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# **Quadruply Twisted Hückel Aromatic Dodecaphyrin**

#### Takanori Soya, Hirotaka Mori, and Atsuhiro Osuka\*

Abstract: Molecular topology of  $\pi$ -conjugated circuits becomes increasingly important in the chemistry of aromatic and antiaromatic compounds. meso-Pentafluorophenyl-substituted 5,35-(1,4phenylene)bridged [56]dodecaphyrin was synthesized by condensation of 1,4-phenylene-bridged dicarbinol dimer and 5,10,15tris-(pentafluorophenyl)tetrapyrrane followed by oxidation with DDQ and was oxidized to its [54]- and [52]congeners in a stepwise manner. Metalation of the [52]dodecaphyrin with Pd2(dba)3 gave two bis-Pd<sup>II</sup> complexes that are isomers of metalation sites, anti and syn with regard to the 1,4-phenylene bridge. The anti-isomer was easily oxidized to its N-fused form, a quadruply twisted non-aromatic or weakly aromatic macrocycle. On the other hand, the syn-isomer was revealed to be the first example of Hückel aromatic molecule with a quadruply twisted structure.

Aromaticity is one of the most fundamental concepts in organic chemistry, since it is important in understanding of energetic, structural, and magnetic properties of  $\pi$ -conjugated cyclic molecules.<sup>[1]</sup> Recent progress in this field has revealed in-plane<sup>[2]</sup> and stacked aromatic<sup>[3]</sup> molecules, demonstrating that aromatic molecules are diverse, not limited to the conventional planar ones. In relation to these, the relationship between the topology of  $\pi$ -conjugated macrocycles and their aromaticities has become increasingly important since the first synthesis of a singly twisted Möbius aromatic molecule by Herges et al. in 2003.<sup>[4–6]</sup>

Topology of  $\pi$ -conjugated macrocycles is defined by the absolute value of linking number  $|L_k|$  that corresponds to the number of half-twist (180°) formally applied to a ribbon, which can experimentally be confirmed by cutting a closed ribbon along the middle. Namely, closed ribbons with  $|L_k| = 0, 1, 2, 3, and 4$  should become two separated rings, a ring, a catenane, a trefoil knot, and Solomon's link, respectively, after the middle cut а procedure.<sup>[4c,8a,9b]</sup> When  $|L_k|$  is even (including zero),  $\pi$ -conjugated macrocycles are aromatic with  $[4n+2]\pi$  electrons and antiaromatic with  $4n\pi$  electrons. In contrast, those with odd values of  $|L_k|$  are aromatic with  $4n\pi$  electrons and antiaromatic with  $[4n+2]\pi$ electrons.<sup>[7]</sup> However, despite the extensive synthetic efforts, there has been no report on aromatic nor antiaromatic molecules possessing more than triply twisted  $(|L_k| \ge 3)$  topology.<sup>[4,9b-e]</sup> As a rare example, [24]annulene 1 was rationally designed and synthesized as the first example of triply twisted  $(|L_k| = 3)$ annulene by Herges et al. in 2014, but this molecule did not show any aromatic character (Figure 1).[8a] Therefore, synthesis of aromatic compounds with more than three molecular twists still remains a big challenge, since it is difficult to accommodate macrocyclic conjugation in such twisted systems.

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Supporting information for this article is given via a link at the end of the document.

In the last two decades, meso-aryl substituted expanded porphyrins consisting of more than four pyrrole units have been demonstrated to serve as effective platforms to realize versatile electronic states including Hückel aromatic and antiaromatic, Möbius aromatic and antiaromatic, and stable radical species.<sup>[9]</sup> Among these, meso-trifluoromethyl substituted [56]dodecaphyrin 2 consisting of twelve pyrrolic units occupies a unique position, in that it has been revealed to take a quadruply twisted topology  $(|L_k|)$ = 4) with a helical conformation in the solid state. But dodecaphyrin 2 has been shown to exist as a mixture of many conformers in solution, hampering the detailed analysis.<sup>[10a]</sup> It occurred to us that an appropriate structural fixation of such large  $\pi$ -conjugated macrocycles would lead to realization of triply or more twisted topologies with aromatic or antiaromatic characters. To test this idea, internally 5,35-(1,4-phenylene)bridged dodecaphyrin 3 was designed as a highly twisted  $\pi$ -conjugated system.<sup>[11]</sup> Herein, we report the synthesis and Pd<sup>II</sup>-metalation of 3. Importantly, one of the bis-Pd<sup>II</sup> complexes has been identified as the first example of quadruply twisted Hückel aromatic molecule.



**Figure 1.** Representative examples of triply twisted ( $|L_k| = 3$ ) and quadruply twisted ( $|L_k| = 4$ )  $\pi$ -conjugated macrocycles. R = CF<sub>3</sub>.

1,4-Phenylene-bridged [56]dodecaphyrin 3 was synthesized via acid catalyzed condensation of a 1:2 mixture of 1,4-phenylene-bridged dicarbinol dimer 8 and 5,10,15-tris-(pentafluorophenyl)tetrapyrrane 9 followed by oxidation with DDQ in 8.3% yield. High-resolution electrospray-ionization time-of-flight mass-spectrometry (HR-ESI-TOF-MS) revealed the parent ion peak at m/z = 2665.2234 ([*M*-H]-; calcd for C<sub>126</sub>H<sub>35</sub>N<sub>12</sub>F<sub>50</sub>, m/z =2665.2315). Fortunately, single crystals of 3 suitable for X-ray analysis were obtained by vapor diffusion of n-heptane into a benzene solution of 3. The solid state structure of 3 has been revealed to be a butterfly-like conformation (Figure 2a).<sup>[12a]</sup> Nontwisted nature of **3** ( $|L_k| = 0$ ) has been confirmed by the middle cut procedure, which gives two separated rings (see Supplemental Movie 1). The <sup>1</sup>H NMR spectrum of **3** shows four singlets in the range of  $\delta$  = 14.03–9.87 ppm due to the eight NHs, a singlet at  $\delta$ = 7.13 ppm due to the four phenylene protons, and eleven signals in the range of  $\delta$  = 7.73–6.04 ppm due to the twenty-four pyrrolic- $\beta$  protons, indicating C<sub>i</sub> symmetry and the absence of macrocyclic ring current effects. In addition to these major signals, there was a set of minor signals, suggesting the existence of minor

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conformers in solution (Figure S5-1 in Supporting Information (SI)).



Scheme 1. Chemical structures of 3, 4, 5, 8, and 9 and the interconversion between 3, 4, and 5. Pentafluorophenyl groups in 3, 4, and 5 are omitted for clarity.

While 3 was not reduced with an excess amount of NaBH4, 3 was smoothly oxidized to [54]dodecaphyrin 4 upon treatment with p-chloranil (1.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub>, which was isolated as violet solids in 29% yield. Further oxidation was accomplished with an excess amount of MnO<sub>2</sub> (10 eq.) to afford [52]dodecaphyrin 5 as red solids in 70% yield. Reductions of 4 and 5 with NaBH4 regenerated 3 quantitatively. We could not get single crystals of 4 because of its easy reduction to 3 under recrystallization conditions, but we obtained single crystals of 5 by vapor diffusion of methanol into a  $\text{CHCl}_3$  solution of  $\mathbf{5}.^{[12b]}$  In the solid state,  $\mathbf{5}$ takes a crescent-like conformation (Figure 2b). The doubly twisted topology  $(|L_k| = 2)$  has been confirmed by the middle cut procedure that gives a catenane (Supplemental Movie 2). The <sup>1</sup>H NMR spectrum of 5 shows a set of sharp signals including two singlets at  $\delta$  = 13.19 and 12.46 ppm due to the two NHs, two signals at  $\delta$  = 8.69 and 7.35 ppm due to the four phenylene protons, and twelve signals in the range of  $\delta$  = 8.17–6.08 ppm due to the twenty-four pyrrolic- $\beta$  protons, indicating the absence of ring

current effects and rigid structure even in solution (Figure S5-3 in SI). In contrast, the <sup>1</sup>H NMR spectrum of **4** is complicated, suggesting that **4** exists as a mixture of several conformers in solution similar to **3** (Figure S5-2 in SI). These results imply that the introduction of a 1,4-phenylene bridge is not sufficient to fix the conformations of the dodecaphyrin.



**Figure 2.** X-Ray crystal structures of (a) **3** and (b) **5**. The thermal ellipsoids are represented at 50% probability level. Solvent molecules, pentafluorophenyl groups, and hydrogen atoms except for NHs are omitted for clarity. Representations of the  $\pi$ -conjugated circuits of (a) **3** and (b) **5**.

In order to further rigidify the structure, we attempted metalations of 5. After many attempts (Table S2-1 in SI), we found that treatment of 5 with Pd2dba3 (5.0 eq.) in the presence of NaOAc (10 eq.) in CH<sub>2</sub>Cl<sub>2</sub> and MeOH gave two bis-Pd<sup>II</sup> complexes 6 and 7 in 15 and 18% yields, respectively, after separation through silica gel column chromatography (Scheme 2).<sup>[13]</sup> HR-ESI-TOF-MS showed the parent ion peaks of 6 and 7 at m/z = 2870.9837 and 2870.9857 ([M-H]-; calcd for C126H29N12F50Pd2, m/z = 2870.9962). The isomers 6 and 7 have been assigned, respectively, as anti and syn isomers with regard to the 1,4phenylene-bridge as revealed by the discussion below. The <sup>1</sup>H NMR spectrum of **6** displays a singlet at  $\delta$  = 16.41 ppm due to the NHs, twelve signals in the range of  $\delta$  = 14.05–3.32 ppm due to the pyrrolic- $\beta$  protons, and two doublets at  $\delta$  = 10.33 and 7.55 ppm due to the bridging phenylene moiety, suggesting its C<sub>2</sub> symmetric structure (Figure 3a). Regrettably, the crystal structure of 6 has not been obtained due to its facile fusion reaction to give 6-fused in solution. Indeed, 6-fused was obtained in 82% yield upon oxidation of 6 with DDQ. The structure of 6-fused was revealed by single crystal X-ray diffraction analysis to take a plectonemic conformation (Figure 4a).<sup>[12c]</sup> The N-fusion reaction occurred at the closely located pyrrolic nitrogen atom and 1,4-phenylene bridge. To our surprise, the quadruply twisted  $\pi$ -conjugated circuit  $(|L_k| = 4)$  has been confirmed by the middle cutting procedure that gives a Solomon's Links. The <sup>1</sup>H NMR spectrum of 6-fused showed a singlet at  $\delta$  = 13.14 ppm due to the NH, twenty-two

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signals in the range of  $\delta$  = 13.07–4.84 ppm due to the twenty-four pyrrolic- $\beta$  protons, and two singlets at  $\delta$  = 11.04 and 6.90 ppm due to the 1,4-phenylene bridge, suggesting the absence of diatropic ring current (Figure 3b).



Scheme 2. Pd<sup>II</sup> metalation of 5 and fusion reaction of 6. Pentafluorophenyl groups are omitted for clarity. A plausible structure is shown for 6.





On the other hand, the <sup>1</sup>H NMR spectrum of the syn-isomer **7** shows a singlet at  $\delta$  = 9.67 ppm due to the NHs, twelve signals in the range of  $\delta$  = 8.59 – 4.22 ppm due to the pyrrolic- $\beta$  protons, and two doublets at  $\delta$  = 4.46 and 3.81 ppm due to the phenylene

moiety located at the inner part of the macrocycle, indicating a substantial diatropic ring current (Figure 3c). The solid state structure of 7 has been revealed by X-ray crystallographic analysis (Figure 4b).[12d] Similarly to 6-fused, 7 displays quadruply twisted topology ( $|L_k| = 4$ ), which gives Solomon's Link by the middle cut procedure (Figure 4b and Supplemental Movie 3). The nucleus independent chemical shift (NICS)<sup>[14]</sup> values at the selected inner positions of 7 were calculated to be -10.72 and -11.50 ppm, also supporting the aromaticity of 7 (positions 29 and 30 in Figure S8-8 in the SI). In addition, the anisotropy of the induced current density (ACID) of 7 was calculated to show a diatropic ring current (Figure S8-14 in the SI).<sup>[15]</sup> In order to realize unprecedented quadruply twisted Hückel antiaromatic molecules, reductions and oxidations of 6-fused and 7 were attempted but all these attempts failed, merely ending as the recovery or decomposition of the starting materials.



**Figure 4.** Left side: X-Ray crystal structures of (a) **6-fused** and (b) **7**. One of two independent molecules of **6-fused** in the unit cell is shown here. The thermal ellipsoids are represented at 50% probability. Pentafluorophenyl groups, solvent molecules, and hydrogen atoms except for NHs were omitted for clarity. Right side: Representations of the  $\pi$ -conjugated circuits of (a) **6-fused** and (b) **7**.



Figure 5. UV/Vis/NIR absorption spectra of 6, 6-fused, and 7 in  $CH_2Cl_2$  at 25 °C. \* indicates absorption due to solvents.

The UV/Vis/NIR absorption spectra showed the absorption maxima at 331, 425, 674, and 1215 nm for **6** and 326, 420, 667,

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and 1118 nm for **6-fused** without any absorption maxima around lower energy region. In contrast, the UV/Vis/NIR absorption spectrum of **7** showed the Soret-like band at 1147 nm and the Q-like bands reaching to the region over 2500 nm, which is in line with its aromatic character (Figure 5).

Finally, the electrochemical properties of the dodecaphyrins were measured by cyclic voltammetry (Figures S6-1 and S6-2 in the Supporting Information). While **3** and **4** showed five and six reversible redox waves respectively, **5** showed seven reversible redox waves. Furthermore, the Pd<sup>II</sup> complexes **6**, **6-fused**, and **7** showed eight reversible redox waves. The observed multiply reversible redox behaviors can be ascribed to the large  $\pi$ -conjugated networks and the rigid structures.

In summary, fully  $\pi$ -conjugated macrocycles possessing quadruply twisted topology ( $|L_k| = 4$ ) **6-fused** and **7** were realized by fixing the conformation of a [54]dodecaphyrin with 1,4-phenylene bridge and Pd<sup>II</sup> ions. While **6-fused** showed no aromatic character, **7** has been identified as a 54 $\pi$  Hückel aromatic species by <sup>1</sup>H NMR and UV/Vis/NIR absorption spectra and NICS and ACID calculations. To the best of our knowledge, **7** is the first quadruply twisted Hückel aromatic molecule.

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**Keywords**: Topology • Quadruple Twist • Solomon's Link • Aromaticity • Porphyrinoids

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- [12] a) Crystallographic data for 3:  $C_{126}H_{36}F_{50}N_{12}\cdot 8(C_6H_6)\cdot 2(C_6)$ ,  $M_r =$ 3436.66; triclinic; space group P-1 (No.2), a = 14.177(2), b = 16.712(4), c = 17.278(3) Å;  $\alpha$  =106.043(5),  $\beta$  = 104.1545(3),  $\gamma$  = 97.629(7)°; V = 3725.5(12) Å<sup>3</sup>;  $\rho_{calcd} = 1.174 \text{ g} \cdot \text{cm}^{-3}$ ; Z = 1;  $R_1 = 0.0531 [I > 2.0 \sigma(I)]$ , w $R_2$ = 0.1666 (all data), GOF = 1.052; b) Crystallographic data for 5:  $C_{126}H_{32}F_{50}N_{12}\cdot 4(CHCI_3), M_r = 3104.82;$  monoclinic; space group C2/c (No.15), a = 63.06(3), b = 20.5623(10), c = 23.476(10) Å;  $\beta =$ 91.853(12)°; V = 30424(19) Å<sup>3</sup>;  $\rho_{calcd}$  = 1.356 g·cm<sup>-3</sup>; Z = 8; R<sub>1</sub> = 0.0865  $[l > 2.0\sigma(l)]$ , wR<sub>2</sub> = 0.2749 (all data), GOF = 1.009; c) Crystallographic data for 6-fused: 2(C126H28F50N12Pd2).6.822(C6H6).2(C2O), Mr = 6379.24; triclinic; space group P-1 (No.2), a = 19.2854(13), b =28.8466(12), c = 30.6271(18) Å;  $\alpha = 108.8038(10)$ ,  $\beta = 108.136(14)$ ,  $\gamma =$ 103.865(15)°; V = 14191(2) Å<sup>3</sup>;  $\rho_{calcd} = 1.493$  g·cm<sup>-3</sup>; Z = 2;  $R_1 = 0.0703$  $[l > 2.0 \sigma(l)]$ , wR<sub>2</sub> = 0.2190 (all data), GOF = 1.009; d) Crystallographic data for 7: C<sub>126</sub>H<sub>30</sub>F<sub>50</sub>N<sub>12</sub>Pd<sub>2</sub>·3(C<sub>6</sub>O)·6(CCl<sub>4</sub>), M<sub>r</sub> = 4061.46; monoclinic; space group C2/c (No.15), a = 26.6753(4), b = 29.1994(4), c = 42.9903(6) Å;  $\beta$  = 105.940(2)°; V = 32197.7(9) Å<sup>3</sup>;  $\rho_{calcd}$  = 1.676 g·cm<sup>-3</sup>; Z = 8;  $R_1 = 0.1759 [l > 2.0 \sigma(l)]$ ,  $wR_2 = 0.4388$  (all data), GOF = 1.081. CCDC- 1868904 (3), 1868905 (5), 1868906 (6-fused), and 1868907 (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. The contributions to the scattering arising from the presence of the disordered solvents in the crystals of 5, 6-fused, and 7 were removed by use of the utility SQUEEZE in the PLATON software package. See; a) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2005; b) P. V. D. Sluis, A. L. Spek, Acta. Crystallogr., Sect. A: Found. Crystallogr. 1990, 46, 194.
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 $\pi$ -Conjugated macrocycles possessing quadruply twisted topology were realized by conformational fixation by insertion of 1,4-phenylene bridge and Pd<sup>II</sup> metalation. Syn-isomer of bis-Pd<sup>II</sup> complexes displays aromatic characters, thus being identified as the first example of quadruply twisted Hückel aromatic molecule.



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