Multiple conformational changes of β-tetraphenyl *meso*-hexakis(pentafluorophenyl) substituted [26] and [28]hexaphyrins(1.1.1.1.1.1)†

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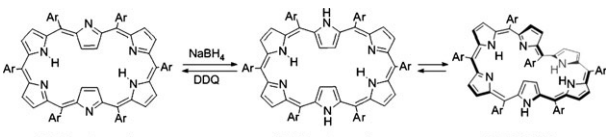
β-Tetraphenyl *meso*-hexakis(pentafluorophenyl) substituted [26]hexaphyrin 3 is conformationally flexible between rectangular and figure-of-eight shapes and its two-electron reduced [28]hexaphyrin 4 takes figure-of-eight conformations, which are changed, upon protonation, to twisted conformations with distinct Möbius aromaticity.

Increasing attention has been focused on expanded porphyrins that are conjugated macrocycles consisting of more than five pyrrolic subunits because of their diverse intriguing electrochemical, optical, structural, and coordination properties.[1] Among these, *meso*-hexakis(pentafluorophenyl) substituted [26]hexaphyrin (**1**)[2] serves as a benchmark molecule, exhibiting a planar molecular shape, strong aromaticity arising from the 26π-electronic system, and versatile metalation behaviors.[3] Curiously, the metalation of **1** with group 10 metals (Ni(II), Pd(II), and Pt(II)) led to the formation of Möbius aromatic molecules with twisted topology.[4,5] Another important chemical reactivity is the reversible interconversion between **1** and [28]hexaphyrin **2** through reduction with $NaBH_4$ and oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Recently, [28]hexaphyrin **2** has been revealed to be a unique macrocycle that exists as a dynamic mixture of several rapidly interconverting Möbius aromatic and Hückel antiaromatic conformers in solution at room temperature (Scheme 1).[6]

Despite these attractive features, the chemistry of *meso*-aryl [26] and [28]hexaphyrins has been rather limited to the parent molecules **1** and **2**, because of the lack of available synthetic methods to fabricate the hexaphyrins. Particularly, peripherally modified [26] and [28]hexaphyrins have been only scarcely reported so far.[7] It was thought that introduction of substituents at the peripheral β-positions would be a useful means to change the electronic and structural properties, hence contributing to expand the chemistry of *meso*-aryl expanded porphyrins. In this communication, we report the synthesis of β-tetraphenyl substituted [26]- and [28]-hexaphyrins **3** and **4** and their intriguing multiple conformational changes.‡

[26]Hexaphyrin **3** was prepared by the condensation reaction of dipyrromethane-dicarbinol **5**[8] and 3,4-diphenylpyrrole (**6**).[9] An equimolar mixture of **5** and **6** was treated with methanesulfonic acid at room temperature for 1 h followed by the oxidation with DDQ for 3 h. Chromatographic separation over a silica gel column gave **3** in 20% yield (Scheme 2). The crystal structure of **3** has been revealed by X-ray crystallographic analysis to be a planar rectangle similar to that of **1** (Fig. 1). Four β-phenyl groups are found at the diagonal peripheral β-positions. Quite unexpectedly, however, the ^1H NMR spectrum of **3** is very broad at room temperature, suggesting rapid conformational changes that are comparable to the NMR measurement time scale. As the temperature was lowered, the signals became sharper, featuring two sets of signals due to different conformations at −60 °C. One set includes a singlet at −0.53 ppm due to the N–H proton and two sets of doublets at 9.02 and 8.67 ppm, and −0.45 and −0.56 ppm due to the outer and inner β-protons, respectively. This has been ascribed to a flat rectangular conformation **3A** that is observed for the crystal. The other set exhibits the NH proton at 9.01 ppm and the β-protons as two sets of doublets at 6.84 and 6.72 ppm, and 5.44 and 4.31 ppm. This set has been assigned as a non-aromatic figure-of-eight conformation **3B** on the basis of the chemical shifts and the simplicity of the spectrum. The moderately highfield shifted signals of the β-protons may suggest a small diatropic ring current also for **3B**.[10] At −60 °C conformational exchange is slow enough to see two separate sets of resonances. Here, it is to be noted that the conformational flexibility of **3** is likely larger than that of **1**, whose rectangular conformation is rather stable in a wide range of temperature.[5] A possible explanation is that the newly introduced four β-phenyl substituents endow additional stabilization for the figure-of-eight conformations *via* π–π interaction between the β-phenyl and *meso*-pentafluorophenyl substituents.

Reduction of **3** with $NaBH_4$ gave [28]hexaphyrin **4** quantitatively (Scheme 3). The crystal structure of **4** has been determined to be figure-of-eight, which is likely stabilized by favorable stacking interaction between the β-phenyl groups



Scheme 1

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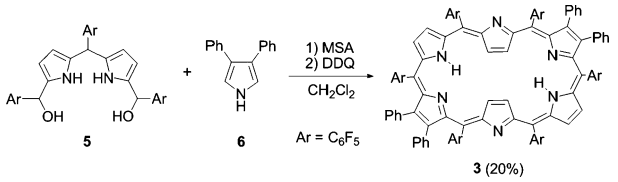
† Electronic supplementary information (ESI) available: Experimental section, spectroscopic data and NMR spectra. CCDC 728271–728273. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b910167e



Scheme 2

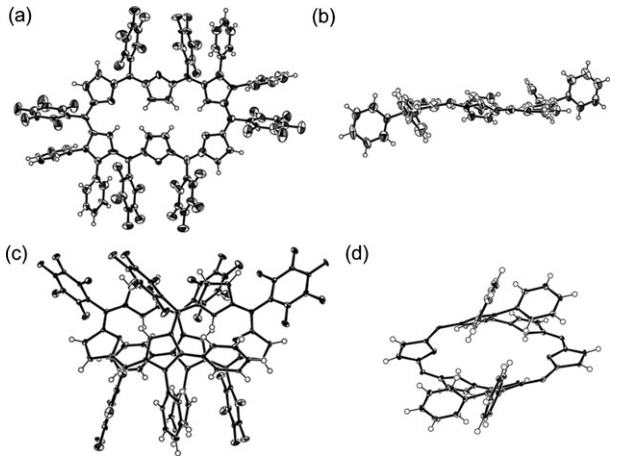
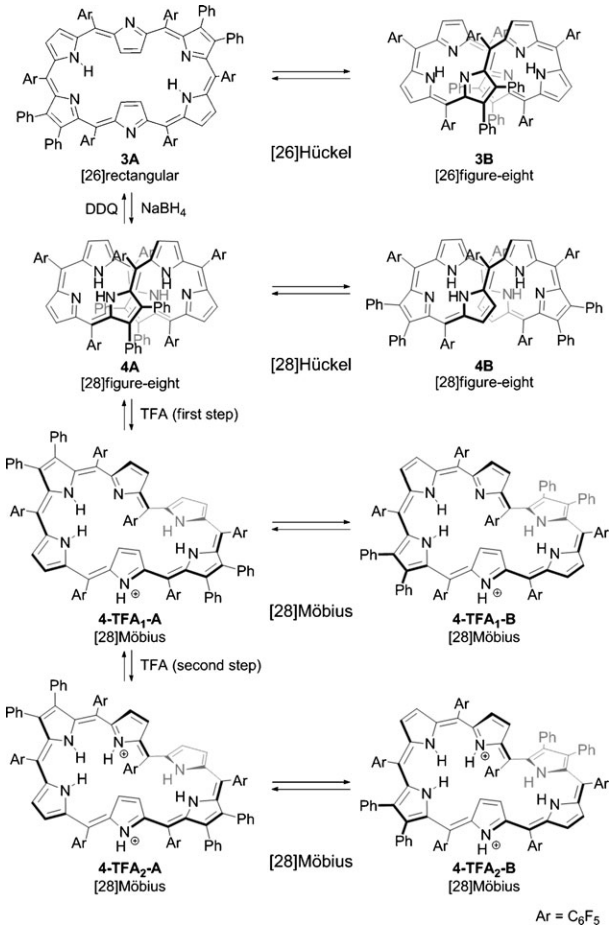


Fig. 1 X-Ray crystal structures of **3** (a) top view and (b) side view and **4** (c) top view and (d) side view. Thermal ellipsoids are scaled to 50% probability level. In the side views, *meso*-pentafluorophenyl substituents are omitted for clarity.

and *meso*-pentafluorophenyl groups. Hydrogen bonding between the pyrrolic amino-NH and imino-N are also supporting the figure-of-eight conformation (Fig. 1). At room temperature the ^{1}H NMR spectrum of **4** in $CDCl_3$ showed two sets of signals due to the N–H protons at 14.68 and 14.05 ppm as sharp signals and at 16.12 and 13.15 ppm as broad signals in a ratio of 1 : 0.72, suggesting that two major figure-of-eight conformers are present in solution. In a region of 8.42–5.56 ppm, a set of β- and phenyl-protons were observed as sharp signals, and the other set was observed as broad signals, which became sharper as the temperature was decreased.

The UV/vis absorption spectrum of **3** in CH_2Cl_2 exhibits split Soret-like bands at 580 and 619 nm and Q-like bands at 731, 796, 896, and 946 nm (Fig. 2), in line with its aromaticity. The splitting of Soret-like bands reflects its molecular symmetry, since two transition dipole moments along the diagonal axes are not equivalent. The absorption spectrum of **4** is ill-defined, being characteristic of non-aromatic or antiaromatic porphyrinoids.[10] The intensity of the Soret-like bands of **3** is not so prominent as compared with that of **1**, probably as a consequence of non-negligible contribution of non-aromatic figure-of-eight conformations.

In the next step, we examined the protonation-induced conformational change of **4** using trifluoroacetic acid (TFA) in CH_2Cl_2, since protonation has been shown to be effective in inducing twisted conformations of Möbius aromaticity for *meso*-aryl substituted [32]heptaphyrins.[11] Addition of TFA indeed induced the absorption spectral changes including the appearance of a prominent sharp Soret-like band at 617 nm and Q-like bands at 828, 869, 928, and 988 nm with isosbestic points at 365, 414, 569, 683, and 744 nm as the first



Scheme 3

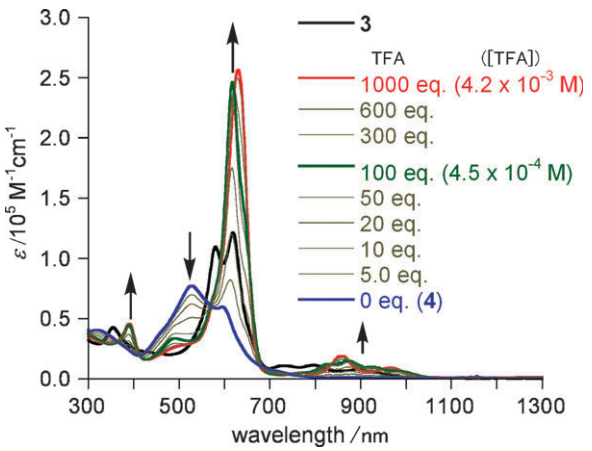


Fig. 2 Absorption spectra of **3** (black solid) and **4** (blue solid) in CH_2Cl_2 and spectral changes for titration experiments of **4** with TFA.

protonation step to form **4·TFA$_1$** up to [TFA] = 4.5×10^{-4} M. Upon further addition of TFA, the Soret-like band was slightly more red-shifted to 631 nm and the Q-like bands appeared at 861 and 967 nm. These secondary spectral changes, which strongly indicated the formation of **4·TFA$_2$**, occurred with different isosbestic points up to [TFA] = 4.2×10^{-3} M (Fig. 2, ESI†). The absorption spectra of **4·TFA$_1$** and **4·TFA$_2$** indicate their strong aromaticity. The protonation steps were also examined by ^{1}H NMR spectroscopy. The

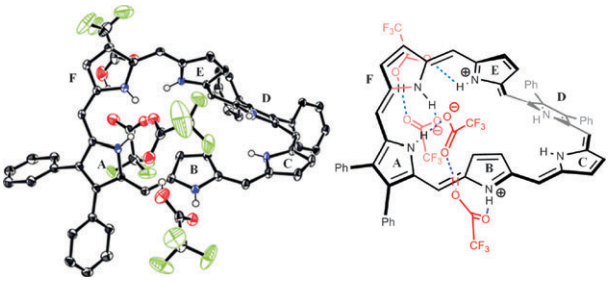


Fig. 3 X-Ray crystal structure of **4·TFA$_2$**. Thermal ellipsoids are scaled to 50% probability level. *meso*-Pentafluorophenyl groups, β- and phenyl-protons, and solvent molecules are omitted for clarity.

^{1}H NMR spectrum of **4·TFA$_1$** in CD_2Cl_2 was very broad at room temperature, indicating rapid conformational interconversion among several aromatic species (ESI†). The spectrum became sharpened at −80 °C, showing two sets of signals in a ratio of 1 : 0.95 due to the inner pyrrolic β-protons in a shielded region. These data indicated the presence of two aromatic species, probably two twisted Möbius aromatic species, for **4·TFA$_1$**. Upon further addition of TFA, the ^{1}H NMR spectrum displayed a different sharp spectrum that contains two sets of signals due to the inner β-protons in a shielded region in a ratio of 1 : 0.88 (ESI†). This spectrum indicates the presence of two twisted conformations of Möbius aromaticity for **4·TFA$_2$**, which differ possibly in position of β-phenyl groups. Upon neutralization with aqueous $NaHCO_3$, **4·TFA$_2$** reverted to **4** with concurrent conformational changes.

Fortunately, crystals suitable for X-ray analysis were obtained from slow diffusion of *n*-hexane into a solution of **4** in CH_2Cl_2–TFA. The structure of this crystal, possibly **4·TFA$_2$**, was revealed to be a twisted Möbius conformation held by hydrogen bonding between TFA molecules and N–H protons in line with the above assignments (Fig. 3). Importantly, the six pyrrolic segments in **4·TFA$_2$** are smoothly linked with dihedral angles of less than 32° to constitute a 28π-electron conjugated electronic circuit.

In summary, β-tetraphenyl substituted [26]hexaphyrin **3** was prepared and has been shown to be conformationally flexible among rectangular and figure-of-eight conformations. Its two-electron reduced congener, [28]hexaphyrin **4**, exists mainly as a dynamic equilibrium of figure-of-eight conformations but acquires Möbius aromaticity upon protonation. Attempts to use these multiple conformational changes for some signaling or switching systems are actively in progress in our laboratory.

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Notes and references

‡ Crystallographic data for **3**: $C_{90}H_{30}F_{30}N_6{\cdot}0.67(CHCl_3)$, M_w = 1844.78, triclinic, $P\bar{1}$ (no. 2), a = 18.209(3) Å, b = 18.259(3) Å, c = 19.016(3) Å, α = 98.298(11)°, β = 105.095(10)°, γ = 94.010(11)°, V = 6002.0(17) Å^3, D_c = 1.531 g cm^{-3}, Z = 3, T = 123(2) K, 50 467 reflections measured, 18 798 unique (R_{int} = 0.0757), R_1 = 0.0808 ($I > 2.0\sigma(I)$), wR_2 = 0.2453 (all data), GOF = 0.800 ($I > 2.0\sigma(I)$). These values have been obtained by removal of the solvent molecules by using the utility SQUEEZE in PLATON software package. SQUEEZE-PLATON: (a) ref. 12; (b) ref. 13. CCDC 728271. Crystallographic data for **4**: $C_{90}H_{32}F_{30}N_6{\cdot}2.62(CH_2Cl_2)$, M_w = 1989.72, monoclinic, $P2_1/c$ (no. 14), a = 13.6922(11) Å, b = 47.412(4) Å, c = 12.5608(10) Å, β = 90.791(2)°, V = 8153.4(11) Å^3, D_c = 1.621 g cm^{-3}, Z = 4, T = 90(2) K, 42 183 reflections measured, 14 315 unique (R_{int} = 0.0662), R_1 = 0.0975 ($I > 2.0\sigma(I)$), wR_2 = 0.2117 (all data), GOF = 1.207 ($I > 2.0\sigma(I)$). CCDC 728273. Crystallographic data for **4-TFA$_2$**: $C_{90}H_{34}F_{30}N_6{\cdot}2(C_2HF_3O_2){\cdot}2(C_2F_3O_2){\cdot}3(CH_2Cl_2)$, M_w = 2478.11, monoclinic, $P2_1/c$ (no. 14), a = 13.8248(14) Å, b = 21.260(2) Å, c = 34.396(4) Å, β = 100.059(2)°, V = 9953.8(18) Å^3, D_c = 1.654 g cm^{-3}, Z = 4, T = 90(2) K, 60 223 reflections measured, 22 188 unique (R_{int} = 0.0415), R_1 = 0.0777 ($I > 2.0\sigma(I)$), wR_2 = 0.2445 (all data), GOF = 1.015 ($I > 2.0\sigma(I)$). CCDC 728272.

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