CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201100919

Synthesis of A_2B_6-Type [36]Octaphyrins: Copper(II)-Metalation-Induced Fragmentation Reactions to Porphyrins and *N*-Fusion Reactions of *meso*-(3-Thienyl) Substituents

Hirotaka Mori,[a] Naoki Aratani,[a, b] and Atsuhiro Osuka*[a]

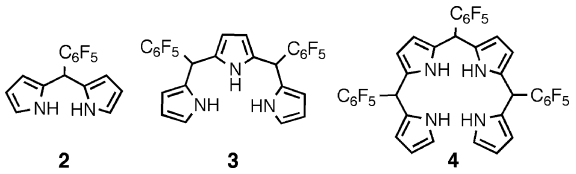
Abstract: 5,10,15-Tris(pentafluorophenyl)tetrapyrromethane was efficiently prepared through a route involving stepwise diaroylation of 5-pentafluorophenyldipyrromethane. A_2B_6-type [36]octaphyrins were prepared by the cross condensation of the tetrapyrromethane with aryl aldehydes in moderate yields. A_2B_6-type [36]octaphyrins bearing 2,4,6-trifluorophenyl, 2,6-dichlorophenyl, and phenyl substituents underwent Cu^{II}-metalation-induced fragmentation to give two molecules of AB_3-type Cu^{II} porphyrins. A_2B_6-type [36]octaphyrin bearing 3-thienyl substituents underwent thermal *N*-thienyl fusion reactions to provide a modestly aromatic [38]octaphyrin, which, upon treatment with MnO_2, underwent further *N*-thienyl fusion and subsequent oxidation to give a nonaromatic doubly *N*-thienyl fused [36]octaphyrin.

Keywords: aromaticity · fragmentation reactions · fusion reactions · octaphyrin · porphyrinoids

Introduction

In the last two decades, considerable efforts have been devoted to the exploration of expanded porphyrins in light of their potential applications in near-IR absorbing dyes, nonlinear optical materials with large two-photon absorption cross sections, anion sensors, explosives sensors, molecular recognition hosts, and so on.[1] We entered this chemistry since our serendipitous finding that a series of *meso*-(pentafluorophenyl)-substituted expanded porphyrins were efficiently formed in the acid-catalyzed condensation of pentafluorobenzaldehyde (**1**) and pyrrole at rather high concentration (ca. 67 mM each).[2] With these expanded porphyrins, we have revealed their intriguing chemistry such as pronounced nonlinear optical properties,[3] rich coordination chemistry,[4] unprecedented skeletal rearrangements,[5,6] and formation of electronically novel species, including stable Hückel antiaromatic molecules, Möbius aromatic and antiaromatic molecules,[7,8] and stable radicals.[9] Among these expanded porphyrins, [36]octaphyrins possess a unique position, since they show unprecedented reactions such as fragmentation to two molecules of porphyrins in a metathesis-like reaction mode[10] and hydrolytic cleavage of a constituent pyrrole.[11a] Furthermore, nonaromatic [36]octaphyrin has been shown to become a Möbius aromatic molecule upon diprotonation.[11b] Despite these findings, the chemistry of [36]octaphyrins has remained at its infant stage, since [36]octaphyrin bearing only *meso*-pentafluorophenyl substituents has been studied so far.[10,11] As a part of our program to explore the chemistry of expanded porphyrins, we decided to investigate the chemistry of A_2B_6 [36]octaphyrins bearing other aryl substituents.

Since the first report on the synthesis of the expanded porphyrins,[2] size-selective syntheses of expanded porphyrins have been developed by using 5-(2,3,4,5,6-pentafluorophenyl)dipyrromethane (**2**) or 5,10-bis(2,3,4,5,6-pentafluorophenyl)tripyrromethane (**3**).[12] In these syntheses, pentafluorophenyl substituent has been commonly employed, because they play an important role in providing steric hindrance at the *meso*-position to direct the condensation reactions towards larger macrocycles and to protect linear and cyclic oligopyrromethane intermediates from oxidative degradation. Dipyrromethane **2** was previously prepared by trifluoroacetic acid (TFA) catalyzed condensation of **1** with pyrrole as a solvent (Lindsey method),[13] and its large-scale preparation was achieved by the condensation in water (Dehaen method).[14] Tripyrromethane **3** was prepared from TFA-catalyzed condensation of **2** with pyrrole[12a,15] or from TFA-catalyzed condensation of dipyrromethane monocarbinol[16] with pyrrole.[12c] Compound **3** is an important precursor in the synthesis of [32]heptaphyrin[17] and *meso*-unsubsti-



[a] H. Mori, Dr. N. Aratani, 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

[b] Dr. N. Aratani
PRESTO Japan Science and Technology Agency (Japan)

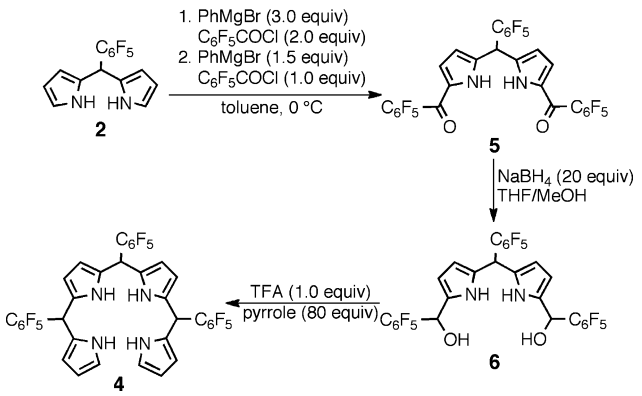
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201100919.

tuted hexaphyrin.[9] 5,10,15-Tris(pentafluorophenyl)tetrapyrromethane (**4**) was prepared from a diacylated dipyrromethane by Lindsey method[16b] and was used for the synthesis of a [32]heptaphyrin.[17]

Herein, we disclose an improved synthesis of **4** and its use for the synthesis of A_2B_6 [36]octaphyrins(1.1.1.1.1.1.1.1) **8** by the cross condensation with aryl aldehydes. This protocol allowed the incorporation of two different *meso*-aryl substituents at the 5- and 25-positions of [36]octaphyrins.

Results and Discussion

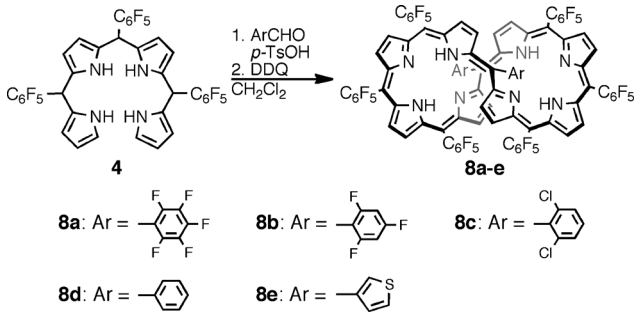
Tetrapyrromethane **4** was prepared by the reaction route shown in Scheme 1, in which the diaroylation of **2** is a key



Scheme 1. Synthesis of tetrapyrromethane **4**.

step. Diaroylated product **5** was originally prepared in 25% yield on the basis of a sequential EtMgBr/C_6F_5COCl procedure developed by Lindsey et al.,[16] and its yield was recently improved to 69% by using mesityl Grignard reagent for activation of dipyrromethane.[18] After extensive experimentation, we found that sequential additions of 1) phenyl Grignard reagent (3.0 equiv) and C_6F_5COCl (2.0 equiv) and 2) phenyl Grignard reagent (1.5 equiv) and C_6F_5COCl (1.0 equiv) in toluene reproducibly provided **5** in more than 83% yield. This reaction protocol allowed large-scale preparation of **5** (18.6 g) from **2** (10.0 g). Diaroylated dipyrromethane **5** was reduced with $NaBH_4$ to dipyrromethane dicarbinol **6**, which reacted with pyrrole with the aid of TFA to give **4**, which was isolated in 73% yield for two steps.

Then, the synthesis of octaphyrins **8** was examined by the cross condensation of **4** with aryl aldehydes (Scheme 2). Initially, the synthesis of **8a** by the reaction of **1** with **4** was examined as a benchmark case. The use of $BF_3{\cdot}OEt_2$ as an acid led to extensive scrambling even at 0°C, as indicated by the formation of heptaphyrin and nonaphyrin detected by TLC analysis and electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. Scrambling was considerably suppressed by the use of methanesulfonic acid; however, scrambled byproducts that hampered the isolation of **8a** were still observed. We found that *p*-toluenesulfonic acid (*p*-TsOH) did not cause scrambling and gave octaphyrin **8a** in



Scheme 2. Synthesis of octaphyrin **8a–e**. DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.

25% yield by the reaction in CH_2Cl_2 at 0°C. The absence of heptaphyrin and nonaphyrin byproducts facilitated the isolation of **8a**. Under similar conditions, octaphyrins **8b** (Ar = 2,4,6-trifluorophenyl), **8c** (Ar = 2,6-dichlorophenyl), and **8d** (Ar = phenyl) were prepared in 15, 10, and 15% yields, respectively. The UV/Vis absorption spectra of **8b–d** in CH_2Cl_2 are similar to that of **8a** with regard to broad bands around 410 and 640 nm (Figure 1). The ^1H NMR spectra of

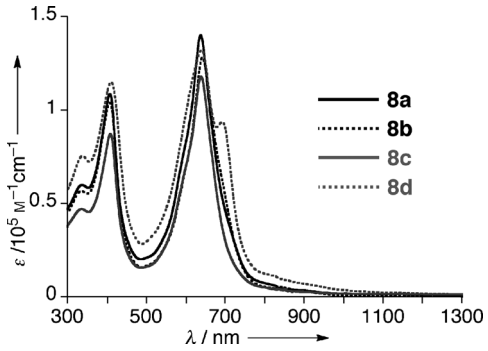


Figure 1. UV/Vis absorption spectra of **8a**, **8b**, **8c**, and **8d** in CH_2Cl_2.

8b–d are also roughly similar to that of **8a**. Crystals of **8b** suitable for X-ray diffraction analysis were obtained from slow diffusion of heptane into its chloroform solution. The solid-state structure of **8b** shows a figure-eight conformation similar to that of **8a**.[2b] Interestingly, less hindered 2,4,6-trifluorophenyl substituents occupy the sterically congested hinge positions of the figure-eight conformation (Figure 2). Bond-length alternation is evident for the structure of **8b**, hence suggesting its nonaromatic character. It is thus conceivable that octaphyrins **8b–d** take figure-eight conformations mainly in nonpolar solvents, while they have considerable conformational flexibility.

First, Cu^{II} metalation reactions of **8b**, **8c**, and **8d** were examined to confirm the generality of the fragmentation reaction (Scheme 3). When the metalation reactions were conducted with $Cu(OAc)_2$ and sodium acetate at 110°C, octaphyrins **8b**, **8c**, and **8d** gave AB_3-type Cu^{II} porphyrins **9bCu**, **9cCu**, and **9dCu** in 83, 89, and 89% yields, respectively. These results indicate a certain generality of the thermal fragmentation reaction for bis-Cu^{II} complexes of [36]octaphyrins despite slight difference in *meso*-aryl substituent.

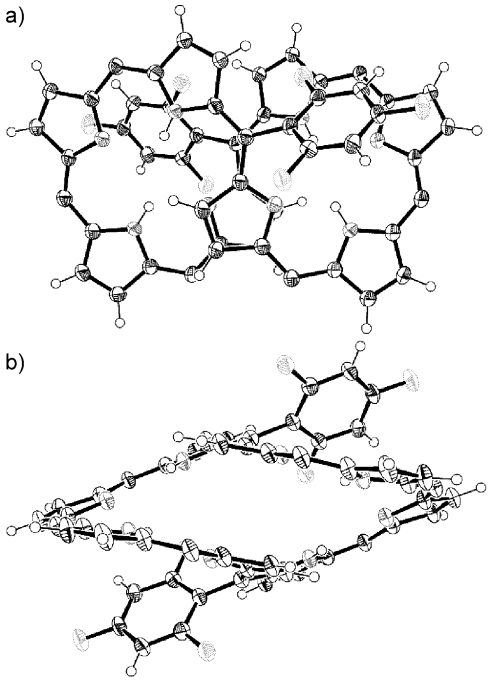
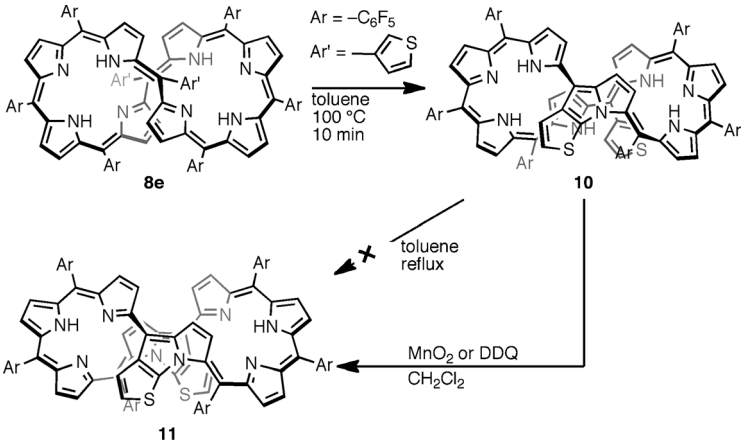


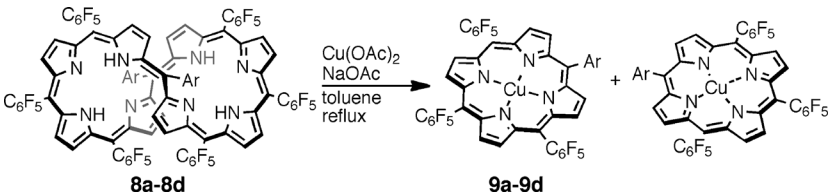
Figure 2. X-ray crystal structure of **8b**. a) Top view. b) Side view. The thermal ellipsoids represent 50% probability. *meso*-Pentafluorophenyl groups and solvent molecules are omitted for clarity.

Fusion reactions of expanded porphyrins have shown promise in creating new conjugated systems, since the resulting rigid and planar tricyclic ring system will lead to significant changes in the structural and electronic properties of porphyrins.[2a,6b,19] As an interesting case, we recently found that a 3-thienyl substituent at the *meso*-position of [26]hexaphyrin triggered a facile fusion reaction with the neighboring pyrrolic nitrogen atom to form an *N*-thienyl fused [28]hexaphyrin with distinct Möbius aromaticity.[19h] Thus, in order to apply this synthetic strategy to octaphyrins, A_2B_6-type [36]octaphyrin **8e** was prepared in 15% yield by the reaction of **4** with 3-thiophenecarbaldehyde. UV/Vis absorption spectrum of **8e** shows two bands at 412 and 622 nm, similar to those of [36]octaphyrins **8a–d** (Figure 1). Interestingly, the ^{1}H NMR spectrum of **8e** shows two sets of signals in a ratio of 3:1, where the minor set has C_2 symmetry and the major set showed a spectrum of higher symmetry (see the Supporting Information). These data indicate that **8e** may adopt two main figure-eight conformations with 3-thienyl substituents at different positions (Scheme 4).[20]

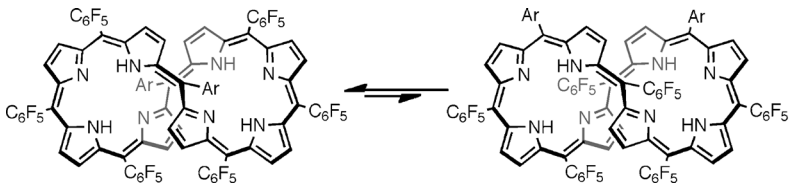
We observed a slow *N*-thienyl fusion reaction of **8e** in solution to provide monofused product **10** (Scheme 5). This *N*-fusion reaction occurred very slowly even in the solid state at room temperature. As a convenient and reproducible method, *N*-thienyl fused octaphyrin **10** was obtained in 70% yield by heating a toluene solution of **8e** at reflux for 10 min. The structure of **10** has been revealed by X-ray diffraction analysis as shown in Figure 3. The coplanar tricyclic segment is located at the hinge position of a roughly figure-eight structure across a [38]octaphyrin electronic network. In line with this nonsymmetric structure, the ^{1}H NMR spectrum of **10** exhibited five signals at $\delta = 11.14$, 10.12, 9.93, 9.21, and 6.86 ppm due to the NH protons, and sixteen signals in the range of $\delta = 6.71$–4.77 ppm due to the β-protons.



Scheme 5. Formation of singly and doubly *N*-thienyl fused octaphyrins **10** and **11**.



Scheme 3. Fragmentation reaction of octaphyrin **8a–d**.



Scheme 4. Conformational equilibrium of **8e** (Ar = 3-thienyl).

The observed deshielded chemical shifts of the β-protons thus can be understood in terms of modest Hückel aromaticity arising from the doubly twisted 38-π-electron network. In line with this interpretation, the UV/Vis absorption spectrum of **10** shows a sharp and strong Soret-like band at 737 nm and low-energy Q-like bands at 985 and 1120 nm (Figure 5). The nucleus-independent chemical shift (NICS) values[21] were calculated to be −11.54, −3.05, and −3.11 ppm at A, B, and C (designated in Figure 3), respectively.

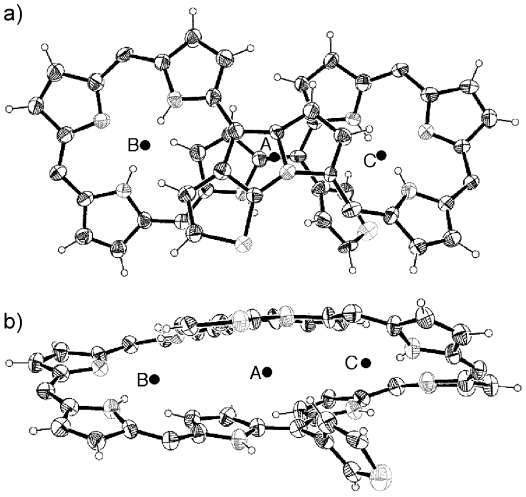


Figure 3. X-ray crystal structure of **10**. a) Top view. b) Side view. The thermal ellipsoids represent 30% probability. *meso*-Pentafluorophenyl groups and solvent molecules are omitted for clarity. A, B, and C indicate points at which nucleus-independent chemical shift (NICS) values were calculated. See text for details.

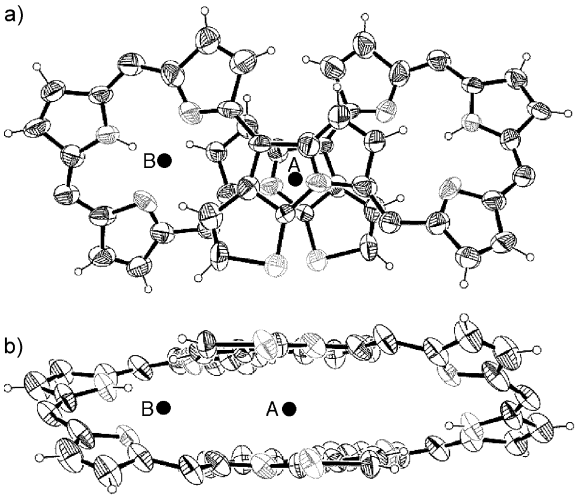


Figure 4. X-ray crystal structure of **11**. a) Top view. b) Side view. The thermal ellipsoids represent 30% probability. *meso*-Pentafluorophenyl groups and solvent molecules are omitted for clarity. A and B indicate points at which NICS values were calculated. See text for details.

The monofused [38]octaphyrin **10** did not show any further *N*-thienyl fusion reactivity under forcing conditions. It was thought that the *N*-thienyl fusion reaction would proceed only from [36]octaphyrin but not from [38]octaphyrin. We thus attempted an oxidation of **10** to the corresponding 36π-congener. A solution of **10** in CH_2Cl_2 was treated with an excess amount of MnO_2 at room temperature, which induced an instantaneous vivid color change from dark green to deep blue to indicate the occurrence of the second *N*-thienyl fusion reaction. After the usual workup, doubly *N*-thienyl-fused [36]octaphyrin **11** was isolated in 80% yield. It is considered that the fusion reaction of a putative singly *N*-thienyl fused [36]octaphyrin is fast at room temperature to provide doubly *N*-thienyl fused [38]octaphyrin that is readily oxidized to **11** under the reaction conditions. The ^{1}H NMR spectrum exhibited broad signal due to NH protons, eight sets of signals due to the β-protons, and two signals due to the 3-thienyl groups. Fortunately, we revealed the structure of **11** by X-ray analysis to be a symmetric figure-eight conformation (Figure 4). The UV/Vis absorption spectrum shows broad bands at 425 and 582 nm, which are similar to those of **8e** (Figure 5). These optical data indicate the nonaromatic properties of **11** with a 36-π-electron circuit. In line with this consideration, the NICS values were calculated at points A and B (designated in Figure 4) to be +4.55 and +4.57 ppm, respectively. As such, the incorporation of 3-thienyl substituents at *meso*-positions of [36]octaphyrin triggered the facile *N*-thienyl fusion reaction, similar to [26]hexaphyrins.[19h]

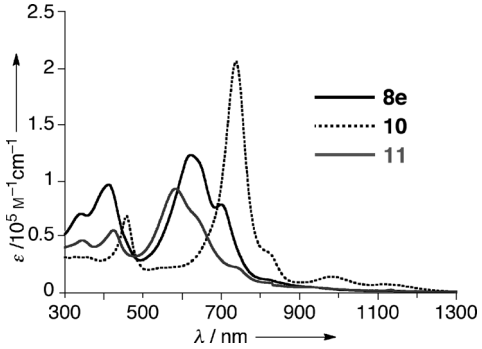


Figure 5. UV/Vis absorption spectra of **8e**, **10**, and **11** in CH_2Cl_2.

Conclusions

The tetrapyrromethane **4**, a key precursor for the synthesis of octaphyrin, was prepared in good yield and on a large scale. A_2B_6-type [36]octaphyrins **8b–e** were prepared by the reaction of **4** with aryl aldehydes in moderate yields and have been shown to take figure-eight structures in solution. [36]Octaphyrins **8b–d** underwent thermal Cu^{II}-metalation-induced fragmentation reaction to two Cu^{II} porphyrins. [36]Octaphyrin bearing 3-thienyl groups at the *meso*-positions underwent facile *N*-thienyl fusion reaction to provide *N*-thienyl fused [38]octaphyrin **10** that is moderately aromatic. Applicability of this synthetic strategy to other expanded porphyrins is being actively studied in our laboratory.

Experimental Section

General: ^{1}H and ^{19}F NMR spectra were recorded on a JEOL ECA-600 spectrometer (600 MHz for ^{1}H and 565 MHz for ^{19}F). Chemical shifts were reported as delta scale in ppm relative to the residual solvent as the internal reference for ^{1}H ($\delta = 7.260$ ppm); hexafluorobenzene was used as

external reference for ^{19}F ($\delta = -162.9$ ppm). NMR signals were assigned from the ^1H–^1H COSY spectra and by comparison with the spectra in the presence of D_2O (signals assigned for NH protons disappear in the presence of D_2O). UV/Vis spectra were recorded on a Shimadzu UV-3100PC spectrometer. High-resolution ESI-TOF mass spectra of samples in acetonitrile were recorded on a BRUKER microTOF instrument in the positive or negative ion mode. X-ray data were recorded on a Rigaku-Raxis imaging plate system. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Silica gel column chromatography was performed on Wakogel C-300 and C-400. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck 5554).

1,9-Bis(pentafluorobenzoyl)-5-(pentafluorophenyl)dipyrromethane (**5**): A solution of 5-(pentafluorophenyl)dipyrromethane (**2**, 10.0 g, 32 mmol) in dry toluene (250 mL) was treated with a solution of PhMgBr in THF (96 mmol; 1.1 M) at 0 °C. After 15 min, pentafluorobenzoyl chloride (9.6 mL, 64 mmol) was added slowly to the reaction mixture, and the resultant solution was stirred for an additional 15 min. Then, the slow addition of PhMgBr (48 mmol; 1.1 M) and the aroyl chloride (4.8 mL, 32 mmol) was repeated over a period of 30 min. After being stirred for 15 min, the reaction mixture was quenched by addition of a saturated aqueous NH_4Cl (100 mL). The product was extracted with ethyl acetate. The combined organic extract was washed with water and dried over anhydrous Na_2SO_4. After the solvent was removed, precipitation from CH_2Cl_2 afforded the crude product, which was purified by recrystallization from CH_2Cl_2/hexane to give a white powder of **5** (18.6 g; 83 %). The spectral data were the same as those in the previous report.[16]

5,10,15-Tris(pentafluorophenyl)tetrapyrromethane (**4**) was prepared by our previous method.[17]

General procedure for synthesis of A_2B_6-type [36]octaphyrins (**8a–e**): A solution of aryl aldehyde (0.62 mmol) and **4** (500 mg, 0.62 mmol) in CH_2Cl_2 (12.5 mL) was placed in a 50 mL round-bottomed flask under nitrogen atmosphere at 0 °C. To the solution was added *p*-toluenesulfuric acid monohydrate (6.0 mg; 5 mol %), and the resulting solution was stirred for 2 h. Then, DDQ (1.1 g; 4.8 mmol) was added and the resulting mixture was stirred for 1 h and was passed through a short alumina column to remove the tar. Repeated silica-gel column chromatography (AcOEt/n-hexane, 1:19; then CH_2Cl_2/*n*-hexane, 1:9) gave **8** as a green fraction. Yields were 25 % for **8a**, 15 % for **8b**, 10 % for **8c**, 15 % for **8d**, and 15 % for **8e**.

5,25-Bis(2,4,6-trifluorophenyl)-10,15,20,30,35,40-hexakis(pentafluorophenyl)-[36]octaphyrin (**8b**): ^1H NMR (600 MHz, $CDCl_3$, 298 K, as conformational mixture; almost exclusively conformer A): $\delta = 13.48$ (br s, 2H; NH), 12.56 (br s, 2H; NH), 9.05 (br s, 2H; β-H), 8.01 (br s, 2H; β-H), 7.81 (br s, 2H; Ar-H), 6.67 (br s, 2H; β-H), 6.25 (br s, 2H; β-H), 6.15 (d, $J = 4.6$ Hz, 2H; β-H), 6.02 (d, $J = 4.6$ Hz, 2H; β-H), and 5.93 ppm (br s, 4H; β-H and Ar-H); ^{19}F NMR (565 MHz, $CDCl_3$): $\delta = -134.28$ (d, $J = 22.0$ Hz, 2F; *o*-F), −137.66 (d, $J = 22.0$ Hz, 2F; *o*-F), −138.14 (d, $J = 22.0$ Hz, 2F; *o*-F), −138.76 (br s, 2F; *o*-F), −138.84 (d, $J = 22.0$ Hz, 2F; *o*-F), −140.22 (d, $J = 22.0$ Hz, 2F; *o*-F), −150.62 (br s, 2F; *p*-F), −152.09 (t, $J = 22.0$ Hz, 2F; *p*-F), −152.19 (t, $J = 22.0$ Hz, 2F; *p*-F), −158.96 (m, 2F; *m*-F), −159.85 (m, 2F; *m*-F), and −160.53 ppm (m, 6F; *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 335 (56600), 408 (104000), and 647 (126000). HR ESI-TOF-MS (positive mode): *m*/*z* 1877.1605 $[M+H]^+$, calcd for $C_{88}H_{25}F_{36}N_8 = 1877.1622$; crystal data: $C_{88}H_{24}F_{36}N_8 \cdot$(heptane)$\cdot(CHCl_3)$, $M_r = 2052.0$, monoclinic, space group *P*2/*c* (No. 13), $a = 8.1869(1)$, $b = 15.0916(3)$, $c = 33.4995(6)$ Å, $\beta = 90.3617(9)°$, $V = 4138.90(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.660$ g cm^{-3}, $T = 93$ K, $R_1 = 0.0798$ [$I > 2\sigma(I)$], $R_w = 0.2341$ (all data), GOF = 1.054. Crystals were grown from $CHCl_3$/heptane.

5,25-Bis(2,6-dichlorophenyl)-10,15,20,30,35,40-hexakis(pentafluorophenyl)-[36]octaphyrin (**8c**): ^1H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 12.97$ (br s, 2H; NH), 12.03 (br s, 2H; NH), 8.61 (br s, 2H; β-H), 7.68 (br s, 2H; β-H), 7.41 (d, $J = 8.2$ Hz, 2H; *m*-H), 7.33 (d, $J = 8.2$ Hz, 2H; *m*-H), 7.29 (d, $J = 7.8$ Hz, 2H; *p*-H), 6.44 (br s, 2H; β-H), 6.28 (br s, 2H; β-H), 6.15 (br s, 2H; β-H), 6.07 (br s, 4H; β-H), and 6.02 ppm (d, $J = 4.1$ Hz, 2H; β-H); ^{19}F NMR (565 MHz, $CDCl_3$): $\delta = -133.40$ (br s, 2F; *o*-F), −134.12 (br s, 2F; *o*-F), −136.02 (dd, $J_1 = 22.0$ Hz, $J_2 = 95.34$, 2F; *o*-F), −137.17 (m, 6F; *o*-F), −150.83 (br s, 2F; *p*-F), −152.76 (t, $J = 22.0$ Hz, 2F; *p*-F), −154.43(br s, 2F; *p*-F), −157.46 (d, $J = 91.7$ Hz, 2F; *m*-F), −159.12 (m, 2F; *m*-F), −160.83 (m, 6F; *m*-F), and −161.07 ppm (m, 2F, *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 336 (47000), 409 (87000), and 639 (118000). HR ESI-TOF-MS (positive mode): *m*/*z* 1907.0638 $[M+H]^+$, calcd for $C_{88}H_{27}N_8F_{30}Cl_4 = 1907.0624$.

5,25-Bis(phenyl)-10,15,20,30,35,40-hexakis(pentafluorophenyl)-[36]octaphyrin (**8d**): ^1H NMR (600 MHz, $CDCl_3$, 298 K, as conformational mixture; conformer A : conformer B = 20:1); conformer A (major): $\delta = 12.90$ (br s, 2H; NH), 11.67 (br s, 2H; NH), 8.77 (br s, 2H; β-H), 7.71 (t, $J = 7.4$ Hz, 2H; *p*-H), 7.60 (br s, 2H; β-H), 6.88 (d, $J = 4.2$ Hz, 2H; β-H), 6.47 (br s, 1H; β-H), 6.21 (d, $J = 4.2$ Hz, 2H; β-H), 6.00 (br s, 2H; β-H), 5.98 (br s, 2H; β-H), and 5.87 ppm (d, 2H; β-H) (*o*-H and *m*-H of phenyl groups are too broad to analyze at 25 °C); ^{19}F NMR (565 MHz, $CDCl_3$): $\delta = -133.80$ (d, $J = 22.0$ Hz, 2F; *o*-F), −137.64 (d, $J = 22.0$ Hz, 2F; *o*-F), −137.80 (d, $J = 22.0$ Hz, 2F; *o*-F), −137.33 (dd, $J_1 = 7.3$ Hz, $J_2 = 22.0$ Hz, 2F; *o*-F), −139.05 (d, $J = 22.0$ Hz, 2F; *o*-F), −140.91 (d, $J = 22.0$ Hz, 2F; *o*-F), −150.26 (t, $J = 22.0$ Hz, 2F; *p*-F), −152.69 (d, $J = 22.0$ Hz, 4F; *p*-F), −159.22 (m, 2F; *m*-F), −160.11 (m, 2F; *m*-F), −160.36 (br s, 2F; *m*-F), and −160.83 ppm (m, 6F; *m*-F). Conformer B (minor): $\delta = 13.25$ (br s, 2H; NH), 12.43 (br s, 2H; NH), 8.67 (d, $J = 4.2$ Hz, 2H; β-H), 7.92 (br s, 2H; β-H), 7.67 (t, $J = 7.4$ Hz, 2H; *p*-H), 7.45 (br s, 2H; β-H), 6.66 (br s, 2H; β-H), 6.51 (d, $J = 4.2$ Hz, 2H; β-H), 6.36 (br s, 2H; β-H), and 5.98 ppm (br s, 2H; β-H). Other peaks are overlapped by the peaks of conformer A or too broad to analyze at 25 °C. ^{19}F NMR (565 MHz, $CDCl_3$): $\delta = -133.47$ (br s, 2F; *o*-F), −136.67 (d, $J = 22.0$ Hz, 2F; *o*-F), −137.10 (d, $J = 22.0$ Hz, 2F; *o*-F), −138.01 (dd, $J_1 = 7.3$ Hz, $J_2 = 22.0$ Hz, 2F; *o*-F), −138.27 (dd, $J_1 = 7.3$ Hz, $J_2 = 22.0$ Hz, 2F; *o*-F), −139.80 (d, $J = 22.0$ Hz, 2F; *o*-F), −151.11 (t, $J = 22.0$ Hz, 2F; *p*-F), −155.06 (d, $J = 22.0$ Hz, 4F; *p*-F), −162.80 (m, 2F; *m*-F), and −163.83 ppm (br s, 2F; *m*-F). Other peaks are overlapped by the peaks of conformer A. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 338 (75000), 411 (115000), 640 (132000), and 692 (94000). HR ESI-TOF-MS (positive mode): *m*/*z* 1769.2167 $[M+H]^+$, calcd for $C_{88}H_{31}N_8F_{30} = 1769.2187$.

5,25-Bis(3-thienyl)-10,15,20,30,35,40-hexakis(pentafluorophenyl)-[36]octaphyrin (**8e**): ^1H NMR (600 MHz, $CDCl_3$, 298 K, as conformational mixture; conformer A : conformer B = 3:1); conformer A (major): $\delta = 12.96$ (br s, 2H; NH), 11.33 (br s, 2H; NH), 8.48 (br s, 2H), 8.06 (br s, 2H), 7.83 (br s, 2H), 7.48 (br s, 2H), 7.03 (d, $J = 4.6$ Hz, 2H; β-H), 6.53 (br s, 2H), 6.20 (d, $J = 4.6$ Hz, 2H; β-H), 6.14 (br s, 2H), 6.06 (d, $J = 4.6$ Hz, 2H; β-H), and 5.99 ppm (br s, 2H). One peak was too broad to analyze at 25 °C. ^{19}F NMR (565 MHz, $CDCl_3$): $\delta = -133.77$ (d, $J = 22.0$ Hz, 2F; *o*-F), −137.20 (br s, 2F; *o*-F), −138.11 (br s, 2F; *o*-F), −138.20 (dd, $J_1 = 7.0$ Hz, $J_2 = 22.0$ Hz, 2F; *o*-F), −138.76 (d, $J = 22.0$ Hz, 2F; *o*-F), −141.12 (br s, 2F; *o*-F), −150.18 (br s, 2F; *p*-F), −152.63 (t, $J = 22.0$ Hz, 4F; *p*-F), −159.19 (m, 2F; *m*-F), −160.12 (m, 2F; *m*-F), −160.25 (br s, 2F; *m*-F), −160.70 (m, 2F; *m*-F), and −160.84 ppm (m, 4F; *m*-F). conformer B (minor): $\delta = 13.59$ (br s, 2H; NH), 12.37 (br s, 2H; NH), 8.64 (br s 2H), 8.62 (d, $J = 4.6$ Hz, 2H; β-H), 8.44 (d, $J = 4.6$ Hz, 2H; β-H), 7.74 (br s, 2H), 7.28 (dd, $J_1 = 2.9$ Hz, $J_2 = 9.7$ Hz, 2H; thienyl-H), 6.58 (br s, 2H), 6.55 (d, $J = 4.6$ Hz, 2H; β-H), 6.43 (d, $J = 4.6$ Hz, 2H; β-H), 6.09 (d, $J = 4.6$ Hz, 2H; β-H), 6.04 ppm (d, $J = 4.6$ Hz, 2H; β-H). Other peaks are overlapped by the peaks of conformer A or too broad to analyze at 25 °C. ^{19}F NMR (565 MHz, $CDCl_3$): $\delta = -134.43$ (br s, 2F; *o*-F), −136.76 (d, $J = 22.0$ Hz, 2F; *o*-F), −137.09 (d, $J = 22.0$ Hz, 2F; *o*-F), −137.80 (dd, $J_1 = 7.3$ Hz, $J_2 = 22.0$ Hz, 2F; *o*-F), −139.42 (dd, $J_1 = 7.3$ Hz, $J_2 = 22.0$ Hz, 2F; *o*-F), −141.12 (br 2F; *o*-F), −151.12 (t, $J = 22.0$ Hz, 2F; *p*-F), −154.84 (d, $J = 22.0$ Hz, 2F; *p*-F), −162.29 (m, 2F; *m*-F), −163.61 ppm (br s, 2F; *m*-F). Other peaks are overlapped by the peaks of conformer A. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 342 (71000), 412 (97000), 622 (122000), and 700 (79000). HR ESI-TOF-MS (negative mode): *m*/*z* 1779.1124 $[M-H]^-$, calcd for $C_{88}H_{25}N_8F_{30}S_2 = 1779.1159$.

General procedure for the fragmentation reaction of A_2B_6-type [36]octaphyrins (**8b–d**): A solution of [36]octaphyrin (**8b–d**; 10 μmol) in toluene was stirred at 110 °C in the presence of $Cu(OAc)_2$ (10 equiv) and of NaOAc (10 equiv) for 12 h under dinitrogen atmosphere in the dark. The reaction was quenched with aqueous $NaHCO_3$ solution and diluted with CH_2Cl_2. The organic layer was dried with anhydrous Na_2SO_4, and the sol-

vent was removed under reduced pressure to give the crude mixture. The separation of the products by silica gel column chromatography gave Cu^{II} porphyrin (**9b–d**) as a red fraction (**9bCu**: 83%, **9cCu**: 89%, and **9dCu**: 89% yield, respectively). These copper(II) porphyrins were demetalated quantitatively upon treatment with H_2SO_4 and TFA to provide corresponding free base porphyrins, **9bH$_2$**, **9cH$_2$**, and **9dH$_2$**, respectively.

5,10,15-Tris(pentafluorophenyl)-20-(2,4,6-trifluorophenyl) copper(II) porphyrin (**9bCu**): UV/Vis (CH_2Cl_2): λ_{max} [nm] = 408, 535, and 570. HR ESI-TOF-MS (positive mode): *m/z* 999.9978 $[M+H]^+$, calcd for $C_{44}H_{11}N_4F_{18}Cu$ = 999.9987.

5,10,15-Tris(pentafluorophenyl)-20-(2,6-dichlorophenyl) copper(II) porphyrin (**9cCu**): UV/Vis (CH_2Cl_2): λ_{max} [nm] = 410, 537, and 572. HR ESI-TOF-MS (positive mode): *m/z* 1015.9453 $[M+H]^+$, calcd for $C_{44}H_{12}N_4F_{15}Cl_2Cu$ = 1015.9464.

5,10,15-Tris(pentafluorophenyl)-20-phenyl copper(II) porphyrin (**9dCu**): UV/Vis (CH_2Cl_2): λ_{max} [nm] = 410, 535, and 570. HR ESI-TOF-MS (positive mode): *m/z* 946.9285 $[M+H]^+$, calcd for $C_{44}H_{14}N_4F_{15}Cu$ = 946.0269.

5,10,15-Tris(pentafluorophenyl)-20-(2,4,6-trifluorophenyl) porphyrin (**9bH$_2$**): ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.95 (d, J = 4.1 Hz, 2H; β-H), 8.90 (br s, 4H; β-H), 8.88 (d, J = 4.1 Hz, 2H; β-H), 7.21 (d, J = 8.3 Hz, 2H; *m*-H), and −2.90 ppm (br s, 2H; inner NH); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −104.98 (m, 2F; trifluorophenyl-*o*-F), −105.02 (m, 1F; trifluorophenyl-*p*-F), −136.43 (m, 6F; *o*-F), −151.41 (m, 3F; *p*-F), and −161.41 ppm (m, 6F; *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] = 412, 505, and 585. HR ESI-TOF-MS (positive mode): *m/z* 939.0810 $[M+H]^+$, calcd for $C_{44}H_{13}N_4F_{18}$ = 939.0847.

5,10,15-Tris(pentafluorophenyl)-20-(2.6-dichlorophenyl) porphyrin (**9cH$_2$**): ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.89 (br s, 4H; β-H), 8.83 (d, J = 4.1 Hz, 2H; β-H), 8.81 (d, J = 4.1 Hz, 2H; β-H), 7.84 (d, J = 7.8 Hz, 2H; *m*-H), 7.76 (d, J = 7.8 Hz, 1H; *p*-H), and −2.80 ppm (br s, 2H; inner NH); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −136.27 (dd, J_1 = 22.0 Hz, J_2 = 7.3 Hz, 4F; *o*-F), −136.45 (dd, J_1 = 25.7 Hz, J_2 = 11.0 Hz, 4F; *o*-F), −151.55 (m, 3F; *p*-F), and −1611.49 ppm (m, 6F; *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] = 413, 505, and 585. HR ESI-TOF-MS (positive mode): *m/z* 953.0317 $[M+H]^+$, calcd for $C_{44}H_{14}N_4F_{15}$ = 953.0351.

5,10,15-Tris(pentafluorophenyl)-20-phenyl porphyrin (**9dH$_2$**): ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.97 (d, J = 4.1 Hz, 2H; β-H), 8.89 (m, 4H; β-H), 8.81 (d, J = 4.1 Hz, 2H; β-H), 8.21 (d, J = 7.3 Hz, 2H; *o*-H), 7.21 (d, J = 7.3 Hz, 1H; *p*-H), 7.79 (m, 2H; *m*-H), and −2.83 ppm (br s, 2H; inner NH); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −136.43 (dd, J_1 = 24.9 Hz, J_2 = 7.3 Hz, 2F; *o*-F), −136.55 (dd, J_1 = 25.7 Hz, J_2 = 7.3 Hz, 4F; *o*-F), −151.70 (m, 3F; *p*-F), and −161.55 ppm (m, 6F; *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] = 413, 509, and 585. HR ESI-TOF-MS (positive mode): *m/z* 885.1108 $[M+H]^+$, calcd for $C_{44}H_{16}N_4F_{15}$ = 885.1130.

Singly *N*-thienyl fused [38]octaphyrin **10**: A solution of **8a** (36 mg, 20 μmol) in toluene (10 mL) was heated at reflux for 10 min. After removal of the solvent by using a rotary evaporator, separation over a silica gel column using CH_2Cl_2/hexane as an eluent gave singly thienyl-fused [38]octaphyrin **10** (25 mg; 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 11.10 (br s, 1H; NH), 10.06 (br s, 1H; NH), 9.89 (br s, 1H; NH), 9.14 (br s, 1H; NH), 6.85 (br s, 1H; NH), 6.79 (m, 2H; β-H), 6.71 (d, J = 4.6 Hz, 1H; β-H), 6.65 (d, J = 5.0 Hz, 1H; β-H), 6.54 (d, J = 4.6 Hz, 1H; β-H), 6.51 (m, 1H; β-H), 6.31 (d, J = 5.0 Hz, 1H; β-H), 6.23 (m, 1H; β-H), 6.04 (d, J = 4.1 Hz, 1H; β-H), 5.89 (d, J = 5.0 Hz, 1H; β-H), 5.66 (d, J = 4.1 Hz, 1H; β-H), 5.62 (d, J = 4.1 Hz, 1H; β-H; β-H), 5.25 (d, J = 5.0 Hz, 1H; β-H^d), 5.15 (m, 2H; β-H^c), 4.77 (d, J = 5.0 Hz, 1H; β-H^b), 4.37 (m, 1H; β-H^a), and 3.28 ppm (m, 1H; thienyl-H). Three thienyl protons were not detected, probably due to severe broadening both at room temperature and at −60 °C.; ^{19}F NMR (565 MHz, $CDCl_3$): δ = −135.34 (d, J = 22.0 Hz, 2F; *o*-F), −135.84 (d, J = 22.0 Hz, 2F; *o*-F), −136.61 (d, J = 22.0 Hz, 2F; *o*-F), −135.34 (d, J = 25.7 Hz, 2F; *o*-F), −136.69 (d, J = 25.7 Hz, 2F; *o*-F), −137.13 (m, 4F; *o*-F), −137.29 (d, J = 22.0 Hz, 2F; *o*-F), −137.46 (dd, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2F; *o*-F), −137.91 (d, J = 22.0 Hz, 2F; *o*-F), −138.09 (d, J = 22.0 Hz, 2F; *o*-F), −138.54 (m, 4F; *o*-F), −150.59 (t, J = 22.0 Hz, 2F; *p*-F), −151.08 (t, J = 22.0 Hz, 2F; *p*-F), −152.72 (t, J = 22.0 Hz, 2F; *p*-F), −153.05 (t, J = 22.0 Hz, 2F; *p*-F), −153.29 (t, J = 22.0 Hz, 2F; *p*-F), −153.67 (t, J = 22.0 Hz, 2F; *p*-F), −159.04 (m, 2F; *m*-F), −159.53 (m, 2F; *m*-F), −160.23 (m, 2F; *m*-F), −160.58 (m, 2F; *m*-F), and −161.10 ppm (m, 8F; *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 458 (69000), 737 (208000), 985 (14000), and 1120 (8000). HR ESI-TOF-MS (positive mode): *m/z* 1781.1289 $[M+H]^+$, calcd for $C_{84}H_{27}N_8F_{30}S_2$ = 1781.1316; crystal data : $C_{84}H_{24}F_{30}N_8S_2\cdot(PhCl)_{2.75}$, M_r = 2087.74, triclinic, space group $P\bar{1}$ (No. 2), a = 19.4720(4), b = 21.0120(4), c = 22.7379(4) Å, α = 76.5557(4), β = 73.7861(4), γ = 83.9060(9)°, V = 8679.8(3) Å^3, Z = 4, ρ_{calcd} = 1.598 g cm^{-3}, T = 93 K, R_1 = 0.1257 [I > 2σ(I)], R_w = 0.3913 (all data), GOF = 1.024. Crystals were grown from PhCl/*n*-nonane.

Doubly *N*-thienyl fused [36]octaphyrin **11**: Under nitrogen atmosphere, an excess amount of MnO_2 (50 mg) was added to a solution of **10** (10.0 mg, 5.6 μmol) in dichloromethane (10 mL), and the resulting solution was stirred for 15 min and was then passed through a short Celite column. Recrystallization from chlorobenzene/*n*-heptane gave **11** (8.0 mg; 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 13.66 (br s, 2H; NH), 8.28 (d, J = 4.9 Hz, 2H; β-H), 7.78 (d, J = 5.9 Hz, 4H; β-H), 7.60 (d, J = 4.8 Hz, 2H; β-H), 7.09 (d, J = 5.5 Hz, 4H; β-H), 6.86 (t, J = 4.8 Hz, 2H; β-H), 6.54 (d, J = 4.9 Hz, 2H; β-H), 6.22 (m, Hz, 4H; 2β-H and thienyl-H), and 6.02 ppm (m, 2H; thienyl-H); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −132.27 (d, J = 22.0 Hz, 2F; *o*-F), −135.19 (d, J = 22.0 Hz, 2F; *o*-F), −136.49 (d, J = 22.0 Hz, 2F; *o*-F), −136.66 (d, J = 20.7 Hz, 2F; *o*-F), −138.12 (d, J = 20.7 Hz, 2F; *o*-F), −138.54 (d, J = 22.0 Hz, 2F; *o*-F), −150.34 (t, J = 22.0 Hz, 2F; *p*-F), −151.31 (t, J = 22.0 Hz, 2F; *p*-F), −151.44 (t, J = 22.0 Hz, 2F; *p*-F), −159.41 (m, 2F; *m*-F), −159.61 (m, 2F; *m*-F), −160.07 (m, 2F; *m*-F), −160.31 (m, 4F; *m*-F), and −160.69 ppm (m, 2F; *m*-F). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 345 (46900), 425 (56000), and 582 (93400). HR ESI-TOF-MS (positive mode): *m/z* 1778.1031 $[M+H]^+$, calcd for $C_{84}H_{23}N_8F_{30}S_2$ = 1778.1035; cryatal data: $C_{84}H_{22}F_{30}N_8S_2\cdot(PhCl)_3$, M_r = 2109.83, orthorhombic, space group $C222_1$ (No. 20), a = 7.9846(5), b = 30.722(3), c = 34.370(3) Å, V = 8431.0(11) Å^3, Z = 4, ρ_{calcd} = 1.662 g cm^{-3}, T = 93 K, R_1 = 0.1534 [I > 2σ(I)], R_w = 0.4309 (all data), GOF = 1.173. Crystals were grown from PhCl/heptane.

Crystallographyic data: CCDC 853155 (**8b**), CCDC 853157 (**10**), and CCDC 853156 (**11**) 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.

Acknowledgements

This work was supported by Grants-in-Aids for Scientific Research (No. 22245006 (A) and 20108001 "pi-Space") from MEXT, Japan.

[1] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267; b) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795; c) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134; d) T. K. Chandrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676; e) Z. S. Yoon, A. Osuka, D. Kim, *Nat. Chem.* **2009**, *1*, 113; f) M. Stępień, N. Sprutta, L. Latos-Grażyński, *Angew. Chem.* **2011**, *123*, 4376; *Angew. Chem. Int. Ed.* **2011**, *50*, 4288; g) S. Saito, A. Osuka, *Angew. Chem.* **2011**, *123*, 4432; *Angew. Chem. Int. Ed.* **2011**, *50*, 4342; h) A. Osuka, S. Saito, *Chem. Commun.* **2011**, *47*, 4330.

[2] a) J.-Y. Shin, H. Furuta, A. Osuka, *Angew. Chem.* **2001**, *113*, 639; *Angew. Chem. Int. Ed.* **2001**, *40*, 619; b) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190.

[3] a) T. K. Ahn, J. H. Kwon, D. Y. Kim, D. W. Cho, D. H. Jeong, S. Keun, M. Suzuki, S. Shimizu, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 12856; b) Z. S. Yoon, J. H. Kwon, M.-C. Yoon, M. K. Koh, S. B. Noh, J. L. Sessler, J. T. Lee, D. Seidel, A. Aguilar, S. Shimizu, M. Suzuki, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2006**, *128*, 14128.

[4] a) S. Shimizu, V. G. Anand, R. Taniguchi, K. Furukawa, T. Kato, T. Yokoyama, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 12280; b) S. Mori, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 8030; c) S. Shimizu, A. Osuka, *Eur. J. Inorg. Chem.* **2006**, 1319.

[5] a) E. Vogel, M. Michels, L. Zander, J. Lex, N. S. Tuzun, K. N. Houk, *Angew. Chem.* **2003**, *115*, 2964; *Angew. Chem. Int. Ed.* **2003**, *42*, 2857; b) S. Saito, K. S. Kim, Z. S. Yoon, D. Kim, A. Osuka, *Angew. Chem.* **2007**, *119*, 5687; *Angew. Chem. Int. Ed.* **2007**, *46*, 5591; c) R. Sakamoto, S. Saito, S. Shimizu, Y. Inokuma, N. Aratani, A. Osuka, *Chem. Lett.* **2010**, *39*, 439; d) K. Moriya, S. Saito, A. Osuka, *Angew. Chem.* **2010**, *122*, 4393; *Angew. Chem. Int. Ed.* **2010**, *49*, 4297; e) T. Yoneda, S. Saito, H. Yorimitsu, A. Osuka, *Angew. Chem.* **2011**, *123*, 3537; *Angew. Chem. Int. Ed.* **2011**, *50*, 3475; f) Y. Tanaka, H. Mori, T. Koide, H. Yorimitsu, N. Aratani, A. Osuka, *Angew. Chem.* **2011**, *123*, 11662; *Angew. Chem. Int. Ed.* **2011**, *50*, 11460.

[6] a) M. Suzuki, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 464; b) M. Suzuki, A. Osuka, *Angew. Chem.* **2007**, *119*, 5263; *Angew. Chem. Int. Ed.* **2007**, *46*, 5171.

[7] a) M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem.* **2007**, *119*, 8015; *Angew. Chem. Int. Ed.* **2007**, *46*, 7869; b) E. Pacholska-Dudziak, J. Skonieczny, M. Pawlicki, L. Szterenberg, Z. Ciunik, L. Latos-Grażyński, *J. Am. Chem. Soc.* **2008**, *130*, 6182; c) M. Stępień, B. Szysko, L. Latos-Grażyński, *J. Am. Chem. Soc.* **2010**, *132*, 3140.

[8] a) Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 693; *Angew. Chem. Int. Ed.* **2008**, *47*, 681; b) J. K. Park, Z. S. Yoon, M.-C. Yoon, K. S. Kim, S. Mori, J.-Y. Shin, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2008**, *130*, 1824; c) J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568; d) S. Saito, J.-Y. Shin, J. M. Lim, K. S. Kim, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 9803; *Angew. Chem. Int. Ed.* **2008**, *47*, 9657; e) T. Higashino, J. M. Lim, T. Miura, S. Saito, J.-Y. Shin, D. Kim, A. Osuka, *Angew. Chem.* **2010**, *122*, 5070; *Angew. Chem. Int. Ed.* **2010**, *49*, 4950.

[9] a) T. Koide, G. Kashiwazaki, M. Suzuki, K. Furukawa, M.-C. Yoon, S. Cho, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 9807; *Angew. Chem. Int. Ed.* **2008**, *47*, 9661; b) T. Koide, K. Furukawa, H. Shinokubo, J.-Y. Shin, K. S. Kim, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2010**, *132*, 7246.

[10] a) Y. Tanaka, W. Hoshino, S. Shimizu, K. Youfu, N. Aratani, N. Maruyama, S. Fujita, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 3046; b) Y. Tanaka, H. Shinokubo, Y. Yoshimura, A. Osuka, *Chem. Eur. J.* **2009**, *15*, 5674.

[11] a) S. Shimizu, Y. Tanaka, K. Youfu, A. Osuka, *Angew. Chem.* **2005**, *117*, 3792; *Angew. Chem. Int. Ed.* **2005**, *44*, 3726; b) J. M. Lim, J.-Y. Shin, Y. Tanaka, S. Saito, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2010**, *132*, 3105; c) H. Hata, Y. Kamimura, H. Shinokubo, A. Osuka, *Org. Lett.* **2006**, *8*, 1169.

[12] a) R. Taniguchi, S. Shimizu, M. Suzuki, J.-Y. Shin, H. Furuta, A. Osuka, *Tetrahedron Lett.* **2003**, *44*, 2505; b) Y. Tanaka, J.-Y. Shin, A. Osuka, *Eur. J. Org. Chem.* **2008**, 1341; c) Y. Kamimura, S. Shimizu, A. Osuka, *Chem. Eur. J.* **2007**, *13*, 1620; d) M. Suzuki, A. Osuka, *Org. Lett.* **2003**, *5*, 3943.

[13] C.-H. Lee, J. S. Lindsey, *Tetrahedron* **1994**, *50*, 11427.

[14] T. Rohand, E. Dolusic, T. H. Ngo, W. Maes, W. Dehaen, *ARKIVOC* **2007**, 307.

[15] J.-W. Ka, W.-S. Cho, C.-H. Lee, *Tetrahedron Lett.* **2000**, *41*, 8121.

[16] a) P. D. Rao, B. J. Littler, G. R. Geier III, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 1084; b) P. D. Rao, S. Dhanalekshmi, B. J. Littler, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 7323.

[17] S. Saito, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 9095.

[18] D. K. Dogutan, D. K. Bediako, T. S. Teets, M. Schwalbe, D. G. Nocera, *Org. Lett.* **2010**, *12*, 1036.

[19] a) S. Mori, J.-Y. Shin, S. Shimizu, F. Ishikawa, H. Furuta, A. Osuka, *Chem. Eur. J.* **2005**, *11*, 2417; b) S. Shimizu, J.-Y. Shin, H. Furuta, R. Ismael, A. Osuka, *Angew. Chem.* **2003**, *115*, 82; *Angew. Chem. Int. Ed.* **2003**, *42*, 78; c) M. Suzuki, R. Taniguchi, A. Osuka, *Chem. Commun.* **2004**, 2682; d) C.-H. Hung, J.-P. Jong, M.-Y. Ho, G.-H. Lee, S.-M. Peng, *Chem. Eur. J.* **2002**, *8*, 4542; e) A. Srinivasan, T. Ishizuka, H. Furuta, *Angew. Chem.* **2004**, *116*, 894; *Angew. Chem. Int. Ed.* **2004**, *43*, 876; f) A. Srinivasan, H. Furuta, *Acc. Chem. Res.* **2005**, *38*, 10–20; g) S. Tokuji, J.-Y. Shin, K. S. Kim, J. M. Lim, K. Youfu, S. Saito, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2009**, *131*, 7240; h) M. Inoue, K. S. Kim, M. Suzuki, J. M. Lim, J.-Y. Shin, D. Kim, A. Osuka, *Angew. Chem.* **2009**, *121*, 6815; *Angew. Chem. Int. Ed.* **2009**, *48*, 6687.

[20] A similar set of conformers in a ratio of 20:1 was detected in the ^{1}H NMR spectrum of **8d**.

[21] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

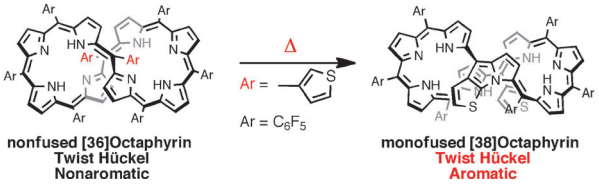
Received: November 10, 2011
Published online: ■■ ■■, 0000

FULL PAPERS

Porphyrinoids

*H. Mori, N. Aratani, A. Osuka** ——— ■■■–■■■

Synthesis of A_2B_6-Type [36]Octaphyrins: Copper(II)-Metalation-Induced Fragmentation Reactions to Porphyrins and *N*-Fusion Reactions of *meso*-(3-Thienyl) Substituents



Make 'em and break 'em: A_2B_6-type [36]octaphyrins were prepared in moderate yields by the cross condensation of tetrapyrromethane with aryl aldehydes. Compounds bearing 2,4,6-trifluorophenyl, 2,6-dichlorophenyl, and phenyl substituents underwent Cu^{II}-metalation-induced fragmentation to give AB_3-type Cu^{II} porphyrins, while that bearing a 3-thienyl substituent underwent *N*-thienyl fusion to provide a modestly aromatic [38]octaphyrin (see scheme).

