Supporting Information

Hindrance-functionalized Vinyl-type π-Stacked Polymer Based On Polystyrene With Pendent Cardo Group for Organic Electronics

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Experimental section.

Chemical and Materials. 9-phenyl-9H-fluoren-9-ol (**1**) was prepared according to our previous report.[1] Solvents were dried using standard procedures. All other reagents were used as received from commercial sources without any purification.

Characterization. ^{1}H- and ^{13}C-NMR in $CDCl_3$ was recorded at 400 MHz using a Varian Mercury 400 plus spectrometer. Absorption and photoluminescence (PL) emission spectra of the materials were measured using a SHIMADZU UV-3150 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. The solution state spectra were measured in chlorobenzene solution. The film was prepared by spin-coating from chlorobenzene solution. Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric with a heating rate 10 °C/min under a nitrogen atmosphere. The Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument 0 at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) was used to obtain the molecular weight of the polymers with reference to polystyrene standards with THF as eluant. The Cyclic Voltammetric (CV) studies were conducted using an Eco Chemie B. V. AUTOLAB potentiostat in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) in dichloromethane (CH_2Cl_2) at a sweeping rate of 0.1 V/s. According to the redox onset potentials of the CV measurements, the HOMO/LUMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO = $-(E_{onset} - 0.01\ \text{V}) - 4.8$ eV, where the value 0.01 V is for FOC vs Ag/Ag^{+}.

Fabrication of Memory Devices. The memory devices with the configuration of ITO/PS or PPFS/Al were fabricated as follows. PS and PPFS are dissolved in toluene (10 mg/ml), respectively. The solution of PS or PPFS is spin-coated on an indium tin oxide (ITO) glass substrate. Subsequently, the sample is annealed at 70 °C for 30 min in air. Finally, a 120 nm Al top electrode is thermally evaporated onto the active layers through a shadow mask at a system pressure of 10^{-6} Torr. The electrical measurements are performed in a glove box by a Keithley 2400 semiconductor parameter analyser. The thickness values of the PS or PPFS film layer measured by scanning electron microscopy (SEM) is 80 nm, respectively.

Fabrication of PPLEDs. PPLEDs were fabricated in the following configuration: indium tin oxide (ITO)/polyethylenedioxythiophene-polystyrene sulfonic acid (PEDOT:PSS, 10 nm)/PPFS: 30% FIrpic (65 nm)/1,3,5-tris(*N*-phenyl benzimidazol -2-yl)benzene (TPBI, 40 nm)/Ca:Ag. A layer of PEDOT:PSS with thickness of 10 nm was spin-coated directly onto the ITO glass and dried at 120 °C for 20 minutes under vacuum to enhance the hole injection ability and to smooth the ITO substrate. The solution of the polymer was prepared under nitrogen atmosphere and spin-coated on PEDOT:PSS layer. The TPBI was used as an electron-transporting/hole-blocking layer as well as excition-confining layer. The cathode Ca:Ag alloy was subsequently deposited onto the TPBI layer. EL spectra and chromaticity coordinates were measured with a SpectraScan PR650 photometer. Current density–voltage–luminance (*J*–*V*–*L*) measurements were conducted simultaneously using a Keithley 4200 semiconductor parameter analyzer combined with a Newport multifunction 2835-C optical meter, with luminance being measured in the forward direction. All device characterizations were carried out under ambient laboratory air at room temperature.

Synthesis of 9-phenyl-9-p-tolyl-fluorene (**2**). To a solution of **1** (5.42 g, 21 mmol) in toluene (75 mL) was added dropwise methanesulfonicacid (CH_3SO_3H) (1.4 ml，21 mmol) in toluene (25 mL). The mixture was heated to 140 °C and stirred for 12 h. In this reaction, toluene is used as not only reactant but also solvent. Then saturated sodium bicarbonate solution was added into the mixture to quench the reaction. The organic phase was separated and washed by saturated sodium bicarbonate, and the water phase was extracted three times with CH_2Cl_2. The combined organic solution was dried with anhydrous magnesium sulfate ($MgSO_4$). The solvent was removed by rotary evaporation, and the residue was purified by column chromatography using petroleum ether/CH_2Cl_2 (10 : 1) as eluent to get a white solid. Yield: 3.49 g (50%). MS (*m*/*z*): [M^+] calcd for, $C_{26}H_{20}$, 407.51; found, 407.00. ^1H NMR (400 MHz, $CDCl_3$--d6) δ (ppm): 7.75–7.79 (d, *J* = 7.5 Hz, 2H), 7.39–7.41 (d, *J* = 7.58 Hz, 2H), 7.33–7.36 (t, 3H), 7.24–7.28 (m, 3H), 7.20 (s, 5H), 7.08–7.10 (d, *J* = 8.02 Hz, 2H), 7.01–7.03 (d, *J* = 8.02 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO--d6) δ (ppm): 20.96, 65.19, 120.13, 126.16, 126.56, 127.39, 127.70, 128.05, 128.14, 128.16, 128.92, 136.21, 140.13, 142.93, 146.09, 151.37. Anal. Calcd. For $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.87; H, 6.28.

Synthesis of 9-(4-(bromomethyl)phenyl)-9-phenyl-fluorene (**3**). **2** (3.19 g, 9.6 mmol) and *N*-bromosuccinimide (NBS) (2.14 g, 12 mmol) were brought to reflux in 100 mL of carbon tetrachloride (CCl_4). A small amount of 2,2'-azobis(isobutyronitrile) (AIBN) was added, and after 1.5 h, another portion of AIBN was added. Refluxing was continued for a total of 4 h. The mixture was cooled, saturated sodium bicarbonate solution (60 mL) was added, and the mixture was filtered giving a white solid that was then air-dried to give **3**, which was used without further purification. Yield: 3.12 g (98%). MS (*m*/*z*): [M^+] calcd for, $C_{26}H_{19}Br$, 411.33; found, 411.00. ^1H NMR (400 MHz, $CDCl_3$--d6) δ (ppm): 7.76-7.78 (d, J = 7.6 Hz, 2H), 7.35–7.39 (m, 5H), 7.23 (s, 2H), 7.20–7.21 (m, 3H), 7.19 (s, 1H), 7.18 (s, 3H), 7.16 (s, 1H), 4.45 (s, 2H). ^{13}C NMR (100 MHz, DMSO--d6) δ (ppm): 33.32, 65.29, 120.23, 126.15, 126.75, 127.61, 127.79, 128.11, 128.18, 128.28, 128.57, 128.95, 136.02, 140.15, 145.56, 146.42, 150.86. Anal. Calcd. For $C_{26}H_{19}Br$: C, 75.92; H, 4.66; Br, 19.43; Found: C, 75.77; H, 4.60; Br, 19.24.

Synthesis of 4-(9-phenyl-fluoren-9-yl)benzaldehyde (**4**). **3** (2.32 g, 5.6 mmol) was stirred in 80 mL of dioxane. A slurry of calcium carbonate ($CaCO_3$) (1.24 g, 12.4 mmol) in 40 mL of water was added and the mixture refluxed for 48 h. The dioxane was removed by rotary evaporation and the residue treated with 6 M HCl until acidic. A white solid was filtered from the mixture, washed well with water, and air-dried. Then this white solid was added to a slurry of crushed molecular sieves and pyridinium chlorochromate (PCC) (3.6 g, 16.8 mmol) in methylene chloride (100 mL), refluxed for 4 h. After cooling, an equal volume of diethyl ether was added and the mixture was filtered through 8 cm of silica gel. The silica gel was washed with 100 mL of hot chloroform. The solution was stripped of solvent, and the residue was recrystallized from chloroform to give 4. Yield: 2.09 g (90%). MS (*m*/*z*): [M$^+$] calcd for, $C_{26}H_{18}O$, 346.42; found, 346.00. ^{1}H NMR (400 MHz, $CDCl_3$--d6) δ (ppm): 9.95 (s, 1H), 7.78–7.80 (d, J = 8.26 Hz, 2H), 7.73–7.75 (m, 2H), 7.39–7.40 (d, 2H), 7.37–7.38 (m, 3H), 7.36 (s,1H), 7.29–7.31 (d, J = 8.55 Hz, 2H), 7.23–7.24 (d, 2H), 7.16–7.19 (m, 3H). ^{13}C NMR (100 MHz, DMSO--d6) δ (ppm): 65.72, 120.40, 126.11, 127.01, 127.89, 127.98, 128.04, 128.46, 128.74, 129.73, 134.95, 140.23, 144.97, 150.22, 153.35, 191.81. Anal. Calcd. For $C_{26}H_{20}$: C, 90.14; H, 5.24; O, 4.62; Found: C, 90.34; H, 5.28; O, 4.72.

Synthesis of 9-phenyl-9-(4-vinylphenyl)-fluorene (**5**). Methyltriphenylphosphonium bromide (CH_3PPh_3Br) (1.42 g, 4 mmol) and dry tetrahydrofuran (THF) (20 mL) were placed in a 150 mL three-necked flask. The hexane solution of *n*-BuLi (2.5 mL, 4 mmol, 1.6 M solution in hexane)was added dropwise to the mixture under a nitrogen atmosphere at room temperature and was vigorously stirred for 2 h. Then, **5** (1.26 g, 3.64 mmol) in dry THF (20 mL) was added gradually to the reaction mixture, which was refluxed for 1.5 h. After the reaction mixture was cooled to room temperature, it was dropped into hexane (40 mL). The precipitate, which corresponds to phosphonium oxide, was filtered off, and the filtrate was evaporated under reduced pressure to give a crude product. The crude monomer was purified by recrystallization from ethanol to give white needles (1.23 g, 98%). MS (*m*/*z*): [M$^+$] calcd for, $C_{27}H_{20}$, 344.45; found, 344.00. ^{1}H NMR (400 MHz, CDCl$_3$--d6) δ (ppm):7.76–7.78 (d, J = 7.52 Hz, 2H), 7.34–7.42 (m, 4H), 7.26–7.29 (m, 5H), 7.21(s, 5H), 7.15–7.17 (d, J = 8.32 Hz,3H), 7.20 (s, 5H), 7.08–7.10 (d, J = 8.02 Hz, 2H), 6.62–6.70 (m, 1H), 5.66–5.70 (d, 1H), 5.18–5.20 (d, 1H). ^{13}C NMR (100 MHz, DMSO--d6) δ (ppm): 65.32, 113.62, 120.19, 126.08, 126.16, 126.67, 127.51, 127.75, 128.13, 128.24, 128.32, 135.98, 136.38, 140.16, 145.61, 145.79, 151.07. Anal. Calcd. For $C_{26}H_{20}$: C, 94.15; H, 5.85. Found: C, 94.79; H, 6.52.

Synthesis of poly(9-phenyl-9-(4-vinylphenyl)- fluorene) (**PPFS**). The monomer **5** (0.433g, 1.0 mmol) was allowed to polymerize carried out in toluene (10 mL) with 10% by weight AIBN (0.043 g) as initiator and refluxed under nitrogen at 85 °C for 2 days. The polymerization was stopped by pouring the reaction mixture into ethanol. The obtained polymer was purified by repeated precipitations followed by drying under vacuum. Yield: 58%. $M_n = 1.1\times10^4$, PDI =1.80. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.40–7.70 (br, ArH). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 29.71, 31.94, 65.13, 120.03, 126.06, 126.56, 127.38, 127.46, 127.59, 127.98, 128.09, 128.12, 139.86, 139.92, 146.02, 146.15, 151.31. Anal. Calcd. For $C_{832}H_{460}$: C, 94.15; H, 5.85. Found: C, 94.29; H, 5.60.

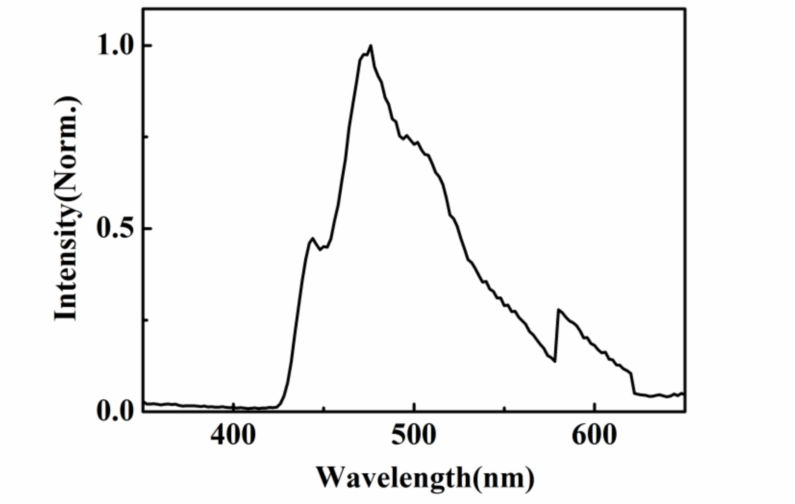

Figure S1. Phosphorescence spectra of PPFS solution at 77 K.

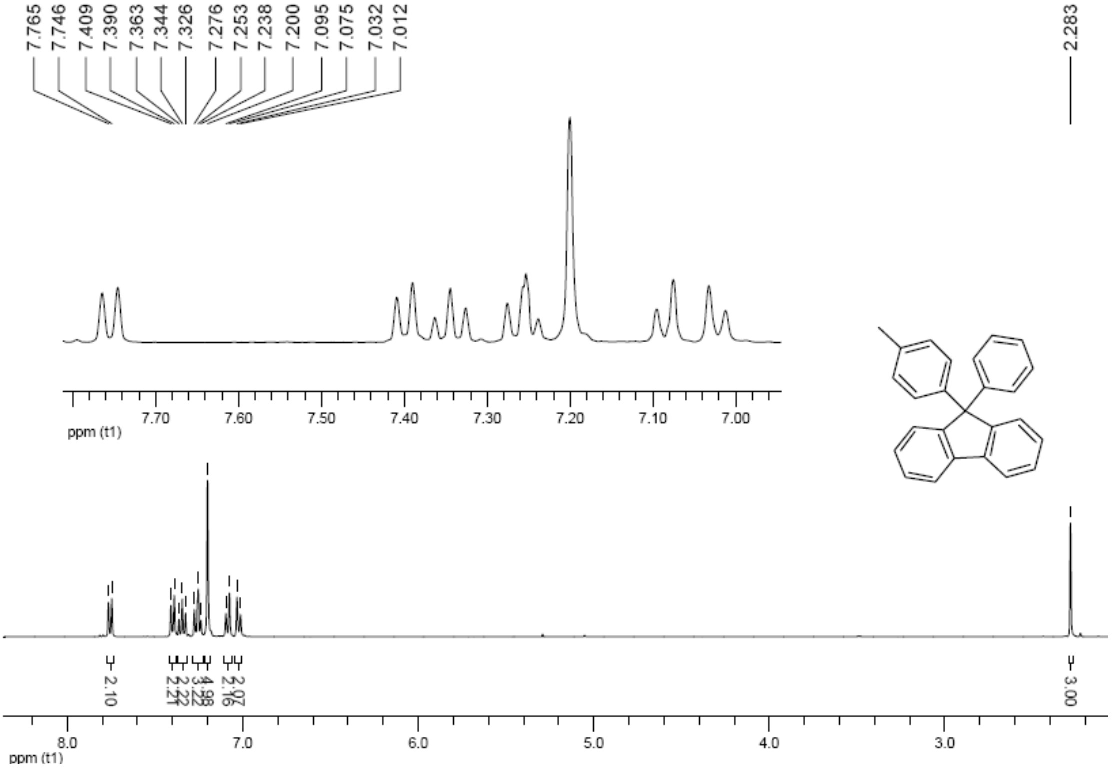

Figure S2. ^{1}HNMR of **2** in $CDCl_3$**.**

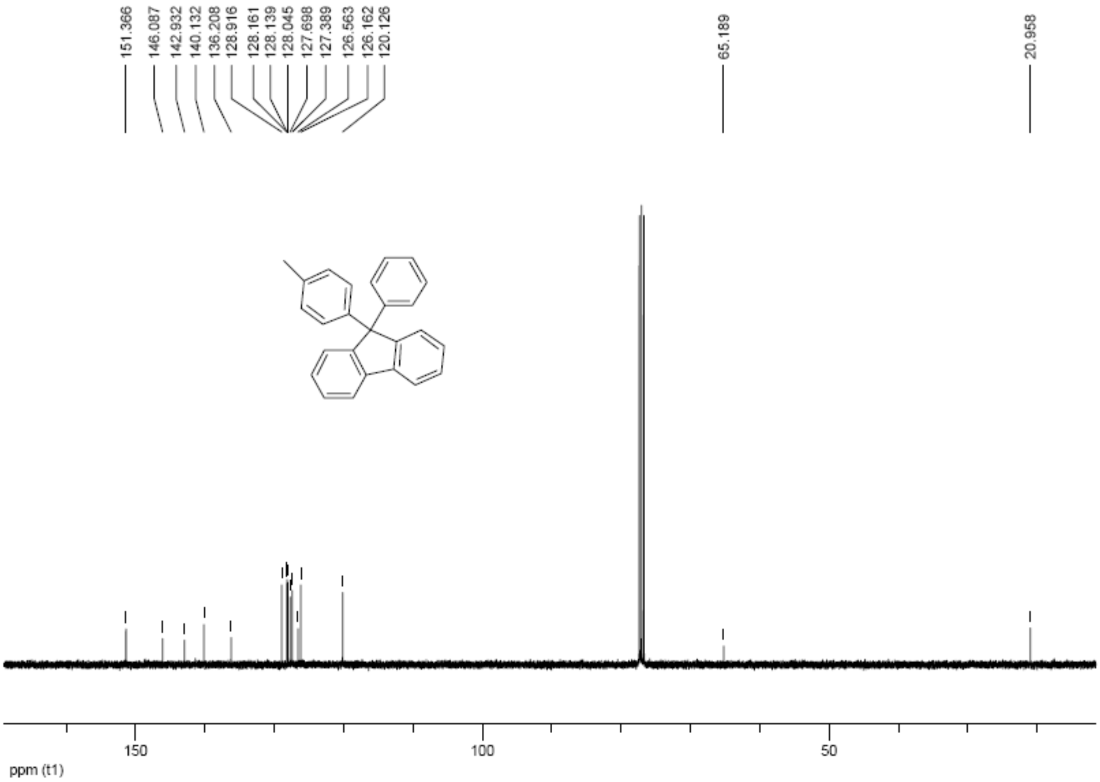

Figure S3. ^{13}CNMR of **2** in CDCl$_3$.

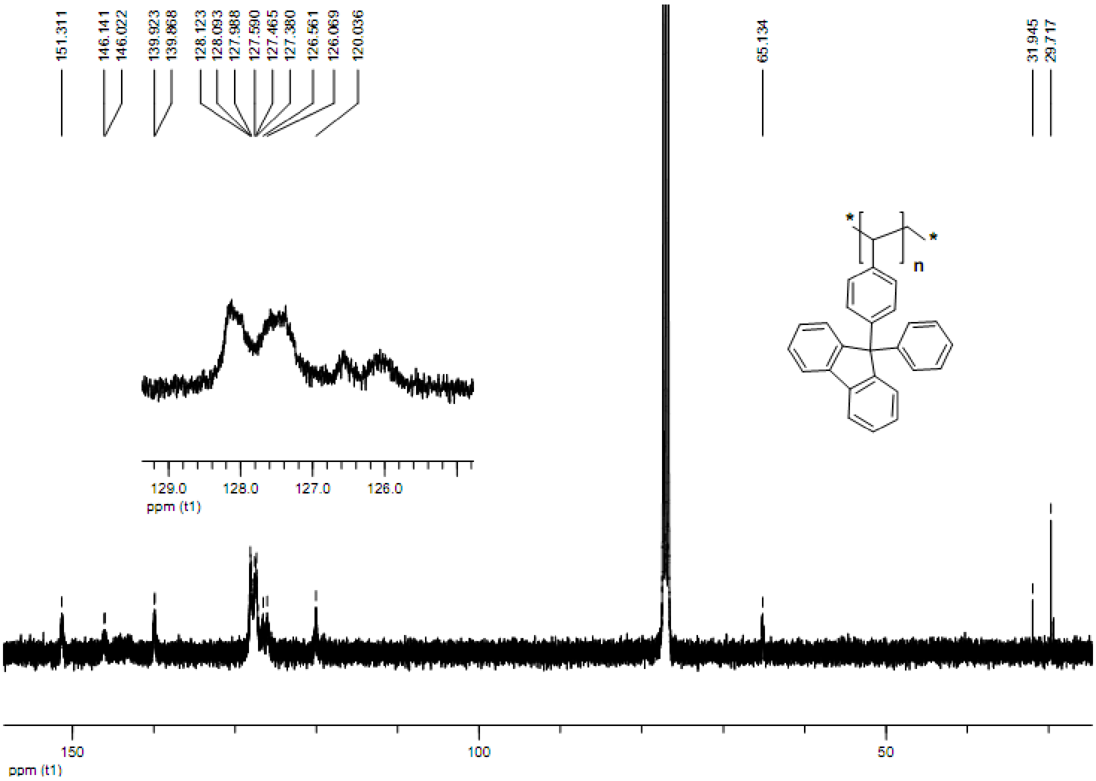

Figure S4. ^{1}HNMR of **3** in CDCl$_3$.

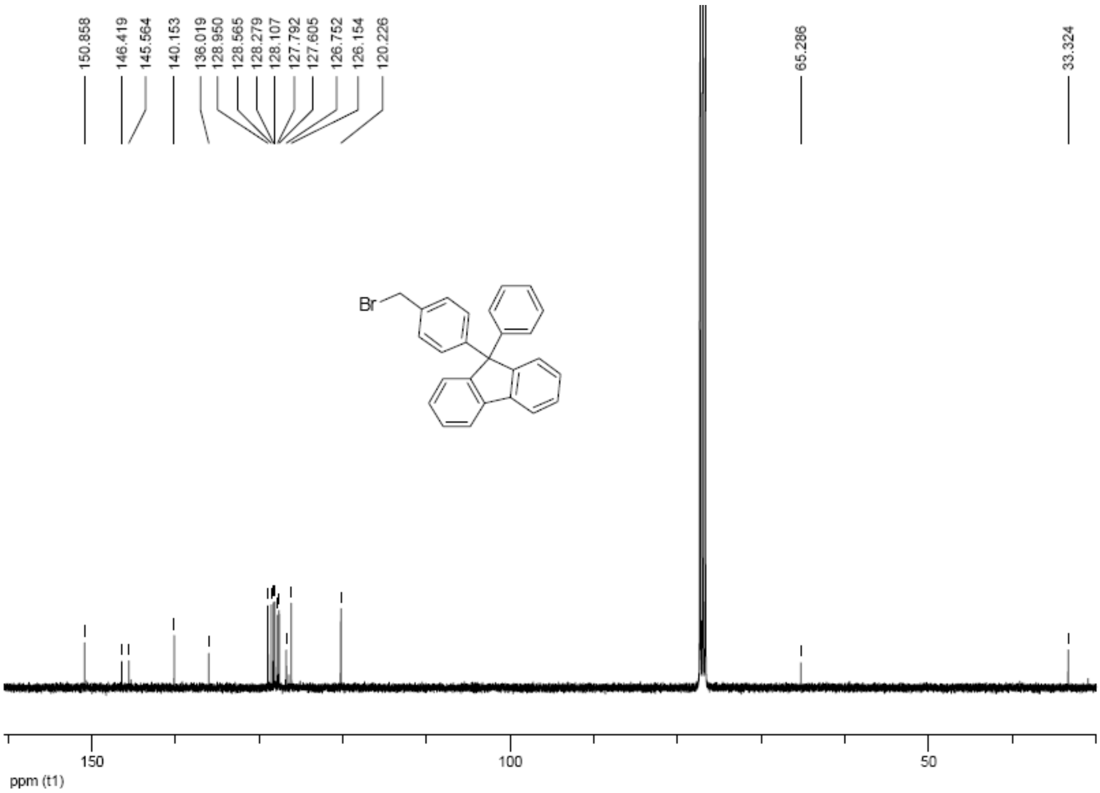

Figure S5. ^{13}CNMR of **3** in $CDCl_3$**.**

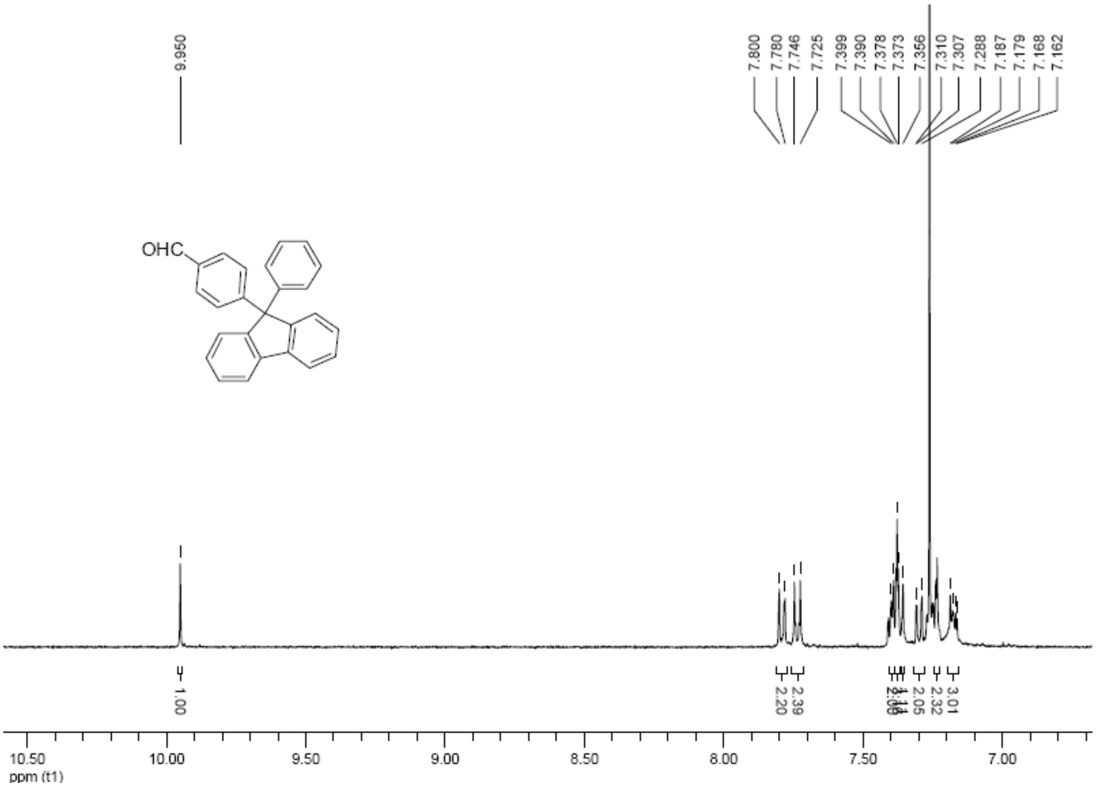

Figure S6. ^{1}HNMR of **4** in $CDCl_3$**.**

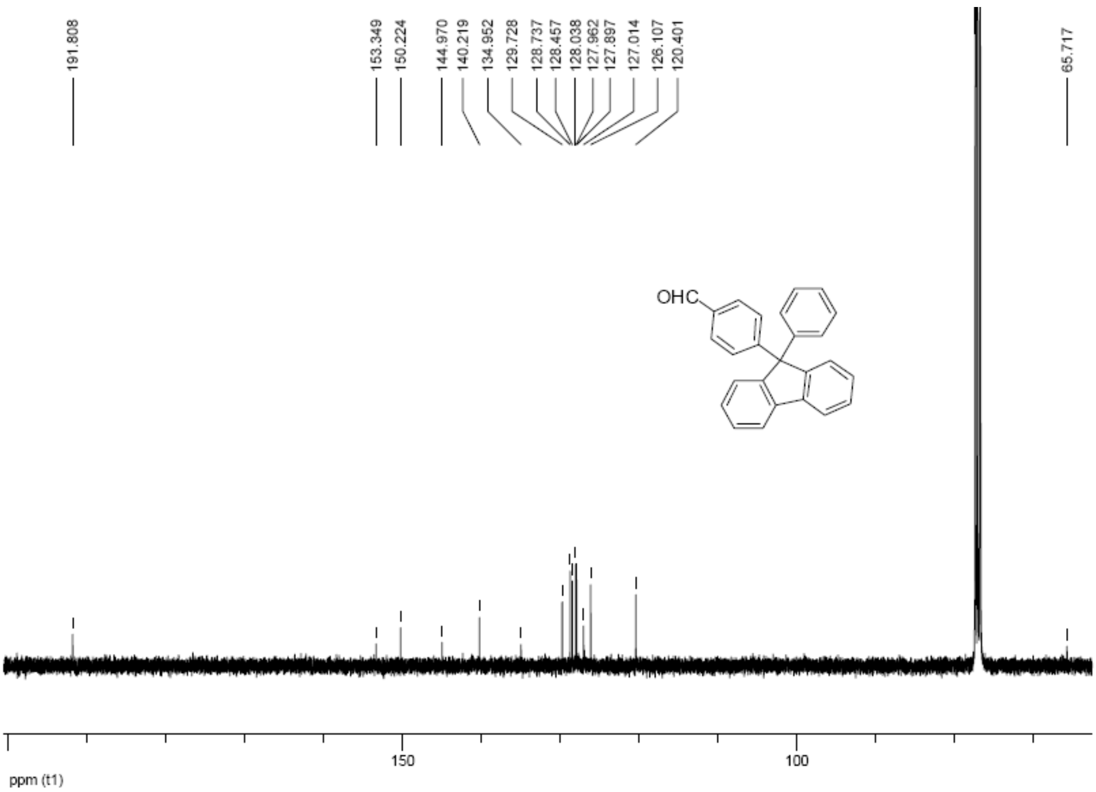

Figure S7. ^{13}CNMR of **4** in $CDCl_3$.

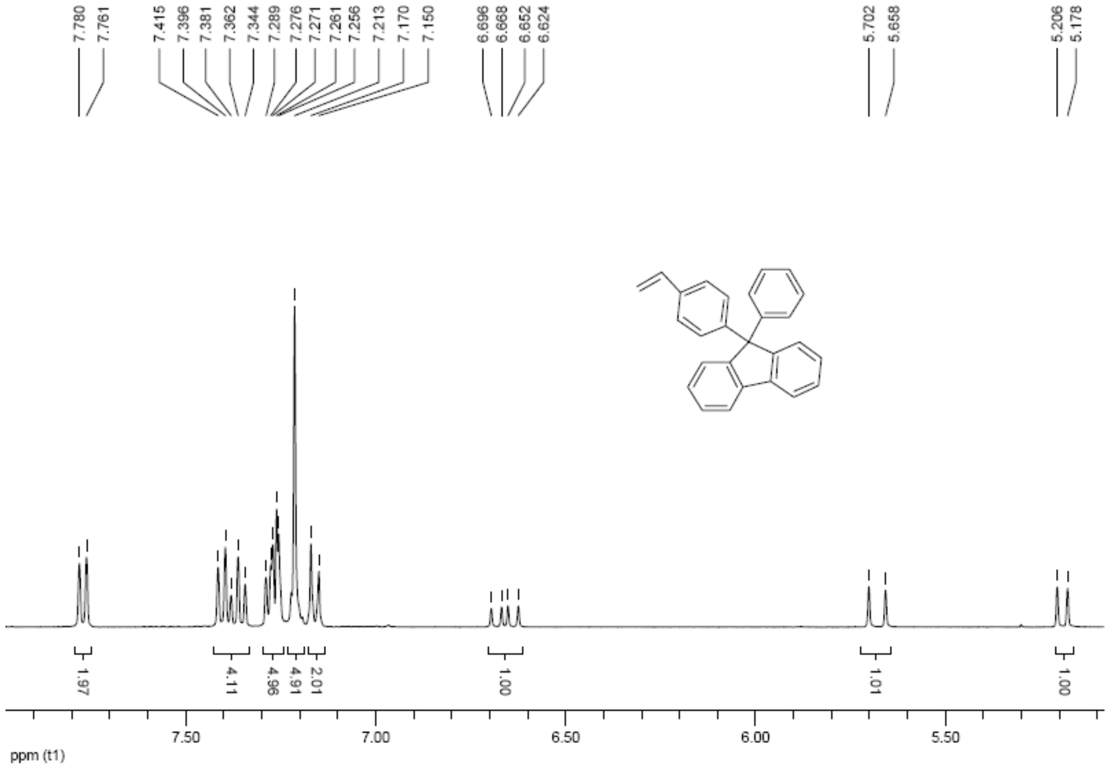

Figure S8. ^{1}HNMR of **5** in $CDCl_3$.

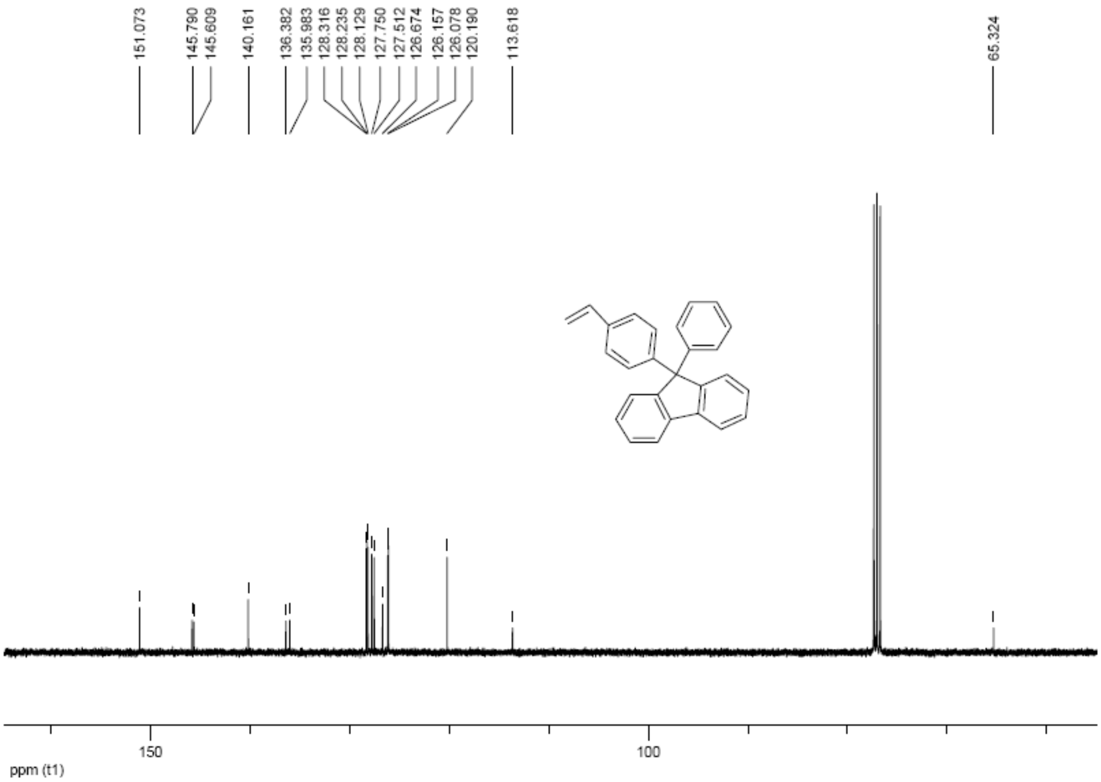

Figure S9. ^{13}CNMR of **5** in $CDCl_3$**.**

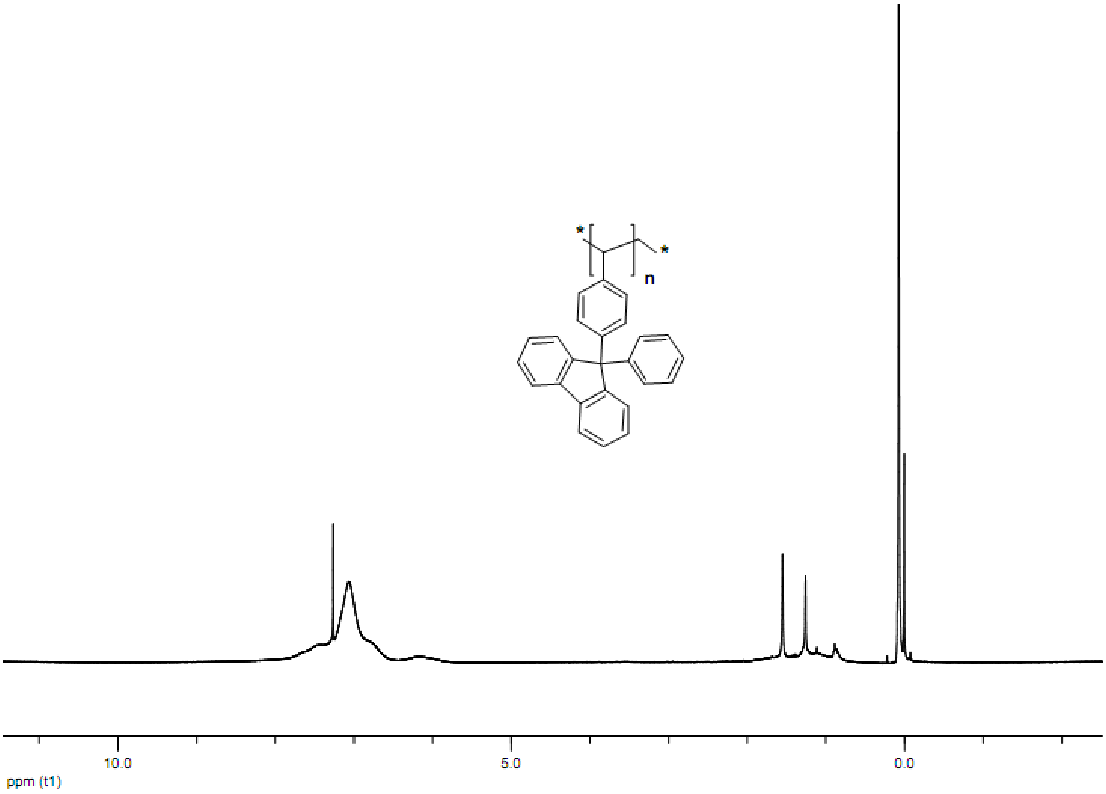

Figure S10. ^{1}HNMR of **PPFS** in $CDCl_3$**.**

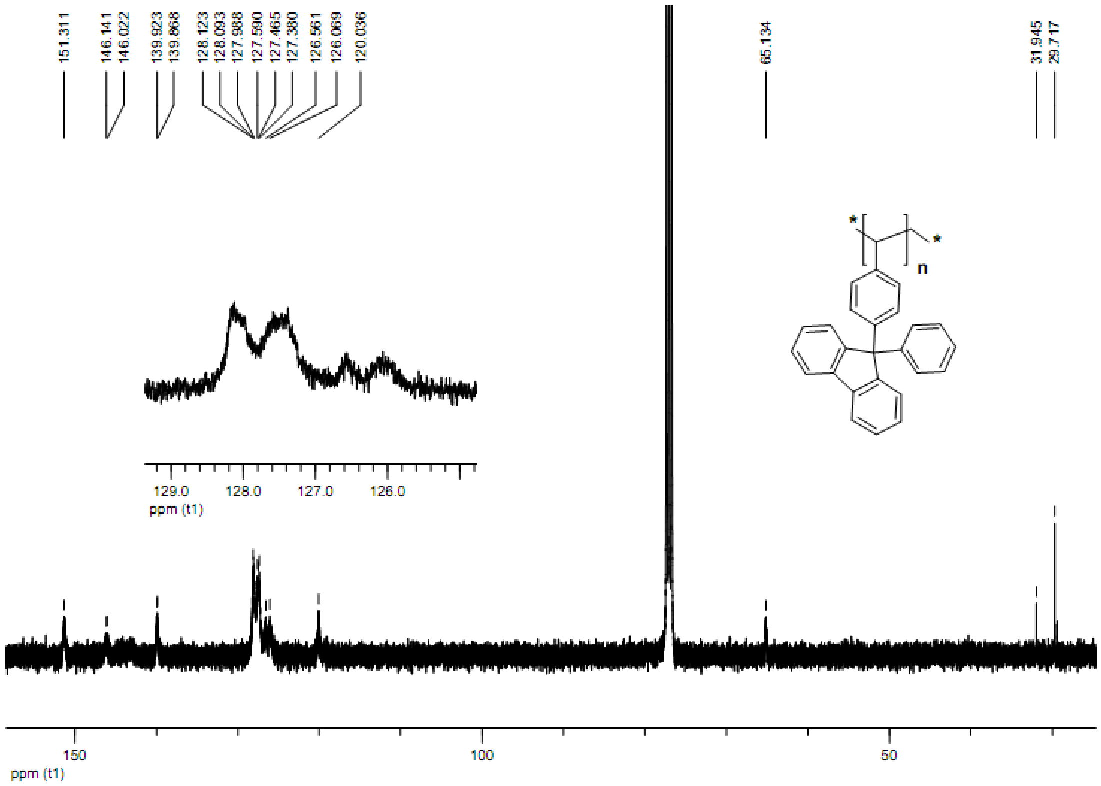

Figure S11. ^{13}CNMR of **PPFS** in $CDCl_3$**.**

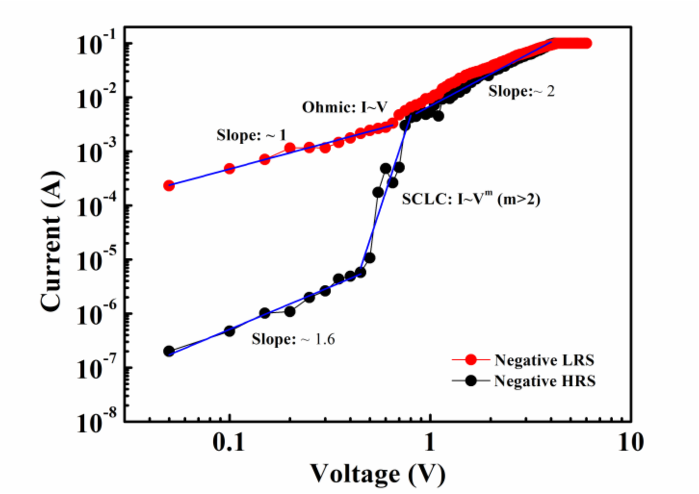

Figure S12. Experimental and fitted I-V curves of the ITO/PPFS/Al memory devices in the OFF and ON state.

References

1 Xie, L. H.; Hou, X. Y.; Hua, Y. R.; Tang, C.; Liu, F.; Fan, Q. L.; Huang, W. *Org. lett.* 2006, **8**. 3701.