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N-Fusion Reaction Sequence of Heptaphyrin(1.1.1.1.1.1.1): Singly, Doubly, and Quadruply N-Fused Heptaphyrins

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Abstract: *meso*-Heptakis(pentafluorophenyl) heptaphyrin(1.1.1.1.1.1.1) (**1**) was prepared by a stepwise route in 39% yield and its unique N-fusion reaction (NFR) sequence has been revealed; this reaction leads to singly-, doubly-, and quadruply N-fused heptaphyrins (**4**, **5**, and **6**) in good yields. These transformations are facilitated by the inherent conformational distortion of **1** as well as the distorted, folded conformations of N-fused heptaphyrins **4** and **5**. The proximate arrangement of the three pyrrole units in **6** allowed for the formation of the tripyrrolylboron(III) complexes **7**, **8**, and **9** with unique coordination features. Molecules **1**, **5**, and **9** were structurally characterized by X-ray crystallography. In addition, the boron complexes **7**, **8**, and **9** displayed weak but distinct fluorescence in the near infrared region.

Keywords: boron · conjugation · macrocycles · N-fusion reaction · porphyrinoids

Introduction

In recent years, expanded porphyrins have emerged as a new class of interesting conjugated macrocycles in respect of their unique optical, electrochemical, and coordination properties that have not been previously reported for porphyrins.[1–3] Some intriguing reactivities of expanded porphyrins stem from their conformational flexibilities, which are in contrast to rigid and planar structures of porphyrins. Among these, N-fusion reactions (NFR), which are characteristic of medium-size-expanded porphyrins when it relieves the macrocycle strain,[4–6] are synthetically attractive, because the resultant fused 5,5,6-tricyclic structures cause substantial influence on the structural and electronic properties, hence leading to the creation of new porphyrinoids. *meso*-Aryl-substituted pentaphyrins exist only as an N-fused pentaphyrin,[3b,5a,b] while *meso*-aryl-substituted hexaphyrins are rather stable and need high temperature for their NFRs.[5c] Here we report NFR sequence of heptaphyrin(1.1.1.1.1.1.1) **1**, which provides, in a stepwise manner, singly, doubly, and quadruply N-fused heptaphyrins all in good yields. In addition, quadruply N-fused heptaphyrin **6** has a unique tripyrrolic coordination site that accommodates boron(III) ion, providing tripyrrolylboron(III) complexes efficiently.

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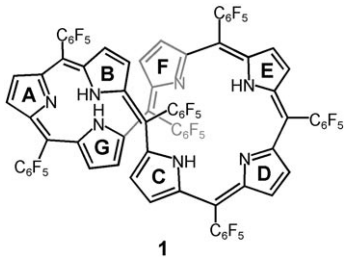
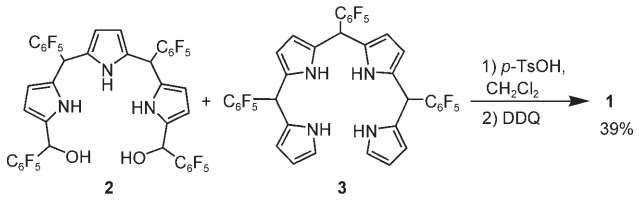
Results and Discussion

Among a series of *meso*-aryl-substituted expanded porphyrins, the chemistry of heptaphyrin(1.1.1.1.1.1.1) **1** has been left almost unexplored mainly because of the difficult synthetic access to its pure form and its facile N-fusion reaction.



1

Although **1** was formed in 4–5% in our synthetic protocol of *meso*-aryl-expanded porphyrins,[3c] its isolation was very difficult, because its elution behavior seriously overlapped with that of octaphyrin(1.1.1.1.1.1.1.1) on a silica gel or alumina column. Therefore, **1** was prepared by a stepwise route as shown in Scheme 1. A solution of tripyrrane dicarbinol **2**[2f] and tetrapyrrane **3**[7] was stirred for 15 min under N_2 atmosphere and treated with *p*-toluenesulfonic acid for 3 h,



Scheme 1. Synthesis of **1**.

and the resulting mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to afford **1** in 39% yield. High-resolution electrospray ionization (HR-ESI) mass spectrometry revealed the parent ion peak at $m/z =$ 1706.1152 (calcd for $C_{77}H_{19}F_{35}N_7$ $[M+H]^+$: $m/z = 1706.1149$) and the ^{1}H NMR spectrum exhibits two broad signals at $\delta =$ 16.59 and 11.82 ppm due to the NH protons, six signals at $\delta = 10.49$, 7.91, 6.68, 6.23, 5.74, and 5.53 ppm due to the peripheral β-protons in a integral ratio of 1:1:1:1:2:1 (Figures 1 and 2), suggesting its symmetric structure and delineating its non-aromatic 32π-electron system. The structure of **1** has been revealed by single-crystal X-ray diffraction analysis to be a distorted figure-of-eight conformation (Figure 3).[8] This is, to the best of our knowledge, the first X-ray crystal structure of an intact heptaphyrin(1.1.1.1.1.1.1).

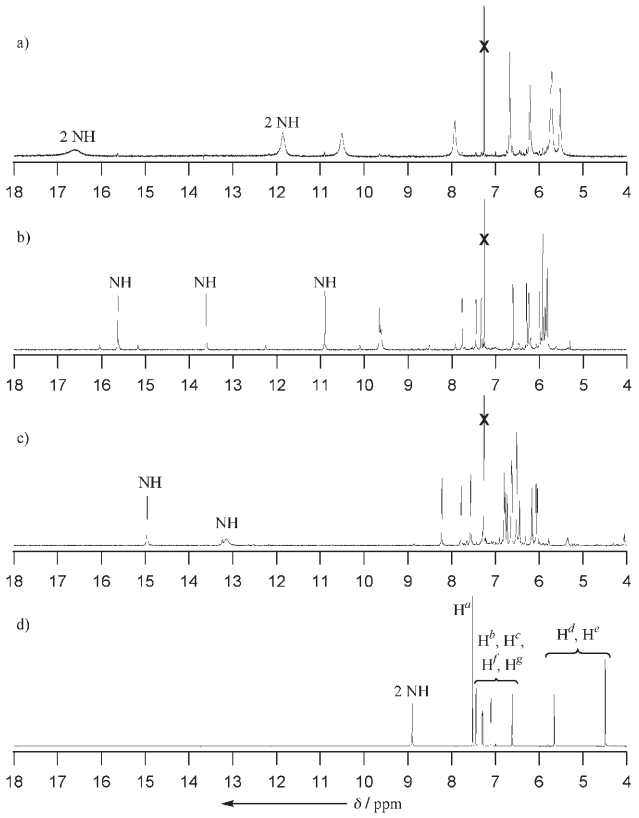


Figure 1. ^{1}H NMR spectra of a) **1**, b) **4**, and c) **5** in $CDCl_3$, and d) **6** in $[D_6]$acetone.

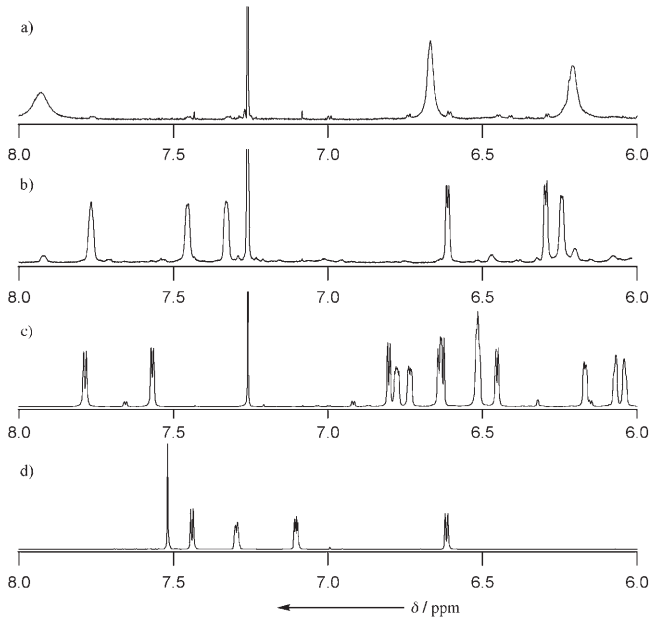


Figure 2. Enlarged ^{1}H NMR spectra of a) **1**, b) **4**, and c) **5** in $CDCl_3$, and d) **6** in $[D_6]$acetone.

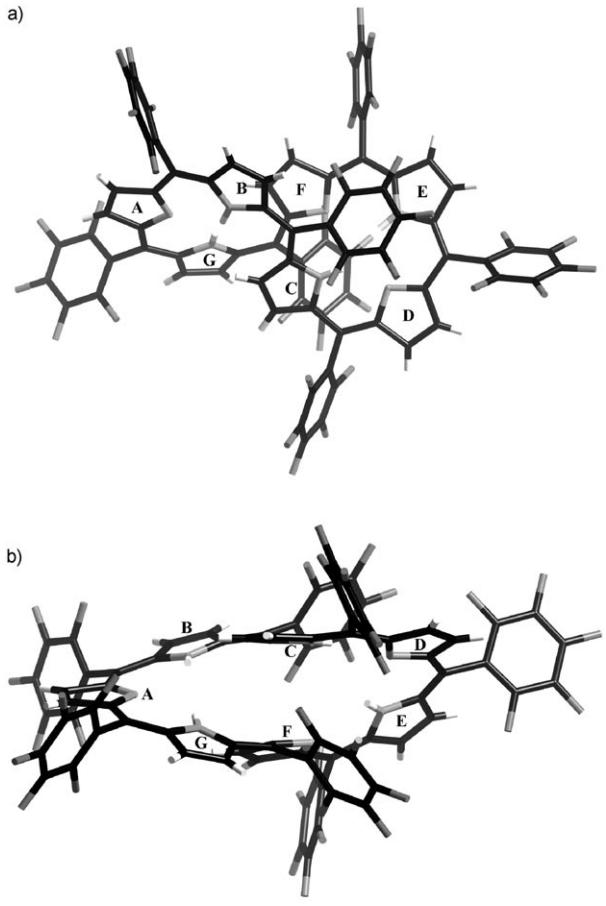
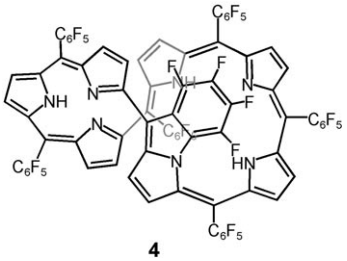


Figure 3. X-ray crystal structure of **1**: a) top view and b) side view.

Similarly to the previously reported *meso*-aryl-substituted heptaphyrin,[5a] **1** underwent NFR slowly but quantitatively to form singly N-fused heptaphyrin **4** just on standing in solution. This conversion was observed in almost all solvents



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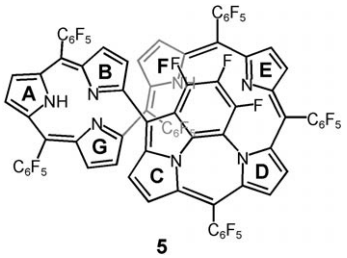
examined except DMF, in which >95% of **1** was recovered intact after standing for one month. HR-ESI mass spectroscopy revealed the elimination of HF during the formation of **4** ($m/z = 1686.1079$; calcd for $C_{77}H_{18}F_{34}N_7$ $[M+H]^+$: $m/z = 1686.1086$). The ^{1}H NMR spectrum of **4** showed three signals due to the NH protons and fourteen signals due to the peripheral β-protons, reflecting its nonsymmetric structure. The structure of **4** has been supported by the similarity of its ^{1}H NMR and absorption spectra with those of singly N-fused perfluorinated heptaphyrin.[5a] Spontaneous NFR propensity of **1** may be accounted for in terms of the inherent distortion of the macrocycle, and the proximity of the pyrrolic nitrogen atoms of the pyrroles C and F atoms to the 2′-carbon atoms of the adjacent *meso*-pentafluorophenyl groups.

Then, we attempted further NFR by refluxing a toluene solution of **4** for 12 h and obtained doubly N-fused heptaphyrin **5** quantitatively. HR-ESI mass spectroscopy revealed



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the parent ion peak of **5** at $m/z = 1666.1024$ (calcd for $C_{77}H_{17}F_{33}N_7$ $[M+H]^+$: $m/z = 1666.1020$), thus indicating further elimination of HF. The ^{1}H NMR spectrum exhibits two signals at $\delta = 14.97$ and 13.14 ppm due to the NH protons and fourteen signals due to the peripheral β-protons, suggesting its nonsymmetric structure (Figures 1 and 2). The structure of **5** has been confirmed by single-crystal X-ray diffraction analysis. Interestingly, the nitrogen atoms of the pyrroles C and D substitute the adjacent 2- and 3-fluorine atoms of the same pentafluorophenyl ring to form a fused pentacyclic structure containing a 1,4-diazepine ring system (Figure 4).[9] Despite differences in the number of N-fusion structures, the absorption spectra of **1**, **4**, and **5** are surprisingly similar to one another exhibiting two bands around 390 and 620 nm (Figure 5a).

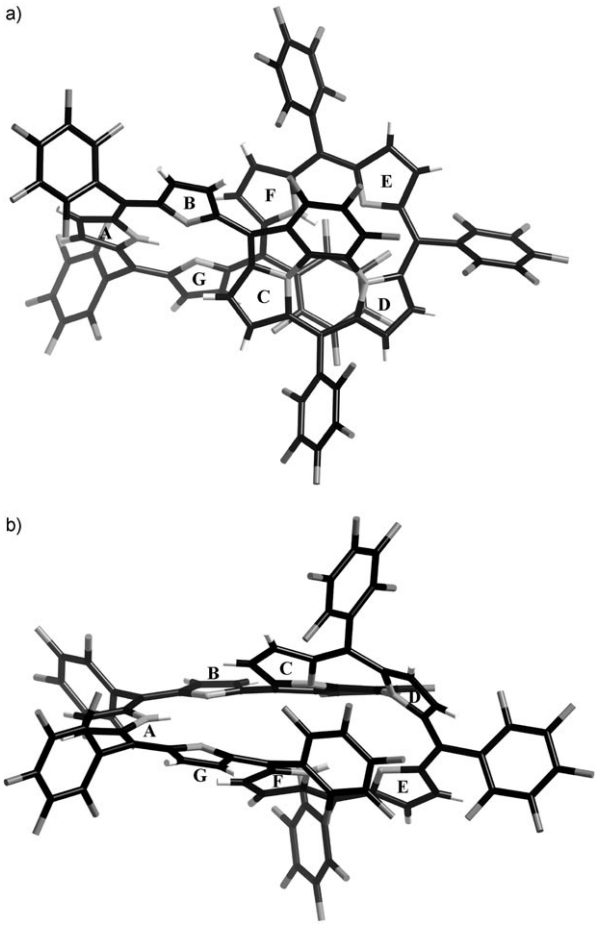
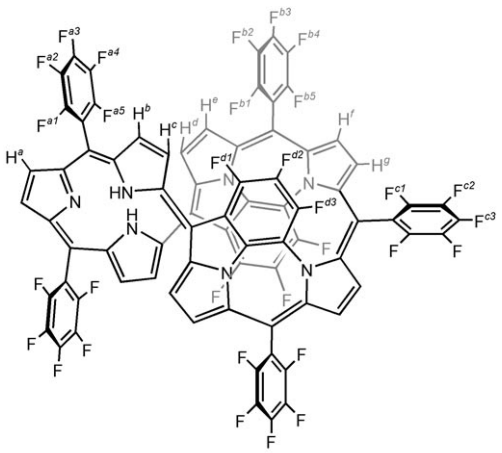


Figure 4. X-ray crystal structure of **5**: a) top view and b) side view.

To our surprise, further double NFR of **5** proceeded smoothly upon treatment with NaH in DMF at 60°C for 4 h,[10] providing quadruply N-fused heptaphyrin **6** as green solids in 71% yield. HR-ESI mass spectroscopy revealed the parent ion peak of **6** at $m/z = 1627.0953$ (calcd for



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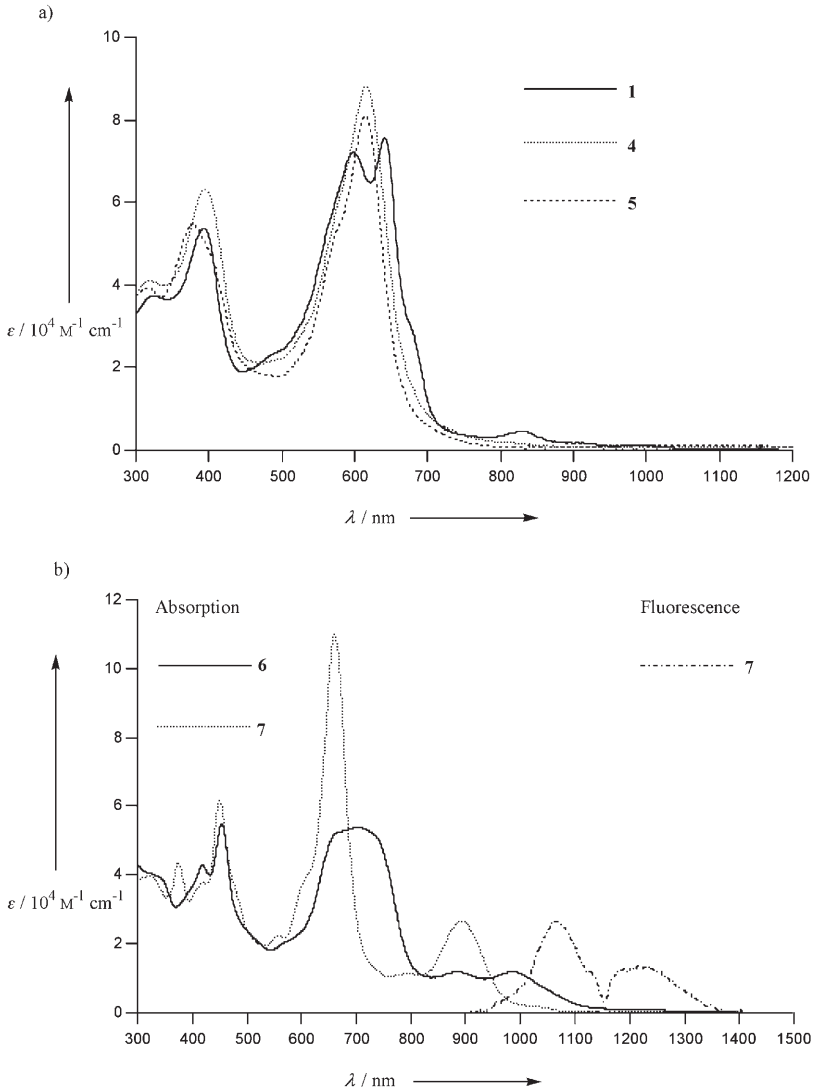


Figure 5. a) Absorption spectra of **1**, **4**, and **5**, and b) those of **6** and **7**, and fluorescence spectrum of **7** in CH_2Cl_2.

$C_{77}H_{16}F_{31}N_7$ $[M]^+$: $m/z =$ 1627.0978) indicating the elimination of two HF units. In line with the expected C_2 symmetric structure, the ^{1}H NMR spectrum of **6** is very simple, exhibiting a signal at $\delta = 8.89$ ppm due to the two NH protons, a singlet at $\delta = 7.52$ ppm due to the peripheral β-protons, six doublets at $\delta = 7.44$, 7.29, 7.11, 6.62, 5.66, and 4.49 ppm due to the peripheral β-protons (Figure 2), reflecting its non-aromatic 34π-electron system. The two upfield proton signals are assigned due to H^d and H^e situated inside of the macrocycle and which are shifted by the local diatropic ring current of pyrroles. The absorption spectrum of **6** exhibits broad bands at 702, 884, and 987 nm (Figure 5b), and are significantly altered from those of **1**, **4**, and **5**. Quadruple NFR in **6** should lead to a helically twisted chiral structure, which has been proved by actual chiral resolution through a chiral HPLC column into optically pure enantiomers,[11] which display the exactly opposite CD signal patterns to each other with prominent Cotton effect around 455 and 755 nm (Figure 6). Despite many attempts, we could not obtain nice crystals of **6** for X-ray diffraction analysis either from racemic or optically pure **6**. However, the quadruple N-fusion structure of **6** has been substantiated from single crystal structure of its boron(III) complex (see below).

As shown in Figures 1 and 2, the ^{1}H NMR spectra become sharper in the order of **1** < **4** < **5** < **6**, reflecting increasing rigidity upon the incorporation of N-fusion structures. Similarly the ^{19}F NMR spectra become sharper in the order of **1** < **4** < **5** < **6** (Supporting Information). In the ^{19}F NMR spectrum of **6**,

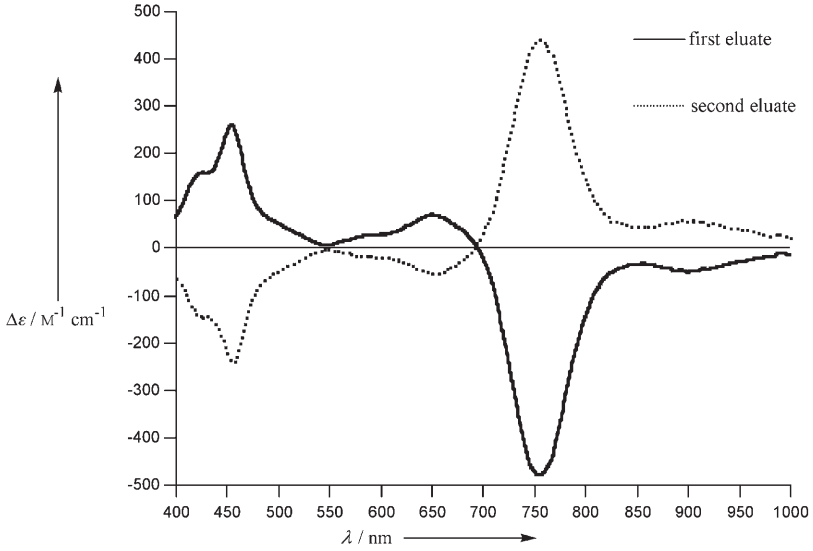


Figure 6. CD spectra of enantiomers of **6** in CH_2Cl_2.

the signals due to the *para*-^{19}F nuclei of the five pentafluorophenyl groups are easily differentiated as clear three triplets in a ratio of 2:2:1 (Figure 7b); starting from these signals, all the ^{19}F NMR signals have been assigned on the basis of extensive 2D-COSY experiments. Curiously, signals due to F^{b1}

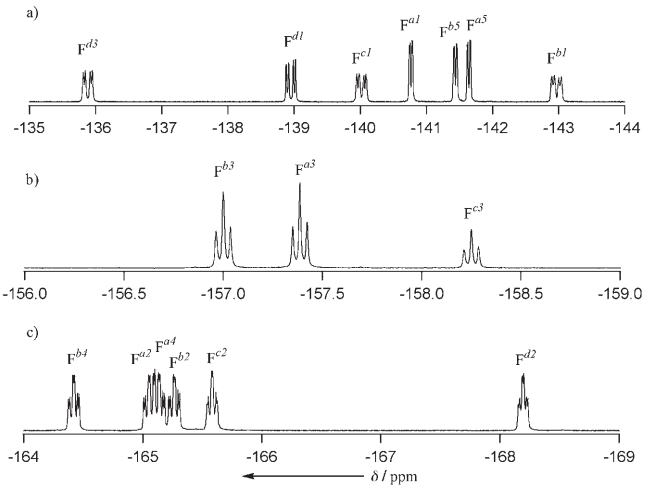
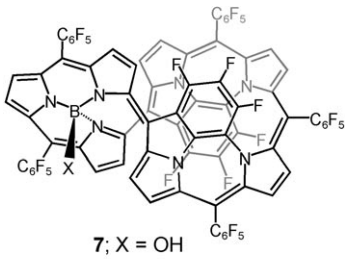


Figure 7. ^{19}F NMR spectra of **6**, a) *ortho*-F region, b) *para*-F region, and c) *meta*-F region in [D_6]acetone.

and F^{d1}, and F^{c1} and F^{d3} are mutually coupled with $J=$ 63 Hz, despite only very small interactions along the through-bond network. Therefore, these coupling are assigned to through-space direct coupling between spatially close two ^{19}F nuclei, which is brought about by the enforced structure of **6**.

Attempts to put boron(III) into the small cavity of **6** failed for the use of $BF_3{\cdot}OEt_2$. In the meantime we found that boron complexation of **6** was effected upon refluxing a solution of **6** in CH_2Cl_2 solution in the presence of BBr_3 and *N*-ethyldiisopropylamine. Subsequent aqueous workup provided hydroxyboron(III) complex **7**, which was converted into alkoxyboron(III) complex **8** (R = methoxy) or **9** (R = isopropoxy) by refluxing in the presence of methanol or isopropyl alcohol. The structure of **9** has been revealed by



single-crystal X-ray diffraction analysis as shown in Figure 8; the two planar pentacyclic frameworks containing a 1,4-diazepine core are folded in a parallel and helical manner with an average interplanar distance of 3.0 Å,

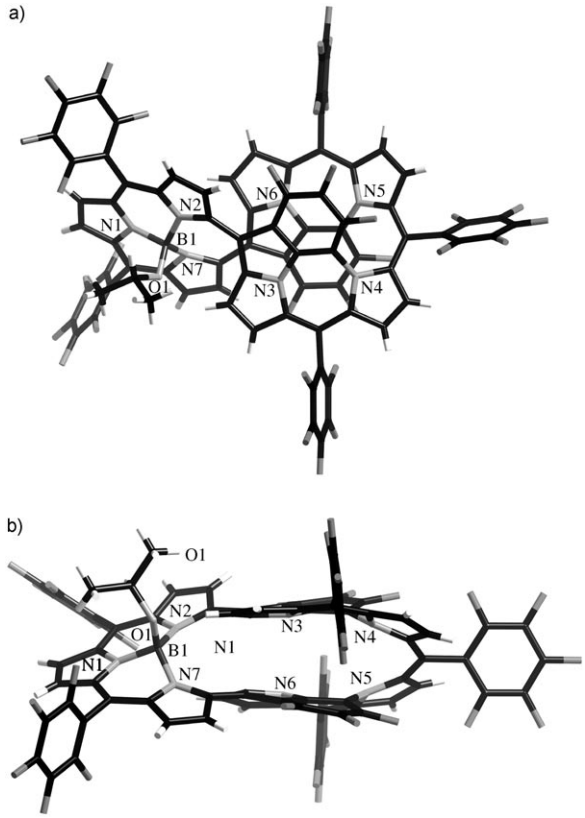


Figure 8. X-ray crystal structure of **9**: a) top view and b) side view.

hinged by the tripyrrolylboronate moiety.[12] Curiously, the boron(III) atom is bound to the three pyrroles in a subphthalocyanine- or subporphine-like manner,[13] with bond distances of 1.562(8) (B1–N1), 1.590(8) (B1–N2), 1.606(8) (B1–N7), and 1.433(8) Å (B1–O1), which are slightly longer than those of subphthalocyanine or subporphyrin (N–B distances are generally 1.49–1.51 Å for tribenzosubporphyrin or subphthalocyanine), and bond angles of 104.2(4) (N1-B1-N2), 122.6(5) (N2-B1-N7), and 101.5(5)° (N7-B1-N1). These data suggest loose boron coordination for **9** relative to that found in subphthalocyanines and subporphyrin. Although some examples have been reported for dipyrromethene boron(III) complexes of porphyrinoids,[14] such a tripyrrolylboron(III) complex is quite rare. In contrast to the inertness of subporphyrins towards acid-induced demetalation, the boron(III) complexes **7**, **8**, and **9** gradually underwent demetalation upon treatment with trifluoroacetic acid. Similar to subphthalocyanines and subporphyrins, the protons of the axial groups of the complexes show substantial upfield shifts in the ^{1}H NMR spectra, which may be attributed to the local diatropic ring currents of the pyrrole rings rather than that of the macrocycle. The ^{11}B NMR spectra show broad signals at $\delta=-5.2$, -5.6, and $-5{,}3$ ppm for **7**, **8**, and **9**, respectively, which are much less down field shifted in comparison to those of subphthalocyanines ($\delta=$ -17.7 to -19.6 ppm),[13a] and of tribenzosubporphyrin ($\delta=$ -13.7 to -14.6 ppm).[13b] These observations indicate the

lack of diatropic ring current of the macrocycles, in line with the ^{1}H NMR analysis.

The absorption spectra of the hydroxyboron(III) complex **7** becomes much sharper with peaks at 660 and 895 nm (Figure 5b). Interestingly, the hydroxyboron(III) complex **7** emits weak fluorescence in the near IR range of 900–1350 nm as a rare case (Figure 5b), while the fluorescence of **6** cannot be detected under the same conditions. The absorption and fluorescence spectra of the alkoxyboron(III) complexes **8** and **9** are similar to those of **7**.

Conclusion

The unique NFR sequence of the heptaphyrin **1** has been revealed, which provides singly-, doubly-, and quadruply N-fused heptaphyrins (**4**, **5**, and **6**) in good yields. These transformations are facilitated by the inherent conformational distortion of **1** as well as the distorted, folded conformations of N-fused heptaphyrins **4** and **5**. The proximate arrangement of the three pyrrole units in **6** allowed for the formation of the tripyrrolylboron(III) complex **7**. Application of the NFR strategy in other medium or large size expanded porphyrins is worthy of further investigations, since it will allow for the creation of expanded porphyrinoids with novel photophysical and electrochemical properties.

Experimental Section

General information: All solvents for reaction were distilled over CaH_2. All reagents were of the commercial reagent grade and were used without further purification except where noted. The spectroscopic grade dichloromethane was used as solvent for all spectroscopic studies. Silica gel column chromatography was performed on Wakogel C-300. UV-visible spectra were recorded on a Shimadzu UV-3100PC spectrometer. ^{1}H, ^{11}B, and ^{19}F NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600.17 MHz for ^{1}H, 192.56 MHz for ^{11}B, and 564.73 MHz for ^{19}F) using the residual solvent as the internal reference for ^{1}H (δ = 7.26 ppm in $CDCl_3$ and δ = 2.09 ppm in [D$_6$]acetone), boron trifluoride diethyl etherate as an external reference for ^{11}B (δ = 0.0 ppm), and hexafluorobenzene as an external reference for ^{19}F (δ = −162.9 ppm). Mass spectra were recorded on a BRUKER microTOF model using positive mode ESI-TOF method for acetonitrile solutions of samples, or on a JEOL HX-110 spectrometer using positive mode FAB ionization method for dichloromethane solutions of samples with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix. CD spectra were recorded on a JASCO J-720W spectropolarimeter. Fluorescence spectra were recorded on a HORIBA Jobin Yvon SPEX fluorolog-NIR-K.

5,10,15-Tris(pentafluorophenyl)tetrapyrrane (3): 1,9-Bis(pentafluorobenzoyl)-5-(pentafluorophenyl)dipyrromethane (6,7 g, 9.6 mmol) was reduced with $NaBH_4$ (3.5 g, 93 mmol) in a 10:1 mixture of THF and methanol (220 mL). After 30 min, the reaction was quenched with saturated aqueous NH_4Cl solution and the products were extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield corresponding dipyrromethane dicarbinol quantitatively, which was unstable at ambient temperature and hence had to be used immediately. The dicarbinol was dissolved in pyrrole (54 mL, 780 mmol), and trifluoroacetic acid (0.74 mL, 9.6 mmol) was added to the solution, which was stirred under N_2 atmosphere for 1 h. The reaction was quenched with triethylamine, and unreacted pyrrole was distilled under reduced pressure. The residue was purified by silica gel chromatography using a 1:1 mixture of hexane and dichloromethane to yield **3** (5.6 g, 73%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (brs, 2H; NH), 8.10–8.06 (br, 2H; NH), 6.72 (m, 2H; pyrrole-β), 6.15 (m, 2H; pyrrole-β), 5.99 (s, 2H; pyrrole-β), 5.91–5.89 (m, 4H; pyrrole-β), 5.85 (s, 2H; *meso*), 5.79 ppm (s, 1H; *meso*); FAB-MS: *m*/*z*: 802.10 $[M]^+$; *m*/*z* calcd for $C_{37}H_{17}F_{15}N_4$: 802.12.

***meso*-Pentafluorophenyl-substituted [32]heptaphyrin(1.1.1.1.1.1.1) 1**: 1,14-Bis(pentafluorobenzoyl)-5,10-bis(pentafluorophenyl)tripyrrane (1220 mg, 1.29 mmol) was reduced with $NaBH_4$ (977 mg, 25.8 mmol) in a 10:1 mixture of THF and methanol (220 mL). After 30 min, the reaction was quenched with saturated aqueous NH_4Cl solution and the products were extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield dicarbinol **2** quantitatively, which was unstable at ambient temperature and hence had to be used immediately. The dicarbinol **2** was added to a solution of **3** (1040 mg, 1.29 mmol) in dry CH_2Cl_2 (200 mL). After the resultant solution was stirred under N_2 atmosphere for 15 min, *p*-toluenesulfonic acid monohydrate (25 mg, 0.13 mmol) was added and stirring was continued for 3 h. DDQ (1760 mg, 7.75 mmol) was added and the resulting solution was opened to the air with constant stirring for further 3 h. The reaction mixture was passed through a basic alumina column followed by evaporation of solvent under reduced pressure. The residue was purified by silica gel chromatography using a 3:1 mixture of hexane and dichloromethane. Evaporation of the dark blue fraction to dryness yielded **1** (861 mg, 39%). Dark blue crystals were obtained by slow vapor diffusion of a pentane solution of **1** in a refrigerator. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 16.59 (brs, 2H; NH), 11.82 (brs, 2H; NH), 10.49 (brs, 2H; pyrrole-β), 7.91 (brs, 2H; pyrrole-β), 6.68 (brs, 2H; pyrrole-β), 6.23 (brs, 2H; pyrrole-β), 5.74 (brs, 4H; pyrrole-β), 5.53 ppm (brs, 2H; pyrrole-β); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −135.1 (d, *J* = 16 Hz, 2F; *o*-F), −136.1 (br, 2F; *o*-F), −136.8 (br, 2F; *o*-F), −137.4 (br, 2F; *o*-F), −138.4 (d, *J* = 20 Hz, 2F; *o*-F), −139.3 (d, *J* = 18 Hz, 2F; *o*-F), −140.0 (d, *J* = 17 Hz, 2F; *o*-F) −152.7 (br, 2F; *p*-F), −153.1 (br, 4F; *p*-F), −153.7 (br, 1F; *p*-F), −161.0 (br, 2F; *m*-F), −161.4 (br, 6F; *m*-F), −162.0 ppm (br, 6F; *m*-F); ESI-MS: *m*/*z*: 1706.1152 $[M+H]^+$; *m*/*z* calcd for $C_{77}H_{19}F_{35}N_7$: 1706.1149; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 394 (5.4), 598 (7.2), 641 (7.6), 827 nm (0.4).

***meso*-Pentafluorophenyl-substituted singly N-fused [32]heptaphyrin 4**: At room temperature, **1** in dichloromethane was gradually changed to **4**, and wholly changed in three days. This fusion reaction proceeded in all solvents examined except DMF, in which **1** was recovered in 95% yield even after one month. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 15.63 (s, 1H; NH), 13.61 (s, 1H; NH), 10.91 (s, 1H; NH), 9.65 (s, 1H; pyrrole-β), 9.62 (s, 1H; pyrrole-β), 7.77 (s, 1H; pyrrole-β), 7.46 (s, 1H; pyrrole-β), 7.33 (s, 1H; pyrrole-β), 6.62 (d, *J* = 4.9 Hz, 1H; pyrrole-β) 6.30 (d, *J* = 4.9 Hz, 1H; pyrrole-β), 6.25 (d, *J* = 4.2 Hz, 1H; pyrrole-β), 6.00 (d, *J* = 2.4 Hz, 1H; pyrrole-β), 5.92 (d, *J* = 4.2 Hz, 2H; pyrrole-β), 5.87 (s, 1H; pyrrole-β), 5.83 ppm (s, 2H; pyrrole-β); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −132.9 (t, *J* = 22 Hz, 1F; C_6F_4N), −134.5 (m, 1F; *o*-F), −135.7 (d, *J* = 22 Hz, 1F; *o*-F), −136.1 (d, *J* = 26 Hz, 1F; *o*-F), −136.8 (br, 1F; C_6F_4N), −138.0 (d, *J* = 22 Hz, 1F; *o*-F), −138.2 (d, *J* = 22 Hz, 2F; *o*-F), −139.2 (br, 2F; *o*-F), −139.9 (d, *J* = 22 Hz, 1F; *o*-F), −140.0 (d, *J* = 22 Hz, 1F; *o*-F), −140.4 (d, *J* = 22 Hz, 1F; *o*-F), −151.1 (t, *J* = 22 Hz, 1F; *p*-F), −151.9 (t, *J* = 22 Hz, 1F; *p*-F), −152.6 (t, *J* = 22 Hz, 1F; *p*-F), −152.7 (t, *J* = 22 Hz, 1F; *p*-F), −152.7 (t, *J* = 23 Hz, 1F; *p*-F), −152.8 (t, *J* = 22 Hz, 1F; *p*-F), −154.3 (m, 1F; C_6F_4N), −159.0 to −159.1 (m, 1F; *m*-F), −159.9 (m, 1F; *m*-F), −160.9 (m, 1F; *m*-F), −161.2 to −161.8 (m, 9F; *m*-F), −162.2 (d, *J* = 18 Hz, 1F; C_6F_4N), −162.5 ppm (m, 1F; C_6F_4N); ESI-MS: *m*/*z*: 1686.1079 $[M+H]^+$; *m*/*z* calcd for $C_{77}H_{18}F_{34}N_7$: 1686.1086; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 320 (4.1), 393 (6.3), 617 nm (8.8).

***meso*-Pentafluorophenyl-substituted doubly N-fused [32]heptaphyrin 5**: Refluxing a solution of **4** (30 mg, 0.018 mmol) in toluene (100 mL) for 12 h gave **5** quantitatively. Recrystallization from a hexane/isopropyl alcohol solution of **5** gave dark blue crystals. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 14.97 (brs, 1H; NH), 13.14 (brs, 1H; NH), 8.23(d, *J* = 5.5 Hz, 1H; pyrrole-β), 7.79 (d, *J* = 5.5 Hz, 1H; pyrrole-β), 7.57 (d, *J* = 4.6 Hz, 1H; pyrrole-β), 6.80 (d, *J* = 4.6 Hz, 1H; pyrrole-β), 6.78 (m, 1H; pyrrole-β), 6.74 (m, 1H; pyrrole-β), 6.64 (d, *J* = 4.6 Hz, 1H; pyrrole-β), 6.63 (d, *J* =

4.6 Hz, 1H; pyrrole-β), 6.52 (br, 2H; pyrrole-β), 6.46 (d, J=4.6 Hz,1H; pyrrole-β), 6.17 (d, J=4.6 Hz, 1H; pyrrole-β), 6.07 (br, 1H; pyrrole-β), 6.04 ppm (br, 1H; pyrrole-β); ^{19}F NMR (565 MHz, $CDCl_3$): δ=−128.0 (dd, J=75, 25 Hz, 1F; *o*-F), −133.3 (dd, J=76, 19 Hz, 1F; $C_6F_3N_2$), −133.5 (d, J=26 Hz, 1F; *o*-F), −134.4 (dd, J=75, 23 Hz, 1F; *o*-F), −135.3 (d, J=24 Hz, 1F; *o*-F), −136.1 (dd, J=45, 20 Hz, 1F; $C_6F_3N_2$), −136.6 to −136.8 (m, 4F; *o*-F), −137.5 (d, J=25 Hz, 1F; *o*-F), −138.6 (dd, J=48, 23 Hz, 2F; *o*-F), −140.3 (d, J=22 Hz, 1F; *o*-F), −150.3 (t, J=22 Hz, 1F; *p*-F), −151.2 (t, J=22 Hz, 1F; *p*-F), −151.6 (t, J=22 Hz, 1F; *p*-F), −151.8 (t, J=22 Hz, 1F; *p*-F), −152.1 (t, J=22 Hz, 1F; *p*-F), −152.7 (t, J=22 Hz, 1F; *p*-F), −159.0 (m, 1F; *m*-F), −160.0 (m, 2F; *m*-F), −160.3 to −160.7 (m, 9F; *m*-F), −164.0 ppm (m, 1F; $C_6F_3N_2$); ESI-MS: m/z: 1666.1020 $[M+H]^+$; m/z calcd for $C_{77}H_{17}F_{33}N_7$: 1666.1024; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon\times10^{-4}$)=316 (4.0), 378 (5.5), 614 nm (8.1).

***meso*-Pentafluorophenyl-substituted quadruply N-fused [34]heptaphyrin 6**: NaH (60% purity, dispersion in paraffin liquid, 35 mg) was added to a solution of **5** (240 mg, 0.14 mmol) in dry DMF (30 mL) and the mixture was stirred under N_2 atmosphere at 60°C for 4 h. After the reaction was quenched by the addition of water (20 mL), the products were extracted with diethyl ether (200 mL). The organic phase was washed with 0.5 M HCl (3×200 mL) and dried over anhydrous Na_2SO_4. After the removal of the solvent, recrystallization from dichloromethane/hexane afforded **6** as a green solid (166 mg, 0.10 mmol, 71%). ^{1}H NMR (600 MHz, [D_6]acetone): δ=8.89 (brs, 2H; NH), 7.52 (s, 2H; pyrrole-β), 7.44 (d, J=4.6 Hz, 2H; pyrrole-β), 7.29 (d, J=3.7 Hz, 2H; pyrrole-β), 7.11 (dd, J=4.6, 1.8 Hz, 2H; pyrrole-β), 6.62 (d, J=5.5 Hz, 2H; pyrrole-β), 5.66 (d, J=4.6 Hz, 2H; pyrrole-β), 4.49 ppm (d, J=5.5 Hz, 2H; pyrrole-β); ^{19}F NMR (565 MHz, [D_6]acetone): δ=−135.9 (dd, J=63, 19 Hz, 2F; $C_6F_3N_2$), −139.0 (dd, J=63, 19 Hz, 2F; $C_6F_3N_2$), −140.0 (dd, J=64, 19 Hz, 2F; *o*-F), −140.8 (dd, J=26, 7.3 Hz, 2F; *o*-F), −141.5 (d, J=24 Hz, 2F; *o*-F), −141.7 (dd, J=25, 7.3 Hz, 2F; *o*-F), −143.0 (dd, J=63, 25 Hz, 2F; *o*-F), −157.0 (t, J=22 Hz, 2F; *p*-F), −157.4 (t, J=22 Hz, 2F; *p*-F), −158.3 (t, J=22 Hz, 1F; *p*-F), −164.4 (dt, J=23, 7.3 Hz, 2F; *m*-F), −165.1 (dt, J=25, 8.8 Hz, 2F; *m*-F), −165.2 (dt, J=26, 8.8 Hz, 2F; *m*-F), −165.3 (dd, J=22, 8.8 Hz, 2F; *m*-F), −165.6 (dt, J=22, 7.2 Hz, 2F; *m*-F), −168.2 ppm (dt, J=21, 7.3 Hz, 2F; $C_6F_3N_2$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=8.87 (brs, 2H; NH), 7.20 (s, 2H; pyrrole-β), 7.03 (d, J=2.8 Hz, 2H; pyrrole-β), 6.99 (d, J=4.6 Hz, 2H; pyrrole-β), 6.86 (d, J=3.7 Hz, 2H; pyrrole-β), 6.08 (d, J=2.8 Hz, 2H; pyrrole-β), 5.20 (d, J=5.5 Hz, 2H; pyrrole-β), 4.32 ppm (d, J=4.6 Hz, 2H; pyrrole-β); ^{19}F NMR (565 MHz, $CDCl_3$): δ=−133.9 (dd, J=63, 22 Hz, 2F; $C_6F_3N_2$), −137.3 to −137.5 (dd, J=65, 22 Hz, 2F; $C_6F_3N_2$), −137.5 to −137.7 (m, 4F; *o*-F), −137.8 (dd, J=26, 7.7 Hz, 2F; *o*-F), −138.7 (dd, J=25, 7.7 Hz, 2F; *o*-F), −140.8 to −141.0 (m, 2F; *o*-F), −152.7 (t, J=23 Hz, 2F; *p*-F), −153.4 (t, J=22 Hz, 2F; *p*-F), −154.1 (t, J=23 Hz, 1F; *p*-F), −161.1 (dt, J=22, 8.4 Hz, 2F; *m*-F), −161.3 (dt, J=22, 9.0 Hz, 2F; *m*-F), −161.9 (dt, J=22, 9.0 Hz, 2F; *m*-F), −162.2 (m, 4F; *m*-F), −166.2 ppm (dt, J=20, 6.6 Hz, 2F; $C_6F_3N_2$); ESI-MS: m/z: 1627.0953 $[M]^+$; m/z calcd for $C_{77}H_{16}F_{31}N_7$: 1627.0978; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon\times10^{-4}$)=419 (4.3), 454 (5.5), 702 (5.4), 884 (1.2), 987 nm (1.2).

Hydroxyboron complex of *meso*-pentafluorophenyl-substituted quadruply N-fused [34]heptaphyrin 7: BBr_3 (2.9 mL, 31 mmol) was added to a solution of **6** (380 mg, 0.23 mmol) in dichloromethane (250 mL) in the presence of distilled ethyldiisopropylamine (EDIPA; 6.1 mL, 35 mmol), and the reaction mixture was refluxed for 28 h under N_2 atmosphere. After the reaction was quenched by the addition of water (50 mL), the products were extracted with diethyl ether (500 mL). The organic phase was washed with 3 M HCl (3×200 mL), neutralized by aqueous $NaHCO_3$, and then dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was subjected to silica gel column chromatography by using a 10:1 mixture of hexane and ethyl acetate. Evaporation of the last green fraction to dryness yielded **7** (262 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$): δ=8.10 (d, J=3.7 Hz, 1H; pyrrole-β), 8.09 (d, J=4.6 Hz, 1H; pyrrole-β), 7.99 (d, J=5.5 Hz, 1H; pyrrole-β), 7.98 (d, J=3.7 Hz, 1H; pyrrole-β), 7.86 (d, J=4.6 Hz, 1H; pyrrole-β), 7.79 (d, J=4.6 Hz, 1H; pyrrole-β), 7.49 (d, J=4.6 Hz, 1H; pyrrole-β), 7.40 (d, J=4.6 Hz, 1H; pyrrole-β), 7.30 (m, 1H; pyrrole-β), 7.20 (m, 1H; pyrrole-β), 7.06 (d, J=4.6 Hz, 1H; pyrrole-β), 6.52 (d, J=5.5 Hz, 1H; pyrrole-β), 6.31 (d, J=4.6 Hz, 1H; pyrrole-β), 3.71 (d, J=4.6 Hz, 1H; pyrrole-β), −1.6 ppm (brs, 1H; OH); ^{19}F NMR (565 MHz, $CDCl_3$): δ=−136.6 (dd, J=58, 20 Hz, 1F; $C_6F_3N_2$), −137.5 (dd, J=26, 5.4 Hz, 1F; *o*-F), −137.7 (dd, J=25, 6.0 Hz, 1F; *o*-F), −137.8 to −137.9 (m, 2F; *o*-F), −138.0 (dd, J=25, 6.6 Hz, 1F; *o*-F), −138.1 (dd, J=25, 6.0 Hz, 1F; *o*-F), −138.8 (m, 3F; *o*-F, $C_6F_3N_2$), −139.1 (dd, J=61, 30 Hz, 1F; $C_6F_3N_2$), −139.5 (dd, J=51, 24 Hz, 1F; *o*-F), −139.7 (dd, J=57, 28 Hz, 1F; $C_6F_3N_2$), −139.8 (dd, J=55, 35 Hz, 1F; *o*-F), −152.3 (t, J=22 Hz, 1F; *p*-F), −152.5 (t, J=22 Hz, 1F; *p*-F), −152.6 (t, J=23 Hz, 1F; *p*-F), −153.0 (t, J=22 Hz, 1F; *p*-F), −153.2 (t, J=22 Hz, 1F; *p*-F), −161.6 to −162.2 (m, 10F, *m*-F), −168.3 (m, 1F; $C_6F_3N_2$), −168.7 ppm (m, 1F; $C_6F_3N_2$); ^{11}B NMR (193 MHz, $CDCl_3$): δ=−5.2 ppm (brs); ESI-MS: m/z (%): 1653.0918 $[M]^+$ (100), 1636.0945 $[M-OH]^+$ (7); UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon\times10^{-4}$)=375 (4.4), 419 (3.8), 450 (6.1), 660 (11.0), 895 nm (2.7); fluorescence (CH_2Cl_2, λ_{ex}= 895 nm): λ_{max}=1068, 1214 nm.

Methoxyboron complex of *meso*-pentafluorophenyl-substituted quadruply N-fused [34]heptaphyrin 8: Methanol (30 mL) was added to a solution of **7** (28 mg, 17 μmol) in ethyl acetate (10 mL), and the solution was refluxed for 12 h to provide **8** (17 mg, 60%) with the recovery of **7** (11 mg, 39%).^{1}H NMR (600 MHz, $CDCl_3$): δ=8.11 (m, 1H; pyrrole-β), 8.08 (d, J=4.6 Hz, 1H; pyrrole-β), 7.99 (d, J=4.6 Hz, 1H; pyrrole-β), 7.98 (d, J=4.1 Hz, 1H; pyrrole-β), 7.86 (d, J=3.7 Hz, 1H; pyrrole-β), 7.78 (d, J=4.6 Hz, 1H; pyrrole-β), 7.50 (d, J=5.0 Hz, 1H; pyrrole-β), 7.40 (d, J=5.0 Hz, 1H; pyrrole-β), 7.32 (dd, J=9.2, 4.6 Hz, 1H; pyrrole-β), 7.20 (d, J=3.7 Hz, 1H; pyrrole-β), 7.03 (d, J=5.0 Hz, 1H; pyrrole-β), 6.31 (m, 2H; pyrrole-β), 3.79 (d, J=4.6 Hz, 1H; pyrrole-β), 1.10 ppm (s, 3H; OMe); ^{19}F NMR (565 MHz, $CDCl_3$): δ=−136.8 (dd, J=56, 19 Hz, 1F; $C_6F_3N_2$), −137.7 to −137.9 (m, 4F; *o*-F, $C_6F_3N_2$), −138.2 (m, 2F; *o*-F), −138.6 to −138.9 (m, 2F; *o*-F, $C_6F_3N_2$), −139.0 (dd, J=25, 6.5 Hz, 1F; *o*-F), −139.0 (dd, J=59, 28 Hz, 1F; *o*-F), −139.4 (dd, J=56, 23 Hz, 1F; *o*-F), −139.7 (m, 2F; *o*-F, $C_6F_3N_2$), −152.3 (t, J=22 Hz, 1F; *p*-F), −152.6 (t, J=22 Hz, 1F; *p*-F), −152.7 (t, J=22 Hz, 1F; *p*-F), −153.1 (t, J=22 Hz, 1F; *p*-F), −153.4 (t, J=22 Hz, 1F; *p*-F), −161.6 (m, 2F; *m*-F), −161.8 to −162.3 (m, 8F; *m*-F), −168.3 (m, 1F; $C_6F_3N_2$), −168.7 ppm (m, 1F; $C_6F_3N_2$); ^{11}B NMR (193 MHz, $CDCl_3$): δ=−5.6 ppm (brs); ESI-MS: m/z (%): 1667.1043 $[M]^+$ (100), 1636.0876 $[M-OMe]^+$; UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon\times10^{-4}$)=374 (3.7), 450 (4.9), 660 (8.5), 892 nm (2.1); fluorescence (CH_2Cl_2, λ_{ex}=892 nm): λ_{max}=1069, 1233 nm.

Isopropoxyboron complex of *meso*-pentafluorophenyl-substituted quadruply N-fused [34]heptaphyrin 9: Isopropyl alcohol (25 mL) was added to a solution of **7** (104 mg, 63 μmol) in ethyl acetate (25 mL), and the solution was refluxed for 12 h to provide **9** (73 mg, 68%) with the recovery of **7** (22 mg, 21%). Recrystallization from 1,2-dichloroethane/isopropyl alcohol gave purple crystals. ^{1}H NMR (600 MHz, $CDCl_3$): δ=8.12 (d, J=4.8 Hz, 1H; pyrrole-β), 8.11 (d, J=4.8 Hz, 1H; pyrrole-β), 8.01 (d, J=4.9 Hz, 1H; pyrrole-β), 7.99 (d, J=5.5 Hz, 1H; pyrrole-β), 7.86 (d, J=4.9 Hz, 1H; pyrrole-β), 7.77 (d, J=4.8 Hz, 1H; pyrrole-β), 7.53 (d, J=5.5 Hz, 1H; pyrrole-β), 7.42 (d, J=5.5 Hz, 1H; pyrrole-β), 7.36 (dd, J=8.9, 4.9 Hz, 1H; pyrrole-β), 7.22 (d, J=2.8 Hz, 1H; pyrrole-β), 7.08 (d, J=4.8 Hz, 1H; pyrrole-β), 6.54 (d, J=5.5 Hz, 1H; pyrrole-β), 6.32 (d, J=4.8 Hz, 1H; pyrrole-β), 3.77 (d, J=4.8 Hz, 1H; pyrrole-β), 1.19 (m, 1H; BOC*H*(CH_3)$_2$), −0.22 (d, J=6.2 Hz, 3H; BOCH(CH_3)$_2$), −0.29 ppm (d, J=6.2 Hz, 3H; BOCH(CH_3)$_2$); ^{19}F NMR (565 MHz, $CDCl_3$): δ=−135.7 to −135.9 (m, 2F; $C_6F_3N_2$), −136.1 (dd, J=26, 7.3 Hz, 1F; *o*-F), −136.3 (dd, J=26, 7.3 Hz, 1F; *o*-F), −136.6 (d, J=21 Hz, 1F; *o*-F), −136.9 (dd, J=25, 5.9 Hz, 1F; *o*-F), −137.1 (dd, J=25, 5.8 Hz, 1F; *o*-F), −137.5 (br, 1F; *o*-F), −137.6 (d, J=21 Hz, 1F; *o*-F), −137.8 to −137.9 (m, 2F; *o*-F, $C_6F_3N_2$), −138.1 to −138.4 (m, 3F; *o*-F, $C_6F_3N_2$), −151.3 (t, J=22 Hz, 1F; *p*-F), −151.4 (t, J=23 Hz, 1F; *p*-F), −151.5 (t, J=22 Hz, 1F; *p*-F), −151.9 (t, J=23 Hz, 1F; *p*-F), −152.2 (t, J=23 Hz, 1F; *p*-F), −160.4 to −161.1 (m, 10F; *m*-F), −167.2 (m, 1F; $C_6F_3N_2$), −167.6 ppm (m, 1F; $C_6F_3N_2$); ^{11}B NMR (193 MHz, $CDCl_3$): δ=−5.3 ppm (brs); ESI-MS: m/z (%): 1695.1427 $[M]^+$ (92), 1636.0954 $[M-OiPr]^+$ (100); UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon\times10^{-4}$)=374 (4.4), 450 (6.3), 659 (11.1), 890 nm (2.7); fluorescence (CH_2Cl_2, λ_{ex}=890 nm); λ_{max}=1069, 1216 nm.

X-ray crystallography: CCDC-604429 (**1**),CCDC-604430 (**5**), CCDC-604431 (**9**) 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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[9] Crystallographic data for **5**: $C_{86}H_{30}F_{33}N_7$, $M_w = 1788.17$, monoclinic, space group $P2_1/n$ (No.14), $a = 13.528(2)$, $b = 12.225(2)$, $c = 44.328(8)$ Å, $\beta = 96.543(3)°$, $V = 7283(2)$ Å^3, $\rho_{calcd} = 1.631$ g cm^{-3}, $Z = 4$, $R_1 = 0.1081$ [$I > 2.0\sigma(I)$], $R_w = 0.2558$ (all data), GOF = 1.154 [$I > 2.0\sigma(I)$].

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