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Möbius Aromaticity

# Thermal Fusion Reactions of *meso*-(3-Thienyl) Groups in [26]Hexaphyrins to Produce Möbius Aromatic Molecules**

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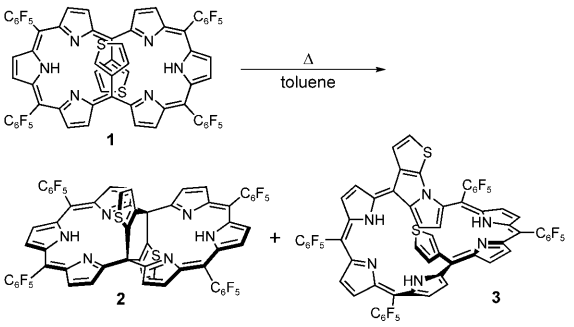
The topology of π-electronic conjugation is an important current topic in structural organic chemistry.[1] This area has been boosted by the seminal paper by Herges et al. on the synthesis of a tetrabenzo[16]annulene as the first stable Möbius aromatic molecule.[2] The concept of Möbius aromaticity was first suggested by Heilbronner in 1964,[3] but its realization has been quite difficult owing to the structural requirements of implementing a smooth conjugated π network and a twisted conformation within a single molecule.[4] Recently, expanded porphyrins, which are pyrrolic conjugated macrocycles, have emerged as a new promising class of molecules for creation of Möbius aromatic systems. Latos-Grażyński et al. reported a di-*p*-benzo[28]hexaphyrin that has a twisted Möbius conformation at low temperature.[5] We found that stable Möbius aromatic molecules were formed from *meso*-aryl expanded porphyrins by metal coordination,[6a,b] temperature control,[6c,d] and protonation.[6e] Recently an additional Möbius aromatic system was found upon heating of *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin in acetic acid.[6f] Despite these efforts, Möbius aromatic molecules are still rare, and a new synthetic strategy to produce Möbius aromatic molecule is highly desirable.

In the course of our studies on the chemistry of *meso*-aryl-substituted [26]hexaphyrins,[7] we have revealed that: 1) there are two major conformations, a spectacles-like shape (type I) and a rectangular shape (type II), both of which are strongly aromatic owing to normal double-sided Hückel topology and 26π-electronic circuits;[8] and 2) transannular interactions in the type I conformation induce intramolecular bridging reactions to create novel skeletons.[9] As a continuation of these studies, we examined the thermal reaction of 5,20-bis(3-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)-substituted [26]hexaphyrin **1** that has the type I conformation.[8] Heating a toluene solution of **1** to reflux for 8 h led to the formation of doubly spiro-annulated product **2** and singly thienyl-fused [28]hexaphyrin **3** in 10 and 82% yields, respectively (Scheme 1).



***Scheme 1.*** Thermal fusion of **1** to give **2** and **3**.

The structure of **2** was determined by X-ray diffraction analysis (Figure 1a).[10] Both 3-thienyl substituents are fused at the opposite *meso*-positions to form a doubly spiro-annulated structure. The central 3,4-dibenzo[1,2,*b*:5,6,*b*′]dithiophene segment bisects the hexaphyrin mean plane with an angle of 87.6°. This symmetric structure is fully consistent with its spectroscopic data (see the Supporting Information). The resulting hybridization of the methene bridges from $sp^2$ to $sp^3$ serves to interrupt the conjugation of the hexaphyrin, which was also confirmed by its less-intense absorption spectrum (Supporting Information). By contrast, the UV/Vis absorption spectrum of **3** has Soret-like bands at 612 nm and Q-like bands in the low-energy region with clear vibronic structure; both bands are characteristic of aromatic expanded porphyrins (Supporting Information). The $^1H$ NMR spectrum of **3** shows two sets of peaks in a ratio of 10:1 at room temperature. A major set includes signals for the two inner β-pyrrolic protons at $\delta = -2.91$ and $-0.86$ ppm, and those for to the outer β-pyrrolic protons in the range $\delta = 6.94$–$8.19$ ppm, which indicates its diatropic ring current. The chemical shift difference between the most shielded and deshielded protons ($\Delta\delta$) is 11.10 ppm. The minor set of signals features three NH protons and three thienyl protons in a strongly deshielded

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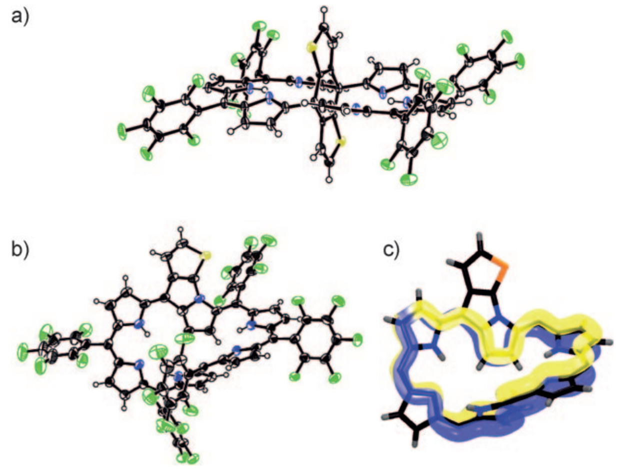
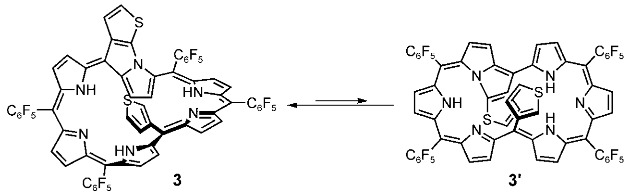


***Figure 1.*** a,b) ORTEPs of a) **2** and b) **5**. N blue, S yellow, F green. Ellipsoids set at 50% probability; solvent molecules are omitted for clarity. c) The molecular topology of **5**, with the phases of the π-electron circuit represented in blue and yellow.

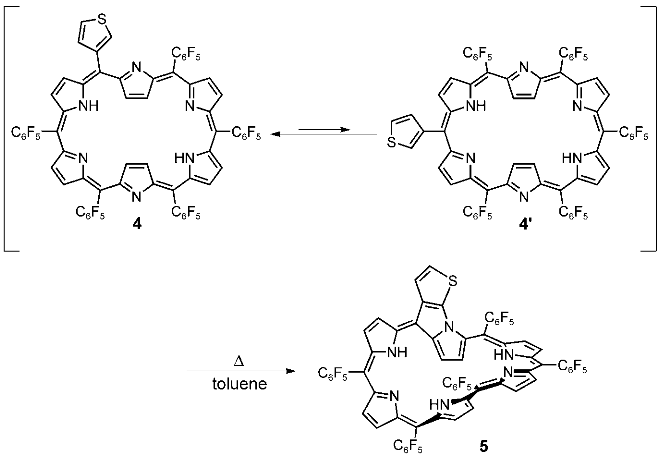
region, indicating a spectacles-like planar conformation and thus Hückel antiaromatic character (**3′**). This spectral feature indicates that there exists a thermal equilibrium between **3** and **3′** (Scheme 2).



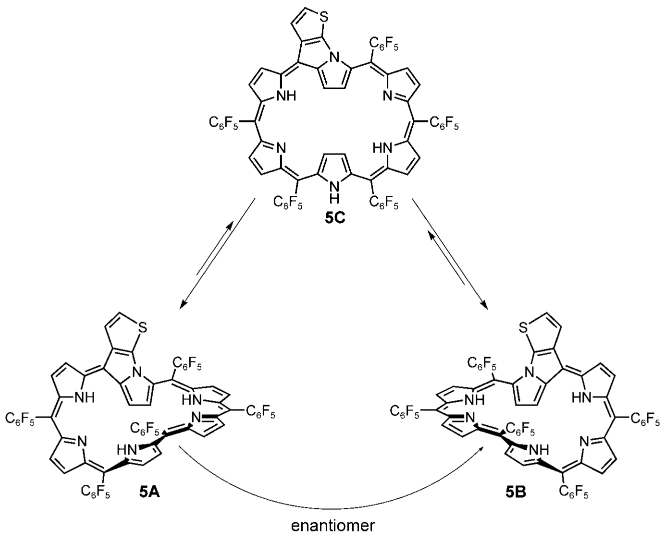
***Scheme 2.*** Representation of an equilibrium between **3** and **3′**.

The femtosecond transient absorption spectra of **1** show only a single decay component with $\tau = 130$ ps by the global fitting analysis. On the other hand, the spectrum of **3** has two transient features in the decay processes; one is composed of a strong bleaching signal along with excited absorption peaks at both sides of the bleaching peak, and the other shows a weak but broad spectral feature, based on the global fitting analysis (Supporting Information). The major species (88%) decays with $\tau_1 = 132$ ps, whilst the minor species (12%) decays with $\tau_2 = 26$ ps. This result also indicates that there is a thermal equilibrium between **3** and **3′**, because it is known that the antiaromatic congener exhibits a relatively short excited state lifetime compared with its aromatic partner.[11] Considering a 28π-electronic circuit, the aromatic features of the major isomer are plausibly ascribed to Möbius aromaticity of a twisted topology of π conjugation.

The formation of **2** and **3** indicates the unique reactivity of *meso*-(3-thienyl) substituents in **1**. Although **2** is most likely formed by the transannular interactions in type I conformation,[9] the formation of **3** can occur from both conformations. The preferential type I conformation of **1** can be ascribed to the presence of two small *meso*-(3-thienyl) substituents.[8] Thus, to suppress the type I conformation and thus block the doubly spiro-annulation reaction, we focused on [26]hexaphyrin **4** by replacing one 3-thienyl group by a larger pentafluorophenyl group. Hexaphyrin **4** was obtained as a mixture of rotational isomers (**4** and **4′**; Scheme 3) in 2.4% yield by a cross-condensation reaction of 5-pentafluorophenyl dipyrromethane, thiophene-3-carbaldehyde, and pentafluorobenzaldehyde. The $^1$H NMR and absorption spectra of **4** and **4′** reveal their rectangular shapes and also strong diatropic ring currents. Remarkably, simple heating of a mixture of **4** and **4′** in toluene gave thienyl-fused product **5** almost quantitatively. The $^1$H NMR spectrum of **5** has signals at $\delta = -2.72$ and $-0.52$ ppm owing to the two inner β-pyrrolic protons, and those in a region of $\delta = 7$–$9$ ppm for the ten outer β-pyrrolic protons. The structure of **5** was unambiguously determined by X-ray single crystal analysis to be a twisted Möbius topology with a 28π-electronic circuit (Figure 1b). Therefore, as we expected, an increase in steric bulk of the *meso*-aryl substituent suppressed a type I conformation, thus improving the yield of the Möbius aromatic product. At first sight, the $^1$H NMR spectrum of **5** seems to indicate a rigid twisted conformation. Considering the restricted rotation of *meso*-pentafluorophenyl substituents, such a rigid structure requires 10 different signals for the *ortho*-$^{19}$F atoms. However, the $^{19}$F NMR spectrum has rather broad peaks for the *ortho*-$^{19}$F atoms of the *meso*-aryl substituents at room temperature. These broad signals were replaced by five sharp signals above 373 K and ten sharp signals below 223 K (Supporting Information). This temperature dependence can be accounted for in terms of conformational dynamics between **5A** and **5B**, and the rate of such conformational dynamics is comparable to the $^1$H NMR time scale at room temperature (Scheme 4). In addition, as the temperature increases, the $^1$H NMR peaks corresponding to the inner β-protons are steadily shifted downfield, which indicates that the conformational equilibrium additionally involves a high-energy antiaromatic isomer **5C**, which increases in contribution at high temperature. Nevertheless, it should be noted that the $^1$H NMR spectrum of **5** still shows the high-field shifted signals for the inner β-protons even at 413 K (Supporting Information).

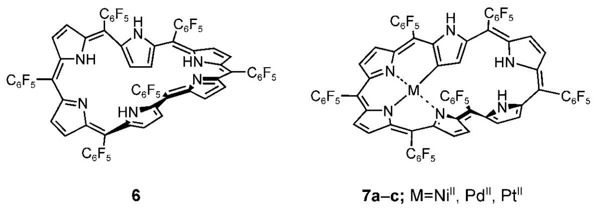


***Scheme 3.*** Thermal fusion reaction of **4** and **4′** to give **5**.



**Scheme 4.** Racemization of **5**.

With a Möbius aromatic [28]hexaphyrin **5** available, we compared its properties with those of free-base [28]hexaphyrin **6** at 173 K[6c,d] and Group 10 metallated [28]hexaphyrin complexes **7a**–**c** (Scheme 5).[6a] The $\Delta\delta$ value of **5** (11.4 ppm) is similar to **6** at 173 K (10.2 ppm), and larger than that of **7a**–**c** (5.9–7.1 ppm), which suggests that the magnitude of diatropic ring current of **5** at room temperature is comparable to that of **6** at 173 K and larger than those of **7a**–**c**. The absorption and fluorescence spectra of **4** and **5** in toluene are shown in Figure 2. Both the absorption spectra of **4** and **5** have general features of an aromatic expanded porphyrin, including an intense Soret-like band and weak Q-like bands.[11] The structured fluorescence spectra, which are also diagnostic of aromatic porphyrinoids, are observed both for **4** and **5** at 1051 and 1233 nm and at 1070 and 1255 nm, respectively (Figure 2).



**Scheme 5.** The structure of **6** and **7a**–**c**.

We measured the excited singlet state ($S_1$) lifetimes of **4** and **5** by femtosecond transient absorption spectroscopy (Supporting Information). The $S_1$ state lifetime of **4** was determined to be about 105 ps, which is quite similar to that of typical free-base [26]hexaphyrins (circa 100 ps).[11,12] In our previous results, the $S_1$ state lifetime of **6** exhibits a double-exponential behavior owing to the presence of Hückel antiaromatic (17 ps) and Möbius aromatic (180 ps) conformers at room temperature.[6d] In contrast, the $S_1$ state decay of **5** was found to obey a single exponential function with $\tau =$ 178 ps (Figure 3), which is quite similar to Möbius aromatic compound **6**. Additionally, we have investigated the excitation and probe wavelength dependence on each split Soret-like band of **5**, which reflects a possibility of conformers (Supporting Information). Despite the alternation of excitation and probe wavelengths, the $S_1$ state dynamics of **5** does not show any significant changes, indicating that the origin of split Soret-like band is not various conformations but electronic transition nature of **5**. Furthermore, the calculated absorption bands of **5** by TD-DFT (B3LYP/6-31G**) method match the Soret-like band splitting well (Supporting Information). Consequently, **5** can be considered to be conformationally locked into a Möbius structure, and the contribution of its Hückel antiaromatic rectangular conformation is almost negligible at room temperature.

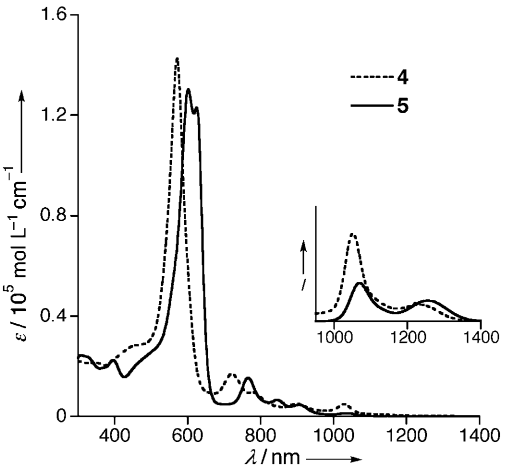


**Figure 2.** Steady-state absorption spectra of **4** (•••••) and **5** (——) in toluene. Inset: fluorescence spectra of **4** and **5** excited by the 442 nm line of a He-Cd laser.

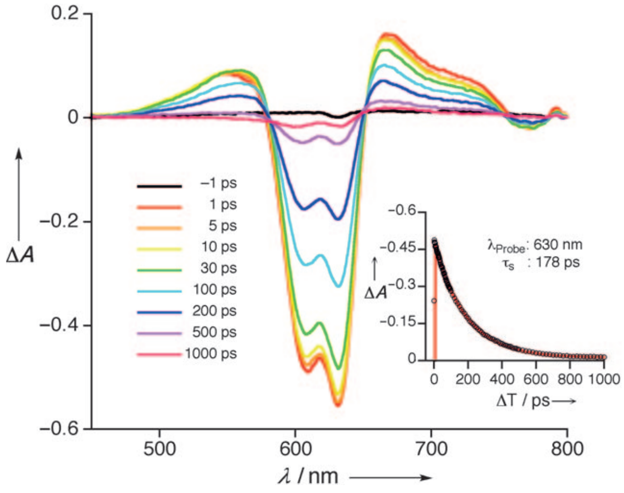


**Figure 3.** Femtosecond transient absorption spectra of **5** under 610 nm excitation in toluene. Inset: decay kinetic profiles at 630 nm.

We also measured the two-photon absorption (TPA) cross-section value $\sigma^{(2)}$ of **5** by an open-aperture *Z*-scan method.[13] Based on previous work, it has been established that the $\sigma^{(2)}$ value can be correlated with the degree of aromaticity in expanded porphyrins within a comparable set of $[4n+2]/[4n]$ systems.[11] The maximum $\sigma^{(2)}$ value of **5** was found to be 8100 GM at 1200 nm, which is comparable to that of **6** at 173 K (9100 GM) and nearly two times larger than those of **7a–c** (4600–5500 GM).

To gain further insight into the Möbius aromaticity of **5**, we performed theoretical calculations using the Gaussian 03 package.[14] These calculations revealed nearly degenerate HOMOs and LUMOs, which are characteristic of aromatic expanded porphyrins (Supporting Information).[11] The harmonic oscillator model of aromaticity (HOMA) value[15] and the nucleus-independent chemical shift (NICS) value[16] at the center of macrocycle were calculated to be 0.61 and −14.9 ppm for **5**, whereas those of **6** (optimized Möbius) and **7a–c** were calculated to be 0.85 and −15.1 ppm and 0.39–0.64 and −11.9–-15.7 ppm, respectively (Supporting Information).

The degree of aromaticity of **5**, as judged from $\Delta\delta$ and $\sigma^{(2)}$ values, is certainly larger than that of **7a–c**. This may be accounted for in terms of smooth connection in constituting Möbius topology. Actually, the largest tilting angles in the conjugated circuit ($\Delta r_m$) are 34.4° for **5**, 26.5° for **6** (optimized Möbius), and 39.9–45.8° for **7a–c**. If the effect of a rigid component is too strong, it gives rise to reduced aromatic character owing to the disturbance of effective π conjugation, as seen for **7a–c**. In this context, the thienyl-fused segment in **5** provides suitable rigidification to sustain the stable Möbius topology and optimal π-electron conjugation in a [28]hexaphyrin macrocycle.

In summary, the unique reactivities of *meso*-(3-thienyl)-substituted [26]hexaphyrins have been used to provide a doubly annulated bis-spiro molecule and stable Möbius aromatic [28]hexaphyrins. Thiophene-fused [28]hexaphyrin **5** features a molecular twist, a distinct diatropic ring current, a large HOMA value, a large negative NICS value, and a large TPA cross-section value even at room temperature, all of which support Möbius aromaticity of **5**.

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**Keywords:** aromaticity · electronic structure · hexaphyrins · Möbius aromaticity · porphyrinoids

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[10] Crystal data for **2**: $C_{66}H_{22}Cl_{12}F_{20}N_6S_2$ ($M_r = 1768$), triclinic, space group $P\bar{1}$ (No. 2), $a = 10.629(5)$, $b = 11.207(6)$, $c = 14.757(6)$ Å, $\alpha = 101.541(20)$, $\beta = 94.327(18)$, $\gamma = 93.703(10)°$, $V = 1711.6(13)$ Å$^3$, $Z = 1$, $\rho_{calcd} = 1.716$ g cm$^{-3}$, $T = 123(2)$ K, $R_1 = 0.0518$ ($I > 2\sigma(I)$), $R_W = 0.1452$(all data), GOF = 1.103. Crystal data for **5**: $C_{76}H_{45}F_{25}N_6O_6S$ ($M_r = 1645$), triclinic, space group $P\bar{1}$ (No. 2), $a = 12.377(5)$, $b = 16.277(5)$, $c = 21.105(9)$ Å, $\alpha = 108.549(11)$, $\beta = 91.396(13)$, $\gamma = 102.304(10)°$, $V = 3919(2)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.394$ g cm$^{-3}$, $T = 123(2)$ K, $R_1 = 0.0847$ ($I > 2\sigma(I)$), $R_W = 0.2578$(all data), GOF = 0.886. In the crystal structure of **5**, there are disordered solvent molecules, and their contribution to the scattering values have been removed by using the PLATON SQUEEZE program.[17] CCDC 729195 (**2**) and CCDC 729196 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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