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A Möbius Aromatic Pd(II) Complex of [28]Hexaphyrin(2.1.1.0.1.1)

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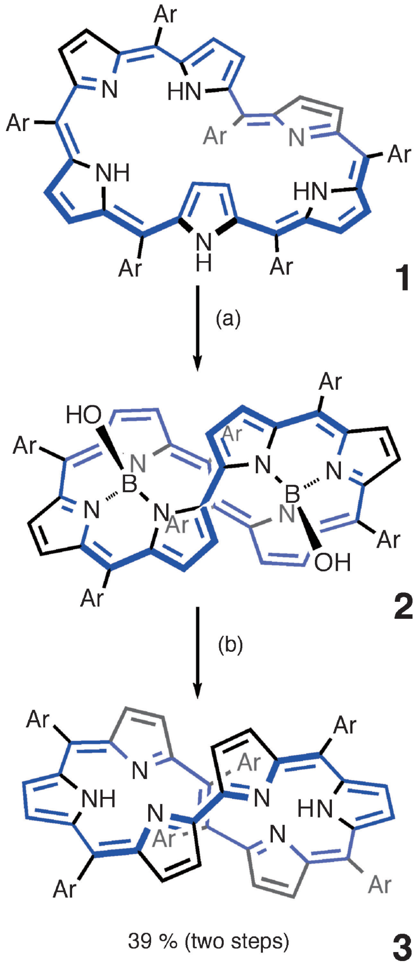
Pd(II) complex of [28]hexaphyrin(2.1.1.0.1.1) **5** was prepared in 36% yield from [26]hexaphyrin(2.1.1.0.1.1) **3** via reduction with $NaBH_4$ and subsequent metalation of **4** with $Pd(OAc)_2$ in the presence of triethylamine. This molecule constitutes the first example of Möbius aromatic species formed from expanded porphyrins other than the regular *meso*-aryl expanded porphyrins with the alternate arrangement of pyrroles and methine carbons.

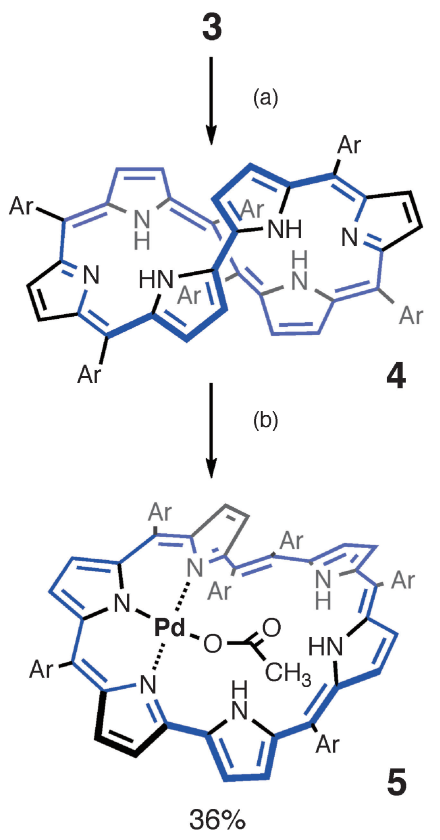
The concept of Möbius aromaticity[1] was first proposed by Heilbronner in 1964 as a complement of Hückel aromaticity.[2] He predicted that $4n\pi$-annulenes should become aromatic when a single molecular twist is incorporated in their cyclic π-conjugation. This prediction was simple and attractive, hence encouraging synthetic chemists to explore such molecules. However, it was only in 2003 that we witnessed the seminal paper by Herges et al. on a [16]annulene that displays modest aromatic character.[3] Expanded porphyrins with more than five pyrrolic subunits hold larger molecular sizes and conformational flexibility and capability to take several stable oxidation states.[4] They have been shown to be a particularly suitable platform to realize Möbius aromatic molecular systems.[5,6] We have demonstrated that the metalation with group 10 metal is an effective means to form conformationally rigid Möbius aromatic species from *N*-fused pentaphyrin,[6b] hexaphyrin,[6a] heptaphyrin,[6a] and octaphyrin.[6a] Beside metalation, protonation,[7] temperature control,[8] and intramolecular fusion[9] have been shown to be also effective for formation of Möbius aromatic species. Despite these efforts, most Möbius aromatic species have been formed from regular *meso*-aryl-substituted expanded porphyrins that are real homologs of porphyrins with respect to the alternate arrangement of pyrroles and methine carbons.[10] Therefore, it is a big question whether the realization of Möbius aromatic systems is really limited to the regular *meso*-aryl-substituted expanded porphyrins, namely the series represented as expanded porphyrins(1.1.1 ... 1), or other uncommon expanded porphyrins can be used to realize Möbius aromatic species. Here, we report the formation of a Möbius aromatic complex from [28]hexaphyrin(2.1.1.0.1.1) **3**.

Quite recently, we found that the insertion of two B(III) ions into [28]hexaphyrin(1.1.1.1.1.1) **1** induced a skeletal rearrangement to bis-B(III) complex of [28]hexaphyrin(2.1.1.0.1.1) **2**, which, upon subsequent oxdation with MnO_2, released B(III) ions to provide [26]hexaphyrin(2.1.1.0.1.1) **3** (Scheme 1).[11] Hexaphyrin **3** is unstable due to a propensity for moisture-sensitive decomposition in solution and has been shown to be nonaromatic on the basis of ^1H NMR and UV–vis absorption properties.[11] This hexaphyrin was reduced with $NaBH_4$ in CH_2Cl_2/MeOH (30:1) to [28]hexaphyrin(2.1.1.0.1.1) **4**, which turned out to be unstable in air. Hexaphyrin **4** shows the parent ion peak at m/z 1461.0865 (calcd for $C_{66}H_{15}F_{30}N_6$, $[M - H]^- = 1461.0874$) in the high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectrum and a symmetric ^1H NMR spectrum.[12] However, further studies on **4** have been severely hampered by its instability. Following our protocol,[6] the hexaphyrin **4** was reacted with $Pd(OAc)_2$ in the presence of triethylamine under argon atmosphere. After being stirred for 16 h, the reaction mixture was poured into water and worked up in a usual manner. TLC analysis indicated the formation of a major blue product, which was isolated and characterized as Pd(II) complex **5**[13] in a two-step yield of 36% from **3** (Scheme 2).

The Pd(II) complex **5** is more stable than **3** and **4** and tolerates usual manipulations including extraction and separation



Scheme 1. Synthesis of [26]hexaphyrin (2.1.1.0.1.1) **3**. Ar: pentafluorophenyl. (a) BBr_3 (200 equiv), diisopropylethylamine (45 equiv), CH_2Cl_2, room temperature, 3 h. (b) MnO_2 (300 equiv), CH_2Cl_2, room temperature, 1 h.



Scheme 2. Synthesis of **5** from **3**. Ar: pentafluorophenyl. (a) $NaBH_4$ (10 equiv), $CH_2Cl_2/MeOH$ (30:1), room temperature, 2.5 h. (b) $Pd(OAc)_2$ (9 equiv), triethylamine (one drop), $CH_2Cl_2/MeOH$ (50:1), room temperature, 16 h.

over a silica gel column. HR-ESI-TOF mass measurement revealed the parent ion peak at m/z 1625.0057 for **5** (calcd for $C_{68}H_{17}O_2N_6F_{30}Pd_1$, $[M - H]^- = 1624.9985$). The absorption spectrum of **5** displays a sharper, red-shifted, and intensified Soret-like band at 606 nm and Q-like bands with a clear vibronic structure at 784, 858, and 961 nm, respectively, which are characteristic of aromatic porphyrinoids (Figure 1).[6,14] The ^1H NMR spectrum of **5** exhibits a signal due to the acetoxy protons at −1.33 ppm, indicating a diatropic ring current. In line with this, the inner NH proton in the pyrrole D is observed at 3.05 ppm, while the inner NH protons in the pyrroles E and F are observed at 6.62 and 6.38 ppm due to the intramolecular hydrogen bonding with the acetoxy carbonyl group.

Fortunately, crystals of **5** suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of octane into a toluene solution. In the solid-state structure, the Pd(II) ion is bound with three pyrrolic nitrogen atoms with Pd–N bond distances of 1.971(4), 2.010(4), and 2.031(4) Å and with the acetoxy group with a Pd–O bond distance of 2.049(4) Å.[15] The remaining three pyrroles are roughly pointed inward albeit with significant deviations (Figure 2). Importantly, a singly twisted molecular topology is achieved by combination of a relatively coplanar subunit around the Pd ion coordination consisting of the pyrroles A, B, C, and D and a distorted subunit consisting of the *trans*-vinylene bridge and the pyrroles E and F. The *trans*-vinylene bridges are considerably tilted with regard to the pyrroles A and F with dihedral angles of 22.0 and 25.6°, and the pyrroles D and E are also tilted with a dihedral angle of 31.3°, hence causing a major twist to achieve an overall Möbius topology.

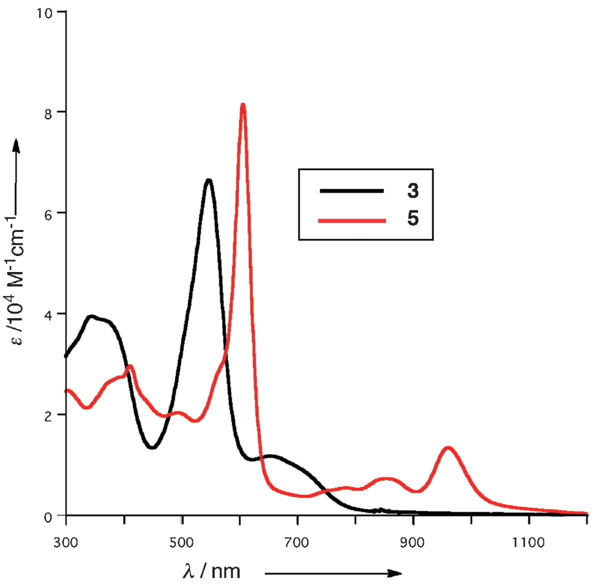


Figure 1. UV–vis absorption spectra of **3** and **5** in CH_2Cl_2.

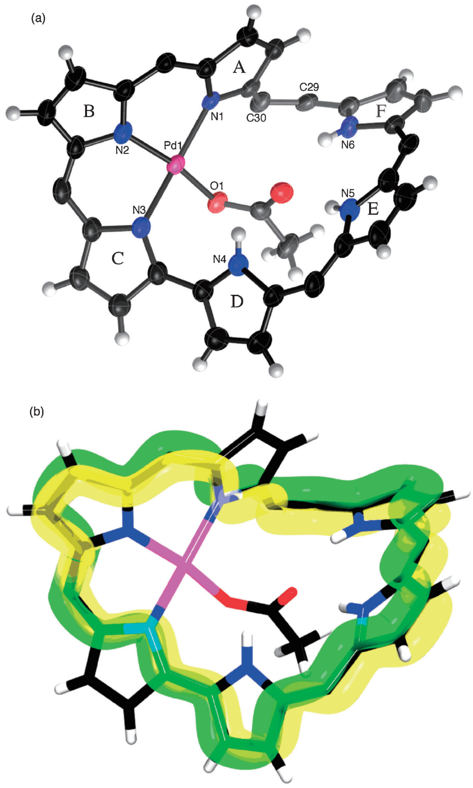


Figure 2. (a) X-ray crystal structure and (b) schematic representation of π-orbital of **5**. *meso*-Pentafluorophenyl substituents and solvent molecules are omitted for clarity. The thermal ellipsoids are drawn at 50% probability level.

The electrochemical properties were studied by cyclic voltammetry in CH_2Cl_2 versus ferrocene/ferrocenium ion (Fc/Fc^+) with tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The complex **5** underwent two reversible oxidations at 0.25 and 0.52 V, and two reversible reductions at -0.98 and -1.38 V, respectively. The electrochemical HOMO–LUMO gap thus determined is 1.23 eV, which is roughly in agreement with the optical HOMO–LUMO gap of 1.29 eV. To obtain further insight, we performed DFT calculations (B3LYP/6-31G(d)/LANL2DZ) (see the Supporting Information).[16] These calculations revealed nearly degenerate HOMO/HOMO−1 and LUMO/LUMO+1 for **5**, which are characteristic of aromatic expanded porphyrins. The nucleus-independent chemical shift (NICS) value[17] at the gravity point of the macrocycle was calculated to be -6.3 ppm, and the harmonic oscillator model of aromaticity (HOMA)[18] was estimated to be 0.46. For the Pd complex of [28]hexaphyrin(1.1.1.1.1.1), the NICS and HOMA value were reported to be -13.3 ppm and 0.64, respectively.[6a] On the basis of these data, the complex **5** is concluded to possess aromatic character originating from its 28π-electronic circuit lying on a twisted Möbius topology and thus be a Möbius aromatic species, but its aromaticity is only modest and weaker than the previously reported [28]hexaphyrin(1.1.1.1.1.1) complex.[6a]

In summary, we isolated and characterized Pd(II) complex of [28]hexaphyrin(2.1.1.0.1.1) **5** as the first example of a Möbius aromatic molecule from expanded porphyrins other than the regular series. In **5**, the *trans*-vinylene part seemingly plays an important role in achieving a smooth molecular twist but the aromaticity of **5** is only modest. This work hence suggests that a wide scope of expanded porphyrins can be used for the formation of Möbius aromatic species. Exploration toward new Möbius aromatic expanded porphyrins along this strategy is now actively studied in our laboratory.

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12 Physical properties of **4**: ^{1}H NMR (600 MHz, $CDCl_3$, −40 °C): δ 8.17 (br s, 2H), 7.46 (d, $J = 4.1$ Hz, 2H, β), 7.09 (d, $J = 4.5$ Hz, 2H, β), 7.06 (d, $J = 4.1$ Hz, 2H, β), 6.79 (br s, 2H, β), and 6.77 (br s, 2H, β) (N–H protons were not clearly observed); HR-ESI TOF-MS m/z: 1461.0865 (calcd for $C_{66}H_{15}N_6F_{30}$: 1461.0874 $[M - H]^-$); UV–vis (in CH_2Cl_2): λ/nm 382, 593, 720, 764, and 898. The optimized structure of **4** was estimated by DFT calculation to be a figure-eight conformation. Thus, the instability of **4** may be ascribed to its Hückel antiaromatic character.

13 Physical properties of **5**: ^{1}H NMR (600 MHz, $CDCl_2CDCl_2$): δ 8.68 (d, $J = 5.0$ Hz, 1H, β), 8.33 (dd, $J_1 = 4.6$ Hz, $J_2 = 2.3$ Hz, 1H, β), 8.12 (d, $J = 5.0$ Hz, 1H, β), 7.58 (dd, $J_1 = 4.6$ Hz, $J_2 = 2.3$ Hz, 1H, β), 7.41 (dd, $J_1 = 3.9$ Hz, $J_2 = 2.2$ Hz, 1H, β), 7.33 (d, $J = 4.8$ Hz, 1H, β), 7.31 (dd, $J_1 = 3.9$ Hz, $J_2 = 2.2$ Hz, 1H, β), 7.26 (d, $J = 5.5$ Hz, 1H, β), 7.24 (d, $J = 5.5$ Hz, 1H, β), 7.06 (d, $J = 4.8$ Hz, 1H, β), 6.80 (s, 1H, N–H), 6.53 (dd, $J_1 = 4.8$ Hz, $J_2 = 0.9$ Hz, 1H, β), 6.45 (s, 1H, N–H), 5.94 (d, $J = 4.8$ Hz, 1H, β), 3.16 (s, 1H, N–H), and −1.29 (d, $J = 4.1$ Hz (coupled with the 4-fluorine atom in the pentafluorophenyl group at 30-position (depicted in Figure 1)), 3H, acetate-CH_3; HR-ESI TOF-MS m/z: 1625.0285 (calcd for $C_{68}H_{17}O_2N_6F_{30}Pd_1$: 1624.9996 $[M - H]^-$); UV–vis (in CH_2Cl_2): λ/nm (ε/$M^{-1}\,cm^{-1}$) 411 (30000), 493 (20000), 606 (82000), 784 (55000), 858 (7300), and 961 (13000).

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15 Crystallographic data for **5**: $C_{68}H_{18}F_{30}N_6O_2Pd\cdot 1.37C_8H_{18}\cdot 0.63C_7H_8$, $M_w = 1841.73$, triclinic, $P\bar{1}$ (No. 2), $a = 15.924(4)$, $b = 16.192(4)$, $c = 17.953(5)$ Å, $\alpha = 73.873(4)$, $\beta = 75.601(5)$, $\gamma = 63.825(5)°$, $V = 3947.9(18)$ Å^3, $D_{calcd} = 1.549$ g cm^{-3}, $Z = 2$, $T = 123(2)$ K, $R_1 = 0.0721$ ($I > 2.0\sigma(I)$), $wR_2 = 0.2122$ (all data), GOF = 1.043 ($I > 2.0\sigma(I)$). CCDC file No. 811685.

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