Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Construction of Polymer Materials with Specific Responses to Violet and Green Lights and Their Potential Applications in Artificial Visual Memory System

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1. Experimental Section

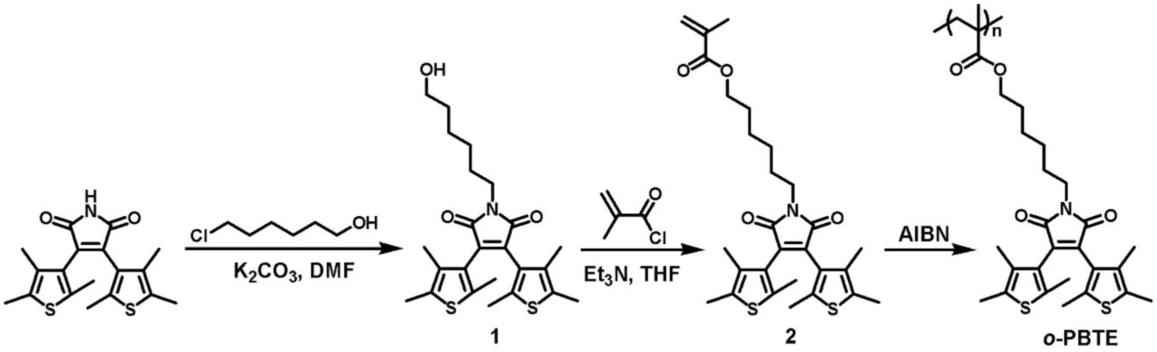
Materials

2,3-Bis(2,4,5-trimethyl-3-thienyl)maleimide (97%), 6-chloro-1-hexanol (95%), methacryloyl chloride (90%), azobisisobutyronitrile (AIBN) (98%) were purchased from TCI. Anhydrous potassium carbonate (K_2CO_3) and other used solvents and salts were purchased from Sinopharm Chemical Reagent Co., Ltd.. AIBN was used after recrystallization in ethanol. Other reagents were used directly without further purification.

Characterization

Nuclear magnetic resonance spectrum (NMR) was measured through INOVA 400 MHz FT-NMR spectrometer with the solvent of $CDCl_3$; Gel Permeation Chromatography (GPC) was carried out by Waters 1515 gel permeation chromatography with THF as the mobile phase to obtain the number average relative molecular weight and molecular weight distribution of the polymer; Thermogravimetric analysis (TGA) was carried out by PE TGA-7 thermogravimetric analyzer with a heating rate of 10 °C/min; Ultraviolet-visible absorption spectrum (UV-vis) was tested on a Shimadzu UV-3600 spectrophotometer; Cyclic Voltammetry (CV) was performed on a CorrTest CS electrochemical workstation analyzer with the scanning speed of 100 mV/s; Atomic Force Microscope (AFM) images were collected on Bruker Icon AFM platform in tapping model then analyzed and exported by NanoScope Analysis software from the same corporation; X-ray diffraction pattern (XRD) was carried out on a X-Pert-Pro MPD X-ray diffractometer; Electrical storage performance (Current-Voltage curve) was performed on a Keithley 4200-SCS semiconductor characterization system. The electrical storage performance (Current-Voltage curve) was performed on a Keithley 4200-SCS semiconductor characterization system. The tests were conducted at room temperature and in atmospheric conditions. Since the organic layer of the device is formed by spin-coating and the polymer covers the entire Indium tin oxide (ITO) surface, a small portion needs to be wiped off and exposed to the bare ITO. The device is tested with two electrode probes, one touching the top electrode (aluminum layer) of the device and the other contacting the bare ITO bottom electrode, thus forming a closed loop. The current signal varies with the applied voltage and is captured by the semiconductor characterization system. XD-300 high brightness cold light source and filter were used as light source, unless specified, the power of the light source used is 190 W.

2. Synthesis Details



Scheme S1. Synthesis procedure of the polymer PBTE

Synthesis of 1-(6-Hydroxyhexyl)-3,4-bis(2,4,5-trimethylthiophen-3-yl)-1H-pyrrole-2,5-dione (Compound 1)[1]

6-chloro-1-hexanol (0.66 g, 4.80 mmol) was dissolved in 60 mL DMF. Potassium carbonate (0.64 g, 4.80 mmol) and 2,3-bis(2,4,5-trimethyl-3-thienyl) maleimide (1.38 g, 4.00 mmol) were then added to the solution, and the reaction was refluxed for 10 h before cooled to room temperature, the mixture was extracted with ethyl acetate and concentrate to obtain a crude product, which purified by a silica gel column chromatography (ethyl acetate/petroleum ether = 1:20) to obtain compound 1 as a yellow-brown oil (1.92 g, 90%). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.16 (t, J = 6.6 Hz, 2H), 3.63 (t, J = 7.2 Hz, 2H), 2.25 (d, J = 10.4 Hz, 6H), 2.05 (s, 3H), 1.89 (s, 6H), 1.73 (s, 3H), 1.67 (p, J = 7.2 Hz, 4H), 1.42 (d, J = 6.3 Hz, 2H), 1.32 – 1.27 (m, 2H).

Synthesis of 6-(2,5-dioxo-3,4-bis(2,4,5-trimethylthiophen-3-yl)-2,5-dihydro-1H-pyrrol-1-yl)methyl Hexyl acrylate (Compound 2)[2]

Compound 1 (1.27 g, 2.85 mmol), tetrahydrofuran (20 mL) and triethylamine (0.6 mL) were added into a 50 mL round bottom flask in an ice bath. Methacryloyl chloride (0.45 g, 4.3 mmol) was diluted with tetrahydrofuran (5 mL) and slowly added to the reaction dropwise. After reacting for 10 h in 0 °C, the reaction solution was poured into water and extracted with dichloromethane, the organic phase was collected and concentrated under reduced pressure to obtain an orange crude product. which purified by a silica gel column chromatography (ethyl acetate/petroleum ether = 1:10) to obtain the compound 2 with a yield of (1.10 g, 75%). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.09 (s, 1H), 5.64 – 5.47 (m, 1H), 4.13 (t, J = 6.6 Hz, 2H), 3.63 (t, J = 7.2 Hz, 2H), 2.25 (d, J = 10.4 Hz, 6H), 2.05 (s, 3H), 1.94 (s, 3H), 1.90 (s, 6H), 1.73 (s, 3H), 1.68 (d, J = 5.4 Hz, 4H), 1.50 – 1.35 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-d) δ 170.42, 170.32, 167.47, 136.90, 136.70, 136.46, 136.13, 135.90, 131.85, 131.51, 130.45, 127.63, 127.48, 125.23, 64.56, 38.26, 38.22, 28.54, 28.47, 26.46, 25.56, 18.34, 14.41, 14.15, 13.31, 13.14, 13.12, 13.02.
Elemental analysis (%) calcd for $C_{28}H_{35}NO_4S_2$: C, 65.46; H, 6.87; N, 2.73; S, 12.48; found: C, 65.34; H, 6.86; N, 2.73; S, 12.24.
MALDI-TOF-MS m/z: calcd 513.20, found 513.242.

Synthesis of the polymer PBTE

Compound 2 (0.26 g, 0.5 mmol), azobisisobutyronitrile (3.3 mg, 0.02 mmol) and cyclohexanone (5 mL) were added into the polymerization tube, the reaction was heated at 80 °C in a nitrogen atmosphere for 24 h. Then the obtained reaction solution was cooled to room temperature and poured into a large amount of methanol to precipitate out the product, which was then filtered out and washed with methanol in a Soxhlet extraction device to remove small molecules and finally obtain a brown product (0.16 g, 62%).

Preparation of the memory device

The indium tin oxide (ITO) glass was washed respectively with deionized water, acetone and ethanol in an ultrasonic bath for 20 minutes. A solution of polymer PBTE in o-dichlorobenzene (10 mg/mL) was prepared and filtered with a 0.22 µm organic filter, the film was formed by spin-coating method (low speed 500 r/min, 10 s; high speed 1500 r/min, 20 s). After the solvent evaporated, a layer of aluminum electrode was vapor-deposited on the film to form a sandwich structure device under 2×10^{-6} Torr through a shadow mask in N_2 atmosphere.

3. Thermal Property

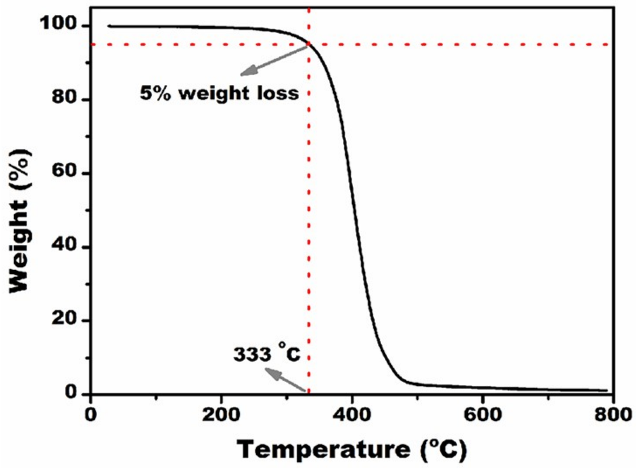


Figure S1. TGA curve of the PBTE at a heating rate of 10 °C/min from 25 °C to 800 °C under N_2 atmosphere.

4. Optical Properties

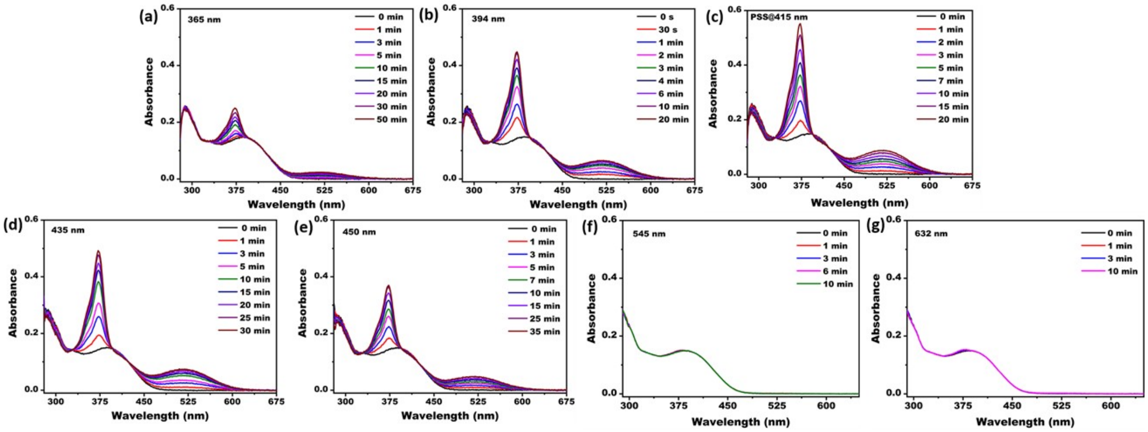


Figure S2. UV-vis absorption spectrum curves of the ring-opened isomer *o*-PBTE in toluene (1×10^{-5} M) under irradiations at (a) 365 nm, (b) 394 nm, (c) 415 nm, (d) 435 nm, (e) 450 nm, (f) 545 nm and (g) 632 nm.

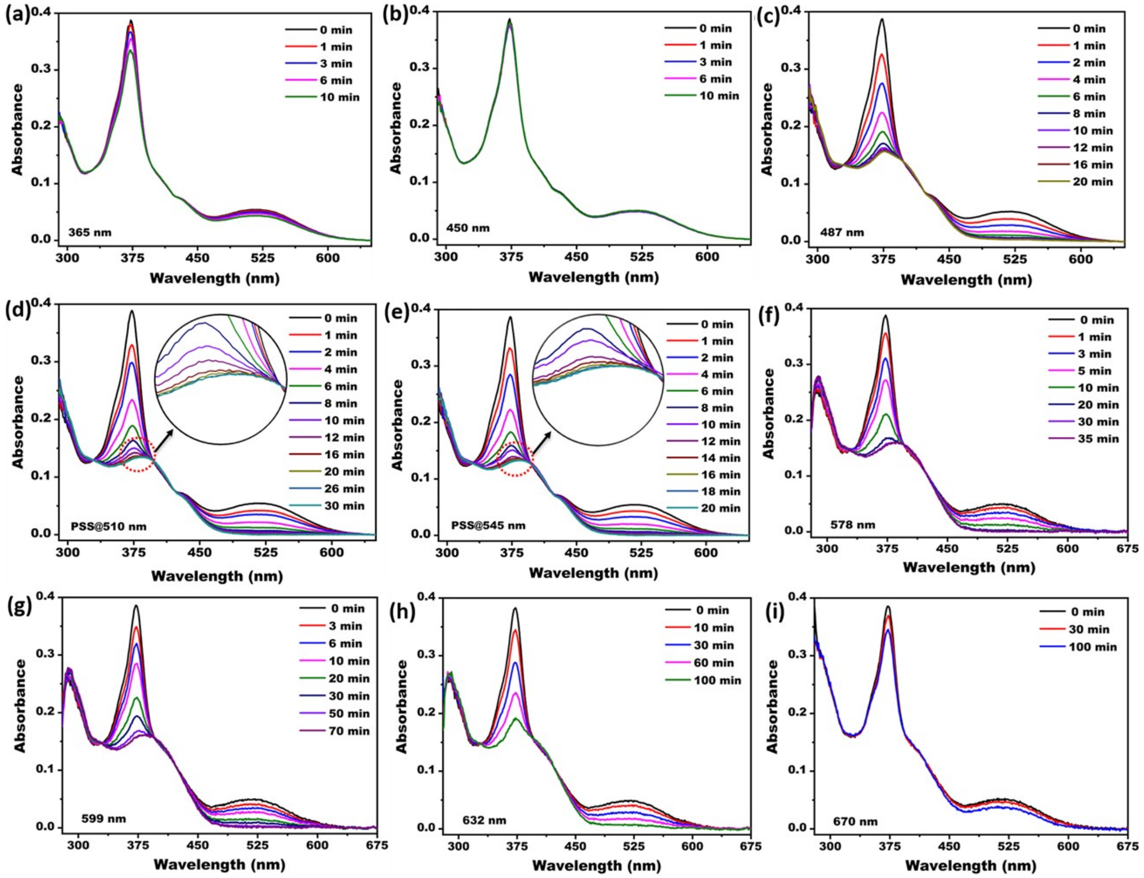


Figure S3. UV-vis absorption spectrum curves of the ring-closed isomer *c*-PBTE in toluene (1×10^{-5} M) under irradiations at (a) 365 nm, (b) 450 nm, (c) 487 nm, (d) 510 nm, (e) 545 nm, (f) 578 nm, (g) 599 nm, (h) 632 nm and (i) 670 nm.

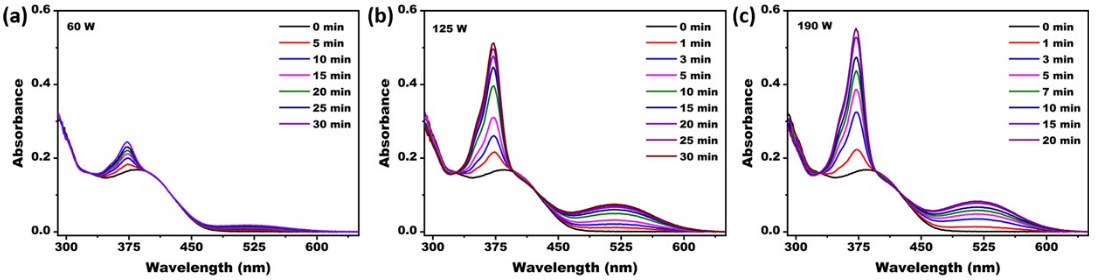


Figure S4. UV-vis absorption spectrum curves of the ring-opened isomer *o*-PBTE in toluene (1×10^{-5} M) under irradiation at 415 nm with different light power: (a) 60 W; (b) 125 W; (c) 190 W.

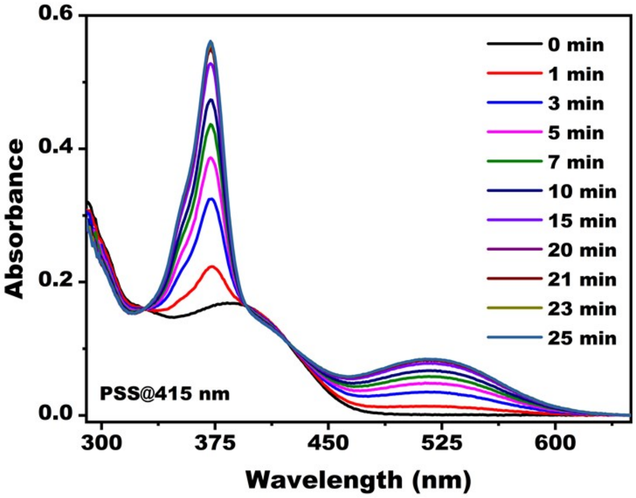


Figure S5. UV-vis absorption spectrum curves of the ring-opened isomer *o*-PBTE in toluene (1×10^{-5} M) under continuous irradiation at 415 nm for 25 min.

5. I-V Performance and Morphology of *o*-PBTE and *c*-PBTE Based Memory Devices

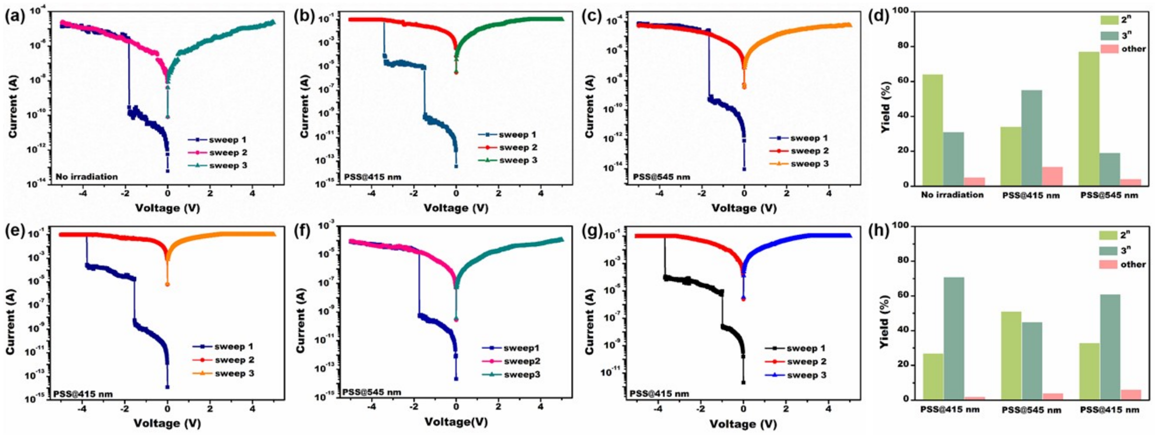


Figure S6. I-V characteristics of *o*-PBTE and *c*-PBTE based memory devices from no irradiation (a) to continuous alternate photoirradiation at 545 nm (c, f) and 415 nm (b, e, g), respectively. And the corresponding statistics distribution diagrams of memory performance (d, h).

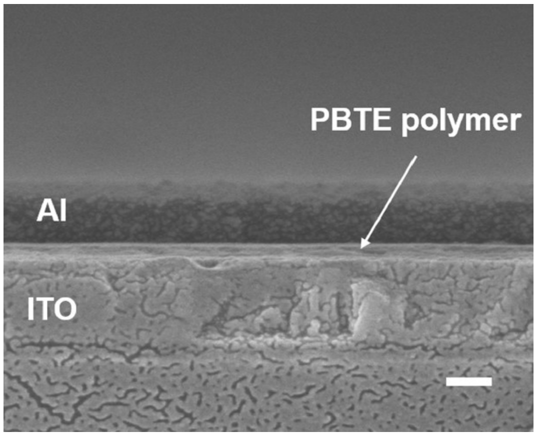


Figure S7. SEM image of a cross-section of the PBTE sandwich device, the scale bar is 100 nm. The thickness of the top electrode aluminum layer is about 130 nm, the middle organic layer is about 40 nm and the ITO bottom electrode layer is about 200 nm.

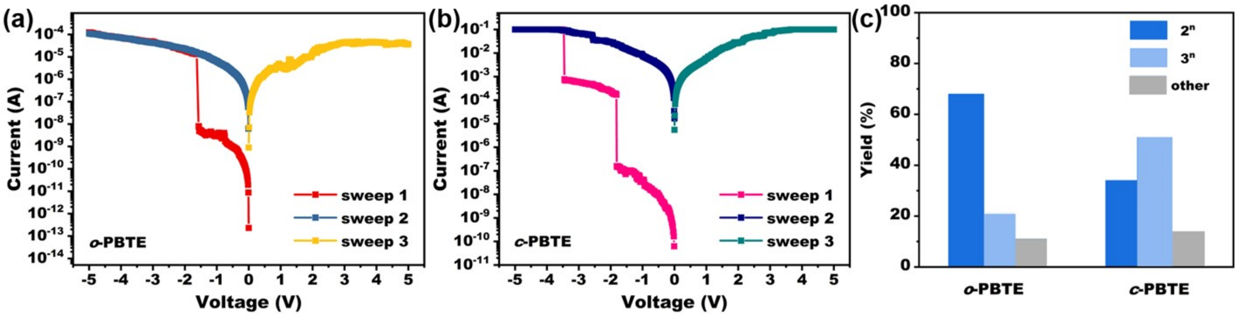


Figure S8. I-V characteristics of *o*-PBTE and *c*-PBTE based memory devices three months later.

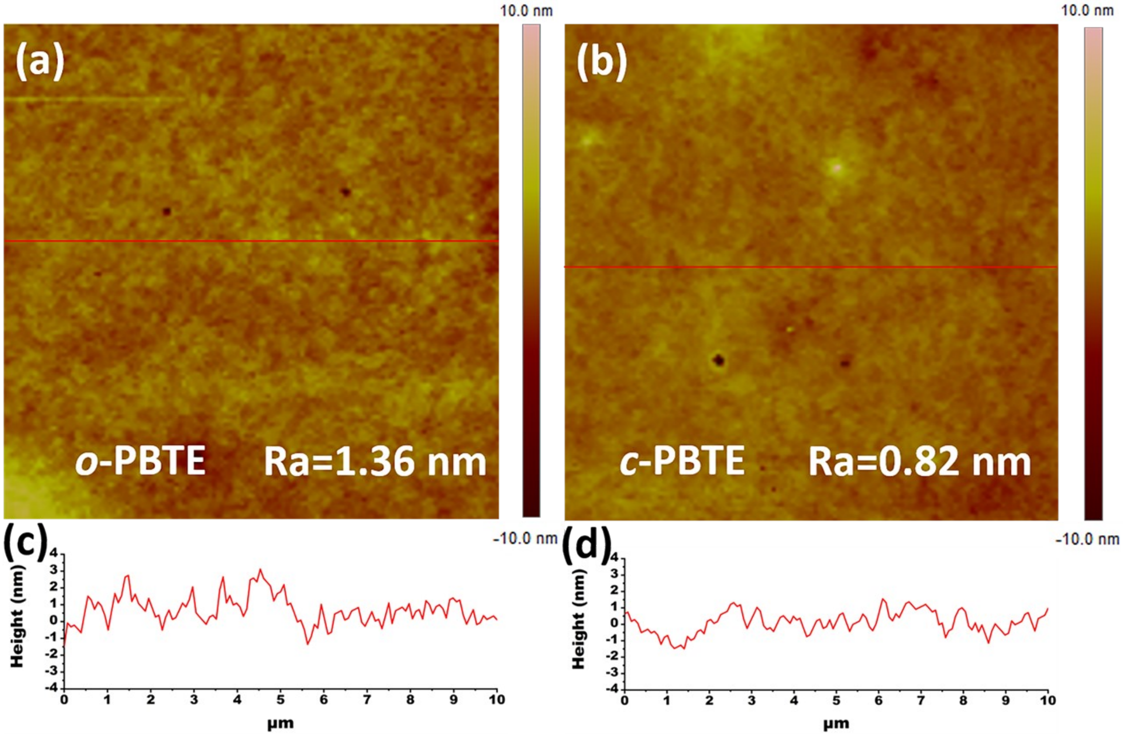


Figure S9. Tapping-mode AFM topographic images in large area (10 μm × 10 μm) and the corresponding roughness curves of (a, c) *o*-PBTE and (b, d) *c*-PBTE.

6. XRD Patterns and UV-vis Absorption Spectra

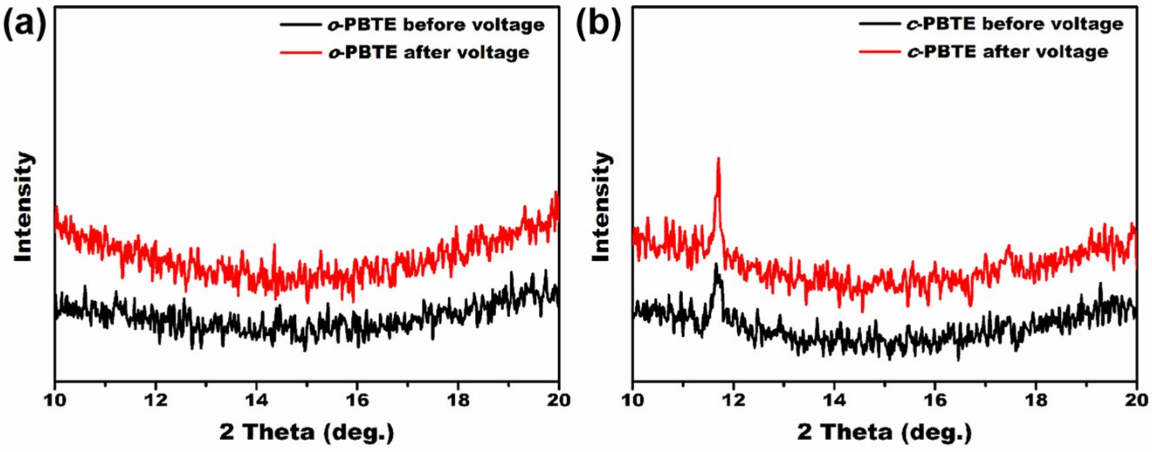


Figure S10. X-ray diffraction patterns of the film (a) *o*-PBTE and (b) *c*-PBTE before and after applying the voltage bias.

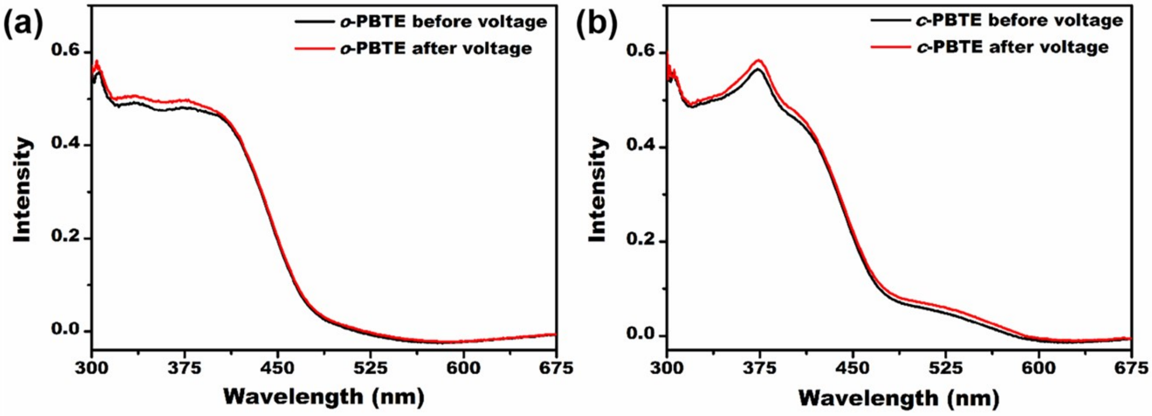


Figure S11. UV-vis absorption spectra of the film (a) *o*-PBTE and (b) *c*-PBTE before and after applying the voltage bias.

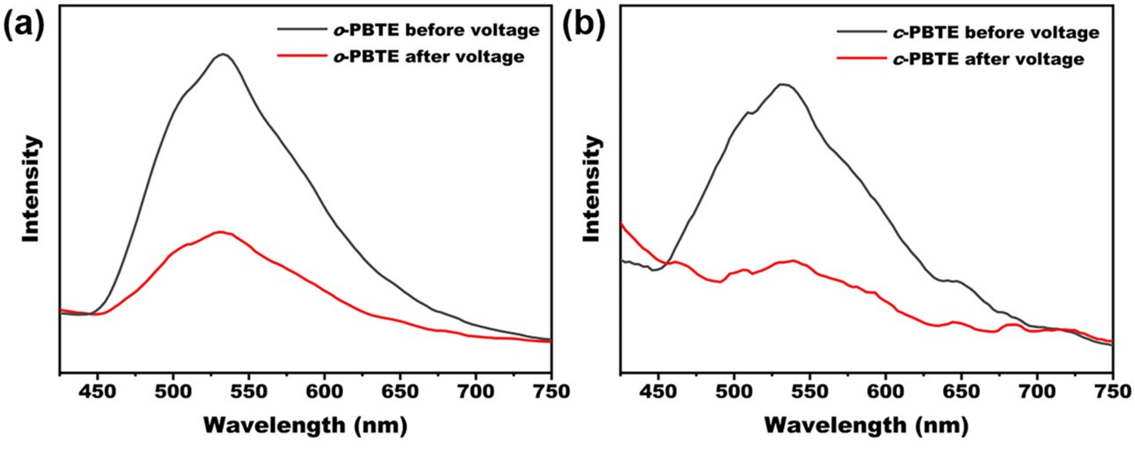


Figure S12. The photoluminescence (PL) measurements of the (a) o-PBTE and (b) c-PBTE based films before and after applying the voltage bias.

7. ^{1}H NMR and ^{13}C NMR Spectra

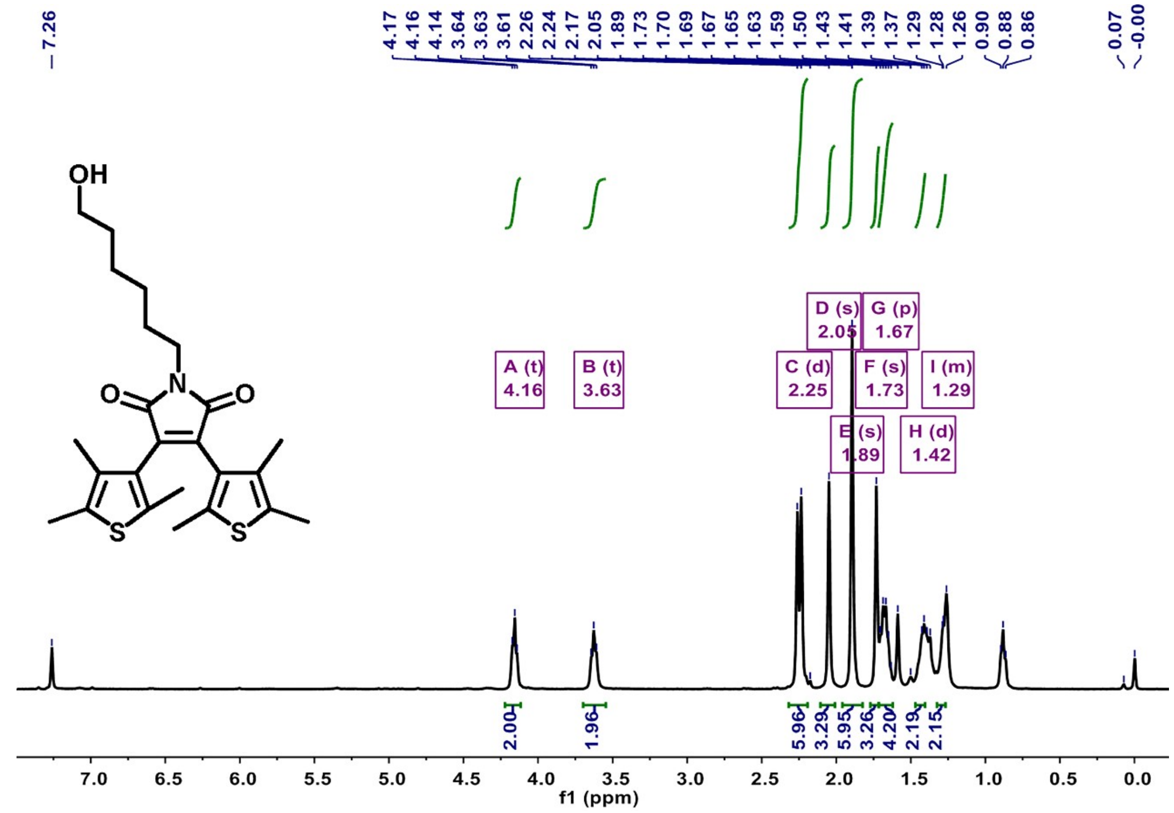


Figure S13. ^{1}H NMR spectrum of compound 1 in $CDCl_3$.

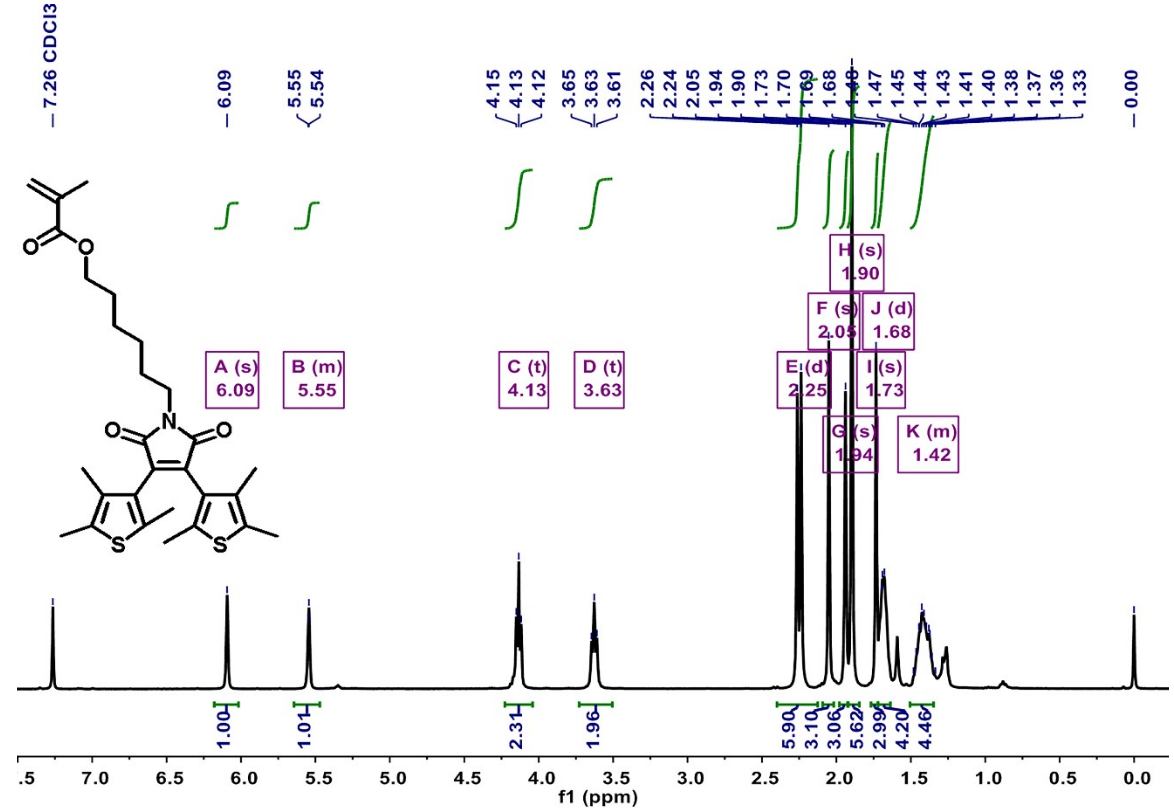


Figure S14. ^{1}H NMR spectrum of compound 2 in $CDCl_3$.

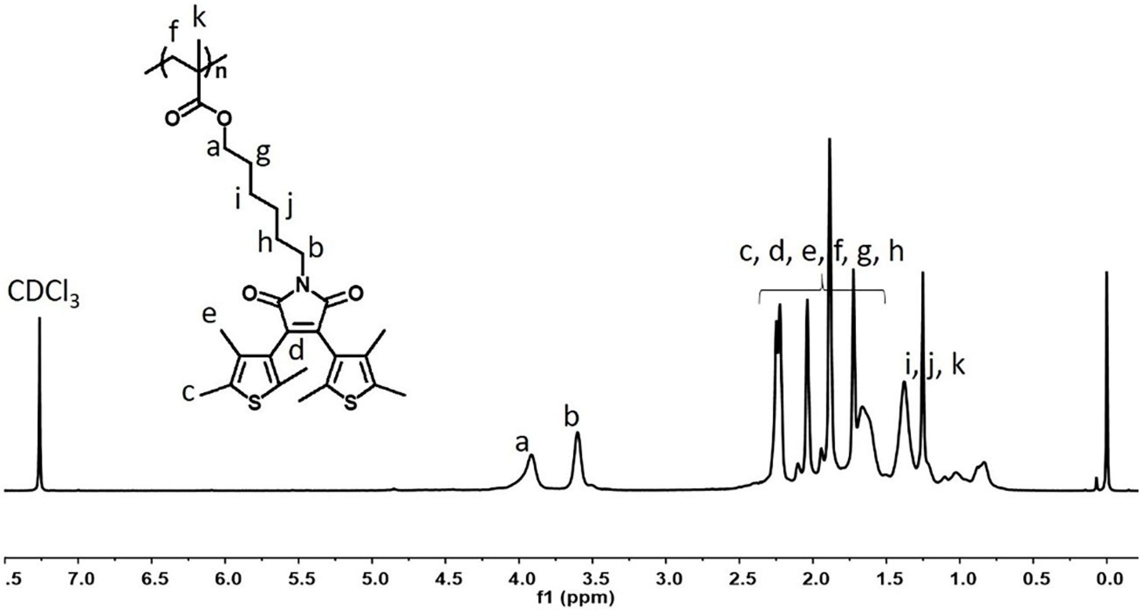


Figure S15. ^{1}H NMR spectrum of PBTE in $CDCl_3$.

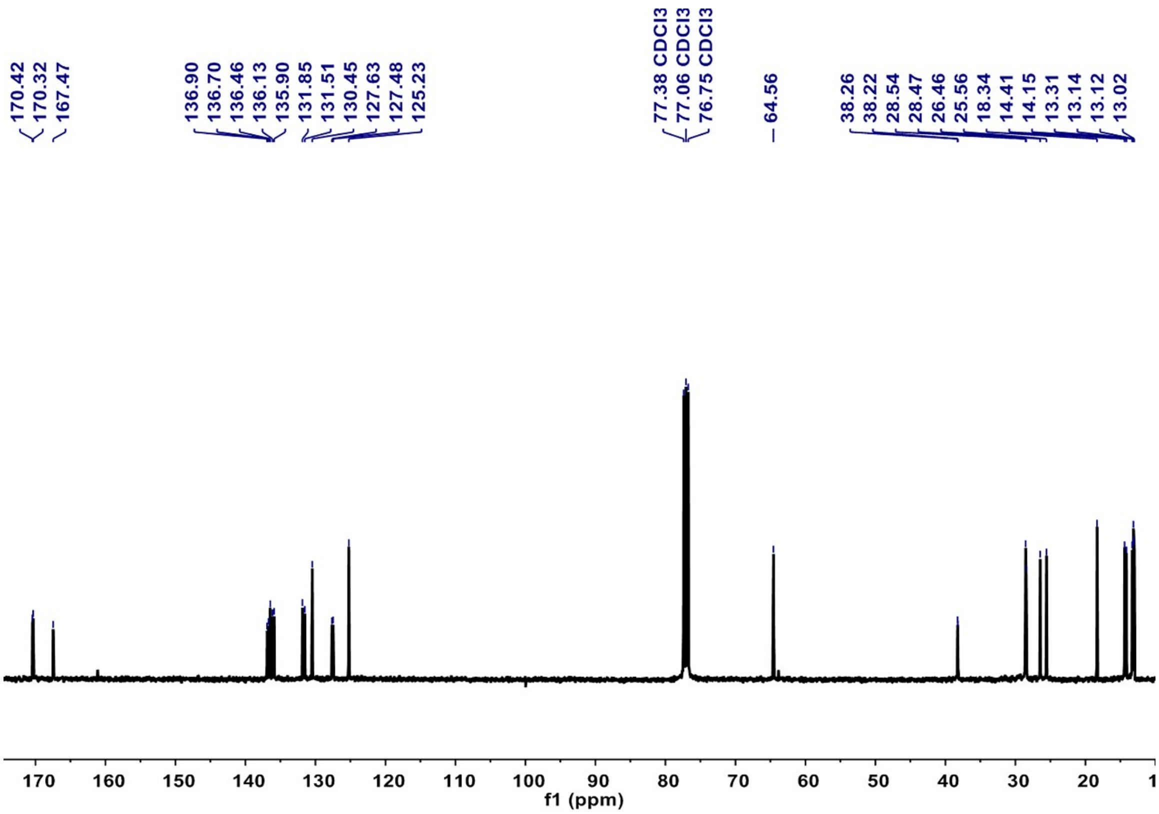


Figure S16. ^{13}C NMR spectrum of compound 2 in $CDCl_3$.

8. MALDI-TOF Mass Spectra

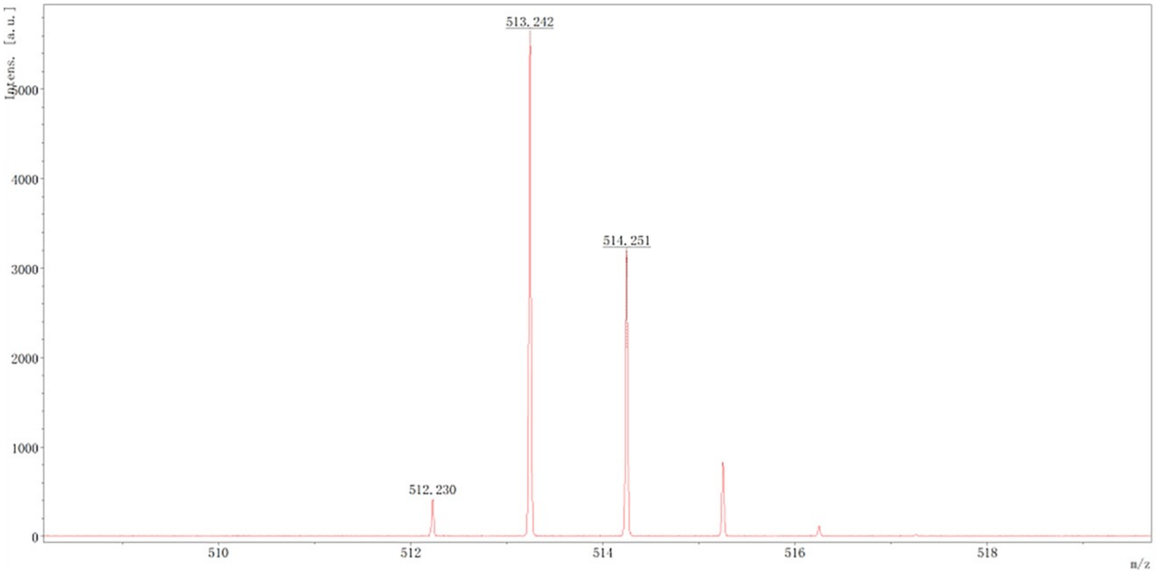


Figure S17. MALDI-TOF mass spectra of compound 2.

9. References

1. Q. Zhou, P. Audebert, G. Clavier, R. Meallet-Renault, F. Miomandre, Z. Shaukat, V. Thanh-Truc and J. Tang, *J. Phys. Chem. C*, 2011, **115**, 21899-21906.
2. Q.-j. Zhang, J.-h. Zhou, H. Li, J.-h. He, N.-j. Li, Q.-f. Xu, D.-y. Chen, H. Li and J.-m. Lu, *Chem-Asian J*, 2018, **13**, 853-860.