Supporting Information

Synthesis of Pyrrolidine-Fused [34]- and [36]Octaphyrins via 1,3-Dipolar Cycloaddition

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Instrumentation and Materials

^{1}H NMR (600 MHz) and ^{19}F NMR (565 MHz) spectra were taken on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ as internal reference for ^{1}H NMR (δ = 7.260 ppm) and hexafluorobenzene as external reference for ^{19}F NMR (δ = –162.9 ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. MALDI-TOF mass spectra were obtained with a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer without matrix. High resolution ESI-TOF mass spectra were taken on a Bruker microTOF. X-Ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector or a Rigaku-Raxis imaging plate system. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure

[3 + 2] Cycloaddition of Azomethine Ylide to Octaphyrin 1

A toluene (10 mL) solution of **1** (195 mg, 0.10 mmol), *N*-methylglycine (35.6 mg, 0.40 mmol) and paraformaldehyde (3.0 mg, 1.00 mmol) was heated at reflux for 2 h under nitrogen atmosphere. After evaporation of the solvent, purification by column chromatography with CH_2Cl_2/hexane (1/5) as eluent yielded bis-pyrrolidine-fused adduct **3** in 34% yield (70.2 mg, 34.0 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.93 (s, 2H, NH), 11.26 (s, 2H, NH), 7.12 (s, 2H, β-H), 7.05 (s, 2H, β-H), 6.64 (d, J = 4.1 Hz, 2H, β-H), 6.49 (d, J = 5.3 Hz, 2H, β-H), 6.36 (d, J = 5.3 Hz, 2H, β-H), 6.08 (d, J = 4.1 Hz, 2H, β-H), 5.24 (dd, J = 7.0, 7.0 Hz, 2H, pyrrolidine β-H), 4.60 (dd, J = 7.0, 7.0 Hz, 2H, pyrrolidine β-H), 3.29 (d, J = 9.0 Hz, 2H, pyrrolidine α-H), 3.27 (d, J = 9.0 Hz, 2H, pyrrolidine α-H), 3.03 (dd, J = 7.0, 9.0 Hz, 2H, pyrrolidine α-H), 2.90 (dd, J = 7.0, 9.0 Hz, 2H, pyrrolidine α-H), 2.35 (s, 6H, CH_3); λ_{max}

(CH_2Cl_2) (ε [$M^{-1}cm^{-1}$]) = 661 (5.5×10^4), 564 (1.0×10^5), 545 (1.0×10^5), 362 nm (4.9×10^4); HR-ESI-MS: *m/z* = 2063.2309. calcd for $C_{94}H_{35}F_{40}N_{10}$: 2063.2402 [$(M+H)^+$].

Compound Data for 2

^{1}H NMR (600 MHz, $CDCl_3$): δ = 12.41 (s, 1H, NH), 12.17 (s, 1H, NH), 12.06 (s, 1H, NH), 11.27 (s, 1H, NH), 8.38 (d, *J* = 5.0 Hz, 1H, β-H), 8.35 (d, *J* = 5.0 Hz, 1H, β-H), 7.74 (s, 1H, β-H), 7.32 (s, 1H, β-H), 7.05 (s, 2H, β-H), 6.65 (d, *J* = 4.6 Hz, 1H, β-H), 6.62 (d, *J* = 4.6 Hz, 1H, β-H), 6.50 (d, *J* = 5.0 Hz, 1H, β-H), 6.48 (d, *J* = 5.0 Hz, 1H, β-H), 6.31 (d, *J* = 5.0 Hz, 1H, β-H), 6.30 (d, *J* = 5.0 Hz, 1H, β-H), 6.08 (d, *J* = 4.6 Hz, 1H, β-H), 6.05 (d, *J* = 4.6 Hz, 1H, β-H), 5.72 (dd, *J* = 7.3, 7.3 Hz, 1H, pyrrolidine β-H), 4.99 (dd, *J* = 7.3, 7.3 Hz, 1H, pyrrolidine β-H), 3.41 (d, *J* = 9.0 Hz, 1H, pyrrolidine α-H), 3.39 (d, *J* = 9.0 Hz, 1H, pyrrolidine α-H), 3.28 (dd, *J* = 7.3, 9.0 Hz, 1H, pyrrolidine α-H), 3.10 (dd, *J* = 7.3, 9.0 Hz, 1H, pyrrolidine α-H), 2.42 (s, 3H, CH_3); λ_{max} (CH_2Cl_2) (ε [$M^{-1}cm^{-1}$]) = 663 (3.6×10^4), 611 (5.5×10^4), 581 (6.0×10^4), 545 (5.2×10^4), 420 (2.9×10^4), 364 nm (3.0×10^4); HR-ESI-MS: *m/z* = 2006.1761. calcd for $C_{91}H_{28}F_{40}N_9$: 2006.1823 [$(M+H)^+$].

MnO_2-Oxidation of [36]Octaphyrin 3 to [34]Octaphyrin 4

To a solution of **3** (41.2 mg, 0.02 mmol) in dichloromethane (50 mL), MnO_2 (17.4 mg 0.20 mmol) was added. After stirring for 10 min, MnO_2 was removed by alumina short column and the solvent was evaporated. Recrystallization from CH_2Cl_2 and hexane afforded purple solid of **4**. Spectroscopic data for **4:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.72 (s, 2H, NH), 6.58 (d, *J* = 4.9 Hz, 2H, β-H), 6.54 (d, *J* = 4.8 Hz, 2H, β-H), 6.52 (d, *J* = 4.7 Hz, 2H, β-H), 6.46 (d, *J* = 4.9 Hz, 2H, β-H), 6.14 (d, *J* = 4.6Hz, 2H, β-H), 5.97 (d, *J* = 4.7 Hz, 2H, β-H), 3.31 (d, *J* = 9.7 Hz, 2H, pyrrolidine α-H), 2.90 (d, *J* = 8.9 Hz,

2H, pyrrolidine α-H), 2.80 (t, J = 7.1 Hz, 2H, pyrrolidine β-H), 2.03 (s, 6H, CH_3), 1.52 (t, J = 8.8 Hz, 2H, pyrrolidine β-H), 1.34 (d, J = 10.6 Hz, 2H, pyrrolidine α-H), 1.32 (d, J = 8.2 Hz, 2H, pyrrolidine α-H); λ_{max} (CH_2Cl_2) (ε [$M^{-1}cm^{-1}$]) = 658 (1.3×10^5), 393 nm (6.0×10^4); HR-ESI-MS: m/z = 2061.2192. calcd for $C_{94}H_{33}F_{40}N_{10}$: 2061.2245 [$(M+H)^+$].

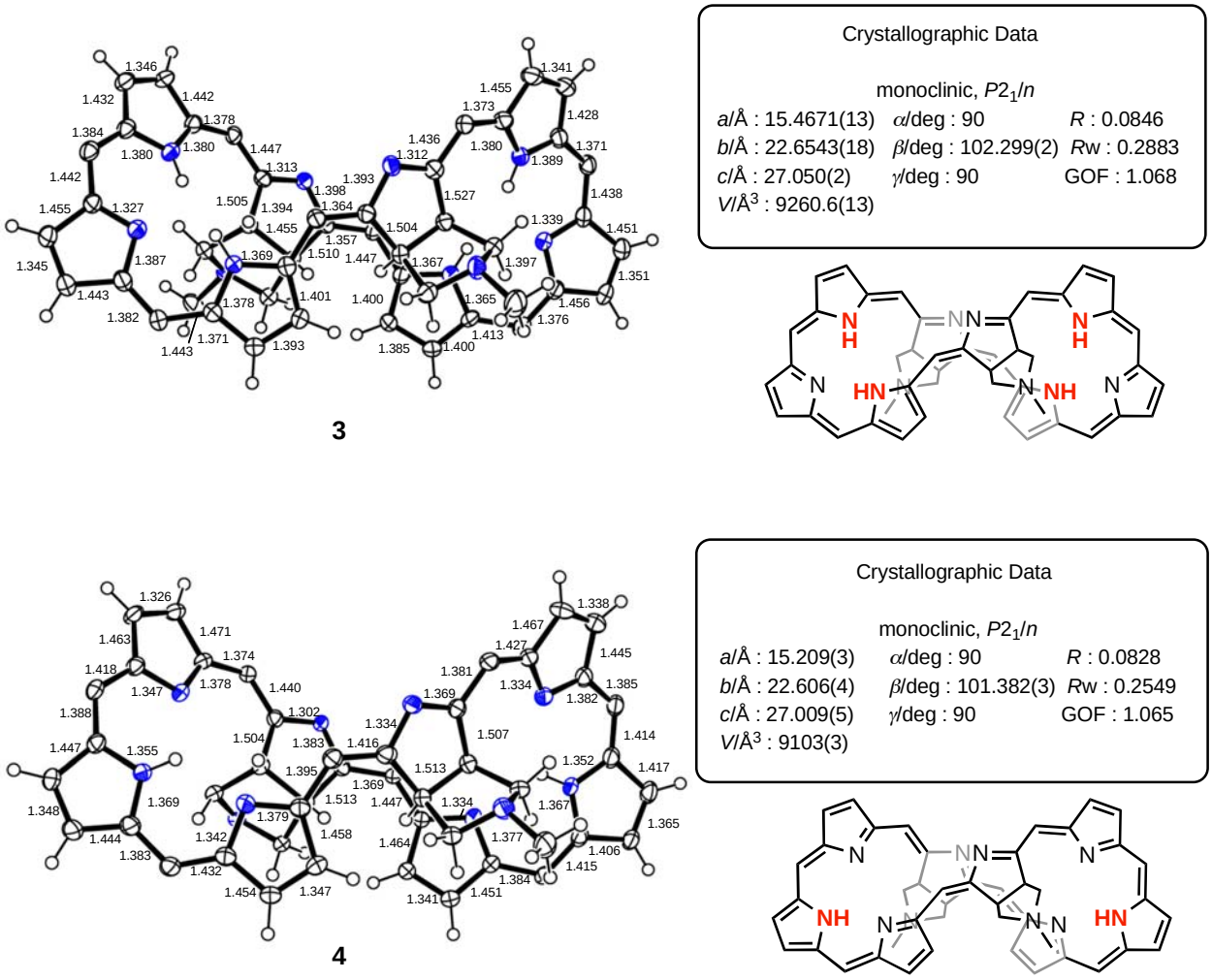
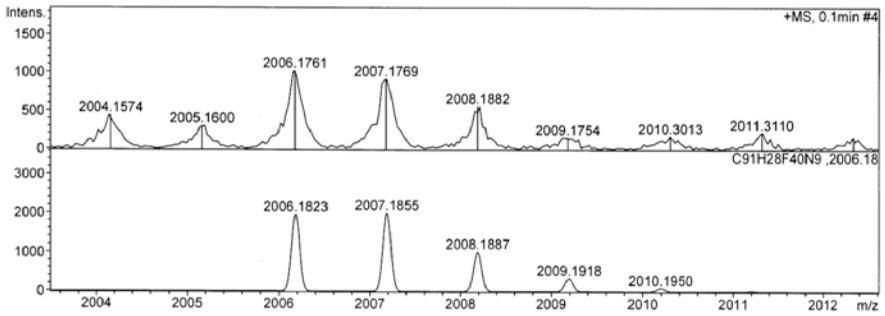


Figure S1. Bond lengths [Å] of **3** and **4**.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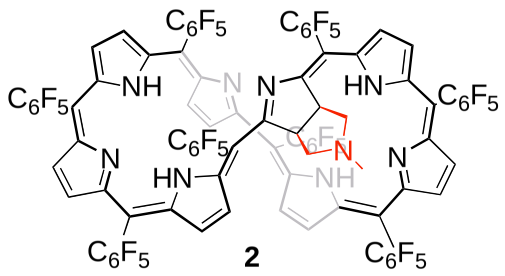
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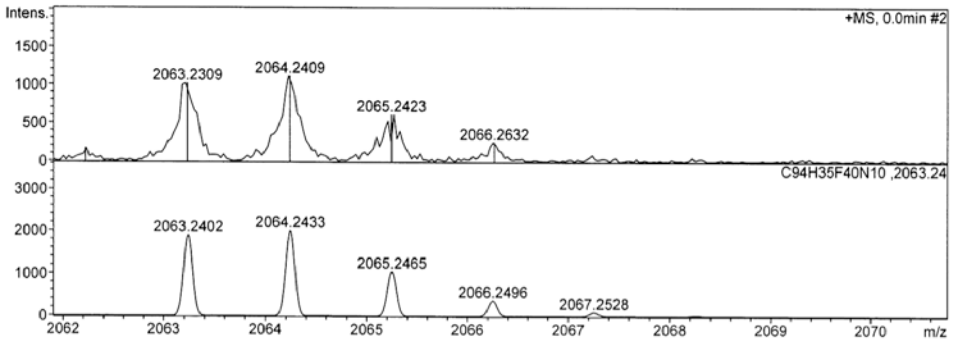
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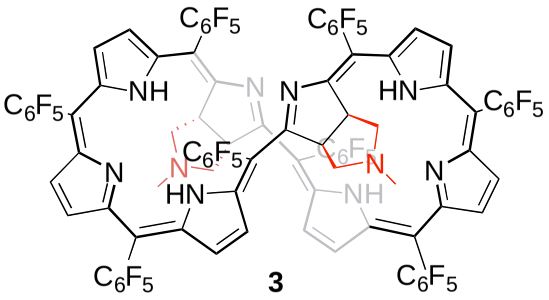
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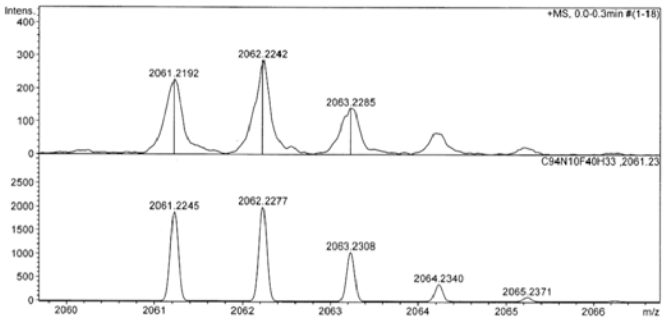
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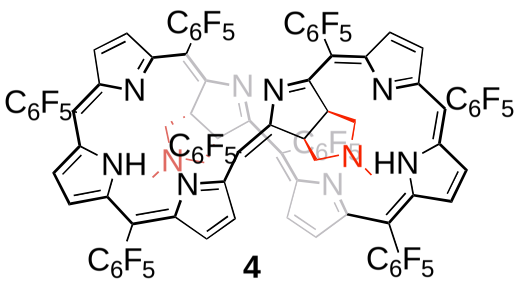
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