Porphyrinoids

Deutsche Ausgabe: DOI: 10.1002/ange.201500099
Internationale Ausgabe: DOI: 10.1002/anie.201500099

A Möbius Aromatic [28]Hexaphyrin Bearing a Diethylamine Group: A Rigid but Smooth Conjugation Circuit**

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Abstract: *The reaction of [26]hexaphyrin with triethylamine in the presence of $BF_3{\cdot}OEt_2$ and O_2 furnished a diastereomeric mixture of a diethylamine-bearing [28]hexaphyrin as a rare example of a Möbius aromatic metal-free expanded porphyrin. The Möbius aromaticity of these molecules is large, as indicated by their large diatropic ring currents, which are even preserved at 100 °C, owing to their internally multiply bridged robust structure with a smooth conjugation network. These molecules were reduced with $NaBH_4$ to give an antiaromatic [28]hexaphyrin, and were oxidized with MnO_2 to give aromatic [26]hexaphyrins, both through a Möbius-to-Hückel topology switch induced by a C–N bond cleavage.*

In recent years, the topology of π conjugation has become increasingly important in discussing the aromaticity of cyclic organic molecules.[1] After the pioneering report by Herges and co-workers, who described the synthesis of a tetrabenzo[16]annulene as the first Möbius aromatic molecule in 2003,[2a] a number of Möbius aromatic compounds have been explored. In these, the macrocyclic [4*n*]π-conjugation system has a singly twisted one-sided topology, such as a Möbius strip (so-called Möbius topology).[2,3] The concept of Möbius aromaticity, first proposed by Heilbronner in 1964,[4] predicts that [4*n*]π- and [4*n*+2]π-conjugated molecules with Möbius topology should be aromatic and antiaromatic, respectively, as a complementary rule of the Hückel rule. *meso*-Aryl-expanded porphyrins have emerged as an effective platform to realize Möbius aromatic and antiaromatic molecules, owing to their macrocyclic π-conjugated system, conformational flexibility, and facile two-electron oxidation and reduction.[3,5] Despite these, examples of metal-free Möbius aromatic expanded porphyrins still remain rather limited because of the intrinsic difficulty in locking singly twisted structures without metal coordination. To the best of our knowledge, to date only peripherally fused [28]hexaphyrins **1** and **2** have been reported as rare examples of metal-free Möbius aromatic molecules that display a diatropic ring current at room temperature (Figure 1.)[3e,f] Herein, we report the unexpected formation of Möbius aromatic [28]hexaphyrin **5** as a metal-free Möbius aromatic molecule that exhibits the strongest diatropic ring current among the Möbius aromatic expanded porphyrins so far explored. Importantly, **5** is a rare example of metal-free Möbius aromatic expanded porphyrins and its aromaticity is preserved even at 100 °C owing to its conformational rigidity.

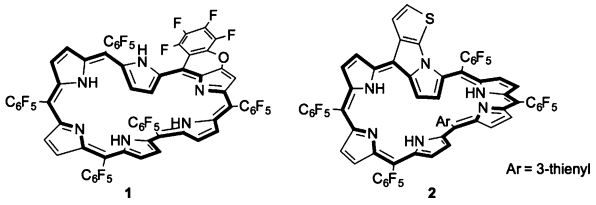

Figure 1. Rare examples of Möbius aromatic [28]hexaphyrin free-bases. **1**: benzopyrane-fused [28]hexaphyrin. **2**: thiophene-fused [28]hexaphyrin.

As a part of our studies on *meso*-aryl-substituted expanded porphyrins,[6] we examined the reactions of [26]- and [28]hexaphyrin with $SiCl_4$ under various conditions with the aim to explore Si-bearing hexaphyrins.[7] In the course of this study, we found that heating of [28]hexaphyrin **3** (see the Supporting Information) or [26]hexaphyrin **4** in the presence of $SiCl_4$, benzoyl peroxide, and NEt_3 under O_2 atmosphere at 50 °C gave NEt_2-bearing hexaphyrin **5** in variable yields. Extensive screening (see the Supporting Information) showed, that the presence of Lewis acid, NEt_3, and molecular oxygen is essential for the formation of **5**. The best yield (45 %) of **5** was accomplished by the reaction of [26]hexaphyrin **4** with $BF_3{\cdot}OEt_2$ (125 equiv) and O_2 in a mixture of 1,2-dichloroethane and NEt_3 atmosphere at room temperature (Scheme 1).

High-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectrometry of **5** showed its parent ion peak at $m/z = 1582.1769$ ($[M+H]^+$; calcd for $C_{74}H_{26}N_7F_{30}$: 1582.1765). ^{1}H NMR spectrum of hexaphyrin **5** in $CDCl_3$ shows two sets of resonances in a 1:1 ratio, which have been ascribed to the presence of two diastereomers, **5a** and **5b**. Analysis of **5** with HPLC on a chiral stationary phase gave three fractions, which were assigned, through their ^{1}H NMR analysis, as follows. The first fraction as an enantiomeric pair of one diastereomer **5b**, and the second and third fractions as

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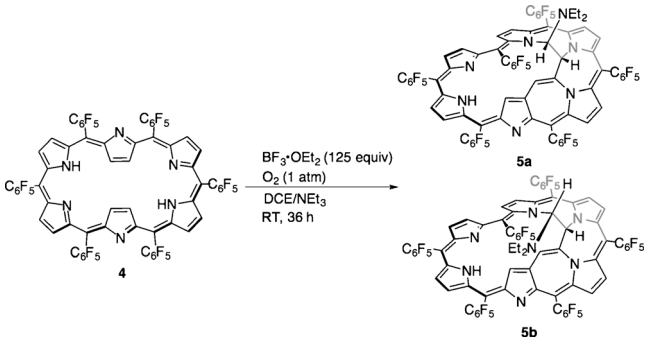
[**] The work at Kyoto University was supported by JSPS KAKENHI (grant numbers 25220802, 25620031, and 20705446). The work at Yonsei University was supported by the Global Research Laboratory (GRL) Program (2013-8-1472) of the Ministry of Education, Science, and Technology (MEST) of Korea.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500099.



Scheme 1. Synthesis of Möbius aromatic heaxaphyrins **5a** and **5b**.

enantiomers of the other diasteromer **5a** (see the Supporting Information).[8] Single crystals of **5a** suitable for X-ray diffraction analysis were obtained from vapor diffusion of hexane into a diisopropyl ether solution of a racemic mixture of **5a**.[9a] The crystal structure showed that the C4 fragment consisting of C73, C74, C75, and C76 is incorporated into its hexaphyrin framework. The β-carbon atom of pyrrole C and the nitrogen atom of pyrrole D are bridged by a vinylene unit of C73 and C74, the nitrogen atoms of pyrroles D and E are bridged by an ethylene unit of C74 and C75, and the nitrogen atoms of pyrroles E and F are bridged by a diethylamino-ethylene unit of C75 and C76. This structure is quite intriguing, allowing a smooth conjugation over the whole macrocycle with the largest dihedral angle of only about 30°, which is the smallest value among the Möbius aromatic [28]hexaphyrins ever reported to date (Figure 2a and b).[3]

The ^{1}H NMR spectrum of **5a** at 25 °C is sharp, except for the broad resonances of the diethylamino moiety. Ten signals of the outer pyrrolic β-H atoms appear in a range of $\delta = 8.91$–5.34 ppm, and a singlet resulting from the inner β-H atom (H^a) was observed at $\delta = -1.29$ ppm, which leads to a huge difference ($\Delta\delta = 12.79$ ppm) between the chemical shifts of the most shielded and deshielded hydrogen atoms, thus

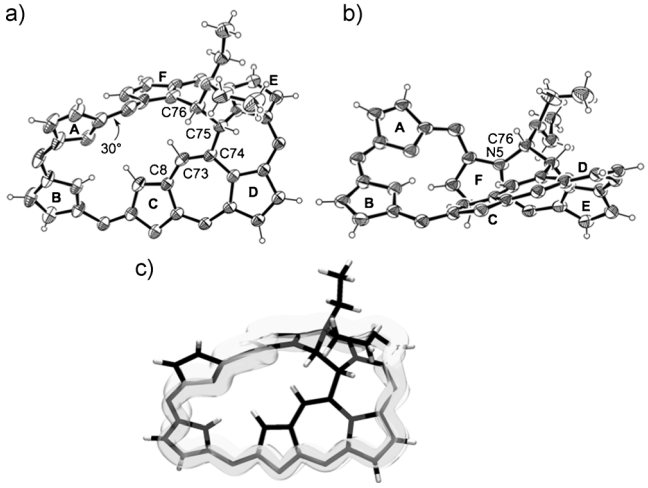


Figure 2. X-ray crystal structures of **5a**: a) top view and b) side view. Thermal ellipsoids represent 30% probability. *meso*-Aryl substituents and solvent molecules are omitted for clarity. c) Schematic representation of the topology of the π-electron system of **5a**.

indicating a strong diamagnetic ring current. Signals resulting from hydrogen atoms H^b-H^d were observed at $\delta = -3.29$, 0.37, and -1.00 ppm, respectively. The broad signals became sharper in [D_2]tetrachloroethane at 100 °C (Figure 3a), and the signals of the ethyl moiety were observed at $\delta = 1.83$, 1.88, and 0.39 ppm. The ^{1}H NMR spectrum of **5b** is essentially the same as that of **5a**, and its $\Delta\delta$ value is 12.82 ppm. Therefore, hexaphyrins **5** are a rare example of 28π Möbius aromatic metal-free [28]hexaphyrins. It is noteworthy that the $\Delta\delta$ values of **5a** are the largest among Möbius aromatic [28]hexaphyrins reported so far. These observations are consistent with its smooth macrocyclic conjugation.[3]

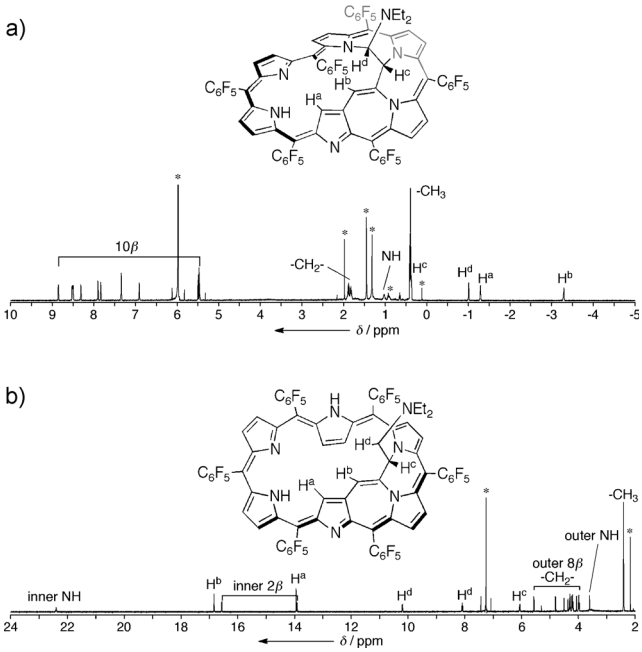
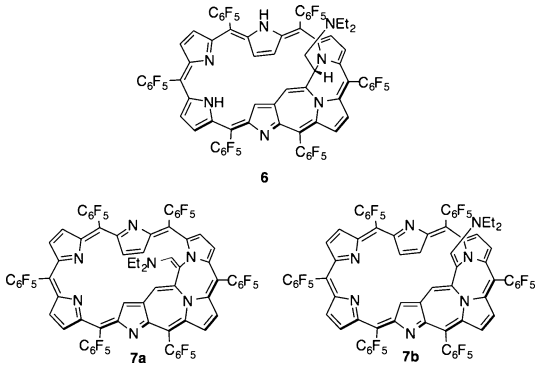


Figure 3. ^{1}H NMR spectra of a) **5a** in 1,1,2,2-[D_2]tetrachloroethane at 100 °C and b) **6** in $CDCl_3$ at 25 °C. Signals marked with * are due to residual solvents.

In the next step, we examined the reduction of **5**, with the expectation that a reduced product might display Möbius antiaromatic properties because of its rigid structure. Unfortunately, however, reduction of **5** with $NaBH_4$ causes a C–N bond cleavage to give a planar hexaphyrin **6** in 25%



yield. The structure of **6** was ambiguously determined by single-crystal X-ray diffraction analysis (Figure 4).[9b] The C76–N5 bond was cleaved, thus allowing pyrrole F to point outward. [28]Hexaphyrin **6** still features internal double bridges and is thus forced to take a planar rectangular

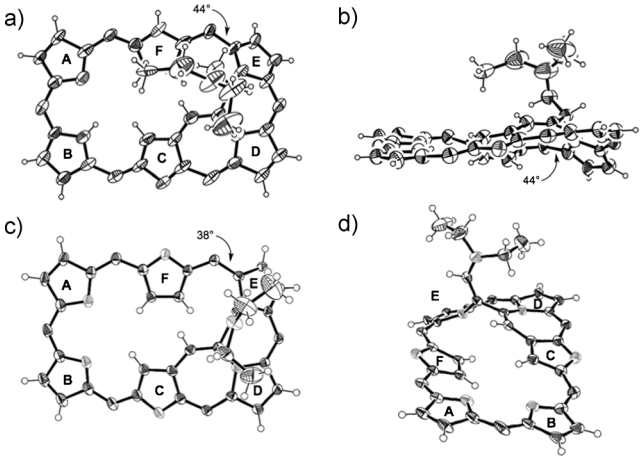


Figure 4. X-ray crystal structures of **6** and **7a**. a) **6**: top view b) **6**: side view c) **7a**: top view d) **7a**: side view. The thermal ellipsoids represent 30% probability about **6** and 50% probability about **7a**, respectively. *meso*-Aryl substituents and solvent molecules are omitted for clarity.

conformation. The mean plane deviation (36 core atoms) is relatively large (ca. 0.41 Å) and the largest dihedral angle along its π conjugation is large (44°). These structural features suggest a Hückel antiaromatic character for **6**, which has been confirmed by its ^{1}H NMR spectrum. The inner NH hydrogen atom was observed at $\delta = 22.41$ ppm, and the inner β-H atoms of pyrrole F were observed as a pair of doublets at $\delta = 16.57$ and 13.91 ppm. The H_a and H_b atoms were observed at $\delta =$ 13.59 and 16.84 ppm, respectively, thus indicating a large paratropic ring current of the [28]hexaphyrin macrocycle. In addition, the signal of the outer NH was observed at $\delta =$ 3.60 ppm and the pyrrolic β-H atoms were observed in a shielded region of $\delta = 5.57$ to about 3.92 ppm. On the other hand, the oxidation of **5** with MnO_2 gave [26]hexaphyrins **7** quantitatively in a stereospecific manner; namely the oxidation of **5a** gave only **7a** and that of **5b** gave only **7b**. The single-crystal X-ray diffraction analysis showed that the C76–N5 bond in **5** was cleaved to relieve the strain associated with the twisted Möbius structure in **7a**, allowing a planar rectangular structure with a smaller mean plan deviation of about 0.32 Å.[9c] The C75–C76 bond in **7a** is a C=C double, and **7a** has been determined to be an *anti* isomer. The ^{1}H NMR spectrum of **7a** shows eight signals corresponding to the outer pyrrolic β-H atoms in a range of $\delta = 9.55$–8.06 ppm and five signals corresponding to the inner pyrrolic β-H atoms in a range of $\delta = 1.63$ to about −3.72 ppm, and three signals corresponding to the diethyl moiety at $\delta = 0.00$, −0.23, and −1.59 ppm. These chemical shifts clearly indicate a strong diatropic ring current stemming from its aromatic character. On the basis of the very similar ^{1}H NMR, HR-ESI-TOF mass, and UV/Vis absorption spectra, the product **7b** has been assigned as a *syn* isomer.

The absorption spectrum of **5** exhibits an intense Soret-like band at 608 nm and Q-like bands at 764, 840, 899, and 1016 nm (Figure 5). These spectral features are consistent with its 28π Möbius aromaticity.[3b,10] The absorption spectrum of **7** also shows an intense Soret-like band at 628 nm and

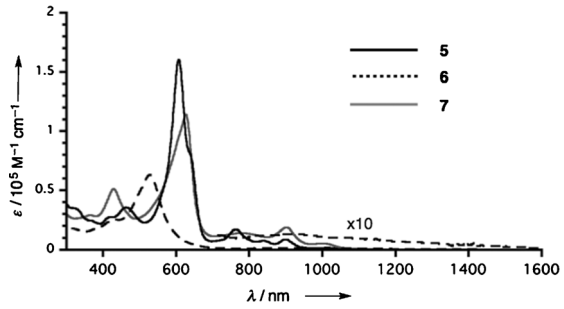


Figure 5. UV/Vis absorption spectra of mixture of **5a** and **5b** (**5**), **6**, and a mixture of **7a** and **7b** (**7**) in CH_2Cl_2.

Q-like bands at 779, 903, and 1005 nm, in line with its 26π Hückel aromaticity. In sharp contrast, the absorption spectrum of **6** displays a broad Soret-like band at 530 nm and no Q-band-like band, but instead displays a very broad and weak absorbance covering a wide range of the NIR region, which may correspond to a prohibited transition to a dark state as characteristic features of antiaromatic porphyrinoids.[10]

It has been established that the aromaticity of porphyrinoids can be evaluated by their excited-state properties.[10] In this regard, we have performed femtosecond transient absorption (fs-TA) measurements for **5**, **6**, and **7** with photoexcitation at the Soret-like band of each compound (Figure S21). The lifetime of the S_1 state of **5** was 170 ps with single-exponential decay function. In addition, the overall TA spectral features of **5** showed a stronger ground-state bleaching (GSB) band compared with relatively weak excited-state absorption (ESA) band. It was noted that these temporal and spectral features strongly represent the aromatic character of **5** as generally observed in Hückel/Möbius aromatic expanded porphyrins.[10c,d] On the other hand, the TA kinetic profile of **6** can be fitted by a double-exponential decay function with two time constants, smaller than 1 and 13 ps, respectively. The former fast decay of **6** can be ascribed to the internal conversion to NIR dark state that acts as a ladder in the deactivation processes, which is characteristic for the decay profile of antiaromatic expanded porphyrins.[10d] The latter decay corresponds to the lifetime of the S_1 state of **6**. The overall TA spectral features of **6** with stronger ESA band compared with relatively weak GSB band also show its obvious antiaromatic characters,[10d] which are in contrast with the TA spectral features of **5**. Interestingly, the lifetime of the S_1 state of **7** was determined to be 11.5 ps, which shows a significantly faster TA kinetic profile compared to the approximately 100 ps of *meso*-pentafluorophenyl [26]hexaphyrin(1.1.1.1.1.1).[10c,d] Nevertheless, the TA spectra of **7**, which are similar to those of **5**, indicate the aromatic character of **7**. We suggest that these distinguishable excited state dynamics of **7**, despite of its aromatic character, can be attributed to perturbed degeneracy of frontier molecular

orbitals (FMOs), particularly HOMO/HOMO-1 and HOMO-2 (Figure S17). Generally, the electronic states of porphyrin-like structures are explained by Gouterman's four-orbital model.[3d] The four FMOs, which consist of nearly degenerated HOMO/HOMO-1 and LUMO/LUMO + 1, participate in configuration interactions in typical aromatic porphyrinoids. However, in the case of **7**, the diethylamine group induces a break of the molecular symmetry, resulting in the perturbation of its electronic states. In other words, owing to its perturbed electronic states, the depopulation rate of the S_1 state of **7** could be accelerated compared with that of *meso*-pentafluorophenyl [26]hexaphyrin(1.1.1.1.1.1), which has nearly degenerated HOMO/HOMO-1 and LUMO/LUMO + 1 states, respectively.[3d]

In summary, the reaction of [26]hexaphyrin with triethylamine in the presence of $BF_3{\cdot}OEt_2$ and O_2 furnished **5**, which is a rare example of a Möbius aromatic metal-free [28]hexaphyrin that displays a smooth conjugation circuit and thus the strongest diatropic ring current ever reported for Möbius aromatic [28]hexaphyrins. The reduction and oxidation of **5** provided **6** and **7**, which are a Hückel antiaromatic [28]hexaphyrin and a Hückel aromatic [26]hexaphyrin, respectively, through a Möbius-to-Hückel topology change that was induced by the C–N bond cleavage. The excited-state decay dynamics of **5**, **6**, and **7** have been shown to be consistent with Möbius aromatic, Hückel antiaromatic, and Hückel aromatic states, respectively.

Keywords: aromaticity · hexaphyrins · Möbius aromaticity · porphyrinoids · radicals

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5456–5459
Angew. Chem. **2015**, *127*, 5546–5549

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[8] One reviewer pointed our the possibility that 1,2-dichloroethane may incorporate into products **5**. But the same products were formed in comparable yield from the reaction in dichloromethane, excluding this possibility.

[9] a) Crystallographic data for **5a**: $C_{74}H_{25}F_{30}N_7{\cdot}C_6H_6O{\cdot}1.25\,(C_6H_{14}O){\cdot}0.25\,(C_7H_{15})$, $M_r = 1844.63$; monoclinic; space group $C2/c$ (No.15), $a = 49.4098(12)$, $b = 14.8089(3)$, $c = 22.8360(4)$ Å; $\beta = 94.5640(10)°$; $V = 16656.2(6)$ Å^3; $\rho_{calcd} = 1.471$ g cm^{-1}; $Z = 8$; $R_1 = 0.0936$ [$I > 2.0\sigma(I)$], $wR_2 = 0.2658$ (all data), GOF = 1.047; b) Crystallographic data for **6**: $C_{77}H_{27}F_{30}N_7{\cdot}C_6H_{14}{\cdot}2(CH_2Cl_2)$, $M_r = 1840.05$; triclinic; space group $P\bar{1}$ (No.2), $a = 13.4102(10)$, $b = 17.9652(11)$, $c = 18.1977(14)$ Å; $\alpha = 116.078(3)$, $\beta = 103.025(4)$, $\gamma = 91.596(3)°$; $V = 3796.0(5)$ Å^3; $\rho_{calcd} = 1.610$ g cm^{-1}; $Z = 2$; $R_1 = 0.1461$ [$I > 2.0\sigma(I)$], $wR_2 = 0.3747$ (all data), GOF = 1.090; c) Crystallographic data for **7a**: $C_{74}H_{23}F_{30}N_7{\cdot}C_5H_{12}$, $M_r = 1652.14$; triclinic; space group $P\bar{1}$ (No.2), $a = 13.088(3)$, $b = 16.497(5)$, $c = 16.902(6)$ Å; $\alpha = 110.565(9)$, $\beta = 95.423(12)$, $\gamma = 93.2299(3)°$; $V = 3385.6(18)$ Å^3; $\rho_{calcd} = 1.621$ g cm^{-1}; $Z = 2$; $R_1 = 0.0623$ [$I > 2.0\sigma(I)$], $wR_2 = 0.1881$ (all data), GOF = 0.996. CCDC 1038037 (**5a**), 1038038 (**6**), and 1038039 (**7a**) contain contains 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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Received: January 6, 2015
Published online: February 4, 2015

