Electronic Supplementary Material (ESI) for Polymer Chemistry

BF_3•Et_2O-mediated Friedel-Crafts C-H Bond Polymerization to Synthesize π-Conjugation-interrupted Polymer Semiconductors

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Experimental Section

Materials

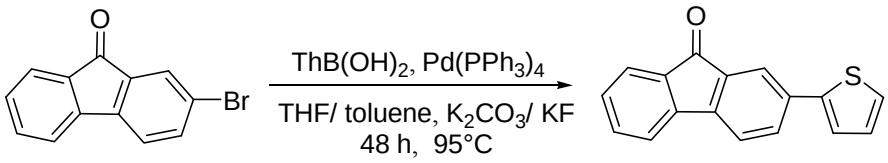
K_2CO_3, KF, toluene, magnesium turnings, CuI, TBAB, $Pd(PPh_3)_4$, $MgSO_4$, $BF_3 \cdot Et_2O$ (> 95%), 1,2-dichlorobenzene, 1-bromo-4-(octyloxy)benzene (> 98%), carbazole (> 95%), acetone, 2,2'-bipyridine, 1,10-phenanthroline were purchased from Aldrich or J&K Chemicals without further purification. 2-bromo-fluoren-9-one (> 99%), 2,7-dibromo-fluoren-9-one (> 99%), thiophen-2-yl boronic acid (> 98%) were obtained from Nanjing Fountain Global Displays Ltd. Co. All experiments were carried out under a nitrogen atmosphere in a dry box or by standard Schlenk techniques. THF was dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. CH_2Cl_2 was distilled at the present of P_2O_5.

Characterization

^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker 400 MHz spectrometer. Chloroform-*d* was used as a solvent. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (TMS) in $CDCl_3$ unless otherwise noted. Gas chromatography-mass spectrum ((GC/MS) were performed with a Shimadzu GCMS 2010, helium used as a carrier gas. The sample (1 mg) was dissolved in dichloromethane (1 mL) and a 2 μL aliquot of the solution was injected. The peaks for products were identified by comparison with pure substance peaks. Molecular weights of the samples were measured by Gel permeation chromatography (GPC) on a Shimadzu LC-20A HPLC system equipped with 7911GP-502 and GP NXC columns. The calibration curves for GPC analysis were obtained using polystyrene standards with a low polydispersity. The sample (10 mg) was dissolved in THF (2 mL) and the solution was filtered through a membrane filter with a 0.45 μm

pore size. Fourier transfer infrared (FT-IR) spectra were measured by neat on a KBr plate. Absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer at 25°C, and photoluminescence spectra were recorded on a Shimadzu RF-5301(PC)S luminescence spectrometer. The sample was measured in CH_2Cl_2 (1.0×10^{-5} mol/L) and in film states. Thermogravimetric analysis (TGA) was undertaken with a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 °C/min under N_2. The electrochemical cyclic voltammetry (CV) was conducted on CHI 600C Electrochemical Workstation, in a 0.1 mol/L acetonitrile solution of tetrabutylammonium hexafluorophosphate (n-$Bu_4N^+PF_6^-$) at a potential scan rate of 100 mV/s with an Ag/Ag^+ reference electrode, a platinum wire counter electrode, and a platinum sheet working electrode, polymer film was formed by drop-casting 1.0 μL of polymer solutions in CH_2Cl_2 (refined, 1 mg/mL) onto the working electrode, and then dried in the air.

Preparation of 2-(thiophen-2-yl)-fluoren-9-one (1)

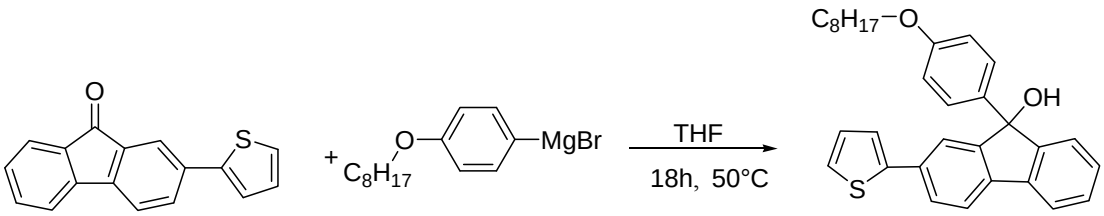


Scheme S1. Synthesis of THFO through the Suzuki cross-coupling reaction.

The K_2CO_3/KF (2 mol/L) solution and the toluene/THF solution should been get rid of oxygen by blowing N_2 directly into the liquid for 2 h. It is also necessary to protect the dryness instrument from light with silver paper. And then, under N_2, 2-bromo-9H-fluoren-9-one (4.0 g, 15.5 mmol), thiophen-2-ylboronic acid (5.0 g, 38.8 mmol), $Pd(PPh_3)_4$ (0.5 g, 5% mmol), were added into the equipment. Besides, toluene/ THF(50 mL) was injected in the flask before heating it in Silicone bath under 95°C. After stirring for 30 min under reflux, the breathed K_2CO_3/KF (39 mL, 78 mmol) into

the flask, held on the reaction for 48 h. After cooling to room temperature, the mixture was quenched with saturated brine (50 mL) and extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (petroleum ether /dichloromethane, 4:1) to get product **1** (3.6 g, 89%) as a yellow solid. GC-MS (EI-m/z): 262 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.88 (s, 1H), 7.71-7.65 (m, 2H), 7.49-7.46 (t, J = 6.7 Hz, 3H), 7.37-7.36 (d, J = 3.5 Hz, 1H), 7.32-7.26 (t, J = 7.2 Hz, 2H), 7.11-7.01 (t, J = 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 193.59, 144.21, 143.12, 142.96, 135.40, 134.87, 134.31, 131.53, 128.99, 128.25, 125.44, 124.40, 123.71, 121.45, 121.43, 120.76, 120.35.

Preparation of 2-(thiophen-2-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-ol (TPFOH)

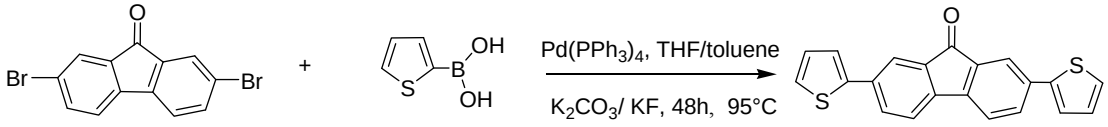


Scheme S2. Synthesis of TPFOH by the Grignard reaction.

Under N_2, a sample of THFO (2.2 g, 8.5 mmol) was dissolved in dry THF (50 mL), and the mixture was dropwise added to a Grignard solution prepared from magnesium turnings (0.5 g, 19.6 mmol) reacted with 1-bromo-4-(octyloxy)benzene (3.7 g, 12.8 mmol) in dry THF (30 mL). After the addition was completed, the reaction carried out in Silicone bath at 50°C for 18 h. After cooling to room temperature, the mixture was quenched with saturated NH_4Cl (30 mL), after the solution was stirred for 30 min,

extracted with CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (petroleum ether /dichloromethane, 3:1) to give colorless solid TPFOH (3.0 g, 75%) . GC-MS (EI-m/z): 468 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.67-7.61 (m, J = 6.7 Hz, 3H), 7.58 (s, 1H), 7.39-7.27 (m, 2H), 7.25-7.24 (d, J = 3.5 Hz, 1H), 7.06-7.04 (m, 1H), 6.71-6.79 (d, J = 8.9 Hz, 2H), 3.92-3.89 (t, J = 6.5 Hz, 2H), 2.46 (s, 1H), 1.76-1.70 (m, 2H), 1.43-1.37 (m, 2H), 1.31-1.24 (m, 8H), 0.90-0.83 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.51, 151.40, 150.79, 144.25, 139.00, 138.82, 134.74, 134.65, 129.11, 128.46, 128.03, 126.86, 126.59, 124.87, 124.73, 123.28, 122.20, 120.52, 120.08, 114.25, 83.39, 67.97, 31.82, 29.36, 29.28, 29.24, 26.06, 22.66, 14.11.

Preparation of 2,7-di(thiophen-2-yl)-fluoren-9-one (DTHFO**, 2)**

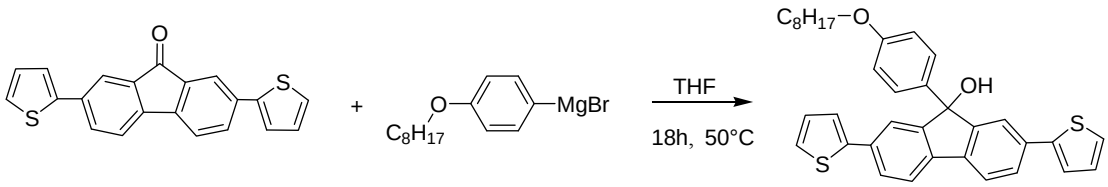


Scheme S3. Synthesis of DTHFO by the Suzuki reaction.

The procedure was similar to the preparation of **1**, 2,7-dibromo-fluoren-9-one (3.0 g, 9 mmol), thiophen-2-ylboronic acid (4.6 g, 36 mmol), $Pd(PPh_3)_4$ (1.0 g, 5%-10% mmol), toluene/THF (54 mL), K_2CO_3/ KF (22.5 mL, 45 mmol). The production was purified by column chromatography (petroleum ether/dichloromethane, 3:1). To recrystallize it from petroleum ether containing a small amount of dichloromethane for three times give product DTHFO (1.2 g, 39%) as a red solid. GC-MS (EI-m/z):

344 (M^+). ^{1}H NMR(400 MHz, $CDCl_3$, TMS, ppm): δ 7.93-7.92 (d, J = 1.5 Hz, 2H), 7.76-7.75 (d, J = 1.8 Hz, 1H), 7.74-7.73 (d, J = 1.7 Hz, 1H), 7.54 (s, 1 H), 7.52 (s, 1H), 7.40-7.39 (d, J = 3.4 Hz, 2H), 7.3 4-7.33 (d, J = 4.9 Hz, 2H), 7.13-7.11 (m, 2H).

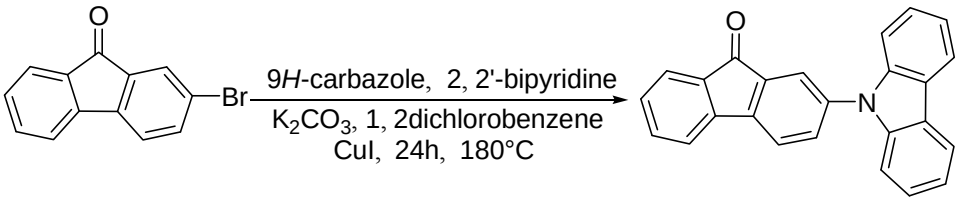
Preparation of 2,7-di(thiophen-2-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-ol (DTPFOH)



Scheme S4. Preparation of DTPFOH by the Grignard reaction.

The process was the same with the preparation of TPFOH wth compound **2** (1.12 g, 3.3 mmol), THF (120 mL), magnesium turnings (0.37 g, 15 mmol), 1-bromo-4-(octyloxy)benzene (2.65 g, 9.3 mmol). The production was purified by column chromatography (petroleum ether /dichloromethane, 2:1) to obtain DTPFOH (0.9 g, 79%) as a light-yellow solid. GC-MS (EI-m/z): 534 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.67-7.61 (m, 4H), 7.58-7.57 (d, J = 1.2 Hz, 2H), 7.37-7.35 (d，d, J = 2.1 Hz, J = 2.1 Hz, 2H), 7.31 -7.30 (d, d, J = 1.1 Hz, J = 1.2 Hz, 2H), 7.26 (s, 1 H), 7.25-7.25 (d, J = 1.0 Hz, 2H), 7.06-7.04 (m, 2H), 6.83-6.80 (d, d, J = 2.1 Hz, J = 2.1 Hz, 2H), 3.92-3.89 (t, J = 6.5 Hz, 2H), 2.46 (s, 1H), 1.76-1.70 (m, 2H), 1.43-1.37 (m, 2H), 1.31-1.26 (m, 8H), 0.88 -0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.56, 151.58, 144.21, 138.30, 134.65, 128.08, 126.92, 126.62, 124.92, 123.37, 122.15, 120.54, 114.37, 83.33, 67.98, 31.84, 29.38, 29.30, 29.27, 26.08, 22.69, 14.15.

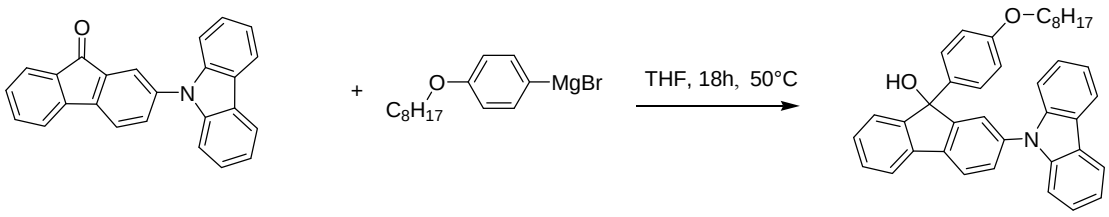
Preparation of 2-(carbazol-9-yl)-fluoren-9-one (3)



Scheme S5. Synthesis of CzFO by the Ullmann reaction.

Under N_2, put 2-bromo-fluoren-9-one (4.00 g, 15 mmol), carbazole (5.20 g, 31 mmol), K_2CO_3 (6.20g, 45 mmol), CuI (3.40 g, 18 mmol), 2,2'-bipyridine (0.005 g), 1,10-phenanthroline (0.005 g) into the dryness flask that protected from light with silver paper, and injected the 1,2-dichlorobenzene (2 mL) into it, then heated the mixture in Silicone bath at 180 °C for 24 h. After the solution cooled to room temperature, the mixture was dissolved in CH_2Cl_2 (35 mL), the solute was filtered and obtained a red-brown solution, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (petroleum ether /dichloromethane, 8:1) to obtain compound **3** (3.7 g, 72%) as a yellow solid. GC-MS (EI-m/z): 345 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.16-8.14 (d, J = 7.7 Hz, 2H), 7.89-7.88 (d, J = 1.8 Hz, 1H), 7.77-7.70 (m, 3H), 7.64-7.55 (m, 2H), 7.44-7.43 (d, J = 3.9 Hz, 4H), 7.38-7.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 192.88, 143.93, 142.99, 140.46, 138.70, 135.98, 135.12, 134.44, 132.71, 129.35, 124.71, 123.66, 122.81, 121.63, 120.57, 120.47, 120.41, 109.77.

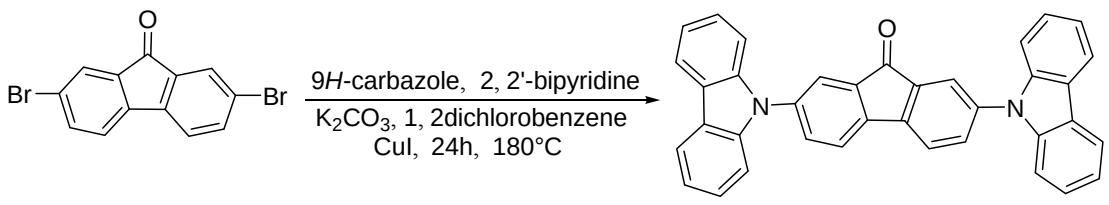
Preparation of 2-(carbazol-9-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-ol (CzPFOH)



Scheme S6. Preparation of CzPFOH by the Grignard reaction.

The process was the same with the preparation of TPFOH with compound **3** (2.52 g, 7.3 mmol), THF (70 mL), magnesium turnings (0.36 g, 13 mmol), 1-bromo-4-(octyloxy)benzene (3.12 g, 11 mmol). The product was purified by column chromatography (petroleum ether /dichloromethane, 4:1). Light-brown viscid solid CzPFOH (3.2 g, 80%) got. GC-MS (EI-m/z): 535 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.13-8.11 (d, J = 7.8 Hz, 2H), 7.87-7.85 (d, J = 8.5 Hz, 1H), 7.75-7.73 (d, J = 7.5 Hz, 1H), 7.58-7.56 (m, 2H), 7.45-7.38 (m, 6H), 7.36-7.28 (m, 5H), 6.81-6.79 (d, J = 8.8 Hz, 2H), 3.91-3.88 (t, J = 6.6 Hz, 2H), 2.55 (s, 1 H), 1.77-1.70 (m, 2H), 1.45-1.37 (m, 2H), 1.32-1.26 (m, 8H), 0.89-0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.64, 152.54, 150.69, 140.68, 138.83, 138.45, 137.66, 134.52, 129.34, 128.70, 127.57, 126.59, 126.00, 124.96, 123.45, 121.24, 120.34, 120.29, 120.04, 114.34, 109.87, 83.43, 68.01, 31.85, 29.39, 29.28, 26.07, 22.70, 14.15.

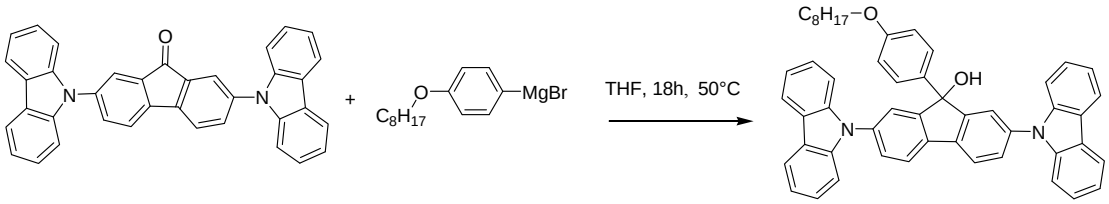
Preparation of 2,7-di(carbazol-9-yl)-fluoren-9-one (4)



Scheme S7. Synthesis of DCzFO by the Ullmann reaction.

The method was similar to the preparation of compound 3 with 2,7-dibromo-fluoren-9-one (6.72 g, 20 mmol), carbazole (8.00g, 48 mmol), CuI(9.12 g, 48 mmol), K_2CO_3 (16.60 g, 120 mol), 2,2'-bipyridine (0.005 g), 1,10-Phenanthroline (0.005 g), 1,2-dichlorobenzene (5 mL), the production was purified by column chromatography (petroleum ether /dichloromethane, 6:1) to obtain compound **4** (5.8 g, 57%) as a yellow solid. GC-MS (EI-m/z): 510 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.18-8.16 (d, J = 7.7 Hz, 4H), 7.97-7.96 (d, J = 1.7 Hz, 2H), 7.87-7.85 (d, J = 7.8 Hz, 2H), 7.80-7.78 (dd, J = 1.95 Hz, J = 1.98 Hz, 2H), 7.47-7.46 (m, 8H), 7.36-7.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ191.86, 142.41, 140.42, 138.97, 136.26, 133.05, 126.25, 123.74, 123.13, 121.86, 120.53, 109.74.

Preparation of 2,7-di(carbazol-9-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-ol (DCzPFOH)

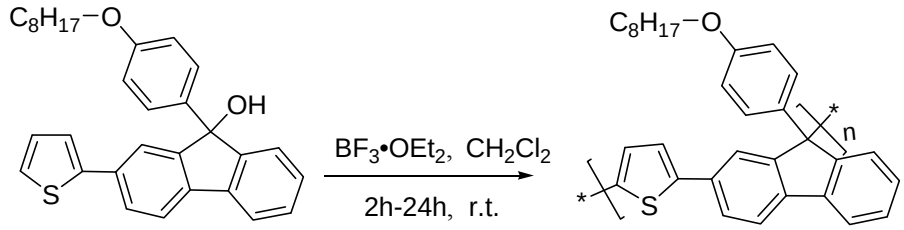


Scheme S8. Preparation of DCzPFOH by the Grignard reaction.

The method was similar to the preparation of TPFOH with compound **4** (2.00 g, 3.9 mmol), THF (75 mL), magnesium turnings (0.30 g, 12.5 mmol), 1-bromo-4-(octyloxy)benzene (2.26g, 7.8 mmol). The production was purified by column chromatography (petroleum ether /dichloromethane, 3:1), and then was recrystallized from petroleum ether containing a small amount of dichloromethane for three times, received DCzPFOH (1.9 g, 68%) as a white solid. ^{1}H NMR(400 MHz, $CDCl_3$, TMS, ppm): δ 8.15-8.13 (d, J = 7.8 Hz, 4H), 7.95-7.93 (d, J = 8.6 Hz, 2H),

7.66-7.64 (t, J = 4.0 Hz, 4H), 7.43-7.39 (t, J = 7.4 Hz, 10H), 7.32-7.28 (m, 4H), 6.82-6.80 (d, J = 8.8 Hz, 2H), 3.91-3.88 (t, J = 6.6 Hz, 2H), 2.69 (s, 1H), 1.76-1.69 (m, 2H), 1.43-1.36 (m, 2H), 1.30-1.25 (m, 8H), 0.87-0.84 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.85, 152.67, 140.64, 137.96, 137.72, 134.00, 127.85, 126.52, 126.04, 123.60, 123.52, 121.45, 120.38, 114.52, 109.80, 83.44, 68.05, 31.80, 29.34, 29.22, 26.02, 22.64, 14.09.

Preparation of poly[2-(thiophen-2-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-yl] (PTPF)

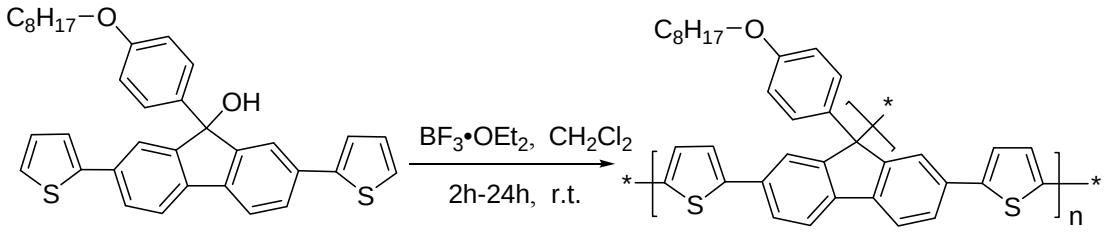


Scheme S9. Preparation of PTPF by the Friedel-Crafts polymerization.

Under N_2, a mixture solution of TPFOH (0.20 g, 0.43 mmol) in appropriate refined CH_2Cl_2 (30 mL) was added dropwise to a solution of $BF_3{\cdot}Et_2O$ complex (0.45 mL, 4.3 mmol) in appropriate refined CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature about 2h-24h. Water (10 mL) was successively added to quench the reaction, and then the phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$). The polymer was purified by dissolving it in a minimum amount of THF or DCM and then precipitating it from methanol (50 mL) at r.t. (25°C), then used Büchner funnel to filtrate the polymer, more pure production obtained after using Soxhlet extractor to distill the polymer. Brown solid PTPF (0.13 g, 65%) was obtained. Mn=1989 g.mol^{-1}, PDI=1.39. IR (KBr), ν_{max}/cm^{-1}: 3047 (Ar-H stretching), 2945(CH_3 asymmetrical stretching), 2918 (CH_2 asymmetrical stretching), 2846 (CH_2 symmetrical stretching), 1602, 1580, 1458 (C=C ring stretching), 810, 796 (Ar-H bending), ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.72-7.24 (6H, Ar-H), 7.15-6.80 (4H, Ar-H), 6.75-6.47 (3H, Ar-H), 3.92-3.73

(2H, OCH_2), 1.78-1.18 (12H, $(CH_2)_6$), 0.95-0.80 (3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.25, 151.73, 151.39, 149.10, 139.14, 138.78, 136.44, 133.96, 128.77, 127.87, 127.73, 127.41, 125.99, 125.68, 122.76, 122.52, 120.57, 120.16, 114.15, 67.84, 64.30, 31.82, 29.50, 29.15, 26.06, 22.67, 14.13.

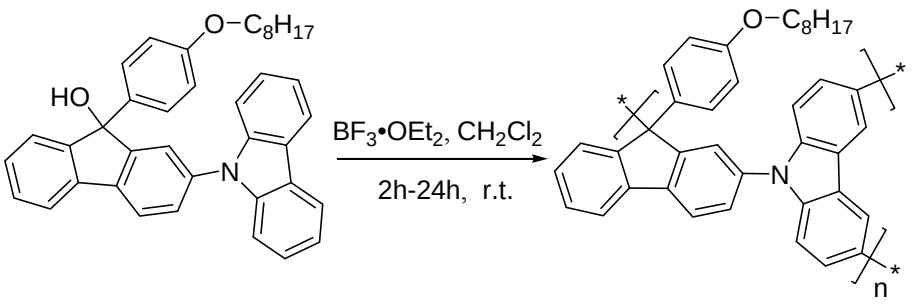
Preparation of poly[2,7-di(thiophen-2-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-yl] (PDTPF)



Scheme S10. Synthesis of PDTPF by the Friedel-Crafts polymerization.

The process was the same with the preparation of PTPF with DTPFOH (0.20 g, 0.36 mmol), CH_2Cl_2 (35 mL), $BF_3{\cdot}Et_2O$ complex (0.39 mL, 3.6 mmol). As a light-brown solid PDTPF (0.16 g, 80%) was obtained. M_n= 2236 g.mol^{-1}, PDI= 1.29. IR (KBr), ν_{max}/cm^{-1}: 3070 (Ar-H stretching), 2951(CH_3 asymmetrical stretching), 2926 (CH_2 asymmetrical stretching), 2848 (CH_2 symmetrical stretching), 1604, 1504, 1467 (C=C ring stretching), 798, 698 (Ar-H bending). ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.72-7.30 (8H, Ar-H), 7.23 -6.54 (8H, Ar-H), 3.94-3.70 (2H, OCH_2), 1.83-1.56 (2H, CH_2), 1.42-1.16 (10H, $(CH_2)_5$), 0.97-0.77 (3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.46, 152.20, 144.59, 138.55, 136.20, 134.00, 128.88, 128.09, 126.05, 124.79, 123.24, 120.72, 114.28, 67.98, 65.50, 31.84, 29.45, 29.25, 26.08, 22.69, 14.14.

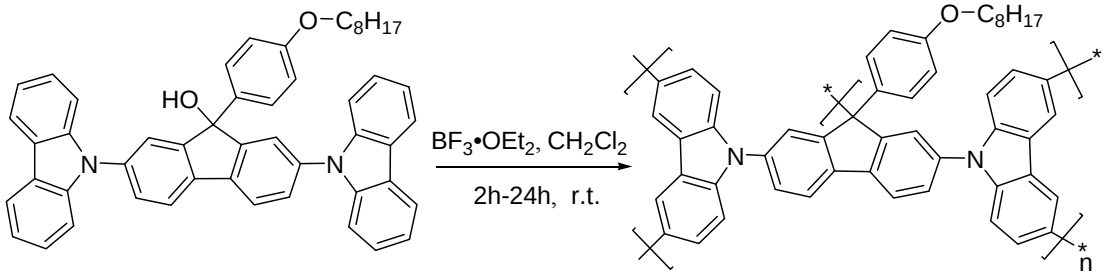
Preparation of poly[2-(carbazol-9-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-yl] (PCzPF)



Scheme S11. Preparation of PCzPF by the Friedel-Crafts polymerization.

The process was similar to the preparation of PTPF with CzPFOH (0.26 g, 0.47 mmol), CH_2Cl_2 (35 mL), $BF_3 \cdot Et_2O$ complex (0.51 mL, 4.7 mmol) to give white solid PCzPF (0.19, 73%). M_n= 9472 g.mol^{-1}, PDI=1.45. IR (KBr), ν_{max}/cm^{-1}: 3059 (Ar-H stretching), 2945(CH_3 asymmetrical stretching), 2926 (CH_2 asymmetrical stretching), 2854 (CH_2 symmetrical stretching), 1600, 1580, 1500 (C=C ring stretching), 804, 746 (Ar-H bending). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.07-7.66 (5H, Ar-H), 7.50-7.33 (6H, Ar-H), 7.19-6.98 (6H, Ar-H), 6.79-6.52 (2H, Ar-H), 3.91-3.59 (2H, OCH_2), 1.78-1.61 (2H, CH_2), 1.38-1.27 (10H, $(CH_2)_5$), 0.88-0.75 (3H, CH_3). ^{13}C NMR (100 MHz; $CDCl_3$, TMS, ppm): δ 206.95, 158.06, 154.14, 152.27, 140.68, 139.21, 137.84, 137.38, 136.73, 129.20, 127.97, 127.57, 126.40, 125.94, 124.47, 123.26, 121.29, 120.35, 120.26, 119.93, 114.26, 109.87, 83.43, 67.94, 65.07, 31.82, 30.95, 29.37, 26.06, 22.66, 14.12.

Preparation of poly[2,7-di(carbazol-9-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-yl] (PDCzPF)



Scheme S12. Synthesis of PDCzPF by the Friedel-Crafts polymerization.

The process was similar to the preparation of PTPF with DCzPFOH (0.30 g, 0.42

mmol), CH_2Cl_2 (35 mL), $BF_3 \cdot Et_2O$ complex (0.43 mL, 4.2 mmol). As a white solid PDCzPF (0.20 g, 68%) was obtained. M_n = 8894 g.mol^{-1}, PDI = 1.39. IR (KBr), ν_{max}/cm^{-1}: 3047 (Ar-H stretching), 2956 (CH_3 asymmetrical stretching), 2920 (CH_2 asymmetrical stretching), 2853 (CH_2 symmetrical stretching), 1608, 1580 (C=C ring stretching), 827, 746 (Ar-H bending), ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.39-7.33 (20H Ar-H), 7.21-6.55 (6H, Ar-H), 3.97-3.62 (2H, OCH_2), 1.78-1.53 (2H, CH_2), 1.40-1.10 (10H, $(CH_2)_5$), 0.88 -0.69 (3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 158.30, 154.27, 140.59, 138.22, 137.10, 129.20, 125.99, 124.91, 123.46, 123.52, 121.54, 120.34, 120.04, 114.41, 109.80, 68.01, 65.22, 31.78, 29.34, 29.22, 29.20, 26.02, 22.60, 14.10.

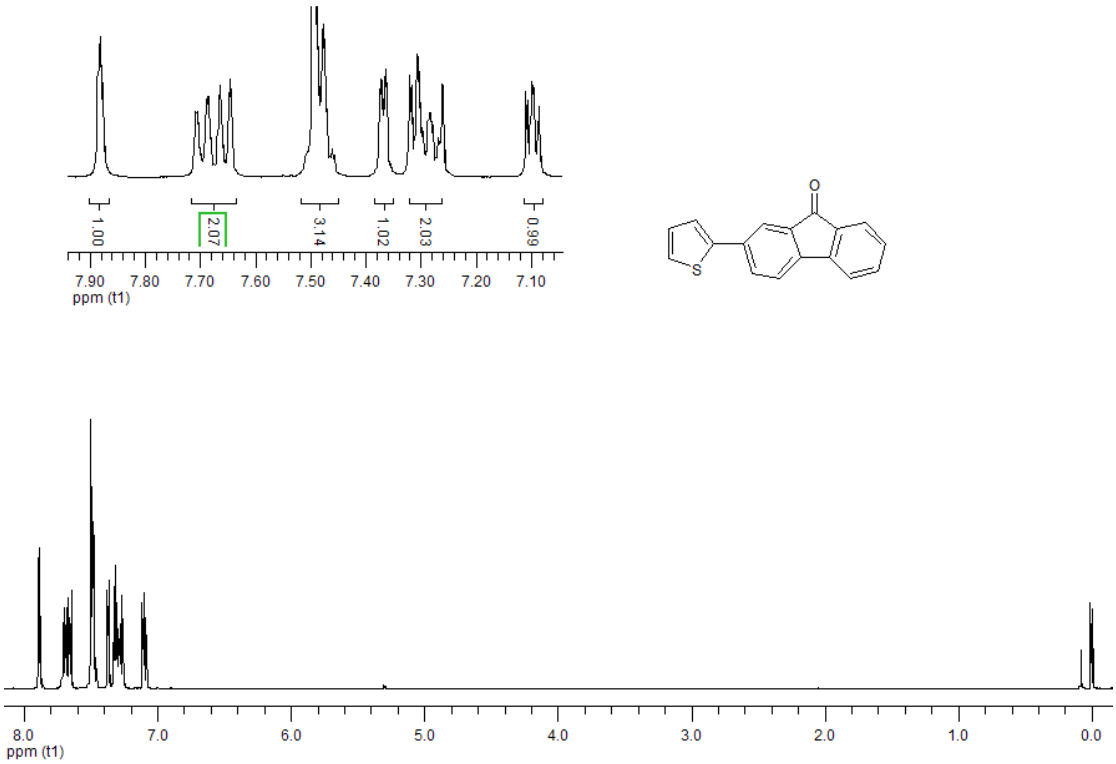


Fig. S-1 ^{1}H NMR spectrum of THFO.

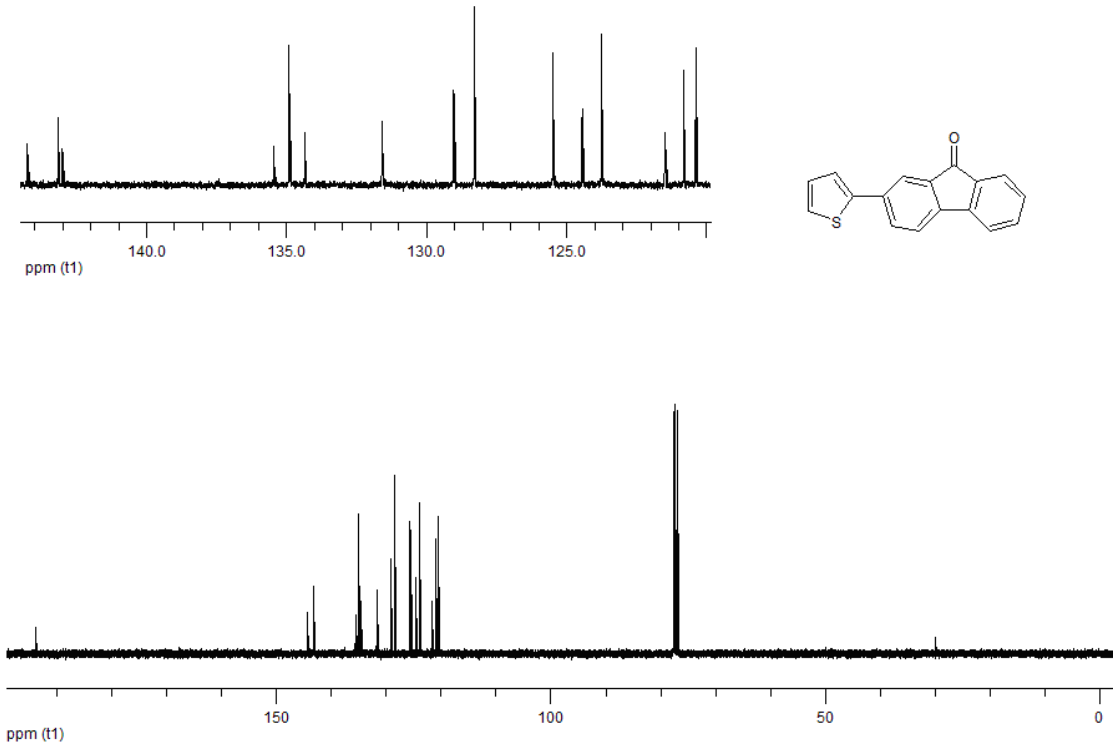


Fig. S-2 ^{13}C NMR spectrum of THFO.

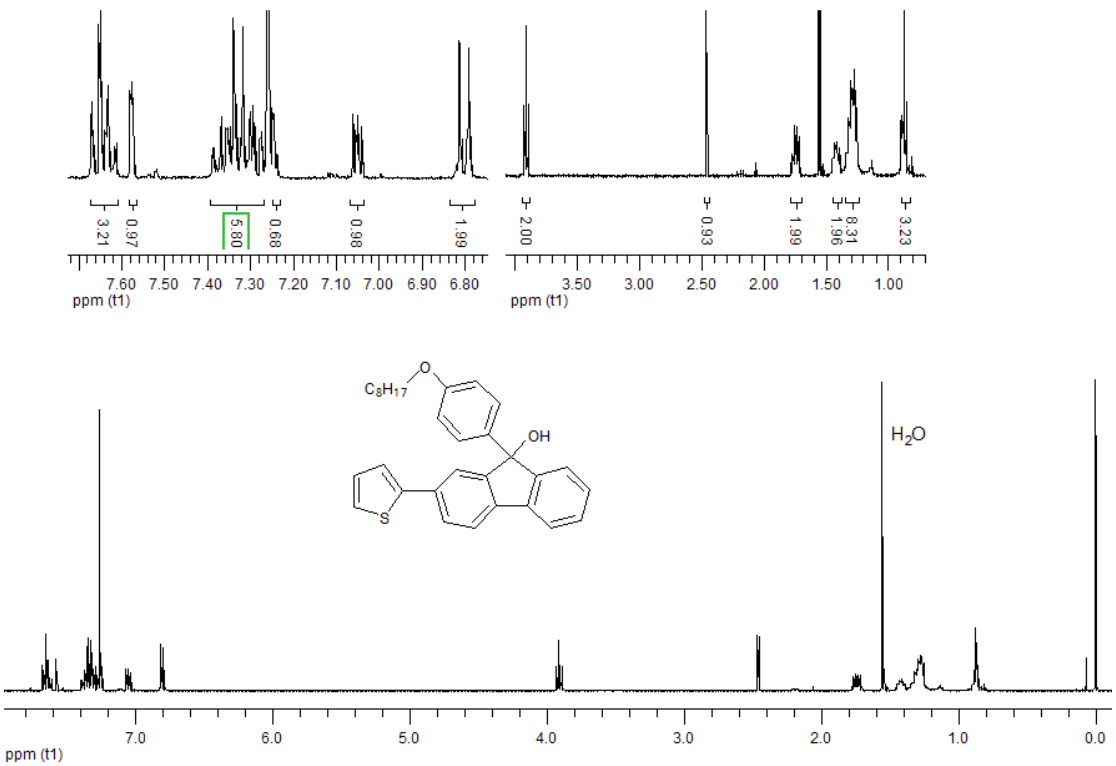


Fig. S-3 ^{1}H NMR spectrum of TPFOH.

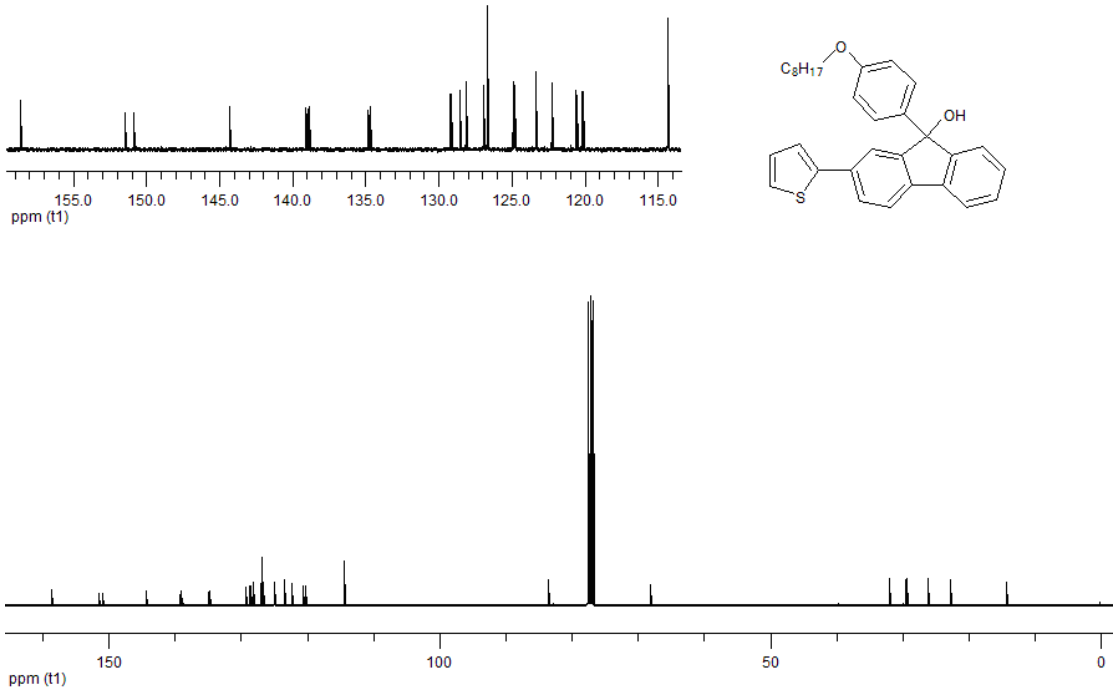


Fig. S-4 ^{13}C NMR spectrum of TPFOH.

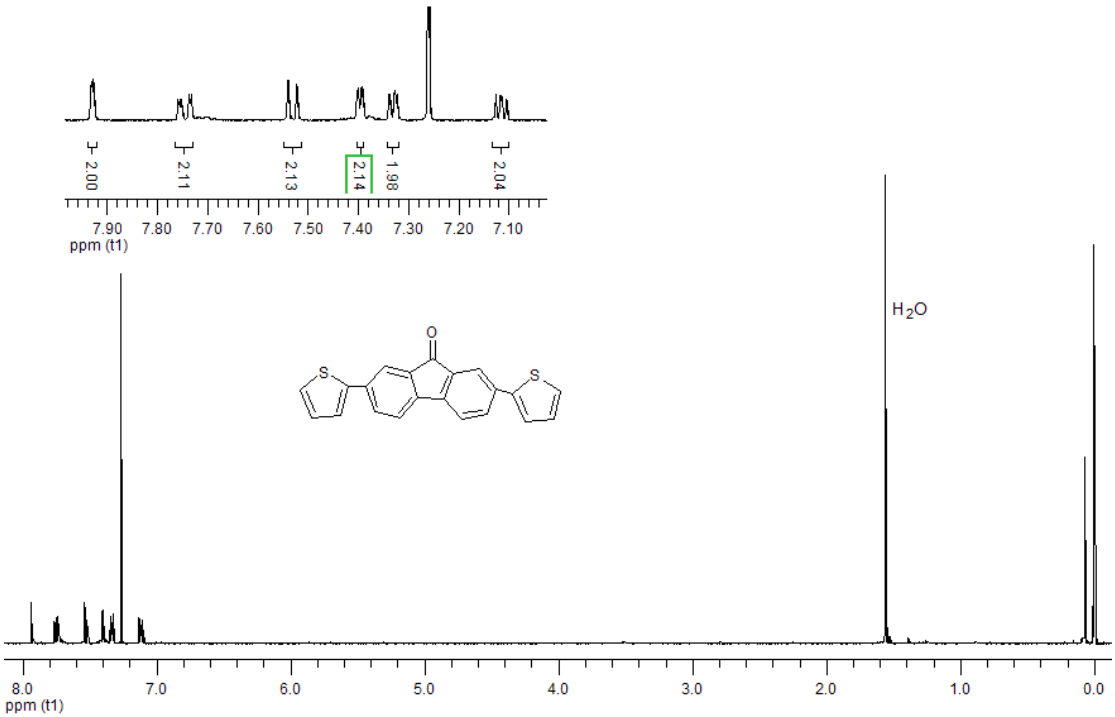


Fig. S-5 ^{1}H NMR spectrum of DTHFO.

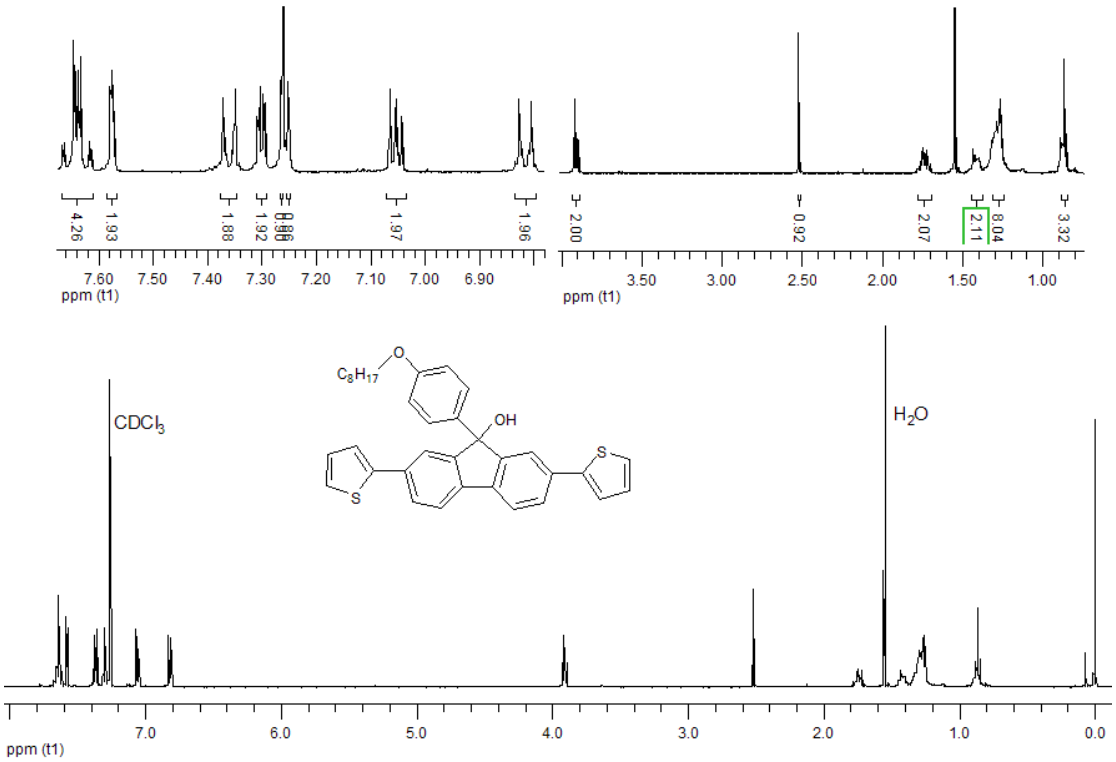


Fig. S-6 ^{1}H NMR spectrum of DTPFOH.

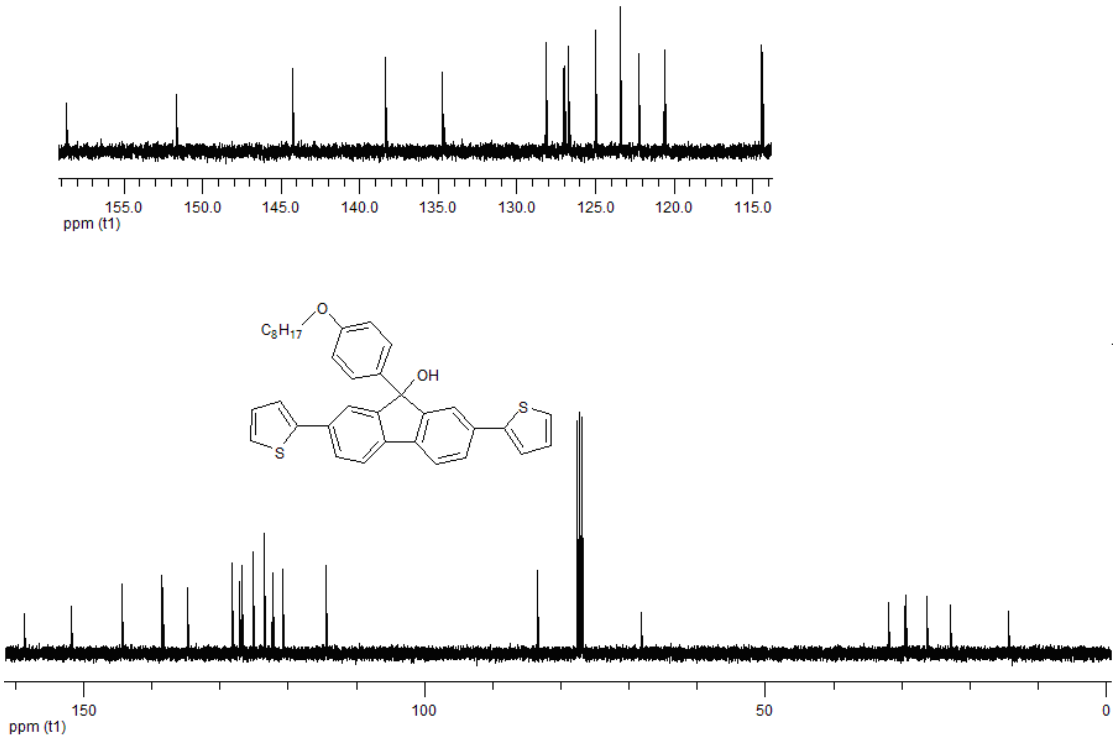


Fig. S-7 ^{13}C NMR spectrum of DTPFOH.

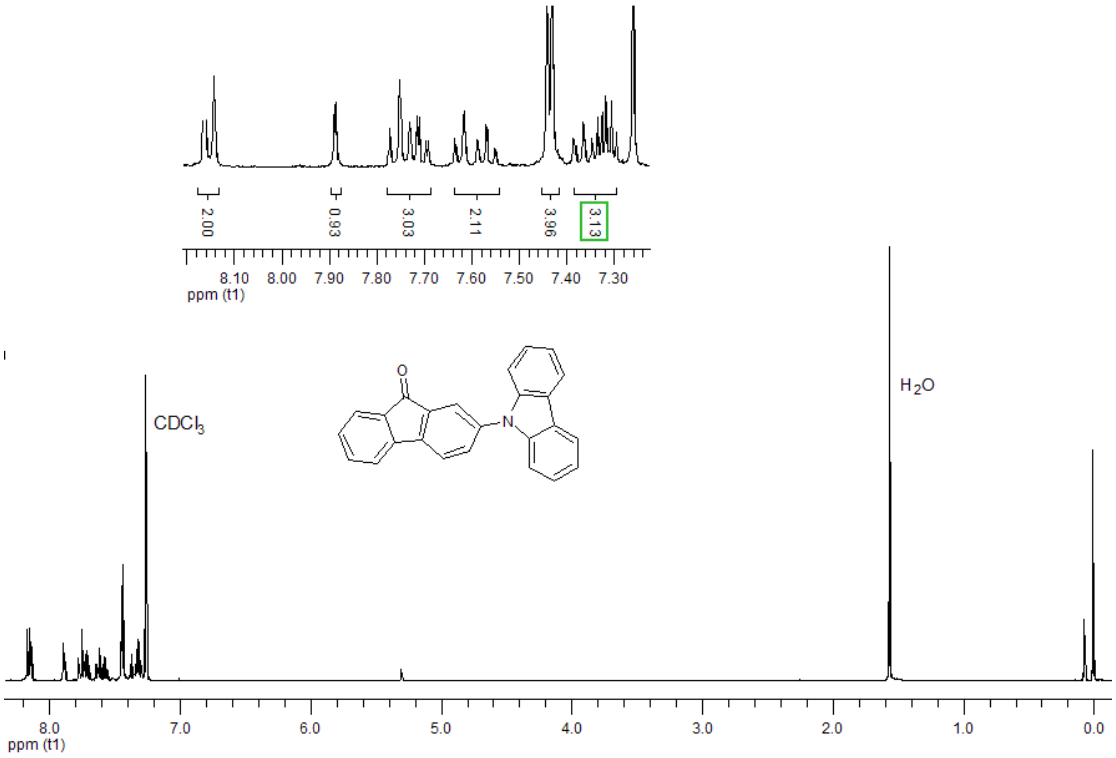


Fig. S-8 ^{1}H NMR spectrum of CzFO.

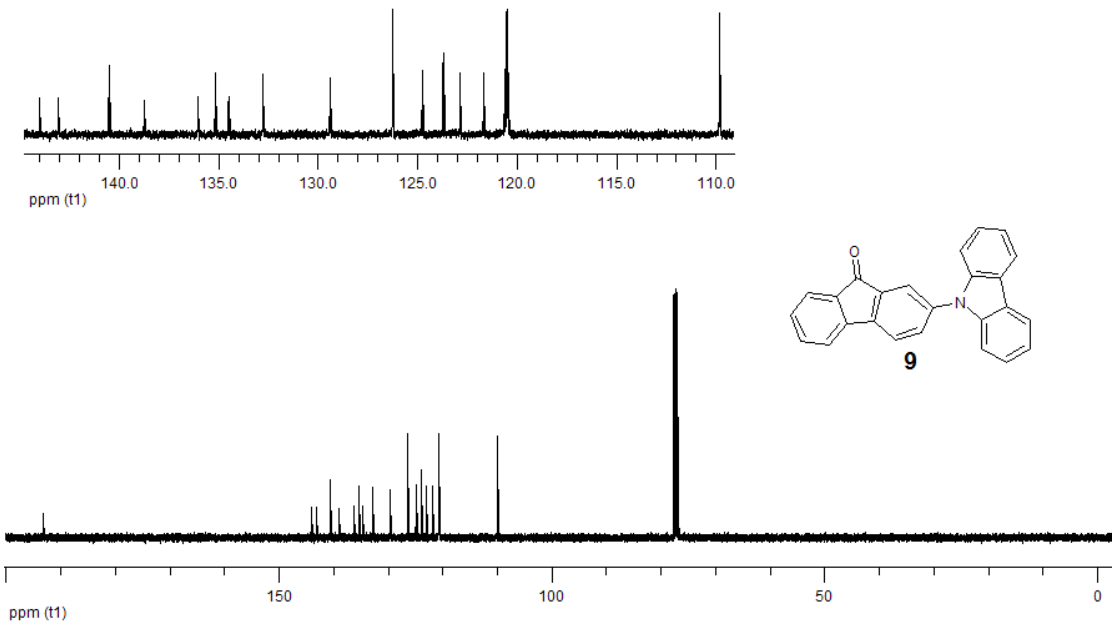


Fig. S-9 ^{13}C NMR spectrum of CzFO.

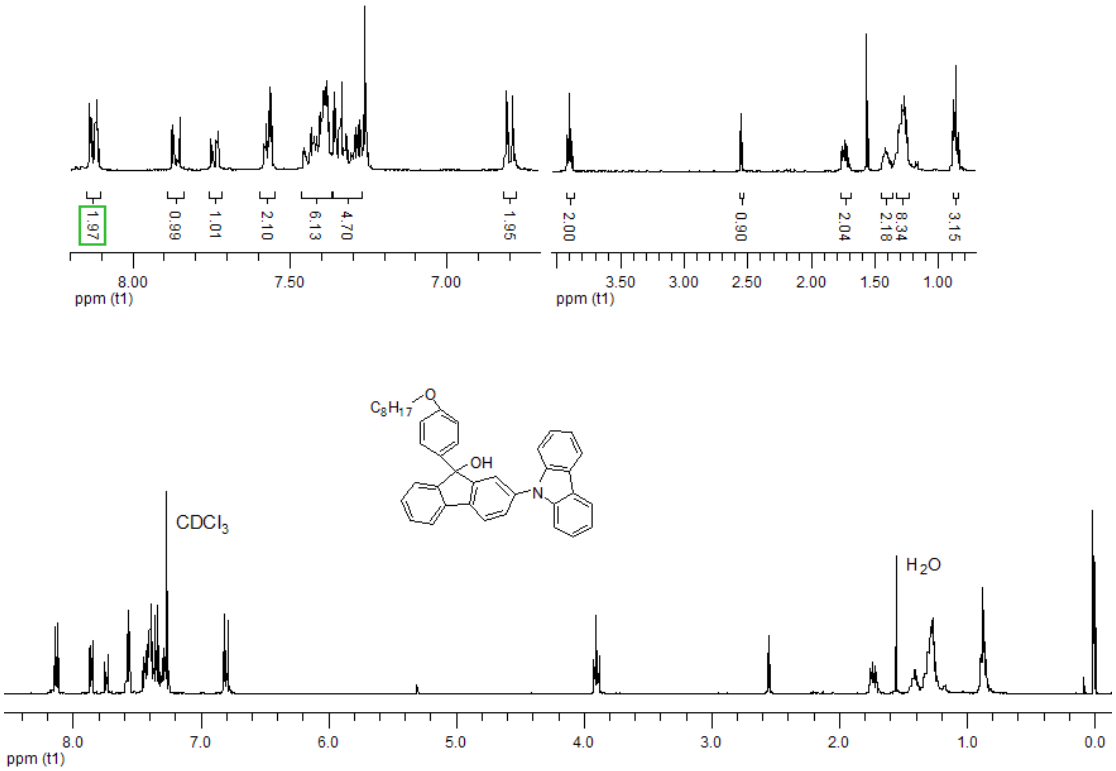


Fig. S-10 ^{1}H NMR spectrum of CzPFOH.

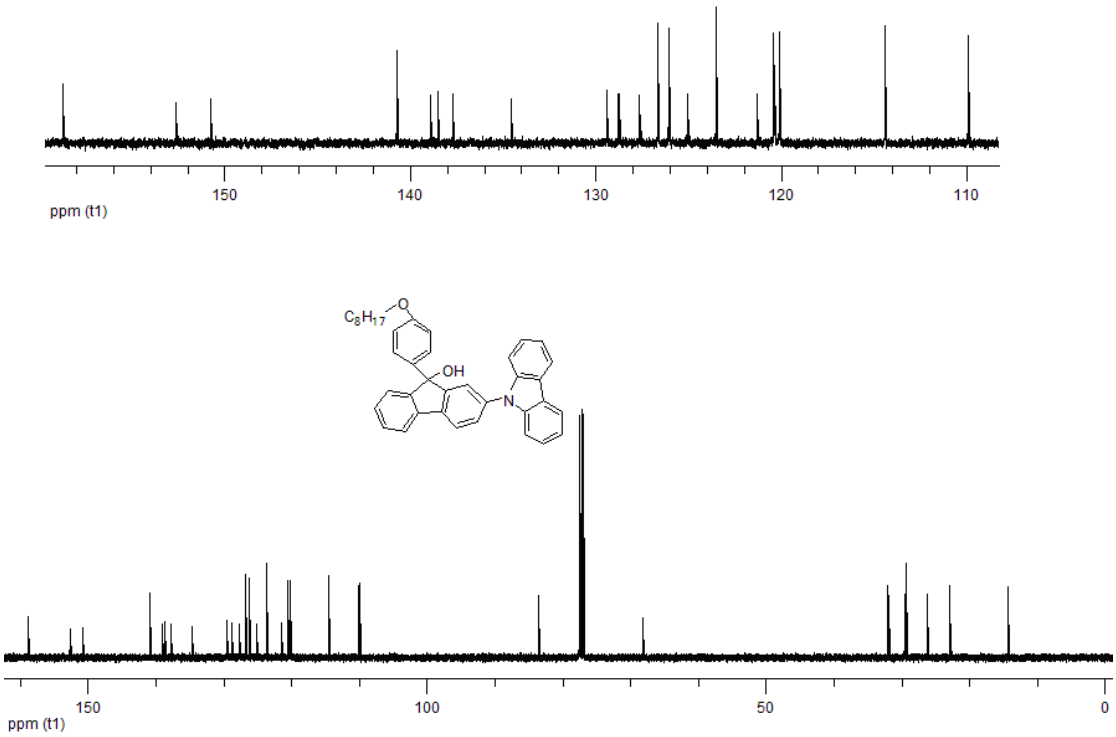


Fig. S-11 ^{13}C NMR spectrum of CzPFOH.

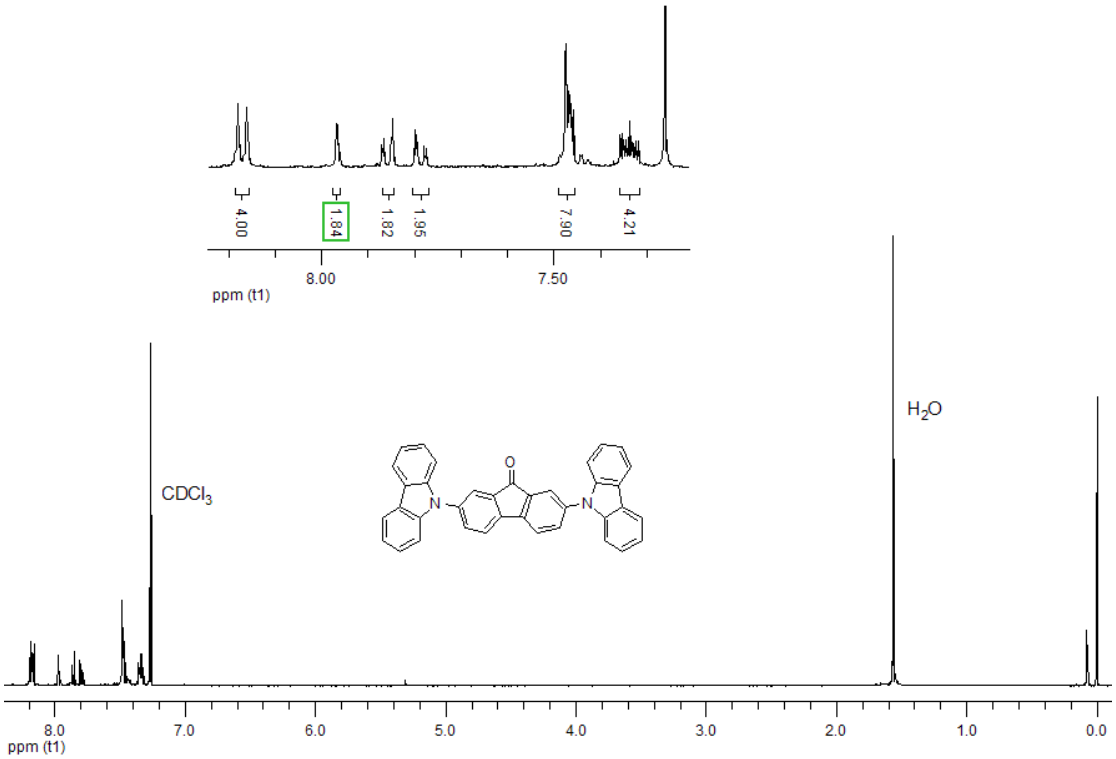


Fig. S-12 ^{1}H NMR spectrum of DCzFO.

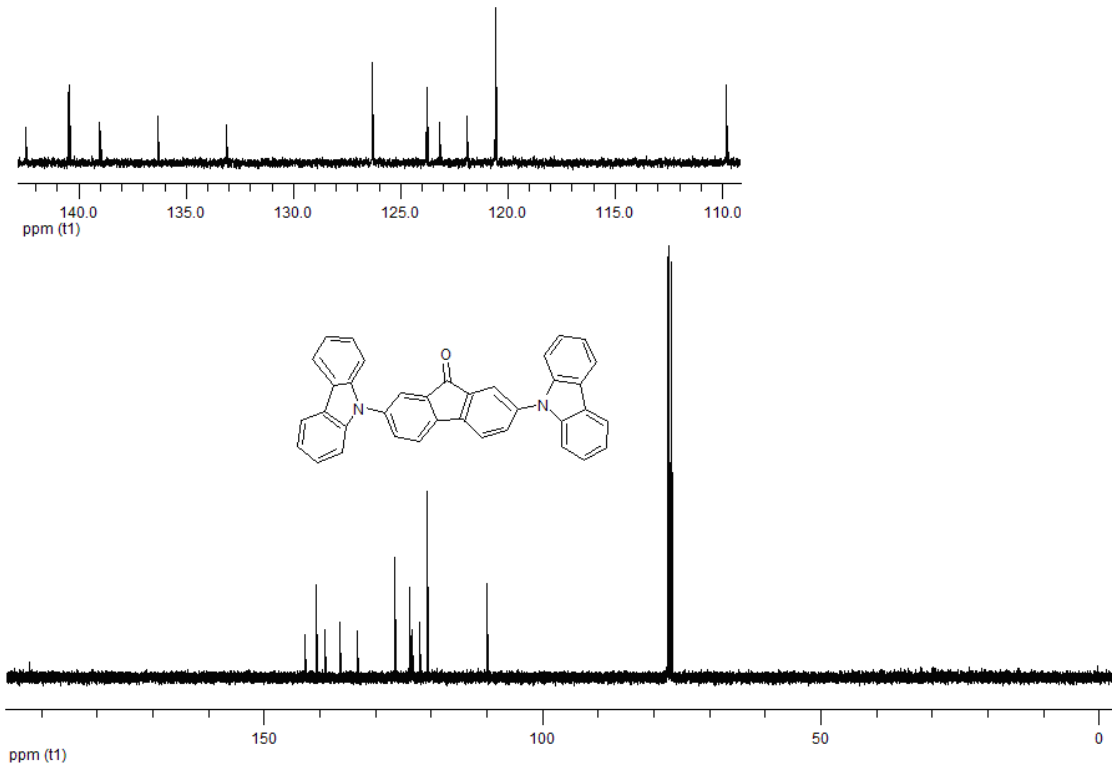


Fig. S-13 ^{13}C NMR spectrum of DCzFO.

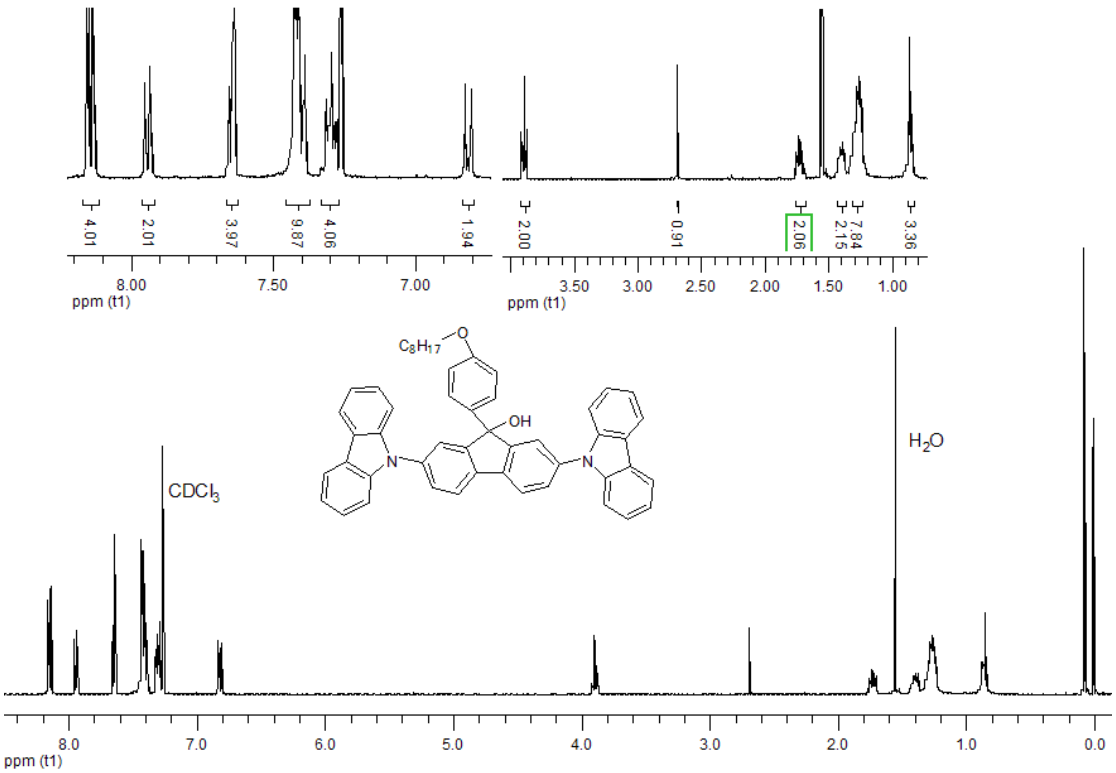


Fig. S-14 ^{1}H NMR spectrum of DCzPFOH.

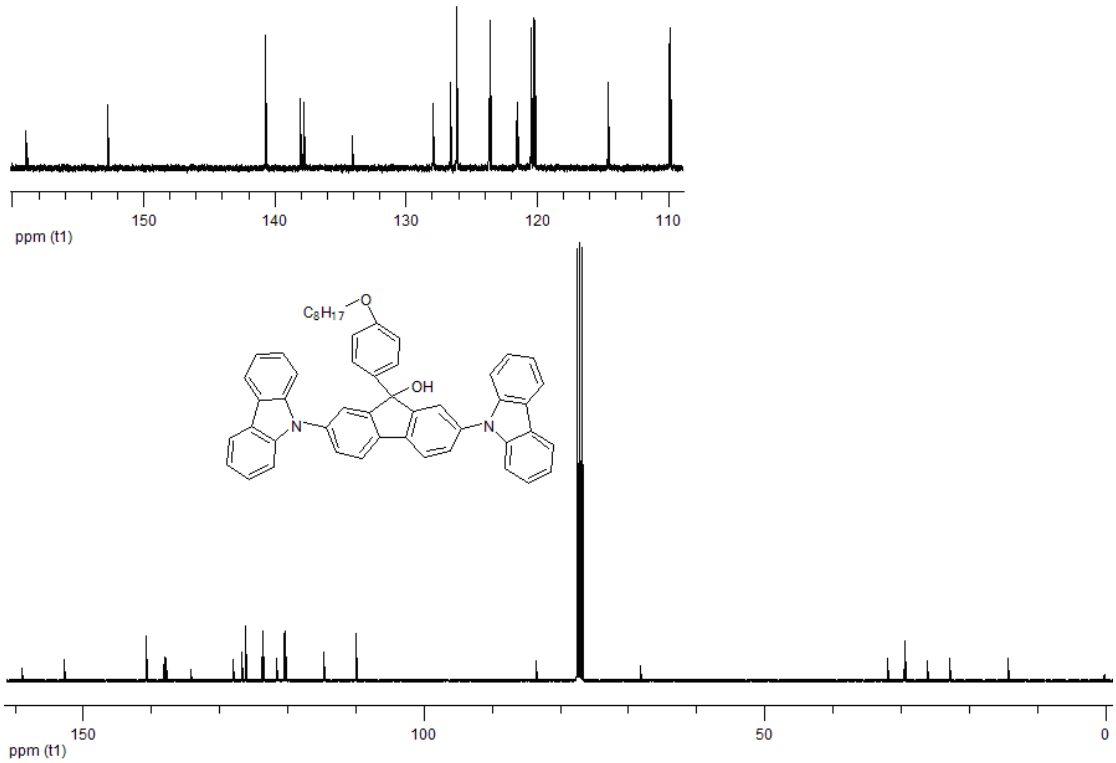


Fig. S-15 ^{13}C NMR spectrum of DCzPFOH.

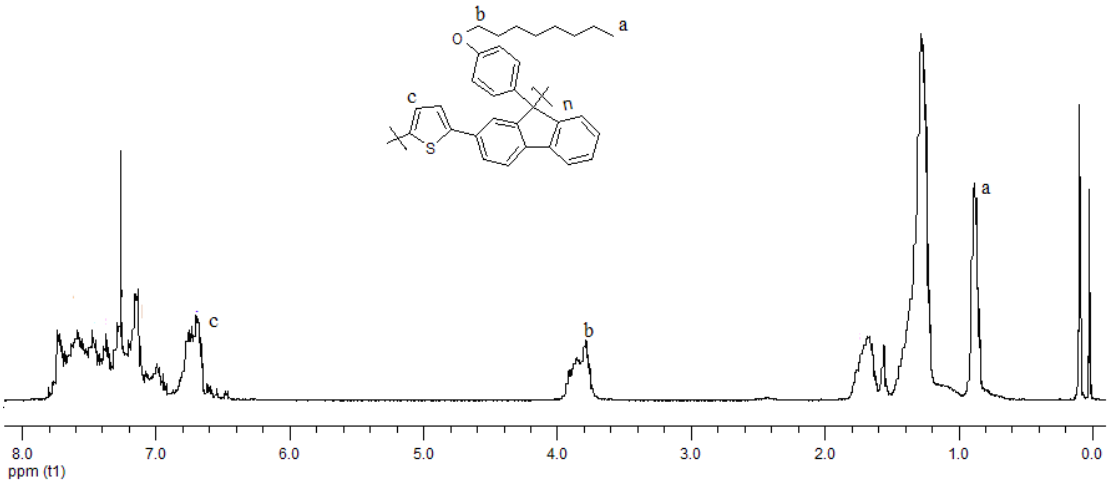


Fig. S-16 ^{1}H NMR spectrum of PTPF.

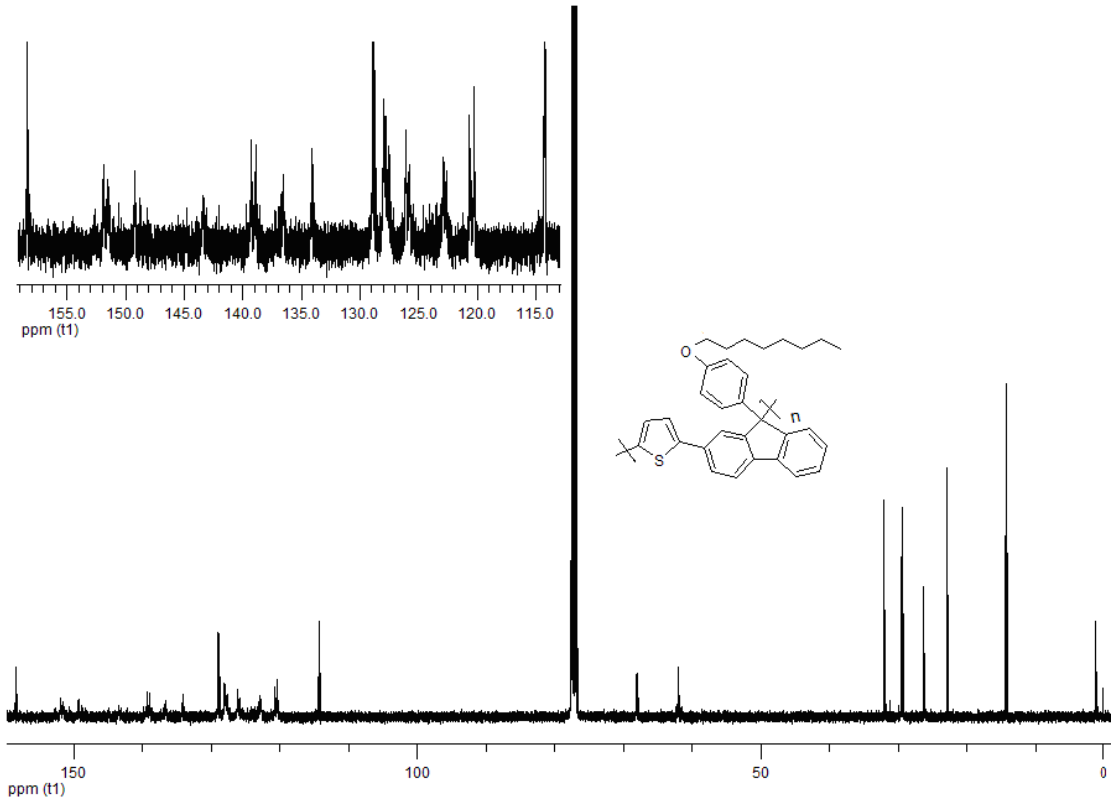


Fig. S-17 ^{13}C NMR spectrum of PTPF.

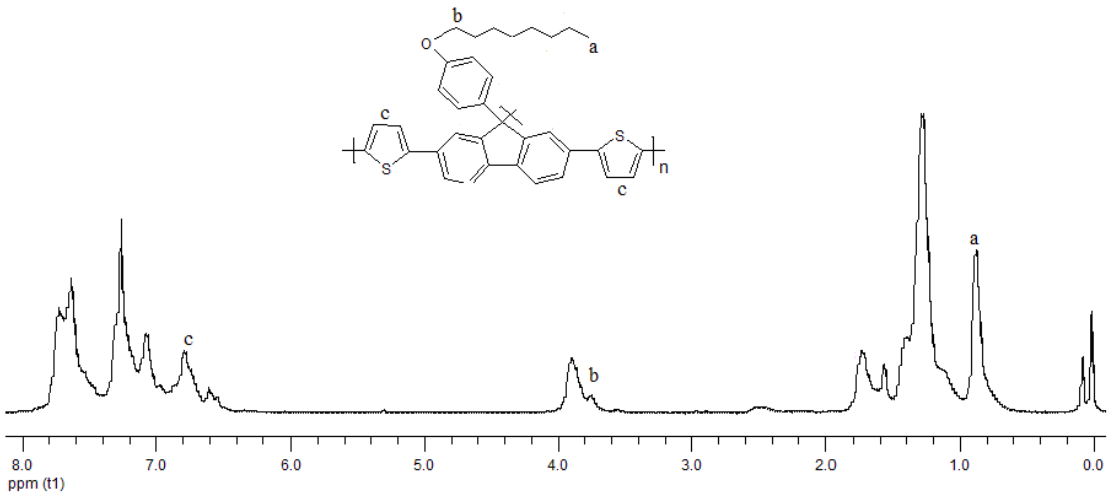


Fig. S-18 ^{1}H NMR spectrum of PDTPF.

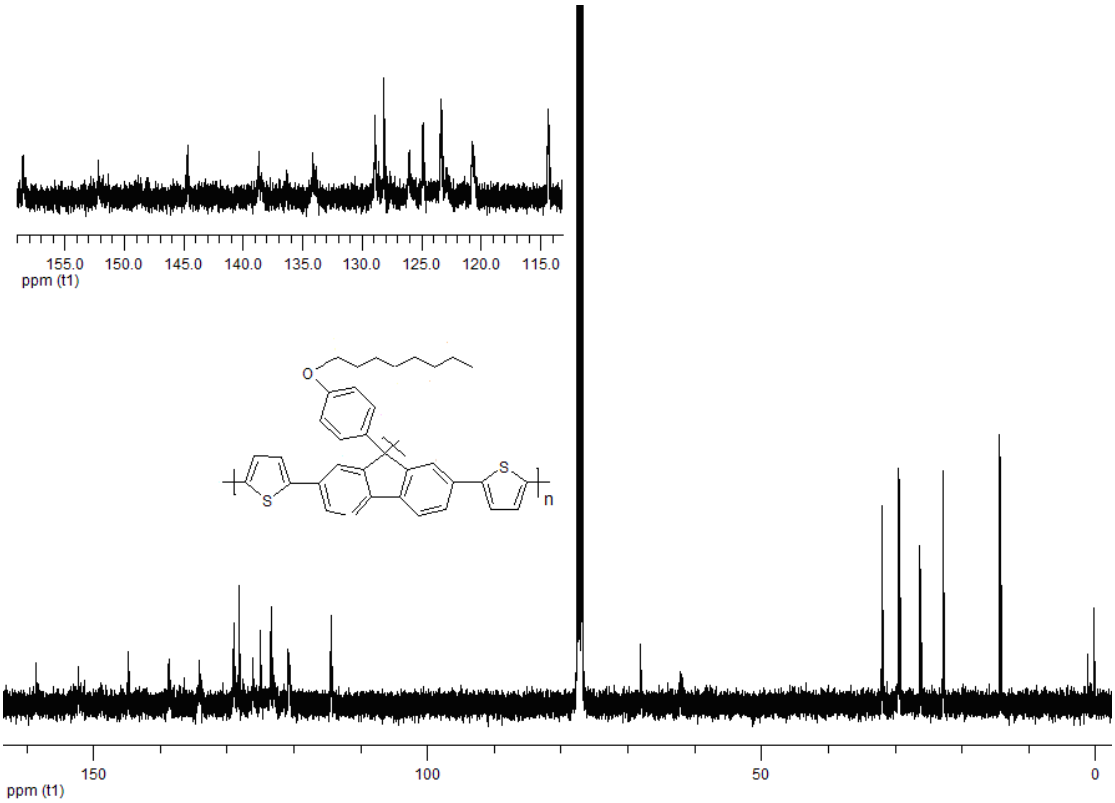


Fig. S-19 ^{13}C NMR spectrum of PDTPF.

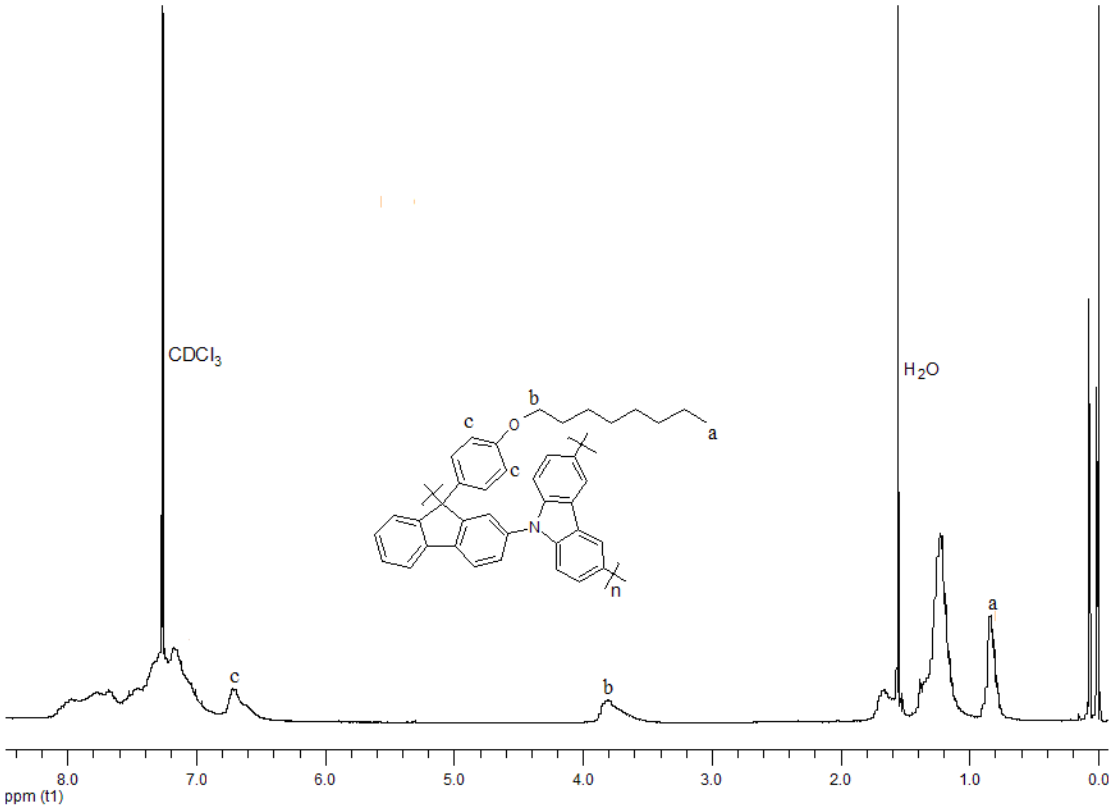


Fig. S-20 ^{1}H NMR spectrum of PCzPF.

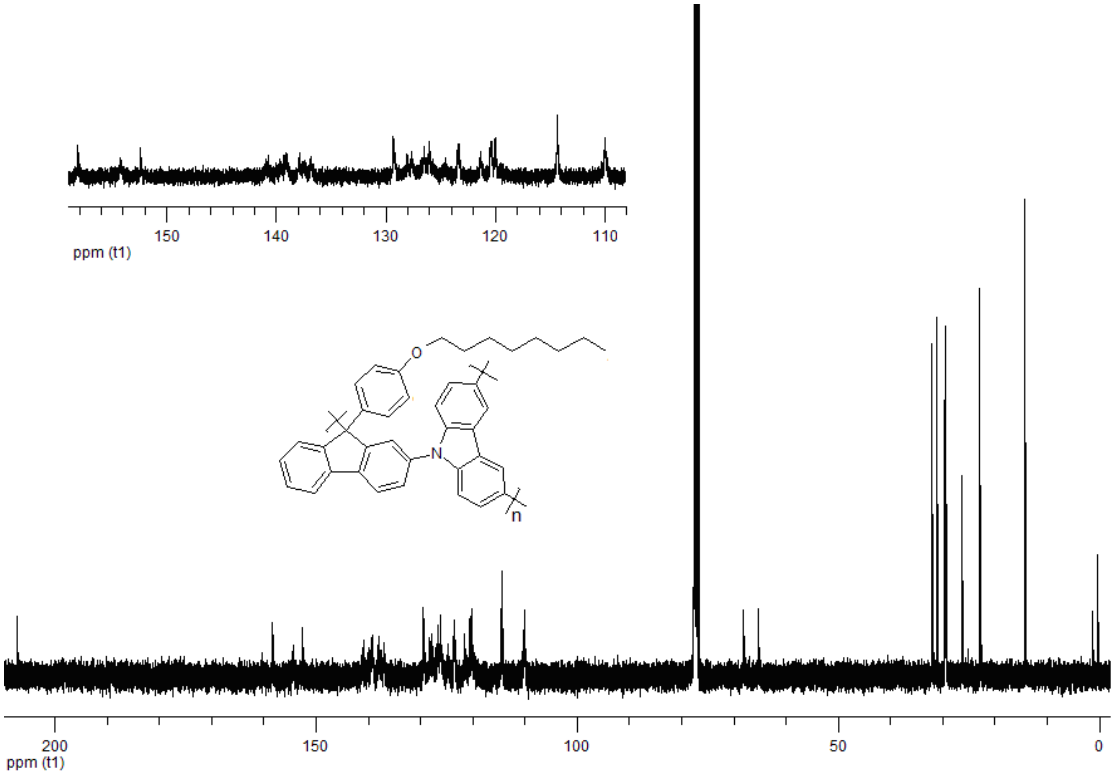


Fig. S-21 ^{13}C NMR spectrum of PCzPF.

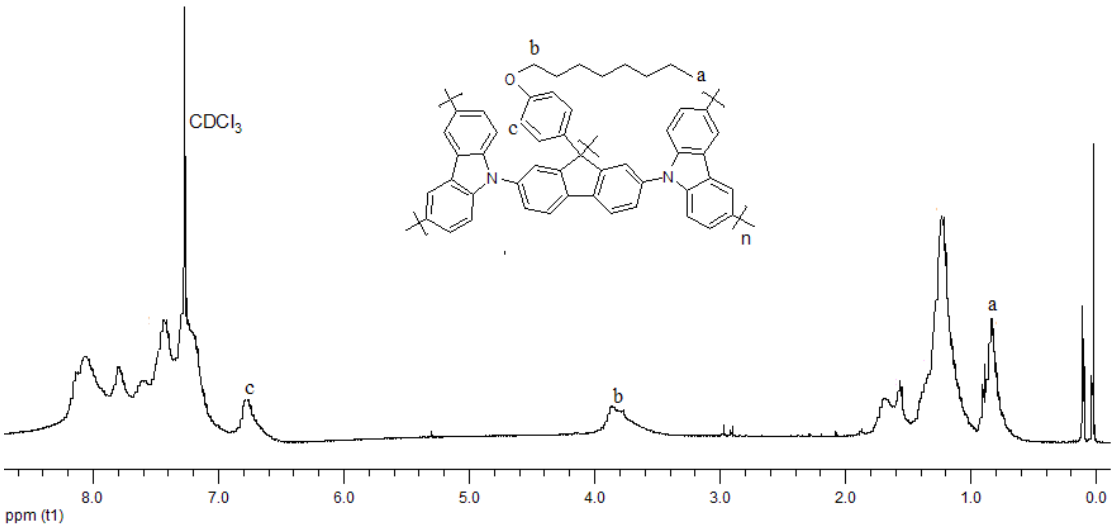


Fig. S-22 ^{1}H NMR spectrum of PDCzPF.

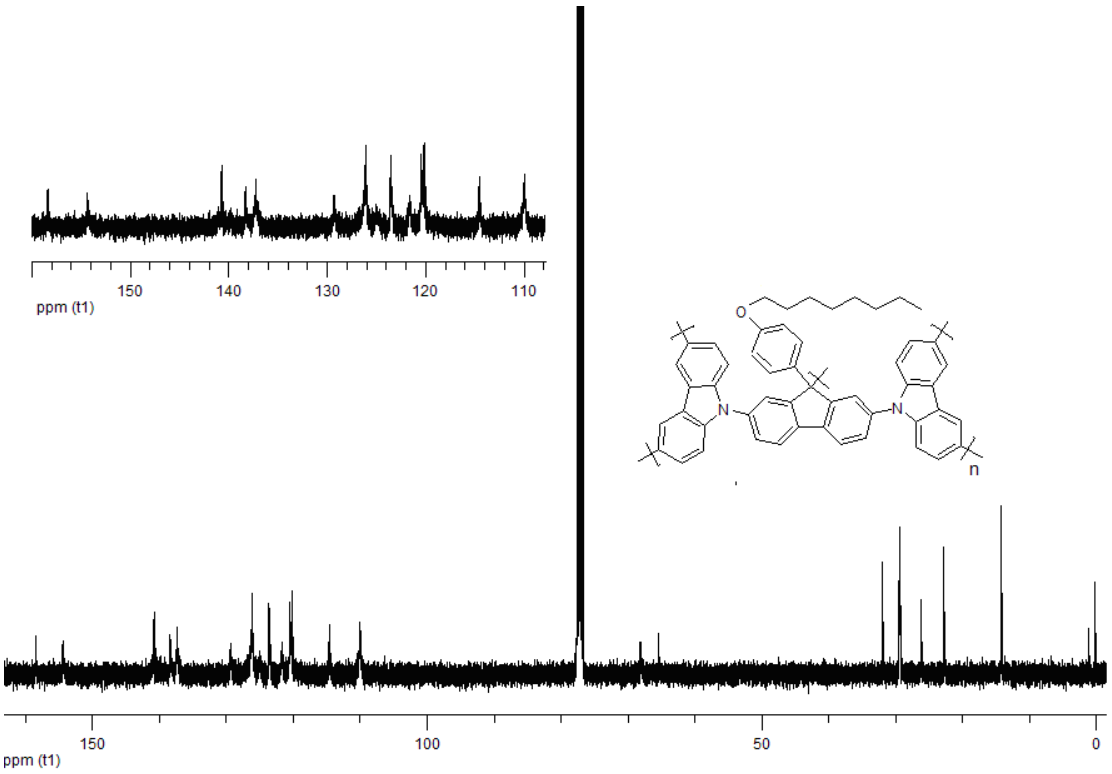


Fig. S-23 ^{13}C NMR spectrum of PDCzPF.

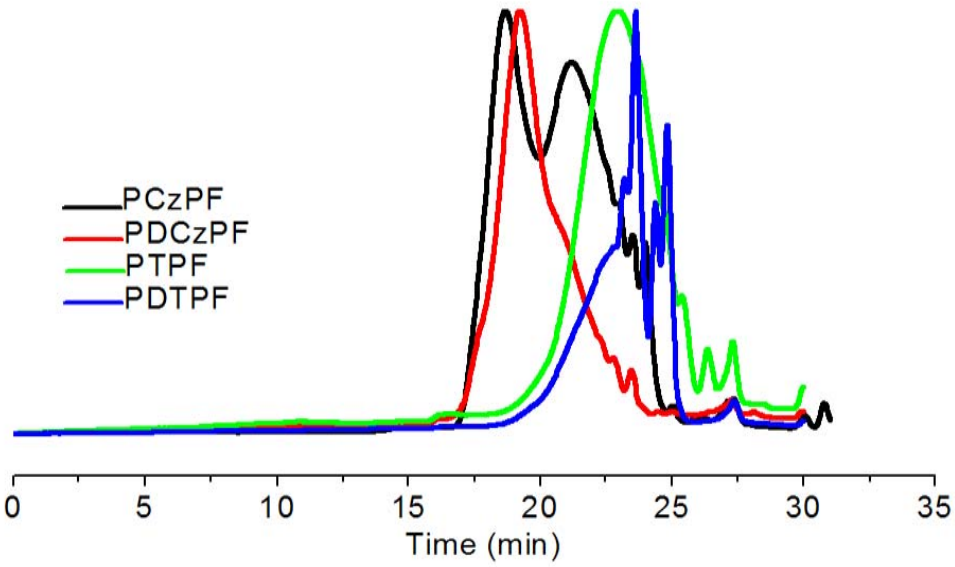


Fig. S-24 GPC curves of the four polymers

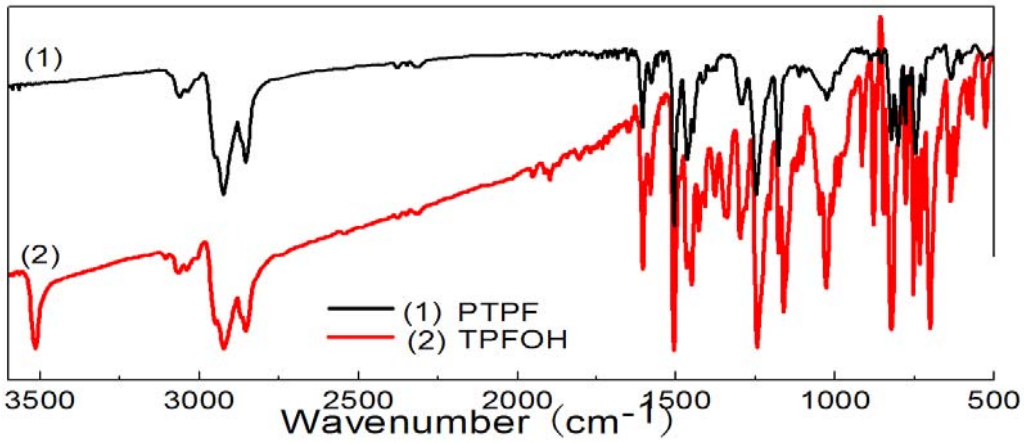


Fig. S-25 FT-IR spectra of the polymer PTPF and the monomer TPFOH.

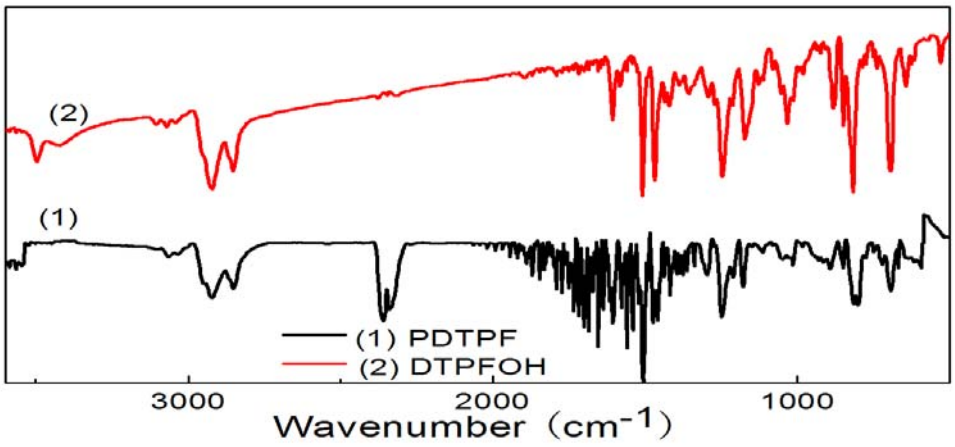


Fig. S-26 FT-IR spectra of the polymer PDTPF and the monomer DTPFOH.

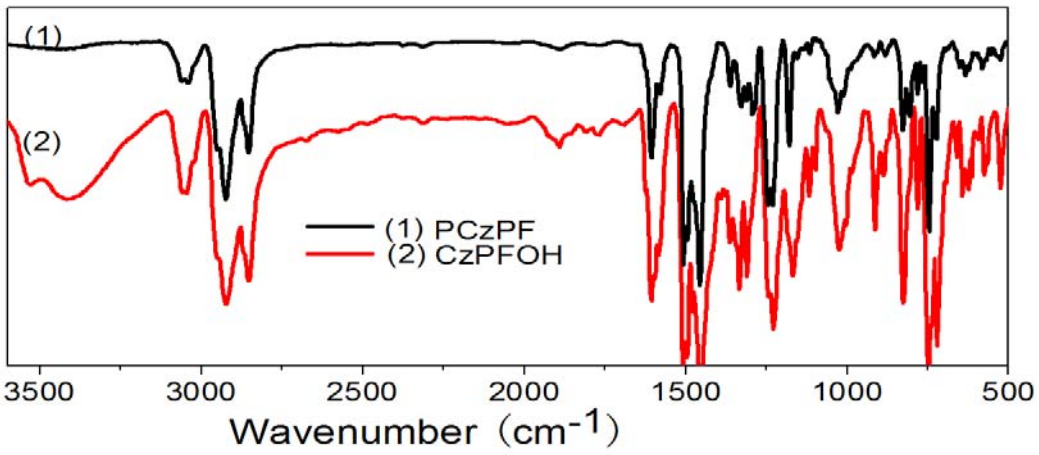


Fig. S-27 FT-IR spectra of the polymer PCzPF and the monomer CzPFOH.

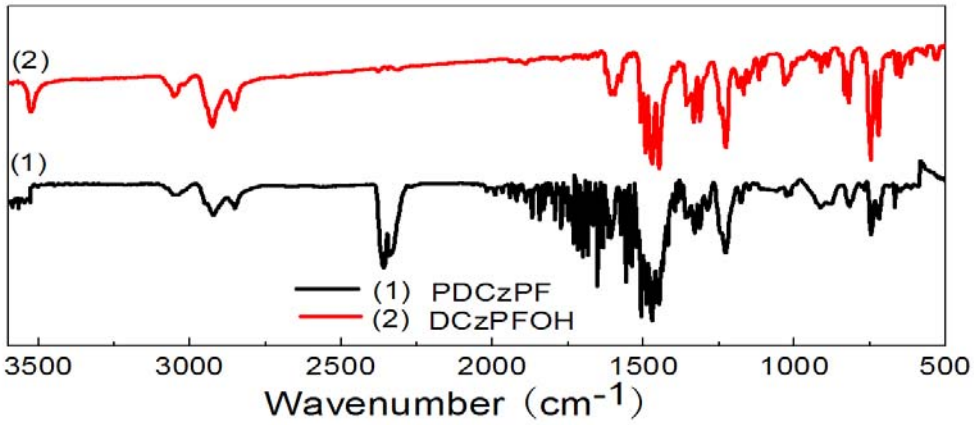


Fig. S-28 FT-IR spectra of the polymer PDCzPF and the monomer DCzPFOH.

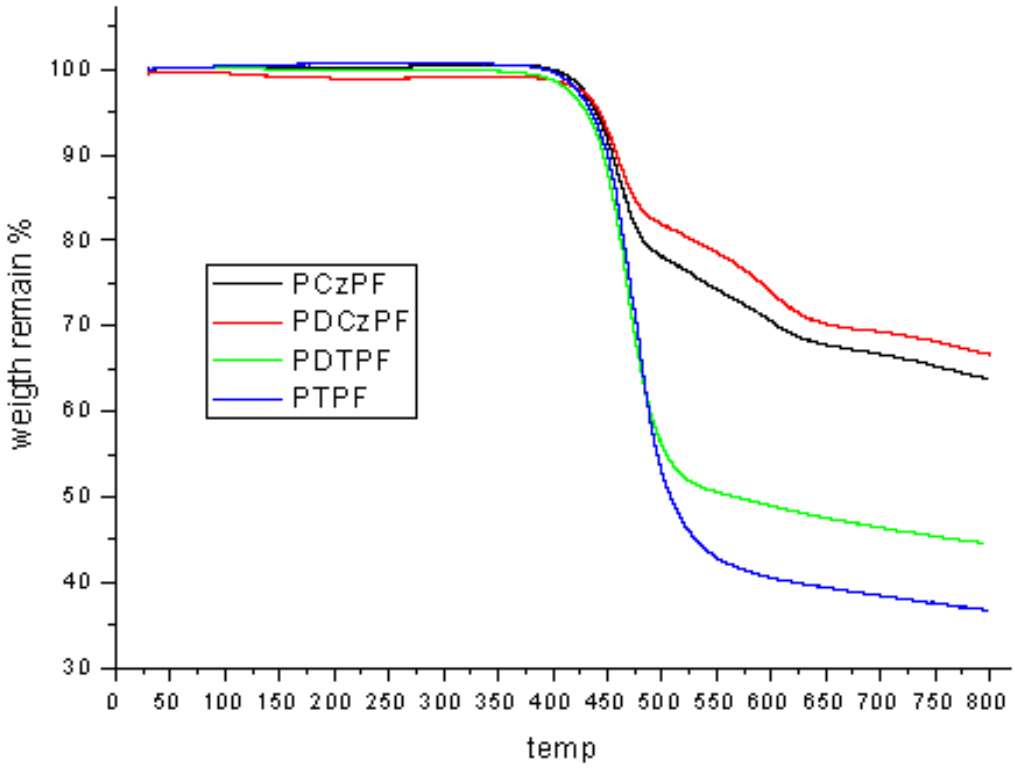


Fig. S-29 TGA curve of the four polymers.