Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Synthesis of Terpyridine-Containing Polycarbonates with Post Polymerization Providing Water-Soluble and Micellar Polymers and Their Metal Complexes

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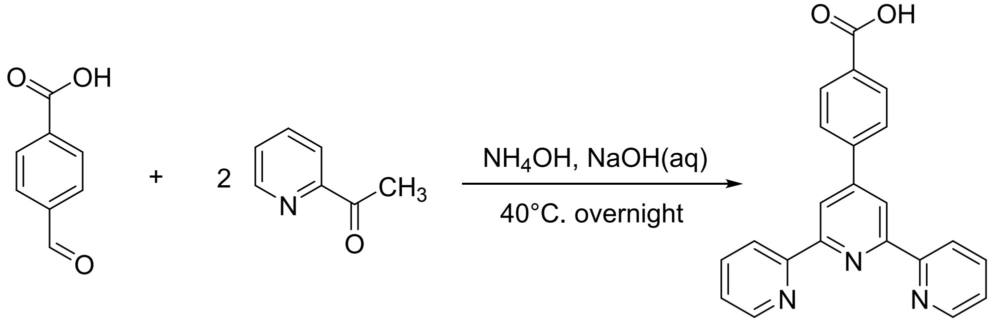
Supplementary Methods

Materials and Methods: All reactions were performed under a nitrogen or argon atmosphere using standard Schlenk line and glovebox techniques. Glassware and stainless-steel reactors were dried at 150 °C for 24 hours prior to use. Solvents were purchased from commercial sources and dried using MBraun manual solvent purification system packed with Alcoa F200 activated alumina desiccant. Allyl glycidyl ether (97%) and propylene oxide (98%) were purchased from Alfa Aesar and distilled over CaH_2 under reduced pressure prior to use. 4-Formylbenzoic acid was purchased from Chem-Impex Int'l. Inc., Sodium hydroxide, AIBN, Thioglycolic acid, and 2-Acetylpyridine from Sigma Aldrich, allyl glycidyl ether from Alfa Aesar, bone-dry CO_2 was supplied from a high-pressure cylinder and equipped with a liquid dip tube purchased from Scott Specialty Gases. The catalyst used for this study was synthesized according to a previously reported procedure.[S1]

NMR spectra were recorded on a 400 MHz Bruker spectrometer with TMS as an internal standard at 0 ppm. Infrared spectra were taken using a Bruker Tensor 27 FT-IR spectrometer and KBr sample cell with 0.02 mm path length. A Malvern modular GPC apparatus with ViscoGEL I-series columns (H&L) and THF eluent was used. M_w and M_n were calculated using data from RI, Right Angle Light Scattering (RALS) and Low Angle Light Scattering (LALS) detectors calibrated against polystyrene standards. The catalyst was synthesized according to a previous procedure.

Synthesis of ([2,2':6',2"-Terpyridin]-4'-yl)benzoic Acid. : The terpy-COOH (HL) was synthesized by a slight modification of previously reported literature procedure.[S2] According to this procedure to a stirred solution of 4-formylbenzoic acid (5.57 g, 37.1 mmol) in 120 mL of ethanol was added 2-acetylpyridine (8.55 g, 70.6 mmol) and 6 mL of concentrated NH_4OH followed by the addition of NaOH (2.5 g dissolved in ~6 mL of H_2O). The reaction mixture obtained was stirred at 40 °C overnight which on cooling result in the formation of a slightly yellow precipitate. The precipitate was filtered and washed thoroughly by cold ethanol and dried to give clean 4-([2,2′:6′,2″-terpyridin]-4′-yl)benzoic acid (7.0 g, 53.8%) . The compound was used without further purification. ^1H NMR (400 MHz, DMSO-d6): δ (ppm) 8.78 (d, 2H), 8.73 (s, 2H), δ 8.66 (d, 2H), δ 8.06 (d, 2H), δ 8.03 (dt, 2H), δ 7.83 (d, 2H), δ 7.53 (dd, 2H).



Scheme S1. Synthesis of **CTA** 4′-(4-carboxyphenyl)-2,2′:6⍰,2⍰⍰-terpyridine (HL) .

Polymer Synthesis**:** Under an argon atmosphere, the catalyst, co-catalyst, monomer, chain transfer agent (HL) and 0.8 mL solvent (DCM:Toluene, 1:1 v/v) were added to a 10 mL stainless steel reactor vessel. All reactions were performed on the scale of 4 mg catalyst, using ratios of 1/1/1000/X for catalyst/co-catalyst/monomer/CTA respectively. CO_2 was added to the vessel pressurizing to 25 bar . After stirring at room temperature for 24 h, the vessel was depressurized, a crude product was taken, and polymer was recrystallized. Initial recrystallization was performed by adding crude product dropwise to acidic methanolic solution (4 drops of conc. HCl/50 mL MeOH), followed by two recrystallizations in neutral methanol. The polymer formed was dried for 24 h under vacuum.

Post polymerization metalation with $ZnCl_2$: To a stirred solution of polycarbonate polymer (600 mg with 0.03 mmol of terpy ligand) in 15 mL of DCM, 10 eq of Zinc Chloride (40 mg, 0.3 mmol) in 1 mL of methanol was added. The resulted reaction mixture was refluxed overnight. The polymer color changed from light yellow to bright yellow during the reaction over time. The metallated polymer was obtained on evaporation of the solvent which was extensively washed with methanol in order to remove the unreacted Zinc Chloride. ^{1}H NMR (DMSO-d6) CTA: δ (ppm) 8.98 (d, 2H), 9.18 (s, 2H), δ 8.89 (d, 2H), δ 8.4 (d, 2H), δ 8.2 (dt, 2H), δ 7.91 (d, 2H), δ 7.58 (dd, 2H).

Post polymerization metalation with $K_2(PtCl_4)$: K_2PtCl_4 (12.5 mg, 0.3 mmol) was dissolved in 1 mL of deionized water and added dropwise to a stirred solution of polycarbonate (500 mg with 0.03 mmol of terpy ligand) in 15 mL of THF and the mixture was refluxed for 24 hrs. A color change from light yellow to red occurs with time during the reaction, indicating the completion of the metalation. DCM was evaporated and the metallated polymer was washed thoroughly with water to remove excess metal precursor and sample was air dried. ^{1}H NMR (DMSO-d6) CTA: δ (ppm) 9.04 (d, 2H), 9.1 (s, 2H), δ 8.9 (d, 2H), δ 8.6 (d, 2H), δ 8.37 (dt, 2H), δ 8.2 (d, 2H), δ 8.02 (dd, 2H).

Thiol-ene click reaction of post-metallated polycarbonate with functional thiols

A solution of the post-metallated polycarbonates (0.78 g, Mn = 17137 g/mol, 4.93 mmol alkenes), Thioglycolic acid (40 eq, 197.2 mmol) in 20 mL of THF was transferred in a schlenk flask and degassed for 15 min then refilled with N_2. AIBN (1.63 mmol, 0.27 g) was added to the mixture under a positive pressure of N_2 followed by refluxing for 24 hrs at 70 °C. The reaction mixture was precipitated from THF into hexanes and the resulted polymer was recrystallized 3 times in hexanes to remove the excess thiol and other by-products.

Deprotonation of thioglycolic acid functionalized polycarbonate

1.0 equiv (based on the molar concentration of the COOH group) of aqueous ammonium hydroxide (28 wt%) was added dropwise to a THF solution of the thiol-functionalized polymer. During stirring, a precipitate was formed which was washed and dried to give the desire product

Synthesis of Triblock Polycarbonates: (salen)cobalt(III)X/PPNX (X = trifluoroacetate) (0.006 mmol), Propylene oxide (0.34 mL, 4.8 mmol) and 0.8 mL solvent (DCM : Toluene 1:1 v/v) with 5 equiv. of HL (10.53 mg, 0.03 mmol) were added to a 10 mL stainless steel reactor in the glovebox, pressurized with CO_2 to 25 bar. After stirring for 24 hrs, the CO_2 was slowly released then the reactor was taken again inside the glovebox where allyl glycidyl ether was added (0.35 mL, 3 mmol). The reactor was recharged with 25 bar of CO_2. The CO_2 was released after 24 hrs. The curde polymer was dissolved in few drops of DCM and recrystallized in methanol. The first recrystallization done by adding crude product dropwise to acidic methanolic solution (4 drops of conc. HCl/50 mL MeOH), followed by two recrystallizations in neutral methanol. then the pure polymer was dried for 24 hrs under vacuum.

Methodology for M_n by ^{1}HNMR

High resolution (>64 scans, 400 MHz) ^{1}HNMR spectra for polymers which were synthesized using chain transfer agents were collected. Number average molecular weight (M_n) was calculated by comparing peak integrations for polymer bound ligand and polymer repeat units according to Eq 1, this method was adapted from the end-group analysis technique.[2]

Ratio of Polymer Repeat unit to Chain Transfer Agent = $\left(i_{\frac{P}{M}}\right) = \frac{Polymer_{int}}{CTA_{int}} * \frac{CTA_{protons}}{Polymer_{protons}}$

$$Mn = MCTA_{mass} + \left(i_{\frac{P}{M}}\right) * Repeat\ Unit_{mass}$$

Equation 1

See the following example for calculation of Mn by ^{1}H NMR using the ^{1}H NMR spectrum in **Figure 3**

Ratio Repeat unit to Metallo-Chain Transfer Agent = $\left(i_{\frac{P}{M}}\right) = \frac{88\ (peak\ f)}{1\ (peak\ \ H2)} * \frac{2}{1}$ = 176

$$M_n = 350\frac{g}{mol} + (176) * 158.144\ Repeat\ Unit_{mass} = 28183\ g/mol$$

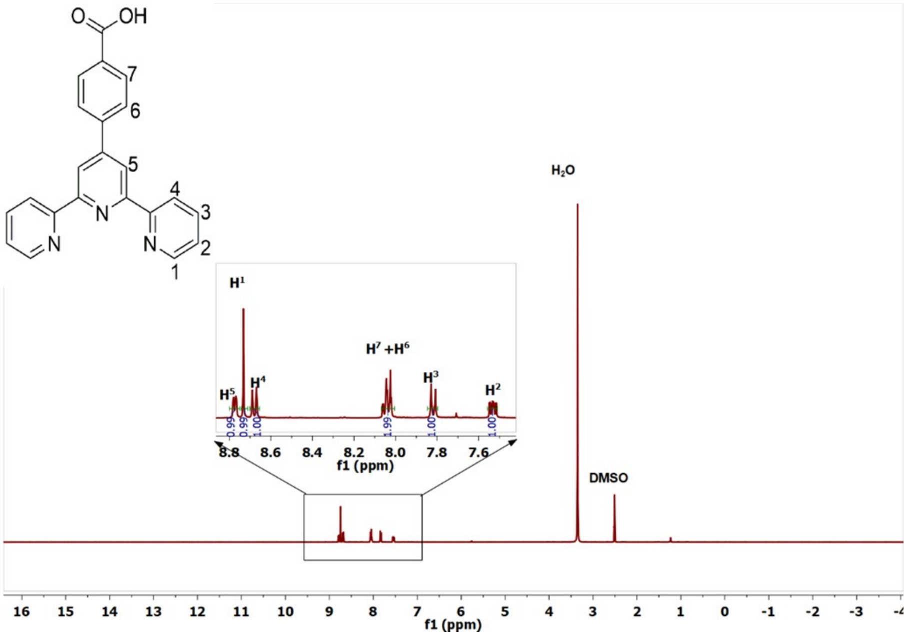


Figure S1. ^{1}H NMR spectrum of **CTA** 4′-(4-carboxyphenyl)-2,2′:6�,2��-terpyridine (HL) (DMSO-d6, 400 MHz)

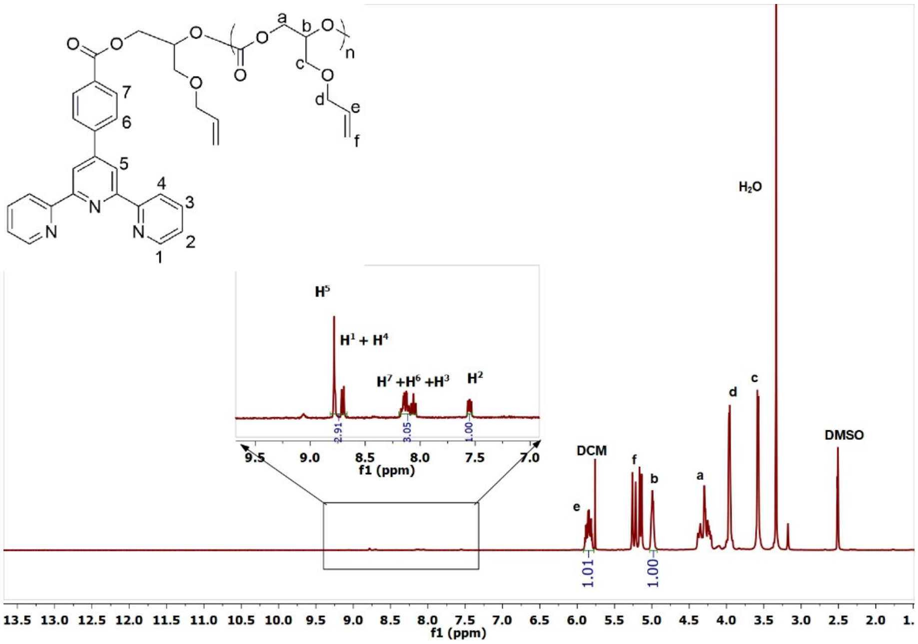


Figure S2. ^{1}H NMR of polycarbonate synthesized using six equivalents (compared to catalyst) of **HL** as a chain transfer agent (DMSO-d6, 400 MHz).

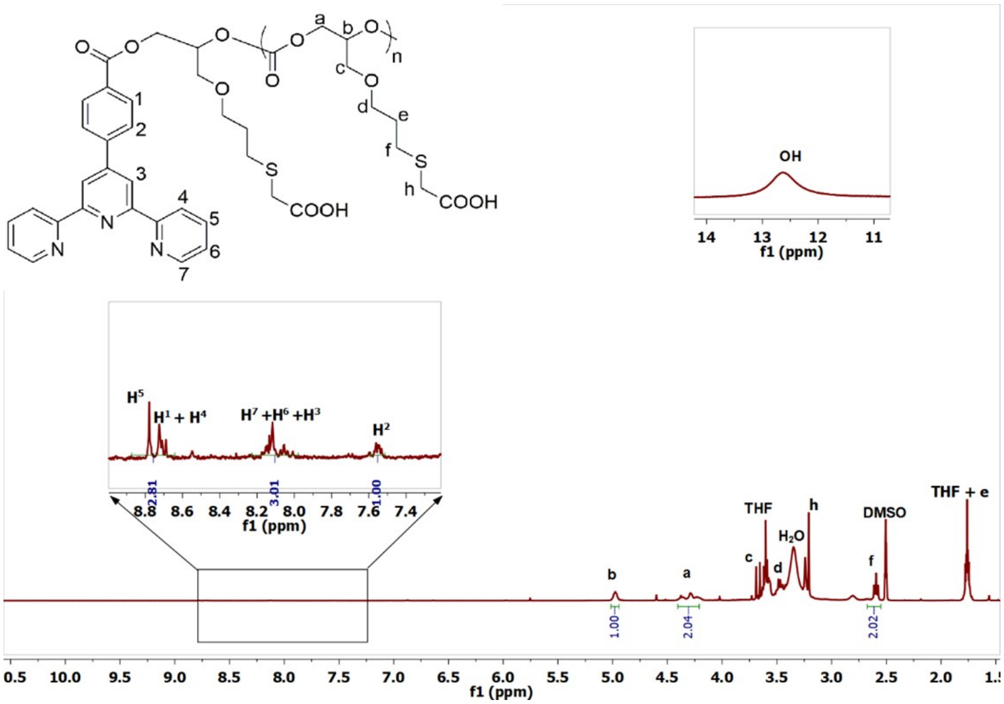


Figure S3. ^{1}H-NMR of functionalized polycarbonates (DMSO-d6 400 MHz).

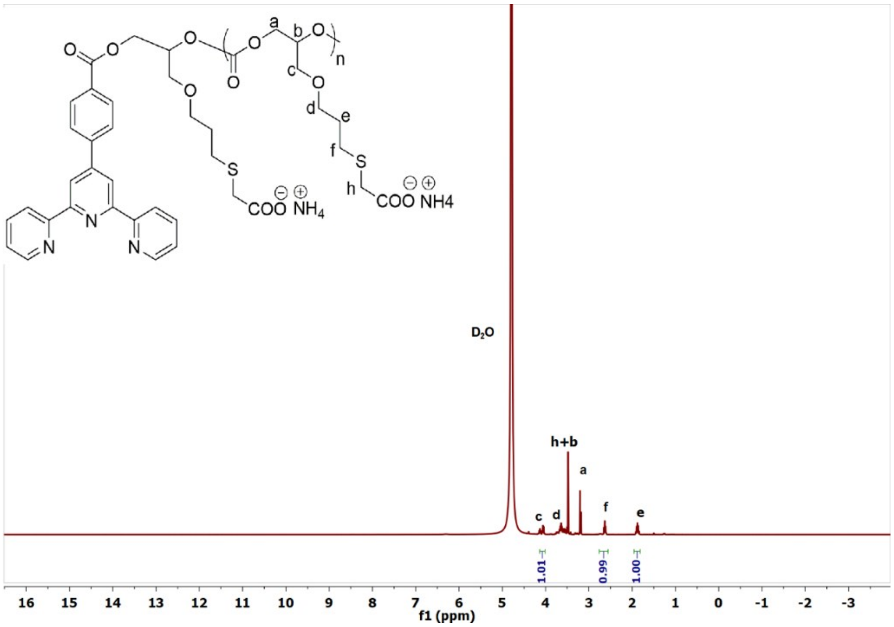


Figure S4. ^{1}H-NMR of functionalized deprotonated copolymer (D_2O - 400 MHz)

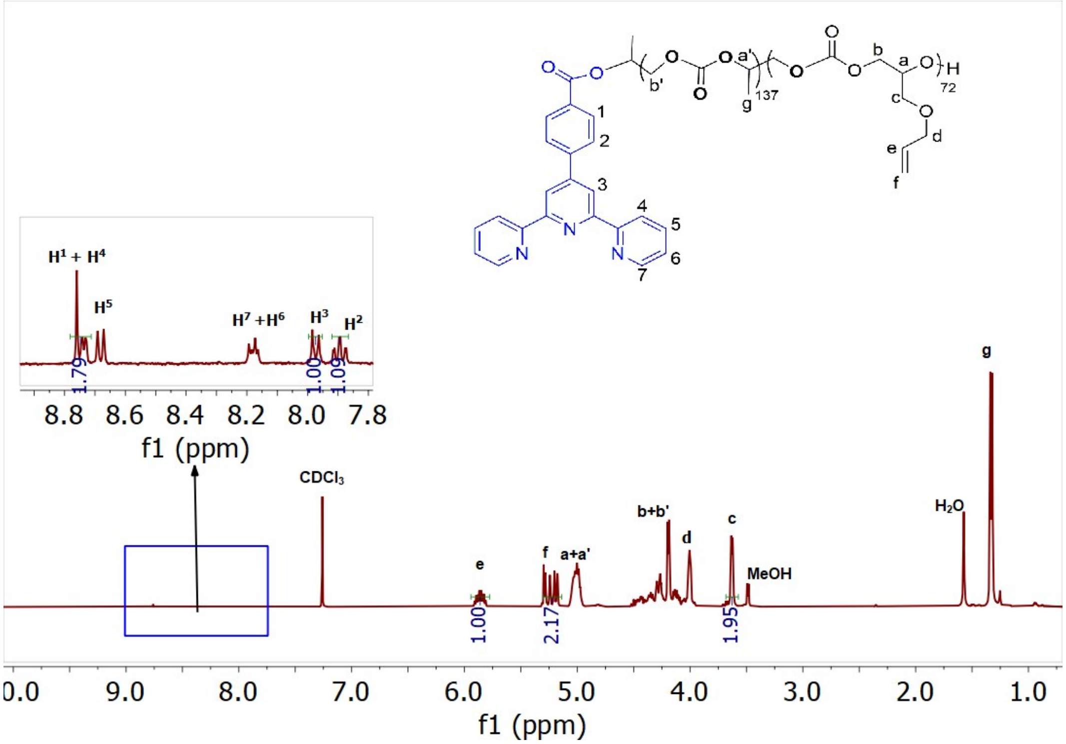


Figure S5. ^{1}H-NMR spectrum of triblock polymer ($CDCl_3$ - 400 MHz).

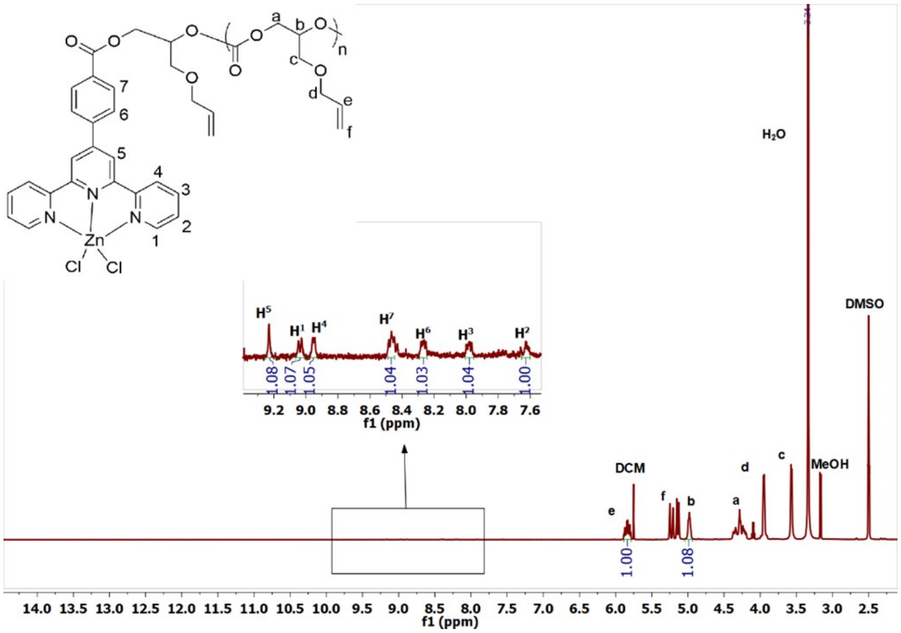


Figure S6. ^{1}H NMR of post-metallated co-polymer synthesized using 10 equivalents (compared to **CTA**) of $ZnCl_2$ (DMSO-d6, 400 MHz).

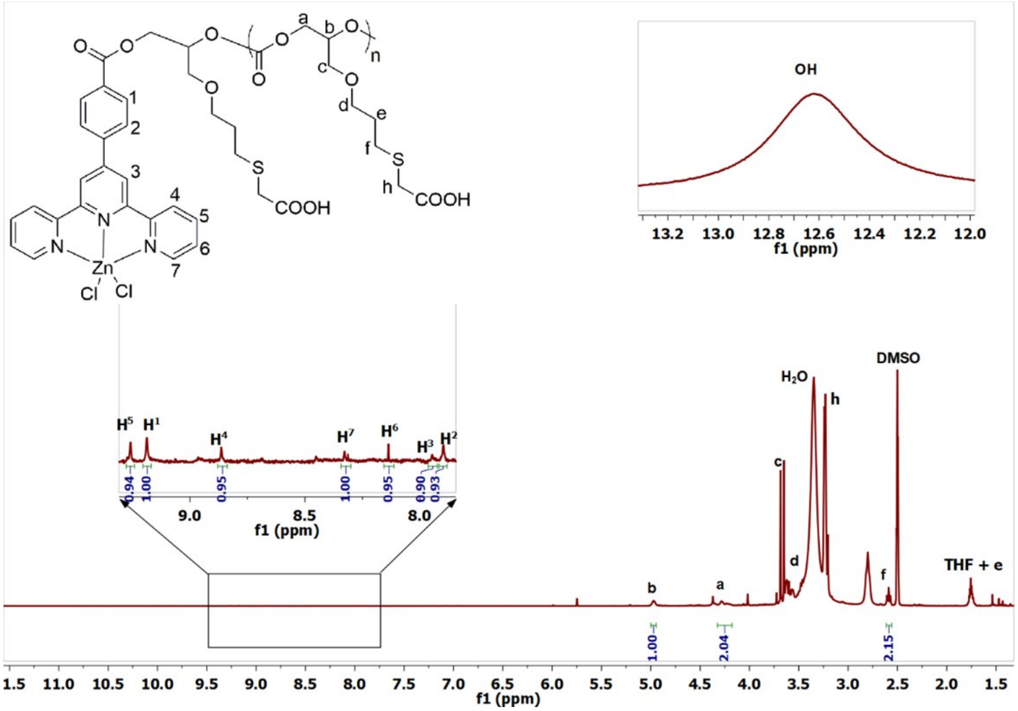


Figure S7. ^{1}H-NMR of functionalized polycarbonates after metalation with $ZnCl_2$ (DMSO-d6 400 MHz).

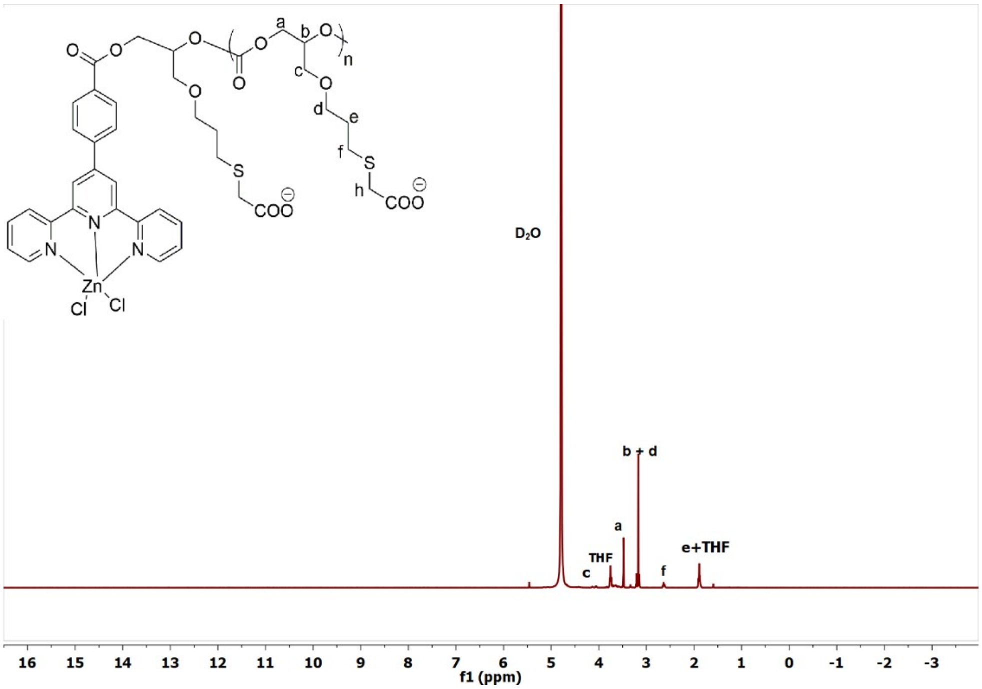


Figure S8. ^{1}H-NMR of deprotonated polycarbonates after metalation with $ZnCl_2$ (D_2O- 400 MHz).

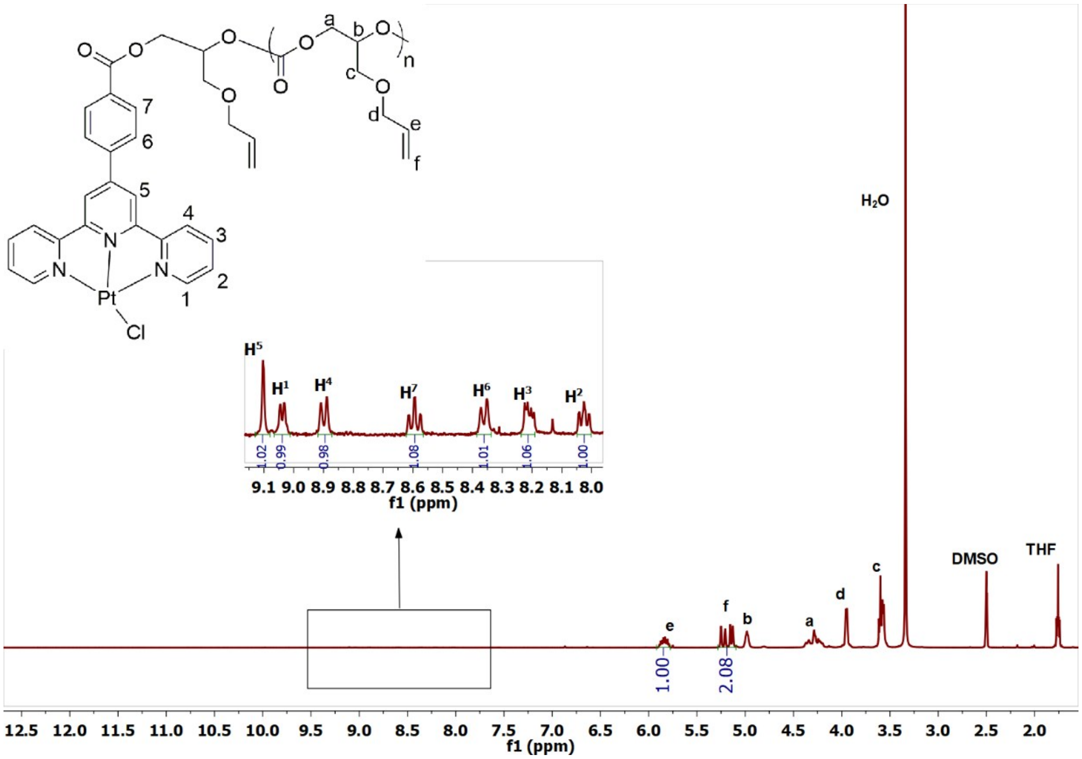


Figure S9. ^{1}H NMR of post-metallated polycarbonates synthesized using 10 equivalents (compared to **CTA**) of K_2PtCl_4 (DMSO-d6, 400 MHz).

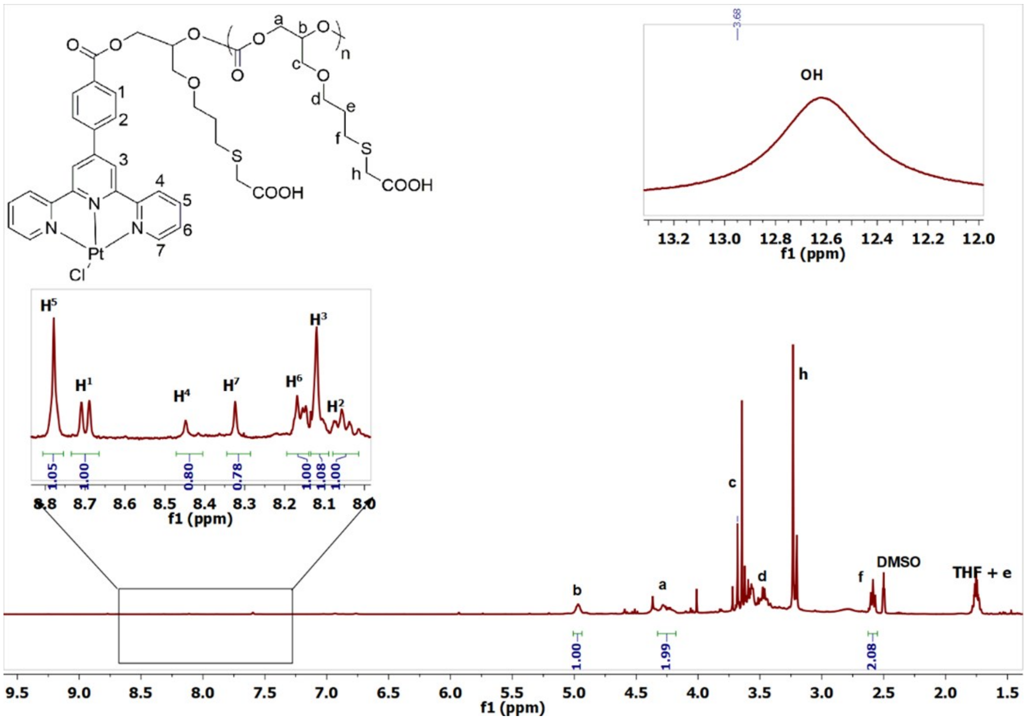


Figure S10. ^{1}H-NMR of functionalized polycarbonates after metalation with K_2PtCl_4 (DMSO-d6

400 MHz)

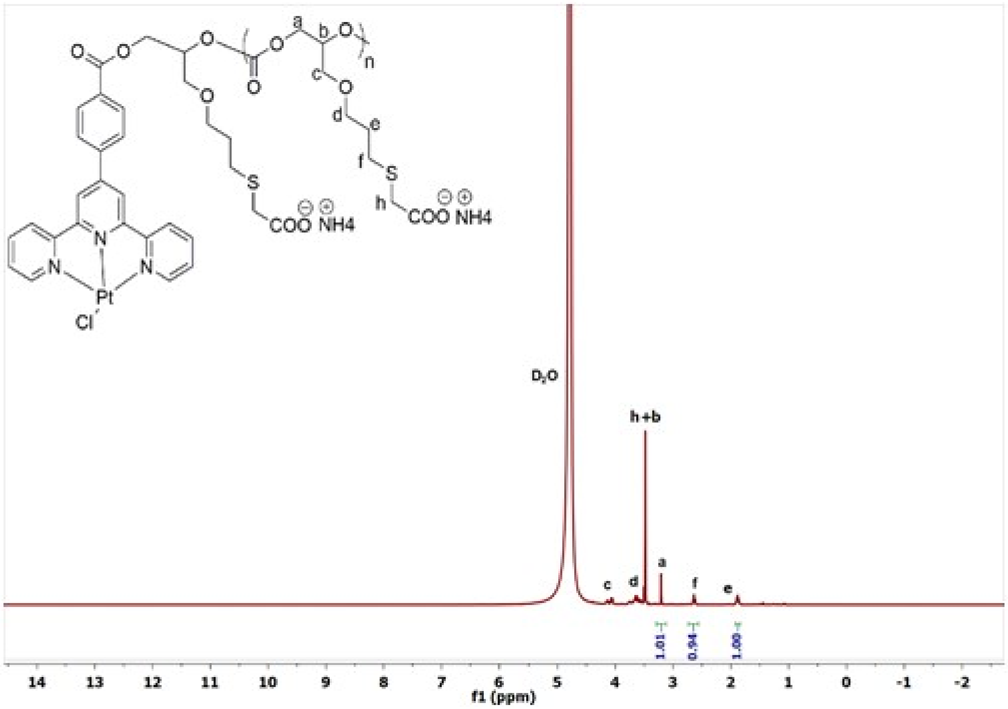


Figure S11. ^{1}H-NMR of deprotonated polycarbonates after metalation with K_2PtCl_4 (D_2O- 400 MHz)

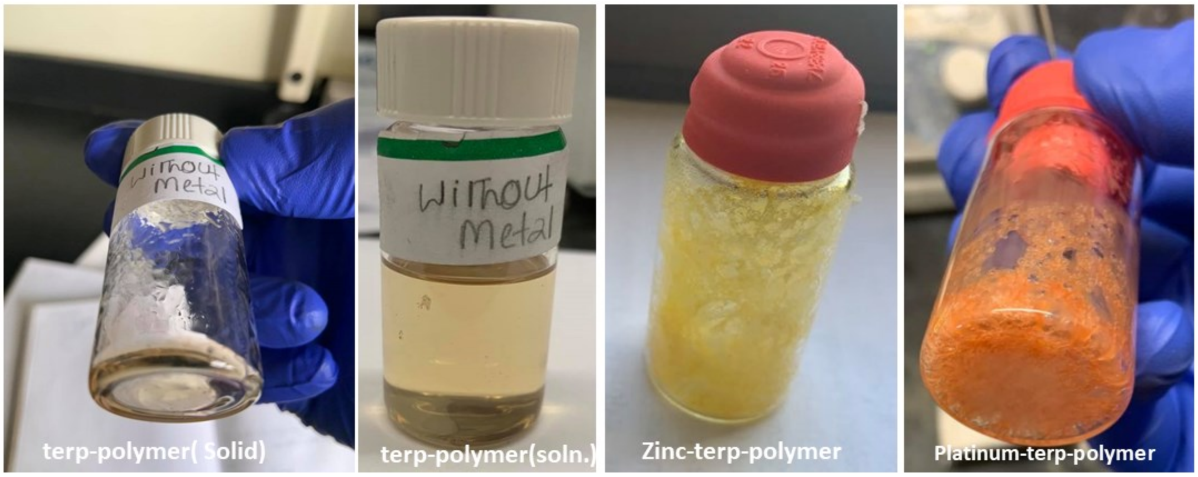


Figure S12. Color of polymers with and without metal.

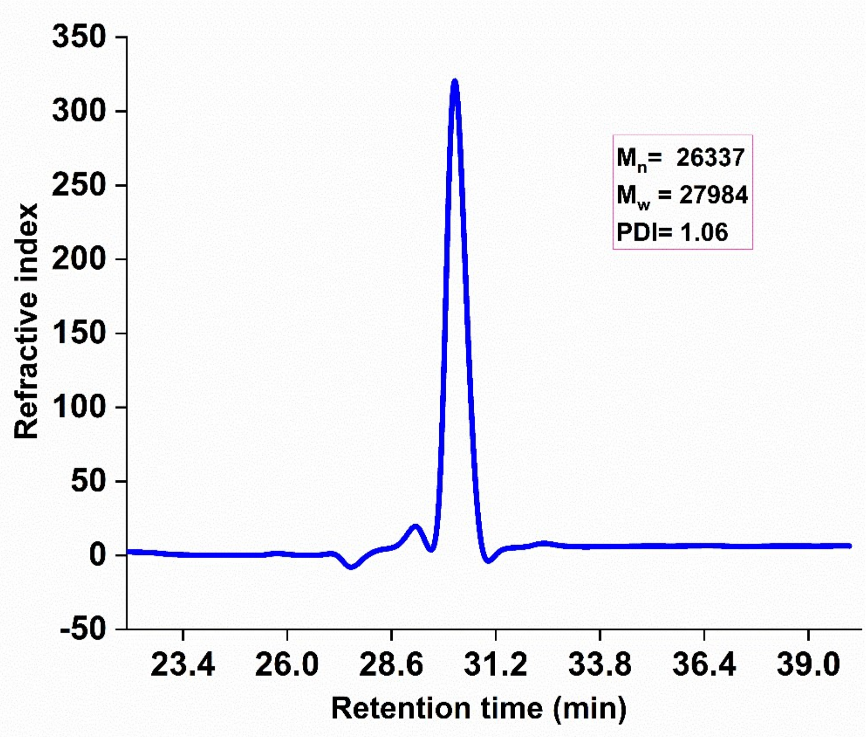


Figure S13. GPC trace of the triblock polymer.

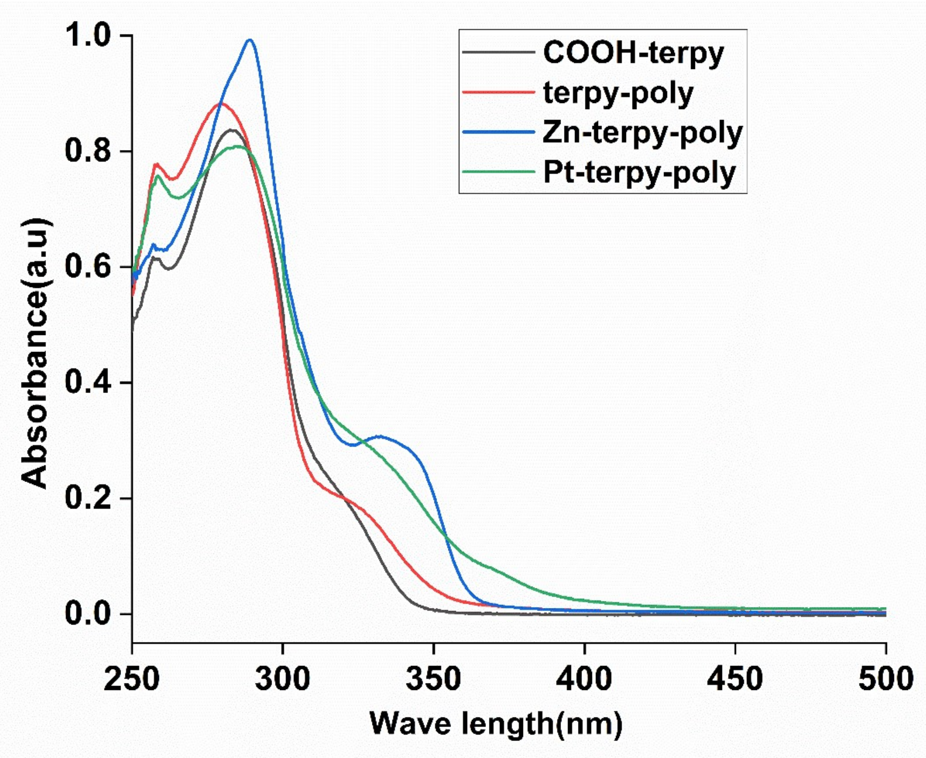


Figure S14. UV-Vis Spectra of **HL, terpy-poly, Zn-terpy poly and Pt-terpy-poly** in DMSO solvent.

References:

S1. Berkessel, A.; Brandenburg, M. *Org. Lett*. **2006**, *8*, 4401–4404

S2. M. A. n. Martínez, M. P. Carranza, A. Massaguer, L. Santos, J. A. Organero, C. Aliende, R. de Llorens, I. Ng-Choi, L. Feliu and M. Planas, *Inorg. Chem.*, 2017, **56**, 13679-13696.