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# Facile Formation of a Benzopyrane-Fused [28]Hexaphyrin That Exhibits Distinct Möbius Aromaticity

Sumito Tokuji,[†] Jae-Yoon Shin,[‡] Kil Suk Kim,[‡] Jong Min Lim,[‡] Katsuyuki Youfu,[†] Shohei Saito,[†] Dongho Kim,*[,‡] and Atsuhiro Osuka*[,†]

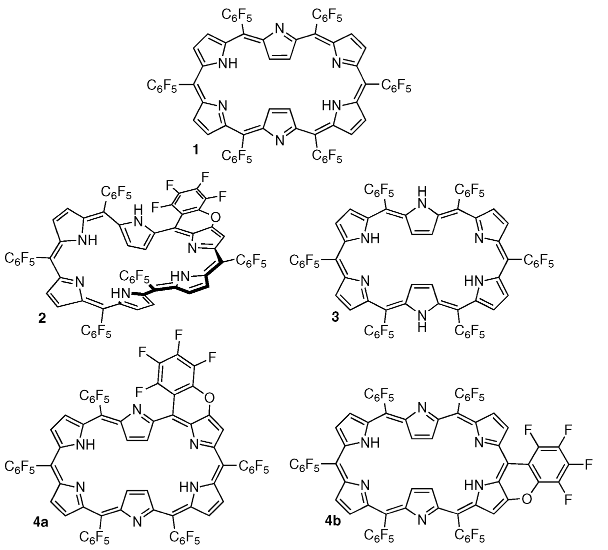
*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, and Spectroscopy Laboratory for Functional π-Electronic Systems and Department of Chemistry, Yonsei University, Seoul 120-749, Korea*

Received April 9, 2009; E-mail: dongho@yonsei.ac.kr; osuka@kuchem.kyoto-u.ac.jp

Möbius aromaticity is one of the current topics in organic chemistry, since it relates to the important topological issue of aromaticity, predicting aromatic character for a cyclic $4n\pi$-electron conjugated system with a molecular twist.[1] This concept, proposed by Heilbronner in 1964,[2] complements the established Hückel aromaticity that is based on the normal nontwisted topology. However, chemists waited for over 40 years to meet the first stable, neutral Möbius aromatic molecule, which was synthesized by Herges et al.[3] in 2003. Difficulties in synthesizing Möbius aromatic systems arise from a need to accommodate both a molecular twist and macrocyclic conjugation within a macrocycle. Through ongoing efforts, expanded porphyrins recently come to the forefront, providing the most promising system for realizing stable Möbius aromatic molecules with distinct aromaticity.[4,5] To date, we have reported three effective strategies for making Möbius aromatic systems: (1) a decrease in temperature for [28]hexaphyrins;[5c] (2) metalation with group 10 metals for [36]octaphyrin, [32]heptaphyrin, and [28]hexaphyrin[5a] and with Rh(I) ion for N-fused [24]pentaphyrin;[5b] and (3) protonation for [32]heptaphyrins.[5d] While these strategies are effective in providing Möbius aromatic molecules, they all have drawbacks, since detailed investigations of intrinsic properties of Möbius expanded porphyrins are hampered by the required low temperature, presence of a coordinated transition metal, or change in charge state. Therefore, a stable Möbius aromatic molecule that can be formed without such assistance is highly desirable for further investigations of Möbius aromatic systems.

Herein, we report the facile and spontaneous formation of benzopyrane-fused [28]hexaphyrin(1.1.1.1.1.1) **2** (Chart 1) as the first example that acquires distinct Möbius aromaticity without any assistance from temperature control, metal coordination, or protonation. The synthesis of **2** is quite simple: heating of [26]hexaphyrin(1.1.1.1.1.1) **1** in acetic acid at 130 °C for 6 h followed by separation over a silica gel column gave fused hexaphyrin **2** (27%) along with [28]hexaphyrin **3** (32%). The structure of **2** was unambiguously determined by single-crystal X-ray diffraction analysis (Figure 1).[6] The ortho position of a pentafluorophenyl group at one of the meso positions is connected through an oxygen atom to the $\beta$-position of the adjacent pyrrole to form a benzopyrane-fused structure. The fused tricyclic segment imparts considerable strain to the hexaphyrin framework in constituting a twisted Möbius topology, even at room temperature. In spite of the molecular twist, the $\pi$ conjugation is relatively smooth, with a largest dihedral angle of 36°. As the most plausible mechanism, the following series of reactions is conceivable: initial formation of $\beta$-acetoxy [28]hexaphyrin, subsequent hydrolysis to give $\beta$-hydroxy [28]hexaphyrin, and a final nucleophilic cyclization to provide **2** [see the Supporting Information (SI)]. Under the reaction conditions, $\beta$-acetoxy [28]hexaphyrin did not persist and was detected only by high-resolution electrospray mass spectroscopy, but $\beta$-hydroxy [28]hexaphyrin was actually isolated and confirmed to be converted to **2** quantitatively upon heating in acetic acid (see the SI).

***Chart 1.*** Structures of Hexaphyrins Studied in This Work



The Möbius aromaticity of **2** was confirmed by its distinct diatropic ring current. The $^1$H NMR spectrum of **2** exhibits highly shielded signals at 2.22 and 1.03 ppm due to the inner $\beta$-protons of inverted pyrrole F, moderately shielded signals at 5.49 and 5.45 ppm due to the $\beta$-protons of the tilted pyrrole C, and deshielded signals in the range 7.44−7.03 ppm due to the outer $\beta$-protons of the remaining pyrroles. Accordingly, the difference between the chemical shifts of the most shielded and deshielded $\beta$-protons is

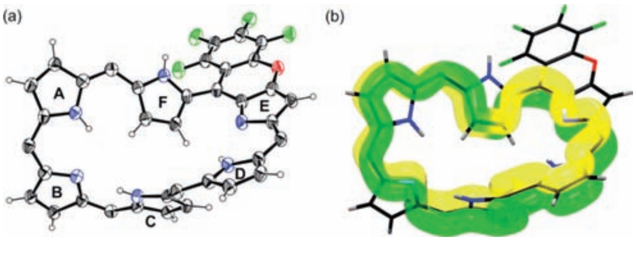


***Figure 1.*** (a) X-ray crystal structure of **2**. (b) Schematic representation of the molecular topology. The thermal ellipsoids in (a) are scaled to the 30% probability level, and the aryl meso substituents have been omitted for clarity.

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[†] Kyoto University.
[‡] Yonsei University.

10.1021/ja902836x CCC: $40.75

6.41 ppm. Importantly, these spectral features are largely preserved over a wide temperature range from −100 to 100 °C, with only small gradual up- or downfield shifts for the inner $\beta$- and NH protons, in contrast to what is observed for nonfused [28]hexaphyrin **3**.[5c,7] This indicates a more robust twisted structure of **2** than **3**. The observed gradual downfield shifts suggest increasing contributions of planar antiaromatic conformers of **2** with increasing temperature, similar to [28]hexaphyrins.[5c] In line with the assignment of **2** as a Möbius aromatic molecule, the harmonic oscillator model of aromaticity (HOMA) value[8] was estimated to be 0.73, and the nucleus-independent chemical shift (NICS) value[9] was evaluated as −11.8 ppm at the central position of the molecule. Furthermore, the molecular orbital energy level of **2** calculated using density functional theory (B3LYP/6-31G**)[10] reveals the same features as those of **3**: nearly degenerate HOMO/HOMO−1 and LUMO/LUMO+1, with a HOMO−LUMO energy gap ($\Delta E_{\mathrm{H-L}}$) of 1.74 eV (see the SI).

In cyclic voltammetry, **2** shows two reversible oxidation waves at −0.04 and 0.22 V versus the ferrocene/ferrocenium ion couple in $CH_2Cl_2$. Encouraged by the structural robustness, we attempted to oxidize **2** to form a Möbius antiaromatic molecule. However, the oxidation of **2** with DDQ proceeded instantaneously to exclusively give Hückel aromatic normal [26]hexaphyrin **4a**, which slowly isomerized under normal conditions to reach a stationary 4:1 mixture of **4a** and **4b**. Interestingly, the reduction of this mixture with $NaBH_4$ gave **2** quantitatively, thus establishing the quantitative interconversion between Möbius and Hückel aromatic systems with a topological switch upon two-electron oxidation and reduction processes.

The steady-state absorption spectrum of **2** exhibited features typical of aromatic expanded porphyrins, namely, an intense, sharp B-like band at 613 nm and distinct Q-like bands at 760, 844, and 968 nm. The fluorescence spectrum was observed at 1058 nm with a vibronic structure (Figure 2). Here it should be noted that the fluorescence spectrum is quite broad and the Stokes shift relatively large (879 cm$^{-1}$). In contrast, the fluorescence spectrum of **3** exhibits relatively sharp bands showing clear vibronic structure and a Stokes shift of 358 cm$^{-1}$ at 293 K.[7] This means larger structural changes in the excited state of **2**. This intimates to us that the $\pi$ conjugation of **2** in the excited state is relatively weak compared with that in **3**. The singlet ($\pi$, $\pi$*) excited-state lifetime of **2** was determined to be ~40 ps by monitoring femtosecond transient absorption spectroscopy decay profiles at 615 and 665 nm (see Figure 2 and the SI). This lifetime is shorter than that of **3** (183 ps).[7] Because the factors that can affect the excited-state lifetimes, such as substituents, $\Delta E_{\mathrm{H-L}}$, and solvents, are the same in both cases, the structural flexibility seems to play an important role in depopulating the singlet excited state of **2**; the conformational flexibility in the excited state can enhance the nonradiative internal-conversion processes. This conjecture was also evidenced by the triplet ($\pi$, $\pi$*) excited-state lifetime measurements (see the SI). At room temperature, we could not observe any triplet-excited-state signals of **2**, presumably because of fast nonradiative decay processes. At low temperature, however, the flexible motion of the molecule became restricted, and the decay processes became observable. Consequently, the triplet-excited-state lifetime of **2** was determined to be 350 ns at 173 K, which is also much shorter than that of **3** (90 $\mu$s) at the same temperature.[7]

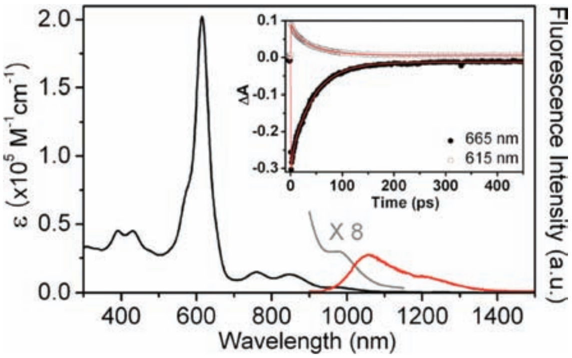

***Figure 2.*** Steady-state absorption (black) and fluorescence (red) spectra and femtosecond transient decay profiles (inset) for **2** in THF. The wavelength of pump excitation was 615 nm, and the fitted time constants of the decay profiles at 615 and 665 nm were 41 and 37 ps, respectively.

Recently, we have suggested that there is a strong correlation between the two-photon absorption (TPA) cross section and the aromaticity of the molecule.[5,11] In this context, TPA measurements on **2** were carried out using the femtosecond Z-scan method, which gave a maximum TPA value of 5400 GM for **2** at 1160 nm (see the SI). This value is comparable to those of group 10 metal complexes of [28]hexaphyrins (4000−5500 GM)[5a] and much larger than that of **3** at room temperature (2100 GM), reflecting its distinct aromatic character.

In summary, simple heating of **1** in acetic acid led to the formation of **2**, which exhibits Möbius aromaticity over a wide temperature range. Reversible interconversions between Möbius aromatic system **2** and Hückel aromatic system **4** have been demonstrated. This rigid Möbius aromatic system may be useful for the realization of Möbius antiaromatic systems. Such a possibility is now being strongly pursued with increasing conformational rigidity in our laboratories.

**Supporting Information Available:** Detailed experimental data, a CIF file for **2**, and complete refs 5c and 10 (as ref S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Crystallographic data for **2**: $C_{72}H_{29}F_{29}N_6O$, $M = 1545.01$; triclinic, space group $P\bar{1}$ (No. 2); $a = 14.19(3)$ Å, $b = 14.83(3)$ Å, $c = 17.49(4)$ Å, $\alpha = 71.79(7)°$, $\beta = 88.10(9)°$, $\gamma = 67.33(9)°$; $V = 3211(13)$ Å$^3$; $Z = 2$; $T = 123(2)$ K; $\rho_{\mathrm{calcd}} = 1.598$ g/cm$^3$; R1 = 0.1057 [$I > 2\sigma(I)$], wR2 = 0.3035 (all data); GOF = 1.029. The data was deposited at the CCDC under deposition no. 722625; also see the SI.
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JA902836X