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$_2$SO$_4$, 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) δ 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$_2$Cl$_2$ (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$_2$Cl$_2$ (100 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and evaporated. Unreacted octylbromide was distilled off under reduced pressure. The product was separated by silica gel chromatography (CH$_2$Cl$_2$). Yield 22.87 g (58 mmol, 83%); $^1$H-NMR (CDCl$_3$) δ 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$_3$) δ 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$_2$Cl$_2$ (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$_3$) δ 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-pyrrol)methane (6) was prepared by the method reported by Lee et al.$^{2}$ 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 CH₂Cl₂ (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 CH₂Cl₂/hexane. The product was recrystallized from CH₂Cl₂-EtOH. Yield; 1.47 g, 44%. This reaction scheme was repeated for 10 times, resulting in the making of 15 g porphyrin.

1H NMR (CDCl₃) δ 10.30 (s, 2H, meso), 9.38 (d, J = 5 Hz, 4H, β), 9.19 (d, J = 5 Hz, 4H, β), 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 C₆₄H₈₆N₄O₄

Zn m/z 974. 6; Anal. Calcd. for C₆₄H₈₆N₄O₄: C, 78.81; H, 8.89; N, 5.74. Found: C, 78.62; H, 8.89; N, 5.73; UV-vis (THF) λmax 407, 501, 537, 574, and 630 nm; Fluorescence (THF, λex = 413 nm) λem 631 and 696 nm.

Z1. 1H NMR (CDCl₃) δ 10.31 (s, 2H, meso), 9.43 (d, J = 5 Hz, 4H, β), 9.26 (d, J = 5 Hz, 4H, β), 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 C₆₄H₈₄N₄O₄Zn m/z 1036.6; Anal. Calcd. for C₆₄H₈₄N₄O₄Zn: C, 74.00; H, 8.15; N, 5.39. Found: C, 73.75; H, 8.21; N, 5.16; UV-vis (THF) λmax (ε) [nm (cm⁻¹M⁻¹)] 413 (645000) and 543 (22000); Fluorescence (THF, λex = 413 nm) λem 584 and 634 nm.

General Procedure for Meso-meso Coupling Reaction of ZnII 5,15-bis(3,5-dioctyloxyphenyl)porphyrin arrays Zn. The reaction vessel containing a
solution of Zn(II) 5,15-bis(3,5-dioctyloxyphenyl)porphyrin array in dry CHCl₃ was covered with foil. A stock solution of AgPF₆ in dry CH₃CN (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 Na₂SO₄. 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 NaHCO₃ solution, and dried over anhydrous Na₂SO₄. 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 CHCl₃ (160 mL). A stock solution of AgPF₆ (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 were separated by a preparative size exclusion column (SEC). Fractions of 2-mer and 3-mer were separated, and the solvent was removed by a rotary evaporator. Recrystallization from CHCl₃/EtOH gave red-blown solids of Z₂ (138 mg, 24%). 

1H NMR (CDCl₃) δ 10.38 (s, 2H, meso), 9.49 (d, J = 5 Hz, 4H, β), 9.28 (d, J = 5 Hz, 4H, β), 8.82 (d, J = 5 Hz, 4H, β), 8.10 (d, J = 5 Hz, 4H, β), 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 C₁₂₈H₁₆₆N₈O₈Zn₂ m/z 2075.1; Anal. Calcd. for C₁₂₈H₁₆₆N₈O₈Zn₂(Η₂O): C, 73.43; H, 8.09; N, 5.35; Found: C, 73.23; H, 8.13; N, 5.34; UV-vis (THF) λₘₐₓ (ε) [nm (cm⁻¹M⁻¹)] 418 (270000), 452 (250000), and 560 (60000); Fluorescence (THF, λₑₓ = 413 nm) λₒₘ 657 nm.

Z₃. 1H NMR (CDCl₃) δ 10.40 (s, 2H, meso), 9.50 (d, J = 5 Hz, 4H, β), 9.29 (d, J = 5 Hz, 4H, β), 8.89 (d, J = 5 Hz, 4H, β), 8.80 (d, J = 5 Hz, 4H, β) 8.24 (d, J = 5 Hz, 4H, β) 8.12 (d,
J = 5 Hz, 4H, J), 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) λ_{max} (nm) 414, 476, and 571; Fluorescence (THF, λ_{ex} = 413 nm) λ_{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}) δ 10.40 (s, 2H, meso), 9.51 (d, J = 5 Hz, 4H, J), 9.30 (d, J = 5 Hz, 4H, J), 8.90 (d, J = 5 Hz, 4H, J), 8.88 (d, J = 5 Hz, 4H, J), 8.82 (d, J = 5 Hz, 4H, J), 8.25 (d, J = 5 Hz, 4H, J), 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) λ_{max} (nm) 414, 494 and 580; Fluorescence (THF, λ_{ex} = 413 nm) λ_{em} 639 and 666 nm.

Z5. ^{1}H NMR (CDCl_{3}) δ 10.41 (s, 2H, meso), 9.52 (d, J = 5 Hz, 4H, J), 9.31 (d, J = 5 Hz, 4H, J), 8.95-8.91 (m, 12H, J), 8.85 (d, J = 5 Hz, 4H, J), 8.35-8.32 (m, 8H, J), 8.28 (d, J = 5 Hz, 4H, J), 8.17 (d, J = 5 Hz, 4H, J), 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) λ_{max} (nm) 414, 494 and 580; Fluorescence (THF, λ_{ex} = 413 nm) λ_{em} 640
1H NMR (CDCl₃) δ 10.42 (s, 2H, meso), 9.52 (d, J = 5 Hz, 4H, β), 9.31 (d, J = 5 Hz, 4H, β), 8.95-8.91 (m, 16H, β), 8.85 (d, J = 5 Hz, 4H, β), 8.35-8.32 (m, 12H, β), 8.28 (d, J = 5 Hz, 4H, β), 8.17 (d, J = 5 Hz, 4H, β), 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 C₃₈₄H₄₉₄N₂₄O₂₄Zn₆ m/z 6221; UV-vis (THF) λ_max (nm) 414, 498 and 582; Fluorescence (THF, λ_ex = 413 nm) λ_em 640 nm.

Z7. 1H NMR (CDCl₃) δ 10.41 (s, 2H, meso), 9.53 (d, J = 5 Hz, 4H, β), 9.31 (d, J = 5 Hz, 4H, β), 8.95-8.91 (m, 20H, β), 8.85 (d, J = 5 Hz, 4H, β), 8.35-8.32 (m, 16H, β), 8.28 (d, J = 5 Hz, 4H, β), 8.17 (d, J = 5 Hz, 4H, β), 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 C₄₄₈H₅₇₆N₂₈O₂₈Zn₇ m/z 7259; UV-vis (THF) λ_max (nm) 414, 500 and 583; Fluorescence (THF, λ_ex = 413 nm) λ_em 642 nm.

Z8. A stock solution of AgPF₆ in CH₃CN (0.047 mL, 0.006 mmol) was added to a solution of Z4 (31 mg, 0.0075 mmol) in CHCl₃ (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 CHCl₃/MeOH gave a pure Z8 (7 mg, 22%). 1H NMR (CDCl₃) δ 10.42 (s, 2H, meso), 9.53 (d, J = 5 Hz, 4H, β), 9.31 (d, J = 5 Hz, 4H, β), 8.95-8.91 (m, 24H, β), 8.85 (d, J = 5 Hz, 4H, β), 8.35-8.32 (m, 20H, β), 8.28 (d, J = 5 Hz, 4H, β), 8.17 (d, J = 5 Hz, 4H, β), 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 C₅₁₂H₆₈₈N₃₂O₃₂Zn₈ m/z 8296; UV-vis (THF) λ_max (e) [nm(cm⁻¹M⁻¹)] 414 (745000), 502 (735000) and 585 (430000); Fluorescence (THF, λ_ex = 413 nm)
\( \lambda_{em} \) 640 nm.

**Z10.** \(^1H\) NMR (CDCl\(_3\)) \( \delta \) 10.41 (s, 2H, meso), 9.53 (br, 4H, \( \beta \)), 9.31 (br, 4H, \( \beta \)), 8.96-8.92 (m, 32H, \( \beta \)), 8.85 (d, \( J = 5 \) Hz, 4H, \( \beta \)), 8.36-8.33 (m, 28H, \( \beta \)), 8.29 (d, \( J = 5 \) Hz, 4H, \( \beta \)), 8.17 (d, \( J = 5 \) Hz, 4H, \( \beta \)), 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\(_4\)O\(_{40}\)Zn\(_{10}\) \( m/z \) 10369; UV (THF) \( \lambda_{max} \) (nm) 414, 505 and 586; Fluorescence (THF, \( \lambda_{ex} \) = 413 nm) \( \lambda_{em} \) 642 nm.

**Z12.** \(^1H\) NMR (CDCl\(_3\)) \( \delta \) 10.41 (s, 2H, meso), 9.52 (br, 4H, \( \beta \)), 9.31 (br, 4H, \( \beta \)), 8.96-8.92 (m, 40H, \( \beta \)), 8.85 (d, \( J = 5 \) Hz, 4H, \( \beta \)), 8.36-8.33 (m, 36H, \( \beta \)), 8.28 (d, \( J = 5 \) Hz, 4H, \( \beta \)), 8.17 (d, \( J = 5 \) Hz, 4H, \( \beta \)), 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), 1.84-1.78 (m, 96H, octyloxy), 1.44-1.20 (m, 640H, 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\(_3\)) \( \lambda_{max} \) (nm) 414, 507 and 587; Fluorescence (CHCl\(_3\), \( \lambda_{ex} \) = 413 nm) \( \lambda_{em} \) 642 nm.

**Z16.** A stock solution of AgPF\(_6\) in CH\(_3\)CN (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%). \(^1H\) NMR (CDCl\(_3\)) \( \delta \) 10.42 (s, 2H, meso), 9.53 (br, 4H, \( \beta \)), 9.31 (br, 4H, \( \beta \)), 8.97-8.85 (m, 60H, \( \beta \)), 8.37-8.17 (m, 60H, \( \beta \)), 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) \( \lambda_{max} \) (\( \epsilon \) [nm (cm\(^2\)M\(^{-1}\)]) \( \lambda_{max} \) 414 (1 300 000), 508 (1 380 000) and 587 (950 000); Fluorescence (THF, \( \lambda_{ex} \) = 413 nm) \( \lambda_{em} \) 642 nm.

**Z20.** \(^1H\) NMR (CDCl\(_3\)) \( \delta \) 10.41 (s, 2H, meso), 9.52 (br, 4H, \( \beta \)), 9.31 (br, 4H, \( \beta \)), 8.96-8.84 (m, 76H, \( \beta \)), 8.36-8.16 (m, 76H, \( \beta \)), 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$_3$) $\lambda_{\text{max}}$ (nm) 414, 506 and 585; Fluorescence (CHCl$_3$, $\lambda_{\text{ex}}$ = 413 nm) $\lambda_{\text{em}}$ 641 nm.

**Z24.** $^1$H NMR (CDCl$_3$) $\delta$ 10.41 (s, 2H, meso), 9.52 (br, 4H, $\beta$), 9.30 (br, 4H, $\beta$), 8.97-8.84 (m, 92H, $\beta$), 8.37-8.16 (m, 92H, $\beta$), 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$_3$) $\lambda_{\text{max}}$ (nm) 414, 506 and 585; Fluorescence (CHCl$_3$, $\lambda_{\text{ex}}$ = 413 nm) $\lambda_{\text{em}}$ 641 nm.

**Z32.** AgPF$_6$ (0.014 mL of 0.138 M stock solution in dry CH$_3$CN, 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%). $^1$H NMR (CDCl$_3$) $\delta$ 10.42 (s, 2H, meso), 9.52 (br, 4H, $\beta$), 9.31 (br, 4H, $\beta$), 8.97-8.85 (m, 124H, $\beta$), 8.38-8.17 (m, 124H, $\beta$), 7.53-7.46 (m, 128H, Ar), 6.86-6.73 (m, 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) $\lambda_{\text{max}}$ ($\epsilon$) [nm (cm$^{-1}$M$^{-1}$)] 414 (2690000), 509 (3070000) and 588 (220000); Fluorescence (THF, $\lambda_{\text{ex}}$ = 413 nm) $\lambda_{\text{em}}$ 642 nm.

**Z40.** $^1$H NMR (CDCl$_3$) $\delta$ 10.42 (s, 2H, meso), 9.52 (br, 4H, $\beta$), 9.31 (br, 4H, $\beta$), 8.97-8.85 (m, 156H, $\beta$), 8.37-8.16 (m, 156H, $\beta$), 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$_3$) $\lambda_{\text{max}}$ (nm) 414, 507 and 586; Fluorescence (CHCl$_3$, $\lambda_{\text{ex}}$ =413 nm) $\lambda_{\text{em}}$ 641 nm.

**Z48.** $^1$H NMR (CDCl$_3$) $\delta$ 10.42 (s, 2H, meso), 9.52 (br, 4H, $\beta$), 9.31 (br, 4H, $\beta$), 8.97 (m,
188 H, β), 8.37-8.16 (m, 188 H, β), 7.52-7.46 (m, 192 H, Ar), 6.86-6.73 (m, 96 H, Ar), 4.07 (m, 384 H, octyloxy), 1.80 (m, 384 H, octyloxy), 1.45-1.22 (m, 1920 H, octyloxy), and 0.87-0.75 (m, 576 H, octyloxy); MALDI-TOF-MS m/z 49447, calcd for C_{3072}H_{3938}N_{192}O_{192}Zn_{48} m/z 49764; UV-vis (CHCl₃) λ_{max} (nm) 413, 508 and 586; Fluorescence (CHCl₃, λ_{ex} = 413 nm) λ_{em} 640 nm.

**Z64.** AgPF₆ (0.004 mL of 0.138 M stock solution in dry CH₃CN, 0.0005 mmol) was added to a solution of Z32 (18 mg, 0.0005 mmol) in CHCl₃ (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 CHCl₃/MeOH gave a pure Z64 (3.7 mg, 22%). ¹H NMR (CDCl₃) δ 10.42 (s, 2 H, meso), 9.52 (br, 4 H, β), 9.31 (br, 4 H, β), 8.97 (m, 252 H, β), 8.38-8.17 (m, 252 H, β), 7.53 (m, 256 H, Ar), 6.86-6.74 (br, 128 H, Ar), 4.07 (m, 512 H, octyloxy), 1.80 (m, 512 H, octyloxy), 1.45-1.22 (m, 2560 H, octyloxy), and 0.85-0.75 (m, 768 H, 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) λ_{max} (nm) 414, 510 and 589; Fluorescence (THF, λ_{ex} = 413 nm) λ_{em} 642 nm.

**Z96.** ¹H NMR (CDCl₃) δ 10.42 (s, 2 H, meso), 9.52 (br, 4 H, β), 9.31 (br, 4 H, β), 8.97 (m, 380 H, β), 8.37-8.16 (m, 380 H, β), 7.52 (m, 384 H, Ar), 6.79 (br, 192 H, Ar), 4.07 (m, 768 H, octyloxy), 1.80 (m, 768 H, octyloxy), 1.45-1.22 (m, 3840 H, octyloxy), and 0.85-0.75 (m, 1152 H, octyloxy); MALDI-TOF-MS m/z 99050, calcd for C_{6144}H_{7874}N_{384}O_{384}Zn_{96} m/z 99503; UV-vis (CHCl₃) λ_{max} (nm) 413, 508 and 586; Fluorescence (CHCl₃, λ_{ex} = 413 nm) λ_{em} 641 nm.

**Z128.** ¹H NMR (CDCl₃) δ 10.40 (s, 2 H, meso), 9.52 (br, 4 H, β), 9.30 (br, 4 H, β), 8.96 (m, 508 H, β), 8.36 (m, 508 H, β), 7.52 (m, 512 H, Ar), 6.79 (br, 256 H, Ar), 4.06 (m, 1024 H, octyloxy), 1.79 (m, 1024 H, octyloxy), 1.44-1.22 (m, 5120 H, octyloxy), and 0.81-0.78 (m, 1536 H, octyloxy); MALDI-TOF-MS m/z 130295, calcd for C_{8192}H_{10496}N_{512}O_{512}Zn_{128} m/z 132702; UV-vis (THF) λ_{max} (nm) 414, 511 and 589; Fluorescence (THF, λ_{ex} = 413 nm) λ_{em} 642 nm.

**Z256.** ¹H NMR (CDCl₃) δ 10.42 (s, 2 H, meso), 9.53 (br, 4 H, β), 9.31 (br, 4 H, β), 8.97 (m, 1020 H, β), 8.37 (m, 1020 H, β), 7.52 (m, 1024 H, Ar), 6.79 (br, 512 H, Ar), 4.06 (m, 2048 H, octyloxy), 1.79 (m, 2048 H, octyloxy), 1.44-1.22 (m, 10240 H, octyloxy), and 0.81-0.78 (m,
3072H, octyloxy); UV-vis (THF) $\lambda_{\text{max}}$ (nm) 414, 511 and 589; Fluorescence (THF, $\lambda_{\text{ex}} = 413$ nm) $\lambda_{\text{em}}$ 642 nm.

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

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

**H2.** Z2 was dissolved in a mixture of CH$_2$Cl$_2$ and 3 N HCl. The resulting solution was stirred for 1 h at room temperature, poured into water, and extracted with CH$_2$Cl$_2$. The organic layer was separated off, and the combined extracts were washed with water, saturated aqueous NaHCO$_3$, water, and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated and the product was recrystallized from CH$_2$Cl$_2$/MeOH to give **H2.**

$^1$H NMR (CDCl$_3$) $\delta$ 10.34 (s, 2H, meso), 9.42 (d, $J = 5$ Hz, 4H, $\beta$), 9.18 (d, $J = 5$ Hz, 4H, $\beta$), 8.72 (d, $J = 5$ Hz, 4H, $\beta$), 8.03 (d, $J = 5$ Hz, 4H, $\beta$), 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$_8$O$_8$ m/z 1947.3; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ (nm) 413, 445, 519, 588, and 644; Fluorescence (CHCl$_3$, $\lambda_{\text{ex}} = 413$ nm) $\lambda_{\text{em}}$ 650 and 711 nm.

**H3.** $^1$H NMR (CDCl$_3$) $\delta$ 10.36 (s, 2H, meso), 9.44 (d, $J = 5$ Hz, 4H, $\beta$), 9.21 (d, $J = 5$ Hz, 4H, $\beta$), 8.81 (d, $J = 5$ Hz, 4H, $\beta$), 8.72 (d, $J = 5$ Hz, 4H, $\beta$), 8.20 (d, $J = 5$ Hz, 4H, $\beta$) 8.09 (d, $J = 5$ Hz, 4H, $\beta$), 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$_{250}$N$_{12}$O$_{12}$ m/z 2922; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ (nm) 410, 469, 528, and 596; Fluorescence (CHCl$_3$, $\lambda_{\text{ex}} = 413$ nm) $\lambda_{\text{em}}$ 661 and 724 nm.
**H4.** $^1$H NMR (CDCl$_3$) $\delta$ 10.37 (s, 2H, meso), 9.44 (d, $J = 5$ Hz, 4H, $\beta$), 9.21 (d, $J = 5$ Hz, 4H, $\beta$), 8.82-8.81 (m, 8H, $\beta$), 8.75 (d, $J = 5$ Hz, 4H, $\beta$), 8.26 (d, $J = 5$ Hz, 4H, $\beta$), 8.22 (d, $J = 5$ Hz, 4H, $\beta$), 8.11 (d, $J = 5$ Hz, 4H, $\beta$), 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$_3$) $\lambda_{max}$ (nm) 411, 480, 535, and 596; Fluorescence (CHCl$_3$, $\lambda_{ex} = 413$ nm) $\lambda_{em}$ 665 and 726 nm.

**H6.** $^1$H NMR (CDCl$_3$) $\delta$ 10.37 (s, 2H, meso), 9.45 (d, $J = 5$ Hz, 4H, $\beta$), 9.22 (d, $J = 5$ Hz, 4H, $\beta$), 8.85-8.83 (m, 16H, $\beta$), 8.76 (d, $J = 5$ Hz, 4H, $\beta$), 8.29-8.28 (m, 12H, $\beta$), 8.23 (d, $J = 5$ Hz, 4H, $\beta$), 8.12 (d, $J = 5$ Hz, 4H, $\beta$), 7.45 (m, 16H, Ar), 7.41 (d, $J = 3$ Hz, 8H, Ar), 6.85 (t, $J = 7$ 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 -2.39 (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$_3$) $\lambda_{max}$ (nm) 412, 489, 541, 599, and 656; Fluorescence (CHCl$_3$, $\lambda_{ex} = 413$ nm) $\lambda_{em}$ 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$_2$Cl$_2$ (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$_2$Cl$_2$. The product was recrystallized from CH$_2$Cl$_2$-n-hexane. Yield; 705 mg,
1H NMR (CDCl$_3$) δ 10.32 (s, 2H, meso), 9.40 (d, J = 5 Hz, 4H, β), 9.09 (d, J = 5 Hz, 4H, β), 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.

**Zp3.** A round-bottomed flask was charged with Zp1 (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 were separated by a preparative size exclusion column. Fractions of 2-mer and 3-mer were separated, and the solvent was removed by a rotary evaporator. Recrystallization from CHCl$_3$/MeOH gave red-blown solids.

**Zp2:** 1H NMR (CDCl$_3$) δ 10.35 (s, 2H, meso), 9.47 (d, J = 5 Hz, 4H, β), 9.12 (d, J = 5 Hz, 4H, β), 8.64 (d, J = 5 Hz, 4H, β), 8.23 (m, 8H, Ar), 8.02 (d, J = 5 Hz, 4H, b), 7.67 (m, 12H, Ar).

**Zp3:** 1H NMR (CDCl$_3$) δ 10.37 (s, 2H, meso), 9.49 (d, J = 5 Hz, 4H, β), 9.15 (d, J = 5 Hz, 4H, β), 8.72 (d, J = 5 Hz, 4H, β), 8.63 (d, J = 5 Hz, 4H, β), 8.28 (m, 8H, Ar), 8.18 (m, 8H, Ar + β), 8.07 (d, J = 5 Hz, 4H, β), 7.71 (m, 12H, Ar), 7.55 (m, 6H, Ar).

**ZnBr$_2$.** 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$_2$SO$_4$ 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.) 1H NMR (CDCl$_3$) δ 9.81 (d, J = 5 Hz, 4H, β), 9.13 (d, J = 5 Hz, 4H, β), 8.71 (d, J = 5 Hz, 4H, β), 8.01 (d, J = 5 Hz, 4H, β), 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$_{160}$N$_8$O$_8$Zn$_2$Br$_2$ m/z 2233.0.

**Z3Br$_2$.** (95%). 1H NMR (CDCl$_3$) δ 9.87 (d, J = 5 Hz, 4H, β), 9.19 (d, J = 5 Hz, 4H, β), 8.81 (d, J = 5 Hz, 4H, β), 8.79 (d, J = 5 Hz, 4H, β) 8.16 (d, J = 5 Hz, 4H, β) 8.14 (d, J = 5 Hz,
1H, β), 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, 12H, octyloxy) and 0.72 (t, j = 7 Hz, 12H, octyloxy); MALDI-TOF-MS m/z 3267, calcd for C\textsubscript{192}H\textsubscript{246}N\textsubscript{12}O\textsubscript{12}Zn\textsubscript{3}Br\textsubscript{2} m/z 3270.

Z4Br\textsubscript{2}. (87%). 1H NMR (CDCl\textsubscript{3}) δ 9.88 (d, j = 5 Hz, 4H, β), 9.20 (d, j = 5 Hz, 4H, β), 8.88 (d, j = 5 Hz, 4H, β), 8.84 (d, j = 5 Hz, 4H, β), 8.81 (d, j = 5 Hz, 4H, β), 8.27 (d, j = 5 Hz, 4H, β), 8.19 (d, j = 5 Hz, 4H, β), 8.16 (d, j = 5 Hz, 4H, β), 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\textsubscript{256}H\textsubscript{328}N\textsubscript{16}O\textsubscript{16}Zn\textsubscript{4}Br\textsubscript{2} m/z 4307.

Z6Br\textsubscript{2}. (78%) 1H NMR (CDCl\textsubscript{3}) δ 9.88 (d, j = 5 Hz, 4H, β), 9.20 (d, j = 5 Hz, 4H, β), 8.94-8.91 (m, 12H, β), 8.86 (d, j = 5 Hz, 4H, β), 8.82 (d, j = 5 Hz, 4H, β), 8.34-8.31 (m, 12H, β), 8.21 (d, j = 5 Hz, 4H, β), 8.18 (d, j = 5 Hz, 4H, β), 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\textsubscript{384}H\textsubscript{492}N\textsubscript{24}O\textsubscript{24}Zn\textsubscript{6}Br\textsubscript{2} m/z 6380.

Z8Br\textsubscript{2}. (83%) 1H NMR (CDCl\textsubscript{3}) δ 9.89 (d, j = 5 Hz, 4H, β), 9.21 (d, j = 5 Hz, 4H, β), 8.95-8.91 (m, 20H, β), 8.86 (d, j = 5 Hz, 4H, β), 8.82 (d, j = 5 Hz, 4H, β), 8.35-8.31 (m, 20H, β), 8.21 (d, j = 5 Hz, 4H, β), 8.18 (d, j = 5 Hz, 4H, β), 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\textsubscript{2}. (92%) 1H NMR (CDCl\textsubscript{3}) δ 9.86 (d, j = 5 Hz, 4H, β), 9.18 (d, j = 5 Hz, 4H, β),
8.90-8.86 (m, 36H, β), 8.80 (d, J = 5 Hz, 4H, β), 8.77 (d, J = 5 Hz, 4H, β), 8.29-8.24 (m, 36H, β),
8.13 (d, J = 5 Hz, 4H, β), 8.07 (d, J = 5 Hz, 4H, β), 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).

\[ \text{Z16Br}_2 \] (84%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.88 (d, J = 5 Hz, 4H, β), 9.02 (d, J = 5 Hz, 4H, β),
8.96 (m, 52H, β), 8.86 (d, J = 5 Hz, 4H, β), 8.82 (d, J = 5 Hz, 4H, β), 8.36 (m, 52H, β), 8.21 (d, J
= 5 Hz, 4H, β), 8.17 (d, J = 5 Hz, 4H, β), 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), 1.77 (m, 192H, octyloxy), 1.44-1.20 (m, 640H, octyloxy), and 0.85-0.75 (m, 192H, octyloxy).

\[ \text{Z24Br}_2 \] (89%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.87 (d, J = 5 Hz, 4H, β), 9.19 (d, J = 5 Hz, 4H, β),
8.95-8.80 (m, 92H, β), 8.35-8.15 (m, 92H, β), 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).

\[ \text{Z48Br}_2 \] (91%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.88 (d, J = 5 Hz, 4H, β), 9.20 (d, J = 5 Hz, 4H, β),
8.95-8.80 (m, 188H, β), 8.35-8.15 (m, 188H, β), 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).

\[ \text{Z64Br}_2 \] (87%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.87 (br, 4H, β), 9.19 (br, 4H, β), 8.93-8.80 (m, 252H, β),
8.32-8.11 (m, 252H, β), 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\(_2\)Cl\(_2\) (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\(_2\)Cl\(_2\)/hexane = 1/4). The product was
given as white crystal (1.48 g, 83%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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) δ 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.

ZnS_2. Bromo porphyrin ZnBr_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) δ 9.14 (d, J = 5 Hz, 4H, β), 8.93-8.91 (m, 16H, β), 8.86-8.85 (m, 4H, β), 8.34-8.31 (m, 12H, β), 8.24 (d, J = 5 Hz, 4H, β), 8.18 (d, J = 5 Hz, 4H, β), 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_{398}H_{496}N_{24}O_{24}Zn_{6}Br_{2} m/z 6380.

Z12S_2. 1H NMR (CDCl_3) δ 9.06 (d, J = 5 Hz, 4H, β), 8.89-8.79 (m, 48H, β), 8.85 (d, J = 5 Hz, 4H, β), 8.29-8.25 (m, 38H, β), 8.17 (d, J = 5 Hz, 4H, β), 8.11 (d, J = 5 Hz, 4H, β), 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).

\textbf{Z24S}_2. (79\%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 9.11 (d, J = 5 Hz, 4H, \(\beta\)), 8.95-8.84 (m, 96H, \(\beta\)), 8.35 (m, 88H, \(\beta\)), 8.22 (d, J = 5 Hz, 4H, \(\beta\)), 8.17 (d, J = 5 Hz, 4H, \(\beta\)), 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).

\textbf{Z48S}_2. (79\%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 9.11 (br, 4H, \(\beta\)), 8.95-8.84 (m, 192H, \(\beta\)), 8.35 (m, 184H, \(\beta\)), 8.24 (d, J = 5 Hz, 4H, \(\beta\)), 8.19 (d, J = 5 Hz, 4H, \(\beta\)), 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).

\textbf{Z64S}_2. (91\%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 9.15 (br, 4H, \(\beta\)), 8.97-8.87 (m, 256H, \(\beta\)), 8.37-8.20 (m, 252H, \(\beta\)), 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. Blue line shows the UV absorbance detected at 413 nm.
**S1 2: ROESY spectrum of Z4 in CDCl3 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

<table>
<thead>
<tr>
<th>compound</th>
<th>absorption peaks (log ε)(^{(a)})</th>
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<tr>
<td></td>
<td>/ nm (M(^{-1})cm(^{-1}))</td>
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<tr>
<td>Z1</td>
<td>413.0 (5.81), 543.0 (4.34)</td>
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<tr>
<td>Z2</td>
<td>418 (5.43), 452 (5.40), 560 (4.78)</td>
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<td>Z3</td>
<td>414 (5.57), 476 (5.51), 571 (4.95)</td>
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<td>Z4</td>
<td>414 (5.64), 488 (5.61), 576 (5.15)</td>
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<tr>
<td>Z5</td>
<td>415 (5.71), 494 (5.69), 580 (5.31)</td>
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<tr>
<td>Z6</td>
<td>414 (5.77), 498 (5.77), 582 (5.45)</td>
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<td>Z7</td>
<td>414 (5.83), 500 (5.82), 583 (5.54)</td>
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<tr>
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<td>414 (5.87), 502 (5.87), 585 (5.63)</td>
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<td>414 (5.95), 505 (5.97), 586 (5.75)</td>
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<td>Z12</td>
<td>414 (6.02), 507 (6.05), 587 (5.86)</td>
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<td>Z16</td>
<td>414 (6.11), 508 (6.14), 587 (5.98)</td>
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<td>414 (6.70), 510 (6.80), 589 (6.66)</td>
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<td>Z128</td>
<td>414 (7.00), 511 (7.10), 589 (6.96)</td>
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<tr>
<td>Z256</td>
<td>414 (7.30), 511 (7.40), 589 (7.26)</td>
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<td>Z384</td>
<td>414 (7.48), 511 (7.58), 589 (7.44)</td>
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<tr>
<td>Z512</td>
<td>414 (7.60), 511 (7.70), 589 (7.56)</td>
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Fluorescence decay profiles for Z256 and Z512.

<table>
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<tr>
<th>Model</th>
<th>256mer (ns, %)</th>
<th>512mer (ns, %)</th>
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<tbody>
<tr>
<td>λ(nm)</td>
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<tr>
<td>600</td>
<td>1.04(25%) + 0.138(75%)</td>
<td>0.965(16%) + 0.124(84%)</td>
</tr>
<tr>
<td>650</td>
<td>1.06(27%) + 0.144(73%)</td>
<td>0.902(14%) + 0.114(86%)</td>
</tr>
<tr>
<td>705</td>
<td>1.07(31%) + 0.148(69%)</td>
<td>0.940(20%) + 0.114(80%)</td>
</tr>
<tr>
<td>(\tau) ave</td>
<td>0.40</td>
<td>0.26</td>
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</table>

SI6. Fluorescence decay profiles for Z256 and Z512.
### Summary of fluorescence data.

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<thead>
<tr>
<th>Model</th>
<th>$\Delta E \text{ (cm}^{-1}\text{)}$</th>
<th>$\Phi$</th>
<th>$\tau_{\text{avg}} \text{ (ns)}$</th>
<th>$\tau_{1} \text{ (ns,%)}$</th>
<th>$\tau_{2} \text{ (ns,%)}$</th>
<th>$r$</th>
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<tbody>
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<td>Z1</td>
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<td>2.64</td>
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<tr>
<td>Z2</td>
<td>2060</td>
<td>0.034</td>
<td>1.83</td>
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<td>0.03</td>
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<tr>
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<td>3176</td>
<td>0.044</td>
<td>1.72</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
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<tr>
<td>Z4</td>
<td>3692</td>
<td>0.055</td>
<td>1.65</td>
<td>-</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>Z6</td>
<td>4104</td>
<td>0.066</td>
<td>1.59</td>
<td>-</td>
<td>-</td>
<td>0.21</td>
</tr>
<tr>
<td>Z8</td>
<td>4283</td>
<td>0.074</td>
<td>1.55</td>
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<td>-</td>
<td>0.29</td>
</tr>
<tr>
<td>Z12</td>
<td>4434</td>
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<td>1.52</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
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<tr>
<td>Z16</td>
<td>4499</td>
<td>0.088</td>
<td>1.50</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
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<tr>
<td>Z24</td>
<td>4557</td>
<td>0.083</td>
<td>1.43</td>
<td>1.49 (95.4)</td>
<td>0.14 (4.6)</td>
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<tr>
<td>Z32</td>
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<td>0.062</td>
<td>1.40</td>
<td>1.48 (92.8)</td>
<td>0.33 (7.2)</td>
<td>0.24</td>
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<tr>
<td>Z48</td>
<td>4595</td>
<td>0.058</td>
<td>0.93</td>
<td>1.47 (61.1)</td>
<td>0.08 (38.9)</td>
<td>0.20</td>
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<tr>
<td>Z64</td>
<td>4595</td>
<td>0.033</td>
<td>0.51</td>
<td>1.47 (31.2)</td>
<td>0.08 (68.8)</td>
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<tr>
<td>Z96</td>
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<td>0.50</td>
<td>1.45 (27.7)</td>
<td>0.14 (72.3)</td>
<td>0.13</td>
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<tr>
<td>Z128</td>
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<td>0.012</td>
<td>0.49</td>
<td>1.42 (21.8)</td>
<td>0.22 (78.2)</td>
<td>0.12</td>
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<tr>
<td>Z256</td>
<td>4615</td>
<td>0.012</td>
<td>0.40</td>
<td>1.05 (28.8)</td>
<td>0.14 (71.2)</td>
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<tr>
<td>Z512</td>
<td>4615</td>
<td>0.006</td>
<td>0.26</td>
<td>0.92 (17.7)</td>
<td>0.12 (82.3)</td>
<td>0.12</td>
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