Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Aldehyde End-Caped CO_2-based Polycarbonates: A Green Synthetic Platform for Site-Specific Functionalization

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General Information

Materials

All manipulations involving air- and/or water-sensitive compounds were performed in a glove box or with the standard Schlenk techniques under dry argon, unless otherwise indicated. Chemicals were obtained from Energy Chemical without further purification unless otherwise stated. Dichloromethane and toluene were purified by distillation from calcium hydride and stored under Argon atmosphere prior to use. The carbon dioxide gas (99.999%) was purchased from Changchun Juyang Co., Ltd. and used without further purification.

Characterization

Solution NMR spectra were collected using Bruker ARX-300 and ARX-400 spectrometer in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO) with tetramethylsilane (TMS) as internal reference. Solvent proton shifts (ppm): $CDCl_3$, 7.26 (s); DMSO-d_6, 2.50 (s). Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker autoflex III mass spectrometer. The molecular weight and molecular weight distribution of the polycarbonates were determined by gel permeation chromatography (GPC) at 35 °C in polystyrene standard on Waters e2695 GPC instrument with dichloromethane as the eluent, where the flow rate was set at 1.0 mL min^{-1}. Contact angel test were conducted by KRUSS contact angle tester. Thermal properties were measured by TA DSC Q2000 and TA TGA Q50 with the heating rate of 10℃/min. Fluorescence spectra were obtained on a Horiba Fluorolog-3 spectrofluorometer.

Synthetic procedures and characterization data for salenCo(III)Cl catalysts

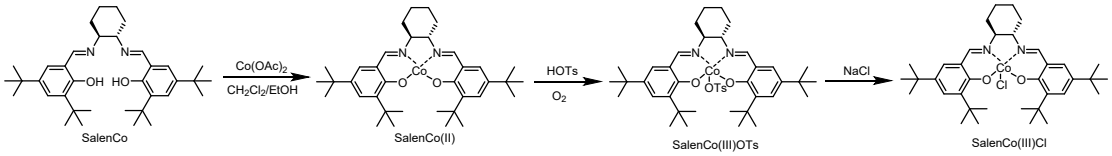

Figure S1. The preparation of salenCo(III)Cl

(R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine (salen) was used as received. A flame-dried, 250 mL round bottom flask was charged with salen ligand (2.00 g, 3.66 mmol) and purged with nitrogen. 25 mL distilled CH_2Cl_2 was added to give a yellow solution. $Co(OAc)_2 \cdot 4H_2O$ (1.09 g, 4.39 mmol) dissolved in ethanol (30 mL, degassed) was added via syringe under stirring. The solution immediately turned dark red and a red precipitate was observed. After stirring for 20 min at room temperature, the mixture was cooled to 0 ℃ by ice water bath and kept for 30 min. The red or orange (salen)Co(II) complex was isolated by filtration and washing with MeOH for several times, then dried in vacuum at 40 ℃. The yield was 80%.

SalenCo(II) (1.00 g, 1.64 mmol) and $TsOH \cdot H_2O$ (0.33 g, 1.72 mmol) were added to a 100 mL round bottom flask. CH_2Cl_2 (50 mL) was added to give a red suspension. The mixture was bubbled with dry oxygen and stirred at room temperature for 8 h. The resulting solid was suspended in pentane and filtered to afford (salen)Co(III)OTs as a dark green solid. The yield was 89%.

SalenCo(III)OTs (1.2 g, 1.55 mmol) was dissolved in CH_2Cl_2 (100 mL) and added to a 1000 mL separatory funnel. The organic layer was washed with saturated aqueous NaCl (4 x 200 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the solid was washed with pentane (3 x 100 mL) to afford (salen)Co(III)Cl as a dark green solid. The yield was 75%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.83 (s, 2H), 7.44 (d, 4H) , 3.66-3.58 (m, 2H), 3.11-3.04 (m, 2H), 2.05-1.97 (m, 2H), 1.96-1.85(m, 2H), 1.74 (s, 18H), 1.62-1.52 (m, 2H) , 1.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.89, 162.52, 142.36, 136.36, 129.15, 119.08, 69.77, 36.21, 33.93, 32.02, 30.86, 29.96, 24.78 ppm. HRMS (ESI): calcd for $C36H52O2N2Co^+$ $[M - Cl]^+$ 603.3361, found 603.3338.

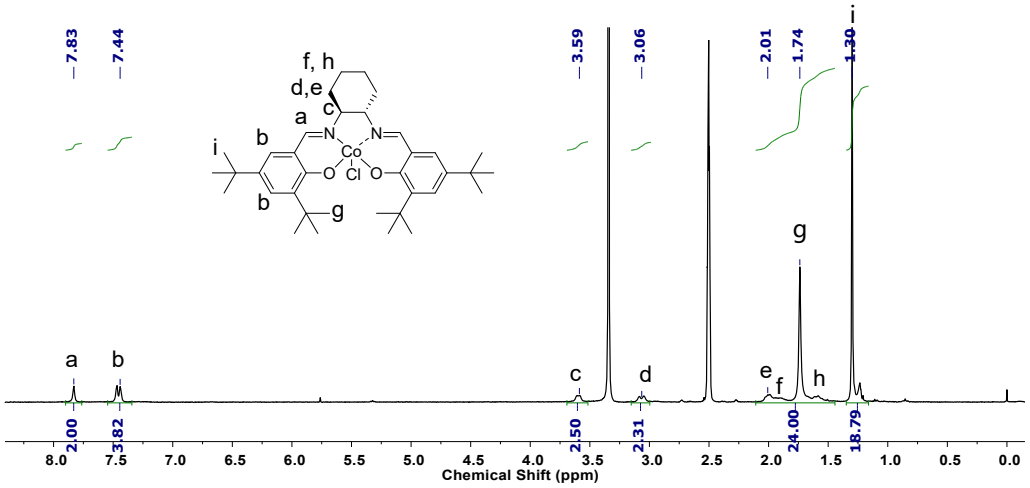

Figure S2. ^{1}H NMR spectrum of salenCo(III)Cl (300 MHz, DMSO-d_6, 25 °C).

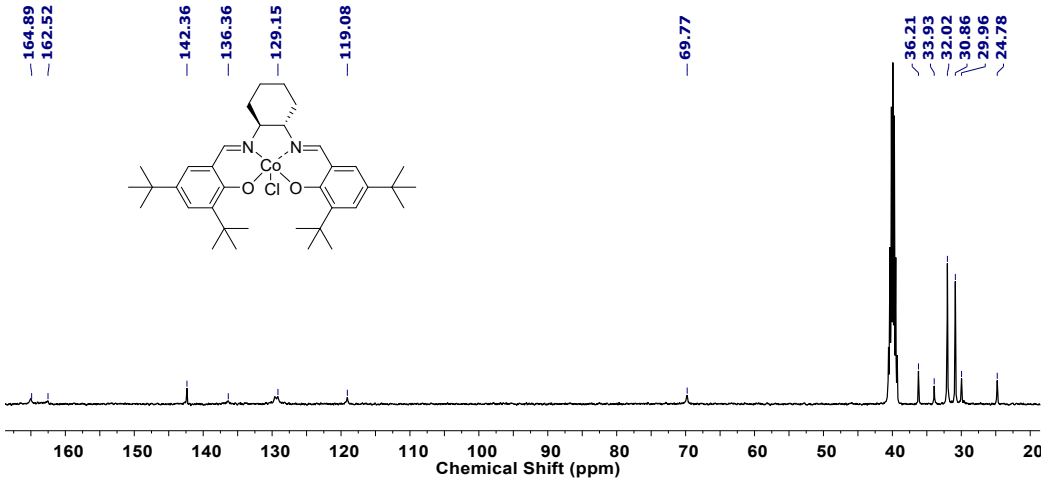

Figure S3. ^{13}C NMR spectrum of salenCo(III)Cl (100 MHz, DMSO-d_6, 25 °C).

General procedure for the copolymerization of CO_2 and PO with 4-formylbenzoic acid (4-FBA) as chain transfer agent using salenCo(III)Cl/PPNCl (1:1) catalyst

Stoichiometric PO (4.0 mL, 57.2 mmol) , salenCo(III)Cl, PPNCl and 4-FBA were added into a 10 mL autoclave, pressurized to 3.0 MPa (30 °C). After the preset reaction time, the CO_2 pressure was released. The crude polymer was dissolved in CH_2Cl_2 and precipitated from methanol for three times. The obtained polymer was dried under vacuum at 60 °C for 12 h.

The methods of post-polymerization functionalization for P-CHO and characterization data

for P-CHO derivatives

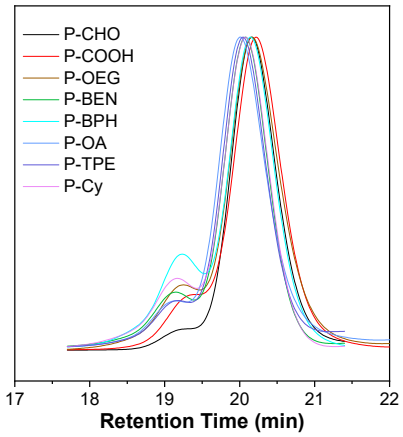

Figure S4. The GPC traces of P-CHO (M_n = 10.6 kg mol^{-1}) and its derivatives.

Table S1. The Molecular Weight and Molecular Weight Distribution of P-CHO and Its Derivatives.[a]

polymer	M_n (kg mol^{-1})	$Đ$
P-CHO	10.6	1.13
P-COOH	10.2	1.18
P-OEG	10.6	1.19
P-BEN	10.7	1.27
P-BPH	10.7	1.21
P-OA	11.0	1.25
P-TPE	10.9	1.23
P-Cy	10.7	1.23

[a] Determined by gel-permeation chromatography in CH_2Cl_2 at 35 °C calibrated with polystyrene standards.

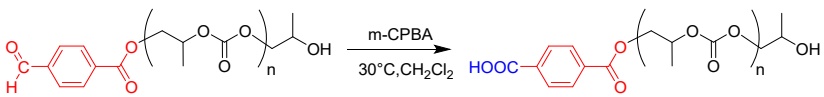

Figure S5. Synthetic route to P-COOH.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL CH_2Cl_2 to give a solution. 19.5 mg m-

chloroperbenzoic acid (m-CPBA) (0.113 mmol, 1.2 eq) was added and the mixture was stirred under 30℃ for 12 h. 100 mL methanol was dropped into the mixture to precipitate P-COOH as white solid. The product was dried under vacuum at 60 °C for 12 h.

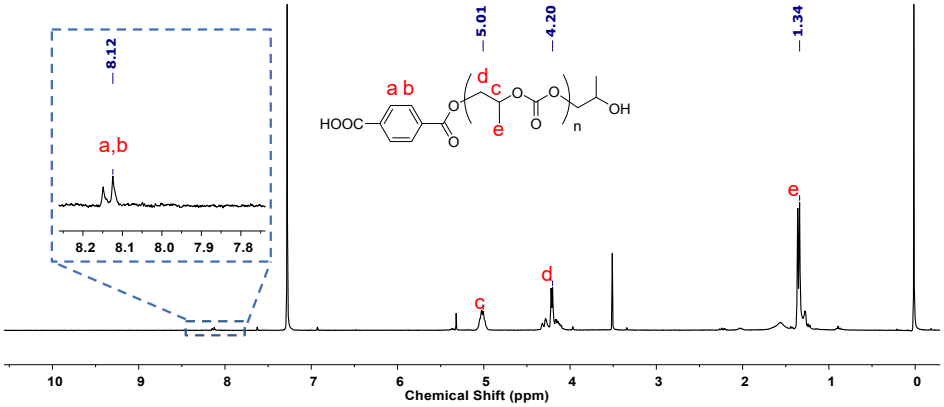

Figure S6. ^{1}H NMR spectrum of P-COOH (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

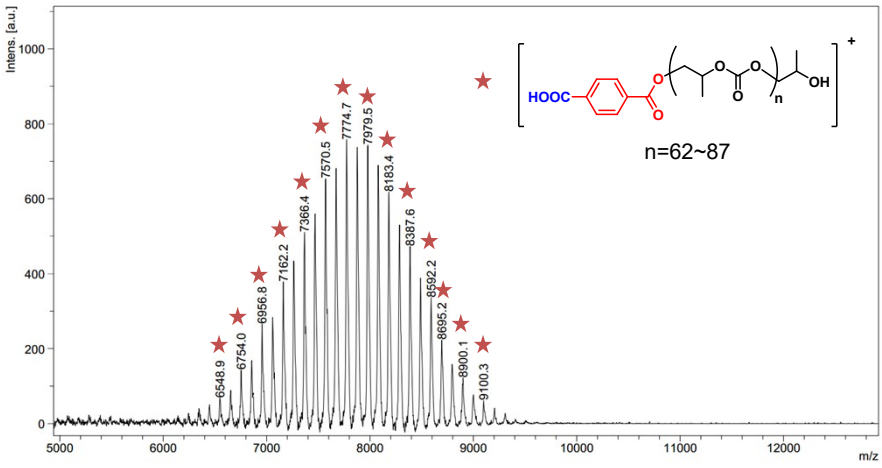

Figure S7. MALDI-TOF-MS spectrum of P-COOH.

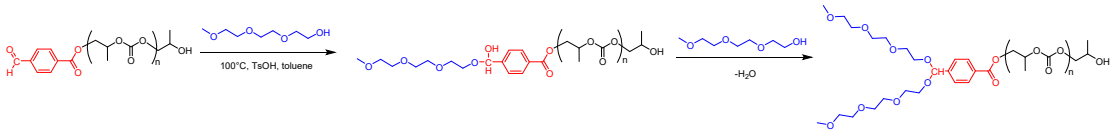

Figure S8. Synthetic route to P-OEG.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL toluene to give a solution. 0.619 g triethylene glycol monomethyl ether (3.77 mmol, 40 eq) was added. The mixture was reflux under 100 ℃ for 12 h with a water knockout trap. 100 mL methanol was dropped into the mixture to precipitate P-OEG as white solid. The product was dried under vacuum at 60 °C for 12 h.

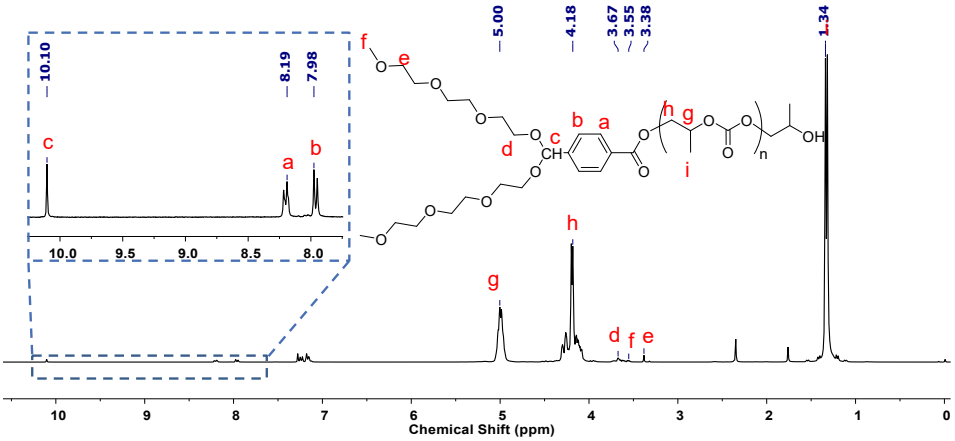

Figure S9. ^{1}H NMR spectrum of P-OA (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

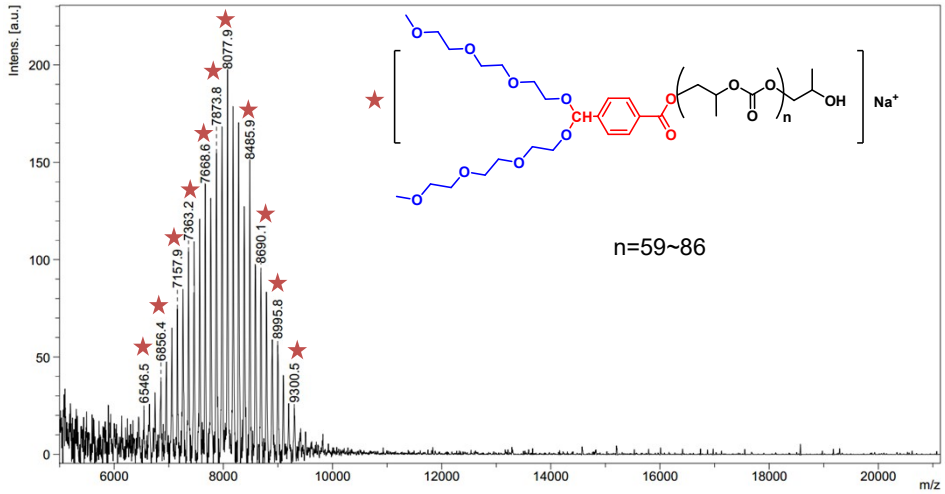

Figure S10. MALDI-TOF-MS spectrum of P-OEG.

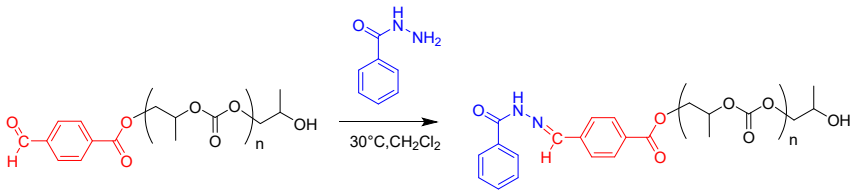

Figure S11. Synthetic route to P-BEN.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL CH_2Cl_2 to give a solution. 64.3 mg benzoyl hydrazine (0.472 mmol, 5 eq) was added and the mixture was stirred under 30 °C for 12 h. 100 mL methanol was dropped into the mixture to precipitate P-BEN as white solid. The product was dried under vacuum at 60 °C for 12 h.

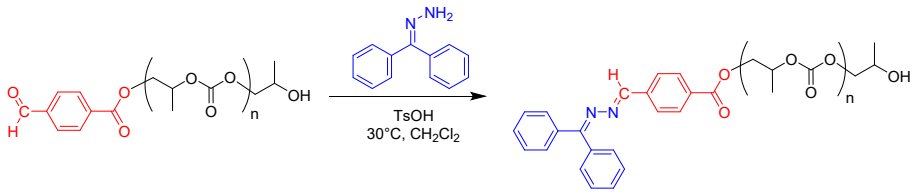

Figure S12. Synthetic route to P-BPH.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL CH_2Cl_2 to give a solution. 92.6 mg benzoyl hydrazine (0.472 mmol, 5 eq) was added and the mixture was stirred under 30 ℃ for 12 h. 100 mL methanol was dropped into the mixture to precipitate P-BPH as white solid. The product was dried under vacuum at 60° C for 12 h.

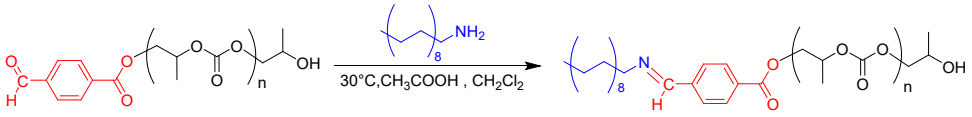

Figure S13. Synthetic route to P-OA.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL CH_2Cl_2 to give a solution. 0.254 g octadecylamine (0.943 mmol, 10 eq) was added to the solution. After dropping 0.2 mL CH_3COOH, the mixture was stirred under 30 ℃ for 48 h. 100 mL methanol was dropped into the mixture to precipitate P-OA as white solid. The product was dried under vacuum at 60 °C for 12 h.

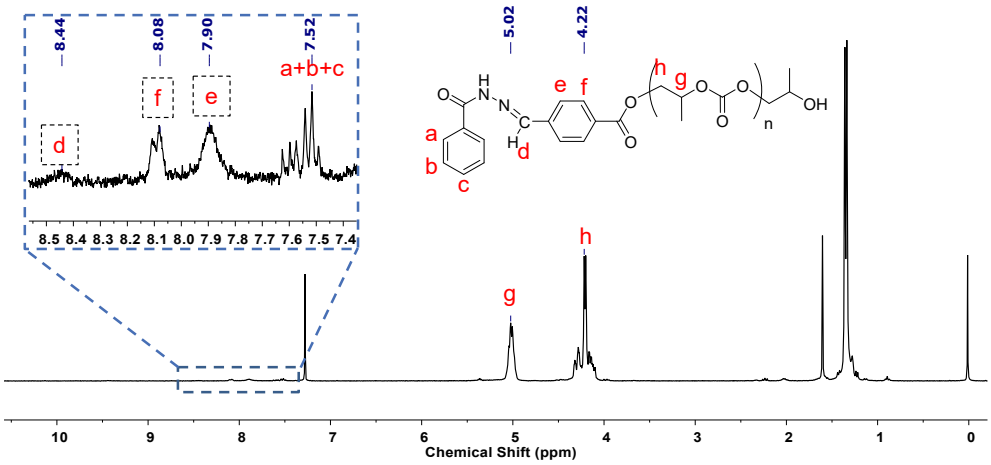

Figure S14. ^{1}H NMR spectrum of P-BEN (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

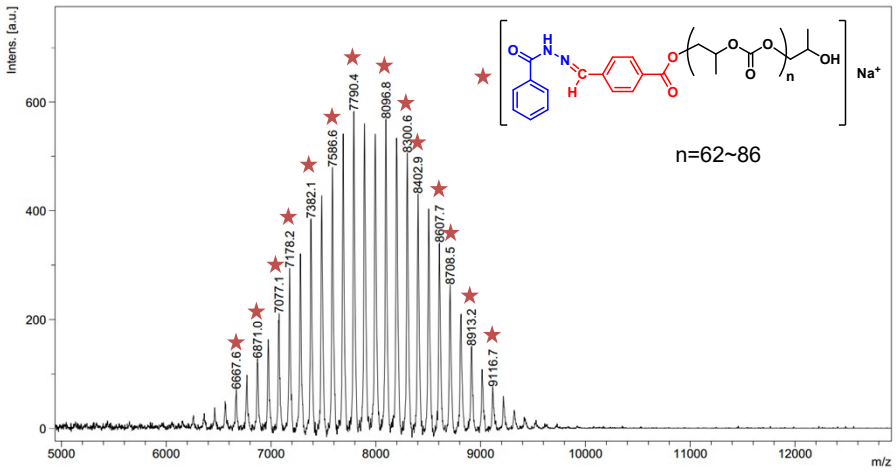

Figure S15. MALDI-TOF-MS spectrum of P-BEN.

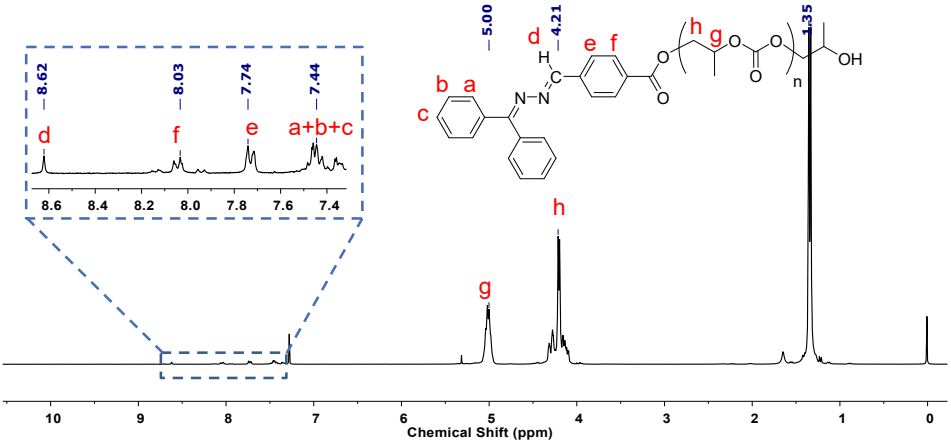

Figure S16. ^{1}H NMR spectrum of P-BPH (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

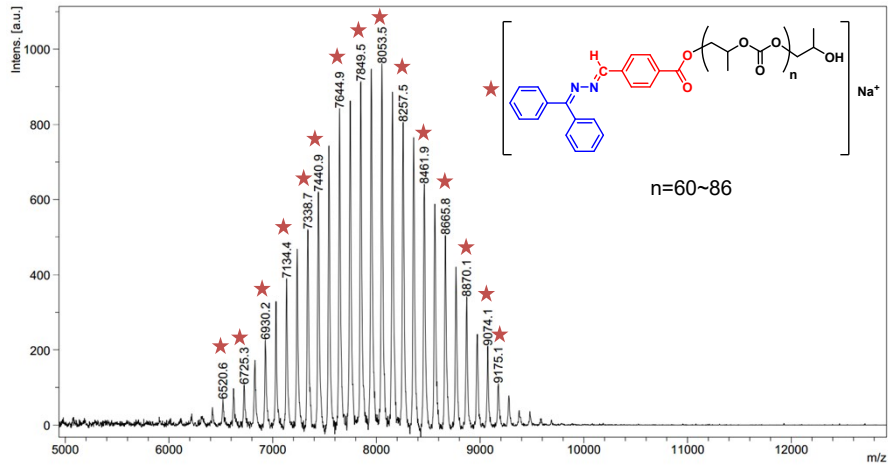

Figure S17. MALDI-TOF-MS spectrum of P-BPH.

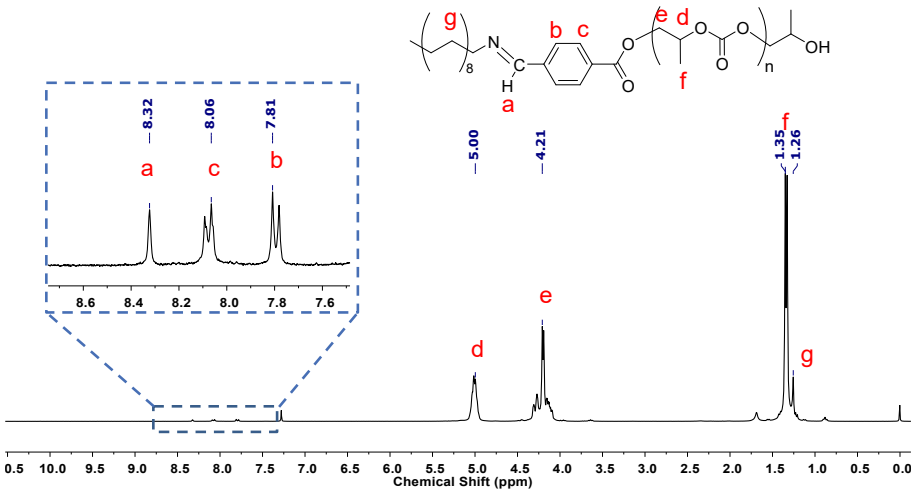

Figure S18. ^{1}H NMR spectrum of P-OA (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

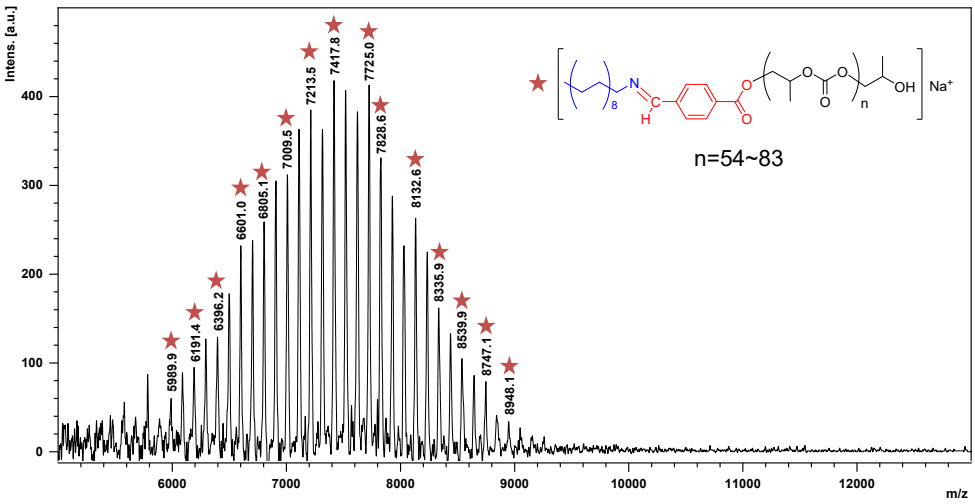

Figure S19. MALDI-TOF-MS spectrum of P-OA.

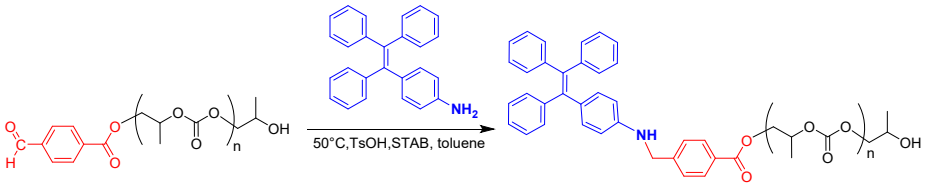

Figure S20. Synthetic route to P-TPE.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL toluene to give a solution. 49.0 mg TPE-NH_2 (0.141 mmol, 1.5 eq), 40.1 mg sodium triacetoxyborohydride (STAB) (0.189 mmol, 2.0eq) and 1.8 mg TsOH·H_2O (0.009 mmol, 0.1eq) was added to the solution. Then, the mixture was stirred

under 50 °C for 12 h. 100 mL methanol was dropped into the mixture to precipitate P-TPE as faint yellow solid. The product was dried under vacuum at 60 °C for 12 h.

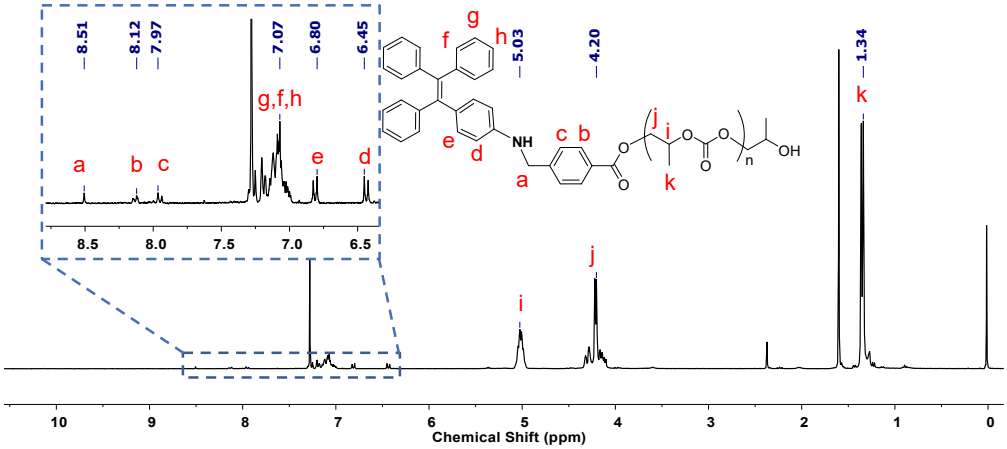

Figure S21. ^{1}H NMR spectrum of P-TPE (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

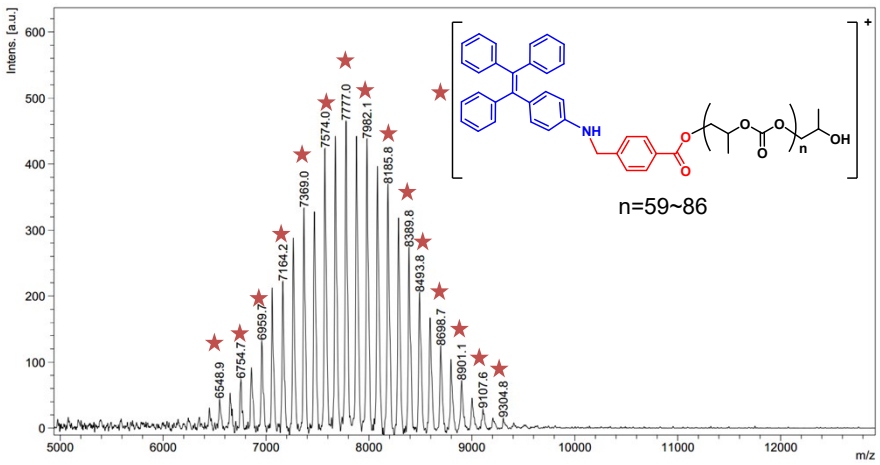

Figure S22. MALDI-TOF-MS spectrum of P-TPE.

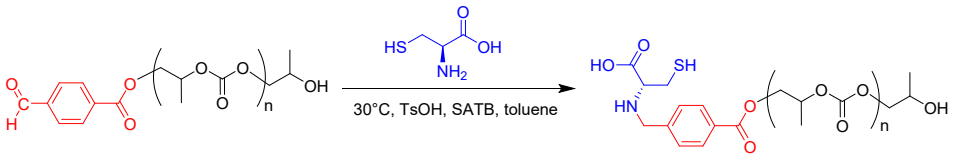

Figure S23. Synthetic route to P-Cy.

1.0 g P-CHO with M_n = 10.6 kg mol^{-1} (containing ~0.0943 mmol –CHO, 1.0 eq) was placed into a 50 mL round bottom flask with the addition of 10 mL toluene to give a solution. 0.114 g L-cysteine (0.943 mmol, 10 eq), 40.1 mg sodium triacetoxyborohydride (STAB) (0.189 mmol, 2.0 eq) and 1.8 mg TsOH·H_2O (0.009 mmol, 0.1 eq) was added to the solution. Then, the mixture was stirred under 50 °C for 12 h. 100 mL methanol was dropped into the mixture to precipitate P-Cy as white solid.

The product was dried under vacuum at 60° C for 12 h.

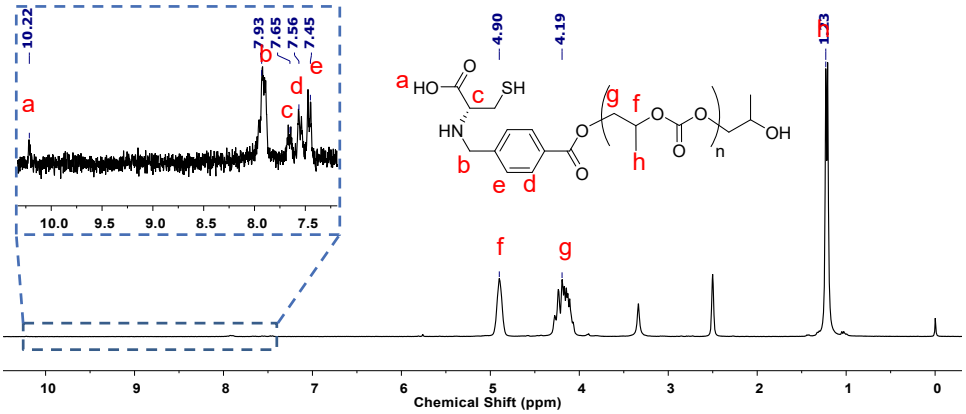

Figure S24. ^{1}H NMR spectrum of P-Cy (300 MHz, $CDCl_3$, 25 °C). Inset: Enlarged proton peaks of end groups.

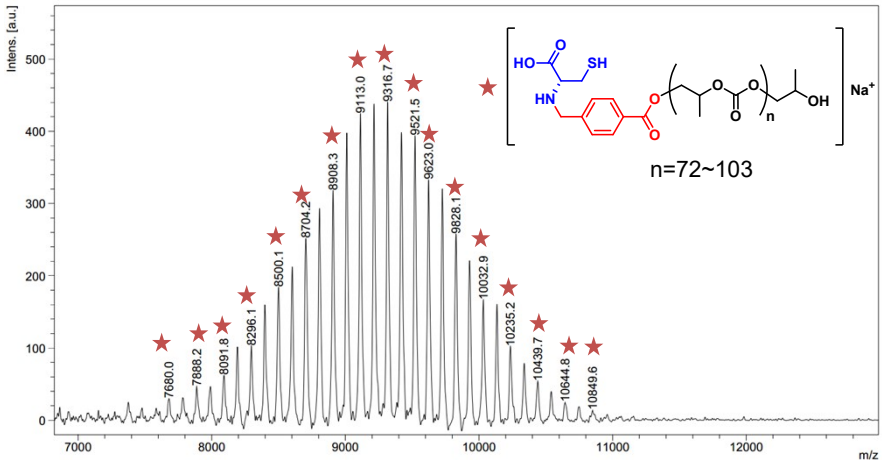

Figure S25. MALDI-TOF-MS spectrum of P-Cy.