

Modulation of Dark Conductivity over a 10^{-12} – 10^{-5} S/cm Range Through Ancillary Group Modification in Amorphous Solids of Ethyne-Bridged (porphinato)zinc(II) Oligomers.

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Experimental Section

Materials. All manipulations were carried out under nitrogen or argon previously passed through an O₂ scrubbing tower (Schweitzerhall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise stated. Air sensitive solids were handled in a Braun 150-M glove box. Standard Schlenk techniques were employed to manipulate air-sensitive solutions. Methylene Chloride (CH₂Cl₂) and tetrahydrofuran (THF) were distilled from CaH₂ and K/4-benzoylbiphenyl, respectively, under N₂. All NMR solvents were used as received. ZnCl₂ was dried by heating under vacuum and stored under N₂. The catalysts Pd(PPh₃)₄, PdCl₂(PPh₃)₂, and tris(dibenzylideneacetone)dipalladium(0) (Pd₂dba₃), copper iodide (CuI), as well as triphenylarsine (AsPh₃) were purchased from Strem Chemicals and used as received.

Chemical shifts for ¹H NMR spectra are relative to tetramethylsilane (TMS) signal in the deuterated solvent (TMS, δ = 0.00 ppm). All *J* values are reported in Hertz. Flash and size exclusion column chromatographies were

performed on the bench top, using respectively silica gel (EM Science, 230–400 mesh) and Bio-Rad Bio-Beads SX-1 (THF as the eluent) as media. Mass spectra were acquired at the Mass Spectrometry Center at the University of Pennsylvania. MALDI-TOF mass spectroscopic data were obtained with a Perspective Voyager DE instrument in the Laboratory of Dr. Bill Degrado (Department of Biophysics, University of Pennsylvania). Samples were prepared as μ molar solutions in CH_2Cl_2 , •-cyano-4-hydroxy cinnamic acid (Aldrich), 1,4-Bis(5-phenyloxazol-2-yl)-benzene (Aldrich), Terthiophene (Aldrich), Anthracene (Aldrich), and TCNQ (Aldrich) were utilized as the matrix.

TGA/DTA samples were purified by silica gel chromatography, filtered and dried under vacuum for 2 days and 2 – 8 mg samples were used and the temperature was increased at a rate of 10 °C/min. XRD data samples were purified by silica gel chromatography, filtered, and slowly dried in a vial over a stream of Nitrogen. Samples were then vacuum dried for another 2 days followed by the thick films being scraped out and loaded into capillary tubes.

Instrumentation. Electronic spectra were recorded on a Shimadzu PharmSpec UV-1700. NMR spectra were recorded on either 250 MHz AC-250, or 500 MHz AMX-500 Brüker spectrometers. TGA/DTA were measured by Dr. A. McGhie (LRSM University of Pennsylvania). XRD data were measured by Dr. P. Heiney (Physics Dept. University of Pennsylvania). For description of equipment and

facilities the reader is referred to the LRSM website,

<http://www.lrsm.upenn.edu/facilities/>.

Purification of samples for 2- and 4-Probe measurements. All samples were purified by a combination of column chromatographies prior to measurements.

Oligomers (dimers, trimers, pentamers) were first purified by size exclusion chromatography (• 61 cm in length), followed by silica gel chromatography using either CHCl_3 or CHCl_3 :MeOH solvents as the eluent to remove excess biobeads, then a final silica gel column using THF:Hexanes as the eluent.

Monomers were not subject to size exclusion chromatography. All samples were filtered through a 50 μm PPE membrane into a vial and dried with a stream of Nitrogen. To prepare press pellets samples were dried 2 days under vacuum and then scraped into solvent washed KBr pellet press. Samples were pressed at 2000 psi and maintained at that pressure for 5 min. Thin film samples were filtered through a 50 μm PPE membrane into a vial and dried with a stream of Nitrogen. Samples were prepared with either HPLC grade solvents or freshly distilled solvents at a concentration of 20-50 mg/mL (concentration depends on ancillary side chains). ESR experiments (mmol concentrations) were performed on monomer and oligomer samples that were exposed to ambient light and temperature (2-4 weeks) all registered isolated spin signals. Following the aforementioned purification procedure, samples prepared for spin casting would not registered any spin signals at maximum gain.

2- and 4-Probe measurements. Pressed pellets were purified until a constant conductivity value was reached. Pellets were pressed in a KBr hydrolic press equipped in a Nitrogen atmosphere glovebox. 5 mm pellets were pressed using a KBr hydrolic press equipped in nitrogen filled glovebox. The pellets were cut down to rectangles with average dimensions of 5 x 2 x 1 mm, with precise dimensions obtained using a dial indicator with 1 μm resolution and microscope. Substrates were subjected to piranha and solvent wash and dried in a 200 °C oven. Electrical contacts were made with micromanipulator electrodes equipped with gold-coated tungsten electrodes, which were cleaned by plasma or solvent wash prior to use. 2- and 4-probe measurements were taken with a Keithley 237. For high resistance samples, measurements were performed using a computer-controlled sequence of opposite polarity voltages.¹ Thin film measurements were done on sapphire substrates (Meller Optics) and samples were deposited by spin coating from concentrated THF solutions, pentamer samples were spin coated from chlorobenzene solutions. Thin film thicknesses were estimated using ellipsometry and verified by RBS measurements (LRSM University of Pennsylvania) where analogous films were spin cast on silicon substrate yielding thicknesses ranging between 200-400 nm. Au contact electrodes were deposited utilizing a shadow mask, for 2-probe measurements, two pairs of electrodes with gap distances of 200 μm and 1 mm apart; 4-probe measurements used a shadow mask that produced 4 sets of electrodes 1 mm apart. All electrical measurements

on films were done under inert conditions with the samples and probe station in a glovebox continuously purged by Ar. Results with pressed pellets were done in air, as there was no observable change in results when done under inert conditions. Resistance values were determined from the linear region of the IV curves. Dark conductivity values were then calculated from the respective dimensions of individual electrode samples and film thicknesses.

Synthetic Procedures

Synthetic details for previously reported compounds refer to the references listed at the end of the synthetic procedure section. For previously reported compounds only characterization data are listed. If a different procedure was used than what is reference full experimental details are listed. The PZn_n -O3Hex synthetic procedures were identical to the PZn_n -O3EHex and only characterization data is listed then for PZn_n -O3Hex series. Abbreviations for mass spectral data are as follows HR MS = High Resolution Mass Spectra, ESI MS = Low Resolution ESI Mass Spectra.

PZn -2,6(OR)Ar Series 2:

10,20-di(2',6'-bis(3'',3''-dimethylbutoxy)phenyl)porphinato)zinc(II) PZn -2,6(OR)Ar.

10,20-di(2',6'-bis(3'',3''-dimethylbutoxy)phenyl)porphyrin (200 mg, 0.234 mmol) was dissolved in 150 mL HPLC grade $CHCl_3$ with 1 mL of TEA. The reaction mixture was heated to reflux and then Zn acetate dihydrate was added in excess

and the reaction was allowed to stir for 2 hrs. After cooling, the reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried with CaCl_2 . Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:4 THF:Hexanes as the eluent. Yield = 208 mg (97% yield based on starting material). ^1H NMR (500 MHz, CDCl_3): δ 9.93(s, 2H), δ 9.15(d, 4H, J = 4.35Hz), δ 8.90(d, 4H, J = 4.35Hz), δ 7.64(t, 2H, J = 8.50Hz), δ 6.97(d, 4H, J = 8.40Hz), δ 3.81(t, 8H, J = 4.65), δ 0.68(t, 8H, J = 7.55), δ 0.22(s, 36H). Vis (THF): 410, 546, 579 nm. ESI-MS m/z : 924.70 $[(M)^+]$ (calcd for $\text{C}_{56}\text{H}_{68}\text{N}_4\text{O}_4\text{Zn}$ 924.4532).

1,2-Bis[(10,20-bis[2',6'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II)-5-yl]ethyne PZn₂-2,6(OR)Ar.

[5-ethynyl-10,20-bis(2',6'-bis(3'',3''-dimethylbutoxy)phenylporphinato)zinc(II) (200 mg, 0.211 mmol), [5-bromo-10,20-bis(2',6'-bis(3'',3''-dimethylbutoxy)phenylporphinato)zinc(II) (201 mg, 0.200 mmol), Pd_2dba_3 (28 mg, 0.03 mmol) and AsPh_3 (78 mg, 1.1 mmol) were charged into a 100 mL Schlenk flask. THF:TEA solvent mixture (50 mL, 9:1) was subjected to 3x freeze-pump-thaw cycles and then transferred to the reaction flask. The reaction mixture was stirred for 16 hrs at 60 °C under Ar. After 16 hrs the reaction mixture was diluted with CHCl_3 and washed 3x with NH_4Cl (aq), organic residue was then dried over Na_2SO_4 , filtered, and solvent removed via vacuum. The product was chromatographed on silica gel using 1:4 THF:hexanes the first band, brown-green, was collected. The solvent was removed via

vacuum yielding **PZn₂-2,6(OR)Ar**. Yield 296 mg (79% yield, based on mono bromo starting material). ¹H NMR (250 MHz, CDCl₃): δ 10.60 (d, 4H, *J* = 4.6), 10.08 (s, 2H), 9.44 (d, 4H, *J* = 4.4), 9.35 (d, 4H, *J* = 4.5), 9.29 (d, 4H, *J* = 4.5), 8.06 (t, 4H, *J* = 8.4), 7.41 (d, 8H, *J* = 8.5), 4.16 (t, 16H, *J* = 7.4), 0.97 (t, 16H, *J* = 7.4), 0.36 (s, 72H). Vis (THF): 413, 480, 551, 693 nm. MS MALDI-TOF *m/z* : 1872.1183 [(M+H)⁺] (calcd for C₁₁₄H₁₃₄N₈O₈Zn₂ 1870.8908).

(5,15-bis[(10',20'-bis[2''',6'''-bis(3''',3'''-dimethyl-1'''-butyloxy)phenyl]porphinato)zinc(II)ethyn-5'-yl]-10,20-bis[2',6'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II) PZn₃-2,6(OR)Ar.

[5-ethynyl-10,20-bis(2',6'-bis(3'',3''-dimethylbutoxy)phenylporphinato)zinc(II) (238 mg, 0.250 mmol), [5,15-dibromo-10,20-bis(2',6'-bis(3,3-dimethylbutoxy)phenylporphinato)zinc(II) (123 mg, 0.114 mmol), Pd₂dba₃ (23 mg, 0.025 mmol) and AsPh₃ (98 mg, 0.300 mmol) were charged into a 100 mL Schlenk flask. THF:TEA solvent mixture (50 mL, 9:1) was subjected to 3x freeze-pump-thaw cycles and then transferred to the reaction flask. The reaction mixture was stirred for 16 hrs at 60 °C under Ar. After 16 hrs the reaction mixture was diluted with CHCl₃ and washed 3x with NH₄Cl (aq), organic residue was then dried over Na₂SO₄, filtered, and solvent removed via vacuum. The product was chromatographed on silica gel using 3:7 THF:hexanes the first band, brown-green, was collected. The solvent was removed and the organic residue was redissolved in THF and further purified by size exclusion column. The solvent was removed via vacuum and chromatographed on silica

gel using CHCl_3 to remove residual biobeads, the first band was collected yielding **PZn₃-2,6**. Yield 254 mg (79% yield, based on dibromo starting material). ^1H NMR (500 MHz, CDCl_3): δ 10.35 (d, 4H, $J = 4.40$ Hz), 10.28 (d, 4H, $J = 4.35$), 9.87 (s, 2H), 9.12 (d, 4H, $J = 4.25$), 9.03 (d, 4H, $J = 4.45$), 8.94 (d, 4H, $J = 4.25$), 8.87 (d, 4H, $J = 4.30$), 7.73 (t, 2H, $J = 8.30$), 7.72 (t, 4H, $J = 8.30$), 7.06 (d, 4H, $J = 8.45$), 7.04 (d, 4H, $J = 8.45$), 3.95 (t, 24H, $J = 7.28$), 0.88 (t, 24H, $J = 7.25$), 0.30 (s, 108H, - CH_3). Vis (THF): 414, 495, 570, 766 nm. MS MALDI-TOF m/z : 2814.7533 [(M)⁺] (calcd for $\text{C}_{172}\text{H}_{200}\text{N}_{12}\text{O}_{12}\text{Zn}_3$ 2817.3283).

PZn-3,5(OR)Ar Series³ :

10,20-di(3',5'-bis(3'',3''-dimethylbutoxy)phenyl)porphinato)zinc(II) PZn-3,5(OR)Ar.

10,20-di(3',5'-bis(3'',3''-dimethylbutoxy)phenyl)porphyrin (200 mg, 0.234 mmol) was dissolved in 150 mL HPLC grade CHCl_3 with 1 mL of TEA. The reaction mixture was heated to reflux and then Zn acetate dihydrate (257 mg, 1.17 mmol) was added and the reaction was allowed to stir for 2 hrs. After cooling, the reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried over CaCl_2 . Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:4 THF:Hexanes as the eluent. Yield = 205 mg (95% yield based on starting material). ^1H NMR (500 MHz, CDCl_3): δ 10.30 (s, 2H), δ 9.43 (d, 4H, $J = 4.50$), δ 9.26 (d, 4H, $J = 4.45$), δ 7.43 (d, 4H, $J = 2.20$), δ 6.91 (t, 2H, $J = 2.20$), δ 4.21 (t, 8H, $J = 7.30$), δ 1.86 (t, 8H, $J = 7.35$), δ 1.01 (s, 36H). Vis

(THF): 410, 546, 579 nm. ESI-MS m/z : 924.90 [(M)⁺] (calcd for C₅₆H₆₈N₄O₄Zn 924.4532).

1,2-Bis[(10,20-bis[3',5'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II)-5-yl]ethyne PZn₂-3,5(OR)Ar.

[5-ethynyl-10,20-bis(3',5'-bis(3'',3''-dimethylbutoxy)phenylporphinato)zinc(II) (210 mg, 0.215 mmol), [5-bromo-10,20-bis(3',5'-bis(3'',3''-dimethylbutoxy)phenylporphinato)zinc(II) (200 mg, 0.200 mmol), Pd₂dba₃ (28 mg, 0.03 mmol) and AsPh₃ (78 mg, 1.1 mmol) were charged into a 100 mL Schlenk flask. THF:TEA solvent mixture (50 mL, 9:1) was subjected to 3x freeze-pump-thaw cycles and then transferred to the reaction flask. The reaction mixture was stirred for 16 hrs at 60 °C under Ar. After 16 hrs the reaction mixture was diluted with CHCl₃ and washed 3x with NH₄Cl (aq), organic residue was then dried over Na₂SO₄, filtered, and solvent removed via vacuum. The product was chromatographed on silica gel using 1:4 THF:hexanes the first band, brown-green, was collected. The solvent was removed via vacuum yielding PZn₂-3,5. Yield 269 mg (72% yield, based on mono ethyne starting material). ¹H NMR (500 MHz, CDCl₃): δ 10.45 (d, 4H, *J* = 4.40 Hz), 10.06 (s, 2H), 9.26 (d, 4H, *J* = 4.45 Hz), 9.24 (d, 4H, *J* = 4.4 Hz), 9.08 (d, 4H, *J* = 4.5 Hz), 7.44 (d, 8H, *J* = 2.05 Hz), 6.89 (d, 4H, *J* = 2.30 Hz), 4.22 (t, 16H, *J* = 7.40 Hz), 1.85 (t, 16H, *J* = 7.40 Hz), 0.99 (s, 72H). Vis (THF): 413, 480, 551, 698 nm. MS MALDI-TOF m/z : 1871.4153 [(M)⁺] (calcd for C₁₁₄H₁₃₄N₈O₈Zn₂ 1870.8908).

(5,15-bis[(10',20'-bis[3''',5'''-bis(3''',3'''-dimethyl-1'''-butyloxy)phenyl]porphinato)zinc(II)ethyn-5'-yl]-10,20-bis[3',5'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II) PZn₃-3,5(OR)Ar.

5-Ethynyl-(10,20-bis[3',5'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II) (248 mg, 2.61×10^{-4} mol) and (5,15-dibromo-10,20-bis[3',5'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II) (135 mg, 1.24×10^{-4} mol) were charged into a Schlenk Flask with AsPh₃ (49 mg, 1.5×10^{-4} mol) and Pd₂dba₃ (17 mg, 1.9×10^{-5} mol). THF:TEA (9:1) solvent mixture was degassed with an Ar purge for 30 min prior to solvent transfer. Once solvent was transferred, the reaction mixture was stirred at 60 °C overnight under Ar. The reaction mixture was poured down a silica plug to removed catalyst and ligand. The solvent was removed via vacuum and the crude reaction mixture subjected to gravimetric size exclusion chromatography using THF as the eluent. The first band was collected, solvent stripped, and then purified by silica gel chromatography using CHCl₃. Yield = 266 mg (77% based on dibromo starting material). ¹H NMR (250 MHz, CDCl₃): δ 10.45 (d, 4H, *J* = 4.50Hz), δ 10.38 (d, 4H, *J* = 4.68Hz), δ 10.08 (s, 2H), δ 9.27 (d, 4H, *J* = 4.38Hz), δ 9.17 (d, 4H, *J* = 4.50Hz), δ 9.09 (d, 4H, *J* = 4.45Hz), δ 7.49 (d, 4H, *J* = 2.10Hz), δ 7.45 (d, 8H, *J* = 2.23Hz), δ 6.91 (m, 6H), δ 4.24 (m, 24H), δ 1.87 (m, 24H), δ 1.00 (s, 108H). Vis (THF): 410, 490, 770 nm. MALDI-TOF MS *m/z*: 2821.2821 [(M)⁺] (calcd for C₁₇₂H₂₀₀N₁₂O₁₂Zn₃ 2823.6716).

PZn-3,5(PEG)Ar Series²:

5,15-bis[3',5'-bis(9''-methoxy-1'',4'',7''-trioxanonyl)phenyl]porphinato)zinc(II)
PZn-(PEG)Ar

5,15-bis[3',5'-bis(9''-methoxy-1'',4'',7''-trioxanonyl)phenyl]porphyrin (222mg, 0.200 mmols) was dissolved in 150 mL HPLC grade CHCl₃ with 1 mL of TEA. The reaction mixture was heated to reflux and then Zn acetate dihydrate (219 mg, 1.0 mmol) was added and the reaction was allowed to stir for 2 hrs. After cooling, the reaction mixture was washed with NH₄Cl (aq) x 3 and the organic layer was collected and dried with CaCl₂. Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:19 MeOH:CHCl₃ as the eluent. Yield = 211 mg (90% yield based on starting material). ¹H NMR (500 MHz, CDCl₃): δ 10.21(s, 2H), δ 9.35(d, 4H, J = 4.50Hz), δ 9.16(d, 4H, J = 4.45Hz), δ 7.45 (d, 4H, J = 2.20Hz), δ 6.92 (t, 2H, J = 2.20Hz), δ 4.34(m, 8H), δ 3.96(m, 8H), δ 3.79(m, 8H), δ 3.71(m, 8H), δ 3.64(m, 8H), δ 3.50(m, 8H), δ 3.32(m, 8H). Vis (THF): 410, 546, 579 nm. ESI-MS m/z: 1174.12 [(M)⁺] (calcd for C₆₀H₇₆N₄O₁₆Zn 1174.6526).

[5,-10,20-bis[3',5'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II)-
[5',-10'',20''-bis[3,5-di(9-methoxy-1,4,7-
trioxanonyl)phenyl]porphinato)zinc(II)]ethyne PZn₂-3,5(PEG)Ar

¹H NMR (500 MHz, CDCl₃): δ 10.45(m, 4H), δ 10.06(s, 2H), δ 9.26(m, 4H), δ 9.20 (d, 2H, J = 4.50Hz), δ 9.10 (d, 4H, J = 4.50Hz), δ 9.04 (d, 2H, J = 4.50Hz), δ 7.48 (d, 4H, J = 2.20Hz), δ 7.45 (d, 4H, J = 2.20Hz), δ 6.96(t, 2H, J = 2.20Hz), δ 6.89 (t, 2H, J = 2.20Hz), δ 4.34(m, 8H), δ 3.96(m, 8H), δ 3.79(m, 8H), δ 3.71(m,

8H), δ 3.64(m, 8H), δ 3.50(m, 8H), δ 3.32(m, 8H), δ 3.29(m, 8H), δ 1.82(m, 8H).

Vis (THF): 410, 496, 698 nm. MS MALDI-TOFF m/z: 2119.80 [(M)⁺] (calcd for

C₁₁₈H₁₄₂N₈O₂₀Zn₂ 2118.8923).

**5,15-bis[[5',-10',2'-bis[3,5-di(3,3-dimethyl-1-butyl-
oxy)phenyl]porphinato)zinc(II)]ethynyl]-10,20-bis[3,5-di[3,5-di(9-
methoxy-1,4,7-trioxanonyl)phenyl]porphinato)zinc(II)] PZn₃-3,5(PEG)₃,5.**

¹H NMR (500 MHz, CDCl₃): δ 10.46(d, 4H, J = 4.45), δ 10.37(d, 4H, J = 4.45), δ 10.08(s, 2H), δ 9.29(d, 4H, J = 4.45), δ 9.27(d, 4H, J = 4.45), δ 9.13(d, 4H, J = 4.50Hz), δ 9.11(d, 4H, J = 4.45Hz), δ 7.53 (d, 4H, J = 2.20Hz), δ 7.45 (d, 8H, J = 2.20Hz), δ 6.99 (t, 2H, J = 2.20Hz), δ 6.91 (t, 4H, J = 2.20Hz), δ 4.34(m, 8H), δ 4.24 (t, 16H, J = 7.85Hz), δ 3.96(m, 8H), δ 3.79(m, 8H), δ 3.71(m, 8H), δ 3.64(m, 8H), δ 3.50(m, 8H), δ 3.32(m, 8H), δ 1.86 (t, 16H, J = 7.80Hz), δ 1.01 (s, 72H). Vis (THF): 413, 490, 543, 770 nm. MALDI-TOF MS m/z: 3066.44 [(M)⁺] (calcd for C₁₇₆H₂₀₈N₁₂O₂₄Zn₃ 3065.33).

**5,15-bis[[15'',-(5',-10',20'-bis[3,5-bis(3,3-dimethyl-1-butyl-
oxy)phenyl]porphinato)zinc(II)]-[5'',-10'',-20''-bis[3,5-di(9-methoxy-1,4,7-
trioxanonyl)phenyl]porphinato)zinc(II)]ethynyl]-10,20-bis[3,5-di(9-methoxy-
1,4,7-trioxanonyl)phenyl]porphinato)zinc(II)] PZn₃-3,5(PEG)₃,5.**

¹H NMR (500 MHz, CDCl₃): δ 10.51(d, 4H, J = 4.45), δ 10.47(d, 4H, J = 4.45), δ 10.40(d, 4H, J = 4.45), δ 10.15(s, 2H), δ 9.34(d, 4H, J = 4.45), δ 9.31(d, 4H, J = 4.45), δ 9.26(d, 4H, J = 4.45), δ 9.22(d, 4H, J = 4.50Hz), δ 9.17(d, 4H, J = 4.45Hz), δ 9.12(d, 4H, J = 4.45Hz), δ 7.51 (br, 8H), δ 7.47 (br, 4H), δ 7.40 (br, 4H),

δ 6.76 (br, 4H), δ 6.66 (br, 4H), δ 6.50 (br, 2H), δ 4.12(m, 16H), δ 4.04 (m, 16H, J = 7.85Hz), δ 3.91(m, 8H), δ 3.52(m, 16H), δ 3.41(m, 8H), δ 3.64(m, 8H), δ 3.31(m, 16H), δ 3.22(m, 8H), δ 3.15(m, 16H), δ 3.08(m, 8H), δ 2.90(m, 16H), δ 2.86(m, 8H), δ 2.72(m, 24H), δ 2.58(m, 36H), δ 1.76 (t, 16H, J = 7.80Hz), δ 0.93 (s, 72H).

Vis (THF): 413, 495, 547, 843 nm. MALDI-TOF MS m/z : 5456.89 [(M)⁺] (calcd for C₁₇₆H₂₀₈N₁₂O₂₄Zn₃ 5454.21).

PZnDPP Series⁴:

ZnTPP

¹H NMR (500 MHz, CDCl₃): δ 8.55(s, 8H), δ 8.15(m, 8H), δ 7.71(m, 12H).

Vis (THF): 420, 570, 590 nm. ESI MS m/z : 6776.50 [(M)⁺] (calcd for C₄₄H₂₈N₄Zn 676.16)

ZnDPP

¹H NMR (250 MHz, CDCl₃): δ 10.31(s, 2H), δ 9.39(d, 4H, J = 4.60), δ 9.07(d, 4H, J = 4.60Hz), δ 8.26(m, 4H), δ 7.80(m, 8H). Vis (THF): 410, 536 nm. ESI MS m/z : 524.50 [(M)⁺] (calcd for C₃₂H₂₀N₄Zn 524.09).

1,2-bis[(10,20-diphenylporphinato)zinc(II)-5-yl]ethyne PZn₂-DPP.

¹H NMR (500 MHz, CDCl₃): δ 10.47(d, 4H, J = 4.40Hz), δ 10.08(s, 2H), δ 9.27(d, 4H, J = 3.0Hz), δ 9.13(d, 4H, J = 4.40Hz), δ 9.05(d, 4H, J = 4.40Hz), δ 8.27(m, 8H), δ 7.78(m, 12H). Vis (THF): 414, 480, 698 nm. MALDI-TOF MS m/z : 1072.8606 [(M)⁺] (calcd for C₆₆H₃₈N₈Zn₂ 1070.1802).

(5,15-bis[(10',20'-(diphenyl)porphinato)zinc(II)ethyn-5'-yl]-10,20-bis(diphenyl)porphinato)zinc(II) PZn₃-DPP.

¹H NMR (500 MHz, CDCl₃): δ 10.47(d, 4H, *J* = 4.50Hz), δ 10.42(d, 4H, *J* = 4.40Hz), δ 10.09(s, 2H), δ 9.26(d, 4H, *J* = 3.80Hz), δ 9.14(d, 4H, *J* = 4.16Hz), δ 9.04(d, 4H, *J* = 4.20Hz), δ 8.96(d, 4H, *J* = 4.32Hz), δ 8.27(m, 12H), δ 7.78(m, 18H). Vis (THF): 414, 490, 770 nm. MALDI-TOF MS *m/z*: 1618.2625 [(M)⁺] (calcd for C₁₀₀H₅₆N₁₂Zn₃).

PZnO1 Series.

1-bromo-3,5,5-trimethyl-hexane (1):

Triphenylphosphine (75.5 g, 0.288 mol) and 3,5,5-trimethylhexanol (50.1 mL, 0.288 mols) were dissolved in 300 mL of CH₂Cl₂ in a 1 L reaction flask and cooled to 0 °C under N₂. Once cooled, small portions, 5 g, of NBS (51.3 g total, 0.288 mol) were added directly to the reaction mixture and allowed to stir for an additional 2 hr. Solvent was removed via vacuum and the solid residue was taken up in ether and sonicated for 60 min. The mixture was filtered and washed with ether. The ether was removed via vacuum and the resulting residue was taken up in cold ether and filtered again. This process was repeated until no precipitate was formed upon dissolving in ether. Compound 1 was purified by silica gel chromatography using straight pentane as the eluent. Yield = 44.32 g (74% based on 3,5,5-trimethylhexanol starting material). ¹H NMR (500 MHz, CDCl₃): δ 3.42(m, 2H), δ 1.86(m, 1H), δ 1.69(m, 2H), δ 1.21(d, 3H, *J* = 3.34Hz), δ

1.18(d, 2H, $J = 3.33\text{Hz}$), δ 0.94(m, 9H). CI MS m/z : 207.0788 $[(M+H)^+]$ (calcd for $C_9H_{19}Br$ 207.0779).

3-(3', 5', 5'-trimethylhexyloxy)-propane-1-ol (2):

KOH (2.0 g, 3.6×10^{-2} mol), 1,3-propanediol (9.68 mL, 0.121 mol), and 50 mL DMSO were charged into a reaction flask and purged with bubbling Ar while being cooled in an ice bath for 30 min. Compound 1 (5.0 g, 2.4×10^{-2} mol) was then added drop-wise to the reaction mixture and stirred for 4 hr. Reaction was quenched with water and the organic phase diluted with CH_2Cl_2 (100 mL) and washed with NH_4Cl (aq), $NaHCO_3$ (aq), and NaCl (aq) and the organic layer collected and dried with $CaCl_2$. The organic layer was then filtered and the solvent removed via vacuum leaving a pale yellow residue. Compound 2 was purified by silica gel chromatography using CH_2Cl_2 . The second band was collected yielding 4.76 g (98% based on Compound 1 starting material). 1H NMR (250 MHz, $CDCl_3$): δ 3.77(dd, 2H, $J = 5.36\text{Hz}$), δ 3.61 (t, 2H, $J = 5.73\text{Hz}$), δ 3.44(t, 2H, $J = 5.68\text{Hz}$), δ 2.57(t, 2H, $J = 5.32\text{Hz}$), δ 1.82(p, 1H, $J = 5.61\text{Hz}$), δ 1.56(m, 2H), δ 1.44(m, 2H), δ 1.24(d, 3H, $J = 3.20\text{Hz}$), δ 1.18(d, 2H, $J = 3.33\text{Hz}$), δ 0.882(m, 9H). CI MS m/z : 203.2012 $[(M+H)^+]$ (calcd for $C_{12}H_{26}O_2$ 203.201).

3-(3', 5', 5'-trimethylhexyloxy)-propane aldehyde (3):

PCC (4.342 g, 2.013×10^{-2} mol) was dissolved in 100 mL of CH_2Cl_2 and degassed with purging Ar for 15 min while stirring at room temperature. Compound 2 was syringed into the reaction flask causing an instant color change from pale orange to dark brown. The reaction mixture was stirred for 3 hr and

then was diluted with ethyl ether and passed through a silica gel plug. A second plug was done if oil appeared turbid. Solvent removed via vacuum leaving behind a clear oil. Yield = 3.4727 g (95% based on Compound 2 starting material). ^1H NMR (250 MHz, CDCl_3): δ 9.79(t, 1H, $J = 1.84\text{Hz}$), δ 3.75(m, 2H), δ 3.50(m, 2H), δ 2.66(m, 2H), δ 1.86(m, 1H), δ 1.56(m, 2H), δ 1.40(m, 2H), δ 1.20(m, 3H), δ 1.06(m, 2H), δ 0.88(m, 9H). CI MS m/z : 201.1848 $[(\text{M}+\text{H})^+]$ (calcd $\text{C}_{12}\text{H}_{24}\text{O}_2$ for 200.1776).

5,15-bis[2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl]porphyrin (4):

2,2'-dipyrrylmethane (4.58 g, 3.14×10^{-2} mol) and compound 3 (6.34 g, 3.14×10^{-2} mol) were dissolved in 4 L HPLC grade CH_2Cl_2 and purged with Ar for 1 hour before TFA (0.6 mL, 7.78×10^{-3} mol) was added via syringe. The reaction mixture was stirred for 20 hours at room temperature. Chloranil (11.61 g, 4.72×10^{-2} mol) was added to the reaction mixture and stirred for an additional 4 hours. The reaction mixture was passed through a silica plug to remove polymer and flushed with CHCl_3 and porphyrin collected. Solvent was removed via vacuum and the dark red residue was chromatographed on silica gel using 1:4 THF:Hexanes as the eluent. Yield= 1.43 g (14% based on 2 equivalents of aldehyde). ^1H NMR (250 MHz, CDCl_3): δ 10.17(s, 2H), δ 9.62(d, 4H, $J = 4.73\text{Hz}$), δ 9.41(d, 4H, $J = 4.63\text{Hz}$), δ 5.31(t, 4H, $J = 13.16\text{Hz}$), δ 4.46(t, 4H, $J = 7.65\text{Hz}$), δ 3.59(t, 4H, $J = 9.04\text{Hz}$), δ 1.161(m, 4H), δ 1.53.(m, 4H), δ 1.27(m, 4H), δ 1.21(m, 6H), δ 1.08(m, 4H), δ 1.00(m, 2H), δ 0.93(m, 18H), δ -3.09(ms, 2H). Vis (CHCl_3):

406, 504, 537, 573, 629 nm. ESI MS m/z : 673.4435 $[M+Na^+]$ (calcd for $C_{42}H_{58}N_4O_2$ 673.4460).

(5,15-bis[2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl]porphinato)zinc(II) (5):

Compound 4 (200 mg, 3.07×10^{-4} mol) was dissolved in 150 mL HPLC grade $CHCl_3$ with 1 mL of TEA. The reaction mixture was heated to reflux and then Zn acetate dihydrate (337 mg, 1.54×10^{-3} mol) was added and the reaction was allowed to stir for 2 hrs. After cooling reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried with $CaCl_2$. Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:4 THF:Hexanes as the eluent. Yield = 213 mg (97% yield based on Compound 4 starting material). 1H NMR (250 MHz, $CDCl_3$): δ 10.07(s, 2H), δ 9.71(d, 4H, J = 4.75Hz), δ 9.40(d, 4H, J = 4.45Hz), δ 5.41(t, 4H, J = 7.86Hz), δ 4.52(t, 4H, J = 7.88Hz), δ 3.65(m, 4H), δ 1.63(m, 4H), δ 1.57(m, 4H), δ 1.29(m, 4H), δ 1.22(m, 4H), δ 1.09(m, 2H), δ 0.93(m, 18H). Vis (THF): 410, 546, 579 nm. ESI MS m/z : 712.3682 $[(M)^+]$ (calcd for $C_{42}H_{56}N_4O_2Zn$ 712.3695).

5-Bromo-10,20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphyrin (6)⁵:

Compound 4 (250 mg, 3.841×10^{-4} mol) was dissolved in $CHCl_3$:MeOH (9:1) and cooled to $-5^\circ C$. N-bromosuccinimide (65.3 mg, 3.841×10^{-4} mol) was dissolved in $CHCl_3$:MeOH (9:1) added to the reaction mixture and stirred at $-5^\circ C$ for 10 min. The reaction was poured through water in a separatory funnel followed by $NaCl$ (aq) washing x3. The organic layer was collected and dried

over CaCl_2 and then filtered followed by solvent removal via vacuum. The residue was then purified by silica gel chromatography 1:4 THF:Hexanes. The first band collected was 5,15-dibromo-10,20-bis(3,5,5-trimethylhexyl-ethyleneglycol)porphyrin (compound 7) (89.7 mg, 15 % based on Compound 4). The second band collect was compound 6 (129 mg, 65 % based on compound 5). ^1H NMR (500 MHz, CDCl_3): δ 9.85(s, 1H), δ 9.71(d, 2H, $J = 4.86\text{Hz}$), δ 9.43(d, 2H, $J = 4.67\text{Hz}$), δ 9.19(d, 2H, $J = 4.56\text{Hz}$), δ 5.11(t, 4H, $J = 7.70\text{Hz}$), δ 4.37(t, 4H, $J = 7.69\text{Hz}$), δ 3.54(t, 4H, $J = 7.61\text{Hz}$), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H), δ -3.80(s, 2H). Vis (CHCl_3): 417, 511, 544, 587, 644 nm. ESI MS m/z : 729.3773 $[(M+H)^+]$ (calcd for $\text{C}_{42}\text{H}_{57}\text{BrN}_4\text{O}_2$ 729.3743)

5,15-dibromo-10,20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphyrin (7):

^1H NMR (500 MHz, CDCl_3): δ 9.40(d, 4H, $J = 4.68\text{Hz}$), δ 9.17(d, 4H, $J = 4.05\text{Hz}$), δ 4.88(t, 4H, $J = 6.30\text{Hz}$), δ 4.22(t, 4H, $J = 7.49\text{Hz}$), δ 5.11(t, 4H, $J = 7.70\text{Hz}$), δ 4.37(t, 4H, $J = 7.69\text{Hz}$), δ 3.54(t, 4H, $J = 7.61\text{Hz}$), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H), δ -4.13(s, 2H). Vis (CHCl_3): 424, 520, 556, 599, 658 nm. ESI MS m/z : 807.2836 $[(M+H)^+]$ (calcd for $\text{C}_{42}\text{H}_{56}\text{Br}_2\text{N}_4\text{O}_2$ 807.2848).

(5-Bromo-10, 20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphinato)zinc(II) (8):

Compound 6 (200 mg, 3.07×10^{-4} mols) was dissolved in 150 mL HPLC grade CHCl_3 with 1 mL of TEA. The reaction mixture was heated to reflux and

then Zn acetate dihydrate (337 mg, 1.54×10^{-3} mol) was added and the reaction was allowed to stir for an additional 2 hrs. After cooling, the reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried with CaCl_2 . Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:4 THF:Hexanes as the eluent. Yield = 233 mg (96% based on compound 6). ^1H NMR (500 MHz, CDCl_3): δ 9.92(s, 1H), δ 9.79(d, 2H, $J = 4.79\text{Hz}$), δ 9.60(d, 2H, $J = 4.57\text{Hz}$), δ 9.29(d, 2H, $J = 4.47\text{Hz}$), δ 5.11(t, 4H, $J = 7.70\text{Hz}$), δ 4.37(t, 4H, $J = 7.69\text{Hz}$), δ 3.54(t, 4H, $J = 7.61\text{Hz}$), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H). Vis (THF): 419, 556, 595 nm. ESI MS m/z : 813.2694 $[(\text{M}+\text{Na})^+]$ (calcd for $\text{C}_{42}\text{H}_{55}\text{BrN}_4\text{O}_2\text{Zn}$ 790.2800).

(5,15-dibromo-10, 20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphinato)zinc(II) (9):

Compound 7 (200 mg, 3.07×10^{-4} mols) was dissolved in 150 mL HPLC grade CHCl_3 with 1 mL of TEA. The reaction mixture was warmed to reflux and then Zn acetate dihydrate (337 mg, 1.54×10^{-3} mol) was added and the reaction was allowed to stir for an additional 2 hrs. After cooling the reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried with CaCl_2 . Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:3 THF:Hexanes as the eluent. Yield = 249 mg (97% based on Compound 7). ^1H NMR (500 MHz, CDCl_3): δ 9.69(d, 4H, $J = 4.70\text{Hz}$), δ 9.50(d, 4H, $J =$

4.70Hz), δ 4.88(t, 4H, J = 6.30Hz), δ 4.22(t, 4H, J = 7.49Hz), δ 4.11(t, 4H, J = 7.70Hz), δ 4.37(t, 4H, J = 7.69Hz), δ 3.54(t, 4H, J = 7.61Hz), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H). Vis (CHCl₃): 426, 559, 601 nm. MALDI-TOF MS m/z : 872.5302 [(M)⁺] (calcd for C₄₂H₅₄Br₂N₄O₂Zn 872.1018).

(5-(trimethylsilyl)ethynyl-10,20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphinato)zinc(II) (10):

THF (10 mL) and (trimethylsilyl)acetylene (0.143 mL, 1.01×10^{-3} mol) were added to a 100 mL Schlenk flask, stirred, and cooled to -78 °C. nBuLi (1.6 M solution in hexanes, 0.633 mL, 1.01×10^{-3} mol) was added via syringe dropwise and the reaction mixture stirred for 30 min under Ar. The reaction mixture was warmed to room temperature and a THF (30 mL) solution of ZnCl₂ (138 mg, 1.01×10^{-3} mols) was added via canula creating a cloudy white solution. The reaction was stirred for 15 min and then canula transferred to a 250 mL reaction flask charged with compound 6 (200 mg, 2.53×10^{-4} mol) and Pd(PPh₃)₄ (29 mg, 2.5×10^{-5} mol). The reaction mixture was stirred at 60 °C under Ar for 8 hours and then quenched with water and extracted with CHCl₃ and washed with NaCl (aq) \times 3. The organic layer was extracted and dried over CaCl₂, filtered and solvent removed via vacuum. The crude product was chromatographed on silica gel using 1:4 THF:Hexanes. Yield = 194 mg (95% based on compound 6). ¹H NMR (500 MHz, CDCl₃): δ 9.94(s, 1H), δ 9.78(d, 2H, J = 4.36Hz), δ 9.61(d, 2H, J = 4.45Hz), δ 9.57(d, 2H, J = 4.40Hz), δ 9.28(d, 2H, J = 4.41Hz), δ 5.28(t, 4H, J =

7.95Hz), δ 4.45(t, 4H, J = 8.28Hz), δ 3.60(t, 4H, J = 6.67Hz), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.30(m, 4H), δ 1.19(m, 2H), δ 1.09(m, 2H), δ 0.87(m, 18H), δ 0.63(m, 9H). Vis (CHCl₃): 427, 554, 594 nm. ESI MS m/z : 831.4008 [(M+Na)⁺] (calcd for C₄₇H₆₄N₄O₂SiZn 831.3990).

(5,15-bis(triisopropylsilylethynyl)-10,20-bis(2'-(3'', 5'', 5'')-trimethylhexyloxy)-ethyl)porphinato)zinc(II) (11):

Compound 7 (270 mg, 3.10×10^{-4} mol) was charged into a 100 mL Schlenk tube and PdCl₂(PPh₃)₂ (65 mg, 1.6×10^{-5} mol) and CuI (18 mg, 9.3×10^{-5} mol) were added in the glovebox. A THF:TEA (30 mL, 9:1) was degassed with Ar purge for 30 min and then canula into the reaction flask while (triisopropylsilyl)acetylene (0.35 mL, 1.6×10^{-3} mol) was added via syringe. The reaction mixture was heated to 60 °C and stirred under Ar overnight. The reaction was quenched with water and diluted with CHCl₃ and washed with NH₄Cl (aq) x 3. The organic layer was extracted and dried over Na₂SO₄, filtered, and solvent removed via vacuum. The crude product was purified on silica gel using 1:4 THF:Hexanes. Yield = 307 mg (92% based on Compound 7). ¹H NMR (500 MHz, CDCl₃): δ 9.72(d, 4H, J = 4.47Hz), δ 9.51(d, 4H, J = 4.52Hz), δ 5.28(t, 4H, J = 7.95Hz), δ 4.45(t, 4H, J = 8.28Hz), δ 3.60(t, 4H, J = 6.67Hz), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.40(m, 18H), δ 1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H). Vis (THF): 439, 586, 640 nm. MALDI-TOF MS m/z : 1075.8249 [(M)⁺] (calcd for C₆₄H₅₆N₄O₂Si₂Zn 1072.6363).

(5-ethynyl-10,20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphinato)zinc(II) (12):

Tetrabutylammonium fluoride (0.1 M in THF, 5.22 mL, 5.22×10^{-4} mol) was added to a solution of 10 (282 mg, 3.48×10^{-4} mol) in 40 mL of THF cooled to 0 °C. The reaction mixture was stirred for 15 min and then directly poured down a short silica gel column with CHCl_3 as the eluent. Yield = 153 mg (65% based on compound 10). ^1H NMR (500 MHz, CDCl_3): δ 9.95(s, 1H), δ 9.81(d, 2H, J = 4.56Hz), δ 9.63(d, 2H, J = 4.50Hz), δ 9.58(d, 2H, J = 4.41Hz), δ 9.29(d, 2H, J = 4.48Hz), δ 5.30(t, 4H, J = 7.99Hz), δ 4.47(t, 4H, J = 4.16Hz), δ 4.17(s, 1H), δ 3.63(t, 4H, J = 8.28Hz), δ 1.62(m, 4H), δ 1.45(m, 4H), δ 1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H). Vis (THF): 424, 559, 604 nm. ESI MS m/z : 675.4646 $[(M+H)^+]$ (calcd for $\text{C}_{64}\text{H}_{56}\text{N}_4\text{O}_2\text{Zn}$ 675.4640).

(5,15-bis-ethynyl-10,20-bis(2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphinato)zinc(II) (13):

Tetrabutylammonium fluoride (0.1 M in THF, 4.43 mL, 4.43×10^{-4} mol) was added to a solution of 11 (307 mg, 4.03×10^{-4} mol) in 20 mL of THF and cooled to 0 °C. The reaction mixture was stirred for 15 min and then directly poured down a short silica gel column with CHCl_3 as the eluent. Yield = 258 mg (84% based on compound 11). ^1H NMR (500 MHz, CDCl_3): δ 9.66(d, 4H, J = 4.41Hz), δ 9.46(d, 4H, J = 4.23Hz), δ 5.15(t, 4H, J = 7.60Hz), δ 4.35(d, 4H, J = 7.79Hz), δ 4.17(s, 8H), δ 3.63(t, 4H, J = 8.28Hz), δ 1.62(m, 4H), δ 1.45(m, 4H), δ

1.30(m, 4H), δ 1.19(m, 4H), δ 1.09(m, 2H), δ 0.87(m, 18H). Vis (THF): 432, 578, 629 nm. ESI MS m/z : 760.40 $[(M)^+]$ (calcd for $C_{46}H_{56}N_4O_2Zn$ 760.3695).

1,2-bis[(10',20'-bis(2''-(3''', 5''', 5'''-trimethylhexyloxy)-ethyl)porphinato)zinc(II)-5'-yl]ethyne PZn₂-O1 (14):

Compounds 6 (53 mg, 6.74×10^{-5} mol) and 12 (50 mg, 7.4×10^{-5} mol) were charged into a 100 mL Schlenk tube along with Pd_2dba_3 (9 mg, 1×10^{-5} mol) and $AsPh_3$ (26 mg, 8.1×10^{-5} mol) which were added in the glovebox. Previously, degassed THF:TEA (9:1) solution was then canula into the reaction flask and the reaction mixture was stirred at 60 °C overnight. The following morning the reaction was quenched with water and then the organics were extracted with $CHCl_3$ and washed with NH_4Cl (aq) x 3. The organic layer was collected and dried with $CaCl_2$, filtered, and solvent removed via vacuum. Compound 17 was purified by silica gel column chromatography using 1:3 THF:Hexanes as the eluent. Yield = 84 mg (86% based on compound 6). 1H NMR (500 MHz, $CDCl_3$): δ 10.56(d, 4H, $J = 4.40Hz$), δ 9.97(s, 2H), δ 9.84(d, 4H, $J = 4.65Hz$), δ 9.64(d, 4H, $J = 4.40Hz$), δ 9.33(d, 4H, $J = 4.45Hz$), δ 5.38(t, 8H, $J = 7.94Hz$), δ 4.56(t, 8H, $J = 8.10Hz$), δ 3.67(m, 8H), δ 1.62(m, 8H), δ 1.45(m, 8H), δ 1.30(m, 8H), δ 1.19(m, 12H), δ 1.09(m, 4H), δ 0.87(m, 36H). Vis (THF): 414, 427, 478, 562, 700 nm. MALDI-TOF MS m/z : 1448.7102 $[(M)^+]$ (calcd for $C_{86}H_{110}N_8O_4Zn_2$ 1446.7233).

1,2-bis[5'-bromo(5',5''-10,20-bis(2''-(3'', 5'', 5''-trimethylhexyloxy)-ethyl)porphinato)zinc(II)]ethyne (15):

Isolated from second size exclusion band from the synthesis of compound 16. Yield = 22 mg (30 %). ^1H NMR (500 MHz, CDCl_3): δ 10.51(d, 2H, J = 4.30 Hz), δ 10.47 (d, 2H, J = 4.55 Hz), δ 9.97(s, 1H), δ 9.83(d, 2H, J = 4.35Hz), δ 9.75(d, 2H, J = 4.75Hz), δ 9.72(d, 2H, J = 4.70Hz), δ 9.55(d, 2H, J = 4.50Hz), δ 5.32(t, 8H, J = 7.50Hz), δ 4.49(t, 8H, J = 7.80Hz), δ 3.67(m, 8H), δ 2.01(m, 8H), δ 1.62(m, 8H), δ 1.45(m, 8H), δ 1.30(m, 8H), δ 1.19(m, 12H), δ 1.09(m, 4H), δ 0.87(m, 36H). Vis (THF): 412, 485, 705 nm. MALDI-TOF MS m/z : 1522.08 [(M) $^+$] (calcd for $\text{C}_{86}\text{H}_{109}\text{N}_8\text{O}_4\text{BrZn}_2$ 1524.63).

5,15-bis[[5',-10',20'-bis([2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl]porphinato)zinc(II)]ethynyl]-10,20-bis([2'-(3'', 5'', 5''-trimethylhexyloxy)-ethyl]porphinato)zinc(II) PZn₃-O1 (16):

Compound 7 (71 mg, 8.1×10^{-5} mol) and 11 (132 mg, 1.79×10^{-4} mo) were charged into a 100 mL Schlenk tube along with Pd_2dba_3 (25 mg, 2.7×10^{-5} mol) and AsPh_3 (70 mg, 2.2×10^{-4} mol). Previously degassed solution of THF:TEA (9:1) were then canula into the reaction flask and heated to 60 °C and stirred overnight under Ar. The reaction was quenched with water and diluted with CHCl_3 and washed with NH_4Cl (aq) 3 x. The organic layer was collected and dried with Na_2SO_4 , filtered, and solvent removed via vacuum. The residue was then put down a silica gel plug using CHCl_3 :Pyridine (99:1) as the eluent to remove catalyst. Solvent was removed by vacuum and then purified by gravimetric size exclusion column (THF as the eluent). The fastest moving band was collected and solvent removed by vacuum. A final silica gel plug was done to remove

residual biobeads using CHCl_3 :Pyridine (99:1) as the eluent. Yield = 137 mg (77% based on compound 7). ^1H NMR (500 MHz, CDCl_3): δ 10.56(d, 4H, J = 4.15Hz), δ 10.49(d, 4H, J = 4.05 Hz), δ 9.96(s, 2H), δ 9.84(d , 4H, J = .3 85Hz), δ 9.77(d , 4H, J = 4.45Hz), δ 9.63(d, 4H, J = 4.30Hz), δ 9.32(d, 4H, J = 4.10Hz), δ 5.38 (br-m, 12H), δ 4.63(t, 12H, J = 8.05Hz), δ 4.57(t, 12H, J = 8.06Hz), δ 3.74(t, 12H, J = 6.55Hz), δ 3.69(t, 12H, J = 5.47Hz), δ 1.62(m, 12H), δ 1.45(m, 12H), δ 1.30(m, 12H), δ 1.19(m, 20H), δ 1.09(m, 6H), δ 0.87(m, 72H). Vis (THF): 414, 494, 574, 774 nm. MALDI-TOF MS m/z : 2182.9642 $[(M)^+]$ (calcd for $\text{C}_{130}\text{H}_{164}\text{N}_{12}\text{O}_6\text{Zn}_3$ 2181.0771).

(5,15-bis(10,20-bis[2-(3', 5', 5'-trimethylhexyloxy)-ethyl]porphinato)zinc(II)-ethyn-5-yl)-10,20-bis[2-(3', 5', 5'-trimethylhexyloxy)-ethyl]porphinato)zinc(II)-ethyn-5-yl)-10,20-bis[2-(3', 5', 5'-trimethylhexyloxy)-ethyl]porphinato]zinc(II) PZn₅-O1 (17).

Compound 15 (62 mg, 4.1×10^{-5} mol) and compound 13 (15 mg, 2.0×10^{-5} mol) were charged into a 100 mL reaction flask. Pd_2dba_3 (15 mg, 1.6×10^{-5} mol), $\text{P}(\bullet\text{-tolyl})_3$ (15 mg, 4.9×10^{-5} mol), and CuI (1 mg, 4×10^{-5} mol) were add to the reaction flask in a glove box. Previously dried and degassed THF:TEA (9:1) was canula into the reaction flask and heated to 60 °C and stirred for 2 days under Ar. The reaction mixture was cooled to room temperature and passed through a silica gel plug washing with THF:Hexanes (1:1) to remove catalyst and baseline material. The organic residue was dried via vacuum and purified via size exclusion chromatography. The fastest moving band was collected and solvent

removed via vacuum. A silica gel column utilizing CHCl_3 :Pyridine (98:2) as the eluent the first band was isolated yielding compound 17. Yield 42 mg (57% yield based on compound 13). ^1H NMR (500 MHz, CDCl_3): δ 10.56(d, 4H, $J = 4.15\text{Hz}$), δ 10.49(d, 4H, $J = 4.05\text{ Hz}$), δ 9.96(s, 2H), δ 9.84(d , 4H, $J = .3\text{ 85Hz}$), δ 9.77(d , 4H, $J = 4.45\text{Hz}$), δ 9.63(d, 4H, $J = 4.30\text{Hz}$), δ 9.32(d, 4H, $J = 4.10\text{Hz}$), δ 5.38 (br-m, 20H), δ 4.63(t, 20H, $J = 8.05\text{Hz}$), δ 4.57(t, 20H, $J = 8.06\text{Hz}$), δ 3.74(t, 20H, $J = 6.55\text{Hz}$), δ 3.69(t, 20H, $J = 5.47\text{Hz}$), δ 1.62(m, 20H), δ 1.45(m, 20H), δ 1.30(m, 20H), δ 1.19(m, 28H), δ 1.09(m, 10H), δ 0.87(m, 90H). Vis (THF): 414, 505, 846 nm. MALDI-TOF MS m/z : 3646.00 $[(M)^+]$ (calcd for $\text{C}_{218}\text{H}_{272}\text{N}_{20}\text{O}_{10}\text{Zn}_5$ 3649.5703).

PZnO3EHex Series:

2-(2'-(2''-ethylhexyloxy)-ethoxy)ethylbromide (18)⁶:

Triphenylphosphine (55.14 g, 0.21 mol) and di(ethylene glycol) 2-ethylhexyl ether (50 mL, 0.21 mol) were dissolved in 300 mL of CH_2Cl_2 in a 1 L reaction flask and cooled to 0 °C under N_2 . Once cooled, small portions, 5 g, of NBS (37.40 g, 0.21 mol) were added producing heat. Reaction mixture was stirred for 4 hours after the last portion of NBS was added. The solvent was removed via vacuum and taken up in ether and sonicated for 60 min. The mixture was filtered and solvent again removed via vacuum. The reaction was again, taken up in cold ether and filtered. This was repeated until no solid is seen in the remaining oil. Compound 18 was purified by silica gel chromatography using ether as the eluent. Yield = 42.52g (72% based on starting material). ^1H NMR (250 MHz, CDCl_3): δ 3.82(t, 2H, $J = 6.38\text{Hz}$), δ 3.66 (m, 2H,), δ

3.59(m, 2H), δ 3.47(t, 2H, J = 6.36Hz), δ 3.33(d, 2H, J = 5.95Hz), δ 1.50(m, 1H), δ 1.32(m, 8H), δ 0.88(m, 6H). CI MS m/z : 305.0932 $[(M+Na)^+]$ (calcd $C_{12}H_{25}BrO_2$ for 303.0932).

12-ethyl-4, 7, 10-trioxahexadecane-1-ol (19):

KOH (60 g, 1.1 mol), 1,3-propanediol (41 mL, 0.57 mol), and 200 mL of DMSO were charged into a reaction flask and purged with bubbling Ar while being cooled by an ice bath. Compound 18 (31.84 g, 0.11 mol) was then added dropwise to the reaction mixture and stirred for 4 hr. The reaction was quenched with water and the organic phase diluted with CH_2Cl_2 (100 mL) and washed with NH_4Cl (aq), $NaHCO_3$ (aq), and $NaCl$ (aq) and the organic layer collected and dried with $CaCl_2$. The organic layer was then filtered and the solvent removed via vacuum leaving a pale yellow residue. Compound 19 was purified by silica gel chromatography using 1:19 MeOH: $CHCl_3$. Yield = 29.25 g (94% based on compound 18). 1H NMR (250 MHz, $CDCl_3$): δ 4.20(d, 2H, J = 2.04Hz), δ 3.98(dd, 4H, J = 2.00Hz), δ 3.77(m, 2H), δ 3.67(m, 2H), δ 3.57(m, 2H), δ 3.31(t, 2H, J = 6.05Hz), δ 2.59(t, 1H, J = 5.62Hz), δ 1.84(m, 2H), δ 1.52(m, 1H), δ 1.39(m, 8H), δ 0.88(m, 6H). CI MS m/z : 299.2189 $[(M+Na)^+]$ (calcd for $C_{15}H_{32}O_4$ 299.2202).

12-ethyl-4, 7, 10-trioxahexadecane-1-one (20):

PCC (25.13 g, 0.116 mol) was dissolved in 100 mL of CH_2Cl_2 and degassed with purging Ar for 15 min while stirring at room temperature. Compound 19 (29.15, 0.11 mol) was syringed into the reaction flask causing an instant color change from pale orange to dark brown. The reaction was stirred for 3 hr and

then diluted with ethyl ether and passed through a silica gel plug. A second plug was done if oil residue appeared turbid. Solvent removed via vacuum leaving behind a clear oil. Yield = 25.57 g (88% based on compound 19). ^1H NMR (250 MHz, CDCl_3): δ 9.79(t, 1H, $J = 1.70\text{Hz}$), δ 4.20(m, 2H), δ 3.82(m, 4H), δ 3.60(m, 2H), δ 3.32(m, 2H), δ 2.66(m, 2H), δ 1.80(m, 2H), δ 1.51(m, 1H), δ 1.32(m, 8H), δ 0.86(m, 6H). CI MS m/z : 297.2053 $[(\text{M}+\text{Na})^+]$ (calcd for $\text{C}_{15}\text{H}_{30}\text{O}_4$ 297.2040).

5,15-bis(11-ethyl-3, 6, 9-trioxapentadecane-1-yl))porphyrin (21):

2,2'-dipyrrylmethane (4.58 g, 3.14×10^{-2} mol) and compound 20 (8.62 g, 3.14×10^{-2} mol) were dissolved in 4 L HPLC grade CH_2Cl_2 and purged with Ar for 1 hour before TFA (0.6 mL, 7.78×10^{-3} mol) was added via syringe. The reaction mixture was stirred for 12 hours at room temperature in the dark. Chloranil (11.61 g, 4.72×10^{-2} mol) was added to the reaction mixture and stirred for an additional 4 hours. The reaction mixture was passed through a silica plug to remove polymer and flushed with CHCl_3 and porphyrin collected. Solvent was removed via vacuum and the dark red residue was chromatographed on silica gel using 3:7 THF:Hexanes as the eluent. Yield = 113 mg (8% based on compound 20). ^1H NMR (500 MHz, CDCl_3): δ 10.06(s, 2H), δ 9.55(d, 4H, $J = 4.50\text{Hz}$), δ 9.31(d, 4H, $J = 4.45\text{Hz}$), δ 5.24(t, 4H, $J = 7.72\text{Hz}$), δ 4.51(t, 4H, $J = 7.60\text{Hz}$), δ 3.82(m, 4H), δ 3.60(m, 4H), δ 3.32(m, 4H), δ 2.66(m, 4H), δ 1.80(m, 4H), δ 1.51(m, 2H), δ 1.32(m, 16H), δ 0.86(m, 12H), δ -3.40 (s, 2H). Vis (CHCl_3):

404, 503, 534, 577, 631 nm. ESI MS m/z : 821.5198 $[(M+Na)^+]$ (calcd for $C_{48}H_{70}N_4O_6$ 798.5295).

5,15-bis([11-ethyl-3, 6, 9-trioxapentadecane-1-yl]porphyrinato)Zn(II) PZn-O3EHex (22)

5,15-bis(11-ethyl-3, 6, 9-trioxapentadecane-1-yl))porphyrin (200 mg, 0.250 mmol) was dissolved in 150 mL HPLC grade $CHCl_3$ with 1 mL of TEA. The reaction mixture was heated to reflux and then Zinc acetate dihydrate (274 mg, 1.25 mol) was added and the reaction was allowed to stir for 2 hrs. After cooling, the reaction mixture was washed with NH_4Cl (aq) \times 3 and the organic layer was collected and dried with $CaCl_2$. Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 3:7 THF:Hexanes as the eluent. Yield = 203 mg (92% yield based on Compound 21 starting material). 1H NMR (500 MHz, $CDCl_3$): δ 10.06(s, 2H), δ 9.55(d, 4H, $J = 4.50Hz$), δ 9.31(d, 4H, $J = 4.45Hz$), δ 5.24(t, 4H, $J = 7.72Hz$), δ 4.51(t, 4H, $J = 7.60Hz$), δ 3.82(m, 4H), δ 3.60(m, 4H), δ 3.32(m, 4H), δ 2.66(m, 4H), δ 1.80(m, 4H), δ 1.51(m, 2H), δ 1.32(m, 16H), δ 0.86(m, 12H). Vis (THF): 410, 546, 579 nm. ESI MS m/z : 883.4288 $[(M+Na)^+]$ (calcd for $C_{48}H_{68}N_4O_6Zn$ 883.4333).

5-Bromo-10,20-bis(11-ethyl-3, 6, 9-trioxapentadecane-1-yl)porphyrin (23):

Compound 21 (234.6 mg, 2.886×10^{-4} mol) was dissolved in $CHCl_3$:MeOH (9:1) and cooled to $-5^\circ C$. N-bromosuccinimide (54 mg, 3.2×10^{-4} mol) was added to the reaction mixture and stirred at $-5^\circ C$ for 10 min and then allowed to cool to

room temperature. Once at room temperature the reaction was poured into water followed by NaCl (aq) washing x 3. The organic layer was collected and dried over CaCl₂ and then filtered followed by solvent removal via vacuum. The residue was then purified by silica gel chromatography 1:9 THF: (CHCl₃:Hexanes 1:1). The first band collect was 5,15-dibromo-10,20-bis(2-ethylhexyl-triethyleneglycol)porphyrin, compound 24. Yield = 110 mg(20% based on compound 21). Second band collect was compound 23. Yield = 139 mg (68% based on compound 21). ¹H NMR (250 MHz, CDCl₃): δ 10.07(s, 1H), δ 9.80(d, 2H, *J* = 4.93Hz), δ 9.53(d, 4H, *J* = 4.95Hz), δ 9.29(d, 2H, *J* = 4.65Hz), δ 5.25(t, 4H, *J* = 7.13Hz), δ 4.49(t, 4H, *J* = 7.52Hz), δ 3.68(m, 4H), δ 3.55(m, 4H), δ 3.45(m, 4H), δ 3.21(m, 4H), δ 1.22(m, 16H), δ 0.84(m, 12H), δ -3.10(s, 2H). Vis (CHCl₃): 414, 512, 544, 590, 648 nm. MS *m/z*: 899.6327 [(M+Na)⁺] (calcd for C₄₈H₆₉BrN₄O₆ 876.4400).

5,15-dibromo-10,20-bis (11-ethyl-3, 6, 9-trioxapentadecane-1-yl)porphyrin (24):

¹H NMR (250 MHz, CDCl₃): δ 9.58(d, 4H, *J* = 4.93Hz), δ 9.36(d, 4H, *J* = 4.95Hz), δ 5.07(t, 4H, *J* = 7.46Hz), δ 4.43(t, 4H, *J* = 8.49Hz), δ 3.66(m, 4H), δ 3.55(t, 4H, *J* = 4.80Hz), δ 3.19(m, 4H), δ 1.22(m, 16H), δ 0.84(m, 12H), δ -3.39(s, 2H). Vis (CHCl₃): 420, 522, 556, 602, 664 nm.

(5-Bromo-10,20-bis(2-ethylhexyl-triethyleneglycol)porphinato)zinc(II) (25):

Compound 23 (150 mg, 1.71 x 10⁻⁴ mol) was dissolved in 150 mL of HPLC grade CHCl₃ with 1 mL of TEA. The reaction mixture was warmed to reflux and then Zn acetate dihydrate (188 mg, 8.55 x 10⁻⁴ mol) was added and the reaction

was allowed to stir for an additional 2 hrs. After cooling the reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried with CaCl_2 . Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:3 THF:Hexanes as the eluent. Yield = 148 mg (92% based on compound 23). ^1H NMR (500 MHz, CDCl_3): δ 9.94(s, 1H), δ 9.78(d, 2H, J = 4.67Hz), δ 9.61(d, 2H, J = 4.68Hz), δ 9.30(d, 2H, J = 4.44Hz), δ 5.31(t, 4H, J = 7.92Hz), δ 4.51(t, 4H, J = 7.90Hz), δ 3.68(m, 4H), δ 3.55(m, 4H), δ 3.45(m, 4H), δ 3.21(m, 4H), δ 1.22(m, 16H), δ 0.84(m, 12H). Vis (CHCl_3): 418, 547, 580 nm. ESI MS m/z : 963.3438 $[(M+\text{Na})^+]$ (calcd for $\text{C}_{48}\text{H}_{67}\text{BrN}_4\text{O}_6\text{Zn}$ 968.3595).

(5,15-dibromo-10,20-bis(11'-ethyl-3',6',9'-trioxapentadecane-1'-yl)porphinato)zinc(II) (26):

Compound 24 (100 mg, 1.05×10^{-4} mols) was dissolved in 150 mL of HPLC grade CHCl_3 with 1 mL of TEA. The reaction mixture was warmed to reflux and then Zn acetate dihydrate (115 mg, 5.25×10^{-4} mol) was added and the reaction was allowed to stir for an additional 2 hrs. After cooling the reaction mixture was washed with NH_4Cl (aq) x 3 and the organic layer was collected and dried with CaCl_2 . Organics were filtered and solvent removed via vacuum leaving behind a red organic residue. The residue was chromatographed on silica gel using 1:3 THF:Hexanes as the eluent. Yield = 99 mg (93% based on compound 24). ^1H NMR (250 MHz, CDCl_3): δ 9.68(d, 4H, J = 4.93Hz), δ 9.51(d, 4H, J = 4.78Hz), δ 5.23(t, 4H, J = 7.77Hz), δ 4.45(t, 4H, J = 3.91Hz), δ 3.68(m, 4H), δ 3.55(

m, 4H), δ 3.45(m, 4H), δ 3.21(m, 4H), δ 1.22(m, 16H), δ 0.84(m, 12H). Vis (CHCl₃): 426, 559, 602 nm. MALDI-TOF MS m/z: 1018.0319 [(M)⁺] (calcd for C₄₈H₆₆Br₂N₄O₆Zn 1018.2797).

(5-Trimethylsilylethynyl-10,20-bis(11'-ethyl-3',6',9'-trioxapentadecane-1'-yl)porphinato)zinc(II) (27):

THF (10 mL) and (trimethylsilyl)acetylene (0.1 mL, 6×10^{-4} mol) were added to a 100 mL Schlenk flask, stirred, and cooled to -78 °C. *n*-BuLi (1.6 M solution in hexanes, 0.396 mL, 6.34×10^{-4} mol) was added via syringe dropwise and the reaction mixture stirred for 30 min under Ar. The reaction mixture was warmed to room temperature and a THF (30 mL) solution of ZnCl₂ (86 mg, 6.3×10^{-4} mol) was added via canula creating a cloudy white solution. The reaction was stirred for 15 min and then canula transferred to a 250 mL reaction flask charged with compound 25 (142 mg, 1.51×10^{-4} mol) and Pd(PPh₃)₄ (17 mg, 1.5×10^{-5} mol). The reaction mixture was stirred at 50 °C under Ar for 8 hours and then quenched with water and extracted with CHCl₃ and washed with NaCl (aq) x 3. The organic layer was extracted and dried over CaCl₂, filtered and solvent removed via vacuum. The crude product was chromatographed on silica gel using 1:4 THF:Hexanes. Yield = 139 mg (96% based on compound 25). ¹H NMR (250 MHz, CDCl₃): δ 9.95(s, 1H), δ 9.76(d, 2H, $J = 4.55$ Hz), δ 9.59(d, 4H, $J = 4.88$ Hz), δ 9.57(d, 2H, $J = 5.33$ Hz), δ 9.28(d, 2H, $J = 4.45$ Hz), δ 5.31(t, 4H, $J = 7.75$ Hz), δ 4.51(t, 4H, $J = 7.71$ Hz), δ 3.69(m, 4H), δ 3.61(m, 4H), δ 3.52(m, 4H), δ

3.27(m, 4H), δ 1.24(m, 2H), δ 0.82(m, 16H), δ 0.62(s, 12H). Vis (THF): 428, 562, 610 nm. MS m/z: 979.4696 [(M+Na)⁺] (calcd for C₅₃H₇₆N₄O₆SiZn 979.4726).

(5,15-bis(triisopropylsilylethynyl)-10,20-bis(11'-ethyl-3',6',9'-trioxapentadecane-1'-yl)porphinato)zinc(II) (28):

Compound 24 (131 mg, 1.28 x 10⁻⁴ mol) was charged into a 100 mL Schlenk tube and PdCl₂(PPh₃)₂ (13.5 mg, 1.92 x 10⁻⁵ mol) and CuI (4 mg, 2 x 10⁻⁵ mol) were added in the glovebox. A THF:TEA (30 mL, 9:1) solution was degassed with Ar purge for 30 min and then canula into the reaction flask while (triisopropylsilyl) acetylene (0.01 mL, 3 x 10⁻⁴ mol) was added via syringe. The reaction mixture was heated to 60 °C and stirred under Ar overnight. Reaction was quenched with water and diluted with CHCl₃ and washed with NH₄Cl (aq) x 3. The organic layer was extracted and dried over Na₂SO₄, filtered, and solvent removed via vacuum. The crude product was purified on silica gel using 1:3

THF:Hexanes. Yield = 138 mg (88% based on compound 24). ¹H NMR (500 MHz, CDCl₃): δ 9.68(d, 4H, *J* = 4.47Hz), δ 9.41(d, 4H, *J* = 4.63Hz), δ 5.12(t, 4H, *J* = 7.50Hz), δ 4.37(t, 4H, *J* = 7.26Hz), δ 3.55(t, 4H, *J* = 4.01Hz), δ 3.46(t, 4H, *J* = 4.84Hz), δ 3.08(t, 4H, *J* = 4.63Hz), δ 2.89(t, 4H, *J* = 4.64Hz), δ 1.50 (m, 42H), δ 1.28(m, 16H), δ 0.89(m, 12H). Vis (THF): 439, 586, 640 nm. MALDI-TOF MS m/z: 1220.8239 [(M)⁺] (calcd for C₇₀H₁₀₈N₄O₆Si₂Zn 1220.7099).

(5-ethynyl-10,20-bis(11'-ethyl-3',6',9'-trioxapentadecane-1'-yl)porphinato)zinc(II) (29):

Tetrabutylammonium fluoride (0.1 M in THF, 3.83 mL, 3.83×10^{-4} mol) was added to a solution of compound 27 (282 mg, 3.48×10^{-4} mol) in 40 mL of THF cooled to 0 °C. The reaction mixture was stirred for 15 min and then directly poured down a short silica gel column with CHCl_3 as the eluent. Yield = 246 mg (80% based on compound 27). ^1H NMR (500 MHz, CDCl_3): δ 9.98(s, 1H), δ 9.80(d, 2H, $J = 4.70\text{Hz}$), δ 9.62(d, 2H, $J = 4.52\text{Hz}$), δ 9.59(d, 2H, $J = 5.59\text{Hz}$), δ 9.31(d, 2H, $J = 4.45\text{Hz}$), δ 5.12(t, 4H, $J = 7.50\text{Hz}$), δ 4.37(t, 4H, $J = 7.26\text{Hz}$), δ 4.12(s, 1H), δ 3.55(t, 4H, $J = 4.01\text{Hz}$), δ 3.46(t, 4H, $J = 4.84\text{Hz}$), δ 3.08(t, 4H, $J = 4.63\text{Hz}$), δ 2.89(t, 4H, $J = 4.64\text{Hz}$), δ 1.28(m, 16H), δ 0.89(m, 12H). Vis (CHCl_3): 422, 552, 590 nm. MS m/z : 907.4291 $[(M+\text{Na})^+]$ (calcd for $\text{C}_{50}\text{H}_{68}\text{N}_4\text{O}_6\text{Zn}$ 907.4330).

(5,15-diethynyl-10,20-bis(11'-ethyl-3',6',9'-trioxapentadecane-1'-yl)porphinato)zinc(II) (30):

Tetrabutylammonium fluoride (0.1 M in THF, 9 mL, 9×10^{-5} mol) was added to a solution of compound 28 (100 mg, 8.19×10^{-5} mol) in 40 mL of THF cooled to 0 °C. The reaction mixture was stirred for 15 min and then directly poured down a short silica gel column with CHCl_3 as the eluent. Yield = 77 mg (94% based on compound 28). ^1H NMR (500 MHz, CDCl_3): δ 9.80(d, 4H, $J = 4.70\text{Hz}$), δ 9.62(d, 4H, $J = 4.52\text{Hz}$), δ 9.59(d, 2H, $J = 5.59\text{Hz}$), δ 9.31(d, 2H, $J = 4.45\text{Hz}$), δ 5.12(t, 4H, $J = 7.50\text{Hz}$), δ 4.37(t, 4H, $J = 7.26\text{Hz}$), δ 4.14(s, 2H), δ 3.55(t, 4H, $J = 4.01\text{Hz}$), δ 3.46(t, 4H, $J = 4.84\text{Hz}$), δ 3.08(t, 4H, $J = 4.63\text{Hz}$), δ 2.89(t, 4H, $J = 4.64\text{Hz}$), δ 1.28(m, 16H), δ 0.89(m, 12H). Vis (THF): 433, 578, 629 nm. MALDI-TOF MS m/z : 909.3127 $[(M+\text{Na})^+]$ (calcd for $\text{C}_{52}\text{H}_{68}\text{N}_4\text{O}_6\text{Zn}$ 908.4430).

5,15-bis[[5',-10',20'-bis([11''-ethyl-3'',6'',9''-trioxapentadecane-1-yl]porphinato)zinc(II)]ethynyl]-10,20-bis([11''-ethyl-3'',6'',9''-trioxapentadecane-1-yl]porphinato)zinc(II) PZn₃-O3EHex (32):

Compound 27 (46.2 mg, 5.21×10^{-5} mol) and 25 (24.2 mg, 2.37×10^{-5} mol) were charged into a 100 mL Schlenk tube along with Pd₂dba₃ (3 mg, 4×10^{-6} mol) and AsPh₃ (10 mg, 2.8×10^{-5} mol). Previously degassed solution of THF:TEA (9:1) were then canula into the reaction flask and heated to 60 °C and stirred overnight under Ar. The reaction was quenched with water and diluted with CHCl₃ and washed with NH₄Cl (aq) 3 x. The organic layer was collected and dried with Na₂SO₄, filtered, and solvent removed via vacuum. The residue was poured down a silica gel plug using CHCl₃:Pyridine (99:1) as the eluent to remove catalyst. Solvent was removed by vacuum and then purified by gravimetric size exclusion column (Biobeads, SX-1, THF). The fastest moving band was collected and solvent removed by vacuum. A final silica gel plug was done to remove residual biobeads using CHCl₃:Pyridine (99:1) as the eluent. Yield = 48 mg (77% based on compound 25). ¹H NMR (500 MHz, CDCl₃): δ 10.56(d, 4H, *J* = 4.45Hz), δ 10.50(d, 4H, *J* = 4.45Hz), δ 9.98(s, 2H), δ 9.87(d, 4H, *J* = 4.50Hz), δ 9.80(d, 4H, *J* = 4.50Hz), δ 9.66(d, 4H, *J* = 4.40Hz), δ 9.33(d, 4H, *J* = 4.35Hz), δ 5.12(t, 12H, *J* = 7.50Hz), δ 4.37(t, 12H, *J* = 7.26Hz), δ 3.55(t, 12H, *J* = 4.01Hz), δ 3.46(t, 12H, *J* = 4.84Hz), δ 3.08(t, 12H, *J* = 4.63Hz), δ 2.89(t, 12H, *J* = 4.64Hz), δ 1.28(m, 48H), δ 0.89(m, 36H). Vis (THF): 414, 494, 574, 774 nm. MALDI-TOF MS *m/z*: 2623.3485 [(M)⁺] (calcd for C₁₄₈H₂₀₀N₁₂O₁₈Zn₃ 2625.2978).

5,15-bis[[5',-10',20'-bis([11-ethyl-3, 6, 9-trioxapentadecane-1-yl]porphinato)zinc(II)]ethynyl]-10,20-bis([3-(3', 5', 5'-trimethylhexyloxy)-ethyl]porphinato)zinc(II) PZn₃-O3EHexO1O3EHex (33):

Compound 9 (237 mg, 2.7×10^{-4} mol) and compound 29 (120 mg, 1.3×10^{-4} mol) were charged into a 50 mL Schlenk flask. Pd2dba3 and AsPh₃ were then charged into the same reaction flask. 30 mL of THF:TEA (9:1, and degassed by Freeze-Pump-thaw cycles) was cannula into the reaction flask. The reaction stirred for 16 hours under Ar. Once cooled the reaction mixture was diluted with CHCl₃ and washed 3 x with NH₄Cl (aq) and the organic layer collected and dried with Na₂SO₄. The organic layer was filtered and solvent removed via vacuum and the residue subjected to silica gel chromatography using THF:Hex (3:7) as the eluent. One large band was collected and the solvent removed via vacuum and the resulting residue was taken up in THF and further purified via size exclusion chromatography. The first band collect was dried by vacuum and one remaining silica gel column was performed to remove residual biobeads using CHCl₃:MeOH (95:5) as the eluent. ¹H NMR (500 MHz, CDCl₃): δ 10.56(d, 4H, *J* = 4.35Hz), δ 10.50(d, 4H, *J* = 4.45Hz), δ 9.98(s, 2H), δ 9.87(d, 4H, *J* = 4.50Hz), δ 9.80(d, 4H, *J* = 4.50Hz), δ 9.66(d, 4H, *J* = 4.40Hz), δ 9.33(d, 4H, *J* = 4.35Hz), δ 5.41(br, 12H), δ 4.63(br, 12H), δ 3.83(br, 12H), δ 3.77(br, 8H), δ 3.68(br, 8H), δ 3.56(br, 8H), δ 3.28(br, 8H), δ 2.89(br, 8H), δ 1.22(br, 18H), δ 0.95(br, 32H), δ 0.84(br, 42H). Vis (THF): 414, 494, 574, 774 nm. MALDI-TOF MS *m/z*: 2476.71 [(M)⁺] (calcd for C₁₄₂H₁₈₈N₁₂O₁₄Zn₃ 2477.2242).

ZnO3Hex Series:

Synthetic procedures were identical to the **ZnO3EHex** series. Listed is only a brief statement concerning purification and characterization, see section for full procedures and reaction details.

2-(2'-(2''-hexyloxy)-ethoxy)ethylbromide (34):

Compound 34 was purified by silica gel chromatography using ether as the eluent. The resulting organic residue was clear with a yield of 74.4 % based on starting material. ^1H NMR (500 MHz, CDCl_3): δ 3.81(t, 2H, J = 6.38Hz), δ 3.66(t, 2H, J = 4.24), δ 3.58(t, 2H, J = 4.15), δ 3.45(qu, 4H, J = 6.37Hz), δ 1.57(q, 2H, J = 6.75Hz), δ 1.31(m, 8H), δ 0.88(t, 3H). CI MS m/z : 253.0802 $[(\text{M}+\text{H})^+]$ (calcd $\text{C}_{12}\text{H}_{25}\text{BrO}_2$ for 252.0725).

4, 7, 10-trioxalhexadecane-1-ol (35):

Compound 35 was purified by silica gel chromatography using 1:19 MeOH:Hexanes and isolated in 33% yield. ^1H NMR (250 MHz, CDCl_3): δ 3.75(m, 2H), δ 3.62(m, 8H), δ 3.46(m, 4H), δ 1.82(m, 2H), δ 1.56(m, 2H), δ 1.29(m, 8H), δ 0.86(m, 3H). CI MS m/z : 249.2054 $[(\text{M}+\text{H})^+]$ (calcd for $\text{C}_{15}\text{H}_{32}\text{O}_4$ 248.1988).

4, 7, 10-trioxalhexadecane-1-one (36):

Repetitive silica gel plugs were done using ether as the eluent until resulting in light yellow oil isolated in 74.9% yield. ^1H NMR (250 MHz, CDCl_3): δ 9.78(t, 1H, J = 1.79Hz), δ 3.82(m, 2H), δ 3.61(m, 4H), δ 3.56(m, 2H), δ 3.47(m, 2H), δ 3.44(m, 2H), δ 1.56(m, 2H), δ 1.30(m, 2H), δ 1.21(m, 8H), δ 0.87(m, 3H). CI MS m/z : 247.3423 $[(\text{M}+\text{H})^+]$ (calcd for $\text{C}_{15}\text{H}_{30}\text{O}_4$ 246.1831).

5,15-bis(-3, 6, 9-trioxapentadecane-1-yl)porphyrin (37):

The dark red residue was chromatographed on silica gel using 3:7 THF:Hexanes as the eluent isolated in 12%. ¹H NMR (500 MHz, CDCl₃): δ 10.12(s, 2H), δ 9.60(d, 4H, *J* = 4.70Hz), δ 9.38(d, 4H, *J* = 4.60Hz), δ 5.28(t, 4H, *J* = 7.71Hz), δ 4.53(t, 4H, *J* = 7.66Hz), δ 3.73(t, 4H, *J* = 4.02), δ 3.67(t, 4H, *J* = 4.8), δ 3.57(t, 4H, *J* = 5.36), δ 3.45(t, 4H, *J* = 5.36), δ 3.32(t, 4H, *J* = 6.81), δ 1.50(m, 4H), δ 1.26(m, 18H), δ 0.87(t, 6H), δ -3.25(s, 2H). Vis (CHCl₃): 404, 503, 534, 577, 631 nm. ESI MS *m/z*: 743.4724 [(M+H)⁺] (calcd for C₄₈H₇₀N₄O₆ 742.4669).

5,15-bis([-3, 6, 9-trioxapentadecane-1-yl]porphyrinato)Zn(II) PZn-O3Hex (38)

The residue was chromatographed on silica gel using THF:Hexanes (3:7) as the eluent. Yield 92%. ¹H NMR (500 MHz, CDCl₃): δ 10.12(s, 2H), δ 9.60(d, 4H, *J* = 4.70Hz), δ 9.38(d, 4H, *J* = 4.60Hz), δ 5.28(t, 4H, *J* = 7.71Hz), δ 4.53(t, 4H, *J* = 7.66Hz), δ 3.73(t, 4H, *J* = 4.02), δ 3.67(t, 4H, *J* = 4.8), δ 3.57(t, 4H, *J* = 5.36), δ 3.45(t, 4H, *J* = 5.36), δ 3.32(t, 4H, *J* = 6.81), δ 1.50(m, 4H), δ 1.26(m, 12H), δ 0.87(t, 6H). Vis (THF): 410, 546, 579 nm.

5-Bromo-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphyrin (39):

The residue was then purified by silica gel chromatography THF:Hexanes (3:7). The first band collected was 5,15-dibromo-10, 20-bis (-3, 6, 9-trioxapentadecane-1-yl)porphyrin (compound 40). Yield = 20%. Second band collect was compound 39. Yield = 68%. ¹H NMR (250 MHz, CDCl₃): δ 9.91(s, 1H), δ 9.73(d, 2H, *J* = 4.80Hz), δ 9.48(d, 2H, *J* = 4.63Hz), δ 9.47(d, 2H, *J* = 4.43Hz), δ 9.23(d, 2H, *J* = 4.61Hz), δ 5.17(t, 4H, *J* = 7.71Hz), δ 4.47(t, 4H, *J* =

7.66Hz), δ 3.71(t, 4H, J = 4.02), δ 3.66(t, 4H, J = 4.8), δ 3.55(t, 4H, J = 5.36), δ 3.43(t, 4H, J = 5.36), δ 3.31(t, 4H, J = 6.81), δ 1.48(m, 4H), δ 1.23(m, 16H), δ 0.85(t, 6H), δ -3.25 (s, 2H). Vis (CHCl₃): 414, 512, 544, 590, 648 nm. MS m/z: 821.3871 [(M+H)⁺] (calcd for C₄₈H₆₉BrN₄O₆ 820.3774).

5,15-dibromo-10,20-bis (3, 6, 9-trioxapentadecane-1-yl)porphyrin (40):

¹H NMR (250 MHz, CDCl₃): δ 9.49(d, 4H, J = 4.75Hz), δ 9.27(d, 4H, J = 4.75Hz), δ 4.99(t, 4H, J = 7.23Hz), δ 4.35(t, 4H, J = 7.56Hz), δ 3.75(t, 4H, J = 4.02), δ 3.65(t, 4H, J = 4.8), δ 3.62(t, 4H, J = 5.36), δ 3.53(t, 4H, J = 5.36), δ 3.30(t, 4H, J = 6.81), δ 1.85(m, 4H), δ 1.28(m, 16H), δ 0.86(t, 6H), δ -3.76 (s, 2H). Vis (CHCl₃): 420, 522, 556, 602, 664nm.

(5-Bromo-10,20-bis((-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II) (41):

The residue was chromatographed on silica gel using 3:7 THF:Hexanes as the eluent. Yield = 92%. ¹H NMR (500 MHz, CDCl₃): δ 9.91(s, 1H), δ 9.77(d, 2H, J = 4.91Hz), δ 9.60(d, 2H, J = 4.22Hz), δ 9.59(d, 2H, J = 4.22Hz), δ 9.29(d, 2H, J = 4.45Hz), δ 5.30(t, 4H, J = 7.82Hz), δ 4.51(t, 4H, J = 7.80Hz), δ 3.73(t, 4H, J = 4.02), δ 3.68(t, 4H, J = 4.8), δ 3.60(t, 4H, J = 5.36), δ 3.49(t, 4H, J = 5.36), δ 3.36(t, 4H, J = 6.81), δ 1.50(m, 4H), δ 1.26(m, 16H), δ 0.87(t, 6H). Vis (CHCl₃): 418, 547, 580 nm.

(5,15-dibromo-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II) (42):

The residue was chromatographed on silica gel using 3:7 THF:Hexanes as the eluent. Yield = 93%. ¹H NMR (250 MHz, CDCl₃): δ 9.69(d, 4H, J = 4.81Hz), δ

9.51(d, 4H, $J = 4.65\text{Hz}$), δ 5.22(t, 4H, $J = 7.72\text{Hz}$), δ 4.67 (t, 4H, $J = 7.80\text{Hz}$), δ 3.70(t, 4H, $J = 4.02$), δ 3.66(t, 4H, $J = 4.8$), δ 3.65(t, 4H, $J = 5.36$), δ 3.48(t, 4H, $J = 5.36$), δ 3.36(t, 4H, $J = 6.81$), δ 1.50(m, 4H), δ 1.22(m, 16H), δ 0.83(t, 6H). Vis (CHCl_3): 426, 559, 602 nm. ESI MS m/z : 983.1932 [(M+Na⁺)] (calcd for $\text{C}_{48}\text{H}_{66}\text{Br}_2\text{N}_4\text{O}_6\text{Zn}$ 960.2015).

(5-Trimethylsilylethynyl-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II) (43):

The crude product was chromatographed on silica gel using THF:Hexanes (3:7). Yield = 98%. ¹H NMR (250 MHz, CDCl_3): δ 9.93(s, 1H), δ 9.75(d, 2H, $J = 4.39\text{Hz}$), δ 9.58(d, 4H, $J = 4.89\text{Hz}$), δ 9.56(d, 2H, $J = 4.41\text{Hz}$), δ 9.27(d, 2H, $J = 4.62\text{Hz}$), δ 5.22(t, 4H, $J = 7.72\text{Hz}$), δ 4.67 (t, 4H, $J = 7.80\text{Hz}$), δ 3.70(t, 4H, $J = 4.02$), δ 3.66(t, 4H, $J = 4.8$), δ 3.65(t, 4H, $J = 5.36$), δ 3.48(t, 4H, $J = 5.36$), δ 3.36(t, 4H, $J = 6.81$), δ 1.50(m, 4H), δ 1.22(m, 16H), δ 0.83(t, 6H). Vis (THF): 428, 562, 610 nm.

(5,15-bis(trimethylsilylethynyl)-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II) (44):

The crude product was purified on silica gel using THF:Hexanes (3:7). Yield = 90%. ¹H NMR (500 MHz, CDCl_3): δ 9.64(d, 4H, $J = 4.53\text{Hz}$), δ 9.49(d, 4H, $J = 4.59\text{Hz}$), δ 5.23(t, 4H, $J = 7.70\text{Hz}$), δ 4.48 (t, 4H, $J = 7.80\text{Hz}$), δ 3.72(t, 4H, $J = 4.02$), δ 3.67(t, 4H, $J = 4.8$), δ 3.59(t, 4H, $J = 5.36$), δ 3.50(t, 4H, $J = 5.36$), δ 3.36(t, 4H, $J = 6.81$), δ 1.51(m, 4H), δ 1.25(m, 16H), δ 0.85(t, 6H, $J = 6.39$), δ 0.62(s, 9H). Vis (THF): 439, 586, 640 nm.

(5-ethynyl-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II) (45):

The reaction mixture was stirred for 15 min and then directly poured down a short silica gel column with CHCl_3 as the eluent. Yield = 99%. ^1H NMR (500 MHz, CDCl_3): δ 9.97(s, 1H), δ 9.78(d, 2H, J = 4.65Hz), δ 9.62(d, 2H, J = 4.40Hz), δ 9.57(d, 2H, J = 4.45Hz), δ 9.29(d, 2H, J = 4.45Hz), δ 5.31(t, 4H, J = 7.80Hz), δ 4.51 (t, 4H, J = 7.80Hz), δ 4.13 (s, 1H), δ 3.72(t, 4H, J = 4.02), δ 3.67(t, 4H, J = 4.8), δ 3.60(t, 4H, J = 5.36), δ 3.50(t, 4H, J = 5.36), δ 3.37(t, 4H, J = 6.81), δ 1.49(m, 4H), δ 1.23(m, 16H), δ 0.83(t, 6H, J = 6.39). Vis (CHCl_3): 422, 552, 590 nm.

(5,15-ethynyl-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II) (46):

The reaction mixture was stirred for 15 min and then directly poured down a short silica gel column with CHCl_3 as the eluent. Yield = 94%. ^1H NMR (500 MHz, CDCl_3): δ 9.70(d, 4H, J = 4.52Hz), δ 9.52(d, 2H, J = 5.59Hz), δ 5.31(t, 4H, J = 7.80Hz), δ 4.51 (t, 4H, J = 7.80Hz), δ 4.14 (s, 2H), δ 3.72(t, 4H, J = 4.02), δ 3.67(t, 4H, J = 4.8), δ 3.60(t, 4H, J = 5.36), δ 3.50(t, 4H, J = 5.36), δ 3.37(t, 4H, J = 6.81), δ 1.49(m, 4H), δ 1.23(m, 16H), δ 0.83(t, 6H, J = 6.39). Vis (THF): 433, 578, 629 nm. ESI MS m/z : 875.3717 [(M+Na) $^+$] (calcd for $\text{C}_{52}\text{H}_{68}\text{N}_4\text{O}_6\text{Zn}$ 852.3804).

1,2-bis[5'-bromo(5',5''-10,20-bis(-3, 6, 9-trioxapentadecane-1-yl)porphinato)zinc(II)]ethyne (47):

Isolated from synthesis of compound 48. Yield 70%. ^1H NMR (500 MHz, CDCl_3): δ 10.52(d, 4H, J = 4.05Hz), δ 10.48(d, 4H, J = 4.10Hz), δ 9.95(s, 1H), δ 9.82(d, 4H, J = 4.30Hz), δ 9.772(d, 4H, J = 4.20Hz), δ 9.70(d, 4H, J = 4.50Hz), δ 9.62(d, 4H, J = 4.25Hz), δ 9.54(d, 4H, J = 4.50Hz), δ 9.31(d, 4H, J = 4.20Hz), δ

5.39(br, 4H), δ 5.29 (br, 4H), δ 4.62 (t, 4H, $J = 7.71$), δ 4.58(t, 4H, $J = 7.71$), δ 3.78(m, 8H), δ 3.72(m, 8H), δ 3.64(m, 8H), δ 3.55(m, 8H), δ 3.38(m, 8H), δ 1.50(m, 8H), δ 1.24(m, 24H), δ 0.84(m, 12H). Vis (THF): 433, 578, 629 nm. MALDI-TOF m/z: 1708.55 [(M)⁺] (calcd for C₅₂H₆₈N₄O₆Zn 1708.6557).

5,15-bis[[5',-10',20'-bis([_3, 6, 9-trioxapentadecane-1-yl]porphinato)zinc(II)]ethynyl]-10,20-bis([_3, 6, 9-trioxapentadecane-1-yl]porphinato)zinc(II) PZn₃-O3Hex (48):

Solvent removed by vacuum and then was purified by gravimetric size exclusion column(Biobeads, SX-1, THF). The fastest moving band was collected and solvent removed by vacuum. A final silica gel plug was done to remove residual biobeads using CHCl₃:Pyridine (99:1) as the eluent. Yield = 30%. ¹H NMR (500 MHz, CDCl₃): δ 10.56(br, 4H), δ 10.50(br, 4H), δ 9.98(br-s, 2H), δ 9.86(br, 4H), δ 9.79(br, 4H), δ 9.65(br, 4H), δ 9.33(br, 4H), δ 5.43(br, 12H), δ 4.71(br, 12H), δ 4.64(br, 12H), δ 3.84(m, 12H), δ 3.75(m, 12H), δ 3.74(m, 12H), δ 3.66(m, 12H), δ 3.55(m, 12H), δ 1.21(m, 36H), δ 0.84(m, 12H). ¹³C NMR (500 MHz, CHCl₃:Pyr 99:1): δ 152.49 (C-C=N), δ 152.22 (C-C=N), δ 151.74 (C-C=N), δ 151.20 (C-C=N), δ 150.72 (C-C=N), δ 150.38 (C-C=N), δ 148.952 (C-C=N), δ 132.41 (beta), δ 131.55 (beta), δ 131.37 (beta), δ 130.00 (beta), δ 129.49 (beta), δ 129.49 (beta), δ 128.49 (beta), δ 116.16 (meso-R), δ 106.92 (meso), δ 102.31 (-CC-), δ 101.57 (-CC-), δ 100.58 (-CC-), δ 100.41 (-CC-), δ 71.72 (O-CH₂), δ 71.10 (O-CH₂), δ 71.03 (O-CH₂), δ 70.99 (O-CH₂), δ 70.29 (O-CH₂), δ 36.15 (C-CH₂-C), δ 34.43 (C-CH₂-C), δ 31.86 (C-CH₂-C), δ 30.54 (C-CH₂-C), δ 29.79 (C-CH₂-C), δ 25.94 (C-CH₂-C), δ 22.79 (C-CH₂-C), δ 22.72 (C-CH₂-C),

δ 21.39 (C-CH₂-C), δ 14.20 (-CH₃), δ 14.16 (-CH₃). Vis (THF): 414, 494, 574, 774 nm.

Anal Calc (found): C – 66.32%(68.63%), H – 7.20%(7.76%), N – 6.82%(5.48).

MALDI-TOF MS *m/z*: 2456.73 [(M)⁺] (calcd for C₁₄₈H₂₀₀N₁₂O₁₈Zn₃ 2457.1100).

5,15-bis[[5',-10',20'-bis([_3, 6, 9-trioxapentadecane-1-yl]porphinato)zinc(II)]ethynyl]-10,20-bis([_3, 6, 9-trioxapentadecane-1-yl]porphinato)zinc(II) PZn₅-O3Hex (49):

Solvent removed by vacuum and then was purified by gravimetric size exclusion column(Biobeads, SX-1, THF). The fastest moving band was collected and solvent removed by vacuum. A final silica gel plug was done to remove residual biobeads using CHCl₃:Pyridine (99:1) as the eluent. Yield = 42%. ¹H NMR (500 MHz, Pyr): δ 10.92(d, 4H, *J* = 4.30 Hz), δ 10.85(m, H), δ 10.26(s, 2H), δ 10.12(d, 4H, *J* = 4.55), δ 10.09(m, 8H), δ 10.06(d, 4H, *J* = 4.60), δ 9.85(d, 4H, *J* = 4.40), δ 9.55(d, 4H, *J* = 4.20), δ 5.59(br, 20H), δ 4.89(br, 20H), δ 3.98(m, 20H), δ 3.87(m, 20H), δ 3.82(m, 20H), δ 3.77(m, 20H), δ 3.66(m, 20H), δ 3.62(m, 20H), δ 3.43(m, 20H), δ 1.50(m, 20H), δ 1.25(m, 20H), δ 1.14(m, 30H), δ 0.80(m, 15H). ¹³C NMR (500 MHz, CHCl₃:Pyr 99:1): δ 152.49 (C-C=N), δ 152.22 (C-C=N), δ 151.74 (C-C=N), δ 151.20 (C-C=N), δ 150.72 (C-C=N), δ 150.38 (C-C=N), δ 148.952 (C-C=N), δ 132.41 (beta), δ 131.55 (beta), δ 131.37 (beta), δ 130.00 (beta), δ 129.49 (beta), δ 129.49 (beta), δ 128.49 (beta), δ 116.16 (meso-R), δ 106.92 (meso), δ 101.57 (-CC-), δ 71.72 (O-CH₂), δ 71.10 (O-CH₂), δ 71.03 (O-CH₂), δ 70.99 (O-CH₂), δ 70.29 (O-CH₂), δ 36.15 (C-CH₂-C), δ 34.43 (C-CH₂-C), δ 31.86 (C-CH₂-C), δ 30.54 (C-CH₂-C), δ 29.79 (C-CH₂-C), δ 25.94 (C-CH₂-C), δ 22.79 (C-CH₂-C), δ 22.72 (C-CH₂-C), δ 21.39 (C-CH₂-C), δ 14.28 (-CH₃),

δ 14.21 (-CH₃), δ 14.18 (-CH₃). Vis (THF): 414 , 505 , 855 nm. Anal Calc (found): C – 66.47%(66.59%), H – 7.14%(8.13%), N – 6.80%(5.20%). MS MALDI-TOF m/z: 4109.94 (calc for C₂₂₈H₂₉₂N₂₀O₃₀Zn₅ 4109.8396).

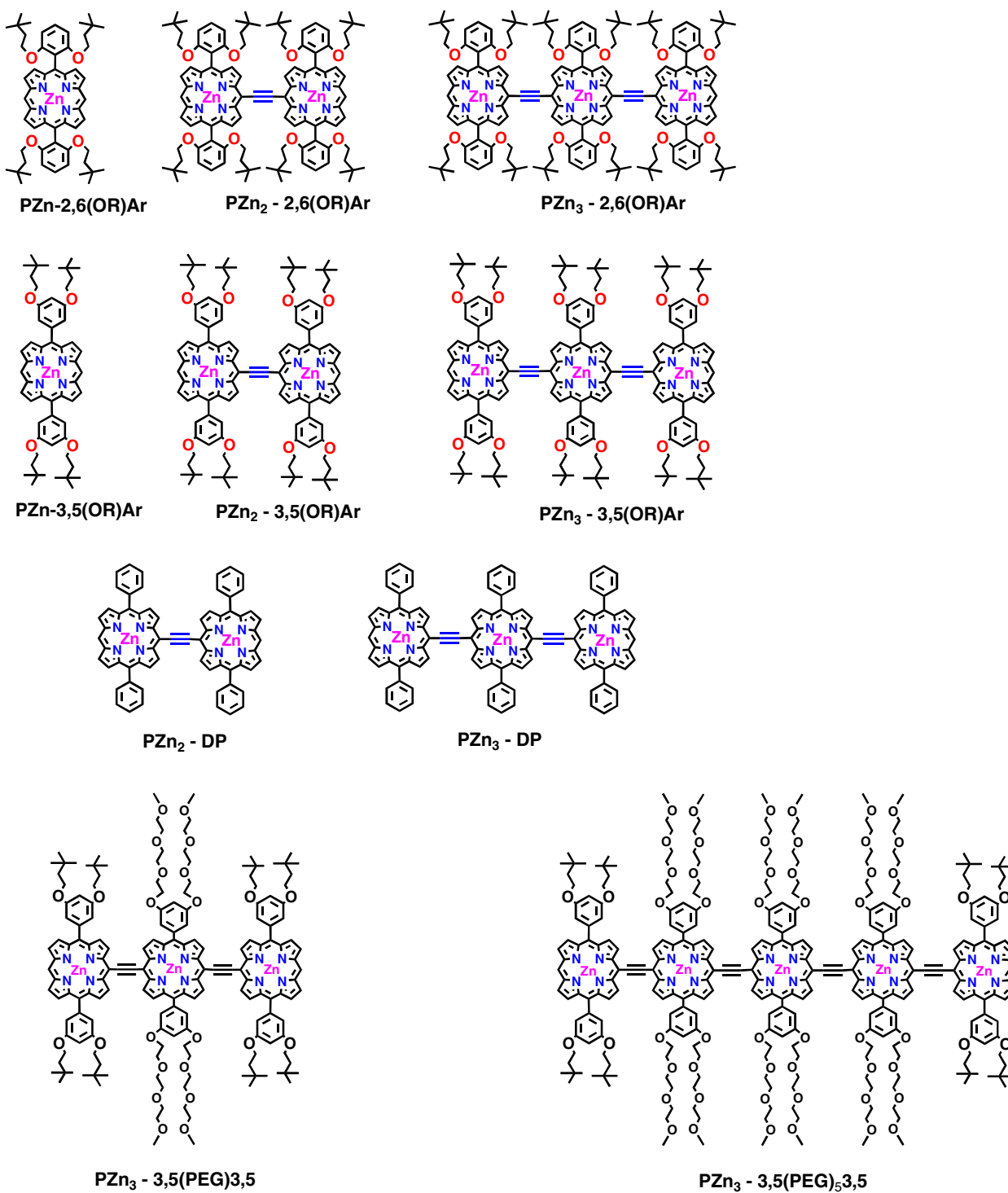
References:

1. Daire, A. *White Paper Report No. 1808* **2001**, Keithley Instruments, Inc.
2. Uyeda, H. T.; Zhao, Y.; Wostyn, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Therien, M. J. *J. Am. Chem. Soc.* **2002**; 124(46), 13806-13813.
3. Susumu, K.; Therien, M. J. *J. Am. Chem. Soc.* **2002** 124, 8550-8552
4. Lin, V. S.-Y; DiMagno, S. G.; Therien, M. J. *Science* **1994**, 264, 1105-1111.
5. Liu, C.; Shen, D.-M.; Chen, Q.-Y. *Chem. Comm.* **2006**, 770-772.

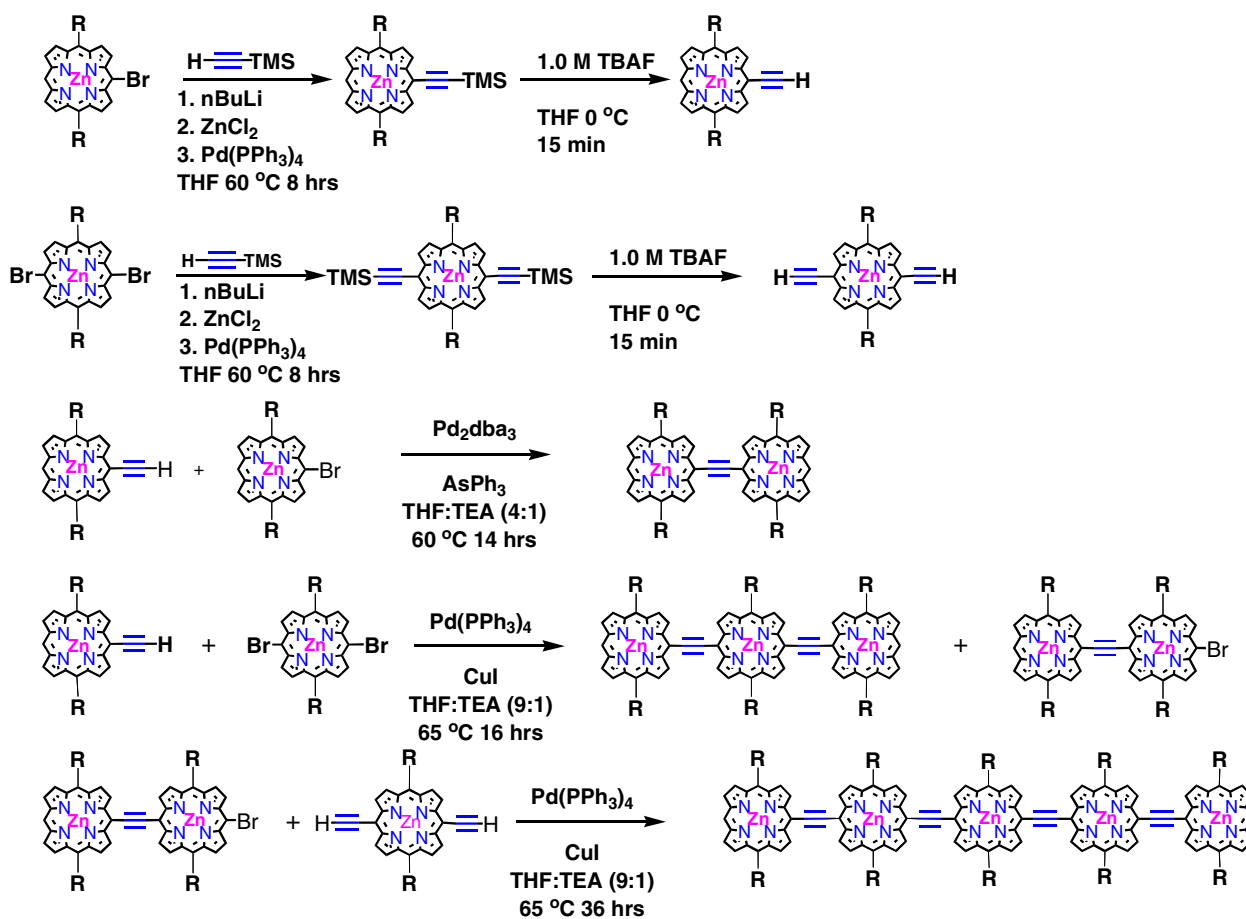
Figure Captions:

- Chart S1.** Compounds used in this study that were previously reported including compound abbreviations.
- Scheme S1.** General Synthetic Reaction scheme for the synthesis of **PZn₂**, **PZn₃**, **PZn₅** oligomers.
- Scheme S2, S3, S4.** Synthetic reaction and numbering scheme for **PZnO1**, **PZnO3EHex**, **PZnO3Hex** series.
- Figure S1.** ¹H NMR of **PZn₃-O1**, **PZn₃-O3Hex**, **PZn₃-O3Hex**, **PZn₅-O1**, **PZn₅-O3Hex**
- Figure S2.** Solution and Thin Film **PZn₁** Electronic Absorption Spectra. Spectra normalized and y-axis offset for clarity.
- Figure S3.** Solution and Thin Film **PZn₂** Electronic Absorption Spectra. Spectra normalized and y-axis offset for clarity.
- Figure S4.** Solution and Thin Film **PZn₃** Electronic Absorption Spectra. Spectra normalized and y-axis offset for clarity.
- Figure S5.** Solution and Thin film **PZn₅** Electronic Absorption Spectra. Spectra normalized and y-axis offset for clarity.
- Figure S6.** TGA/DTA of **PZn₃-3,5OR**
- Figure S7.** TGA/DTA of **PZn₃-O1**
- Figure S8.** TGA/DTA of **PZn₃-O3Hex**
- Figure S9.** TGA/DTA of **PZn₅-O1**
- Figure S10.** TGA/DTA of **PZn₅-O3Hex**
- Figure S11.** Powder XRD (small/intermediate/wide angle) of **PZn₃-3,5OR**
- Figure S12.** Powder XRD (small/intermediate/wide angle) of **PZn₅-O3Hex**
- Figure S13.** Analytical GPC Traces of **PZn₃-O3Hex** and **PZn₅-O3Hex**
- Figure S14.** Summary of **PZn_n** Ionization and Electron Affinity potentials
- Table S1.** Summary of **PZn_n-O3Hex** cyclic voltammetry results.
- Table S2.** Complete **PZn_n** Pressed Pellet and Thin Film Conductivities (2- and 4- probe) S cm⁻¹.

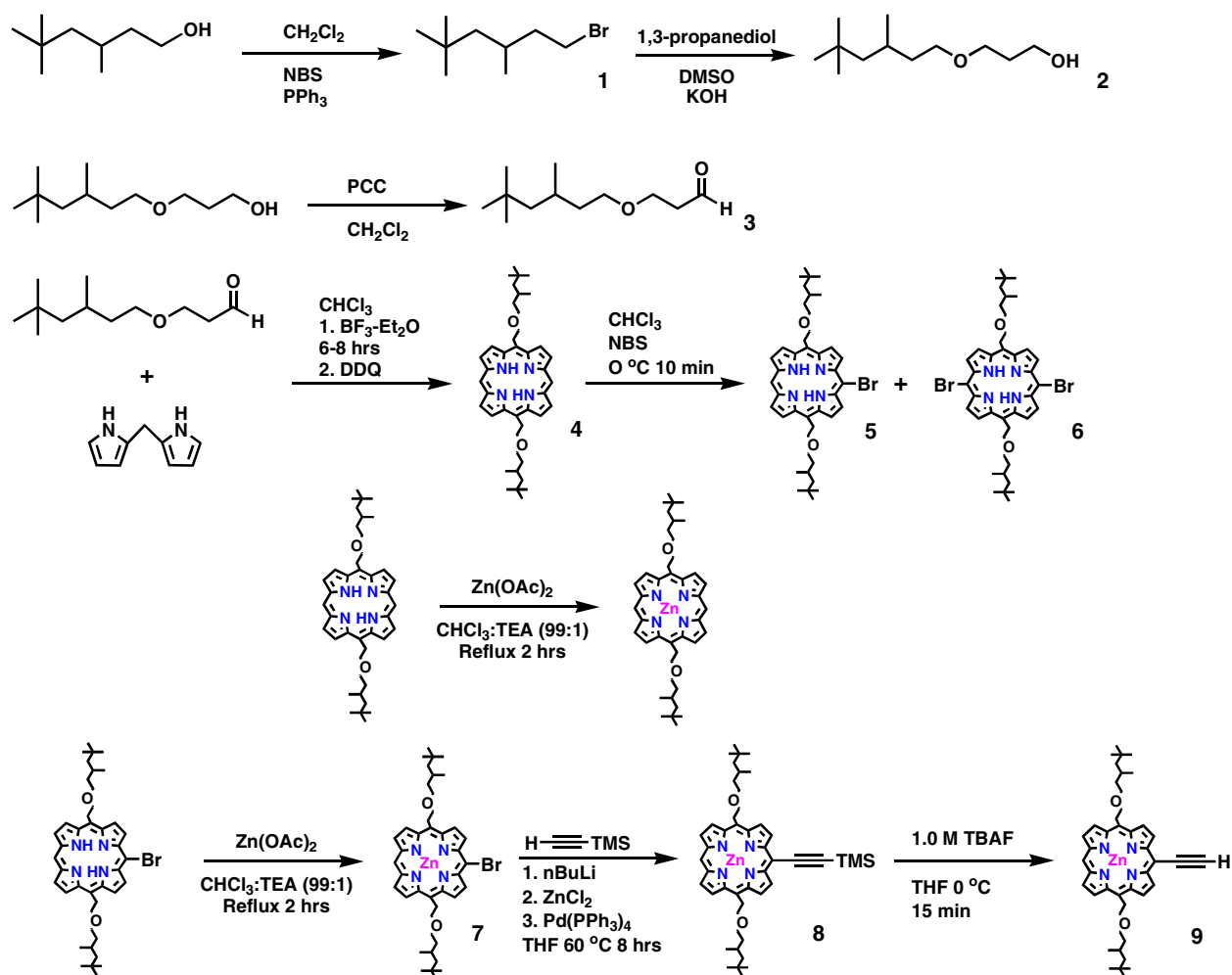
Chart S1.

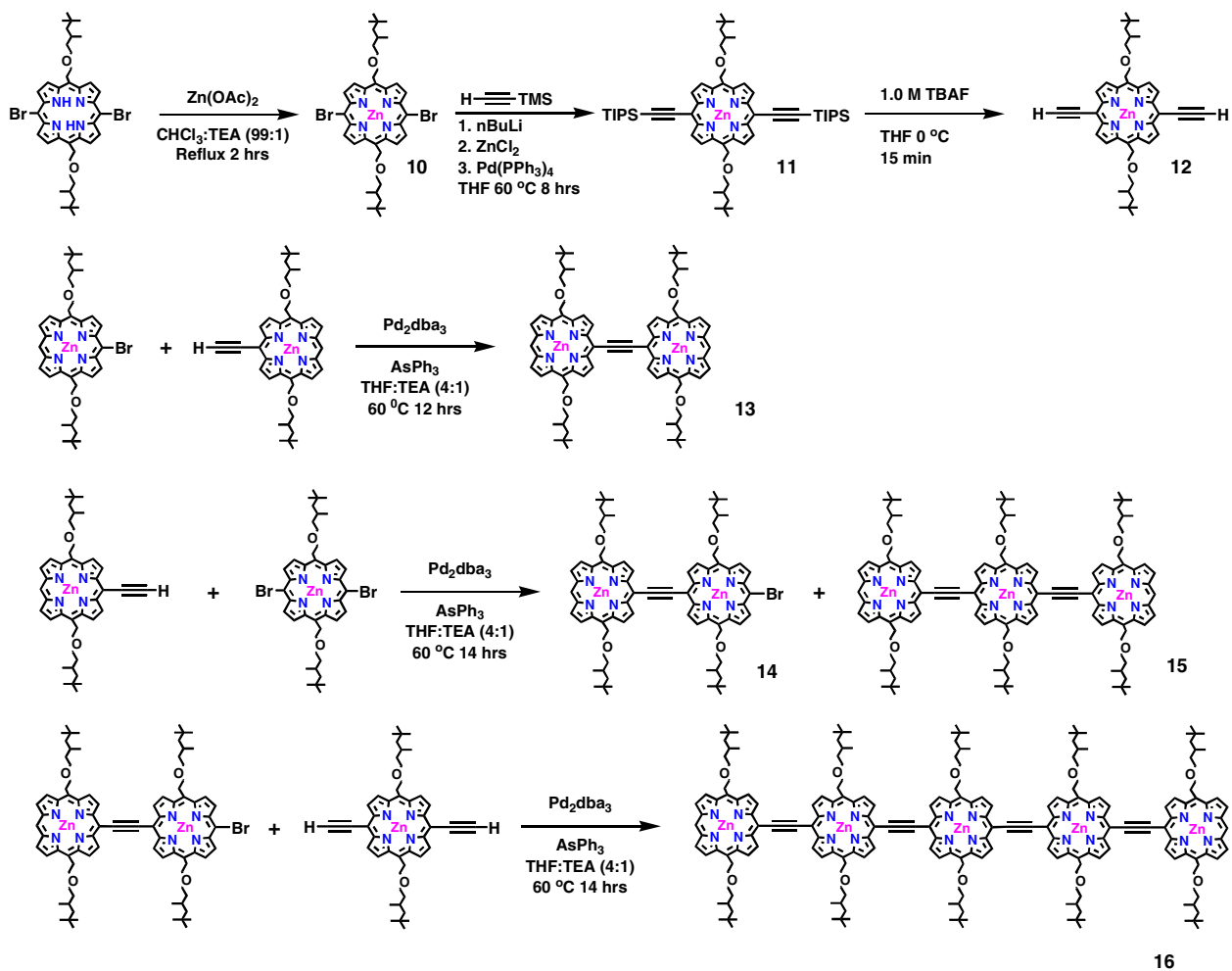


Scheme S1.

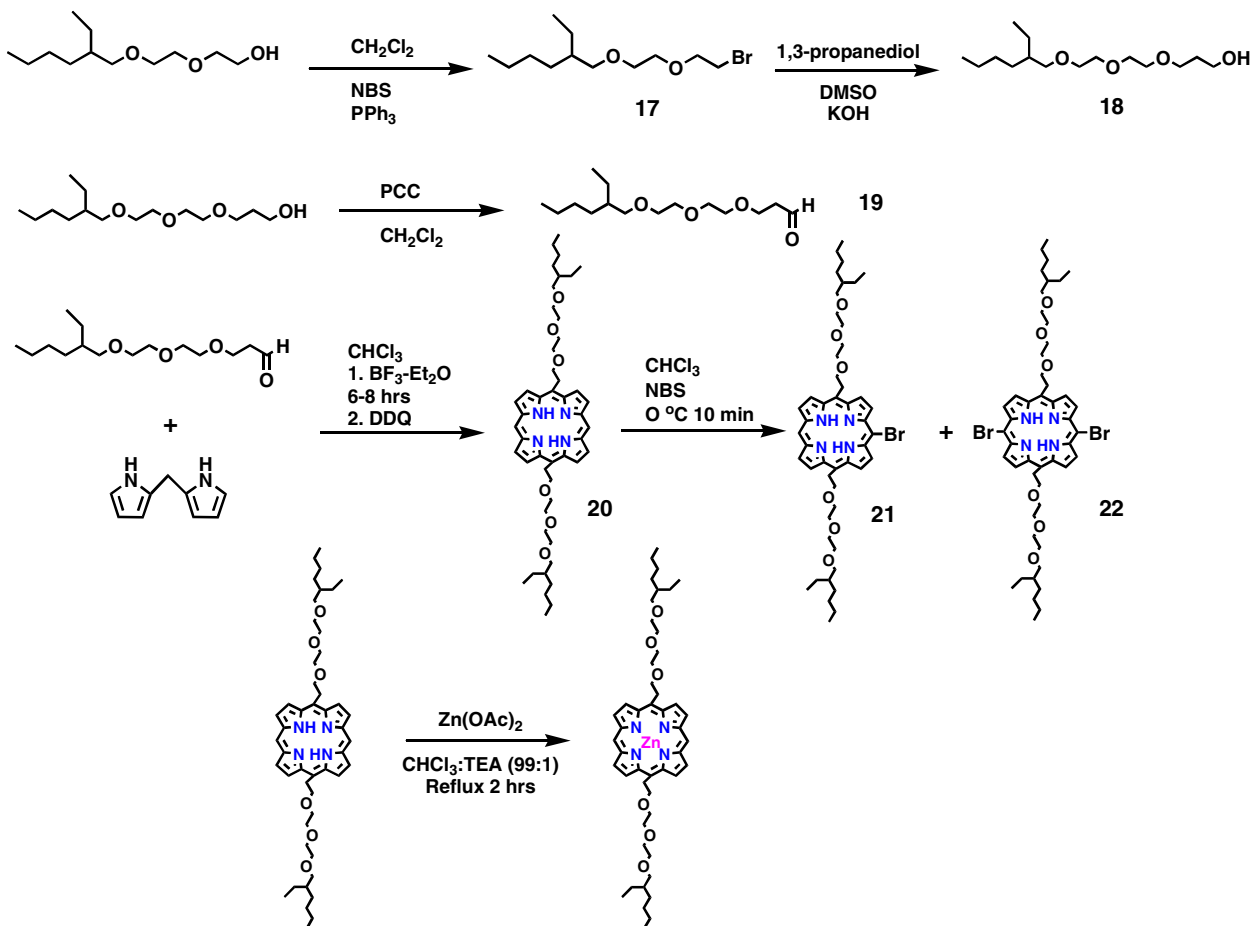


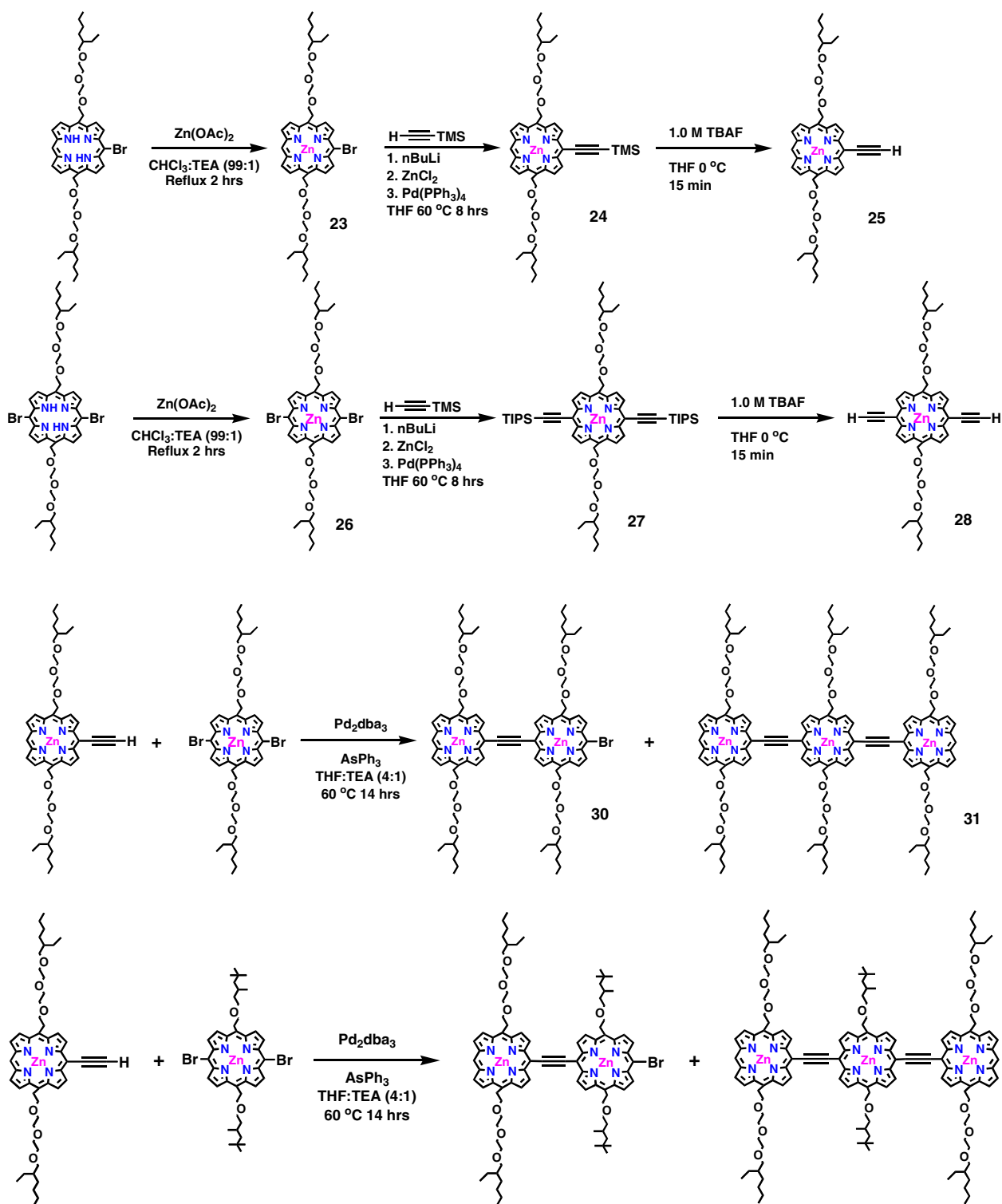
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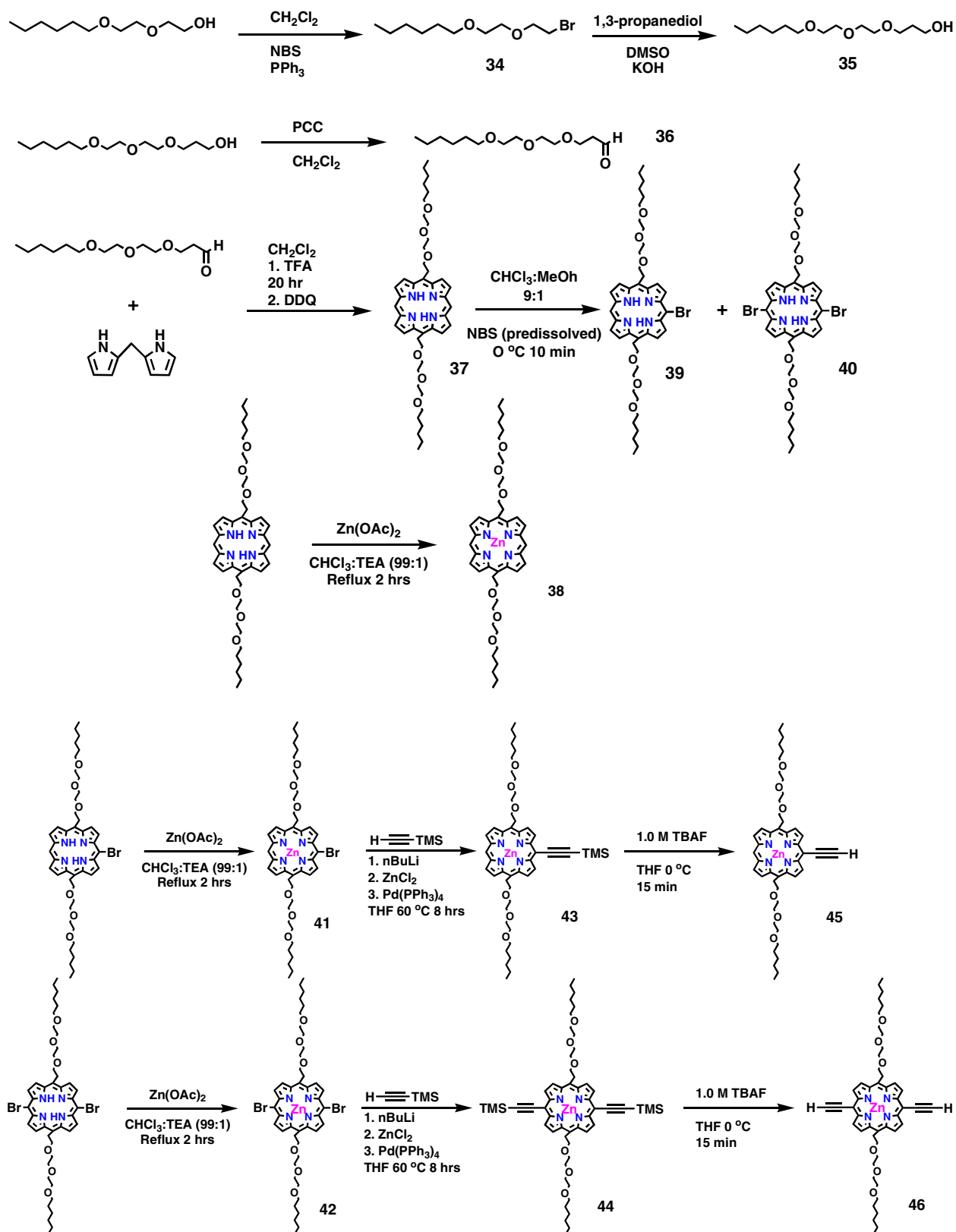


Scheme S3.





Scheme S4.



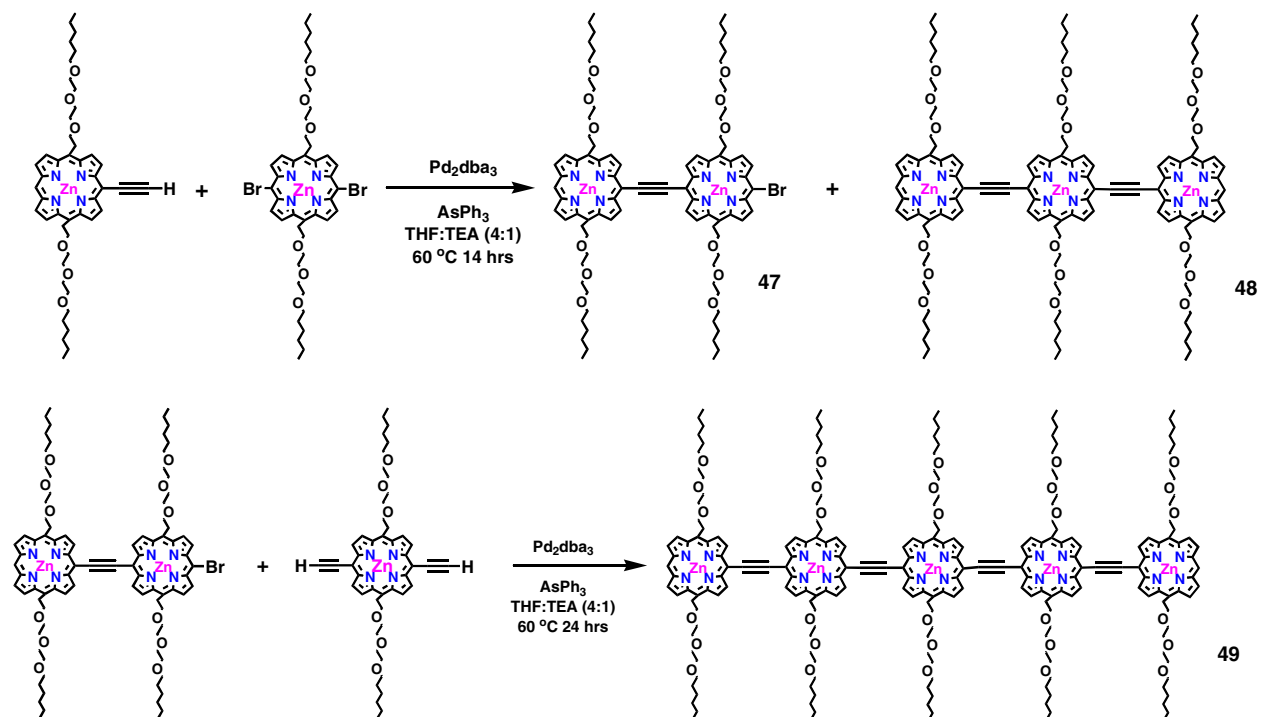


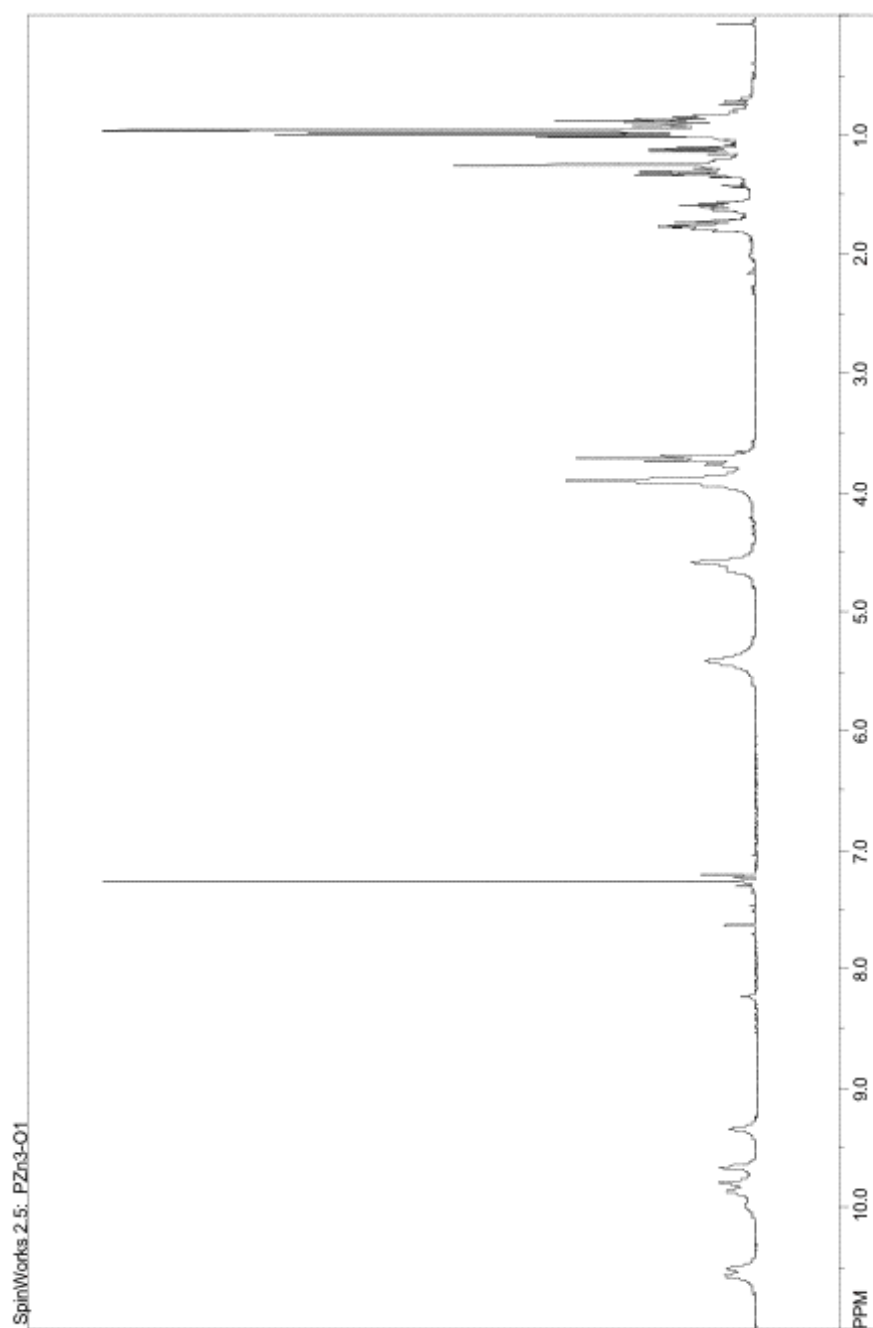
Figure 1a. ^1H NMR of $\text{PZn}_3\text{-O1}$. Solvent: $\text{CHCl}_3\text{:Pyr}$ (99:1)

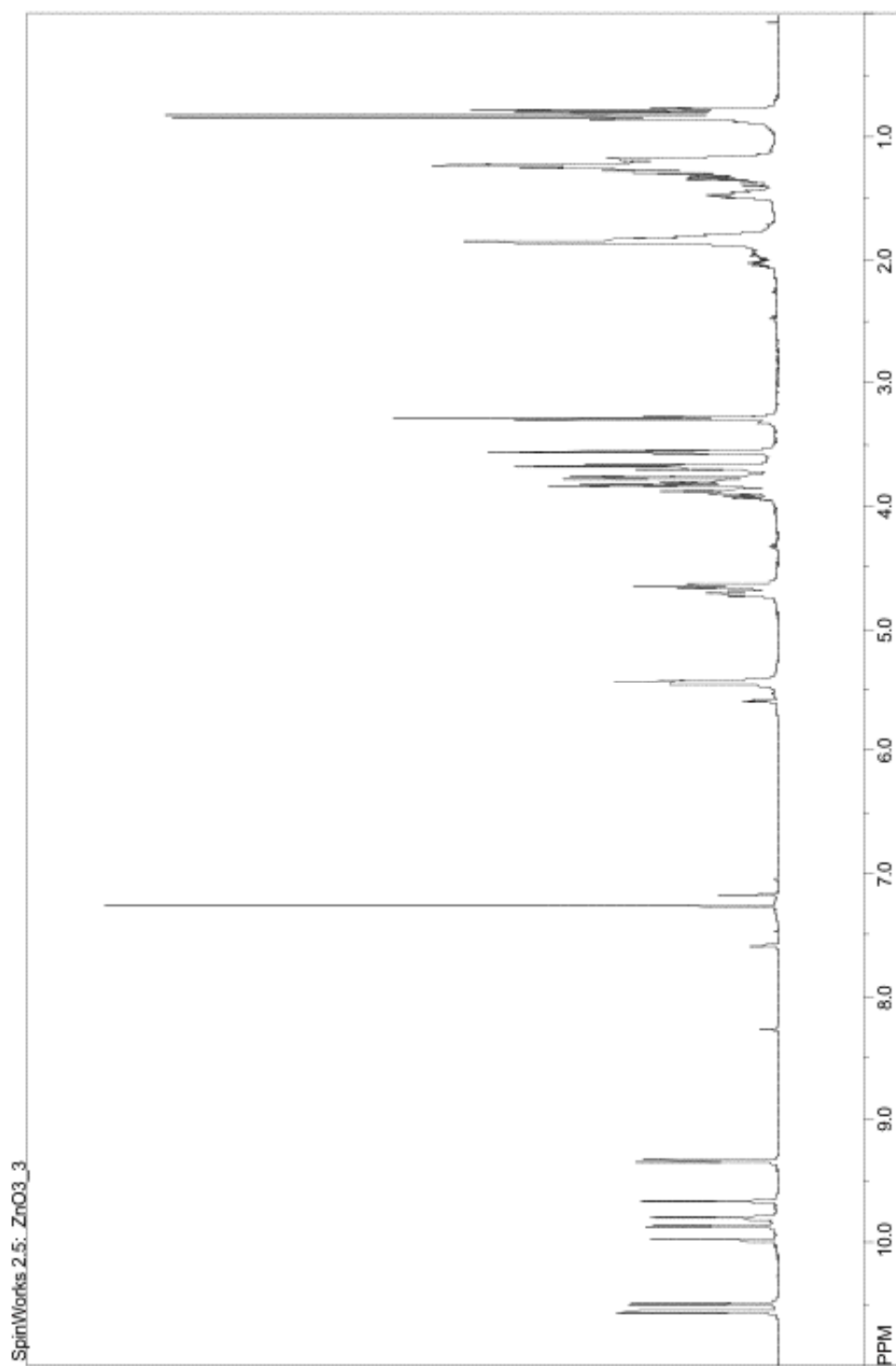
Figure S1b. ^1H NMR of $\text{PZn}_3\text{-O3EHex}$. Solvent: $\text{CHCl}_3\text{:Pyr}$ (99:1)

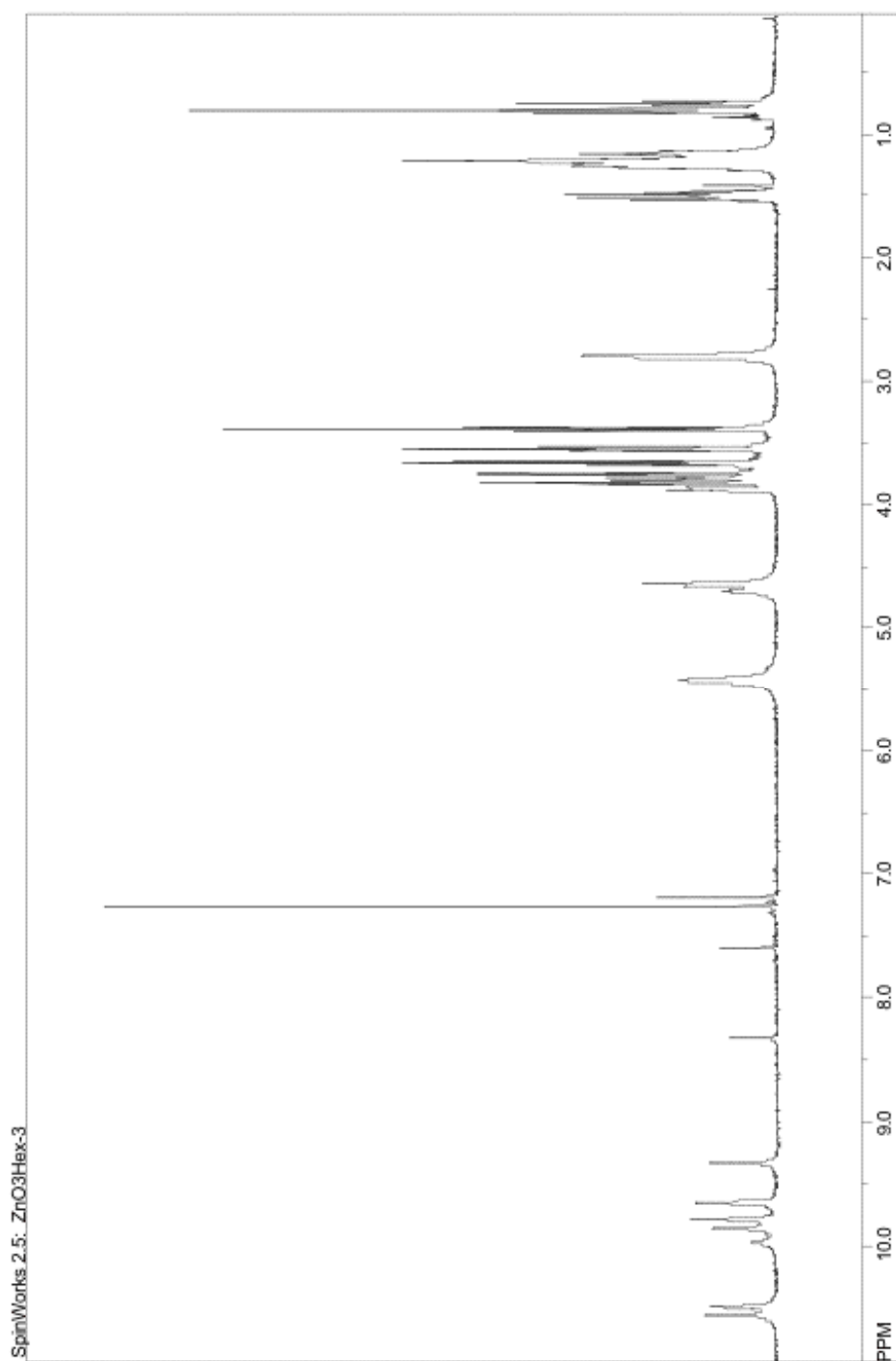
Figure S1c. ^1H NMR of $\text{PZn}_3\text{-O3Hex}$. Solvent: $\text{CHCl}_3\text{:Pyr}$ (99:1)

Figure S1d. ^1H NMR of $\text{PZn}_5\text{-O3Hex}$. Solvent: Pyridine – d_5

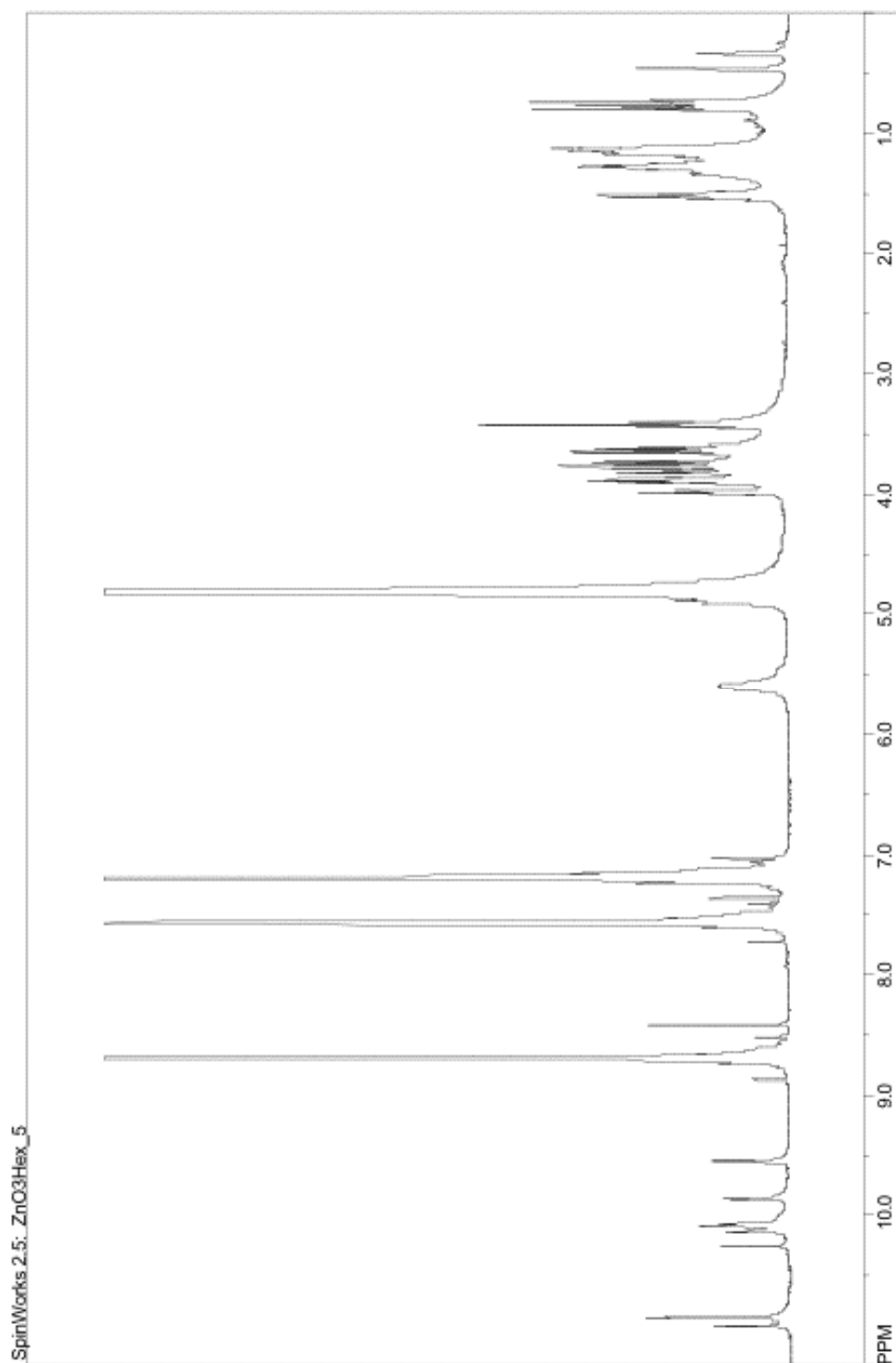


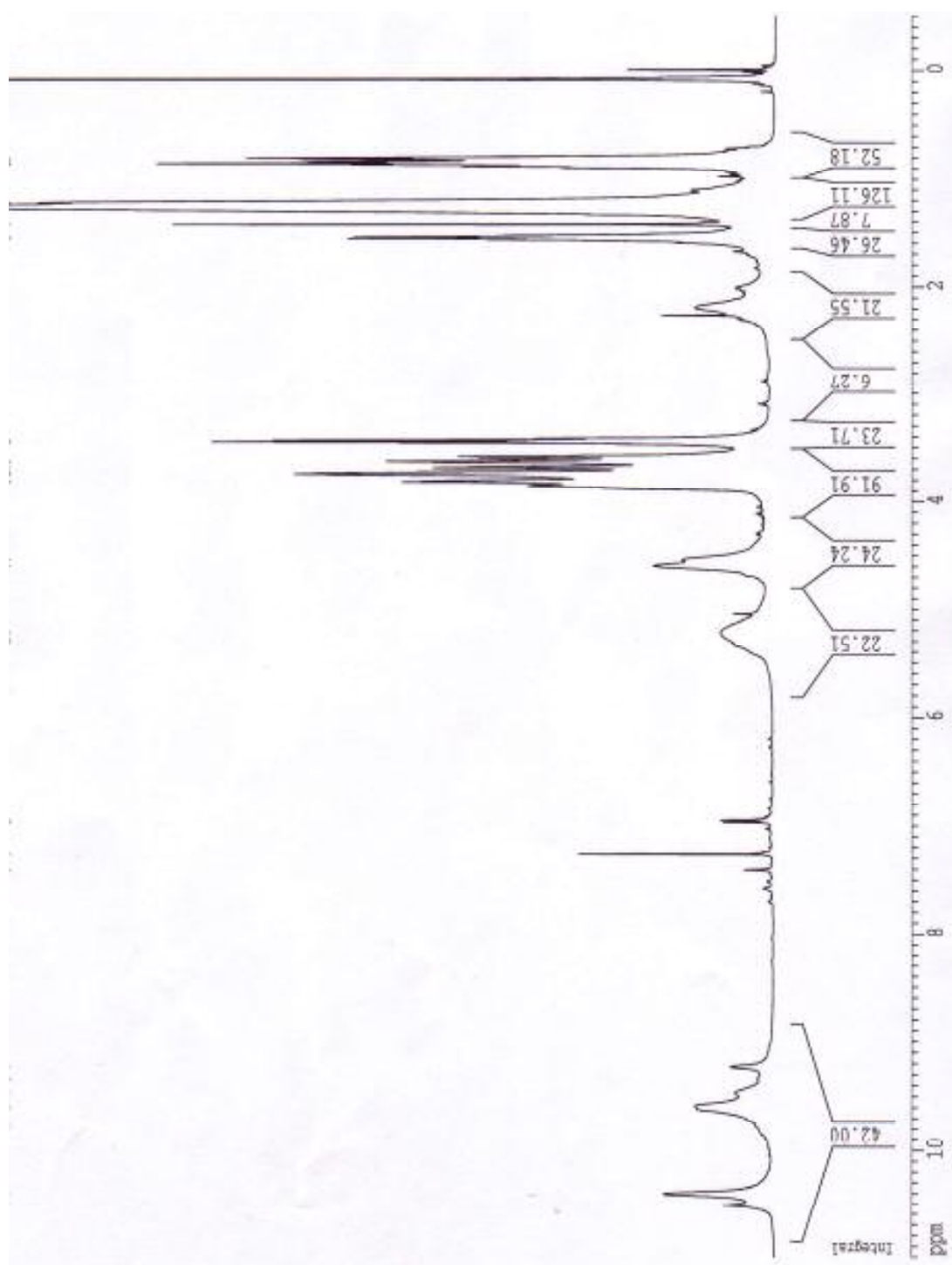
Figure S1dd. ^1H NMR of $\text{PZn}_5\text{-O3Hex}$. Solvent: $\text{CHCl}_3\text{:Pyr}$ (99:1)

Figure S2.

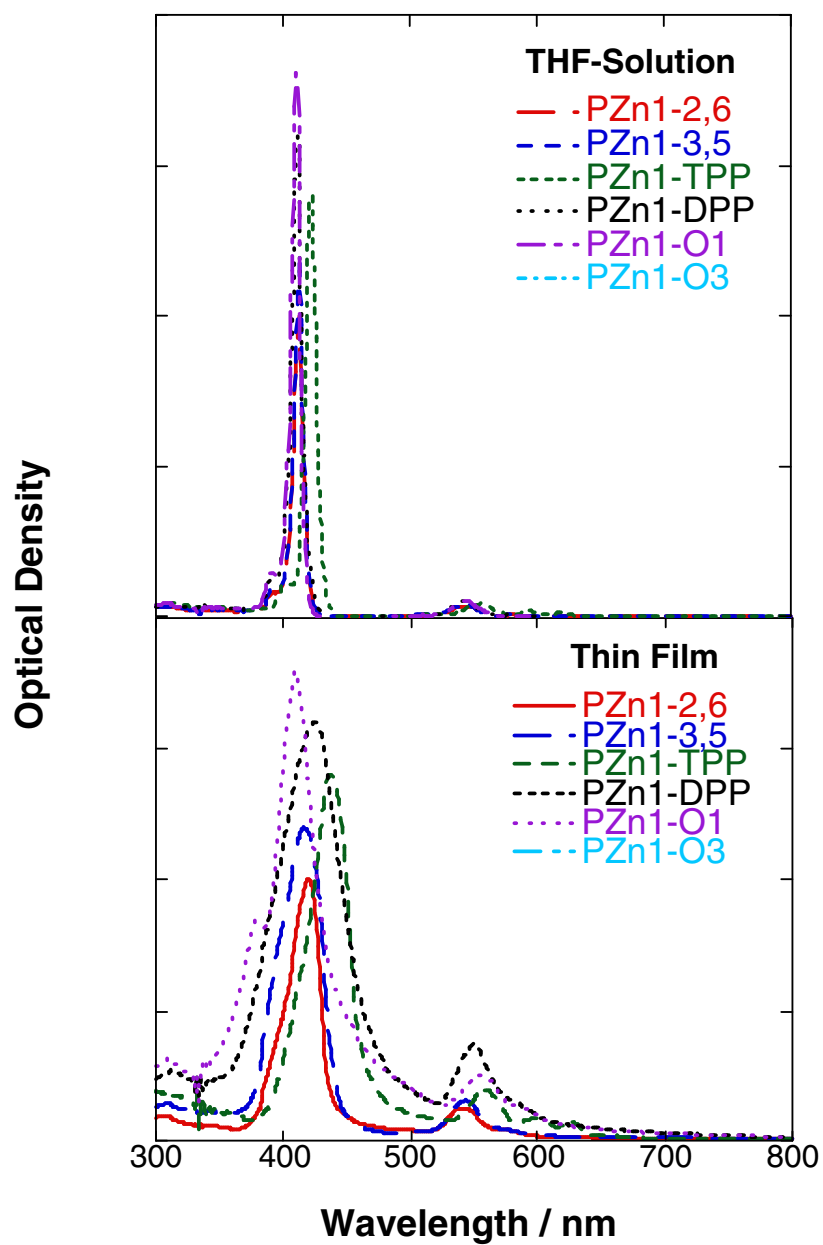


Figure S3.

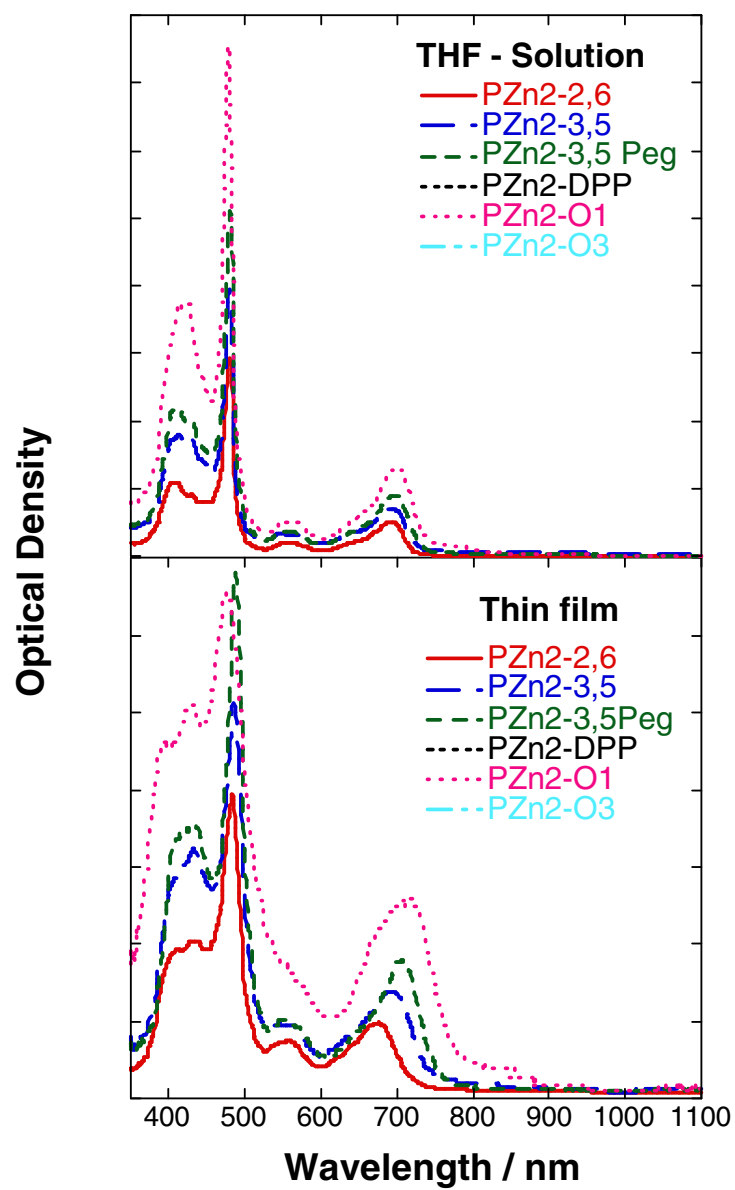


Figure S4.

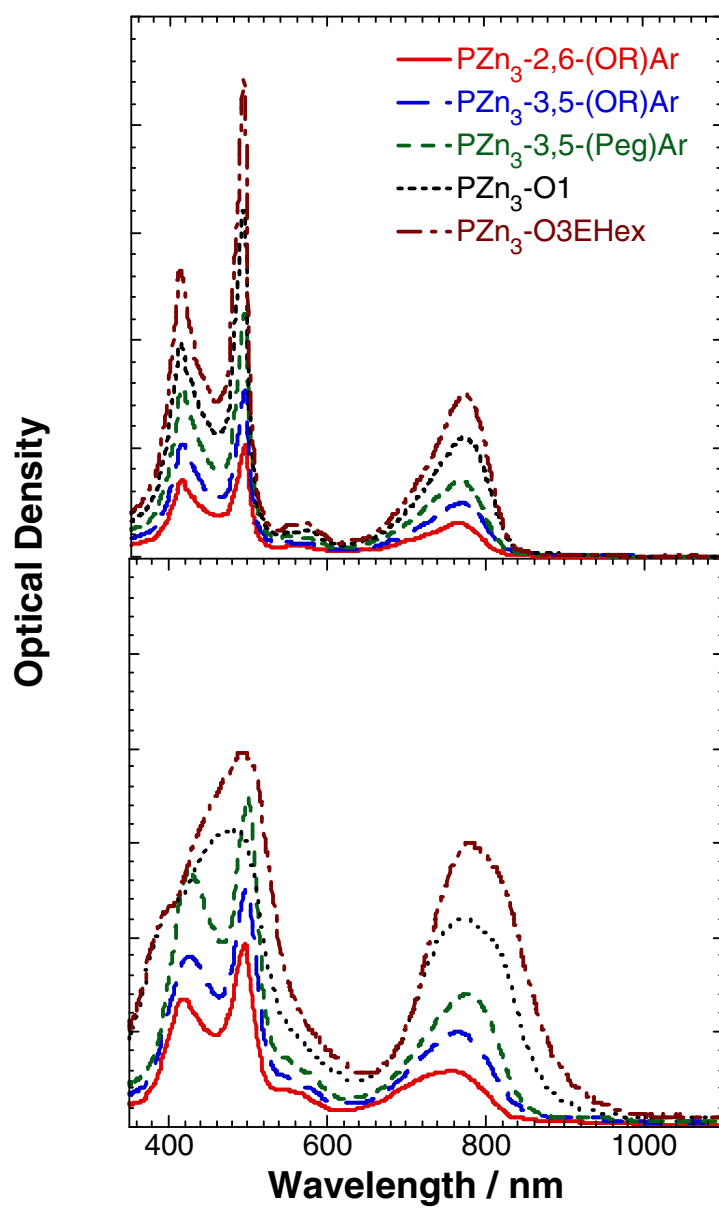


Figure S5.

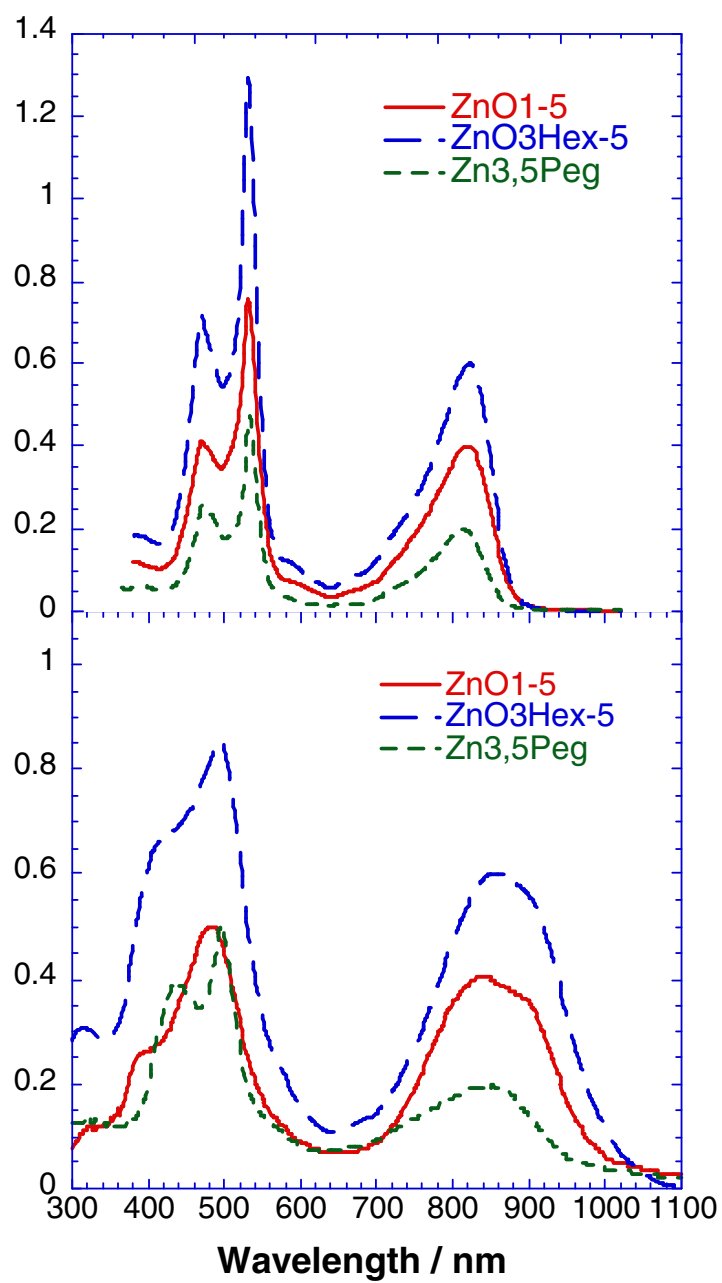
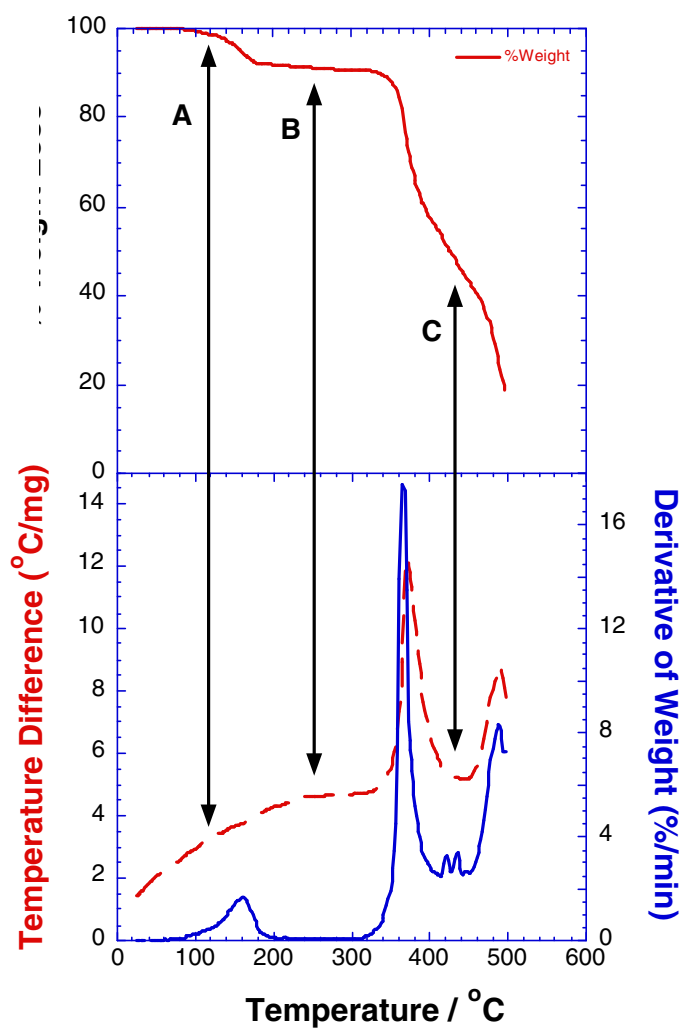
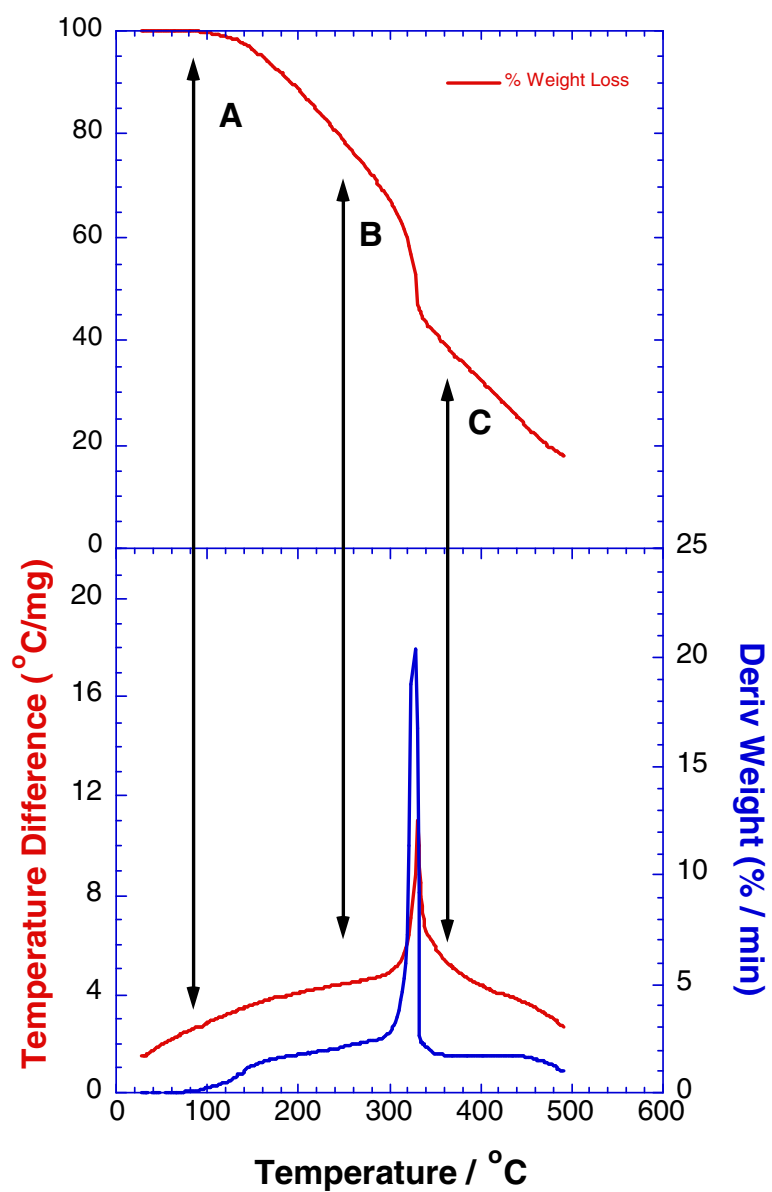


Figure S6. TGA/DTA of $\text{PZn}_3\text{-3,5}$ 

A = onset at 90 $^{\circ}\text{C}$ - attributed to trap solvent

B = onset at 250 $^{\circ}\text{C}$ - first decomposition process

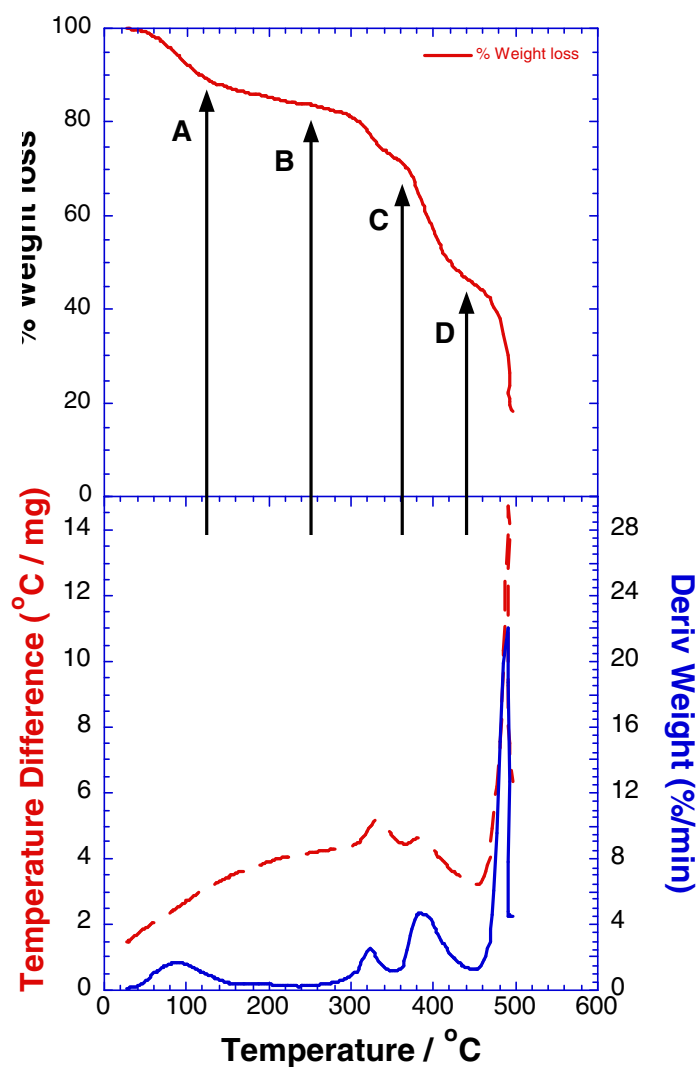
C = onset at 420 $^{\circ}\text{C}$ - second decomposition process

Figure S7. TGA/DTA PZn₃-O1

A = onset at 90 °C – loss of solvent and diffusion controlled decomposition

B = onset at 282 °C – second decomposition process

C = onset at 350 °C – third decomposition process

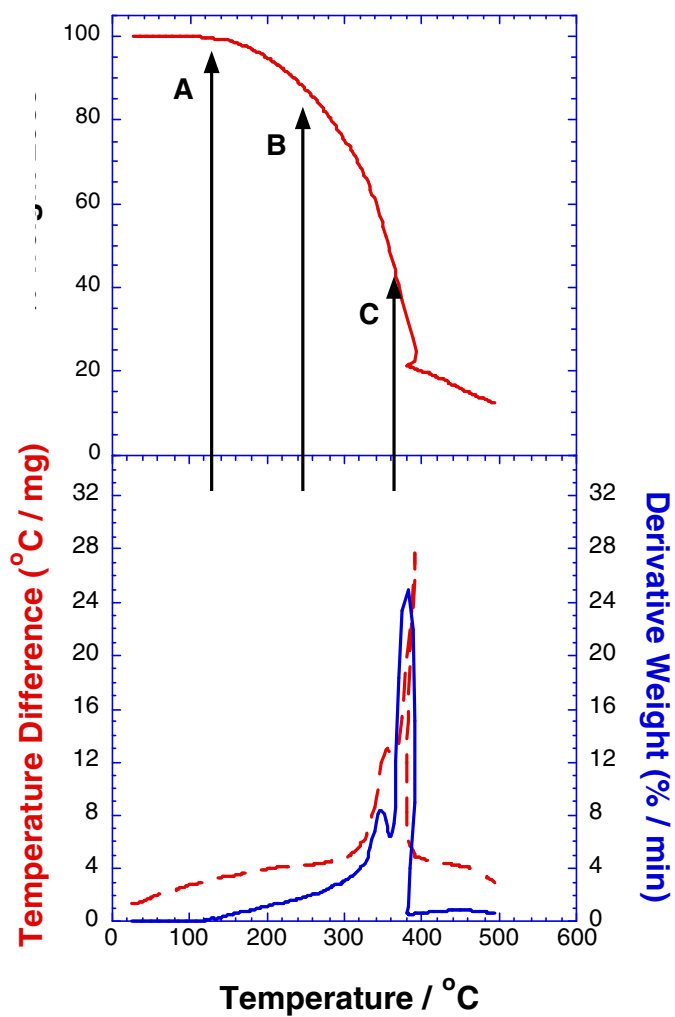
Figure S8. TGA/DTA PZn₃-O3Hex

A = onset at 80 °C – loss of solvent

B = onset at 250 °C – first decomposition process

C = onset at 350 °C – second decomposition process

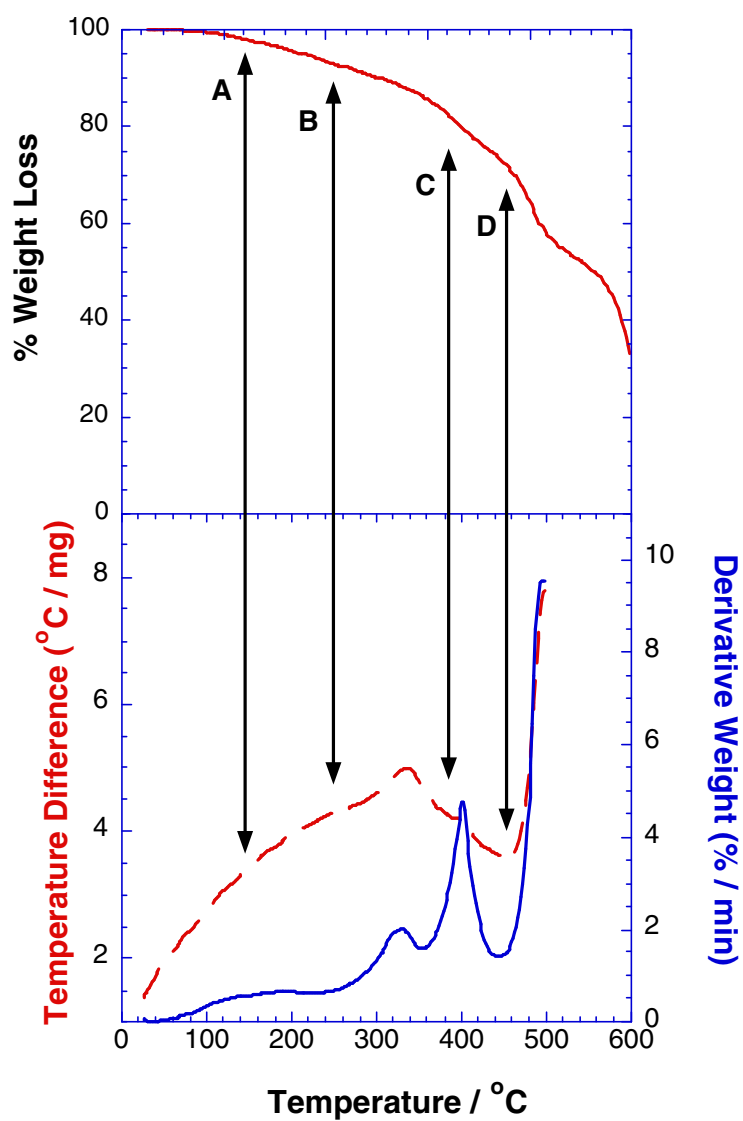
D = onset at 450 °C – third decomposition process

Figure S9. TGA/DTA PZn₅-O1

A = onset at 110 °C – diffusion controlled air decomposition

B = onset at 240 °C – second decomposition process

C = onset at 360 °C – third decomposition and combustion

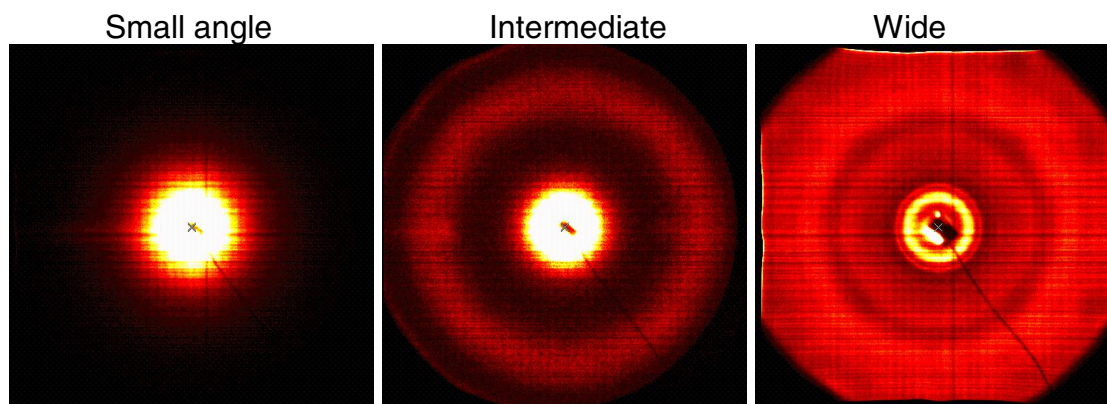
Figure S10. TGA/DTA of $\text{PZn}_5\text{-O3Hex}$ 

A = onset at 140 $^{\circ}\text{C}$ – loss of solvent

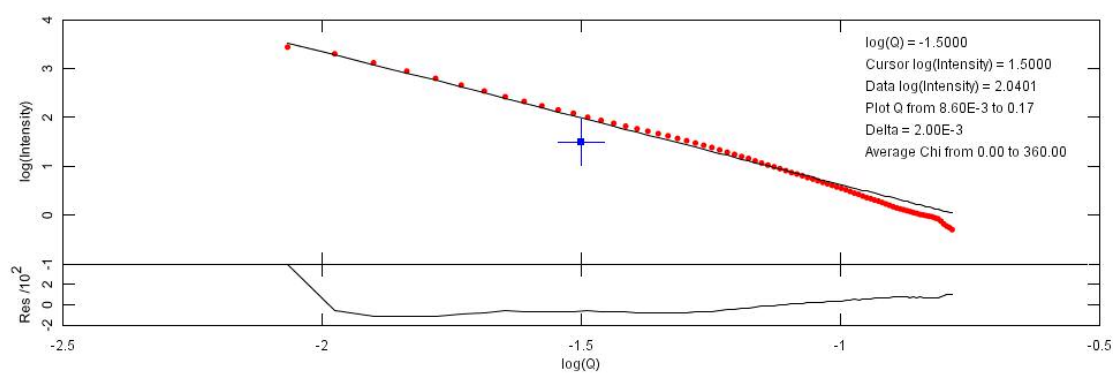
B = onset at 240 $^{\circ}\text{C}$ – first decomposition process

C = onset at 360 $^{\circ}\text{C}$ – second decomposition process

D = onset at 440 $^{\circ}\text{C}$ – third decomposition process

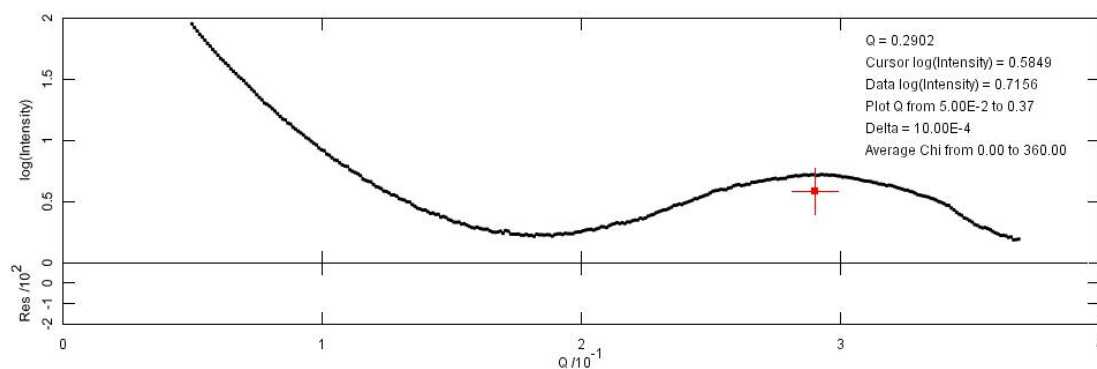
Figure S11. PZn₃-3,5(OR)

Small angle Log-log scale



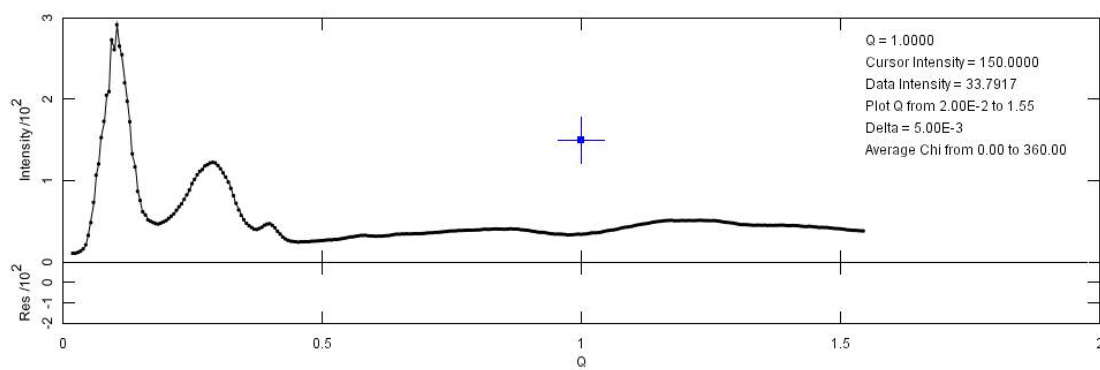
Solid line is fit to power law. Power fits to -2.7. Power of -2 would correspond to random coils; power of -4 would correspond to point-like defects. Sample 1
 $z=25.3$

Intermediate Angle Line plot (semilog scale)

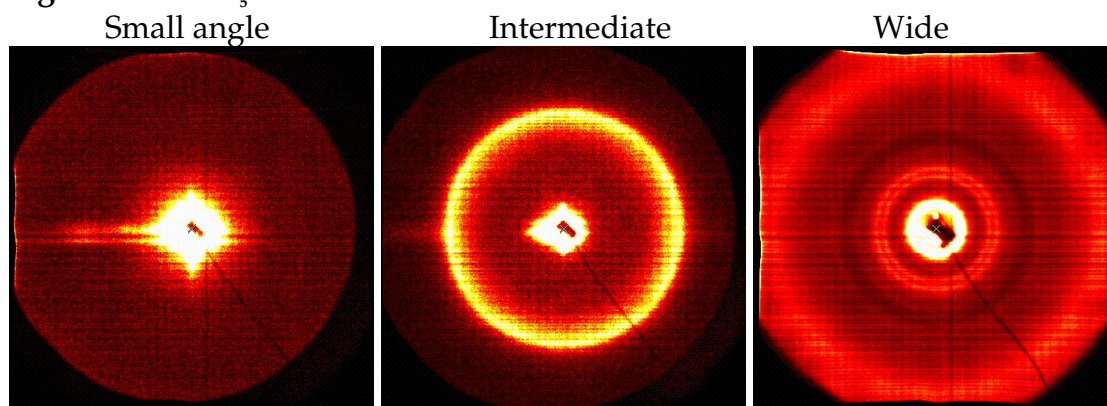
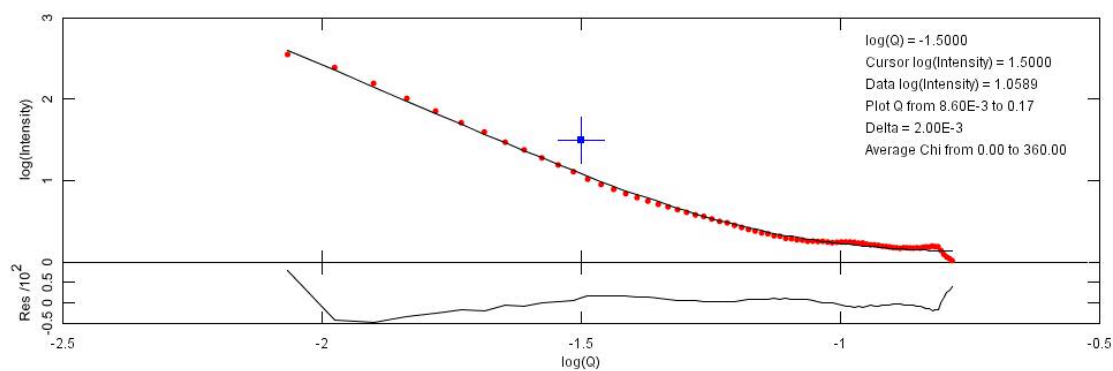


Broad peak at $q=0.291$ ($d=21.6$) HWHM=0.058 corresponding to correlation length

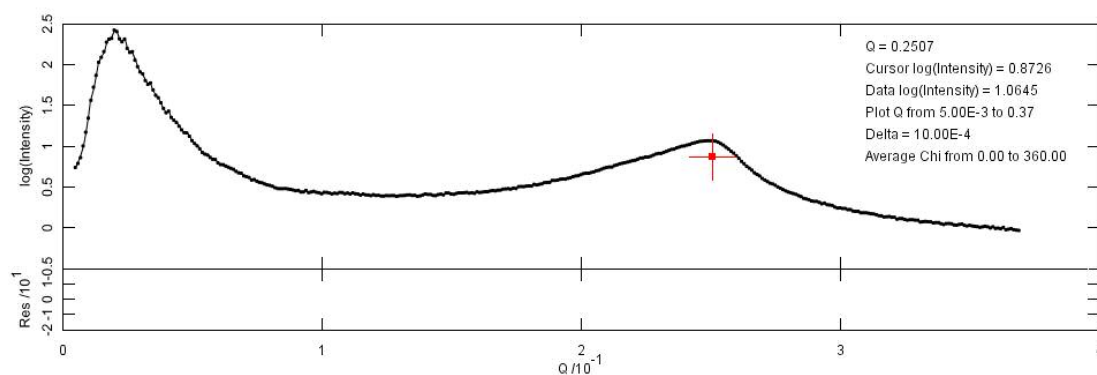
Wide angle linear scale



Broad peaks at $q=0.289$ ($d=21.7\text{\AA}$), $q=0.398$ ($d=15.8\text{\AA}$), $q=1.2$ ($d=5.2\text{\AA}$)

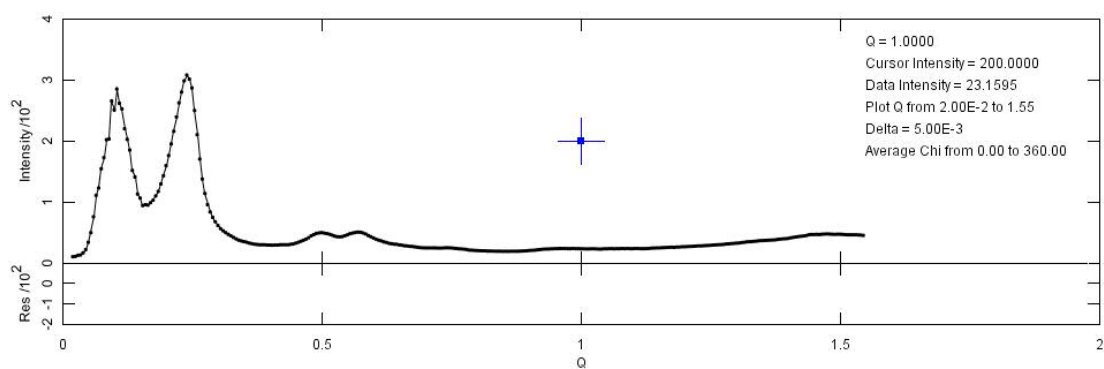
Figure S12. PZn₅-O3Hex**Small angle Log-log plot**

Fit to power law + constant. Power law is still -2.7. Looks similar except amplitude is down by a factor of 10. Sample 2 z=50.8

Intermediate angle semilog scale

Peak at $q=0.251$ ($d=25.0$) Sample 2 z=50.8

Wide angle linear scale



Peaks at $q=0.240$ ($d=26.2$ Å), 0.498 ($d=12.6$ Å), 0.569 ($d=11.0$ Å), 1.45 ($d=4.3$ Å)

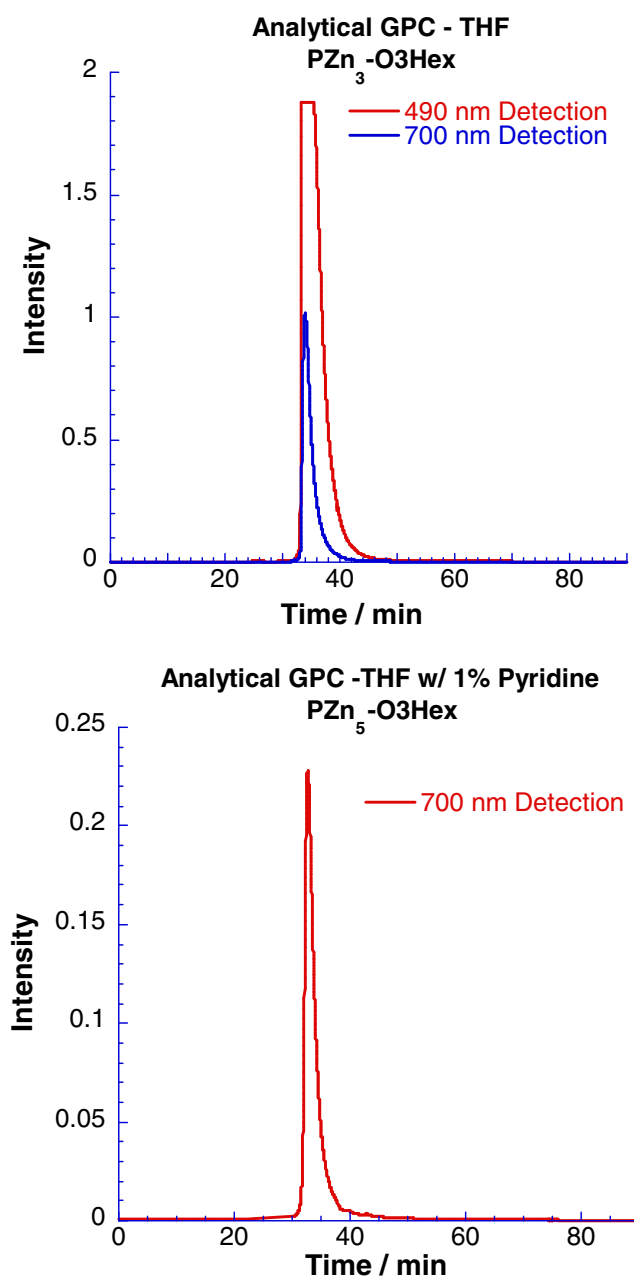
Figure S13. Analytical GPC traces of $\text{PZn}_{3.5}\text{-O3Hex}$ 

Figure S14.

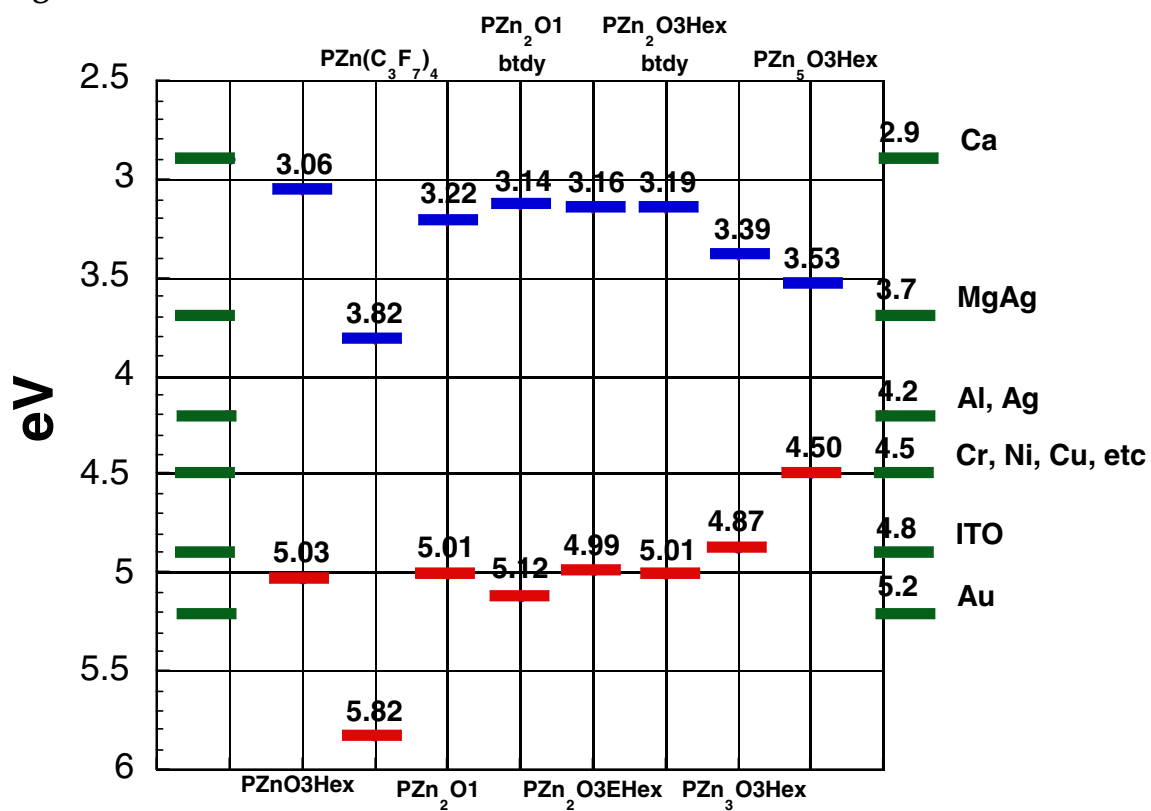


Table S1.

	PZn ₃ O3Hex		PZn ₅ O3Hex	
	Solution (eV)	Film (eV)	Solution (eV)	Film (eV)
$E_{op}(\lambda_{max})^a$	1.60	782	1.45	146
$E_{op}(edge)^b$	1.49	1.39	1.34	1.22
$E_{1/2}^{0/+}$	0.40	0.50 ^f	0.39	0.10 ^f
$E_{1/2}^{-/0}$	-1.10	-1.01 ^f	-1.02	-0.88 ^f
E_a^c		3.39g		3.52 ^g
I_p^c		4.90g		4.50g
E_p	1.50 ^d	1.51 ^e	1.41 ^d	0.98 ^e

PZn_n-(OR) oligomer's potentiometric data has been reported elsewhere.¹

- Measured as the maximum absorption of the lowest energy transition.
- Measured as the point where the slope changes on the red edge of the lowest energy transition.
- E_a and I_p were estimated from the onset electrochemical potentials via cyclic voltammetry of thin films on glassy carbon electrode. $E_a = E_{red} + 4.4$ eV and $I_p = E_{ox} + 4.4$ eV where E_{red} and E_{ox} the onset potentials for reduction and oxidation relative to Ag/AgCl reference electrode.²
- E_p for solution was determined by $E_p = E_{1/2}^{0/+} - E_{1/2}^{-/0}$. $E_{1/2}$ values were measured in 1 mM porphyrin solution in 0.2 M TBAPF₆ in CH₂Cl₂ using glassy carbon as the electrode. Potentiometric values are reported using SCE as the reference electrode.
- E_p for thin films was determined as $E_p = I_p - E_a$.
- Values represent the onset potentials of thin films on glassy carbon electrode relative to the Ag/AgCl reference electrode.
- For reference concerning the possibility of charge injection listed are work functions for various metal electrodes: Au (5.2), ITO (4.8 – 5.0), Ca (2.9), MgAg (3.7), and Al (4.2).¹

- (a) Uyeda, H. T.; Zhao, Y.; Wostyn, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Therien, M. J. *J. Am. Chem. Soc.* **2002**; 124(46), 13806-13813.
(b) Susumu, K.; Therien, M. J. *J. Am. Chem. Soc.* **2002** 124, 8550-8552
(c) Lin, V. S.-Y.; DiMaggio, S. G.; Therien, M. J. *Science* **1994**, 264, 1105-1111.
- Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. *P. Appl. Phys. Lett.* **1998**, 73, 2453-2455.

Table 1.

* = not measurable because material remained soft after drying

** = not measurable because there was not enough material to press a pellet or poor film quality

Error listed as standard deviation for a minimum of 3 independent samples.

Standard deviation not listed when there were fewer than 3 independent samples.

Compound	Pressed Pellet / S cm ⁻¹		Thin Film / S cm ⁻¹	
	2 - Probe	4 - Probe	2 - Probe	4 - Probe
<u>Monomers</u>				
PZn ₁ - 2,6(OR)Ar	8.67 x 10 ⁻¹¹		> 10 ⁻¹¹	
PZn ₁ - 3,5(OR)Ar	2.74 x 10 ⁻¹²		> 10 ⁻¹¹	
PZn ₁ - TPP	(7.60±0.11) x 10 ⁻¹¹		> 10 ⁻¹¹	
PZn ₁ - DPP	6.86 x 10 ⁻¹²		> 10 ⁻¹¹	
PZn ₁ - O1	2.07 x 10 ⁻¹²		> 10 ⁻¹¹	
PZn ₁ - O3EHex	*		*	
PZn1-O3Hex	*		*	
<u>Dimers</u>				
PZn ₂ - 2,6(OR)Ar	(9.59±0.13) x 10 ⁻¹¹		4.20 x 10 ⁻¹⁰	
PZn ₂ - 3,5(OR)Ar	(8.82±5.49) x 10 ⁻¹²		5.18 x 10 ⁻¹⁰	
PZn ₂ - 3,5(PEG)Ar	1.62 x 10 ⁻¹²		4.44 x 10 ⁻¹⁰	
PZn ₂ - O1	**		5.52 x 10 ⁻¹²	
PZn ₂ - O3EHex	**		**	
PZn ₂ - O3Hex	**		**	
<u>Trimers</u>				
PZn ₃ - 2,6(OR)Ar	8.54 x 10 ⁻¹¹		3.92 x 10 ⁻¹⁰	
PZn ₃ - 3,5(OR)Ar	(2.62±2.58) x 10 ⁻⁹		1.40 x 10 ⁻⁹	

PZn₃ - 3,5(PEG)Ar	(7.14±7.73) × 10 ⁻¹²		4.91 × 10 ⁻¹⁰	
PZn₃ - O1	6.00 × 10 ⁻⁸	5.95 × 10 ⁻⁸	(1.85±0.14) × 10 ⁻⁸	
PZn₃ - O3HexO1	4.69 × 10 ⁻⁷	5.29 × 10 ⁻⁷		
PZn₃ - O3Hex	6.99 × 10 ⁻⁸	2.96 × 10 ⁻⁷	(5.38±1.70) × 10 ⁻⁷	(1.07±0.10) × 10 ⁻⁶
PZn₃ - O3Hex	*		(5.24±2.40) × 10 ⁻⁷	(8.60±4.83) × 10 ⁻⁷
<u>Pentamers</u>				
PZn₅-3,5(PEG)Ar	**		(1.49±2.49) × 10 ⁻⁸	
PZn₅-3,5(OR)Ar	**		2.74 × 10 ⁻¹⁰	
PZn₅-O1	**		(3.24±3.20) × 10 ⁻⁸	
PZn₅-O3Hex	*		(3.83±1.11) × 10 ⁻⁵	(4.60±2.22) × 10 ⁻⁶