Supporting Information

Probing Secondary Coordination Sphere interactions within Porphyrin-Cored Polymer Nanoparticles

Brian F. Patenaude†, Erik B. Berda†‡, Samuel Pazicni*

†University of New Hampshire, Department of Chemistry, 23 Academic Way, Durham, NH 03824, USA

‡University of New Hampshire, Materials Science Program, 23 Academic Way, Durham, NH 03824, USA

** Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States*

E-mail: erik.berda@unh.edu , sam.pazicni@chem.wisc.edu

Table of Contents

Table of Figures

Materials

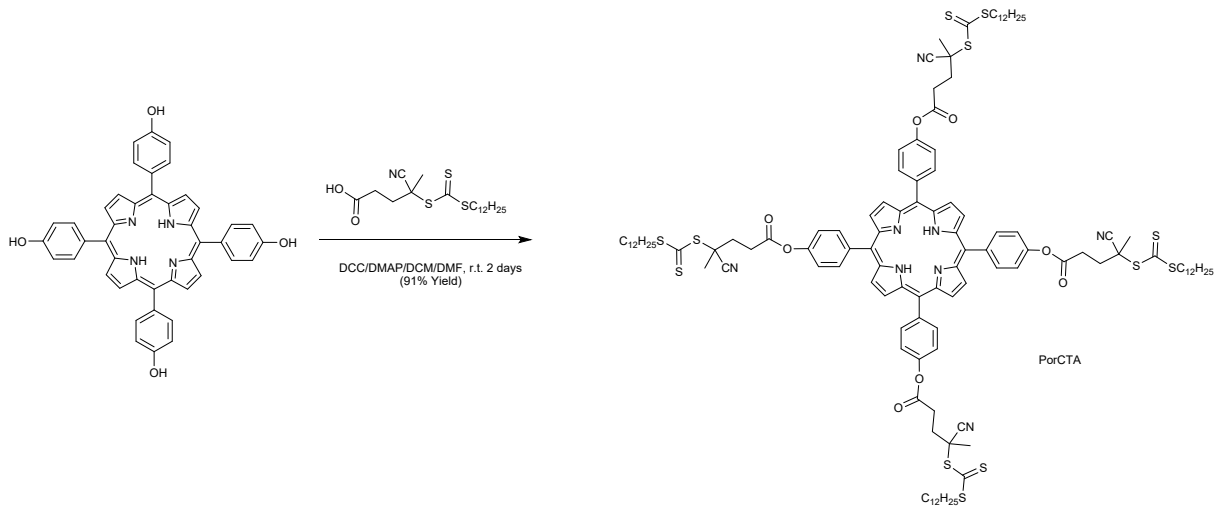
The following reagents were obtained from the indicated commercial suppliers and used as received unless otherwise noted: 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (THPP) (Sigma Alrich), 4-cyano-4-[(dodecyl-sulfanylthiocarbonyl)sulfanyl]-penatanoic acid (Sigma Aldrich), N,N'-dicyclohexylcarbodiimide (DCC) (Sigma Aldrich), 4-(Dimethylamino)pyridine (DMAP) (Sigma Aldrich), sodium sulfate (Fisher Scientific), 9-anthraldehyde (Sigma Aldrich), sodium borohydride (Sigma Aldrich), methacrylic acid (Sigma Aldrich), ethyl acetate (Fisher Scientific), pentafluorophenol (Oakwood Products,

Inc), methacrylol chloride (Sigma Aldrich), methyl methacrylate (MMA) (Sigma Aldrich), azobisisobutyronitrile (AIBN) (Sigma Aldrich), Chloroform (Fisher Scientific), zinc acetate hydrate (Sigma Aldrich), n-hexylamine (Sigma Aldrich), Acetone (Pharmco Products Inc), isopropylamine (Alfa Aesar), 2-aminoethanol (TCI America), N,N-dimethylformamide (DMF) (Fisher Scientific), sodium cyanide (Sigma Aldrich), Sodium Acetate (Mallinckrodt), Sodium Carbonate (Alfa Aesar), dimethyl sulfoxide (DMSO) (Fisher Scientific), dichloromethane (DCM) (Fisher Scientific), methanol (Fisher Scientific), tetrahydrofuran (THF) (Fisher Scientific), silica gel (230400 mesh) (SiliCycle), chloroform-d (Cambridge Isotope Laboratories), and N,N-dimethylformamide-d_7(Cambridge Isotope Laboratories). Dry toluene, DCM, DMF, and THF were obtained from an Innovative Technology solvent purification system model SPS-400-5 and stored over molecular sieves.

Instrumentation

Photodimerization reactions were conducted in a Luzchem photo-reactor CCP-4V equipped with 4 UVA (350 nm centered) and 4 UVC (254 nm centered) lamps. ^{1}H NMR and ^{13}C NMR Spectra were acquired with a Varian Mercury 400 BB NMR or Varian UnityINOVA 500 NMR. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Solvents ($CDCl_3$ & DMF-D_7) contained 0.03% v/v TMS as an internal reference. NMR samples were prepared at a concentration of 50 mg/mL. The PCSP species were prepared for NMR by dissolving 25 mg of polymer in 500 µL of solvent. The PCPN species were prepared for NMR by dissolving 13 mg of nanoparticles in 260 µL of solvent. Peak abbreviations are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. NMR spectra were processed with MestReNova Software (Ver. 14.0.0). ^{1}H DOSY NMR were acquired with a Varian UnityINOVA 500 NMR using a ledbpgp2s pulse pattern with 25 gradient steps (2% to 95% gradient amplitude) and 8 scans per step. Varian UnityINOVA 500 NMR magnetic field gradient calibrated against D_2O. ^{1}H DOSY NMR spectra were processed in MestReNova Software (Ver. 14.0.0) using Bayesian transformations with 2 repetitions, 0.1 resolution, and 256 points in the diffusion dimension. Viscosity of DOSY solutions were assumed to be that of pure DMF (0.802 cP at 25 °C).[1] UV-Vis spectra were obtained using a Shimadzu UV-2450 UV-Vis spectrophotometer equipped with a S-1700 thermoelectric single cell holder and a Lauda RE 200 chiller. Infrared spectra were obtained using a Thermo Nicolet iS10 FTIR equipped with a diamond plate Smart iTR™ attenuated total reflectance (ATR) sampling accessory. UV-Vis and ATR-IR spectra were processed with Matlab R2019b software by The MathWorks, Inc.

Experimental Procedures



Scheme S1: Synthesis of PorCTA

Synthesis and Characterization of 5,10,15,20-tetrakis(4-(4-cyano-4[(dodecylsulfanylthiocarbonyl)sulfanyl]phenyl pentanoate)-21H,23H-porphine (PorCTA)[2]

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with dry dichloromethane (30 mL), dry N,N-dimethylformamide (1 mL), 5,10,15,20-tetrakis(4-hydroxyphenol)-21H,23H-porphine (0.1790 g, 0.2637 mmol), 4-cyano-4-[(dodecyl-sulfanylthiocarbonyl)sulfanyl]-penatanoic acid (0.5414g, 1.341 mmol), Dicyclohexylcarbodiimide (0.2980 g, 1.444 mmol) , and 4-Dimethylaminopyridine (0.0283 g, 0.1883 mmol). The solution sparged with nitrogen then allowed to stir for 20 hours at room temperature. The solution was then vacuum filtered. The filtrate was then washed with water (4 x 50 mL) and dried with sodium sulfate. The solution was then concentrated under reduced pressure and the product was isolated by column chromatography using silica (9:1 toluene/ ethyl acetate, Rf = 0.7). The product fraction was concentrated under reduced pressure to yield 5,10,15,20-tetrakis(4-(4-cyano 4[(dodecylsulfanylthiocarbonyl)sulfanyl]phenyl pentanoate)-21H,23H-porphine as a purple tar (0.5323 g, 0.2396 mmol, 90.86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.90 (s, 8H), 8.25 (d, 8H), 7.55 (d, 8H), 3.43-3.40 (m, 8H), 3.14-3.11 (m, 8H), 2.86-2.66 (m, 8H), 2.07 (s, 12H), 1.79-1.68 (m, 8H), 1.47-1.25 (m, 72H), 0.92-0.89 (m, 12H), -2.80 (br s, 2NH)

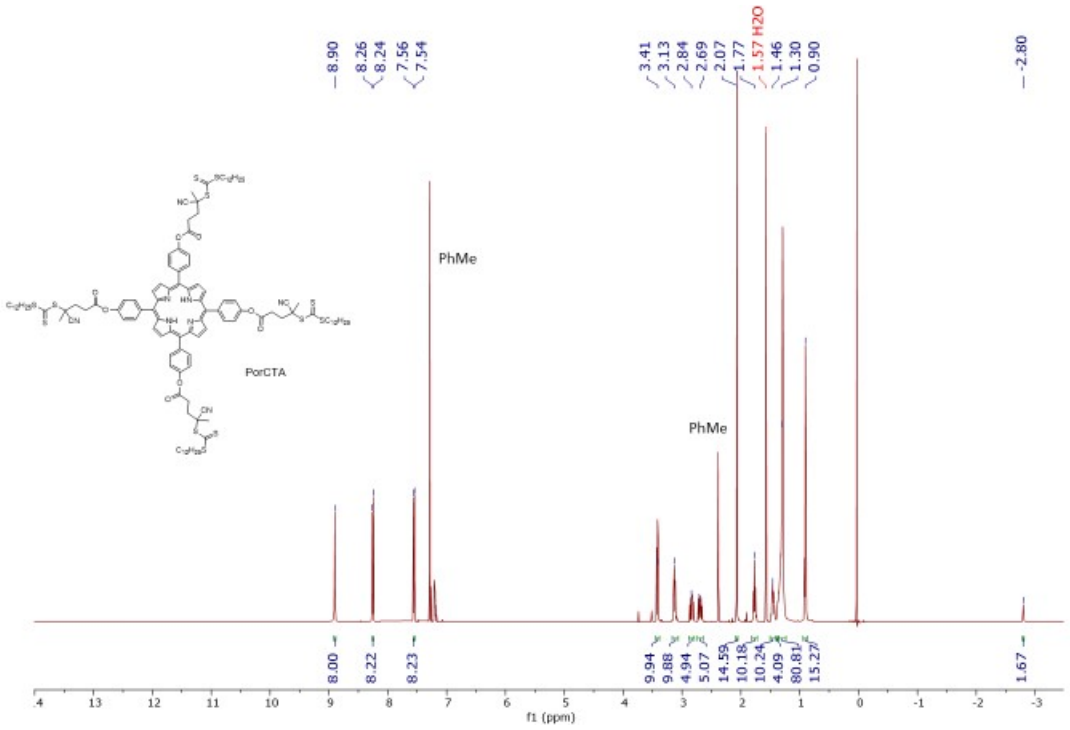


Figure S1: [1]H NMR (CDCl3, 400 MHz) spectrum of PorCTA

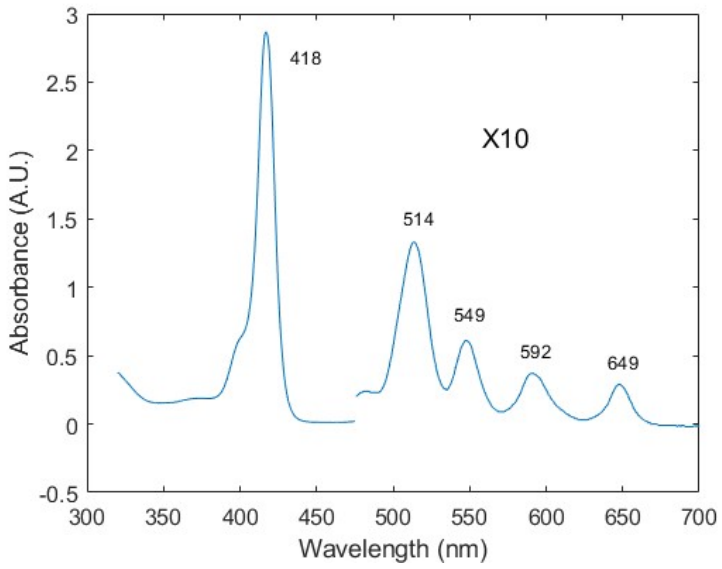
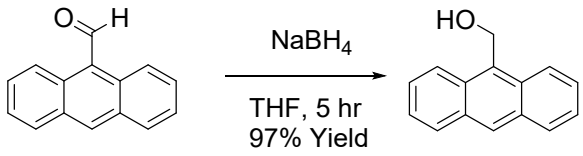


Figure S2: UV-Vis Spectrum of PorCTA at 0.020 mg/mL in THF. Absorbance from 475 to 700 nm magnified X 10



Scheme S2: Synthesis of 9-Anthracene methanol

Synthesis and Characterization of 9-anthracene methanol[3]

A 500 mL round bottom flask equipped with a magnetic stir bar was charged with dry tetrahydrofuran (120 mL), 9-anthraldehyde (3.0199 g, 14.643 mmol) and sodium borohydride (0.6475 g, 17.116 mmol). The solution was stirred under nitrogen at room temperature for 5 hours. The solution was then poured into 1 L beaker containing 500 mL of cold water. The resulting yellow precipitate was isolated by vacuum filtration and dried under vacuum to yield 9-antrhacene methanol as a yellow powder (2.962 g, 14.223 mmol, 97.131% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (s, 1H), 8.42 (dq, *J* = 8.9, 1.0 Hz, 2H), 8.04 (ddt, J = 8.4, 1.4, 0.7 Hz, 2H), 7.58 (ddd, , J = 8.9, 6.5, 1.4 Hz, 2H), 7.51 (ddd, , J = 8.4, 6.5, 1.1 Hz, 2H), 5.66 (d, J = 5.6 Hz, 2H), 1.81 (t, J = 5.6 Hz, OH)

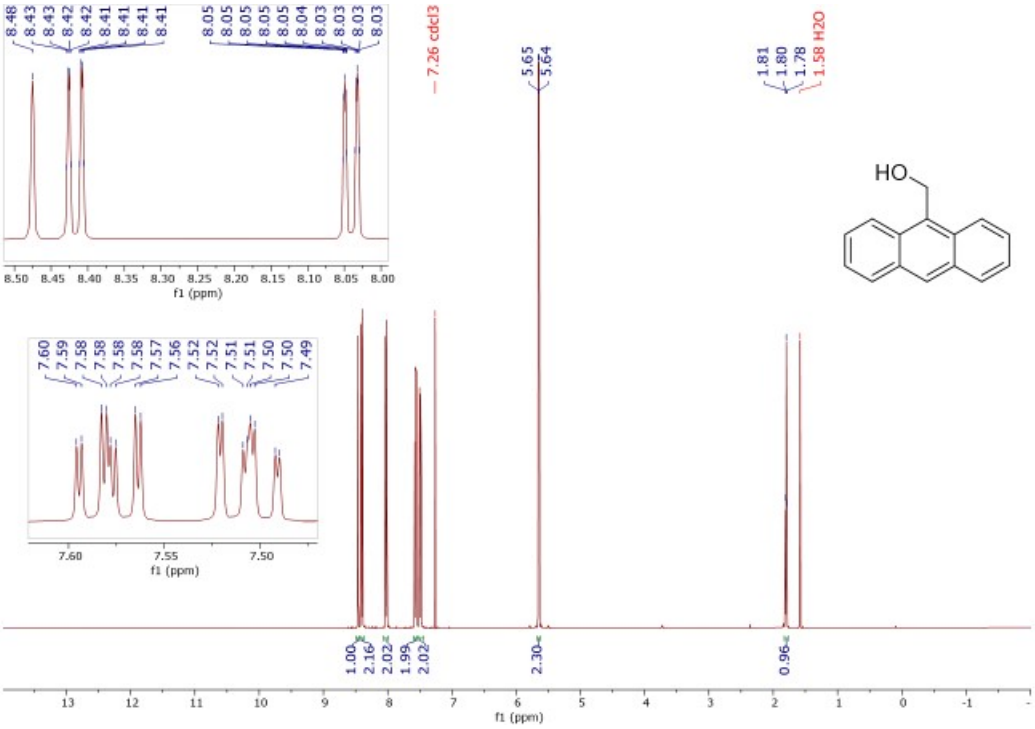
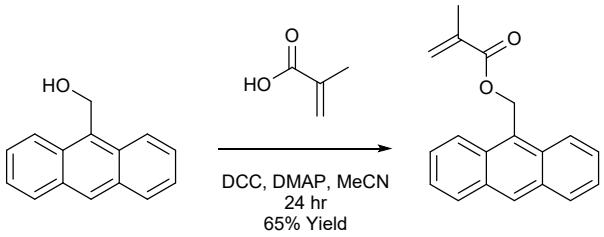


Figure S3: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 9-anthracenemethanol



Scheme S3: Synthesis of 9-Anthraceynlmethyl methacrylate

Synthesis and Characterization of 9-anthracynlmethyl methacrylate (AMMA)[3]

A 500 mL round bottom flask equipped with a magnetic stir bar was charged with dry acetonitrile (60 mL), 9-anthracene methanol (2.5068 g, 12.037 mmol), methacrylic acid (2.06 mL, 24.4 mmol), N,N-Dicyclohexylcarbodiimide (5.0407 g, 24.430 mmol), and 4-Dimethylaminopyridine (0.2314 g, 1.8941 mmol). The mixture was stirred at room temperature for 24 hours under nitrogen. The solution was vacuum filtered, and the filtrate was concentrated under reduced pressure. The product was isolated via column chromatography using silica (5:1 toluene/ ethyl acetate). The product fraction was concentrated under reduced pressure and precipitated in methanol. The resulting precipitate was vacuum filtered and dried under vacuum to yield 9-anthracynlmethyl methacrylate as a pale-yellow powder (2.1736 g, 7.8657 mmol, 65.346% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.38 (dq, J = 8.9, 1.0 Hz, 2H), 8.04 (ddt, J = 8.5, 1.4, 0.7 Hz, 2H), 7.58 (ddd, J = 8.9, 6.5, 1.4 Hz, 2H), 7.50 (ddd, J = 8.4, 6.5, 1.1 Hz, 2H), 6.23 (s, 2H), 6.06 (dq, J = 2.0, 1.0 Hz, 1H), 5.51 (p, J = 1.6 Hz, 1H), 1.93 (dd, J = 1.6, 0.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.75, 136.28, 131.54, 131.26, 129.27, 129.22, 126.73, 126.55, 126.15, 125.24, 124.19, 59.29, 18.49.

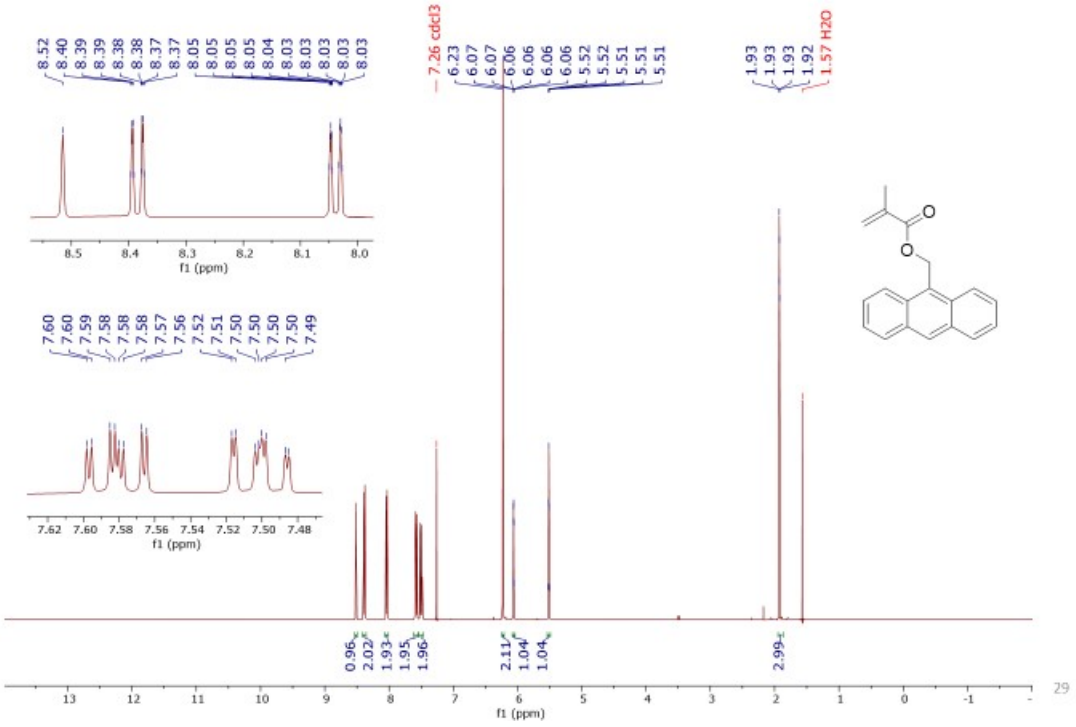


Figure S4: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of AMMA

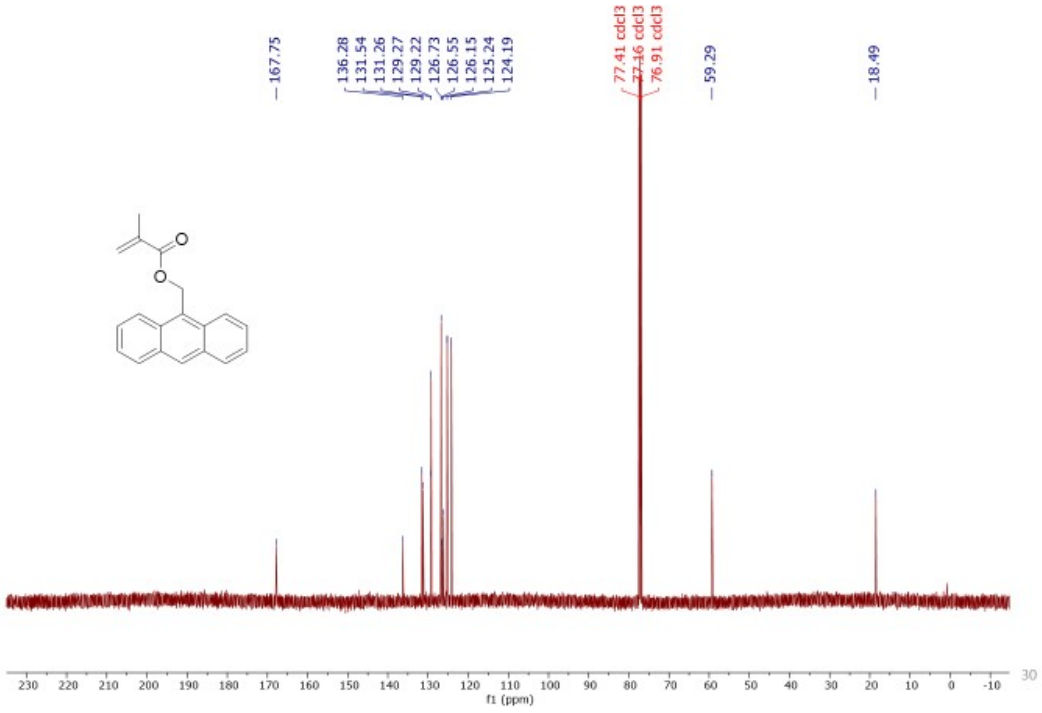


Figure S5: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of AMMA

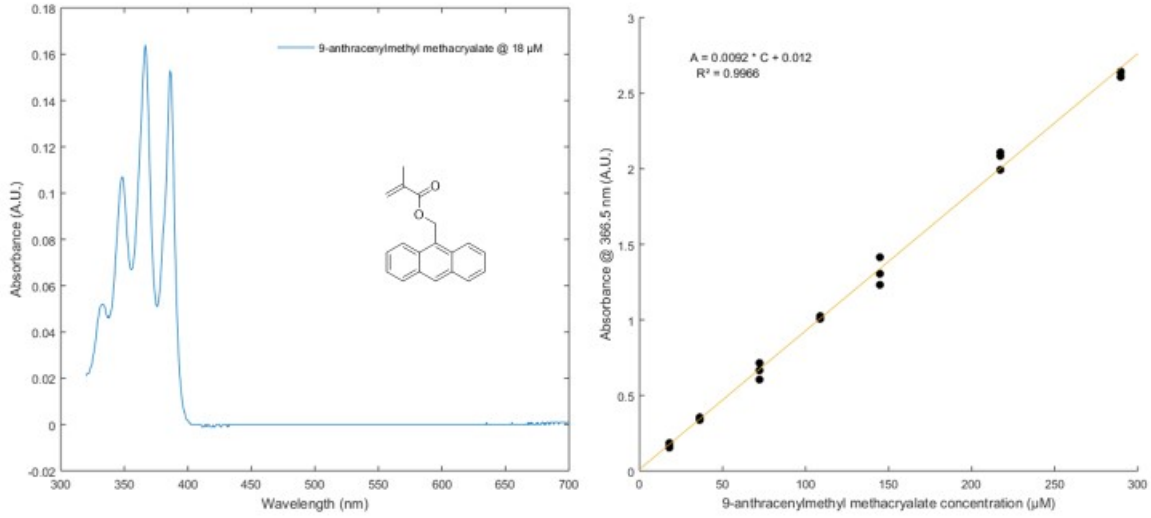
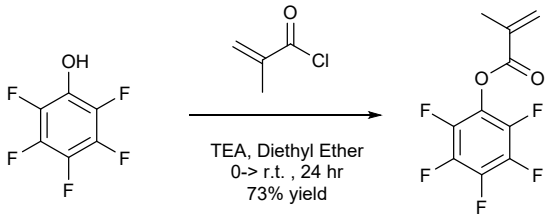


*Figure S6: (Left) UV-Vis Spectrum of 18µM AMMA in THF, (Right) Concentration curve of AMMA at 366.5 nm; Absorbance = 0.0092 * Concentration (µM) + 0.012, R^2 = 0.9966*



Scheme S4: Synthesis of Pentafluorophenyl methacyrlate

Synthesis and Characterization of pentafluorophenyl methacrylate (PFPMA)[4]

A 250 mL round bottom flask equipped with a magnetic stir bar was charged with diethyl ether (100 mL), Pentafluorophenol (4.3537 g, 23.652 mmol), and triethylamine (3.9 mL, 28 mmol). The solution was sparged with nitrogen and cooled to 0°C. While stirring methacryloyl chloride (2.8 mL, 29 mmol) was added dropwise to the solution. The solution was then stirred for an additional 24 hours at room temperature under nitrogen. The solution was vacuum filtered, and the filtrate was then concentrated under reduced pressure. The product was isolated via column chromatography using silica (petroleum ether). The product fraction was concentrated under reduced pressure to yield pentafluorophenol methacrylate as a clear oil (4.3404 g, 17.214 mmol, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (p, J = 1.0 Hz, 1H), 5.92 – 5.90 (m, 1H), 2.08 (dd, J = 1.6, 1.0 Hz, 3H). ^{19}F NMR ($CDCl_3$, 376.1 MHz): δ -152.86 (d, 2F), -158.31 (t, 1F), -162.59 (t, 2F)

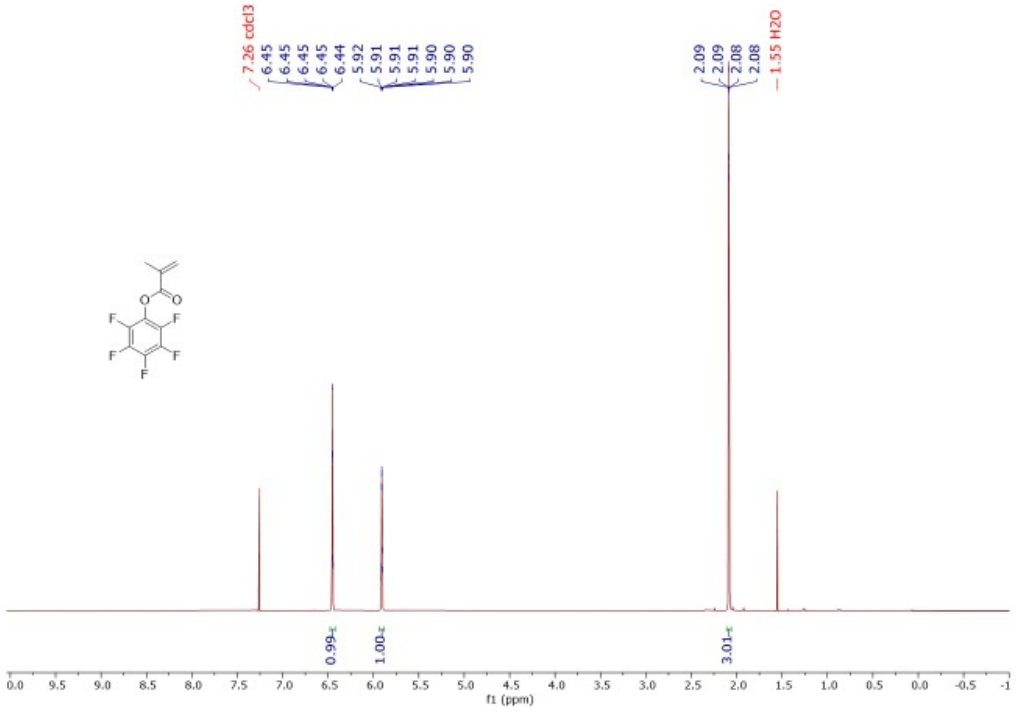


Figure S7: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of PFPMA

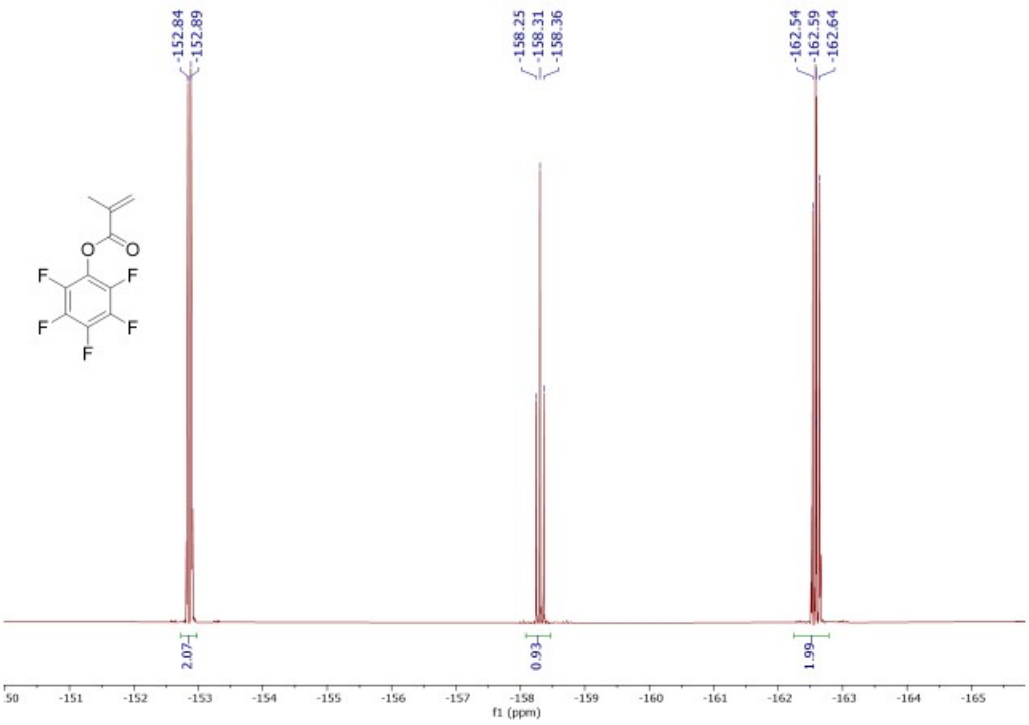
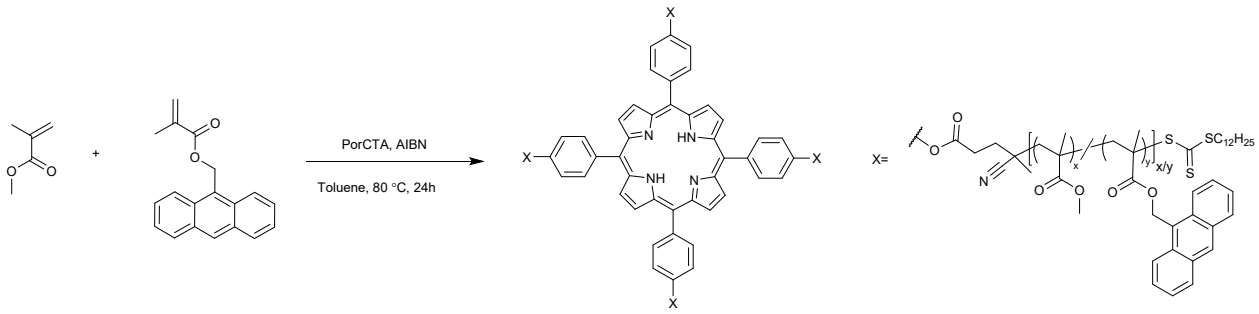


Figure S8: ^{19}F NMR ($CDCl_3$, 376.1 MHz) spectrum of PFPMA



Scheme S5: Synthesis of Por[poly(MMA-co-AMMA)]$_4$

Synthesis and Characterization of Por[poly(MMA-co-AMMA)]$_4$ [2]

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with PorCTA in toluene solution (1.079 ml, 0.176g PorCTA, 0.079 mmol), 9-anthracynlmethyl methacrylate (0.4160 g, 1.5054 mmol), methyl methacrylate (0.6060 g, 6.0529 mmol), and azobisisobutyronitrile (0.0145 g, 0.0883 mmol). The mixture was sparged with argon for 1 hour while stirring. After, the flask was placed in an oil bath preheated to 80°C and the solution was stirred under argon for 18 hours. The solution was then concentrated under reduced pressure, dissolved in minimal dichloromethane, then precipitated in cold methanol. The collected solids were dialyzed against tetrahydrofuran. The polymer solution was then concentrated under reduced pressure, dissolved in minimal dichloromethane, and precipitated in cold methanol. The precipitate was collected via vacuum filtration and dried under vacuum to yield Por[poly(MMA-co-AMMA)]$_4$ as a tan powder (0.8819 g, M_n = 17.2 kDa, AMMA incorporation = 22.8%). M_n calculated based on Equation 1. %AMMA incorporation calculated based on Equation 2. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.87 (br s), 8.55-8.10 (br m), 8.10-7.70 (br m), 7.67-7.10 (br m), 6.32-5.60 (br m), 3.86-3.00 (br m), 2.50-0.36 (br m), -2.85 (br s)

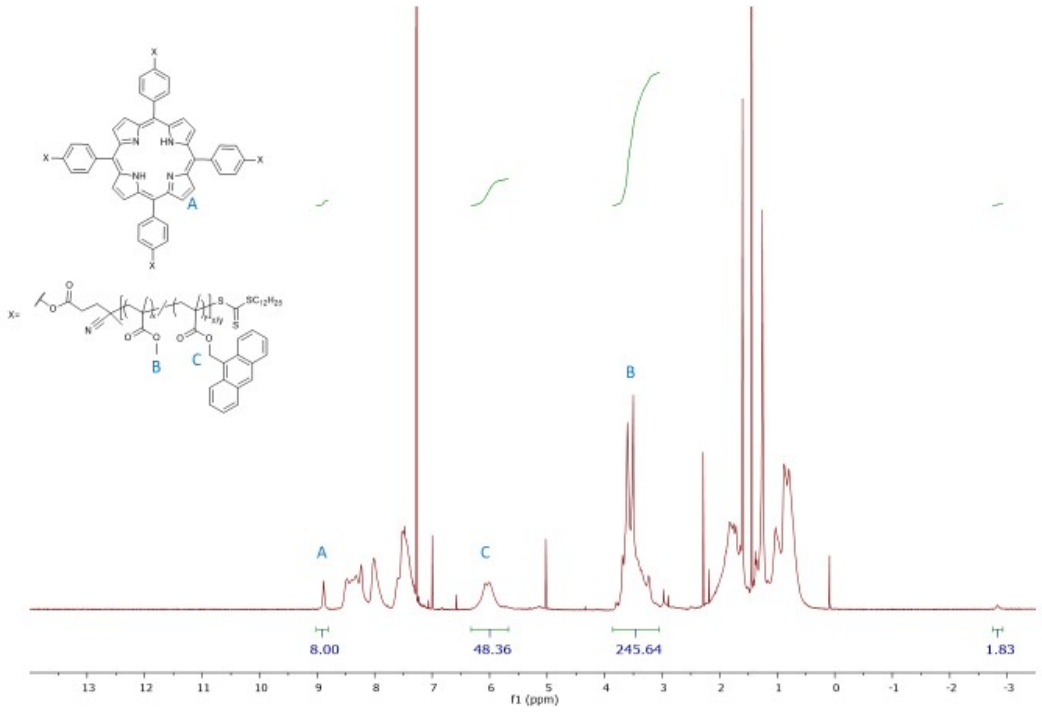


Figure S9: ^1H NMR ($CDCl_3$, 500 MHz) spectrum of Por[poly(MMA-co-AMMA)]$_4$

$$Equation\ 1:\ M_n = M_{porCTA}\frac{\int A}{H_A} + M_{MMA}\frac{\int B}{H_B} + M_{AMMA}\frac{\int C}{H_C}$$

$$Equation\ 2:\ \%\ AMMA = \frac{\frac{\int C}{H_C}}{\frac{\int B}{H_B} + \frac{\int C}{H_C}} \times 100$$

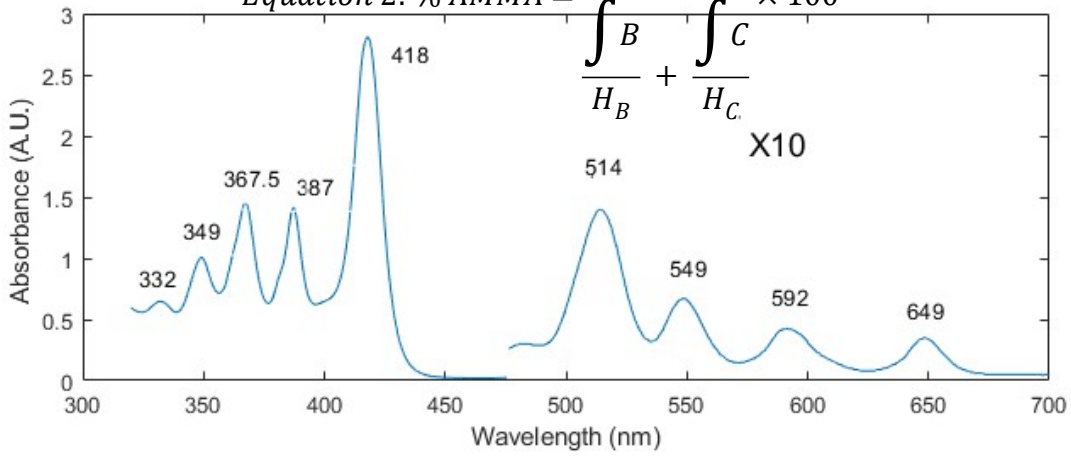
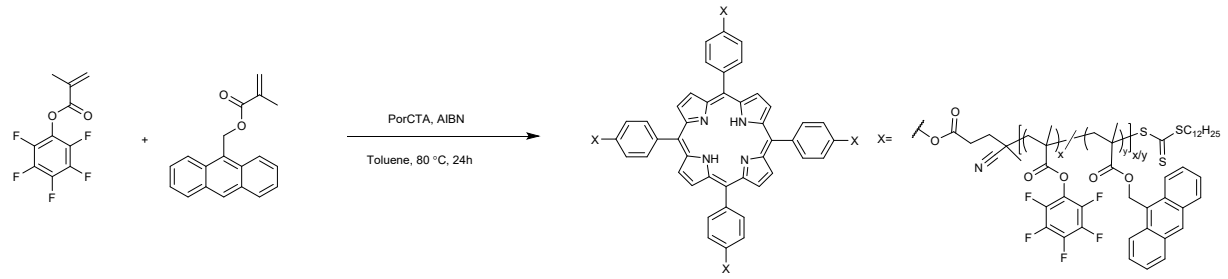


Figure S10: UV-Vis Spectrum of Por[poly(MMA-co-AMMA)]$_4$ at 0.1 mg/mL in THF. Absorbance from 475 to 700 nm magnified X 10



Scheme S6: Synthesis of Por[poly(PFPMA-co-AMMA)]$_4$

Synthesis and Characterization of Por[poly(PFPMA-co-AMMA)]$_4$ [4]

A 50 mL round bottom flask equipped with a stir bar was charged with PorCTA (0.4550 g, 0.2049 mmol) , toluene (2 mL), 9-anthracenylmethyl methacrylate (0.8350 g, 3.022 mmol), pentafluorophenyl methacrylate (3.0444 g, 12.074 mmol) and azobisisobutyronitrile (0.0261 g, 0.1589 mmol). The mixture was sparged with argon for 1 hour while stirring. After, the flask was placed in an oil bath preheated to 80°C and the solution was stirred under argon for 18 hours. The solution was then concentrated under reduced pressure, dissolved in minimal dichloromethane, then precipitated in cold methanol. The collected solids were dialyzed against tetrahydrofuran. The polymer solution was then concentrated under reduced pressure, dissolved in minimal dichloromethane, and precipitated in cold methanol. The precipitate was collected via vacuum filtration and dried under vacuum to yield Por[poly(PFPMA-co-AMMA)]$_4$ as a red powder. (4.1863 g, M_n = 33.2 kDa, AMMA incorporation = 14.6%) M_n Calculated based on equation 3. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.87 (br s), 8.54 -8.06 (br m), 8.06-7.65 (br m), 7.65-7.00 (br m), 6.49-5.62 (br m), 2.75 -0.6 (br m), -2.84 (br s) ^{19}F NMR ($CDCl_3$, 376.1 MHz): δ -149.2 to -152.5(br m), -156.5 to -158.2 (br m), -161.2 to -163.0 (br m)

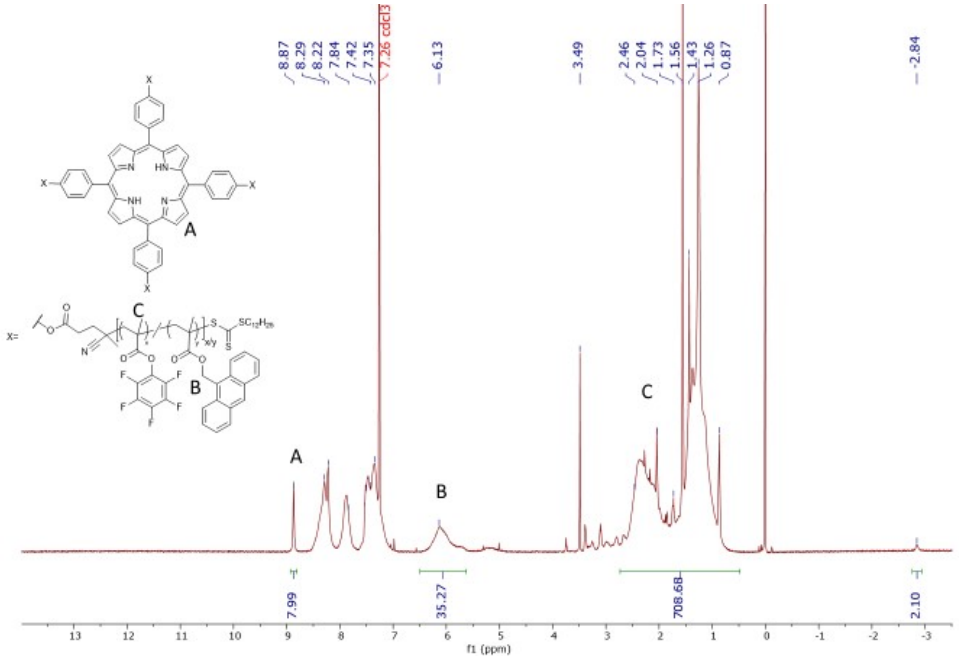


Figure S11: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Por[poly(PFPMA-co-AMMA)]$_4$

$$Equation\ 3: M_n = M_{porCTA}\frac{\int A}{H_A} + M_{AMMA}\frac{\int B}{H_B} + M_{PFPMA}\frac{\left[\int C - H_{c,AMMA}\frac{\int B}{H_B} - H_{C,porCTA}\frac{\int A}{H_A}\right]}{H_{C,PFPMA}}$$

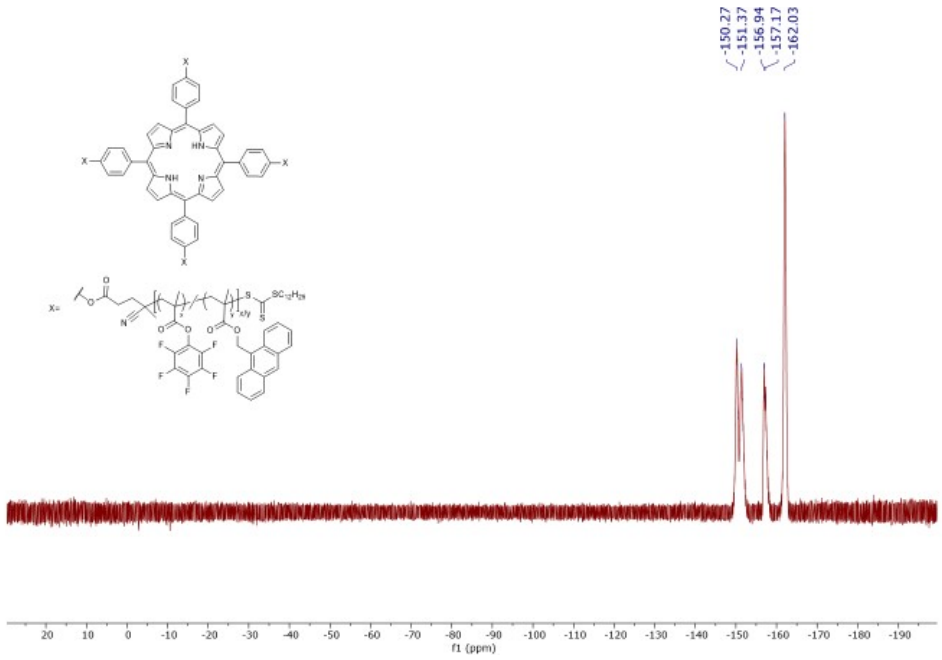
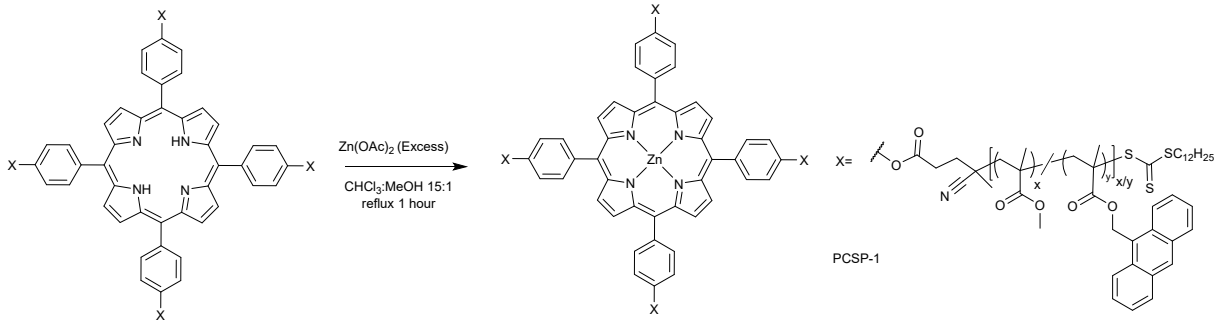


Figure S12: ^{19}F NMR ($CDCl_3$, 376.1 MHz) spectrum of Por[poly(PFPMA-co-AMMA)]$_4$



Scheme S7: Synthesis of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)

Synthesis and Characterization of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)

A 1 L round bottom flask equipped with a magnetic stir bar was charged with Por(MMA-co-AMMA (0.5014 g, 0.0292 mmol), chloroform (140 mL), methanol (10 mL), and zinc acetate hydrate (0.1283 g, 0.5886 mmol). The solution was refluxed with stirring for 1 hour. The solution was concentrated under reduced pressure, dissolved in minimal dichloromethane, and precipitated in cold methanol. The precipitate was collected via vacuum filtration then dried under vacuum to yield Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) as a red powder (0.4537g). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.93 (br s), 8.55-8.10 (br m), 8.10-7.70 (br m), 7.67-7.10 (br m), 6.32-5.60 (br m), 3.86-3.00 (br m), 2.50-0.36 (br m)

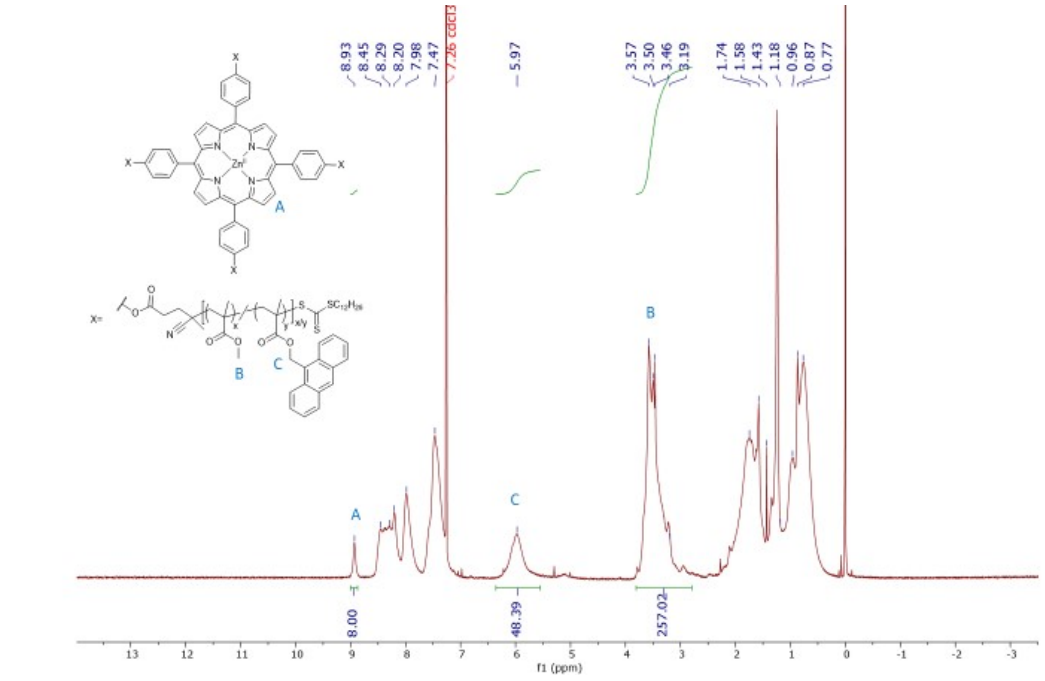


Figure S13: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)

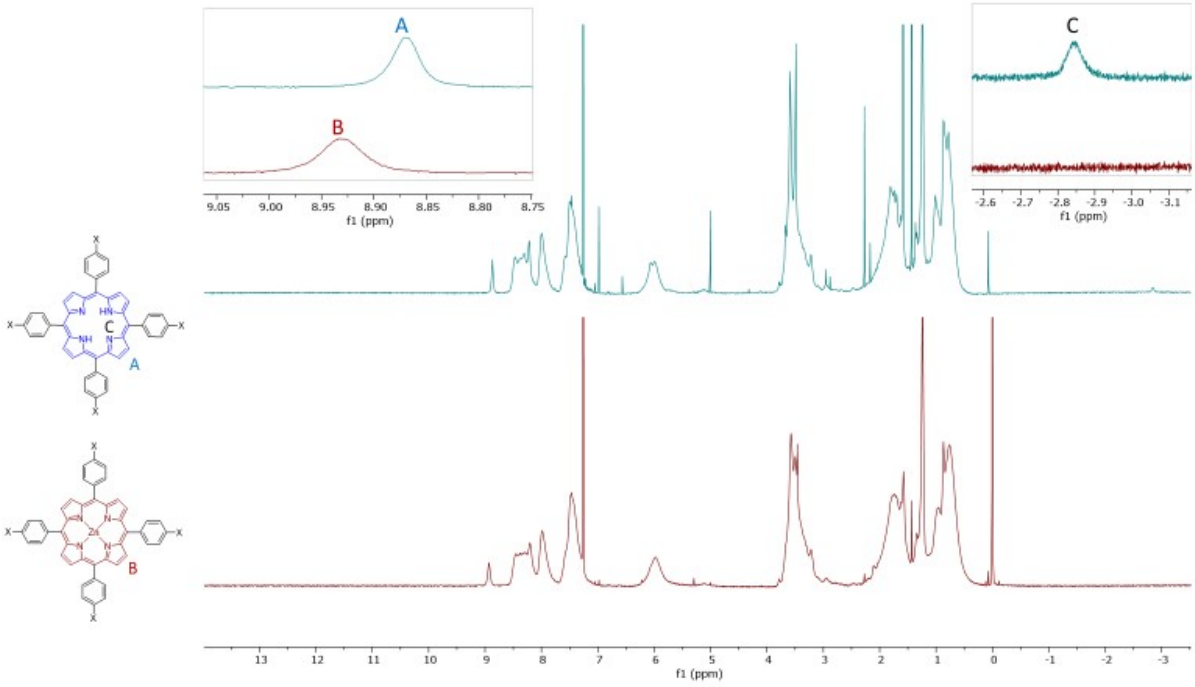


Figure S14: Comparison of ^{1}H NMR ($CDCl_3$, 500 MHz) spectrums for Por[poly(MMA-co-AMMA)]$_4$ (Blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (Red)

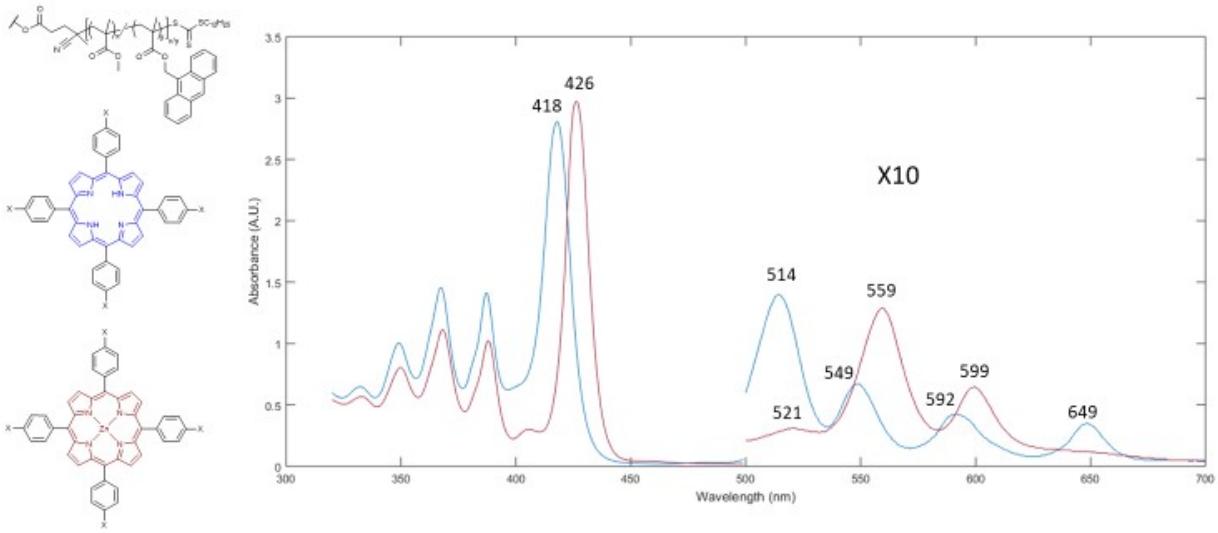


Figure S15: Comparison of UV vis spectrum of Por[poly(MMA-co-AMMA)]$_4$ (Blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (Red) at 0.1 mg/mL in THF, Absorbance from 500 to 700 nm magnified X 10

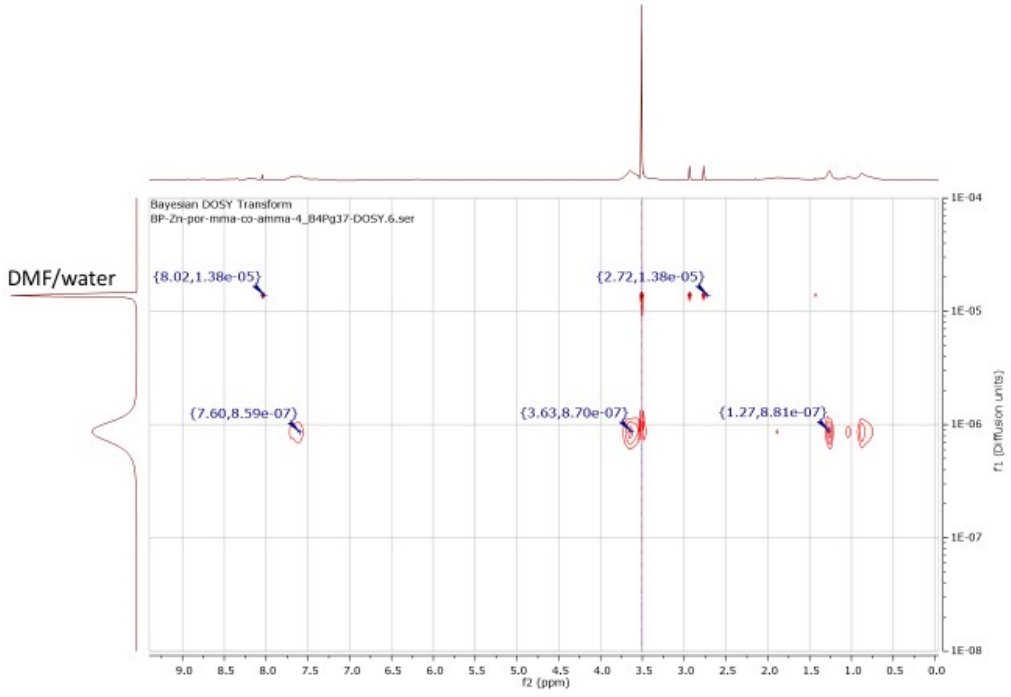
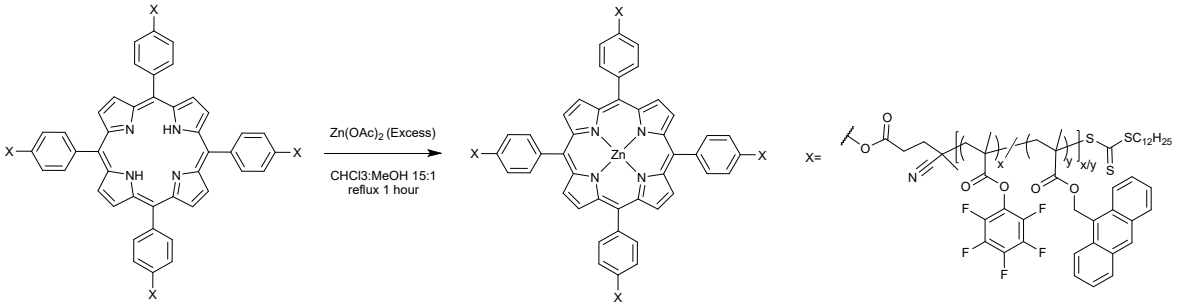


Figure S16: ^{1}H DOSY NMR (DMF-D$_7$, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)



Scheme S8: Synthesis of Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$)

Synthesis and Characterization of Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$)

A 1 L round bottom flask equipped with a magnetic stir bar was charged with Por(PFPMA-co-AMMA (1.2173 g, 0.0429 mmol), chloroform (337 mL), methanol (24 mL), and zinc acetate hydrate (0.3101 g, 1.4226 mmol). The solution was refluxed with stirring for 1 hour. The solution was concentrated under reduced pressure, dissolved in minimal dichloromethane, and precipitated in cold methanol. The precipitate was collected via vacuum filtration then dried under vacuum to yield Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$) as a pink powder (1.0447 g). . ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.96 (br s), 8.54 -8.06 (br m), 8.06-7.65 (br m), 7.65-7.00 (br m), 6.49-5.62 (br m), 2.75 -0.60 (br m)

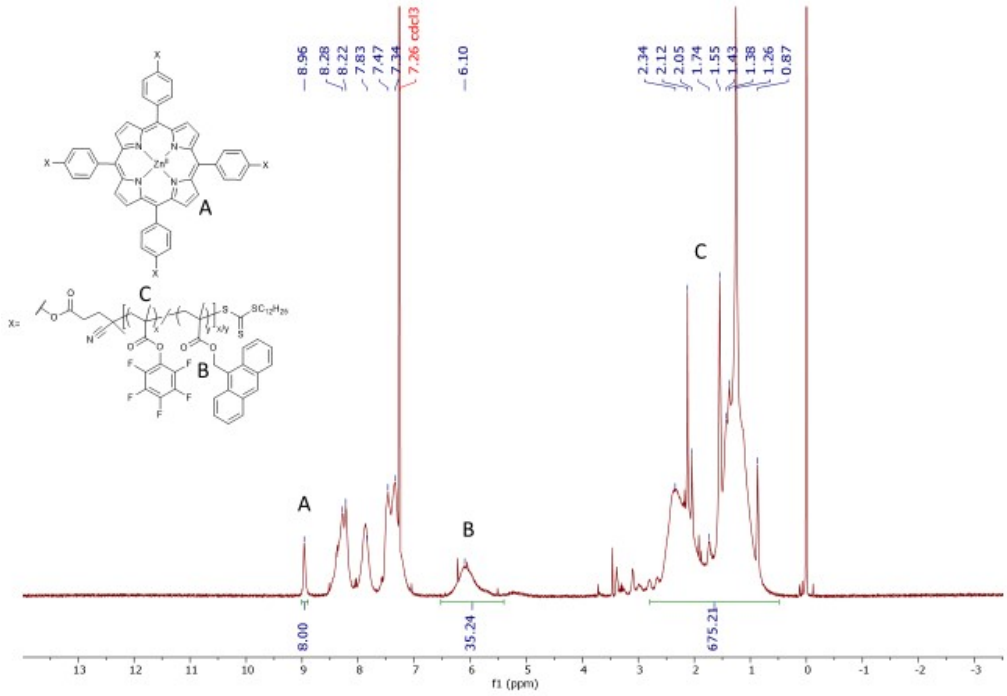


Figure S17: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Zn^{II}(Por(PFPMA-co-AMMA)$_4$)

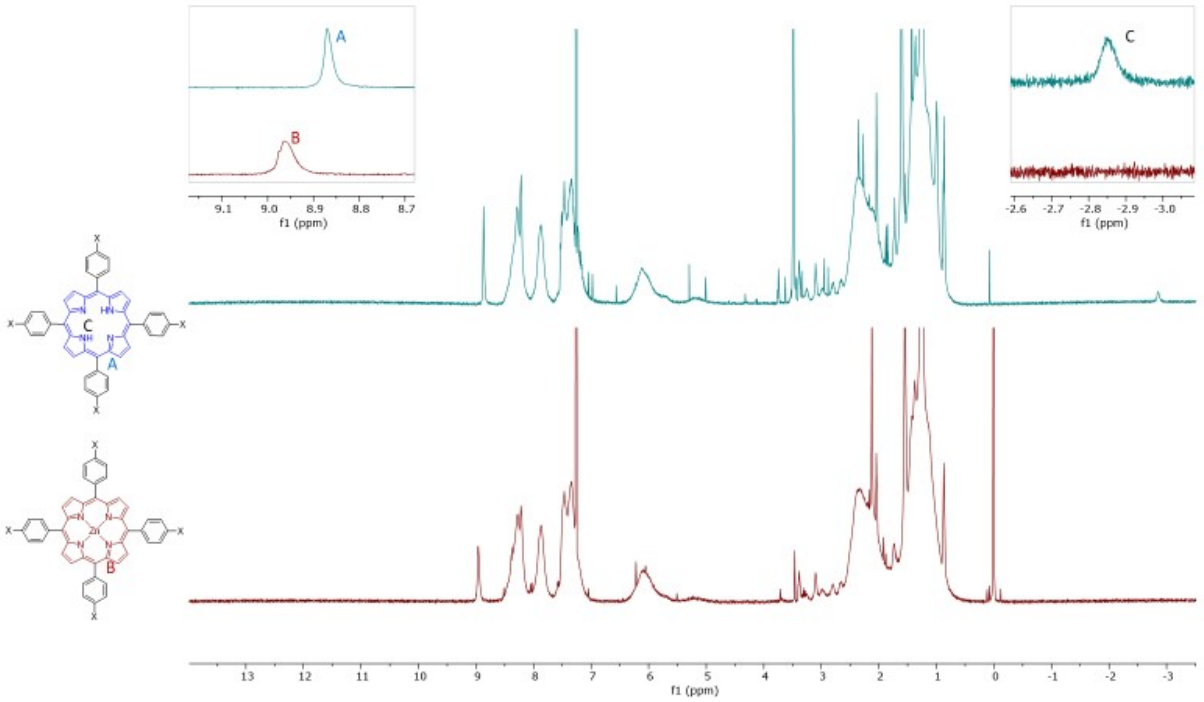


Figure S18:Comparison of ^{1}H NMR ($CDCl_3$, 500 MHz) spectrums for Por[poly(PFPMA-co-AMMA)]$_4$ (Blue) and Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$) (Red)

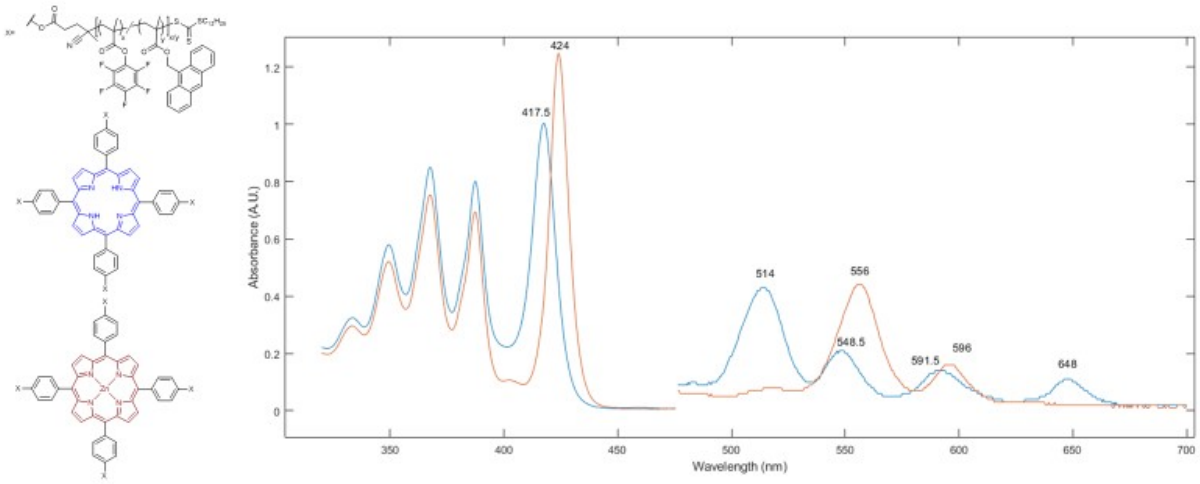
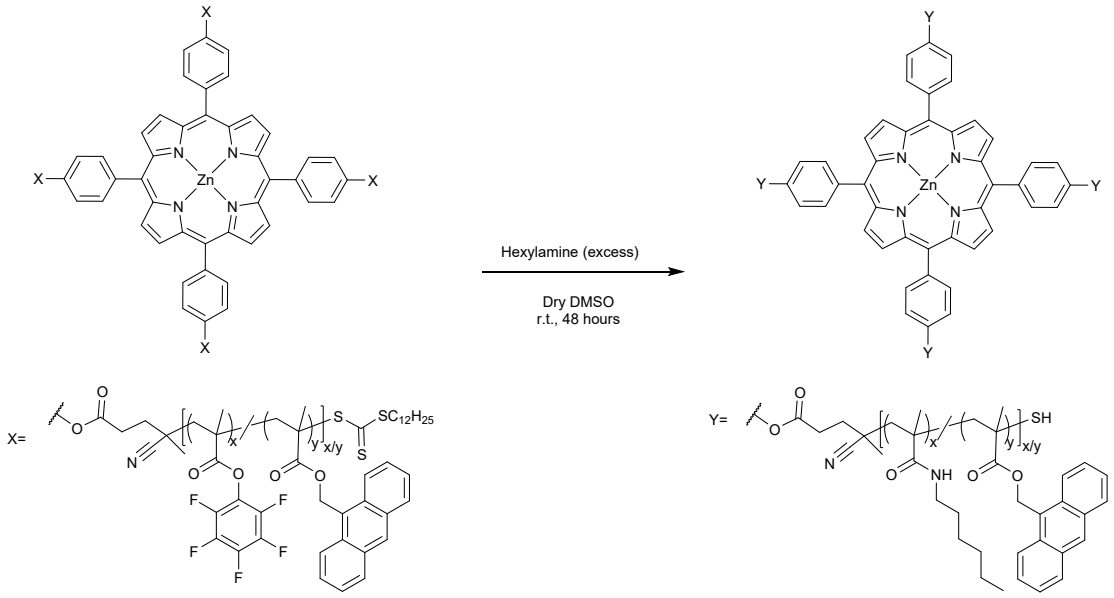


Figure S19: Comparison of UV vis spectrum of Por[poly(MMA-co-AMMA)]$_4$ (Blue) at 0.20 mg/mL in THF and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (Red) at 0.17 mg/mL in THF, Absorbance from 475 to 700 nm magnified X 10



Scheme S9: Synthesis of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$)

Synthesis and Characterization of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$)

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$) (0.3992 g, 1.238 mmol PFPMA), dry dimethyl sulfoxide (15.5 mL), and hexylamine (800 μL, 6.05 mmol). The mixture was allowed to stir for 48 hours at room temperature under nitrogen to yield a green solution. The solution was dialyzed against acetone for 3 hours, replacing the dialysis tube every 30 minutes. The solution was then concentrated under reduced pressure and dialyzed against tetrahydrofuran for 24 hours to yield a reddish tan solution. The solution was concentrated under reduced pressure and dried under vacuum to yield Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$) as green solids (0.3385 g). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.87 (br s), 8.60-8.12 (br m), 8.12-7.71 (br m), 7.71-6.99 (br m), 6.42-4.90 (br m), 3.86-0.16 (br m)

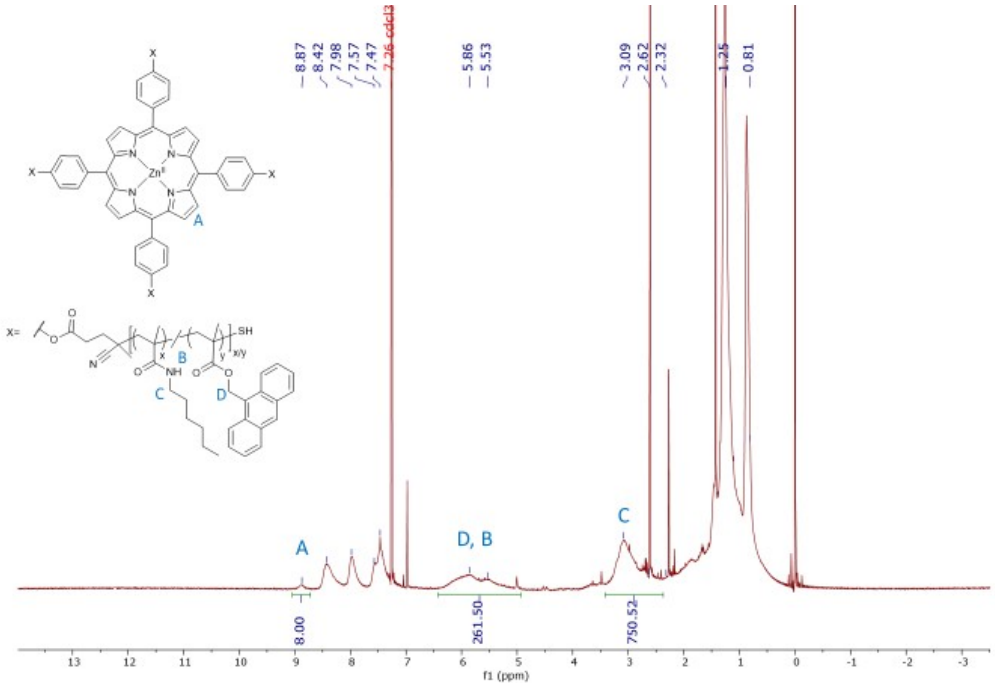


Figure S20: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Zn^{II}(Por(HexMAAm -co-AMMA)$_4$)

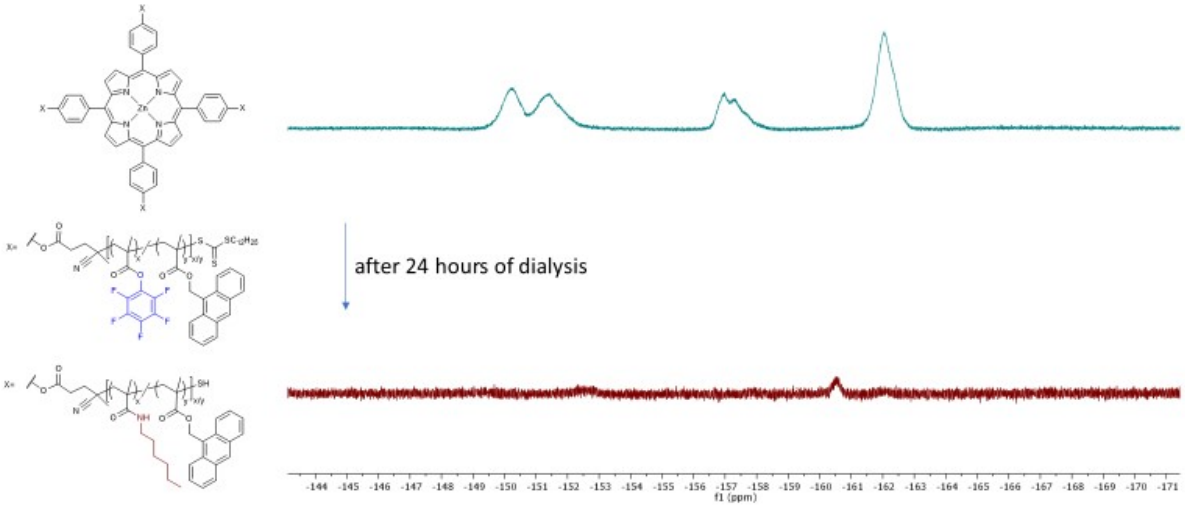


Figure 21: (Top) ^{19}F NMR ($CDCl_3$, 376.1 MHz) spectrum of Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$), (Bottom) ^{19}F NMR ($CDCl_3$, 376.1 MHz) spectrum of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$) after dialysis.

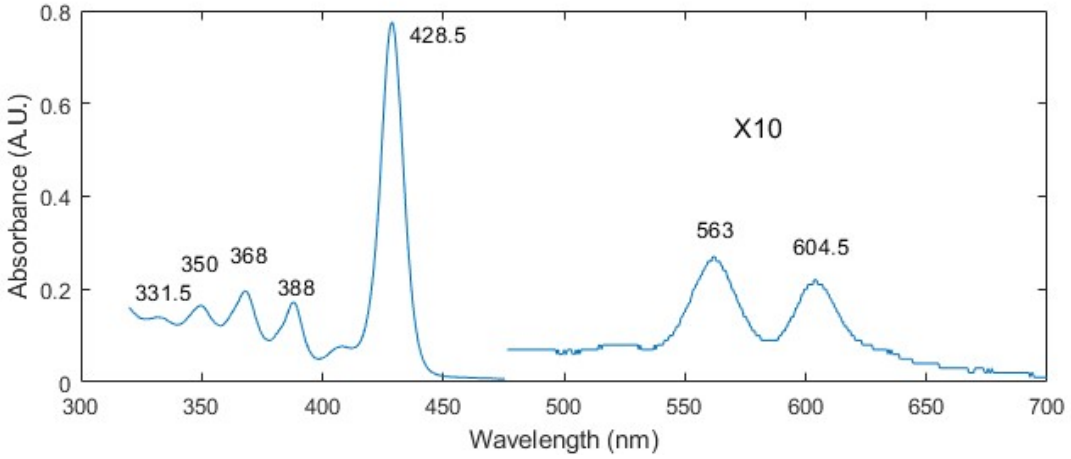


Figure S22: UV-Vis Spectrum of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$) at 2.9 μM in DMF. Absorbance from 475 to 700 nm magnified X 10

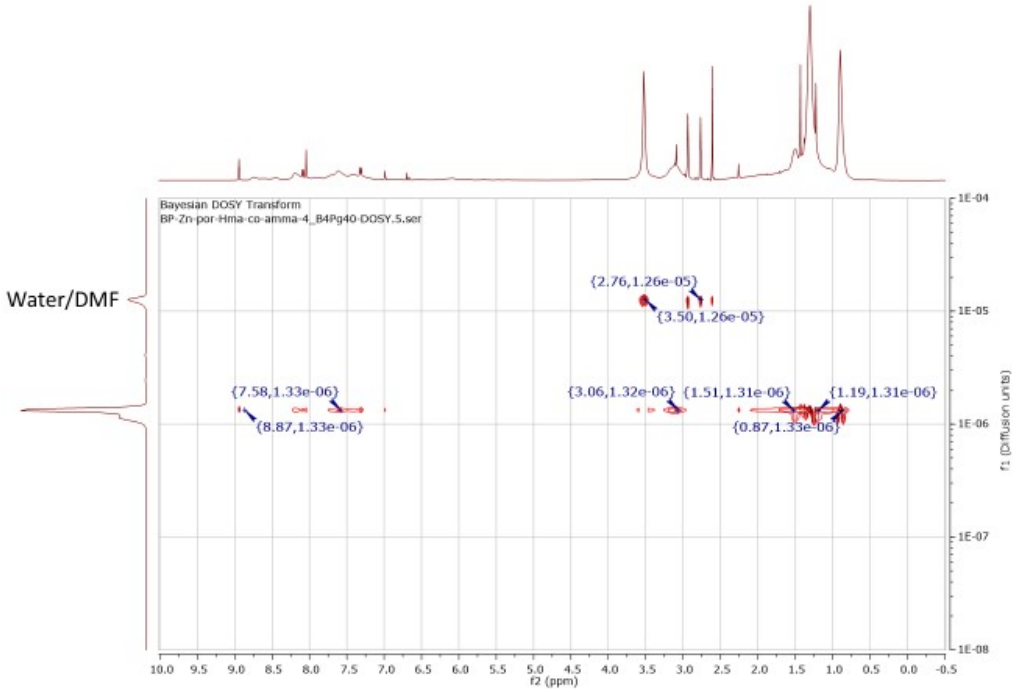
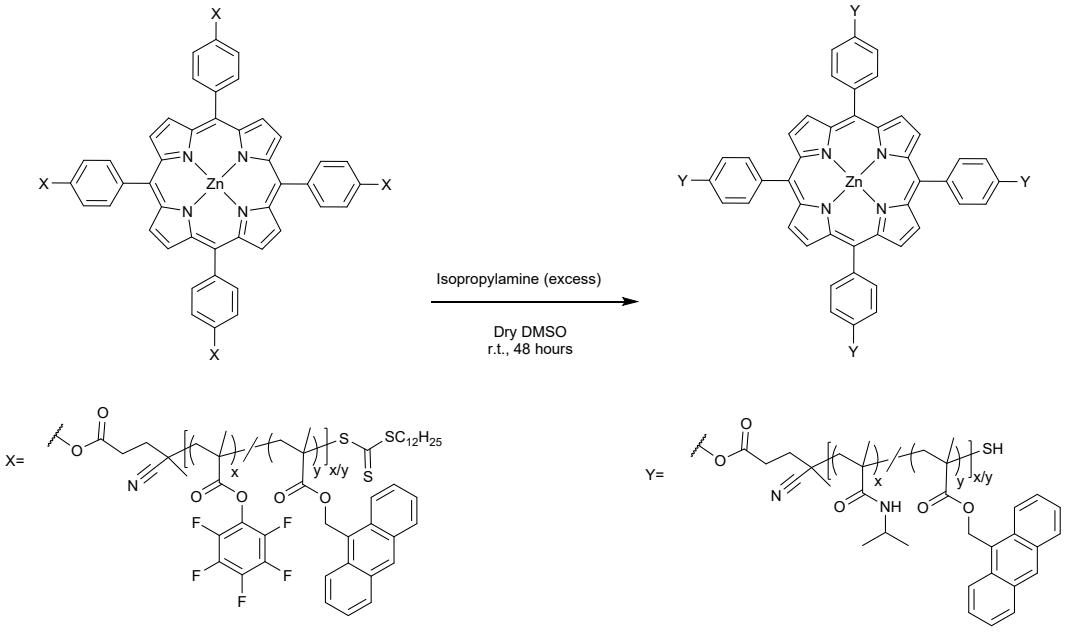


Figure S23: ^{1}H DOSY NMR (DMF-D7, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$)



Scheme S10: Synthesis of Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)

Synthesis and Characterization of Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$) (0.4019 g, 1.247 mmol PFPMA), dry dimethyl sulfoxide (16 mL), and isopropylamine (800 µL, 9.31 mmol). The mixture was stirred for 48 hours at room temperature under nitrogen. The solution was dialyzed against acetone for 5 hours, replacing the dialysis tube every hour. The solution was then concentrated under reduced pressure and dialyzed against tetrahydrofuran for 48 hours to yield a reddish tan solution. The solution was concentrated under reduced pressure and dried under vacuum to yield Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$) as green solids (0.2686 g) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.88 (br s), 8.60-8.12 (br m), 8.12-7.71 (br m), 7.71-6.99 (br m), 6.48-4.88 (br m), 4.30-3.26 (br m), 2.71-0.15 (br m)

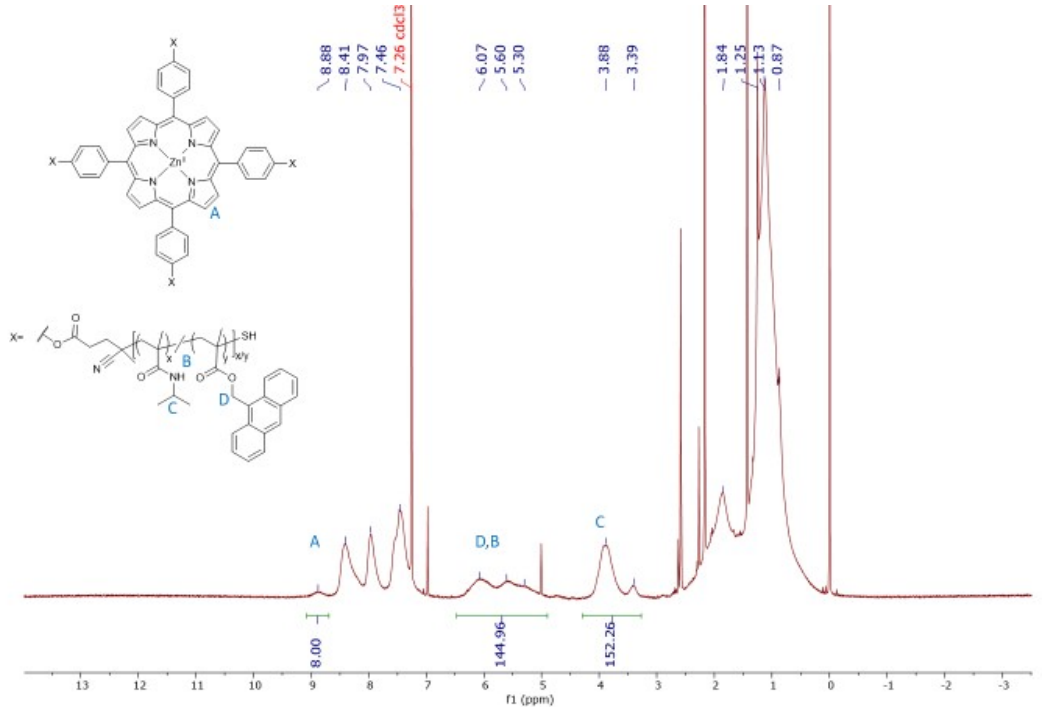


Figure S24: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)

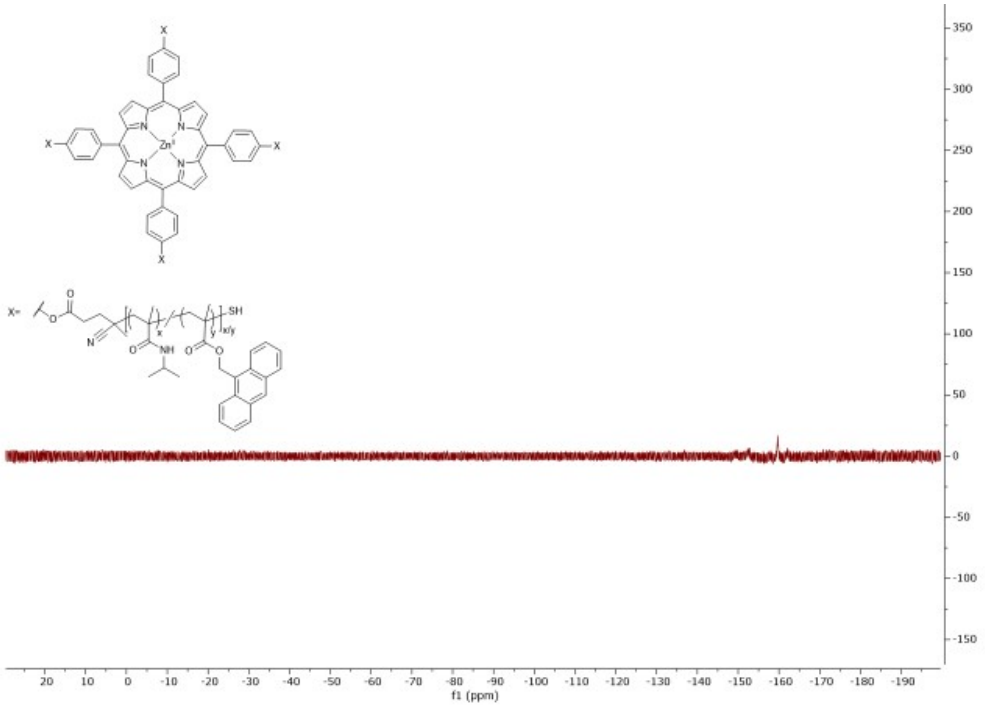


Figure S25: ^{19}F NMR ($CDCl_3$, 376.1 MHz) spectrum of Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)

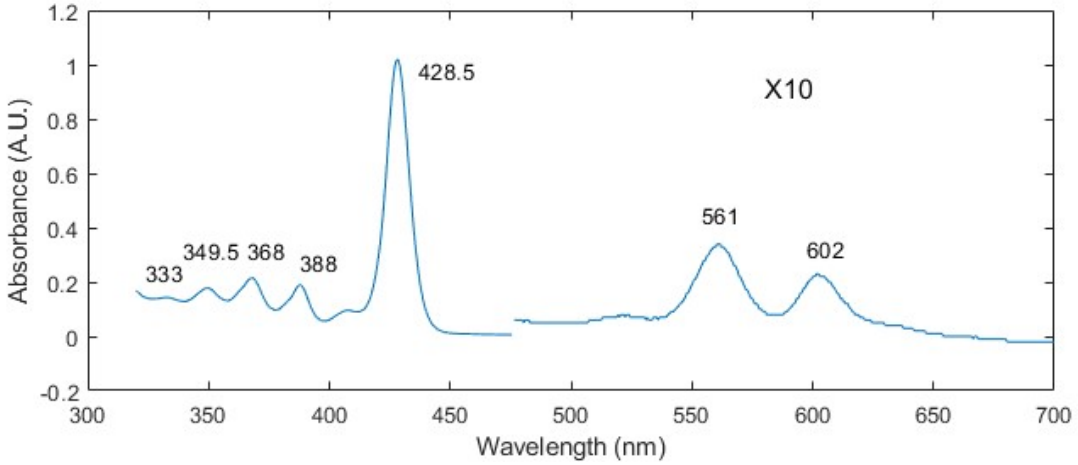


Figure S26: UV-Vis Spectrum of Zn^{II}(Por(iPMAAm -co-AMMA)$_4$) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

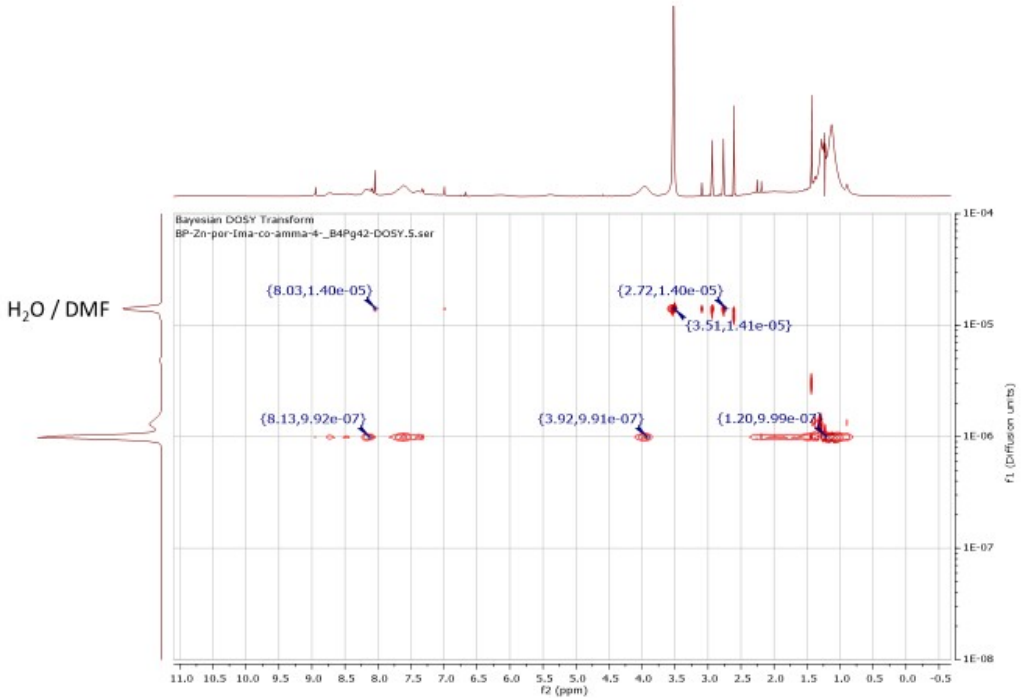
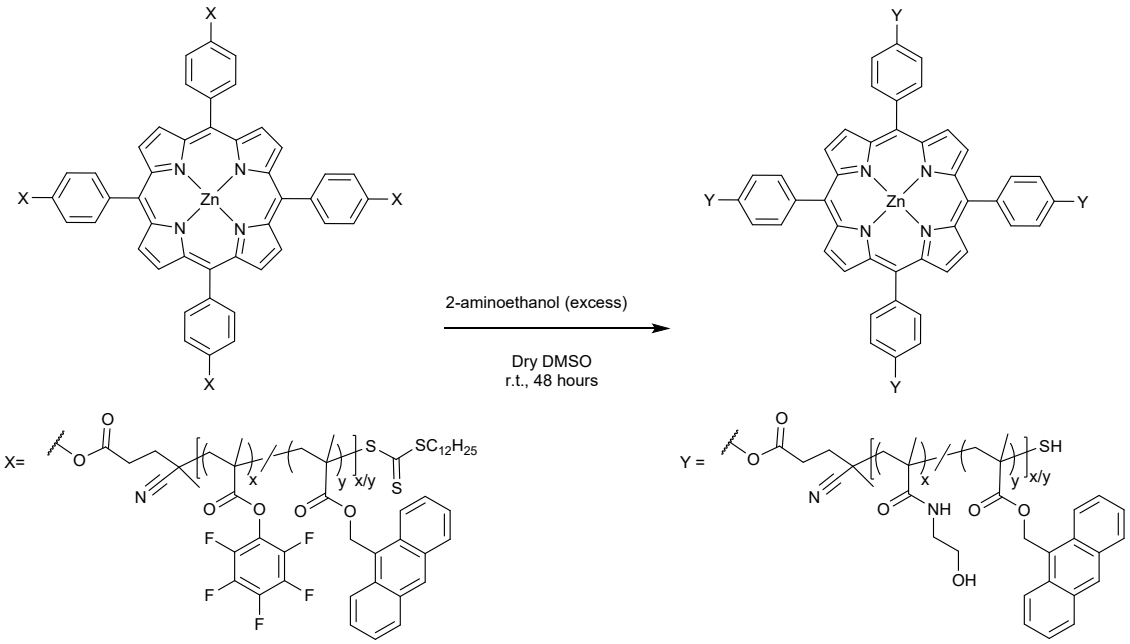


Figure S27: ^{1}H DOSY NMR (DMF-D7, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)



Scheme S11: Synthesis of Zn^{II}(Por((HEMA-co-AMMA)$_4$)

Synthesis and Characterization of Zn^{II}(Por((HEMA-co-AMMA)$_4$)

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with Zn^{II}(Por[poly(PFPMA-co-AMMA)]$_4$) (0.4007 g, 1.243 mmol PFPMA), dry dimethyl sulfoxide (16 mL), and 2-aminoethanol (360 µL, 5.9 mmol). The mixture was stirred for 24 hours at room temperature under nitrogen. The solution was dialyzed against acetone for 48 hours, replacing the dialysis tube every 30 minutes for the first 3 hours, and again after 24 hours resulting in green solids plated to the dialysis tubes and a purple solution. The solids were collected from the dialysis bags and dried under vacuum to yield Zn^{II}(Por((HEMA-co-AMMA)$_4$) as green solids (0.1291 g) ^{1}H NMR (DMF-d$_7$, 400 MHz): δ 8.93 (br s), 8.82-8.29 (br m) 8.29-7.93 (br m) 7.93-7.10 (br m) 6.43-5.60 (br m) 5.05-4.58 (br m), 4.16-3.00 (br m), 2.51-0.26 (br m)

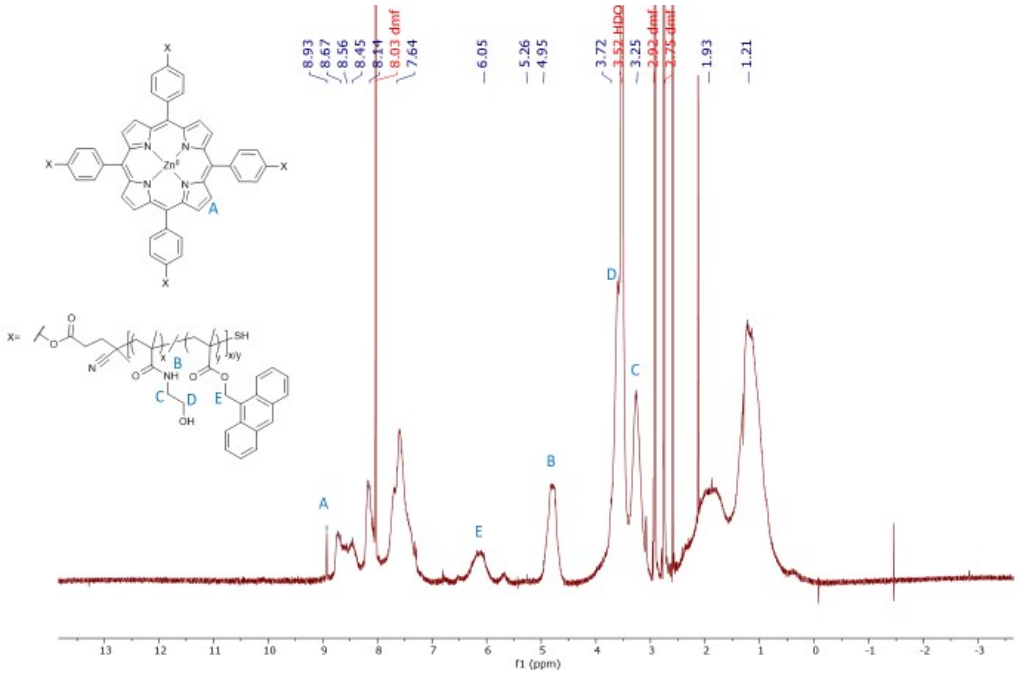


Figure S28:[1]H NMR (DMF-d_7, 400 MHz) spectrum of Zn^{II}(Por((HEMA-co-AMMA)$_4$)

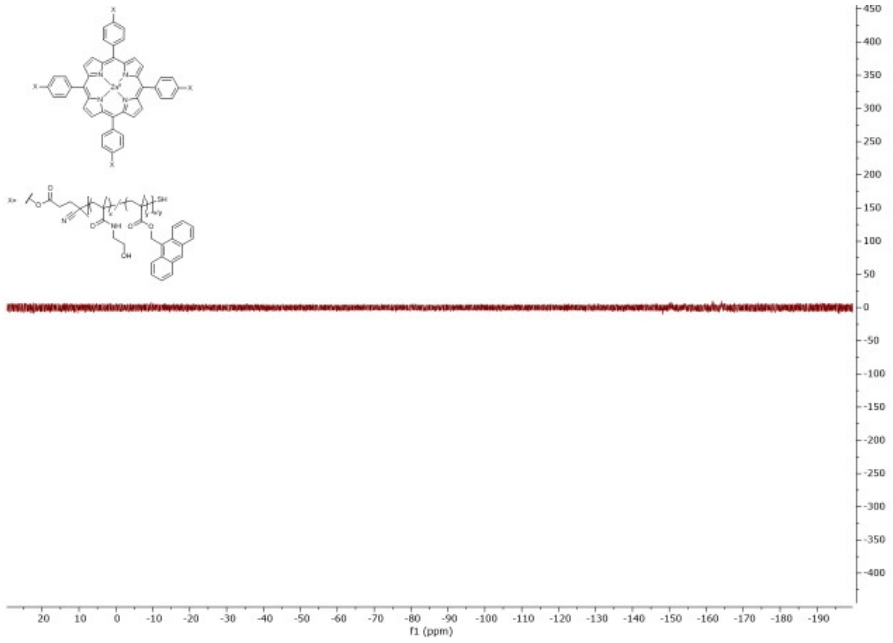


Figure S29:[19]F NMR (DMF-d_7, 376.1 MHz) spectrum of Zn^{II}(Por((HEMA-co-AMMA)$_4$)

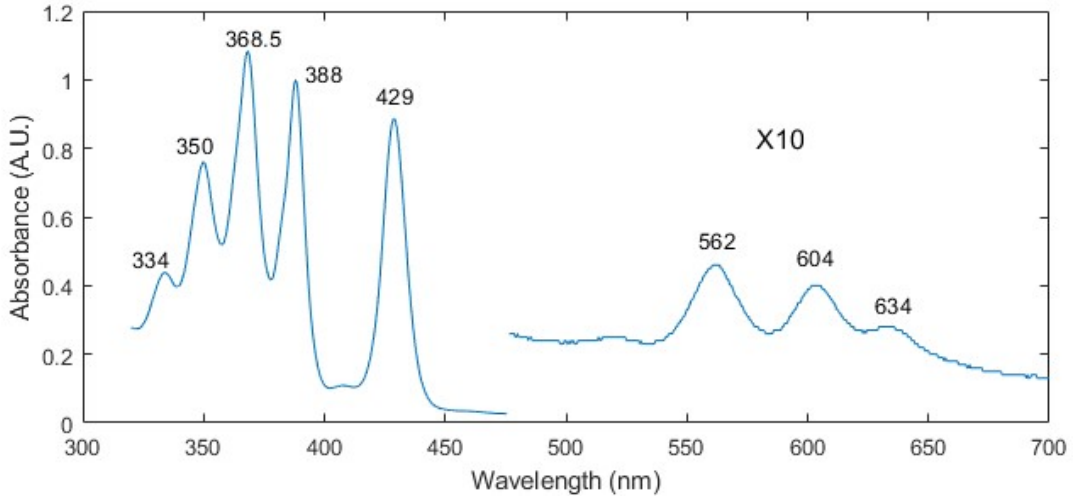


Figure S30: UV-Vis Spectrum of Zn^{II}(Por((HEMA-co-AMMA)$_4$) at 0.1 mg/mL in DMF. Absorbance from 475 to 700 nm magnified X 10

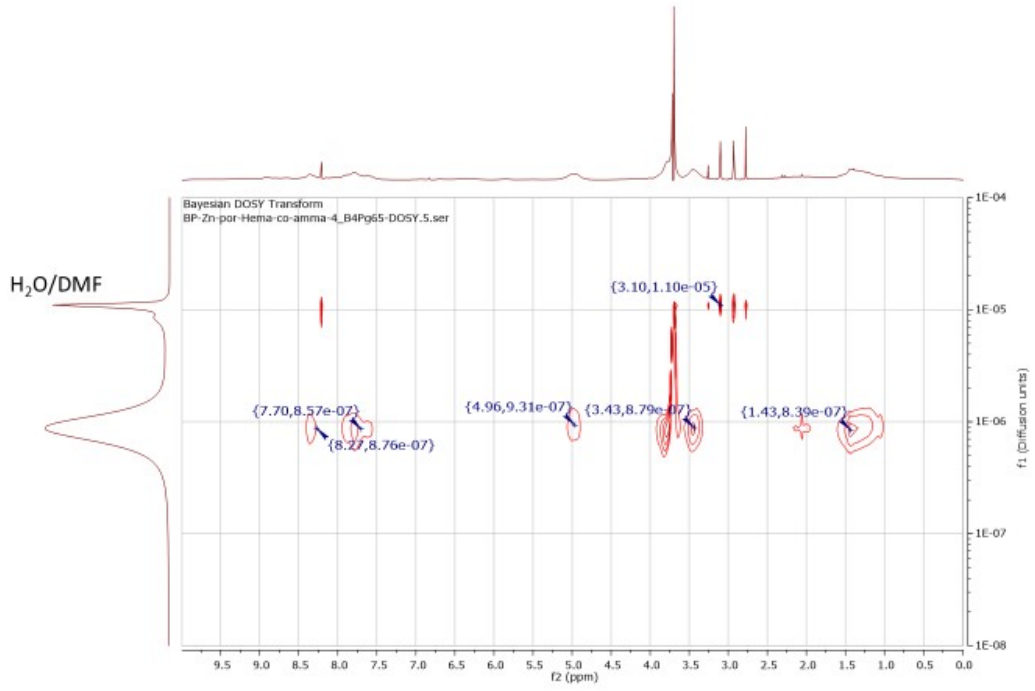
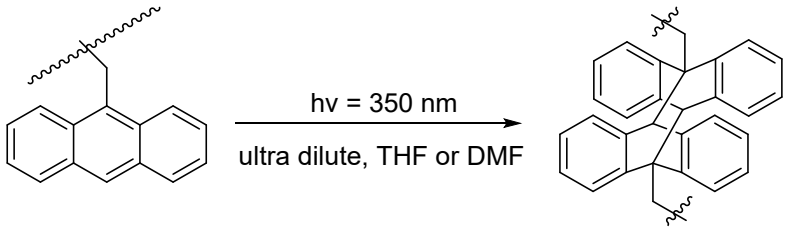


Figure S31: ^{1}H DOSY NMR (DMF-D7, 500 MHz, 298 K) spectrum of Zn^{II}(Por((HEMA-co-AMMA)$_4$)



Scheme S12:Photo-induced [4+4] cycloaddition of anthracene

General procedure for photoinduced dimerization of anthracene

A 250 mL quartz round bottom flask equipped with a stir bar was charged with polymer (15 mg) and dry N,N-dimethylformamide (150 mL) sparged with nitrogen. The solution was stirred for 1 hour and a 10 mL aliquot was taken. The bulk solution was then submitted to 350 nm light for 2 hours at room temperature with stirring. A second 10 mL aliquot was taken then the bulk was concentrated under reduced pressure. Collapse of the polymers to nanoparticles were monitored by UV-Vis spectroscopy and DOSY NMR. Percent conversion of Anthracene to the anthracene dimer calculated based on the UV-Vis absorbance at 366.5 nm.

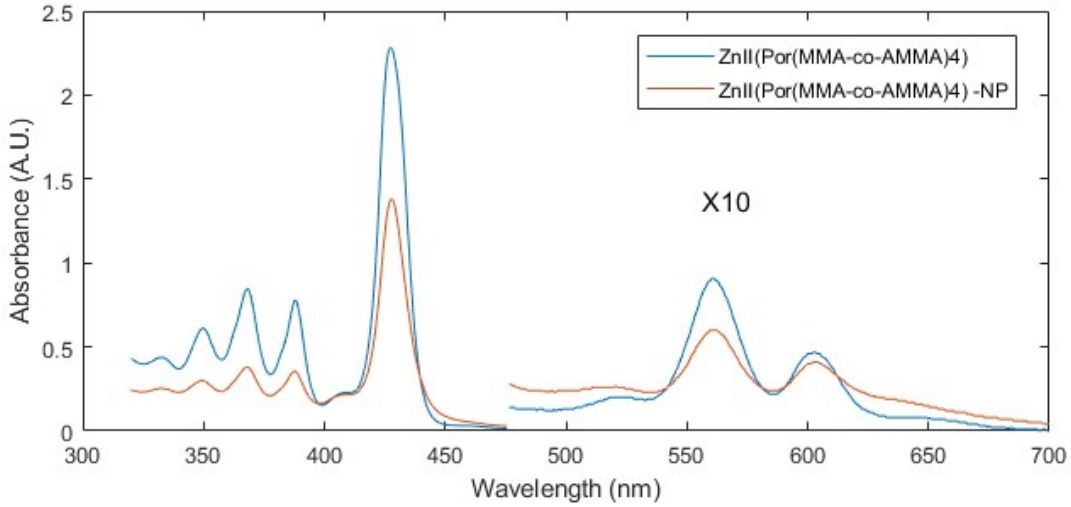


Figure S32: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP (red) at 0.1 mg/mL in DMF. Absorbance from 475 to 700 nm magnified X 10

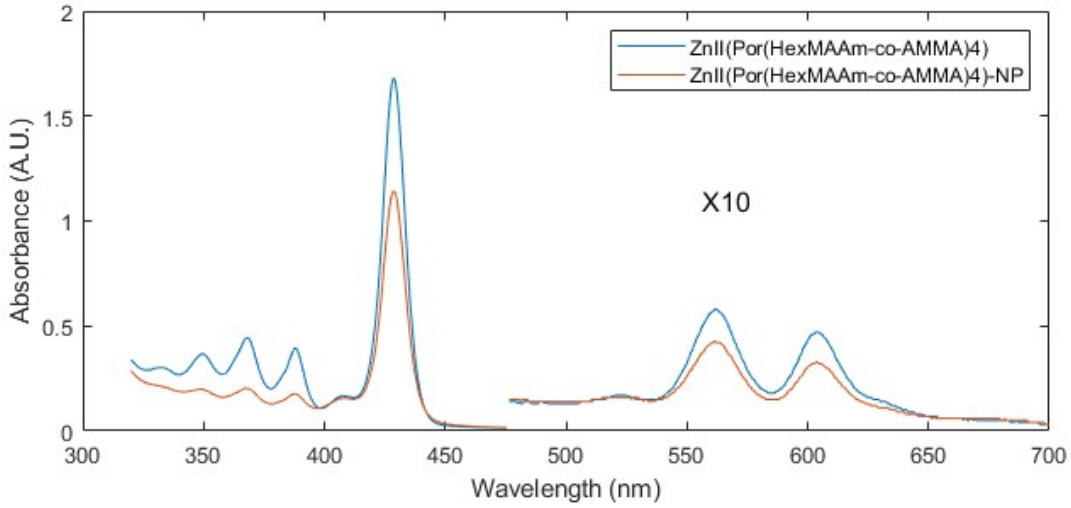


Figure S33:Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$) (blue) and Zn^{II}(Por(HexMAAm -co-AMMA)$_4$)-NP (red) at 0.1 mg/mL in DMF. Absorbance from 475 to 700 nm magnified X 10

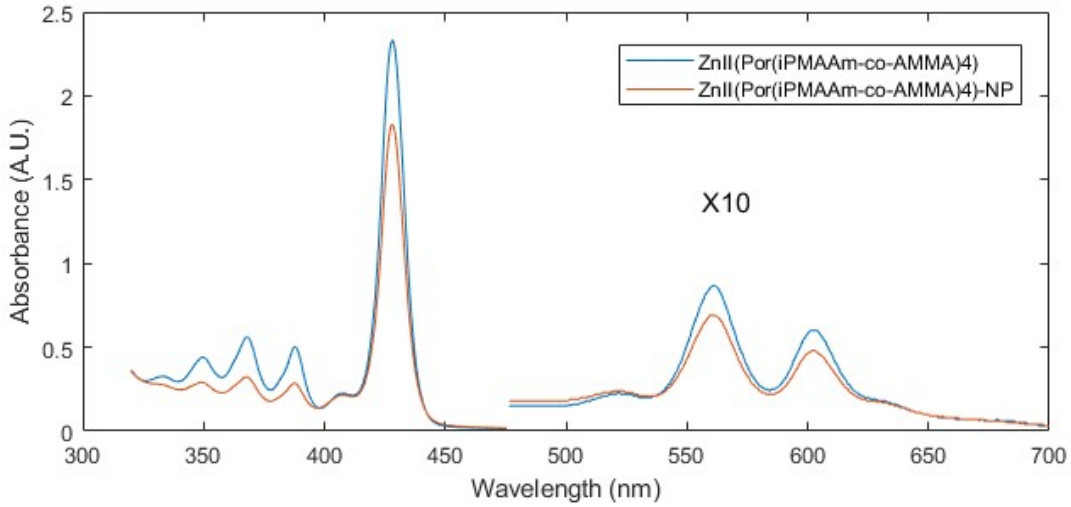


Figure S34: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$) (blue) and Zn^{II}(Por(iPMAAm -co-AMMA)$_4$)-NP (red) at 0.1 mg/mL in DMF. Absorbance from 475 to 700 nm magnified X 10

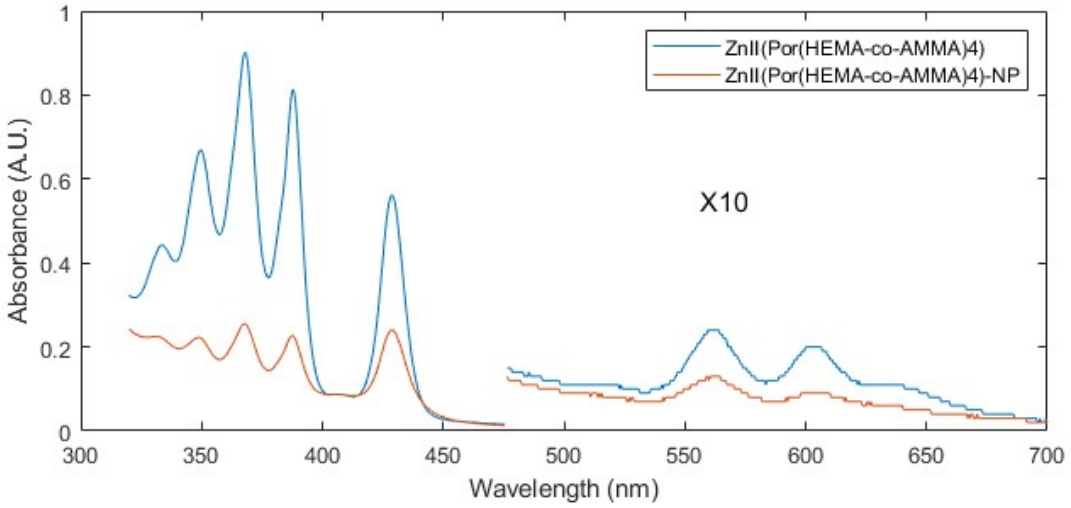


Figure S35: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$) (blue) and Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$)-NP (red) at 0.1 mg/mL in DMF. Absorbance from 475 to 700 nm magnified X 10

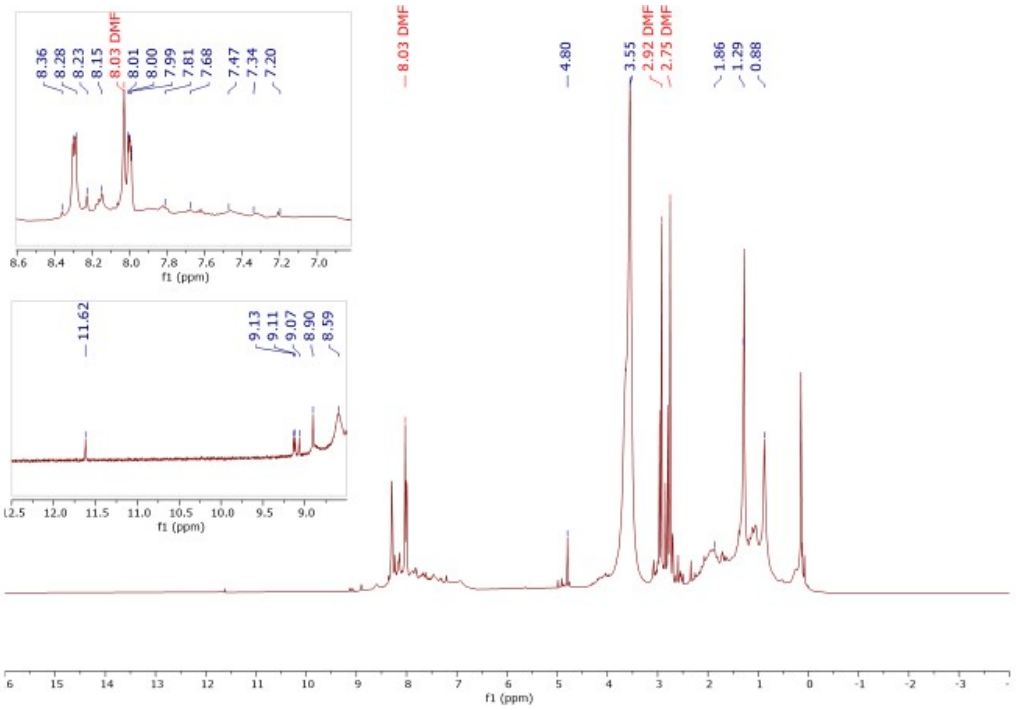


Figure S36 :^{1}H NMR (DMF-d_7, 500 MHz) spectrum of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP

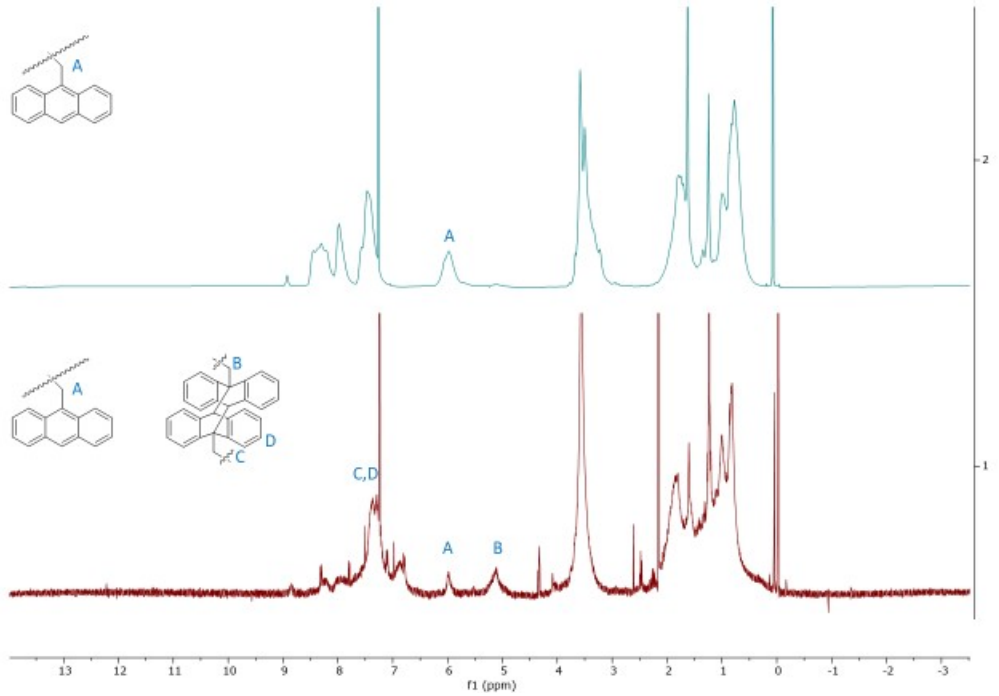


Figure S37: Comparison of ^{1}H NMR ($CDCl_3$, 500 MHz) spectrums for Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (Blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP after 2 hours of 350nm UV radiation (Red)

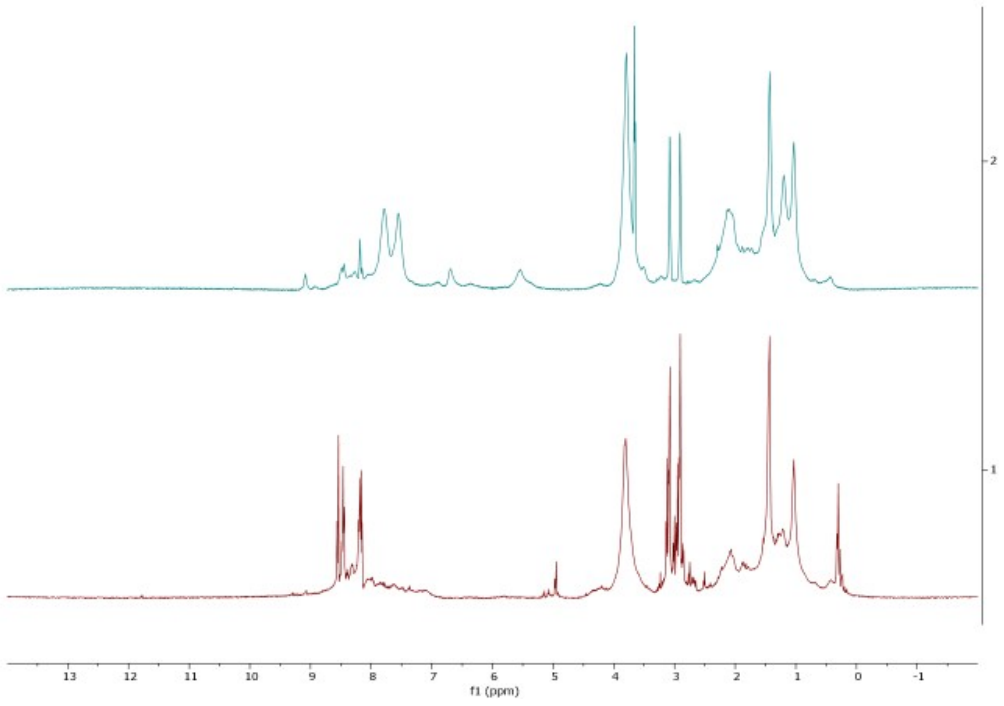


Figure 38: Comparison of 1H NMR (DMF-d7, 400 MHz) spectrums for Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (Blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP after 2 hours of 350nm UV radiation (Red)

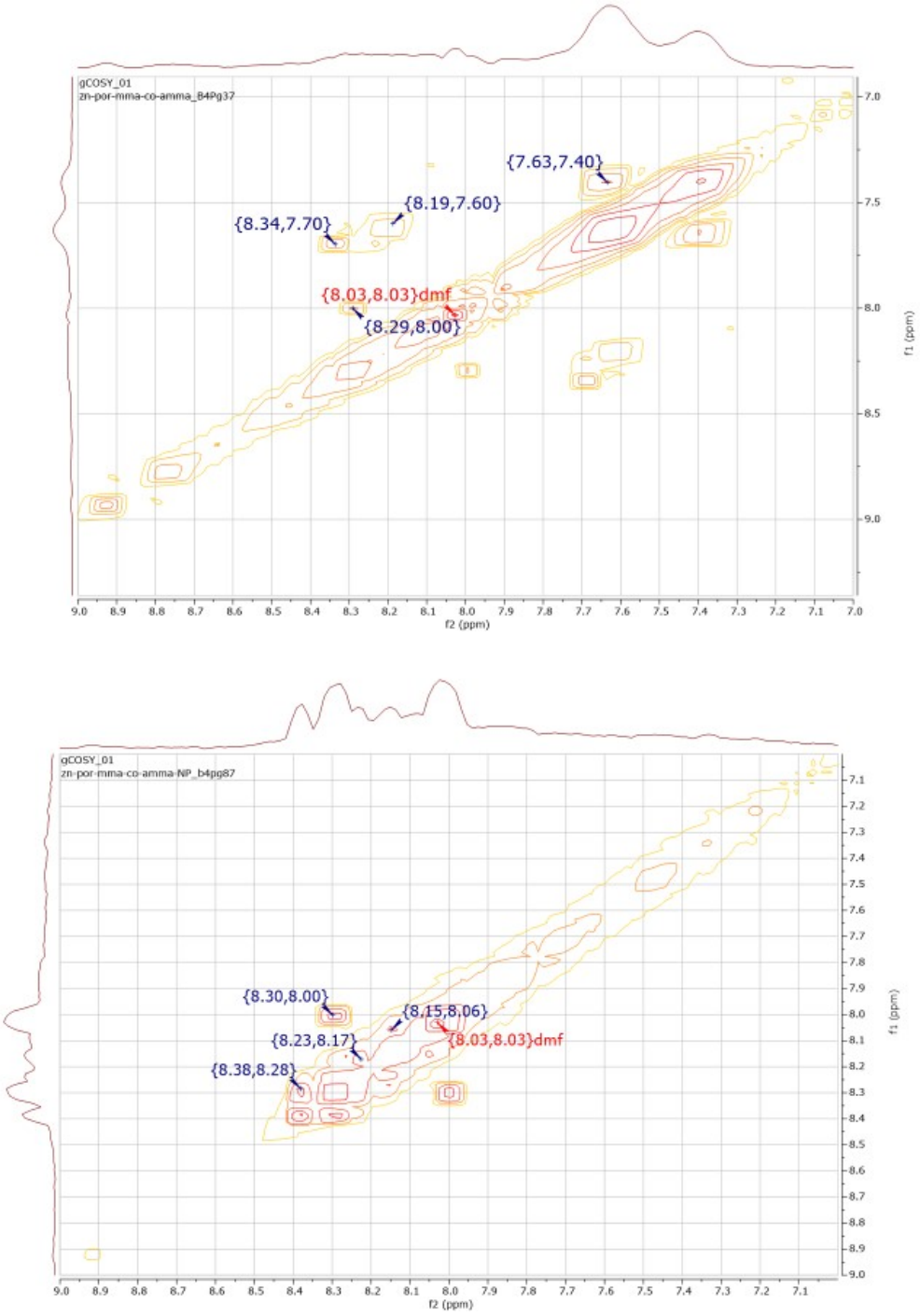


Figure S39: gCOSY NMR (DMF-d_7, 400 MHz) spectrums [δ 9.0 to 7.0] for Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (top) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP (bottom)

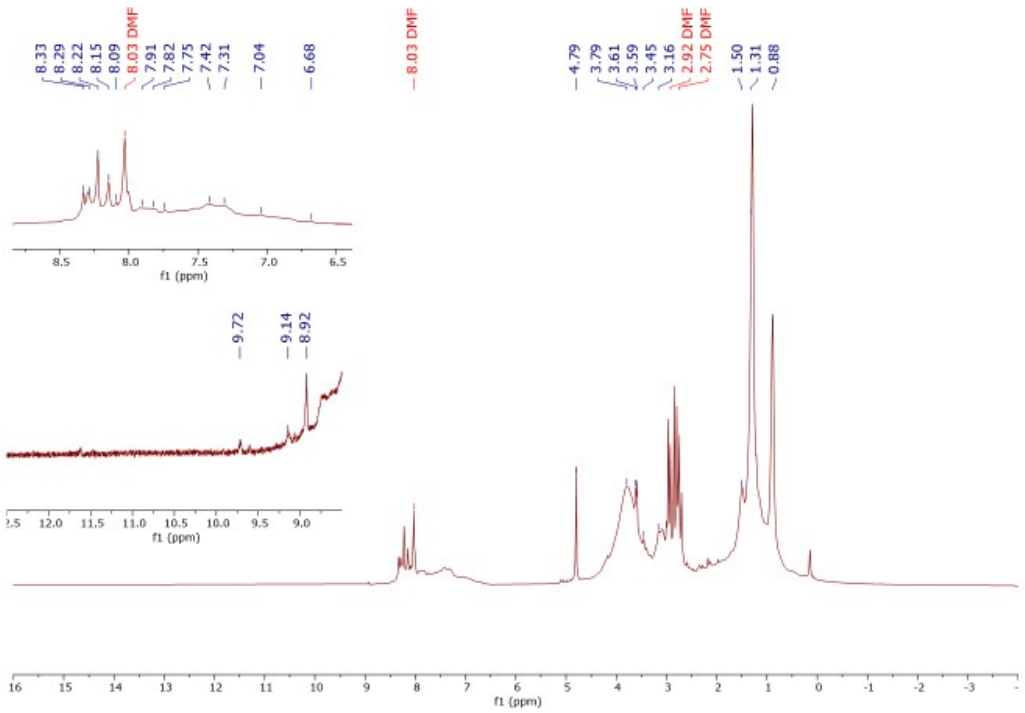


Figure S40: [1]H NMR (DMF-d7, 500 MHz) spectrum of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$)-NP

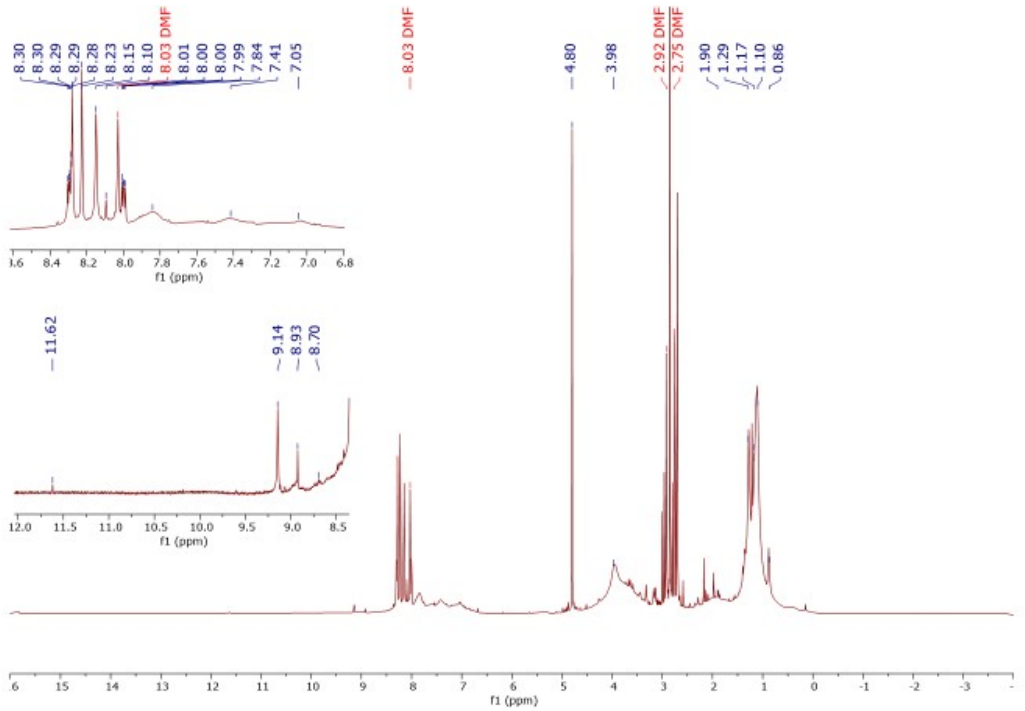


Figure S41: 1H NMR (DMF-d7, 500 MHz) spectrum of Zn^{II}(Por(iPMAAm -co-AMMA)$_4$)-NP

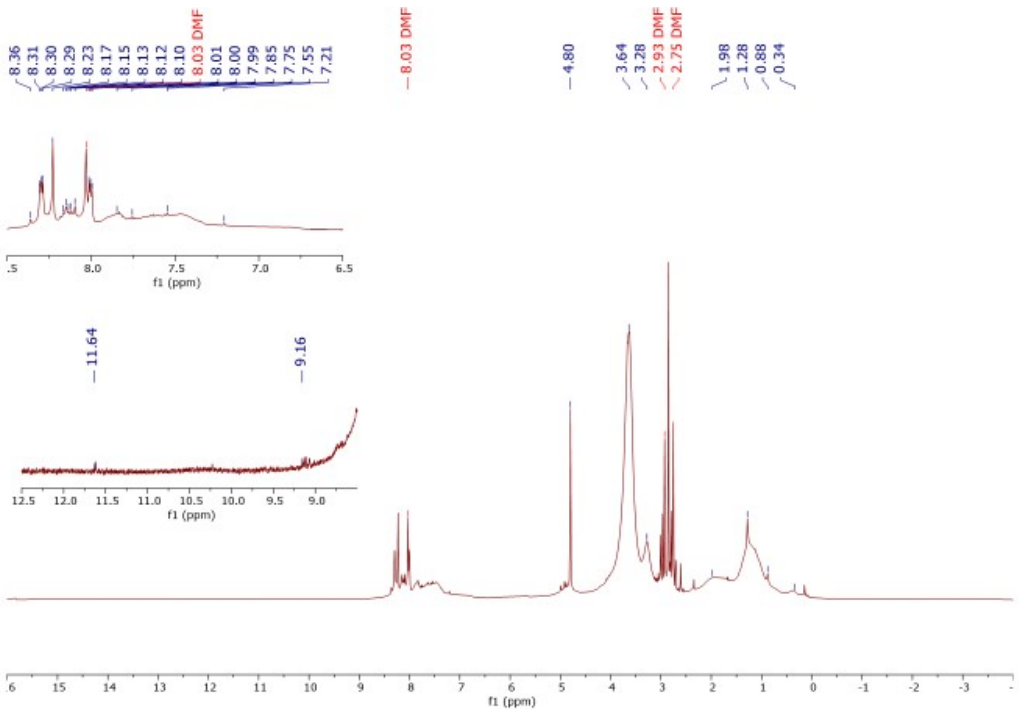


Figure S42: [1]H NMR (DMF-d7, 500 MHz) spectrum of Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$)-NP

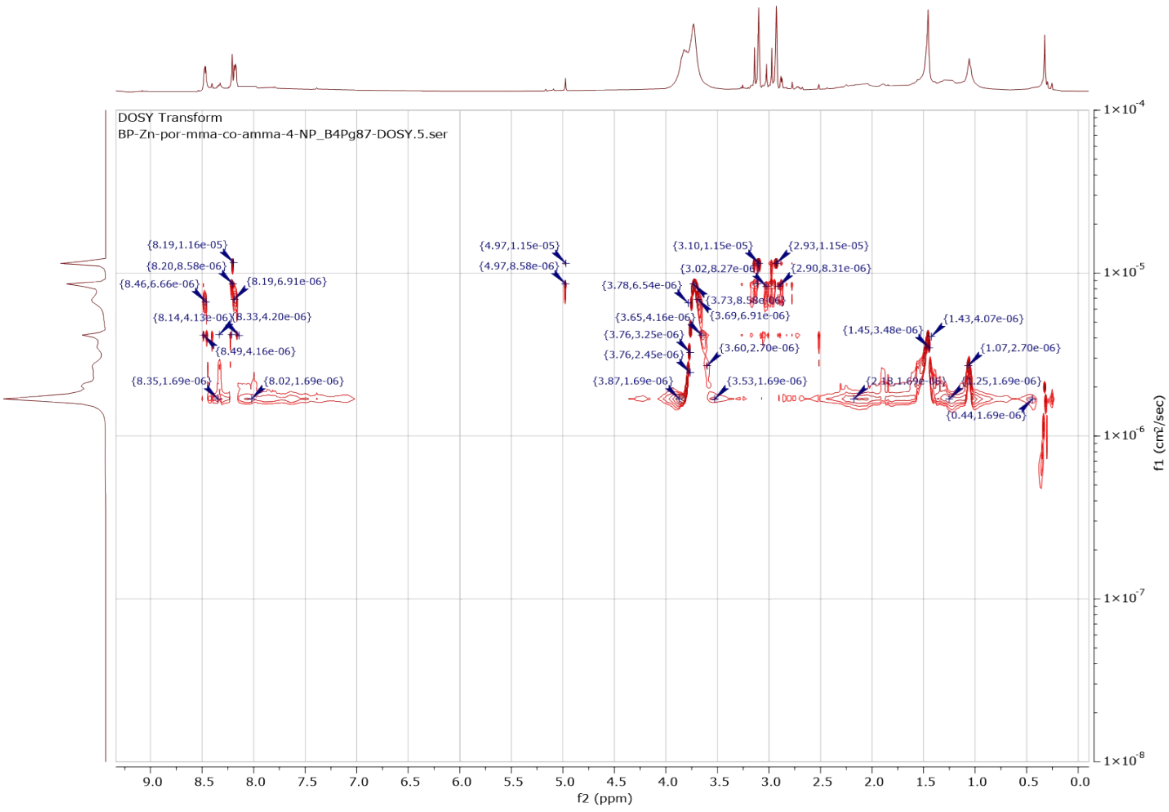


Figure S43: [1]H DOSY NMR (DMF-d_7, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP

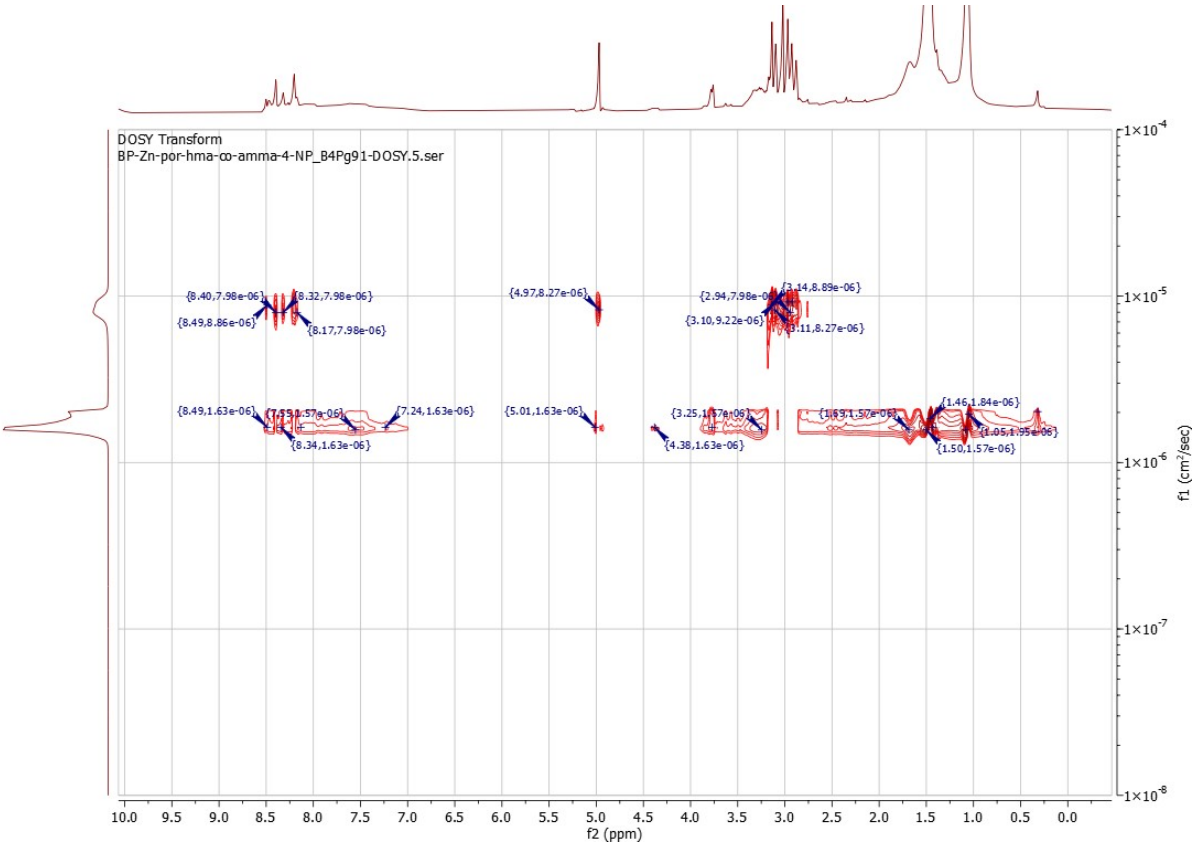


Figure S44: ^{1}H DOSY NMR (DMF-d_7, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$)-NP

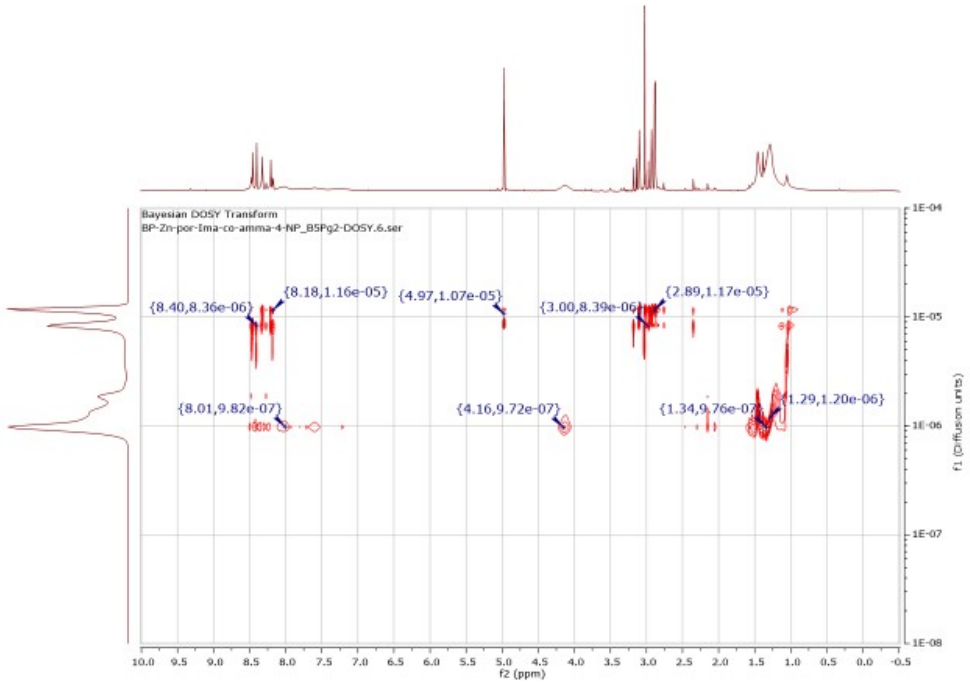


Figure S45: ^{1}H DOSY NMR (DMF-d_7, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)-NP

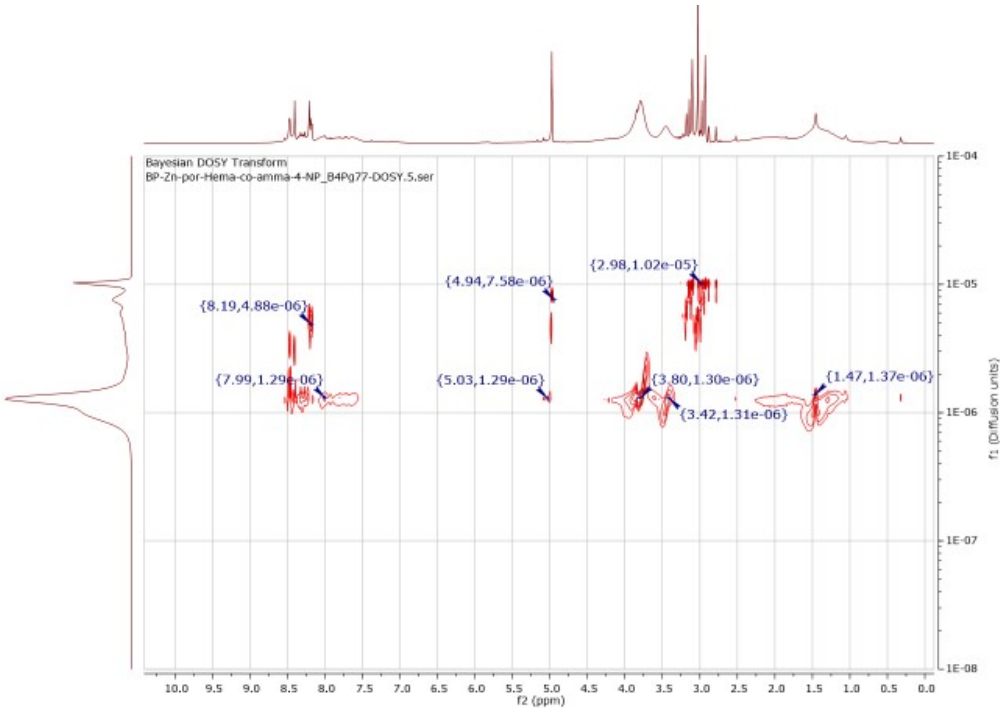


Figure S46: ^{1}H DOSY NMR (DMF-d_7, 500 MHz, 298 K) spectrum of Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$)-NP

General procedure for CN binding

(Note: Sodium cyanide and hydrogen cyanide are highly toxic compounds. Sodium cyanide and hydrogen cyanide may be fatal if inhaled, swallowed, or absorbed through skin. Ensure that adequate safety precautions been taken prior to working with these compounds)

In a quartz cuvette stock polymer in dry degassed DMF solution (0.1 mg/mL) was diluted to ~3 µM in dry degassed DMF. Initial spectrum (700 to 320 nm) was obtained, then stock sodium cyanide in dry DMF solution (4.4 mg/mL) was spiked into the cuvette and kinetics was immediately monitored at 428.5 and 439 nm. Shimadzu kinetics module was set to collect spectra every 15 minutes for 24 hours. After 24 hours a full spectrum (700 to 320 nm) scan was performed, and the solution was transferred to a scintillation vial and stored at room temperature. Kinetic experiments were run in triplicate for each PCSP and PCPN species.

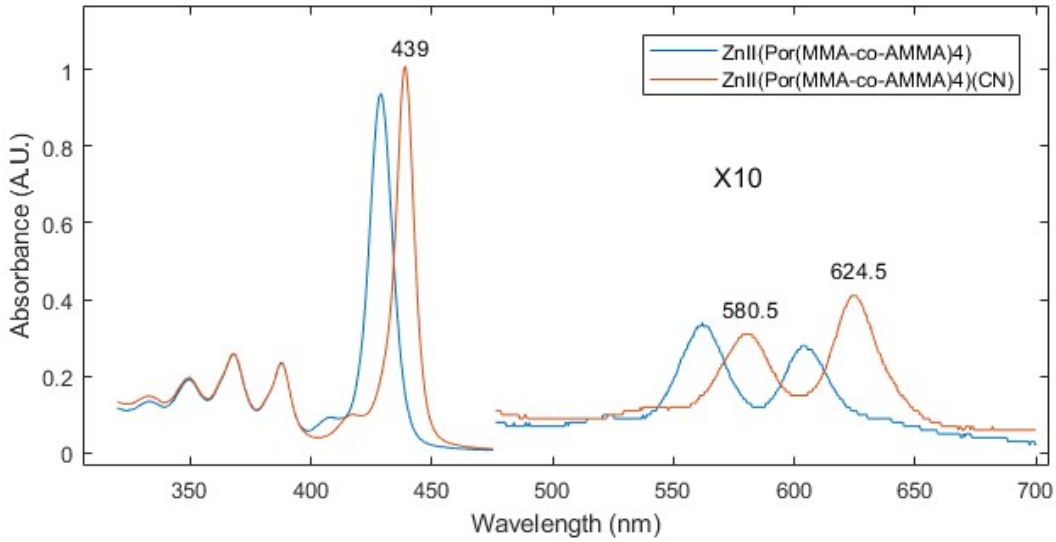


Figure S47: : Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) (blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)(CN) (red) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

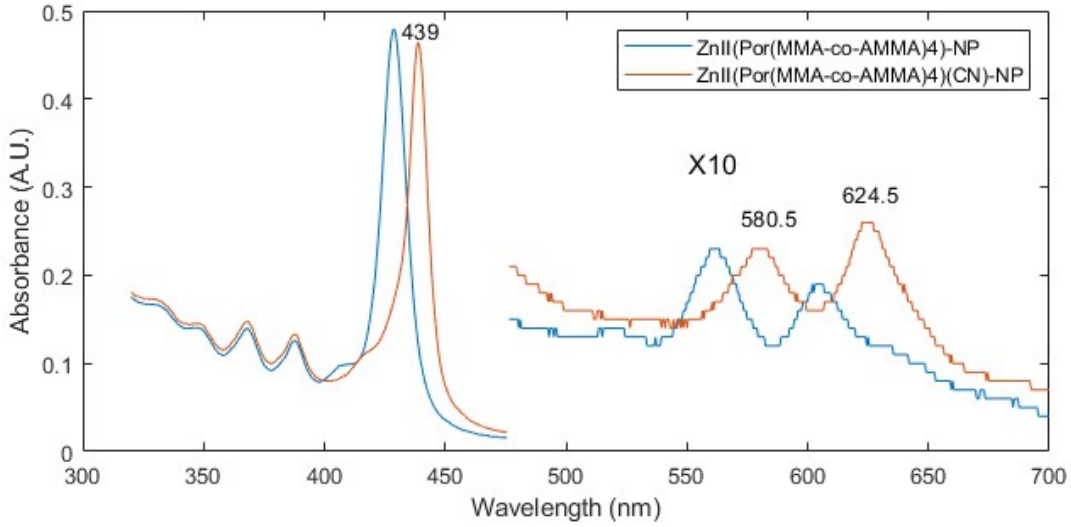


Figure S48: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP (blue) and Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)(CN)-NP (red) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

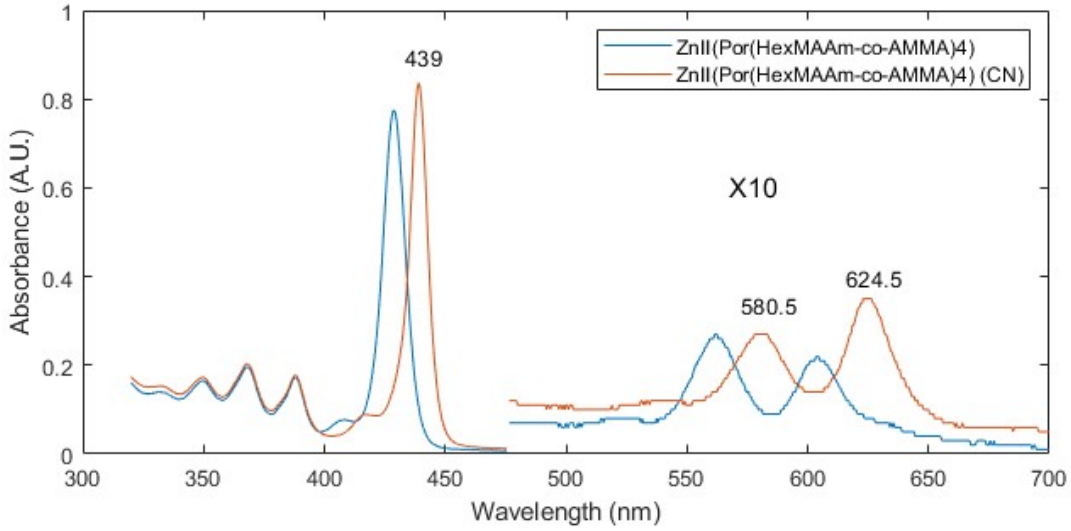


Figure S49: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$) (blue) and Zn^{II}(Por(HexMAAm -co-AMMA)$_4$)(CN) (red) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

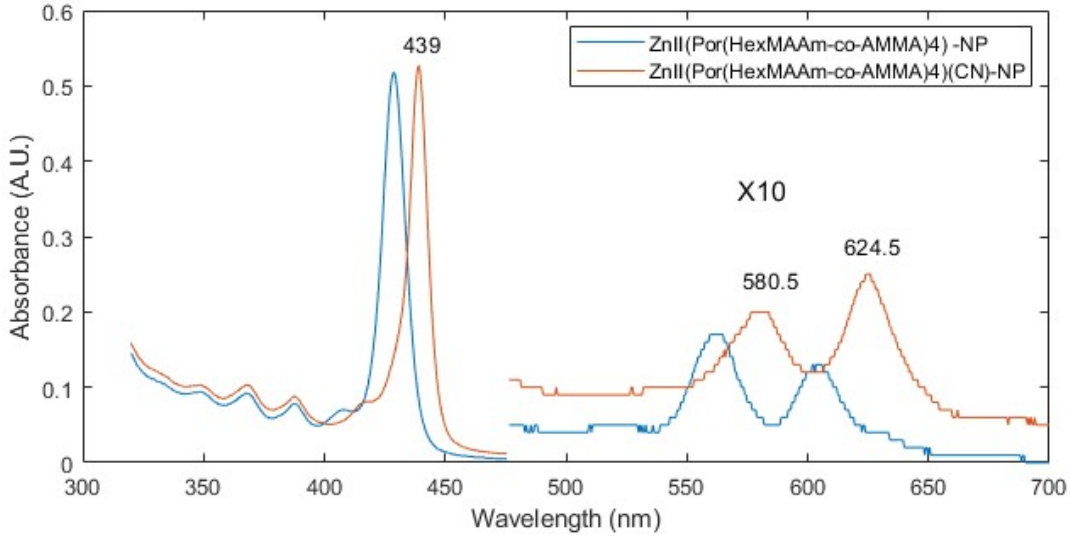


Figure S50: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(HexMAAm-co-AMMA)]$_4$)-NP (blue) and Zn^{II}(Por(HexMAAm -co-AMMA)$_4$)(CN)-NP (red) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

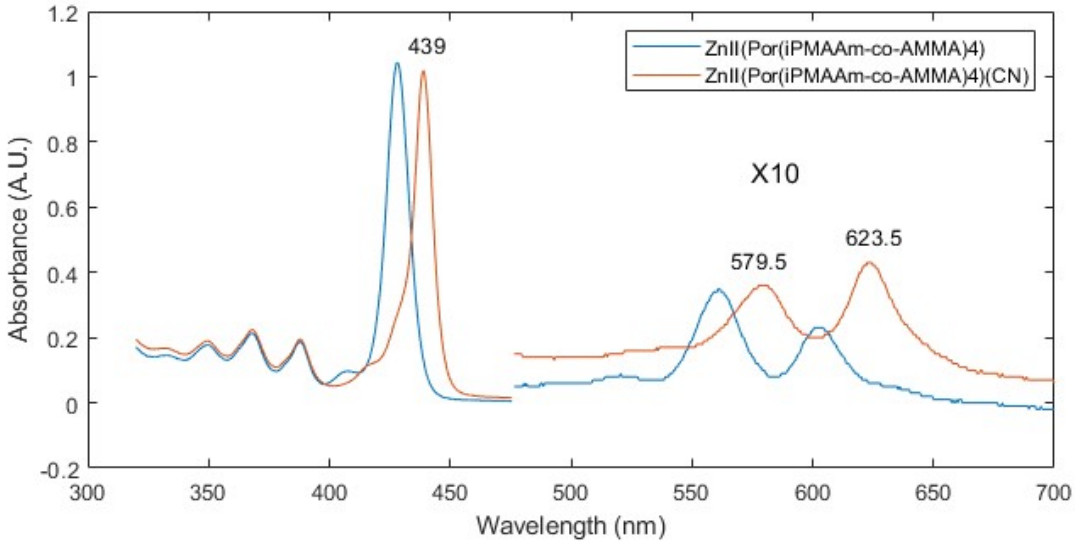


Figure S51: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$) (blue) and Zn^{II}(Por(iPMAAm -co-AMMA)$_4$)(CN) (red) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

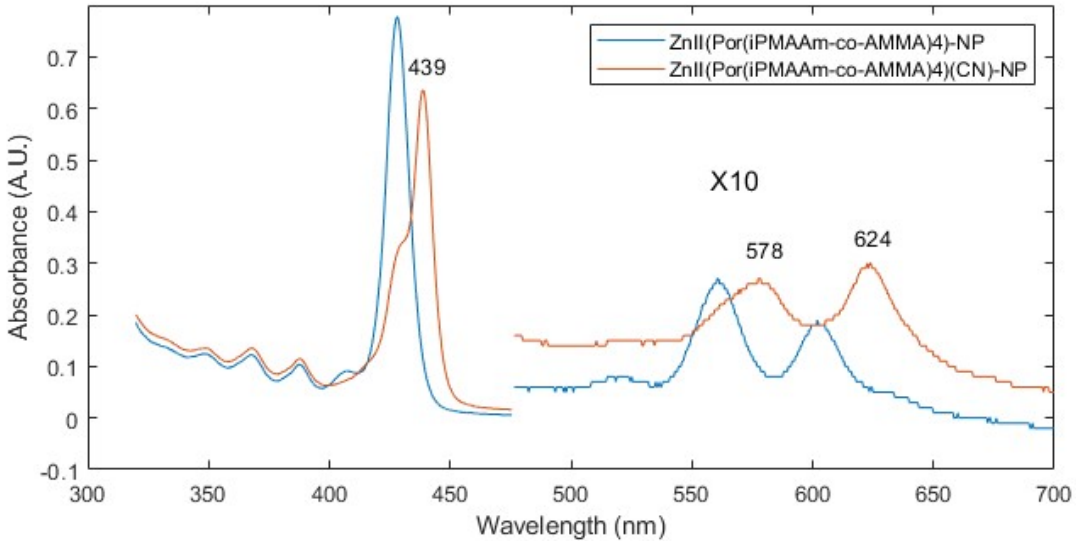


Figure S52: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(iPMAAm-co-AMMA)]$_4$)-NP (blue) and Zn^{II}(Por(iPMAAm -co-AMMA)$_4$)(CN)-NP (red) at 2.9 µM in DMF. Absorbance from 475 to 700 nm magnified X 10

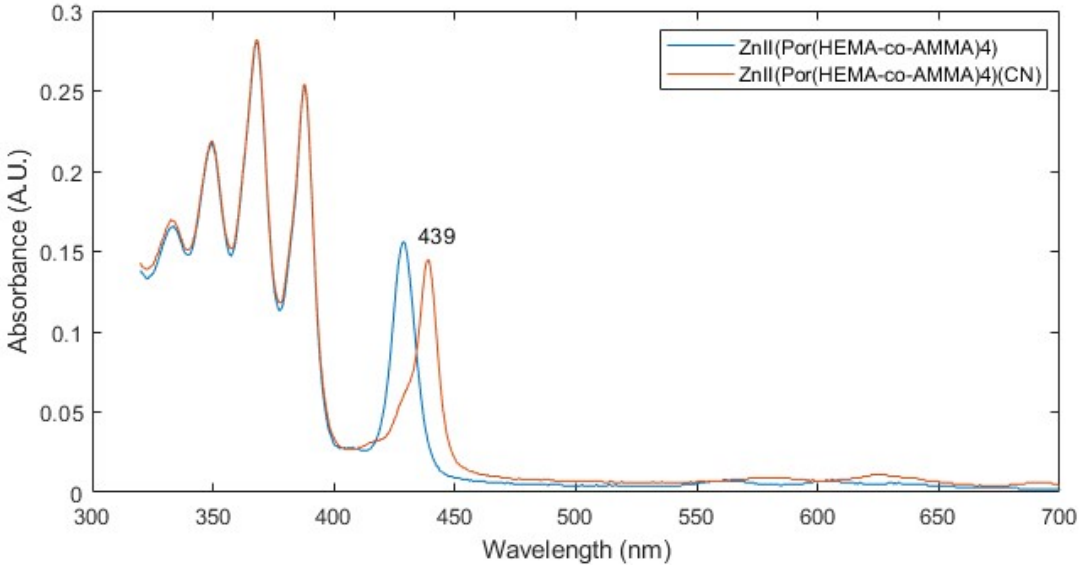


Figure S53: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$) (blue) and Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$)(CN) (red) at 2.9 µM in DMF.

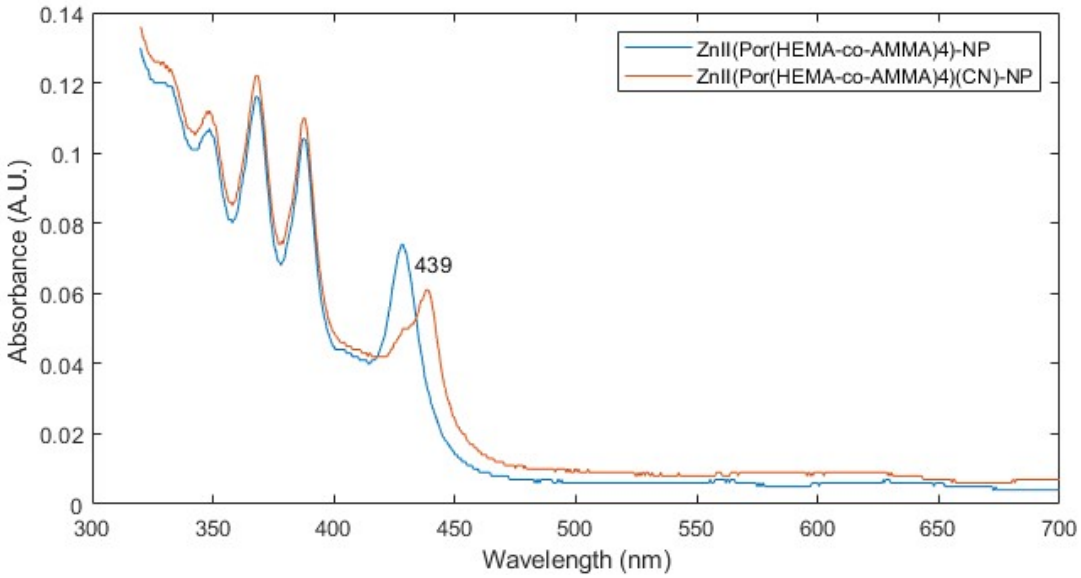


Figure S54: Comparison of UV-Vis Spectrums for Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$)-NP (blue) and Zn^{II}(Por[poly(HEMA-co-AMMA)]$_4$)(CN)-NP (red) at 2.9 µM in DMF.

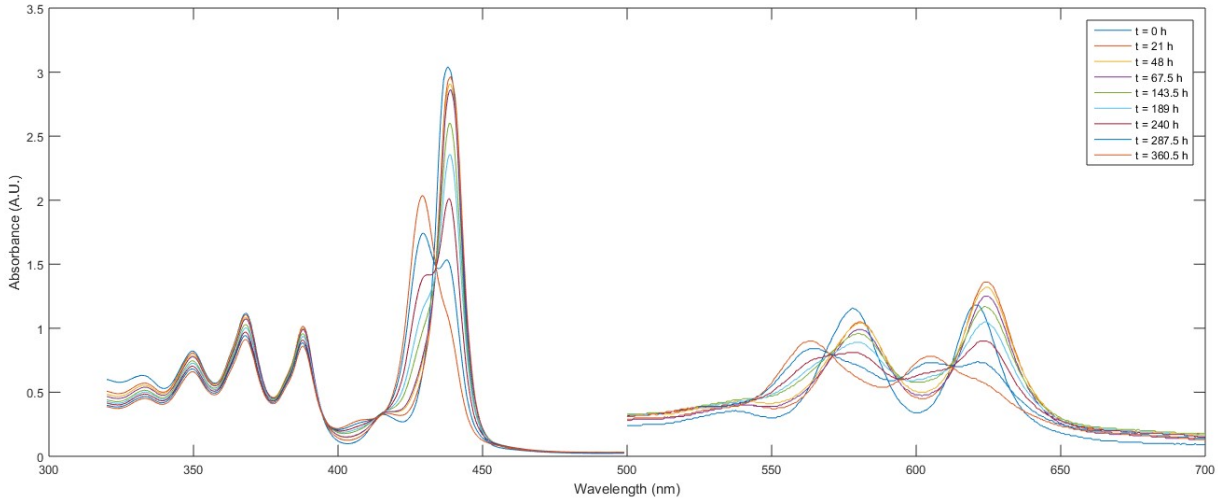


Figure S55: UV-Vis spectrums of the evolution of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$) at 0.1 mg/ml and 0.5 mM in DMF over time. Absorbance from 500 to 700 nm magnified X 10

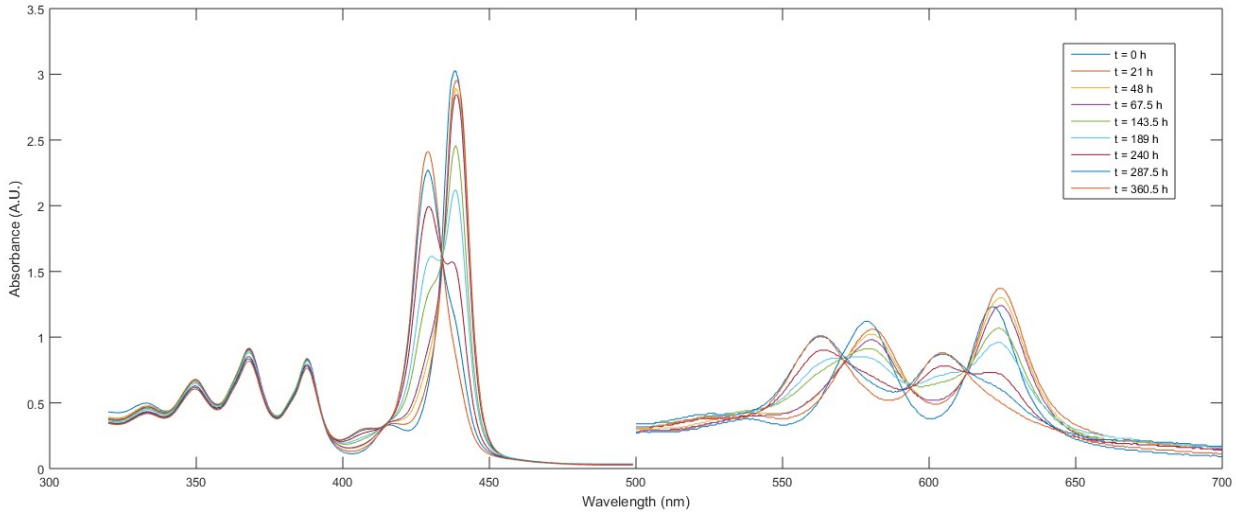


Figure S56: UV-Vis spectrums of the evolution of Zn^{II}(Por[poly(MMA-co-AMMA)]$_4$)-NP at 0.1 mg/ml and 0.5 mM in DMF over time. Absorbance from 500 to 700 nm magnified X 10

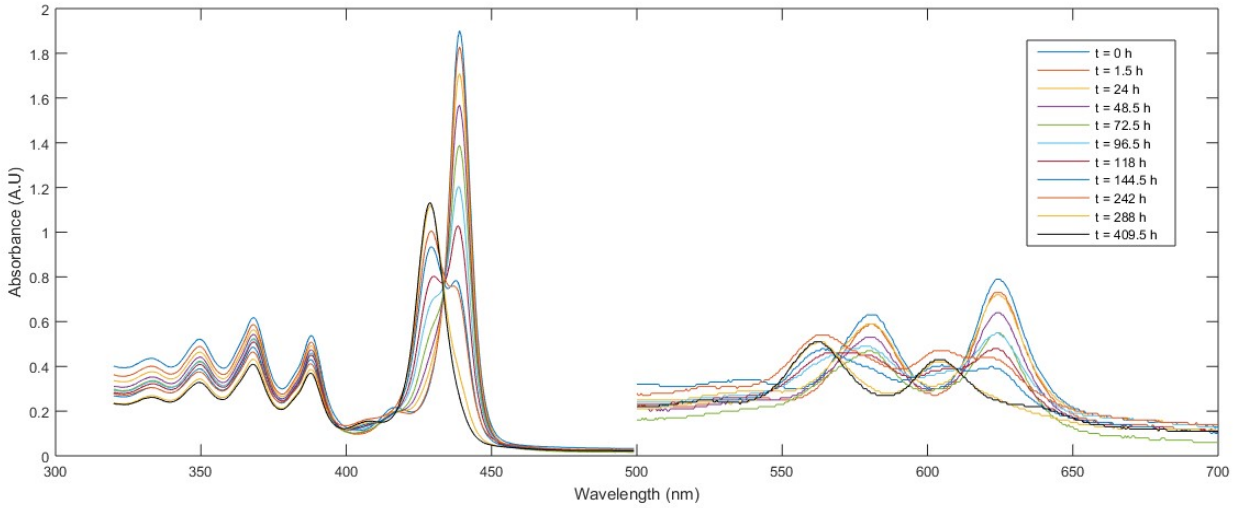


Figure S57: UV-Vis spectrums of the evolution of Zn^{II}(Por(HexMAAm -co-AMMA)$_4$) over time. Absorbance from 500 to 700 nm magnified X 10

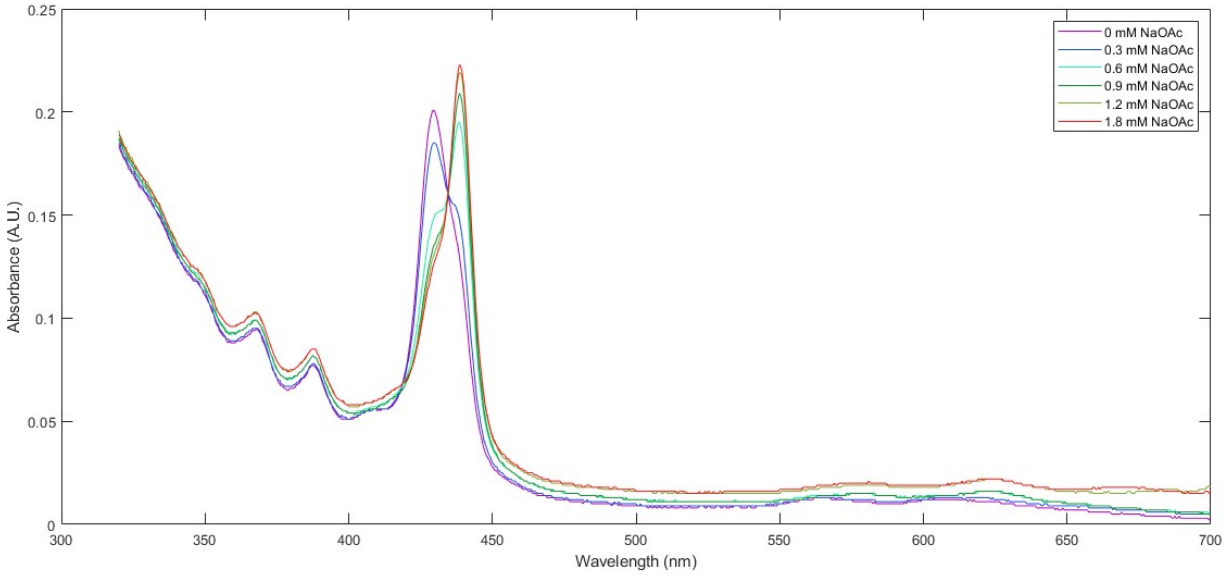


Figure S58: UV-Vis spectrums of Zn^{II}(Por(HexMAAm -co-AMMA)$_4$) at 2.9 µM and 0.5 mM in DMF titrated with sodium acetate two weeks after cyanide addition.

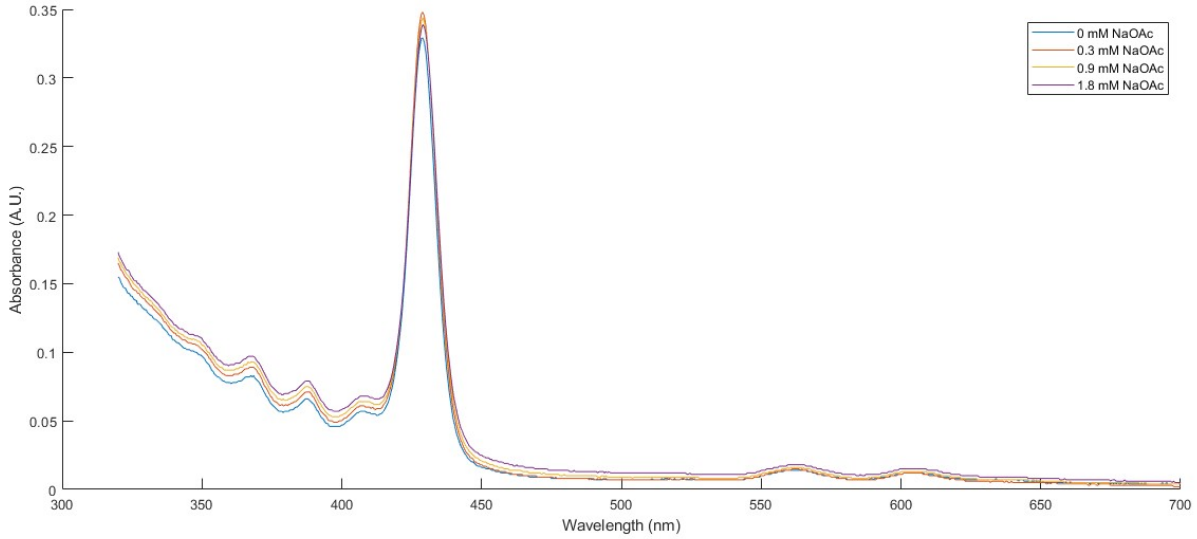


Figure S59: UV-Vis spectrums of fresh Zn^{II}(Por(HexMAAm -co-AMMA)$_4$) at 2.9 µM in DMF solution titrated with sodium acetate.

General procedure for isolating Zn-CN adduct precipitate

(Note: Sodium cyanide and hydrogen cyanide are highly toxic compounds. Sodium cyanide and hydrogen cyanide may be fatal if inhaled, swallowed, or absorbed through skin. Ensure that adequate safety precautions have been taken prior to working with these compounds)

Sodium cyanide (74.0 mg, 1.51 mmol) and DMF (2 mL) were added to a 20 mL scintillation vial equipped with a magnetic stir bar. The sodium cyanide was crushed with a spatula then stock Zn^{II}(Por(HexMAAm -co-AMMA)$_4$)-NP solution in DMF solution (0.1 mg/mL, 2.000 mL) was added and the solution was stirred for 48 hours. The solution was vacuum filtered, and the white precipitate was rinsed with dry DCM (10 mL). The precipitate was dried to yield sodium carbonate as a white powder (0.0641 g, 0.6048 mmol, 80.1 % Yield). The reactions for each polymer and the control were run in triplicate. ^{13}C NMR (101 MHz, d2o) δ 168.08. ATR-IR v = 1422, 1413, 878, 702, 695 cm^{-1}.

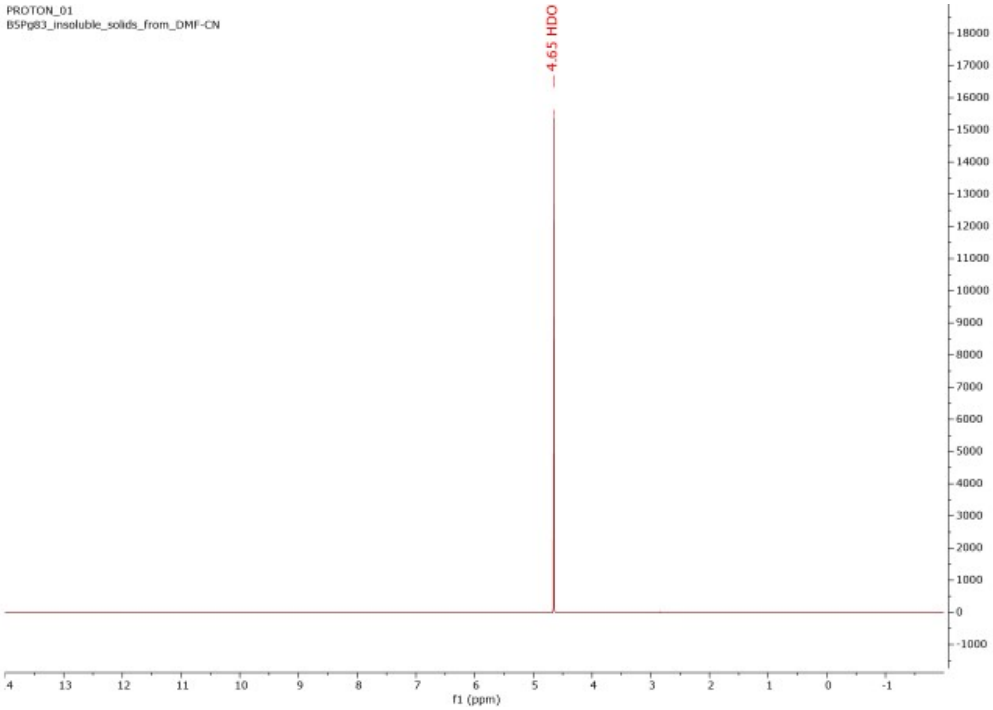


Figure S60: ^{1}H NMR (D_2O, 400 MHz) spectrum of white precipitates from reaction of Zn^{II}(Por(HexMAAm -co-AMMA)$_4$), NaCN, and DMF under ambient conditions.

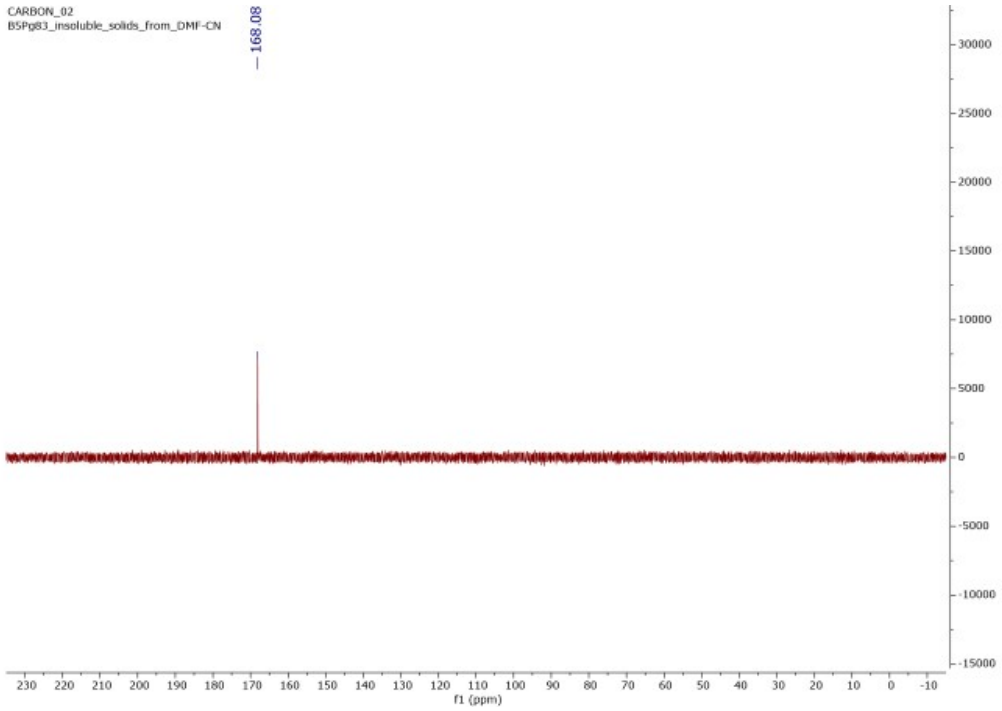


Figure S61: ^{13}C NMR (D2O, 101 MHz) spectrum of white precipitates from reaction of Zn^{II}(Por(HexMAAm -co-AMMA)$_4$), NaCN, and DMF under ambient conditions.

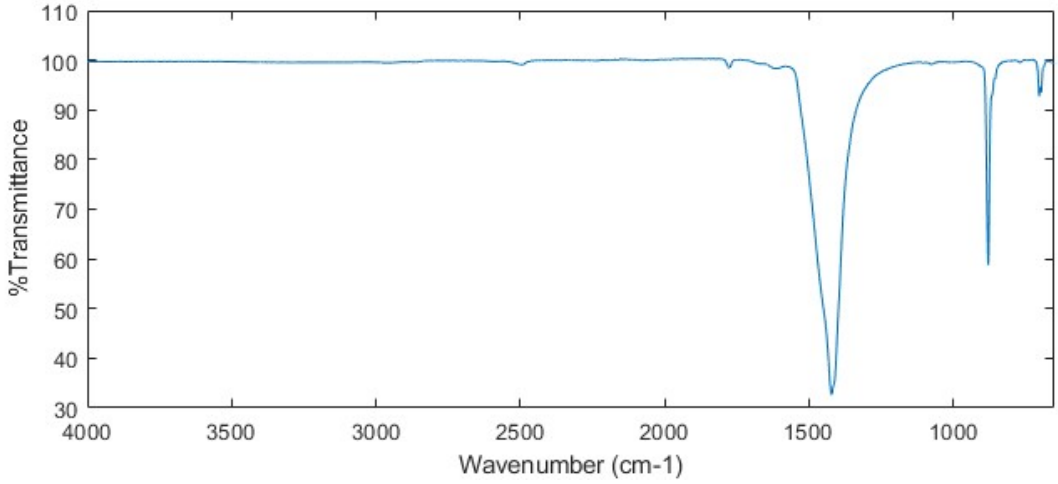


Figure S62: ATR-IR spectrum of white precipitates from reaction of Zn^{II}(Por(HexMAAm -co-AMMA)$_4$), NaCN, and DMF under ambient conditions.

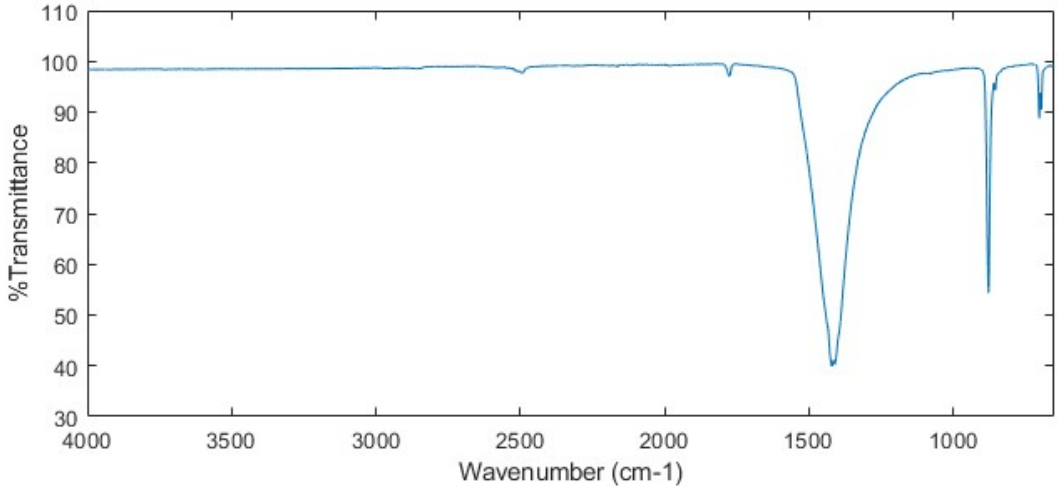


Figure S63: ATR-IR spectrum of Sodium Carbonate, 98% purity from Alfa Aesar

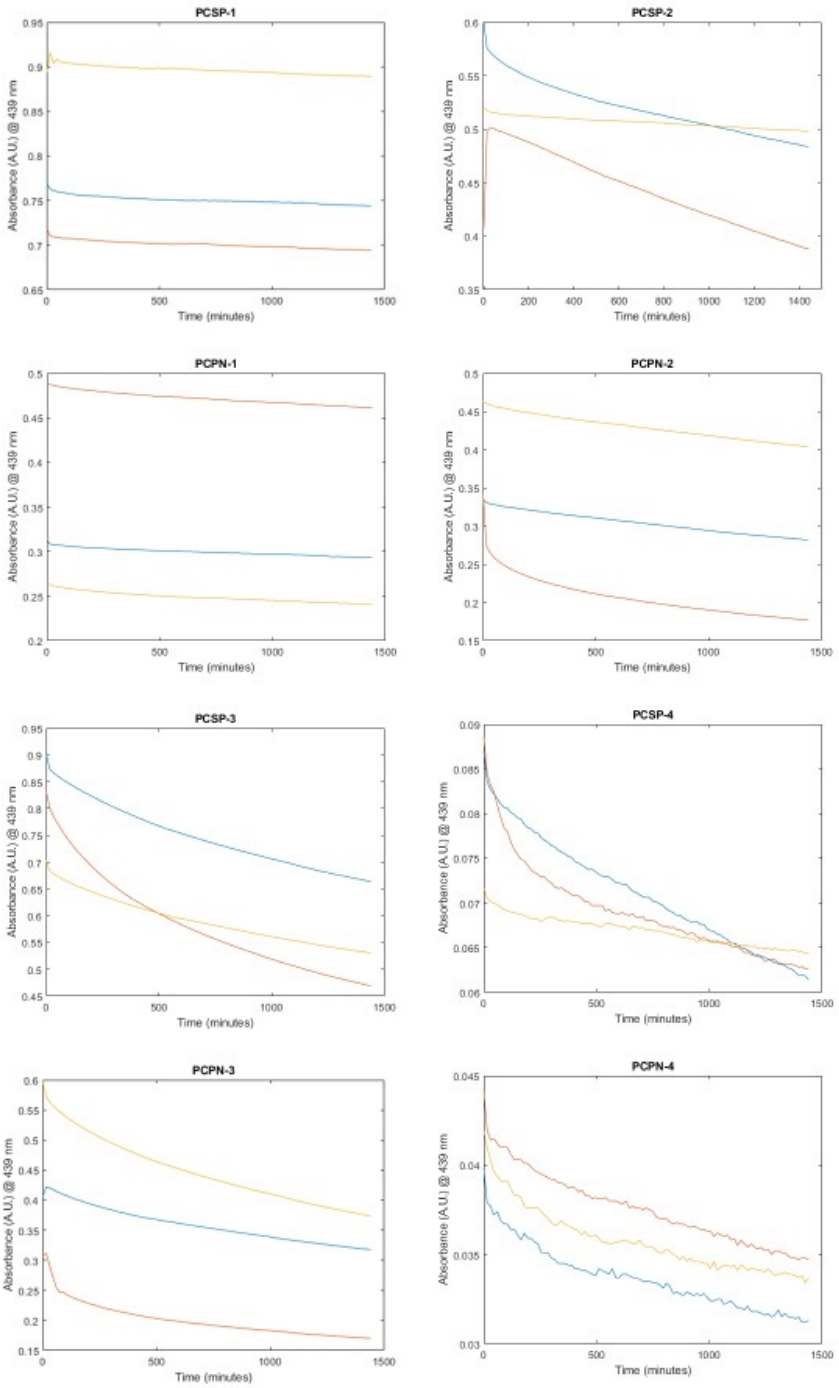


Figure S64: UV-Vis kinetic data over 24 hours after cyanide addition to PCSP-1, PCNP-1, PCSP-2, PCPN-2, PCSP-3, PCPN-3, PCSP-4, and PCPN-4. Data was collected at 25 °C.

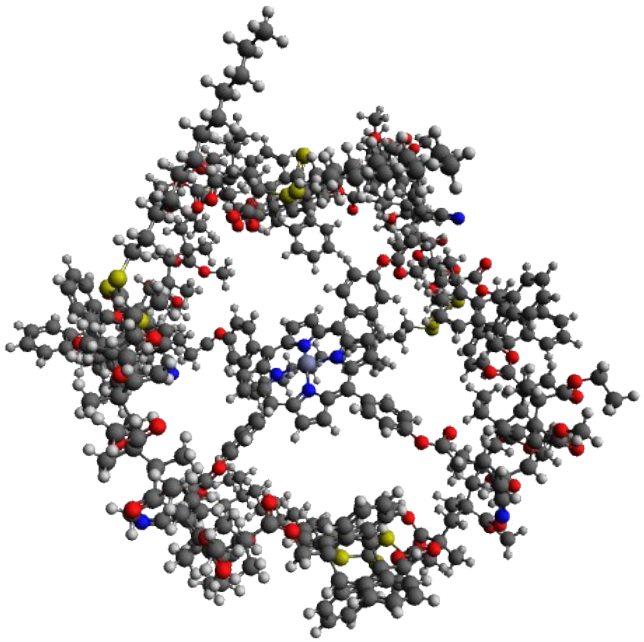


Figure S65: Expanded table of content structure. The Zn^{II}(por[poly(MMA-co-AMMA)]$_4$) nanoparticle structure used in the table of contents graphic was formed by manually making bonds between anthracene units of adjacent polymer arms. Geometries Optimized via universal force fields (UFF) in Avogadro.

References

(1) N,N-Dimethylformamide | HCON(CH3)2 - PubChem https://pubchem.ncbi.nlm.nih.gov/compound/dimethylformamide (accessed Feb 18, 2020).

(2) Rodriguez, K. J.; Hanlon, A. M.; Lyon, C. K.; Cole, J. P.; Tuten, B. T.; Tooley, C. A.; Berda, E. B.; Pazicni, S. Porphyrin-Cored Polymer Nanoparticles: Macromolecular Models for Heme Iron Coordination. *Inorg. Chem.* **2016**, *55* (19), 9493–9496.

(3) Frank, P. G.; Tuten, B. T.; Prasher, A.; Chao, D.; Berda, E. B. Intra-Chain Photodimerization of Pendant Anthracene Units as an Efficient Route to Single-Chain Nanoparticle Fabrication. *Macromol. Rapid Commun.* **2014**, *35* (2), 249–253.

(4) Rodriguez, K. J. Modeling Secondary Coordination Sphere Interactions in Heme Proteins: From Small Molecule Ligands to Macromolecular Porphyrin-Cored Polymer Nanoparticles, University of New Hampshire, 2017.