Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

A *meso-meso* Directly Linked Octameric Porphyrin Square

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Contents

1. Experimental Section

General Procedures: All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dry toluene was obtained by distilling over CaH_2. ^1H NMR spectra were recorded on a JEOL ECA-delta-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.26). The spectroscopic grade THF and $CHCl_3$ were used as solvents for all spectroscopic studies. UV/visible absorption spectra were recorded on a Shimadzu UV-2500 spectrometer. Steady-state fluorescence emission spectra were recorded on a Shimadzu RF-5300PC spectrometer. Mass spectra were recorded on a JEOL HX-110 spectrometer, using positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix, and/or a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using positive-MALDI ionization method with matrix. Preparative separations were performed by silica gel flash column chromatography (Merck Kieselgel 60H Art. 7736) and silica gel gravity column chromatography (Wako gel C-200). Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). Recycling preparative GPC-HPLC was carried out on a JAI LC-908 using preparative JAIGEL-2.5H, 3H, and 4H columns (chloroform eluant; flow rate 3.8 $mLmin^{-1}$).

5,10-Bis(3,5-di-*t*-butylphenyl)-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrin zinc(II) complex 2a: To a solution of 5,10-bis(3,5-di-*t*-butylphenyl)porphyrin (250 mg, 0.36 mmol) in CH_2Cl_2 and a drop of pyridine under N_2 at 0 °C was added NBS (84 mg, 1.3 eq.), and the solution was stirred for 3 h. The reaction mixture was added to water and extracted with CH_2Cl_2. The organic layer was washed with brine and water, and dried over anhydrous Na_2SO_4, and then evaporated to remove the solvent. The residue was recrystallized from CH_2Cl_2/MeOH. A saturated solution of $Zn(OAc)_2$ in methanol was added to a solution of a mixture of brominated porphyrins thus obtained in $CHCl_3$, and the resulting mixture was stirred for 3 h at room temperature. The reaction mixture was washed with aqueous $NaHCO_3$, water, and the organic layer was dried over anhydrous Na_2SO_4, passed through a short silica-gel column, evaporated to remove the solvent. A solution of a mixture of obtained zincated porphyrins in 20 ml of freshly distilled 1,2-dichloroethane was added via syringe to a mixture of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.68 ml, 4.7 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg), and triethylamine (1.0 ml, 7.4 mmol). The solution was stirred for 2 h at reflux under Ar atmosphere. The reaction mixture was added to water and extracted with CH_2Cl_2. The organic layer was washed with saturated KCl solution and water, and dried over anhydrous Na_2SO_4, and then evaporated to remove the solvent. The residue was separated with silica-gel column chromatography (CH_2Cl_2/hexane). The second fraction was 5,10-bis(3,5-di-*t*-butylphenyl)-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) zinc(II) porphyrin **2a**. Yield 211 mg (66%). ^1H NMR ($CDCl_3$): δ 10.22 (s, 1H, *meso*), 10.03 (d, *J* = 4.6 Hz, 1H, β), 9.93 (d, *J* = 4.6 Hz, 1H, β), 9.49 (d, *J* = 4.6 Hz, 1H, β), 9.37 (d, *J* = 4.6 Hz, 1H, β), 9.12 (d, *J* = 4.6 Hz, 1H, β), 9.11 (d, *J* = 4.6 Hz, 1H, β), 9.02 (d, *J* = 4.6 Hz, 1H, β), 8.99 (d, *J* = 4.6 Hz, 1H, β), 8.08 (d, *J* = 1.8 Hz, 2H, Ar), 8.06 (d, *J* = 1.8 Hz, 2H, Ar), 7.79 (t, *J* = 1.8 Hz, 1H, Ar), 7.79 (t, *J* = 1.8 Hz, 1H, Ar), 1.89 (s, 12H, Me), and 1.50 (s, 36H, ^{t}Bu) ppm; FAB-MS: *m/z* 874.53, calcd for $C_{54}H_{63}N_4O_2BZn$ = 874.43.

5,15-Dibromo-10,20-dibutyl zinc(II) porphyrin (3a): To a solution of 5,15-dibutylporphyrin (100 mg, 0.24 mmol) in CH_2Cl_2 and a drop of pyridine, NBS (92 mg, 0.52 mmol) was added, and the solution was stirred for 1 h at 0 °C. The reaction mixture was added to water and extracted with CH_2Cl_2. The organic layer was washed with brine and water, and dried over anhydrous Na_2SO_4, and then evaporated to remove the solvent. The residue was zincated by using the same procedure of **2a**, and recrystallized from $CHCl_3$/MeOH. Yield 115 mg (75%). ^1H NMR ($CDCl_3$): δ 9.74 (d, *J* = 4.6 Hz, 4H, β), 9.51 (d, *J* = 4.8 Hz, 4H, β), 4.91 (t, *J* = 8.1 Hz, 4H, C_4H_9), 2.49 (m, 4H, C_4H_9), 1.15 (m, 4H, C_4H_9), and 0.83 (t, *J* = 8.1 Hz, 6H, C_4H_9) ppm; FAB-MS: *m/z* 642.07, calcd for $C_{28}H_{26}N_4ZnBr_2$ 642.00.

***syn*-Zinc(II) porphyrin trimer 4a**: **2a** (175 mg, 0.20 mmol), **3a** (64 mg, 0.10 mmol), Pd(PPh_3)$_4$ (10 mg), Cs_2CO_3 (100 mg, 0.30 mmol) were dissolved in a mixture of toluene (10 ml) and DMF (5 ml). The solution was deoxygenated via three freeze-pump-thaw cycles, and the resulting solution was heated at 80 °C for 20 h under Ar atmosphere. After cooling down, the reaction mixture was washed with water and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4, passed through a short silica-gel column, and evaporated to remove the solvent. The product was separated with recycling preparative GPC-HPLC and silica gel column. Recrystallization gave **4a** (4.5 mg, 2.3%) **5a** (4.5 mg, 2.3 %), and **6a** (19 mg, 13%). **4a**: ^{1}H NMR ($CDCl_3$) δ 10.38 (s, 2H, *meso*), 9.51 (d, *J* = 5.0 Hz, 2H, β), 9.33 (d, *J* = 5.0 Hz, 4H, β), 9.27 (d, *J* = 5.0 Hz, 2H, β), 9.23 (d, *J* = 5.0 Hz, 2H, β), 9.17 (d, *J* = 5.0 Hz, 2H, β), 9.11 (d, *J* = 5.0 Hz, 2H, β), 8.81 (d, *J* = 5.0 Hz, 4H, β), 8.41 (d, *J* = 4.5 Hz, 2H, β), 8.27 (d, *J* = 5.0 Hz, 2H, β), 8.24-8.23 (m, 8H, β+Ar-*o*), 8.13 (d, *J* = 2.0 Hz, 4H, Ar-*o*), 7.89 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 7.73 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 4.97 (t, *J* = 8.0 Hz, 4H, C_4H_9), 2.58 (t-t, *J* = 8.0 Hz, 4H, C_4H_9), 1.77 (t-t, *J* = 8.0 Hz, 4H, C_4H_9), 1.62 (s, 36H, ^{t}Bu), 1.47 (s, 36H, ^{t}Bu), and 1.03 (t, *J* = 8.0 Hz, 6H, C_4H_9) ppm; FAB-MS: *m/z* 1981.84, calcd for $C_{124}H_{128}N_{12}Zn_3$ 1981.83. **5a**: ^{1}H NMR ($CDCl_3$) δ 10.38 (s, 2H, *meso*), 9.51 (d, *J* = 5.0 Hz, 2H, β), 9.33 (d, *J* = 5.0 Hz, 4H, β), 9.27 (d, *J* = 5.0 Hz, 2H, β), 9.22 (d, *J* = 5.0 Hz, 2H, β), 9.17 (d, *J* = 5.0 Hz, 2H, β), 9.11 (d, *J* = 5.0 Hz, 2H, β), 8.83 (d, *J* = 5.0 Hz, 4H, β), 8.39 (d, *J* = 4.5 Hz, 2H, β), 8.29 (d, *J* = 5.0 Hz, 2H, β), 8.24-8.23 (m, 8H, β+Ar-*o*), 8.15 (d, *J* = 2.0 Hz, 4H, Ar-*o*), 7.89 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 7.74 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 4.97 (t, *J* = 8.0 Hz, 4H, C_4H_9), 2.58 (t-t, *J* = 8.0 Hz, 4H, C_4H_9), 1.83 (t-t, *J* = 8.0 Hz, 4H, C_4H_9), 1.63 (s, 36H, ^{t}Bu), 1.48 (s, 36H, ^{t}Bu), and 1.03 (t, *J* = 8.0 Hz, 6H, C_4H_9) ppm; FAB-MS: *m/z* 1981.85, calcd for $C_{124}H_{128}N_{12}Zn_3$ 1981.83. **6a**: ^{1}H NMR ($CDCl_3$) δ 10.33 (s, 2H, *meso*), 9.47 (d, *J* = 5.0 Hz, 2H, β), 9.24 (d, *J* = 5.0 Hz, 2H, β), 9.15 (d, *J* = 5.0 Hz, 2H, β), 9.14 (d, *J* = 4.5 Hz, 2H, β), 8.73 (d, *J* = 5.0 Hz, 2H, β), 8.28 (d, *J* = 5.0 Hz, 2H, β), 8.21 (d, *J* = 1.5 Hz, 2H, Ar), 8.19 (d, *J* = 1.5 Hz, 2H, Ar), 8.14 (d, *J* = 5.0 Hz, 2H, β), 8.09-8.08 (m, 4H, Ar), 7.86 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 7.69 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 1.60 (s, 18H, ^{t}Bu), 1.59 (s, 18H, ^{t}Bu), 1.44 (s, 18H, ^{t}Bu), and 1.43 (s, 18H, ^{t}Bu) ppm; FAB-MS: *m/z* 1494.68, calcd for

$C_{96}H_{102}N_8Zn_2$ 1494.68.

5,10-Bis(3,5-dioctyloxyphenyl)-15-bromoporphyrin 2b: To a solution of 5,10-bis(3,5-dioctyloxyphenyl)porphyrin (340 mg, 0.35 mmol) in CH_2Cl_2 and five drops of pyridine was added NBS (74 mg, 0.42 mmol), and the solution was stirred for 3 h under N_2 at 0 °C. The reaction mixture was added to water and extracted with CH_2Cl_2. The organic layer was washed with brine and water, and dried over anhydrous Na_2SO_4, and then evaporated to remove the solvent. The residue was separated over silica gel with CH_2Cl_2/hexane. Yield 294 mg, 80%. ^1H NMR ($CDCl_3$): δ10.11 (s, 1H, *meso*), 9.74 (d, *J* = 4.6 Hz, 1H, β), 9.64 (d, *J* = 4.6 Hz, 1H, β), 9.35 (d, *J* = 4.6 Hz, 1H, β), 9.26 (d, *J* = 4.6 Hz, 1H, β), 9.07 (d, *J* = 4.6 Hz, 1H, β), 8.94 (d, *J* = 4.6 Hz, 1H, β), 7.33 (d, *J* = 1.8 Hz, 2H, Ar), 7.32 (d, *J* = 1.8 Hz, 2H, Ar), 6.88 (t, *J* = 1.8 Hz, 1H, Ar), 6.87 (t, *J* = 1.8 Hz, 1H, Ar), 4.12-4.09 (m, 8H, C_8H_{17}), 1.88-1.83 (m, 8H, C_8H_{17}), 1.50-1.44 (m, 8H, C_8H_{17}), 1.36-1.23 (m, 36H, C_8H_{17}), 0.85 (m, 12H, C_8H_{17}), and -3.0 (s, 2H, NH) ppm; FAB-MS: *m/z* 1053.47, calcd for $C_{64}H_{85}N_4O_4Br$ = 1053.58.

5,15-Dihexyl-10,20-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) zinc(II) porphyrin 3b: 5,15-Dibromo-10,20-dihexyl zinc(II) porphyrin was prepared by the same procedure for **3a**. A solution of dibrominated zinc(II) porphyrin (200 mg, 0.34 mmol) in 100 ml of freshly distilled 1,2-dichloroethane was added via syringe to a mixtutere of 4,4,5,5- tetramethyl-1,3,2-dioxaborolane (1.0 ml), $Pd(PPh_3)_2Cl_2$ (30 mg), and triethylamine (1.2 ml). The solution was stirred overnight at reflux under Ar atmosphere. The reaction mixture was added to water and extracted with CH_2Cl_2. The organic layer was washed with saturated KCl solution and water, and dried over anhydrous Na_2SO_4, then evaporated to remove the solvent. The residue was separated with silica-gel column chromatography (CH_2Cl_2/hexane). The second fraction was **3b**. Yield 153 mg, 57%. ^1H NMR ($CDCl_3$): δ9.95 (d, *J* = 4.6 Hz, 4H, β), 9.68 (d, *J* = 4.8 Hz, 4H, β), 5.05 (t, *J* = 8.1 Hz, 4H, C_6H_{13}), 2.57 (t-t, *J* = 8.1 Hz, 4H, C_6H_{13}), 1.88 (s, 24H, Me), 1.85 (t-t, *J* = 8.1 Hz, 4H, C_6H_{13}), 1.53 (t-t, *J* = 8.1 Hz, 4H, 6_4H_{13}), 1.43 (t-t, *J* = 8.1 Hz, 4H, C_6H_{13}), and 0.94 (t, *J* = 8.1 Hz, 6H, C_6H_{13}) ppm; MALDI-TOF-MS: *m/z* 795.4, calcd for $C_{44}H_{58}N_4ZnB_2O_4$ 794.0.

***syn*-Zinc(II) porphyrin trimer 4b**: **2b** (290 mg, 0.27 mmol), **3b** (109 mg, 0.137 mmol), $Pd(PPh_3)_4$ (32 mg, 10 mol%), Cs_2CO_3 (134 mg, 0.41 mmol) were dissolved in a mixture of toluene (20 ml) and DMF (10 ml). The solution was deoxygenated via three freeze-pump-thaw cycles, and the resulting solution was heated at 90 °C for 10 h under Ar atmosphere. After cooling down, the reaction mixture was washed with water and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4, passed through a short plug of silica-gel column, and evaporated to remove the solvent. The product was separated with recycling preparative GPC-HPLC and then silica gel column. Recrystallization gave **4b** (70 mg, 20%) and **5b** (55 mg, 16%). **4b**: ^1H NMR ($CDCl_3$) δ 10.33 (s, 2H, *meso*), 9.43 (d, *J* = 5.0 Hz, 2H, *β*), 9.34 (d, *J* = 5.0 Hz, 4H, *β*), 9.25 (d, *J* = 5.0 Hz, 2H, *β*), 9.15 (d, *J* = 5.0 Hz, 2H, *β*), 9.11 (d, *J* = 5.0 Hz, 2H, *β*), 9.07 (d, *J* = 5.0 Hz, 2H, *β*), 8.78 (d, *J* = 5.0 Hz, 2H, *β*), 8.33 (d, *J* = 4.5 Hz, 2H, *β*), 8.25 (d, *J* = 5.0 Hz, 4H, *β*), 8.15 (d, *J* = 4.5 Hz, 2H, *β*), 7.50 (d, *J* = 2.0 Hz, 4H, Ar-*o*), 7.42 (d, *J* = 2.0 Hz, 4H, Ar-*o*), 6.97 (br, 2H, Ar-*p*), 6.82 (br, 2H, Ar-*p*), 4.96 (t, *J* = 8.0 Hz, 4H, C_6H_{13}), 4.21 (t, *J* = 8.0 Hz, 8H, C_8H_{17}), 4.07 (t, *J* = 8.0 Hz, 8H, C_8H_{17}), 2.59 (t-t, *J* = 8.0 Hz, 4H, C_6H_{13}), 1.94 (t-t, *J* = 8.0 Hz, 4H, C_8H_{17}), 1.83-1.75 (m, 12H, C_6H_{13}+C_8H_{17}), 1.62-1.22 (m, 88H, C_6H_{13}+C_8H_{17}), 0.90 (t, *J* = 8.0 Hz, 12H, C_8H_{17}), 0.82-0.76 (m, 18H, C_6H_{13}+ C_8H_{17}), and -2.41 (br, 4H, NH) ppm; MALDI-TOF-MS: *m/z* 2489.5, calcd for $C_{160}H_{204}N_{12}ZnO_8$ 2488.7. **5b**: ^1H NMR ($CDCl_3$) δ 10.32 (s, 2H, *meso*), 9.53 (d, *J* = 5.0 Hz, 2H, *β*), 9.35 (d, *J* = 5.0 Hz, 4H, *β*), 9.25 (d, *J* = 5.0 Hz, 2H, *β*), 9.12 (m, 4H, *β*), 9.07 (d, *J* = 5.0 Hz, 2H, *β*), 8.80 (d, *J* = 5.0 Hz, 2H, *β*), 8.28 (d, *J* = 4.5 Hz, 2H, *β*), 8.25 (d, *J* = 5.0 Hz, 4H, *β*), 8.19 (d, *J* = 5.0 Hz, 2H, *β*), 7.51 (d, *J* = 2.0 Hz, 4H, Ar-*o*), 7.43 (d, *J* = 2.0 Hz, 4H, Ar-*o*), 6.96 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 6.83 (t, *J* = 2.0 Hz, 2H, Ar-*p*), 4.96 (t, *J* = 8.0 Hz, 4H, C_6H_{13}), 4.22 (t, *J* = 8.0 Hz, 8H, C_8H_{17}), 4.08 (t, *J* = 8.0 Hz, 8H, C_8H_{17}), 2.59 (t-t, *J* = 8.0 Hz, 4H, C_6H_{13}), 1.94 (t-t, *J* = 8.0 Hz, 4H, C_8H_{17}), 1.83-1.74 (m, 12H, C_6H_{13}+C_8H_{17}), 1.57-1.22 (m, 88H, C_6H_{13}+C_8H_{17}), 0.90 (t, *J* = 8.0 Hz, 12H, C_8H_{17}), 0.82-0.79 (m, 18H, C_6H_{13}+ C_8H_{17}), and -2.36 (br, 4H, NH) ppm; MALDI-TOF-MS: *m/z* 2487.2, calcd for $C_{160}H_{204}N_{12}ZnO_8$ 2488.7.

***meso,meso′-Dibromo-syn-*zinc(II) porphyrin trimer 7b**: To a solution of **4b** (85 mg, 0.034 mmol) in CH_2Cl_2 was added NBS (13 mg, 0.075 mmol) and the solution was stirred for 2 h under N_2 atmosphere at 0 °C. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with brine and water, and dried over anhydrous Na_2SO_4 and then evaporated to remove the solvent. Yield 75 mg, 83%; **7b**: ^{1}H NMR ($CDCl_3$) δ 9.75 (d, *J* = 4.8 Hz, 2H, *β*), 9.45 (d, *J* = 4.4 Hz, 2H, *β*), 9.35 (d, *J* = 4.8 Hz, 4H, *β*), 9.14 (d, *J* = 4.8 Hz, 2H, *β*), 9.02 (d, *J* = 4.8 Hz, 2H, *β*), 8.99 (d, *J* = 4.8 Hz, 2H, *β*), 8.70 (d, *J* = 4.8 Hz, 2H, *β*), 8.22 (d, *J* = 4.8 Hz, 4H, *β*), 8.19 (d, *J* = 5.0 Hz, 2H, *β*), 8.06 (d, *J* = 4.5 Hz, 2H, *β*), 7.46 (d, *J* = 2.4 Hz, 4H, Ar-*o*), 7.38 (d, *J* = 2.4 Hz, 4H, Ar-*o*), 6.97 (t, *J* = 2.4 Hz, 2H, Ar-*p*), 6.81 (t, *J* = 2.4 Hz, 2H, Ar-*p*), 4.96 (t, *J* = 8.0 Hz, 4H, C_6H_{13}), 4.20 (t, *J* = 8.0 Hz, 8H, C_8H_{17}), 4.07 (t, *J* = 8.0 Hz, 8H, C_8H_{17}), 2.59 (t-t, *J* = 8.0 Hz, 4H, C_6H_{13}), 1.94 (t-t, *J* = 8.0 Hz, 4H, C_8H_{17}), 1.83-1.75 (m, 12H, C_6H_{13}+C_8H_{17}), 1.62-1.22 (m, 88H, C_6H_{13}+C_8H_{17}), 0.90 (t, *J* = 8.0 Hz, 12H, C_8H_{17}), 0.82-0.80 (m, 18H, C_6H_{13}+ C_8H_{17}), and -2.12 (br, 4H, NH) ppm; MALDI-TOF-MS: *m/z* 2647.2, calcd for $C_{160}H_{202}N_{12}ZnO_8Br_2$ 2646.6.

***meso-meso* Linked cyclo porphyrin octamer 1**: **7b** (26 mg, 10 μmol), **3b** (8.0 mg, 10 mol), $Pd(PPh_3)_4$ (2 mg), Cs_2CO_3 (40 mg) were dissolved in a mixture of toluene (2.0 ml) and DMF (1.0 ml). The solution was deoxygenated via freeze-pump-thaw cycles, and the resulting solution was heated at 90 °C for 17 h under Ar atmosphere. After cooling down, the reaction mixture was washed with water and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4, passed through a short plug of silica-gel column, and evaporated to remove the solvent. The product was separated with recycling preparative GPC-HPLC and silica-gel column chromatography (CH_2Cl_2/hexane). Yield 2.3 mg, 8%. ^{1}H NMR ($CDCl_3$): δ 9.26 (d, *J* = 5.0 Hz, 16H, *β*), 9.13 (s, 8H, *β*), 8.82 (d, *J* = 4.5 Hz, 8H, *β*), 8.29 (d, *J* = 4.9 Hz, 16H, *β*), 8.15 (d, *J* = 4.5 Hz, 8H, *β*), 7.61 (s, 8H, *β*), 7.50 (d, *J* = 2.2 Hz, 16H, Ar), 6.87 (d, *J* = 2.1 Hz, 8H, Ar), 4.83 (br, 16H, C_6H_{13}), 4.13 (t, *J* = 6.4 Hz, 32H, C_8H_{17}), 2.41 (br, 16H, C_6H_{13}), 1.87 (m, 32H, C_8H_{17}), 1.69 (br, 16H, C_6H_{13}), 1.60-1.15 (m, 192H, C_6H_{13} +C_8H_{17}), 0.84 (t, *J* = 8.0 Hz, 48H, C_8H_{17}), 0.73 (t, *J* = 8.0 Hz, 24H, C_6H_{13}), and -1.58 (s, 8H, NH) ppm; MALDI-TOF-MS: *m/z* 6053.5, calcd for $C_{384}H_{472}N_{32}O_{16}Zn_4$ 6053.7.

2. GPC Chromatogram

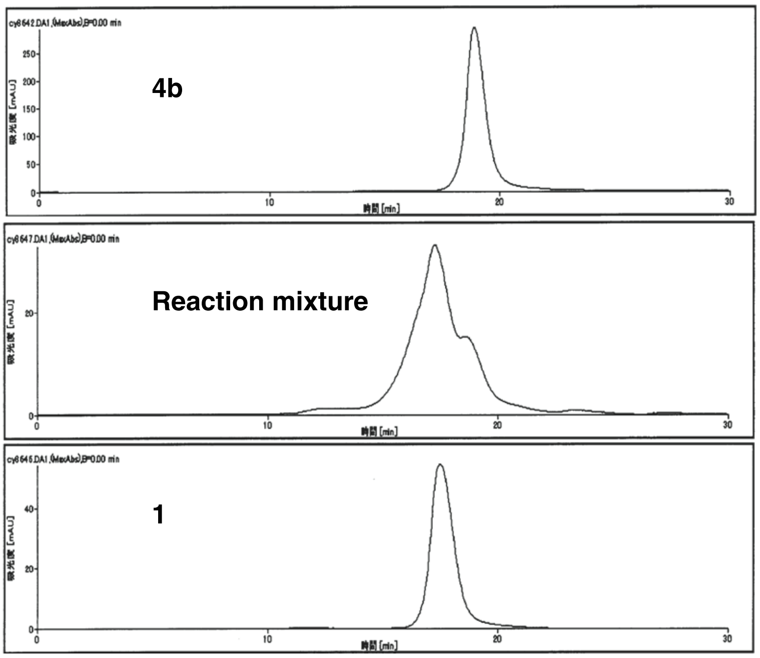


Figure S1. GPC-HPLC chromatograms of coupling reaction were detected by absorbance maxima at 35°C. GPC setup is the combination of JAI-GEL 4H-AF, 3H-AF, and 2.5H-AF.

3. MALDI-TOF mass spectrum of 1

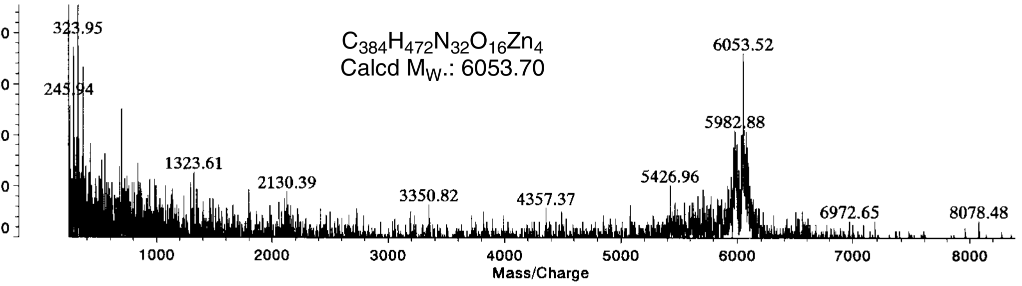


Figure S2. MALDI-TOF mass spectrum of **1**.

4. ¹H NMR spectrum of 1

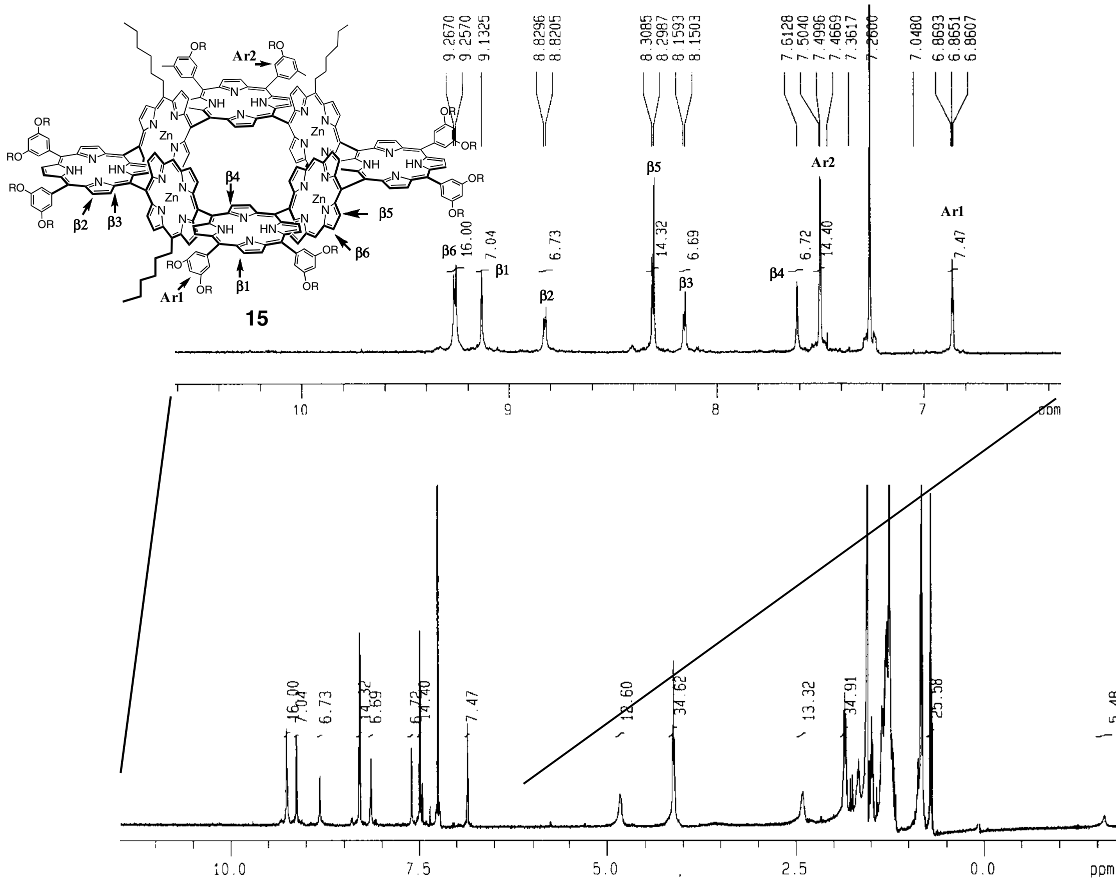
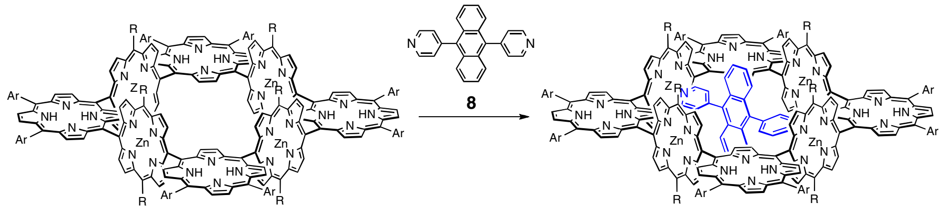


Figure S3. ¹H NMR spectrum of **1**.

5. Titration Experiment of 1 with 8



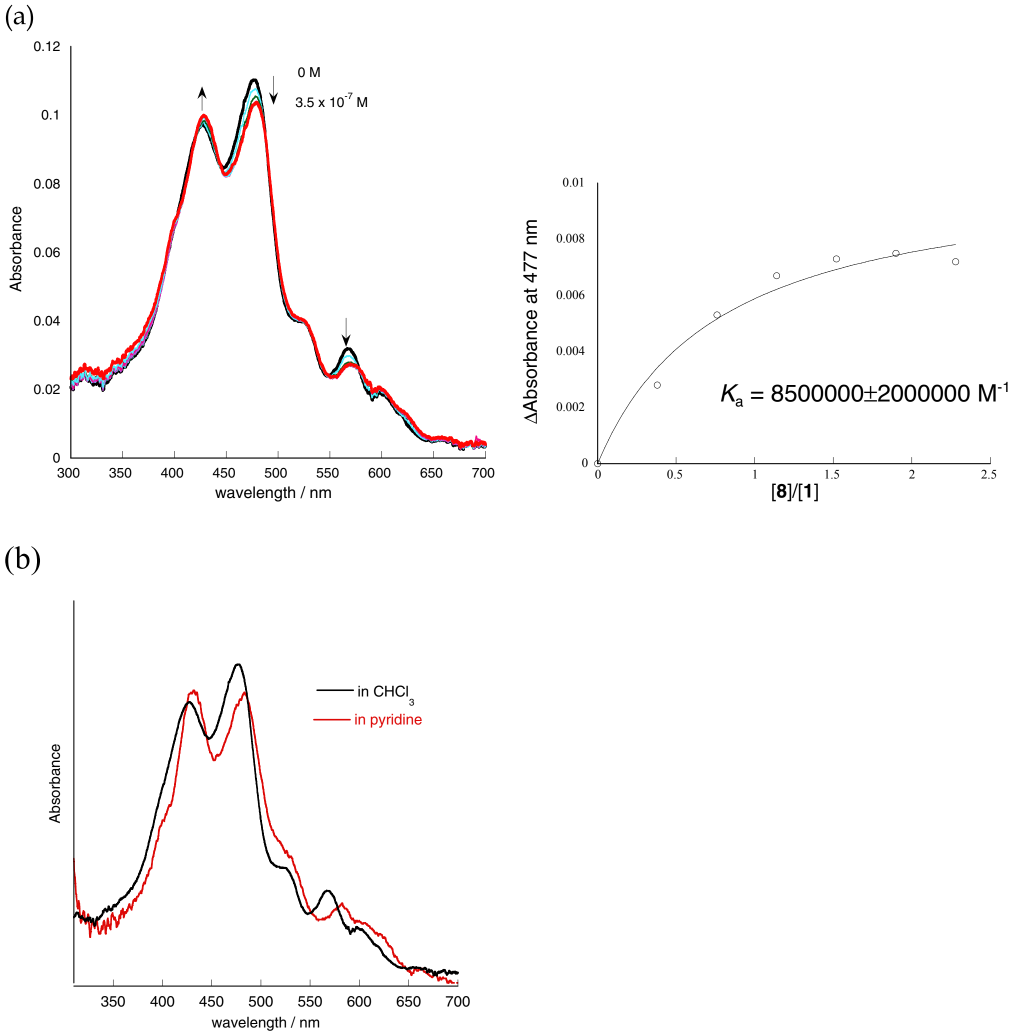


Figure S4. (a) UV-vis absorption spectra of titration for binding of **1** and **8** in $CHCl_3$. [**1**] = 1.5 x 10^{-7} M. (b) UV-vis absorption spectra of 1 in $CHCl_3$ and in pyridine.

^{1}H NMR spectral Change of 1 with 8 in $CDCl_3$

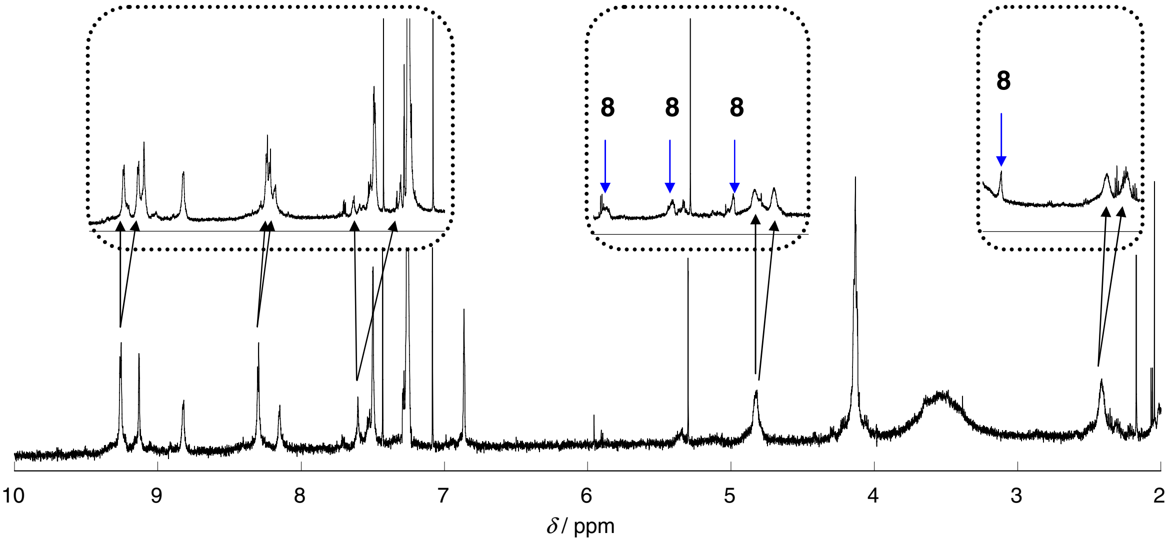


Figure S5. ^{1}H NMR spectra of **1** in $CDCl_3$ without (bottom) and with (insets) **8**. [**1**] = 3.0×10^{-5} M. [**8**] = 3.0×10^{-5} M (inset).

6. X-ray Crystal Structure of 5a

Single crystals of **5a** suitable for X-ray crystal analysis were obtained by slow diffusion of methanol into a dichloromethane solution of **5a**. X-Ray data at 123 K were taken on a Rigaku Raxis-Rapid X-Ray diffractometer equipped with an imaging plate detector with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 30819 reflections were measured at a maximum 2θ angle of 55°, of which 14119 were independent reflections (R_{int} = 0.0339). Structure was processed by CrystalStructure and then refined by SHELXL-97. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated in ideal positions. Three methanol molecules were found to coordinate on the zinc ions. The other solvent molecules contained in the lattice were severely disordered. Zinc ion in the central porphyrin core, and dichloromethane and methanol molecules in the large void space between the large molecules were disordered over two symmetrically equivalent positions. Totally 4.70 methanol molecules including the coordination ones and 3.795 dichloromethane molecules were assigned. The crystal data are as follows: $C_{132.50}H_{151.41}Cl_{7.59}N_{12}O_{4.70}Zn_3$; F_W = 2452.58, crystal size 0.45 × 0.30 × 0.15 mm^3, Triclinic, P-1 (No. 2), a = 9.299(3) Å, b = 14.420(4) Å, c = 24.109(8) Å, α = 92.761(10)°, β = 90.922(13)°, γ = 105.825(10)°, V = 3105.2(16) Å^3, Z = 1, D_c = 1.312 g cm^{-3}, R_1 = 0.0511 ($I > 2\sigma(I)$), R_w (all data) = 0.1490, GOF = 1.053. CCDC 683676.

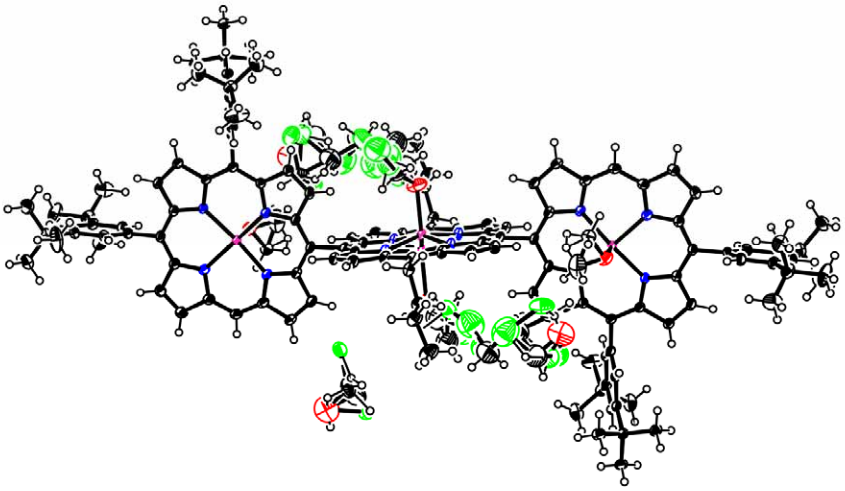


Figure S6. X-Ray crystal structure of **5a**.