Porphyrins

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Internally 1,4-Phenylene-Bridged *meso* Aryl-Substituted Expanded Porphyrins: The Decaphyrin and Octaphyrin Cases**

*Venkataramanarao G. Anand, Shohei Saito, Soji Shimizu, and Atsuhiro Osuka**

The chemistry of expanded porphyrins is the current focus of intensive research because of their unique properties.[1,2] Among their many expected properties, extensive aromaticity is realized in expanded porphyrins such as sapphyrins,[3] rubyrins,[1d,4] and hexaphyrins.[5] However, such aromaticity becomes increasingly difficult to obtain with larger expanded porphyrins, particularly for systems larger than octapyrroles, mainly because of intrinsic conformational distortion from planarity.[2c,d,6] Rare examples are the 34π-electron core-modified octaphyrin[1d,7] and 30π-electron cyclo[8]pyrrole,[8] both of which exhibit planar conformations and strong aromaticity, thus underscoring the influence of the conformation of the expanded porphyrins upon their electronic structures.

Several years ago we found that a series of *meso* aryl-substituted expanded porphyrins could be prepared by a simple one-pot reaction by using modified Rothemund–Lindsey conditions.[5c,9] These *meso* aryl expanded porphyrins can be regarded as real homologues of porphyrins in terms of regular alternate arrangements of pyrrole rings and methine carbon atoms. These molecules become more twisted with increasing number of pyrrolic subunits. It then occurred to us that suppression of this intrinsic twisting attribute may be a promising means to tune their conformational and electronic properties to generate large aromatic ring systems. We now report the influence of an internal 1,4-phenylene bridge that bisects large *meso* aryl-substituted expanded porphyrins—particularly the cases of decaphyrin and octaphyrin—on their structural and electronic properties.

A solution of one equivalent of 1,4-phenylene-bridged bis(dipyrromethane) **1a**[10] and two equivalents of tripyrrane diol **2** in dichloromethane was stirred in the presence of *p*-toluenesulfonic acid for 1 h, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.6 equivalents relative to **1a**) for an additional 1 h. Separation of the products by column chromatography on silica gel gave internally 1,4-phenylene-bridged [46]decaphyrin **4a** as a major product with a green metallic luster in 7% yield. Neither the 1,4-phenylene-bridged pentaphyrin dimer nor its derived products[11] were detected in the reaction mixture. Treatment of **4a** with 10 equivalents of DDQ resulted in its quantitative conversion into [44]decaphyrin **5a**, with a color change from dark red to dark green. [44]Decaphyrin **5a** was in turn quantitatively reduced to **4a** with $NaBH_4$, thus indicating a reversible redox interconversion. Electrospray ionization mass spectrometry revealed a parent ion peak for **4a** at *m*/*z* 2179.2163 (calcd for $C_{104}H_{31}F_{40}N_{10}$ $[M+H]^+$, *m*/*z* 2179.2100) and that for **5a** at *m*/*z* 2177.2032 (calcd for $C_{104}H_{29}F_{40}N_{10}$ $[M+H]^+$, *m*/*z* 2177.1943).

The structures of both **4a** and **5a** have been confirmed by X-ray diffraction analyses. Decaphyrin **4a** exhibits a C_2-symmetric nonplanar, but not a "figure-eight", structure (Figure 1),[12a] in which the two twisted pentapyrrolic subunits are interconnected by the central 1,4-phenylene bridge. Each pentapyrrolic arm consists of a dipyrromethene unit (pyrrole rings A and B or F and G) and a tripyrrodimethene unit (pyrrole rings C, D, and E or H, I, and J), both of which are roughly planar but almost opposite each other. The central 1,4-phenylene unit (ring K) is tilted relative to the neighboring pyrrole rings A and J as well as E and F, with dihedral angles of 60.1° and 59.8°, respectively, hence allowing its deconjugation from the rest of the conjugated network.

[*] Dr. V. G. Anand, S. Saito, S. Shimizu, 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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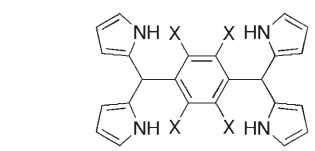

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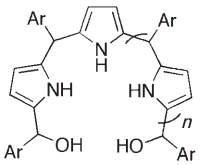

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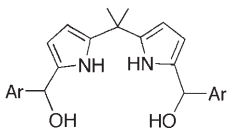

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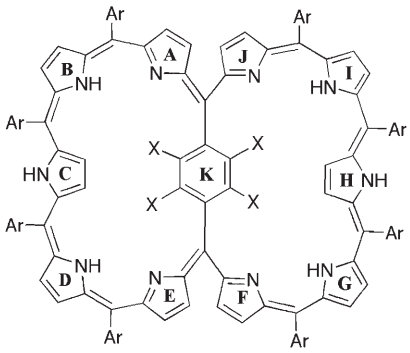

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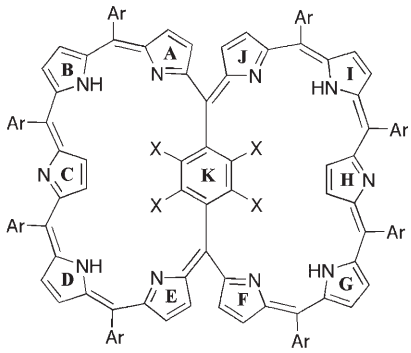

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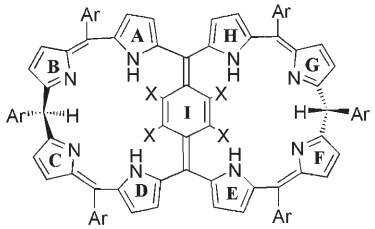

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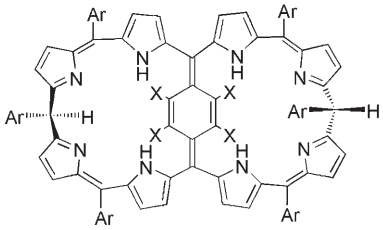
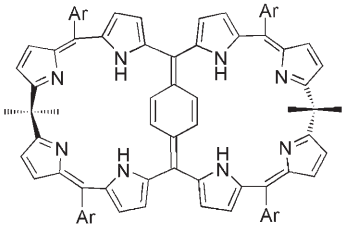


7a: X = H
7b: X = D



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Ar = pentafluorophenyl

Interestingly, the two C(pyrrole-α)–C(*meso*) bond lengths at the bridging positions are quite similar, thus suggesting effective conjugation over the overall macrocycle and in line with the 46π electronic circuit. The ^{1}H NMR spectrum of **4a** was quite broad at room temperature, indicative of fast conformational dynamics in solution relative to the NMR time scale. However, the spectrum became well resolved at 233 K with distinct differences in chemical shifts evident between the outer and inner protons of the macrocycle: the outer two NH protons at $\delta = 9.01$ ppm versus the inner four NH protons at $\delta = 5.84$ ppm; the outer β protons as two sets of mutually coupled doublets at $\delta = 7.36$ and 6.84 ppm and $\delta = 7.31$ and 7.19 ppm versus the inner β protons as a singlet at $\delta = 1.2$ ppm. The protons of the 1,4-phenylene bridge, assigned by comparison of the spectrum with that of the corresponding deuterated decaphyrin **4b**, appear as a sharp singlet at $\delta = 3.78$ ppm. These data support a diatropic ring current in **4**.

On the other hand, [44]decaphyrin **5a** shows a D_2-symmetric framework that is distinctly different from that of **4a** (Figure 2).[12b] Pairs of neighboring pyrrole rings (A and B, D and E, F and G, and I and J) constitute planar dipyrromethene units, and the pyrrole rings C and H are completely inverted, with the pyrrolic nitrogen atoms pointing outward. Each pentapyrrolic arm adopts a twisted but relatively planar structure, which constitutes a so-called benzihexaphyrin macrocycle. The arms are connected by the central 1,4-phenylene spacer in an almost perpendicular arrangement. Decaphyrin **5a** exhibits a well-resolved ^{1}H NMR spectrum at room temperature, with the inner four NH protons as a singlet at $\delta = 13.6$ ppm; the outer β protons as doublets at $\delta =$ 6.82 and 6.30 ppm and a multiplet at $\delta = 6.36$ ppm; the inverted pyrrole β protons as a singlet at $\delta =$ 7.78 ppm, and the bridging 1,4-phenylene protons as a singlet at $\delta =$ 8.98 ppm. The protons of the 1,4-phenylene bridge were assigned by comparison with the ^{1}H NMR spectrum of **5b**. There is no distinct difference between the chemical shifts of the inner and outer protons in **5a**, which is indicative of its non-aromatic character, and in line with its 44π electronic circuit and solid-state structure. The absorption spectrum of **4a** shows a Soret-like band at 505 nm and strong Q-like split bands at 800 and 856 nm, while that of **5a** exhibits broad bands at 454 and 619 nm (Figure 3). Interestingly, protonation of **4a** with trifluoroacetic acid (TFA) led to an intense and sharp Soret-like band at 846 nm and a Q-like band at 1221 nm.

We then examined the reaction of **1a** with dipyrromethane diol **3**. A solution of **1a** and **3** in dichloromethane and THF (3:1) was treated with methanesulfonic acid for 1 h and the resulting solution was oxidized with *p*-chloranil for 2 h. Together with the expected 1,4-phenylene-linked porphyrin dimer[14] (1–2% yield) which appeared as a red band by TLC analysis of the reaction mixture, two violet bands were observed and the products were isolated in yields of 0.6 and 0.5%. Despite the low yields, the formation of these products is quite reproducible when *p*-chloranil is used as the oxidant and the reaction time of the secondary oxidation step is maintained at 2 h. High-resolution electrospray ionization mass spectrometry revealed the parent ion peak at *m*/*z*

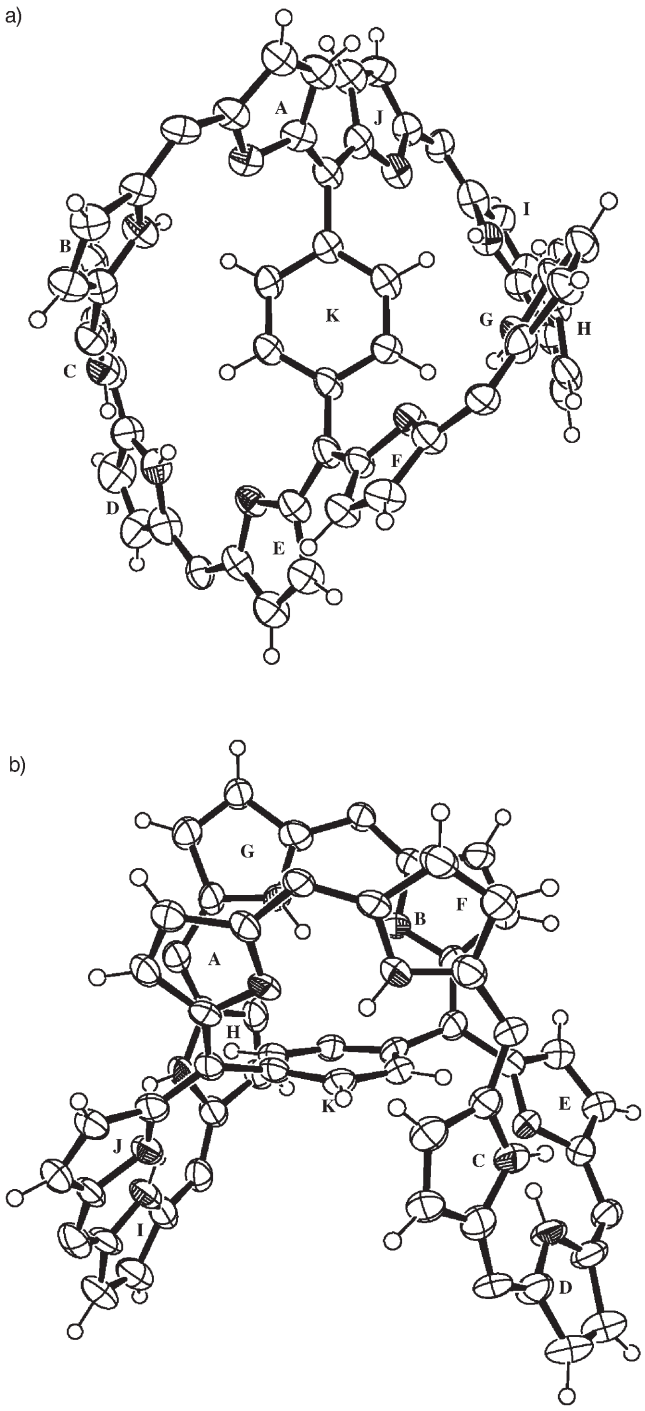

Figure 1. X-ray crystal structure of **4a**: a) top view and b) side view. Solvent molecules and *meso*-pentafluorophenyl groups are omitted for clarity.

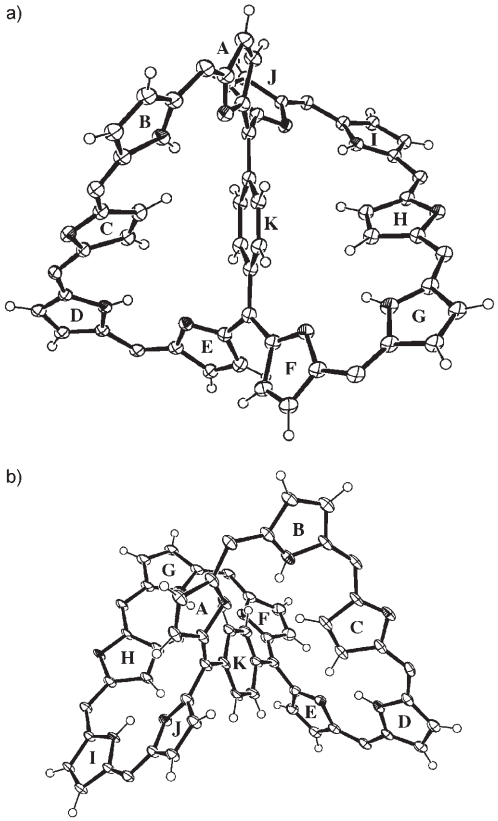

Figure 2. X-ray crystal structure of **5a**: a) top view and b) side view. Solvent molecules and *meso*-pentafluorophenyl groups are omitted for clarity.

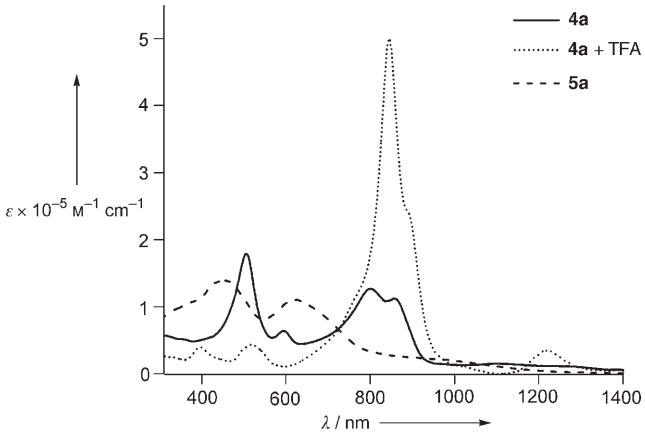

Figure 3. Absorption spectra of **4a**, **4a** + TFA, and **5a** in dichloromethane.

1693.1920 for **6a** (calcd for $C_{82}H_{27}F_{30}N_8$ $[M+H]^+$, m/z 1693.1874) and 1693.1915 for **7a** (calcd for $C_{82}H_{27}F_{30}N_8$ $[M+H]^+$, m/z 1693.1874). The absorption spectra of **6a** and **7a** are also quite similar to each other, with bands at 394, 593, and 895 nm, and 392, 593, and 898 nm, respectively. The structure of **6a** has been unambiguously revealed by X-ray diffraction analysis to be a *p*-quinodimethane-bridged calixoctaphyrin with two sp^3 meso carbon atoms at the diagonal positions and overall C_{2h} symmetry (Figure 4).[13] The bicyclic macrocycle adopts a saddle conformation consisting of four planar dipyrromethene units rather than a non-figure-eight structure. The quinodimethane structure is evident from a distinctly shorter C(22)–C(23) bond (1.367(4) Å) relative to that of C(21)–C(22) (1.430(4) Å). The angle C(23)*-C(21)-C(22) is 115.6(2)°, which is distinctly smaller than that of C(21)-C(22)-C(23) (122.7(3)°) and C(22)-C(23)-C(21)*

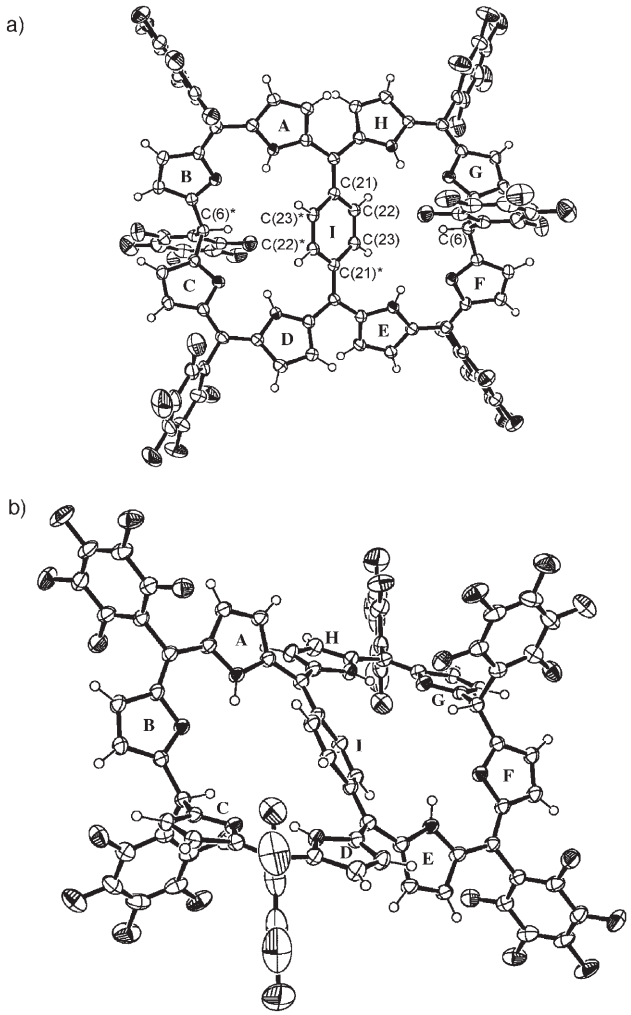

Figure 4. X-ray crystal structure of **6a**: a) top view and b) side view. Solvent molecules are omitted for clarity.

(121.7(3)°). The exo-methylene moieties in the quinodimethane unit are tilted by 18.1° relative to the six-membered ring. The dipyrromethene units are all maintained planar by hydrogen bonding, and thus all the pyrrolic nitrogen atoms point inward. The dipyrromethene units A, B and C, D are arranged with a dihedral angle of 60.9°, which are tilted relative to the central quinodimethane unit by 46.0 and 49.4°, respectively. The two pentafluorophenyl substituents at C(6) take anti and exo positions. The symmetric structure of **6a** is supported by its simple ^{1}H NMR spectrum, in which the central quinodimethane protons appear as a singlet at $\delta =$ 5.09 ppm and the meso protons appear as a singlet at $\delta =$ 2.71 ppm. The structure of **7a** has been revealed by a preliminary X-ray diffraction analysis to be almost the same as that of **6a** except for the positions of the pentafluorophenyl groups at C(6), which are both anti but not identical, each exo and endo (Supporting Information). The nonsymmetric structure of **7a** is in good agreement with the NMR data, with the central quinodimethane protons appearing as two singlets at $\delta = 5.21$ and 4.85 ppm and the *meso* protons appearing as two singlets at $\delta = 6.42$ and 2.45 ppm.

The reaction of **1** with dipyrromethane diol **8** afforded calixoctaphyrin **9** as a single major product as a violet solid in 3% yield. In the ^{1}H NMR spectrum of **9** the internal *p*-quinodimethane protons appear as a singlet at $\delta = 4.65$ ppm and the *gem*-dimethyl protons as two singlets at $\delta = 1.39$ and -1.03 ppm. The high chemical shifts of one of the dimethyl groups can be ascribed to its positioning just above the central bridge. Therefore, a *p*-quinodimethane structure may be considered to be a general concequence when a 1,4-phenylene bridge is incorporated in *meso* aryl-substituted calixoctaphyrins. In sharp contrast to **6a** and **7a** the calixoctaphyrin **9** is quite stable under oxidizing conditions.

This study shows that the incorporation of a 1,4-phenylene bridge into *meso* aryl-substituted expanded porphyrins has a profound impact on the structural and electronic properties of the macrocycles. Such modifications lead to suppression of the intrinsic property to take a twisting conformation and result in planar conformations. The structural modification result in diatropic ring current in the decaphyrin case, and forces a macrocycle to become calixoctaphyrin with an internal *p*-quinodimethane bridge in the octaphyrin case. Lastly, it is interesting to note that [46]decaphyrin is, to the best of our knowledge, the largest macrocycle that exhibits a diatropic ring current.

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[12] a) Crystallographic data for **4a**: $C_{113}H_{50}Cl_4F_{40}N_{10}O_6$, $M_r = 2545.43$, triclinic, space group $P\bar{1}$ (No. 2), $a = 17.897(2)$, $b = 18.824(2)$, $c = 19.929(3)$ Å, $\alpha = 62.486(3)$, $\beta = 78.326(3)$, $\gamma = 62.418(3)°$, $V = 5277.3(11)$ Å^3, $\rho_{calcd} = 1.602\ mg\,mm^{-3}$, $Z = 2$, $R_1 = 0.1069$, R_w (all data) $= 0.3199$, GOF $= 1.044$ ($I > 2.0\sigma(I)$); b) crystallographic data for **5a**: $C_{254}H_{160}Cl_8F_{80}N_{20}$, $M_r = 5343.62$, monoclinic, space group Cc (No. 9), $a = 32.0109(8)$, $b = 21.9539(5)$, $c = 37.7303(10)$ Å, $\beta = 111.0570(10)°$, $V = 24744.9(11)$ Å^3, $\rho_{calcd} = 1.434\ mg\,mm^{-3}$, $Z = 4$, $R_1 = 0.0956$, R_w (all data) $= 0.2966$, GOF $= 1.028$ ($I > 2.0\sigma(I)$).

[13] Crystallographic data for **6a**: $C_{86}H_{26}F_{30}N_{10}$, $M_r = 1769.17$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.002(5)$, $b = 11.829(5)$, $c = 16.816(10)$ Å, $\alpha = 77.742(18)$, $\beta = 80.313(19)$, $\gamma = 62.352(14)°$, $V = 1888.3(16)$ Å^3, $\rho_{calcd} = 1.556\ mg\,mm^{-3}$, $Z = 1$, $R_1 = 0.0678$, R_w (all data) $= 0.1726$, GOF $= 1.063$ ($I > 2.0\sigma(I)$). CCDC-280276–280278 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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