Supporting Information

for

A meso-meso Directly Linked Octameric Porphyrin Square

Naoki Aratani* and Atsuhiro Osuka*

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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$_2$. $^1$H 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$_3$ ($\delta = 7.26$). 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$_2$Cl$_2$ 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$_2$Cl$_2$. The organic layer was washed with brine and water, and dried over anhydrous Na$_2$SO$_4$, and then evaporated to remove the solvent. The residue was recrystallized from CH$_2$Cl$_2$/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 
NaHCO₃ water, and the organic layer was dried over anhydrous Na₂SO₄ 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(PPh₃)₂Cl₂ (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 
CH₂Cl₂. The organic layer was washed with saturated KCl solution and water, and dried 
over anhydrous Na₂SO₄ and then evaporated to remove the solvent. The residue was 
separated with silica-gel column chromatography (CH₂Cl₂/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 (CDCl₃): 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, tBu) ppm; FAB-MS: m/z 874.53, calcd for 
C₅₄H₆₃N₄O₂BZn = 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 CH₂Cl₂ and a drop of pyridine, NBS (92 mg, 0.52 mmol) was added, 
and the solution was stirred for 1 h at 0 ºC. The reaction mixture was added to water and 
extracted with CH₂Cl₂. The organic layer was washed with brine and water, and dried over 
anhydrous Na₂SO₄ and then evaporated to remove the solvent. The residue was zincated by 
using the same procedure of 2a, and recrystallized from CHCl₃/MeOH. Yield 115 mg (75%). 
¹H NMR (CDCl₃): 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, 
C₄H₉), 2.49 (m, 4H, C₄H₉), 1.15 (m, 4H, C₄H₉), and 0.83 (t, J = 8.1 Hz, 6H, C₄H₉) ppm; FAB-MS: 
m/z 642.07, calcd for C₃₈H₃₆N₄ZnBr₂ 642.00.
**syn-Zinc(II) porphyrin trimer 4a:** 2a (175 mg, 0.20 mmol), 3a (64 mg, 0.10 mmol), Pd(PPh₃)₄ (10 mg), Cs₂CO₃ (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 Na₂SO₄, 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: ¹H NMR (CDCl₃) 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), 7.74 (t, J = 2.0 Hz, 2H, Ar-p), 4.97 (t, J = 8.0 Hz, 4H, C₄H₉), 2.58 (t-t, J = 8.0 Hz, 4H, C₄H₉), 1.78 (t-t, J = 8.0 Hz, 4H, C₄H₉), 1.62 (s, 36H, tBu), 1.47 (s, 36H, tBu), and 1.03 (t, J = 8.0 Hz, 6H, C₄H₉) ppm; FAB-MS: m/z 1981.84, calcd for C₁₂₄H₁₂₈N₁₂Zn₃ 1981.83.

5a: ¹H NMR (CDCl₃) 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), 7.74 (t, J = 2.0 Hz, 2H, Ar-p), 4.97 (t, J = 8.0 Hz, 4H, C₄H₉), 2.58 (t-t, J = 8.0 Hz, 4H, C₄H₉), 1.77 (t-t, J = 8.0 Hz, 4H, C₄H₉), 1.62 (s, 36H, tBu), 1.47 (s, 36H, tBu), and 1.03 (t, J = 8.0 Hz, 6H, C₄H₉) ppm; FAB-MS: m/z 1981.85, calcd for C₁₂₄H₁₂₈N₁₂Zn₃ 1981.83.

6a: ¹H NMR (CDCl₃) 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, tBu), 1.59 (s, 18H, tBu), 1.44 (s, 18H, tBu), and 1.43 (s, 18H, tBu) ppm; FAB-MS: m/z 1494.68, calcd for
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 CH₂Cl₂ and five drops of pyridine was added NBS (74 mg, 0.42 mmol), and the solution was stirred for 3 h under N₂ at 0 ºC. The reaction mixture was added to water and extracted with CH₂Cl₂. The organic layer was washed with brine and water, and dried over anhydrous Na₂SO₄, and then evaporated to remove the solvent. The residue was separated over silica gel with CH₂Cl₂/hexane. Yield 294 mg, 80%. ¹H NMR (CDCl₃): δ 10.11 (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, C₈H₁₇), 1.88-1.83 (m, 8H, C₈H₁₇), 1.50-1.44 (m, 8H, C₈H₁₇), 1.36-1.23 (m, 36H, C₈H₁₇), 0.85 (m, 12H, C₈H₁₇), and -3.0 (s, 2H, NH) ppm; FAB-MS: m/z 1053.47, calcd for C₆₄H₈₅N₄O₄Br = 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 mixture of 4,4,5,5-tetramethyl-1,3,2-dioxaborolan (1.0 ml), Pd(PPh₃)₂Cl₂ (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 CH₂Cl₂. The organic layer was washed with saturated KCl solution and water, and dried over anhydrous Na₂SO₄, then evaporated to remove the solvent. The residue was separated with silica-gel column chromatography (CH₂Cl₂/hexane). The second fraction was 3b. Yield 153 mg, 57%. ¹H NMR (CDCl₃): δ 9.95 (d, J = 4.6 Hz, 4H, β), 9.68 (d, J = 4.8 Hz, 4H, β), 5.05 (t, J = 8.1 Hz, 4H, C₆H₁₃), 2.57 (t-t, J = 8.1 Hz, 4H, C₆H₁₃), 1.88 (s, 24H, Me), 1.85 (t-t, J = 8.1 Hz, 4H, C₆H₁₃), 1.53 (t-t, J = 8.1 Hz, 4H, C₆H₁₃), 1.43 (t-t, J = 8.1 Hz, 4H, C₆H₁₃),
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$_2$CO$_3$ (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$_2$SO$_4$, 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: $^1$H NMR (CDCl$_3$) $\delta$ 10.33 (s, 2H, meso), 9.43 (d, $J = 5.0$ Hz, 2H, $\beta$), 9.34 (d, $J = 5.0$ Hz, 4H, $\beta$), 9.25 (d, $J = 5.0$ Hz, 2H, $\beta$), 9.15 (d, $J = 5.0$ Hz, 2H, $\beta$), 9.11 (d, $J = 5.0$ Hz, 2H, $\beta$), 9.07 (d, $J = 5.0$ Hz, 2H, $\beta$), 8.78 (d, $J = 5.0$ Hz, 2H, $\beta$), 8.33 (d, $J = 4.5$ Hz, 2H, $\beta$), 8.25 (d, $J = 5.0$ Hz, 4H, $\beta$), 8.15 (d, $J = 4.5$ Hz, 2H, $\beta$), 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, $C_6H_{13}$), 4.22 (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, $C_8H_{17}$), 0.82-0.76 (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: $^1$H NMR (CDCl$_3$) $\delta$ 10.32 (s, 2H, meso), 9.53 (d, $J = 5.0$ Hz, 2H, $\beta$), 9.35 (d, $J = 5.0$ Hz, 4H, $\beta$), 9.25 (d, $J = 5.0$ Hz, 2H, $\beta$), 9.12 (m, 4H, $\beta$), 9.07 (d, $J = 5.0$ Hz, 2H, $\beta$), 8.80 (d, $J = 5.0$ Hz, 2H, $\beta$), 8.28 (d, $J = 4.5$ Hz, 2H, $\beta$), 8.25 (d, $J = 5.0$ Hz, 4H, $\beta$), 8.19 (d, $J = 5.0$ Hz, 2H, $\beta$), 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,
meso-meso’-Dibromo-syn-zinc(II) porphyrin trimer 7b: To a solution of 4b (85 mg, 0.034 mmol) in CH₂Cl₂ was added NBS (13 mg, 0.075 mmol) and the solution was stirred for 2 h under N₂ atmosphere at 0 ºC. The reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was washed with brine and water, and dried over anhydrous Na₂SO₄ and then evaporated to remove the solvent. Yield 75 mg, 83%; 7b: ¹H NMR (CDCl₃) 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), 7.38 (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-ο), 6.81 (t, J = 2.4 Hz, 2H, Ar-p), 4.96 (t, J = 8.0 Hz, 4H, C₆H₁₃), 4.20 (t, J = 8.0 Hz, 8H, C₈H₁₇), 2.59 (t-t, J = 8.0 Hz, 4H, C₆H₁₃), 1.94 (t-t, J = 8.0 Hz, 4H, C₈H₁₇), 1.83-1.75 (m, 12H, C₆H₁₃+C₈H₁₇), 1.62-1.22 (m, 88H, C₆H₁₃+C₈H₁₇), and -2.12 (br, 4H, NH) ppm; MALDI-TOF-MS: m/z 2647.2, calcd for C₁₆₀H₂₅₀N₁₂ZnO₈Br₂ 2646.6.

meso-meso Linked cyclo porphyrin octamer 1: 7b (26 mg, 10 μmol), 3b (8.0 mg, 10 mol), Pd(PPh₃)₄ (2 mg), Cs₂CO₃ (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 ºC 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 Na₂SO₄, 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 (CH₂Cl₂/hexane). Yield 2.3 mg, 8%. ¹H NMR (CDCl₃): 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\textsubscript{6}H\textsubscript{13}), 4.13 (t, \(J = 6.4\) Hz, 32H, C\textsubscript{8}H\textsubscript{17}), 2.41 (br, 16H, C\textsubscript{6}H\textsubscript{13}), 1.87 (m, 32H, C\textsubscript{8}H\textsubscript{17}), 1.69 (br, 16H, C\textsubscript{6}H\textsubscript{13}), 1.60-1.15 (m, 192H, C\textsubscript{6}H\textsubscript{13} + C\textsubscript{8}H\textsubscript{17}), 0.84 (t, \(J = 8.0\) Hz, 48H, C\textsubscript{8}H\textsubscript{17}), 0.73 (t, \(J = 8.0\) Hz, 24H, C\textsubscript{6}H\textsubscript{13}), and -1.58 (s, 8H, NH) ppm; MALDI-TOF-MS: \(m/z\) 6053.5, calcd for C\textsubscript{384}H\textsubscript{472}N\textsubscript{32}O\textsubscript{16}Zn\textsubscript{4} 6053.7.
2. GPC Chromatogram

![GPC Chromatogram of 4b](image1)

**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

![MALDI-TOF Mass Spectrum](image2)

**Figure S2.** MALDI-TOF mass spectrum of 1.
4. $^1$H NMR spectrum of 1

Figure S3. $^1$H NMR spectrum of 1.
5. Titration Experiment of 1 with 8

![Titration Diagram](image)

**Figure S4.** (a) UV-vis absorption spectra of titration for binding of 1 and 8 in CHCl₃. [1] = 1.5 x 10⁻⁷ M. (b) UV-vis absorption spectra of 1 in CHCl₃ 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 55º, of which 14119 were independent reflections (Rint = 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_{132.56}H_{151.41}Cl_{7.59}N_{12}O_{4.70}Zn; FW = 2452.58, crystal size 0.45 × 0.30 × 0.15 mm³, Triclinic, P-1 (No. 2), a = 9.299(3) Å, b = 14.420(4) Å, c = 24.109(8) Å, α = 92.761(10)º, β = 90.922(13)º, γ = 105.825(10)º, V = 3105.2(16) Å³, Z = 1, Dc = 1.312 g cm⁻³, R₁ = 0.0511 (I > 2σ(I)), R_w (all data) = 0.1490, GOF = 1.053. CCDC 683676.

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