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One-Pot Synthesis of Core-Modified *meso*-Aryl Calix[5]phyrin and N-Fused [24]Pentaphyrin

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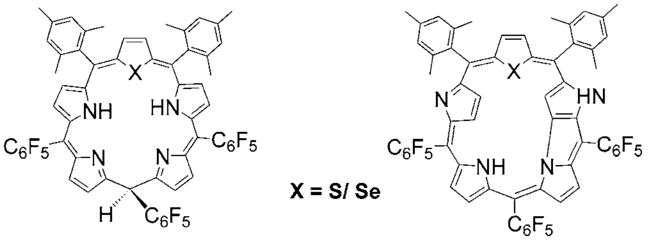
ABSTRACT



meso-aryl Calix[5]phyrin

meso-aryl N-Fused[24]pentaphyrin

Synthesis and characterization of core-modified *meso*-aryl calix[5]phyrins and N-fused pentaphyrins are reported.

Expanded porphyrins with more than four pyrrolic/ heterocyclic rings are a class of functional macrocycles being utilized for anion recognition, neutral substrate binding, electrochemical and interesting optical properties.[1] Expanded porphyrins are generally synthesized by an acid-catalyzed Mac-Donald type condensation reaction or by an oxidative coupling reaction of appropriate precursors.[2] Specifically pentaphyrin **1** (Figure 1) was first synthesized by Gossauer et al. through a [2+3] Mac-Donald condensation between diformyl tripyrrane and an α-free dipyrromethane.[3] Later, Sessler and co-workers reported an improved synthesis of *meso*-free β-alkyl-substituted pentaphyrin and a solid-state structure of corresponding uranium complex.[4] On the other

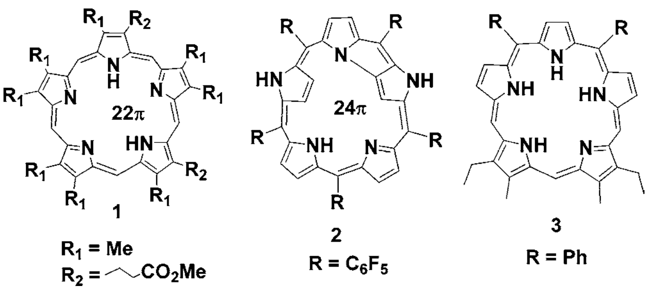


Figure 1. Pentaphyrins reported in literature.

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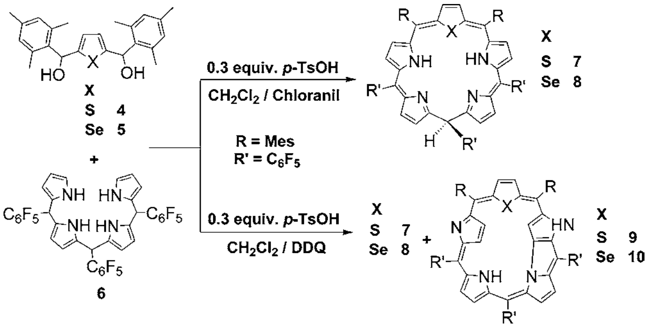
hand, Furuta et al. reported the *meso*-aryl- substituted N-fused pentaphyrin **2** containing a tripentacyclic ring by a one-pot reaction of modified Rothemund-Lindsey method between pyrrole and corresponding benzaldehyde.[5] Thus, it is clear that use of precursors with substituents on pyrrole and no substituents on meso carbons leads to open chain pentaphyrin **1**, while aryl substituents at meso position and no substituents on β-pyrrole rings leads to N-fused pentaphyrin **2**. Use of one precursors with β-pyrrole substituents and other with meso-aryl substituents also leads to formation of open chain pentaphyrin **3**.[6] We speculated the core-modification with bigger sulfur or selenium instead of pyrrole nitrogens might prevent the N-fusion reaction in meso-aryl pentaphyrins and to test this idea, we have performed an acid catalyzed [4+1] Mac-Donald type condensation reaction of core-modified diols **4** or **5**[7] and tetrapyrrane **6**[8] as precursor. Scheme 1 depicts the synthetic methodology adopted. Reaction of **4** or **5** with tetrapyrrane precursor **6** in presence of *p*-toluenesulphonic acid (*p*-TSA) followed by oxidation with chloranil leads to the formation of calixthia[5]phyrin **7** or calixselena[5]phyrin **8** as green solids in approximately 20% yield as a single product. However, change of the oxidant from chloranil to stronger oxidant 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) under the same condition gave **7** or **8** in approximately 12% yield, in addition to the formation of N-fused thiapentaphyrin **9** or N-fused selenapentaphyrin **10** as a stable green metallic solid in 15% yield. Thus by controlling the nature of the oxidant used it is possible to synthesize either calix[5]phyrin or the N-fused core-modified pentaphyrin by this methodology. Also it will be interesting to see what happens when one or more of the pyrrole ring in **6** is replaced by either thiophene or selenophene. Attempts to interconvert calix[5]phyrin **8** to N-fused pentaphyrin **10** using DDQ and **8** from **10** in presence of $NaBH_4$ was not fruitful implying the stability of **8** and **10** at room temperature. Further oxidation of **10** with DDQ/MnO_2 did not yield the corresponding oxidized N-fused[22]pentaphyrin.

Scheme 1. Synthesis of Core-modified Calix[5]phyrin and N-fused Pentaphyrins



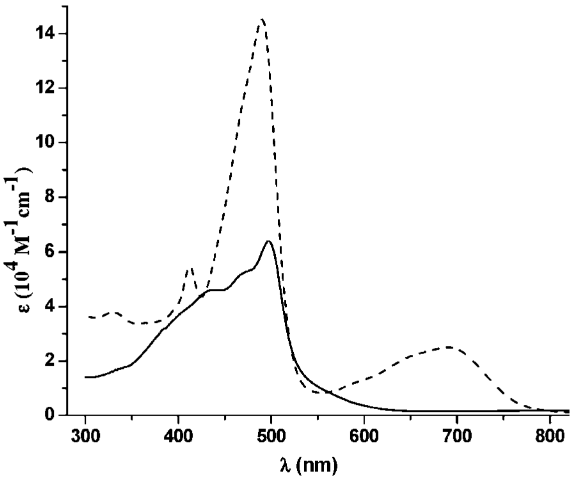


Figure 2. Electronic absorption spectra of **8** (0.66 × 10^{-5}M- - - -) and **10** (0.13 × 10^{-4}M—) in CH_2Cl_2.

The proposed structure of the macrocycle comes from various spectroscopic analyses and the single-crystal X-ray structure obtained for **8**. The FAB mass spectrum of calixselena[5]phyrin **8** exhibits a molecular ion signal at m/z = 1187. The UV/vis spectrum of **8,** (Figure 2) is characterized by a broad Soret type band at 490 nm ($\epsilon = 1.45 \times 10^5$) followed by a Q-band like absorption at 691 nm ($\epsilon = 2.5 \times 10^4$). The broad Soret-like absorption suggests the nonplanar structure of the macrocycle. FAB mass spectrum of N-fused pentaphyrin **10** showed a molecular ion signal at m/z = 1186. The electronic spectrum of **10** exhibits a Soret like band at 498 nm ($\epsilon = 0.64 \times 10^5$). Upon protonation, the Soret-like band experiences a small blue shift of 25 nm ($\epsilon = 0.56 \times 10^5$) with a slight decrease in the ϵ value (see Supporting information). The ^{1}H NMR spectrum of **8** in CD_2Cl_2 shows a C_2 symmetric signal pattern containing four pairs of doublets due to pyrrolic β−CH protons between 6.68 and 7.9 ppm, whereas the peaks at 7.09 and 7.03 ppm have been assigned to the phenyl protons of the mesityl rings and the signals between 2.43 and 1.97 ppm has been assigned for the methyl protons of the mesityl rings (see Supporting Information). On the other hand, two distinct singlets at 2.86 and 7.36 ppm were observed without having any correlation in the two dimensional ^{1}H-^{1}H COSY spectrum for *meso*-hydrogen and selenophene β−CH's respectively and a broad singlet at 9.04 ppm integrating two pyrrolic NH's supports its nonconjugated nature. The structure of compound **10** was determined by ^{1}H NMR and the completely assigned spectrum is shown in Figure 3. The greater number of signals

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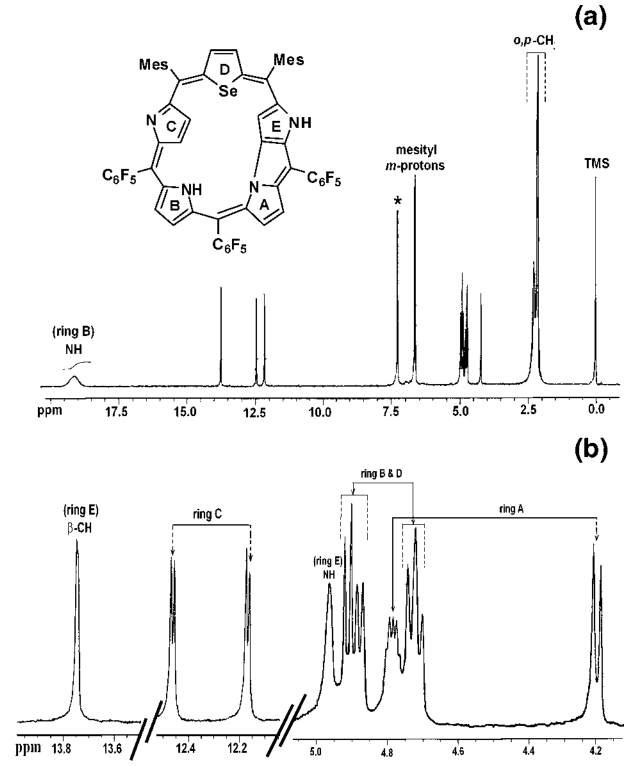

Figure 3. ^{1}H NMR spectrum of **10** in CD_2Cl_2 with assignments observed are marked. (a) complete spectrum and (b) expanded spectrum in the specific regions.

in the spectrum reflects the lowering of molecular symmetry in **10** exhibits a mutually coupled doublet at 4.2 ppm with a multiplet at 4.79 ppm due to the β-protons of pyrrole **A**. The outer β-protons of pyrrole **B** and **D** exhibits a pair of doublets and a multiplet between 4.7 and 4.95 ppm. Interestingly, the inner β-protons of pyrrole **C** are observed as mutually coupled pair of doublets at exceptionally low field region between 12.46 and 12.17 ppm, while the inner β-proton of fused pyrrole **E** appeared as singlet at 13.73 ppm. In contrast, the outer NH proton at 4.97 ppm and the inner NH proton as a broad singlet at 19.2 ppm clearly indicate a 24π nonaromatic nature of macrocycle **10**. This is also supported by the absorption spectrum consisting of ill-defined Soret-like band without Q-like bands.[5]

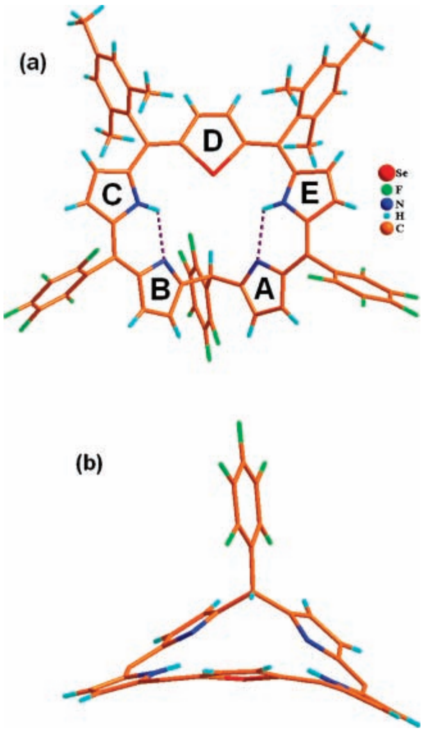

Figure 4. X-ray crystal structure of **8** (a) top view (dotted lines shows intramolecular hydrogen-bonding) and (b) side view (some *meso*-phenyl groups are omitted for clarity).

The structure of **8** has been determined by X-ray diffraction analysis, which shows a pentapyrrolic core with a distorted ruffled conformation containing an sp^3 carbon (Figure 4).[9] All the pyrrolic nitrogens are pointing inward to the center of the macrocycle.[10] This is in contrast to the structure observed for all pyrrole calix[5]phyrin, where one of the pyrrole rings are inverted with 120° ring flipped.[11] Of the four pyrroles, two of them are imino pyrroles (ring A and B) whose α-carbons are directly connected to the *meso*-sp^3 carbon are canted significantly and orienting in the same direction: the tilt angles are 40.95 and 36.14° to the mean plane defined by four *meso*-sp^2 carbons. The remaining two amino pyrroles (ring C and D) are slightly tilted by the angles of 22.97 and 19.73° respectively, thus nearly coplanar to the selenophene ring (ring D). The selenophene ring is almost planar with a tilt angle of 7.52° with respect to the mean plane leading to a symmetric distorted conformation. The important feature of the structure is the presence of two strong intramolecular hydrogen-bonding interactions in the cavity between N1−H1−N2 (2.22 (2) Å and N4−H1−N3 (2.18 (2) Å).

The packing diagram shown in Figure 5 reveals the presence of four intermolecular hydrogen bonds: (a) one β-CH of the pyrrole ring of one molecule with *ortho*-fluorine of the pentafluorobenzene unit of other molecule (C18−H18−F6 2.74 (4) Å, 165.4°) to form a self-assembled dimer; (b) one of the three pentafluorogroups (connected through sp^3 meso carbon) of **8** is involved in C23−H23−F9 (2.69 (4) Å, 161.2°) interactions for the construction of 2D sheet-like structure from the self-assembled dimer. This is one of the predominant structure-building interactions in the solid-state structure of **8**. Further, two more C−H−F (C22−H22−

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(10) Crystal data for **8**: $C_{67}H_{49}F_{15}N_4Se_1$, $M = 1187.89$, triclinic, space group $P1$, $a = 14.317(3)$ Å, $b = 14.494(3)$ Å, $c = 15.344(5)$ Å, $\alpha = 87.74(9)°$, $\beta = 69.23(10)°$, $\chi = 74.18(2)°$, $V = 2858(5)$ Å^3, $Z = 2$, $T = 100(2)$ K, 16276 reflections measured, 11021 independent, giving $R1 = 0.0803$, w$R2 = 0.1849$ for observed unique reflection ($I > 2\sigma(I)$), and $R1 = 0.1277$, w$R2 = 0.2237$, Go$F^2 = 1.025$.

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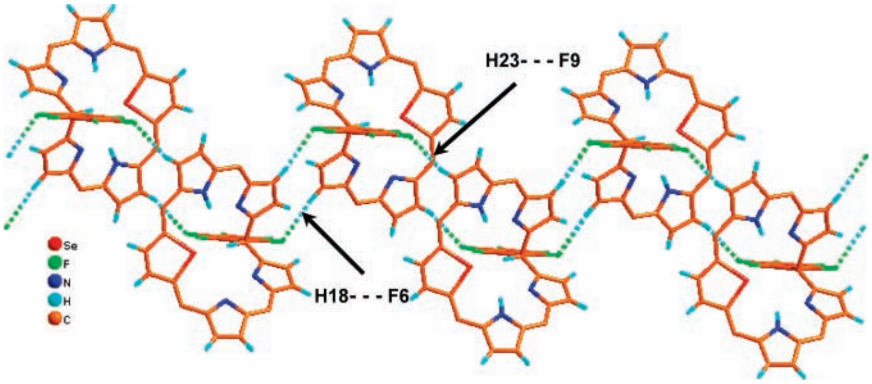

Figure 5. Molecular packing diagram of **8** showing two-dimensional ladder structure. Hydrogen-bonding interactions are represented by dotted lines and indicated by arrows.

F14; 2.592 Å, 146.29(4)°, C8−H8−F8; 2.696 Å, 155.78(4)°) interactions between the 2D layers leads to a 3D caged-like architecture (see Supporting Information for the complete structure). Overall, due to the presence of extensive intermolecular C−H−F interactions may further add to the stability of the compound in **8**.

In conclusion, we have described an efficient methodology to synthesize core-modified calix[5]phyrins and N-fused[24]-pentaphyrins using easily available stable precursors. Further studies of these systems, particularly coordination chemistry are currently in progress.

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Supporting Information Available: Experimental procedures and characterization of all new compounds including UV−vis spectra of **7**−**10** along with its protonated forms, crystallographic data for compound **8** (CIF), and views of the supramolecular structure of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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