Supporting Information

π-Conjugation-Interrupted Hyperbranched Polymer Electrets for Organic Nonvolatile Transistor Memory Devices

Jinyi Lin,[a] Wen Li,[a] Zhenzhen Yu,[b] Mingdong Yi,*[a] Haifeng Ling,[a] Linghai Xie,*[a] Shengbiao Li,[b] Wei Huang*[c, a]

[a] *Center for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Nanjing, 210023, P. R.. China. Fax: +86 025 8586 6396; E-mail: (W.H.)* iamwhuang@njupt.edu.cn*; (L.X.)* iamlhxie@njupt.edu.cn*; (M.Y.)* iammdyi@njupt.edu.cn*;*

[b]*Department of Chemistry, Central China Normal University, Wuhan, 430079, P. R. China.*

[c]*Jiangsu-Singapore Joint Research Center for Organic/Bio Electronics & Information Displays, Institute of Advanced Materials, Nanjing Tech University, Nanjing 211816, P. R. China.*

EXPERIMENTAL SECTION

Chemicals. All reagents were purchased from Sigma-Aldrich, Merck and Alfa Aesar, and used as received unless stated otherwise. Anhydrous THF (HPLC grade) was collected from Solvent Purification Systems (Innovative Technology, Inc.). Anhydrous chloroform was pre-dried over molecular sieves.

Characterization: ^{1}H-NMR were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS 2010 PLUS. Gel permeation chromatography (GPC) analysis was performed on a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent/? at a flow rate of 1.0 mL/min at 25 ^oC. Absorption spectra (1 μM in toluene) were measured with a Shimadzu UV-3600 spectrometer at 25 ^oC, and emission spectra (1 μM in toluene) were recorded on a Shimadzu RF-5301(PC) luminescence spectrometer. DSC measurement was acquired using a Shimadzu Instruments DSC-60A. DSC data were collected from 30 to 250 ^oC at a rate of 5 ^oC/min for both of the baseline and sample. Thermogravimetric analyses (TGA) were conducted by a Shimadzu DTG-60H under a heating rate of 5 ^oC/min and a nitrogen flow rate of 50 cm^3/min. Cyclic voltammetric (CV) studies were conducted using an CHI660C Electrochemical Workstation 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 (n-Bu_4NPF_6) in 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 = $-[E_{onset} - E(\mathrm{Fc/Fc^+}) + 4.8]$ eV. PPF and PPF8 films were spin-coating from a 5 mg/mL toluene. The samples were then examined with a field emission SEM (Hitachi, S-4800) at an accelerating voltage of 3 kV. Atomic force microscopy (AFM) measurements were obtained with a NanoScope IIIa AFM at room temperature. Commercial silicon cantilevers with typical spring constants of 21-78 $\mathrm{Nm^{-1}}$ were used to operate the AFM in tapping mode. X-ray diffraction (XRD) was performed using an X'Pert PRO X-ray diffractometer using Cu-Kα radiation (λ= 1.5418 Å) with a scan range typically of 5-30 degrees, 0.2 degrees per step.

Fabrication of pentacene-based transistor memory devices. The schematic configuration of the fabricated pentacene-based OFET memory devices is shown in Figure 3. Highly doped n-type Si(100) wafer was used as the substrate. A 300 nm thick SiO_2 layer as a gate dielectric was thermally grown onto the Si substrates. The substrate was rinsed with toluene, acetone, isopropyl alcohol and dried with a steam of nitrogen. A toluene solution of polymer (10 mg/ml) was stirred overnight to form a homogeneous solution. Thereafter, the solution was filtered through a 0.22 mm pore size PTFE membrane syringe filter and spin-coating at 1000 rpm for 60 s onto the wafer substrate. The polymer thin film was dried under vacuum (10^{-4} torr) at 70 °C for 1 h to remove residual solvents. The thickness of the prepared thin film was estimated to be 60 nm. The pentacene was thermally deposited with a deposition rate of 0.3-0.4 nm s^{-1} at 137.8 °C under vacuum (2.9×10^{-4} torr) to form a 50 nm thick film. A 25.5 nm thick gold electrode was subsequently deposited by thermal deposition through a shadow mask under vacuum (2.4×10^{-4} torr). The channel length (L) and width (W) of the devices were 50 and 1000 mm, respectively.

Preparation of PFOH.

Under N_2, a sample of fluorenone (1.8 g, 10 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 bromobenzene (1.87 g, 12 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 to give colorless solid PFOH (2.0 g, 80 %) . ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.69-7.67 (d, J=7.6 Hz, 2H, Ar-H), 7.41-7.33 (m, 6H, Ar-H), 7.29-7.24 (m, 5H, Ar-H), 2.51 (s, 1H, OH).

Preparation of PFO8H.

The process was the same with the preparation of PFO8H with PFOH. As a light-brown liquid PPF8 (3.01 g, 80%) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.68-7.65 (d, 2H, Ar-H), 7.38-7.24 (m, 8H, Ar-H), 6.80-6.78 (d, 2H, Ar-H), 3.91-3.89 (t, 2H, OCH_2), 2.40 (s, 1H, OH), 1.78-1.70 (m, 2H, CH_2), 1.35-1.25 (m, 10H, CH_2), 0.90-0.87 (t, 3H, CH_3).

Preparation of PPF.

Under N_2, a mixture solution of PFOH (0.20 g, 0.40 mmol) in appropriate refined CH_2Cl_2 (30 mL) was added dropwise to a solution of CF_3SO_3H (0.45 mL, 4.3 mmol) in appropriate refined CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature about 48 h. 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. As a white solid PPF (0.16 g, 80 %) was obtained. M_n= 6846 g mol^{-1}, PDI= 2.86. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.82-7.52 (2H, Ar-H), 7.48-7.29 (2H, Ar-H), 7.23-7.19 (2H, Ar-H), 7.14-7.01 (2H, Ar-H), 7.00-6.81 (2H, Ar-H), 6.73-6.46 (1H, Ar-H).

Preparation of PPF8.

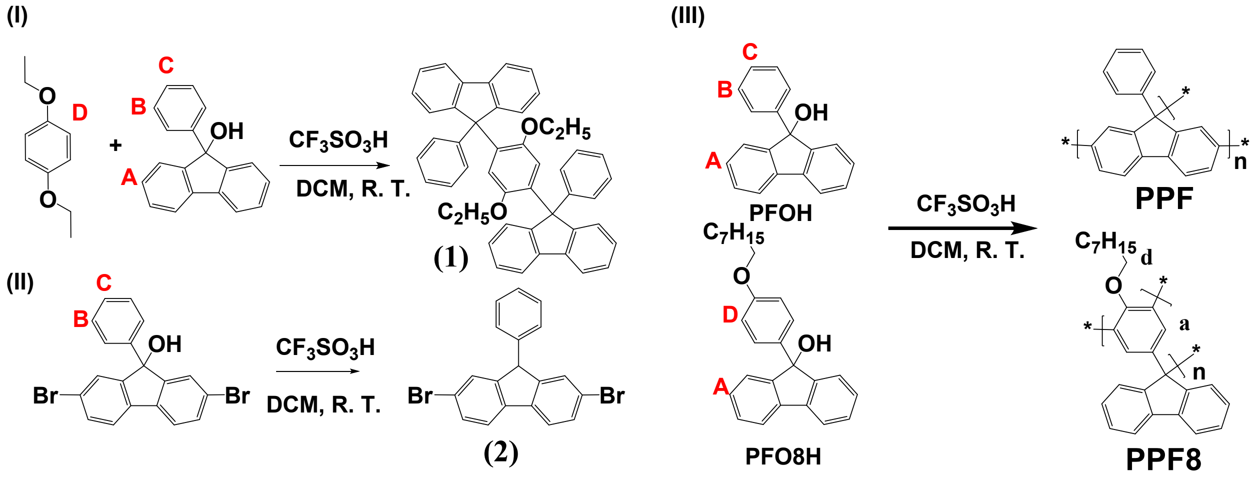
The process was the same with the preparation of PPF8 with PPF. As a light-brown solid PPF8 (0.16 g, 80%) was obtained. M_n= 8687 g mol^{-1}, PDI= 2.62. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.77-7.65 (2H, Ar-H), 7.43-7.29 (2H, Ar-H), 7.20-6.94 (4H, Ar-H), 6.76-6.63 (1H, Ar-H), 3.91-3.85 (2H, OCH_2), 1.75-1.74 (2H, CH_2), 1.30-1.29 (10H, $(CH_2)_5$), 0.91-0.90 (3H, CH_3).

Controlled experiment I (1).

The experiment I process (Preparation of 1) was the same with the preparation of PPF. As a white I (70 %) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.72 (d, J = 7.5 Hz, 4H, Ar-H), 7.66 (d, J = 7.6 Hz, 4H, Ar-H), 7.33 (t, J = 7.3 Hz, 4H, Ar-H), 7.23 (dd, J = 10.9, 4.2 Hz, 4H, Ar-H), 7.09 (t, J = 5.0 Hz, 10H, Ar-H), 6.42 (s, 2H, Ar-H), 3.28 (q, J = 6.9 Hz, 4H, CH_2), 1.38-0.73 (m, 6H, CH_3).

Controlled experiment II (2).

The experiment I process (Preparation of 2) was the same with the preparation of PPF. As a white II (68 %) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.64-7.61 (d, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.31-7.26 (m, 2H, Ar-H), 7.07-7.04 (d, 2H, Ar-H), 5.00 (s, 1H, C-H).



Scheme S1. (I, II) Research on the active site of phenyl fluorene tertiary alcohol in F-C polymerization. (III) Synthetic Routes for PPF and PPF8.

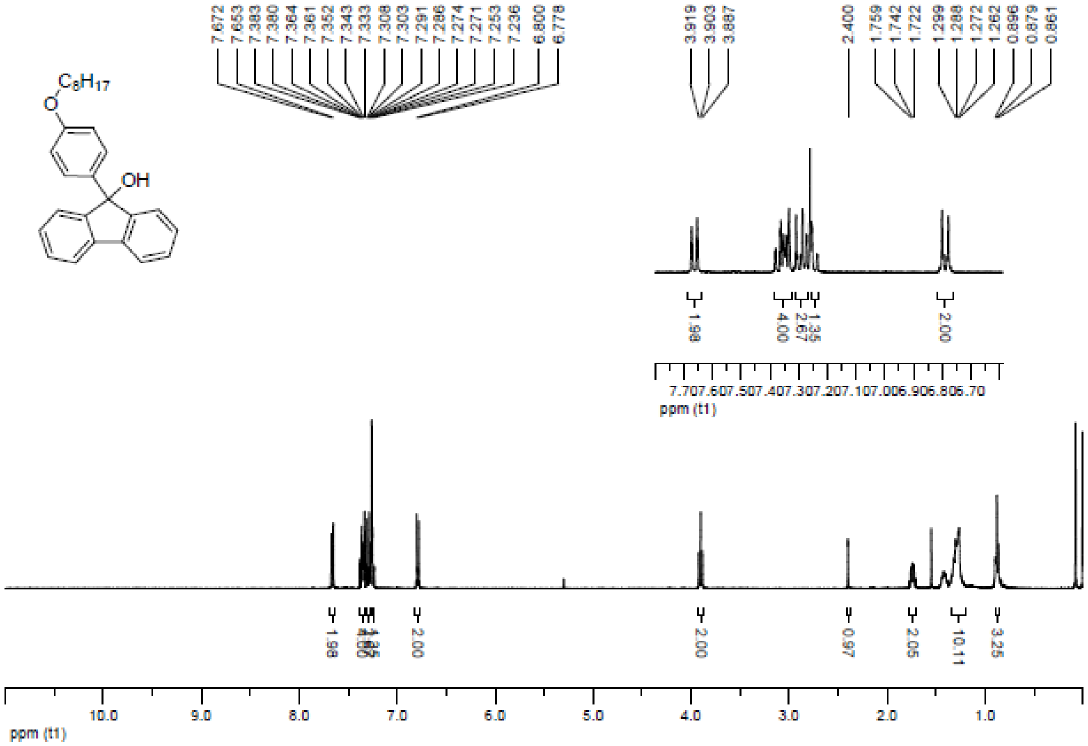


Figure S1-1. ^{1}H spectra of PF8OH in $CDCl_3$.

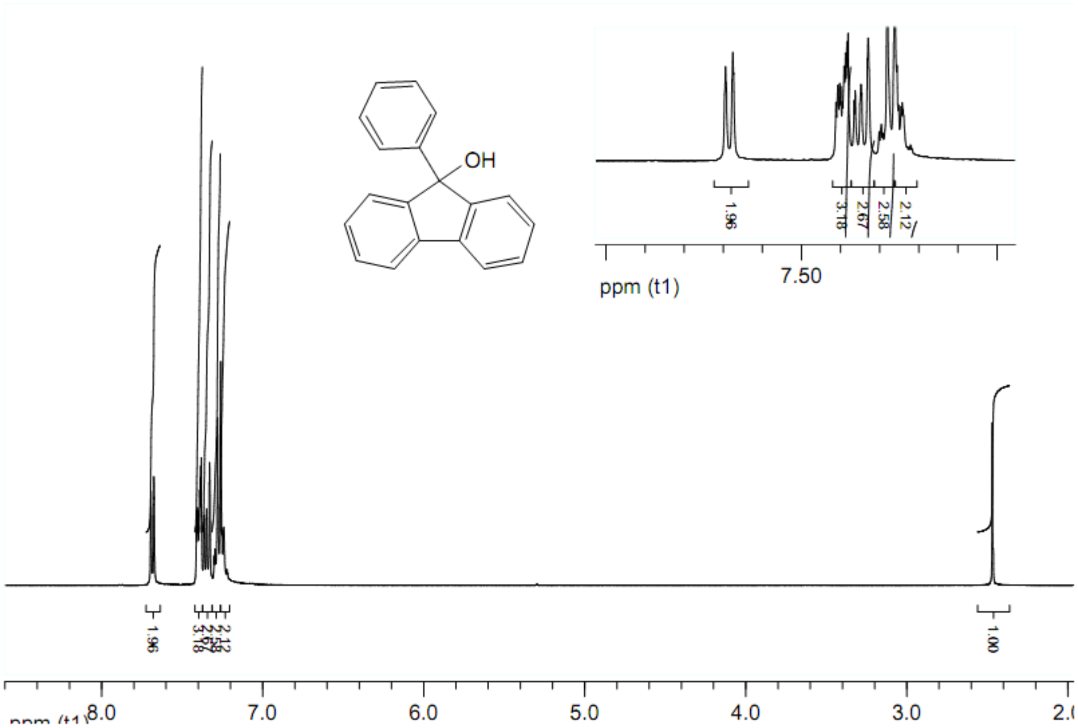


Figure S1-2. ^{1}H spectra of PFOH in $CDCl_3$.

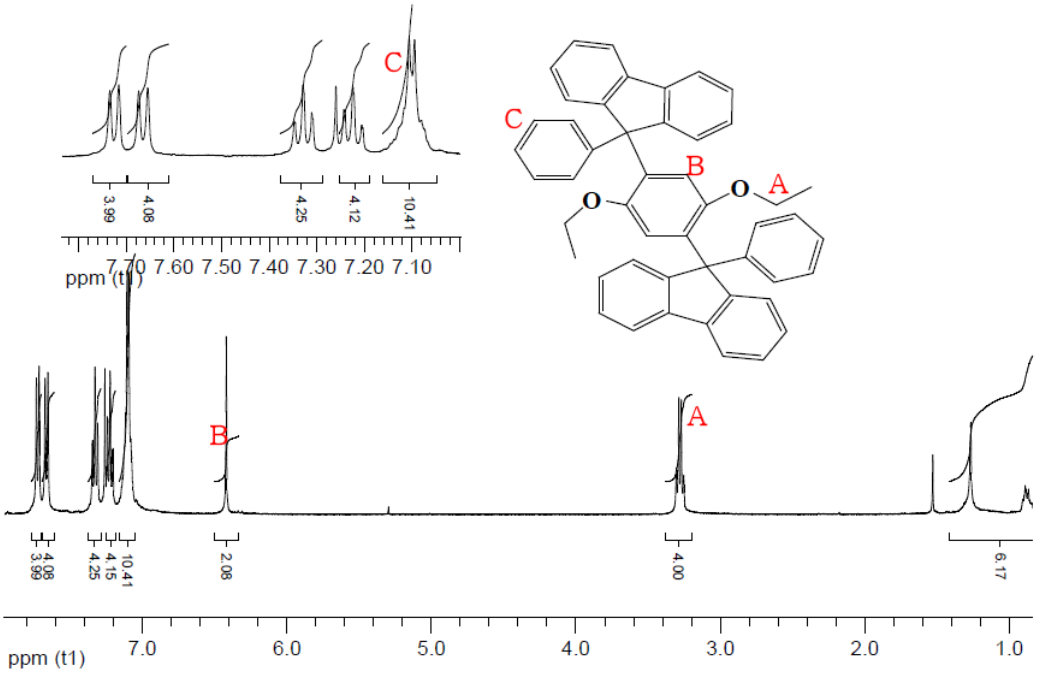


Figure S1-3. ^{1}H spectra of **(1)** in $CDCl_3$.

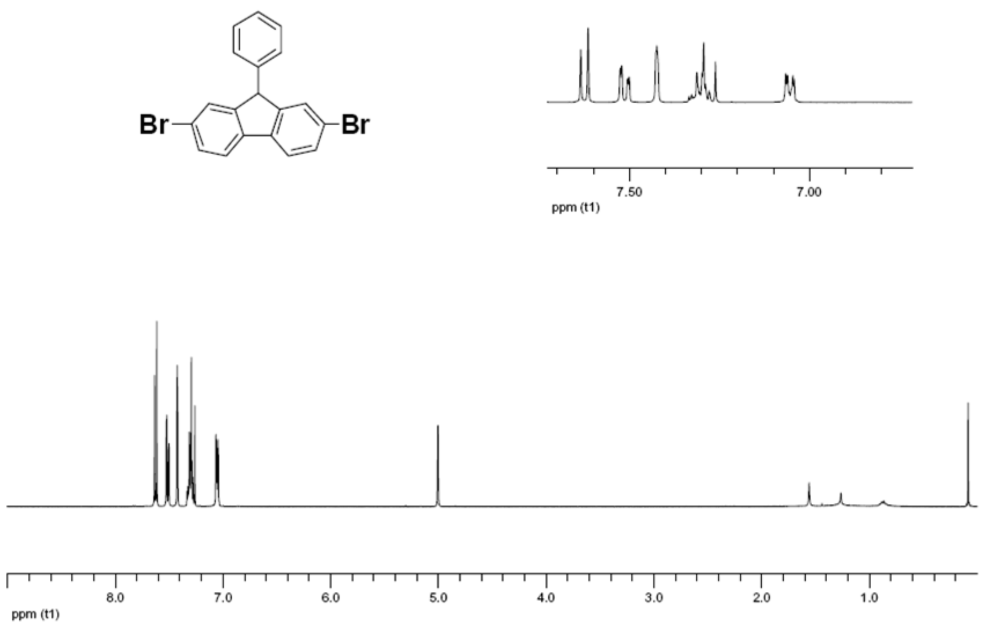


Figure S1-4. ^{1}H spectra of **(2)** in $CDCl_3$.

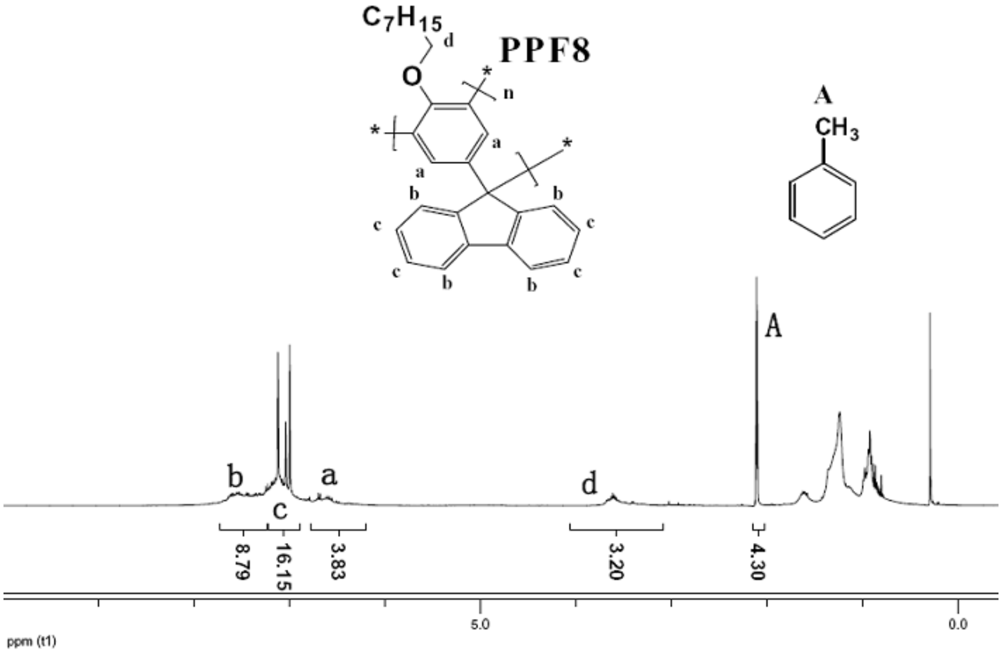


Figure S1-5. ^{1}H spectra of **PPF8** in d_6-toluene.

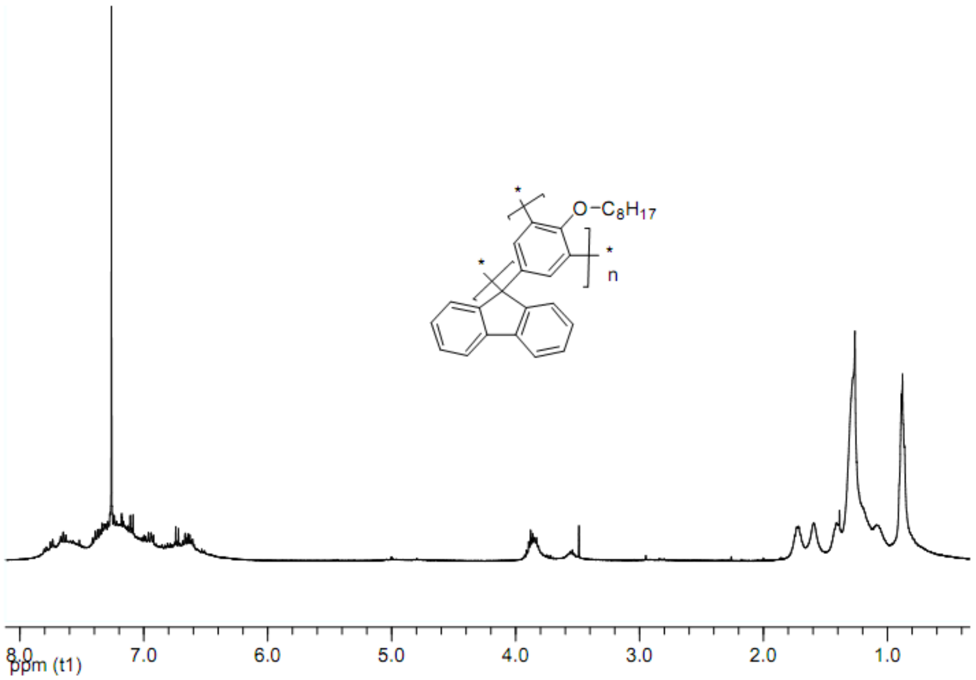


Figure S1-6. ^{1}H spectra of **PPF8** in $CDCl_3$.

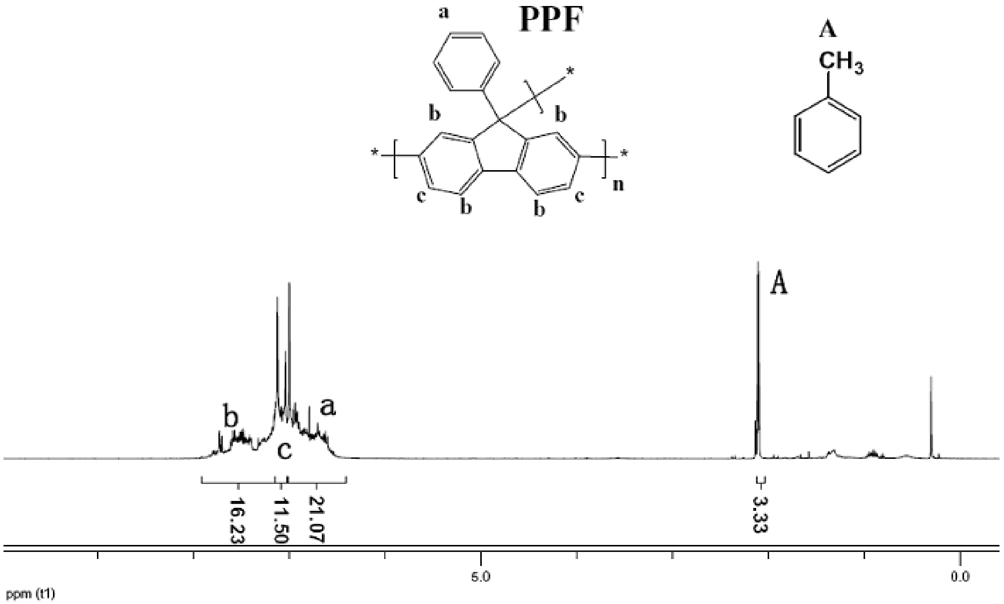


Figure S1-7. ^{1}H spectra of **PPF** in d_6-toluene.

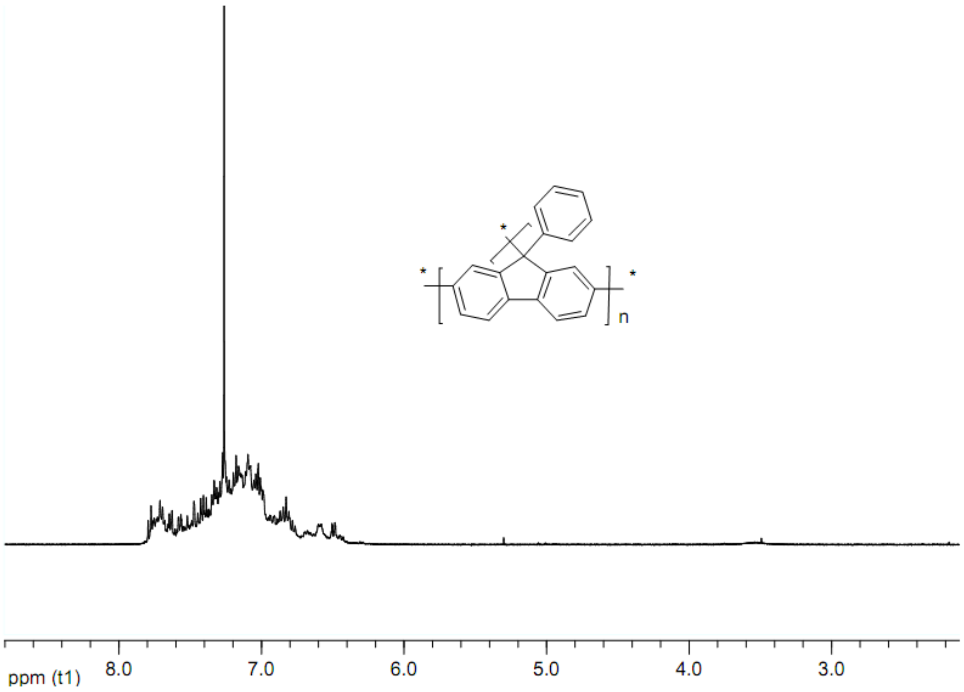


Figure S1-8. ^{1}H spectra of **PPF** in $CDCl_3$.

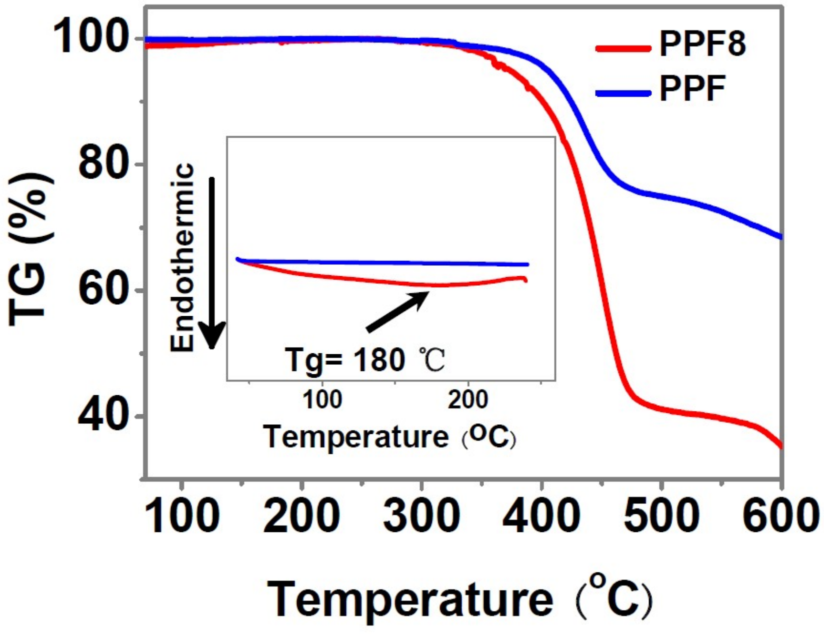


Figure S2. TGA curve of PPF and PPF8 recorded at a heating rate of 5 °C/min (decomposition temperature from the position of 5 % weight loss). Inset: DSC trace of PPF and PPF8 recorded at a heating rate of 5 °C/min from 50 to 250 °C.

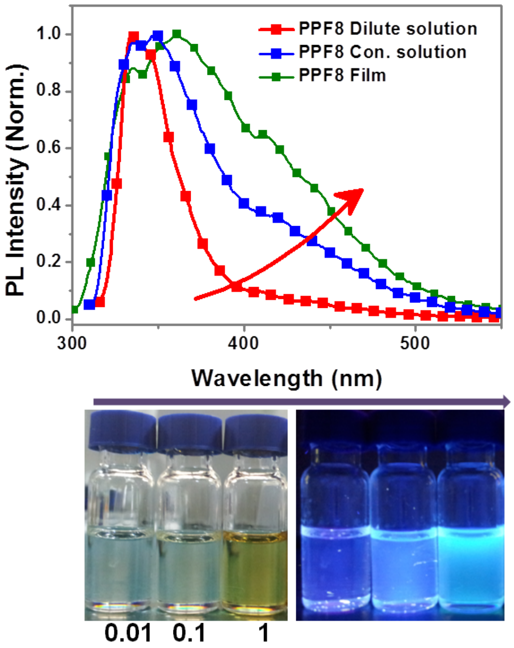


Figure S3. PL spectra of PPF8 in toluene solution at various concentrations.

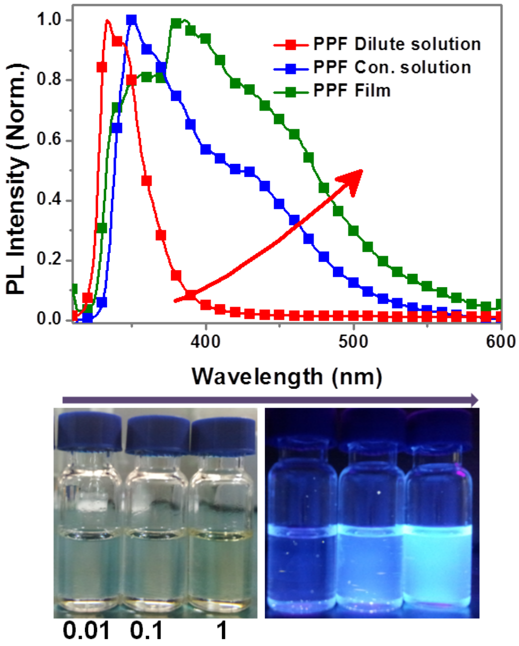


Figure S4. PL spectra of PPF in toluene solution at various concentrations.

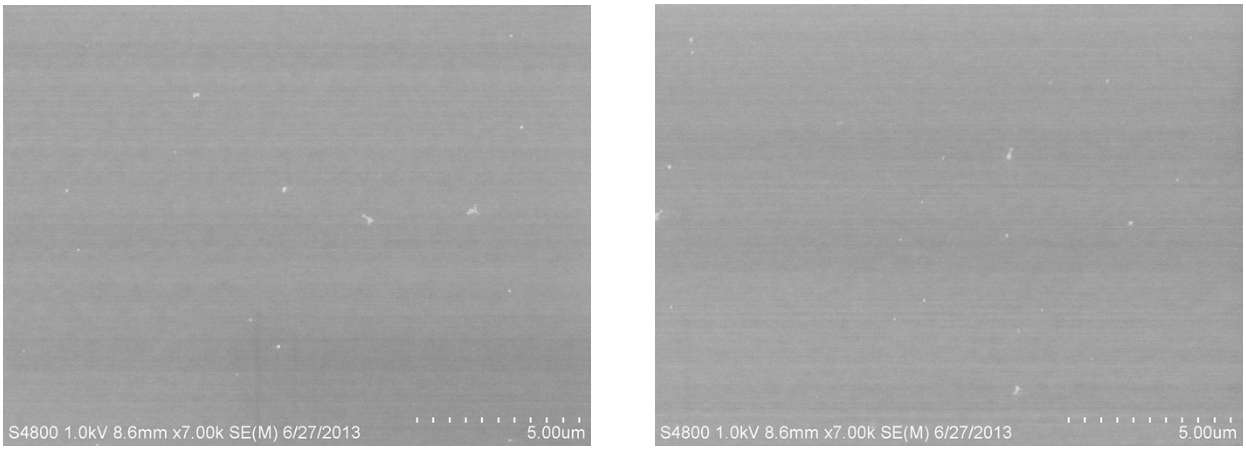


Figure S5. SEM topographic images of PPF8 (right) and PPF (left) film on SiO_2 substrates.

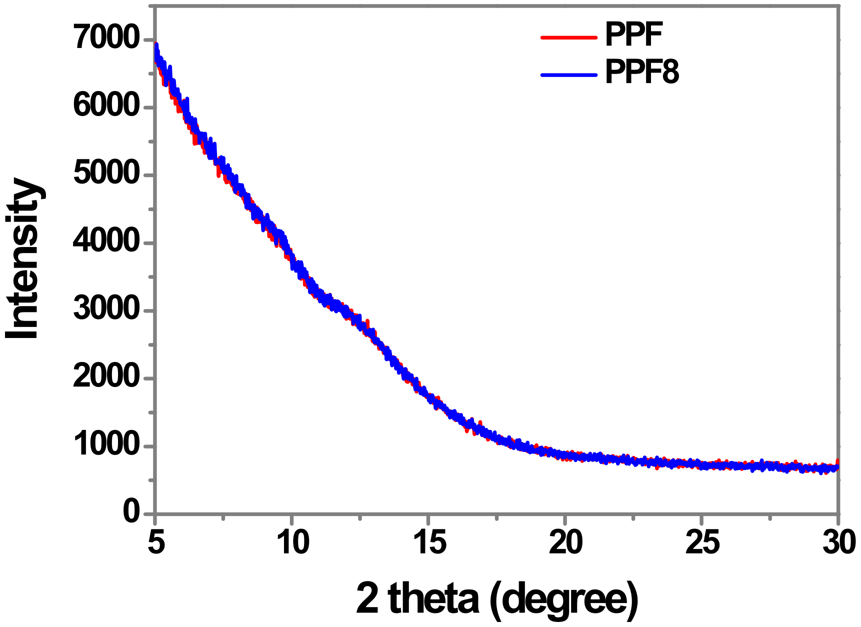


Figure S6. Out-of-plane X-ray diffraction patterns of PPF8 and PPF spin-coating from toluene solution (10 mg/ml) on SiO_2 substrates.

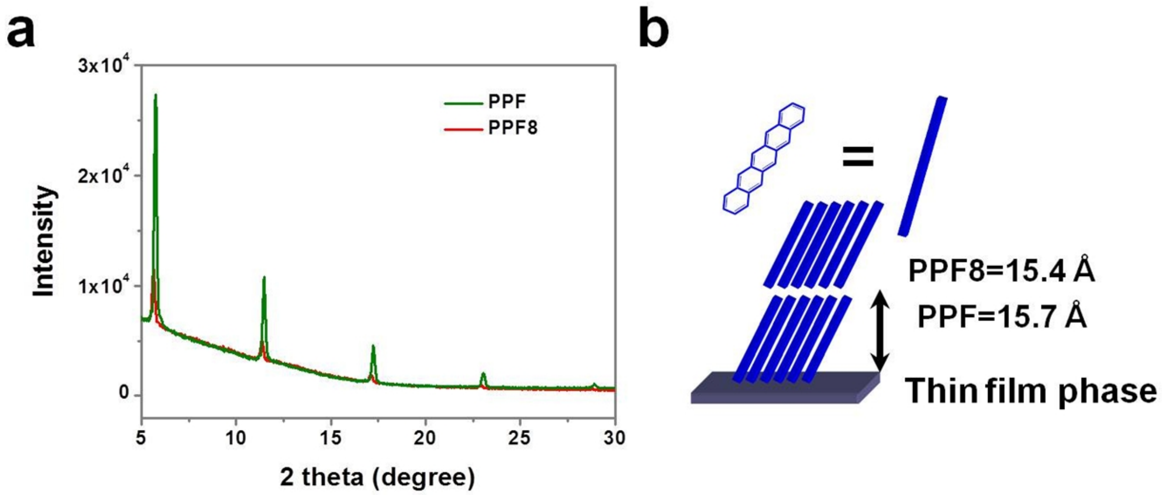
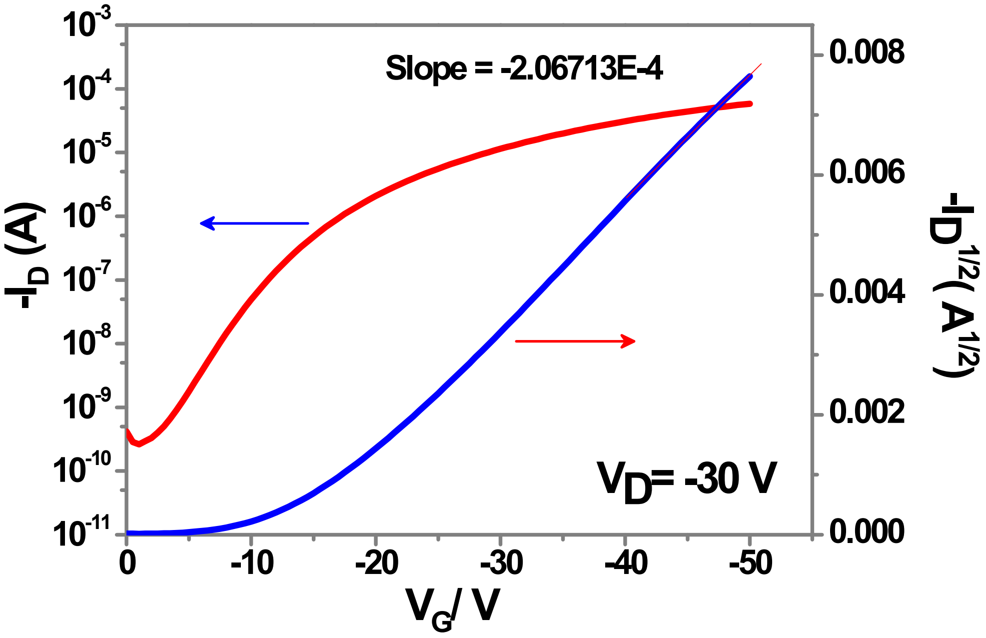


Figure S7. (a) Out-of-plane X-ray diffraction patterns of pentacene on PPF8 and PPF, and (b) Schematic of pentacene morphology on the polymers: thin-film phase.



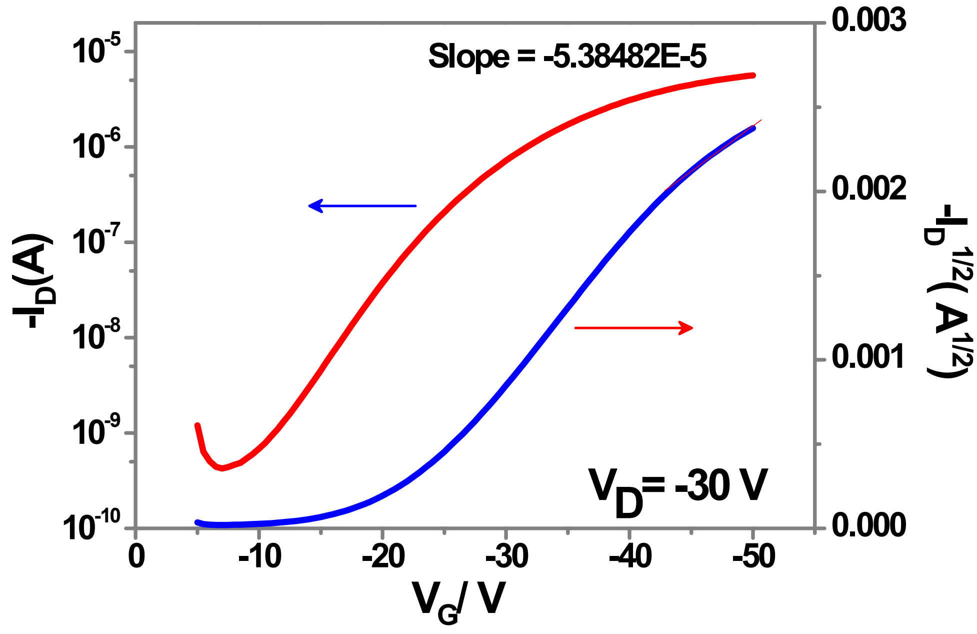
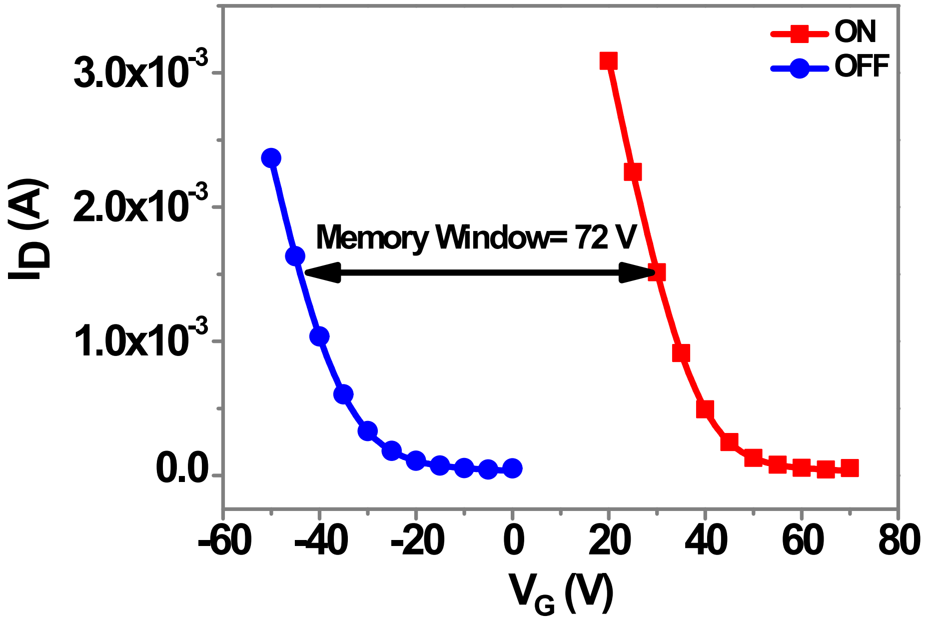


Figure S8. Transfer characteristics of transistor memory devices with PPF (Top) and PPF8 (Bottom) as the polymer electret.



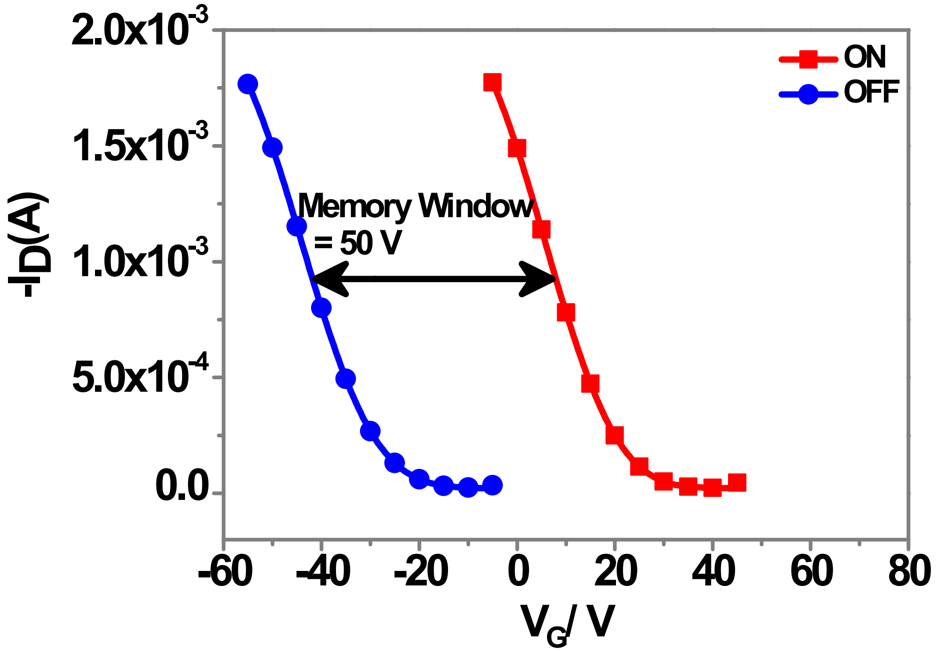


Figure S9. Memory windows of transistor memory devices with PPF (Top) and PPF8 (Bottom) as the polymer electret.

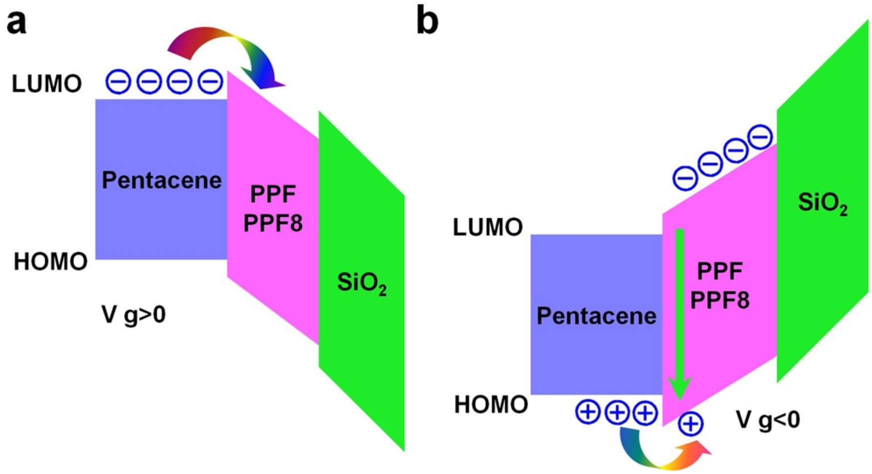


Figure S10. Energy band diagrams under (a) a positive gate voltage and (b) a negative gate voltage.