## Communications

**Expanded Porphyrins** 



Perfluorinated *meso*-Aryl-Substituted Expanded Porphyrins\*\*

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In recent years there has been a considerable upsurge in the development of expanded porphyrins with five or more conjugated pyrrolic rings, because of their ability to exhibit a variety of interesting optical, electrochemical, stereochemical, and coordination properties.<sup>[1,2]</sup> Among such macrocyclic systems, there are only scattered reports on meso-arylsubstituted expanded porphyrins that are structurally homologous to tetrakis-meso-aryl porphyrin in respect of the alternate conjugative arrangement of pyrrole and methine carbon atoms. Recently, we reported that simple modified Rothemund-Lindsey reaction of pentafluorobenzaldehyde and pyrrole unexpectedly allowed the formation of a series of meso-aryl-substituted expanded porphyrins ranging from pentaphyrin to dodecaphyrin.<sup>[3]</sup> meso-Aryl-substituted expanded porphyrins thus formed have received particular attention as a result of their ability to chelate multimetal ions as well as the multitude of oxidation states. In addition, meso-aryl-substituted expanded porphyrins can be structurally diverse, depending on the ring size, the metalation, and the degree of protonation.<sup>[3,4]</sup> For example, in the solid states, [26]hexaphyrin takes a flat rectangular conformation with two inverted pyrrole rings,<sup>[4]</sup> [36]octaphyrin exhibits a figure-

of-eight conformation,<sup>[3]</sup> and the [42]nonaphyrin-trifluoroacetic acid (TFA) complex shows a butterfly conformation with a central cleft in which TFA is bound by two inverted pyrrole rings.<sup>[3]</sup> Finally, these *meso*-aryl-substituted expanded porphyrins and other related large macrocycles offer a good opportunity to study the interplay between the aromaticity/ non-aromaticity that may be brought about by the twoelectron oxidation/reduction of the macrocycle.

Provided that the successful formation of *meso*-arylsubstituted expanded porphyrins is mainly a consequence of the steric congestion around the formyl group and the

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electron-deficient property of the aryl aldehyde, the similar reaction of pentafluorobenzaldehyde and 3,4-difluoropyr-role<sup>[5,6]</sup> may be facilitated by the additional steric crowding as well as by the electron-deficient nature of the fluorine substituents in the pyrrole ring. Furthermore, perfluorinated *meso*-aryl-substituted expanded porphyrins may be interesting as robust oxidation catalysts and functional dyes.<sup>[7]</sup>

Here we report the synthesis of a series of perfluorinated expanded porphyrins that possess fluorine substituents at both the *meso*-aryl and  $\beta$ -pyrrole positions. In a typical synthesis, a solution of 3,4-difluoropyrrole and pentafluorobenzaldehyde (66.7 mM each) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 8 h with BF<sub>3</sub>·OEt<sub>2</sub>. After oxidation with DDQ for 10 h, chromatographic separation on silica gel gave porphyrin **1** (6–9%),<sup>[7]</sup> pentaphyrin **2** (about 1%),<sup>[8]</sup> hexaphyrin **3** (2–5%), hepta-



Figure 1. UV/Vis spectra of meso-aryl-substituted expanded porphyrins.

phyrin **4** (4–6%), octaphyrin **5** (4–7%), nonaphyrin **6** (~2%), and decaphyrin **7** (about 2%; Scheme 1). The X-ray crystal structures of the hexaphyrin and octaphyrin were found to be particularly interesting, in that both these structures are quite different from those of the corresponding  $\beta$ -hydrogen ( $\beta$ -H) expanded porphyrins.

The yield of the initial hexaphyrin product 3 was variable for each batch, probably because of its very poor solubility in common organic solvents. The isolated hexaphyrin 3 exhibited a sharp Soret-like band at 560 nm ( $\varepsilon = 1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and Q-type bands at 717, 779, 907, and 1048 nm in the UV/Vis spectrum (Figure 1). These band positions are quite similar to those of  $\beta$ -H [26]hexaphyrin and suggest that **3** has aromatic character. This hexaphyrin was converted into a reduced form upon treatment with NaBH4 which was found to be more soluble in many solvents. Thus, a better yield (about 5-7%) of hexaphyrin has been constantly achieved by the treatment of the product mixture with NaBH<sub>4</sub> before the chromatographic separation. The reduced hexaphyrin was quantitatively oxidized back to its poorly soluble oxidized form upon treatment with DDQ. The reduced hexaphyrin exhibits two singlets at  $\delta = 15.39$  and 11.93 ppm in the <sup>1</sup>H NMR spectrum (Table 1) and a broad band at 492 nm ( $\varepsilon = 5.1 \times 10^4 \,\mathrm{M^{-1} \, cm^{-1}}$ ) without a Q-band-like absorption band, which suggests it has nonaromatic character (Figure 1). The structure of the reduced hexaphyrin has been revealed by X-ray crystallography to be [28]hexaphyrin (Scheme 2), with a twisted figure-of-eight-like



Scheme 1. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.



Scheme 2. Structures of selected meso-aryl-substituted perfluorinated porphyrins.

conformation consisting of two tripyrrolic "hemimacrocycles", in which the two tripyrrolic subunits are almost planar and the two planes are canted by approximately 60° (Figure 2).<sup>[9]</sup> It is interesting to note that a distinct alternation in the bond lengths of the  $\pi$ -electronic system is evident from the detailed analysis of its X-ray structure, and this is, to the best of our knowledge, the smallest expanded porphyrin that takes a twisted figure-of-eight conformation.

The heptaphyrin **4** exhibited a parent ion at m/z 1959 (calcd: m/z 1957) in the FABMS spectrum and quite simple

## Communications



Figure 2. X-ray crystal structure of [28]hexaphyrin 3. Top view (top) and side view (bottom).

<sup>1</sup>H NMR and <sup>19</sup>F NMR spectra (see below), which suggests it has a symmetric conformation in CDCl<sub>3</sub> solution, although its detailed X-ray structure has not been determined. The signals of the inner NH protons appear at  $\delta = 14.25$  and 11.34 ppm in the <sup>1</sup>H NMR spectrum of the compound, which suggests there is no specific ring current effect. The UV/Vis spectrum of heptaphyrin 4 exhibits an absorption band at 557 nm without any low-energy band. During many attempts to make single crystals, we found that 4 was converted slowly into its fused form (4-HF) in solutions containing methanol, as evident from the parent ion in the FAB mass spectrum. The fused form exhibited a parent molecular ion peak at m/z 1938, which was smaller than the original heptaphyrin by an equivalent of HF (m/z 20). Unlike the case with 4, it was possible to obtain crystals of the fused heptaphyirn 4-HF suitable for X-ray analysis (Figure 3).<sup>[10,11]</sup> The structure is a methanol adduct of N-fused [32]heptaphyrin, MeO-4-HF, in which the macrocycle adopts a twisted figure-of-eight-like conformation with a fused tripyrrolic ring formed by a nucleophilic substitution of the ortho fluorine atom by the inverted pyrrole nitrogen atom and with the  $\beta$ -fluorine atom of the fused pyrrole ring substituted by methanol. MeO-4-HF exhibits the bond alternation and shows signals for the inner NH protons at  $\delta = 13.59$ , 12.97, and 12.21 ppm, and its absorption spectrum is similar to that of nonfused heptaphyrin 4 with some bathochromic shifts. Collectively, N-fused



*Figure 3.* X-ray crystal structure of methanol-adduct of N-fused [32]heptaphyrin MeO-4–HF.

[32]heptaphyrins, **4**–HF and MeO-**4**–HF, can be considered to be non-aromatic.

The FAB mass spectrum of octaphyrin 5 (obtained from the reaction mixture) exhibits a molecular ion at m/z 2236 (calcd: m/z 2236) and the <sup>1</sup>H NMR spectrum shows four NH signals at  $\delta = 13.80, 12.42, 11.30, \text{ and } 7.95 \text{ ppm}$ . The UV/Vis spectrum shows broad bands at 401, 576, and 616 nm without noticeable Q-band-like transitions in the longer wavelength region. All these data suggest that it has a non-aromatic character that may be delineated as a  $36\pi$ -electronic system. The firm structural evidence for this supposition came from its X-ray crystal structure, which shows a cyclic ellipsoidal conformation, in which two sets of three pyrrole rings (1), (2), and (4)', and (1)', (2)', and (4), constitute a relatively planar arrangement but the pyrrole rings (3) and (3)' are largely canted from such planes (Figure 4).<sup>[12]</sup> As seen in the side view, the (3) and (3)' pyrrole rings are almost parallel with their nitrogen atoms pointing inward toward the center of the macrocycle. Of the eight pyrrole rings, the (1), (3), (1)', and (3)' rings bear hydrogen atoms while (2), (4), (2)', and (4)' do not. In line with the assignment as a 36π-electron nonaromatic system, the bond alternation of the conjugated double bonds is evident from the X-ray structure. It is interesting to note that the solid-state structure of the present [36] octaphyrin is a rare example, since most of the octaphyrin derivatives reported so far take figure-of-eight conformations.<sup>[2d,3b,13]</sup> This [36] octaphyrin was reduced to [38] octaphyrin upon stirring with NaBH<sub>4</sub>. This reduced octaphyrin exhibited a molecular ion peak at m/z 2238 (calcd: m/z2238) in the mass spectrum and showed a sharp Soret-like band at 681 nm ( $\varepsilon = 1.5 \times 105 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$ ) and Q-band-like absorptions at 907 and 1020 nm in the UV/Vis spectrum. The <sup>1</sup>H NMR spectrum revealed the presence of six NH signals at  $\delta$  = 7.95, 7.46, 7.19, 5.38, 5.31, and 5.23 ppm, while the <sup>19</sup>F NMR spectrum revealed 16 signals for the ortho F atoms, which suggests that the [38]octaphyrin has a nonsymmetric structure. In comparison to [28]hexaphyrin, the reoxidation of [38] octaphyrin with DDQ was found to be rather slow. The Xray structure of [38]octaphyrin shows a twisted macrocyclic

80





*Figure 4.* X-ray crystal structure of [36]octaphyrin **5**. Top view (top) and side view (bottom).



Figure 5. X-ray crystal structure of [38]octaphyrin (5 + 2 H).

conformation consisting of the two-edge iminopyrroles and the rest six aminopyrroles (Figure 5).<sup>[14]</sup>

An interesting correlation exists between the absorption spectral properties and the number of  $\pi$  electrons in the conjugated rings. The spectral characteristic for [4n]- $\pi$  electronic systems is the presence of only a single broad Soret-like band without Q-band-like low energy bands in the

**Table 1:** Selected physical data for [28]hexaphyrin, [32]heptaphyrin, N-fused [32]heptaphyrin, [36]octaphyrin, and [38]octaphyrin.

[28]hexaphyrin: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 303 K):  $\delta$  =15.39 (s, 2 H; NH), 11.93 ppm (s, 2 H; NH); <sup>19</sup>F NMR (470.40 MHz, CDCl<sub>3</sub>, 222 K, C<sub>6</sub>F<sub>6</sub>):  $\delta$  = -136.64 (d, <sup>3</sup>*J* = 18.3 Hz, 2 F; o-F), -137.54 (d, <sup>3</sup>*J* = 21.2 Hz, 2 F; o-F), -140.87 (d, <sup>3</sup>*J* = 21.2 Hz, 2 F; o-F), -141.12 (d, <sup>3</sup>*J* = 21.2 Hz, 2 F; o-F), -141.85 (brs, 2 F; o-F), -142.56 (brs, 2 F; o-F), -147.79 (t, <sup>3</sup>*J* = 18.3 Hz, 2 F; p-F), -148.08 (s, 2 F; \beta-F), -149.15 (t, <sup>3</sup>*J* = 21.6 Hz, 2 F; p-F), -149.38 (s, 2 F; \beta-F), -151.65 (t, <sup>3</sup>*J* = 21.2 Hz, 2 F; p-F), -153.87 (s, 2 F; β-F), -153.82 (s, 2 F; β-F), -154.37 (s, 2 F; β-F), -157.98 (t, <sup>3</sup>*J* = 24.5 Hz, 2 F; m-F), -160.16 (t, <sup>3</sup>*J* = 21.2 Hz, 2 F; m-F), -160.31 (s, 2 F; β-F), -160.50 (t, <sup>3</sup>*J* = 15.5 Hz, 2 F; m-F), -161.57 ppm (m, 6 F; m-F); UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ [m<sup>-1</sup>cm<sup>-1</sup>]) = 492 nm (51000); FABMS: *m/z* (% intensity): 1678 (100) [*M*<sup>+</sup>]

[32]heptaphyrin: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 296 K):  $\delta$  = 14.25 (2 H; NH), 11.34 ppm (s, 2 H; NH); <sup>19</sup>F NMR (470.40 MHz, CDCl<sub>3</sub>, 297 K, C<sub>6</sub>F<sub>6</sub>):  $\delta$  = -137.06 (d, <sup>3</sup>*J* = 21.2 Hz, 2 F; o-F), -138.97 (d, <sup>3</sup>*J* = 21.6 Hz, 2 F; o-F), -139.44 (m, 2 F; o-F), -140.44 (m, 6 F; o-F), -141.69 (d, <sup>3</sup>*J* = 27.8 Hz, 2 F; o-F), -146.00 (s, 2 F; β-F), -148.52 (s, 2 F; β-F), -149.26 (t, <sup>3</sup>*J* = 18.35 Hz, 2 F; p-F), -150.20 (t, <sup>3</sup>*J* = 21.6 Hz, 2 F; p-F), -150.33 (s, 2 F; β-F), -151.16 (t, <sup>3</sup>*J* = 18.35 Hz, 2 F; p-F), -151.63 (s, 2 F; β-F), -151.85 (t, <sup>3</sup>*J* = 21.2 Hz, F; p-F), -151.95 (s, 2 F; β-F), -153.71 (s, 2 F; β-F), -156.82 (s, 2 F; β-F), -159.77 (t, <sup>3</sup>*J* = 24.0 Hz, 2 F; m-F), -161.58 ~162.29 ppm (12 F; m-F); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ [m<sup>-1</sup> cm<sup>-1</sup>]) =557 (76000), 368 nm (64000); FABMS: *m/z* (% intensity): 1958 (100) [M<sup>+</sup>+H]

N-fused [32]heptaphyrin: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 296 K):  $\delta$  = 12.91 (1H; NH), 12.68 (s, 1H; NH), 11.82 ppm (s, 1H; NH); <sup>19</sup>F NMR (470.40 MHz, CDCl<sub>3</sub>, 297 K, C<sub>6</sub>F<sub>6</sub>):  $\delta$  = -136.70 (m, 3 F; *o*-F), -137.91 (d, <sup>3</sup>*J* = 18.3 Hz, 2 F; *o*-F), -140.05 (d, <sup>3</sup>*J* = 18.3 Hz, 1 F; *o*-F), -140.17 (d, <sup>3</sup>*J* = 21.2 Hz, 1 F; *o*-F), -140.54 (d, <sup>3</sup>*J* = 18.3 Hz, 2 F; *o*-F), -140.78 (2 F; *o*-F), -141.46 (d, <sup>3</sup>*J* = 18.3 Hz, 1 F; *o*-F), -141.66 (s, 1 F; β-F), -141.86 (s, 1 F; β-F), -142.50 (s, 2 F; β-F), -142.80 (d, <sup>3</sup>*J* = 9.41 Hz, 1 F; *o*-F), -145.63 (s, 1 F; β-F), -145.78 (s, 1 F; β-F), -146.65 (t, <sup>3</sup>*J* = 16.0 Hz, 1 F; *p*-F), -147.65 (t, <sup>3</sup>*J* = 18.3 Hz, 1 F; *p*-F), -148.34 (s, 1 F; β-F), -149.03 (s, 1 F; β-F), -149.50 (t, <sup>3</sup>*J* = 21.6 Hz, 1 F; *p*-F), -150.62 (t, <sup>3</sup>*J* = 21.6 Hz, 1 F; *p*-F), -150.95 (m, 2 F; *p*-F), -151.44 (t, <sup>3</sup>*J* = 21.6 Hz, 1 F; *p*-F), -152.80 (t, <sup>3</sup>*J* = 17.4 Hz, 1 F; *p*-F), -153.17 (s, 1 F; β-F), -154.76 (s, 1 F; β-F), -152.45 (s, 1 F; β-F), -158.57 (s, 2 F; β-F), -158.72 (s, 1 F; β-F), -160.44 -162.55 ppm (14 F; *m*-F); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 385, 607 nm; FABMS: *m/z* (% intensity): 1938 (100) [*M*<sup>+</sup>]

[36]octaphyrin: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 223 K):  $\delta$ =13.79 (s, 1 H; NH), 12.42 (s, 1 H; NH), 11.30 (1 H; NH), 7.97 ppm (1 H; NH); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ [m<sup>-1</sup>cm<sup>-1</sup>])=616 (68 000), 576 (74 000), 401 nm (53 000); FABMS: *m/z* (% intensity): 2236 (100) [*M*<sup>+</sup>]

[38]octaphyrin: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 296 K):  $\delta = 7.96$  (1 H; NH), 7.46 (s, 1H; NH), 7.19 (s, 1H; NH), 5.39 (1H; NH), 5.31 (s, 1H; NH), 5.23 ppm (s, 1 H; NH); <sup>19</sup>F NMR (470.40 MHz, CDCl<sub>3</sub>, 297 K, C<sub>6</sub>F<sub>6</sub>):  $\delta =$ -135.72 (d,  ${}^{3}J = 24.5$  Hz, 1 F; o-F), -136.56 (d,  ${}^{3}J = 21.2$  Hz, 1 F; o-F), -136.68 (d,  ${}^{3}J = 18.3$  Hz, 1F; o-F), -137.12 (d,  ${}^{3}J = 21.2$  Hz, 1F; o-F), -139.62 (d,  ${}^{3}J = 21.2$  Hz, 1F; o-F), -139.80 (d,  ${}^{3}J = 21.6$  Hz, 1F; o-F), -140.43 (d,  ${}^{3}J = 21.6$  Hz, 1F; o-F), -140.92 (d,  ${}^{3}J = 27.8$ , 1F; o-F), -141.88 (m, 2F; o-F), -142.34 (brs, 1F; o-F), -142.70 (d, <sup>3</sup>J=24.5 Hz, 1F; o-F), -143.65 (brs, 1F; o-F), -145.13 (brs, 1F; o-F), -147.10 (brs, 1 F; o-F), -147.60 (m, 1 F; o-F), -148.95 (s, 1 F;  $\beta$ -F), -149.42 (t,  $^{3}J =$ 33.9 Hz, 5 F; *p*-F), -149.72 (s, 1 F; β-F), -150.48 (s, 5 F; β-F), -151.09 (t, <sup>3</sup>*J* = 18.3 Hz, 1 F; *p*-F), -151.46 (t, <sup>3</sup>*J* = 18.3 Hz, 1 F; *p*-F), -151.56 (s, 1 F;  $\beta$ -F), -151.94 (t,  ${}^{3}J$  = 21.6 Hz, 1 F; p-F), -152.53 (s, 1 F;  $\beta$ -F), -153.71 (s, 1 F; β-F), -154.69 (s, 1 F; β-F), -155.18 (s, 1 F; β-F), -157.20 (s, 1 F; β-F), -157.42 (s, 1F;  $\beta$ -F), -158.21 (s, 1F;  $\beta$ -F), -164.18 (s, 1F;  $\beta$ -F), -158.41 - 163.84 ppm (16 F; *m*-F); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  $(\varepsilon[M^{-1}cm^{-1}]) = 681 \text{ nm} (154000); \text{ FABMS: } m/z (\% \text{ intensity}): 2238$ (100) [M<sup>+</sup>]

## Communications

UV/Vis spectrum ([28]hexaphyrin, [32]heptaphyirn, and [36]octaphyrin), whereas the  $[4n+2]-\pi$  electronic systems have a remarkably sharp Soret-like band with several Q-band-like low energy absorption bands ([26]hexaphyrin and [38]octaphyrin). This trend seems to suggest that the Hückel rule may still be valid for the prediction of absorption properties of the *meso*-aryl-substituted expanded porphyrins. However, the upfield shifts for the inner NH protons of [38]octaphyrin are only modest, thus not indicating a strong ring current. The detailed analysis of the X-ray structure has revealed an alternation in the bond length of this octaphyrin, thus posing a question on the aromaticity of this large expanded porphyrin macrocycle.

In summary, a range of perfluorinated meso-aryl-substituted expanded porphyrins are readily formed from the reaction of 3,4-difluropyrrole and pentafluorobenzaldehyde followed by the oxidation with DDQ. Of these, the solid-state structures of the perfluorinated [28]hexaphyrin and [36]octaphyrin are markedly different from those of their β-H counterparts. The [36]octaphyrin has been reduced with NaBH4 to [38]octaphyrin and generated large structural changes. Furthermore, the perfluorinated heptaphyrin has been shown to be readily converted into its fused form upon treatment with alcohol. The absorption spectral characteristics have been found to be a function of the number of  $\pi$  electrons. The porphyrin-like sharp Soret band and lowenergy Q-band-like bands are observed for macrocycles with [4n+2]- $\pi$  electrons, which do not exhibit a strong ring current effect. The applications of these perfluorinated expanded porphyrins as robust oxidation catalysts and as long-wavelength absorbing dyes are interesting future targets and such studies are actively in progress.

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- [8] This pentaphyrin product was considered to be a fused pentaphyrin as judged from its parent ion signal (m/z 1379) on the basis of FABMS, see ref. [3a]. We, however, noted the formation of nonfused pentaphyrin, the complete characterization of which could not be carried out because of its instability.
- [9] Crystal data of [28]hexaphyrin **3**:  $C_{66}H_4F_{42}N_6$ ,  $M_r = 1678.7(1)$ , triclinic, space group  $P\bar{I}$ , a = 11.5000(5), b = 14.7625(9), c = 19.673(1) Å,  $\alpha = 71.876(1)$ ,  $\beta = 83.702(2)$ ,  $\gamma = 86.999(2)^{\circ}$ , V = 3154.4(3) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.822$  g cm<sup>-3</sup>, T = 123 K, crystal size  $0.50 \times 0.20 \times 0.10$  mm<sup>3</sup>, R = 0.071,  $R_w = 0.081$ , GOF = 2.177 for 10238 reflections with  $I > 2.0\sigma(I)$ . CCDC-185842 (**3**), CCDC-185846 (MeO-**4**-HF), CCDC-185847 (**5**), and CCDC-190412 (**5**+2H) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).
- [10] Crystal data of methanol-adduct of N-fused [32]heptaphyrin MeO-4–HF: C<sub>78</sub>H<sub>6</sub>F<sub>47</sub>N<sub>7</sub>O,  $M_r$ =1949.8(5), triclinic, space group  $P\bar{I}$ , a=14.4773(7), b=16.305(2), c=17.212(2) Å, a=96.39(1),  $\beta$ =110.150(4),  $\gamma$ =92.28(1)°, V=3777.4(7) Å<sup>3</sup>, Z=2,  $\rho_{calcd}$ = 1.807 g cm<sup>-3</sup>, T=123 K, crystal size 0.10×0.10×0.05 mm<sup>3</sup>, R= 0.092,  $R_w$ =0.094, GOF=0.120 for 8688 reflections with  $I > 2.0\sigma(I)$ .
- [11] In a similar manner, the single crystals of a fused heptaphyrin obtained from a solution of  $CH_2Cl_2$  and *i*PrOH showed the almost same crystal structure (see Supporting Information).
- [12] Crystal data of [36]octaphyrin **5**: C<sub>88</sub>H<sub>4</sub>F<sub>56</sub>N<sub>8</sub>,  $M_r$ =2235.9(7), triclinic, space group  $P\bar{1}$ , a=11.0672(2), b=13.8090(9), c=19.033(1) Å, a=93.641(2),  $\beta$ =96.243(4),  $\gamma$ =108.931(3)°, V=2719.9(2) Å<sup>3</sup>, Z=1,  $\rho_{calcd}$ =1.720 gcm<sup>-3</sup>, T=123 K, crystal size 0.50 × 0.25 × 0.25 mm<sup>3</sup>, R=0.081,  $R_w$ =0.087, GOF=2.366 for 9209 reflections with  $I > 2.0\sigma(I)$ .
- [13] Quite recently, a completely flat ring-shape [30]octaphyrin(0.0.0.0.0.0.0) was reported, see: ref. [2h].
- [14] Crystal data of [38]octaphyrin (5+2H):  $C_{88}H_6F_{56}N_8$ ,  $M_r$ = 2237.9(8), triclinic, space group  $P\bar{I}$ , a = 13.839(2), b = 18.629(2), c = 19.712(2) Å, a = 61.763(3),  $\beta = 74.599(5)$ ,  $\gamma = 71.470(8)^\circ$ , V =4204.4(9) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.802$  g cm<sup>-3</sup>, T = 123 K, crystal size  $0.20 \times 0.20 \times 0.05$  mm<sup>3</sup>, R = 0.084,  $R_w = 0.104$ , GOF = 1.216 for 5530 reflections with  $I > 2.0\sigma(I)$ .