

## Supporting information

### Wide-Band-Gap Phthalimide-Based D- $\pi$ -A Polymers for Nonfullerene Organic Solar Cells: The Effect of Conjugated $\pi$ -Bridge from Thiophene to Thieno[3,2-*b*]thiophene

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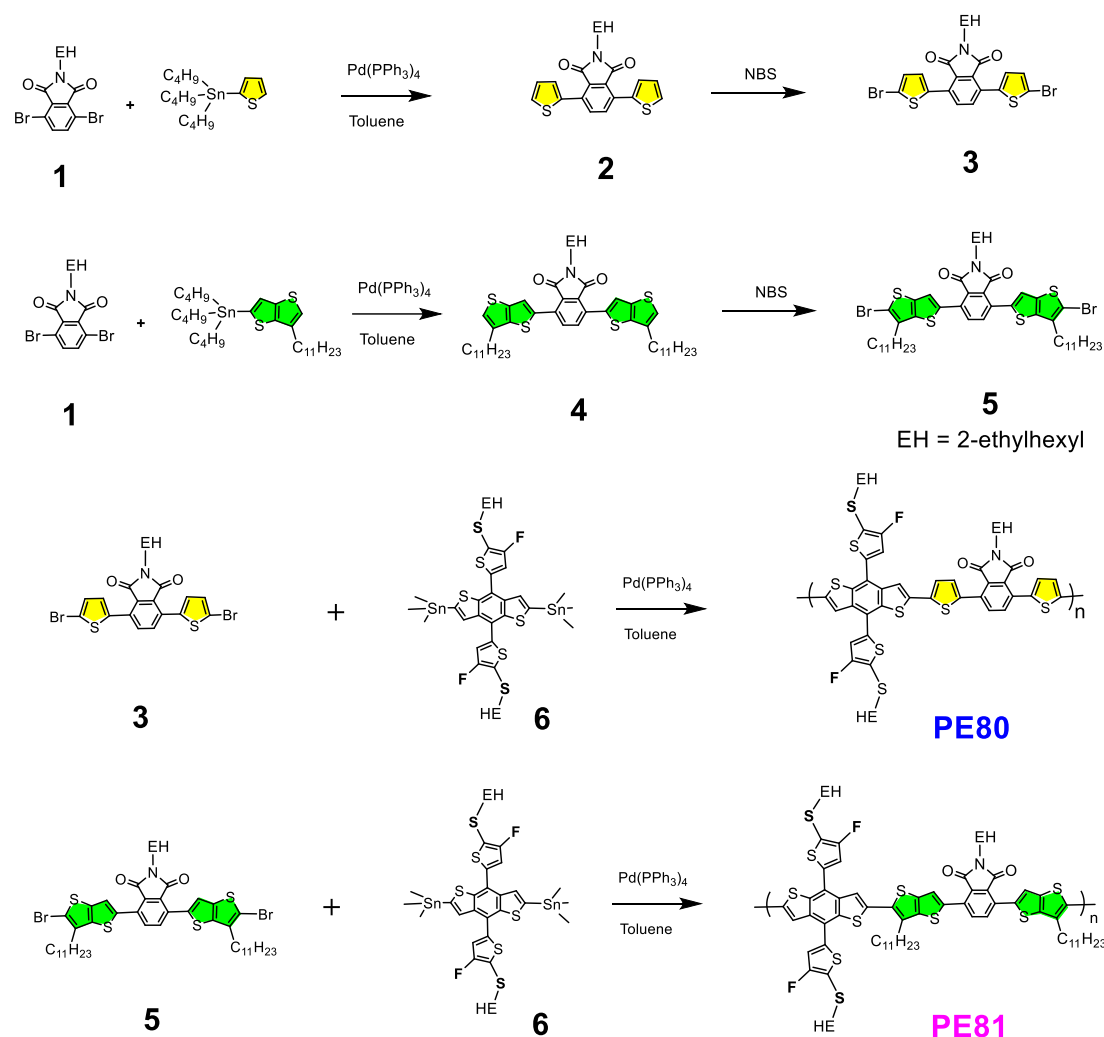
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#### Materials and Synthesis

**Materials.** The monomer **3**, **5**, **PE80** and **PE81** were synthesized according to the literatures. Toluene was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were commercial grade and used as received without further purification. All reactions were performed under nitrogen atmosphere.



**Scheme S1.** Synthesis of the monomers and the polymers of **PE80** and **PE81**.

### N-(2-ethylhexyl)-3,6-di(thiophen-2-yl)phthalimide (**2**)

N-(2-ethylhexyl)-3,6-dibromophthalimide (417 mg, 1.0 mmol), tributyl(thiophen-2-yl)stannane (783 mg, 2.1 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) were dissolved in 20 mL anhydrous toluene in a well-dried round flask under nitrogen atmosphere. The mixture was refluxed for 24 hours and then cooled to room temperature. Potassium fluoride saturated solution (30 mL) was added and stirred for 6 hours. The mixture was extracted with dichloromethane (3 × 100 mL). The organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel petroleum ether/dichloromethane (1:1), to give compound **2** as a yellow solid (380 mg, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (s,

4H), 7.47 (d,  $J = 4.0$  Hz, 2H), 7.17 (t,  $J = 4.0$  Hz, 2H), 3.57 (d,  $J = 8.0$  Hz, 2H), 1.88 – 1.80 (m, 1H), 1.30 (m, 8H), 0.93 – 0.84 (m, 6H).

### **N-(2-ethylhexyl)-3,6-bis(5-bromothiophen-2-yl)phthalimide (3)**

Compound 2 (380 mg, 0.89 mmol) was added to a mixture of chloroform (50 mL) and acetic acid (50 mL). After cooling the mixture to 0°C, the N-bromosuccinimide (NBS) (351 mg, 1.97 mmol) was added and the mixture was stirred at room temperature in dark overnight. Then the reaction mixture was poured into water (200 mL) and extracted with dichloromethane ( $3 \times 50$  mL). The extracts were combined and washed with water then dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica, eluting with petroleum ether/dichloromethane (5:1) to give **3** as a yellow solid (416 mg, 80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (s, 2H), 7.51 (d,  $J = 4$  Hz, 2H), 7.12 (d,  $J = 4$  Hz, 2H), 3.56 (d,  $J = 4$  Hz, 2H), 1.87 – 1.77 (m, 1H), 1.30 (m, 8H), 0.92 – 0.85 (m, 6H).

### **N-(2-ethylhexyl)-3,6-bis(6-undecylthieno[3,2-b]thiophen-2-yl)phthalimide (4)**

N-(2-ethylhexyl)-3,6-dibromophthalimide (417 mg, 1.0 mmol), tributyl (6-undecylthieno[3,2-b]thiophen-2-yl)stannane (1.23 g, 2.1 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (35 mg, 0.03 mmol) were dissolved in 20 mL anhydrous toluene in a well-dried round flask under nitrogen atmosphere. The mixture was refluxed for 24 hours and then cooled to room temperature. Potassium fluoride saturated solution (30 mL) was added and stirred for 6 hours. The mixture was extracted with dichloromethane ( $3 \times 50$  mL). The organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel petroleum ether/dichloromethane (1:1), to give compound **4** as a yellow solid (734 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (s, 2H), 7.83 (s, 2H), 7.07 (s, 2H), 3.60 (d,  $J = 4$  Hz, 2H), 2.76 (t,  $J = 8$  Hz, 4H), 1.85 (m, 1H), 1.82–1.73 (m, 4H), 1.39–1.23 (m, 40H), 0.88 (m, 12H).

### **N-(2-ethylhexyl)-3,6-bis(5-bromo-6-undecylthieno[3,2-b]thiophen-2-yl)phthalimide (5)**

Compound **4** (730 mg, 0.86 mmol) was added to a mixture of chloroform (50 mL) and acetic acid (50 mL). After cooling the mixture to 0°C, the N-bromosuccinimide (NBS) (338 mg, 1.90 mmol) was added and the mixture was stirred at room temperature in dark overnight. Then the reaction mixture was poured into water (200 mL) and extracted with dichloromethane (3 × 50 mL). The extracts were combined and washed with water then dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica, eluting with petroleum ether/dichloromethane (5:1) to give compound **5** as a yellow solid (788 mg, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 2H), 7.81 (s, 2H), 3.60 (d, *J* = 8 Hz, 2H), 2.76 (t, *J* = 8 Hz, 4H), 1.84 (m, 1H), 1.77 – 1.69 (m, 4H), 1.26 (m, 40H), 0.87 (m, 12H).

### **Synthesis of PE80**

The monomer **3** (116.3 mg, 0.2 mmol) and monomer **6** (201.0 mg, 0.2 mmol) were put into a 25 mL two-neck flask, and 10 mL of anhydrous toluene was added. The mixture was stirred and purged with nitrogen for 10 min, and then Pd(PPh<sub>3</sub>)<sub>4</sub> (7 mg, 0.006 mmol) was added. After being purged for 15 min, the mixture was heated at 105 °C for 48 h. Blocking agent of tributyl(thiophen-2-yl)stannane and 2-bromothiophene was injected six hours apart, respectively. After cooled to room temperature, the reaction mixture was added dropwise to 50 mL CH<sub>3</sub>OH, then collected by filtration and washed with methanol. The solid was filtered into a Soxhlet funnel and extracted by methanol, hexane, dichloromethane chloroform and chlorobenzene successively. The solution extracted from chloroform and chlorobenzene was concentrated and then precipitated from ethanol. Finally, the precipitate was dried under vacuum to obtain reddish brown compound **PE80** (167 mg, 74%, *M<sub>n</sub>* = 8.9 kDa, *M<sub>w</sub>* = 17.3 kDa, PDI = 1.93).

### **Synthesis of PE81**

The synthesis method is the same as **PE80**. Differently, the corresponding reagents are monomer **5** (200.5 mg, 0.2 mmol) and the monomer **6** (201.0 mg, 0.2 mmol). Finally, the precipitate was dried under vacuum to obtain reddish brown compound **PE81** (279 mg, 90%,  $M_n = 31.5$  kDa,  $M_w = 81.0$  kDa, PDI = 2.63).

### Measurements and characterizations

$^1\text{H}$  NMR (400 MHz) spectra were obtained using a Bruker AVANCE III HD 400 with tetramethyl silane as an internal standard. Chemical shifts of  $^1\text{H}$  NMR were reported in ppm. UV-vis spectra were identified with a Lambda 950 spectrophotometer. Electrochemical cyclic voltammetry (CV) was conducted on an electrochemical workstation (VMP3 Biologic, France) with a Pt disk coated with a molecular film, a Pt plate, and an Ag/AgCl electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1 mol/L tetrabutylammonium phosphorus hexafluoride ( $\text{Bu}_4\text{NPF}_6$ ) acetonitrile solution. The J-V curves were measured in air with a Keithley 2420 source measure unit. The photocurrent was obtained under illumination using an Oriel Newport 150W solar simulator (AM 1.5G), and the light intensity was calibrated with a Newport reference detector (Oriel PN 91150 V). The EQE measurements of the devices were performed in air with an Oriel Newport system (Model 66902). The thickness of the active layer was measured on a Kla-Tencor Alpha-StepD-120 Stylus Profiler. The thickness of the **PE80**:Y6 and **PE81**:Y6 based films are estimated to be 130 and 110 nm, respectively. AFM images were obtained on a Multimode Digital Instrument (D3100) in ScanAsyst mode. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses were measured at the XEUSS SAXS/WAXS equipment. The data were obtained with an area Pilatus 100k detector with a resolution of  $195 \times 487$  pixels ( $0.172 \text{ mm} \times 0.172 \text{ mm}$ ). The X-ray wavelength was  $1.54 \text{ \AA}$ , and the incidence angle was  $0.2^\circ$ . The samples were spin-coated onto the PEDOT:PSS/Si substrate.

### Photovoltaic device fabrication

The PSC devices were fabricated with a configuration of ITO/ PEDOT:PSS/active layer/Ca/Al. A thin layer of PEDOT: PSS (40 nm, Baytron PH1000) was spin-cast on pre-cleaned ITO-coated glass at 3000 rpm, 30s. After baking at 150 °C for 15 min, the substrates were transferred into glovebox. Optimized devices were prepared under the following conditions. The active layer was dissolved in chloroform (CF) with D:A ratio of 1:1 (w/w) or :1.2 (w/w) and a total concentration of 18 mg/mL or 12 mg/mL for **PE80**:Y6 and **PE81**:Y6, respectively. Then they were stirred for 1 hour at 40 °C. Afterwards, the active layers were spin-coated from the above solution with a speed of 1500 rpm for 30s onto the PEDOT: PSS layer. The thickness of the photoactive layer is in the range of 110-130 nm. Subsequently, PE80-based and PE81-based devices were annealed at 110 °C and 150 °C for 10 min, respectively. Finally, a Ca (20 nm)/Al (80 nm) metal top electrode was thermal evaporated onto the active layer under about  $3 \times 10^{-4}$  Pa. The active area of the device was 0.04 cm<sup>2</sup> defined by shadow mask.

### Carrier Mobilities

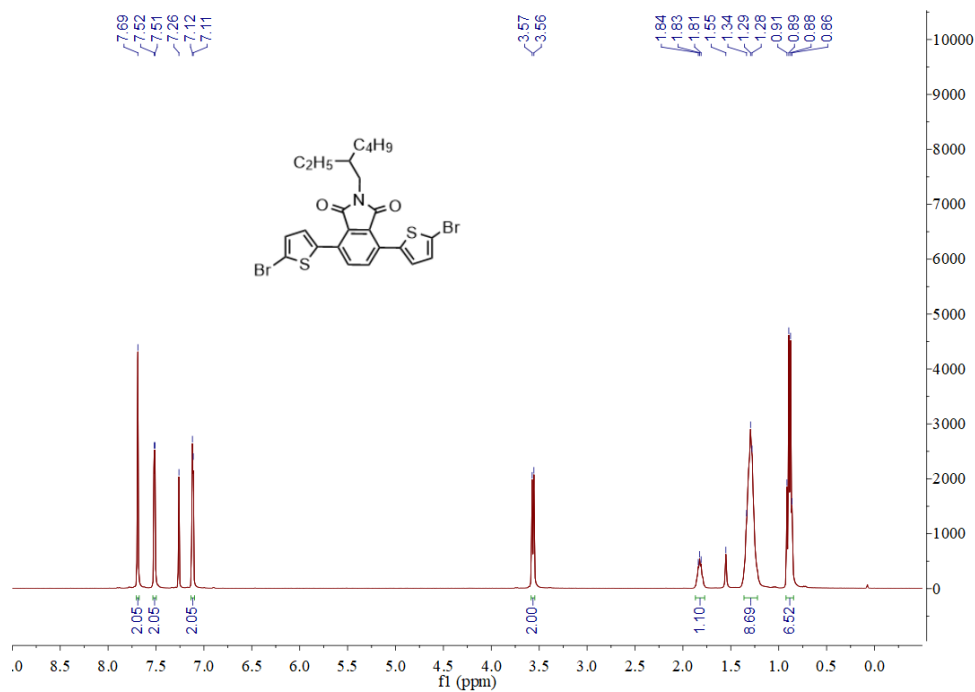
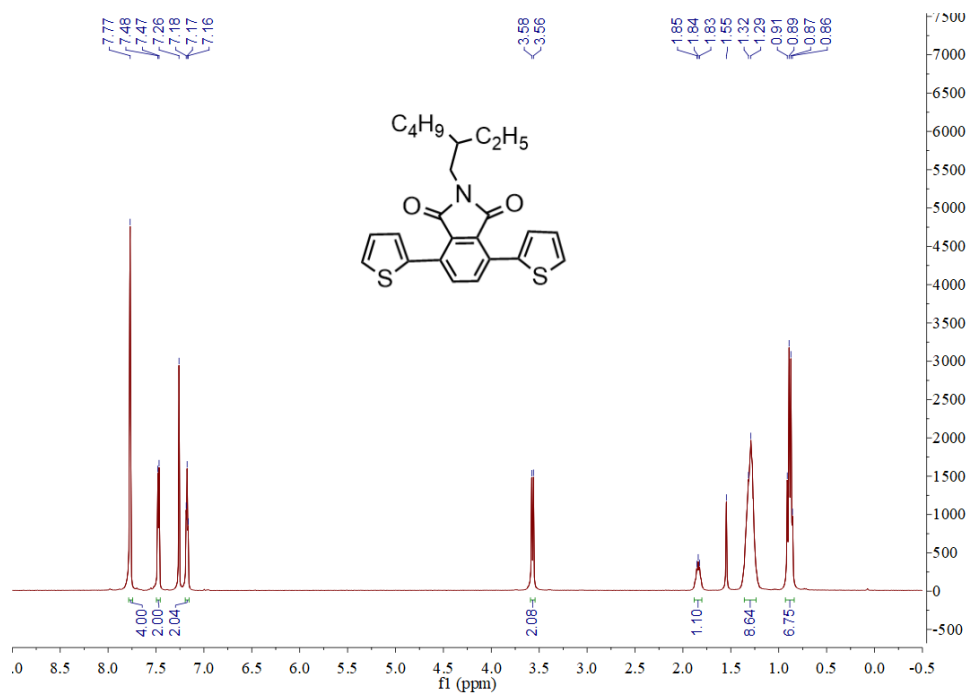
The carrier mobilities of the polymer were investigated by the space charge limited current (SCLC) method. The hole mobility of the blend films was measured with the device structure of ITO/PEDOT:PSS/active layer/Au (80 nm) while the electron mobility of the blends was measured with the device structure of ITO/TiOx/active layer/ Al (80 nm).

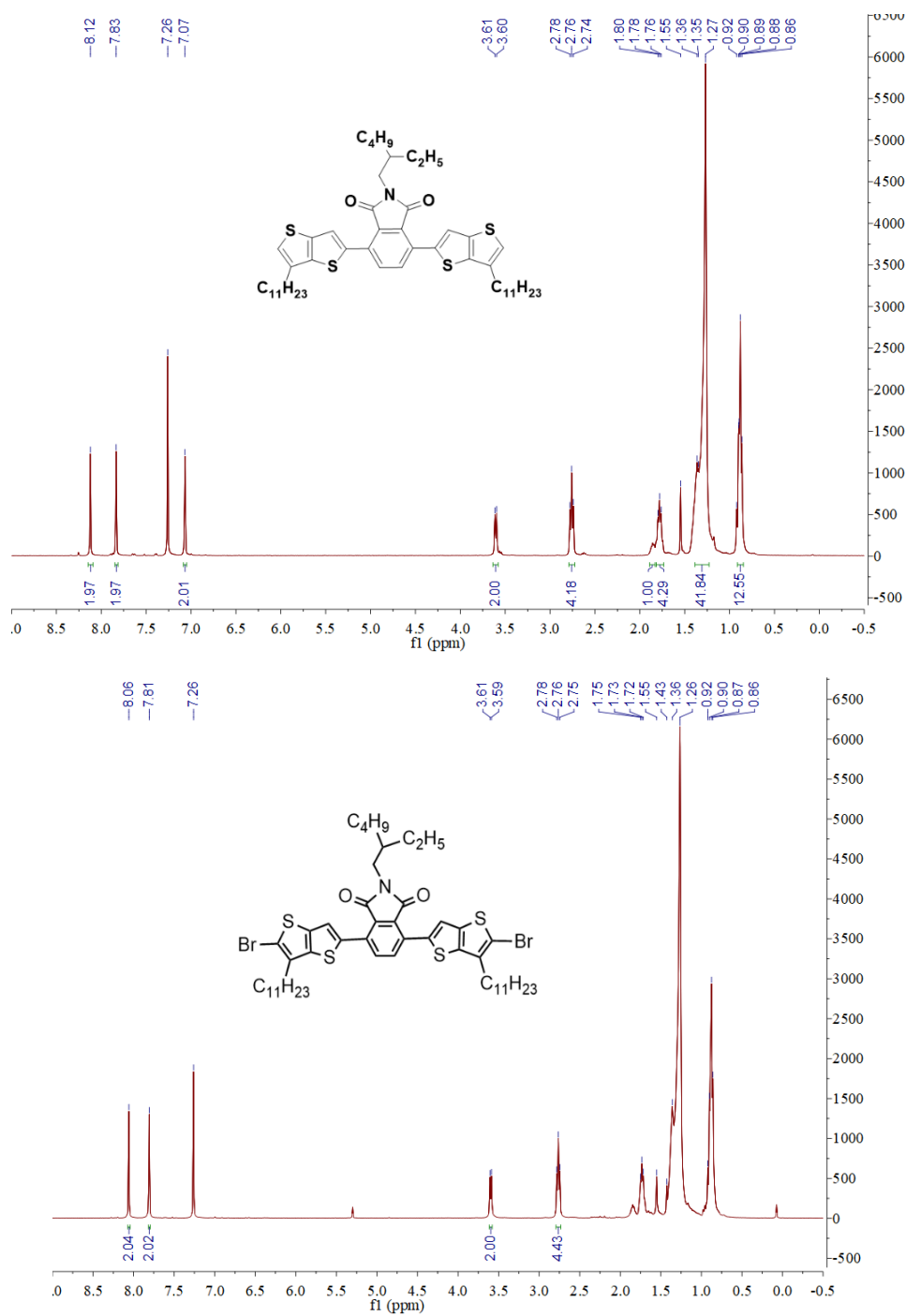
The SCLC model is described by modified Mott-Gurney law:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^3}$$

where J stands for current density,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  C V<sup>-1</sup> m<sup>-1</sup>),  $\epsilon_r$  is the relative dielectric constant of the transport medium (assuming that of 3.0),  $\mu$  is the carrier mobility, and L is the thickness of the active layer. V is the internal potential in the device, and  $V = V_{app} - V_{bi}$ , where  $V_{app}$  is the voltage applied to the device, and  $V_{bi}$  is the built-in voltage resulting from the relative work function

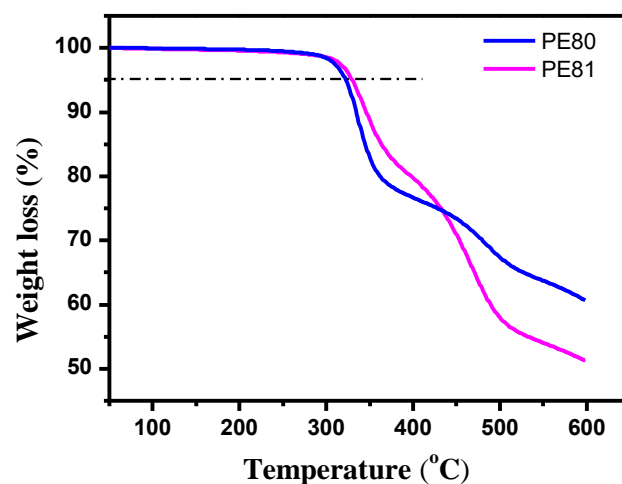
difference between the two electrodes (the  $V_{bi}$  values of hole-only and electron-only devices were all selected as 0 V).<sup>[1-2]</sup>



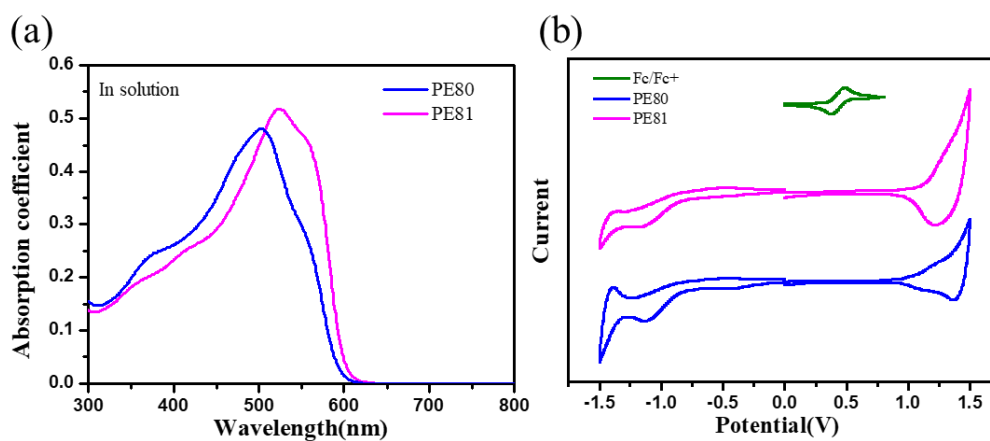


**Figure S1.**  $^1\text{H}$  NMR spectra of monomers.





**Figure S2.** TGA plots of the polymers with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere.



**Figure S3.** (a) UV-vis absorption spectra of **PE80** and **PE81** in chloroform solution, (b) Cyclic voltammograms of the **PE80** and **PE81** in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution with Fc/Fc<sup>+</sup> couple as an external standard possessing an oxidation potential of +0.454 V vs Ag/AgCl.

## References

- [1] Chen, Y.; Zhang, Q.; Du, M.; Li, G.; Li, Z.; Huang, H.; Geng, Y.; Zhang, X.; Zhou, E., Benzotriazole-Based p-Type Polymers with Thieno[3,2-b]thiophene  $\pi$ -Bridges and Fluorine Substituents To Realize High VOC. *ACS Appl. Polym. Mater.* **2019**, *1*, 906-913.

[2] Li, S.; Ye, L.; Zhao, W.; Liu, X.; Zhu, J.; Ade, H.; Hou, J., Design of a New Small-Molecule Electron Acceptor Enables Efficient Polymer Solar Cells with High Fill Factor. *Adv. Mater.* **2017**, 29 ,1704051.