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Supporting Information

Giant *meso-meso* Linked Porphyrin Arrays of Micrometer Molecular Length and Their Fabrications

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Experimental Procedures

Methyl 3,5-dihydroxybenzoate (2). 3,5-Dihydroxybenzoic acid (**1**) (25.00 g, 162 mmol) was dissolved in methanol (500 mL). Conc. sulfuric acid (7 mL) was added to this mixture, and the solution was refluxed overnight, and then methanol was evaporated. The residue was dissolve in ethyl acetate and washed with water. The organic layer was separated and dried over anhydrous Na_2SO_4, and evaporated. The methyl ester **2** that was precipitated during evaporation was collected by filtration, and washed with hexane to give white crystals of **2**. Yield 26.02 g (155 mmol, 95%); mp 163.5-164.0°C; ^{1}H-NMR (DMSO) *d* 9.61 (s, 2H, OH), 6.80 (d, *J* = 2 Hz, 2H, Ar-2,6-H), 6.43 (t, *J* = 2 Hz, 1H, Ar-4-H), 3.78 (s, 3H, Me); IR (KBr) 3383 + 3319 (br, m, OH), 1695 (s, C=O), 1169 (m, C-O) cm^{-1}.

Methyl 3,5-dioctyloxybenzoate (3). The methyl ester **2** (11.87 g, 70.7 mmol) was dissolved in acetone (300 mL). To this solution was added potassium carbonate (24.4 g, 177 mmol) and octylbromide (25.6 mL, 148 mmol). The mixture was heated under reflux for 2 days. The precipitates in formal were filtered, and the filtrate was concentrated by a rotary evaporator. To the resultant residue was added CH_2Cl_2 (100 mL), and water (300 mL) was finally poured into this reaction mixture. The organic layer was separated. The aqueous layer was further extracted with CH_2Cl_2 (100 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. Unreacted octylbromide was distilled off under reduced pressure. The product was separated by silica gel chromatography (CH_2Cl_2). Yield 22.87 g (58 mmol, 83%); ^{1}H-NMR ($CDCl_3$) *d* 7.16 (d, *J* = 2 Hz, 2H, Ar-2,6-H), 6.64 (t, *J* = 2 Hz, 1H, Ar-4-H), 3.97 (t, *J* = 7 Hz, 4H, octyloxy), 3.89 (s, 3H, Me), 1.77 (t-t, *J* = 7 Hz, 4H, octyloxy), 1.43 (m, 4H, octyloxy), 1.29 (m, 16H, octyloxy), and 0.88 (t, *J* = 7 Hz, 6H, octyloxy). Anal. Calcd. for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27. Found: C, 73.29; H, 10.57.

3,5-Dioctyloxybenzyl alcohol (4). Lithium aluminum hydride (2.73 g, 72 mmol) was suspended in dry THF (100 mL) and then cooled to 0°C under nitrogen. The methyl ester **3** (40 g, 100 mmol) was dissolved in dry THF (200 mL), and this was added dropwise to above mentioned $LiAlH_4$/THF suspension at 0°C under nitrogen. After the mixture was stirred for 1 h, water was carefully added dropwise. The solid was deposited during addition of water and removed by filtration under reduced pressure. The filtrate was extracted with diethyl ether, and the organic layer was separated, washed with brine, dried over anhydrous sodium sulfate, and evaporated. Colorless crystal. Yield 34.17 g (94 mmol, 92%); ^{1}H-NMR ($CDCl_3$) *d* 6.50 (d, *J* = 2 Hz, 2H, Ar-2,6-H), 6.38 (t, *J* = 2 Hz, 1H, Ar-4-H), 4.61 (d, *J* = 6 Hz, 2H, benzyl), 3.97 (t, *J* = 7 Hz, 4H, octyloxy), 1.78 (t-t, *J* = 7 Hz, 4H, octyloxy), 1.61 (t, *J* = 6 Hz, 1H, OH), 1.43 (m, 4H, octyloxy), 1.29 (m, 16H, octyloxy), and 0.89 (t, *J* = 7 Hz, 6H, octyloxy); FAB MS *m/z* 364.5, calcd for $C_{23}H_{40}O_3$ *m/z* 364.3. Anal. Calcd. for $C_{23}H_{40}O_3$: C, 75.77; H, 11.06. Found: C, 75.49; H, 10.83.

3,5-Dioctyloxybenzaldehyde (5). Alcohol **4** (33 g, 90 mmol) was dissolved in dry CH_2Cl_2 (200 mL). Sodium acetate (14.7 g, 180 mmol) was suspended in this solution, and the resultant suspension was cooled to 0°C. Pyridinium chlorochromate (PCC) (29 g, 200 mmol) was carefully added to the suspension at 0°C. After stirring for 2 h diethyl ether was added to the reaction mixture, and the liquid phase was separated by decantation. The residual gummy solid was washed with diethyl ether several times. The combined liquid phase was passed though a florisil short column. Diethyl ether was evaporated. The product was crystallized during evaporation. Colorless oil. Yield 30 g (81 mmol, 91%); ^{1}H-NMR ($CDCl_3$) *d* 9.90 (s, 1H, CHO), 6.98 (d, *J* = 2 Hz, 2H, Ar-2,6-H), 6.70 (t, *J* = 4 Hz, 1H, Ar-4-H), 3.99 (t, *J* = 7 Hz, 4H, octyloxy), 1.80 (t-t, *J* = 7 Hz, 4H, octyloxy), 1.43 (m, 4H, octyloxy), 1.29 (m, 16H, octyloxy), and 0.89 (t, *J* = 7 Hz, 6H, octyloxy); FAB MS *m/z* 362.4, calcd for $C_{23}H_{38}O_3$ *m/z* 362.3. Anal. Calcd. for $C_{23}H_{38}O_3$: C, 76.20; H, 10.56. Found: C, 76.02; H, 10.76.

Bis(2-pyrryl)methane (**6**) was prepared by the method reported by Lee *et al.*[25e] A solution of formalin (12 mL, 0.14 mol) and pyrrole (50 mL, 0.72 mol) was stirred for 15 min at 50°C then carefully added TFA (1.1 ml, 0.014 mol). After the work-up, **6** (5.23 g, 26%) was obtained.

5,15-Bis(3,5-dioctyloxyphenyl)porphyrin H1. A solution of **6** (1.00 g, 6.85 mmol) and 3,5-dioctyloxybenzaldehyde (2.48 g, 6.85 mmol) in dry CH_2Cl_2 (1.3 L) was stirred under Ar, the flask was shielded from light. Trifluoroacetic acid (0.328 mL, 4.26 mmol) was added via syringe, and the solution was stirred for 2-3 h at room temperature. DDQ (2.32 g, 10.3 mmol) was added to the solution, and the resulting solution was stirred for an additional 2-3 h. After the reaction mixture was neutralized by triethylamine and passed over Alumina column to remove polymeric materials, the solvent was removed by a rotary evaporator and the residue was purified by a silica gel flash column chromatography with CH_2Cl_2/hexane. The product was recrystallized from CH_2Cl_2-EtOH. Yield; 1.47 g, 44%. This reaction scheme was repeated for 10 times, resulting in the making of 15 g porphyrin. ^1H NMR ($CDCl_3$) *d* 10.30 (s, 2H, *meso*), 9.38 (d, *J* = 5 Hz, 4H, *b*), 9.19 (d, *J* = 5 Hz, 4H, *b*), 7.43 (d, *J* = 3 Hz, 4H, Ar), 6.92 (t, *J* = 3 Hz, 2H, Ar), 4.12 (t, *J* = 7 Hz, 8H, octyloxy), 1.89 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.51 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.38-1.27 (m, 32H, octyloxy), 0.87 (t, *J* = 7 Hz, 12H, octyloxy), and -3.15 (s, 2H, N-H); FAB MS *m/z* 974.6, calcd for $C_{64}H_{86}N_4O_4$ *m/z* 974.7; Anal. Calcd. for $C_{64}H_{86}N_4O_4$: C, 78.81; H, 8.89; N, 5.74. Found: C, 78.62; H, 8.89; N, 5.73; UV-vis (THF) l_{max} 407, 501, 537, 574, and 630 nm; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 631 and 696 nm.

Z1. ^1H NMR ($CDCl_3$) *d* 10.31 (s, 2H, *meso*), 9.43 (d, *J* = 5 Hz, 4H, *b*), 9.26 (d, *J* = 5 Hz, 4H, *b*), 7.43 (d, *J* = 3 Hz, 4H, Ar), 6.92 (t, *J* = 3 Hz, 2H, Ar), 4.15 (t, *J* = 7 Hz, 8H, octyloxy), 1.89 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.51 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.39-1.27 (m, 32H, octyloxy), and 0.87 (t, *J* = 7 Hz, 12H, octyloxy); FAB MS *m/z* 1036.4, calcd for $C_{64}H_{84}N_4O_4Zn$ *m/z* 1036.6; Anal. Calcd. for $C_{64}H_{86}N_4O_4Zn$: C, 74.00; H, 8.15; N, 5.39. Found: C, 73.75; H, 8.21; N, 5.16; UV-vis (THF) l_{max} (*e*) [nm ($cm^{-1}M^{-1}$)] 413 (645000) and 543 (22000); Fluorescence (THF, l_{ex} = 413 nm) l_{em} 584 and 634 nm.

General Procedure for *Meso-meso* Coupling Reaction of Zn^{II} 5,15-bis(3,5-dioctyloxyphenyl)porphyrin arrays Z*n*. The reaction vessel containing a solution of Zn(II) 5,15-bis(3,5-dioctyloxyphenyl)porphyrin array in dry $CHCl_3$ was covered with foil. A stock solution of $AgPF_6$ in dry CH_3CN (0.127 M) was added to that solution, and the resulting mixture was stirred at 30°C or room temperature, while the progress of the reaction was monitored by the analytical GPC-HPLC. The reaction was stopped by adding water and the reaction mixture was dried over anhydrous Na_2SO_4. A solution of $Zn(OAc)_2$ in methanol was added, and the solution was stirred at refluxed temperature for 1-2 h. Then it was washed successively with water, and saturated $NaHCO_3$ solution, and dried over anhydrous Na_2SO_4. The solvent was removed by a rotary evaporator. The product separation was performed on a preparative size exclusion column (a medium-pressure size-exclusion column (SEC) chromatography for **Z2**, **Z3**, and **Z4**, and recycling preparative GPC-HPLC for larger arrays).

Z2. A round-bottomed flask was charged with **Z1** (570 mg, 0.55 mmol) and dry $CHCl_3$ (160 mL). A stock solution of $AgPF_6$ (4.78 mL, 0.66 mmol) in acetonitrile was added at once. The reaction mixture was stirred for 10 h at 30°C. After the usual work-up, the oligomers ware separated by a preparative size exclusion column (SEC). Fractions of 2-mer and 3-mer ware separated, and the solvent was removed by a rotary evaporator. Recrystallization from $CHCl_3$/EtOH gave red-blown solids of **Z2** (138 mg, 24%). ^{1}H NMR ($CDCl_3$) *d* 10.38 (s, 2H, *meso*), 9.49 (d, *J* = 5 Hz, 4H, *b*), 9.28 (d, *J* = 5 Hz, 4H, *b*), 8.82 (d, *J* = 5 Hz, 4H, *b*), 8.10 (d, *J* = 5 Hz, 4H, *b*), 7.42 (d, *J* = 3 Hz, 8H, Ar), 6.92 (t, *J* = 3 Hz, 4H, Ar), 4.06 (t, *J* = 7 Hz, 16H, octyloxy), 1.80 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.44 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.32-1.21 (m, 64H, octyloxy), and 0.81 (t, *J* = 7 Hz, 24H, octyloxy); MALDI-TOF-MS *m/z* 2076, calcd for $C_{128}H_{166}N_8O_8Zn_2$ *m/z* 2075.1; Anal. Calcd. for $C_{128}H_{166}N_8O_8Zn_2(H_2O)$: C, 73.43; H, 8.09; N, 5.35; Found: C, 73.23; H, 8.13; N, 5.34; UV-vis (THF) l_{max} (*e*) [nm ($cm^{-1}M^{-1}$)] 418 (270000), 452 (250000), and 560 (60000); Fluorescence (THF, l_{ex} = 413 nm) l_{em} 657 nm.

Z3. ^{1}H NMR ($CDCl_3$) *d* 10.40 (s, 2H, *meso*), 9.50 (d, *J* = 5 Hz, 4H, *b*), 9.29 (d, *J* = 5 Hz, 4H, *b*), 8.89 (d, *J* = 5 Hz, 4H, *b*), 8.80 (d, *J* = 5 Hz, 4H, *b*) 8.24 (d, *J* = 5 Hz, 4H, *b*) 8.12 (d, *J* = 5 Hz, 4H, *b*), 7.45 (d, *J* = 3 Hz, 8H, Ar), 7.38 (d, *J* = 3 Hz, 4H, Ar), 6.84 (t, *J* = 3 Hz, 4H, Ar), 6.67 (t, *J* = 3 Hz, 2H, Ar), 4.09 (t, *J* = 7 Hz, 16H, octyloxy), 3.95 (t, *J* = 7 Hz, 8H, octyloxy), 1.82 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.69 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.46 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.33-1.13 (m, 104H, octyloxy), 0.81 (t, *J* = 7 Hz, 24H, octyloxy) and 0.72 (t, *J* = 7 Hz, 12H, octyloxy); MALDI-TOF-MS *m/z* 3114, calcd for $C_{192}H_{248}N_{12}O_{12}Zn_3$ *m/z* 3112; UV-vis (THF) l_{max} (nm) 414, 476, and 571; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 632 and 669 nm.

Z4. A round-bottomed flask was charged with **Z2** (90 mg, 0.043 mmol) and dry $CHCl_3$ (60 mL). A stock solution of $AgPF_6$ (0.26 mL, 0.033 mmol) was added at once. The reaction mixture was stirred for 5 h at room temperature. After the usual work up, the separation over SEC and recrystallization from $CHCl_3$/MeOH gave a pure **Z4** (24 mg, 27%). ^{1}H NMR ($CDCl_3$) *d* 10.40 (s, 2H, *meso*), 9.51 (d, *J* = 5 Hz, 4H, *b*), 9.30 (d, *J* = 5 Hz, 4H, *b*), 8.90 (d, *J* = 5 Hz, 4H, *b*), 8.88 (d, *J* = 5 Hz, 4H, *b*), 8.82 (d, *J* = 5 Hz, 4H, *b*), 8.28 (d, *J* = 5 Hz, 4H, *b*), 8.25 (d, *J* = 5 Hz, 4H, *b*), 8.14 (d, *J* = 5 Hz, 4H, *b*), 7.46 (d, *J* = 3 Hz, 8H, Ar), 7.43 (d, *J* = 3 Hz, 8H, Ar), 6.85 (br, 4H, Ar), 6.71 (br, 4H, Ar), 4.10 (t, *J* = 7 Hz, 16H, octyloxy), 4.00 (t, *J* = 7 Hz, 16H, octyloxy), 1.83 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.73 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.47 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.38-1.16 (m, 144H, octyloxy), 0.82 (t, *J* = 7 Hz, 24H, octyloxy), and 0.75 (t, *J* = 7 Hz, 24H, octyloxy); MALDI-TOF-MS *m/z* 4146, calcd for $C_{256}H_{330}N_{16}O_{16}Zn_4$ *m/z* 4148; UV-vis (THF) l_{max} (*e*) [nm ($cm^{-1}M^{-1}$)] 414 (440000), 488 (410000) and 576 (140000); Fluorescence (THF, l_{ex} = 413 nm) l_{em} 639 and 666 nm.

Z5. ^{1}H NMR ($CDCl_3$) *d* 10.41 (s, 2H, *meso*), 9.52 (d, *J* = 5 Hz, 4H, *b*), 9.31 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.91 (m, 12H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.35-8.32 (m, 8H, *b*), 8.28 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.48 (d, *J* = 2 Hz, 12H, Ar), 7.45 (d, *J* = 2 Hz, 8H, Ar), 6.85 (br, 4H, Ar), 6.76 (br, 2H, Ar) 6.72 (br, 4H, Ar), 4.11-4.01 (m, 40H, octyloxy), 1.85-1.72 (m, 40H, octyloxy), 1.49-1.17 (m, 200H, octyloxy), 0.83 (t, *J* = 7 Hz, 20H, octyloxy), and 0.78-0.74 (m, 40H, octyloxy); MALDI-TOF-MS *m/z* 5183, calcd for $C_{320}H_{412}N_{20}O_{20}Zn_5$ *m/z* 6221; UV-vis (THF) l_{max} (nm) 414, 494 and 580; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 640 nm.

Z6. ^{1}H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.52 (d, *J* = 5 Hz, 4H, *b*), 9.31 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.91 (m, 16H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.35-8.32 (m, 12H, *b*), 8.28 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.48 (d, *J* = 2 Hz, 8H, Ar), 7.47 (d, *J* = 3 Hz, 8H, Ar), 7.45 (d, *J* = 2 Hz, 8H, Ar), 6.85 (br, 4H, Ar), 6.76 (br, 4H, Ar) 6.72 (br, 4H, Ar), 4.11-4.01 (m, 48H, octyloxy), 1.85-1.72 (m, 48H, octyloxy), 1.49-1.17 (m, 240H, octyloxy), 0.83 (t, *J* = 7 Hz, 24H, octyloxy), and 0.78-0.74 (m, 48H, octyloxy); MALDI-TOF-MS *m/z* 6214, calcd for $C_{384}H_{494}N_{24}O_{24}Zn_6$ *m/z* 6221; UV-vis (THF) l_{max} (nm) 414, 498 and 582; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 640 nm.

Z7. ^{1}H NMR ($CDCl_3$) *d* 10.41 (s, 2H, *meso*), 9.53 (d, *J* = 5 Hz, 4H, *b*), 9.31 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.91 (m, 20H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.35-8.32 (m, 16H, *b*), 8.28 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.51-7.46 (m, 28H, Ar), 6.86 (br, 4H, Ar), 6.77 (br, 6H, Ar), 6.73 (br, 4H, Ar), 4.11-4.02 (m, 56H, octyloxy), 1.83-1.73 (m, 56H, octyloxy), 1.48-1.20 (m, 280H, octyloxy), 0.83 (t, *J* = 7 Hz, 21H, octyloxy), and 0.80-0.74 (m, 63H, octyloxy); MALDI-TOF-MS *m/z* 7253, calcd for $C_{448}H_{576}N_{28}O_{28}Zn_7$ *m/z* 7259; UV-vis (THF) l_{max} (nm) 414, 500 and 583; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z8. A stock solution of $AgPF_6$ in CH_3CN (0.047 mL, 0.006 mmol) was added to a solution of **Z4** (31 mg, 0.0075 mmol) in $CHCl_3$ (40 mL), and stirred for 3 h at room temperature. After the usual work-up, the separation over a recycling preparative GPC-HPLC and recrystallization from $CHCl_3$/MeOH gave a pure **Z8** (7 mg, 22%). ^{1}H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.53 (d, *J* = 5 Hz, 4H, *b*), 9.31 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.91 (m, 24H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.35-8.32 (m, 20H, *b*), 8.28 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.51-7.46 (m, 32H, Ar), 6.86 (br, 4H, Ar), 6.77 (br, 8H, Ar), 6.73 (br, 4H, Ar), 4.11-4.02 (m, 64H, octyloxy), 1.83-1.73 (m, 64H, octyloxy), 1.48-1.20 (m, 320H, octyloxy), 0.83 (t, *J* = 7 Hz, 24H, octyloxy), and 0.80-0.74 (m, 72H, octyloxy); MALDI-TOF-MS *m/z* 8303, calcd for $C_{512}H_{658}N_{32}O_{32}Zn_8$ *m/z* 8296; UV-vis (THF) l_{max} (*e*) [nm ($cm^{-1}M^{-1}$)] 414 (745000), 502 (735000) and 585 (430000); Fluorescence (THF, l_{ex} = 413 nm)

l_{em} 640 nm.

Z10. ^{1}H NMR ($CDCl_3$) *d* 10.41 (s, 2H, *meso*), 9.53 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.96-8.92 (m, 32H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.36-8.33 (m, 28H, *b*), 8.29 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.52-7.46 (m, 40H, Ar), 6.87 (br, 4H, Ar), 6.78 (br, 12H, Ar), 6.74 (br, 4H, Ar), 4.12-4.07 (m, 80H, octyloxy), 1.86-1.74 (m, 80H, octyloxy), 1.50-1.19 (m, 400H, octyloxy), and 0.85-0.75 (m, 120H, octyloxy); MALDI-TOF-MS *m/z* 10351, calcd for $C_{640}H_{822}N_{40}O_{40}Zn_{10}$ *m/z* 10369; UV (THF) l_{max} (nm) 414, 505 and 586; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z12. ^{1}H NMR ($CDCl_3$) *d* 10.41 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.96-8.92 (m, 40H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.36-8.33 (m, 36H, *b*), 8.28 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.52-7.46 (m, 48H, Ar), 6.86 (br, 4H, Ar), 6.79 (br, 16H, Ar), 6.73 (br, 4H, Ar), 4.07 (m, 96H, octyloxy), 1.86-1.76 (m, 96H, octyloxy), 1.50-1.19 (m, 480H, octyloxy), and 0.85-0.75 (m, 144H, octyloxy); MALDI-TOF-MS *m/z* 12416, calcd for $C_{768}H_{986}N_{48}O_{48}Zn_{12}$ *m/z* 12443; UV ($CHCl_3$) l_{max} (nm) 414, 507 and 587; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 642 nm.

Z16. A stock solution of $AgPF_6$ in CH_3CN (0.012 mL, 0.0015 mmol) was added to a solution of **Z8** (18 mg, 2.2 mmol) in $CHCl_3$ (20 mL), and stirred for 12 h at room temperature. After the usual work-up, the separation over a recycling preparative GPC-HPLC and recrystallization from $CHCl_3$/MeOH gave a pure **Z16** (5 mg, 27%). ^{1}H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.53 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97-8.85 (m, 60H, *b*), 8.37-8.17 (m, 60H, *b*), 7.52-7.46 (m, 64H, Ar), 6.86-6.73 (br, 32H, Ar), 4.07 (m, 128H, octyloxy), 1.84-1.78 (m, 128H, octyloxy), 1.44-1.20 (m, 640H, octyloxy), and 0.85-0.75 (m, 192H, octyloxy); MALDI-TOF-MS *m/z* 16620, calcd for $C_{1024}H_{1314}N_{64}O_{64}Zn_{16}$ *m/z* 16590; UV-vis (THF) l_{max} (*e*) [nm (cm^{-1}M^{-1})] l_{max} 414 (1 300 000), 508 (1 380 000) and 587 (950 000); Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z20. ^{1}H NMR ($CDCl_3$) *d* 10.41 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.96-8.84 (m, 76H, *b*), 8.36-8.16 (m, 76H, *b*), 7.52-7.45 (m, 80H, Ar), 6.86-6.73 (m, 40H, Ar), 4.07 (m, 160H, octyloxy), 1.79 (m, 160H, octyloxy), 1.44-1.21 (m, 800H, octyloxy), and 0.84-0.75 (m, 240H, octyloxy); MALDI-TOF-MS *m/z* 20769, calcd for $C_{1280}H_{1642}N_{80}O_{80}Zn_{20}$ *m/z* 20736; UV-vis ($CHCl_3$) l_{max} (nm) 414, 506 and 585; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 641 nm.

Z24. ^1H NMR ($CDCl_3$) *d* 10.41 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.30 (br, 4H, *b*), 8.97-8.84 (m, 92H, *b*), 8.37-8.16 (m, 92H, *b*), 7.52-7.45 (m, 96H, Ar), 6.86-6.73 (m, 48H, Ar), 4.07 (m, 192H, octyloxy), 1.79 (m, 192H, octyloxy), 1.44-1.21 (m, 960H, octyloxy), and 0.84-0.74 (m, 288H, octyloxy); MALDI-TOF-MS *m/z* 24465, calcd for $C_{1536}H_{1970}N_{96}O_{96}Zn_{24}$ *m/z* 24884; UV-vis ($CHCl_3$) l_{max} (nm) 414, 506 and 585; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 641 nm.

Z32. $AgPF_6$ (0.014 mL of 0.138 M stock solution in dry CH_3CN, 0.0019 mmol) was added to a solution of **Z16** (40 mg, 0.0024 mmol) in $CHCl_3$ (20 mL), and stirred for 4 h at room temperature. Again $AgPF_6$ solution (0.014 mL) was added and the mixture was stirred for more 5 h. After the usual work-up, the separation over a recycling preparative GPC-HPLC and recrystallization from $CHCl_3$/MeOH gave a pure **Z32** (10 mg, 25%). ^1H NMR ($CDCl_3$) *d* 10.42 (s, 2H, meso), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97-8.85 (m, 124H, *b*), 8.38-8.17 (m, 124H, *b*), 7.53-7.46 (m, 128H, Ar), 6.86-6.73 (br, 64H, Ar), 4.08 (m, 256H, octyloxy), 1.80 (m, 256H, octyloxy), 1.46-1.21 (m, 1280H, octyloxy), and 0.85-0.75 (m, 384H, octyloxy); MALDI-TOF-MS *m/z* 33790, calcd for $C_{2048}H_{2626}N_{128}O_{128}Zn_{32}$ *m/z* 33178; UV-vis (THF) l_{max} (*e*) [nm ($cm^{-1}M^{-1}$)] 414 (2690000), 509 (3070000) and 588 (220000); Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z40. ^1H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97-8.85 (m, 156H, *b*), 8.37-8.16 (m, 156H, *b*), 7.52-7.46 (m, 160H, Ar), 6.86-6.73 (m, 80H, Ar), 4.07 (m, 320H, octyloxy), 1.80 (m, 320H, octyloxy), 1.44-1.22 (m, 1600H, octyloxy), and 0.88-0.75 (m, 480H, octyloxy); MALDI-TOF-MS *m/z* 41177, calcd for $C_{2560}H_{3282}N_{160}O_{160}Zn_{40}$ *m/z* 41470; UV-vis ($CHCl_3$) l_{max} (nm) 414, 507 and 586; Fluorescence ($CHCl_3$, l_{ex} =413 nm) l_{em} 641 nm.

Z48. ^1H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97 (m, 188H, *b*), 8.37-8.16 (m, 188H, *b*), 7.52-7.46 (m, 192H, Ar), 6.86-6.73 (m, 96H, Ar), 4.07 (m, 384H, octyloxy), 1.80 (m, 384H, octyloxy), 1.45-1.22 (m, 1920H, octyloxy), and 0.87-0.75 (m, 576H, octyloxy); MALDI-TOF-MS *m/z* 49447, calcd for $C_{3072}H_{3938}N_{192}O_{192}Zn_{48}$ *m/z* 49764; UV-vis ($CHCl_3$) l_{max} (nm) 413, 508 and 586; Fluorescence ($CHCl_3$, l_{ex} =413 nm) l_{em} 640 nm.

Z64. $AgPF_6$ (0.004 mL of 0.138 M stock solution in dry CH_3CN, 0.0005 mmol) was added to a solution of **Z32** (18 mg, 0.0005 mmol) in $CHCl_3$ (3 mL), and stirred for 7 h at room temperature. After the usual work-up, the separation over a recycling preparative GPC-HPLC and recrystallization from $CHCl_3$/MeOH gave a pure **Z64** (3.7 mg, 22%). ^1H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97 (m, 252H, *b*), 8.38-8.17 (m, 252H, *b*), 7.53 (m, 256H, Ar), 6.86-6.74 (br, 128H, Ar), 4.07 (m, 512H, octyloxy), 1.80 (m, 512H, octyloxy), 1.45-1.22 (m, 2560H, octyloxy), and 0.85-0.75 (m, 768H, octyloxy); MALDI-TOF-MS *m/z* 66258, calcd for $C_{4096}H_{5250}N_{256}O_{256}Zn_{64}$ *m/z* 66350; UV-vis (THF) l_{max} (nm) 414, 510 and 589; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z96. ^1H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97 (m, 380H, *b*), 8.37-8.16 (m, 380H, *b*), 7.52 (m, 384H, Ar), 6.79 (br, 192H, Ar), 4.07 (m, 768H, octyloxy), 1.80 (m, 768H, octyloxy), 1.45-1.22 (m, 3840H, octyloxy), and 0.88-0.76 (m, 1152H, octyloxy); MALDI-TOF-MS *m/z* 99050, calcd for $C_{6144}H_{7874}N_{384}O_{384}Zn_{96}$ *m/z* 99503; UV-vis ($CHCl_3$) l_{max} (nm) 413, 508 and 586; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 641 nm.

Z128. ^1H NMR ($CDCl_3$) *d* 10.40 (s, 2H, *meso*), 9.52 (br, 4H, *b*), 9.30 (br, 4H, *b*), 8.96 (m, 508H, *b*), 8.36 (m, 508H, *b*), 7.52 (m, 512H, Ar), 6.79 (br, 256H, Ar), 4.06 (m, 1024H, octyloxy), 1.79 (m, 1024H, octyloxy), 1.44-1.22 (m, 5120H, octyloxy), and 0.81-0.78 (m, 1536H, octyloxy); MALDI-TOF-MS *m/z* 130295, calcd for $C_{8192}H_{10498}N_{512}O_{512}Zn_{128}$ *m/z* 132702; UV-vis (THF) l_{max} (nm) 414, 511 and 589; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z256. ^1H NMR ($CDCl_3$) *d* 10.42 (s, 2H, *meso*), 9.53 (br, 4H, *b*), 9.31 (br, 4H, *b*), 8.97 (m, 1020H, *b*), 8.37 (m, 1020H, *b*), 7.52 (m, 1024H, Ar), 6.79 (br, 512H, Ar), 4.06 (m, 2048H, octyloxy), 1.79 (m, 2048H, octyloxy), 1.44-1.22 (m, 10240H, octyloxy), and 0.81-0.78 (m, 3072H, octyloxy); UV-vis (THF) l_{max} (nm) 414, 511 and 589; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z384. UV-vis (THF) l_{max} (nm) 414, 511 and 589; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

Z512. UV-vis (THF) l_{max} (nm) 414, 511 and 589; Fluorescence (THF, l_{ex} = 413 nm) l_{em} 642 nm.

H2. **Z2** was dissolved in a mixture of CH_2Cl_2 and 3 N HCl. The resulting solution was stirred for 1 h at room temperature, poured into water, and extracted with CH_2Cl_2. The organic layer was separated off, and the combined extracts were washed with water, saturated aqueous $NaHCO_3$, water, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the product was recrystallized from CH_2Cl_2/MeOH to give **H2**. ^{1}H NMR ($CDCl_3$) ***d*** 10.34 (s, 2H, *meso*), 9.42 (d, *J* = 5 Hz, 4H, ***b***), 9.18 (d, *J* = 5 Hz, 4H, ***b***), 8.72 (d, *J* = 5 Hz, 4H, ***b***), 8.03 (d, *J* = 5 Hz, 4H, ***b***), 7.39 (d, *J* = 3 Hz, 8H, Ar), 6.80 (t, *J* = 3 Hz, 4H, Ar), 4.06 (t, *J* = 7 Hz, 16H, octyloxy), 1.79 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.44 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.32-1.21 (m, 64H, octyloxy), 0.80 (t, *J* = 7 Hz, 24H, octyloxy), and -2.44 (s, 4H, inner-NH); FAB-MS *m/z* 1947.2, calcd for $C_{128}H_{170}N_8O_8$ *m/z* 1947.3; UV-vis ($CHCl_3$) l_{max} (nm) 413, 445, 519, 588, and 644; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 650 and 711 nm.

H3. ^{1}H NMR ($CDCl_3$) ***d*** 10.36 (s, 2H, *meso*), 9.44 (d, *J* = 5 Hz, 4H, ***b***), 9.21 (d, *J* = 5 Hz, 4H, ***b***), 8.81 (d, *J* = 5 Hz, 4H, ***b***), 8.72 (d, *J* = 5 Hz, 4H, ***b***) 8.20 (d, *J* = 5 Hz, 4H, ***b***) 8.09 (d, *J* = 5 Hz, 4H, ***b***), 7.43 (d, *J* = 2 Hz, 8H, Ar), 7.35 (d, *J* = 2 Hz, 4H, Ar), 6.84 (t, *J* = 2 Hz, 4H, Ar), 6.67 (br, 2H, Ar), 4.10 (t, *J* = 7 Hz, 16H, octyloxy), 3.96 (t, *J* = 7 Hz, 8H, octyloxy), 1.84 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.70 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.46-1.13 (m, 120H, octyloxy), 0.82 (t, *J* = 7 Hz, 24H, octyloxy), 0.73 (t, *J* = 7 Hz, 12H, octyloxy), -1.65 (s, 2H, inner-NH), -2.40 (s, 4H, inner-NH); MALDI-TOF-MS *m/z* 2917, calcd for $C_{192}H_{254}N_{12}O_{12}$ *m/z* 2922; UV-vis ($CHCl_3$) l_{max} (nm) 410, 469, 528, and 596; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 661 and 724 nm.

H4. ^{1}H NMR ($CDCl_3$) *d* 10.37 (s, 2H, *meso*), 9.44 (d, *J* = 5 Hz, 4H, *b*), 9.21 (d, *J* = 5 Hz, 4H, *b*), 8.82-8.81 (m, 8H, *b*), 8.75 (d, *J* = 5 Hz, 4H, *b*), 8.26 (d, *J* = 5 Hz, 4H, *b*), 8.22 (d, *J* = 5 Hz, 4H, *b*), 8.11 (d, *J* = 5 Hz, 4H, *b*), 7.44 (d, *J* = 3 Hz, 8H, Ar), 7.40 (d, *J* = 3 Hz, 8H, Ar), 6.84 (br, 4H, Ar), 6.71 (br, 4H, Ar), 4.10 (t, *J* = 7 Hz, 16H, octyloxy), 4.00 (t, *J* = 7 Hz, 16H, octyloxy), 1.83 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.73 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.47 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.38-1.16 (m, 144H, octyloxy), 0.82 (t, *J* = 7 Hz, 24H, octyloxy), 0.75 (t, *J* = 7 Hz, 24H, octyloxy), -1.62 (s, 4H, inner-NH), and -2.39 (s, 4H, inner-NH); MALDI-TOF-MS *m/z* 3894, calcd for $C_{256}H_{338}N_{16}O_{16}$ *m/z* 3894; UV-vis ($CHCl_3$) l_{max} (nm) 411, 480, 535, and 596; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 665 and 726 nm.

H6. ^{1}H NMR ($CDCl_3$) *d* 10.37 (s, 2H, *meso*), 9.45 (d, *J* = 5 Hz, 4H, *b*), 9.22 (d, *J* = 5 Hz, 4H, *b*), 8.85-8.83 (m, 16H, *b*), 8.76 (d, *J* = 5 Hz, 4H, *b*), 8.29-8.28 (m, 12H, *b*), 8.23 (d, *J* = 5 Hz, 4H, *b*), 8.12 (d, *J* = 5 Hz, 4H, *b*), 7.45 (m, 16H, Ar), 7.41 (d, *J* = 3 Hz, 8H, Ar), 6.85 (t, *J* = 2 Hz, 4H, Ar), 6.76 (t, *J* = 2 Hz, 4H, Ar) 6.72 (t, *J* = 2 Hz, 4H, Ar), 4.12-4.01 (m, 48H, octyloxy), 1.85-1.72 (m, 48H, octyloxy), 1.49-1.17 (m, 240H, octyloxy), 0.83 (t, *J* = 7 Hz, 24H, octyloxy), 0.78-0.74 (m, 48H, octyloxy), -1.57 (s, 4H, inner-NH), -1.60 (s, 4H, inner-NH), and -2.38 (s, 4H, inner-NH); MALDI-TOF-MS *m/z* 5839, calcd for $C_{384}H_{506}N_{24}O_{24}$ *m/z* 5841; UV-vis ($CHCl_3$) l_{max} (nm) 412, 489, 541, 599, and 656; Fluorescence ($CHCl_3$, l_{ex} = 413 nm) l_{em} 667 and 727 nm.

5,15-Diphenylporphyrin. A solution of 2,2'-dipyrrylmethane (1.15 g, 7.84 mmol) and benzaldehyde (0.796 mL, 7.84 mmol) in freshly distilled CH_2Cl_2 (1.5 L) was stirred under N_2, and the flask was shielded from light. Trifluoroacetic acid (0.376 mL, 4.88 mmol) was added via syringe, and the solution was stirred for 3 h at room temperature. DDQ (2.67 g, 11.75 mmol) was added to the solution, and the resulting solution was stirred for an additional 2 h. After the reaction mixture was neutralized by triethylamine and passed over Alumina column to remove polymeric materials, the solvent was removed by a rotary evaporator and the residue was purified by a silica gel column chromatography with CH_2Cl_2. The product was recrystallized from CH_2Cl_2-*n*-hexane. Yield; 705 mg, 39%. ^{1}H NMR ($CDCl_3$) ***d*** 10.32 (s, 2H, *meso*), 9.40 (d, *J* = 5 Hz, 4H, ***b***), 9.09 (d, *J* = 5 Hz, 4H, ***b***), 8.28 (m, 4H, Ar), 7.82 (m, 6H, Ar), and -3.10 (s, 2H, N-H); FAB MS *m/z* 462.2, calcd for $C_{32}H_{22}N_4$ *m/z* 462.2.

Z$_P$3. A round-bottomed flask was charged with **Z$_P$1** (100 mg, 0.19 mmol) and dry $CHCl_3$ (100 mL). A stock solution of $AgPF_6$ (1.80 mL, 0.23 mmol) in acetonitrile was added at once. The reaction mixture was stirred for 10 h at 30°C. After the usual work-up, the oligomers ware separated by a preparative size exclusion column. Fractions of 2-mer and 3-mer ware separated, and the solvent was removed by a rotary evaporator. Recrystallization from $CHCl_3$/MeOH gave red-blown solids. **Z$_P$2**: ^{1}H NMR ($CDCl_3$) ***d*** 10.35 (s, 2H, *meso*), 9.47 (d, *J* = 5 Hz, 4H, ***b***), 9.12 (d, *J* = 5 Hz, 4H, ***b***), 8.64 (d, *J* = 5 Hz, 4H, ***b***), 8.23 (m, 8H, Ar), 8.02 (d, *J* = 5 Hz, 4H, b), 7.67 (m, 12H, Ar). **Z$_P$3**; ^{1}H NMR ($CDCl_3$) ***d*** 10.37 (s, 2H, *meso*), 9.49 (d, *J* = 5 Hz, 4H, ***b***), 9.15 (d, *J* = 5 Hz, 4H, ***b***), 8.72 (d, *J* = 5 Hz, 4H, ***b***), 8.63 (d, *J* = 5 Hz, 4H, ***b***), 8.28 (m, 8H, Ar), 8.18 (m, 8H, Ar + ***b***), 8.07 (d, *J* = 5 Hz, 4H, ***b***), 7.71 (m, 12H, Ar), 7.55 (m, 6H, Ar).

Z*n*Br$_2$. *Meso-meso* linked porphyrin arrays was dissolved in a mixture of $CHCl_3$ and pyridine (0.5%). NBS (2.2 equiv.) was added to this solution and the resulting solution was stirred for 2 h. The mixture was poured into water and extracted with $CHCl_3$. After the combined organic extract was dried over Na_2SO_4 and passed through a short silica gel column, the solvent was removed by a rotary evaporator. The product was recrystallized from $CHCl_3$-MeOH.

Z2Br$_2$. (quant). ^{1}H NMR ($CDCl_3$) ***d*** 9.81 (d, *J* = 5 Hz, 4H, ***b***), 9.13 (d, *J* = 5 Hz, 4H, ***b***), 8.71 (d, *J* = 5 Hz, 4H, ***b***), 8.01 (d, *J* = 5 Hz, 4H, ***b***), 7.34 (d, *J* = 3 Hz, 8H, Ar), 6.77 (t, *J* = 3 Hz, 4H, Ar), 4.02 (t, *J* = 7 Hz, 16H, octyloxy), 1.78 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.43 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.32-1.10 (m, 64H, octyloxy), and 0.80 (t, *J* = 7 Hz, 24H, octyloxy); MALDI-TOF-MS *m/z* 2232.4, calcd for $C_{128}H_{164}N_8O_8Zn_2Br_2$ *m/z* 2233.0.

Z3Br$_2$. (95%). ^{1}H NMR ($CDCl_3$) ***d*** 9.87 (d, *J* = 5 Hz, 4H, ***b***), 9.19 (d, *J* = 5 Hz, 4H, ***b***), 8.81 (d, *J* = 5 Hz, 4H, ***b***), 8.79 (d, *J* = 5 Hz, 4H, ***b***) 8.16 (d, *J* = 5 Hz, 4H, ***b***) 8.14 (d, *J* = 5 Hz, 4H, *b*), 7.39 (d, *J* = 3 Hz, 8H, Ar), 7.37 (d, *J* = 3 Hz, 4H, Ar), 6.82 (t, *J* = 3 Hz, 4H, Ar), 6.68 (t, *J* = 3 Hz, 2H, Ar), 4.08 (t, *J* = 7 Hz, 16H, octyloxy), 3.95 (t, *J* = 7 Hz, 8H, octyloxy), 1.81 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.69 (t-t, *J* = 7 Hz, 8H, octyloxy), 1.45 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.33-1.13 (m, 104H, octyloxy), 0.81 (t, *J* = 7 Hz, 24H, octyloxy) and 0.72 (t, *J* = 7 Hz, 12H, octyloxy); MALDI-TOF-MS *m/z* 3267, calcd for $C_{192}H_{246}N_{12}O_{12}Zn_3Br_2$ *m/z* 3270.

Z4Br$_2$. (87%). ^{1}H NMR ($CDCl_3$) ***d*** 9.88 (d, *J* = 5 Hz, 4H, *b*), 9.20 (d, *J* = 5 Hz, 4H, *b*), 8.88 (d, *J* = 5 Hz, 4H, *b*), 8.84 (d, *J* = 5 Hz, 4H, *b*), 8.81 (d, *J* = 5 Hz, 4H, *b*), 8.27 (d, *J* = 5 Hz, 4H, *b*), 8.19 (d, *J* = 5 Hz, 4H, *b*), 8.16 (d, *J* = 5 Hz, 4H, *b*), 7.41 (d, *J* = 3 Hz, 8H, Ar), 7.40 (d, *J* = 3 Hz, 8H, Ar), 6.83 (br, 4H, Ar), 6.71 (br, 4H, Ar), 4.09 (t, *J* = 7 Hz, 16H, octyloxy), 3.99 (t, *J* = 7 Hz, 16H, octyloxy), 1.82 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.72 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.47 (t-t, *J* = 7 Hz, 16H, octyloxy), 1.38-1.15 (m, 144H, octyloxy), 0.82 (t, *J* = 7 Hz, 24H, octyloxy), and 0.74 (t, *J* = 7 Hz, 24H, octyloxy); MALDI-TOF-MS *m/z* 4310, calcd for $C_{256}H_{328}N_{16}O_{16}Zn_4Br_2$ *m/z* 4307.

Z6Br$_2$. (78%) ^{1}H NMR ($CDCl_3$) ***d*** 9.88 (d, *J* = 5 Hz, 4H, *b*), 9.20 (d, *J* = 5 Hz, 4H, *b*), 8.94-8.91 (m, 12H, *b*), 8.86 (d, *J* = 5 Hz, 4H, *b*), 8.82 (d, *J* = 5 Hz, 4H, *b*), 8.34-8.31 (m, 12H, *b*), 8.21 (d, *J* = 5 Hz, 4H, *b*), 8.18 (d, *J* = 5 Hz, 4H, *b*), 7.48 (d, *J* = 2 Hz, 8H, Ar), 7.44 (d, *J* = 3 Hz, 8H, Ar), 7.42 (d, *J* = 2 Hz, 8H, Ar), 6.83 (br, 4H, Ar), 6.76 (br, 4H, Ar) 6.73 (br, 4H, Ar), 4.11-4.00 (m, 48H, octyloxy), 1.85-1.72 (m, 48H, octyloxy), 1.49-1.17 (m, 240H, octyloxy), 0.83 (t, *J* = 7 Hz, 24H, octyloxy), and 0.78-0.72 (m, 48H, octyloxy); MALDI-TOF-MS *m/z* 6381, calcd for $C_{384}H_{492}N_{24}O_{24}Zn_6Br_2$ *m/z* 6380.

Z8Br$_2$. (83%). ^{1}H NMR ($CDCl_3$) ***d*** 9.89 (d, *J* = 5 Hz, 4H, *b*), 9.21 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.91 (m, 20H, *b*), 8.86 (d, *J* = 5 Hz, 4H, *b*), 8.82 (d, *J* = 5 Hz, 4H, *b*), 8.35-8.31 (m, 20H, *b*), 8.21 (d, *J* = 5 Hz, 4H, *b*), 8.18 (d, *J* = 5 Hz, 4H, *b*), 7.50-7.49 (m, 16H, Ar), 7.44 (d, *J* = 3 Hz, 8H, Ar), 7.42 (d, *J* = 3 Hz, 8H, Ar), 6.84 (br, 4H, Ar), 6.77 (br, 8H, Ar), 6.73 (br, 4H, Ar), 4.10-4.02 (m, 64H, octyloxy), 1.85-1.73 (m, 64H, octyloxy), 1.48-1.20 (m, 320H, octyloxy), 0.83 (t, *J* = 7 Hz, 24H, octyloxy), and 0.80-0.71 (m, 72H, octyloxy).

Z12Br$_2$. (92%) ^{1}H NMR ($CDCl_3$) ***d*** 9.86 (d, *J* = 5 Hz, 4H, *b*), 9.18 (d, *J* = 5 Hz, 4H, *b*), 8.90-8.86 (m, 36H, *b*), 8.80 (d, *J* = 5 Hz, 4H, *b*), 8.77 (d, *J* = 5 Hz, 4H, *b*), 8.29-8.24 (m, 36H, *b*), 8.13 (d, *J* = 5 Hz, 4H, *b*), 8.07 (d, *J* = 5 Hz, 4H, *b*), 7.50-7.48 (m, 32H, Ar), 7.43 (d, *J* = 3 Hz, 8H, Ar), 7.41 (d, *J* = 3 Hz, 8H, Ar), 6.84 (br, 4H, Ar), 6.77 (br, 16H, Ar), 6.73 (br, 4H, Ar), 4.06 (m, 96H, octyloxy), 1.84-1.76 (m, 96H, octyloxy), 1.50-1.19 (m, 480H, octyloxy), and 0.85-0.75 (m, 144H, octyloxy).

Z16Br$_2$. (84%). ^{1}H NMR ($CDCl_3$) *d* 9.88 (d, *J* = 5 Hz, 4H, *b*), 9.02 (d, *J* = 5 Hz, 4H, *b*), 8.96 (m, 52H, *b*), 8.86 (d, *J* = 5 Hz, 4H, *b*), 8.82 (d, *J* = 5 Hz, 4H, *b*), 8.36 (m, 52H, *b*), 8.21 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 7.52-7.42 (m, 64H, Ar), 6.85 (d, *J* = 3 Hz, 4H, Ar), 6.78 (br, 24H, Ar), 6.73 (d, *J* = 3 Hz, 4H, Ar), 4.06 (m, 128H, octyloxy), 1.84-1.78 (m, 128H, octyloxy), 1.44-1.20 (m, 640H, octyloxy), and 0.85-0.75 (m, 192H, octyloxy).

Z24Br$_2$. (89%). ^{1}H NMR ($CDCl_3$) *d* 9.87 (d, *J* = 5 Hz, 4H, *b*), 9.19 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.80 (m, 92H, *b*), 8.35-8.15 (m, 92H, *b*), 7.50-7.41 (m, 96H, Ar), 6.83-6.72 (m, 48H, Ar), 4.06 (m, 192H, octyloxy), 1.77 (m, 192H, octyloxy), 1.42-1.23 (m, 960H, octyloxy), and 0.84-0.72 (m, 288H, octyloxy).

Z48Br$_2$. (91%). ^{1}H NMR ($CDCl_3$) *d* 9.88 (d, *J* = 5 Hz, 4H, *b*), 9.20 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.80 (m, 188H, *b*), 8.35-8.15 (m, 188H, *b*), 7.50-7.41 (m, 192H, Ar), 6.83-6.72 (m, 96H, Ar), 4.06 (m, 384H, octyloxy), 1.77 (m, 384H, octyloxy), 1.42-1.24 (m, 1920H, octyloxy), and 0.84-0.71 (m, 576H, octyloxy).

Z64Br$_2$. (87%). ^{1}H NMR ($CDCl_3$) *d* 9.87 (br, 4H, *b*), 9.19 (br, 4H, *b*), 8.93-8.80 (m, 252H, *b*), 8.32-8.11 (m, 252H, *b*), 7.50 (m, 256H, Ar), 6.77 (br, 128H, Ar), 4.08 (m, 512H, octyloxy), 1.80 (m, 512H, octyloxy), 1.45-1.22 (m, 2560H, octyloxy), and 0.85-0.77 (m, 768H, octyloxy).

9. 4-Bromobenzenethiol (**8**) (920 mg, 5.0 mmol) was dissolved in a mixture of TFA (9 ml) and CH_2Cl_2 (2 ml) and stirred for 15 min under Ar at room temperature. To the solution was added benzhydrol (**7**) (945 mg, 5.0 mmol). After 5 min, the precipitate was collected and purified over a silica gel column (CH_2Cl_2/hexane = 1/4). The product was given as white crystal (1.48 g, 83%). ^{1}H NMR ($CDCl_3$) *d* 7.37 (d, *J* = 8 Hz, 4H, Ar), 7.30-7.19 (m, 8H, Ar), 7.06 (d, *J* = 8 Hz, 2H, Ar), and 5.48 (s, 1H, benzyl). FAB MS *m/z* 402.3, calcd for $C_{32}H_{22}N_4$ *m/z* 402.2.

10. **9** (178 mg, 0.5 mmol) was mixed with bispinacolate diboron (125 mg, 0.5 mmol), KOAc (125 mg), and $PdCl_2$(dppf) (12 mg) in DMF (2 ml) and toluene (2 ml). The mixture was degassed 3 times by freeze-pump thaw cycles and stirred at 80°C for 6 h. Then the mixture was washed with water, and organic layer was extracted with ether, dried over Na_2SO_4 and evaporated. The residue was separated by a silica gel column (benzene). The boronate was obtained as a white solid (96 mg, 48%). ^1H NMR ($CDCl_3$) *d* 7.59 (d, *J* = 8 Hz, 2H, Ar), 7.42 (d, *J* = 8 Hz, 4H, Ar), 7.29 (t, *J* = 8 Hz, 4H, Ar), 7.21 (t, *J* = 8 Hz, 2H, Ar), 7.19 (d, *J* = 8 Hz, 2H, Ar), 5.64 (s, 1H, benzyl), and 1.30 (s, 12H, Me). FAB MS *m/z* 402.3, calcd for $C_{32}H_{22}N_4$ *m/z* 402.2.

Z*n*S$_2$. Bromo porphyrin **Z*n*Br$_2$** was mixed with boronate **10** (10 equiv), Cs_2CO_3 (15 equiv), and $Pd(PPh_3)_4$ (10 mol%) in a mixed solvent of toluene (1 ml) and DMF (1 ml). The mixture was degassed 3 times by freeze-pump thaw cycles and stirred at 80°C for 5 h. Then the mixture was washed with water, extracted with $CHCl_3$, dried over Na_2SO_4 and evaporated. After passed through a short silica gel column, the residue was loaded in GPC (THF) to remove unreacted **10**. The porphyrin fraction was collected and the solvent was evaporated. The residue was recrystallized with $CHCl_3$/Methanol.

Z6S$_2$. (90%). ^1H NMR ($CDCl_3$) *d* 9.14 (d, *J* = 5 Hz, 4H, *b*), 8.93-8.91 (m, 16H, *b*), 8.86-8.85 (m, 4H, *b*), 8.34-8.31 (m, 12H, *b*), 8.24 (d, *J* = 5 Hz, 4H, *b*), 8.18 (d, *J* = 5 Hz, 4H, *b*), 8.12 (d, *J* = 8 Hz, 4H, Ph), 7.68-7.67 (m, 12H, Ph + Ar), 7.48 (m, 16H, Ph + Ar), 7.44 (d, *J* = 3 Hz, 8H, Ar), 7.42 (d, *J* = 2 Hz, 8H, Ar), 7.38 (t, *J* = 8 Hz, 4H, Ph), 6.83 (br, 4H, Ar), 6.75 (br, 4H, Ar) 6.72 (br, 4H, Ar), 4.10-4.01 (m, 48H, octyloxy), 1.82-1.72 (m, 48H, octyloxy), 1.48-1.17 (m, 240H, octyloxy), 0.82 (t, *J* = 7 Hz, 24H, octyloxy), and 0.78-0.74 (m, 48H, octyloxy); MALDI-TOF-MS *m/z* 6381, calcd for $C_{384}H_{492}N_{24}O_{24}Zn_6Br_2$ *m/z* 6380.

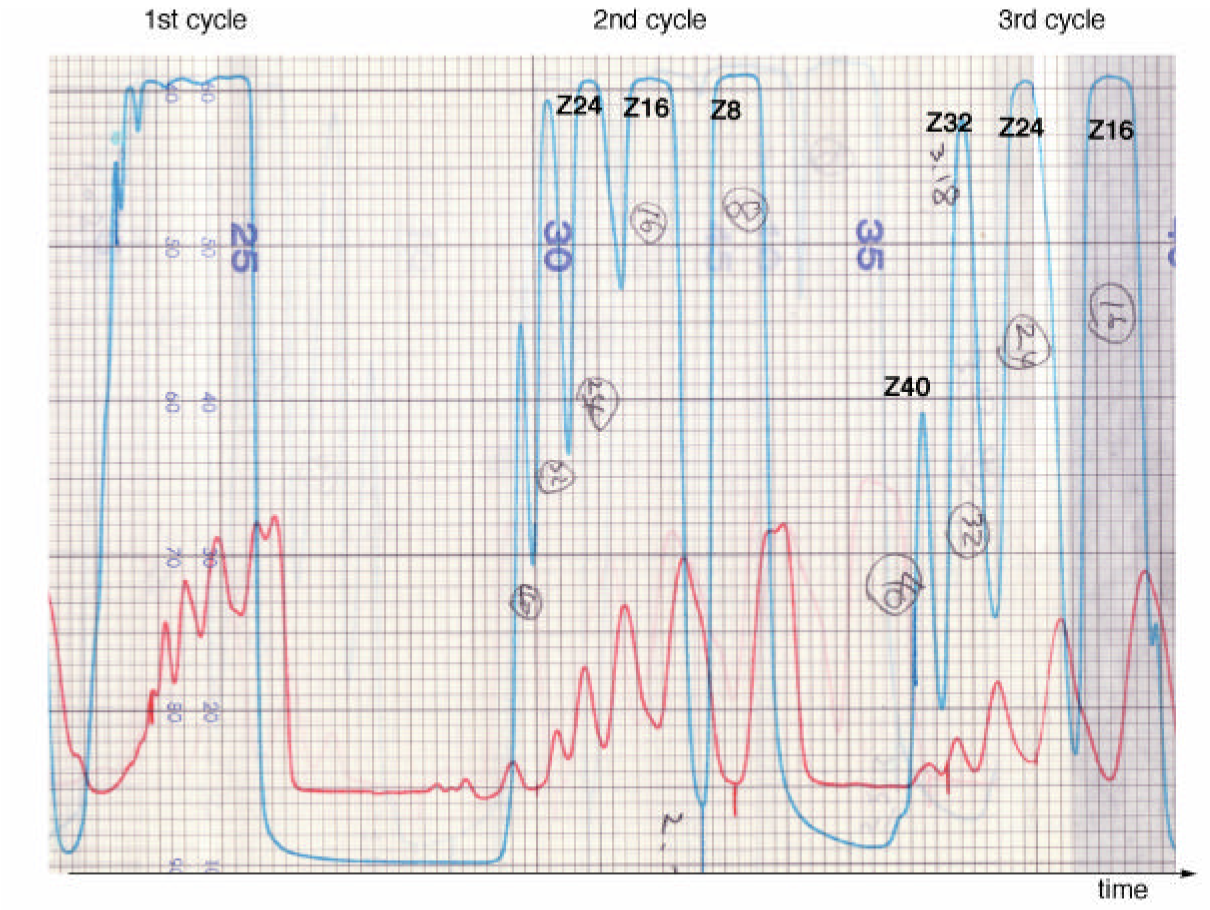
Z12S$_2$. ^1H NMR ($CDCl_3$) *d* 9.06 (d, *J* = 5 Hz, 4H, *b*), 8.89-8.79 (m, 48H, *b*), 8.85 (d, *J* = 5 Hz, 4H, *b*), 8.29-8.25 (m, 38H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 8.11 (d, *J* = 5 Hz, 4H, *b*), 8.06

(d, *J* = 8 Hz, 4H, Ph), 7.61-7.59 (m, 12H, Ph + Ar), 7.45-7.28 (m, 60H, Ph + Ar), 6.77 (br, 4H, Ar), 6.71 (br, 16H, Ar), 6.66 (br, 4H, Ar), 5.84 (s, 2H, benzyl), 4.07 (m, 96H, octyloxy), 1.86-1.76 (m, 96H, octyloxy), 1.50-1.19 (m, 480H, octyloxy), and 0.85-0.75 (m, 144H, octyloxy).

Z24S$_2$. (79%). ^{1}H NMR (CDCl$_3$) *d* 9.11 (d, *J* = 5 Hz, 4H, *b*), 8.95-8.84 (m, 96H, *b*), 8.35 (m, 88H, *b*), 8.22 (d, *J* = 5 Hz, 4H, *b*), 8.17 (d, *J* = 5 Hz, 4H, *b*), 8.12 (d, *J* = 8 Hz, 4H, Ph), 7.65 (m, 12H, Ph + Ar), 7.45-7.41 (m, 108H, Ph + Ar), 6.83-6.72 (m, 48H, Ar), 5.89 (s, 2H, benzyl), 4.06 (m, 192H, octyloxy), 1.77 (m, 192H, octyloxy), 1.42-1.23 (m, 960H, octyloxy), and 0.84-0.72 (m, 288H, octyloxy).

Z48S$_2$. (79%). ^{1}H NMR (CDCl$_3$) *d* 9.11 (br, 4H, *b*), 8.95-8.84 (m, 192H, *b*), 8.35 (m, 184H, *b*), 8.24 (d, *J* = 5 Hz, 4H, *b*), 8.19 (d, *J* = 5 Hz, 4H, *b*), 8.15 (d, *J* = 8 Hz, 4H, Ph), 7.65 (m, 12H, Ph + Ar), 7.45-7.41 (m, 204H, Ph + Ar), 6.83-6.72 (m, 96H, Ar), 5.89 (s, 2H, benzyl), 4.06 (m, 384H, octyloxy), 1.77 (m, 384H, octyloxy), 1.42-1.23 (m, 1920H, octyloxy), and 0.84-0.72 (m, 576H, octyloxy).

Z64S$_2$. (91%). ^{1}H NMR (CDCl$_3$) *d* 9.15 (br, 4H, *b*), 8.97-8.87 (m, 256H, *b*), 8.37-8.20 (m, 252H, *b*), 8.13 (br, 4H, Ph), 7.67 (d, *J* = 7 Hz, 12H, Ph + Ar), 7.52 (m, 268H, Ar), 6.79 (br, 128H, Ar), 5.92 (s, 2H, benzyl), 4.08 (m, 512H, octyloxy), 1.80 (m, 512H, octyloxy), 1.45-1.22 (m, 2560H, octyloxy), and 0.85-0.77 (m, 768H, octyloxy).



SI 1 GPC chromatogram of the reaction of **Z8**. Brue line shows the UV absorbance detected at 413 nm.

```
COMNT : DOPZN4 2D
EXMOD : ROESY
IRMOD : NON
POINT :       512
FREQU :  2136.30 Hz
SCANS :        16
DUMMY :         4
ACQTM :       0.2397 sec
PD    :       1.5000 sec
RGAIN :        16

CLFRQ :  2136.30 Hz
CLPNT :       512
TOSCN :       256
CINWT :      3.00 usec
CINTV :    468.10 usec

PW1   :     37.50 usec
PW2   :     12.50 usec
PW3   :     37.50 usec
PW4   :     10.40 usec
PI1   : 250.0000 msec
PI3   :    7.4458 msec
OBATN :         0

OBNUC : 1H
OBFRQ :    500.00 MHz
OBSET : 164194.00 Hz

IRNUC : 1H
IRFRQ :    500.00 MHz
IRSET : 164393.28 Hz
IRATN :       150
IRRPW :      50.0 usec
IRBP1 :        30
IRBP2 :         6
IRRNS :         0

ADBIT :        16
CTEMP :      25.0 c
CSPED :        14 Hz
SLVNT : CDCL3

RESOL :      4.17 Hz
CLRSO :      4.17 Hz
TLINE :         8
THTOP :    1.0000
THBTM :    0.1277
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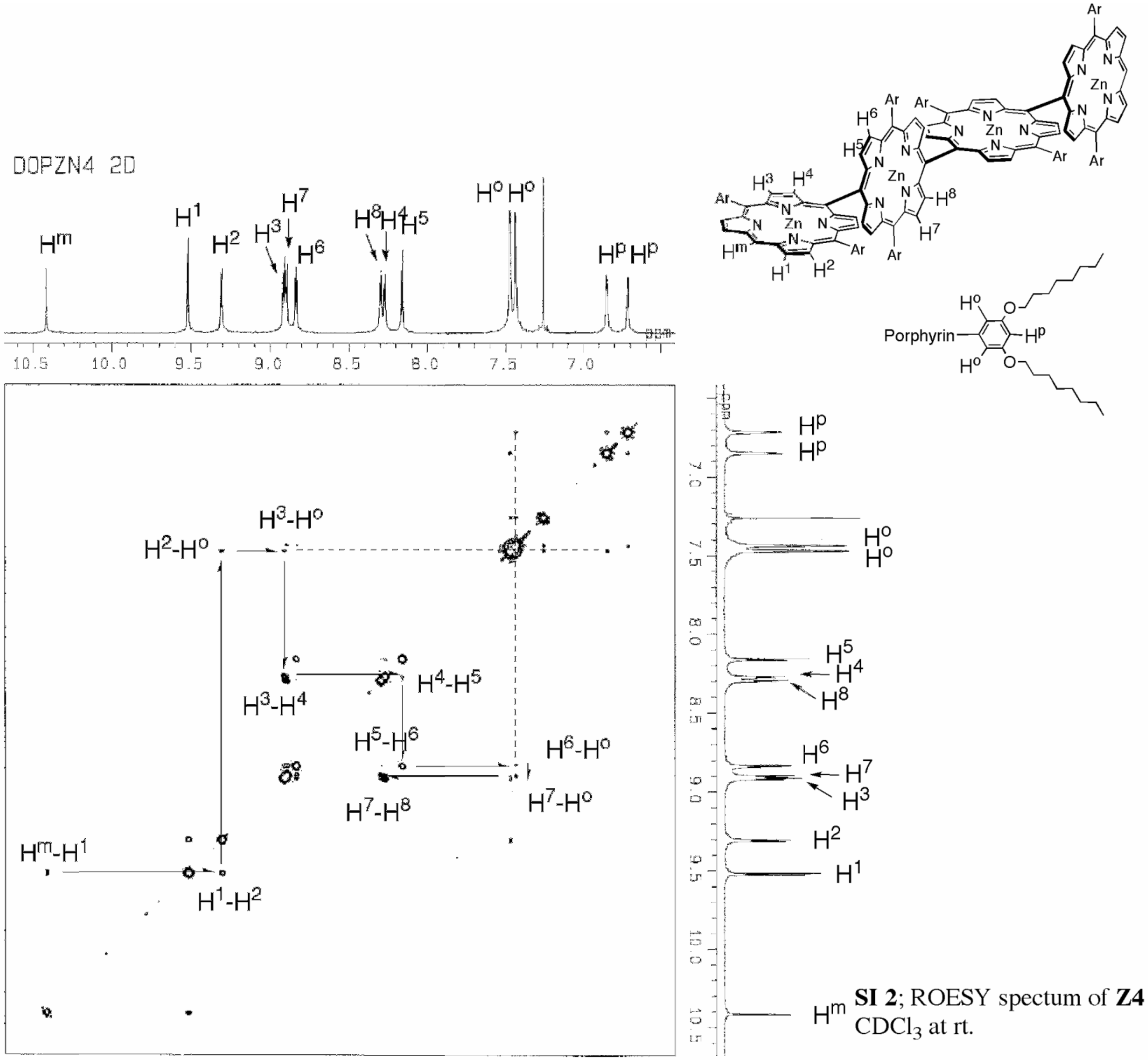
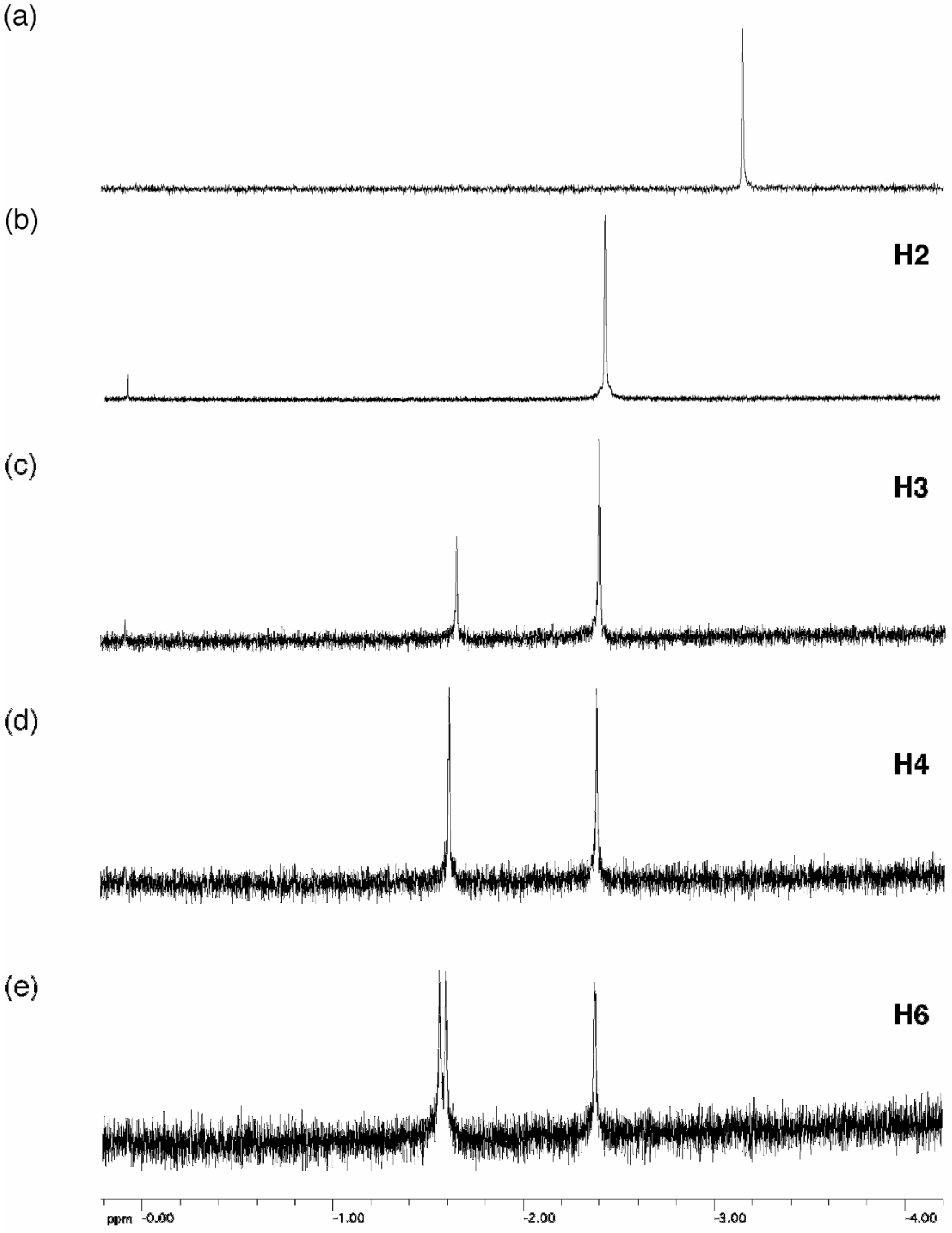
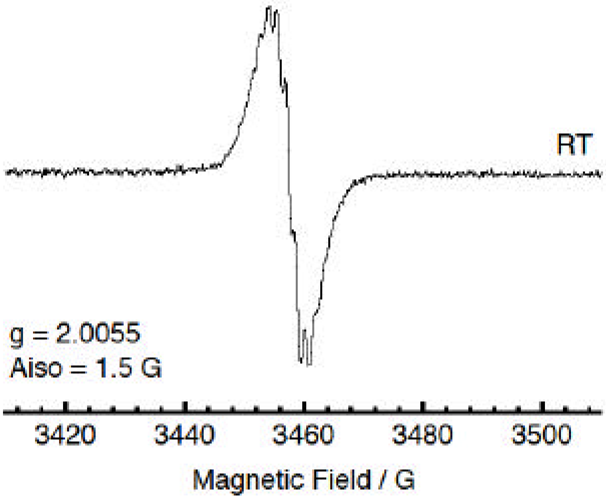


SI 2; ROESY spectum of **Z4** in $CDCl_3$ at rt.



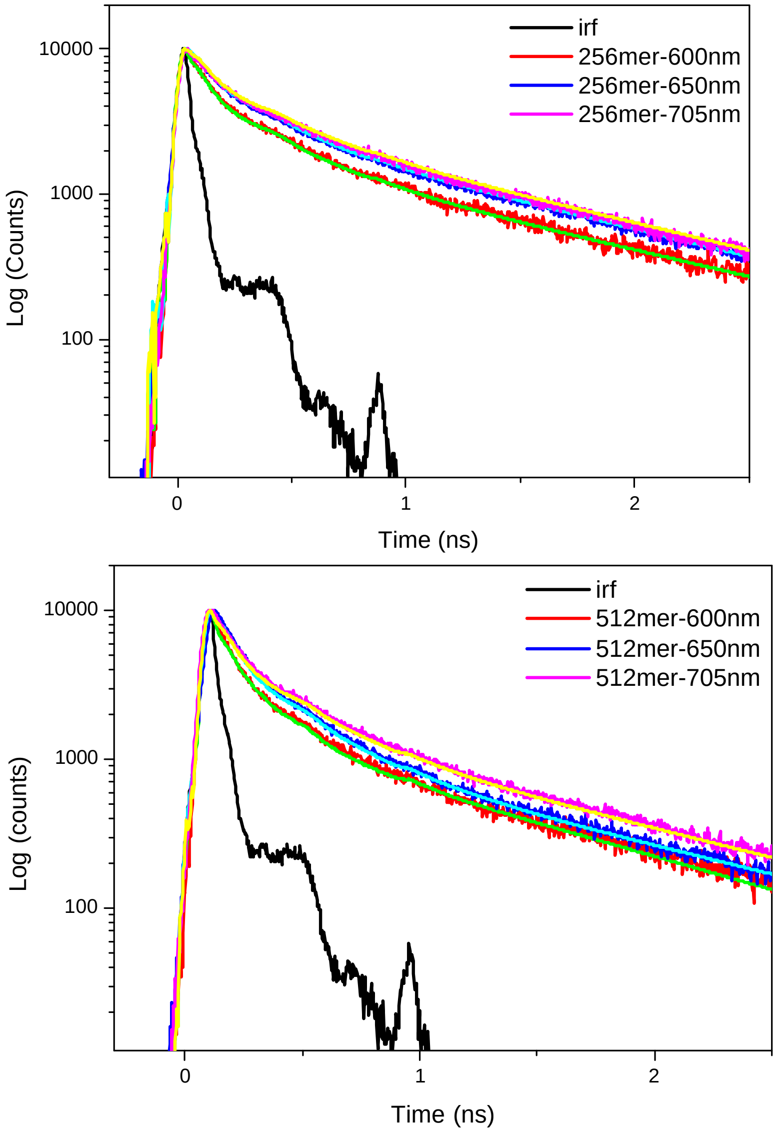
SI 3; ^{1}H-NMR spectra from -4.00 to 0.00 ppm, (a) **H1**, (b) **H2**, (c) **H3**, (d) **H4**, and (e) **H6.**



SI4. ESR spectra of 5,15-bis(3,5-di-*t*-butylphenyl)porphyrin zinc complex cation radical formed by electrochemical oxidation.

SI 5. Table ; Absorption spectral data of *meso*-*meso* linked porphyrin arrays in THF

compound	absorption peaks (log *e*)$^{(a)}$ / nm ($M^{-1}cm^{-1}$)
Z1	413.0 (5.81), 543.0 (4.34)
Z2	418 (5.43), 452 (5.40), 560 (4.78)
Z3	414 (5.57), 476 (5.51), 571 (4.95)
Z4	414 (5.64), 488 (5.61), 576 (5.15)
Z5	415 (5.71), 494 (5.69), 580 (5.31)
Z6	414 (5.77), 498 (5.77), 582 (5.45)
Z7	414(5.83), 500 (5.82), 583 (5.54)
Z8	414 (5.87), 502 (5.87), 585 (5.63)
Z10	414 (5.95), 505 (5.97), 586 (5.75)
Z12	414 (6.02), 507 (6.05), 587 (5.86)
Z16	414 (6.11), 508 (6.14), 587 (5.98)
Z32	414 (6.41), 509 (6.49), 588 (6.34)
Z64	414 (6.70), 510 (6.80), 589 (6.66)
Z128	414 (7.00), 511 (7.10), 589 (6.96)
Z256	414 (7.30), 511 (7.40), 589 (7.26)
Z384	414 (7.48), 511 (7.58), 589 (7.44)
Z512	414 (7.60), 511 (7.70), 589 (7.56)



Model λ (nm)	256mer (ns, %)	512mer (ns, %)
600	**1.04(25%) + 0.138(75%)**	**0.965(16%) + 0.124(84%)**
650	**1.06(27%) + 0.144(73%)**	**0.902(14%) + 0.114(86%)**
705	**1.07(31%) + 0.148(69%)**	**0.940(20%) + 0.114(80%)**
$\tau_{\mathbf{ave}}$	**0.40**	**0.26**

SI6. Fluorescence decay profiles for **Z256** and **Z512**.

model	ΔE (cm^{-1})[a]	Φ_F[b]	τ_{avg}(ns)[c]	τ_1(ns,%)[d]	τ_2(ns,%)[e]	r[f]
Z1	-	0.022	2.64			0.008
Z2	2060	0.034	1.83			0.03
Z3	3176	0.044	1.72			0.05
Z4	3692	0.055	1.65			0.16
Z6	4104	0.066	1.59			0.21
Z8	4283	0.074	1.55			0.29
Z12	4434	0.080	1.52			0.31
Z16	4499	0.088	1.50			0.31
Z24	4557	0.083	1.43	1.49(95.4)	0.14(4.6)	0.27
Z32	4569	0.062	1.40	1.48(92.8)	0.33(7.2)	0.24
Z48	4595	0.058	0.93	1.47(61.1)	0.08(38.9)	0.20
Z64	4595	0.033	0.51	1.47(31.2)	0.08(68.8)	0.17
Z96	4615	0.031	0.50	1.45(27.7)	0.14(72.3)	0.13
Z128	4615	0.012	0.49	1.42(21.8)	0.22(78.2)	0.12
Z256	4615	0.012	0.40	1.05 (28.8)	0.14(71.2)	0.12
Z512	4615	0.006	0.26	0.92 (17.7)	0.12(82.3)	0.12

SI7. Summary of fluorescence data.