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Facile Synthesis of Large *meso*-Pentafluorophenyl-Substituted Expanded Porphyrins

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Acid-catalyzed condensation of *meso*-pentafluorophenyl dipyrromethane **1** (100 mM) and pentafluorobenzaldehyde **2** (100 mM) at 0 °C gave a series of expanded porphyrins with even number of pyrrolic subunits up to octadecaphyrin-(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1) **18** in improved yields, particularly for larger expanded porphyrins. The solid-state structure of decaphyrin(1.1.1.1.1.1.1.1.1.1) **10** was revealed by X-ray diffraction analysis to be a crescent-like conformation. The Soret-like absorption bands are increasingly redshifted as the size of the ring increases, but such a trend becomes nearly saturated for hexadecaphyrin-(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1) **16** and **18**, which exhibit bands in the near-infrared region at 939 and 953 nm, respectively.

Introduction

In recent years, there has been a growing interest in the chemistry of expanded porphyrins that consist of more than five conjugated pyrrolic rings or heterocyclic congeners, as expanded porphyrins display attractive properties such as conformational flexibility, multitude of oxidation states, multiple metalation, small HOMO–LUMO gaps, absorption bands reaching the near-infrared region, large two-photon absorption cross sections, and facile aromatic–antiaromatic switching upon two-electron oxidation and reduction processes.[1] A promising and challenging direction is to explore larger expanded porphyrins with the hope of finding novel functions and properties that arise from the expansion of the π conjugation.[2] However, the synthesis of large expanded porphyrins is not easy and often needs lengthy tedious steps and repeated separation. Despite these difficulties, remarkably large expanded porphyrins were synthesized by Vogel,[3] Sessler,[2a,4] Chandrashekar,[5] and Setsune[6] so far.

Among these expanded porphyrins, we reported a facile synthesis of a series of *meso*-pentafluorophenyl-substituted expanded porphyrins under modified Rothemund–Lindsey conditions either from acid-catalyzed condensation of pyrrole and pentafluorobenzaldehyde **2**[7a,7b] or from dipyrromethane **1**[8] and **2** in a size-selective manner.[7c,7d] High concentrations of the substrates (67 mM each), about tenfold of the recommended concentrations for porphyrin synthesis,[9] were crucial for the effective formation of the expanded porphyrins.[7] These expanded porphyrins are fully conjugated macrocycles with regular alternating arrangements of the pyrrole and methine carbon atoms, and they exhibit structural diversity,[10] intriguing linear and nonlinear optical properties,[11] multiple metalations that afford unique metal complexes with notable metal–metal interactions,[12] and unprecedented chemical reactivities.[13] [26]Hexaphyrin **6** first reported by Cavaleiro in 1999[14] is an aromatic molecule that takes a planar and rectangular shape and exhibits a strong diatropic ring current. This macrocycle coordinates two metal ions in many ways to provide various bis(metalated) complexes[15] and exhibits several unique reactivities.[13,16] [32]Heptaphyrin **7** undergoes sequential N-fusion reactions to finally give a quadruply N-fused heptaphyrin[17a] and, upon cooperative Cu^{II} and B^{III} metalation, gives tris(pentafluorophenyl)-substituted boron(III) subporphyrin along with Cu^{II} tetrakis(pentafluorophenyl)porphyrin.[17b] [36]Octaphyrin **8** is an interesting macrocycle, as its bis[copper(II)] complex undergoes an amazing splitting reaction to afford quantitatively two copper(II) porphyrins upon heating by a formal metathesis-like topological process.[18] [40]Nonaphyrin **9** displays unique metalation behavior by accommodating a Zn^{II} ion and two Pd^{II} ions in a cooperative fashion.[19] Furthermore, we recently reported that Pd^{II} complexes of **6**, **7**, and **8** take Möbius topology and exhibit distinct Möbius aromaticity.[20] These results amply demonstrated the novel chemistry of *meso*-aryl-expanded porphyrins, but larger expanded porphyrins have been only poorly studied mainly due to their synthetic difficulties.

Here we explored the synthesis of larger expanded porphyrins by employing more concentrated solutions of the substrates at low temperature.

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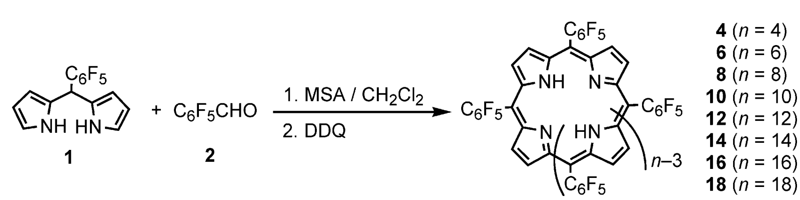
Results and Discussion

Initially, we examined the concentration effect upon the yields of expanded porphyrins. Upon an increase in the concentrations of **1** and **2** from 33.3 mM to 100 mM, the yields of porphyrin **4** and hexaphyrin **6** decreased, but the yields of larger expanded porphyrins **8**–**18** increased slightly (Table 1, Runs 1 and 2; Scheme 1). Further increase in the concentrations to 200 mM caused an overall decrease in the yields of the expanded porphyrins owing to increased formation of polymerized material under the concentrated conditions (Table 1, Run 3). To suppress the possible scrambling of expanded porphyrinogen precursors, the reaction temperature was decreased whilst keeping the concentrations of the substrates at 100 mM (Table 1, Runs 4 and 5). In the meantime, we found the reaction conditions (Table 1, Run 5) that allowed the formation of large expanded porphyrins in improved yields. Production of expanded porphyrins up to octadecaphyrin was indicated by MALDI-TOF mass analysis of the reaction mixture (Figure 1). Separation of the reaction mixture was performed as following: (1) initial elution of the reaction mixture by using a 1:4 mixture of CH_2Cl_2/*n*-hexane as an eluent separated **4** (1.1%), **6** (8.6%), and **8** (10.2%) from the rest of the larger expanded porphyrin products; (2) second elution by using a gradient mixture of ethyl acetate/*n*-hexane from 1:19 to 1:4 allowed the separation of the larger expanded porphyrins in the following order: decaphyrin **10** (5.5%) as a dark yellow-green fraction, tetradecaphyrin **14** (1.5%) as a dark-green fraction, octadecaphyrin **18** (0.8%) as a dark-purple fraction, dodecaphyrin **12** (1.1%) as a reddish-brown fraction, and hexadecaphyrin **16** (1.2%) as a dark-red fraction. The yields of the expanded porphyrins were small but reproducible. These expanded porphyrins are stable under aerobic conditions either in solution or the solid state, and they were characterized by electrospray-ionization time-of-flight high-

Table 1. Conditions and yields of the synthesis of **4**–**18**.

Run	Concentration [mM]	Temperature [°C]	**4** [%]	**6** [%]	**8** [%]	**10** [%]	**12** [%]	**14** [%]	**16** [%]	**18** [%]
1	33.3	20	9.8	15.9	7.6	2.8	0.1	0.6	trace	–
2	100	20	3.1	10.4	7.8	4.8	0.7	1.2	0.6	0.1
3	200	20	1.5	10.0	5.6	3.4	0.6	1.0	0.2	0.2
4	100	–10	0.6	4.1	6.3	3.2	0.9	0.6	0.4	0.1
5	100	0	1.1	8.6	10.2	5.5	1.1	1.5	1.2	0.8



Scheme 1. Synthesis of expanded porphyrins **4**–**18**.

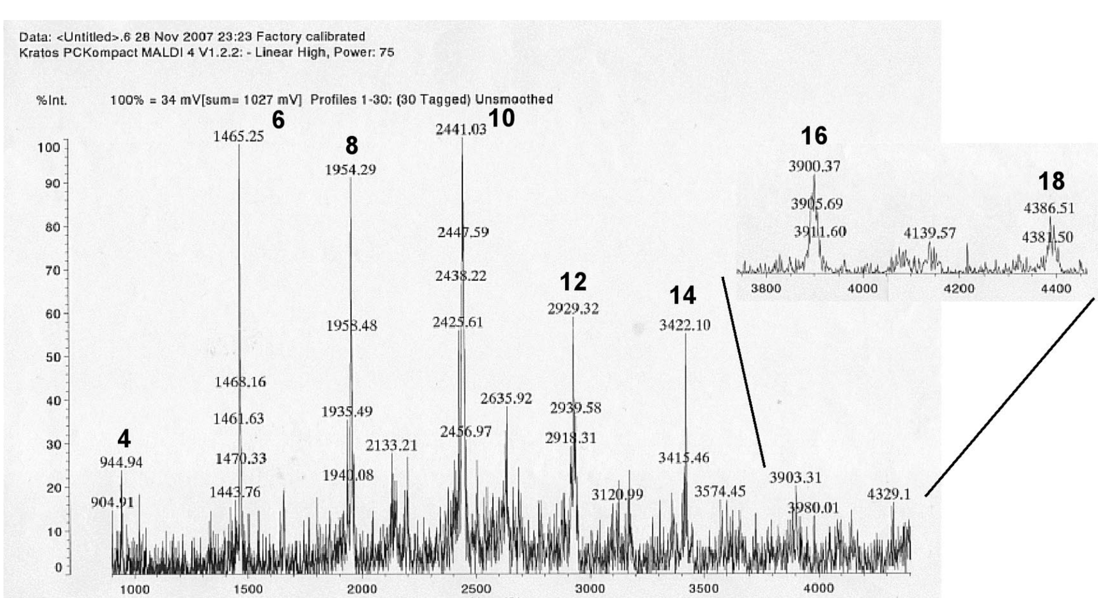


Figure 1. MALDI-TOF mass spectrum of the reaction mixture of expanded porphyrins.

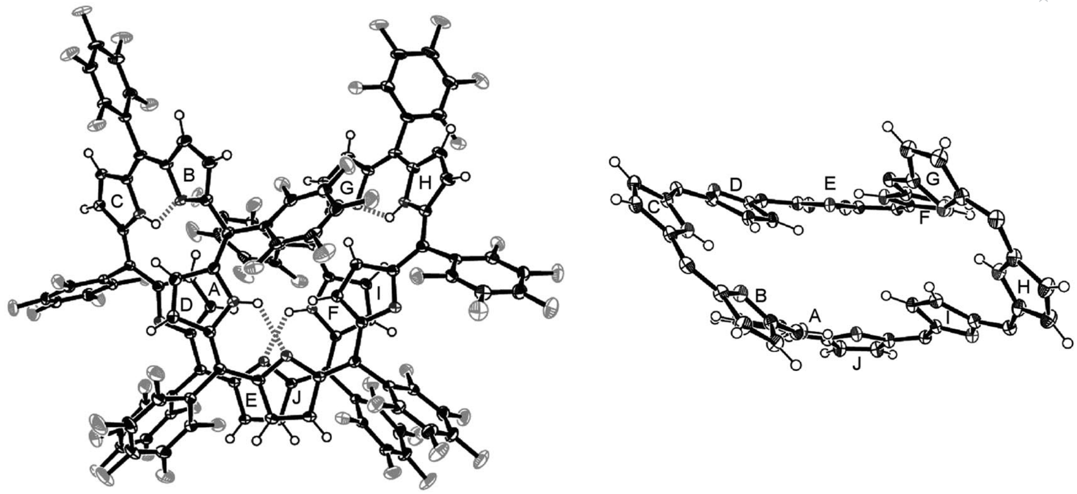


Figure 2. Crystal structure of **10** with intramolecular hydrogen-bonding network: top view (left) and side view (right). Thermal ellipsoids were scaled to the 50% probability level; *meso*-pentafluorophenyl substituents were omitted for clarity for the side view.

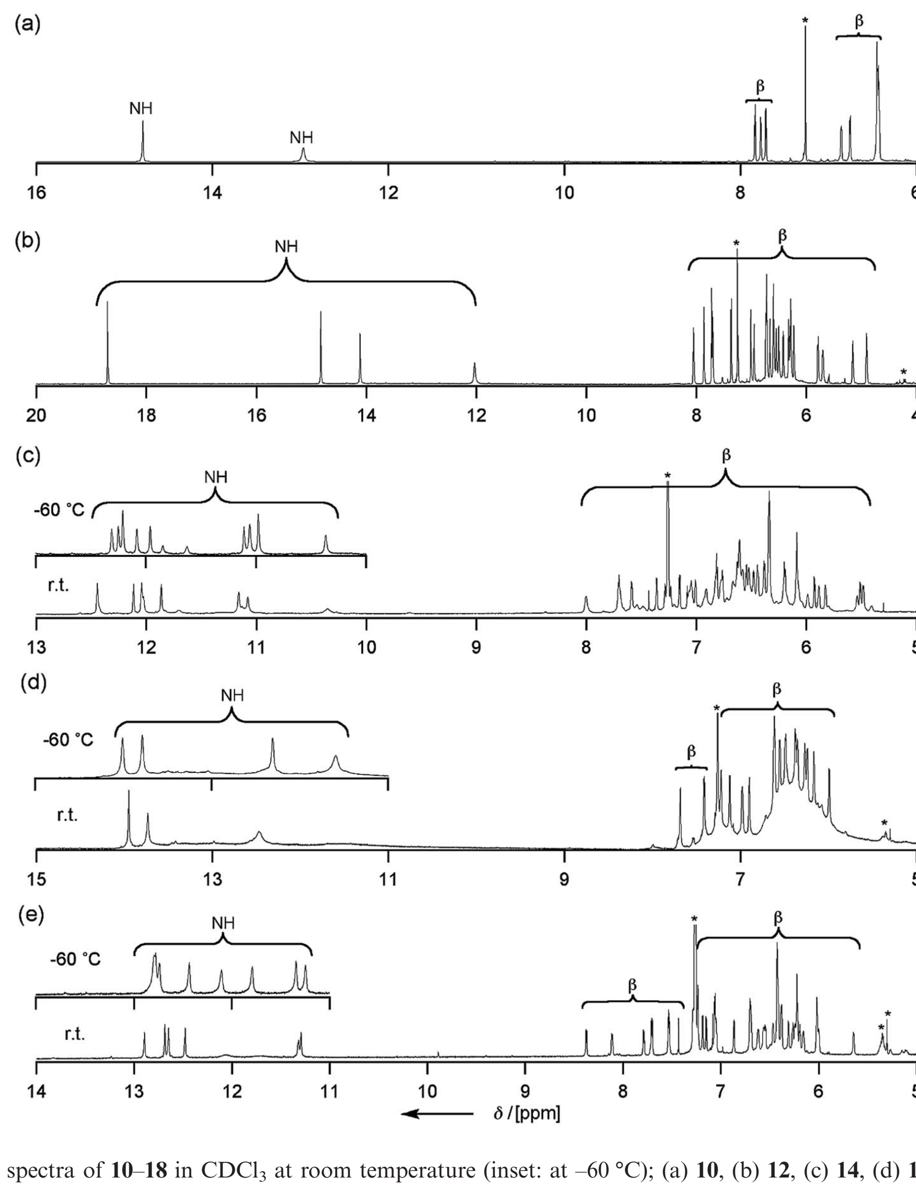


Figure 3. ^{1}H NMR spectra of **10**–**18** in $CDCl_3$ at room temperature (inset: at –60 °C); (a) **10**, (b) **12**, (c) **14**, (d) **16**, and (e) **18**. *Solvent and impurities.

resolution mass spectrometry [HRMS (ESI-TOF)], and NMR and UV/Vis absorption spectroscopic measurements.

Fortunately, we obtained nice crystals of **10** suitable for X-ray diffraction analysis by slow diffusion of *n*-heptane vapor into its benzene solution. The solid-state structure of **10** reveals a C_2-symmetric crescent-like conformation that is supported with the aid of an intramolecular hydrogen-bonding network (Figure 2). As judged from the C–N–C bond angles, the pyrrole rings A, C, F, and H (110.20–110.78°) are amino-type pyrrole units, and the pyrrole rings B, D, E, G, I, and J (105.37–106.45°) are imino-type pyrrole units, which leads to the formulation of **10** as a 44π-electron-conjugated macrocycle. This macrocycle consists of four dipyrromethene units, B–C, E–F, G–H, and J–A, which are held by hydrogen bonds to form almost planar subunits with mean plane deviations of 0.049 Å for unit B–C, 0.085 Å for unit E–F, 0.030 Å for unit G–H, and 0.065 Å for unit J–A; the remaining pyrrole rings D and I are inverted without hydrogen-bonding interactions to other pyrrole rings. Its C_2-symmetric conformation is kept in the solution state, as judged by its ^1H NMR spectrum, which exhibits 2 signals due to NH protons at δ = 14.79 and

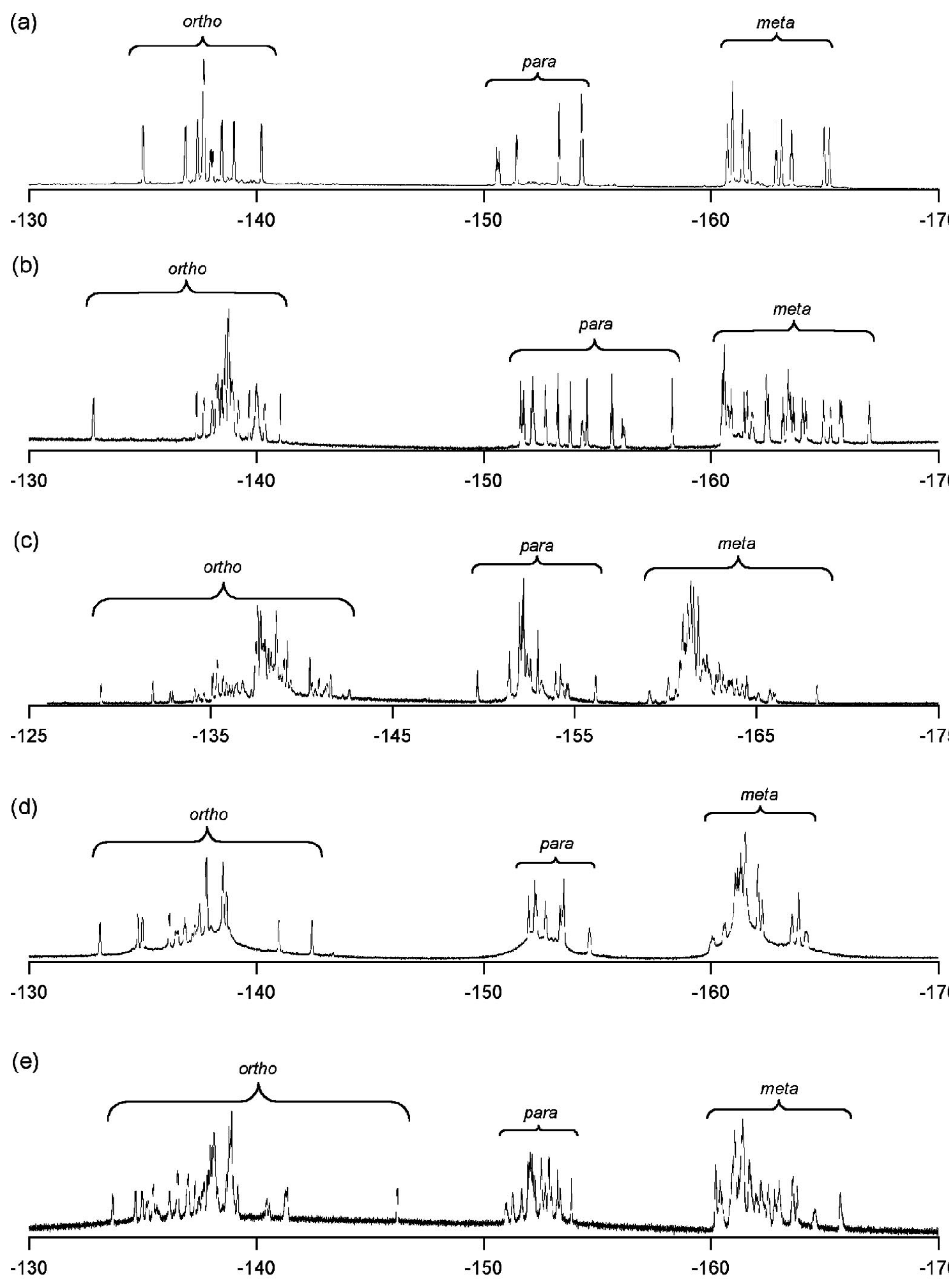


Figure 4. ^{19}F NMR spectra of **10**–**18** in $CDCl_3$ at room temperature; (a) **10**, (b) **12**, (c) **14**, (d) **16**, and (e) **18**.

12.97 ppm and 6 signals due to pyrrole β protons at 7.83, 7.76, 7.71, 6.85, 6.75, and 6.43 ppm (Figure 3a), and by its ^{19}F NMR spectrum, where 5 sets of aryl *para*-fluorine signals and 10 sets of aryl *ortho*- and *meta*-fluorine signals can be seen (Figure 4a). The HRMS (ESI-TOF) revealed a parent ion peak at m/z = 2434.1375 (calcd. for $C_{110}H_{23}F_{50}N_{10}$ [M – H]$^-$ 2434.1346), which also supports its assignment as [44]decaphyrin(1.1.1.1.1.1.1.1.1.1) (Figure 5).

The HRMS (ESI-TOF) revealed the parent ion peak of **12** at m/z = 2920.1550 (calcd. for $C_{132}H_{27}F_{60}N_{12}$ [M – H]$^-$ 2920.1561), and the ^{1}H NMR spectrum of **12** displays 4 signals due to the NH protons at 18.7, 14.8, 14.1, and 12.0 ppm and 21 signals due to the β-CH protons at 8.05, 7.87, 7.72, 7.37, 7.01, 6.96, 6.74, 6.72, 6.66, 6.60, 6.55, 6.50, 6.42, 6.33, 6.30, 6.28, 6.23, 5.79, 5.70, 5.15, and 4.91 ppm (Figure 3b), which thus indicates the formation of a macrocycle composed of 20 pyrrole units with a 52π electronic system.[21] Its ^{19}F NMR spectrum shows 20 triplet signals assigned to aryl *para*-fluorine atoms at –151.63 to –158.30 ppm (Figure 4b). These data indicate its nonsymmetric conformation and suggest its formulation as [52]dodecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1). The absence of particular high-field-shifted proton signals suggests its nonaromatic character due to its nonplanar conformation, and the observed relatively sharp ^{1}H and ^{19}F NMR spectra indicate that **12** takes a stable single conformation at room temperature.

The ^{1}H NMR spectrum of **14** shows a complicated feature that includes six NH proton signals at 12.45, 12.12, 12.04, 11.86, 11.16, and 11.08 ppm with a minor set of signals at room temperature and at –60 °C (Figure 3c). Thus, **14** may have several conformations even at –60 °C. The ^{19}F NMR spectrum also displays an intricate signal pattern,

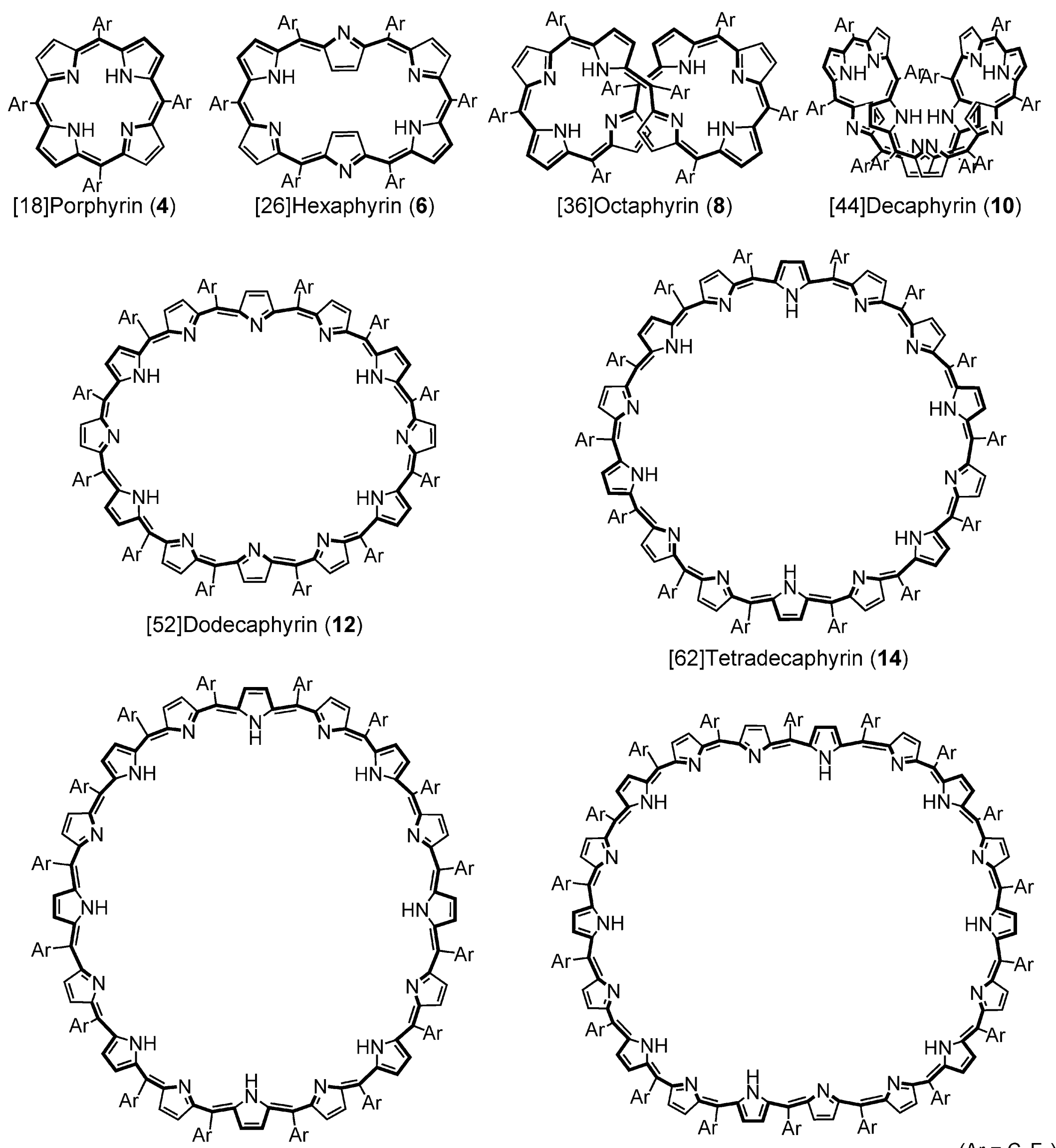


Figure 5. Structures of porphyrin **4** and expanded porphyrins **6**–**18**. Those for **12**–**18** are plausible π-conjugation networks.

which suggests its nonsymmetric conformation and the existence of minor conformers (Figure 4c). These NMR spectroscopic data, as well as its HRMS (ESI-TOF) where the parent ion peak was observed at m/z = 1703.5998 (calcd. for $C_{154}H_{32}F_{70}N_{14}$ $[M - 2H]^{2-}$ 1703.5930), allowed us to assign **14** as [62]tetradecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1.1.1).

The HRMS (ESI-TOF) revealed parent ion peaks of **16** and **18** at m/z = 1947.6161 (calcd. for $C_{176}H_{38}F_{80}N_{16}$ $[M - 2H]^{2-}$ 1947.6155) and at m/z = 2191.1253 (calcd. for $C_{198}H_{42}F_{90}N_{18}$ $[M - 2H]^{2-}$ 2191.1239), respectively. Although the signals in the ^1H NMR spectra of **16** and **18** are too broad to be analyzed at room temperature, their signals become sharper when the temperature is lowered. The ^1H NMR spectrum of **16** at –60 °C revealed that this macrocycle displays four signals assigned for pyrrole NH protons at 14.01, 13.78, 12.31, and 11.59 ppm, each corresponding to two protons (Figure 3d). In addition to these ^1H NMR spectroscopic data, a relatively simple ^{19}F NMR signal pattern, which contains eight sets of fluorine signals (Figure 4d) suggests that **16** has a symmetric conformation. In contrast, **18** shows a ^1H NMR signal pattern where eight pyrrole NH signals are observed at 12.79, 12.77, 12.73, 12.43, 12.10, 11.78, 11.34, and 11.24 ppm at –60 °C (Figure 3e), which suggests its nonsymmetric conformation. The NMR spectroscopic data display no minor sets of signals, which suggests that, unlike **14**, compounds **16** and **18** adopt one stable conformation, and these NMR studies are consistent with the mass analyses. In both cases, the pyrrolic β protons appear in the range 5–9 ppm, which is indicative of nonaromatic character. These data reveal the formulation of [72]hexadecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1) for **16** and [80]octadecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1) for **18**.

Figure 6 shows the absorption spectra of **4**, **6**, **8**, **10**, **12**, **14**, **16**, and **18** in CH_2Cl_2. Whereas porphyrin **4** and hexaphyrin **6** display spectra characteristic of aromatic macrocycles featuring strong and sharp Soret bands and Q-band-like bands, the other larger expanded porphyrins exhibit much broader spectra without Q-band-like bands, which are characteristic of nonaromatic expanded porphyrins.

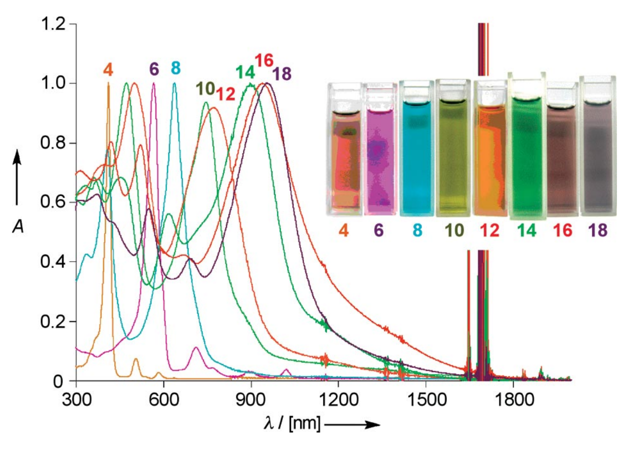


Figure 6. UV/Vis absorption spectra of **4**–**18** in CH_2Cl_2 normalized at their respective Soret-like bands and pictures of their CH_2Cl_2 solutions.

This nonaromatic character seemingly arises from distorted nonplanar conformations, which are often found in larger expanded porphyrins. A figure-eight conformation was revealed for **8**,[7a] a crescent-like conformation was revealed here for **10**, and similar nonplanar conformations are also expected for **12**–**18**. As the size of the expanded porphyrin increases, the absorption bands are redshifted: 411 nm for **4**, 567 nm for **6**, 638 nm for **8**, 746 nm for **10**, 773 nm for **12**, 892 nm for **14**, 939 nm for **16**, and 953 nm for **18**. Their absorption maxima indicate progressive redshifting as the number of the pyrrolic units is increased until it reaches saturation for the larger expanded porphyrins. Interestingly, the Soret-like bands of **14**, **16**, and **18** enter into the near-infrared region.

Conclusion

We confirmed the formation of expanded porphyrins up to octadecaphyrin **18**. Further studies of these expanded porphyrins with regard to aromaticity, multiple oxidation states, metal complexation, and ion sensing are actively in progress in our laboratory.

Experimental Section

General: Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry CH_2Cl_2 was obtained by refluxing and distillation over CaH_2. Silica-gel column chromatography was performed on Wakogel C-200, C-300, or C-400. Alumina column chromatography was performed on Sumitomo Active alumina or Merck aluminum oxide 90 active neutral. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck 5554). UV/Vis spectra were recorded with a Shimadzu UV-3100PC spectrometer. ^1H and ^{19}F NMR spectra were recorded with a JEOL ECA-600 spectrometer (operating at 600.17 MHz for ^1H and 564.73 MHz for ^{19}F) by using the residual solvent as the internal reference for ^1H ($CDCl_3$: δ = 7.260 ppm) and hexafluorobenzene as the external reference for ^{19}F (δ = –162.9 ppm). Mass spectra were recorded with a Shimadzu KRATOS KOMPACT MALDI4 by using the positive-MALDI-TOF method and with a BRUKER microTOF LC by using the ESI-TOF method in the negative ion mode in an acetonitrile solution. Single-crystal diffraction analysis data were collected at –153 ± 1 °C with a Bruker SMART diffraction by using graphite monochromated Mo-K_α radiation (λ = 0.71069 Å) to a maximum 2θ value of 56.6°.

***meso*-Pentafluorophenyl-Substituted Expanded Porphyrins (4–18):** A solution of pentafluorobenzaldehyde (3 mmol, 100 mM) and dipyrromethane (3 mmol, 100 mM) in CH_2Cl_2 (30 mL) was placed in a 100 mL round-bottomed flask under an atmosphere of nitrogen at 0 °C. To the solution was added methanesulfonic acid (MSA; 2.5 M in CH_2Cl_2, 120 µL), and the resulting solution was stirred for 2 h. After the addition of DDQ (1.36 g, 6 mmol), the solution was stirred for 10 h and then passed through a short alumina column to remove the tar. The reaction mixture was separated by silica-gel column chromatography (CH_2Cl_2/n-hexane, 1:4; then AcOEt/n-hexane, 1:19→1:4) to give [18]porphyrin (**4**; 16 mg, 1.1 %), [26]hexaphyrin (**6**; 126 mg, 8.6 %), [36]octaphyrin (**8**; 149 mg, 10.2 %), [44]decaphyrin (**10**; 74 mg, 5.5 %), [52]dodecaphyrin (**12**; 16 mg, 1.1%), [62]tetradecaphyrin (**14**; 21 mg, 1.5%), [72]hexadecaphyrin (**16**; 18 mg, 1.2%), and [80]octadecaphyrin (**18**; 12 mg, 0.8%).

***meso*-Pentafluorophenyl-Substituted [44]Decaphyrin(1.1.1.1.1.1.1.1.1.1) (10):** ^{1}H NMR (600.17 MHz, $CDCl_3$, r.t.): δ = 14.79 (br. s, 2 H, NH), 12.97 (br. s, 2 H, NH), 7.83 (d, J = 4.6 Hz, 2 H), 7.76 (d, J = 4.1 Hz, 2 H), 7.71 (d, J = 5.0 Hz, 2 H), 6.85 (d, J = 4.6 Hz, 2 H), 6.75 (d, J = 4.1 Hz, 10 H), 6.43 (m, 10 H) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$, r.t.): δ = –135.03 (d, J = 20.1 Hz, 2 F, *o*-F), –136.91 (d, J = 25.6 Hz, 2 F, *o*-F), –137.44 (d, J = 23.8 Hz, 2 F, *o*-F), –137.72 (d, J = 22.0 Hz, 6 F, *o*-F), –138.05 (dd, J = 23.8 Hz, J = 60.0 Hz, 2 F, *o*-F), –138.50 (d, J = 20.2 Hz, 2 F, *o*-F), –139.04 (d, J = 23.8 Hz, 2 F, *o*-F), –140.26 (d, J = 22.0 Hz, 2 F, *o*-F), –150.65 (dt, J = 22.0 Hz, J = 58.6 Hz, 2 F, *p*-F), –151.47 (t, J = 20.2 Hz, 2 F, *p*-F), –153.34 (t, J = 22.0 Hz, 2 F, *p*-F), –154.31 (t, J = 22.0 Hz, 2 F, *p*-F), –154.37 (t, J = 22.0 Hz, 2 F, *p*-F), –160.75 (t, J = 22.0 Hz, 2 F, *m*-F), –160.97 (t, J = 23.8 Hz, 4 F, *m*-F), –161.40 (t, J = 22.0 Hz, 2 F, *m*-F), –161.72 (br. s, 2 F, *m*-F), –162.89 (t, J = 23.8 Hz, 2 F, *m*-F), –163.13 (t, J = 22.0 Hz, 2 F, *m*-F), –163.57 (t, J = 22.0 Hz, 2 F, *m*-F), –165.00 (t, J = 22.0 Hz, 2 F, *m*-F), –165.23 (t, J = 20.2 Hz, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 361 (63200), 473 (93300), 745 (88000) nm. HRMS (ESI-TOF–): calcd. for $C_{110}H_{23}F_{50}N_{10}$ [M – H]$^-$ 2434.1346; found 2434.1375. Crystallographic data: $C_{132}H_{66}F_{50}N_{10}$, M_w = 2741.95, triclinic, space group $P\bar{1}$ (No. 2), a = 16.3373(13) Å, b = 18.1522(14) Å, c = 22.7004(18) Å, α = 86.3690(10)°, β = 70.7440(10)°, γ = 68.2890(10)°, V = 5891.3(8) Å^3, $D_{calcd.}$ = 1.546 g cm^{-3}, Z = 2, R = 0.0575, R_1 [$I > 2.0\sigma(I)$] = 0.1655, GOF = 1.024. CCDC-647365 contains 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.

***meso*-Pentafluorophenyl-Substituted [52]Dodecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1) (12):** ^{1}H NMR (600.17 MHz, $CDCl_3$, r.t.): δ = 18.71 (s, 1 H, NH), 14.83 (s, 1 H, NH), 14.12 (s, 1 H, NH), 12.03 (s, 1 H, NH), 8.05 (t, J = 3.7 Hz, 1 H), 7.87 (d, J = 4.6 Hz, 1 H), 7.72 (dd, J = 4.6 Hz, J = 14.7 Hz, 2 H), 7.37 (d, J = 4.6 Hz, 1 H), 7.01 (d, J = 5.5 Hz, 1 H), 6.96 (d, J = 4.6 Hz, 1 H), 6.74 (d, J = 4.6 Hz, 1 H), 6.72 (t, J = 5.5 Hz, 2 H), 6.66 (d, J = 4.6 Hz, 1 H), 6.60 (t, J = 5.5 Hz, 1 H), 6.55 (d, J = 4.6 Hz, 1 H), 6.50 (d, J = 4.6 Hz, 1 H), 6.42 (br. s, 1 H), 6.33 (d, J = 3.7 Hz, 1 H), 6.30 (d, J = 3.7 Hz, 1 H), 6.28 (d, J = 4.7 Hz, 1 H), 6.23 (t, J = 3.7 Hz, 1 H), 5.79 (d, J = 4.2 Hz, 1 H), 5.70 (br. s, 1 H), 5.15 (d, J = 4.6 Hz, 1 H), 4.91 (d, J = 5.5 Hz, 1 H) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$, r.t.): δ = –132.83 (d, J = 23.1 Hz, 1 F, *o*-F), –137.37 (d, J = 24.2 Hz, 1 F, *o*-F), –137.68 (m, 1 F, *o*-F), –138.05 (br. s, 1 F, *o*-F), –138.26 (m, 3 F, *o*-F), –138.49 (t, J = 25.3 Hz, 2 F, *o*-F), –138.63 (t, J = 26.4 Hz, 2 F, *o*-F), –138.80 (m, 3 F, *o*-F), –138.93 (m, 3 F, *o*-F), –139.21 (br. s, 1 F, *o*-F), –139.69 (t, J = 19.7 Hz, 1 F, *o*-F), –140.01 (t, J = 19.7 Hz, 3 F, *o*-F), –140.37 (br. s, 1 F, *o*-F), –141.06 (t, J = 24.2 Hz, 1 F, *o*-F), –151.63 (t, J = 22.0 Hz, 1 F, *p*-F), –151.75 (t, J = 23.0 Hz, 1 F, *p*-F), –152.13 (t, J = 22.0 Hz, 1 F, *p*-F), –152.21 (t, J = 22.0 Hz, 1 F, *p*-F), –152.72 (t, J = 22.0 Hz, 1 F, *p*-F), –153.25 (t, J = 22.0 Hz, 1 F, *p*-F), –153.80 (t, J = 20.1 Hz, 1 F, *p*-F), –154.34 (m, 1 F, *p*-F), –154.55 (t, J = 20.9 Hz, 1 F, *p*-F), –155.64 (t, J = 22.0 Hz, 1 F, *p*-F), –156.14 (m, 1 F, *p*-F), –158.30 (t, J = 22.0 Hz, 1 F, *p*-F), –160.65 (m, 4 F, *m*-F), –160.75 (br. s, 1 F, *m*-F), –160.87 (dt, J = 6.6 Hz, J = 22.5 Hz, 1 F, *m*-F), –161.45 (dt, J = 7.7 Hz, J = 22.5 Hz, 1 F, *m*-F), –161.59 (dt, J = 8.8 Hz, J = 23.1 Hz, 1 F, *m*-F), –161.79 (m, 1 F, *m*-F), –162.44 (m, 3 F, *m*-F), –163.17 (dt, J = 8.8 Hz, J = 19.8 Hz, 1 F, *m*-F), –163.40 (m, 2 F, *m*-F), –163.50 (dt, J = 7.7 Hz, J = 20.3 Hz, 1 F, *m*-F), –163.63 (dt, J = 7.7 Hz, J = 19.3 Hz, 1 F, *m*-F), –164.03 (t, J = 22.0 Hz, 1 F, *m*-F), –164.17 (dt, J = 6.6 Hz, J = 23.6 Hz, 1 F, *m*-F), –164.96 (t, J = 22.0 Hz, 1 F, *m*-F), –165.26 (m, 1 F, *m*-F), –165.72 (m, 2 F, *m*-F), –166.97 (t, J = 23.1 Hz, 1 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 376 (57000), 493 (120000), 773 (64000) nm. HRMS (ESI-TOF–): calcd. for $C_{132}H_{27}F_{60}N_{12}$ [M – H]$^-$ 2920.1561; found 2920.1550.

***meso*-Pentafluorophenyl-Substituted [62]Tetradecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1.1.1) (14):** ^{1}H NMR (600.17 MHz, $CDCl_3$, r.t.): δ = 12.45 (s, 1 H, NH), 12.12 (s, 1 H, NH), 12.04 (s, 1 H, NH), 11.86 (s, 1 H, NH), 11.16 (s, 1 H, NH), 11.08 (s, 1 H, NH), 8.00 (br. s, 1 H), 7.70 (t, J = 5.5 Hz, 1 H), 7.59 (d, J = 5.5 Hz, 1 H), 7.36 (d, J = 4.6 Hz, 1 H), 7.15 (d, J = 5.1 Hz, 1 H), 7.05 (m, 1 H), 7.01 (d, J = 4.6 Hz, 1 H), 6.91 (br. s, 1 H), 6.82 (t, J = 4.6 Hz, 1 H), 6.77 (d, J = 5.5 Hz, 1 H), 6.67 (br. s, 1 H), 6.63 (d, J = 4.1 Hz, 1 H), 6.61 (br. s, 1 H), 6.58 (br. s, 1 H), 6.55 (d, J = 4.6 Hz, 1 H), 6.52 (br. s, 1 H), 6.48 (d, J = 5.5 Hz, 1 H), 6.44 (d, J = 5.0 Hz, 1 H), 6.38 (d, J = 4.6 Hz, 1 H), 6.34 (br. s, 1 H), 6.20 (d, J = 5.0 Hz, 1 H), 6.09 (br. s, 1 H), 5.93 (d, J = 4.6 Hz, 1 H), 5.88 (br. s, 1 H), 5.82 (br. s, 1 H), 5.54 (br. s, 1 H), 5.51 (d, J = 5.0 Hz, 1 H), 5.48 (d, J = 5.0 Hz, 1 H) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$, r.t.): δ = –129.02 (d, J = 28.4 Hz, *o*-F), –131.85 (d, J = 22.0 Hz, *o*-F), –132.80 (d, J = 20.2 Hz, *o*-F), –132.94 (d, J = 20.2 Hz, *o*-F), –134.15 (br. s, *o*-F), –134.37 (br. s, *o*-F), –134.64 (br. s, *o*-F), –135.15 (d, J = 22.0 Hz, *o*-F), –135.40 (t, J = 20.2 Hz, *o*-F), –135.71 (d, J = 24.7 Hz, *o*-F), –135.88 (br. s, *o*-F), –136.07 (br. s, *o*-F), –136.21 (br. s, *o*-F), –136.48 (m, *o*-F), –136.78 (br. s, *o*-F), –137.25 (br. s, *o*-F), –137.50 (m, *o*-F), –137.59 (br. s, *o*-F), –137.78 (d, J = 26.6 Hz, *o*-F), –137.95 (br. s, *o*-F), –138.19 (d, J = 26.6 Hz, *o*-F), –138.35 (d, J = 26.6 Hz, *o*-F), –138.05 (m, *o*-F), –138.65 (br. s, *o*-F), –138.97 (m, *o*-F), –139.07 (d, J = 26.6 Hz, *o*-F), –139.24 (br. s, *o*-F), –139.42 (br. s, *o*-F), –140.48 (d, J = 22.0 Hz, *o*-F), –140.59 (d, J = 22.0 Hz, *o*-F), –140.80 (br. s, *o*-F), –140.98 (d, J = 22.0 Hz, *o*-F), –141.44 (m, *o*-F), –141.63 (m, *o*-F), –142.70 (br. s, *o*-F), –149.71 (t, J = 22.9 Hz, *p*-F), –151.47 (t, J = 21.1 Hz, *p*-F), –152.02 (m, *p*-F), –152.24 (m, *p*-F), –152.44 (m, *p*-F), –152.63 (m, *p*-F), –153.01 (t, J = 22.0 Hz, *p*-F), –153.21 (br. s, *p*-F), –154.01 (t, J = 25.6 Hz, *p*-F), –154.26 (t, J = 22.0 Hz, *p*-F), –154.66 (t, J = 27.5 Hz, *p*-F), –156.19 (m, *p*-F), –159.15 (br. s, *m*-F), –160.20 (m, *m*-F), –160.58 (br. s, *m*-F), –160.82 (m, *m*-F), –161.01 (m, *m*-F), –161.26 (br. s, *m*-F), –161.43 (d, J = 21.1 Hz, *m*-F), –161.60 (br. s, *m*-F), –161.83 (br. s, *m*-F), –162.08 (m, *m*-F), –162.28 (m, *m*-F), –162.84 (d, J = 16.5 Hz, *m*-F), –162.97 (m, *m*-F), –163.11 (d, J = 21.1 Hz, *m*-F), –163.61 (m, *m*-F), –163.96 (m, *m*-F), –164.26 (br. s, *m*-F), –164.51 (t, J = 27.4 Hz, *m*-F), –165.16 (br. s, *m*-F), –165.78 (m, *m*-F), –166.03 (m, *m*-F), –168.37 (br. s, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 333 (80000), 377 (80000), 451 (83000), 671 (63000), 898 (110000) nm. HRMS (ESI-TOF–): calcd. for $C_{154}H_{32}F_{70}N_{14}$ [M – 2H]$^{2-}$ 1703.5930; found 1703.5998.

***meso*-Pentafluorophenyl-Substituted [72]Hexadecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1) (16):** ^{1}H NMR (600.17 MHz, $CDCl_3$, r.t.): δ = 13.94 (br. s, 2 H, NH), 13.73 (br. s, 2 H, NH), 12.47 (br. s, 2 H, NH), 11.59 (br. s, 2 H, NH), 7.68 (d, J = 4.1 Hz, 2 H), 7.41 (d, J = 4.6 Hz, 2 H), 7.22 (d, J = 3.7 Hz, 2 H), 7.12 (d, J = 5.0 Hz, 2 H), 6.98 (br. s, 2 H), 6.90 (d, J = 4.1 Hz, 2 H), 6.61 (br. s, 2 H), 6.60 (d, J = 5.0 Hz, 2 H), 6.55 (d, J = 4.1 Hz, 2 H), 6.48 (d, J = 4.6 Hz, 2 H), 6.37 (d, J = 4.6 Hz, 2 H), 6.34 (br. s, 2 H), 6.26 (br. s, 2 H), 6.24 (d, J = 3.7 Hz, 2 H), 6.16 (d, J = 4.6 Hz, 2 H), 5.99 (d, J = 3.7 Hz, 2 H) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$, r.t.): δ = –133.14 (d, J = 24.7 Hz, 2 F, *o*-F), –134.80 (d, J = 24.5 Hz, 2 F, *o*-F), –135.00 (d, J = 21.1 Hz, 2 F, *o*-F), –136.17 (d, J = 22.0 Hz, 2 F, *o*-F), –136.45 (m, 2 F, *o*-F), –136.88 (br. s, 2 F, *o*-F), –137.32 (br. s, 2 F, *o*-F), –137.51 (br. s, 2 F, *o*-F), –137.82 (m, 4 F, *o*-F), –137.88 (s, 2 F, *o*-F), –138.53 (d, J = 24.7 Hz, 4 F, *o*-F), –138.72 (dt, J = 8.3 Hz, J = 25.8 Hz, 2 F, *o*-F), –141.00 (s, 2 F, *o*-F), –142.47 (d, J = 22.0 Hz, 2 F, *o*-F), –152.00 (t, J = 21.1 Hz, 2 F, *p*-F), –152.26

(m, 4 F, *p*-F), –152.74 (t, *J* = 22.0 Hz, 2 F, *p*-F), –153.72 (t, *J* = 22.0 Hz, 2 F, *p*-F), –153.55 (m, 4 F, *p*-F), –154.68 (br. s, 2 F, *p*-F), –160.04 (br. s, 2 F, *m*-F), –160.60 (br. t, *J* = 24.7 Hz, 2 F, *m*-F), –161.0, –161.6 (m, 14 F, *m*-F), –162.10 (t, *J* = 22.0 Hz, 4 F, *m*-F), –162.14 (t, *J* = 22.0 Hz, 2 F, *m*-F), –163.58 (br. s, 2 F, *m*-F), –163.89 (br. s, 4 F, *m*-F), –164.18 (m, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 315 (81000), 420 (89000), 522 (85000), 671 (46000), 939 (100000) nm. HRMS (ESI-TOF–): calcd. for $C_{176}H_{38}F_{80}N_{16}$ $[M-2H]^{2-}$ 1947.6155; found 1947.6161.

***meso*-Pentafluorophenyl-Substituted [80]Octadecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1) (18):** ^{1}H NMR (600.17 MHz, $CDCl_3$, r.t.): δ = 12.90 (s, 1 H, NH), 12.69 (s, 1 H, NH), 12.65 (s, 1 H, NH), 12.48 (s, 1 H, NH), 12.07 (br. s, 1 H, NH), 11.72 (br. s, 1 H, NH), 11.32 (s, 1 H, NH), 11.29 (s, 1 H, NH), 8.38 (d, *J* = 5.5 Hz, 1 H), 8.11 (d, *J* = 4.6 Hz, 1 H), 7.79 (d, *J* = 5.5 Hz, 1 H), 7.43 (s, 1 H), 7.24 (d, *J* = 4.6 Hz, 1 H), 7.19 (d, *J* = 5.0 Hz, 1 H), 7.15 (d, *J* = 5.5 Hz, 1 H), 7.06 (m, 3 H), 6.87 (d, *J* = 4.6 Hz, 1 H), 6.70 (d, *J* = 4.1 Hz, 2 H), 6.62 (br. s, 1 H), 6.55 (m, 2 H), 6.47 (d, *J* = 3.2 Hz, 1 H), 6.42 (br. s, 4 H), 6.38 (d, *J* = 4.6 Hz, 1 H), 6.31 (d, *J* = 4.6 Hz, 1 H), 6.26 (d, *J* = 3.2 Hz, 1 H), 6.24 (m, 1 H), 6.22 (br. s, 3 H), 6.19 (br. s, 1 H), 6.17 (br. s, 1 H), 6.02 (d, *J* = 4.6 Hz, 2 H), 6.00 (br. s, 1 H), 5.65 (br. s, 1 H), 5.35 (m, 2 H) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$, r.t.): δ = –133.62 (d, *J* = 18.3 Hz, 1 F, *o*-F), –134.63 (d, *J* = 24.7 Hz, 1 F, *o*-F), –134.93 (d, *J* = 30.2 Hz, 1 F, *o*-F), –135.17 (m, 1 F, *o*-F), –135.42 (d, *J* = 22.9 Hz, 1 F, *o*-F), –136.12 (t, *J* = 20.2 Hz, 1 F, *o*-F), –136.49 (br. s, 2 F, *o*-F), –136.92 (br. s, 2 F, *o*-F), –137.25 (d, *J* = 24.7 Hz, 1 F, *o*-F), –137.45 (br. s, 1 F, *o*-F), –137.58 (br. s, 1 F, *o*-F), –137.64 (d, *J* = 24.7 Hz, 1 F, *o*-F), –138.03 (m, 10 F, *o*-F), –138.63 (d, *J* = 24.0 Hz, 1 F, *o*-F), –138.80 (m, 6 F, *o*-F), –139.14 (d, *J* = 24.0 Hz, 1 F, *o*-F), –140.39 (br. s, 1 F, *o*-F), –140.52 (br. s, 1 F, *o*-F), –141.29 (m, 2 F, *o*-F), –146.14 (d, *J* = 20.2 Hz, 1 F, *o*-F), –150.96 (t, *J* = 25.7 Hz, 1 F, *p*-F), –151.23 (d, *J* = 22.0 Hz, 1 F, *p*-F), –151.63 (d, *J* = 22.0 Hz, 1 F, *p*-F), –152.00 (m, 6 F, *p*-F), –152.52 (d, *J* = 24.7 Hz, 2 F, *p*-F), –152.67 (br. s, 1 F, *p*-F), –152.81 (d, *J* = 21.1 Hz, 2 F, *p*-F), –152.94 (br. s, 1 F, *p*-F), –153.20 (t, *J* = 22.0 Hz, 1 F, *p*-F), –153.6 (d, *J* = 21.1 Hz, 1 F, *p*-F), –153.80 (t, *J* = 23.8 Hz, 1 F, *p*-F), –160.17 (t, *J* = 21.1 Hz, 2 F, *m*-F), –160.34 (m, 2 F, *m*-F), –161.00 (m, 6 F, *m*-F), –161.30 (m, 8 F, *m*-F), –161.66 (m, 4 F, *m*-F), –161.95 (m, 2 F, *m*-F), –162.17 (d, *J* = 24.8 Hz, 2 F, *m*-F), –162.45 (t, *J* = 24.7 Hz, 1 F, *p*-F), –162.74 (t, *J* = 24.7 Hz, 1 F, *p*-F), –162.93 (t, *J* = 33.0 Hz, 2 F, *p*-F), –163.55 (d, *J* = 20.2 Hz, 2 F, *p*-F), –163.74 (t, *J* = 20.2 Hz, 1 F, *p*-F), –164.53 (m, 1 F, *m*-F), –165.66 (s, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 372 (70000), 469(50000), 559 (61000), 696 (50000), 953 (110000) nm. HRMS (ESI-TOF–): calcd. for $C_{198}H_{42}F_{90}N_{18}$ $[M-2H]^{2-}$ 2191.1239; found 2191.1253.

Supporting Information (see footnote on the first page of this article): HRMS (ESI-TOF) of **12**–**18**.

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