

Hollow porphyrin prisms: modular formation of permanent, torsionally rigid, nanostructures via templated olefin metathesis

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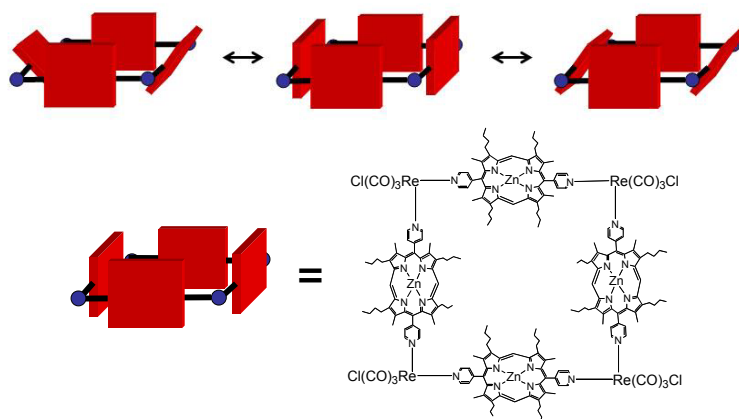


Figure S1. A schematic illustration of the fluxional behavior in $M_4\text{Por}_4$ “molecular squares” complex. See also discussion in L. Miljacic; L. Sarkisov; D. E. Ellis and R. Q. Snurr, *J. Chem. Phys.* 2004, **121**, 7228-7236.

General Information. All chemicals were obtained from commercial and used without further purification. (4-Allyloxyphenyl)dipyromethane and (4-(1-pentenloxy)phenyl)dipyromethane were prepared according to literature procedures.¹ All reactions and manipulations were carried out under dry N_2 gas using standard Schlenk techniques, unless otherwise noted.

UV-Vis spectra were obtained in CH_2Cl_2 on a Varian Cary 500 spectrophotometer unless otherwise noted. Fluorescence emission spectra were recorded on an ISA instruments Fluorolog fluorescence spectrometer. Nuclear magnetic resonance (NMR) spectra for all the synthesized compounds were recorded on either a Varian INOVA 500 NMR spectrometer (499.773 MHz for ^1H NMR, 125.669 MHz for ^{13}C NMR). ^1H NMR data are reported as follows: Chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, and m = multiplet)).

High-resolution fast-atom-bombardment mass spectrometric (HRFABMS) data were obtained from the Mass Spectrometry Laboratory at University of Illinois at Urbana Champaign. MALDI-TOF MS was conducted on an Applied Biosystems PE Voyager DE Pro MALDI-TOF mass spectrometer.

Analytical gel-permeation chromatography (GPC) analyses of the reaction mixtures were carried out on an automated Agilent 1100 series HPLC equipped with a multi-wavelength detector using a Phenomenex Phenogel 100-Å column packed in CH_2Cl_2 with a 7.80-mm inner diameter and a 300-mm length (flow rate = 1 mL/min). Samples were eluted using CH_2Cl_2 and monitored at 453 nm. ($\text{Zn}_2\text{-AA}$ and $\text{Zn}_2\text{-PP}$), 491 nm ($(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$ and $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$) and 420 nm ($(\text{AA})_3$).

I. Preparative procedures concerning porphyrin possessing allyloxyphenyl substituents

(4-Allyloxyphenyl)dipyromethane (1). 4-Allyloxybenzaldehyde (2.48 mL, 14.49 mmol) was combined with pyrrole (100 mL) in a 250-mL Schlenk flask equipped with a magnetic stir bar. This mixture was degassed for 10 min with a stream of N_2 . InCl_3 (0.32 g, 1.45 mmol) was then added in a portion, and the reaction mixture was stirred at room temperature. After 2 h, NaOH (1.74 g) was added to quench the reaction, followed by additional stirring for 1 h. The reaction mixture was filtered and the volatiles were evaporated from the filtrate using a rotary evaporator. The residue was subjected to column chromatography over silica gel (hexanes/ethyl acetate 5:1 v/v) to yield the desired product as a yellow oil (3.2 g, 79%). ^1H NMR (CDCl_3): δ 7.85 (broad s, 2H), 7.14 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 6.67 (d, J = 1.5 Hz, 2H), 6.20 (m, 2H), 6.10 (m, 1H), 5.94 (s, 2H), 5.46 (d, J = 17.5 Hz, 1H, vinyl CH), 5.40 (s, 1H), 5.34 (d, J = 10.5 Hz, 1H, vinyl CH), 5.06 (d, J = 5.5 Hz, 2H, allylic H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.64, 134.55, 133.43, 133.03, 129.52, 117.87, 117.31, 114.92, 108.47, 107.24, 68.99, 43.21.

[5,15-Bis(4-allyloxyphenyl)-10,20-bis(trimethylsilyl)ethynyl]-21H,23H-porphine (2). Compound **1** (1.715 g, 6.3 mmol) and trimethylsilylpropynal (1 mL, 6.8 mmol) were combined with CH_2Cl_2 (530 mL) in a 1000-mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed for 5 min and cooled to -5°C . After $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.16 mL) was added, the reaction mixture was stirred for 2 h at -5°C before being warmed up to room temperature. After stirring for an additional 12 h at room temperature, DDO (2.1 g) was added and the resulting mixture was then stirred for 2 h more. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The crude product was purified by silica column chromatography (hexanes/ CH_2Cl_2 1:1 v/v) to yield the desired product as a purple powder (0.485 g, 20.2%). ^1H NMR (CDCl_3): δ 9.60 (d, J = 4.5 Hz, 4H), 8.85 (d, J = 4.5 Hz, 4H), 8.08 (d, J = 8.5 Hz, 4H), 7.33 (d, J = 8.5 Hz, 4H), 6.29 (m, 2H), 5.64 (d, J = 17 Hz, 2H), 5.47 (d, J = 10.5 Hz, 2H), 4.85 (d, J = 5.5 Hz, 4H), 0.60 (s, 18H), -2.18 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.85, 135.82, 134.01, 133.53, 121.72, 118.31, 113.42, 107.11, 102.75, 100.89, 69.39, 0.43. HRFABMS: m/z = 766.3161 for M^+ , Calcd. 766.3159.

¹ J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambrose, and J. S. Lindsey, *Org. Process Res. Dev.*, 2003, **7**, 799-812.

[[5,15-Bis(4-allyloxyphenyl)-10,20-bis(trimethylsilyl)ethynyl]-21H,23H-porphinato]zinc (3). A solution of ZnOAc₂·2H₂O (0.65 g, 2.7 mmol) in MeOH (15 mL) was added to a solution of **2** (0.45 g, 0.59 mmol) in CH₂Cl₂ (150 mL) in a 250-mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was stirred for 4 h at room temperature. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. Purification of the crude product by silica column chromatography (hexanes/THF 3:1 v/v) yielded the desired product as a purple microcrystalline solid (0.45 g, 94%). ¹H NMR (CDCl₃): δ 9.68 (d, *J* = 5 Hz, 4H), 8.94 (d, *J* = 5 Hz, 4H), 8.07 (d, *J* = 8.5 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 6.27 (m, 2H), 5.64 (d, *J* = 17.5 Hz, 2H), 5.47 (d, *J* = 10.5 Hz, 2H), 4.84 (d, *J* = 5.5 Hz, 4H), 0.61 (s, 18H). ¹³C{¹H} NMR (CDCl₃): δ 158.64, 152.33, 150.79, 135.67, 134.83, 133.58, 132.99, 131.40, 122.61, 118.27, 113.23, 107.59, 102.12, 101.53, 69.40, 0.58. HRFABMS: *m/z* = 828.2295 for M⁺, Calcd. 828.2291.

[[5,15-Bis(4-allyloxyphenyl)-10,20-bis(ethynyl)-21H,23H-porphinato]zinc (4). A solution of TBAF (1.2 mL of a 1-M solution in THF) was added to a solution of **3** (0.385 g, 0.46 mmol) in CH₂Cl₂ (50 mL) in a 100-mL Schlenk flask equipped with a magnetic stir bar. After stirring for 20 min, the reaction mixture was quenched with HOAc (90 μL) and MeOH (150 mL). The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. Recrystallization of the crude product in THF/MeOH gave **4** as a purple microcrystalline solid (0.25 g, 79%). ¹H NMR (THF-*d*₈): δ 9.66 (d, *J* = 4.5 Hz, 4H), 8.89 (d, *J* = 4.5 Hz, 4H), 8.08 (d, *J* = 8.5 Hz, 4H), 7.35 (d, *J* = 8.5 Hz, 4H), 6.28 (m, 2H), 5.62 (d, *J* = 17 Hz, 2H), 5.39 (d, *J* = 10.5 Hz, 2H), 4.85 (d, *J* = 5.5 Hz, 4H), 4.63 (s, 2H). ¹³C{¹H} NMR (THF-*d*₈): δ 159.85, 153.20, 151.70, 136.47, 136.14, 135.18, 133.36, 131.63, 123.17, 117.49, 100.72, 87.41, 85.37, 68.90, 68.39. HRFABMS: *m/z* = 684.1503 for M⁺, Calcd. 684.1500.

[[5,15-Bis(4-allyloxyphenyl)-10-ethynyl-20-(triheptylsilyl)ethynyl]-21H,23H-porphinato]zinc (Zn-A). *n*-BuLi (0.36 mL of a 1.6-M solution in hexane, 0.58 mmol) was added to a solution of **5** (200 mg, 0.29 mmol) in THF (50 mL) at -78 °C. After stirring for 1 h at -78 °C the reaction mixture was allowed to warm to 0 °C before being cooled down to -78 °C again. Chlorotriheptylsilane (0.27 mL, 0.73 mmol) was then added and the reaction mixture was stirred for an additional 1 h at -78 °C. The reaction mixture was then allowed to warm up to RT and stirred for more 1 h before being filtered through a short silica plug with THF/hexanes (1:1 v/v) eluent. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remained residue was subjected to column chromatography over silica-gel (THF/hexanes 1:9 v/v) to afford pure Zn-A as a purple microcrystalline solid (68 mg, 24.2%). ¹H NMR (THF-*d*₈): δ 9.69 (d, *J* = 4 Hz, 2H), 9.67 (d, *J* = 4 Hz, 2H), 8.89 (d, *J* = 2.5 Hz, 4H), 8.09 (d, *J* = 8 Hz, 4H), 7.36 (d, *J* = 8 Hz, 4H), 6.29 (m, 2H), 5.63 (d, *J* = 17 Hz, 2H), 5.40 (d, *J* = 10.5 Hz, 2H), 4.86 (d, *J* = 5.5 Hz, 4H), 4.64 (s, 1H), 1.87 (m, 6H), 1.62 (m, 6H), 1.5 – 1.35 (m, 12H), 1.10 (m, 6H), 0.94 (t, *J* = 6.5 Hz, 9H). ¹³C{¹H} NMR (THF-*d*₈): δ 159.85, 153.20, 153.15, 151.67, 151.64, 136.50, 136.14, 135.16, 133.31, 133.23, 131.63, 123.31, 117.50, 113.80, 110.81, 101.71, 101.75, 99.86, 87.43, 85.39, 69.89, 34.54, 32.82, 25.56, 23.78, 14.89, 14.73. HRFABMS: *m/z* = 966.4243 for M⁺, Calcd. 966.4246.

[5,5'-(1,3-Butyne-1,4-diyl)-bis[10,20-bis[2,6-bis(4-allyloxyphenyl)-15-[(triheptylsilyl)ethynyl]porphinato]]dizinc (Zn₂-AA). A solution of Zn-A (147 mg, 0.152 mmol), pyridine (3 mL), and TMEDA (2.6 mL) in CH₂Cl₂ (320 mL) was bubbled with a stream of dry-air for 15 min. Next, CuCl (1 g) was added in one portion and the reaction mixture was allowed to stir for an additional 30 min under a stream of dry air. The reaction was then quenched with water (200 mL). The organic layer was collected, washed with water until the wash remains clear, and dried over MgSO₄. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remaining residue was subjected to column chromatography over silica gel (THF/hexanes 1:3 v/v) to afford Zn₂-AA as a dark solid (89.6 mg, 61%). ¹H NMR (CDCl₃): δ 9.63 (d, *J* = 4 Hz, 4H), 9.44 (d, *J* = 4 Hz, 4H), 8.91 (d, *J* = 4.5 Hz, 4H), 8.81 (d, *J* = 4 Hz, 4H), 8.08 (d, *J* = 8 Hz, 8H), 7.33 (d, *J* = 8 Hz, 8H), 6.28 (m, 4H), 5.64 (d, *J* = 17.5 Hz, 4H), 5.46 (d, *J* = 10.5 Hz, 4H), 4.85 (d, *J* = 4 Hz, 8H), 1.75 (m, 12H), 1.56 (m, 12H), 1.5-1.3 (m, 24H), 1.03 (m, 12H), 0.93 (t, *J* = 6.5 Hz, 18H). ¹³C{¹H} NMR (CDCl₃): δ 158.57, 152.42, 151.83, 150.62, 150.12, 136.01, 134.68, 133.55, 133.02, 132.62, 131.00, 130.55, 122.77, 118.22, 113.25, 108.20, 101.95, 100.84, 99.75, 87.32, 82.46, 69.38, 33.68, 31.99, 24.65, 22.98, 14.48, 14.06. HRFABMS: *m/z* = 1930.8343 for M⁺, Calcd. 1930.8336. UV-Vis (nm, (ε × 10³ / M⁻¹cm⁻¹)): 706.7 (8.28), 654.5 (5.12), 575.6 (1.67), 486.7 (16.27), 453.4 (30.64), 426.7 (14.04).

Covalently linked zincated trigonal prism incorporating Py₃T template ((Zn₂-AA)₃(Py₃T)₂). A solution of Zn₂-AA (24 mg, 12.4 μmol) and Py₃T (2.6 mg, 8.3 μmol) in CH₂Cl₂ (40 mL) was allowed to stir for 30 min. A solution of Grubbs' 1st-generation catalyst (5.1 mg, 25 mol%) in CH₂Cl₂ (2 mL) was then added to the reaction mixture. After stirring at room temperature overnight, the reaction mixture was opened to air and acetone (~ 10 mL) was added. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remaining residue was extracted with CH₂Cl₂ (~ 10 mL) and subjected to size-exclusion chromatography (Bio-Rad Bio-Beads S-X1, CH₂Cl₂) to afford (Zn₂-AA)₃(Py₃T)₂ as a dark solid (20 mg, 77%). ¹H NMR (CDCl₃): δ 9.63 (s, 12H), 9.47 (s, 12H), 8.93 (s, 12H), 8.83 (s, 12H), 8.39 (s, 12H), 7.99 (s, 12H), 7.52 (s, 12H), 7.50 (s, 12H), 6.48 (s, 4H, *Z*-vinyl), 6.37 (s, 8H, *E*-vinyl), 5.91 (s, 12H, β-Py), 5.37 (s, 16H, *E*-allyl), 5.22 (s, 8H, *Z*-allyl), 2.44 (s, 12H, α-Py), 1.6-0.7 (m, 78H). UV-Vis (nm, (ε × 10⁴ / M⁻¹cm⁻¹)): 738.9 (71.48), 678.9 (11.56), 587.8 (5.42), 491.1 (97.38), 485.6 (36.03), 442.2 (48.87), 428.9 (54.35). MALDI-TOF: *m/z* = 5634.93 for [M-2Py₃T]⁺, Calcd. 5637.64.

Covalently linked hollow trigonal prism comprising of free base porphyrin ((AA)₃). A solution of (Zn₂-AA)₃(Py₃T)₂ (17 mg, 2.71 μmol) in CH₂Cl₂ (40 mL) was treated with TFA (5 mL). After stirring for 30 min, the reaction mixture was washed with water (3 x 30 mL) and purified using size-exclusion chromatography (Bio-Rad Bio-Beads S-X1, CH₂Cl₂) to afford (AA)₃ as a dark solid (14 mg, 94%). ¹H NMR (CDCl₃): δ 9.63 (s, 12H), 9.43 (s, 12H), 8.82 (s, 12H), 8.71 (s, 12H), 8.25 (s, 12H), 7.76 (s, 12H), 7.43 (s, 12H), 7.39 (s, 12H), 6.39 (s, 4H, *Z*-vinyl), 6.33 (s, 8H, *E*-vinyl), 5.22 (s, 16H, *E*-allyl), 5.10 (s, 8H, *Z*-allyl), 1.8-0.6 (m, 78H), -2.07 (s, 12H). UV-Vis (nm, (ε × 10⁴ / M⁻¹cm⁻¹)): 733.3 (35.44), 644.4 (10.39), 630.0 (16.88), 536.5 (4.06), 481.1 (40.38), 455.6 (32.10), 435.6 (38.79), 420.1 (45.01). MALDI-TOF: *m/z* = 5257.76 for M⁺, Calcd. 5257.39.

Covalently linked zincated trigonal prism from (AA)₃ ((Zn₂-AA)₃). A solution of Zn(OAc)₂·2H₂O (24 mg, 0.11 mmol) in MeOH (2 mL) was added to a solution of (AA)₃ (7.8 mg, 1.5 μmol) in CH₂Cl₂ (15 mL) in a 25-mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was stirred for 4 h at room temperature. The volatiles were removed from the reaction mixture under reduced

pressure using a rotary evaporator. The residue was subject to size-exclusion chromatography (Bio-Rad Bio-Beads S-X1, CH₂Cl₂) to afford (Zn₂-AA)₃ as a dark solid (7.3 mg, 86%). ¹H NMR (THF-*d*₈): δ 9.67 (s, 4H), 9.47 (s, 12H), 8.87 (s, 12H), 8.74 (s, 12H), 8.19 (s, 12H), 7.77 (s, 12H), 7.47 (s, 12H), 7.40 (s, 12H), [6.42 (s, *Z*-vinyl), 6.30 (s, *E*-vinyl), 12H], [5.29 (s, *E*-allyl), 5.13 (s, 8H, *Z*-allyl), 24H] 1.9-0.7 (m, 78H). UV-Vis (nm, (ε × 10⁴ / M⁻¹cm⁻¹)) in THF: 725.6 (41.45), 668.9 (8.98), 581.1 (5.18), 487.8 (68.07), 438.9 (48.69), 426.7 (48.56). MALDI-TOF: *m/z* = 5635.63 for M⁺, Calcd. 5637.64.

Covalently linked cobaltated trigonal prism from (AA)₃ ((Co₂-AA)₃). A solution of Co(OAc)₂·4H₂O (14 mg, 56 μmol) in MeOH (2 mL) was added to a solution of (AA)₃ (4.5 mg, 0.80 μmol) in CHCl₃ (150 mL) in a 250-mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was refluxed for overnight. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The residue was subject to size-exclusion chromatography (Bio-Rad Bio-Beads S-X1, CH₂Cl₂) to afford (Co₂-AA)₃ as a dark solid (4.0 mg, 88%). UV-Vis (nm, (ε × 10⁴ / M⁻¹cm⁻¹)) in THF: 682.2 (13.77), 558.9 (3.36), 473.3 (35.32), 431.1 (24.26). MALDI-TOF: *m/z* = 5598.79 for M⁺, Calcd. 5598.90.

II. Preparative procedures concerning porphyrin possessing pentenyloxyphenyl substituents.

(4-(1-pentenyloxy)phenyl)dipyrrromethane (5). 4-Pentenyloxybenzaldehyde (3 g, 16.2 mmol)² was combined with pyrrole (200 mL) in a 300-mL Schlenk flask equipped with a magnetic stir bar. This mixture was degassed for 10 min with a stream of N₂. InCl₃ (0.36 g, 1.45 mmol) was then added in one portion, and the reaction mixture was stirred at room temperature. After 2 h, NaOH (1.96 g) was added to quench the reaction, followed by additional stirring for 1h. The reaction mixture was filtered and the volatiles were evaporated from the filtrate using a rotary evaporator. The residue was subjected to column chromatography over silica gel (hexanes/CH₂Cl₂/ethyl acetate 9:1:1 v/v/v) to yield the desired product as a white powder (3.1 g, 79 %). ¹H NMR (CDCl₃): δ 7.92 (broad s, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 1.5 Hz, 2H), 6.15 (m, 2H), 5.91 (s, 2H), 5.85 (m, 1H), 5.43 (s, 2H), 5.05 (d, *J* = 17.5 Hz, 1H, vinyl CH), 4.99 (d, *J* = 10.5 Hz, 1H, vinyl CH), 3.95 (t, *J* = 6.5 Hz, 2H, allylic H). ¹³C{¹H} NMR (CDCl₃): δ 158.24, 138.02, 134.23, 133.07, 129.57, 117.28, 117.21, 115.41, 114.80, 114.73, 67.40, 43.35, 30.33, 28.64.

[5,15-bis(4-(1-pentenyloxy)phenyl)-10,20-bis(trimethylsilyl)ethynyl]-21H,23H-porphine (6). Compound 5 (2.9 g, 9.47 mmol) and trimethylsilylpropynal (1.53 mL, 10.4 mmol) were combined with CH₂Cl₂ (850 mL) in a 1-L Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed for 5 min and cooled to -5 °C. After BF₃·Et₂O (0.23 mL) was added, the reaction mixture was stirred for 2 h at -5 °C before being warmed up to room temperature. After stirring for an additional 12 h at room temperature, DDQ (3.2 g) was added and the resulting mixture was then stirred for 2 h more. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The crude product was purified by silica column chromatography (hexanes/CH₂Cl₂ 1:2 v/v) to yield the desired product as a purple powder (0.75 g, 19.2%). ¹H NMR (CDCl₃): δ 9.59 (d, *J* = 4.5 Hz, 4H), 8.85 (d, *J* = 4.5 Hz, 4H), 8.07 (d, *J* = 8.5 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 4H), 6.00 (m, 2H), 5.21 (d, *J* = 17.5 Hz, 2H), 5.12 (d, *J* = 10.5 Hz, 2H), 4.29 (t, *J* = 6 Hz, 4H), 2.44 (m, 4H), 2.11(m, 4H), 0.60 (s, 18H), -2.18 (s, 2H). ¹³C{¹H} NMR (CDCl₃): δ 159.30, 138.13, 135.85, 133.73, 130.53, 121.83, 115.60, 113.20, 107.14, 102.72, 100.86, 67.77, 30.52, 28.86, 0.52. HRFABMS: *m/z* = 822.3789 for M⁺, Calcd. 822.3785.

[5,15-bis(4-(1-pentenyloxy)phenyl)-10,20-bis(trimethylsilyl)ethynyl]-21H,23H-porphinato]zinc (7). A solution of Zn(OAc)₂·2H₂O (1.1 g, 4.5 mmol) in MeOH (30 mL) was added to a solution of 6 (0.75 g, 0.91 mmol) in CH₂Cl₂ (200 mL) in a 300-mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was stirred for 4 h at room temperature. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. Purification of the crude product by silica column chromatography (hexanes/THF 3:2 v/v) yielded the desired product as a purple microcrystalline solid (0.657 g, 81%). ¹H NMR (CDCl₃): δ 9.68 (d, *J* = 4.5 Hz, 4H), 8.95 (d, *J* = 4.5 Hz, 4H), 8.07 (d, *J* = 8 Hz, 4H), 7.29 (d, *J* = 8 Hz, 4H), 6.00 (m, 2H), 5.21 (d, *J* = 17.5 Hz, 2H), 5.12 (d, *J* = 10 Hz, 2H), 4.29 (t, *J* = 6.5 Hz, 4H), 2.44 (m, 4H), 2.11(m, 4H), 0.60 (s, 18H). ¹³C{¹H} NMR (CDCl₃): δ 159.12, 152.34, 150.85, 138.17, 135.70, 134.57, 131.39, 122.74, 115.59, 113.00, 107.64, 102.09, 101.50, 67.77, 30.52, 28.89, 0.52. HRFABMS: *m/z* = 884.2921 for M⁺, Calcd. 884.2920.

[5,15-bis(4-(1-pentenyloxy)phenyl)-10,20-bis(ethynyl)-21H,23H-porphinato]zinc (8). A solution of TBAF (0.93 mL of a 1-M solution in THF) was added to a solution of 7 (0.28 g, 0.31 mmol) in CH₂Cl₂ (50 mL). After stirring for 20 min, the reaction mixture was quenched with HOAc (50 μL) and MeOH (200 mL). The mixture was stored at -10 °C for overnight to precipitate purple microcrystals of 8 (0.21 g, 85 %). ¹H NMR (THF-*d*₈): δ 9.65 (d, *J* = 4.5 Hz, 4H), 8.89 (d, *J* = 4.5 Hz, 4H), 8.06 (d, *J* = 8.5 Hz, 4H), 7.32 (d, *J* = 8.5 Hz, 4H), 6.02 (m, 2H), 5.19 (d, *J* = 17.5 Hz, 2H), 5.08 (d, *J* = 10 Hz, 2H), 4.62 (s, 1H), 4.30 (t, *J* = 6.5 Hz, 4H), 2.44 (m, 4H), 2.08 (m, 4H). ¹³C{¹H} NMR (THF-*d*₈): δ 160.25, 153.18, 151.72, 139.23, 136.47, 135.92, 133.33, 131.60, 123.24, 115.59, 113.54, 100.69, 87.41, 85.33, 68.89, 31.46, 29.96. HRFABMS: *m/z* = 740.2129 for M⁺, Calcd. 740.2130.

[5,15-bis(4-(1-pentenyloxy)phenyl)-10-ethynyl-20-(triethylsilyl)ethynyl]-21H,23H-porphinato]zinc (Zn-P). *n*-BuLi (252 μL of a 1.6-M solution in hexane, 0.42 mmol) was added to a solution of 8 (150 mg, 202 μmol) in THF (35 mL) at -78 °C. After stirring for 1 h at -78 °C the reaction mixture was allowed to warm to 0 °C before being cooled down to -78 °C again. Chlorotriethylsilane (189 μL, 405 μmol) was then added and the reaction mixture was stirred for an additional 1 h at -78 °C. The reaction mixture was then allowed to warm up to RT and stirred for more 1 h before being filtered through a short silica plug with THF/hexanes (1:1 v/v) eluent. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remained residue was subjected to column chromatography over silica-gel (THF/hexanes 1:9 v/v) to afford pure Zn-P as a purple microcrystalline solid (73 mg, 35%). ¹H NMR (THF-*d*₈): δ 9.65 (m, 4H), 8.87 (m, 4H), 8.06 (d, *J* = 8 Hz, 4H), 7.32 (d, *J* = 8 Hz, 4H), 6.02 (m, 2H), 5.20 (d, *J* = 17 Hz, 2H), 5.08 (d, *J* = 10 Hz, 2H), 4.62 (s, 1H), 4.30 (t, *J* = 6.5 Hz, 4H), 2.44 - 0.92 (m, 39H). ¹³C{¹H} NMR (THF-*d*₈): δ 160.26, 153.17, 153.12, 151.69, 151.65, 139.23, 136.50, 135.92, 133.31, 133.22, 131.58, 123.37, 115.60, 113.55, 110.81, 108.31, 101.66, 100.71, 99.80, 87.42, 85.34, 68.37, 34.52, 32.81, 31.45, 29.95, 25.54, 23.76, 14.87, 14.70. HRFABMS: *m/z* = 1022.4868 for M⁺, Calcd. 1022.4872.

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[[5,5'-(1,3-butynyl-1,4-bisyl)-bis[10,20-bis[2,6-bis(4-(1-pentenyl)oxy)phenyl]-15-[(triethyl)ethynyl]porphinato]]]dizinc (Zn₂-PP). A solution of Zn-P (76 mg, 74.1 μmol), pyridine (1.6 mL), and TMEDA (1.3 mL) in CH₂Cl₂ (160 mL) was bubbled with a stream of dry-air for 15 min. Next, CuCl (0.52 g) was added in one portion and the reaction mixture was allowed to stir for an additional 30 min under a stream of dry air. The reaction was then quenched with water (100 mL). The organic layer was collected, washed with water until the wash remains clear, and dried over MgSO₄. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remaining residue was subjected to column chromatography over silica gel (THF/hexanes 1:5 v/v) to afford Zn₂-PP as a dark solid (33 mg, 44 %). ¹H NMR (CDCl₃): δ 9.69 (d, *J* = 4 Hz, 4H), 9.50 (d, *J* = 4 Hz, 4H), 8.93 (d, *J* = 4.5 Hz, 4H), 8.83 (d, *J* = 4 Hz, 4H), 8.07 (d, *J* = 8 Hz, 8H), 7.29 (d, *J* = 8 Hz, 8H), 6.00 (m, 4H), 5.21 (d, *J* = 17 Hz, 4H), 5.12 (d, *J* = 10 Hz, 4H), 4.26 (t, *J* = 6.5 Hz, 8H), 2.44 – 0.92 (m, 78H). ¹³C {¹H} NMR (CDCl₃): δ 159.08, 152.81, 152.17, 150.08, 150.40, 138.17, 134.88, 134.55, 133.26, 132.83, 131.27, 130.84, 123.03, 115.59, 113.04, 108.54, 102.25, 100.88, 99.87, 87.72, 82.59, 67.78, 33.65, 31.95, 30.54, 28.89, 24.64, 22.96, 14.46, 14.07. MALDI-TOF: *m/z* = 2048.56 for M⁺, Calcd. 2047.53. UV-Vis (nm, (ε × 10³ /M⁻¹cm⁻¹): 708.9 (8.11), 658.9 (5.05), 576.6 (1.72), 486.7 (16.05), 453.3(30.65), 430.0 (15.30).

Covalently linked zincated trigonal prism incorporating TPEB template ((Zn₂-PP)₃(TPEB)₂). A solution of Zn₂-PP (12 mg, 5.8 μmol) and TPEB (1.5 mg, 3.9 μmol) in CH₂Cl₂ (35 mL) was allowed to stir for 30 min. A solution of Grubbs' 1st-generation catalyst (2 mg, 25 mol%) in CH₂Cl₂ (1 mL) was then added to the reaction mixture. After stirring at room temperature overnight, the reaction mixture was opened to air and acetone (~ 5 mL) was added. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remaining residue was extracted with CH₂Cl₂ (~ 10 mL) and subjected to size-exclusion chromatography (Bio-Rad Bio-Beads S-X1, CH₂Cl₂) to afford (Zn₂-PP)₃(TPEB)₂ as a dark solid (10 mg, 76 %). ¹H NMR (CDCl₃): δ 9.76 (s, 12H), 9.55 (d, *J* = 4Hz, 12H), 8.95 (d, *J* = 4 Hz, 12H), 8.84 (s, 12H), 8.43 (s, 12H), 7.62 (s, 12H), 7.42 (s, 12H), 7.18 (s, 12H), 6.50 (s, 6H) 5.80 (s, 4H, *Z*-vinyl), 5.70 (s, 8H, *E*-vinyl), 5.29 (s, 12H, β-Py), 4.33 (s, 24H), 2.34 (s, 12H, α -Py), 2.6 – 0.8 (m, 234H). MALDI-TOF: *m/z* = 5972.76 amu for (M-2TPEB)⁺, Calcd. 5674.27. UV-Vis (nm, (ε × 10⁴ /M⁻¹cm⁻¹)), 742.2 (43.83), 680.0 (8.38), 586.7 (4.64), 493.3 (56.82), 464.4 (27.56), 443.3 (38.86), 430.0 (40.95).

III. Spectroscopic and analytical data

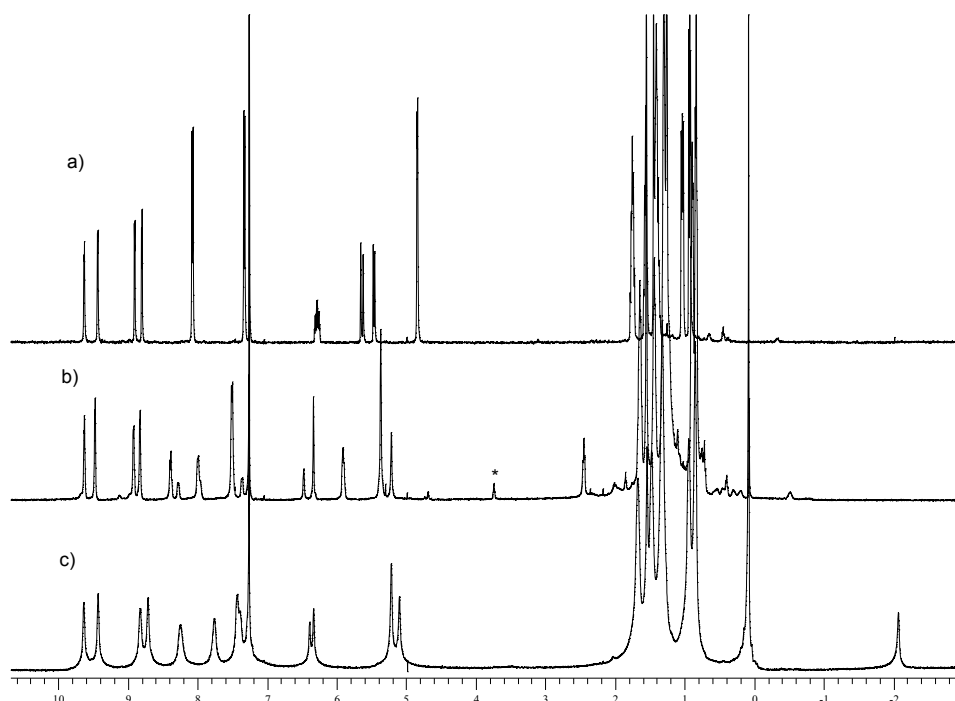


Figure S2. The ¹H NMR spectra of: a) Zn₂-AA, b) (Zn₂-AA)₃(Py₃T)₂, and c) (AA)₃.

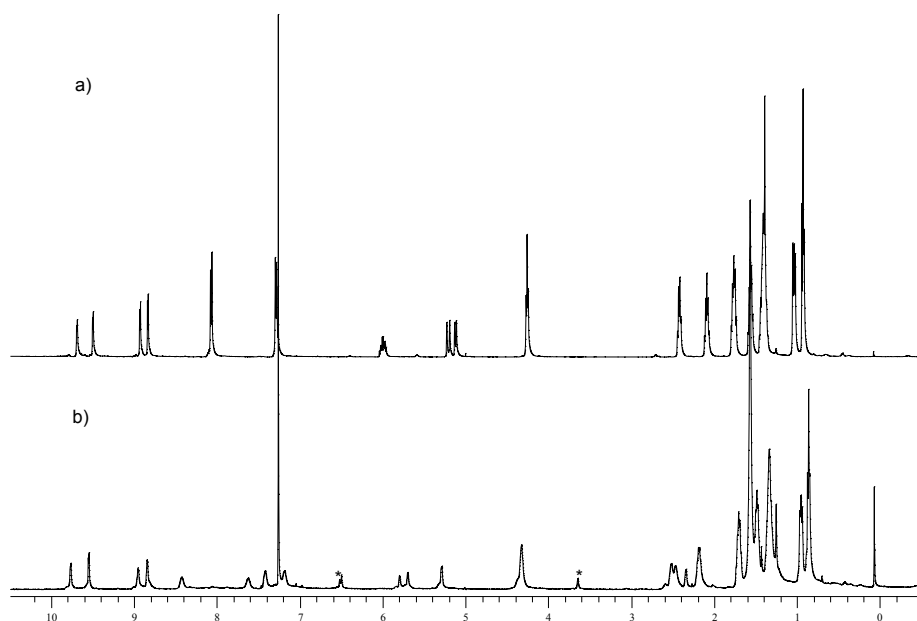


Figure S3. The ^1H NMR spectra of: a) $\text{Zn}_2\text{-PP}$ and b) $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$.

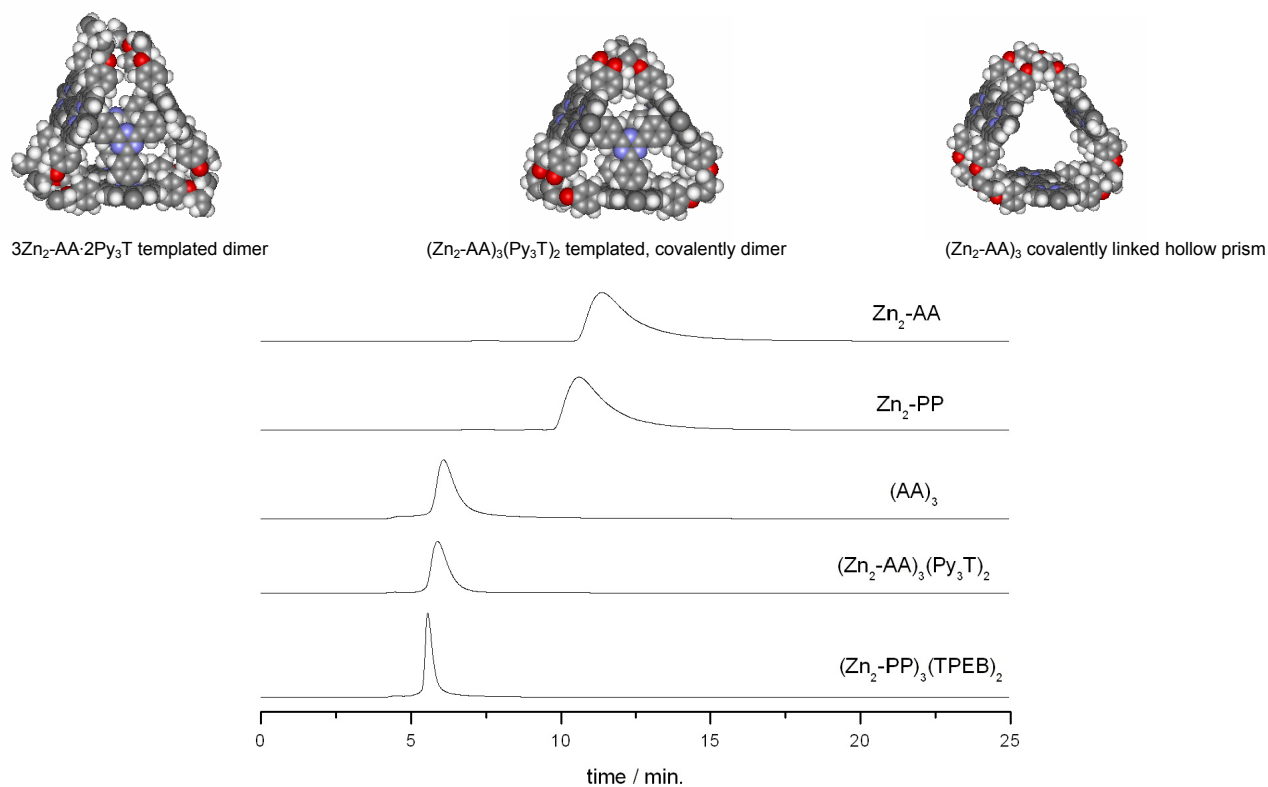


Figure S4. Top: Molecular-packing diagram for $3\text{Zn}_2\text{-AA}\cdot 2\text{Py}_3\text{T}$ templated dimer; $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$ templated, covalently dimer; and $(\text{Zn}_2\text{-AA})_3$ covalently linked hollow prism. Bottom: Analytical GPC traces of $\text{Zn}_2\text{-AA}$, $\text{Zn}_2\text{-PP}$, $(\text{AA})_3$, $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$, and $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$

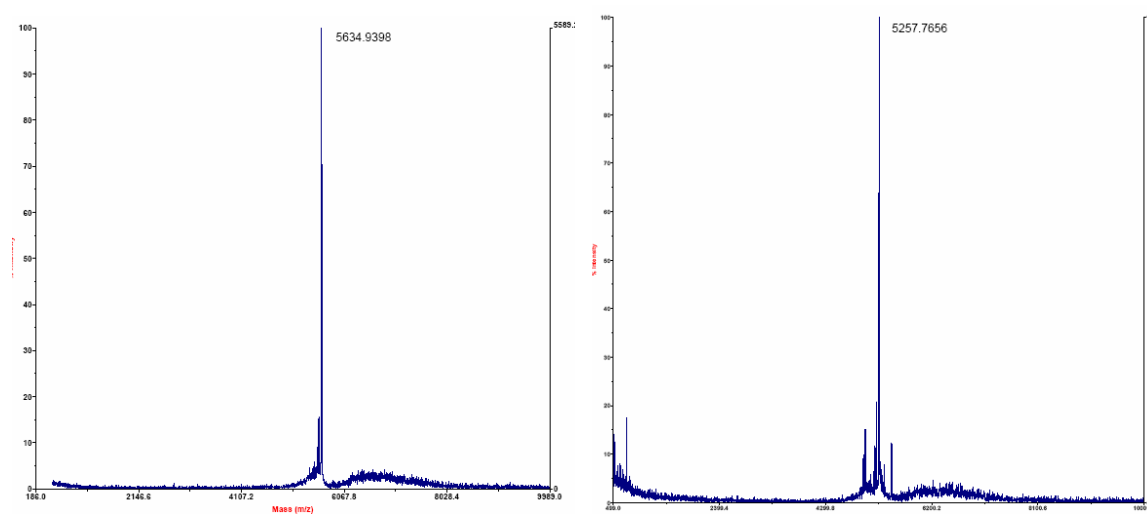


Figure S5. The MALDI-TOF mass spectra of $(Zn_2-AA)_3(Py_3T)_2$ (left) and $(AA)_3$ (right).

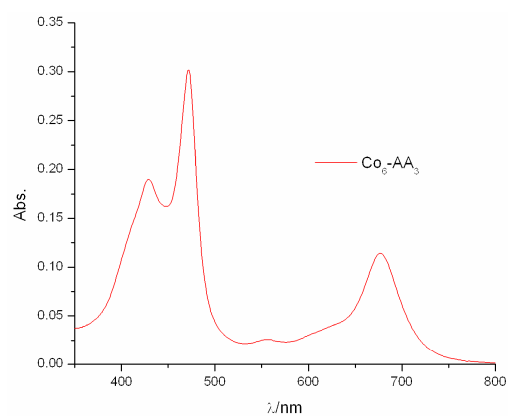


Figure S6. The UV-Vis spectrum of $(Co_2-AA)_3$.

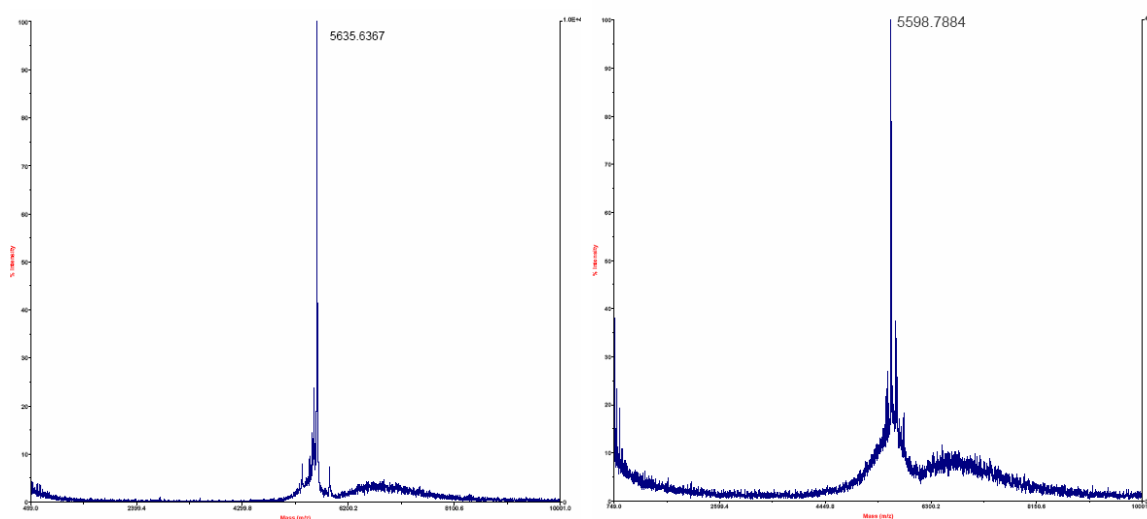


Figure S7. The MALDI-TOF mass spectra of $(Zn_2-AA)_3$ (left) and $(Co_2-AA)_3$ (right).

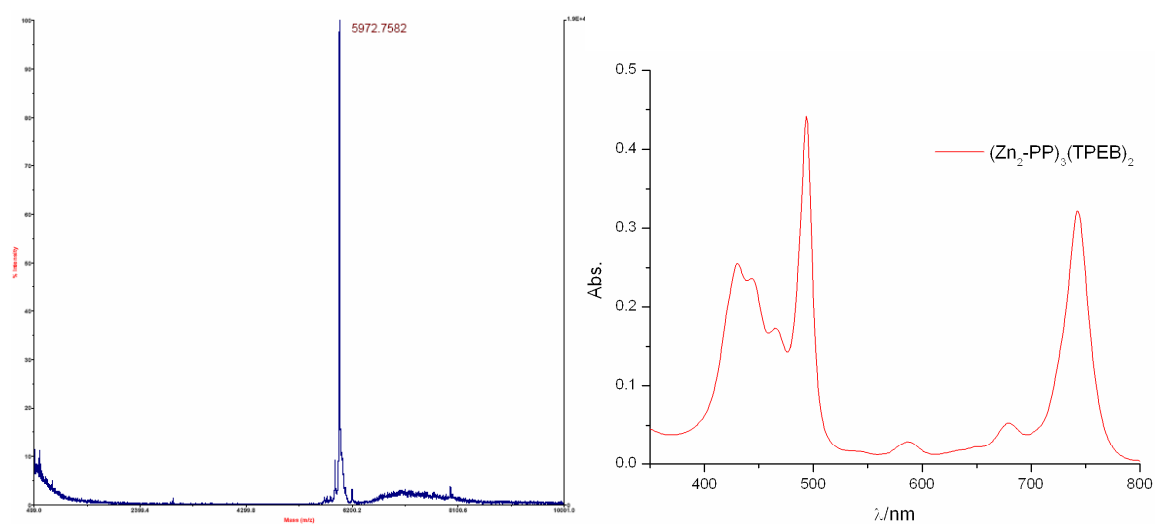


Figure S8. The MALDI-TOF mass spectrum (right) and UV-Vis spectrum (left) of $(Zn_2-PP)_3(TPEB)_2$.