.01 and 7.1 ppm integrate into four protons and overlap significantly with the  $\beta$ -CH's of rings **A** and **C**. Further, two doublets at 7.87 and 8.07 ppm, which are considerably down-field shifted, integrate into two protons that correlate with each other, and are apparent for the  $\beta$ -CH's of the inverted ring **D**.  $\text{D}_2\text{O}$  experiments were performed in order to prove the presence of NH's in the macrocycle and the corre-

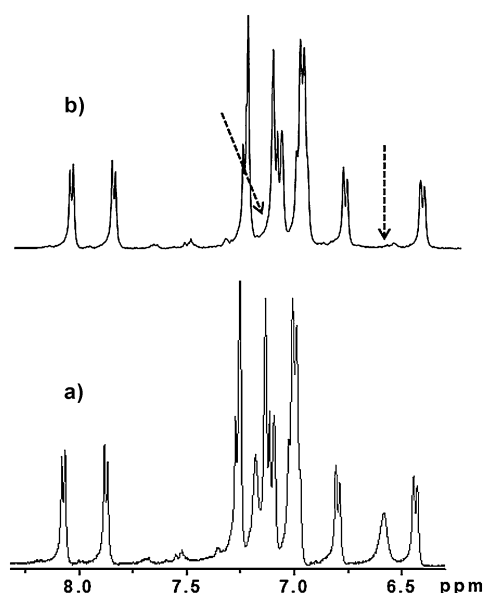


Figure 6.  $^1\text{H}$  NMR spectrum of **10** in the 8.5 to 6.5 ppm range a) in  $\text{CDCl}_3$  and b) 10:1  $\text{CDCl}_3$  and  $\text{D}_2\text{O}$  (arrows indicate the disappearance of NH signals on the addition of  $\text{D}_2\text{O}$ ).

### Conformational Analysis

Failure to obtain suitable single crystals for X-ray diffraction studies compelled us to use energy optimization techniques to understand the preferred orientations of the six pyrrolic/heterocyclic rings in the hexaphyrin system **12**. We have performed theoretical calculations using a model compound (**12a**) wherein the *meso* substituents of the hexaphyrin **12** are replaced with hydrogen atoms. The structures of seven different conformations (conformation 1 to conformation 7) are optimized at the B3LYP/6-31G\*\*(d,p)<sup>[22]</sup> level of density functional theory with the restriction of  $C_s$  symmetry. For all the calculations, the Gaussian03 suite of programs were used.<sup>[23]</sup> In conformation 1, none of the rings are inverted. Arising from experimental investigation strongly suggesting the inversion of at least one ring in the system, only six different conformations (conformation 2 to conformation 7) are possible by inverting ring **A** to **F** in conformation 1. The optimized structures of all the conformations (conformation 1 to conformation 7) are presented in Figure 7 along

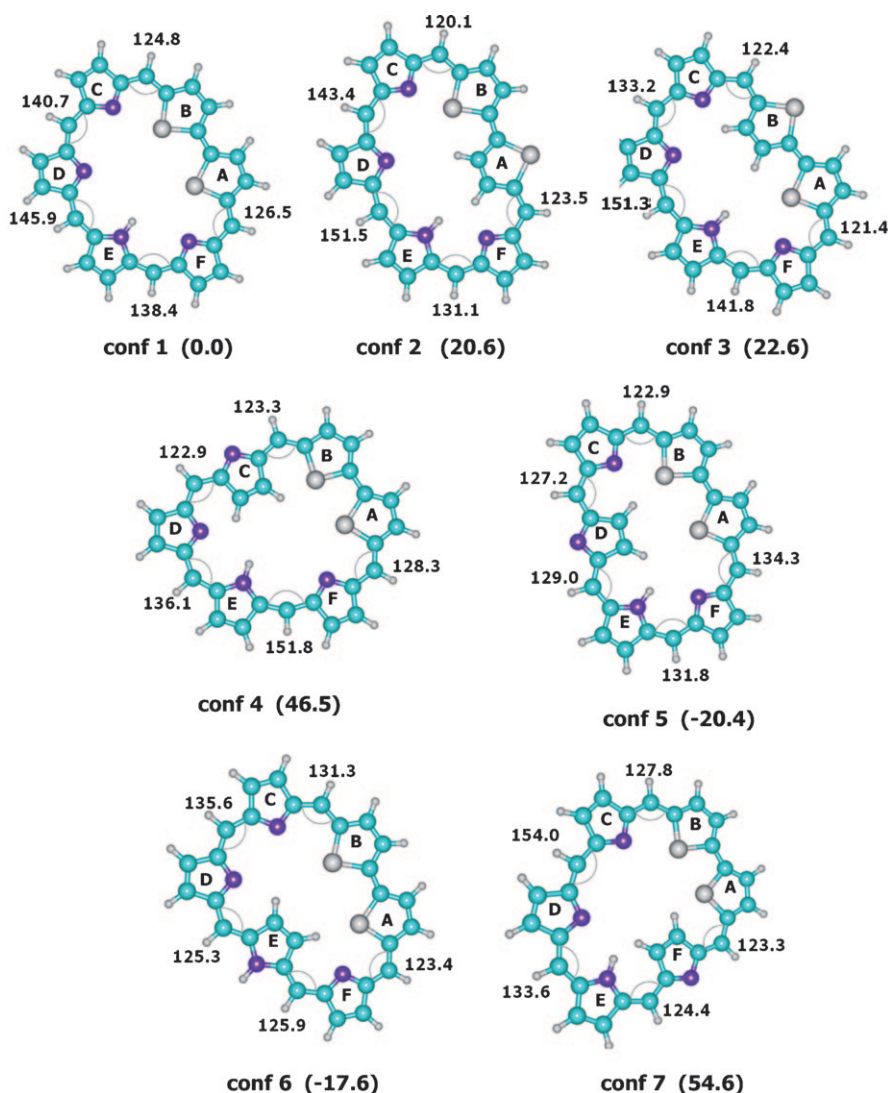


Figure 7. Optimized structures of the different conformations of the model compound **12a** with  $C_s$  symmetry. The relative energy values ( $\text{kcal mol}^{-1}$ ) are given in parenthesis and the *meso* bond angles (in degrees) are also given.

with important structural parameters and the relative energy values. The relative energy values obtained suggests that conformation 5 and conformation 6 are considerably more stable than conformation 1, while the remaining four conformations are quite unstable when compared to conformation 1. In addition, conformation 5 is more stable by  $2.8 \text{ kcal mol}^{-1}$  than the conformation 6. The stable conformations 5 and 6 are further optimized with no symmetry constraints and in the corresponding optimized structures, the inverted ring (ring **D** in conformation 5 and ring **E** in conformation 6) was found to be slightly tilted away from the nearly planar arrangement of the remaining pyrrolic/heterocyclic rings (twist is  $18^\circ$  in conformation 5 and  $14^\circ$  in conformation 6). In the fully optimized structure, the relative energy for conformation 5 and 6 were found to be  $-21.8$  and  $-18.6 \text{ kcal mol}^{-1}$  respectively. Thus, the hexaphyrin skeleton **12** studied here has a strong preference for inversion in ring **D** rather than the other ring inverted structure. It may be

noted that the bond angle around the  $\text{sp}^2$  hybridized carbon atom in a strain free environment is close to  $120^\circ$  and in the present case, all the C–C–C bond angles at the *meso* positions of all the conformations are significantly deviated from the  $\text{sp}^2$  angle, which indicates considerable strain in the hexaphyrin system. In fact, the relative energy of the system can be correlated with the largest C–C–C angle at the *meso* positions, which means that the system with the most deviated C–C–C angle from the  $\text{sp}^2$  value is the most unstable and vice versa (*cf.* Figure 8). In other words, the ring inversion in conformation 1 is inevitable in order to release the strain energy and this process is most effective when ring **D** is inverted which releases  $21.8 \text{ kcal mol}^{-1}$  energy when compared to the energy of conformation 1. Thus, theoretical results strongly support the fact that the ring **D** in hexaphyrin **12** is inverted and slightly tilted away from the planar geometry and has an excellent agreement with the proposed structures on the basis of the solution NMR spectral data.

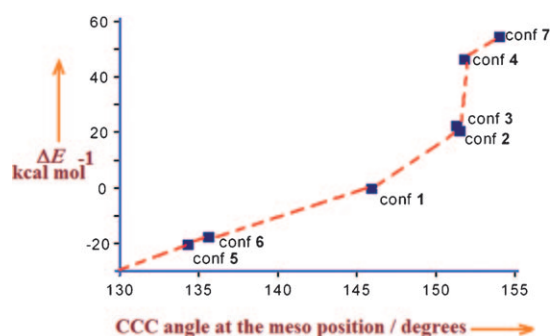


Figure 8. Correlation between the relative energy of the conformations for **12a** and the largest C–C–C bond angle at the *meso* positions.

### Electrochemical Properties

The redox behavior of both non-aromatic [28]hexaphyrins **9** and **10**, and aromatic [26]hexaphyrins **11** and **12** were stud-

ied by cyclic voltammetry and differential pulse voltammetry using 0.1 M TBAPF<sub>6</sub> (tetra-*n*-butylammonium hexafluorophosphate) as the supporting electrolyte in CH<sub>2</sub>Cl<sub>2</sub>, in the potential range –2.0 to 2.0 versus SCE (Figure 9). In gener-

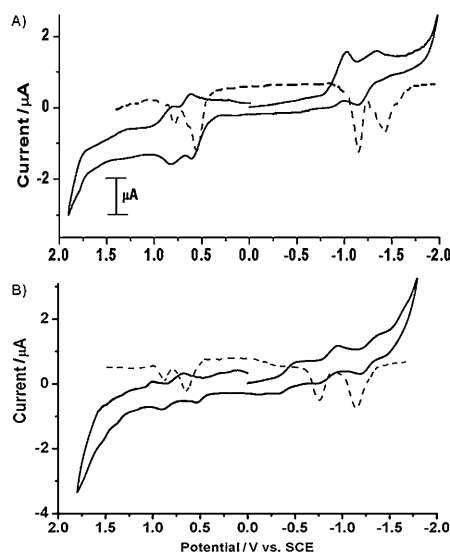


Figure 9. Cyclic voltammogram (—) and differential pulse voltammogram (----) of A) **10** and B) **12** in anhydrous CH<sub>2</sub>Cl<sub>2</sub> versus SCE containing 0.1 M TBAPF<sub>6</sub>, recorded at 100 mV s<sup>–1</sup> scan rate.

al, the hexaphyrins reported here show two one-electron oxidations and two one-electron reductions. The respective half-wave redox potentials are presented in Table 1. The im-

Table 1. Electrochemical data for hexaphyrins **9–12**.

Compound	E <sub>1/2</sub> <sup>red</sup> (1) <sup>[b]</sup>	E <sub>1/2</sub> <sup>red</sup> (2)	E <sub>1/2</sub> <sup>ox</sup> (1)	E <sub>1/2</sub> <sup>ox</sup> (2)	Δ <sub>redox</sub> <sup>[a]</sup> (V)
<b>9</b>	–1.07	–1.35	0.62	0.83	1.69
<b>10</b>	–1.08	–1.36	0.61	0.81	1.69
<b>11</b>	–0.72	–1.16	0.75	1.44	1.47
<b>12</b>	–0.72	–0.84	0.73	1.03	1.45

[a] Calculated from the difference between E<sub>1/2</sub><sup>ox</sup>(1) and E<sub>1/2</sub><sup>red</sup>(1). [b] Quasi-reversible waves were observed. [c] Irreversible-waves were observed.

portant observation is that the Δ<sub>redox</sub> values for aromatic hexaphyrins **11** and **12** are 1.47 and 1.45 V, respectively, which on comparison with other aromatic systems H2TPP (2.26 V), sapphyrin (1.88 V) and rubyrin (1.64 V),<sup>[24]</sup> show significant reduction in the HOMO–LUMO gap which are consistent with the observed red-shift of the Soret and Q-bands in the electronic absorption spectra.

## Conclusions

In this study, we have successfully described the syntheses of core-modified 26π and 28π hexaphyrins, which contain five *meso* carbon bridges, by an efficient acid-catalyzed [4+2] MacDonald-type condensation. Using extensive spectro-

scopic analyses, both aromatic 26π and non-aromatic 28π hexaphyrins were isolated and thoroughly characterized. These can be reversibly interconverted into the oxidized (26π) and reduced (28π) forms with the use of simple oxidizing and reducing agents. The above-mentioned methodology is simple and efficient because of the absence of side products and easy purification. The results of theoretical studies have further support the analysis and sheds light on the exact conformation of the aromatic 26π hexaphyrin system.

## Experimental Section

### General Procedure

All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran, methanol, toluene, and *n*-hexane were purified and distilled by standard procedure. Electronic spectra were recorded on a Perkin–Elmer Lambda 20 UV/Vis spectrophotometer in 1 cm pathlength cuvettes. Proton NMR spectra were recorded on a 300 MHz JEOL spectrometer. Cyclic voltammetric studies were performed on CH instruments (CH 620B). A three electrode system consisting of a platinum working electrode, a platinum mesh counter electrode and a commercially available saturated calomel electrode (SCE) as the reference electrode were used. Tetra-*n*-butylammonium hexafluorophosphate from Fluka was used as the supporting electrolyte. FAB-MS spectra were obtained on a JEOL-SX-120/DA6000 spectrometer. Thin-layer chromatography was carried out on Silica Gel 60 F<sub>254</sub> aluminium plates (Merck). Bithiophene diol, biselenophene diol, and tetrapyrane were synthesized using methods described in literature<sup>[11,18]</sup> and stored under inert atmosphere at –10 °C.

### Syntheses

**Hexaphyrin (9 and 11):** A mixture of **6** (0.340 g, 0.74 mmol) and tetrapyrane **8** (0.500 g, 0.62 mmol) were dissolved in dry dichloromethane (200 mL) and stirred under nitrogen atmosphere for 5 min. *p*-Toluenesulfonic acid (PTSA) (0.036 g, 0.19 mmol) was added and the stirring was continued for 90 min. DDQ (0.426 g, 19 mmol) was added and the reaction mixture was stirred for a further 90 min. The solvent was then evaporated in vacuum and the residue was purified by chromatography on a basic alumina column. The first red band was eluted with dichloromethane/petroleum ether (1:4), which gave **9** (0.03 g, 5%) followed by elution of a violet band with dichloromethane/petroleum ether (3:2), which yielded a greenish metallic solid on evaporation of solvent that was identified as **11** (0.06 g, 10%).

**Data for Compound 9:** UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε × 10<sup>4</sup> M<sup>–1</sup> cm<sup>–1</sup>): 400 (4.4), 547 (8.2), 692 (1.3), 756 (1.2); (CH<sub>2</sub>Cl<sub>2</sub>/TFA): λ<sub>max</sub> (ε × 10<sup>4</sup> M<sup>–1</sup> cm<sup>–1</sup>): 440 (4.9), 529 (5.0), 613 (9.2), 849 (1.9), 925 (2.2); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 1.78 (s, 3H, *p*-CH<sub>3</sub>), 2.13 (s, 3H, *p*-CH<sub>3</sub>), 2.41 (dd, *J* = 2.2 Hz, 12H, *o*-CH<sub>3</sub>), 5.43 (m, 1H, β-H), 5.7 (brs, 1H, NH), 6.36 (d, *J* = 5.4 Hz, 1H, β-H), 6.72 (d, *J* = 4.8 Hz, 1H, β-H), 6.84 (d, *J* = 3.9 Hz, 1H), 6.98 (7.01 (m, 2H), 7.03 (m, 2H, β-H), 7.09 (m, 2H), 7.14 (d, 1H, *J* = 3.6 Hz, β-H), 7.41 (brs, 2H, NH), 7.44 (d, 1H, *J* = 3.2 Hz, β-H), 7.76 ppm (d, 1H, *J* = 3.9 Hz, β-H); FAB-MS: *m/z* (%) calcd for C<sub>65</sub>H<sub>37</sub>F<sub>15</sub>N<sub>4</sub>S<sub>2</sub>: 1223 (100) [*M*<sup>+</sup>]; elemental analysis: calcd (%) for C<sub>65</sub>H<sub>37</sub>F<sub>15</sub>N<sub>4</sub>S<sub>2</sub>: C 63.83, H 3.05, N 4.58; found: C 63.25, H 2.95, N 4.15.

**Data for Compound 11:** UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε × 10<sup>4</sup> M<sup>–1</sup> cm<sup>–1</sup>): 546 (13.9), 611 (3.8), 707 (2), 765 (2), 868 (1.2); (CH<sub>2</sub>Cl<sub>2</sub>/TFA): λ<sub>max</sub> (ε × 10<sup>4</sup> M<sup>–1</sup> cm<sup>–1</sup>): 558 (22), 597 (12.2), 814 (2.7), 849 (2.4), 907 (2.4); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = –1.34 (d, *J* = 4.2 Hz, 1H, β-H), –0.41 (d, *J* = 4.2 Hz, 1H, β-H), 2.03 (d, *J* = 6.4 Hz, 12H, *o*-CH<sub>3</sub>), 2.68 (d, *J* = 14.4 Hz, 6H, *p*-CH<sub>3</sub>), 7.38 (d, *J* = 10.8 Hz, 4H, Ar-*mes*; *m*-H), 8.32 (d, *J* = 4.5 Hz, 1H, β-H), 8.51 (d, *J* = 4.8 Hz, 1H, β-H), 8.61 (m, 2H, β-H), 8.69 (d, 2H, *J* = 4.8 Hz, β-H), 9.06 (d, *J* = 4.8 Hz, 1H, β-H), 9.62 (d, *J* = 4.5 Hz, 2H, β-H), 10.28 ppm (d, *J* = 4.2 Hz, 2H, β-H). FAB-MS: *m/z* (%) calcd



for  $C_{65}H_{35}F_{15}N_4S_2$ : 1221 (100) [ $M^+$ ]; elemental analysis: calcd (%) for  $C_{65}H_{35}F_{15}N_4S_2$ : C 63.93, H 2.89, N 4.59; found: C 63.65, H 2.47, N 4.32.

Hexaphyrin (**10** and **12**): A mixture of **7** (0.340 g, 0.62 mmol) and tetrapyrane **8** (0.500 g, 0.62 mmol) were dissolved in dry dichloromethane (200 mL) and stirred under a nitrogen atmosphere for 5 min. *p*-Toluenesulfonic acid (PTSA) (0.036 g, 0.19 mmol) was added and the stirring was continued for 90 min. DDQ (0.426 g, 19 mmol) was added and the reaction mixture was stirred for a further 90 min. The solvent was then evaporated in vacuum and the residue was purified by chromatography on a basic alumina column. The first red band which was eluted with dichloromethane/petroleum ether (1:4) gave **10** (0.03 g, 5%) and a violet band was eluted with dichloromethane/petroleum ether (3:2), which yielded a greenish metallic solid on evaporation of solvent that was identified as **12** (0.06 g, 10%).

Data for Compound **10**: UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  ( $\epsilon \times 10^4 M^{-1} cm^{-1}$ ): 403 (3.8), 561 (6.8), 716 (1.4), 786 (1.2); ( $CH_2Cl_2$ /TFA):  $\lambda_{max}$  ( $\epsilon \times 10^4 M^{-1} cm^{-1}$ ): 444 (3.8), 541 (3.9), 624 (8.3), 850 (1.6), 993 (1.6);  $^1H$  NMR (300 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 1.75 (s, 3H, *p*-CH<sub>3</sub>), 2.1 (s, 3H, *p*-CH<sub>3</sub>), 2.38 (dd,  $J$  = 2.2 Hz, 12H, *o*-CH<sub>3</sub>), 5.23 (m, 1H,  $\beta$ -H), 5.28 (m, 1H,  $\beta$ -H), 6.44 (d,  $J$  = 4.8 Hz, 1H,  $\beta$ -H), 6.58 (brs, 1H, NH), 6.8 (d,  $J$  = 3.6 Hz, 1H), 7.01 (m, 4H,  $\beta$ -H and Mesityl *m*-H), 7.09 (m, 2H,  $\beta$ -H), 7.14 (s, 2H), 7.18 (brs, 2H, NH), 7.28 (d, 2H overlapped,  $\beta$ -H), 7.87 (d, 1H,  $J$  = 4.5 Hz,  $\beta$ -H), 8.07 ppm (d, 1H,  $J$  = 4.5 Hz,  $\beta$ -H). FAB-MS:  $m/z$  (%) calcd for  $C_{65}H_{35}F_{15}N_4Se_2$ : 1317 (100) [ $M^+$ ]; elemental analysis: calcd (%) for  $C_{65}H_{35}F_{15}N_4Se_2$ : C 59.28, H 2.83, N 4.25; found: C 59.02, H 2.79, N 4.12.

Data for Compound **12**: UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  ( $\epsilon \times 10^4 M^{-1} cm^{-1}$ ): 558 (15.2), 586 (6.8), 713 (1.7), 776 (1.8), 887 (1.2); ( $CH_2Cl_2$ /TFA):  $\lambda_{max}$  ( $\epsilon \times 10^4 M^{-1} cm^{-1}$ ): 568 (20.3), 610 (10.2), 834 (2.1), 871 (1.7), 928 (1.4);  $^1H$  NMR (300 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = -2.28 (d,  $J$  = 4.2 Hz, 1H,  $\beta$ -H), -1.26 (d,  $J$  = 4.2 Hz, 1H,  $\beta$ -H), 2.04 (d,  $J$  = 6.4 Hz, 12H, *o*-CH<sub>3</sub>), 2.76 (d,  $J$  = 14.4 Hz, 6H, *p*-CH<sub>3</sub>), 7.49 (d,  $J$  = 10.8 Hz, 4H, Ar-mes; *m*-H), 8.86 (d,  $J$  = 4.5 Hz, 1H,  $\beta$ -H), 8.88 (d,  $J$  = 4.8 Hz, 1H,  $\beta$ -H), 8.97 (d,  $J$  = 4.5 Hz, 1H,  $\beta$ -H), 9.21 (d,  $J$  = 4.8 Hz, 1H,  $\beta$ -H), 9.26 (d,  $J$  = 4.5 Hz, 1H,  $\beta$ -H), 9.62 (d,  $J$  = 4.5 Hz, 1H,  $\beta$ -H), 10.48 (d,  $J$  = 4.2 Hz, 1H,  $\beta$ -H), 10.52 (d,  $J$  = 4.5 Hz, 1H,  $\beta$ -H), 11.55 ppm (d,  $J$  = 4.5 Hz, 1H,  $\beta$ -H). FAB-MS:  $m/z$  (%) calcd for  $C_{69}H_{39}F_{15}N_4S_3$ : 1315 (100) [ $M^+$ ]; elemental analysis: calcd (%) for  $C_{69}H_{39}F_{15}N_4S_3$ : C 59.37, H 2.68, N 4.26; found: C 64.25, H 2.89, N 3.15.

Reduction of [26]hexaphyrin **12** to [28]hexaphyrin **10**:  $NaBH_4$  (3.8 mg, 100 mmol, 10 equiv) was carefully added in small portions to a stirred solution of **12** (12.23 mg, 10 mmol) in a 1:1 mixture of  $CH_2Cl_2$ /methanol; stirring was continued for a further 30 min. The reaction was then quenched with water and the mixture was washed with brine and dried over  $Na_2SO_4$ . Removal of the solvent gave a quantitative yield of [28]hexaphyrin **10** as a dark reddish solid.

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