Electronic Supporting Information

Exploring the Supramolecular Chemistry of Cyclopropeniums: Halogen-Bonding-Induced Electrostatic Assembly of Polymers

Shiwen Huang[1], *Jianlin Zheng*[1], *Zihao Jiang*[1], *Jiaxiong Liu*[1], *Yiliu Liu*[1,2]*

[1] South China Advanced Institute for Soft Matter Science and Technology, School of Emergent Soft Matter, South China University of Technology, Guangzhou 510640, China

[2] Guangdong Provincial Key Laboratory of Functional and Intelligent Hybrid Materials and Devices, South China University of Technology, Guangzhou 510640, China

* *Corresponding Author: Yiliu Liu, liuyiliu@scut.edu.cn*

Table of Contents

1. Materials and Methods

Materials:

All chemical reagents were purchased from commercial suppliers (Energy Chemical, TCI, Inno-chem). All reagents and solvents were used as supplied without further purification.

Instruments & Methods:

Nuclear magnetic resonance (NMR). The NMR data was performed on JEOL 500 MHz spectrometer at 298 K.

Electrospray mass spectrometry (ESI-MS). The synthetic compounds were firstly dissolved in methanol with a concentration of 5 mg/L, and then subjected to Agilent1290/Bruker maXis spectrometer to collect the mass information.

Gel permeation chromatography (GPC). The GPC analysis with a dimethyl formamide (DMF) eluent was made on a liquid chromatograph pump equipped with two Shodex mixed gel columns (KD-801, KD-804*2 and; 300*8.0 mm; bead size = 7 μm; pore size = 20~200 Å). The flow rate of 1.0 mL/min (40°C). Sample detection and quantification were made with a Shodex differential refractometer RI-102 calibrated with known concentrations of polymer in solvent. The column system was calibrated with standard PMMAs.

Rheological Test. Rheological investigations were performed at TA Instruments rheometer equipped with a temperature controlling system. Parallel plates with a diameter of 25 mm were used in the rheology experiments. Small-amplitude oscillatory shear (SAOS) data were subsequently collected under different temperatures with a fixed normal force. The fitting operation was carried out with the Trios platform. The horizontal shift factors(α_T) and vertical shift factors(b_T) was established. Herein, WLF equation ($log a_T = \frac{-C_1(T-T_0)}{C_2+(T-T_0)}$) was applied to monitor the variation trend of α_T toward the testing temperature. For the WLF formula, T_0 denoted the reference temperature and C_1, C_2 represented two empirical constants. The fitting curves all matched with the experimental data points. As is shown in Figrue S17, strain range for test was $\leqslant$10%.

Dynamic light scattering (DLS). DLS was carried out within 8 h of completion of the assembly protocol. Samples was prepared in 3.00 mL acetone solution. Data were collected with a Brookhaven BI-200SM research goniometer and laser Light scattering system. Measurements were

made at 25℃ with a HeNe laser (633 nm) and at a scattering angle of 90˚. Particle sizes were determined by treating the data with a non-negatively constrained least squares algorithm.

Electron Microscopy. Transmission electron microscopy (TEM) was accomplished using a JEOL instrument operating at 1200 kV accelerating voltage. The samples were prepared by dissolving the polymer mixture in acetone followed by direct drop casting onto a carbon coated copper grid. The solvent was allowed to evaporate at ambient conditions for 24 h before measurement.

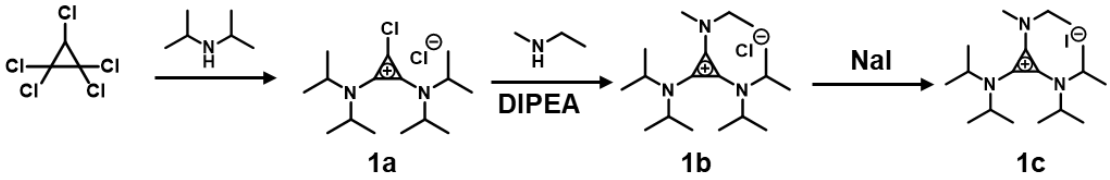
UV-vis Spectroscopy. UV-vis absorption spectra in solution were recorded using a UV-3600Plus (Shimadzu) spectrophotometer.

Fourier Transform Infrared Spectroscopy (FT-IR). FI-IR spectra were collected on a Bruker Vector 33 FT-IR spectrometer in the 500~4000 cm^{-1} region. The samples were dispersed in anhydrous KBr powder, piled into thin tablets, and then subjected to the FT-IR spectrometer. The raw data was processed using Win-IR software.

Thermogravimetric Analysis (TGA). TGA was conducted using a TGA 5500 (TA Instruments) from 30℃ to 800 ℃ at a heating rate of 10 ℃/min under a nitrogen flow, where the samples were placed in platinum crucibles. Samples was dried by freeze drier for 24 h before testing.

Dynamic Scanning Calorimetry (DSC). DSC measurements were performed using a calorimeter (DSC 2500, TA Instruments) under a nitrogen flow, where the samples were placed in alumina crucibles (flow rate: 50 mL/min; temperature range: −160℃ to 100℃; heating rate: 10℃/min). Samples was dried by freeze drier for 24 h before testing.

2. Synthetic procedures and characterization.

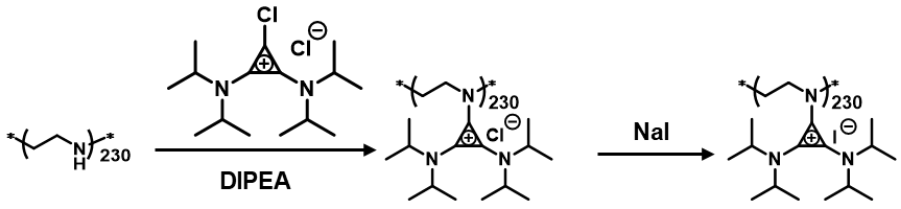


1a: 1a was synthesized according to the reported procedure[1]. Spectral data agreed with those reported in the literature[1].

1b: A 500 mL round bottom flask was charged with DCM (250 mL), **1a** (1.55 g, 5.00 mmol, 1.00 equiv) and N, N-Diisopropylethylamine (DIPEA) (970 mg, 7.50 mmol, 1.50 equiv). The flask was cooled to 0℃ and N-Ethyl methylamine (355 mg, 6.00 mmol, 1.20 equiv) was added slowly. The

reaction was stirred for 4 h at 0°C, then the DCM layer was washed with 1M HCl (100 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash chromatography on silica gel, using DCM: MeOH (10: 1) as eluent. **1b** was isolated as a yellow solid in 75% yield (1.43 g, 4.32 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 3.94 - 3.83 (m, 4H), 3.60 (q, *J* = 7.0 Hz, 2H), 3.29 (s, 3H), 1.38 (dd, *J* = 6.9 Hz, 24H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm)=119.06, 116.83, 51.53, 49.63, 39.65, 22.06, 13.47. MS (ESI-MS, *m/z*): Calc. for $C_{18}H_{36}N_3^+$: 294.2904. Found: 294.2926.

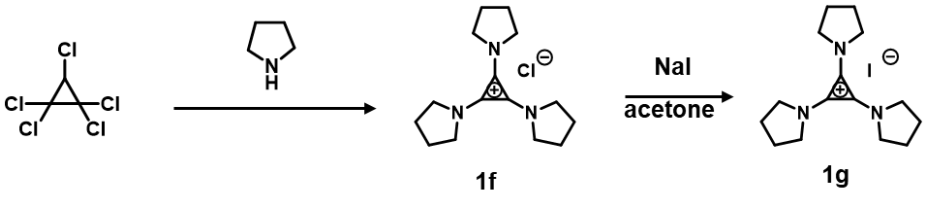
1c: Anion exchange was accomplished by mixing an acetone (15.0 mL) solution of the corresponding **1b** (1.43 g, 4.32 mmol, 1.0 equiv) with an acetone (15.0 mL) solution of sodium iodide (1.30 g, 8.64 mmol, 2.0 equiv). The reaction mixture was stirred at room temperature for 2 h. as sodium chloride was allowed to precipitate. The reaction mixture was then filtered and an additional equivalent of sodium iodide was added to the filtrate. No further precipitation was observed over the course of 2 h. The reaction solution was then concentrated in vacuo to a solid mixture of cyclopropenium iodide and sodium iodide. Cyclopropenium iodide was extracted in pure form from this solid mixture with dichloromethane followed by a water wash to remove trace sodium iodide. The title cyclopropenium salt **1c** was isolated as a light-yellow solid in 98% yield (1.76 g, 2.95 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 3.92 (p, *J* = 6.9 Hz, 4H), 3.61 (q, *J* = 7.2 Hz, 2H), 3.29 (s, 3H), 1.40 (d, *J* = 6.9 Hz, 24H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 119.29, 117.12, 51.54, 49.79, 39.65, 22.25, 13.59. MS (ESI-MS, m/z): Calc. for $C_{18}H_{36}N_3^+$: 294.29. Found: 294.2917.



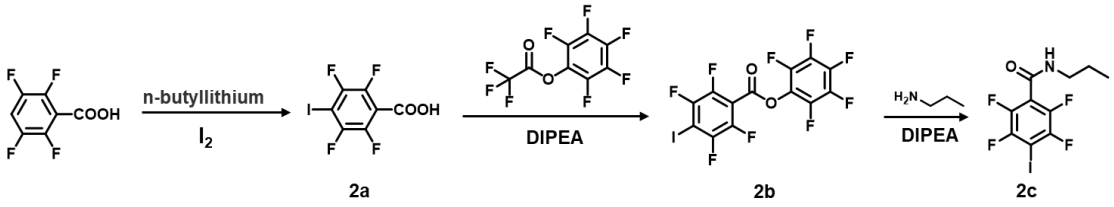
1d **1e**

1e: This procedure was performed open to the atmosphere. Linear polyethyleneimine (M_n=10000) (1.00 g, 23.3 mmol, 1.0 equiv) was dissolved in chloroform (15.0 mL) in a scintillation vial. To the vial was added DIPEA (9.00 g, 70.0 mmol, 3.0 equiv) and the 1a (10.8 g, 35.0 mmol, 1.50 equiv). The reaction mixture was allowed to stir overnight at 65 °C. The resulting solution was concentrated

in vacuo and then dissolved in water and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against methanol. The resulting solution was concentrated under vacuum to yield **1d** a yellow-brown powder (1.20 g, 60% yield). **1e** was synthesized with **1d** through the similar procedure of **1c**. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.45~3.15 (b, 1860H, $(CH_2CH_2N)_{230}$, $NCH(CH_3)_2$), 1.90-0.65 (5501H, $NCH(CH_3)_2$).



1g: A round bottom flask was charged with 40 mL of DCM and pentachlorocyclopropane (1.00 mL, 7.00 mmol). The flask was cooled to 0 ℃ and pyrrolidine (4.70 mL, 56.0 mmol) was added dropwise. The reaction was stirred for 1 h at 0 ℃ and then for 24 h at rt. The reaction was transferred to a separatory funnel and washed with twice with 1M HCl (20 mL) and brine (20.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give **1f** as a yellow solid, which was carried to the next step without further purification (2.13 g, 6.58 mmol, 94% yield). **1g** was synthesized with **1f** through the similar procedure of **1c**. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 3.52~3.55(m, 1H), 2.02~2.06(m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 113.88, 50.99, 25.88; MS (ESI-MS, m/z): Calc. for $C_{15}H_{24}N_3^+$ $[M]^+$: 246.1964. Found $[M]^+$:.246.1966.

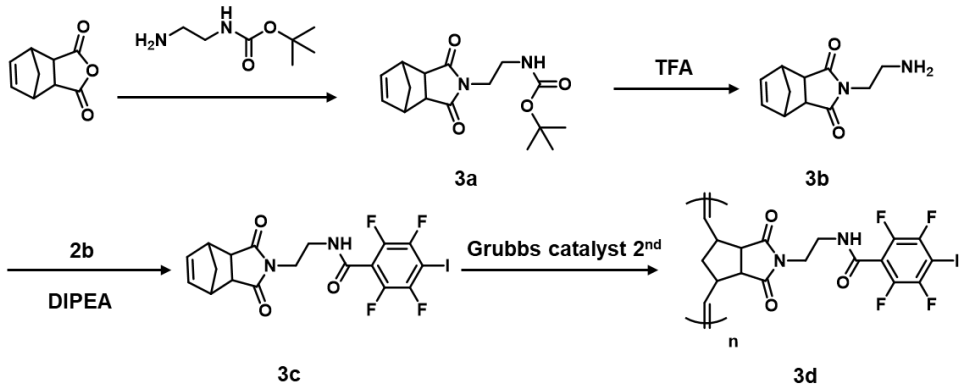


2a: 2a was synthesized according to the reported procedure[2]. Spectral data agreed with those reported in the literature.

2b: A 100 mL round bottom flask was charged with DCM (20.0 mL), **2a** (960 mg, 3.00 mmol, 1.00 equiv), and DIPEA (465 mg, 3.60 mmol, 1.20 equiv). To the mixture, pentafluoro phenyl trifluoroacetate (336 mg, 1.20 mmol, 1.20 equiv) was added. The reaction was stirred for 3 h. Solvents removed under reduced pressure. The crude was purified by silica gel chromatography (Petroleum ether/DCM = 95/5) to give pure **2b** as a white solid (1.2 g, 2.5 mmol, 90%). ^{19}F NMR

(376 MHz, $CDCl_3$): δ(ppm) = -117.03 (q, *J* (C, F) = 9.1 Hz), -134.59 (q, *J* (C, F) = 9.1 Hz), -151.53 (d, *J* (C, F) = 17.9 Hz), -155.97 (t, *J*(C, F) = 21.6 Hz), -161.17 (dd, *J* (C, F) = 21.6, 17.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 155.63, 148.83, 146.86, 145.76, 143.75, 142.02, 141.28, 140.01, 139.11, 137.08, 124.27, 109.78, 80.14.

2c: A 100 mL round bottom flask was charged with DCM (20.0 mL), **2b** (1.20 g, 2.50 mmol, 1 equiv), and DIPEA (388 mg, 3.00 mmol, 1.20 equiv). To the mixture, Propylamine (148 mg, 2.50 mmol, 1.00 equiv) was added. The reaction was stirred overnight. Solvents removed under reduced pressure. The crude was purified by silica gel chromatography (Petroleum ether/DCM = 85/15) to give pure **2c** as a white solid in 90% yield (850 mg, 2.35 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ(ppm) = 5.93 (br,1H, NHCO), 3.45 (q, *J* = 6.9 Hz, 2H), 1.65 (q, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) = -118.35~-118.43 (m, 2F, *J* (C, F) =11.9Hz), -139.28~-134.37(m, 2F, *J* (C, F) = 11.9Hz). 157.98, 148.24, 146.27, 144.14, 141.91, 117.11, 42.1, 22.64, 11.28. MS (ESI-MS, m/z): Calc. for $C_{10}H_8F_4INO$ $(M+Na)^+$: 383.9479. Found $(M+Na)^+$: 383.9488.



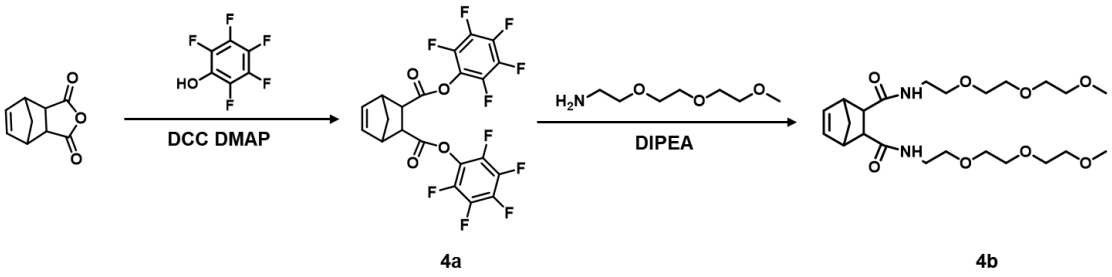
3a: Cis-5-Norbornene-exo-2,3-dicarboxylic anhydride (3.00 g, 18.3 mmol), N-Boc-Ethylenediamine (3.52 g, 22.0 mmol, 1.00 equiv), and triethylamine (2.23 g, 22.0 mmol, 1.00 equiv) were mixed with 80 mL toluene in a 250 mL round-bottom flask fitted with a Dean-Stark apparatus. After refluxing the reaction for around 12 h, the reaction solution was cooled and concentrated. The resulting crude solid was then dissolved in DCM (150 mL) and washed by 1M HCl. After drying the DCM phase by anhydrous Na_2SO_4, the DCM was evaporated to produce **3a** as the white solid product in a yield of 80% (4.48 g, 14.6 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ(ppm) = 6.29 (s, 2H), 4.77(br, 1H, NHCO), 3.66 ~ 3.60 (m, 2H), 3.38 ~ 3.31 (m, 2H), 3.28 (s, 2H), 2.70 (s, 2H), 1.51 (d, *J* = 9.9 Hz, 1H), 1.41 (s, 9H), 1.25 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ(ppm) =

178.31, 155.97, 137.91, 79.55, 47.98, 45.23, 42.93, 39.17, 38.51, 28.40. MS (ESI-MS, m/z): Calc. for $C_{16}H_{22}N_2O_4$ $(M+Na)^+$: 329.1471. Found $(M+Na)^+$: 329.1483.

3b: A 100 mL round bottom flask was charged with DCM (20.0 mL), 3a (2.24 g, 7.32 mmol, 1.00 equiv). To the mixture, trifluoroacetic acid (TFA) (8.35 g, 73.2 mmol, 10.0 equiv) was added. The reaction was stirred for 6 h. Solvents and TFA were removed under reduced pressure. The organic layer was concentrated in vacuo and the solids were triturated with Et_2O, collected via filtration, and washed twice more with Et_2O to give **3b** as white solid (1.21 g, 5.87 mmol, 80 yield). ^{1}H NMR (500 MHz, CD_3OD): δ(ppm) = 6.34 (s, 2H), 3.79 ~ 3.77(t, 2H, *J*=10 Hz), 3.21 (s, 2H), 3.14 ~ 3.12 (t, 2H, *J*=10Hz), 1.52 ~ 1.50(dd, 1H, *J*=10Hz),1.26~1.24(dd, 1H, *J*=10 Hz). ^{13}C NMR (126 MHz, CD_3CN): δ(ppm) = 179.39, 138.7, 48.85, 45.88, 43.55, 39.08, 36.86. MS (ESI-MS, m/z): Calc. for $C_{11}H_{14}N_2O_2$ $(M+H)^+$: 207.1128. Found $(M+H)^+$: 207.1135.

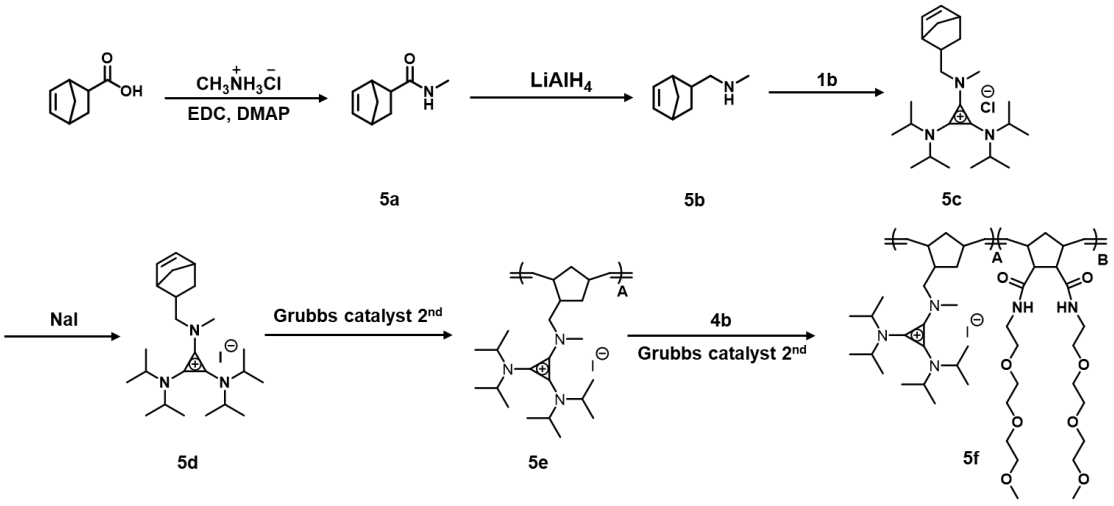
3c: A 100ml round bottom flask was charged with DCM (20 mL), 3b (1.21 g, 5.86 mmol,1.00 equiv) and DIPEA (907 mg, 7.03 mmol, 1.20 equiv). To the mixture 2b (2.85g, 5.86 mmol, 1.00 equiv) was added. The reaction was stirred overnight. Solvents was removed under reduced pressure. The crude was purified by silica gel chromatography (DCM) to give pure **3c** as a white solid (2.379 g, 4.68 mmol, 80%). ^{1}H NMR (500 MHz, Acetone-d_6): δ(ppm) = 7.99(br, 1H, NHCO), 6.32 (s, 2H), 3.71 ~ 3.67 (m, 2H), 3.65 (q, *J* = 5.3 Hz, 2H), 3.15 (s, 2H), 2.68 (s, 2H), 1.40 (s, 1H), 1.32 (s, 1H). ^{19}F NMR (376 MHz, Acetone-d_6): δ(ppm) = -121.61 ~ -121.79 (m), -141.27~-141.45(m). MS (ESI-MS, m/z): Calc. for $C_{18}H_{13}IF_4N_2O_3$ $(M+Na)^+$: 530.9799. Found $(M+Na)^+$: 530.9804.

3d: 3d were synthesized using ring-opening metathesis polymerization (ROMP). Grubbs catalyst 2nd (G_2) and 3c were respectively dissolved in a 25.0 mL Schlenk tube with 2.50 mL DMF. The pre-polymerization mixture was respectively brought into a nitrogen glovebox. The 3c solution was added to the catalyst G_2 solution at room temperature under N_2 while stirring vigorously. After reacting for 4h, the reaction was quenched by addition of 0.50 mL Ethyl Vinyl Ether (EVE). The mixture was concentrated and then precipitated in Et_2O to obtain **3d**. GPC/DMF for 3d(n=15): M_n=15 kDa, Đ=1.12. GPC/DMF for 3d(n=40) M_n=35.7 kDa, Đ(n=40) = 1.22.



4a: 4a was synthesized according to the reported procedure[3]. Spectral data were in agreement with those reported in the literature.

4b: A 100 mL round bottom flask was charged with DCM (20.0 mL), 4b (1.03 g, 2.00 mmol,1.00 equiv) and DIPEA (517 mg, 4.00 mmol, 4.00 equiv). To the mixture, 2-(2-(2-methoxyethoxy)ethoxy) ethanamine (326 mg, 4.00 mmol, 2.00 equiv) was added. The reaction was stirred for overnight. Solvents was removed under reduced pressure. The crude was purified by silica gel chromatography (DCM: MeOH= 98: 2) to give pure **4b** as a white solid in 90% yield (718 mg, 1.50 mmol). ^{1}H NMR (500 MHz, CD_3OD): δ(ppm) = 7.62 (br, 2H, NHCO), 6.23 (s, 2H), 3.62 (ddd, *J* = 7.1, 4.9, 2.8 Hz, 12H), 3.56 ~ 3.49 (m, 8H), 3.36 (s, 6H), 2.91 (s, 2H), 2.45 (s, 2H), 2.38 (d, *J* = 8.5 Hz, 1H), 1.41 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 173.28, 138.45, 71.97, 70.57~69.97, 59.06, 48.76, 45.23, 39.33. MS (ESI-MS, m/z): Calc. for $C_{23}H_{40}N_2O_8$ $(M+Na)^+$: 495.2677. Found $(M+Na)^+$: 495.2685.



5a: A 100 mL round bottom flask was charged with DCM (20 mL), DMAP (122 mg, 1.00 mmol, 0.100 equiv) and 5-Norbornene-2-carboxylic acid (1.38 g, 10.0 mmol, 1.00 equiv). To the mixture, Methylamine hydrochloride (676 mg, 10.0 mmol, 1.00 equiv), EDC (1.92 g, 10 mmol, 2.0 equiv)

was added. The reaction was stirred for 24 h. The mixture was washed by saturated $NaHCO_3$ solvent, brine. After dried by Na_2SO_4. Solvents was removed under reduced pressure. The crude was purified by silica gel chromatography (DCM: MeOH= 98: 2) to give pure **5a** as a white solid in 90% yield (718 mg, 1.5 mmol). ^{1}H NMR (500 MHz, CD_3OD): δ(ppm) = 6.25 ~ 6.21 (m, 1H), 5.97 ~ 5.92 (m, 1H), 3.98 ~ 3.88 (m, 4H), 3.25 (s, 4H), 3.15 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.86 (s, 2H), 2.58 ~ 2.48 (m, 1H), 1.97 ~ 1.89 (m, 1H), 1.53 ~ 1.48 (m, 1H), 1.40 ~ 1.32 (m, 24H), 1.31 ~ 1.22 (m, 1H), 0.60 (dd, *J* = 4.3, 2.6 Hz, 1H). ^{13}C NMR (126 MHz, CD_3OD): δ(ppm) =175.15, 137.83, 132.46, 50.12, 46.26, 44.86, 42.81,30.17, 26.40.MS (ESI-MS, m/z): Calc. for $C_9H_{13}NO$ $(M+Na)^+$: 174.0889. Found $(M+Na)^+$: 174.0893.

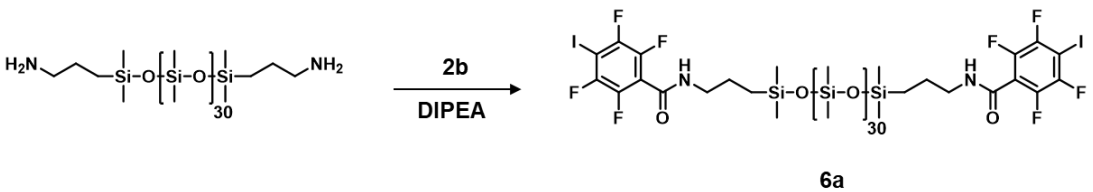
5b: A 100 mL round bottom flask was charged with dry THF (20.0 mL), $LiAlH_4$ (190 mg, 35.0 mmol, 5.00 equiv) under N_2 atmosphere at 0℃. 5a (1.06 g, 7.00 mmol,1.00 equiv) was dissolved by dry THF and the solution was slowly injected in the round bottom flask with a syringe. The reaction was stirred for 48 h. The mixture was quenched by water before 15% NaOH and water slowly were injected in the flask. The white solid was filtered and the filtrate was immediately used for next procedure without purification.

5d: A 100 mL round bottom flask was charged with DCM (20.0 mL), 1a (1.08 g, 3.50 mmol, 0.500 equiv) and DIPEA (1.80 g, 14.0 mmol, 2.00 equiv). To the mixture, the filtrate of **5b** (960 mg, 7.00 mmol, 1.00 equiv) was added dropwise. The reaction was stirred for overnight at 0℃. Solvents was removed under reduced pressure and the mixture was dissolved by DCM. Then the DCM layer was washed with 1M HCl (100 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash chromatography on silica gel, using DCM: MeOH (10:1) as eluent. 5c was isolated as a yellow solid in 61% yield (1.75 g, 4.27 mmol). Anion exchange was accomplished by mixing an acetone solution of the corresponding **5c** (1.75 g, 4.27 mmol, 1.00 equiv) with an acetone (15.0 mL) solution of sodium iodide (1.28 g, 8.54 mmol, 2.00 equiv). The reaction mixture was stirred at room temperature for 2 h. as sodium chloride was allowed to precipitate. The reaction mixture was then filtered, and an additional equivalent of sodium iodide was added to the filtrate. No further precipitation was observed over the course of 2 h. The reaction solution was then concentrated in vacuo to a solid mixture of cyclopropenium iodide and sodium iodide. Cyclopropenium iodide was extracted in pure form from this solid mixture with

dichloromethane followed by a water wash to remove trace sodium iodide. The title cyclopropenium salt **5d** was isolated as a light-yellow solid in 98% yield (2.1 g, 4.18 mmol). ^{1}H NMR (500 MHz, CD_3OD): δ(ppm) = 6.23 (dd, *J* = 5.7, 3.1 Hz, 1H), 5.94 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.92 (p, J = 6.9 Hz, 4H), 3.25 (s, 4H), 3.15 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.86 (s, 2H), 2.52 (dd, *J* = 12.1, 7.9, 4.0 Hz, 1H), 1.97 ~ 1.89 (m, 1H), 1.50 (d, *J* = 8.2 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 24H), 1.31 ~ 1.22 (m, 1H), 0.60 (dd, *J* = 11.7, 4.3, 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 138.75, 131.97, 120.05, 117.77, 59.08, 51.63, 49.97, 44.68, 42.38, 40.61, 38.05, 29.92, 22.38. MS (ESI-MS, m/z): Calc. for $C_{24}H_{42}N_3^+$ $(M)^+$:372.3373. Found $(M)^+$: 372.3392.

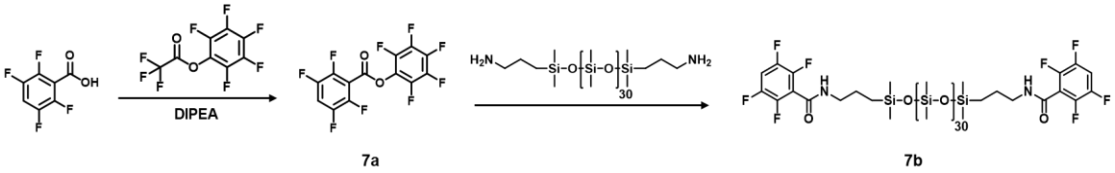
5e: A TACs based polymer was synthesized using ring-opening metathesis polymerization (ROMP). G_2 and **5d** were respectively dissolved in a 25.0 mL Schlenk tube with 2.50 mL DMF. The pre-polymerization mixture was respectively brought into a nitrogen glovebox. The **5d** solution was added to the catalyst G_2 solution at room temperature under N_2 while stirring vigorously. After a completed reaction monitored by ^{1}H NMR, the reaction was quenched by addition of 0.5 mL EVE. The mixture was concentrated and then precipitated in Et_2O to obtain in a yield of 90%. GPC/DMF for 5e(A=20): M_n=85.8 kDa, $Đ$=1.16. GPC/DMF for 5f (A=10, B=18): M_n=16.5 kDa, $Đ$=1.20.

5f: A block copolymer was synthesized using ring-opening metathesis polymerization (ROMP). G_2 and **5d** were respectively dissolved in a 25.0 mL Schlenk tube with 2.50 mL DMF. The pre-polymerization mixture was respectively brought into a nitrogen glovebox. The 5d solution was added to the G_2 solution at room temperature under N_2 while stirring vigorously. After a completed reaction monitored by ^{1}H NMR, **4b** dissolved in 1ml DMF was added to the completed reacted mixture. After a completed reaction monitored by ^{1}H NMR, the reaction was quenched by addition of 0.5 mL EVE. The mixture was concentrated and then precipitated in Et_2O to obtain in a yield of 90% (1.0 g, 90%).



6a

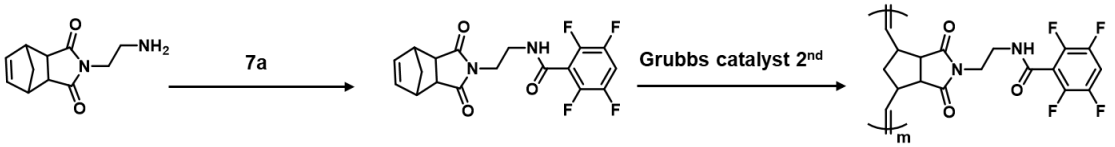
6a: A 100mL round bottom flask was charged with DCM (10.0 mL), poly(dimethylsiloxane)-[bis(3-aminopropyl) terminated] (1.00 g, 0.40 mmol, M_n=2500) and DIPEA (310 mg, 2.4 mmol), To the mixture, **2b** (389 mg, 0.8 mmol) was added. The reaction was stirred for overnight. Solvents was removed under reduced pressure. The mixture was concentrated and then precipitated in CH_3CN to obtain **6a** in a yield of 85%. (850 mg, 0.34 mmol). ^{1}H NMR (500 MHz, $CDCl_3$ without TMS): δ(ppm) = 5.96 (br, NHCO, 2H), 3.39(q, 4H, *J* = 6.8 Hz), 1.57~1.64(m, 4H, *J* = 10Hz), 0.51~0.54(m, 4H, *J* =15Hz), 0.01(m, 250H). ^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) = -118.13~-118.58 (m), -139.15~-139.45 (m).



7a 7b

7a: 7a (90% yield) was synthesized through the similar procedure of **2b** with 2, 3, 5, 6-tetrafluoro benzoic acid. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 7.43 ~ 7.33(m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) = -135.98 ~ -136.14 (m, 2F), -136.24 ~ -136.38 (m, 2F), -151.60 ~ -151.77 (m, 2F), -156.11 ~ -156.32 (m, 1F), -161.29~-161.49 (m, 2F). MS (ESI-MS, m/z): Calc. for $C_{13}HF_9O_2$ $[M]^+$:359.9827. Found $[M]^+$: 360.3244.

7b: 7b (85% yield) was synthesized through the similar procedure of **6b** with **7a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 7.16 ~ 7.06 (m, 1H), 3.46 (q, *J* = 6.7 Hz, 2H), 1.69 ~ 1.61 (m, 2H), 0.61 ~ 0.55 (m, 2H), 0.14 (s, 204H). ^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) = -137.06~ -137.21 (m, 2F), -141.15 ~ -141.32 (m, 2F).



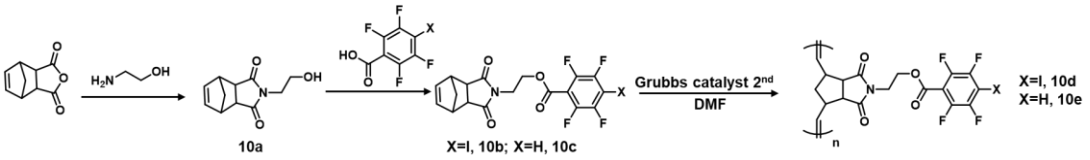
8a 8b

8a: 8a(90%, yield) was synthesized through the similar procedure of **3b** with **7a**. ^{1}H NMR (500 MHz, Acetone-d_6): δ(ppm) = 7.98 (br, 1H), 7.61 ~ 7.54(m, 1H), 6.29(s, 1H), 3.65 ~ 3.67(m, 2H), 3.6~3.63(m, 2H), 3.12(s, 2H), 2.65(s, 2H), 1.37 ~ 1.39(dd, *J* = 10Hz, 1 H), 1.27 ~ 1.29(dd, *J* = 10Hz

1H).[19]F NMR (376 MHz, Acetone-d_6): δ(ppm) = -139.96(m, 2F), -143.46(m, 2F). [13]C NMR (126 MHz, Acetone-d_6) δ(ppm):178.66, 158.65, 147.02, 145.02, 144.53, 142.49, 137.91, 116.81, 107.74, 48.02, 45.29, 42.93, 39.78, 37.61. MS (ESI-MS, m/z): Calc. for $C_{18}H_{14}F_4N_2O_3$ $(M+Na)^+$:405.0833. Found $(M+Na)^+$: 405.0847. GPC/DMF for 8b(m=15): M_n=23.6 kDa, $Đ$=1.81. GPC/DMF for 8b (m=40) : M_n=57.17 kDa, $Đ$=1.27.

8b: 8b (90%, yield) was synthesized through the similar procedure of **5e** with **8a** and G_2.

9a: 9a (90%, yield) was synthesized through the similar procedure of **3d** with 1,6-hexanediamine and **2b**. [1]H NMR (500 MHz, Acetone-d_6): δ(ppm) = 7.92(br, 2H), 3.41 (q, J = 6.9 Hz, 4H), 1.65~1.58 (m, 4H), 1.47~1.41(m, 4H). [19]F NMR (376 MHz, Acetone-d_6): δ(ppm) = -121.74(m, 2F), -142.09(m, 2F). MS (ESI-MS, m/z): Calc. for $C_{20}H_{14}F_8I_2NO_2$ $(M+Na)^+$:742.8909. Found $(M+Na)^+$: 742.8933.



10a: 10a (90%, yield) was synthesized according to the literature with cis-5-norbornene-exo-2,3-dicarboxylic anhydride and 2-aminoethanol. [4] Spectral data were in agreement with those reported in the literature.[4]

10b/10c: To a solution of 10a (414 mg, 2.00 mmol) and 2a (640 mg, 2.00 mmol) in CH_2Cl_2 (12.0 mL) were added DMAP (24.0 mg, 0.20 mmol) and EDC (3.00 mmol). The reaction mixture was stirred at room temperature for 24 h, then washed with 5% aqueous HCl (15.0 mL), 5% aqueous $NaHCO_3$ (20.0 mL), H_2O (20.0 mL), and brine (20.0 mL), and dried (Na_2SO_4). Purification by flash chromatography (DCM/EtOAc=99/1) afforded **10b** in 80% yield as a white powder. [1]H NMR (500 MHz, $CDCl_3$): δ(ppm) = 6.27 (s, 2H), 4.53 (s, 2H), 3.88 (s, 2H), 3.26 (s, 2H), 2.70 (s, 2H), 1.50 (dd, J = 9.9 Hz, 1H), 1.26 (dd, J = 9.9 Hz, 1H).[19]F NMR (376 MHz, $CDCl_3$): δ(ppm) = -118.18~-118.36 (m), -136.63~-136.77 (m). [13]C NMR (126 MHz, $CDCl_3$) δ(ppm):177.89, 159.33, 146.55, 137.92,

63.04, 47.96, 45.31, 42.84, 37.32.

10c was synthesized through the similar procedure of **10b** with 2,3,5,6-tetrafluorobenzoic acid and 10a. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 7.23 ~7.14 (m, 1H), 6.25 (s, 2H), 4.52 (t, 2H), 3.87 (t, 2H), 3.23 (s, 2H), 2.69 (s, 2H), 1.47 (dd, *J* = 11.4 Hz, 1H), 1.25 (dd, *J* = 9.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ(ppm) = -137.06 ~ -137.20 (m), -138.61~-138.68 (m). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.85, 159.44, 137.89, 111.01, 62.88, 47.93, 45.93, 42.81, 37.29.

10d/10e: 10d/10e (90%, yield) was synthesized through the similar procedure of **5e** with **10b/10c** and G_2. GPC/DMF for 10d(m=27): M_n=23.9 kDa, $Đ$=1.37. GPC/DMF for 10e (n=35): M_n=21.1 kDa, $Đ$=1.33.

3. Experimental Conditions.

^{19}F NMR Titrations:

Job plot for TFAI/TACE-I. According to those reported in the literature[5], Job plot for the TFAI/TACE-I blend was created using ^{19}F NMR by plotting $|\Delta\delta\cdot\chi|$ against χ. For each tested sample, the total concentration of [TFAI+TACE-I] was 5mM in acetone-d_6. χ was the concentration percentage of TACE-I. The chemical shifts of the signals near -121.78 ppm were tracked. $|\Delta\delta|$ was the changes in chemical shift ($|\Delta\delta|$) relative to -121.78 ppm.

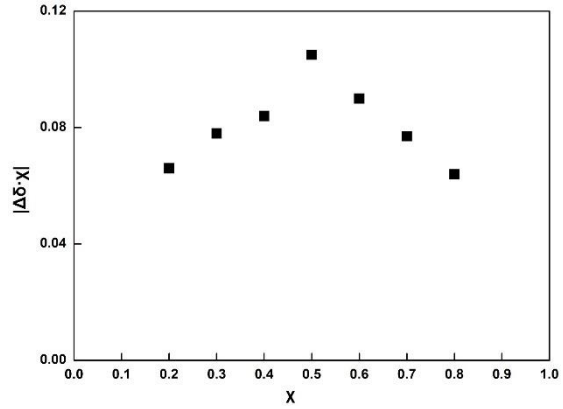


Figure S1: Job Plot of $|\Delta\delta\cdot\chi|$ against χ for the ^{19}F NMR titration of TFAI with TACE-I.

Association constant of TACE-I/TFAI and pTACE-1/TFAI. According to those reported in the literature[5,6], a parent solution of the TFAI (1mM of iodo groups, halogen bond (XB) donors) was first prepared in acetone. This parent solution was then used to prepare a solution of TACE-I or pTACE-1 (XB acceptors). The samples for titration were then prepared by mixing the two solutions

in varying proportions using a syringe. The chemical shifts of the signals near -121.78 ppm were tracked. Changes in chemical shift (|Δδ|) relative to -121.78 ppm and XB acceptors concentration (concentration of iodide ions) were curve fitted using web software (supramolecular.org) in order to solve for the association constants (K_a) using a 1:1 binding stoichiometry of iodo groups and iodide ions according to the Job's plot (Figure S1).

Association constant of NaI/TFAI and DMIM-I/TFAI. A parent solution of the TFAI (4 mM of iodo groups, XB donors) was first prepared in acetone. This parent solution was then used to prepare a solution of NaI or DMIM-I (XB acceptors). The samples for titration were then prepared by mixing the two solutions in varying proportions using a syringe. The chemical shifts of the signals near -121.78 ppm were tracked. Changes in chemical shift (|Δδ|) relative to -121.78 ppm and XB acceptors concentration (concentration of iodide ions) were curve fitted using web software (supramolecular.org) in order to solve for the association constants (K_a) using a 1:1 binding stoichiometry of iodo groups and iodide ions.

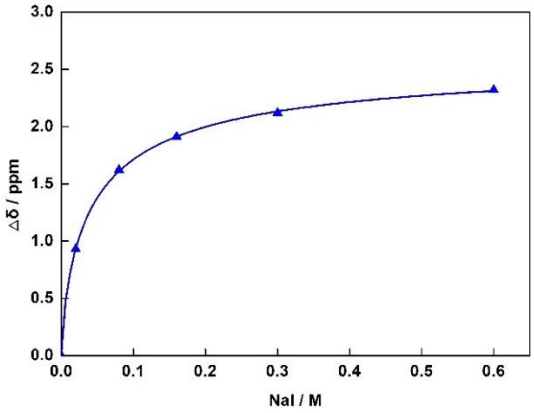


Figure S2: NMR titration curves obtained from titrating TFAI with NaI (K_a=29.6 M^{-1}).

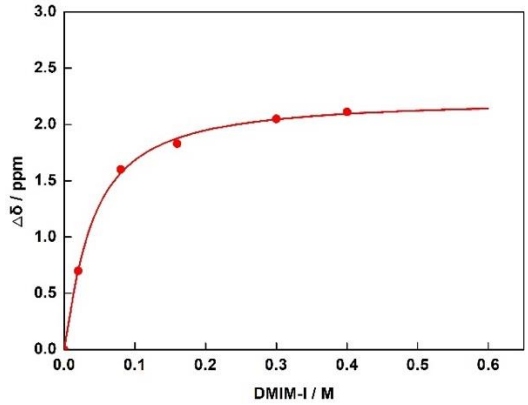


Figure S3: NMR titration curves obtained from titrating TFAI with DMIM-I (K_a=24.3 M^{-1}).

^{13}C NMR Titrations:

Similar to those ^{19}F NMR Titrations, a parent solution of the TFAI (200 mM of iodo groups, halogen bond (XB) donors) was first prepared in acetone. TACE-I (XB acceptors) was added to the parent solution. The samples for titration were then prepared by mixing the two solutions in varying proportions using a syringe. The chemical shifts of the signals near 74.23 ppm were tracked.

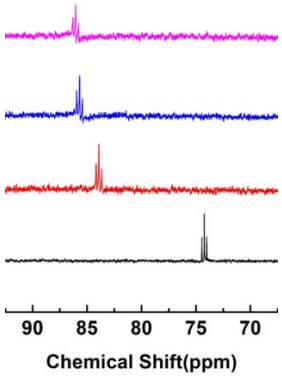


Figure S4: ^{13}C NMR titration curves obtained from titrating TFAI with TACE-I. (TFAI/TACE-I=1/0, black, 1/1, red, 1/2, blue, 1/3, pink).

^{1}H NMR Titrations:

Similar to those ^{19}F NMR Titrations, a parent solution of the TFAH (2 mM of hydrogen groups) was first prepared in acetone. TACE-I was added to the parent solution. The samples for titration were then prepared by mixing the two solutions in varying proportions using a syringe. The chemical shifts of the signals near 7.90 ppm were tracked.

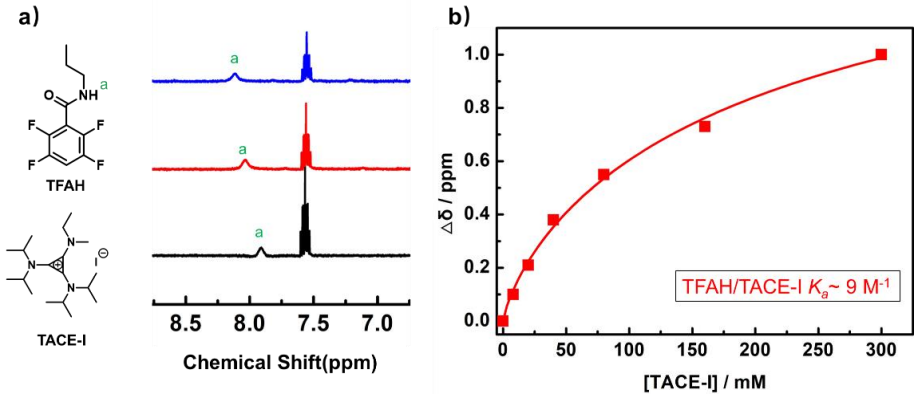


Figure S5: a) ^{1}H NMR spectra recorded upon titrating TACE-I into TFAH (signals from the fluoro-substituents neighboring the iodo-substituent; ratio of TACE-I increases from bottom to top); b) titration curves obtained from titrating TFAH with TACE-I.

The synthesis of TFAI/TACP-I adduct. Mixing TFAI (361 mg, 1.0 mmol) and TACP-I (373 mg, 1.00 mmol) in dichloromethane (1.00 mL) then dropwise adding into diethyl ether resulted a precipitate after 2 h, which was identified to be the adduct of TFAI and TACP-I with a 1:1 stoichiometry. TFAI itself is highly soluble in diethyl ether, which indicates the strong complexation between TFAI and TACP-I. Yield: 81% (white solid); ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm)= 3.61~3.58 (m, 12H), 3.49~3.42 (m, 2H), 2.1~2.04 (m, 12H), 1.69~1.62 (m, 2H), 1.0(t, *J* = 7.4Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm)= -118.17~-118.43(m, 2F), -139.08~-139.42(m, 2F)

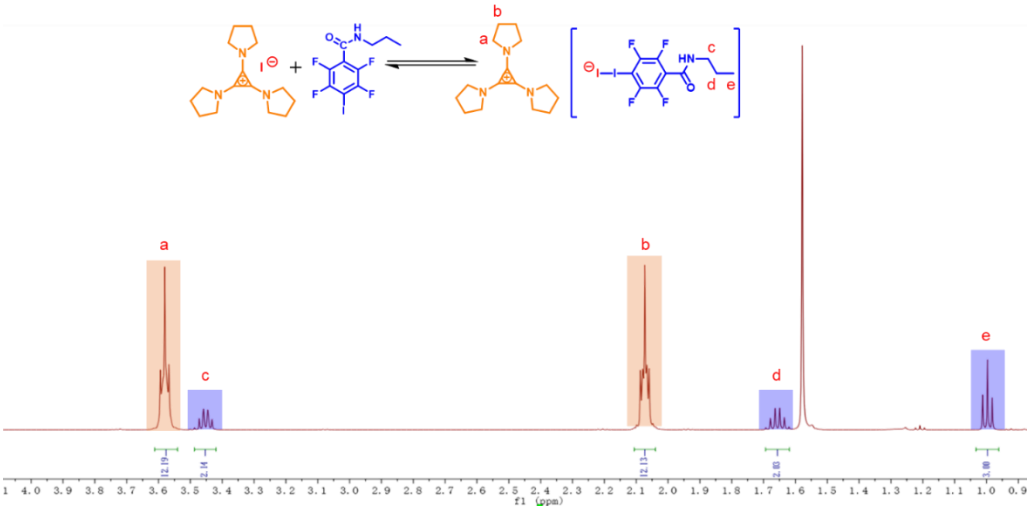


Figure S6: ^{1}H NMR spectrum of TFAI/TACP-I adduct.

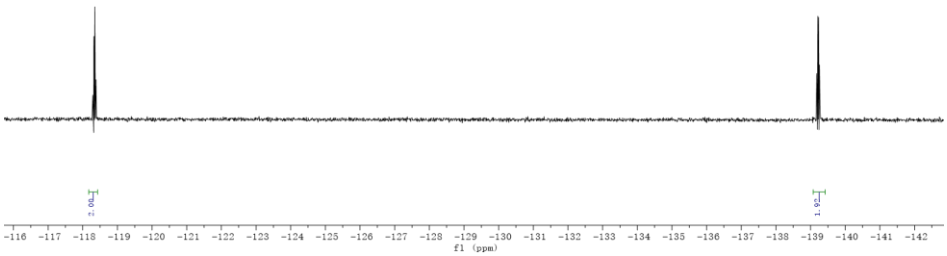


Figure S7: ^{19}F NMR spectrum of TFAI/TACP-I adduct.

Crystal structure analysis:

Suitable crystal for single-crystal X-ray diffraction were obtained by crystallization from CH_2Cl_2/Et_2O. The single-crystal X-ray diffraction experiment was carried out on a Supernova diffractometer with PHOTON III CMOS detector at 150 K.

Comparison of TAC-based polymer, TFAI(H) based dimer/polymers and their mixture:

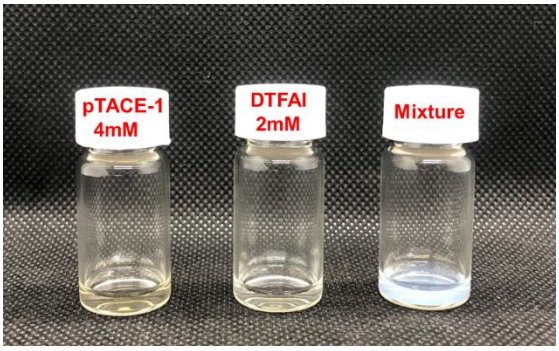


Figure S8: Appearance of pTACE-1(4.0 mM of iodide ions), DTFAI (2.0 mM of iodo groups) and their mixture in acetone at room temperature.

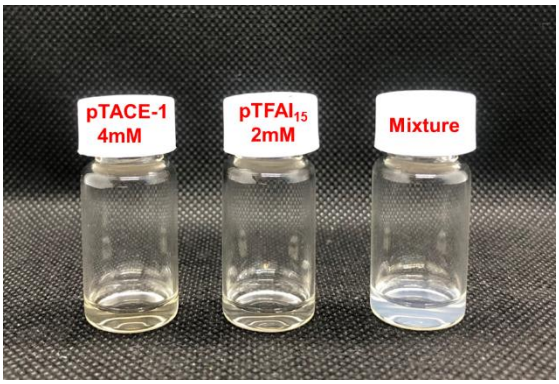


Figure S9: Appearance of pTACE-1(4.0 mM of iodide ions), $pTFAI_{15}$ (2.0 mM of iodo groups) and their mixture in acetone at room temperature.

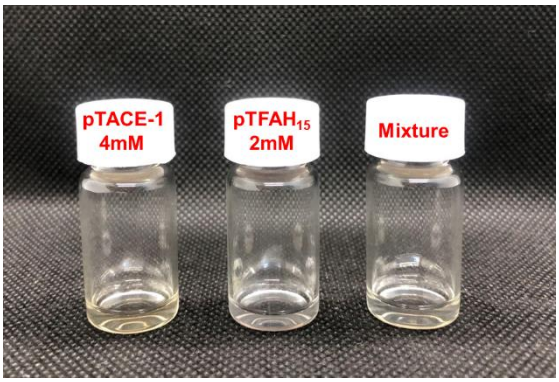


Figure S10: Appearance of pTACE-1 (4.0 mM of iodide ions), $pTFAH_{15}$ (2.0 mM of hydrogen groups) and their mixture in acetone at room temperature.

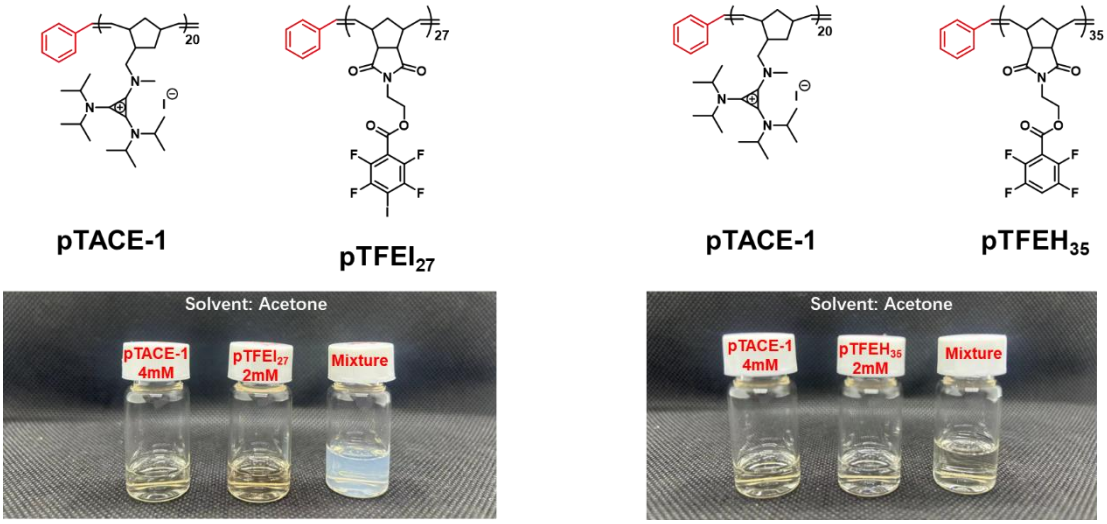


Figure S11: Appearance of pTACE-1(4.0 mM of iodide ions), $pTFEI_{27}$ (2.0 mM of hydrogen groups), $pTFEH_{35}$ and their mixture in acetone at room temperature.

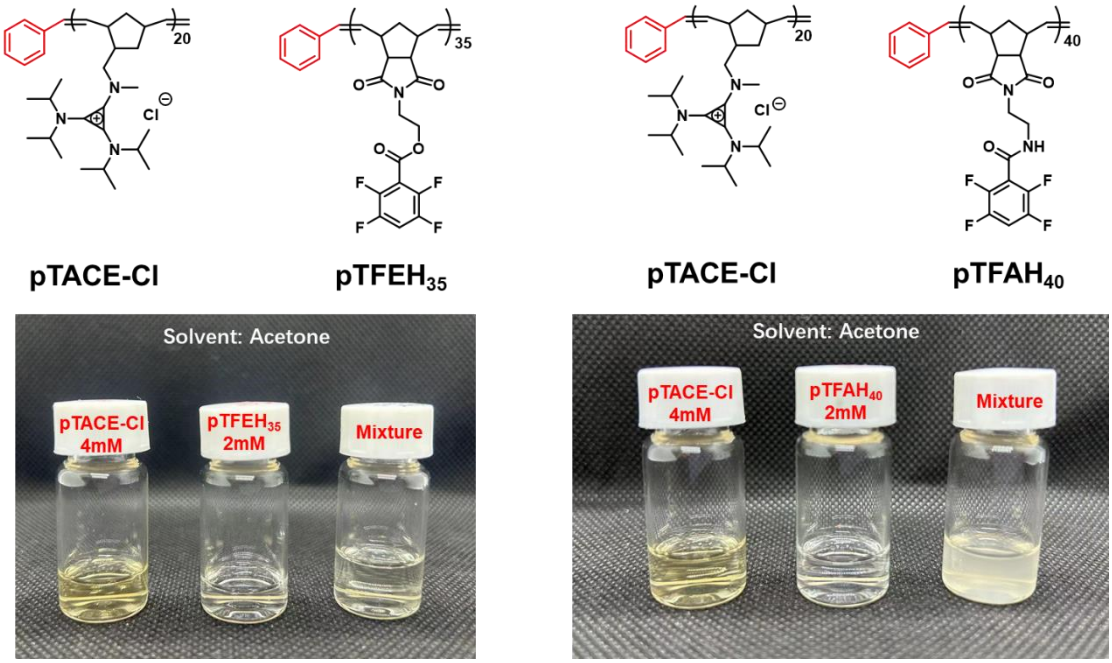


Figure S12: Appearance of pTACE-Cl (4.0 mM of chloride ions), $PTFEH_{35}$ (2.0 mM of hydrogen groups), $pTFAH_{40}$ (2.0 mM of hydrogen groups) and their mixture in acetone at room temperature.

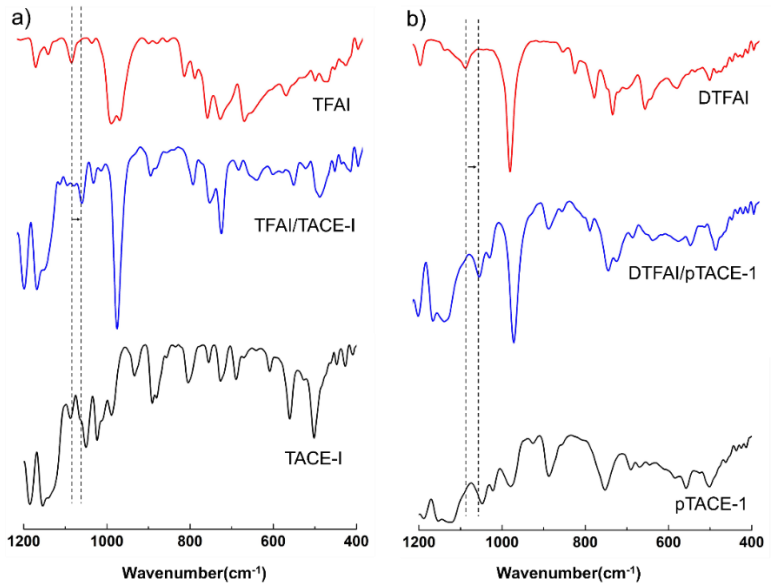


Fig. S13: FT-IR (1200~400 cm^{-1}) of model molecules, dimer, macromolecules and their blends (1:1).

DLS data of pTACE-2/pTFAI$_{15}$ assemblies:

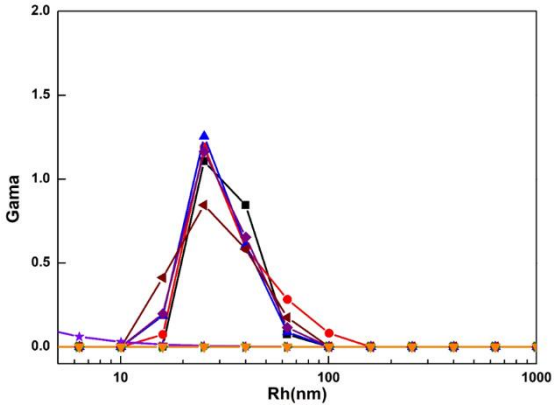


Figure S14: DLS data of pTACE-2/pTFAI$_{15}$ assemblies with the ratio of 0.2:1.0(◀, brown), 0.4:1.0(◆, purple), 0.6:1.0(▲, blue), 0.8:1.0(●, red), 1.0 :1.0(■, black), pTACE-2 (1.4mM of iodide ions, ▶, green), pTFAI$_{15}$ (1.4mM of iodo groups, ★, orange), and pTFAH$_{15}$ (1.4mM of hydrogen groups, ▼, violet) in acetone solution, respectively.

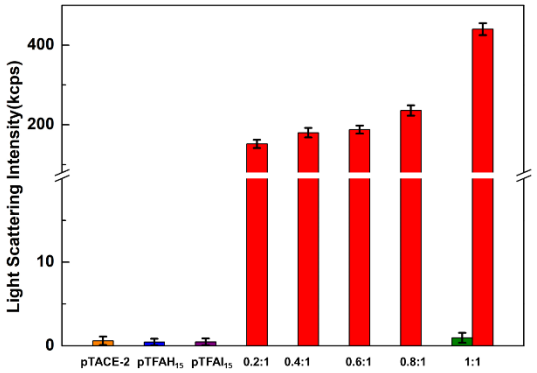


Figure S15: Light scattering intensity of pTACE-2/pTFAI$_{15}$ assemblies of 0.2:1.0, 0.4:1.0, 0.6:1.0, 0.8:1.0, 1.0:1.0 ratio of iodide ions/iodo groups (red), the control sample pTACE-2/pTFAH$_{15}$ of 1.0:1.0 of iodide ions/hydrogen groups(green), pTACE-2 (1.4mM of iodide ions, orange), and pTFAI$_{15}$(1.4mM of iodo groups, blue), pTFAH$_{15}$ (1.4mM of hydrogen groups, purple) in acetone, respectively.

Hydrophilic treatment of quartz crystal plate. Ultrasonic treatment was used for the pretreatment of quartz crystal plate in acetone, anhydrous ethanol and ultra-pure water successively for 5 min. After rinsed with ultra-pure water and dried with pure nitrogen, the quartz crystal plate were treated hydrophilically in a solution of (H_2SO_4): (H_2O_2) = 7:3 for 1 h. Then the quartz crystal plate was rinsed with ultra-pure water and dried with pure nitrogen.

Layer-by-layer (LbL) assembly. According to the literature[7]. LbL assembly of pTACE-3 and $pTFAI_{40}$ (around 40 units per chain) was carried out in acetone solution. An OH-tailored substrate of quartz crystal plate was first immersed in pTACE-3 solution (1.9 mM of repeat units) for 10 min. After being rinsed three times in the solvent (1 min each time) and dried in the ambient atmosphere, a pTACE-3-covered substrate was obtained. Then the substrate was immersed in $pTFAI_{40}$ solution (1.9 mM of repeat units) for 10 min, resulting in a polymer $pTFAI_{40}$ covered substrate. By repeating the above two steps in a cyclic fashion, we obtained a (pTACE-3 and $pTFAI_{40}$)$_n$ multilayer film, where n is the bilayer number. As a control, pTACE-3/$pTFAH_{40}$ (without XB donors) multilayer films were prepared by the same procedure above.

UV-vis spectra of the control multilayer films:

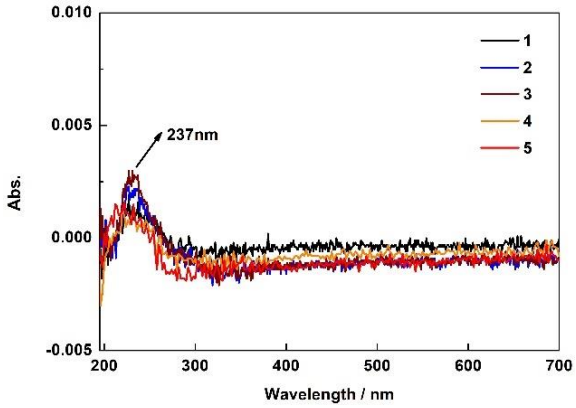


Figure S16: UV-vis spectra of [pTACE-3/$pTFAH_{40}$]$_n$ multilayer films.

Supplementary data for PDMS-DI/pTACE-3 blend:

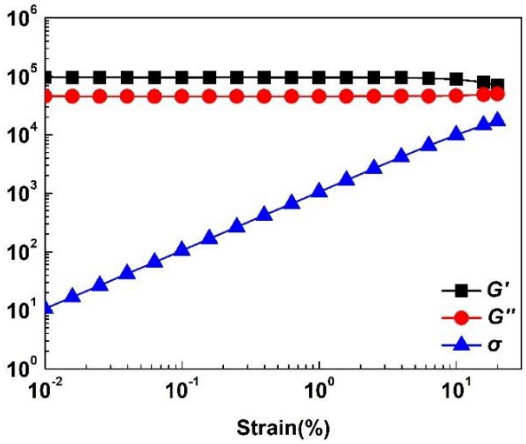


Figure S17: The curve of stress(σ)-strain to determine the strain range for rheological test of PDMS-DI/pTACE-3 blend(1/0.6).

PDMS-DI/pTACE-3 blend was characterized by temperature-sweep analysis for twice. The modulus curves at 25℃-75℃ are basically consistent, indicating that the blends have relatively stable rheological properties.

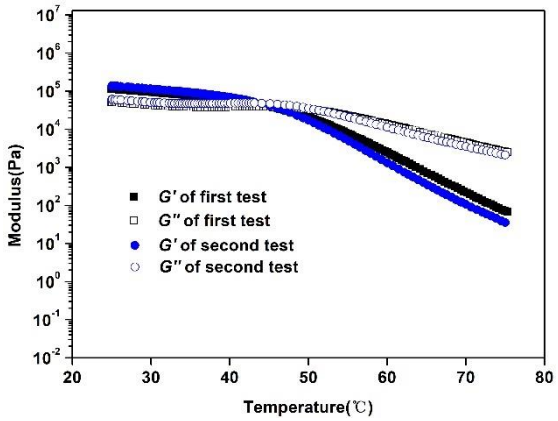


Figure S18: Two tests about temperature dependence of storage modulus (*G′*) and loss modulus (*G″*) for PDMS-DI/pTACE-3 blend (1.0 : 0.4 ratio of XB donor/acceptor groups). The experiments were performed at 6.28 rad/s at a strain of 1.0%.

Results exhibit a smooth curve of δ vs the complex modulus(*G**) curve in the range of performed temperature, indicating that the weak bonds (XB) have the same temperature dependence, and the physical mixtures showed this thermorheologically simple behavior[8].

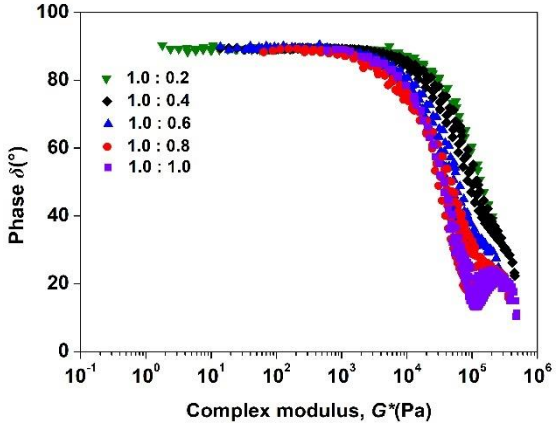


Figure S19: Relationship between *G** and phase angle δ of PDMS-DI/pTACE-3 blend with different ratio of XB donor/acceptor groups.

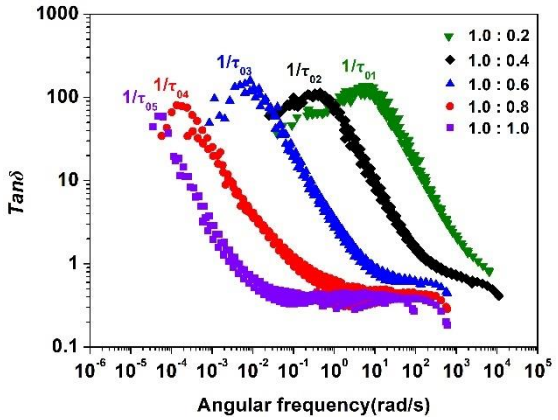


Figure S20: Frequency dependence of loss factors tanδ of PDMS-DI/pTACE-3 complexes with different ratio of XB donor/acceptor groups following TTS (Reference temperature=25 ℃).

Table S1 The rheological parameters of PDMS-DI/pTACE-3 blends

PDMS-DI/pTACE-3	**1.0:0.2**	**1.0:0.4**	**1.0:0.6**	**1.0:0.8**	**1.0:1.0**
C_1	6.55	8.60	12.27	16.66	30.91
C_2(K)	146.55	155.53	183.75	257.19	384.10
E_a (kJ/mol)	77.05	94.28	106.73	130.54	140.69

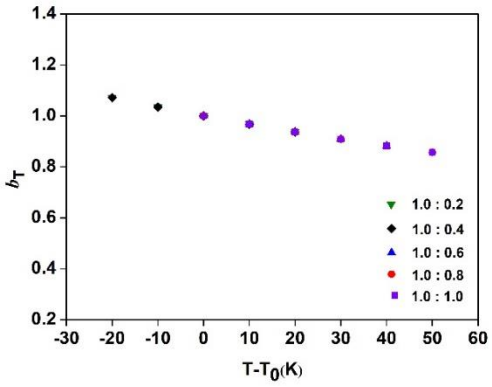


Figure S21: Time-temperature vertical shift factor(b_T) of PDMS-DI/pTACE-3 complexes with different ratio of XB donor/acceptor groups as a function of temperature. (Reference temperature T_0 = 25 ℃).

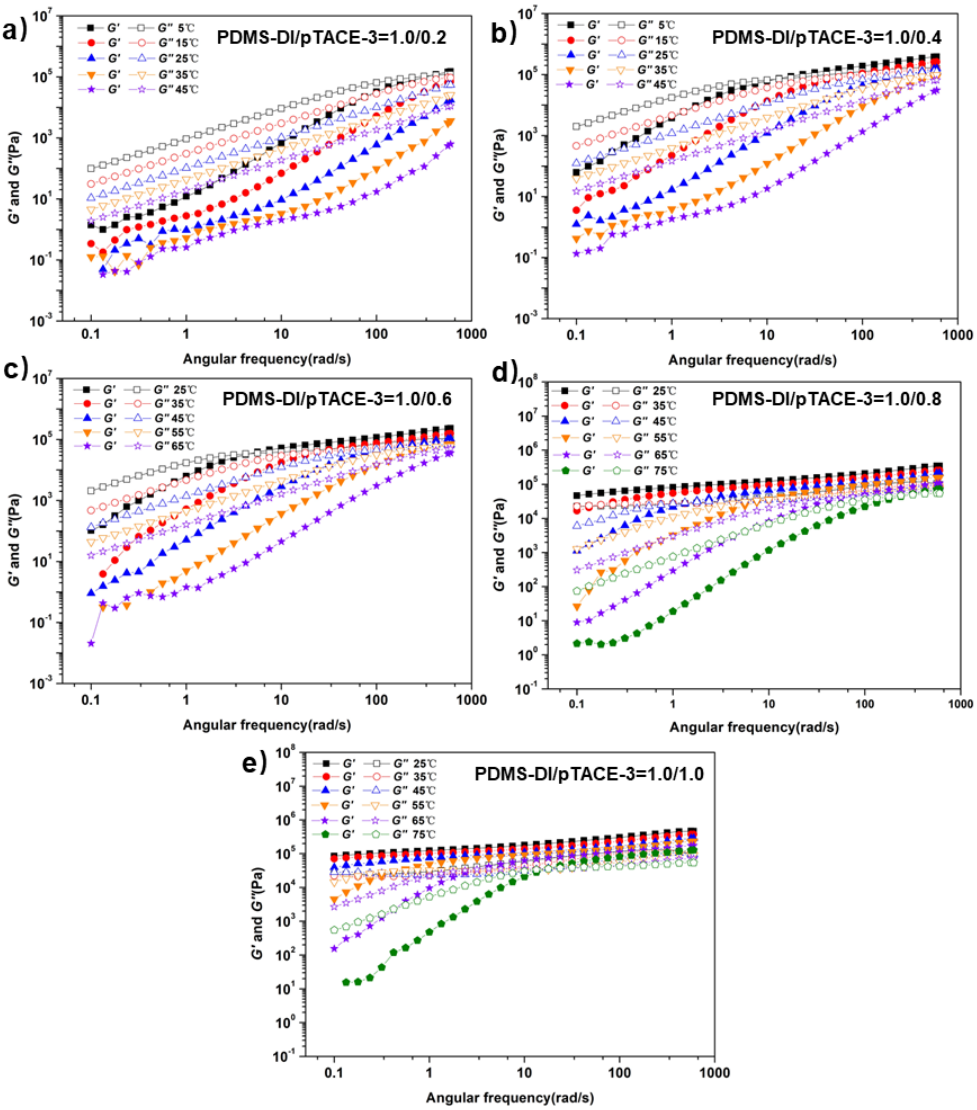


Figure S22: SAOS raw data for blends of PDMS-DI/pTACE-3 with different ratio of XB donor/acceptor groups. The storage modulus (*G′*) and loss modulus (*G″*) for PDMS-DI/pTACE-3=(a)1.0 : 0.2; (b)1.0 : 0.4; (c)1.0 : 0.6; (d)1.0 : 0.8; (e)1.0 : 1.0 under different temperature.

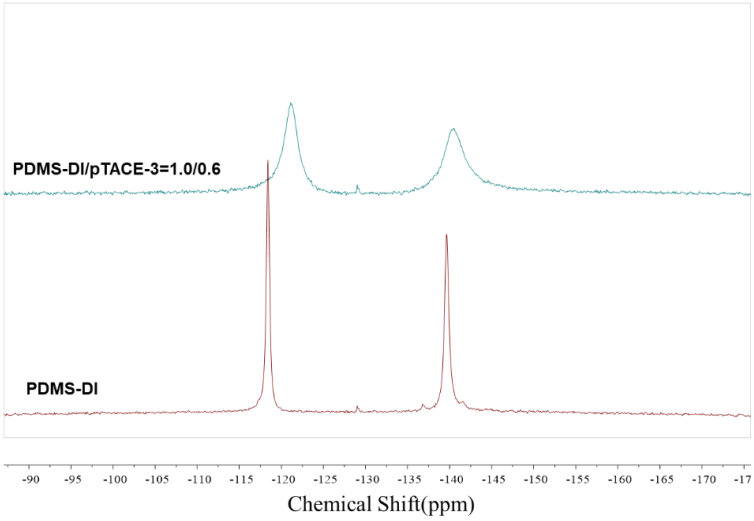


Figure S23: ^{19}F NMR of PDMS-DI and PDMS-DI/pTACE-3(1.0/0.6) blends.

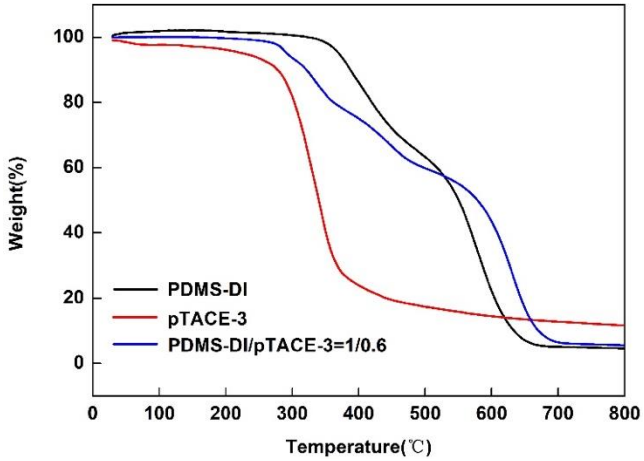


Figure S24: TGA results of pure PDMS-DI, pTACE-3 and PDMS-DI/pTACE-3 blends with XB donor/acceptor groups (1.0/0.6).

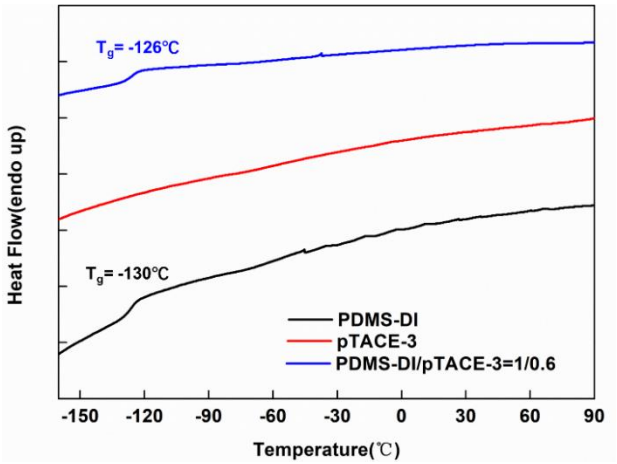


Figure S25: DSC results of pure PDMS-DI, pTACE-3 and PDMS-DI/pTACE-3 blends with XB donor/acceptor groups (1.0/0.6).

4. Appendix

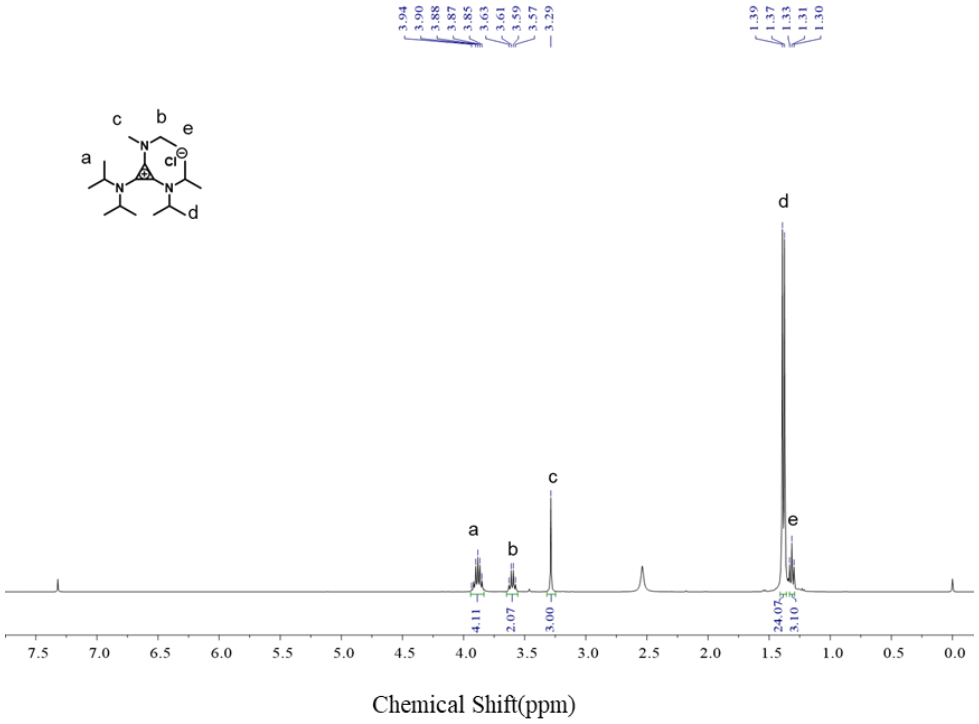


Figure S26: ^{1}H NMR spectrum of 1b.

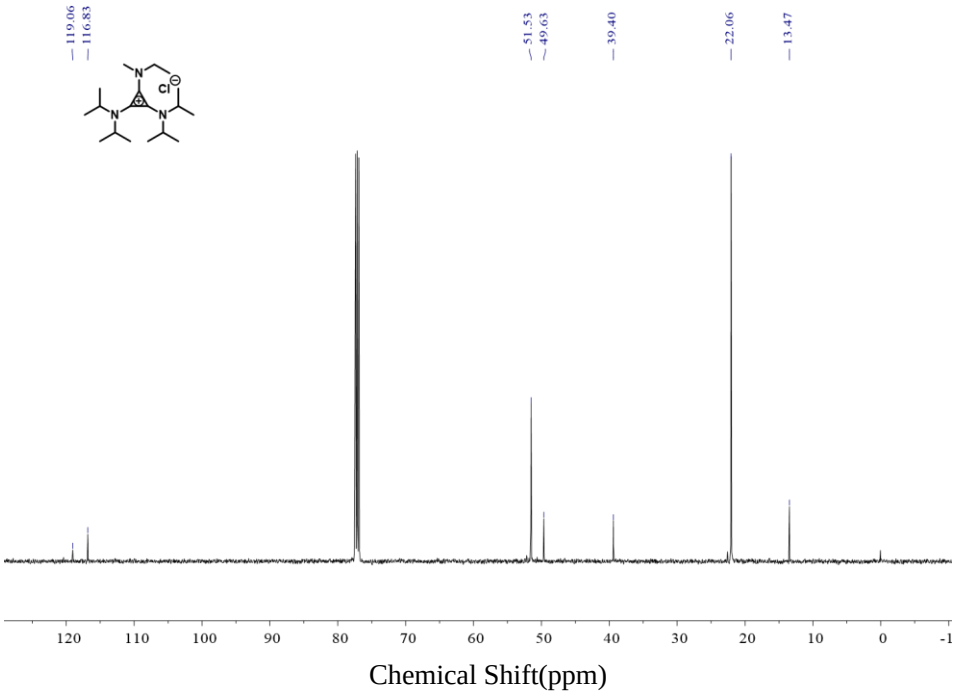


Figure S27: ^{13}C NMR spectrum of 1b.

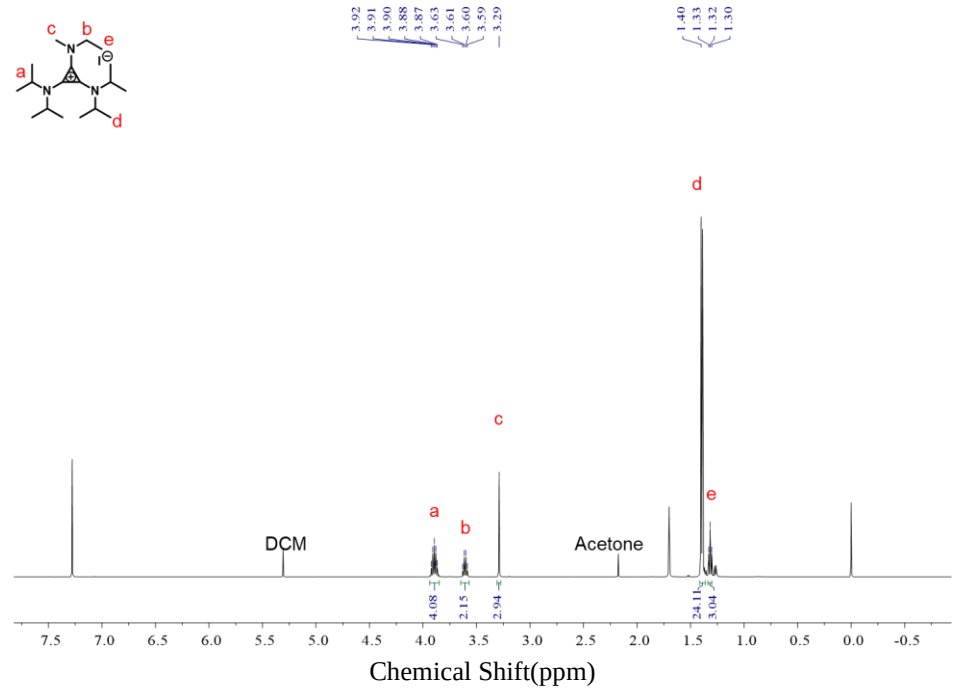


Figure S28: ^{1}H NMR spectrum of 1c.

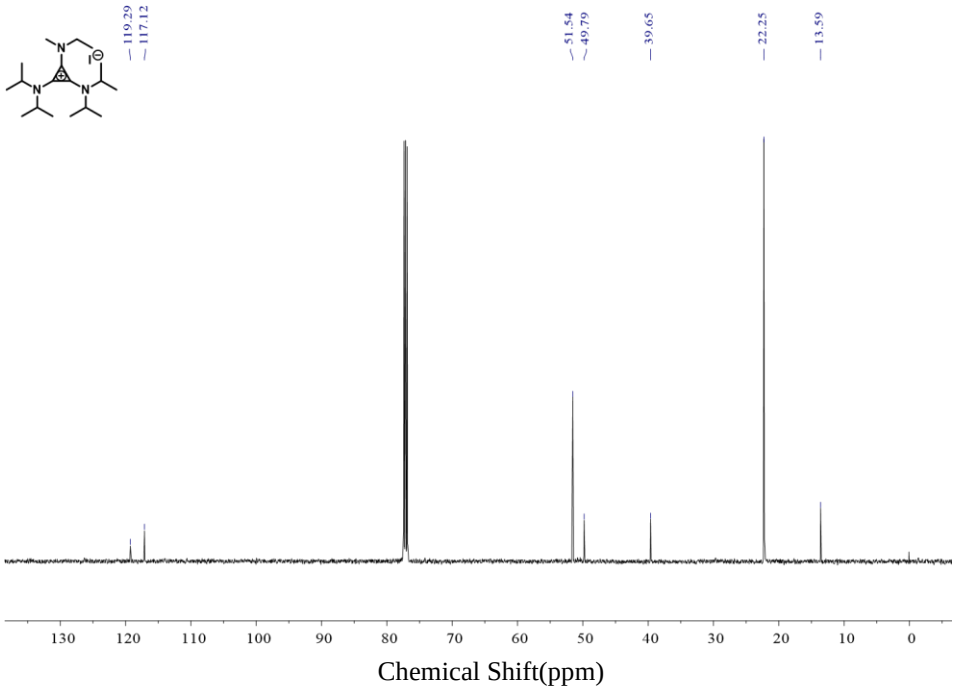


Figure S29: ^{13}C NMR spectrum of 1c.

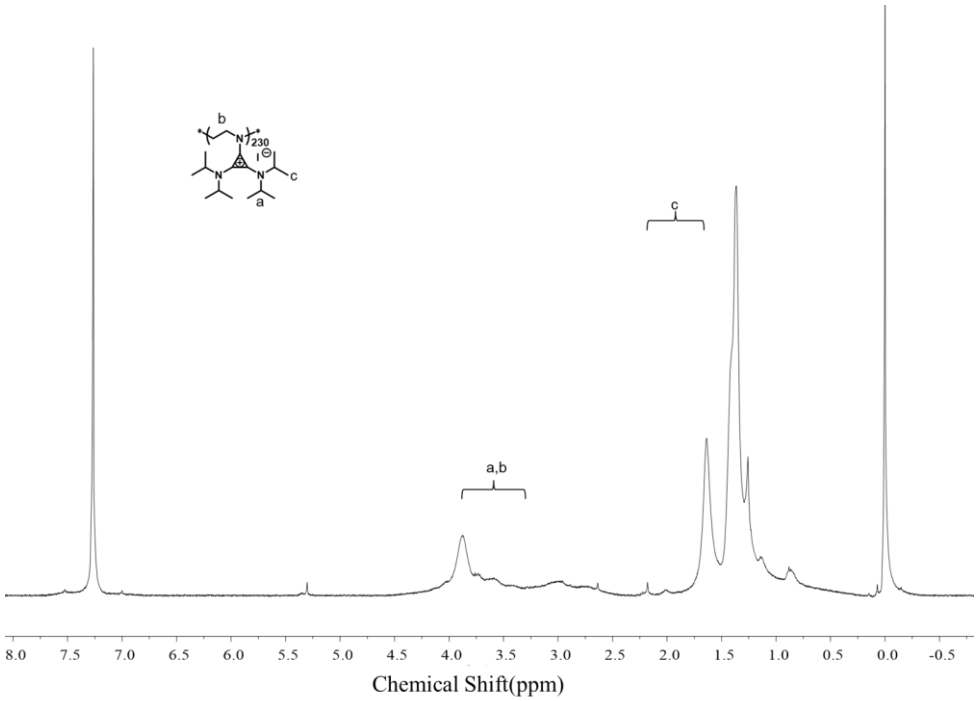


Figure S30: ^{1}H NMR spectrum of 1e.

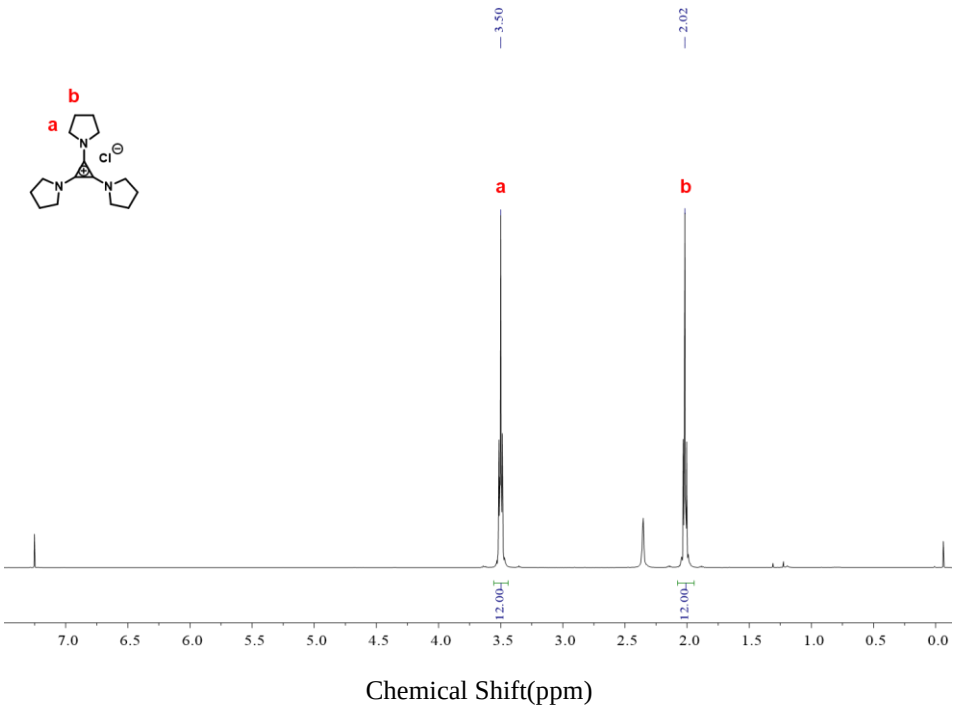


Figure S31: ^{1}H NMR spectrum of 1f.

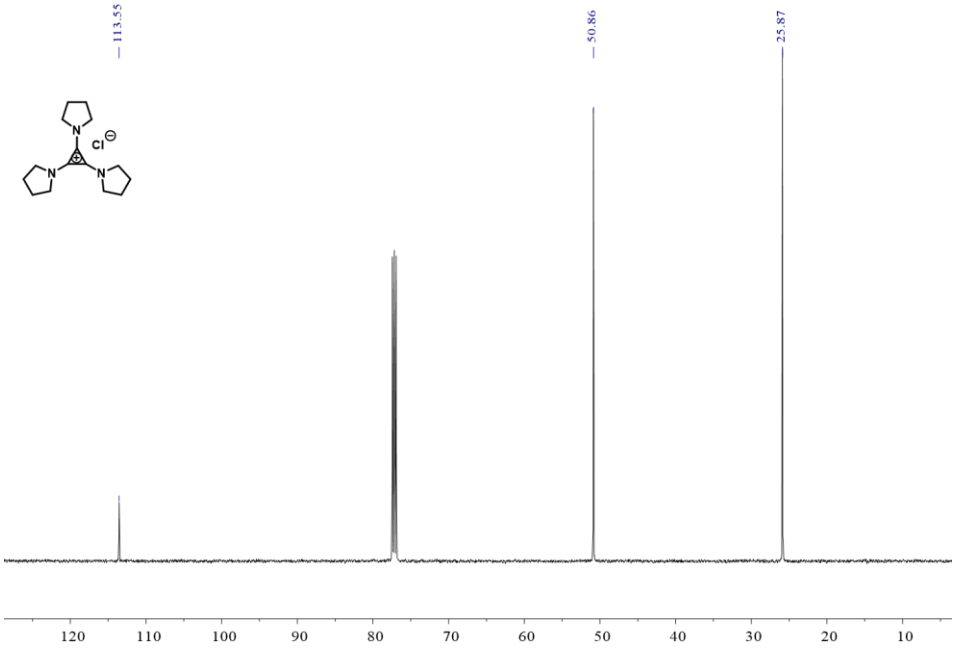


Figure S32: ^{13}C NMR spectrum of 1f.

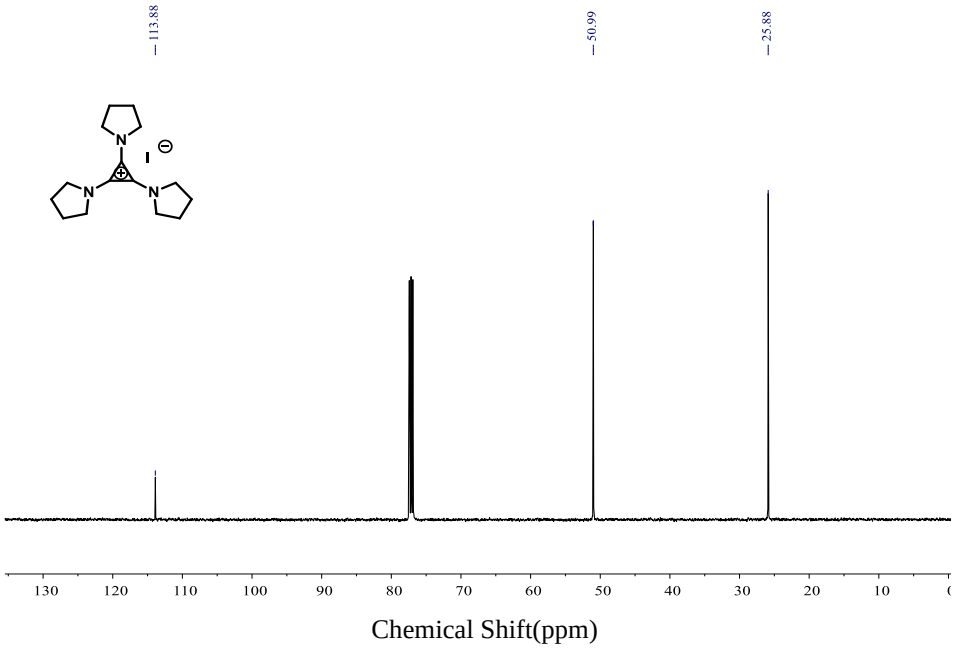


Figure S33: ^{1}H NMR spectrum of 1g.

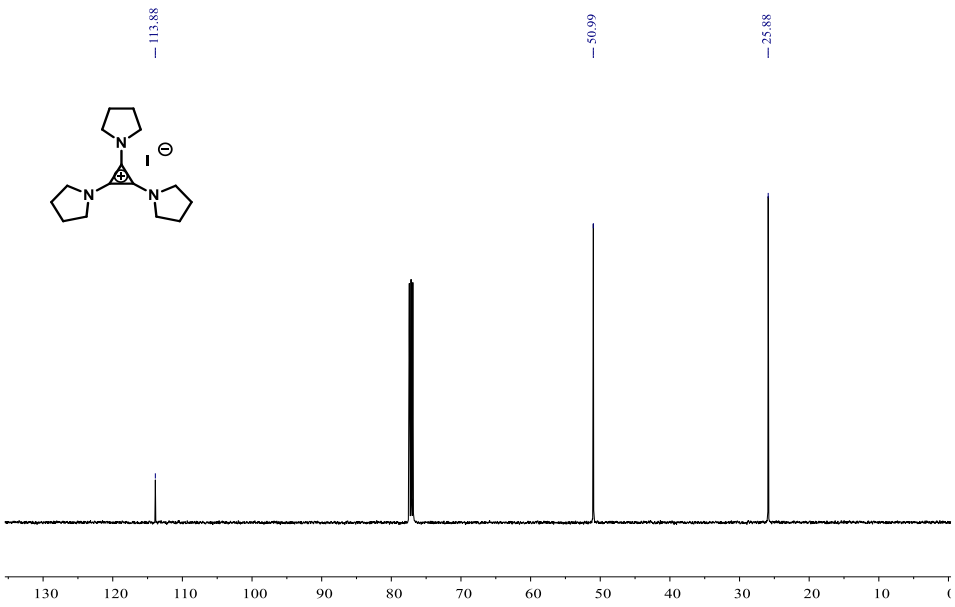


Figure S34: ^{13}C NMR spectrum of 1g.

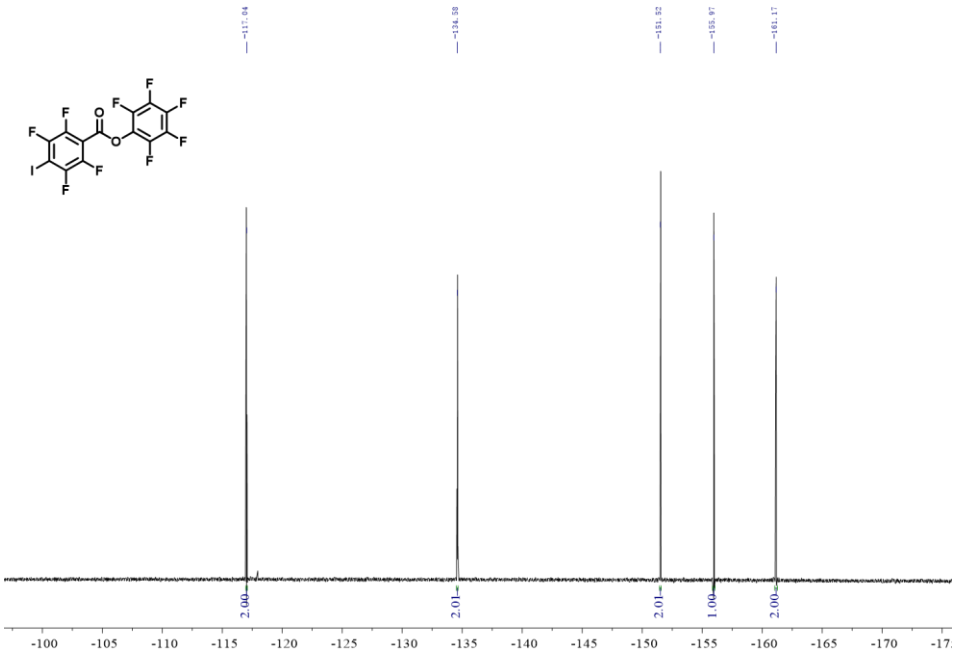


Figure S35: ^{19}F NMR spectrum of 2b.

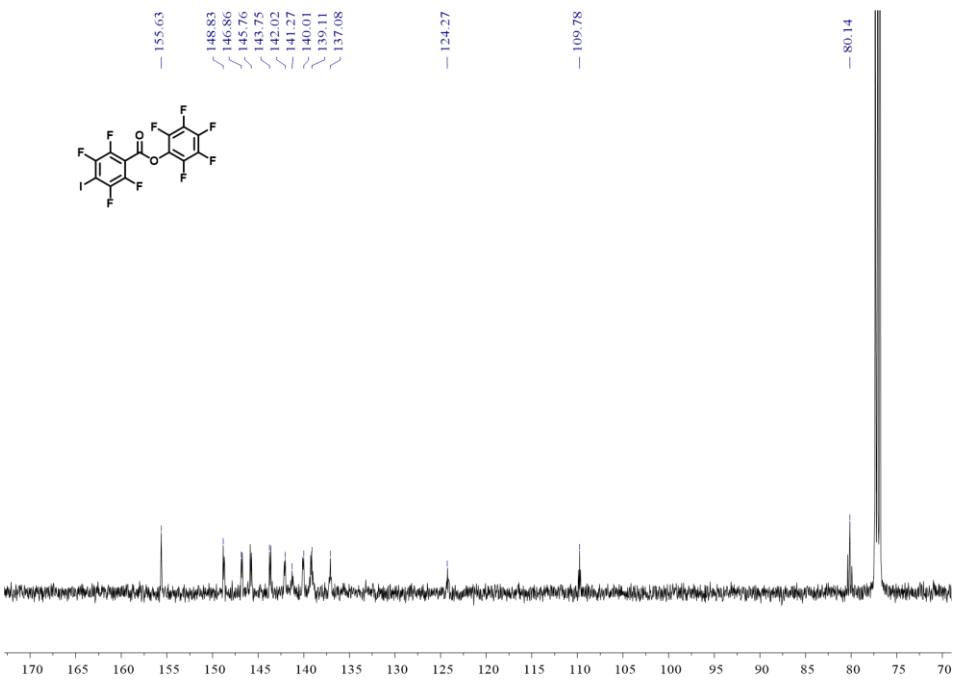


Figure S36: ^{13}C NMR spectrum of 2b.

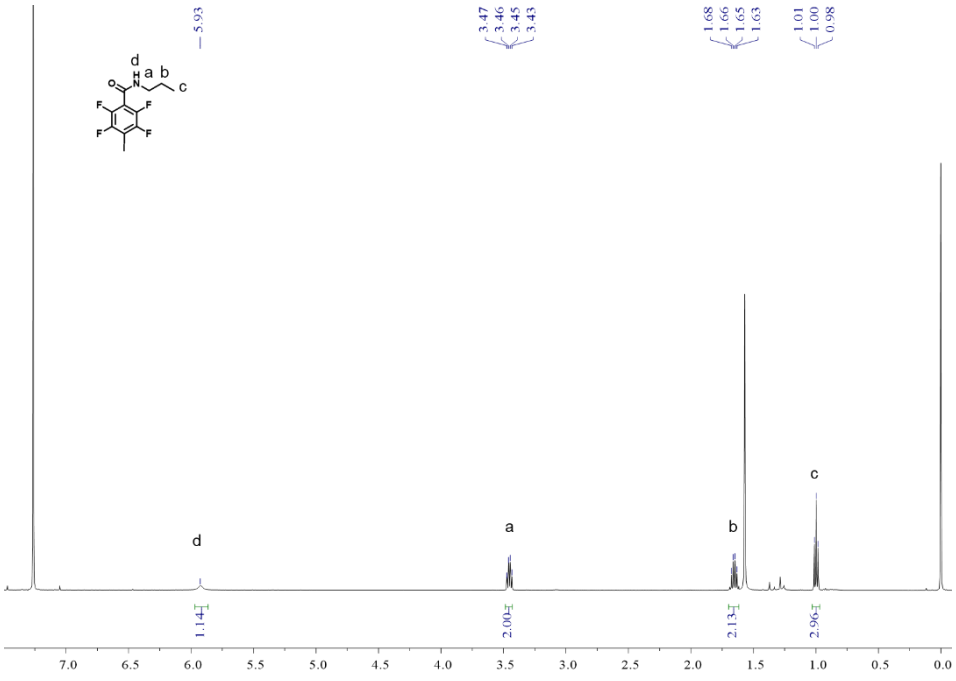


Figure S37: ^{1}H NMR spectrum of 2c.

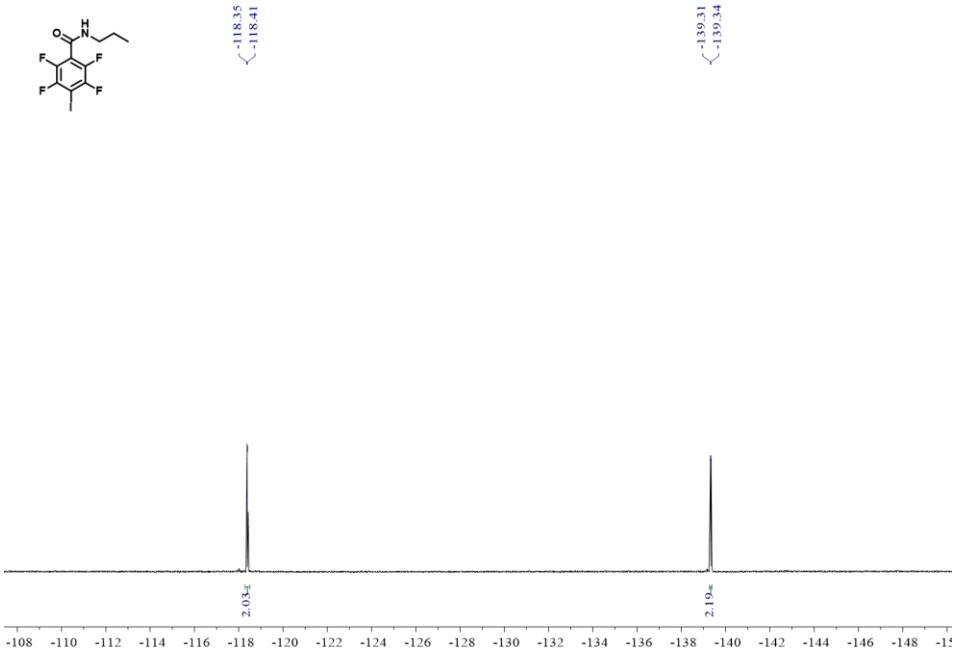


Figure S38: ^{19}F NMR spectrum of 2c.

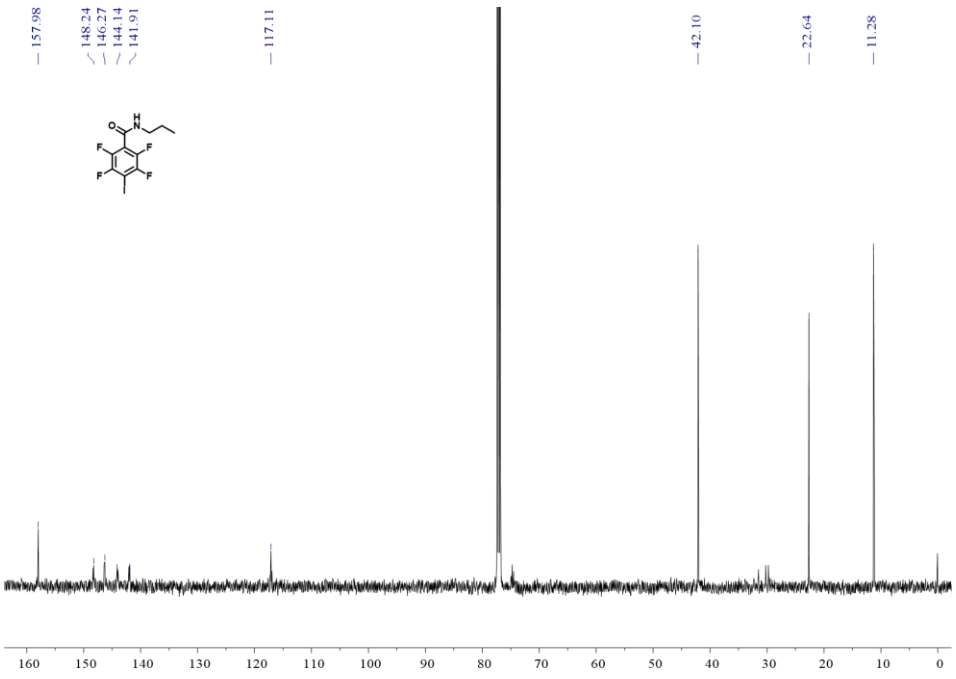


Figure S39: ^{13}C NMR spectrum of 2c.

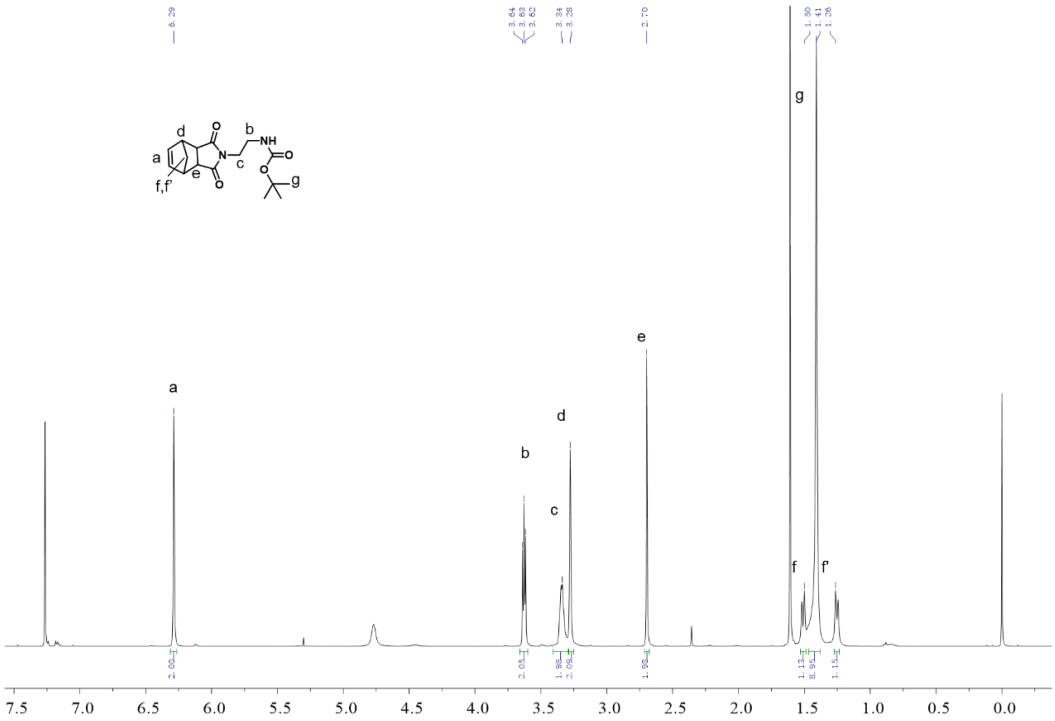


Figure S40: ^{1}H NMR spectrum of 3a.

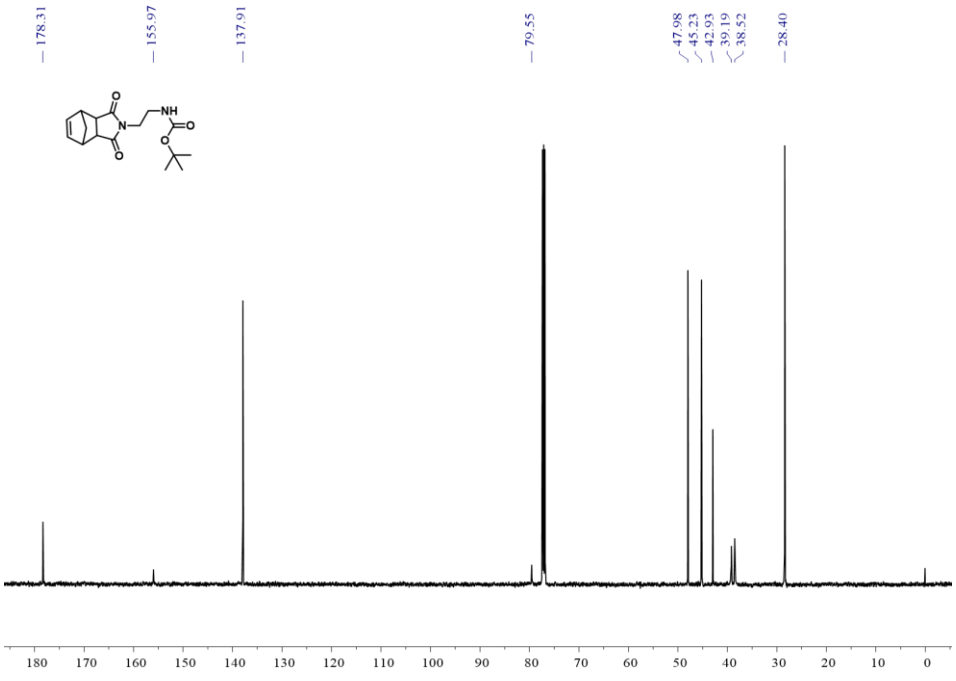


Figure S41: ^{13}C NMR spectrum of 3a.

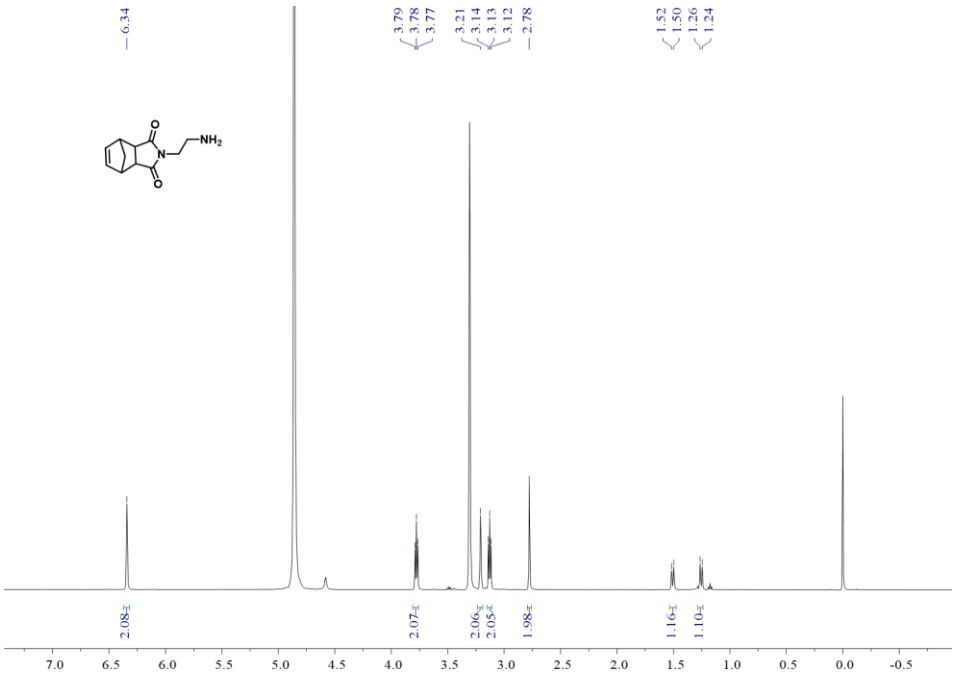


Figure S42: ^{1}H NMR spectrum of 3b.

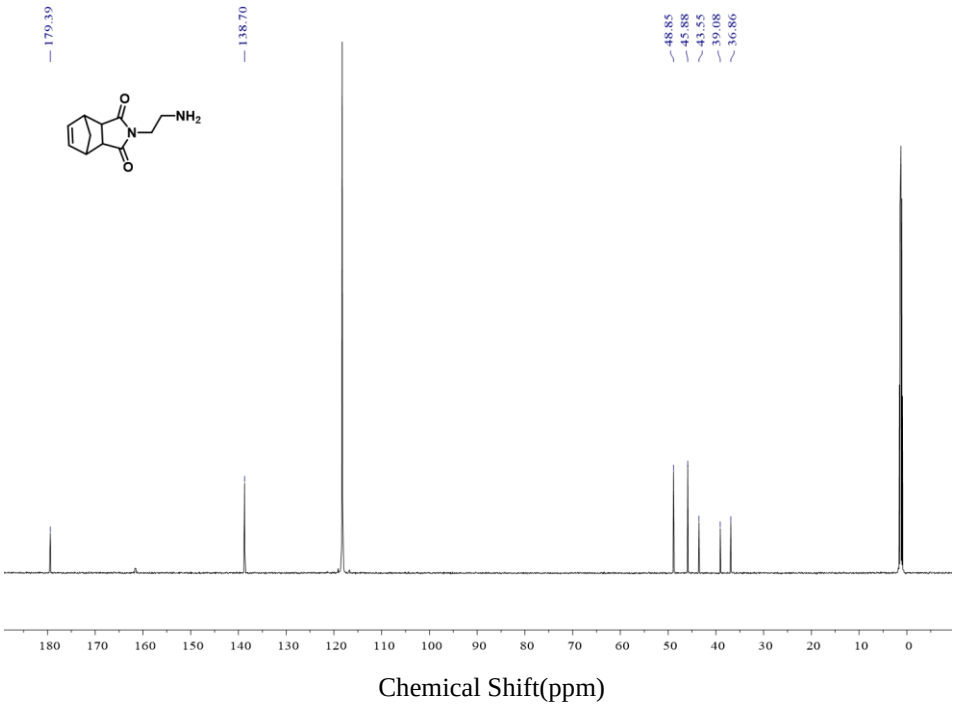


Figure S43: ^{13}C NMR spectrum of 3b.

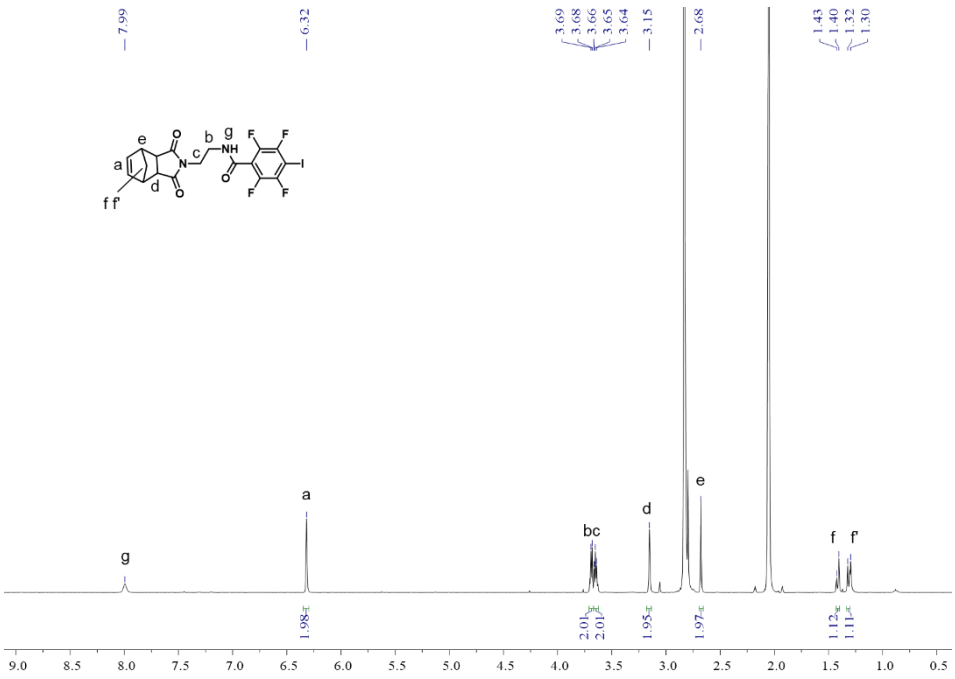


Figure S44: ^{1}H NMR spectrum of 3c.

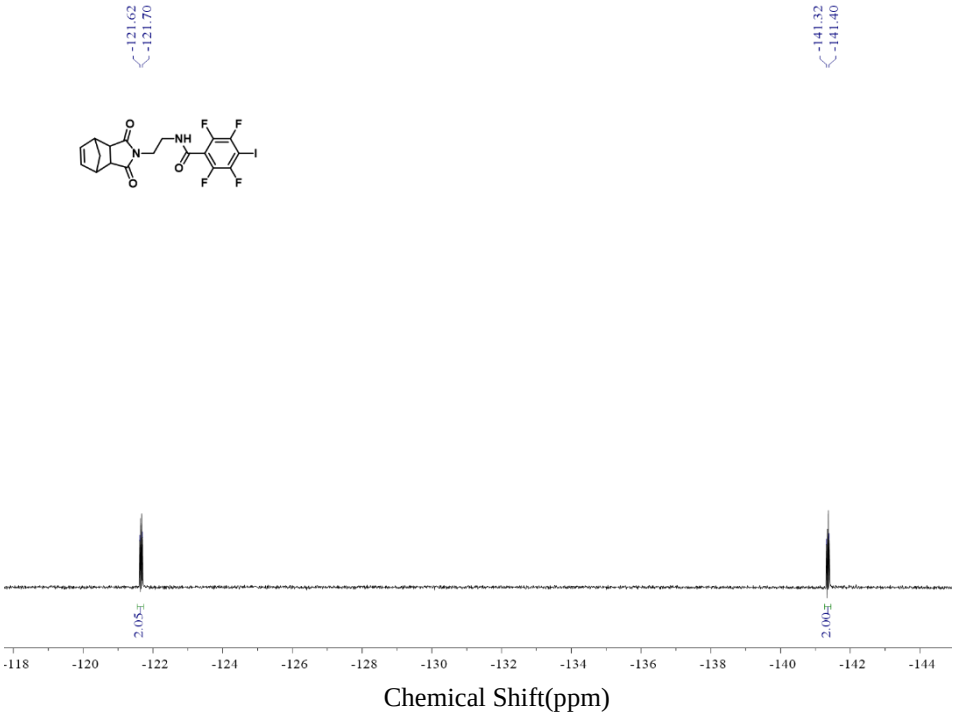


Figure S45: ^{19}F NMR spectrum of 3c.

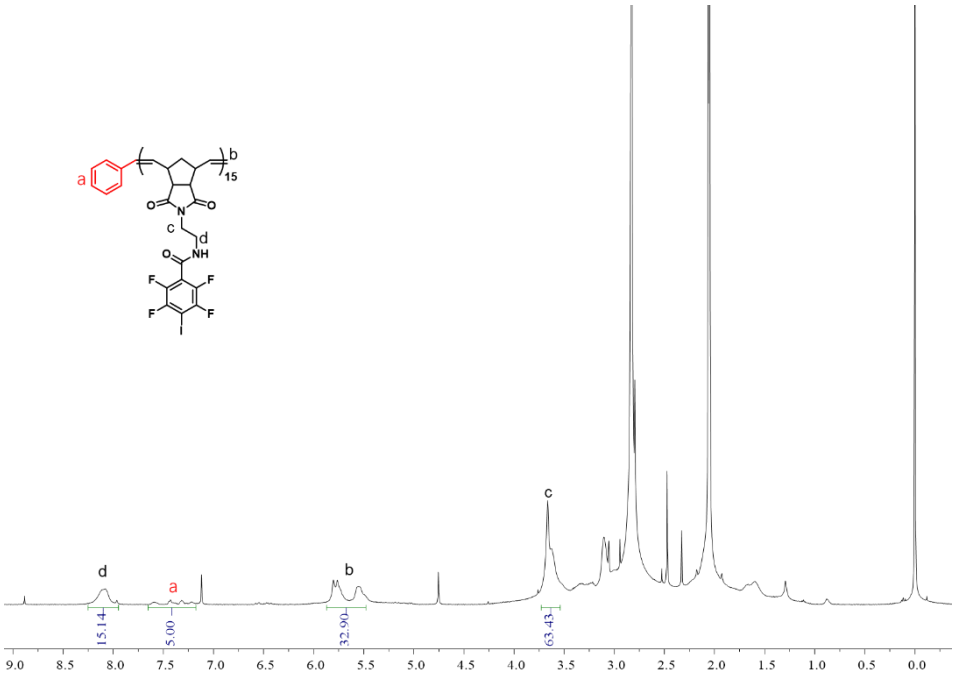


Figure S46: ^{1}H NMR spectrum of 3d (X_n=15).

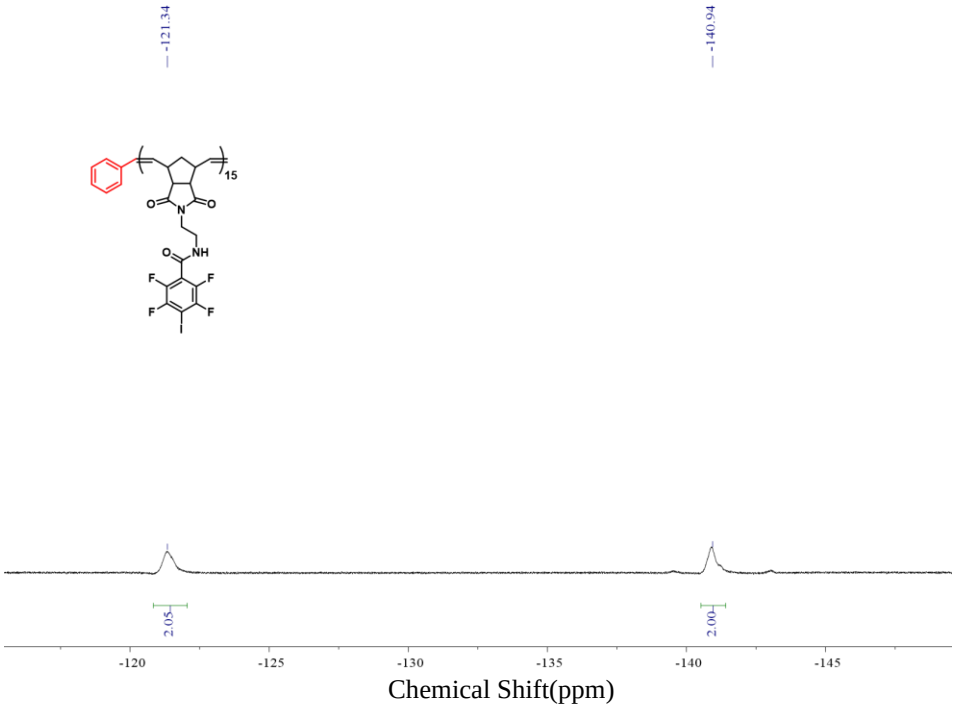


Figure S47: ^{19}F NMR spectrum of 3d (X_n=15).

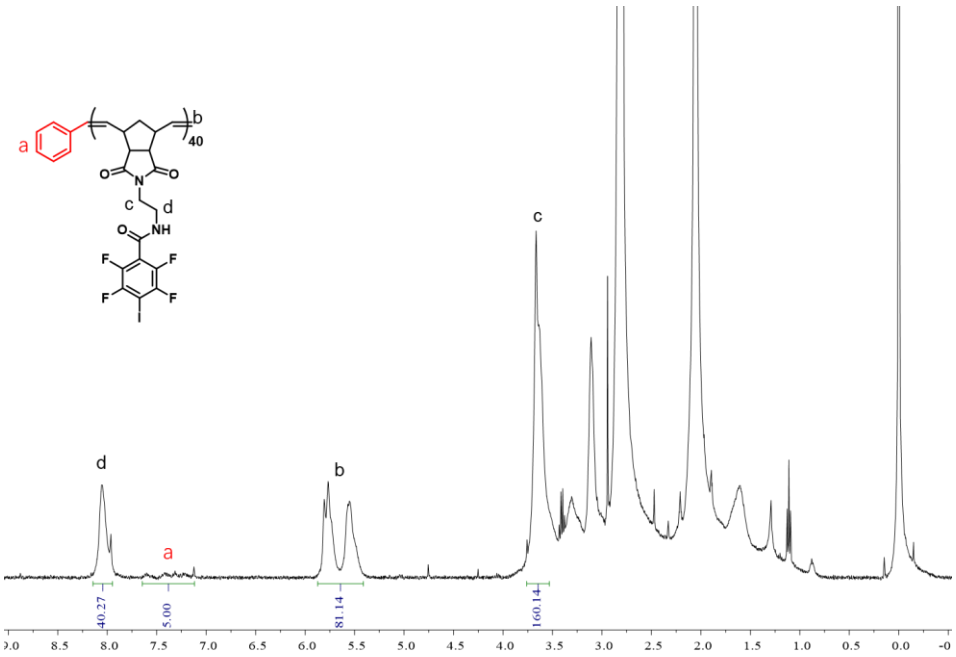


Figure S48: ^{1}H NMR spectrum of 3d (X_n=40).

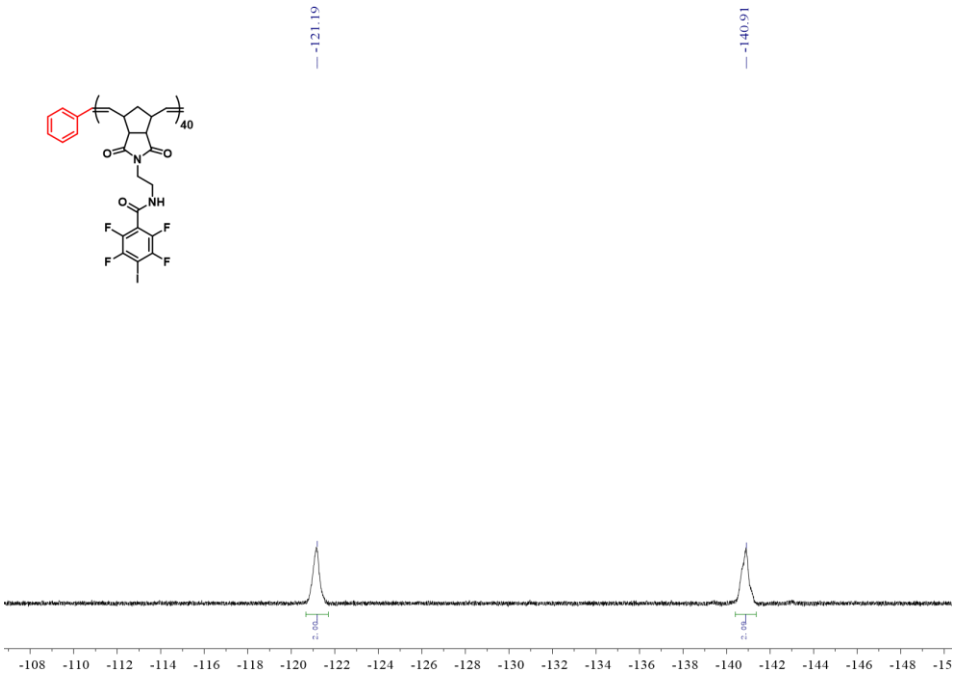


Figure S49: ^{19}F NMR spectrum of 3d (X_n=40).

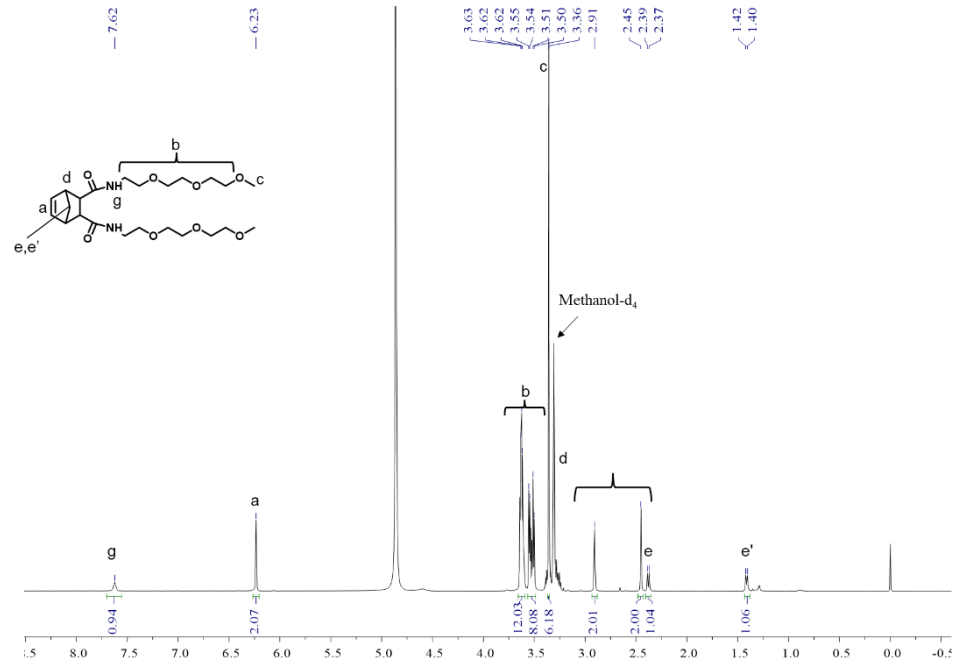


Figure S50: ^{1}H NMR spectrum of 4b.

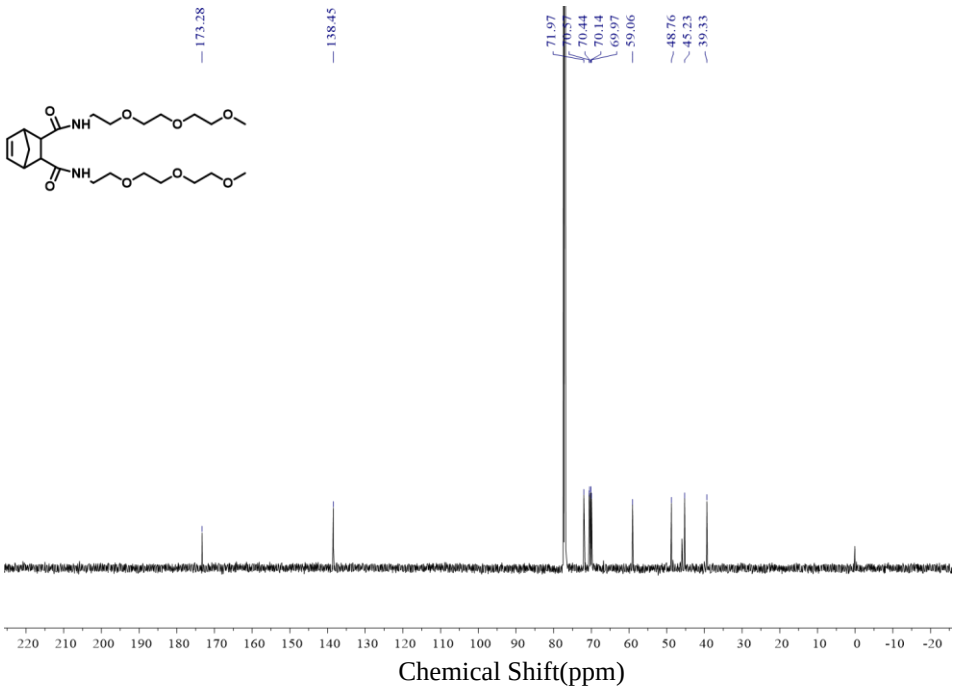


Figure S51: ^{13}C NMR spectrum of 4b.

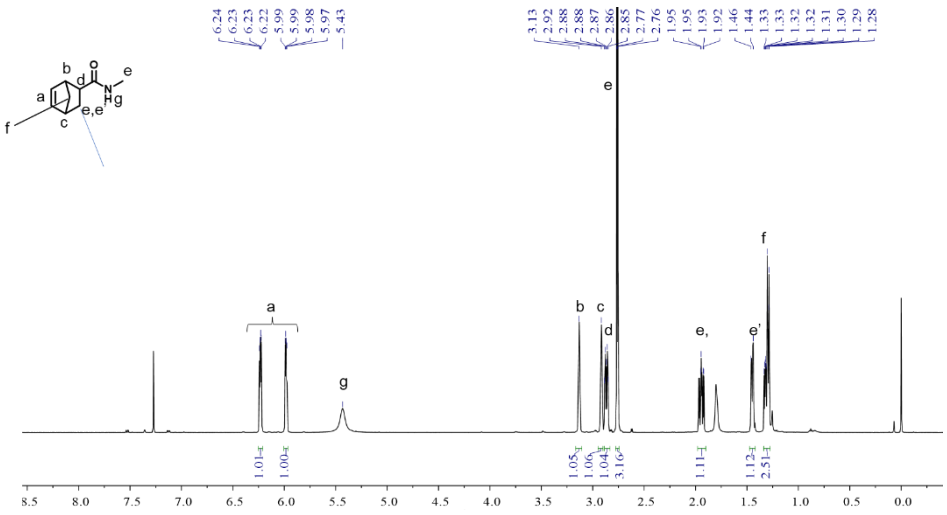


Figure S52: ^{1}H NMR spectrum of 5a.

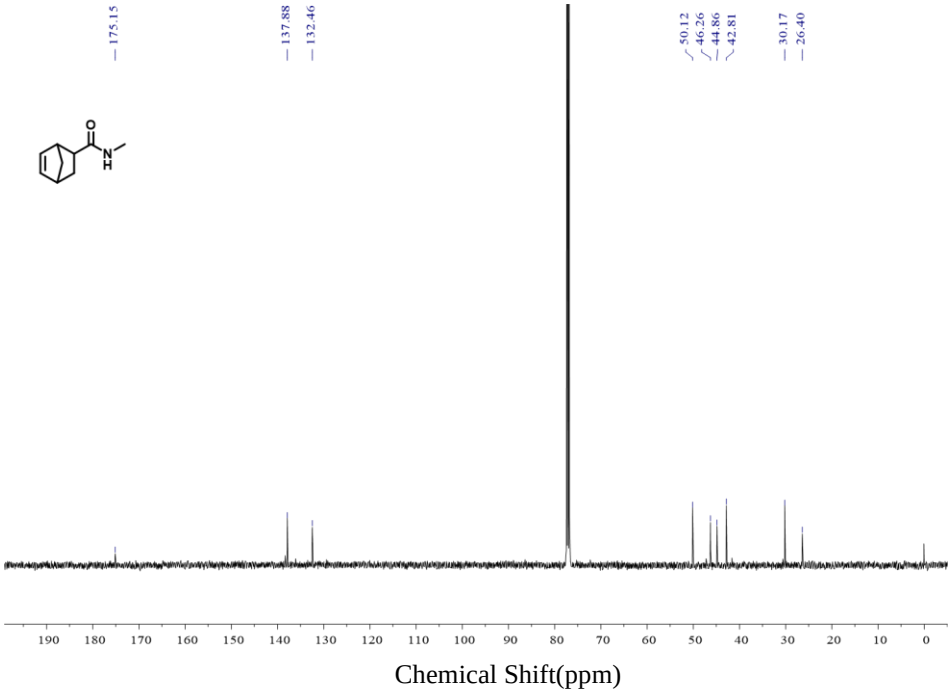


Figure S53:^{13}C NMR spectrum of 5a.

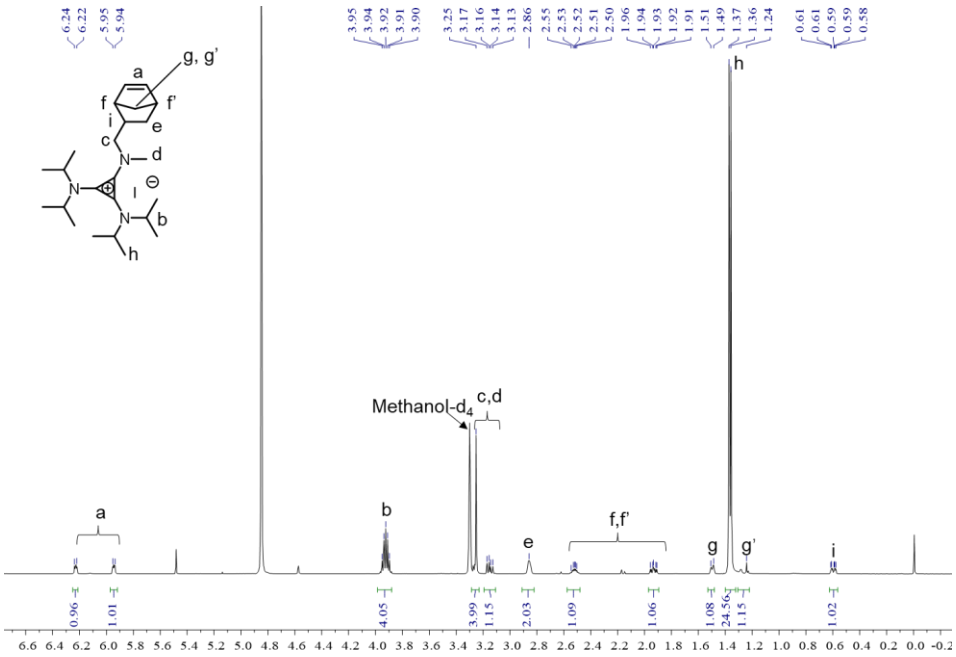


Figure S54: ^{1}H NMR spectrum of 5d.

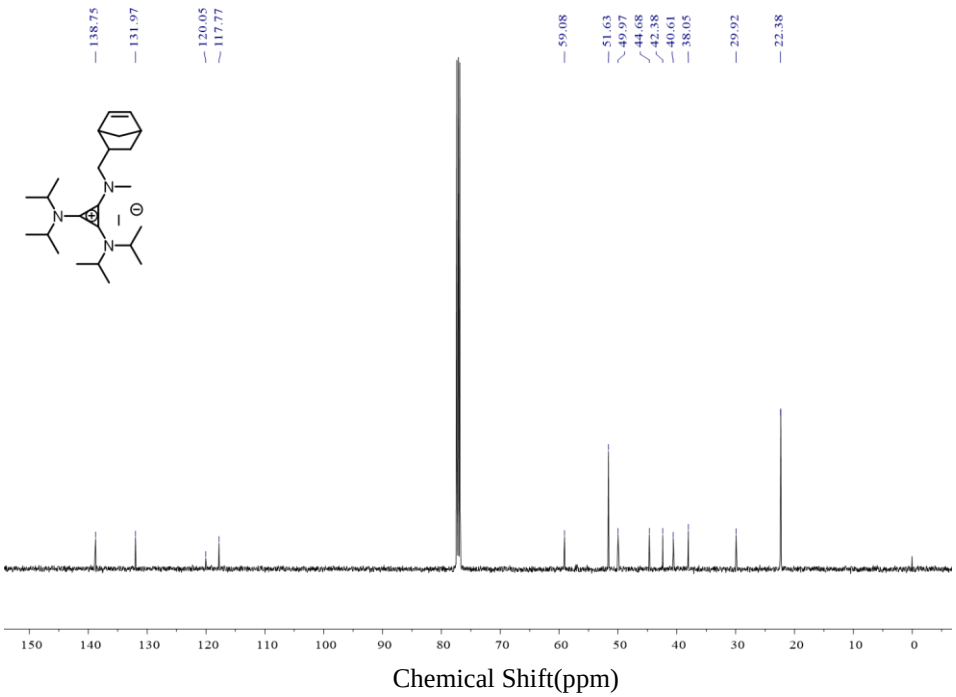


Figure S55: ^{13}C NMR spectrum of 5d.

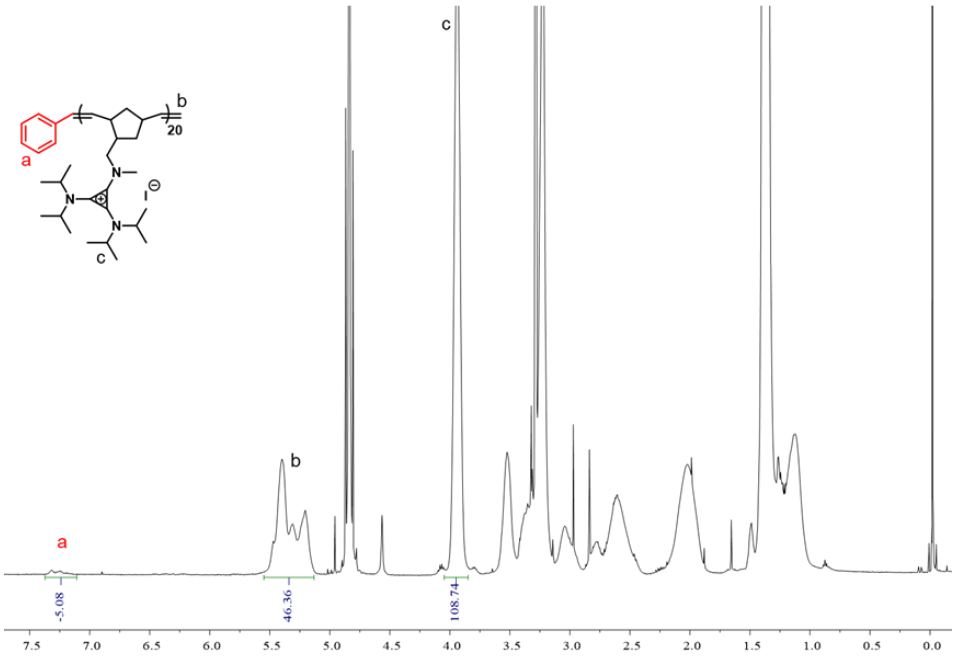


Figure S56: ^{1}H NMR spectrum of 5e(X_n=20) (CD_3OD).

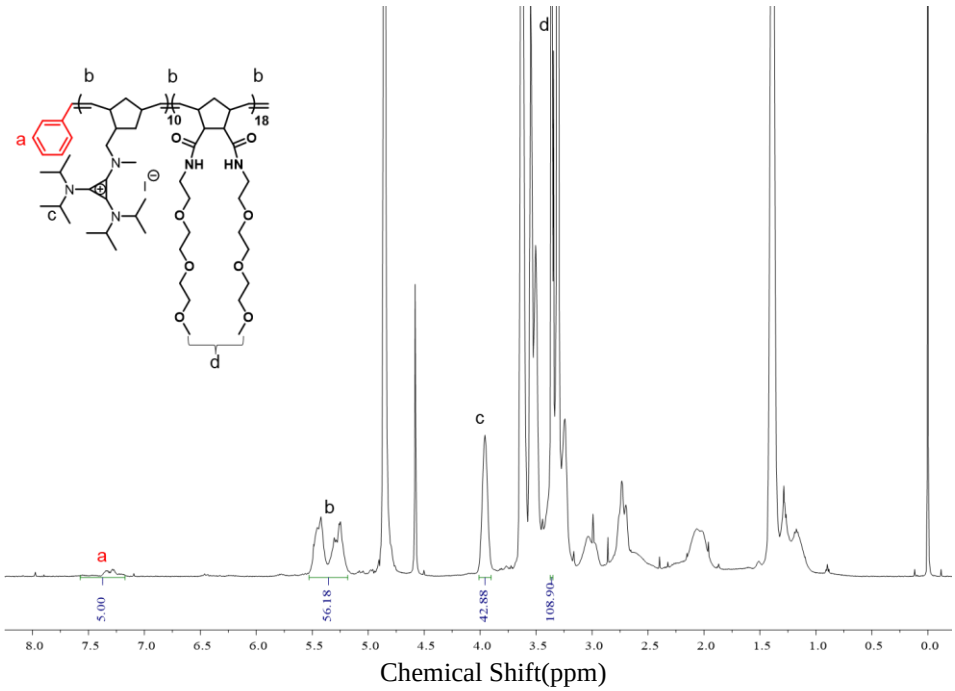


Figure S57: ^{1}H NMR spectrum of 5f (CD_3OD).

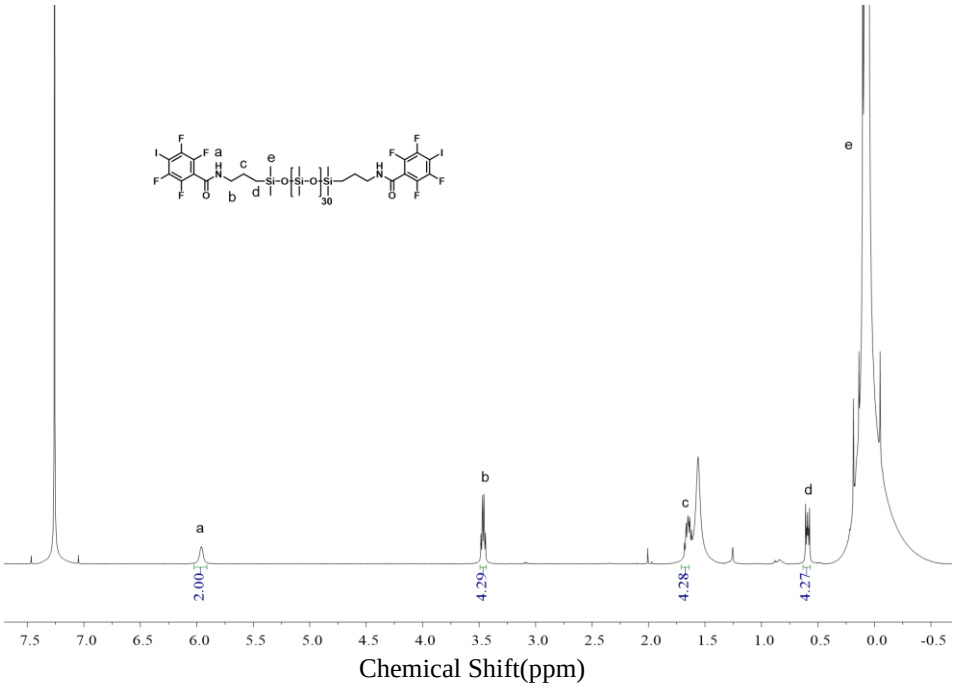


Figure S58: 1H NMR spectrum of 6a.

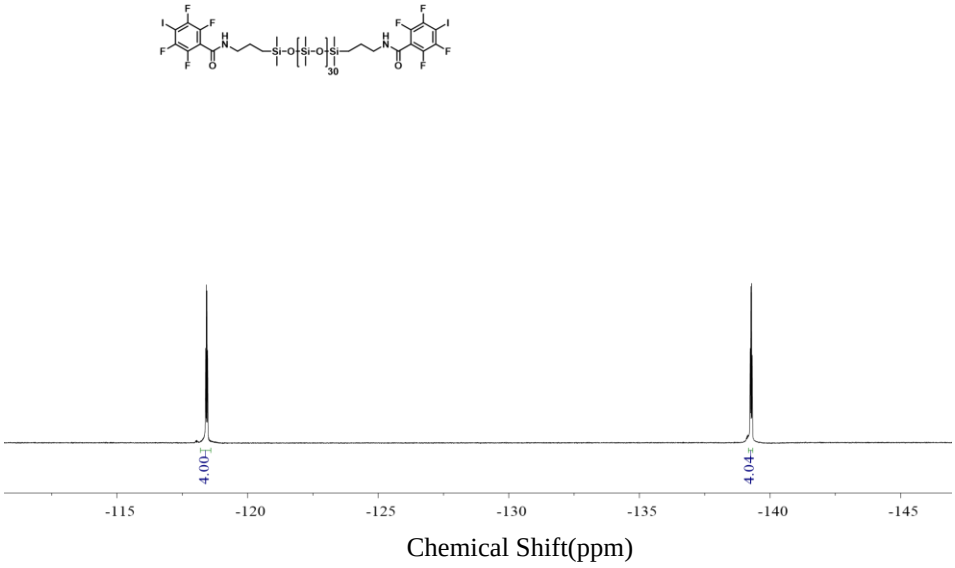


Figure S59: ^{19}F NMR spectrum of 6a.

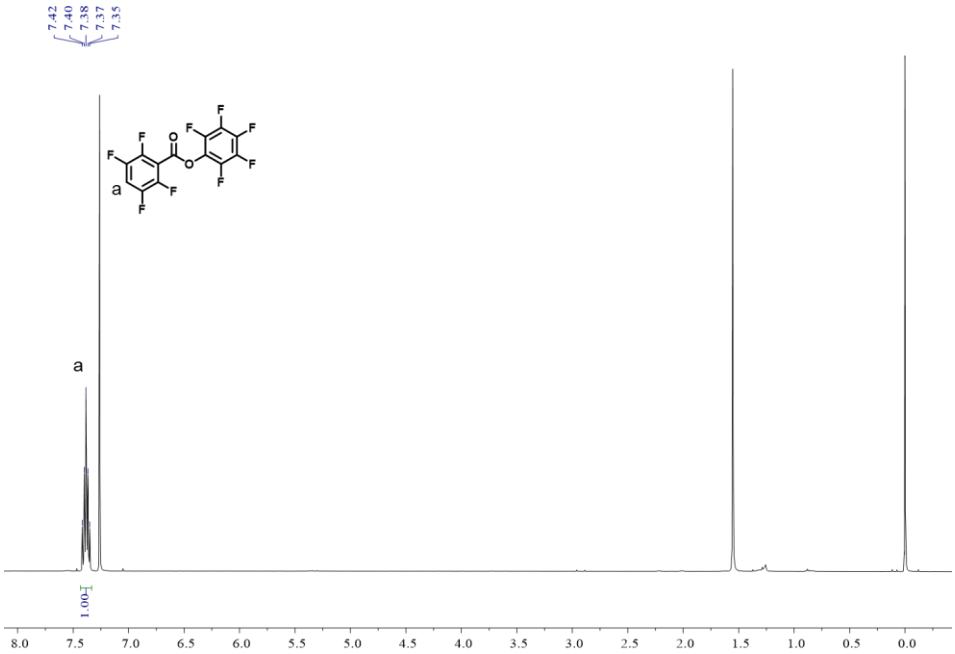


Figure S60: ^{1}H NMR spectrum of 7a.

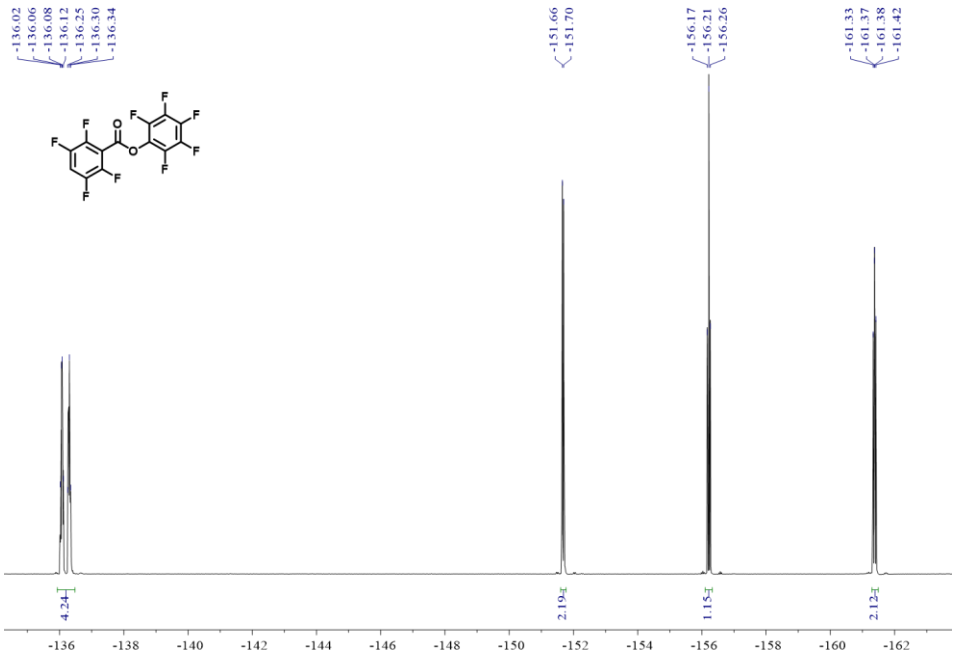


Figure S61: ^{19}F NMR spectrum of 7a.

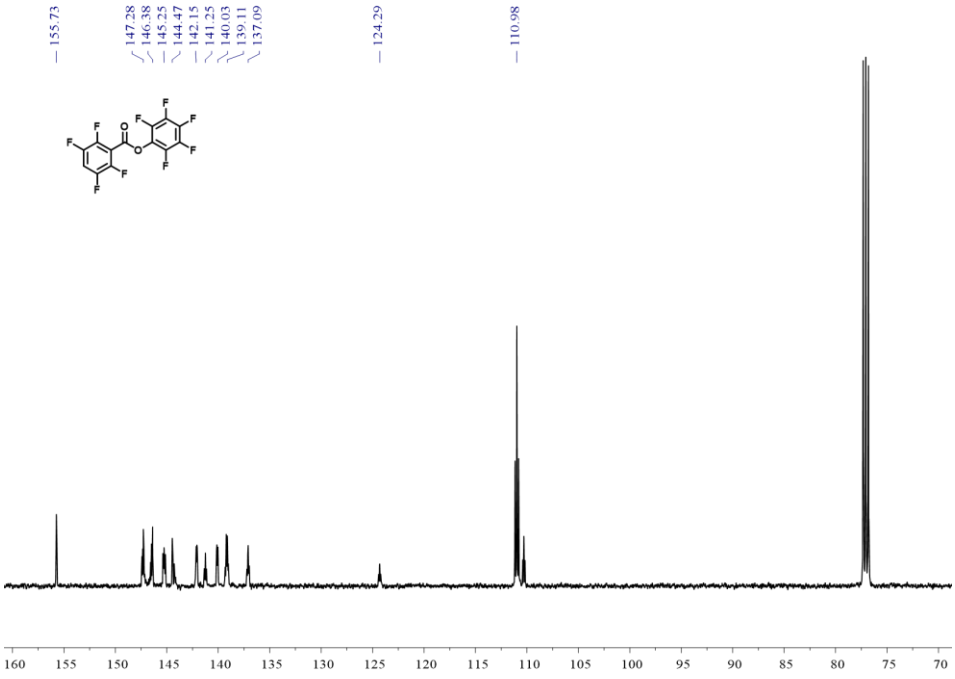


Figure S62: ^{13}C NMR spectrum of 7a.

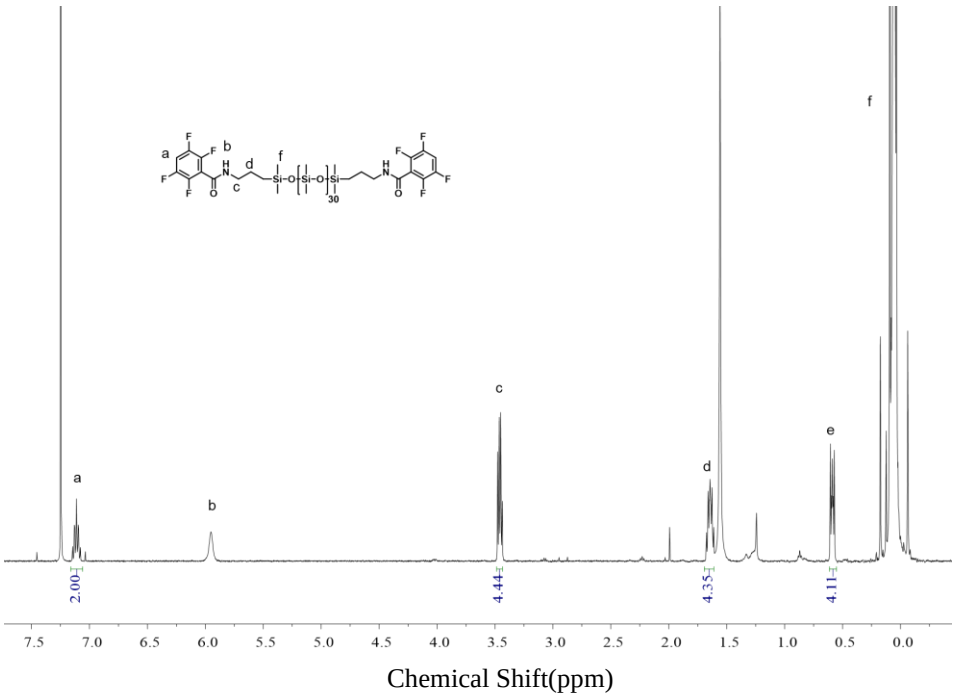


Figure S63: ^{1}H NMR spectrum of 7b.

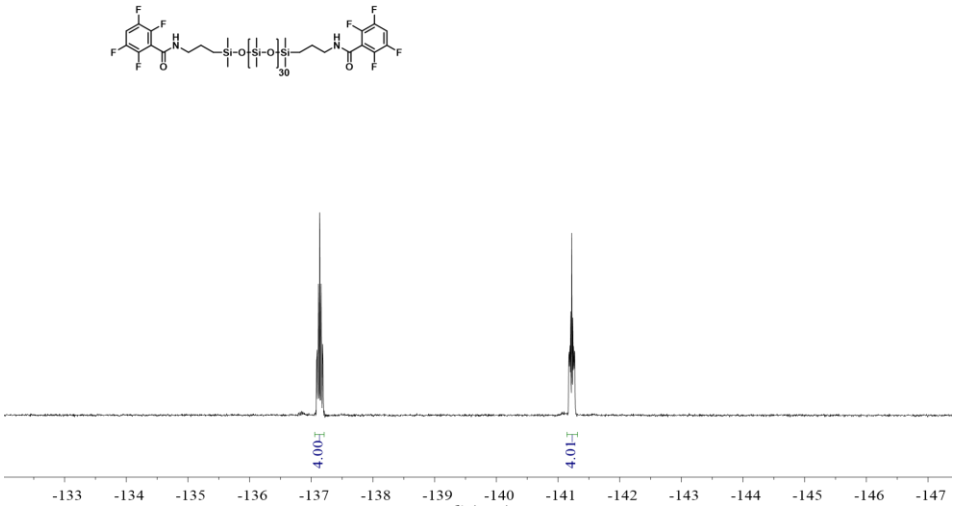


Figure S64: ^{19}F NMR spectrum of 7b.

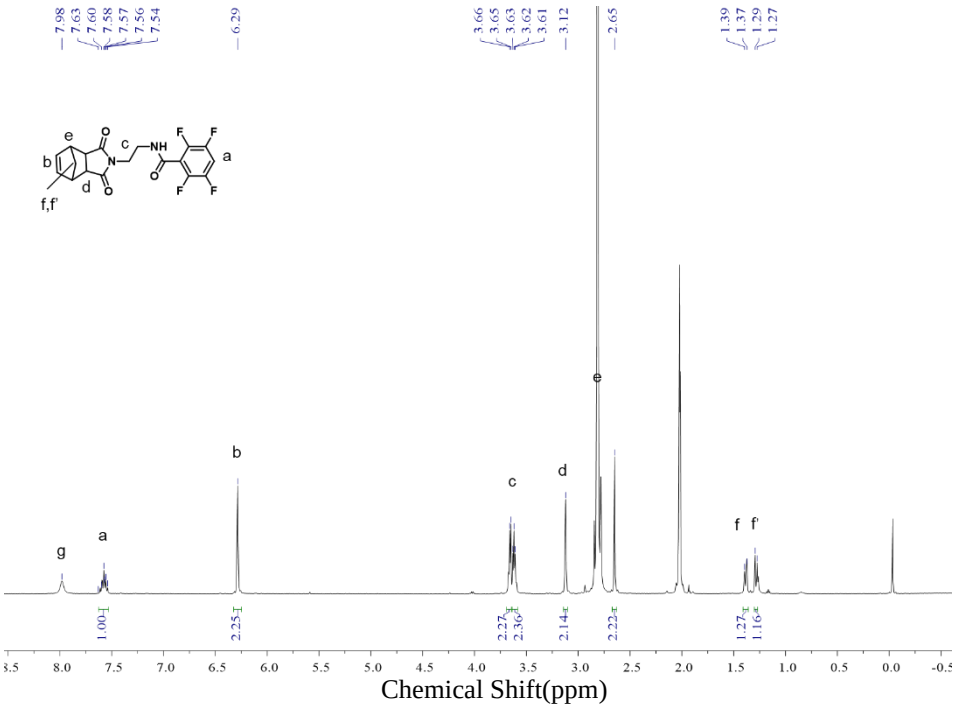


Figure S65: ^{1}H NMR spectrum of 8a.

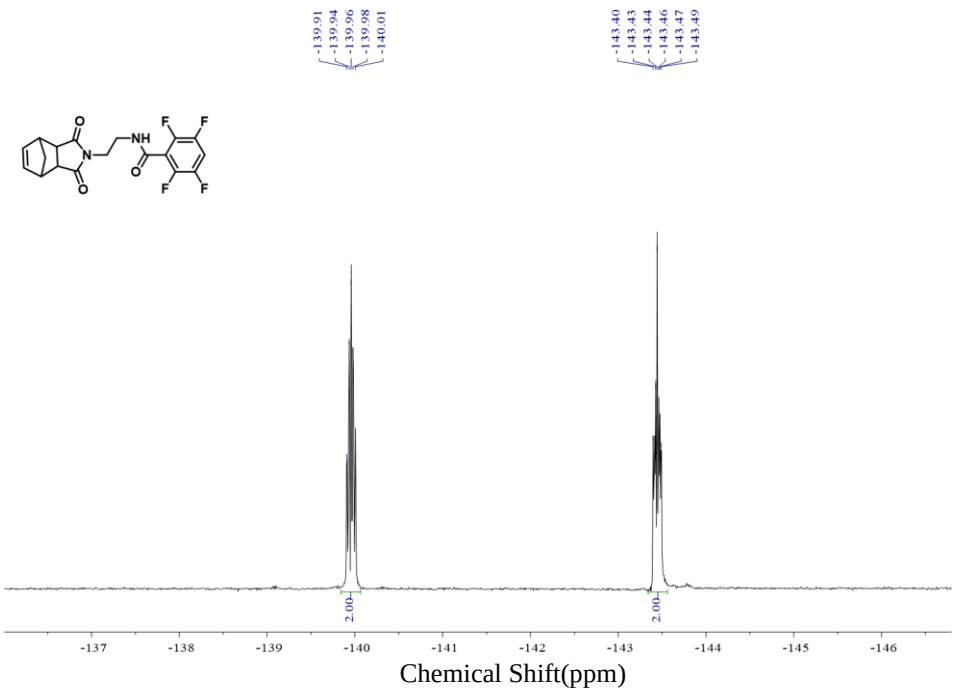


Figure S66: ^{19}F NMR spectrum of 8a.

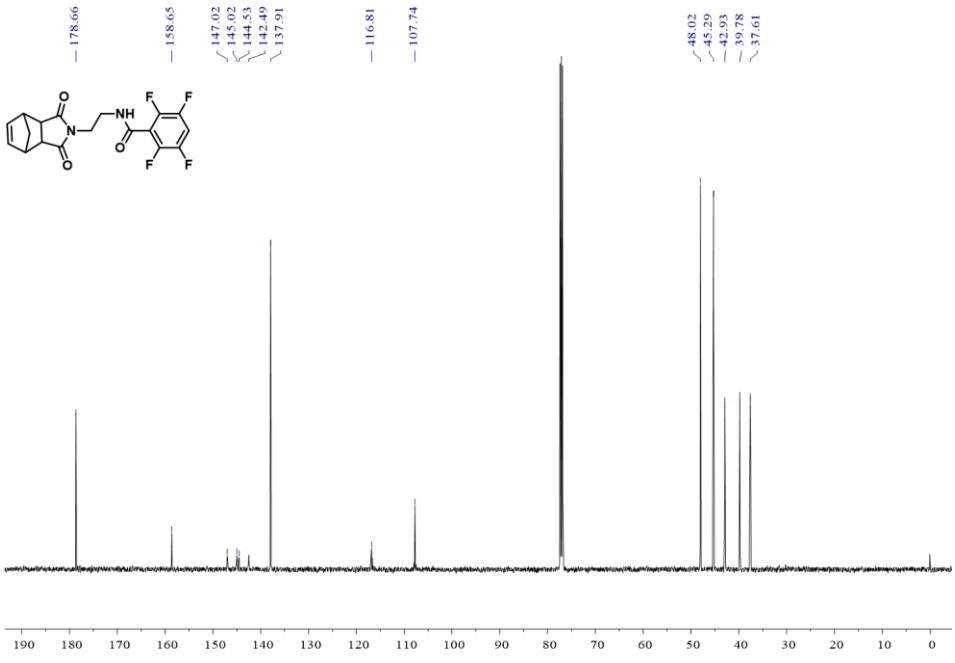


Figure S67: ^{13}C NMR spectrum of 8a.

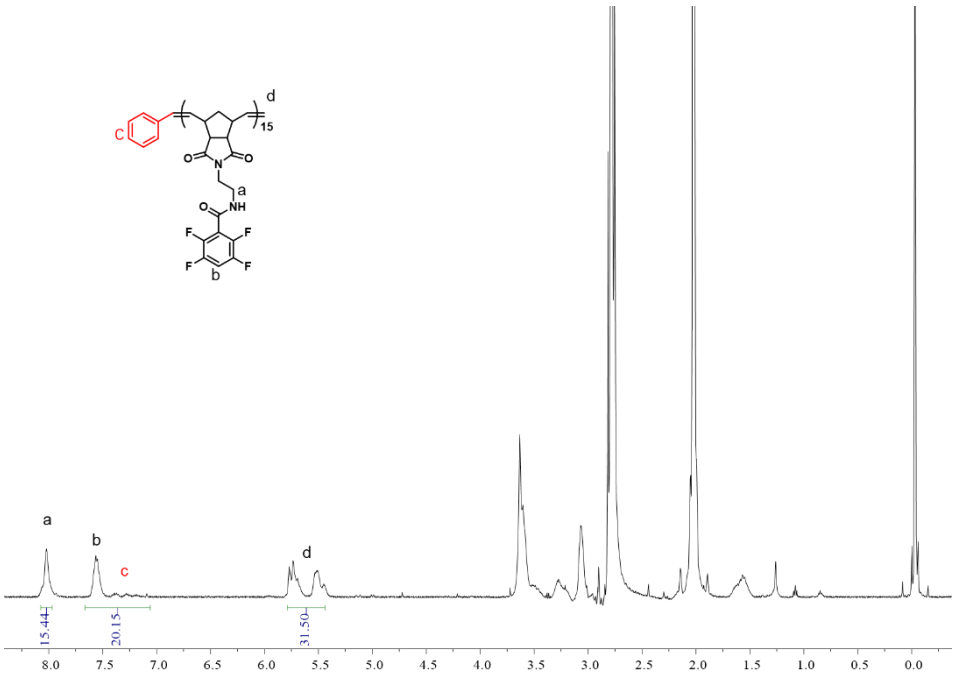


Figure S68: ^{1}H NMR spectrum of 8b (X_n=15) (Acetone-d_6).

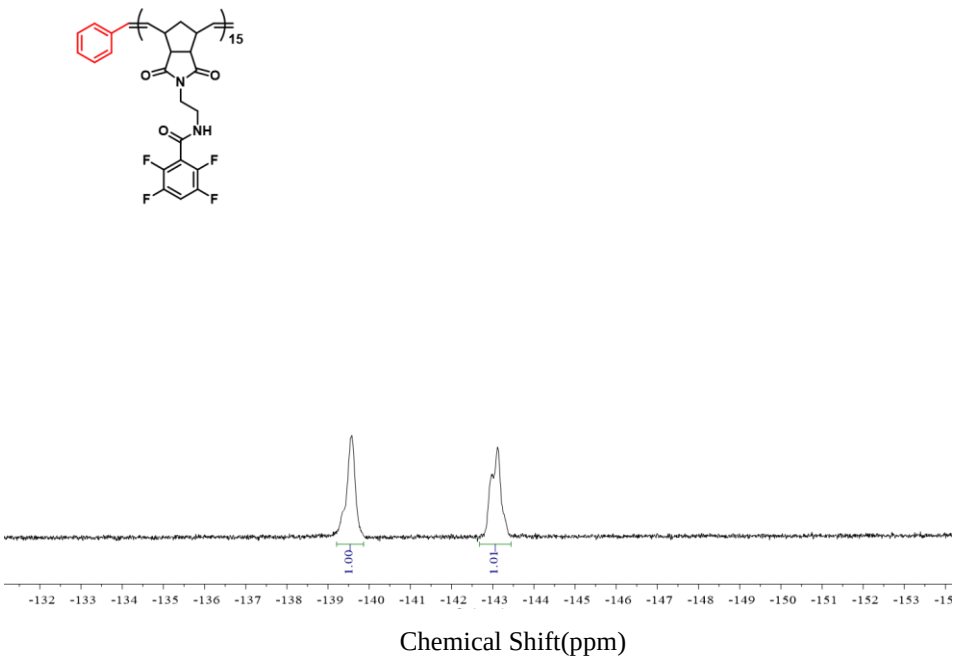


Figure S69: ^{19}F NMR spectrum of 8b (X_n=15) (Acetone-d_6).

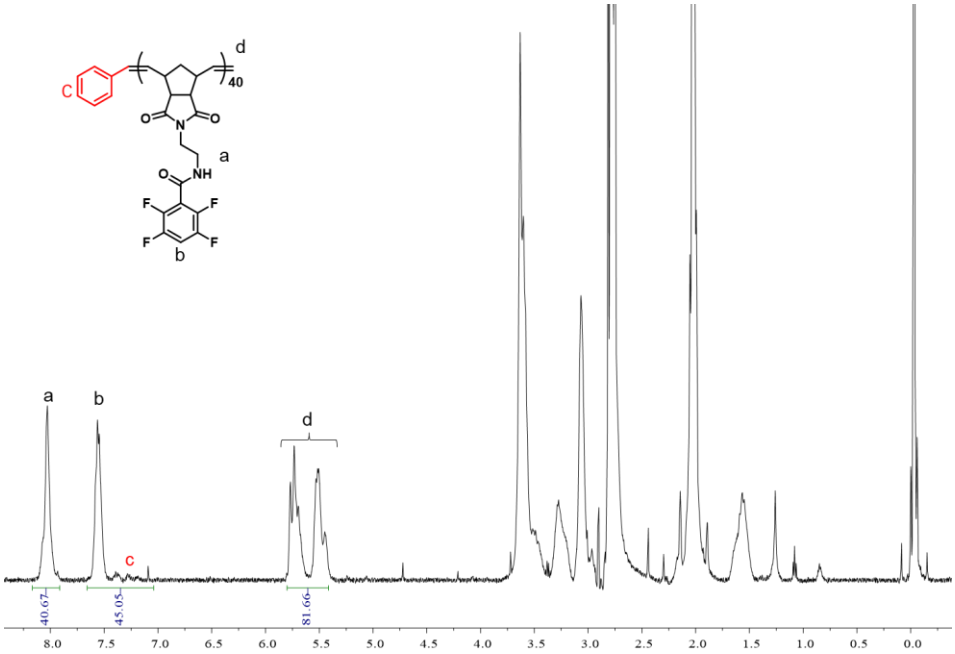


Figure S70: ^{1}H NMR spectrum of 8b (X_n=40)(Acetone-d_6).

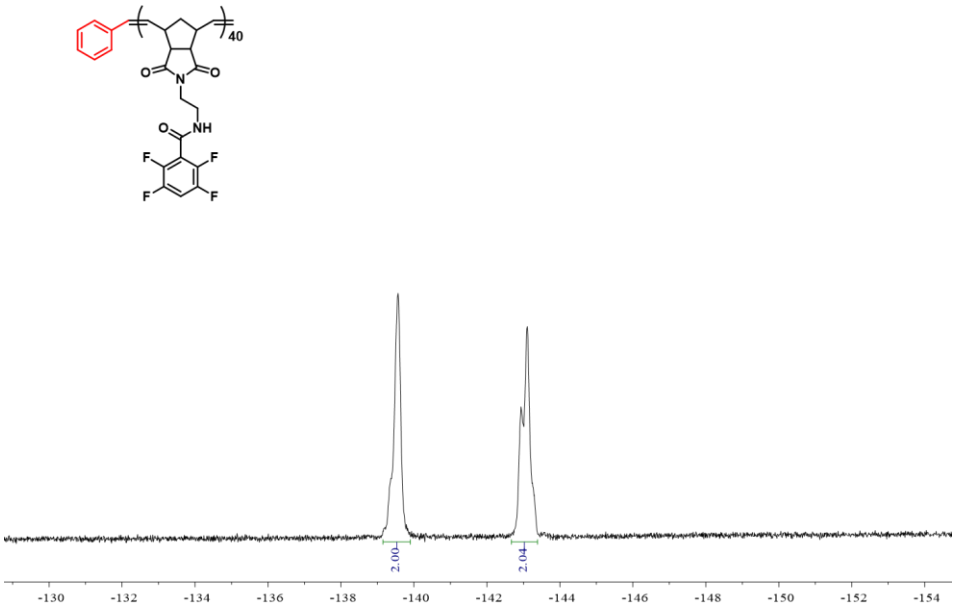


Figure S71: ^{19}F NMR spectrum of 8b (X_n=40) (Acetone-d_6).

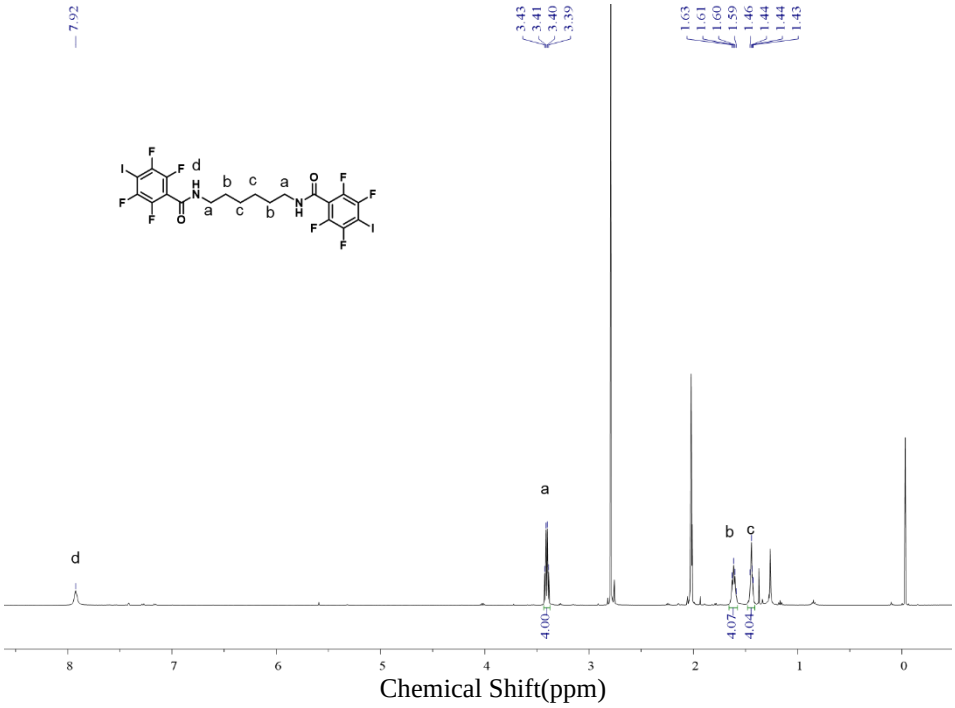


Figure S72: ^{19}F NMR spectrum of 9a.

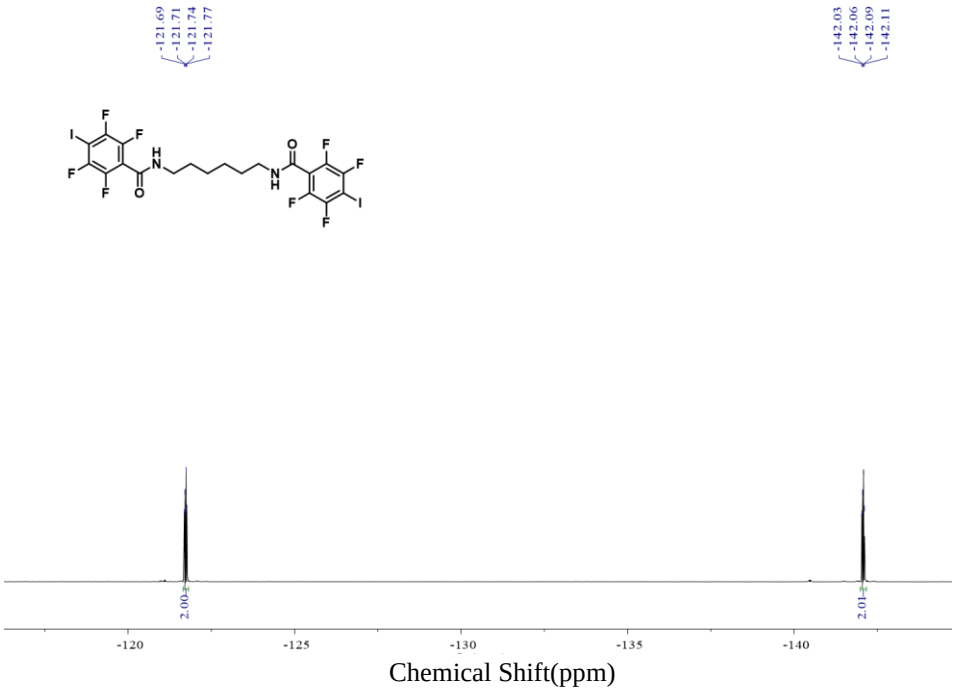


Figure S73: ^{19}F NMR spectrum of 9a.

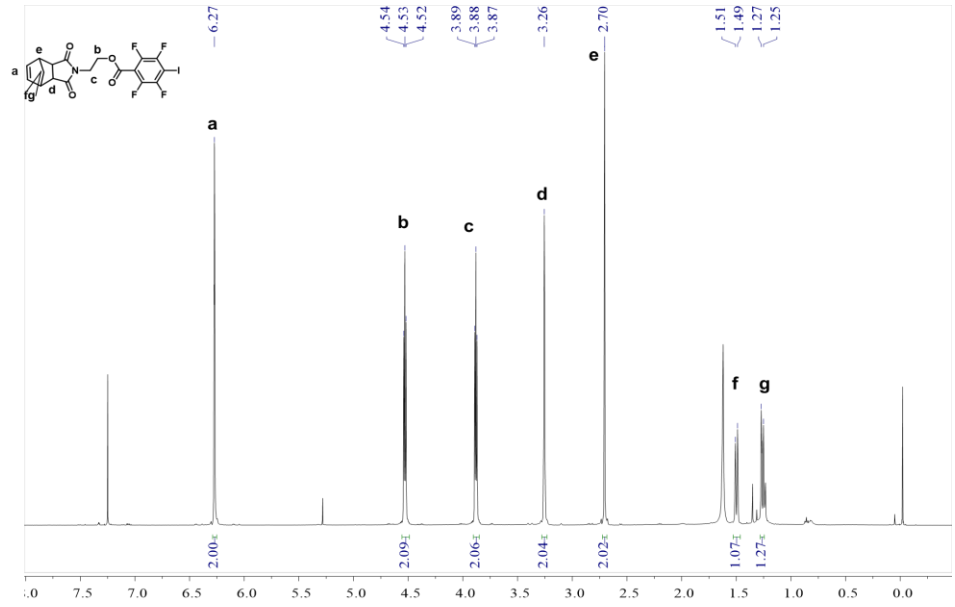


Figure S74: ^{1}H NMR spectrum of 10b.

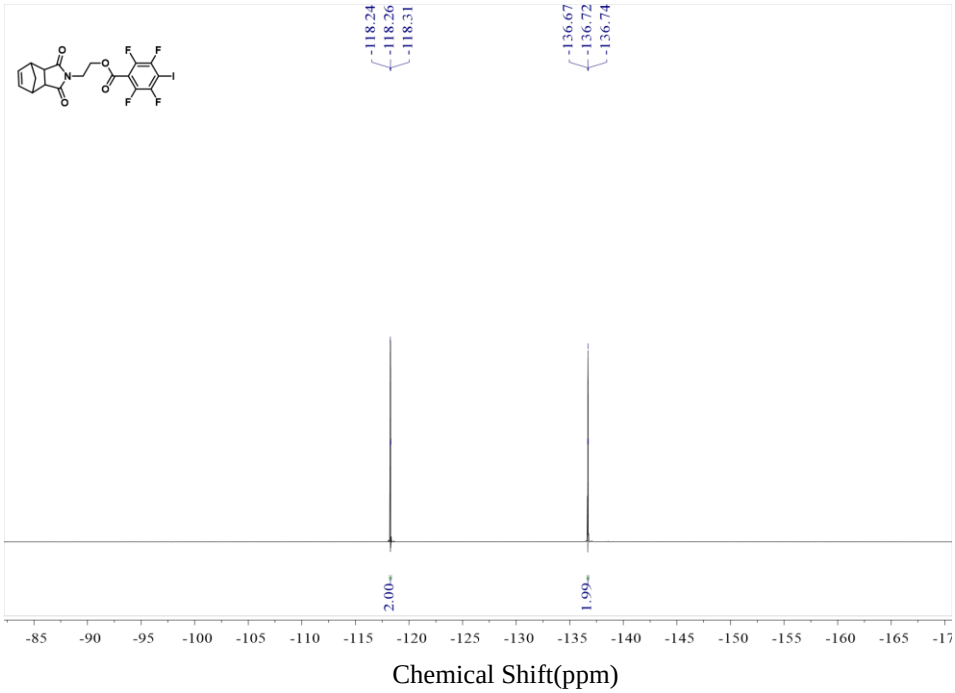


Figure S75: ^{19}F NMR spectrum of 10b.

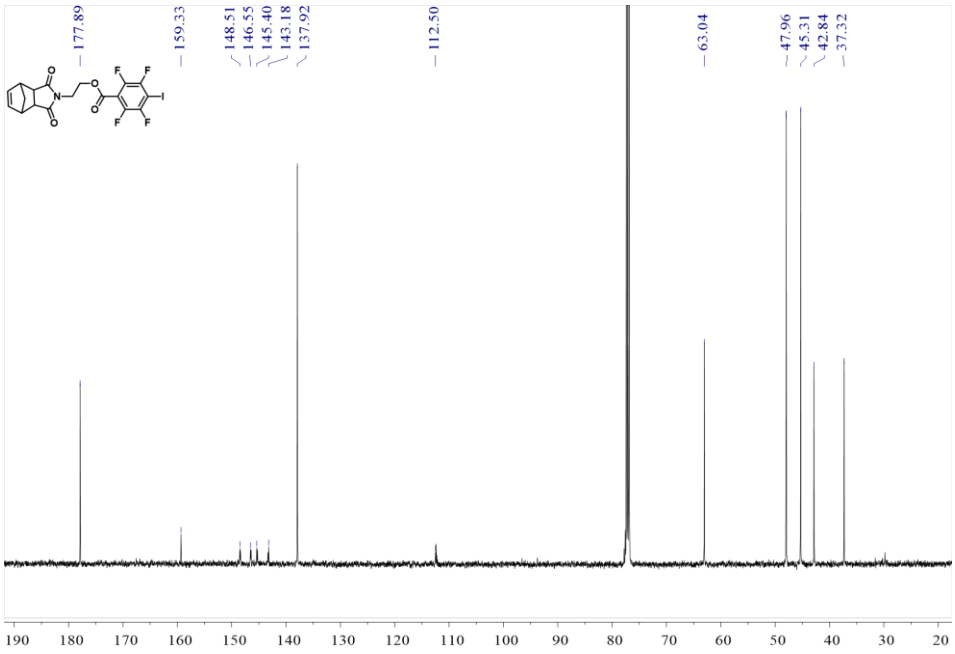


Figure S76: ^{13}C NMR spectrum of 10b.

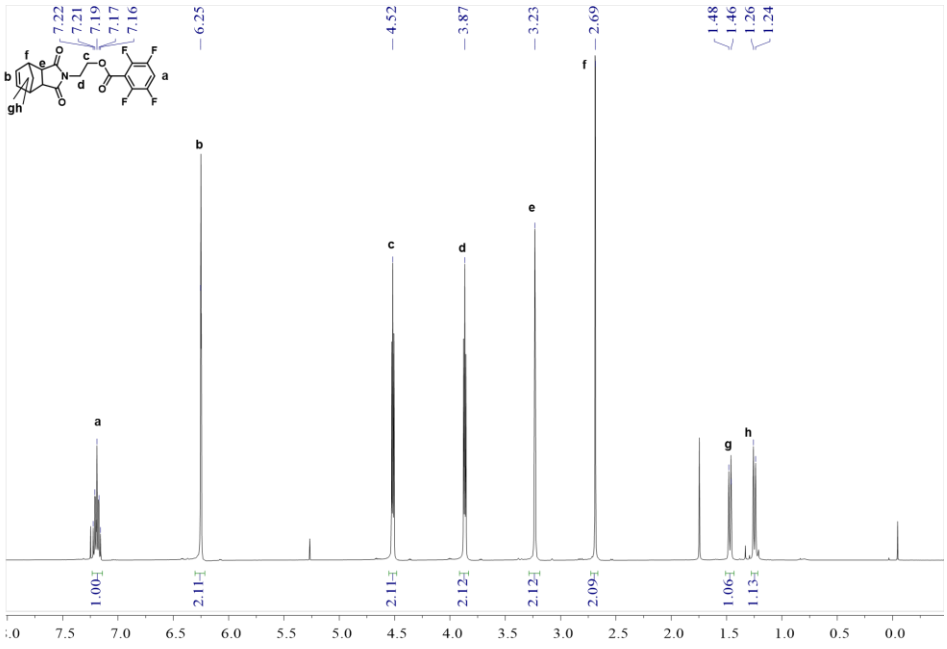


Figure S77: ^{1}H NMR spectrum of 10c.

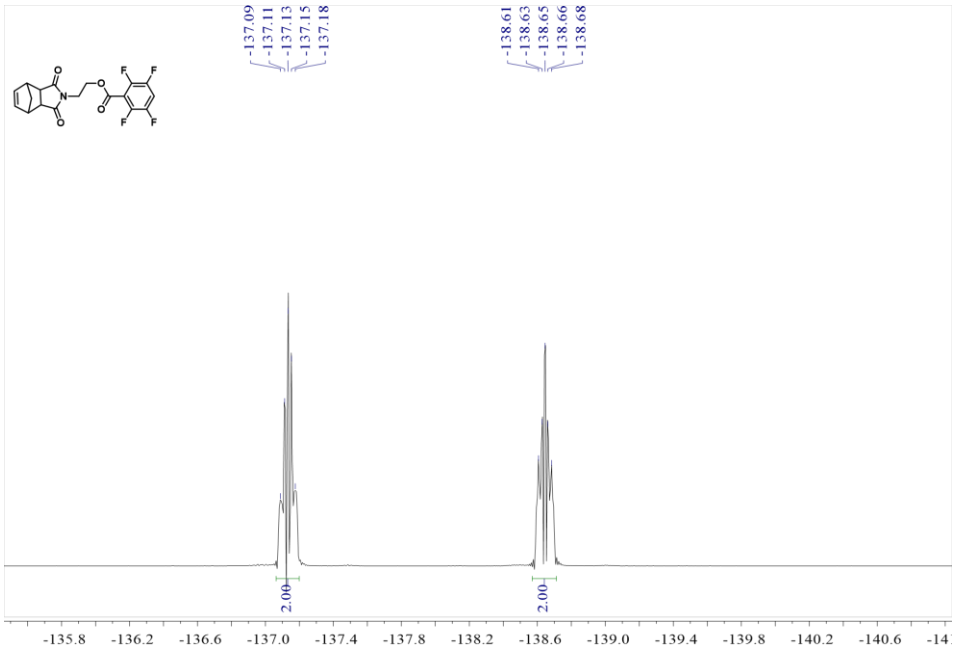


Figure S78: ^{19}F NMR spectrum of 10c.

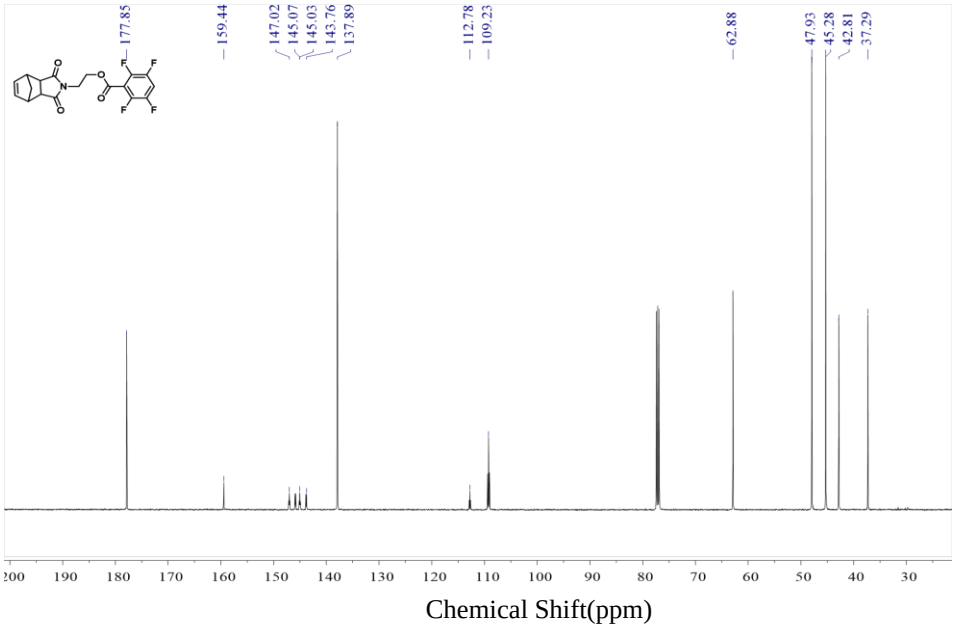


Figure S79: ^{13}C NMR spectrum of 10c.

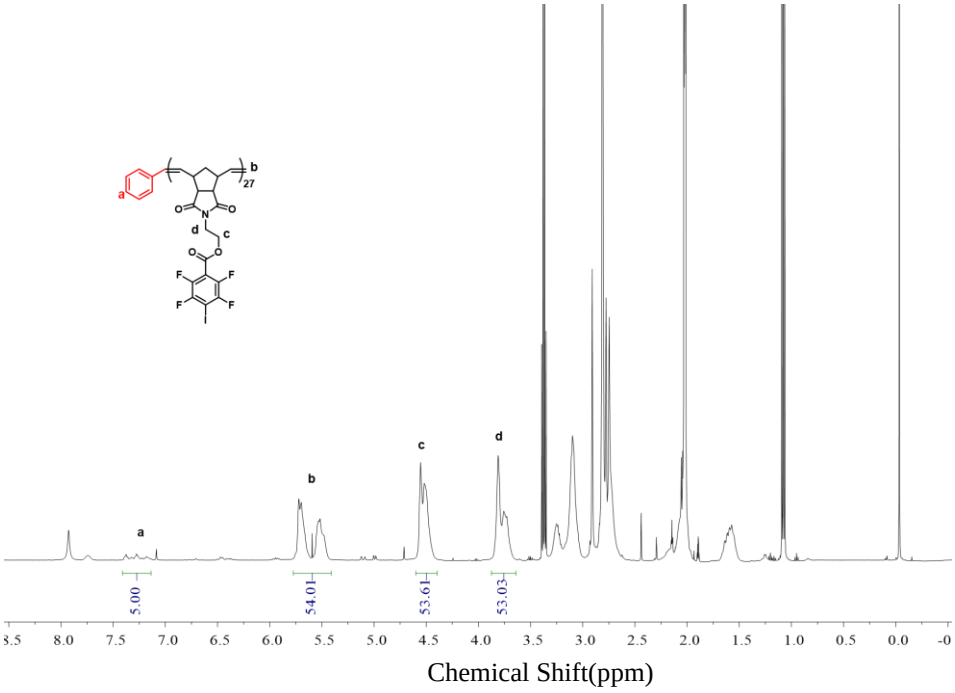


Figure S80: ^{1}H NMR spectrum of 10d (Acetone-d_6).

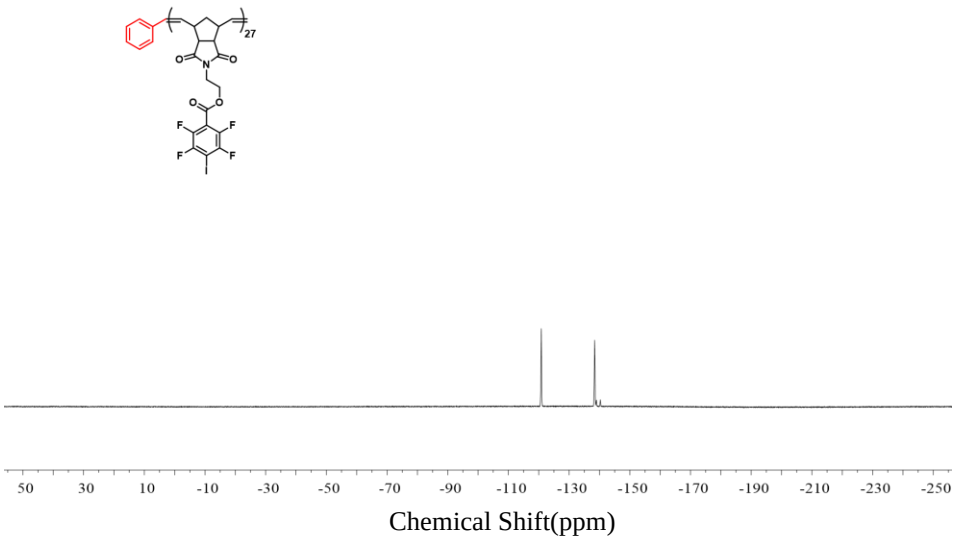


Figure S81: ^{19}F NMR spectrum of 10d (Acetone-d_6).

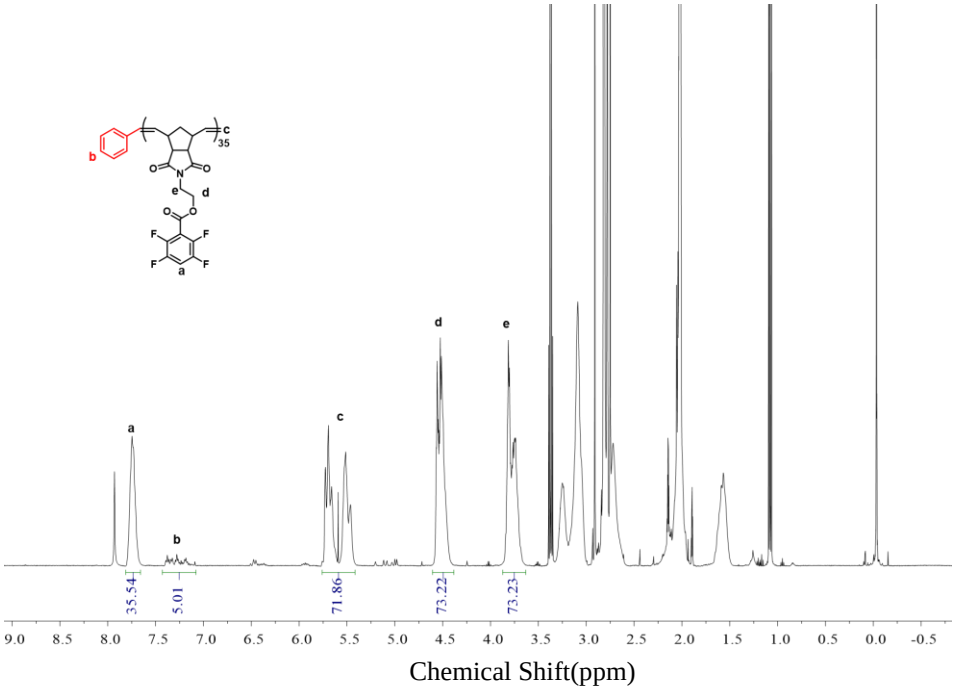


Figure S82: ^{1}H NMR spectrum of 10e (Acetone-d_6).

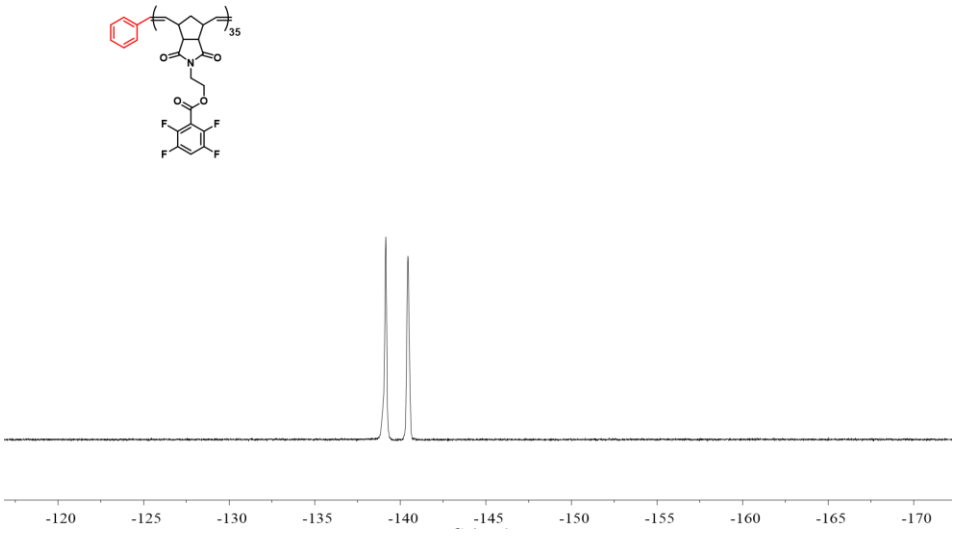


Figure S83: ^{19}F NMR spectrum of 10e (Acetone-d_6).

5. References

[1] Z. M. Strater, M. Rauch, S. Jocksch, T. H. Lambert, *Angew. Chem. Int. Ed.* 2019, **58**, 8049-8052.

[2] N. Biot, D. Bonifazi, *Chem-Eur J.* 2020, **26**, 2904-2913.

[3] Y. Zhao, K. Zhang, *Polym. Chem.* 2016, **7**, 4081-4089.

[4] R. Kumar, S. K. Ray, Dr. S. Mukherjee, S. Saha, A. Bag, P. K. Ghorai, N. Ghosh, R. Shunmugam, *Chem. Eur. J.* 2019, **25**, 13514-13522.

[5] M. G. Chudzinski, C. A. McClary, M. S. Taylor, *J. Am. Chem. Soc.* 2011, **133**, 10559-10567.

[6] A. Vanderkooy, M. S. Taylor, *J. Am. Chem. Soc.* 2015, **137**, 5080-5086.

[7] F. Wang, N. Ma, Q. Chen, W. Wang, L. Wang, *Langmuir* 2007, **23**, 9540-9542.

[8] T. L. Sun, F. Luo, W. Hong, K. Cui, Y. Huang, H. J. Zhang, D. R. King, T. Kurokawa, T. Nakajima, J. P. Gong, *Macromolecules* 2017, **50**, 2923-2931.