Preparation of Cationic Cobaltocenium Polymers and Block Copolymers by "Living" Ring-Opening Metathesis Polymerization

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Supplementary Information

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I. Experimental and Characterization

Materials *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (95%, NDA), *exo*-5-norbornenecarboxylic acid (97%), 3-amino-1-propanol, and ethyl vinyl ether (99%, EVE) were purchased from Aldrich, and used directly. Cobaltocenium acyl chloride was synthesized according to earlier reports.[1-3] Grubbs catalyst, 3rd generation, was synthesized following a procedure reported in literature.[4] *N,N*-dimethylformamide (DMF) was dried and freshly distilled. Sodium tetraphenylborate (99%, $NaBPh_4$, Alfa Aesar) was used as received. IRA-400 (Cl) ion-exchange resin (Alfa) was washed with water before usage. All other chemicals were from commercial sources and used as received.

Characterization ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury 400 spectrometer with tetramethylsilane (TMS) as an internal reference. ^{19}F NMR (376 MHz) spectra were recorded on a Varian Mercury 400 spectrometer with CHF_3 as an internal reference. Gel permeation chromatography (GPC) was performed in DMF (containing 0.1% LiBr) at a flow rate of 0.8 mL/min at 50 ºC on a Varian system equipped with a ProStar 210 pump and a Varian 356-LC RI detector and three 5 μm phenogel columns (Phenomenex Co.) with narrow dispersed polystyrene as standards. Mass Spectrometry (MS) was conducted on a Waters Micromass quadropole-Time of Flight (Q-Tof) mass spectrometer, using electrospray ionization in a positive ion mode. Elemental analysis was conducted on a CHNOS 440 Elemental analyzer (Exeter Analytical).

II. Synthesis of Monomers and Polymers

Synthesis of *N*-[3-Hydroxylpropyl]-*cis*-5-Norbornene-*exo*-2,3-Dicarboximide (NPH). NDA (0.328 g, 2.0×10^{-4} mol) and 3-amino-1-propanol (0.016 g, 2.2×10^{-4} mol) were dissolved in 10 mL dichloromethane (DCM), stirred, and then evaporated all solvents. The mixture was heated to 110 ˚C and maintained overnight. The product was purified by passing through a short alumina column. Yield: 98%. ^1H NMR (**Figure S1**) ($CDCl_3$, δ): 6.27 (s, 2H, $CH{=}CH$), 3.64 (t, 2H, NCH_2CH_2), 3.53 (CH_2CH_2OH), 3.26 (s, 2H, $CHCON$), 2.71 (m, 2H, CH_2CH), 1.77 (m, 2H, $CH_2CH_2CH_2$), 1.23, 1.54 (m, 2H, CH_2CH). ^{13}C

NMR (**Figure S2**) ($CDCl_3$, δ): 178.4 (*C*ON), 137.7 (*C*H=*C*H), 58.9 (*C*H_2OH), 47.6 (CH_2*C*HCHCO), 44.9 (CH_2CH*C*HCO), 42.6 (*C*H_2CHCHCO), 35.3 (N*C*H_2CH_2), 30.4 (NCH_2*C*H_2).

Synthesis of *N*-[3-Cobaltoceniumcarboxyl Propyl]-*cis*-5-Norbornene-*exo*-2,3-Dicarboximide Hexafluorophosphate (MPF6) Monomer. NPH (0.442 g, 2.0 × 10^{-3} mol) and cobaltocenium acyl chloride (1.000 g, 2.5 × 10^{-3} mol) were added into a dry round bottom flask with 100 mL dry THF. Triethylamine (1 mL, 7.0 × 10^{-3} mol) was added into the solution slowly. The mixture was stirred at room temperature for 4 days. The product was purified by extraction with water and then precipitated from diethyl ether. The final product MPF6 was a yellow solid. Yield: 90%. ^{1}H NMR (MPF6, acetone-d_6, δ): 6.40 (d, 2H, Cp), 6.32 (s, 2H, C*H*=C*H*), 6.10 (m, 7H, Cp), 4.33 (t, 2H, C*H_2*COO), 3.70 (t, 2H, NC*H_2*CH_2), 3.17 (s, 2H, C*H*CON), 2.76 (s, 2H, CH_2C*H*CH), 2.05 (s, 2H, NCH_2C*H_2*), 1.45 and 1.28 (m, 2H, C*H_2*CHCH). ^{13}C NMR (Figure S3) (MPF6, acetone-d_6, δ): 178.2 (*C*ON), 162.3 (*C*OOCH_2), 137.6 (vinyl group), 82.2-85.6 (Cp), 61.8 (*C*H_2COO), 47.5, 45.8 (*C*H_2*C*HCH), 40.7 (*C*HCON), 30.9 (N*C*H_2CH_2), 25.2 (NCH_2*C*H_2). ^{19}F NMR (**Figure S7**) (MPF6, CHF_3, δ): -73.23 (d, P*F6*). MS (**Figure S4**): theoretical m/e 436, founded m/e 436. Elemental analysis (%): theoretical C: 47.52, H: 3.99, N: 2.41; experimental C: 47.52, H: 4.01, N: 2.39.

Synthesis of *N*-[3-Cobaltoceniumcarboxyl Propyl]-*cis*-5-Norbornene-*exo*-2,3-Dicarboximide Chloride (MCl) and *N*-[3-Cobaltoceniumcarboxyl Propyl]-*cis*-5-Norbornene-*exo*-2,3-Dicarboximide Tetraphenylborate (MBPh4). MCl was synthesized by ion-exchange of MPF6 with IRA-400(Cl) ion-exchange resin. The acetone solution of MPF6 (50 mg/mL, 4 mL) was added into the aqueous dispersion solution of IRA-400(Cl) (1 g/mL, 20 mL), and stirred for 4 h. The aqueous solution was collected after filtration. The solvent was evaporated under pressure. The MBPh4 was prepared by the following procedure. In the aqueous solution of NaBPh4 (1 mol/L, 20 mL), MPF6 acetone solution (0.5 g/mL, 1 mL) was added into the solution, and stirred for 2 h. The yellow precipitate was filtered out and washed with water to remove excess NaBPh4. ^{1}H NMR (**Figure S5**) (MCl, acetone-d_6, δ): 6.20 (d, 2H, Cp), 6.15 (s, 2H, C*H*=C*H*), 5.69 (m, 7H, Cp), 4.21 (t, 2H, C*H_2*COO), 3.49 (t, 2H, NC*H_2*CH_2), 3.00 (s, 2H, C*H*CON), 2.68 (s, 2H, CH_2C*H*CH), 1.80 (s, 2H, NCH_2C*H_2*), 1.05 and 1.38 (m, 2H, C*H_2*CHCH). ^{1}H NMR

(**Figure S6**) (MBPh4 acetone-d_6, δ): 7.21 (s, 8H, Ph), 6.96 (t, 8 H, Ph), 6.81 (t, 4H, Ph), 6.32 (d, 2H, Cp), 6.28 (s, 2H, C*H*=C*H*), 5.95 (m, 7H, Cp), 4.32 (t, 2H, CH_2COO), 3.69 (t, 2H, NCH_2CH_2), 3.17 (s, 2H, C*H*CON), 2.74 (s, 2H, CH_2C*H*CH), 2.05 (s, 2H, NCH_2CH_2), 1.44 and 1.27 (m, 2H, CH_2CHCH).

Synthesis of PMPF6 via ROMP. Grubbs 3rd catalyst (0.004 g, 5.0×10^{-6} mol) was dissolved in 0.5 mL dry DMF. MPF6 (0.145 g, 2.5×10^{-4} mol) in dry DMF (2 mL) was added into the catalyst solution drop wise under open air with vigorous stirring. The reaction was stopped after 10 min by adding EVE (0.2 mL). The orange solid polymers were purified by precipitating in dichloromethane three times and dried under vacuum until constant weight. Yield: 98%. ^{1}H NMR (**Figure S8**) (PMPF6, acetonitrile-d_3, δ): 7.21-7.50 (m, 5H, phenyl), 6.17 (broad, 100H, Cp), 5.84 (broad, 350H, Cp), 5.52 and 5.74 (double broad, 100H, C*H*=C*H*), 4.26 (Broad, 100H, OCH_2CH_2), 3.59 (broad, 100H, NCH_2CH_2), 3.04 (m, 100H, CH=CHC*H*CH_2), 2.67 (broad, 50H, CH=CHCHCH_2), 2.23 (broad, OCH_2CH_2 and H_2O), 1.53 (broad, 50H, CH=CHCHCH_2). Elemental analysis (%): theoretical C:58.55, H: 4.91, N: 2.97; Experimental C: 57.89, H: 5.19, N: 3.26.

Kinetic Study of ROMP of Monomer MPF6. In order to verify the living character of ROMP of cobaltocenium monomer, kinetic studies were conducted at two different conditions. 1): MPF6 (0.116 g, 2.0×10^{-4} mol) was added into a solution of Grubbs 3rd catalyst (0.002 g, 2.0×10^{-6} mol) in DMF at a concentration of 58.1 mg/mL. Calculated amount of samples (0.3 mL) were taken at 1 min intervals, and added into a DMF solution with 0.1 mL EVE directly to terminate the polymerization. The conversion of the monomer was calculated by comparing the vinyl group of the monomer (6.32 ppm) and polymer (5.52-5.74 ppm). Semilogrithmic plots were made based on the conversion analysis. 2): A series of reactions were conducted with different molar ratios of catalyst to monomer using the procedure described above. All polymerizations were stopped with nearly 100% monomer conversion. The degree of polymerization was calculated by comparing the integration of phenyl group from polymer chain end (7.21-7.50 ppm) and the protons from Cp rings (5.84 and 6.17 ppm).

Synthesis of High Molecular Weight PMPF6-2. The procedure was similar to the synthesis of PMPF6 described in the main text, but the molar ratio of MPF6 to Grubbs 3rd catalyst was 300 : 1. The

PMPF6-2 was purified by precipitating in dichloromethane followed by drying under vacuum. The signal at 7.21-7.50 ppm was assigned to the phenyl group of the end group of the polymer. By comparing the integration of phenyl group (7.21-7.50 ppm) and the signals from Cp rings (5.84 and 6.17 ppm), the degree of polymerization (DP) of this polymer was calculated to be DP = 287, which was very close to the feed ratio of monomer to catalyst (**Figure S9**).

Synthesis of PMCl Homopolymer. The PMCl homopolymers were synthesized by either direct ROMP polymerization of MCl monomer in DMF or by the ion-exchange of PMPF6 in the presence of with IRA-400(Cl) ion-exchange resin.

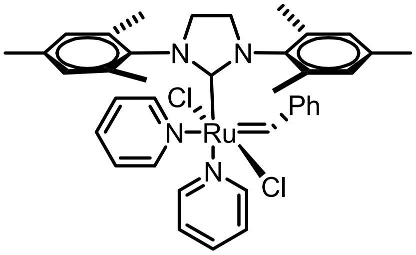
Hydrolysis of PMPF6 Polymer. PMPF6 (50 mg) was dissolved in acetonitrile followed by adding two drops of concentrated hydrochloride solution and stirred for 2 days at room temperature. After reaction, the crude product was neutralized to pH = 7 and dialyzed against water to remove small molecules. The product was freeze-dried to produce white powder. ^{1}H NMR (DMSO-d$_6$, δ): 7.21-7.48 (m, 5H, phenyl), 5.45 and 5.68 (double broad, 2H, $CH{=}CH$), 4.39 (broad, 1H, CH_2OH), 3.50 (broad, 2H, NCH_2CH_2), 3.23 (Broad, 2H, $HOCH_2CH_2$), 3.04 (m, 4H, $CH{=}CHCHCH_2$), 2.65 (broad, 1H, $CH{=}CHCHCH_2$), 2.26 (broad, OCH_2CH_2 and H_2O), 1.57 (m, 2H, CH_2CH), 1.43 (broad, 1H, $CH{=}CHCHCH_2$). GPC (M_n: 58,000 g/mol; PDI: 1.12).

Synthesis of PNPH Homopolymers without Cobaltocenium via ROMP. The synthesis of PNPH followed a similar procedure to the synthesis of PMPF6. In a vial with deoxygenated Grubbs 3rd catalyst (1 mg, 0.0014mmol) in dry DMF solution (0.5 mL), NPH (21.0 mg, 0.095 mmol) in DMF (1 mL) was added under vigorous stirring. The polymerization was stopped by adding EVE (0.1 mL). The product was purified by precipitating in dichloromethane three times and dried under vacuum until constant weight. Yield: 93 %. ^{1}H NMR (DMSO-d$_6$, δ): 7.25-7.48 (m, 5H, phenyl), 5.45 and 5.68 (double broad, 2H, $CH{=}CH$), 4.41 (broad, 1H, CH_2OH), 3.53 (broad, 2H, NCH_2CH_2), 3.25 (Broad, 2H, $HOCH_2CH_2$), 3.04 (m, 4H, $CH{=}CHCHCH_2$), 2.67 (broad, 1H, $CH{=}CHCHCH_2$), 2.23 (broad, OCH_2CH_2 and H_2O), 1.65 (m, 2H, CH_2CH), 1.52 (broad, 1H, $CH{=}CHCHCH_2$). GPC (**Figure S10**) M_n: 107,000 g/mol; PDI: 1.04.

Synthesis of PMPF6-*b*-poly(cis-5-norbornene-exo-2-carboxylic acid) (PMPF6-*b*-PNCA). A mixture of MPF6 (0.058 g, 1.0 × 10^{-4} mol) and Grubbs 3rd catalyst (0.004 mg, 5.0 × 10^{-6} mol) in dry DMF reacted for 10 min. NCA (0.065 g, 4.0 × 10^{-4} mol) solution in DMF was then added to the above mixture under the protection of nitrogen gas. The polymerization was stopped by adding EVE (0.3 mL). Yellow solid polymers were purified by precipitating from diethyl ether three times and dried under vacuum until constant weight. Yield: 98 %. ^{1}H NMR (DMSO-d_6, δ): 12 (s, 82H, COO*H*), 7.2 (m, 5H, Ph), 6.2 (broad, 40H, Cp), 5.9 (broad, 140H, Cp), 5.0-5.8 (multi broad, 200H, C*H*=C*H*), 4.2 (Broad, 40H, OC*H*$_2$CH$_2$).

III. Schemes, Figures and Tables

Scheme S1. The structure of Grubbs 3rd catalyst.



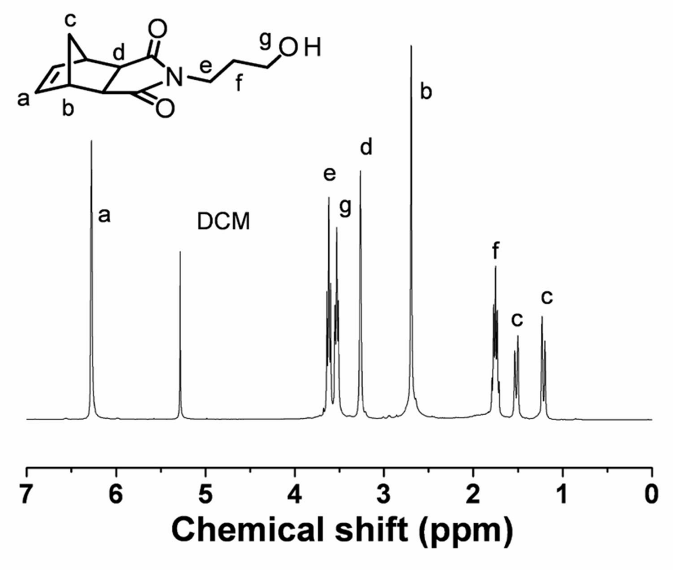


Figure S1. ^{1}H NMR spectrum of *N*-[3-hydroxylpropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide (NPH).

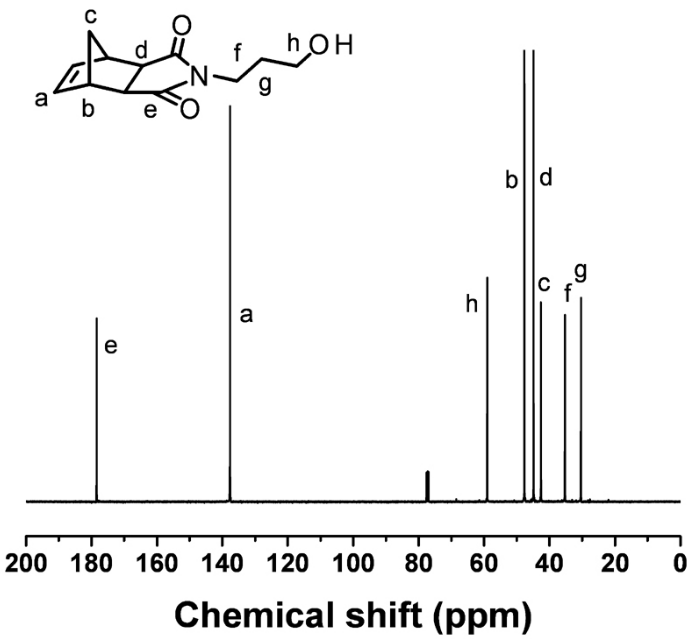


Figure S2. ^{13}C NMR spectrum of *N*-[3-hydroxylpropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide (NPH).

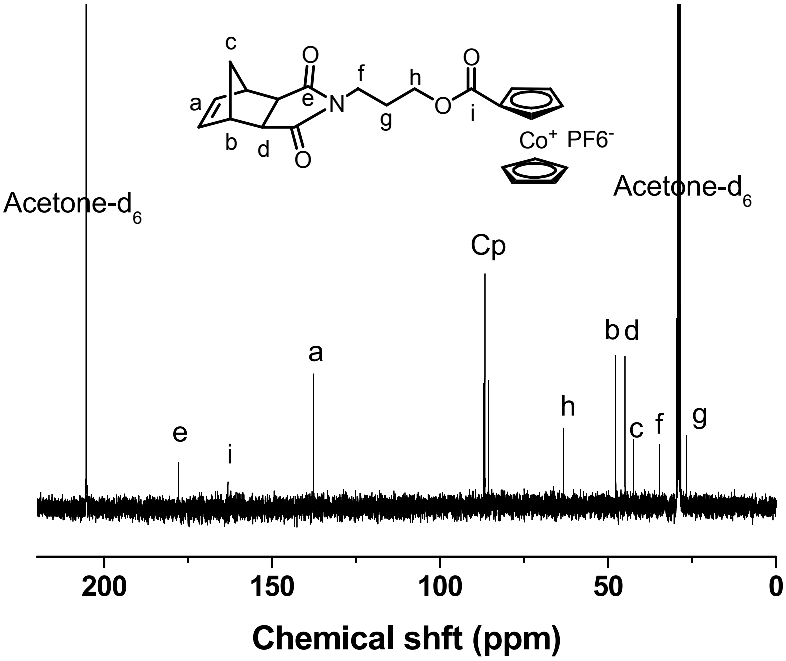


Figure S3. ^{13}C NMR spectrum of *N*-[3-cobaltoceniumcarboxyl propyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide hexafluorophosphate (MPF6).

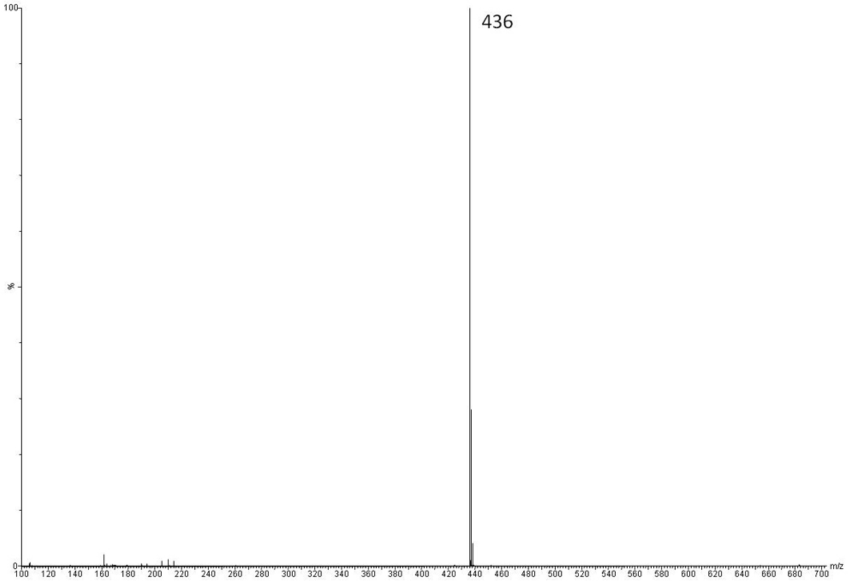


Figure S4. Mass spectrum of *N*-[3-cobaltoceniumcarboxyl propyl]-*cis*-5-norbornene-*exo*-2,3-dicarboxymide hexafluorophosphate (MPF6).

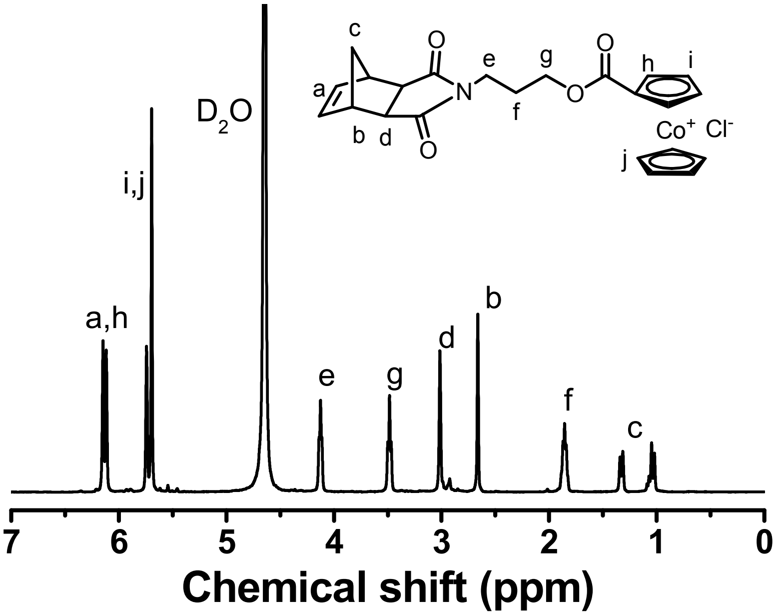


Figure S5. ^{1}H NMR spectrum of *N*-[3-cobaltoceniumcarboxyl propyl]-*cis*-5-norbornene-*exo*-2,3-dicarboxymide chloride (MCl).

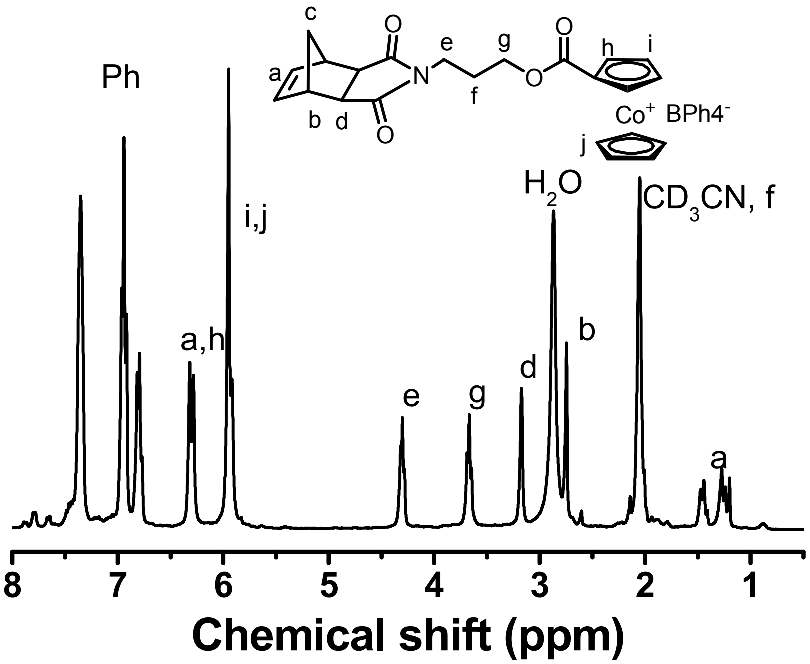


Figure S6. ^{1}H NMR spectrum of *N*-[3-cobaltoceniumcarboxyl propyl]-*cis*-5-norbornene-*exo*-2,3-dicarboxamide tetraphenyborate (MBPh4).

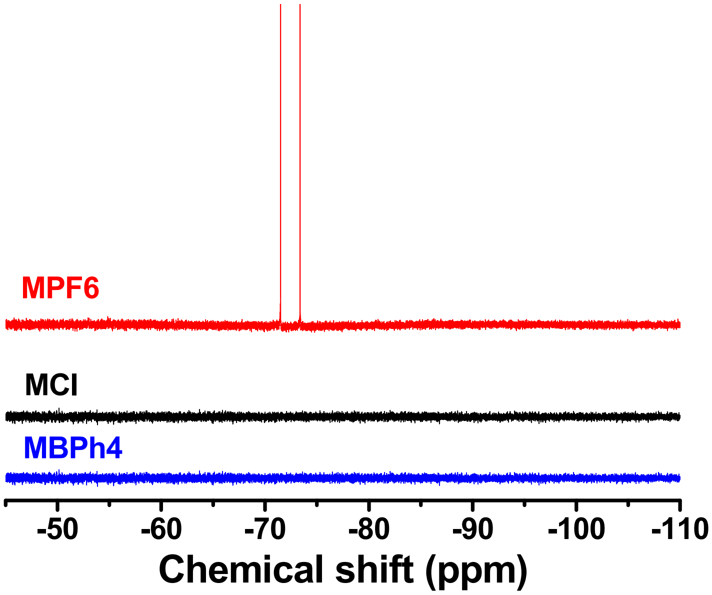


Figure S7. ^{19}F NMR spectra of cobaltocenium-containing monomers MPF6, MCl and MBPh4.

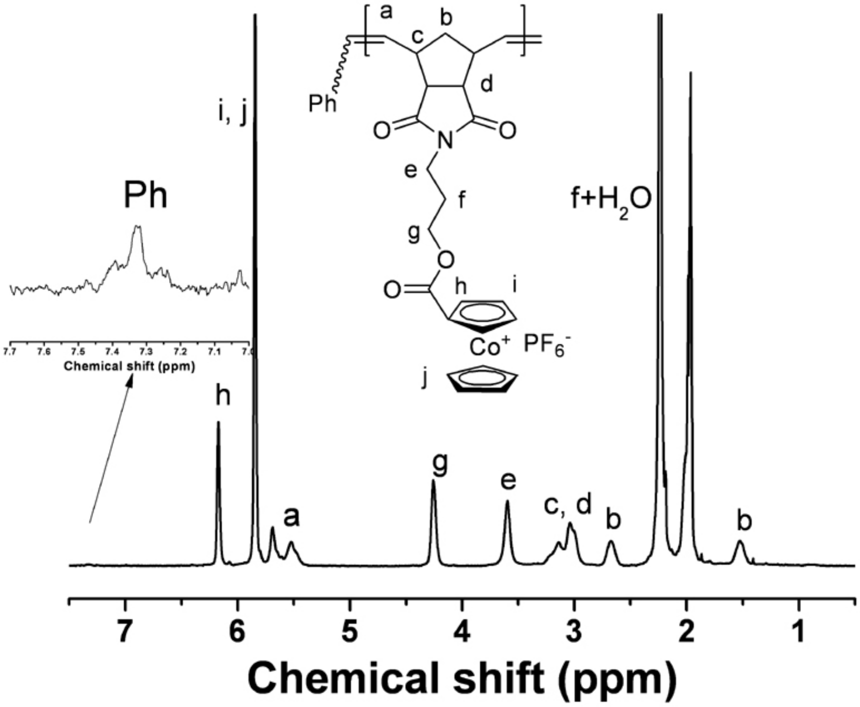


Figure S8. High-resolution ^{1}H NMR spectrum of PMPF6.

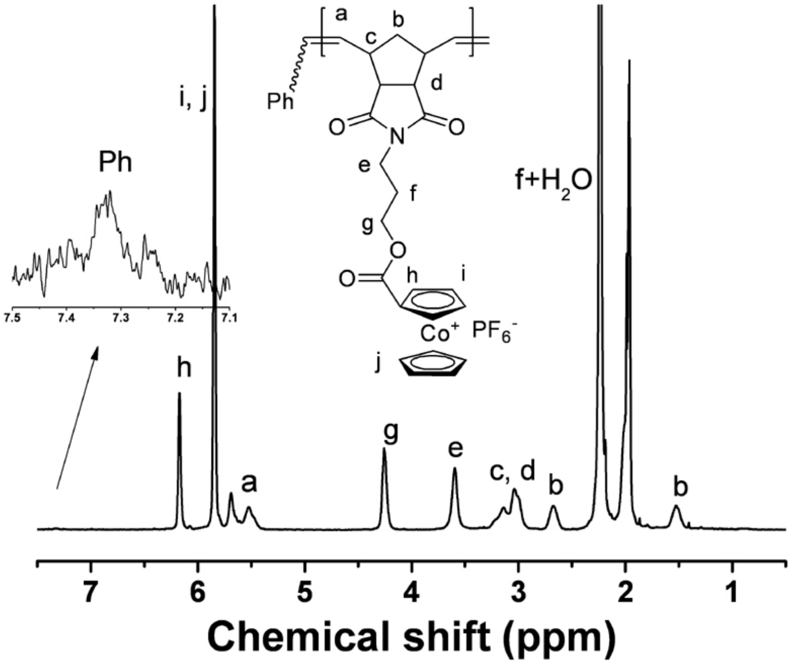


Figure S9. High-resolution ^{1}H NMR spectrum of PMPF6-2.

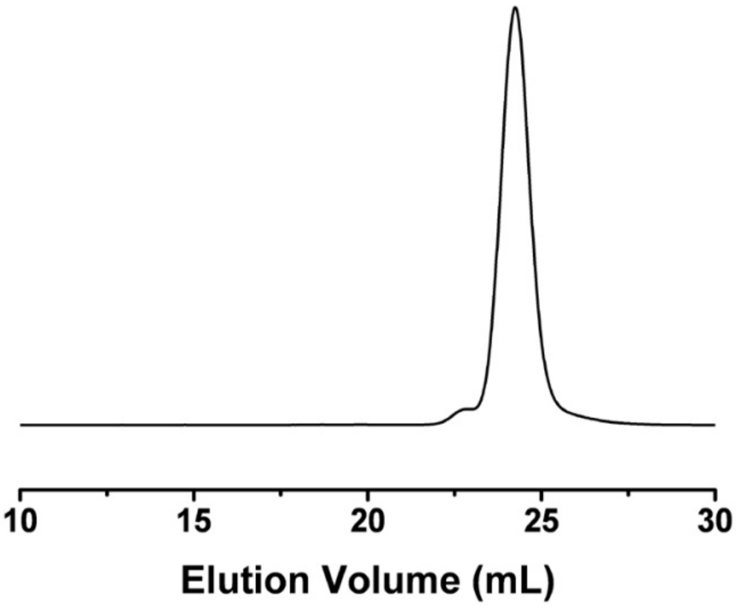


Figure S10. GPC trace of PNPH, which was prepared by direct ROMP of NPH monomer.

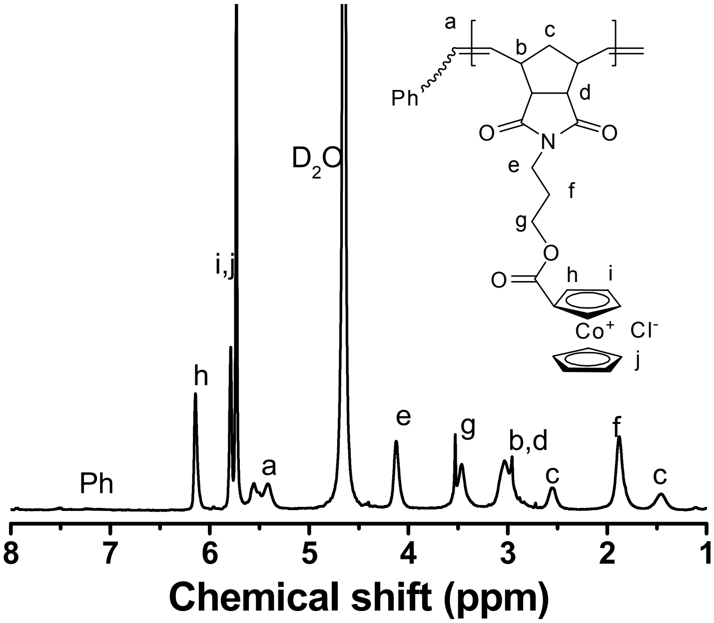


Figure S11. ^{1}H NMR spectrum of poly(*N*-[3-cobaltoceniumcarboxyl propyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide chloride) (PMCl).

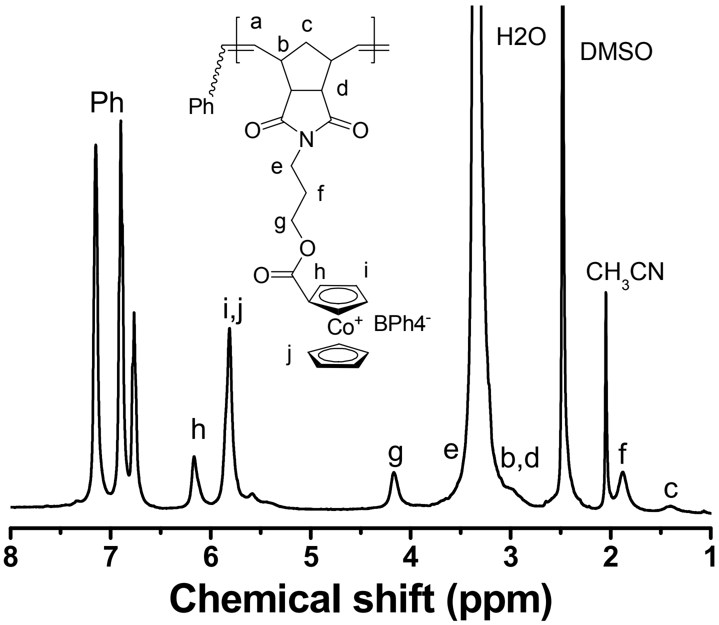


Figure S12. ^{1}H NMR spectrum of poly(*N*-[3-cobaltoceniumcarboxyl propyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide tetraphenyborate) (PMBPh4).

Table S1. Summary of side-chain Cobaltocenium-containing polymers.

Polymer	[M]:[G3][a]	DP (theorectical)	DP[b] (Experimental)	M_n (g/mol)[c]	PDI[d]
PMPF6	100:1	100	100	58,000	1.12
PMPF6-2	300:1	300	287	167,000	-
PMCl	100:1	100	100	47,000	-
PMBPh4	100:1	100	100	64,000	-
PNPH	100:1	100	100	22,000	1.04

[a] feed ratio of monomer to Grubbs 3rd initiator; [b] degree of polymerization of the corresponding polymer calculated from ^{1}H NMR by conversion; [c] number average molecular weight obtained by end group analyses from ^{1}H NMR; [d] polydispersity index characterized by GPC in DMF (0.1 % LiBr) at the flow rate of 0.8 mL/min at 50 °C.

IV. References

1. J. E. Sheats, M. D. Rausch, *J. Org. Chem*. **1970**, *35*, 3245-.
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4. M. S. Sanford, J. A. Love, R. H. Grubbs, *Organometallics* **2001**, *20*, 5314.