Aromaticity

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Redox-Induced Palladium Migrations that Allow Reversible Topological Changes between Palladium(II) Complexes of Möbius Aromatic [28]Hexaphyrin and Hückel Aromatic [26]Hexaphyrin**

*Mitsunori Inoue and Atsuhiro Osuka**

Möbius aromaticity is the concept that complements the Hückel aromaticity by predicting aromatic and antiaromatic characters for [4nπ] and [(4n+2)π] annulenes having a Möbius topology.[1] Since its first proposal by Heilbronner in 1964,[2a] this concept has encouraged both experimental and theoretical studies. Importantly, the seminal papers by Herges and co-workers[3] have regenerated interest in this concept leading to reports on a [16]annulene that possesses a twisted conformation and a moderate aromatic character.[4] Recently, expanded porphyrins[5] have emerged as a nice platform to realize various Möbius aromatic molecules.[6–8] Although these molecules are important and interesting, displaying singly twisted conformations and diatropic ring currents originating from their aromatic characters, their chemical reactivity has been hardly unexplored thus far. Herein we report the novel reactivity of the Möbius aromatic [28]hexaphyrin/palladium(II) complex **3** (Figure 1), which undergoes a molecular topology change to give Hückel aromatic [26]hexaphyrin/palladium(II) complex **4** upon oxidation with tris(4-bromophenyl)aminium hexachloroantimonate (TBAH). Interestingly, the reverse transformation from **4** into **3** can be effected by reduction with $NaCNBH_3$.

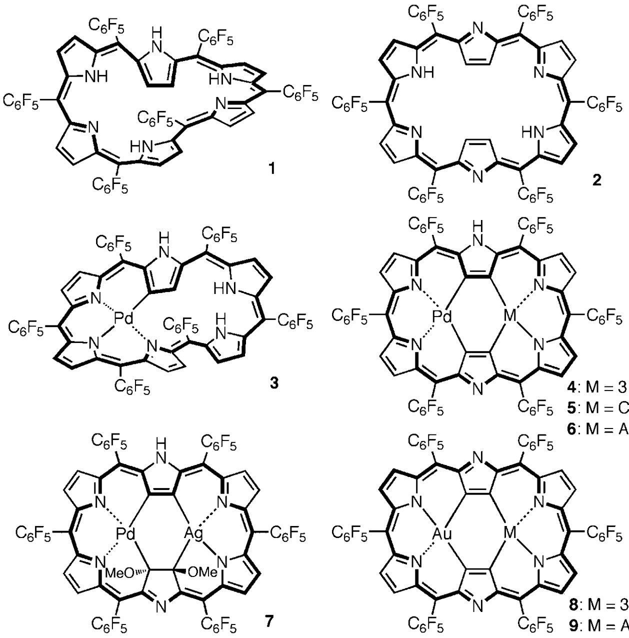

Figure 1. Hexaphyrins and their metal complexes in this paper. Bold bonds represent π-conjugated circuits.

In the course of our studies on Möbius aromatic molecules, we have revealed that although [26]hexaphyrin (**2**) is a Hückel aromatic molecule with certain structural rigidity, and its two-electron reduced congener [28]hexaphyrin (**1**) has been shown to exist in solution at 25 °C largely as an equilibrium of several rapidly interconverting twisted Möbius conformations having distinct aromaticities.[8a] In contrast, the rigid conformation of the [28]hexaphyrin/palladium(II) complex **3** was determined on the basis of its temperature-independent ^1H NMR spectrum.[7a] We thought that the two-electron oxidation of **3** might give a Möbius antiaromatic [26]hexaphyrin with a twisted conformation. Isolation of stable Möbius antiaromatic molecules is quite important to confirm that the [4nπ] and [(4n+2)π] rule is also valid for conjugated macrocycles of Möbius topology, but such Möbius antiaromatic molecules have been quite scarce.[9] We thus attempted the oxidation of **3** with various oxidants. Whereas **3** was found to be inert towards oxidants such as P_2O_5, $NaIO_4$, and $NaBrO_3$, it was readily decomposed upon treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *para*-chloranil, MnO_2, *meta*-chloroperbezoinc acid (MCPBA), and ceric ammonium nitrate (CAN). Fortunately, we found that clean oxidation of **3** proceeded with TBAH in acetonitrile. An acetonitrile solution of **3** was stirred in the presence of TBAH for 10 minutes at room temperature, and then the reaction mixture was quenched by the addition of methanol. After the usual work-up, a single product was isolated in 71 % yield, and has been identified as the planar and rectangular macrocycle **4** on the basis of single-crystal X-ray diffraction analysis (Figure 2).[10] Interestingly, NNNC Pd^{II} coordination in **3** is changed to NNCC Pd^{II} coordination in **4** with a molecular topology change from a twisted Möbius conformation to a planar Hückel conformation. In **4**, the representative bond distances are 2.105(19) Å for Pd-N(2), 2.105(2) Å for Pd-N(3), 1.996(2) Å for Pd-C(3), and 1.990(2) Å for Pd-C(17), and the pyrrolic interior angles of C-N(4)-C and C-N(1)-C are 109.1(18) and 105.7(2)°, indicating the location of amino-type and imino-type pyrroles,

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[*] M. Inoue, Prof. Dr. A. Osuka
Department of Chemistry, Graduate School of Science
Kyoto University, Sakyo-ku, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp

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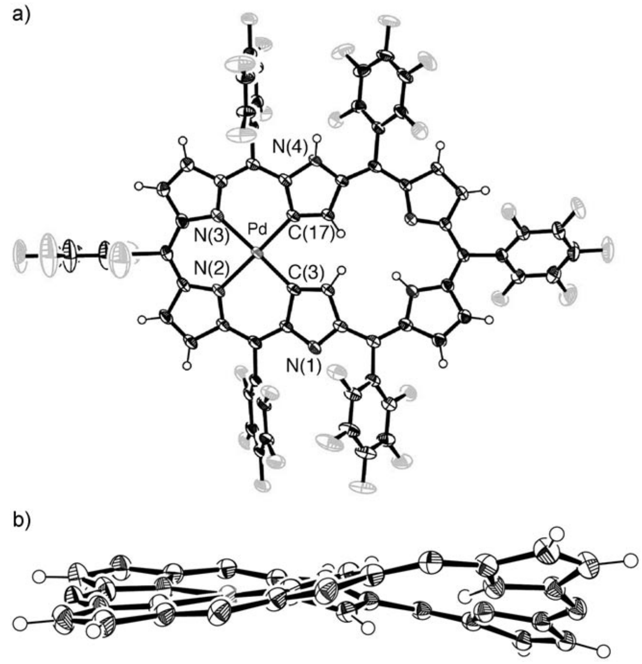


Figure 2. X-ray crystal structure of **4**: a) top view and b) side view. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

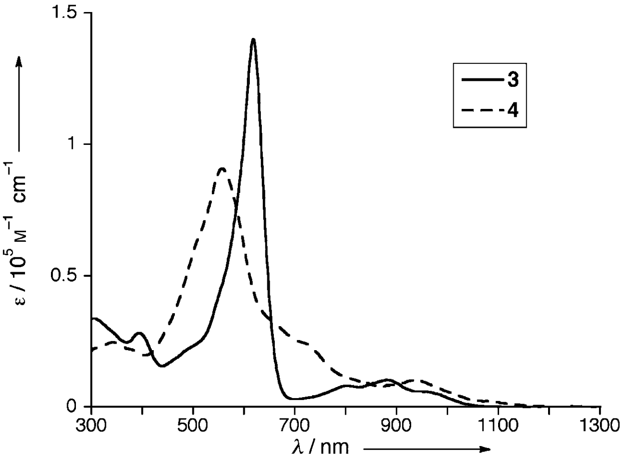
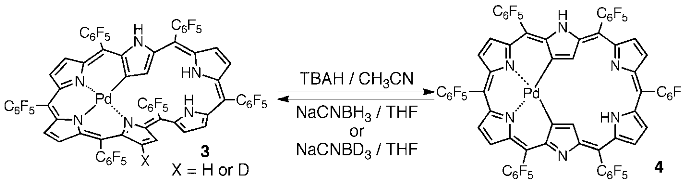


Figure 3. UV/Vis absorption spectra of **3** and **4** in CH_2Cl_2.

respectively. The structure of **4** confirms the conjugated 26π circuit as shown in Figure 1. Importantly, the complex **4** cannot be obtained directly by the metallation of hexaphyrin **1** or **2** with palladium salts.[7a, 11] It is likely that the Pd^{II} metal migrates from N(1) to C(3) with C–H activation during the oxidation to avoid unfavorable Möbius topology with a 26π electronic circuit. Previously, we reported that the metallation of **2** with $NaAuCl_4$ in the presence of sodium acetate led to the formation of complexes **8** and **9**, in which the Au^{III} ions are coordinated to NNCC, similar to the Pd^{II} ion in **4**.[12a] However, the structure of **4** differs from that of **8** in terms of the presence of the outer NH group, which balances the overall charge and causes the nonsymmetric structure. The ^{1}H NMR spectrum of **4** is consistent with its nonsymmetric structure, exhibiting a singlet at $\delta = 11.8$ ppm that results from the outer NH, eight doublets in the range of $\delta = 9.58$–8.93 ppm that result from the outer β protons, a singlet at $\delta = -2.70$ ppm that results from the inner NH, and two singlets at $\delta = -3.62$ and -3.73 ppm, respectively that result from the inner β protons. The UV/Vis absorption spectrum of **4** shows a distinct Soret-like band at 557 nm and Q-like bands at 941 nm which are signatures of its aromatic nature (Figure 3). The spectrum of **4** is however considerably broader than that of **3**.

To test the reversibility of the palladium(II) rearrangement, the reduction of **4** was examined. Whereas the reduction of **4** with $NaBH_4$ caused immediate decomposition, the reduction of **4** was successful when using $NaCNBH_3$ in THF, thus regenerating **3** in 74% yield (Scheme 1). Therefore, the reverse palladium(II) rearrangement has been confirmed through reduction. With $NaCNBD_3$, C3-deuterated **3** was obtained, suggesting that the Pd–C3 bond is reductively cleaved, and subsequent Pd–N1 bond formation achieves the twisted Möbius aromatic [28]hexaphyrin. Therefore, it may be concluded that the hexaphyrin/monopalladium(II)complex is a unique platform, wherein the Pd^{II} metal rearranges between N1 and C3 to achieve the topologically different aromatic molecular systems, thus responding to the number of π electrons involved in the conjugation circuit.



Scheme 1. Redox interconversions between **3** and **4**.

In the next step, the metallation of **4** in the preorganized vacant CCNN cavity has been performed to create hetero-bis(metal) complexes.[12] The reaction of **4** with $Cu(OAc)_2$ in a 4:1 mixture of CH_2Cl_2 and methanol in the presence of NaOAc for 3 hours at room temperature afforded the [26]hexaphyrin/Pd^{II}/Cu^{III} complex **5** in 90% yield. The high-resolution electrospray-ionization time-of-flight mass spectroscopy (HR-ESI-TOF/MS) revealed m/z 1624.8671-($[M-H]^-$) as the parent ion peak of **5** (calcd for $C_{66}H_8N_6F_{30}PdCu$, $m/z = 1624.8682$). The ^{1}H NMR spectrum of **5** exhibits a singlet at $\delta = 11.5$ ppm that results from the outer NH and eight doublets in the range of $\delta = 9.28$–8.76 ppm that result from the outer β protons. The clean ^{1}H NMR spectrum indicated the presence of Cu^{III} ion in the pocket, hence confirming that the NNCC core in **4** can serve as a tridentate ligand to realize the high valent Cu^{III} state in a similar manner as the carbaporphyrins.[13] The UV/Vis absorption spectrum of **5** exhibits a rather broad and split Soret-like band and Q-like bands that extend up to 1200 nm.

Similarly, the metallation of **4** with AgOTf in acetonitrile after 30 hours at room temperature provided a Pd^{II}/Ag^{III}

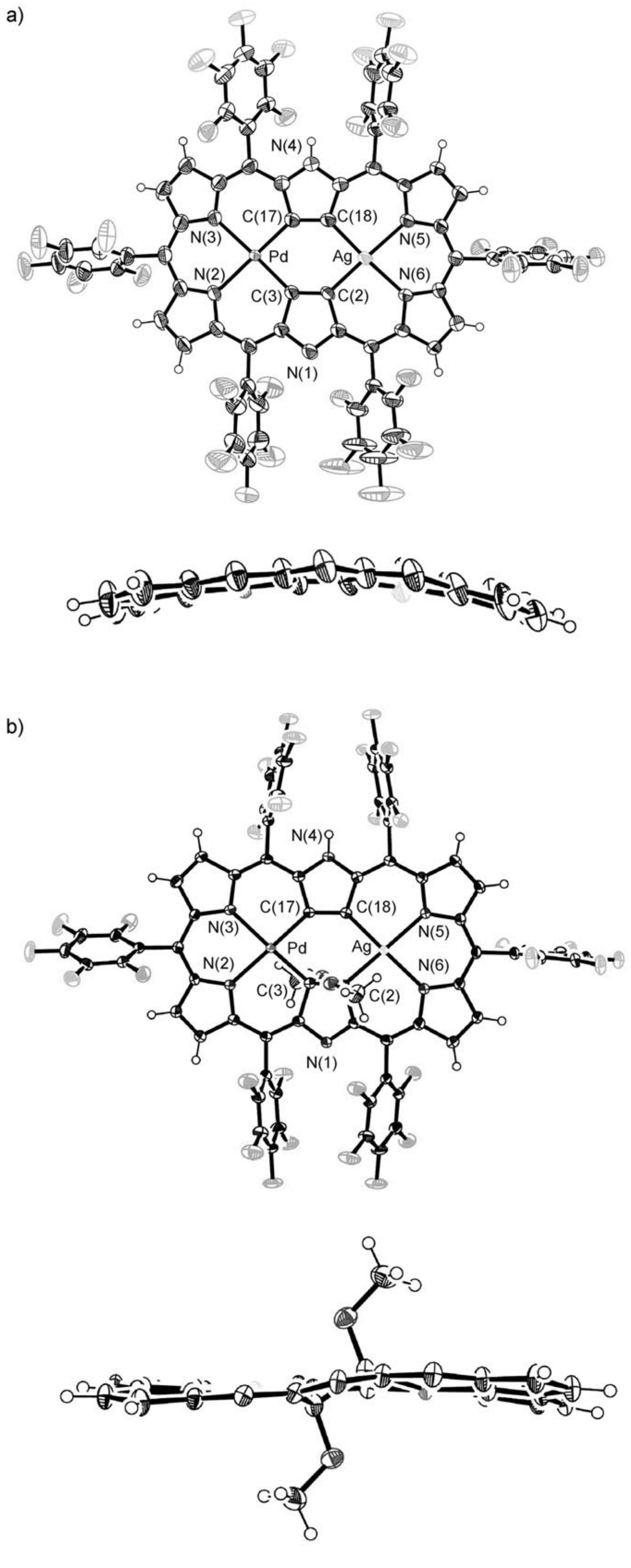


Figure 4. X-ray crystal structures of **6** (a) and **7** (b); for each structure a top and side view are shown. In **7**, solvent molecules are omitted for clarity. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

complex of [26]hexaphyrin (**6**) in 93% yield. The structure of **6** was unambiguously confirmed by the single-crystal X-ray diffraction analyses.[10] In **6**, the Pd^{II} ion and Ag^{III} ion are coordinated to two pyrrolic nitrogen atoms and two β carbon atoms with following bond lengths: 2.137(4) Å for Pd-N(2), 2.121(4) Å for Pd-N(3), 2.010(4) Å for Pd-C(3), 1.979(5) Å for Pd-C(17); 2.157(5) Å for Ag-N(5), 2.113(4) Å for Ag-N(6), 1.970(6) Å for Ag-C(2), 2.041(5) Å for Ag-C(18). The pyrrole interior angles of C-N(4)-C and C-N(1)-C are 109.3(3) and 105.2(3)°, indicating the location of amino-type and imino-type pyrroles, respectively. Compared with **4**, **6** is more planar with the smaller mean plane deviation of 36 atoms (**4**, 0.425 Å; **6**, 0.349 Å). ^{1}H NMR and ^{19}F NMR data as well as UV/Vis absorption spectra of **6** are very similar to those of **5**.

Refluxing a solution of **6** in CH_2Cl_2 containing methanol for 48 hours in the presence of AgOTf and NaOAc led to production of the bis(methoxy) adduct **7** in 86% yield. X-Ray diffraction analysis revealed the structure of **7**, in which two methoxy groups are attached to the inner pyrrolic β positions in an *anti* manner (Figure 4B).[10] The C–C bond distances of the reacted pyrrolic unit are 1.553(5), 1.549(5), and 1.539(5) Å, which are well within the typical single C–C bond distance. The ^{1}H NMR, ^{19}F NMR, and HR-ESI-TOF data are fully consistent with the solid-state structure. The ^{1}H NMR spectrum exhibits two highly shielded singlets at $\delta = -2.41$ and -2.75 ppm that result from the two methoxy groups, indicating that a strong diatropic ring current is preserved in **7**. The UV/Vis absorption spectrum of **7** exhibits a sharp and split Soret-like band and intensified Q-like bands, which also supports the aromatic nature and expanded chlorin-like structure of **7** (Figure 5).

In summary, the oxidation of the Möbius aromatic hexaphyrin **3** with TBAH induced a topological change (from twisted to planar) to produce the Hückel aromatic hexaphyrin **4** with Pd^{II} migration from N1 to C3, and the reverse topological change was effected by the reduction of **4** with $NaCNBH_3$ to regenerate **3**. The complex **4** has a preorganized cavity that has been used as a binding site for another metal ion to produce hetero-bis(metal) complexes such as the Pd^{II}/Cu^{III} complex **5** and Pd^{II}/Ag^{III} complex **6**. Finally, the silver(I)-catalyzed addition reaction of methanol

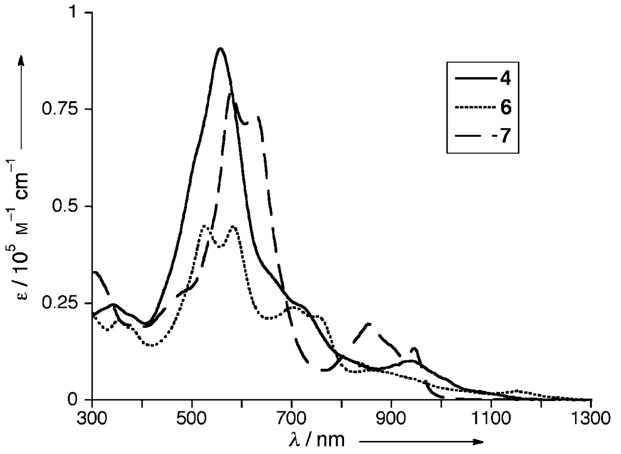


Figure 5. UV/Vis absorption spectra of **4**, **6**, and **7** in CH_2Cl_2.

to **6** provided the bis(methoxy) adduct **7**, which holds a diatropic ring current owing to its chlorin-like [26]hexaphyrin network.

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[10] Crystal data for **4**: $C_{66}H_{12}F_{30}N_6Pd$ ($M_r = 1565$), triclinic, space group $P\bar{1}$ (No. 2), $a = 12.756(3)$, $b = 15.649(5)$, $c = 18.135(5)$ Å, $\alpha = 101.791(12)$, $\beta = 103.460(9)$, $\gamma = 98.606(11)$, $V = 3371.6(16)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.542\ g\,cm^{-3}$, $T = 123(2)$ K, $R_1 = 0.0418$ ($I > 2\sigma(I)$), $R_W = 0.1227$(all data), GOF = 1.118. Crystal data for **6**: $C_{66}H_9AgF_{30}N_6Pd$ ($M_r = 1670$), orthorhombic, space group *Pbca* (No. 61), $a = 18.0763(17)$, $b = 27.081(3)$, $c = 27.320(3)$ Å, $V = 13374(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.659\ g\,cm^{-3}$, $T = 90(2)$ K, $R_1 = 0.0566$ ($I > 2\sigma(I)$), $R_W = 0.1717$(all data), GOF = 1.033. In these crystal structures, there are disordered solvent molecules, and their contribution to the scattering values have been removed by using the PLATON SQUEEZE program.[14] Crystal data for **7**: $C_{70}H_{19}AgCl_4F_{30}N_6O_2Pd$ ($M_r = 1901$), monoclinic, space group $P2_1/n$ (No. 11), $a = 19.043(6)$, $b = 16.649(4)$, $c = 20.854(5)$ Å, $\beta = 102.423(11)°$, $V = 6457(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.956\ g\,cm^{-3}$, $T = 123(2)$ K, $R_1 = 0.0480$ ($I > 2\sigma(I)$), $R_W = 0.1285$-(all data), GOF = 1.044. CCDC 790146 (**4**), CCDC 790147 (**6**), CCDC 790148 (**7**) contain 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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