Electronic Supplementary Information for

"A New Glass-forming Molecule Having Fluorene Skeleton : Synthesis and Conversion to the Polymer with Low Dielectric, High Hydrophobicity and Thermostability"

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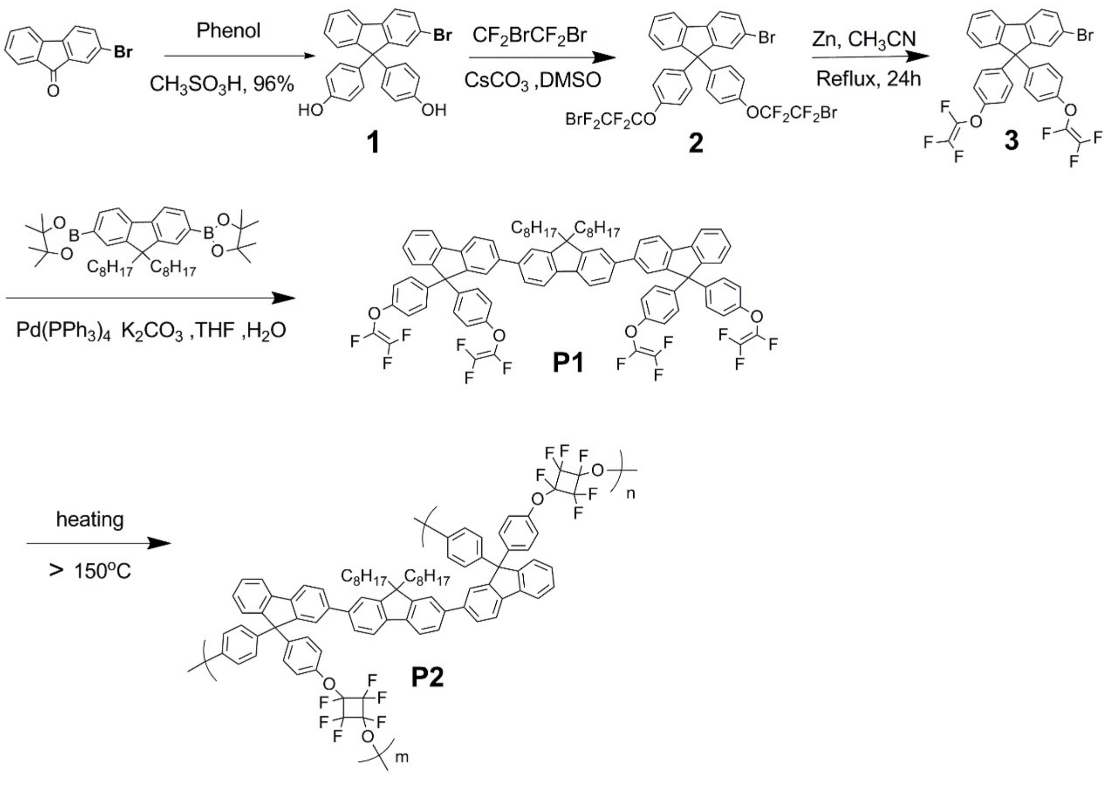
1. Experimental Section

Materials. 2-Bromofluoren-9-one and 9,9-dioctylfluorene-2,7-bis(boronic acid pinacal ester) were purchased from Aladdin Industrial Corporation and used as received. 1,2-Dibromotetrafluoroethane was purchased from Top Fluorochem Co., Ltd, China and used without purification. Other starting materials were purchased from TCL and used without any further purification. All solvents were dried over CaH_2 and distilled before use.

Instrumentation. ^1H NMR, ^{19}F NMR and ^{13}C NMR were measured on a Bruker AV400 instrument. Mass spectrometry was performed on Agilgent Technologies 5973N and Thermo Fisher Scientific LTQ FT Ultra. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetric (DSC) analysis was determined with TA Instrument DSC Q200 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Dielectric properties were investigated at room temperature on a 4294A Precision Impedance Analyzer (Agilent) by the standard capacitance method at the various frequencies. The thickness of the films used for calculation of the dielectric constant was obtained from field emission scanning electron microscopy (FE-SEM) on a Hitachi FE-SEM S-4800. Thermo-gravimetric analysis (TGA) was measured on a TG 209F1 apparatus with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Ultraviolet-visible Near Infrared (UV-vis NIR) spectrum was measured on UV-vis spectrophotometer CARY 5000 (Varian). Using a sessile drop method, the contact angle of water on the film was characterized at the 20 °C on a dynamic contact angle measurement instrument (JC2000C). Surface toughness of cured film was measured by atom force microscopy (AFM) on an environment control scanning probe microscope (Nanonavi E-sweep). The mechanical properties of cured films were measured on a nano-indenter system named as UNHT/NST (CSM Company).

Synthesis and Characterization



Synthesis of 2-bromo-9,9-bis(4-hydroxyphenyl)fluorene (1).

A mixture of 2-bromofluoren-9-one (100.0 g, 385.9mmol), phenol (83.5 g, 887.7 mmol), and methansulfonic acid (300 mL) was stirred at room temperature for 24 h. Then the mixture was poured into water, and the precipitate was filtered and dissolved in ethyl acetate. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was re-dissolved in ethyl acetate, and the solution was added dropwise to *n*-hexane to obtain a precipitate, which was filtered and dried under reduce pressure to give pure product as a white solid in a yield of 96%. ^{1}H NMR (400 MHz, acetone-d_6, ppm): δ 8.28 (s, 2H), 7.85 (dd, 1H), 7.80 (dd, 1H), 7.55~7.52(m, 2H), 7.40~7.28 (m, 3H), 6.98 (dd, 4H), 6.66 (dd, 4H). ^{13}C NMR (101 MHz, acetone-d_6, ppm): δ 157.13, 155.37. 152.81, 140.02, 139.48, 136.97, 131.23, 129.84, 129.86, 128.91, 128.32, 126.92, 122.75, 121.51, 121.18, 115.87, 65.14. HR-MS (*m/z*): $[M]^+$ Calcd for $C_{25}H_{17}BrO_2$, 428.0412. Found 428.0414.

Synthesis of 2-bromo-9,9-bis(4′-[trifluorovinyloxy]-phenyl)fluorene (3).

To a mixture of 2-bromo-9,9-bis(4-hydroxyphenyl)fluorene (compound **1**, 30.0 g, 69.9 mmol), Cs_2CO_3 (68.3g, 209.6 mmol) and DMSO (100 mL), was added dropwise $BrCF_2CF_2Br$ (33.4 mL, 279.5 mmol) during a period of 1 h at room temperature under N_2. The mixture was allowed to heat to 50 °C and kept at the temperature for overnight. After being cooled to room temperature, the solution was diluted by water of 150 mL and extracted withy ethyl acetate (3×100 mL). The combined organic phase was washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude compound **2** was obtained, which was further purified by flash column chromatography on SiO_2 using CH_2Cl_2 as the eluent.

To a solution of compound **2** in CH_3CN (150 mL) was added zinc powder (18.3 g, 279.5 mmol), and the mixture was heated to 60 °C under N_2. After being stirred at 60 °C for 1 h, the mixture was heated to 90 °C and kept at the temperature for 5 h. The mixture was stirred until compound **2** was completely consumed (monitored by ^{19}F spectra). The mixture was filtered, and the filtrate cake was washed with ethyl acetate. The organic phase was combined and concentrated. The obtained residue was purified by flash column chromatography on SiO_2 using hexane as the eluent to give pure **3** as colorless sticky oil with a yield of 51%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.74~7.71 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.37 (m, *J* = 7.6, 5.7, 2.8 Hz, 1H), 7.32~7.28 (m, 1H), 7.16~7.13 (m, 4H), 6.96 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (101 MHz, actone-d_6, ppm): δ 154.79, 153.77, 151.29, 148.04(td), 142.86, 140.16, 139.64, 134.37 (dt), 132.02, 130.64, 129.64, 129.39, 129.22, 126.91, 123.14, 121.99, 121.48, 116.56, 65.26. ^{19}F NMR (376 MHz, acetone-d_6, ppm): δ -120.7 8~-121.20 (m, 2F), -127.95~-128.50 (m, 2F), -135.41~-135.86 (m, 2F). HR-MS (*m/z*): $[M]^+$ Calcd for $C_{29}H_{15}BrF_6O_2$, 589.3226. Found 589.0232.

Synthesis of P1.

To a mixture of compound **3** (5.73 g, 9.73 mmol), 9,9-dioctylfluorene-2,7-bis(boronic acid pinacal ester) (2.50 g, 3.89 mmol), $Pd(PPh_3)_4$ (0.36 g, 0.311 mmol), and THF (20 mL), was added an aq. K_2CO_3 solution (10 mL, 2M) via a syringe under argon. The mixture was heated to 50 ^oC and maintained at the temperature for 16 h. The clear solution was extracted with ethyl acetate (20×2 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by flash column chromatography on SiO_2 using a mixture solvent of petroleum ether and CH_2Cl_2 as the eluent (10:1, v/v) to give **P1** as a white solid with a yield of 73%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.68 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.61 (s, 2H), 7.53~7.49 (m, 4H), 7.40 (td, *J* = 7.4, 1.0 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (d, **J** = 7.4 Hz, 2H), 7.25 (d, 8H), 6.98 (d, *J* = 8.7 Hz, 8H), 2.05~1.96 (m, 4H), 1.16~1.02 (m, 20H), 0.76 (t, J = 7.0 Hz, 6H), 0.70 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 154.10, 151.92, 151.47, 151.08, 147.32 (td), 142.41, 141.65, 140.22, 139.98, 139.77, 139.24, 134.53 (dt), 129.79, 128.08, 127.28, 126.29, 126.06, 124.55, 121.48, 120.80, 120.59, 120.17, 115.88, 64.51, 55.41, 40.38, 31.82, 30.10, 29.30, 23.96, 22.67, 14.11. ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ -119.48~-119.89 (m, 4F), -126.18~-126.73 (m, 4F), -133.60~-134.05 (m, 4F). HR-MS (*m/z*): $[M]^+$ Calcd for $C_{87}H_{70}F_{12}O_4$, 1406.5082. Found 1406.5089. Anal. Calcd for $C_{87}H_{70}F_{12}O_4$: C, 74.24; H, 5.01; F, 16.20. Found: C, 74.22; H, 5.00; F, 15.92.

2. NMR spectra of the intermediates and the monomers

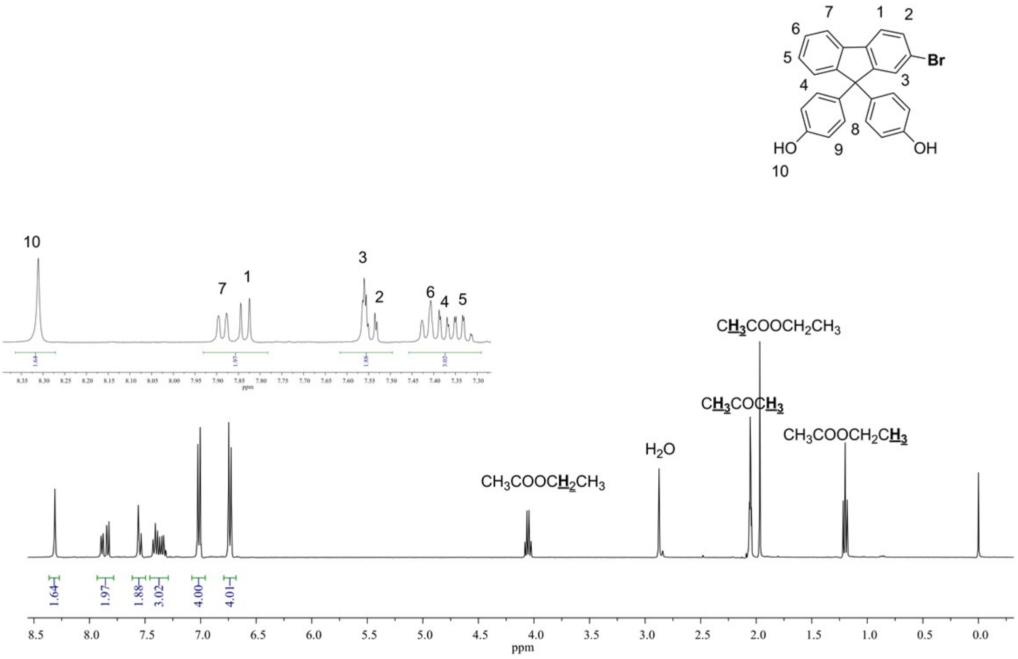


Figure S$_1$. ^{1}H NMR spectrum of compound **1** (400 MHz, acetone-*d$_6$*).

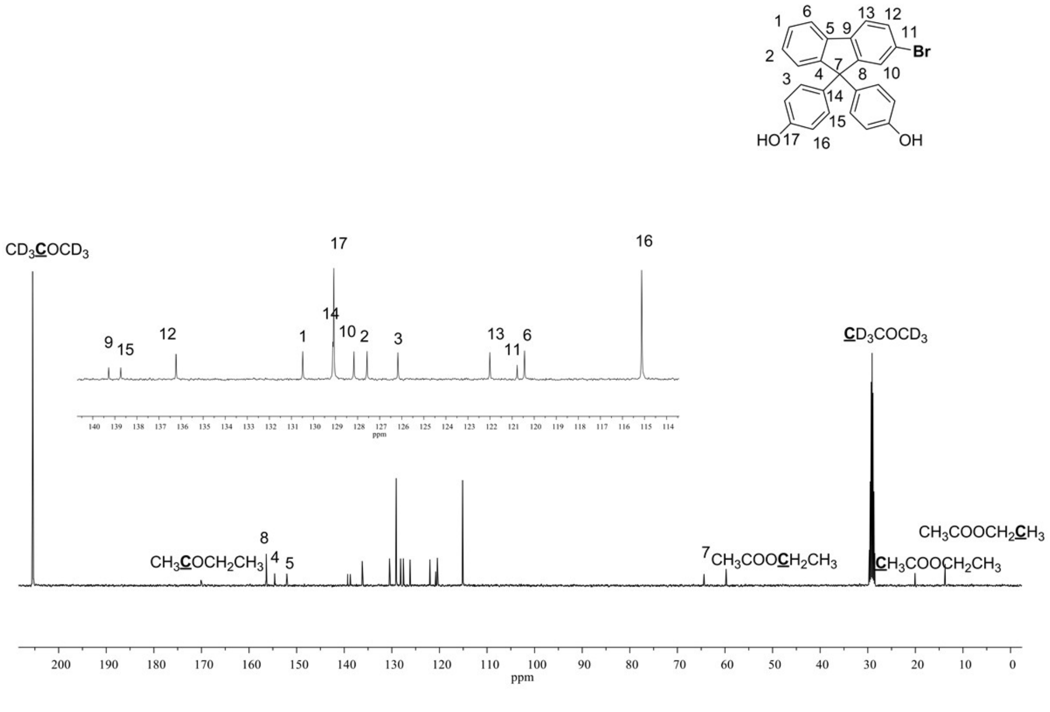


Figure S$_2$. ^{13}C NMR spectrum of compound **1** (101 MHz, acetone-*d$_6$*).

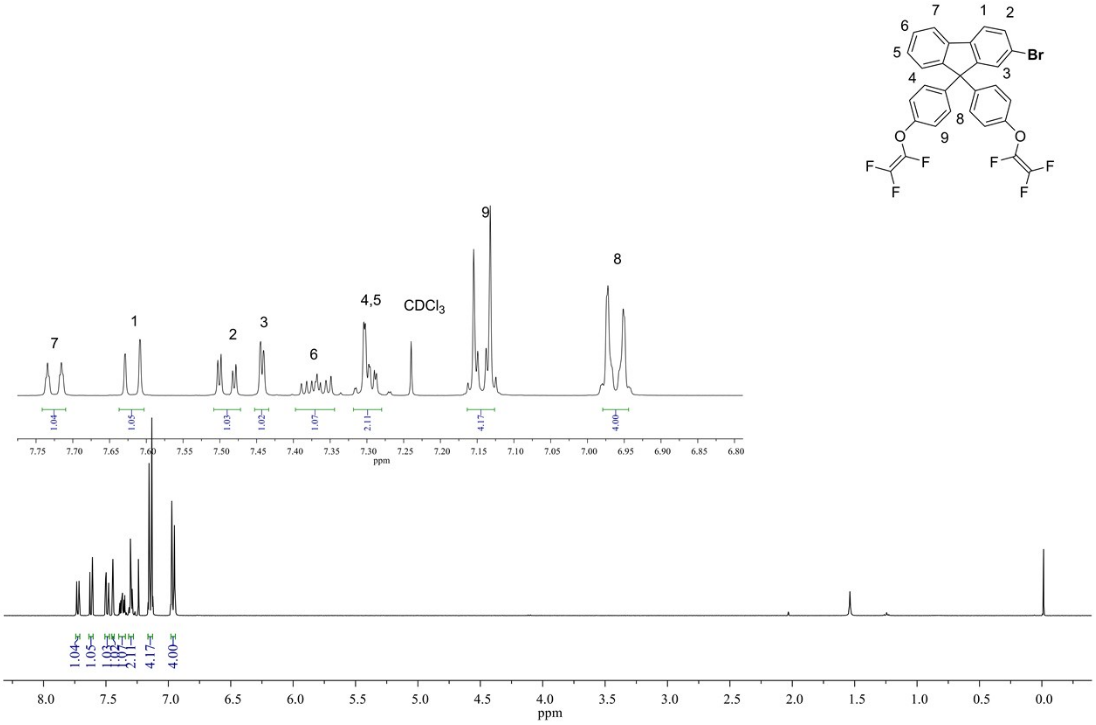


Figure S$_3$. ^{1}H NMR spectrum of compound **3** (400 MHz, CDCl$_3$).

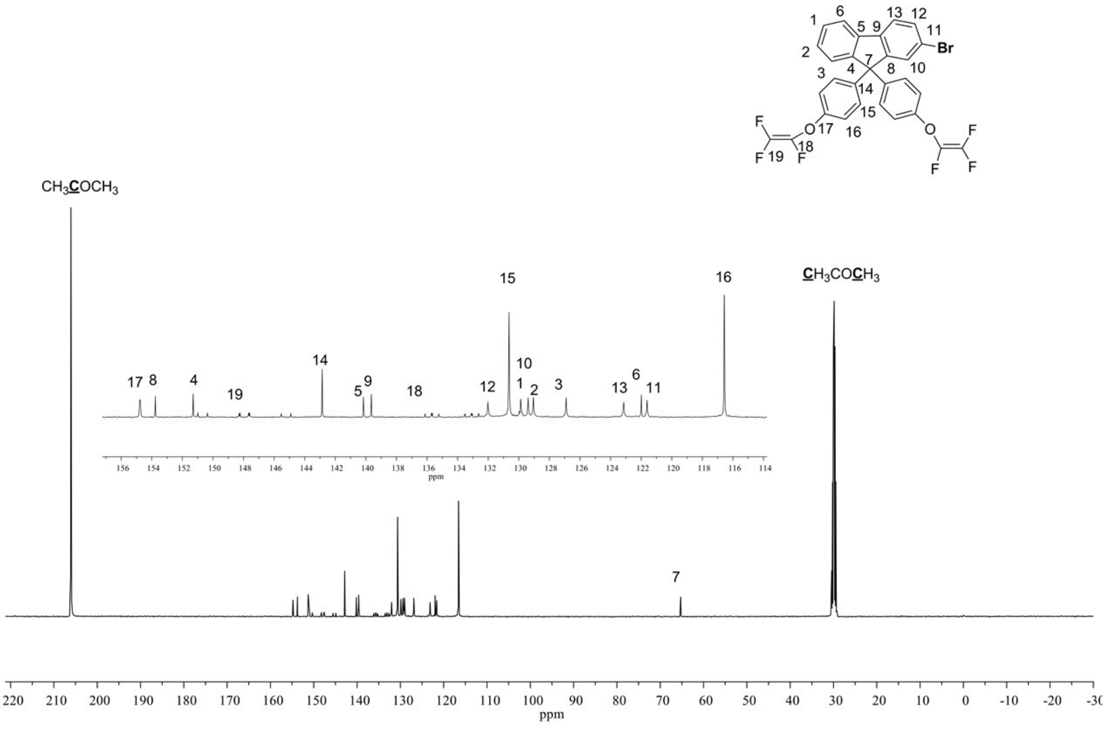


Figure S$_4$. ^{13}C NMR spectrum of compound **3** (101 MHz, acetone-*d$_6$*).

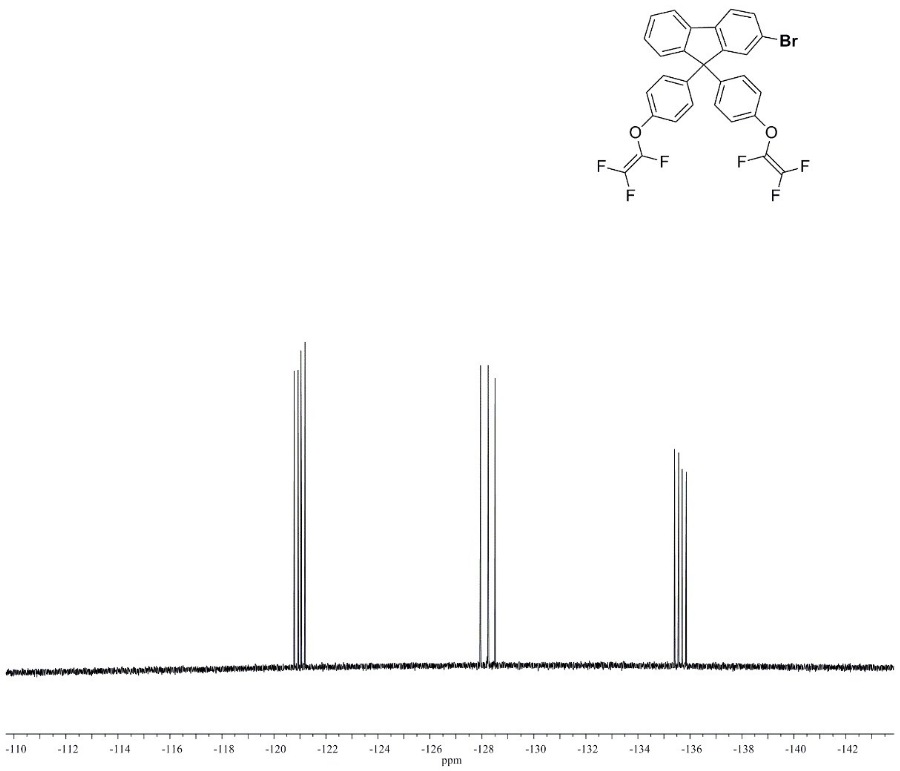


Figure S₅. ^{19}F NMR spectrum of compound **3** (376 MHz, acetone-*d₆*).

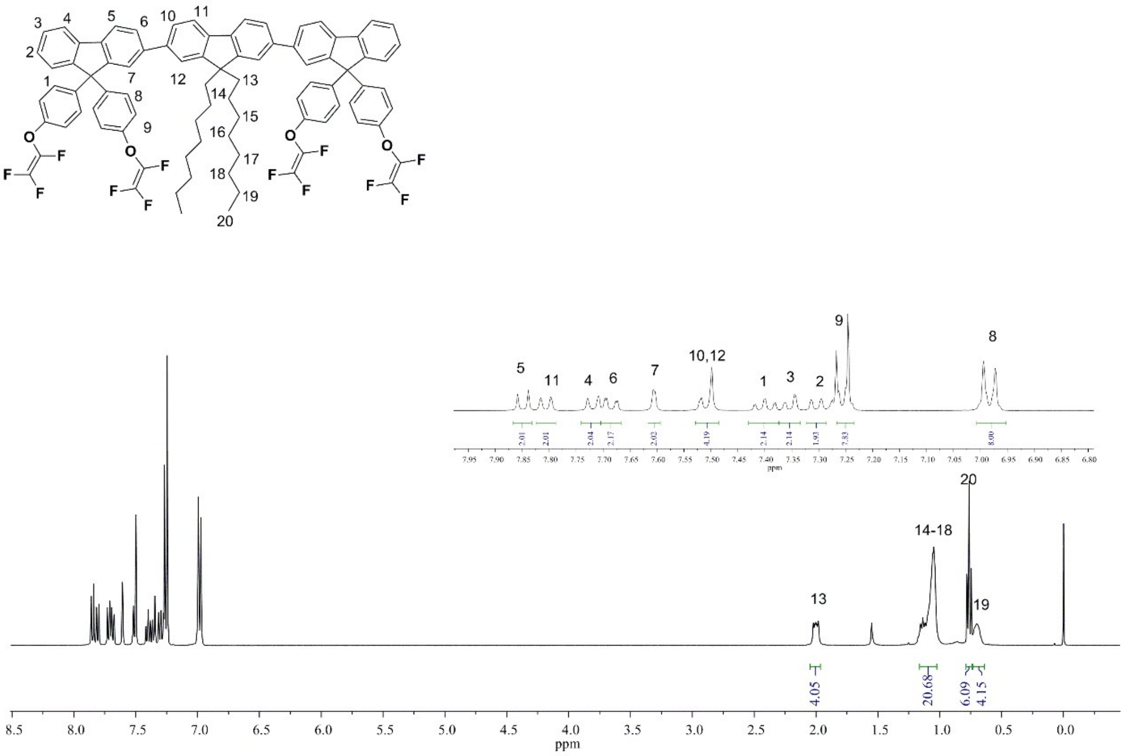


Figure S₆. ^{1}H NMR spectrum of **P1** (400 MHz, CDCl$_3$).

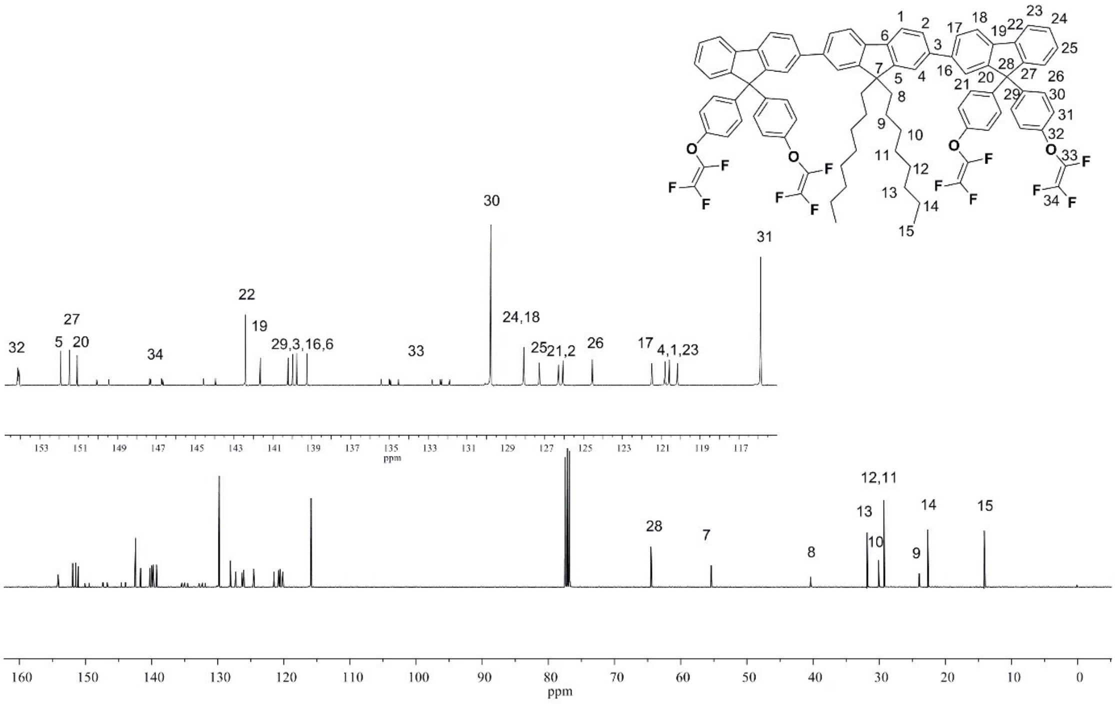


Figure S₇. ^{13}C NMR spectrum of **P1** (101 MHz, acetone-*d₆*).

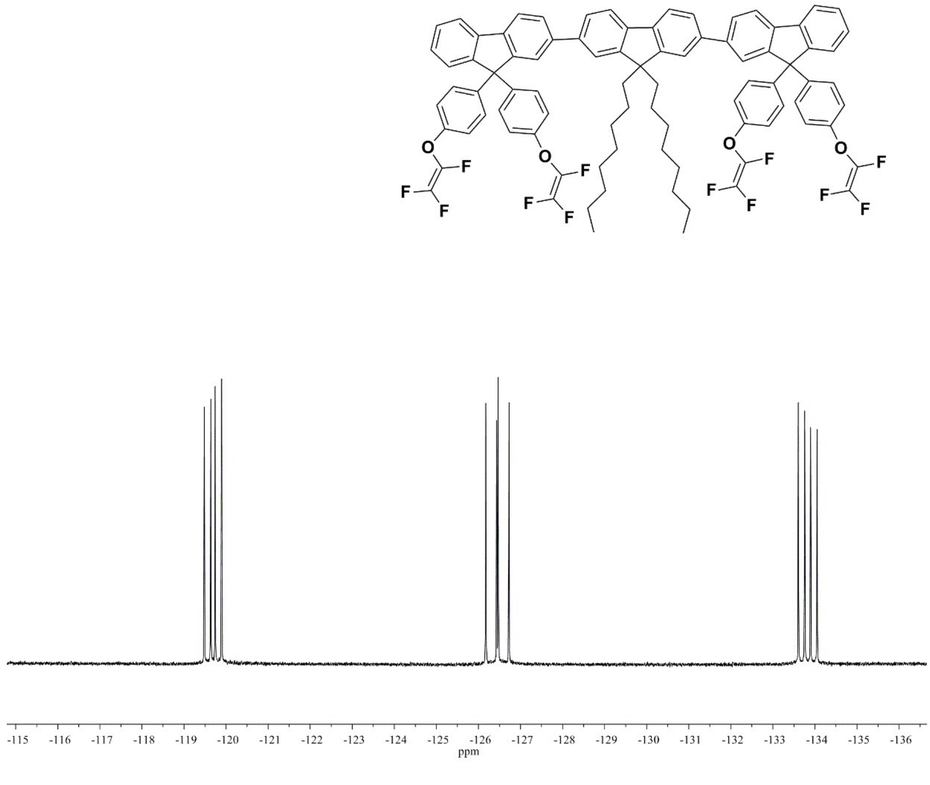


Figure S₈. ^{19}F NMR spectrum of **P1** (376 MHz, acetone-*d₆*).

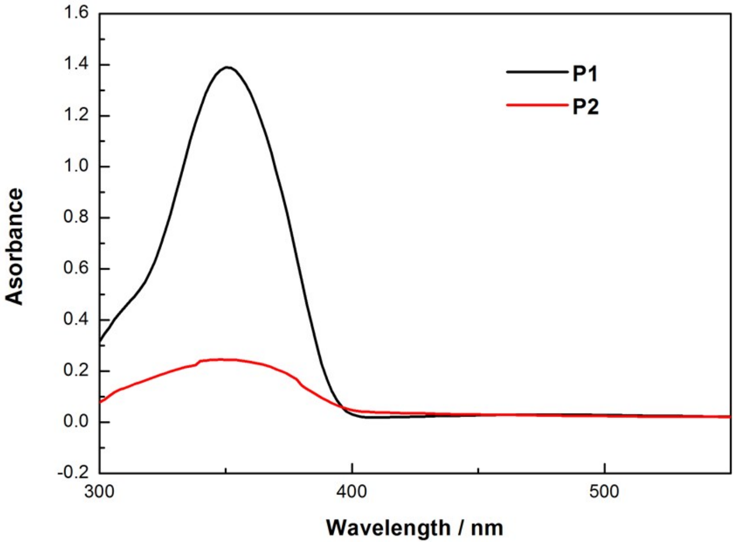


Figure S$_9$. UV–vis absorption spectra of **P1** and **P2** films.

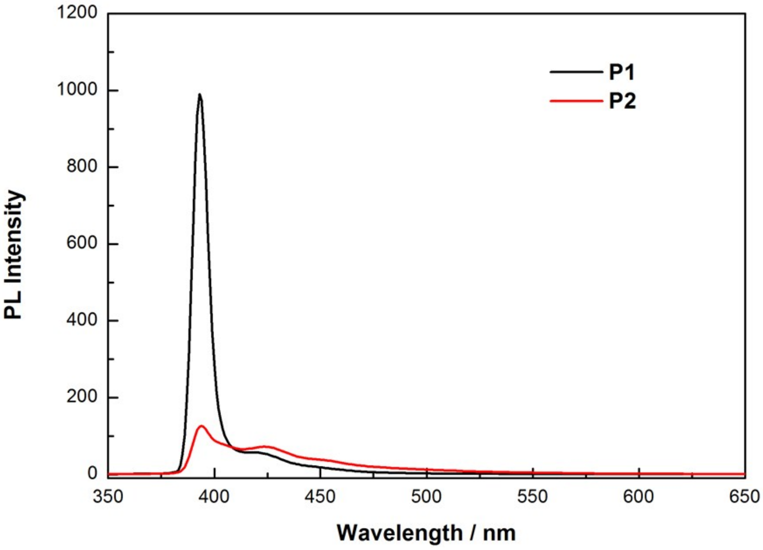


Figure S$_{10}$. PL emission spectra of **P1** and **P2** films.