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Möbius Aromatic Palladium(II) Complexes of a β-Tetraphenyl *meso*-Hexakis(pentafluorophenyl) Substituted Hexaphyrin(1.1.1.1.1.1)

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Two isomeric Pd^{II} complexes, **4** and **5**, of a β-tetraphenyl *meso*-hexakis(pentafluorophenyl) substituted [28]hexaphyrin were isolated, both of which exhibited distinct diatropic ring currents and electronic absorption spectra characteristic of aromatic porphyrinoids. These complexes have been designated Möbius aromatic species on the basis of their twisted conformations and 28π-electronic networks.

The concept of Möbius aromaticity was proposed by Heilbronner in 1964.[1] However, related chemistry had been largely confined to the theoretical world until recently because of the difficulty in preparing molecules that possess a smoothly twisted 4$n\pi$ cyclic conjugated system with a certain level of rigidity. A singly twisted [16]annulene was reported as the first stable and neutral Möbius aromatic molecule in 2003 by Herges and co-workers.[2] Recently, Latos-Grażyński and co-workers reported the temperature- and solvent-dependent conformational changes between Hückel- and Möbius-conformations for di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1).[3] Soon after that, we discovered that a series of *meso*-aryl-substituted expanded porphyrins are a nice platform to realize Möbius aromatic molecules. This remarkable property can be ascribed largely to a flexible π-conjugated circuit and facile two-electron redox reactions that allow various stable and neutral oxidation states.[4] We have explored several methods to realize Möbius aromatic expanded porphyrins by metallation,[4a,4b] temperature control,[4c] solvent polarity control,[5] protonation,[5] and intramolecular fusion of peripheral positions.[6] Despite these efforts, the number of Möbius aromatic expanded porphyrins still remains small. In this paper, we report that Pd^{II} metallation provides stable Möbius aromatic systems and, at the same time, confers sufficient conformational rigidity, which allows us to separate two Möbius isomers (Figure 1).

Quite recently, we reported that [26]- and [28]-β-tetraphenyl *meso*-hexakis(pentafluorophenyl) substituted hexaphyrins, **1** and **2**, showed multiple conformational changes that were induced by two-electron redox reactions and/or protonation.[7] [28]Hexaphyrin **2** showed stepwise and drastic changes from nonaromatic figure-eight conformations into twisted Möbius aromatic conformations upon addition of TFA. Both the monoprotonated and diprotonated states were detected in the ^{1}H and ^{19}F NMR spectra. The ^{1}H NMR spectrum of the diprotonated species **2-TFA** showed broad signals at room temperature, which became two sets of sharp signals in a ratio of 1:0.88 at −80 °C in CD_2Cl_2. These results indicated that **2-TFA** took two different twisted Möbius conformations in solution (Scheme 1), whose interconversion was slow on an NMR time scale at −80 °C but faster at room temperature. The structure of one conformer (**2-TFA-A**) was elucidated by X-ray crystallographic analysis, and the other was thought to be a conformational isomer (**2-TFA-B**). However it was difficult to identify the putative minor conformer, since the protonated species are present only under considerably acidic conditions and the interconversion is fast at room temperature.

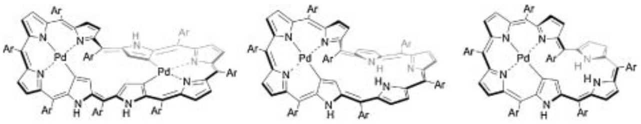
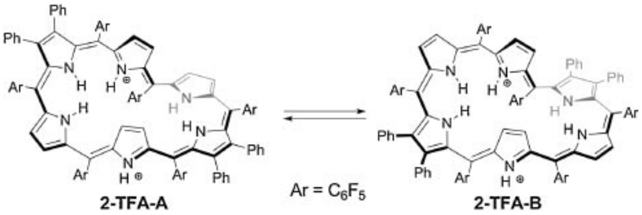


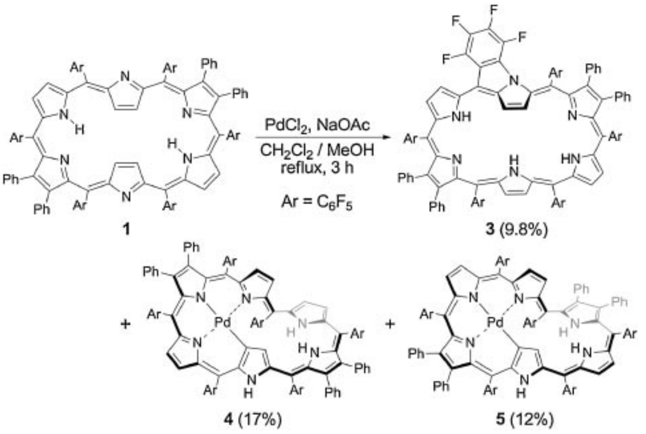
Figure 1. Examples of Pd complexes of expanded porphyrins.



Scheme 1. A conformational equilibrium between two isomers of **2-TFA**.

With these results, it occurred to us that the fixation of the putative two Möbius conformers might be possible by Pd^{II}-metallation. Thus, Pd^{II}-metallation of **1** was attempted by refluxing a CH_2Cl_2/MeOH solution of **1** with $PdCl_2$ in the presence of sodium acetate for 3 h, which led to the isolation of N-fused [28]hexaphyrin **3** (9.8%), and two isomeric Pd^{II} complexes **4** (17%) and **5** (12%) after silica gel column chromatography (Scheme 2).

The high-resolution electrospray-ionization time-of-flight (HR-ESI-TOF) mass spectrum of **3** exhibited a parent ion peak at $m/z = 1746.2194$ (calcd for $C_{90}H_{31}N_6F_{29}$ $[M]^+$, 1746.2142). Absence of a Q-like band in the UV–vis absorption spectrum of **3** suggested it to be nonaromatic or antiaromatic. The ^{1}H NMR spectrum of **3** in $CDCl_3$ exhibited signals due to the β-protons at 9.64, 8.48, 7.24, 7.03, 6.64, 6.02, 5.99, and 5.77 ppm. Signals due to the three N–H protons were observed at 17.92, 17.61, and 14.02 ppm. The ^{19}F NMR of **3** showed eleven signals due to the *ortho*-F, six signals due to the *para*-F, and twelve signals due to the *meta*-F of pentafluorophenyl substituents, in accord with its nonsymmetric N-fused structure.[8]



Scheme 2. Pd^{II} metallation of **1**.

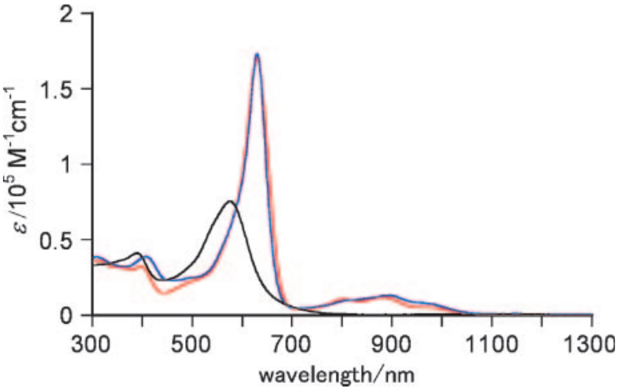


Figure 2. UV–vis absorption spectra of **3** (black), **4** (red), and **5** (blue) in CH_2Cl_2.

The HR-ESI-TOF mass spectra showed the parent ion peaks of **4** and **5** at 1870.0971 and 1870.1131, respectively (calcd for $C_{90}H_{30}N_6F_{30}Pd$ $[M]^+$, 1870.1109). The ^1H NMR spectrum of the complex **4** exhibited the signals due to the N–H protons at 9.47, 4.24, and 0.07 ppm and those due to the outer β-protons at 7.80, 7.63 (2H), 7.23, 6.78, and 5.46 ppm, and that of inner β-proton at 0.18 ppm. Thus, the chemical shift difference between the outer and inner β-proton was 7.62 ppm, indicating a large diatropic ring current. The aromaticity of **4** was also seen from the UV–vis absorption spectrum that showed a Soret-like band at 630 nm and Q-like bands at 805, 882, and 973 nm (Figure 2). The other complex **5** exhibited a ^1H NMR spectrum that showed signals due to the N–H protons at 9.14, 4.92, and 1.79 ppm, and those due to the outer β-protons at 7.79, 7.74, 7.48, 7.45, and 7.40 (2H) ppm, and that of the inner β-proton at 1.28 ppm. Here again, the chemical shift difference between the outer and inner β-protons is comparable, being 6.51 ppm. The UV–vis absorption spectrum of **5** exhibited a Soret-like band at 630 nm and Q-like bands at 810, 895, and 975 nm. Both these data indicate the aromaticity of **5**.

Finally, the structures of **4** and **5** have been proven by single-crystal X-ray crystallographic analysis to be singly twisted Möbius conformations in which the cyclic π-electronic conjugation is reasonably preserved with the largest tortional angle of 36° for **4** and 43° for **5** (Figure 3).[9,10] In both cases, the Pd^{II} ion is accommodated within a NNNC ligand in a roughly square-planar coordination, with distances of 1.991 (Pd–N6), 2.042 (Pd–N1), 2.002 (Pd–N2), and 1.992 Å (Pd–C12) for **4**, and 1.996 (Pd–N5), 2.022 (Pd–N6), 2.011 (Pd–N1), and 1.943 Å (Pd–C7) for **5**. These two complexes show similar structures with regards to the overall macrocyclic shape and π-conjugation network but differ only in the location of β-phenyl substituents. Since the structure of **4** is similar to that of **2-TFA-A**, the structure of **5** is suggested to be similar to that of **2-TFA-B**. While the protonated species undergo rapid conformational interconversion at room temperature, the conformational rigidity is enhanced for the Pd^{II} complexes **4** and **5**. This feature is useful for detailed studies of Möbius aromatic compounds.

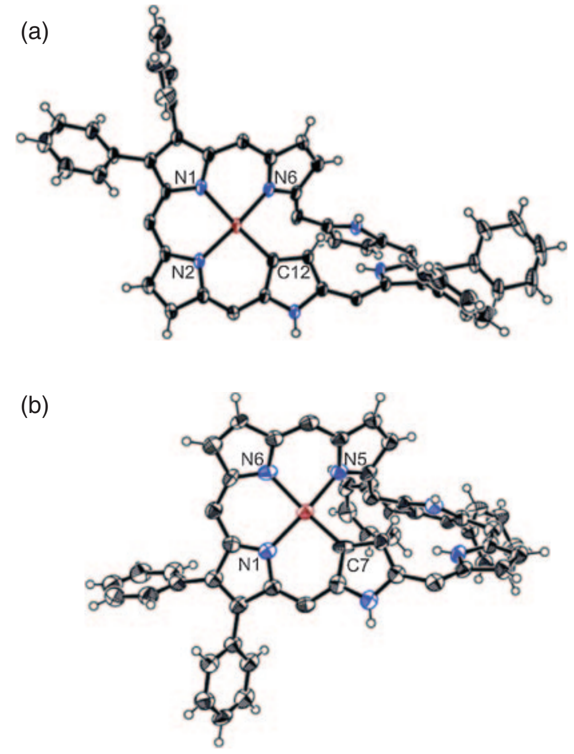


Figure 3. X-ray crystal structures of **4** (a) and **5** (b). Thermal ellipsoids are scaled to 50% probability level. Solvents and *meso*-pentafluorophenyl substituents are omitted for clarity.

In summary, the two Pd^{II} complexes of a β-tetraphenyl *meso*-hexakis(pentafluorophenyl) substituted hexaphyrin were isolated and characterized because of the enhanced conformational rigidity caused by Pd^{II} metallation. These complexes have been determined to be Möbius aromatic species on the basis of the singly twisted structures and the diatropic ring currents and the absorption spectra characteristic of aromatic porphyrinoids.

Experimental

To a solution of β-tetraphenyl *meso*-hexakis(pentafluorophenyl)[26]hexaphyrin(1.1.1.1.1.1) **1** (17.7 mg, 10.0 µmol) in CH_2Cl_2/MeOH (10 mL, 2 mL), $PdCl_2$ (17.7 mg, 100 µmol) and NaOAc (8.2 mg, 100 µmol) were added. After refluxing for 3 h, the reaction mixture was poured into water and the products were extracted with CH_2Cl_2. The organic phase was washed with water, dried over anhydrous Na_2SO_4. After the solvent was removed by a rotary evaporator, the products were separated over a silica gel column with a mixture of 10% CH_2Cl_2/hexane and then CH_2Cl_2 as an eluent, giving three fractions. The first purple fraction was recrystallized from hexane to give **3** (1.7 mg, 9.8%) as brown solids. The second blue fraction was recrystallized from CH_2Cl_2/hexane to give **4** (3.2 mg, 17%) as brown solids and the third bluish green fraction was recrystallized from CH_2Cl_2/hexane to give **5** (2.3 mg, 12%) as brown solids.

N-Fused β-tetraphenyl *meso*-hexakis(pentafluorophenyl)-[28]hexaphyrin(1.1.1.1.1.1) **3**: ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 17.92 (s, 1H, N–H), 17.61 (s, 1H, N–H), 14.02 (s, 1H, N–H), 9.64 (d, $J = 4.6$ Hz, 1H, β-H), 8.48 (d, $J = 4.6$ Hz, 1H, β-H), 7.24 (d, $J = 5.8$ Hz, 1H, β-H), 7.03 (d, $J = 4.6$ Hz, 1H, β-H), 7.0–6.75 (m, 15H, phenyl-H), 6.64 (s, 1H, β-H), 6.61 (d, $J = 6.9$ Hz, 2H, phenyl-H), 6.58 (s(sh), 1H, phenyl-H), 6.53 (d, $J = 6.9$ Hz, 2H, phenyl-H), 6.02 (d, $J = 4.6$ Hz, 1H, β-H), 5.99 (d, $J = 4.6$ Hz, 1H, β-H), 5.77 (d, $J = 3.4$ Hz, 1H, β-H); UV–vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 390 (41200) and 576 (75400); ESI-TOF-MS (positive-mode) (%intensity): $C_{90}H_{31}F_{29}N_6$ ([M]$^+$): calcd: 1746.2142, found: 1746.2194 (100%).

Mono-Pd^{II} complexes of β-tetraphenyl *meso*-hexakis(pentafluorophenyl)[28]hexaphyrin(1.1.1.1.1.1) **4** and **5**.

4: ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 9.47 (s, 1H, N–H), 7.80 (d, $J = 4.9$ Hz, 1H, β-H), 7.71 (d, $J = 9.0$ Hz, 1H, phenyl-H), 7.63 (s, 2H, β-H), 7.47 (d, $J = 7.6$ Hz, 1H, phenyl-H), 7.42 (m, 2H, phenyl-H), 7.26–7.19 (m, 4H, phenyl-H), 7.23 (d, $J = 4.9$ Hz, 1H, β-H), 7.17 (t, $J = 7.6$ Hz, 1H, phenyl-H), 7.11–7.03 (m, 7H, phenyl-H), 6.99 (t, $J = 7.6$ Hz, 1H, phenyl-H), 6.78 (m, 1H, β-H + 2H, phenyl-H), 6.27 (d, $J = 7.6$ Hz, 1H, phenyl-H), 5.46 (d, $J = 4.6$ Hz, 1H, β-H), 4.24 (s, 1H, N–H), 0.18 (s, 1H, β-H), 0.07 (s, 1H, N–H); UV–vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 397 (32400), 630 (170000), 805 (10800), 882 (12100), and 973(sh) (5290); ESI-TOF-MS (positive-mode) (%intensity): $C_{90}H_{30}F_{30}N_6Pd$ ([M]$^+$): calcd: 1870.1109, found: 1870.0971 (100%).

5: ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 9.14 (s, 1H, N–H), 7.79 (d, $J = 4.8$ Hz, 1H, β-H), 7.74 (br s, 1H, β-H), 7.59 (d, $J = 7.6$ Hz, 1H, phenyl-H), 7.53 (d, $J = 7.6$ Hz, 1H, phenyl-H), 7.48 (br s, 1H, β-H), 7.45 (d, $J = 4.8$ Hz, 1H, β-H), 7.40 (s, 2H, β-H), 7.14–6.93 (m, 8H, phenyl-H), 6.85 (br s, 2H, phenyl-H), 6.81 (t, $J = 7.6$ Hz, 1H, phenyl-H), 6.63 (br s, 1H, phenyl-H), 6.57 (d, $J = 5.5$ Hz, 4H, phenyl-H), 6.53 (d, $J = 7.6$ Hz, 1H, phenyl-H), 6.31 (d, $J = 7.6$ Hz, 1H, phenyl-H), 4.92 (s, 1H, N–H), 1.79 (s, 1H, N–H), 1.28 (s, 1H, β-H); UV–vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 408 (38800), 630 (173000), 810(sh) (9930), 895 (13400), and 975(sh) (7660); ESI-TOF-MS (positive-mode) (%intensity): $C_{90}H_{30}F_{30}N_6Pd$ ([M]$^+$): calcd: 1870.1109, found: 1870.1131 (100%).

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Supporting Information

The general experimental methods and physical data of ^{19}F NMR spectra are described. Figures of ^{1}H and ^{19}F NMR spectra of **3**, **4**, and **5** are shown. This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

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9 Crystallographic data for **4**: $C_{90}H_{30}F_{30}N_6Pd \cdot C_6H_{14} \cdot CH_2Cl_2$, $M_w = 2042.70$, triclinic, $P\bar{1}$ (No. 2), $a = 12.961(4)$ Å, $b = 18.246(6)$ Å, $c = 18.785(7)$ Å, $\alpha = 82.34(1)°$, $\beta = 80.07(1)°$, $\gamma = 69.21(1)°$, $V = 4078(2)$ Å^3, $D_{calcd} = 1.663$ g cm^{-3}, $Z = 2$, $T = 123(2)$ K, $R_1 = 0.0720$ ($I > 2.0\sigma(I)$), $wR_2 = 0.2138$ (all data), GOF = 1.059 ($I > 2.0\sigma(I)$). CCDC file No. 767702.

10 Crystallographic data for **5**: $C_{90}H_{30}F_{30}N_6Pd \cdot 2(C_6H_5Cl)$, $M_w = 2096.70$, triclinic, $P\bar{1}$ (No. 2), $a = 14.124(6)$ Å, $b = 18.742(6)$ Å, $c = 19.552(6)$ Å, $\alpha = 113.84(1)°$, $\beta = 101.79(1)°$, $\gamma = 96.28(1)°$, $V = 4527(3)$ Å^3, $D_{calcd} = 1.538$ g cm^{-3}, $Z = 2$, $T = 123(2)$ K, $R_1 = 0.0916$ ($I > 2.0\sigma(I)$), $wR_2 = 0.2879$ (all data), GOF = 1.087 ($I > 2.0\sigma(I)$). These values have been obtained by removal of the solvent molecules by using the utility SQUEEZE in PLATON software package.; SQUEEZE-PLATON: a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2005**. b) P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194, CCDC file No. 767703.