Driving High Quantum Yield NIR Emission through Proquinoidal Linkage Motifs in Conjugated Supermolecular Arrays

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1. Materials and Instrumentation

Materials. All manipulations were carried out under argon previously passed through an O_2 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. Unless otherwise noted, all solvents utilized in this work were obtained from Fisher Scientific (HPLC grade); tetrahydrofuran (THF) was distilled from Na/4-benzoylbiphenyl under N_2. Diisopropylamine, Triethylamine, MeOH, $CHCl_3$ and CH_2Cl_2 were distilled from CaH_2 under N_2. Pyridine and piperidine was also dried over CaH_2 and distilled under reduced pressure. The catalysts tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), bis(triphenylphosphine)-palladium(II) chloride ($Pd(PPh_3)_2Cl_2$), tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3), copper iodide (CuI), triphenylarsine ($AsPh_3$) and triphenylphosphine ($P(o\text{-tol})_3$) were purchased from Strem Chemicals and used as received. 4-Bromo-benzo[*c*][1,2,5]thiadiazole and 4,7 Dibromobenzo[*c*][1,2,5]thiadiazole[1] were prepared by literature methods. All NMR solvents were used as received. All the other chemicals were used as received.

Instrumentation. NMR spectra were recorded on a 500 MHz AC-Brucker instrument. All chemical shifts for ^{1}H NMR spectra are relative to tetramethylsilane (TMS) signal in the deuterated solvent (TMS = 0.00 ppm). All *J* values are reported in Hertz. Flash and size exclusion column chromatography were performed on the bench top, using silica gel (EM Science, 230–400 mesh) and Bio-Rad Bio-Beads SX-1, respectively, as media. MALDI-TOF spectroscopic data were obtained with a Perspective Voyager DE instrument; samples for these experiments were prepared as micromolar solutions in THF or CH_2Cl_2, and dithranol in THF or cyano-4-hydroxycinnamic acid in CH_2Cl_2/isopropyl alcohol (4:1) were utilized as the matrix.
Steady State Absorption. Absorption measurements were performed on a Shimadzu UV-1700 spectrophotometer in the same 1 cm quartz cell used for the quantum yield measurements.
Steady State Emission. Steady state emission spectra were recorded on an Edinburgh FLSP920, equipped with a Xe-lamp for excitation and an R2658 PMT (Hamamatsu) for detection, in the same 1 cm quartz cell used for the quantum yield measurements. The emission spectra were corrected for system and detector response using a correction file generated from traceable standard lamps.
Quantum Yield System. A Hamamatsu C9920-03 Absolute Quantum Yield Measurement System was employed to make the quantum yield measurements. Excitation initiates from a Xe-lamp, where the wavelength is selected by a monochromator, and passed through a 1 mm optical excitation fiber. The inside of the sphere is coated with Spectralon (Labsphere, Inc.) that has 99% reflectance from at least 350 – 1650 nm. The light transmitted, light scattered, and emitted light are collected through a second optical fiber protected by a baffle. The baffle ensures that each photon bounces twice within the sphere before being collected, which homogenizes the collected light such that no detected photons are from direct injection of scattered or emitted light into the fiber. Therefore, the individual signals of the light being detected is truly representative of the distribution of the light within the sphere. The collected light is then sent into a photonic multichannel analyzer (PMA-12) that contains a BT-CCD based spectrometer for light detection. The system response to wavelength and intensity are fully calibrated and corrected based on the output of traceable lamp sources to the National Metrology Institute of Japan.
Quantum Yield Measurement. A dilute stock solution of each sample was made fresh daily. For each sample, at least two sets of four concentrations were measured to show the precision of

the methodology. For each set, a low chromophore concentration (~0.025 OD) at the excitation wavelength was prepared, measured, and subsequently diluted 3 additional times until the final OD was roughly 0.005. Each measurement was checked for absorption prior to measurement to ensure this range. The reference sample of each measurement was a 1 cm cuvette filled with the solvent being used, and the same 1 cm cell was used for the whole set of measurement.

Density Functional Theory Calculations. All electronic structure calculations were performed upon model compounds in which the aliphatic chains were truncated to methyl groups. Structure optimization was performed with density functional theory using Gaussian 16.[2, 3] The M11 functional[4] was employed for all calculations. Optimizations were performed with minimal symmetry constraints using tight optimization criteria and the 6-311g(d) basis set was implemented. Selected frontier orbital wavefunctions were plotted as isosurfaces (iso = 0.02) using Avogadro.[5] TD-DFT result files were post-processed using the GaussSum package;[6] this software partitions the wavefunction amplitudes onto molecular fragments using Mulliken population analysis.[7]

2. Synthetic Procedures and Schemes

Synthesis.
For synthesis of previously made porphyrin compounds see supplemental literature.[8, 9]

4,7-Bis[(10,20-bis[2',6'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II)-5-ylethynyl]benzo[*c*][1,2,5]thiadiazole (PZn-BTD-PZn) (1). (5-Ethynyl-10, 20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (0.100 g, 1.05×10^{-4} mol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (12.9 mg, 4.4×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (12.1 mg, 1.32×10^{-5} mol) and $AsPh_3$ (32.3 mg, 1.05×10^{-4} mol). THF:$^{i}Pr_2NH$ (9:1 mL) 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 50 ºC overnight under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluent. Yield = 82 mg (91.6 % based on 12.9 mg of the dibromobenzo[*c*][1,2,5]thiadiazole starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.12 (d, 4H, J = 4.4 Hz, β-H), 10.04 (s, 2H, *meso*-H), 9.21 (d, 4H, J = 4.4 Hz, β-H), 9.06 (d, 4H, J = 4.5 Hz, β-H), 8.92 (d, 4H, J = 4.3 Hz, β-H), 8.37 (s, 2H, Ph-H), 7.74 (t, 4H, J = 8.6 Hz, Ph-H), 7.04 (d, 8H, J = 8.6 Hz, Ph-H), 3.94 (t, 16H, J = 7.2 Hz, -O-CH_2-C), 0.87 (t, 16H, J = 7.6 Hz, -O-C-CH_2-C), 0.24 (s, 72H, -C-CH_3). MALDI-TOF MS m/z : 2029.98 $(M+H)^+$ (calcd 2029.89).

(5-[7'-Bromobenzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl] -10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (2). (5-Ethynyl-10,20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (0.100 g, 1.05×10^{-4} mol) and 4, 7-dibromobenzo[*c*][1,2,5]thiadiazole (123.7 mg, 4.21×10^{-4} mol) were charged into a Schlenk flask with Pd_2dba_3 (14.4 mg, 1.57×10^{-5} mol) and $AsPh_3$ (38.5 mg, 1.26×10^{-4} mol). THF: $^{i}Pr_2NH$ (9:1

mL) 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 50 ºC overnight under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluent. Yield = 0.118 g (96.6 % based on 100 mg of the porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.06 (s, 1H, *meso*-H), 10.01 (d, 2H, J = 4.4 Hz, β-H), 9.22 (d, 2H, J = 4.4 Hz, β-H), 9.02 (d, 2H, J = 4.5 Hz, β-H), 8.91 (d, 2H, J = 4.5 Hz, β-H), 8.07 (d, 1H, J = 7.4 Hz, Ph-H), 8.01(d, 1H, J = 7.5 Hz, Ph-H), 7.71 (t, 2H, J = 8.6 Hz, Ph-H), 7.01 (d, 4H, J = 8.6 Hz, Ph-H), 3.90 (t, 8H, J = 7.3 Hz, -O-CH_2-C), 0.87 (t, 8H, J = 7.0 Hz, -O-C-CH_2-C), 0.22 (s, 36H, -C-CH_3).

(5, 15-Bis[7'-([10''',20'''-bis[2'''',6''''-bis(3''''',3''''')-dimethyl-1'''''-butyloxy)phenyl]porphinato)zinc(II)-5''-ylethynyl]benzo[*c*][1,2,5]thiadiazole-ethyn-4'-yl] 10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (PZn-(BTD-PZn)$_2$ (3). Compound 2 (0.100 g, 8.59×10^{-5} mol) and (5, 15-diethynyl-10, 20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (34.9 mg, 3.58×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (9.83 mg, 1.07×10^{-5} mol) and P(*o*-tol)$_3$ (26.1 mg, 8.59×10^{-5} mol). A THF: TEA (9:1 mL) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected, and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected, and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 114 mg (58% based on diethynyl starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.02 (d, 4H, J = 4.4 Hz, β-H), 9.94 (d, 4H, J = 4.5 Hz, β-H), 9.86 (s, 2H, *meso*-H), 9.08 (d, 4H, J = 4.2 Hz, β-H), 8.96 (d, 4H, J = 4.3 Hz, β-H), 8.86 (d, 4H, J = 4.5 Hz, β-H), 8.81(d, 4H, J = 4.2 Hz, β-H), 8.26 (s, 4H, Ph-H), 7.70 (t, 6H, J = 8.6 Hz, Ph-H), 7.02 (d, 6H, J = 4.6 Hz, Ph-H), 7.00 (d, 6H, J = 4.7 Hz, Ph-H), 3.89 (m, 24H, -O-CH_2-C), 0.87 (m, 24H, -O-C-CH_2-C), 0.34 (s, 36H, -C-CH_3), 0.30 (s, 72H, -C-CH_3). MALDI-TOF MS m/z: 3136.72 $(M+H)^+$ (calcd 3134.33).

(5-Ethynyl-15-[7'-bromobenzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl] -10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (4). (5-Ethynyl-15-triisopropylsilylethynyl-10,20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (0.100 g, 0.94×10^{-4} mol) and 4, 7-dibromobenzo[*c*][1,2,5]thiadiazole (110.7 mg, 3.77×10^{-4} mol) were charged into a Schlenk flask with Pd_2dba_3 (12.9 mg, 1.40×10^{-5} mol) and $AsPh_3$ (34.5 mg, 1.13×10^{-4} mol). THF: ^{i}Pr$_2$NH (9:1 mL) 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 50 ºC overnight under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluent. Yield = 0.117 g (92.4 % based on 100 mg of the porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 9.85 (d, 2H, β-H), 9.57 (d, 2H, J = 4.6 Hz, β-H), 8.83 (d, 2H, J = 4.5 Hz, β-H), 8.79 (d, 2H, J = 4.7 Hz, β-H), 7.69 (t, 2H, J = 8.5 Hz, Ph-H), 7.56 (m, 1H, Ph-H), 7.29 (m, 1H, Ph-H), 6.98 (d, 4H, J = 8.6 Hz, Ph-H), 1.43(m, 42H, -SiCH(CH_3)$_2$), 3.88 (t, 8H, J = 7.4 Hz, -O-CH_2-C), 0.87 (t, 8H, J = 7.3 Hz, -O-C-CH_2-C), 0.24 (s, 36H, -C-CH_3).

5, 15-Bistriisopropylsilylethynyl- (5, 15-bis[7'-([10''',20'''-bis[2'''',6''''-bis(3''''',3'''''-dimethyl-1''''''-butyloxy)phenyl]porphinato)zinc(II)-5''-ylethynyl]benzo[*c*][1,2,5]thiadiazole-ethyn-4'-yl]-10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (5). Compound 4 (0.100 g, 7.44×10^{-5} mol) and (5, 15-diethynyl-10, 20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (30.3 mg, 3.10×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (8.52 mg, 0.93×10^{-5} mol) and P(*o*-tol)$_3$ (22.6 mg, 7.44×10^{-5} mol). A THF:TEA (9:1 mL) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$:MeOH (49:1 mL) as the eluent. A large band was collected, the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 56.4 mg (52% based on diethynyl starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.02 (d, 4H, *J* = 4.4 Hz, β-H), 9.94 (d, 4H, *J* = 4.5 Hz β-H), 9.86 (s, 2H, *meso*-H), 9.08 (d, 4H, *J* = 4.2 Hz, β-H), 8.96 (d, 4H, *J* = 4.3 Hz, β-H), 8.86 (d, 4H, *J* = 4.5 Hz, β-H), 8.81(d, 4H, *J* = 4.2 Hz, β-H), 8.26 (s, 4H, Ph-H), 7.70 (t, 6H, *J* = 8.6 Hz, Ph-H), 7.02 (d, 6H, *J* = 4.6 Hz, Ph-H), 7.00 (d, 6H, *J* = 4.7 Hz, Ph-H), 3.89 (m, 24H, -O-CH_2-C), 1.42 (m, 42H, -SiCH(CH_3)$_2$), 0.87 (m, 24H, -O-CCH_2- C), 0.34 (s, 36H, -C-CH_3), 0.30 (s, 72H, -C-CH_3). MALDI-TOF MS m/z: 3136.72 $(M+H)^+$ (calcd 3134.33).

5, 15-Ethynyl- (5, 15-bis[7'-([10''',20'''-bis[2'''',6''''-bis(3''''',3'''''-dimethyl-1''''''butyloxy)phenyl]porphinato)zinc(II)-5''-ylethynyl]benzo[*c*][1,2,5]thiadiazole-ethyn-4'-yl]-10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (6). Compound 5 (100 mg, 2.63×10^{-5} mol) was dissolved in THF and cooled down to 0 ºC under Ar. TBAF (0.526 mL, 0.1 M TBAF in THF solution, 5.26×10^{-5} mol) was then added dropwise and the reaction mixture was allowed to stir for 15 min at 0 ºC. The reaction mixture was then directly poured down a short silica gel column using $CHCl_3$ as the eluent. Yield = 75 mg (82.3% based on compound 5). ^{1}H NMR (500 MHz, $CDCl_3$): 10.05 (d, 4H, *J* = 4.4 Hz, β-H), 9.96 (d, 4H, *J* = 4.5 Hz, β-H), 9.02 (d, 4H, *J* = 4.2 Hz, β-H), 8.96 (d, 4H, *J* = 4.3 Hz, β-H), 8.87 (d, 4H, *J* = 4.5 Hz, β-H), 8.80 (d, 4H, *J* = 4.2 Hz, β-H), 8.26 (s, 4H, Ph-H), 7.72 (t, 6H, *J* = 8.6 Hz, Ph-H), 7.02 (d, 6H, *J* = 4.6 Hz, Ph-H), 7.00 (d, 6H, *J* = 4.7 Hz, Ph-H), 4.13 (s, 2H), 3.89 (m, 24H, -O-CH_2-C), 0.87 (m, 24H, -O-C-CH_2-C), 0.34 (s, 36H, -CCH_3), 0.30 (s, 72H, -C-CH_3).

(5, 15-Bis[7''-([10'''',20''''-bis[2''''',6''''']-bis(3''''''',3''''''-dimethyl-1''''''-butyloxy)phenyl]porphinato)zinc(II)-5'''-ylethynyl]benzo[*c*][1,2,5]thiadiazole-ethyn-4''-yl]-(5, 15-bis[7'-([10''',20'''-bis[2'''',6''''-bis(3''''',3''''')-dimethyl-1''''''-butyloxy)phenyl]porphinato)zinc(II)-5''-ylethynyl]benzo[*c*][1,2,5]thiadiazole-ethyn4'-yl] 10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (PZn-(BTD-PZn)$_4$ (7). Compound 2 (0.100 g, 8.59×10^{-5} mol) and compound 6 (114.1 mg, 3.58×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (9.83 mg, 1.07×10^{-5} mol) and P(*o*-tol)$_3$ (26.1 mg, 8.59×10^{-5}mol). A THF:TEA (9:1 mL) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$:MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and

then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected, solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$: MeOH (49:1 mL) as the eluent. Yield = 61.2 mg (32% based on compound 6). ^{1}H NMR (500 MHz, $CDCl_3$): 10.02 (d, 4H, J = 4.4 Hz, β-H), 9.94 (d, 4H, J = 4.5 Hz, β-H), 9.86 (s, 2H, *meso*-H), 9.08 (d, 4H, J = 4.2 Hz, β-H), 8.96 (d, 4H, J = 4.3 Hz, β-H), 8.86 (d, 4H, J = 4.5 Hz, β-H), 8.81(d, 4H, J = 4.2 Hz, β-H), 8.26 (s, 4H, Ph-H), 7.70 (t, 6H, J = 8.6 Hz, Ph-H), 7.02 (d, 6H, J = 4.6 Hz, Ph-H), 7.00 (d, 6H, J = 4.7 Hz, Ph-H), 3.89 (m, 24H, -O-CH_2-C), 0.87 (m, 24H, -O-C-CH_2-C), 0.34 (s, 36H, -C-CH_3), 0.30 (s, 72H, -C-CH_3). MALDI-TOF MS *m/z*: 5366.7 $(M+Na)^+$ (calcd 5367.18).

(5, 15-Bis[benzo[*c*][1,2,5]thiadiazole-ethyn-4'-yl] -10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (BTD-PZn-BTD) (8). (5, 15-Diethynyl-10,20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (50.0 mg, 5.13×10^{-5} mol), and 4 bromobenzo[*c*][1,2,5]thiadiazole (26.5 mg, 1.23×10^{-4} mol) were charged into a Schlenk flask with Pd_2dba_3 (14.1 mg, 1.54×10^{-5} mol) and $AsPh_3$ (37.7 mg, 1.23×10^{-4} mol). THF: ^{i}Pr$_2$NH (9:1 mL) 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 50 ºC overnight under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluent. Yield = 57.2 mg (90.2 % based on 50 mg of the porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 9.82 (d, 4H, J = 4.5 Hz, β -H), 8.85 (d, 4H, J = 4.5 Hz, β-H), 7.97 (d, 2H, J = 6.4 Hz, Ph-H), 7.68 (t, 2H, J = 8.5 Hz, Ph-H), 7.47 (m, 2H, Ph-H), 7.01 (t, 2H, J = 8.6 Hz, Ph-H), 6.98 (m, 6H, Ph-H), 3.86 (t, 8H, J = 7.3 Hz, -O-CH_2-C), 0.77 (t, 8H, J = 7.3 Hz, -O-CCH_2-C), 0.19 (s, 36H, -C-CH_3). MALDI-TOF MS m/z: 1239.53 $[(M+H)^+]$ (calcd 1240.44).

4-(Trimethylsilyl)ethynylbenzo[*c*][1,2,5]thiadiazole (9). 4-Bromobenzo[*c*][1,2,5]thiadiazole (0.378 g, 1.76×10^{-3} mol), $Pd(PPh_3)_4$ (0.125 g, 1.68×10^{-4} mol), CuI (0.014 g, 7.4×10^{-5} mol), THF (20 mL), diisopropylamine (1.00 mL), and (trimethylsilyl)acetylene (1.00 mL, 7.1×10^{-3} mol) were added to a 50 mL Schlenk tube. N_2 was bubbled through the mixture for 5 min, following which the reaction was stirred at 45 ºC for 20 h under N_2. After cooling, the solvent was evaporated, and the residue was chromatographed on silica gel with 1:1 hexanes:$CHCl_3$ as the eluent. Yield = 0.398 g (97.3 % based on 0.378 g of 4-bromobenzothiadiazole). ^{1}H NMR (500 MHz, $CDCl_3$): 7.88 (m, 1H, Ph-H), 7.67 (m, 1H, Ph-H), 7.45 (m, 1H, Ph-H), 0.33 (s, 9H, -Si-CH_3).

4-Ethynylbenzo[*c*][1,2,5]thiadiazole (10). 4-(Trimethylsilyl)ethynylbenzo[*c*][1,2,5]thiadiazole (0.100 g, 4.30×10^{-4} mol), K_2CO_3 (78.6 mg, 5.71×10^{-4} mol), THF (3 mL), and MeOH (2 mL) were added to a 25 mL Schlenk tube. N_2 was bubbled through the mixture for 5 min, following which the reaction was stirred at room temperature for 1.5 h under N_2. The reaction mixture was then filtered and the filtrate was evaporated. The residue was chromatographed on silica gel with 5:1 hexanes:THF as the eluent. Yield = 63 g (91.4% based on 0.100 g of 4-(trimethylsilyl)-ethynylbenzothiadiazole). ^{1}H NMR (500 MHz, $CDCl_3$): 8.01 (m, 1H, Ph-H), 7.78 (m, 1H, Ph-H), 7.56 (m, 1H, Ph-H), 3.56 (s, 1H, -CC-H).

(5-Bromo-15-[benzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl] -10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (11). (5, 15-Dibromo-10,20-bis[2",6"-bis(3,3-

dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (0.200 g, 1.84×10^{-4} mol) and 4-ethynylbenzo[*c*][1,2,5]thiadiazole (14.8 mg, 8.22×10^{-5} mol) were charged into a Schlenk flask with $Pd(PPh_3)_4$ (26.6 mg, 2.30×10^{-5} mol) and CuI (8.8 mg, 4.62×10^{-4} mol). THF:piperidine (9:1 mL) 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 50 ºC overnight under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluent. Yield = 0.076 g (64.9 % based on the 4-ethynylbenzothiadiazole starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 9.75 (d, 2H, β-H), 9.57 (d, 2H, J = 4.6 Hz, β-H), 8.88 (d, 2H, J = 4.5 Hz, β-H), 8.81 (d, 2H, J = 4.7 Hz, β-H), 8.00 (m, 1H, Ph-H), 7.69 (t, 2H, J = 8.5 Hz, Ph-H), 7.56 (m, 1H, Ph-H), 7.29 (m, 1H, Ph-H), 6.98 (d, 4H, J = 8.6 Hz, Ph-H), 3.88 (t, 8H, J = 7.4 Hz, -O-CH_2-C), 0.87 (t, 8H, J = 7.3 Hz, -O-C-CH_2-C), 0.24 (s, 36H, -C-CH_3).

(5-Triisopropylsilylethynyl-15-[benzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl] -10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (12). (5-Bromo-15-triisopropylsilylethynyl-10,20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (0.200 g, 1.69×10^{-4} mol) and 4-ethynylbenzo[*c*][1,2,5]thiadiazole (32.5 mg, 2.03×10^{-4} mol) were charged into a Schlenk flask with $Pd(PPh_3)_4$ (29.3 mg, 2.53×10^{-5} mol) and CuI (9.6 mg, 5.06×10^{-5} mol). THF:piperidine (9:1 mL) 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 50 ºC overnight under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluent. Yield = 164.4 mg (76.8 % based on the porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 9.87 (d, 2H, β-H), 9.61 (d, 2H, J = 4.5 Hz, β-H), 8.86 (d, 2H, J = 4.5 Hz, β-H), 8.80 (d, 2H, J = 4.5 Hz, β-H), 8.07 (m, 1H, Ph H), 7.67 (t, 2H, J = 8.5 Hz, Ph-H), 7.60 (m, 1H, Ph-H), 7.49 (m, 1H, Ph-H), 6.98 (d, 4H, J = 8.5 Hz, Ph-H), 3.88 (t, 8H, J = 7.4 Hz, -O-CH_2-C), 1.41 (m, 21H, -Si-$(CH(CH_3)_2)_3$), 0.88 (t, 8H, J = 7.3 Hz, -O-C-CH_2-C), 0.27 (s, 36H, -C-CH_3).

(5-Ethynyl-15-[benzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl] -10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (13). Compound 12 (160 mg, 1.26×10^{-4} mol) was dissolved in THF under Ar. TBAF (2.5 mL, 0.1 M TBAF in THF solution, 2.5×10^{-4} mol) was then added dropwise and the reaction mixture was allowed to stir for 5 min at room temperature. TLC analysis (5:1 hexanes:THF) showed complete formation of the product and consumption of the starting material. The reaction mixture was then quenched with 10 mL water, extracted with $CHCl_3$ and evaporated. The residue was chromatographed on silica gel using 5:1 hexanes:THF as the eluant. Yield = 125.5 mg (89.5% based on compound 12). ^{1}H NMR (500 MHz, $CDCl_3$): 9.86 (d, 2H, β-H), 9.57 (d, 2H, J = 4.1 Hz, β-H), 8.85 (d, 2H, J = 4.8 Hz, β-H), 8.81 (d, 2H, J = 4.5 Hz, β-H), 8.03 (m, 1H, Ph-H), 7.69 (t, 2H, J = 8.5 Hz, Ph-H), 7.56 (m, 1H, Ph-H), 7.49 (m, 1H, Ph-H), 6.98 (m, 4H, Ph-H), 4.07 (S, 1H, -CC-H), 3.88 (t, 8H, J = 7.4 Hz, -O-CH_2-C), 0.87 (t, 8H, J = 6.8 Hz, -O-C-CH_2-C), 0.29 (s, 36H, -C-CH_3).

1,2-Bis[(15-(benzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl)-10,20-bis[3',5'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II)-5-yl]ethyne (BTD-PZn$_2$-BTD) (14). Compound 11 (50.0 mg, 4.30×10^{-5} mol) and compound 13 (57.0 mg, 5.16×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (5.9 mg, 6.45×10^{-6} mol) and $AsPh_3$ (15.8 mg, 5.16×10^{-5} mol). A THF:TEA (9:1 mL) 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 ºC overnight under

Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$:MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 45 mg (47.8% based on 50 mg of compound 11). ^{1}H NMR (500 MHz, $CDCl_3$): 10.19 (d, 4H, J = 4.4 Hz, β-H), 9.85 (d, 4H, J = 4.3 Hz, β-H), 8.88 (d, 4H, J = 4.4 Hz, β-H), 8.84 (d, 4H, J = 4.5 Hz, β-H), 8.10 (d, 2H, J = 6.1 Hz, Ph-H), 8.07 (m, 2H, Ph-H), 7.66 (t, 4H, J = 8.6 Hz, Ph-H), 7.00 (d, 8H, J = 8.6 Hz, Ph-H), 3.89 (t, 16H, J = 7.5 Hz, -O-CH_2-C), 0.82 (t, 16H, J = 6.6 Hz, -O-C-CH_2-C), 0.32 (s, 72H, -C-CH_3). MALDI-TOF MS *m/z*: 2182.14 $(M+H)^+$ (calcd 2187.89).

(5, 15-Bis[15'-benzo[*c*][1,2,5]thiadiazole-ethyn-4'-yl-(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) (BTD-PZn$_3$-BTD) (15). Compound 13 (60 mg, 5.42×10^{-5} mol) and (5, 15-dibromo-10, 20-bis[2",6"-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (24.5 mg, 2.26×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (6.2 mg, 6.78×10^{-6} mol) and P(*o*-tol)$_3$ (16.5 mg, 5.42×10^{-5} mol). A THF:TEA (9:1 mL) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 48.4 mg (68.2% based on dibromo starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.16 (d, 4H, J = 4.4 Hz, β-H), 10.14 (d, 4H, J = 4.3 Hz, β-H), 9.81 (d, 4H, J = 4.4 Hz, β-H), 8.87 (d, 4H, J = 4.4 Hz, β-H), 8.85 (d, 4H, J = 4.4 Hz, β-H), 8.81 (d, 4H, J = 4.4 Hz, β-H), 8.02 (d, 2H, J = 6.0 Hz, Ph-H), 7.90 (d, 2H, J = 8.7 Hz, Ph-H), 7.63 (m, 8H, Ph-H), 6.96 (m, 12H, J = 4.6 Hz, Ph-H), 3.89 (m, 24H, -O-CH_2-C), 0.81 (m, 24H, -O-C-CH_2-C), 0.28 (s, 36H, -C-CH_3), 0.26 (s, 72H, -C-CH_3). MALDI-TOF MS *m/z*: 3136.80 $(M+H)^+$ (calcd 3134.33).

(5,15-Bis[(15'-triisopropylsilylethynyl-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) (16): (5-bromo-15-triisopropylsilylethynyl-10,20-bis[2",6"-bis(3"",3""-dimethyl-1""butyloxy)phenyl]porphinato)zinc(II) (120 mg, 1.01×10^{-4} mol) and (5,15-diethynyl-10,20-bis[2",6"-bis(3"",3""dimethyl-1""-butyloxy)phenyl]porphinato)zinc(II) (41.1 mg, 4.21×10^{-5} mol) were charged into a Schlenk flask with $AsPh_3$ (30.9 mg, 1.01×10^{-4} mol) and Pd_2dba_3 (11.6 mg, 1.26×10^{-5} mol). A THF:TEA (9:1 mL) solvent mixture was degassed with an Ar purge for 30 min and then transferred to the reaction flask. The reaction mixture was stirred at 60 ºC under Ar overnight. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$: MeOH (49:1 mL) as the eluent. Yield =

114 mg (85% based on diethynyl starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.35 (d, 8H, β-H), 9.64 (d, 4H, β-H), 9.01 (d, 8H, β-H), 8.86 (d, 4H, β-H), 7.72 (d, 6H, β-H), 7.05 (d, 12H, J = 4.6 Hz, Ph-H), 3.98 (m, 24H, -O-CH_2-C), 1.40 (m, 42, -SiCH(CH_3)$_2$), 0.89 (m, 24H, -O-C-CH_2-C), 0.40 (s, 36H, -C-CH_3), 0.37 (s, 72H, -C-CH_3).

(5,15-Bis[(15'-ethynyl-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) (17): Compound 16 (114 mg, 3.58×10^{-5} mol) was dissolved in THF and cooled down to 0 ºC under Ar. TBAF (0.716 mL, 0.1 M TBAF in THF solution, 7.16×10^{-5} mol) was then added dropwise and the reaction mixture was allowed to stir for 15 min at 0 ºC. The reaction mixture was then directly poured down a short silica gel column using $CHCl_3$ as the eluent. Yield = 101.2 mg (98.4% based on compound 16). ^{1}H NMR (500 MHz, $CDCl_3$): 10.35 (d, 8H, β-H), 9.64 (d, 4H, β-H), 9.01 (d, 8H, β-H), 8.86 (d, 4H, β-H), 7.72 (d, 6H, β-H), 7.05 (d, 12H, J = 4.6 Hz, Ph-H), 4.11 (s, 2H), 3.98 (m, 24H, -O-CH_2-C), 0.89 (m, 24H, -O-C-CH_2-C), 0.40 (s, 36H, -C-CH_3), 0.37 (s, 72H, -C-CH_3).

[5,15-Bis(15'''-[(15''''''- benzo[*c*][1,2,5]thiadiazole-ethyn-4'''''''-yl -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)-ethyn-5'''-yl)-10,20-bis[2',6'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl)phenyl]porphinato]zinc(II) (BTD-PZn$_5$-BTD) (18): Compound 11 (50 mg, 4.13×10^{-5} mol), compound 17 (47.4 mg, 1.65×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (5.7 mg, 4.95×10^{-6} mol) and P(*o*-tol)$_3$ (12.1 mg, 3.96×10^{-5} mol), CuI (0.31mg, 1.65×10^{-6} mol). A THF:TEA (9:1 ml) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 55 mg (68.2% based on compound 17). ^{1}H NMR (500 MHz, $CDCl_3$): 10.39 (m, 8H, β-H), 10.35 (m, 8H, β-H), 9.84 (d, 4H, β-H), 9.04 (m, 16H, β-H), 8.88 (d, 4H, β-H), 7.77 (d, 2H, Ph-H), 7.74 (m, 12H, Ph-H), 7.55 (d, 2H, Ph-H), 7.07 (m, 20H, Ph-H), 4.03 (m, 40H, -O-CH_2-C), 0.89 (m, 40H, -O-C-CH_2-C), 0.38 (m, 180H, -C-CH_3). MALDI-TOF MS *m/z*: 5046.80 $(M+Na)^+$ (calcd 5049.18).

(5- Triisopropylsilylethynyl-15-[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) (19). (5-Bromo-15-triisopropylsilylethynyl-10,20-bis[2'',6''-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (74.8 mg, 6.31×10^{-5} mol) and (5-ethynyl-10,20-bis[2'',6''-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)zinc(II) (50 mg, 5.26×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (7.2 mg, 7.89×10^{-6} mol) and $AsPh_3$ (19.2 mg, 6.31×10^{-5} mol). A THF:TEA (9:1 mL) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel

column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 82 mg (75.8 % based on the 50 mg of 5-Bromo-15-triisopropylsilylethynyl porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl^3$): 10.43 (d, 2H, J = 4.6 Hz, β-H), 10.42 (d, 2H, J = 4.4 Hz, β-H), 10.03 (s, 1H, *meso*-H), 9.65 (d, 2H, J = 4.5 Hz, β-H), 9.23 (d, 2H, J = 4.4 Hz, β-H), 9.10 (d, 2H, J = 4.6 Hz, β-H), 8.99 (d, 2H, J = 4.4 Hz, β-H), 8.95 (d, 2H, J = 4.4 Hz, β-H), 8.86 (d, 2H, J = 4.4 Hz, β-H), 7.73 (m, 4H, Ph-H), 7.05 (m, 8H, Ph-H), 3.98 (m, 16H, -O-CH_2-C), 1.43 (m, 21, -SiCH(CH_3)$_2$), 0.89 (m, 16H, -O-C-CH_2-C), 0.45 (s, 36H, -C-CH_3), 0.42 (s, 36H, -C-CH_3).

(5-Ethynyl-15-[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) (20). Compound 19 (80 mg, 3.89×10^{-5} mol) was dissolved in THF and cooled down to 0 ºC under Ar. TBAF (0.778 mL, 0.1 M TBAF in THF solution, 7.78×10^{-5} mol) was then added dropwise and the reaction mixture was allowed to stir for 15 min at 0 ºC. The reaction mixture was then directly poured down a short silica gel column using $CHCl_3$ as the eluent. Yield = 65 mg (87.9% based on compound 16). ^{1}H NMR (500 MHz, $CDCl_3$): 10.43 (d, 2H, J = 4.6 Hz, β-H), 10.42 (d, 2H, J = 4.4 Hz, β-H), 10.03 (s, 1H, *meso*-H), 9.65 (d, 2H, J = 4.5 Hz, β-H), 9.23 (d, 2H, J = 4.4 Hz, β-H), 9.10 (d, 2H, J = 4.6 Hz, β-H), 8.99 (d, 2H, J = 4.4 Hz, β-H), 8.95 (d, 2H, J = 4.4 Hz, β-H), 8.86 (d, 2H, J = 4.4 Hz, β-H), 7.73 (m, 4H, Ph-H), 7.05 (m, 8H, Ph-H), 4.10 (s, 2H), 3.98 (m, 16H, -O-CH_2-C), 0.89 (m, 16H, -O-C-CH_2-C), 0.45 (s, 36H, -C-CH_3), 0.42 (s, 36H, -C-CH_3).

4,7-Diiodobenzo[*c*][1,2,5]thiadiazole (21). Benzo[*c*][1,2,5]thiadiazole (3.20 g, 2.35×10^{-2} mol), I_2 (13.2 g, 5.20×10^{-2} mol) and Ag_2SO_4 (7.34 g, 2.35×10^{-2} mol) were added to a 100 mL three neck round bottom flask. 35 mL concentrated H_2SO_4 was added to the mixture and the reaction mixture was stirred at 110 ºC for 14 hours under N_2. After cooling, the reaction mixture was poured into ice water and the precipitate was collected by filtration. This precipitate was washed with $CHCl_3$. The organic solution was then washed with saturated $NaHSO_3$ aqueous solution and brine respectively for three times and dried over Na_2SO_4. The product was then chromatographed on silica gel with 1:1 hexanes:$CHCl_3$ as the eluant. Yield = 3.95 g (43.3 % based on 3.20 g of benzothiadiazole). ^{1}H NMR (500 MHz, $CDCl_3$): 7.75 (s, 12H, Ph-H).

4,7-Bis[(15-(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)-5-ylethynyl]benzo[*c*][1,2,5]thiadiazole (PZn_2-BTD-PZn_2) (22). Compound 20 (50.0 mg, 2.63×10^{-5} mol) and Compound 21 (4.27 mg, 1.10×10^{-6} mol) were charged into a Schlenk flask with Pd_2dba_3 (3.03 mg, 3.31×10^{-7} mol) and $AsPh_3$ (8.05 g, 2.63×10^{-5} mol). THF:^{i}Pr$_2$NH (9:1 mL) 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 ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed

via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 35 mg (80.6 % based on 4.27 mg of compound 21). ^{1}H NMR (500 MHz, THF-d^8): 10.33 (d, 4H, J = 7.3 Hz, β-H), 10.28 (d, 4H, J = 7.0 Hz, β-H), 10.07 (d, 4H, J = 8.3 Hz, β-H), 9.90(s, 2H, *meso*-H), 9.13 (d, 4H, J = 7.0 Hz, β-H), 9.06 (d, 4H, J = 7.4 Hz, β-H), 8.94 (m, 8H, β-H), 8.88 (d, 4H, J = 4.2 Hz, β-H), 8.40 (s, 2H, Ph-H), 7.79 (m, 8H, Ph-H), 7.17 (m, 16H, Ph-H), 4.01 (m, 32H, -O-CH_2-C), 0.87 (m, 32H, -O-C-CH_2-C), 0.41 (d, 72H, J = 5.2 Hz, -C-CH_3), 0.36 (d, 72H, J = 5.1 Hz, -C-CH_3). MALDI-TOF MS *m/z*: 3942.10 $(M+H)^+$ (calcd 3938.80).

1,2-Bis[(15-triisoprpylsilylethynyl-10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II)-5-yl]ethyne (23). (5-Bromo-15-triisopropylsilylethynyl-10,20-bis[2'',6''-bis(3'''',3''''-dimethyl-1''''butyloxy)phenyl]porphinato)zinc(II) (150 mg, 1.26 x 10^{-4} mol) and (5-ethynyl-15-triisopropylsilylethynyl-10,20-bis[2'',6''-bis(3'''',3''''-dimethyl-1''''butyloxy)phenyl]porphinato)zinc(II) (106 mg, 9.40×10^{-5} mol) were charged into a Schlenk flask with $AsPh_3$ (46.3 mg, 1.51×10^{-4} mol) and Pd_2dba_3 (17 mg, 1.89×10^{-5} mol). A THF:TEA (9:1 mL) solvent mixture was degassed with an Ar purge for 30 min and then transferred to the reaction flask. The reaction mixture was stirred at 60 ºC under Ar overnight. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$: MeOH (49:1 mL) as the eluent. Yield = 164 mg (78.1% based on 106 mg 5-ethynyl-15-triisopropylsilylethynyl porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.36 (d, 4H, β-H), 9.67 (d, 4H, β-H), 9.00 (d, 4H, β-H), 8.88 (d, 4H, β-H), 7.75 (m, 4H, Ph-H), 7.06 (m, 8H, Ph-H), 3.98 (m, 16H, -O-CH_2-C), 1.46 (m, 21H, -SiCH(CH_3)$_2$), 0.91 (m, 16H, -O-C-CH_2-C), 0.38 (d, 72H, -C-CH_3).

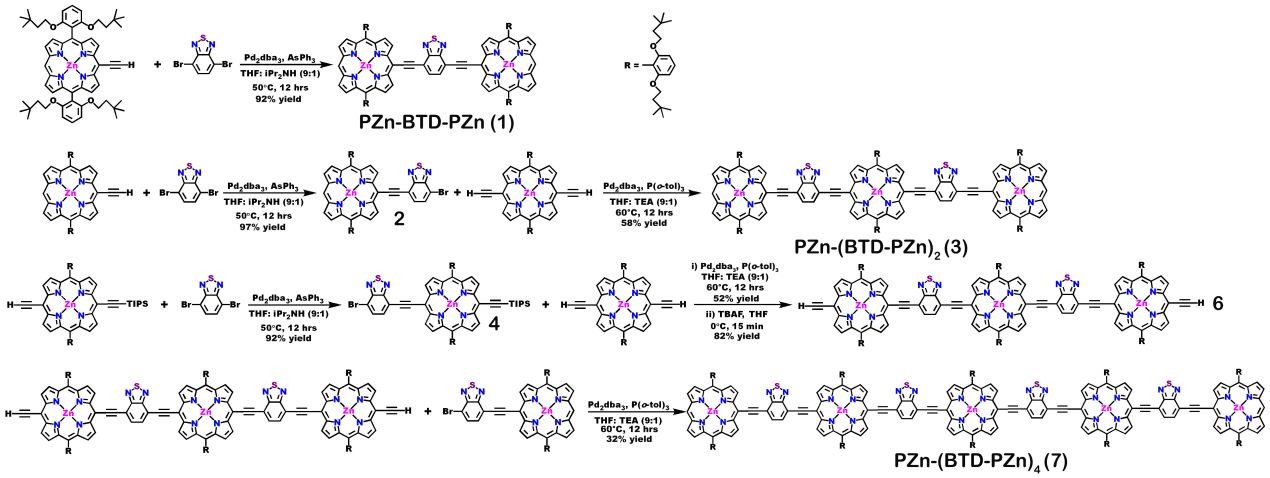
1,2-Bis[(15-ethynyl-10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II)-5-yl]ethyne (24). Compound 23 (150 mg, 6.71×10^{-5} mol) was charged in a Schlenk flask and dissolved in THF and cooled to 0 ºC while under Ar. TBAF (1.34 mL, 0.1 M TBAF solution in THF, 1.34×10^{-4} mol) was added dropwise to the reaction mixture and allowed to stir for 15 min at 0 ºC under Ar. At 15 min the reaction mixture was poured down a prepacked $CHCl_3$ silica gel plug and the first band was collected and solvent removed via vacuum. Yield = 115 mg (89.1% based on compound 23). ^{1}H NMR (500 MHz, $CDCl_3$):10.32 (d, 4H, β-H), 9.58 (d, 4H, β-H), 8.96 (d, 4H, β-H), 8.84 (d, 4H, β-H), 7.73 (m, 4H, Ph-H), 7.06 (m, 8H, Ph-H), 4.10 (s, 2H), 3.96 (m, 16H, -O-CH_2-C), 0.91 (m, 16H, -O-CCH_2-C), 0.40 (d, 72H, -C-CH_3).

(5-(10',20'-Bis[2'',6''-bis(3''',3'''-dimethyl-1'''butyloxy)phenyl]porphinato)zinc(II)-ethyn-5'-yl)-15-[7'-bromobenzo[*c*][1,2,5]thiadiazole- ethyn-4'-yl] -10,20-bis[2',6'-bis(3'',3''-dimethyl-1''butyloxy)phenyl]porphinato)zinc(II) (25). Compound 20 (0.200 g, 1.05×10^{-4} mol) and 4, 7-dibromobenzo[*c*][1,2,5]thiadiazole (123.8 mg, 4.21×10^{-4} mol) were charged into a Schlenk flask with Pd_2dba_3 (14.4 mg, 1.57×10^{-5} mol) and $AsPh_3$ (38.6 mg, 1.26×10^{-4} mol). A THF:TEA (9:1 mL) solvent mixture was degassed with an Ar purge for 30 min prior to solvent

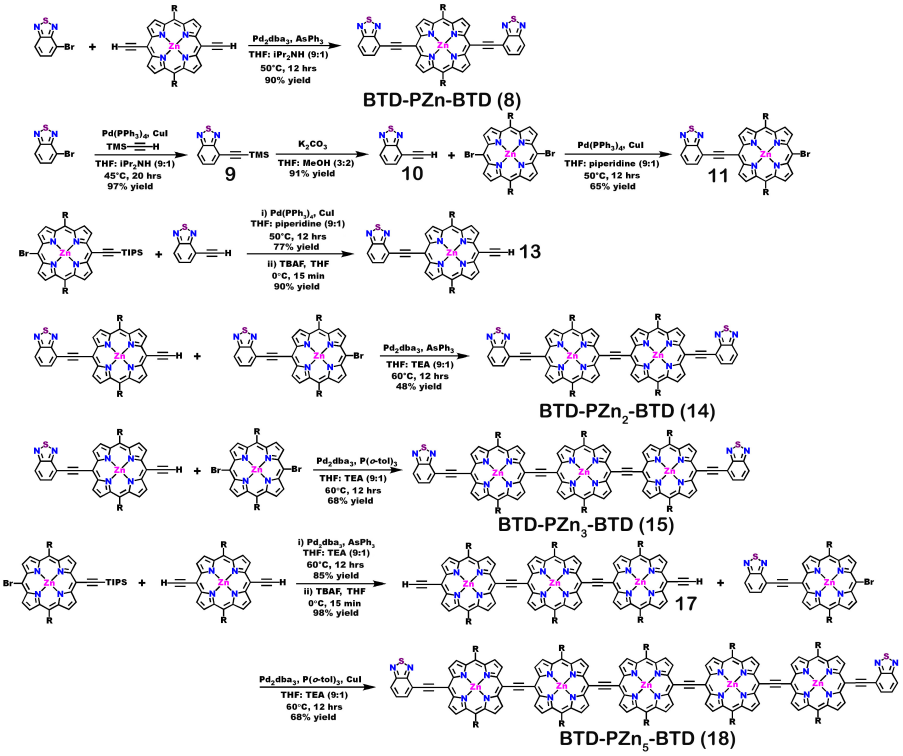
transfer. Once solvent was transferred, the reaction mixture, was stirred at 50 ºC overnight under Ar. After the solvent was evaporated, the residue was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The second band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$:MeOH (49:1 mL) as the eluent. Yield = 108 mg (48.7 % based on 0.200 mg of the porphyrin starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.43 (d, 2H, J = 4.6 Hz, β-H), 10.42 (d, 2H, J = 4.4 Hz, β-H), 10.03 (s, 1H, *meso*-H), 9.65 (d, 2H, J = 4.5 Hz, β-H), 9.23 (d, 2H, J = 4.4 Hz, β-H), 9.10 (d, 2H, J = 4.6 Hz, β-H), 8.99 (d, 2H, J = 4.4 Hz, β-H), 8.95 (d, 2H, J = 4.4 Hz, β-H), 8.86 (d, 2H, J = 4.4 Hz, β-H), 8.10 (d, 1H, J = 6.1 Hz, Ph-H), 7.73 (m, 5H, Ph-H), 7.05 (m, 8H, Ph-H), 3.98 (m, 16H, -O-CH_2-C), 1.43 (m, 21, -SiCH(CH_3)$_2$), 0.89 (m, 16H, -O-C-CH_2-C), 0.45 (s, 36H, -C-CH_3), 0.42 (s, 36H, -C-CH_3).

1,2-Bis(4-[10,20-bis[2',6'-bis(3'',3''-dimethyl-1''-butyloxy)phenyl]porphinato)zinc(II)-5-ylethynyl],7-[(15-(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)-5-ylethynyl]benzo[*c*][1,2,5]thiadiazole (PZn_2-(BTD-PZn_2)$_2$ (26). Compound 25 (181.4 mg, 8.59×10^{-5} mol) and compound 24 (68.9 mg, 3.58×10^{-5} mol) were charged into a Schlenk flask with Pd_2dba_3 (9.83 mg, 1.07×10^{-5} mol) and P(*o*-tol)$_3$ (26.1 mg, 8.59×10^{-5} mol). A THF:TEA (9:1 mL) 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 60ºC overnight under Ar. The reaction mixture was then poured down a short silica gel column using $CHCl_3$: MeOH (49:1 mL) as the eluent. A large band was collected and the solvent stripped and then the residue was taken up in THF and put down a size exclusion column (BioRad Biobeads, SX-1) and chromatographed gravimetrically. The first band was collected and solvent removed via vacuum and the residue was purified by silica gel chromatography using $CHCl_3$: MeOH (49:1 mL) as the eluent. Yield = 68.9 mg (32% based on diethynyl starting material). ^{1}H NMR (500 MHz, $CDCl_3$): 10.02 (d, 4H, J = 4.4 Hz, β-H), 9.94 (d, 4H, J = 4.5 Hz, β-H), 9.86 (s, 2H, *meso*-H), 9.08 (d, 4H, J = 4.2 Hz, β-H), 8.96 (d, 4H, J = 4.3 Hz, β-H), 8.86 (d, 4H, J = 4.5 Hz, β-H), 8.81(d, 4H, J = 4.2 Hz, β-H), 8.26 (s, 4H, Ph-H), 7.70 (t, 6H, J = 8.6 Hz, Ph-H), 7.02 (d, 6H, J = 4.6 Hz, Ph-H), 7.00 (d, 6H, J = 4.7 Hz, Ph-H), 3.89 (m, 24H, -O-CH_2-C), 0.87 (m, 24H, -O-C-CH_2-C), 0.34 (s, 36H, -C-CH_3), 0.30 (s, 72H, -C-CH_3). MALDI-TOF MS *m/z*: 6017.79 $(M+Na)^+$ (calcd 6023.65).

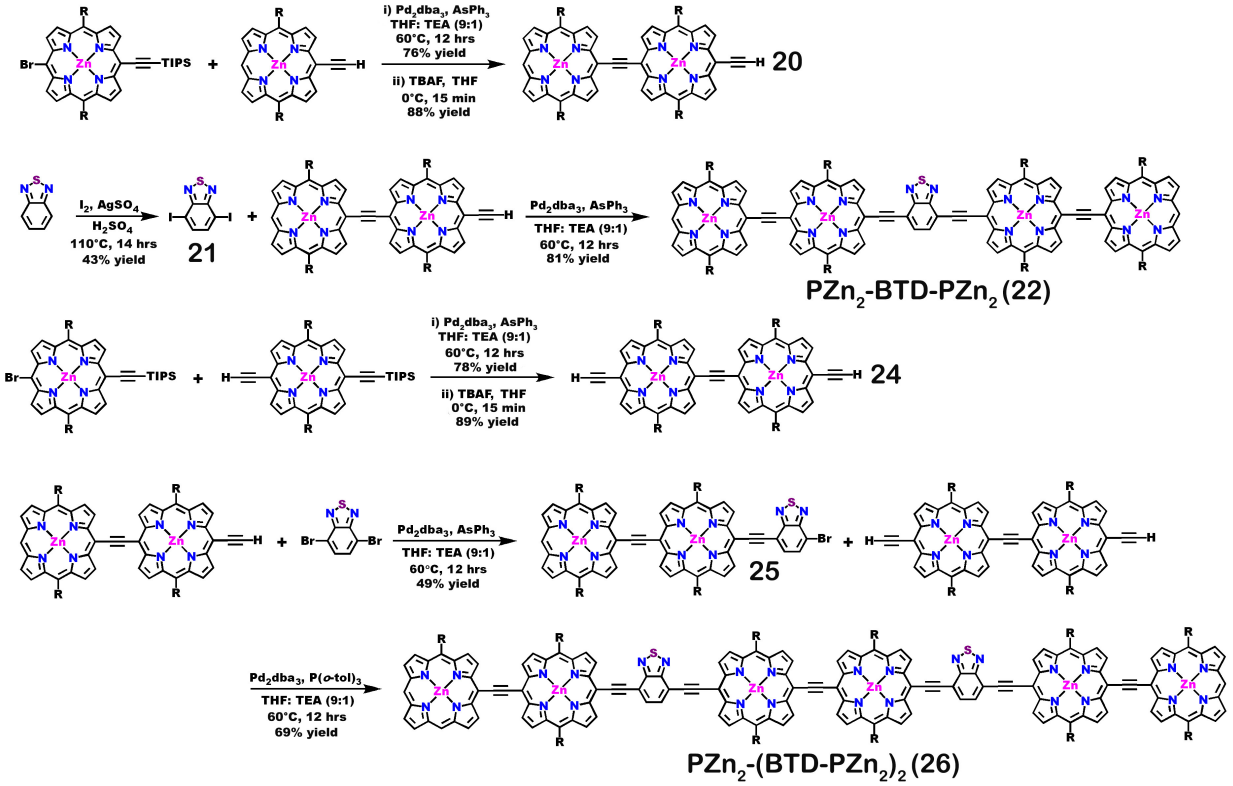
Synthetic Schemes.



Scheme 1. Syntheses of **PZn-(BTD-PZn)$_n$** compounds.



Scheme 2. Syntheses of **BTD-PZn$_n$-BTD** compounds.



Scheme 3. Syntheses of **$(PZn)_2$-$(BTD\text{-}PZn_2)_n$** compounds.

3. Characterization and Additional Spectra

^{1}H NMR Spectra.

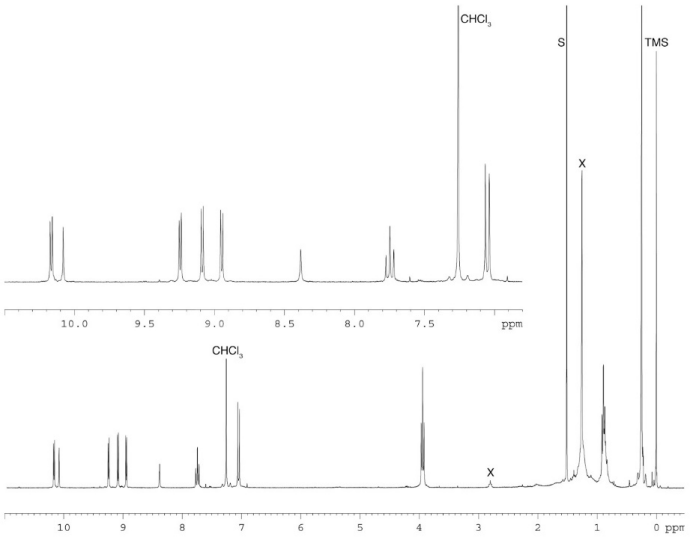


Figure S1. ^{1}H NMR (500 MHz) of **PZn-BTD-PZn** in $CDCl_3$. The designations s and x denote solvent and impurity peaks, respectively.

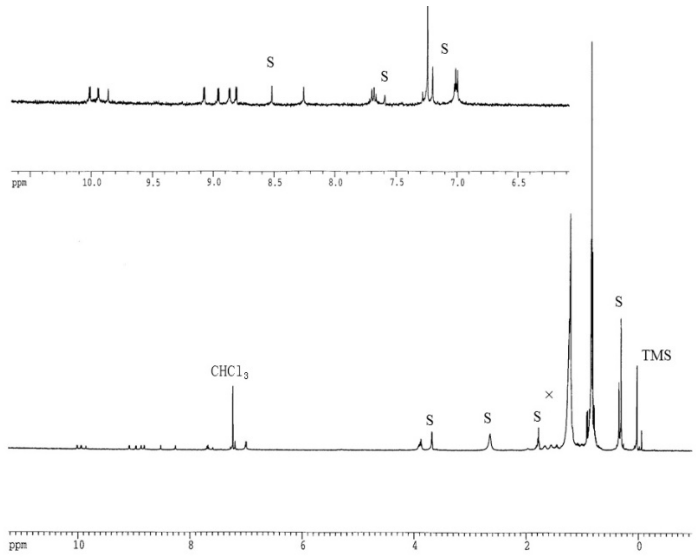


Figure S2. ^{1}H NMR (500 MHz) of **PZn-(BTD-PZn)$_2$** in $CDCl_3$ with 1 drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

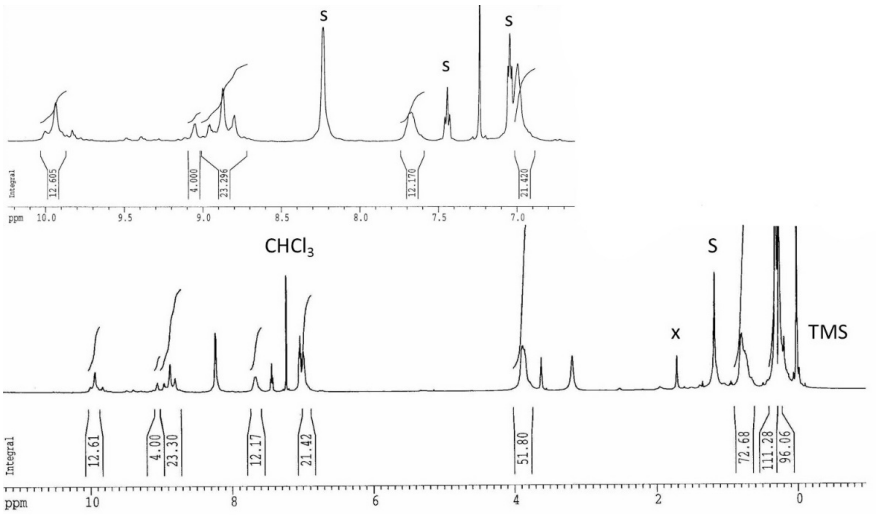


Figure S3. ^{1}H NMR (500 MHz) of **PZn-(BTD-PZn)$_4$** in $CDCl_3$ with 1 drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

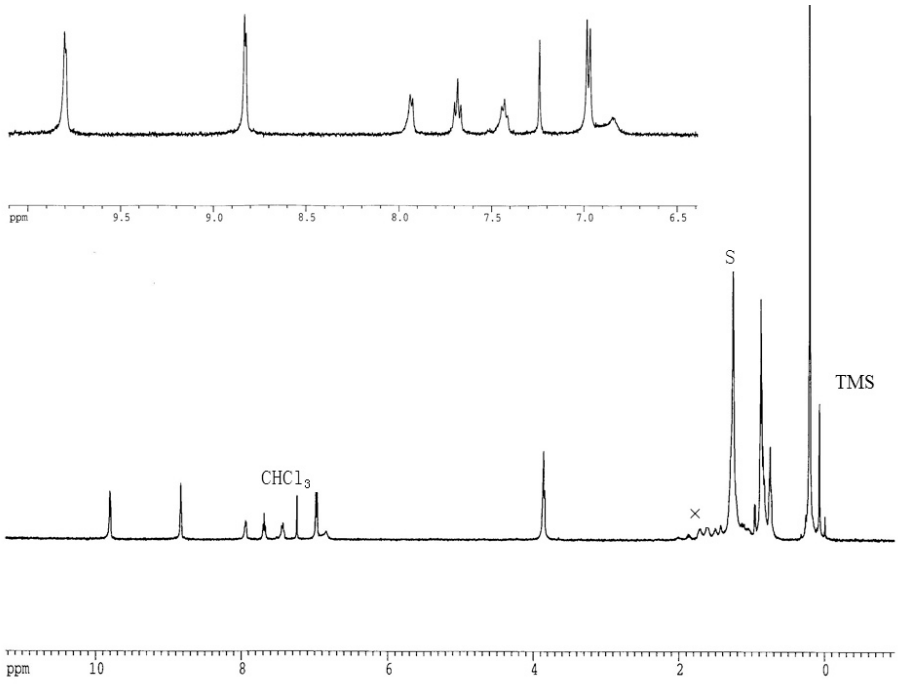


Figure S4. ^{1}H NMR (500 MHz) of **BTD-PZn-BTD** in $CDCl_3$. The designations s and x denote solvent and impurity peaks, respectively.

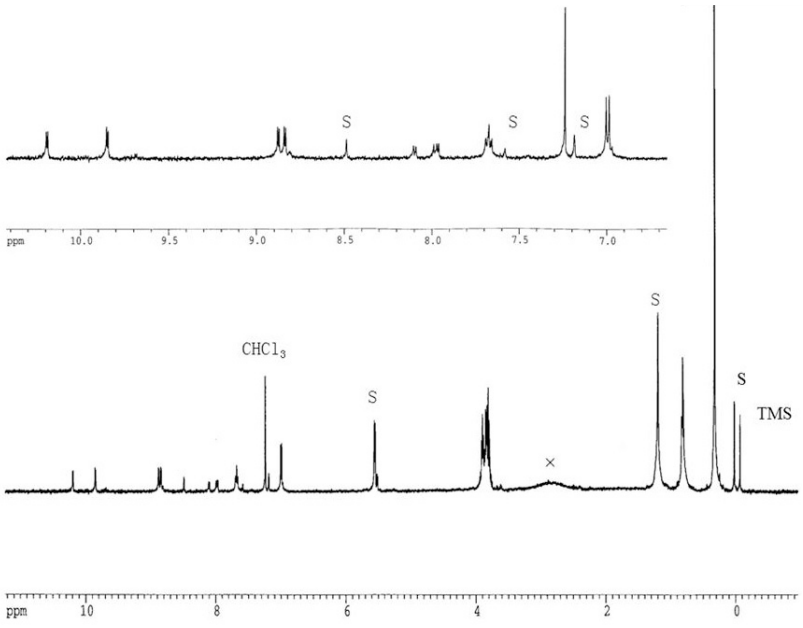


Figure S5. ^{1}H NMR (500 MHz) of **BTD-PZn$_2$-BTD** in $CDCl_3$ with one drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

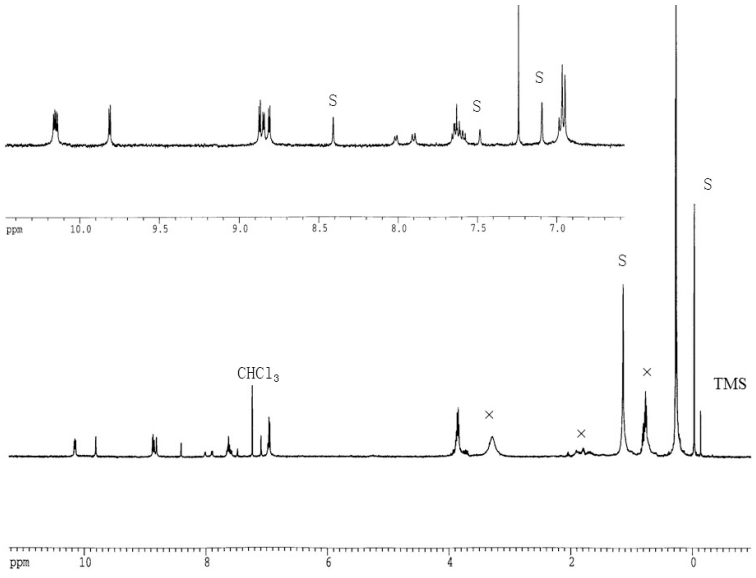


Figure S6. ^{1}H NMR (500 MHz) of **BTD-PZn$_3$-BTD** in $CDCl_3$ with 1 drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

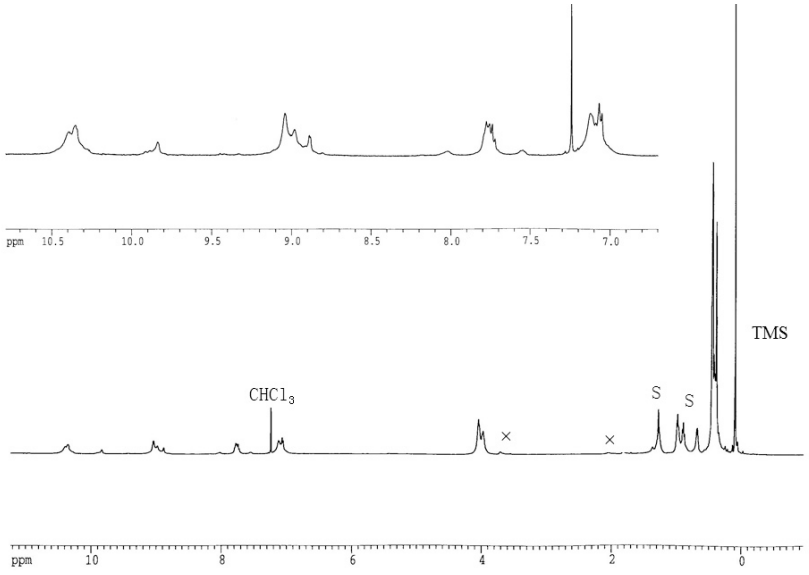


Figure S7. ^{1}H NMR (500 MHz) of **BTD-PZn$_5$-BTD** in $CDCl_3$ with 1 drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

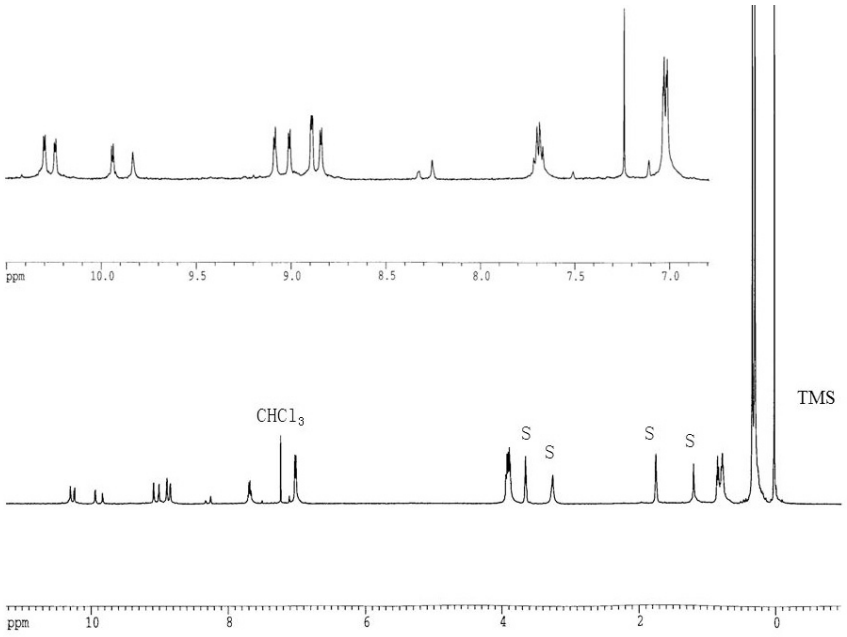


Figure S8. ^{1}H NMR (500 MHz) of **PZn$_2$-BTD-PZn$_2$** in $CDCl_3$ with 1 drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

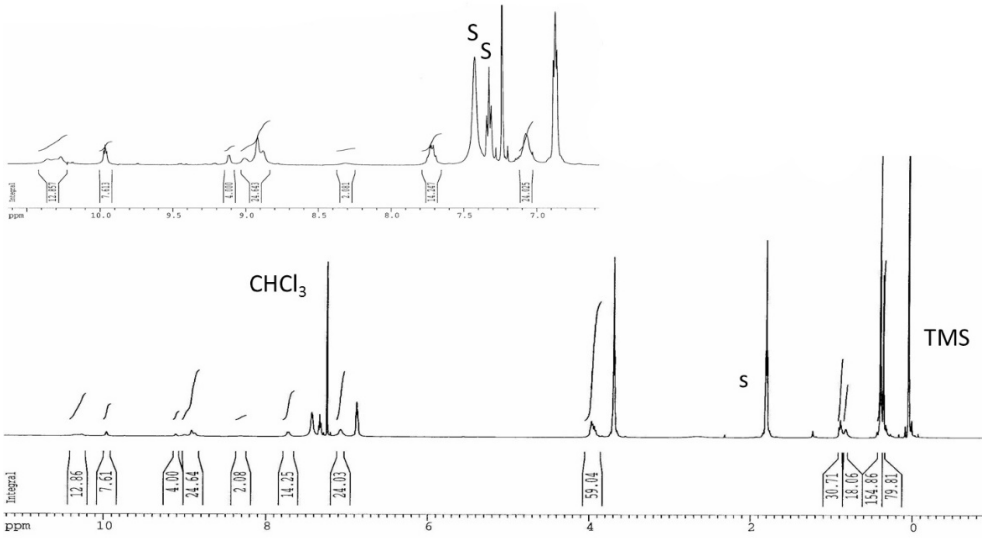


Figure S9. ^{1}H NMR (500 MHz) of **PZn_2-(BTD-PZn_2)$_2$** in $CDCl_3$ with 1 drop of pyridine-d_5. The designations s and x denote solvent and impurity peaks, respectively.

Additional Electronic Spectral Data.

Table S1 | Prominent absorption band wavelength and energies of BTD-incorporated arrays in THF solvent.

	B-Band			**Q-Band**			
	λ(nm)	ν(cm^{-1})	Log(ε)	λ(nm)	ν(cm^{-1})	FWHM (cm^{-1})	Log(ε)
PZn-BTD-PZn	426 465 530 566	23,474 21,505 18,868 17,668	5.16 4.79 4.55 4.34	689	14,514	1194	4.81
PZn-(BTD-PZn)$_2$	427 486 524 572	23,419 20,576 19,084 17,483	5.42 5.01 4.94 4.53	628 745	15,924 13,423	1178	4.48 5.13
PZn-(BTD-PZn)$_4$	428 530	23,364 18,868	5.46 5.05	642 712 776	15,576 14,045 12,887	1558	4.68 4.94 5.26
BTD-PZn-BTD	432 468	23,148 21,368	4.97 5.25	674	14,837	672	4.92
BTD-PZn$_2$-BTD	467 495	21,413 20,202	5.20 5.40	586 640 705 766	17,065 15,625 14,184 13,056	1243	4.26 4.21 4.73 5.04
BTD-PZn$_3$-BTD	422 492	23,697 20,325	5.16 5.43	588 812	17,007 12,315	1663	4.38 5.20
BTD-PZn$_5$-BTD	424 498	23,585 20,080	5.31 5.67	590 686 846	16,949 14,577 11,820	1675	4.53 4.69 5.38
PZn$_2$-BTD-PZn$_2$	415 488 564	24,096 20,491 17,730	5.33 5.61 4.61	781	12,804	1822	5.16
PZn$_2$-(BTD-PZn$_2$)$_2$	416 489	24,038 20,450	5.23 5.50	818	12,225	1582	5.24

Table S2 | Prominent absorption band wavelength, energies, and Stokes shifts of BTD arrays in toluene solvent.

	B-band region		Q-band region			$S_1 \rightarrow S_0$		Stokes' Shift	
	λ (nm)	ν(cm^{-1})	λ (nm)	ν(cm^{-1})	FWHM (cm^{-1})	λ (nm)	ν(cm^{-1})	FWHM (cm^{-1})	ν(cm^{-1})
PZn-BTD-PZn	423 462 519 560	23,641 21,645 19,268 17,857	667	14,993	949	689	14,514	886	479
PZn-(BTD-PZn)$_2$	427 485 522 568	23,419 20,619 19,157 17,606	614 656 720	16,287 15,244 13,889	1014	738	13,550	787	339
PZn-(BTD-PZn)$_4$	427 488 525	23,419 20,492 19,048	633 689 756	15,798 14,514 13,228	1655	764	13,089	811	139
BTD-PZn-BTD	426 468	23,474 21,368	660	15,152	663	669	14,948	606	204
BTD-PZn$_2$-BTD	430 467 496	23,256 21,413 20,161	578 626 685 737	17,301 15,974 14,599 13,569	1564	763	13,106	753	463
BTD-PZn$_3$-BTD	414 467 496	24,155 21,413 20,161	584 770	17,123 12,970	1630	810	12,346	871	624
BTD-PZn$_5$-BTD	420 456 498	23,810 21,930 20,080	583 797	17,153 12,547	1564	841	11,891	939	656
PZn$_2$-BTD-PZn$_2$	412 487	24,272 20,534	748	13,369	1609	781	12,804	907	565
PZn$_2$-(BTD-PZn$_2$)$_2$	414 488	24,155 20,492	777	12,870	1339	806	12,407	829	463

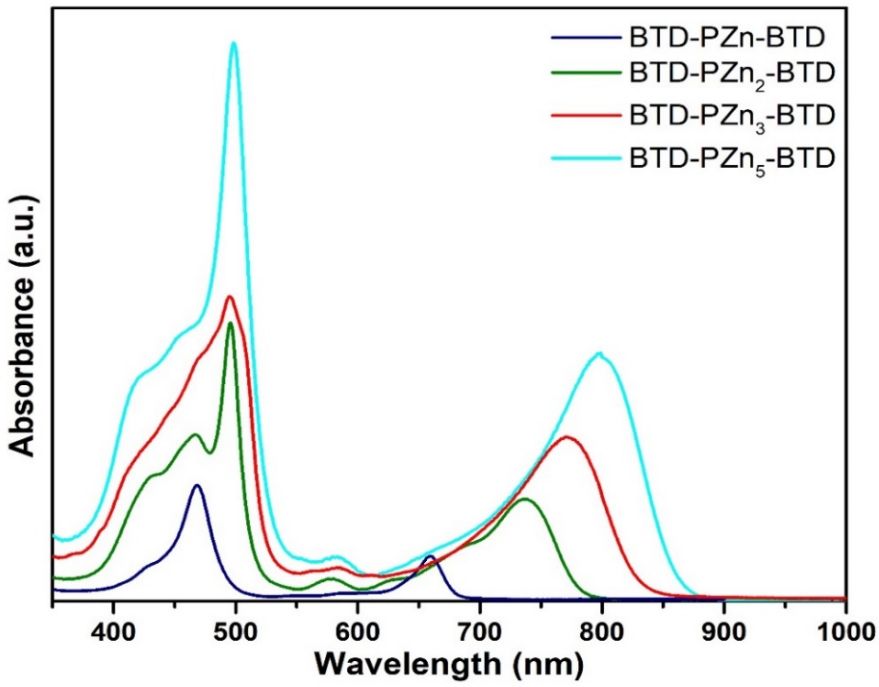


Figure S10. Electronic absorption spectra of **BTD-PZn$_n$-BTD** fluorophores in toluene solvent.

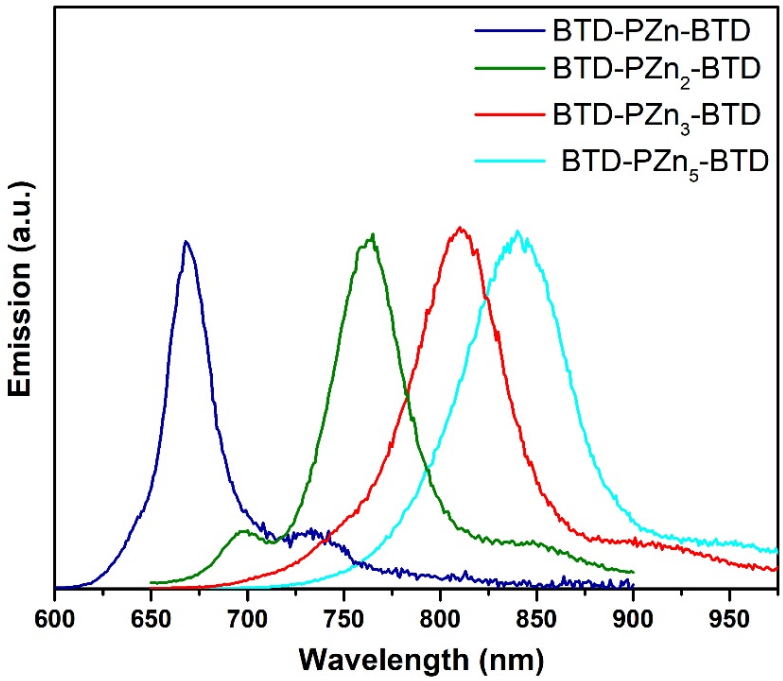


Figure S11. Emission spectra of **BTD-PZn$_n$-BTD** fluorophores in toluene solvent.

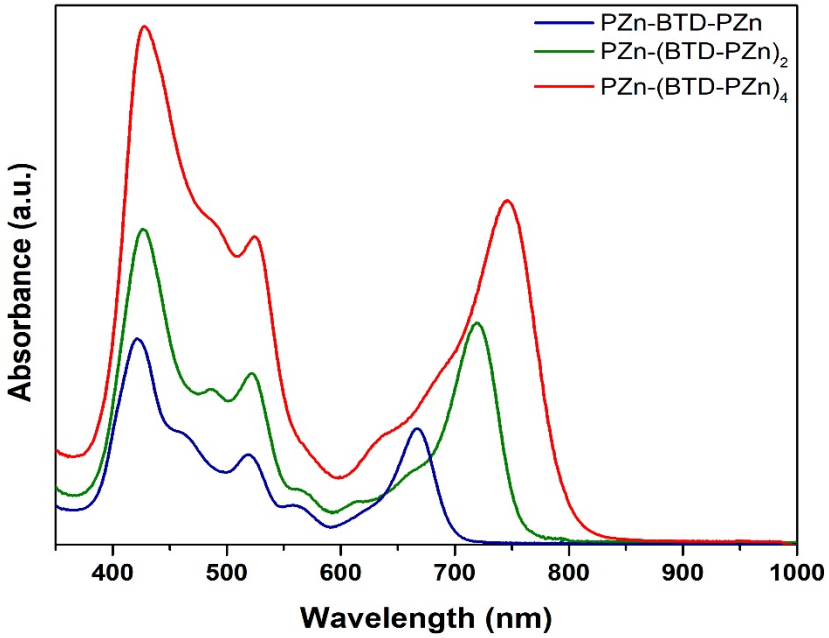


Figure S12. Electronic absorption spectra of **PZn-(BTD-PZn)$_n$** fluorophores in toluene solvent.

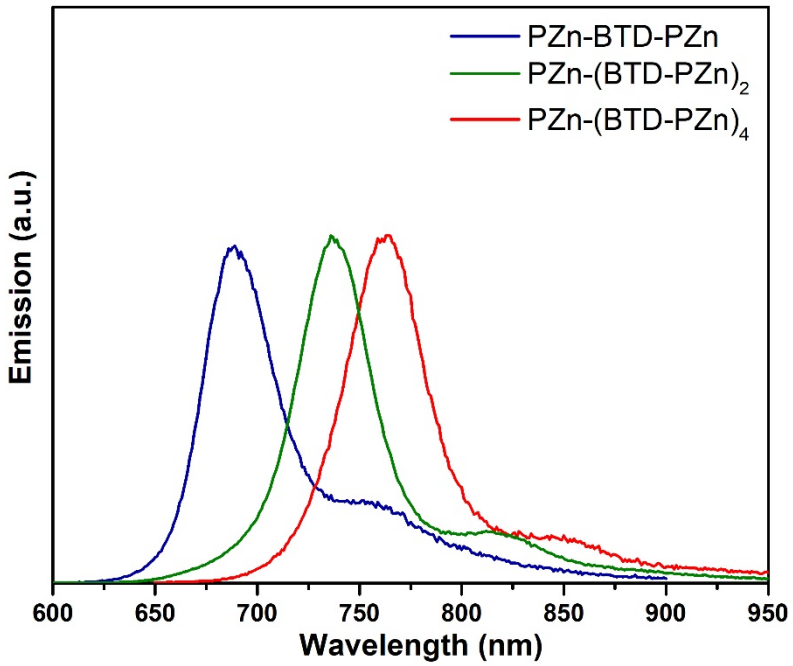


Figure S13. Emission spectra of **PZn-(BTD-PZn)$_n$** fluorophores in toluene solvent.

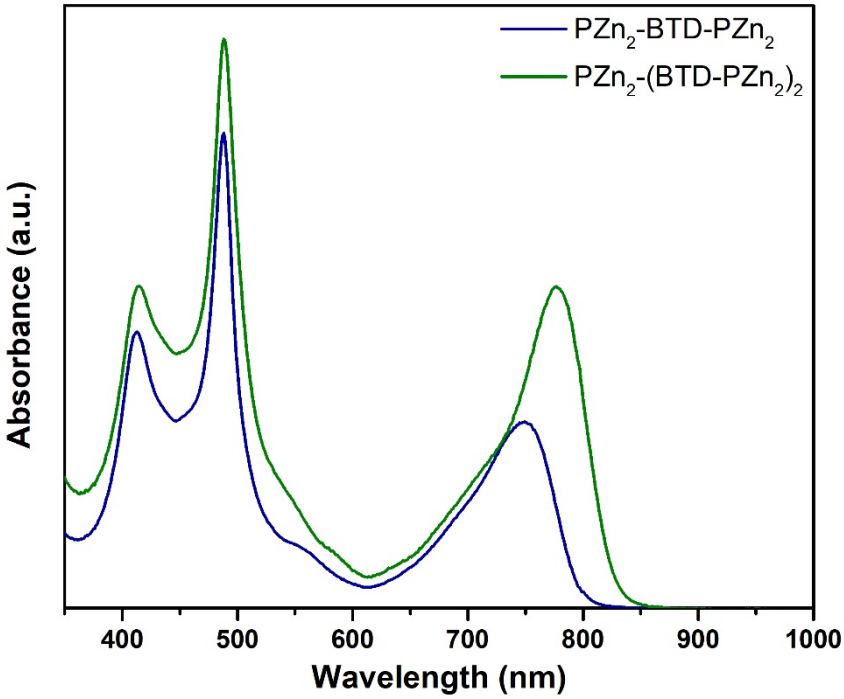


Figure S14. Electronic absorption spectra of **PZn_2-(BTD-PZn_2)$_n$** fluorophores in toluene solvent.

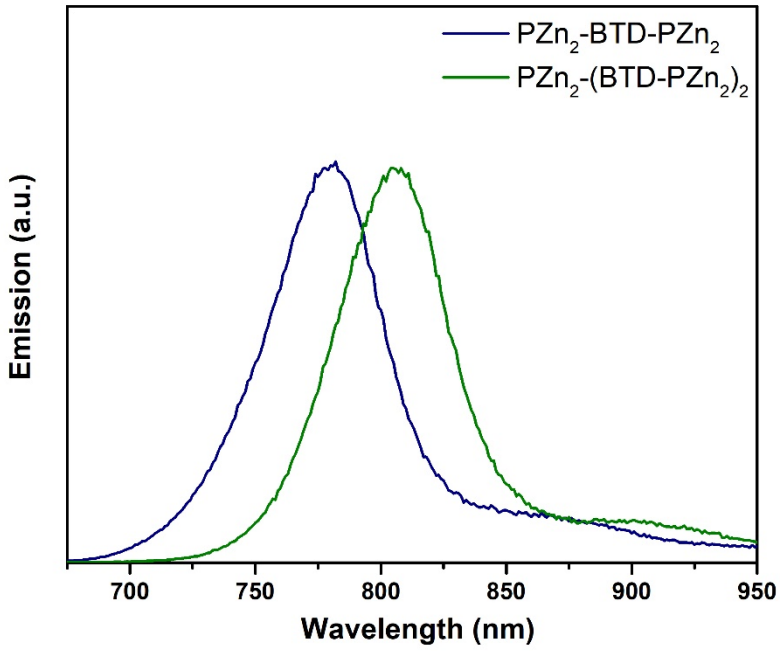


Figure S15. Emission spectra of **PZn_2-(BTD-PZn_2)$_n$** fluorophores in toluene solvent.

Exemplary Concentration Dependence

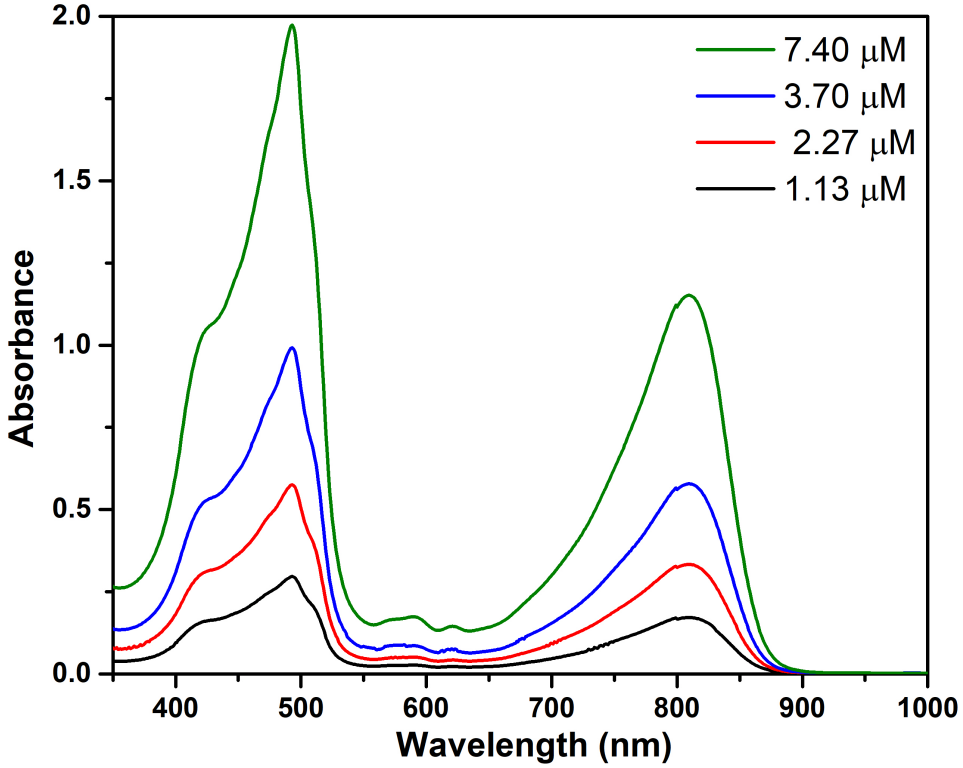


Figure S16. Absorbance spectra of **BTD-PZn$_3$-BTD** in THF at varying concentrations.

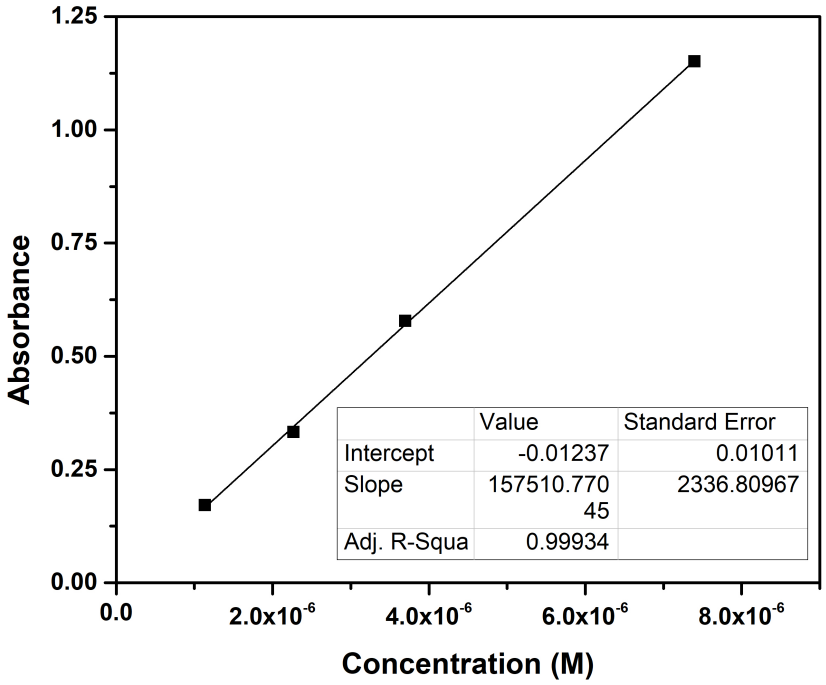


Figure S17. Beer's law plot of **BTD-PZn$_3$-BTD** in THF at varying concentrations for lowest-energy (Q_x) transition.

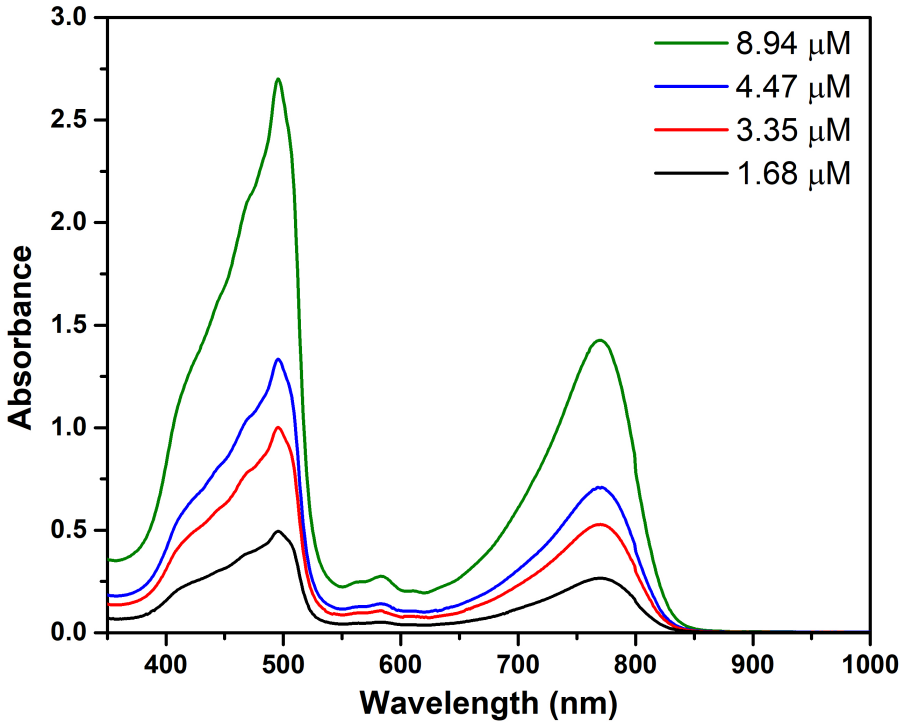


Figure S18. Absorbance spectra of **BTD-PZn$_3$-BTD** in toluene at varying concentrations.

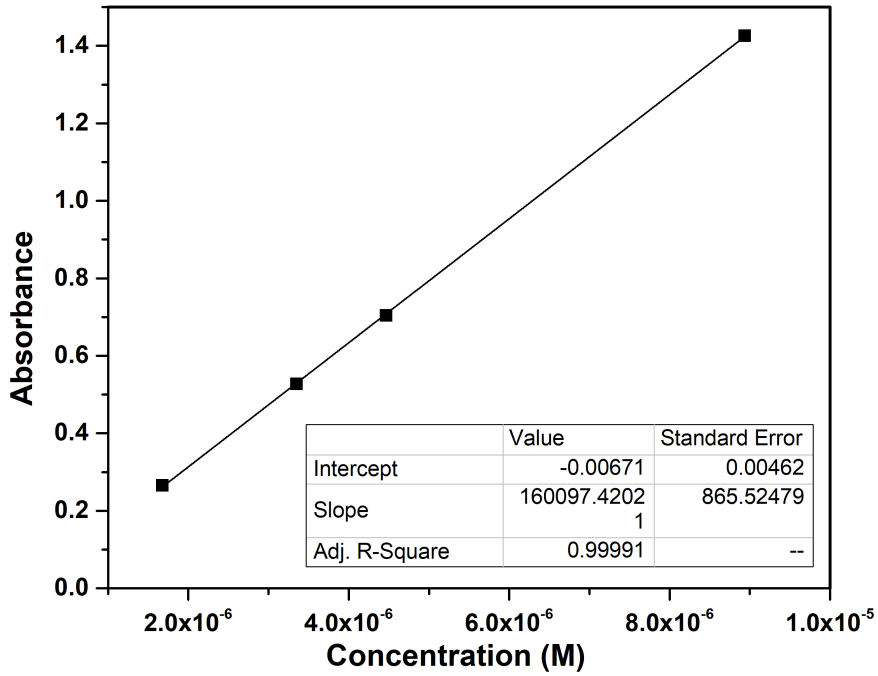


Figure S19. Beer's law plot of **BTD-PZn$_3$-BTD** in toluene at varying concentrations for the lowest-energy (Q_x) transition.

4. DFT and TD-DFT Calculations.

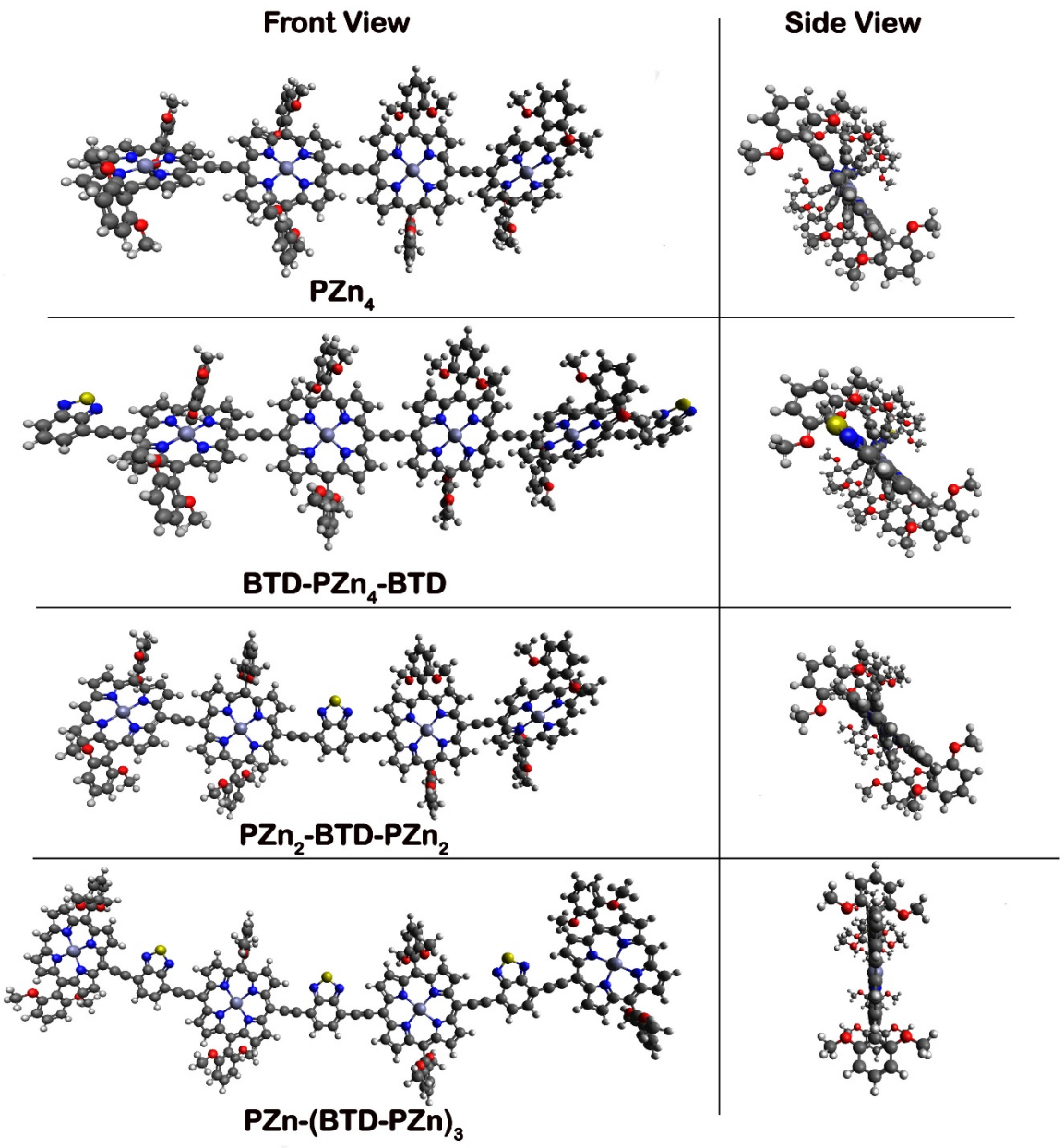


Figure S20. Front and side view of optimized ground state structures of representative tetramers.

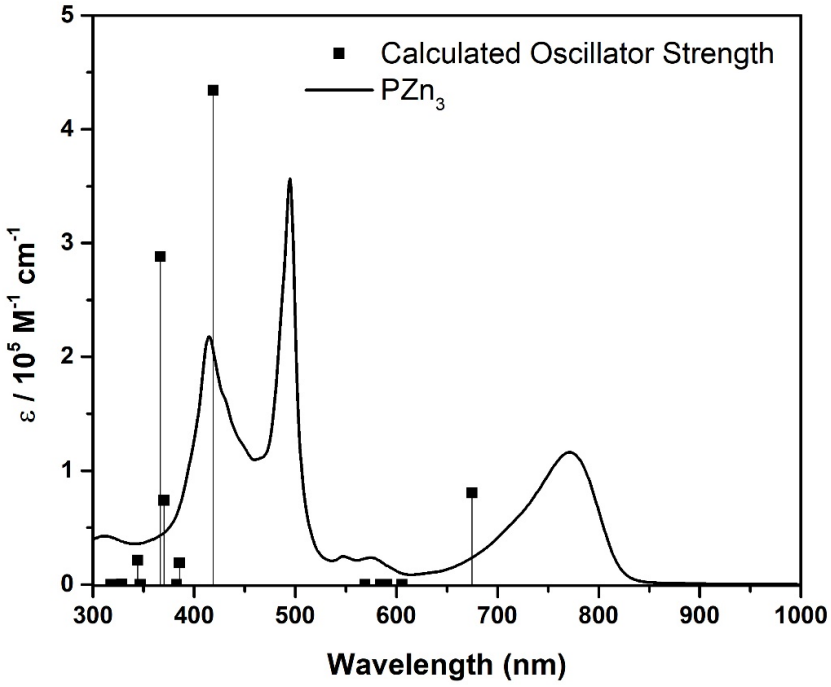


Figure S21. Electronic absorbance spectrum of **PZn_3** in toluene solvent with calculated oscillator strengths overlaid.

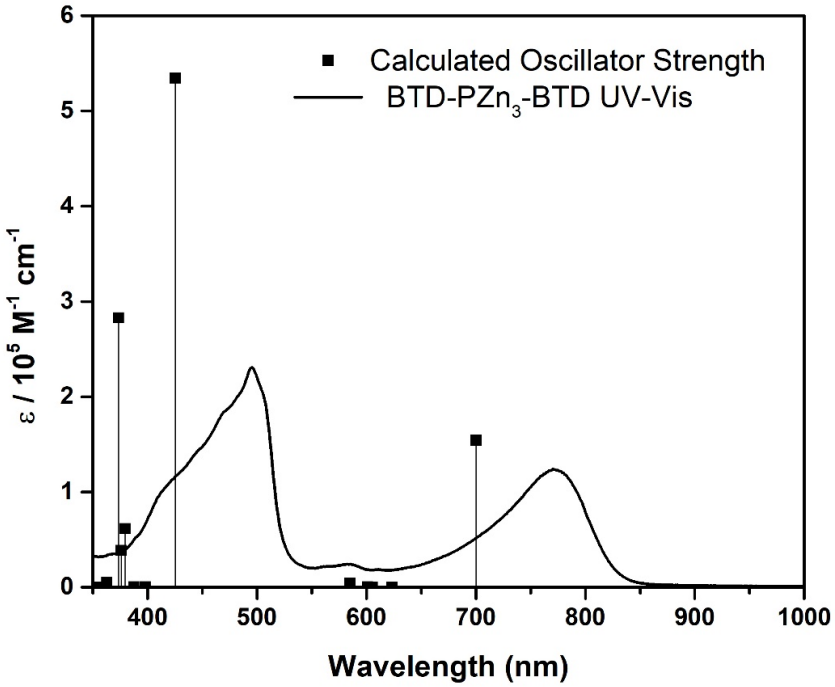


Figure S22. Electronic absorbance spectrum of **BTD-PZn_3-BTD** in toluene solvent with calculated oscillator strengths overlaid.

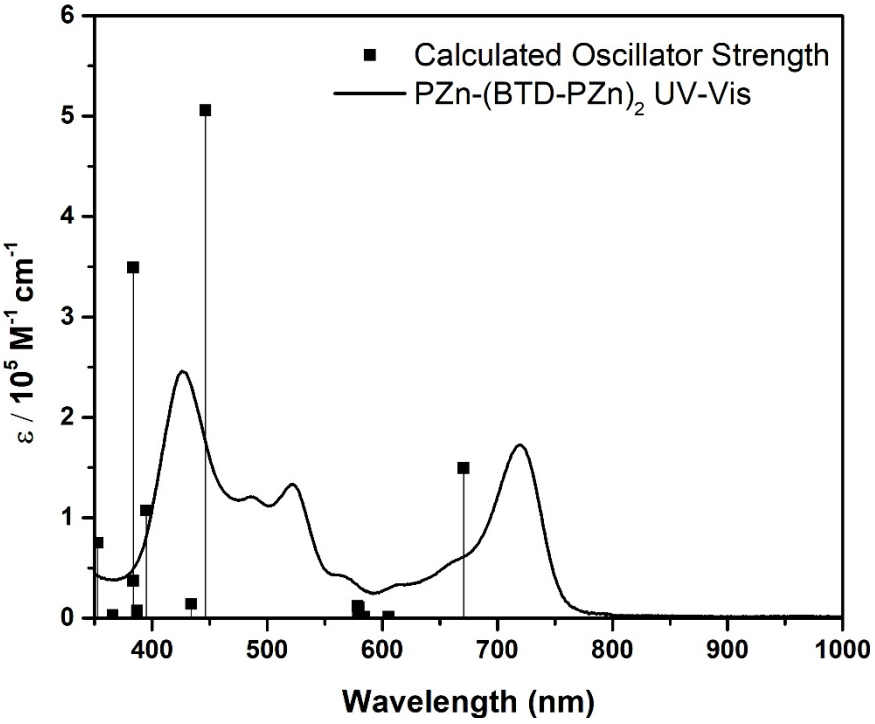


Figure S23. Electronic absorbance spectrum of **PZn-(BTD-PZn)$_2$** in toluene solvent with calculated oscillator strengths overlaid.

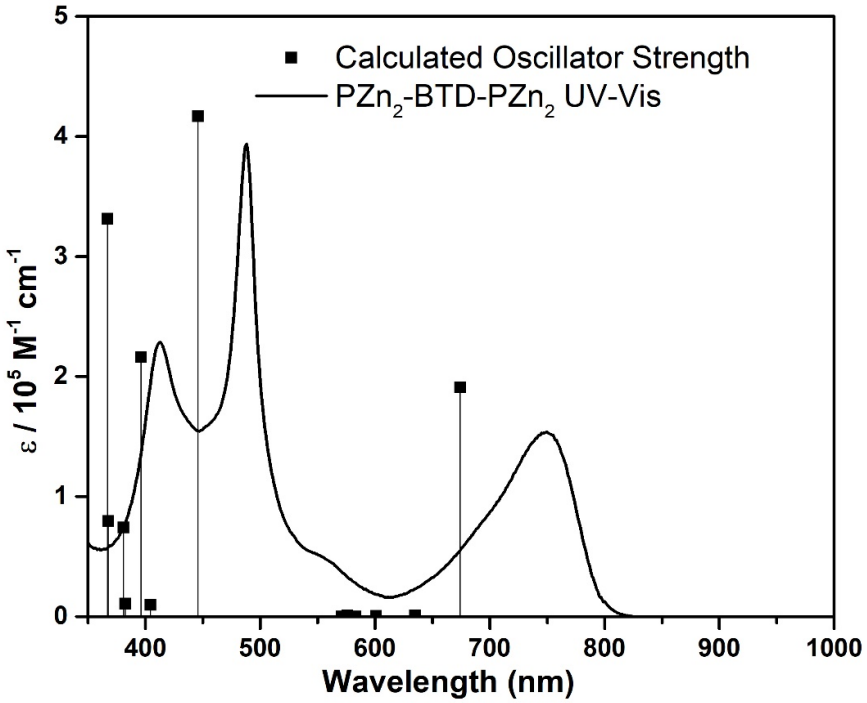


Figure S24. Electronic absorbance spectrum of **PZn$_2$-BTD-PZn$_2$** in toluene solvent with calculated oscillator strengths overlaid.

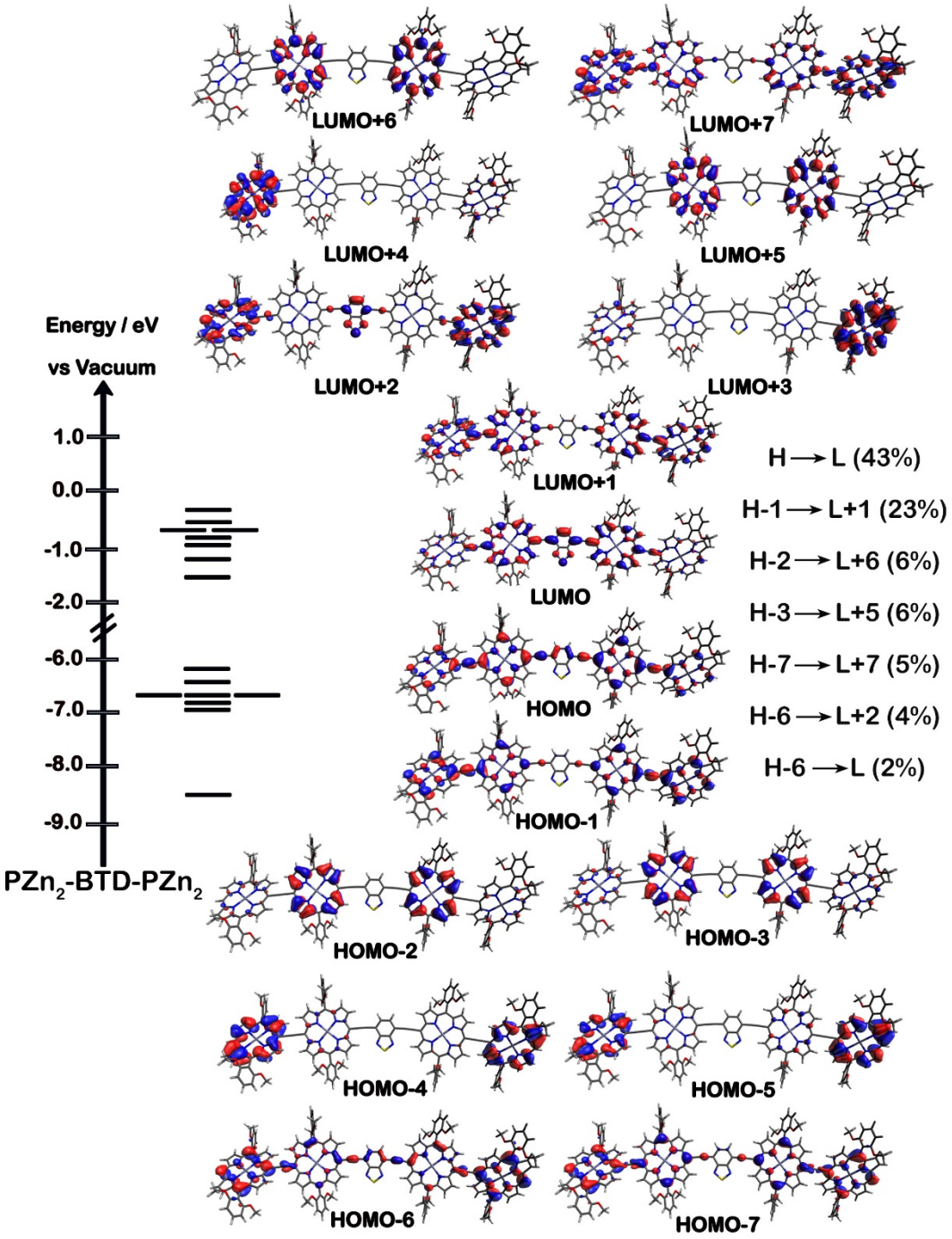


Figure S25. Calculated frontier molecular orbitals, energies, and relative one electron contributions to the lowest energy (Q_x) transition for **PZn_2-BTD-PZn_2**.

Delocalization Range Function Calculation. Using the electron delocalization range function (EDR) developed by Frisch and coworkers,[10] the degree to which electrons in a calculated wavefunction delocalize over a given length scale may be quantified. Here, we computed weighted averages over the EDR using the S_1 state density obtained at the S_1 minimum geometry to quantify the average number of electrons that delocalize over length scale d. This approach is especially helpful as it provides a quantitative comparison of both the number of delocalized electrons and how far that delocalization holds. Figure S26 displays the results of these calculations, indicating that both **BTD-PZn$_3$-BTD** and **PZn-(BTD-PZn)$_2$** have more delocalized wavefunctions than benchmark **PZn$_3$** as on average both systems possess a larger number of electrons delocalized over longer distance relative to that for **PZn$_3$**.

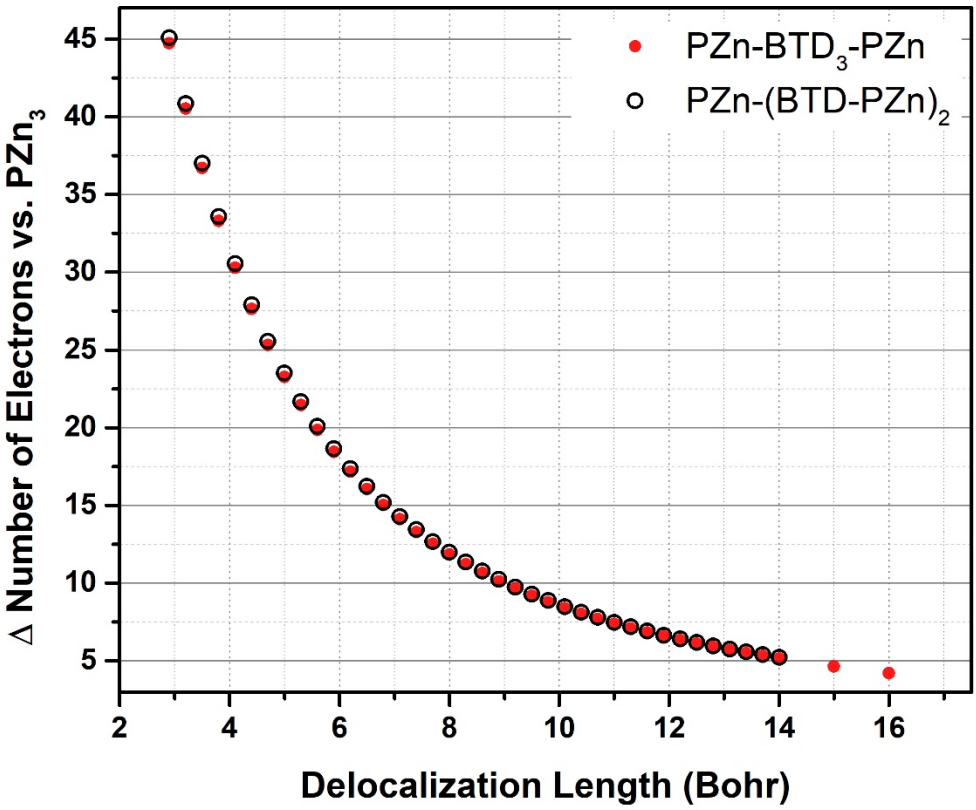


Figure S26. Calculated delocalization via electron density range function for **BTD-PZn$_3$-BTD** and **PZn-(BTD-PZn)$_2$** as compared to benchmark **PZn$_3$**.

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