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Doubly N-fused *meso*-aryl substituted hexaphyrins(1.1.1.1.1.1)

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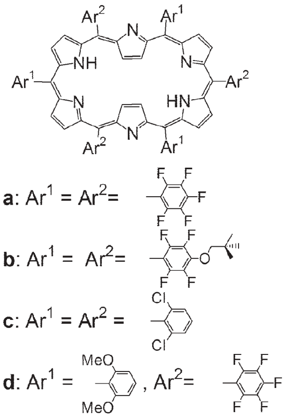
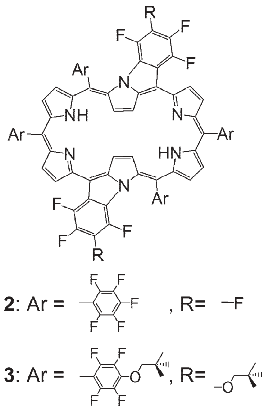
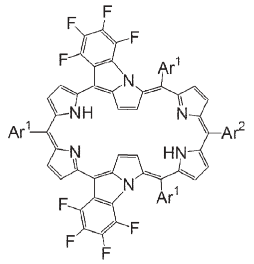
Doubly N-fused hexaphyrins were synthesized from *meso*-aryl substituted hexaphyrins and X-ray crystallography revealed that *syn*- or *anti*-double N-fusion occurred, depending on the positions of *meso*-substituents.

In recent years, expanded porphyrins have attracted considerable interest because of their fascinating optical and electrochemical properties as well as unprecedented reactivities that are not known for porphyrins.[1–3] Among these, N-fused structures were reported for N-fused porphyrin (**NFP**),[4a,b] N-fused pentaphyrin(1.1.1.1.1) (**NFP5**),[3b] and doubly N-fused pentaphyrin,[4c] as a consequence of nucleophilic attack of a pyrrolic nitrogen atom at the β-position of the neighboring pyrrole. Another mode of N-fusion reaction is nucleophilic substitution of *ortho*-halogen at *meso*-aryl substituent by an adjacent pyrrolic nitrogen atom, which is reported only for trithiahexaphyrin(1.1.1.1.1.1)[5] and *meso*-aryl perfluorinated heptaphyrin(1.1.1.1.1.1.1).[3d] These transformations are attractive, since the incorporation of a 5,5,6-tricyclic ring system leads to creation of a novel N-fused expanded porphyrin with unique optical and electrochemical properties. Here, we report facile double N-fusion reactions of *meso*-aryl substituted [26]hexaphyrins(1.1.1.1.1.1) **1**, which are more general, being aided by the outward-pointing two pyrroles and reactive pentafluorophenyl substituents in the hexaphyrins.[3a]

Initially, a solution of [26]hexaphyrin **1a** in toluene was refluxed in the presence of an excess amount of sodium acetate. The reaction was rather slow but gave, after a week, one major product **2** as a less polar red compound in 30% yield. When subjected to the conditions used for similar N-fusion reaction of a trithiahexaphyrin (refluxing in DMF in the presence of CuCl),[5] **1a** was merely decomposed. Refluxing of **1a** in DMF without any additive for 1.5 h led to the formation of **2** with many other complicated products. In this run, repeated tedious separations were needed to isolate **2** in 37% yield. In the meantime, we found that **2** was formed in 55% yield by refluxing **1** in chlorobenzene in the presence of Fe(III) acetylacetonate. It is important to note that [28]hexaphyrin, a reduced form of **1a**, could not be converted into **2** under the reaction conditions examined above.







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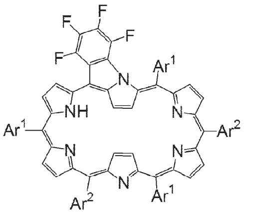

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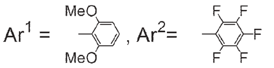

The structure of **2** has been determined by X-ray analysis of its trifluoroacetic acid salt, **2**-TFA (**2**-bis(trifluoroacetate)) (Fig. 1a). Important structural features are 1) N-fusion reaction occurred at the 5- and 15-pentafluorophenyl substituents, causing two 5,5,6-tricyclic ring units at *anti*-positions, 2) the fused pyrrolic nitrogens are pointing outward in a rectangular macrocyclic conformation as

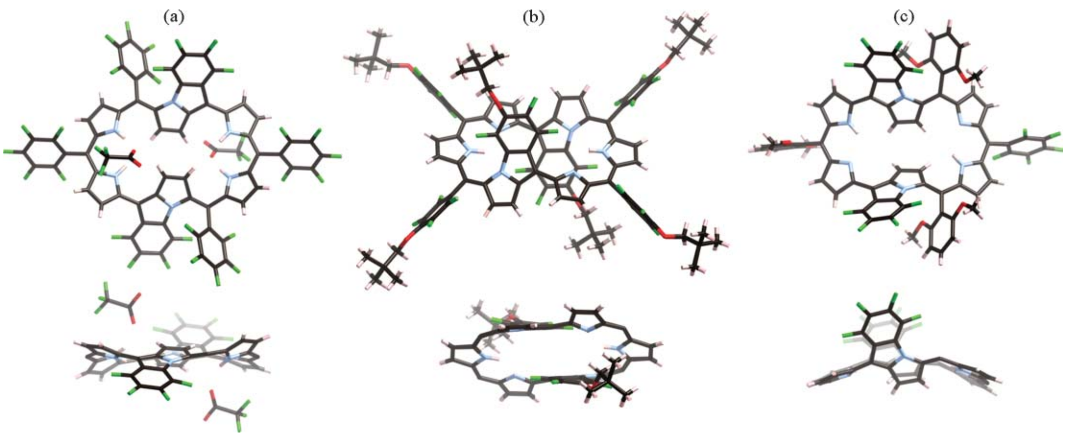

Fig. 1 Crystal structures of (a) **2**-TFA, (b) **3**, and (c) **4**. Some *meso*-aryl groups were omitted for clarity. Upper, top view; lower, side views.

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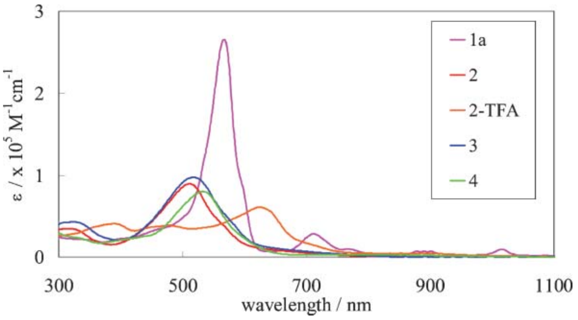

Fig. 2 UV/vis absorption spectra in CH_2Cl_2.

observed for **1**, 3) the diagonal two pyrrolic nitrogens are protonated to form a diprotonated species, and 4) the conjugated electronic system is a 28π-electron non-aromatic network. The 5,5,6-tricyclic ring system constitutes a flat framework with mean-plane deviation of 0.039 Å, while the overall doubly N-fused hexaphyrin macrocycle exhibits a larger mean-plane deviation of 0.204 Å. A neutral form of **2** exhibits a parent molecular ion peak at $m/z = 1420$ (calcd: m/z 1422) in the mass spectrum and mutually coupled three pairs of doublets at 5.90 and 5.49 ppm, 5.09 and 4.68 ppm, and 4.69 and 4.24 ppm due to the pyrrolic β-protons and a singlet at 20.0 ppm due to the inner NH protons in the ^{1}H NMR spectrum. The high chemical shifts of the pyrrolic β-protons and the exceptionally low chemical shift of the inner NH proton may suggest non-aromatic or rather anti-aromatic nature of the macrocycle. The latter one also indicates an additional contribution of strong hydrogen bonding between NH···N.The absorption spectra of **2**-TFA and **2** differ significantly from that of **1a** in respect of less intense Soret-like bands and the absence of a Q-band like band, reflecting their non-aromatic nature (Fig. 2).†

Although we could not get crystals of neutral **2** suitable for X-ray crystallography, we obtained good crystals of **3**, which was prepared from **1b**. Interestingly, the X-ray crystal structure of **3** (Fig. 1b) is quite different from that of **2**-TFA, in that all the pyrrolic nitrogens are pointing inward towards the center of the macrocycle and the fused tricyclic rings are laid over the marocycle to form a symmetric distorted conformation. The ^{1}H NMR spectrum of **3** shows the pyrrolic β-protons in 4.33–5.12 ppm and the inner NH proton at 22.1 ppm that are similar to **2**, thus suggesting that doubly N-fused hexaphyrins **2** and **3** take a similar distorted conformation in their neutral forms. The absorption spectrum of **3** is quite similar to that of neutral **2**, again suggesting its non-aromatic property.

N-fusion reactions of hexaphyrins **1c** and **1d** were also examined. The former was practically unreactive under the same conditions, indicating that the 2,6-dichlorophenyl substituent is much less reactive compared with the pentafluorophenyl substituent. Hexaphyrin **1d**[3e] was chosen to synthesize a *syn*-doubly N-fused hexaphyrin, since *syn*-type double N-fusion reaction is only possible for **1d**. By refluxing **1d** in DMF for 8 h, *syn*-doubly fused hexaphyrin **4** and singly N-fused hexaphyrin **5** were obtained in 3 and 17% yields, respectively. These products both exhibited parent molecular ion peaks at the expected positions; $m/z = 1330$ for **4** and $m/z = 1349$ for **5**, respectively. Heating a solution of **5** led to the formation of **4**. Such a mono N-fused hexaphyrin product was also detected only in a trace amount in the reaction of **1a**. The solid-state structure of **4** determined by the X-ray diffraction technique revealed a distorted saddle conformation with the two inverted pyrroles, at which sites the N-fusion reaction took place (Fig. 1c). The 5,5,6-tricyclic rings are both quite planar and directed to the same side. The ^{1}H NMR spectrum of **4** in CD_2Cl_2 exhibits four doublets due to the peripheral outer β-protons in a range of 5.28–5.93 ppm and a broad signal due to the inner NH protons at 16.9 ppm. Interestingly, the inner β-protons are observed as two doublets at exceptionally low fields 9.91 and 11.0 ppm. These data again suggest a 28π-electron non-aromatic network, which is also supported by the absorption spectrum of **4** that is similar to those of **2** and **3**.

In summary, appropriately *meso*-aryl substituted [26]hexaphyrins are converted into doubly N-fused [28]hexaphyrins upon heating. Doubly N-fused hexaphyrins thus formed take variable conformations depending upon the degree of protonation and the arrangement of N-fusion sites. The N-fusion reactivity of hexaphyrin lies between those of porphyrin and pentaphyrin, since such reaction is not known or impossible for porphyrins but N-fusion reaction seems mandatory for pentaphyrins, since all *meso*-aryl substituted pentaphyrins isolated so far have an N-fused structure like **NFP5**.[3b]

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Notes and references

† *Crystal data for* **2**-TFA: $C_{70}H_{16}O_4N_6F_{34}\cdot 2(C_4H_7O)\cdot 6(C_2F_3O_2) = 2245.14$, triclinic, space group *P*-1 (No. 2), $a = 8.995$ (2), $b = 14.081$ (3), $c = 17.398$ (3) Å, $\alpha = 73.42$, $\beta = 86.77$, $\gamma = 85.54°$, $V = 2104$ (6) Å^3, $Z = 1$, $D_{\text{calcd.}}$ 1.772 g cm^{-3}, $T = -150$ °C, $R = 0.057$ ($I > 3\sigma(I)$), $R_W = 0.079$ (all data), GOF = 1.029 ($I > 3\sigma(I)$). CCDC 242616; *Crystal data for* **3**: $C_{96}H_{80}O_6N_6F_{22}\cdot 4(O) = 1895.69$, tetragonal, space group *I*4/*m* (No. 88), $a = 34.436$ (8), $b = 34.436$ (8), $c = 17.721$ (7) Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$, $V = 21014$ (9) Å^3, $Z = 8$, $D_{\text{calcd.}}$ 1.198 g cm^{-3}, $T = -150$ °C, $R = 0.094$ ($I > 3\sigma(I)$), $R_W = 0.138$ (all data), GOF = 1.147 ($I > 3\sigma(I)$). CCDC 242617; *Crystal data for* **4**: $C_{72}H_{41}O_6N_6F_{13}\cdot 2(CHCl_3) = 1571.89$, triclinic, space group *P*-1 (No. 2), $a = 7.9826$ (7), $b = 15.903$ (1), $c = 27.941$ (2) Å, $\alpha = 77.88$, $\beta = 89.14$, $\gamma = 83.14°$, $V = 3443$ (5) Å^3, $Z = 2$, $D_{\text{calcd.}}$ 1.516 g cm^{-3}, $T = -150$ °C, $R = 0.100$ ($I > 3\sigma(I)$), $R_W = 0.152$ (all data), GOF = 1.478 ($I > 3\sigma(I)$). CCDC 242615. See http://www.rsc.org/suppdata/cc/b4/b410011e/ for crystallographic data in .cif or other electronic format.

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