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Aromatic Core-Modified Twisted Heptaphyrins[1.1.1.1.1.1.0]: Syntheses and Structural Characterization

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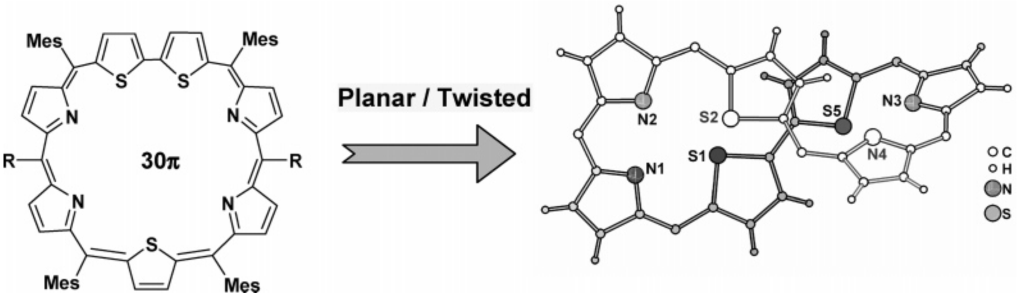
ABSTRACT



First examples of aromatic core-modified twisted heptapyrrolic systems with six *meso* links have been obtained via a general [3 + 4] acid-catalyzed condensation method. Despite the twisted conformation, these heptaphyrins exhibit aromaticity in solution, unlike most of the all-aza analogues.

Expanded porphyrins continue to attract the attention of researchers, undoubtably in view of their diverse applications in a variety of modern technologies. For example, they have been identified to be potential candidates as anion receptors, sensitizers for PDT, and contrast agents in MRI.[1] Most recently, in the fledgling era of nonlinear optics, these macrocycles have been found to exhibit moderate to large second- and third-order nonlinear optical response by virtue of their aromatic nature and extended π-conjugation.[2] Such intriguing applications are attributed not only to their inherent optical and electrochemical properties but also to their structural diversity. Expanded porphyrins with 26 or more π electrons exhibit planar, twisted, and figure-eight conformations depending upon the number and nature of the *meso* links connecting the heterocyclic units. Such a conformational flexibility affects the aromatic nature of the macrocycle, leading to altered optical and electrochemical properties.[3] In this context, heptapyrrolic macrocycles possess very limited history. For example, **1**,[4] which has only two *meso* carbon linkages with 28 π electrons is nonaromatic; **2**,[5] which has a 30 π electron system with four *meso* linkages is planar and aromatic, and **3**,[6] which is formally a 30 π

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system with five *meso* linkages, is aromatic despite a twisted conformation. Heptaphyrins with seven *meso* linkages are found to be nonaromatic; however, little information regarding the exact nature of this macrocycle is available at present.[7] Thus, there remains a challenge to synthesize and study the structure−property correlation in heptapyrrolic systems with six *meso* linkages whose all-aza analogues are yet to be synthesized. More likely, such systems would be helpful in understanding the effect of aromaticity on increasing the number of *meso* carbons. Furthermore, development of easy and efficient methodology to synthesize these expanded porphyrins in multigram quantities is still a synthetic goal to exploit their various applications. In this context, very recently, we have reported the large third-order nonlinear optical response of [34] octaphyrin (1.1.1.0.1.1.1.0) and its smaller homologue [26] hexaphyrin (1.1.1.1.1.1).[8]

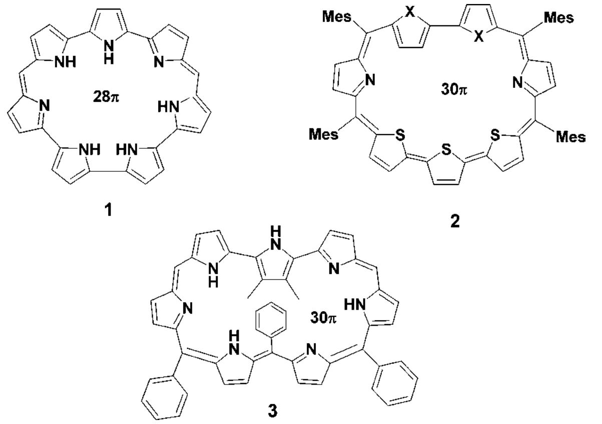
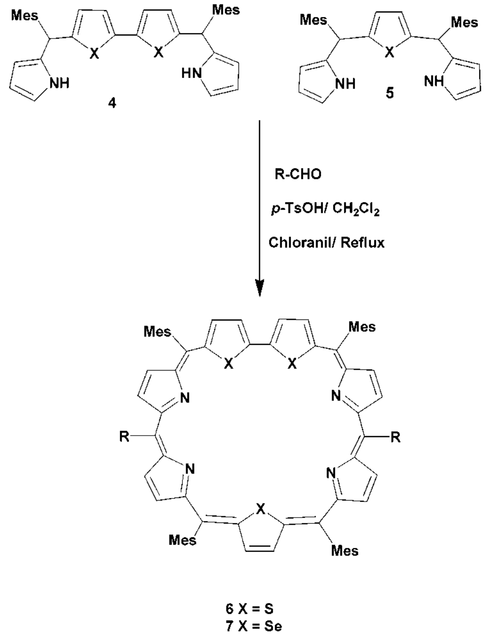


Figure 1. Schematic representation of hitherto reported heptapyrrolic systems.

In this communication, we wish to report the first structurally characterized aromatic core-modified heptaphyrins bearing six *meso* linkages and their solution-state properties. To the best of our knowledge, these systems constitute the first expanded porphyrins with seven heterocyclic rings connected through six *meso* linkages.

From a synthetic perspective, pyrrole and aldehydes condense to form a series of porphyrinic macrocycles, but the main disadvantage lies in the purification and isolation of the products where repeated silicagel column chromatography leads to isolation of distinct products in poor yields. Most of the synthetic methodologies known in the literature require sensitive precursors that involve multistep synthesis before the final condensation step, thus restricting the yield of the final product. Thus, there remains a challenge in utilizing synthetic strategy and suitable precursors that can lead to the production of hitherto unknown systems with interesting properties. Our strategy for the synthesis involves an acid-catalyzed [4 + 3] condensation using modified tetrapyrrane **4** and tripyrrane **5**, which are easily accessible through condensation of corresponding diols and pyrrole. Here it is noteworthy to mention that our effort in making planar octaphyrins with six *meso* links via a change of *meso*-aryl substituents in the precursors from mesityl to xylyl was not fruitful.[9] Thus, in this present synthesis, we have taken the starting precursors with *meso*-mesityl substituents. Of course, the primary criteria is based on the well-known fact that bulky *meso* substituents lead to the formation of higher-order expanded porphyrins.[10] The reaction of **4** and **5** with reactive pentafluoro benzaldehyde in the absence of any acid catalyst gave corresponding octaphyrin[9] analogues as a result of the self-condensation of **4** with the aldehyde instead of the expected heptaphyrin **6**. However, our desired product **6** was obtained in good yields when the reaction was performed in the presence of protic acid catalysts such as *p*-toluenesulfonic acid and methane sulfonic acid in dichloromethane followed by chloranil oxidation. The product distribution and the yields were found to be dependent on the concentration of acid catalyst and the aldehyde used for carrying out the condensation reactions. In general, *p*-toluenesulfonic acid is well-suited for our reaction when we used 0.5 equiv of the same with respect to the starting precursor, i.e., modified tetrapyrane and tripyrrane, where the desired product **6** was obtained in almost 10% yield. Increasing the acid concentra-

Scheme 1. Core-Modified Heptapyrrolic Systems via a [4 + 3] Acid-Catalyzed Condensation Reaction



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tion to 1 and 2 equiv reduces the yield to almost 1%, but increasing the aldehyde concentration to more than 2-fold with respect to tetrapyrrane and tripyrrane gave the self-condensed products of these precursors, leading to the formation of hexaphyrins[11] and octaphyrins[9] in accordance with our previous results. Thus, 2 equiv of the aldehyde was found to be best suited for our reaction conditions. In the same way, 0.3 equiv of methane sulfonic acid gave the total yield of **6** in 8%, whereas 0.5 and 1 equiv of the aforesaid acid reduces the percentage yield of the final product **6** to nearly 1−2%. The interesting feature of the present method is the isolation of only the single desired product when the reaction conditions are met, thus making the purification handy.

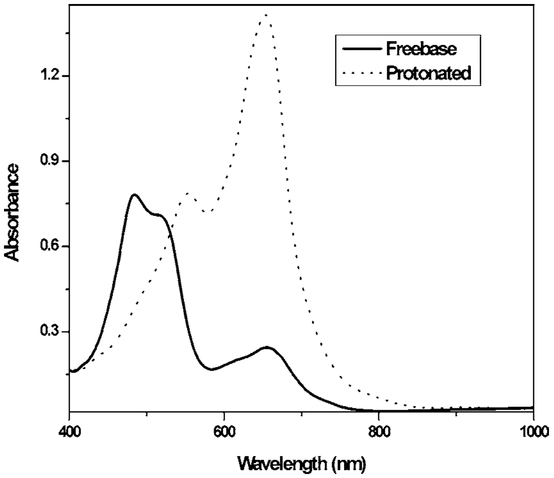

Figure 2. UV−vis spectra of **6** and its protonated derivative. Protonation is achieved by the addition of a dilute solution of TFA in CH_2Cl_2.

The constitutional structures of these novel macrocycles were characterized by FAB mass, UV−vis, ^{1}H NMR, and electrochemical study. Structural proof for these macrocycles was obtained from single-crystal X-ray diffraction analysis of the free base form of **6**. FAB mass data confirm the proposed composition of the free-base forms of **6** and **7** (see Suppoting Information). The UV−vis spectra of these macrocycles are dominated by a split Soret-type band with λ_{max} at 483 nm ($\epsilon = 9.89 \times 10^4$) and Q-band like absorption at 685 nm, which upon protonation undergoes a bathochromic shift up to 100 nm. Such observation of red shift upon protonation is the signature of *meso*-aryl substituted aromatic core-modified expanded porphyrins.[12]

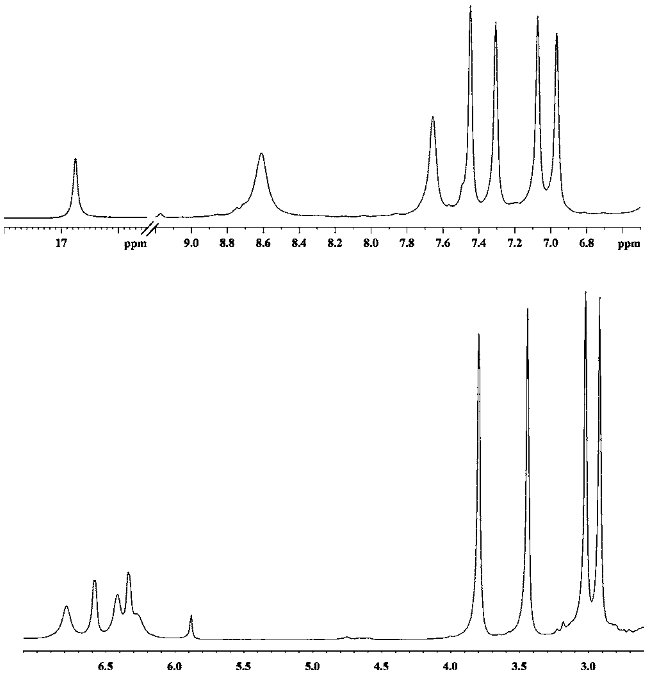

Figure 3. Complete ^{1}H NMR spectra for the free base form of **6** in CD_2Cl_2 at 298 K.

A fairly well-resolved ^{1}H NMR spectrum was obtained at room temperature for the macrocycle **6**. The peaks in the region 6−6.5 ppm have been assigned to the phenyl protons of *meso*-mesityl rings, whereas the peaks in the region 2.5−3.5 ppm have been assigned to the methyl protons of the *meso*-mesityl substituents. The singlets in the region 7−17 ppm are mainly due to the β-CH protons of the seven heterocyclic rings. Absence of any correlation in the COSY spectra prevented us from assigning the signals for the respective β-CH proton resonances of the heterocyclic units. However, a $\Delta\delta$ value of 16 ppm for the chemical shift

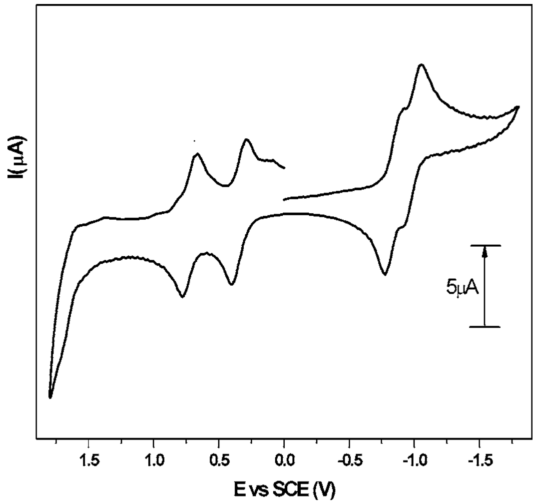

Figure 4. Cyclic voltammogram of **6** in CH_2Cl_2 with TBAP (0.1 M) as supporting electrolyte with scanrate 100 mV/s.

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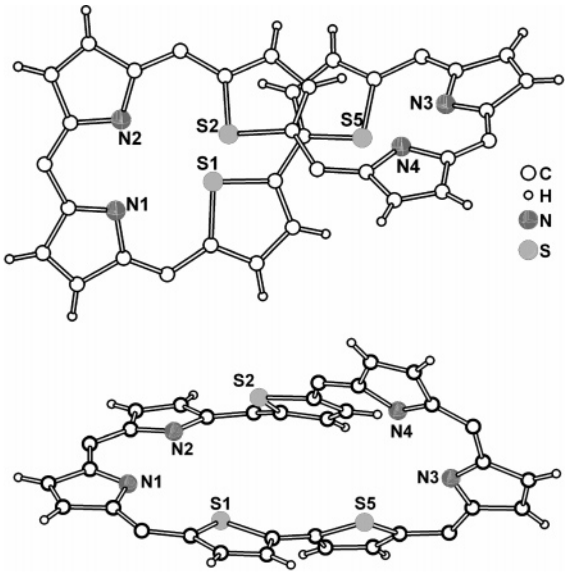

Figure 5. Single-crystal X-ray structure of **6**: (top) plane view; (bottom) side view. *meso*-Aryl substituents have been omitted for clarity.

difference between the most deshielded proton resonance and the most shielded proton resonance is the primary evidence for the aromatic nature of this macrocycle in the solution state. Further insight into this aromaticity comes from the electrochemical studies.

The redox behavior of these heptaphyrin analogues was studied with cyclic voltammetry studies using 0.1 M TBAP (tetra-*n*-butylammoniumhexafluoro phosphate) as supporting electrolyte in dichloromethane solution in the potential range −1.8 to 1.8 V vs SCE. A typical cyclic voltammogram with scan rate of 100 mV/s for macrocycle **6** as a representative example is shown in Figure 4. The observation of two reversible oxidation couples [$E_{1/2}{}^{ox1} = 0.34$ V and $E_{1/2}{}^{ox2} = 0.72$ V] and two reversible reduction couples [$E_{1/2}{}^{\mathrm{red1}} = -0.84$ V and $E_{1/2}{}^{\mathrm{red2}} = -1.02$ V] suggest the aromatic nature of this macrocycle.

The Δ_{redox} value calculated from the electrochemical data of 1.18 V indicates a reduction in the HOMO−LUMO gap consistent with the observed redshift in the absorption spectra.

Final proof for the formation of these macrocycles comes from the single-crystal X-ray diffraction structure of the macrocycle **6**. The solid-state crystal structure of the macrocycle was found to exhibit a nonplanar figure-eight conformation as shown in Figure 5. It is inferred that the twisting of the macrocycle is anticipated mainly due to the inversion of one of the thiophene rings of bithiophene moiety with a torsional angle of 37.1° between the two thiophene rings (S1−C2−C4−S5). Another ring inversion is noted where the thiophene of the tripyrrane moiety is linked with the neighboring pyrrole ring through a *meso* carbon with a torsional angle of 19.5° (S2−C27−C50−N4). These inversions make the macrocyclic core flexible enough to deviate from a planar conformation towards a figure-eight like structure. Another important point here is that an increase in the number of *meso* linkages also relaxes the basic framework of the macrocycle to adopt a nonplanar structure.

In conclusion, we have successfully synthesized the first heptapyrrolic expanded porphyrins with six *meso* links and have shown that core-modified heptaphyrins deviate from planarity upon increase of *meso* links beyond four; nevertheless aromaticity is still sustained in solution state. These observations are concordant with our previous reports for core-modified octaphyrin analogues with six *meso* linkages.[9] Further studies in finding such interesting phenomena in case of core-modified expanded porphyrins with six *meso* links are currently in progress.

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Supporting Information Available: Experimental procedures, FAB MS, and UV−vis spectra for selected compounds, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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