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*-arylsubstituted [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

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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 1 a).^[10] Both 3-thienyl substituents are fused at the opposite meso-positions to form a doubly spiroannulated 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 sp² to sp³ 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]hex-

aphyrin 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%



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

yield by a cross-condensation reaction of 5-pentafluorophenyl dipyrromethane, thiophene-3-carbaldehyde, and pentafluorobenzaldehyde. The ¹H 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 ¹H 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 ¹H 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 ¹⁹F NMR spectrum has rather broad peaks for the ortho-¹⁹F 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 ¹H NMR time scale at room temperature (Scheme 4). In addition, as the temperature increases, the ¹H 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 ¹H NMR spectrum of **5** still shows the high-field shifted signals for the inner β -protons even at 413 K (Supporting Information).



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



Scheme 5. The structure of 6 and 7 a-c.

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).

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 doubleexponential 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 $\tau =$



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

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-



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

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 conformation of its Hückel antiaromatic rectangular conformation is almost negligible at room temperature.

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

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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 (Δr_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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