

## Supplementary Information

### Acceptor-Quantity Modulation Strategy for High-Performance Ambipolar Semiconducting Polymers: from Dual-Acceptor to Quad-Acceptor Backbone

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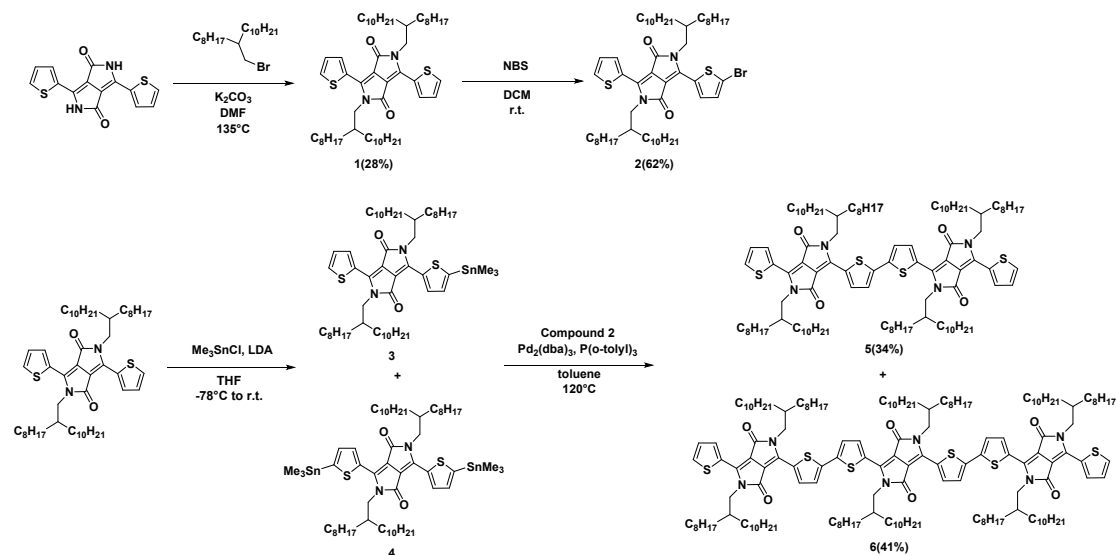
## 1. Instruments and Measurements

All commercially available reagents and chemicals were purchased from Adamas, Greagent, CIL and used as received unless otherwise specified. All reactions were carried out with the use of standard inert atmosphere and Schlenk tubes. Silica gel (100~200 mesh) was used for column chromatography.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. Deuterated chloroform and methylene chloride- $\text{d}_2$  were used as the solvents.  $^1\text{H}$  NMR (600 MHz) spectra were measured on a Ascend 600 spectrometer. 1,1,2,2-tetrachloroethane- $\text{d}_2$  was used as the solvent. The NMR chemical shifts were reported in ppm (parts per million) relative to the residual solvent peak at 7.26 ppm (deuterated chloroform), 5.32 ppm (methylene chloride- $\text{d}_2$ ) and 6.00 ppm (1,1,2,2-tetrachloroethane- $\text{d}_2$ ) for the  $^1\text{H}$  NMR spectroscopy and 77.6 ppm (deuterated chloroform) for the  $^{13}\text{C}$  NMR spectroscopy. The MALDI-TOF mass spectra were measured by a Bruker autoflex max MALDI-TOF mass spectroscopy. TGA measurement was carried out on Mettler STARe (TA Instrument) with a heating ramp of  $20\text{ }^\circ\text{C min}^{-1}$  under nitrogen flow. DSC measurement was carried out on Mettler STARe (TA Instrument) with a heating (or cooling) ramp of  $20\text{ }^\circ\text{C min}^{-1}$  under nitrogen flow. UV-Vis absorption spectra were acquired from Shimadzu UV3600i Plus spectrophotometer. All film samples were spin-cast on glass substrates. All the solution of polymers were measured with a concentration of  $1.0 \times 10^{-5}\text{ M}$  in chloroform. CV measurements of films were performed under argon atmosphere using a CHI760E voltametric analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate ( $n\text{Bu}_4\text{NPF}_6$ ) in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode were employed. The scanning rate was  $0.1\text{ V s}^{-1}$ . Films were drop-casted from chloroform solutions of polymers on a Pt working electrode (2 mm in diameter). The supporting electrolyte solution was thoroughly purged with argon before all CV measurements. For calibration, the redox potential of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was measured under the same conditions. It was assumed that the redox potential of  $\text{Fc}/\text{Fc}^+$  has an absolute energy level of -4.80 eV to a vacuum. The HOMO energy levels were

determined by HOMO (eV) =  $-(E_{\text{ox}} + 4.8 - \varphi_{Fe})$ , while the LUMO energy levels were determined by LUMO (eV) =  $-(E_{\text{red}} + 4.8 - \varphi_{Fe})$ . Polymer molecular weights were characterized on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system (Agilent Technologies) at 150 °C vs polystyrene standards using 1,2,4-trichlorobenzene as the eluent. Geometry optimizations and HOMO/LUMO calculations of monomers and repeat units of polymers were performed at the B3LYP/6-31G (d) level using the Gaussian 09 program package. All the model compounds have methyl groups at their amide moieties to simplify the calculations. AFM measurements were performed by using Bruker's Dimension Icon with true noncontact mode. All film samples were spin-cast on glass substrates according to device fabrication conditions.

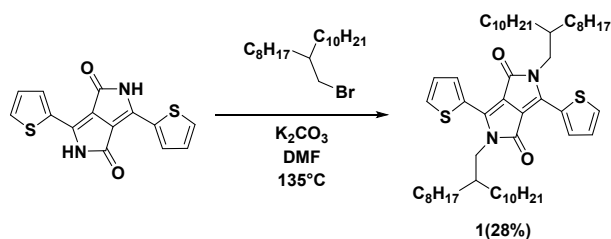
## 2. Materials and Synthesis

All commercially available reagents and chemicals were purchased from Adamas, Greagent, CIL and used as received unless otherwise specified. All reactions were carried out with the use of standard inert atmosphere and Schlenk tubes.



**Scheme S1.** Synthesis routes to the monomers.

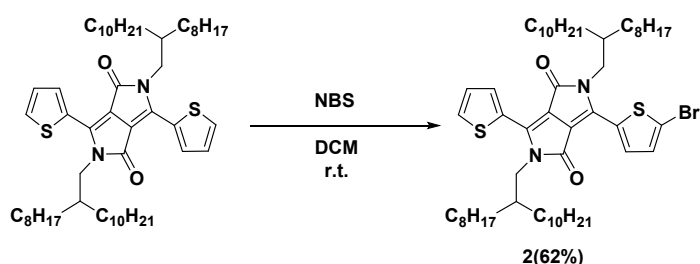
### (1) Synthesis of Compound 1



A 100 ml Schlenk flask charged with 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo [3,4-*c*] pyrrole-1,4-dione (1.0 g, 3.329 mmol) and  $K_2CO_3$  (1.4 g, 10.13 mmol) was evacuated and back-filled with  $N_2$ . Anhydrous DMF (15 ml) was injected under a  $N_2$  atmosphere. The reaction mixture was stirred at 120 °C for 1 h. Then, 3.0 ml 9-(bromomethyl) nonadecane (8.134 mmol) was successively injected and the reaction mixture was maintained at 135 °C overnight. After the mixture was cooled to room temperature, it was extracted in DCM, washed with brine, dried over  $MgSO_4$ , and evaporated in vacuo to give a crude product, which was purified by column chromatography (silica gel, PE/EA = 100:1 v/v) to give compound **1** (803 mg, 28%) as a red solid.

$^1H$  NMR (400 MHz,  $CD_2Cl_2$ ) of compound **1**:  $\delta$  (ppm): 8.75 (d,  $J=4.8$  Hz, 2H), 7.60 (d,  $J=5.2$  Hz, 2H), 7.21 (t,  $J=9.2$  Hz, 2H), 3.92 (d,  $J=7.6$  Hz, 4H), 1.79 (s, 2H), 1.21 (m,  $J=27.2$  Hz 74H), 0.81 (m,  $J=18.8$  Hz 13H). MS (MALDI-TOF,  $m/z$ ):  $[M^+]$  calc: 860.6287, found: 860.8675.

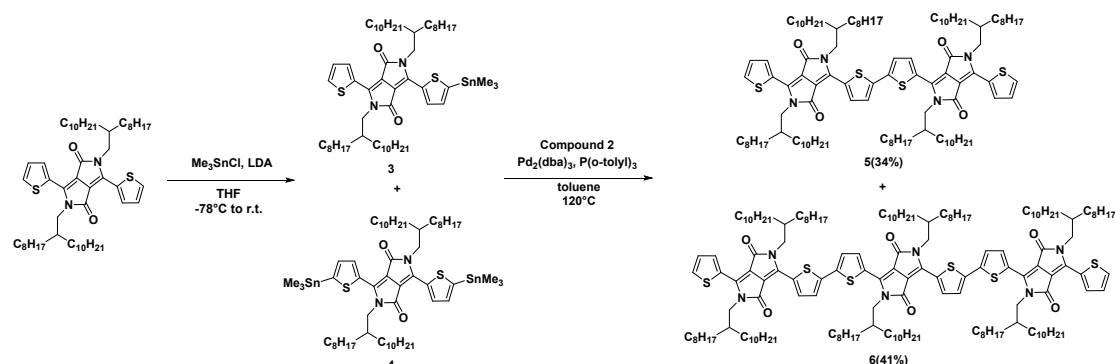
## (2) Synthesis of Compound 2



*N*-Bromosuccinimide (NBS) (0.744 g, 4.185 mmol) was added slowly to a solution of compound **1** (3.6g, 4.180 mmol) in DCM (100 ml). The solution was protected from light and stirred at room temperature for 30 min. Then, the reaction mixture was extracted in DCM, washed with brine, dried over  $MgSO_4$ , and evaporated in vacuo to give a crude product, which was purified by column chromatography (silica gel, PE/DCM = 4:1~3:1 v/v) to give compound **2** (2.35g, 62%) as a red solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound **2**:  $\delta$  (ppm): 8.87 (d,  $J=3.6$  Hz, 1H), 8.50 (d,  $J=4.4$  Hz, 1H), 7.61 (d,  $J=4.8$  Hz, 1H), 7.21 (t,  $J=9.2$  Hz, 1H), 7.17 (d,  $J=4.0$  Hz, 1H), 3.92 (d,  $J=7.6$  Hz, 2H), 3.84 (d,  $J=7.6$  Hz, 2H), 1.78 (s, 2H), 0.81 (m,  $J=18.8$  Hz, 13H). MS (MALDI-TOF,  $m/z$ ):  $[\text{M}^+]$  calc: 938.5392, found: 940.8251.

### (3) Synthesis of Compound **5** and **6**



Compound **5** and compound **6** were synthesized through one pot method. A 100 ml Schlenk flask charged with compound **1** (1.4 g, 1.625 mmol) was evacuated and back-filled with  $\text{N}_2$ . Anhydrous THF (20 ml) was injected under a  $\text{N}_2$  atmosphere and the reaction mixture was stirred at  $-78^\circ\text{C}$  for 10 min. Then, 2.9 ml LDA (2.0 M, 5.8 mmol) was slowly added dropwise by a syringe under a  $\text{N}_2$  atmosphere and the reaction mixture was stirred at  $-78^\circ\text{C}$  for 1 h. Then, 5.8 ml  $\text{Me}_3\text{SnCl}$  (1.0 M, 5.8 mmol) was injected, and the reaction mixture was maintained at room temperature overnight. After the reaction, 30 ml KF solution was poured into the reaction mixture stirring for 2 h. Then, the reaction mixture was extracted in DCM, washed with brine, dried over  $\text{MgSO}_4$ , evaporated in vacuo and dried under vacuum at  $55^\circ\text{C}$  for 48 h to get the mixture organotin compound **3** and compound **4** as black oil.

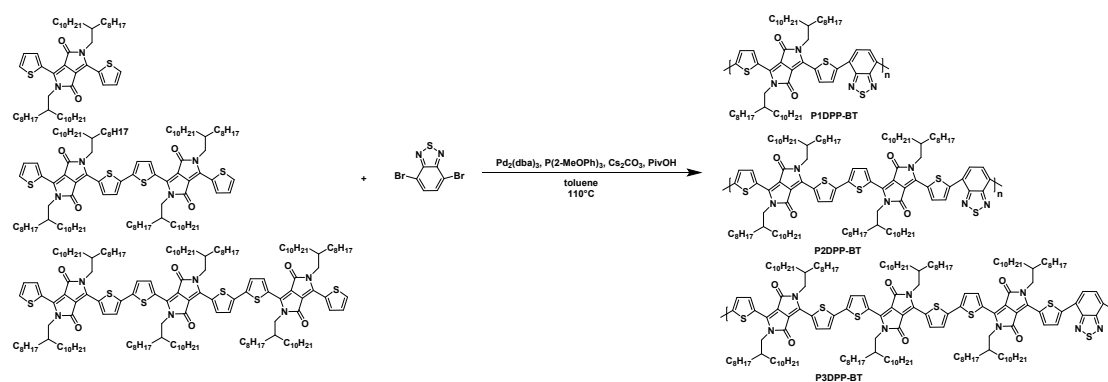
Then, a 100 ml Schlenk flask charged with these two reaction intermediates, compound **2** (3.0 g, 3.190 mmol),  $\text{Pd}_2(\text{dba})_3$  (75 mg, 0.08190 mmol),  $\text{P}(o\text{-tolyl})_3$  (99 mg, 0.3253 mmol) was evacuated and back-filled with  $\text{N}_2$ . Anhydrous toluene (30 ml) was injected under a  $\text{N}_2$  atmosphere. The reaction mixture was maintained at  $120^\circ\text{C}$  overnight. After the mixture was cooled to room temperature, it was extracted in DCM, washed with brine, dried over  $\text{MgSO}_4$ , and evaporated in vacuo to give a crude product, which was purified by column chromatography (silica gel, PE/DCM = 2:1~1:1 v/v) to

give compound **5** (950 mg, 34%) as a black solid and compound **6** (1720 mg, 41%) as a black solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound **5**:  $\delta$  (ppm): 8.87 (d,  $J=4.4$  Hz, 2H), 8.80 (d,  $J=4.8$  Hz, 2H), 7.61 (d,  $J=5.2$  Hz, 2H), 7.40 (d,  $J=4.4$  Hz, 2H), 3.96 (q,  $J=11.6$  Hz, 8H), 1.97-1.78 (s, 4H), 1.30-1.14 (m, 150H), 0.80 (m,  $J=24.0$  Hz 28H). MS (MALDI-TOF,  $m/z$ ):  $[\text{M}^+]$  calc:1719.2418, found: 1721.7595.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound **6**:  $\delta$ (ppm): 8.94 (d,  $J=4.0$  Hz, 2H), 8.88 (d,  $J=4.4$  Hz, 2H), 8.80 (d,  $J=4.0$  Hz, 2H), 7.54 (d,  $J=4.8$  Hz, 2H), 7.32 (d,  $J=4.0$  Hz, 4H), 7.17 (t,  $J=8.8$  Hz 2H), 3.96 (q,  $J=19.6$  Hz 12H), 1.97-1.78 (s, 6H), 1.32-1.14 (m, 226H), 0.79 (m,  $J=20.4$  Hz 40H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **6**:  $\delta$ (ppm): 161.70, 161.58, 141.41, 141.06, 139.16, 135.82, 130.92, 130.02, 129.83, 128.64, 126.04, 109.24, 108.99, 108.31, 46.54, 38.30, 38.01, 32.16, 32.13, 31.45, 30.36, 30.30, 29.95, 29.89, 29.82, 29.77, 29.63, 29.60, 29.56, 26.53, 26.45, 22.93, 14.36. MS (MALDI-TOF,  $m/z$ ):  $[\text{M}^+]$  calc: 2577.8549, found: 2579.6638.

#### (4) Synthesis of the three polymers



**Scheme S3.** Synthesis routes to **P(nDPP-BT)** ( $n=1,2,3$ ).

#### **P1DPP-BT**

In a 10ml Schlenk flask, compound **1** (172.3 mg, 0.2 mmol), 4,7-dibromobenzothiazole (58.8 mg, 0.2 mmol),  $\text{Pd}_2(\text{dba})_3$  (7.3 mg, 0.008mmol),  $\text{P}(2\text{-MeOPh})_3$  (11.3 mg, 0.032 mmol),  $\text{Cs}_2\text{CO}_3$  (195.5 mg, 0.6 mmol),  $\text{PivOH}$  (20.4 mg, 0.2 mmol) was evacuated and back-filled with  $\text{N}_2$ . Anhydrous toluene (2.0 ml) was injected under a  $\text{N}_2$  atmosphere. The reaction mixture was maintained at  $110^\circ\text{C}$  for 0.5 h. The resulting

mixture was poured into methanol (50 ml) and stirred for 1 h and then extracted sequentially with methanol, acetone, hexane and chloroform by Soxhlet extractor. Finally, polymer products were collected and dried under vacuum at 65 °C for 10 h. The purified polymer was collected to give a black solid (195mg, 98%).  $M_w/M_n$  (HT-GPC) = 52.6/19.2 kg mol<sup>-1</sup>. Anal. cacl'd for (C<sub>60</sub>H<sub>90</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>)<sub>n</sub> (%): C, 72.39; H, 9.11; N, 5.63; S, 9.66. Found (%): C, 70.55; H, 8.60; N, 5.56; S, 9.31.

### **P2DPP-BT**

In a 10 ml Schlenk flask, compound **5** (344.2 mg, 0.2 mmol), 4,7-dibromobenzo [*c*] [1,2,5] thiadiazole (58.8 mg, 0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (7.3 mg, 0.008mmol), P(2-MeOPh)<sub>3</sub> (11.3 mg, 0.032 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol), PivOH (20.4 mg, 0.2 mmol) was evacuated and back-filled with N<sub>2</sub>. Anhydrous toluene (2.0 ml) was injected under a N<sub>2</sub> atmosphere. The reaction mixture was maintained at 110 °C for 0.5 h. The resulting mixture was poured into methanol (50 ml) and stirred for 1 h, and then extracted sequentially with methanol, acetone, hexane and chloroform by Soxhlet extractor. Finally, polymer products were collected and dried under vacuum at 65 °C for 10 h. The purified polymer was collected to give a black solid (363 mg, 98%).  $M_w/M_n$  (HT-GPC) = 75.6/24.9 kg mol<sup>-1</sup>. Anal. cacl'd for (C<sub>114</sub>H<sub>176</sub>N<sub>6</sub>O<sub>4</sub>S<sub>5</sub>)<sub>n</sub> (%): C, 73.81; H, 9.56; N, 4.53; S, 8.64. Found (%): C, 71.32; H, 8.60; N, 4.27; S, 7.97.

### **P3DPP-BT**

In a 10 ml Schlenk flask, compound **6** (516.0 mg, 0.2 mmol), 4,7-dibromobenzo [*c*] [1,2,5] thiadiazole (58.8 mg, 0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (7.3 mg, 0.008mmol), P(2-MeOPh)<sub>3</sub> (11.3 mg, 0.032 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol), PivOH (20.4 mg, 0.2 mmol) was evacuated and back-filled with N<sub>2</sub>. Anhydrous toluene (2.0 ml) was injected under a N<sub>2</sub> atmosphere. The reaction mixture was maintained at 110 °C for 0.5 h. The resulting mixture was poured into methanol (50 ml) and stirred for 1 h, and then extracted sequentially with methanol, acetone, hexane and chloroform by Soxhlet extractor. Finally, polymer products were collected and dried under vacuum at 65 °C for 10 h. The purified polymer was collected to give a black solid (505 mg, 93%).  $M_w/M_n$  (HT-



GPC) = 39.5/13.8 kg mol<sup>-1</sup>. Anal. cacl'd for (C<sub>168</sub>H<sub>262</sub>N<sub>8</sub>O<sub>6</sub>S<sub>7</sub>)<sub>n</sub> (%): C, 74.34; H, 9.73; N, 4.13; S, 8.27. Found (%): C, 71.6; H, 8.80; N, 3.85; S, 7.57.

### 3. Fabrication of Thin-Film Transistors

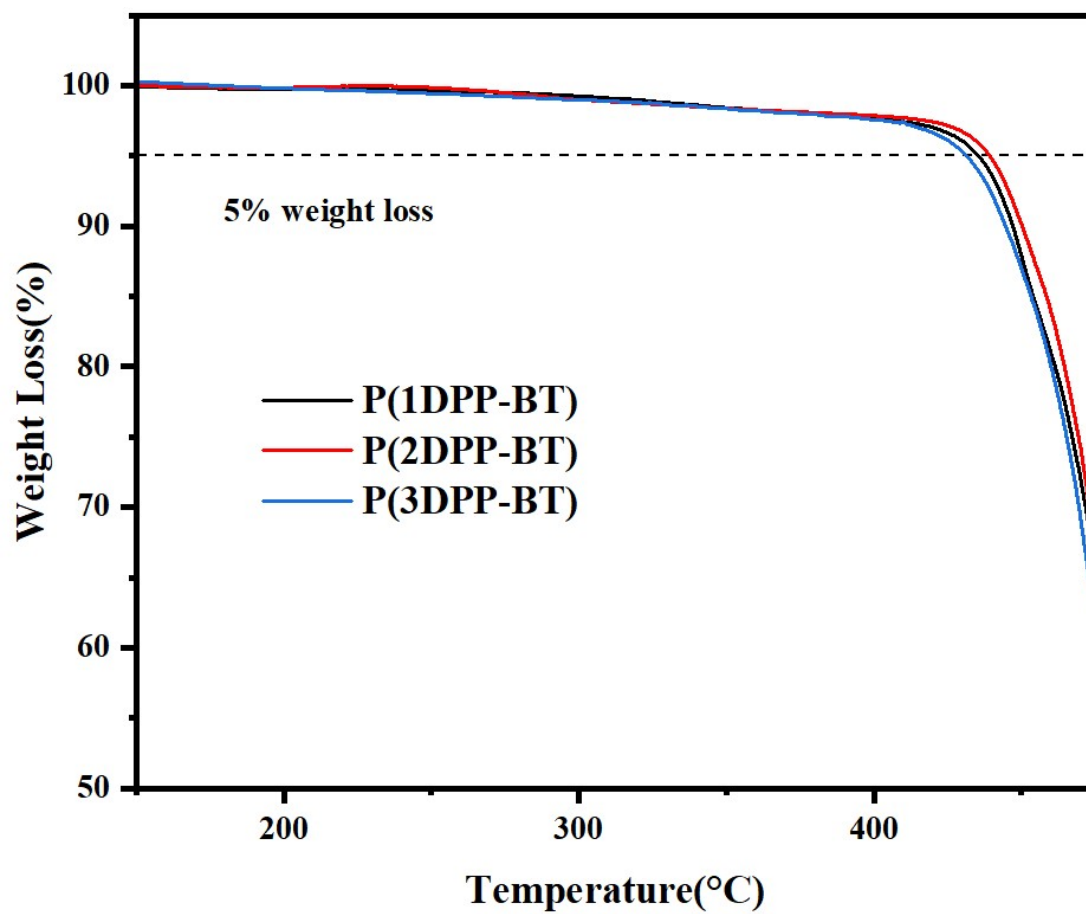
The charge-transport properties of the prepared DPP-based polymers were investigated by fabricating organic field-effect transistor (OFET) devices with a top-gate/bottom contact (TGBC) architecture. The substrate material, polyethylene glycol terephthalate (PET), was purchased from Yingkou OPV Tech New Energy Co., Ltd, which was cleaned with deionized water and ethanol. By using a shadow mask technique, 30 nm of Au film was deposited on the surface of PET substrate as the source/drain (S/D) electrodes with the channel length (L) and channel width (W) of 4200 and 50 μm, respectively. The DPP-based polymers were dissolved in bi-component solvent containing chlorobenzene (CB) to obtain a ≈5 mg/mL concentration solution, which was spin-coated (800 rpm for 2s and 1800 rpm for 60s) on the PET substrates, and then annealed at 160 °C for 20 min in a nitrogen (N<sub>2</sub>)-filled glove box (O<sub>2</sub>, H<sub>2</sub>O concentration < 0.1 ppm). After that, 900 nm of polymethyl methacrylate (PMMA, M<sub>w</sub> = 996 KDa, C<sub>i</sub> ≈ 3.6 nF cm<sup>-2</sup>) dielectric was deposited on the surface of the active layer by spin-coating a PMMA solution (80 mg mL<sup>-1</sup>) in n-butyl acetate, and then annealed at 90 °C for 30 min in order to remove organic solvent in a N<sub>2</sub> glove box. The PMMA used here was purchased from Adamas. Finally, 80 nm of Ag gate electrode was deposited on the surface of PMMA dielectric layer via thermal evaporation technique. Under N<sub>2</sub> protection, the electrical characteristics were measured by using a semiconductor parameter analyzer (Platform Design Automation FS380 Pro). The charge mobility was extracted from the saturation regime and calculated from the following equation:

$$I_{DS} = \frac{W}{2L} C_i \mu (V_{GS} - V_T)^2$$

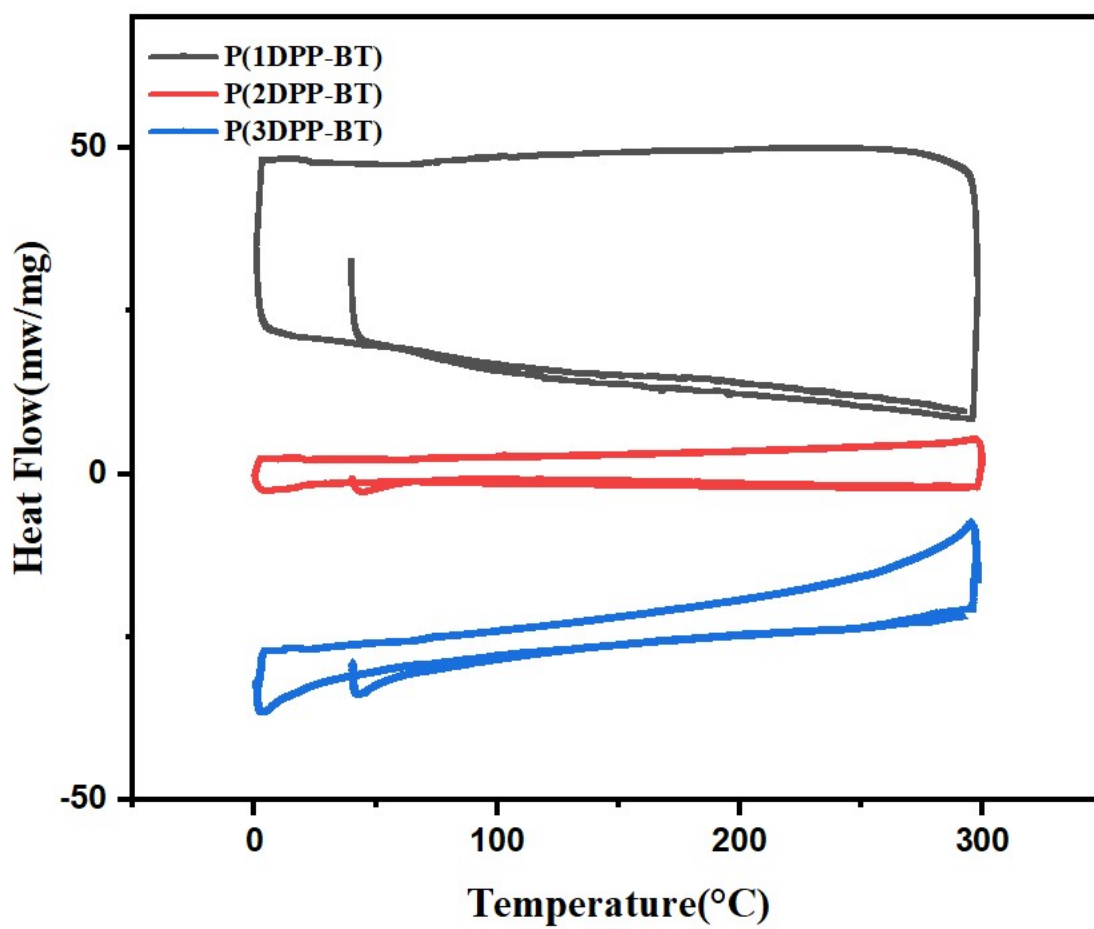
Where W/L is the channel width/length, C<sub>i</sub> is the capacitance per unit area of gate dielectric layer, and V<sub>G</sub> and V<sub>T</sub> are the gate voltage and threshold voltage, respectively.



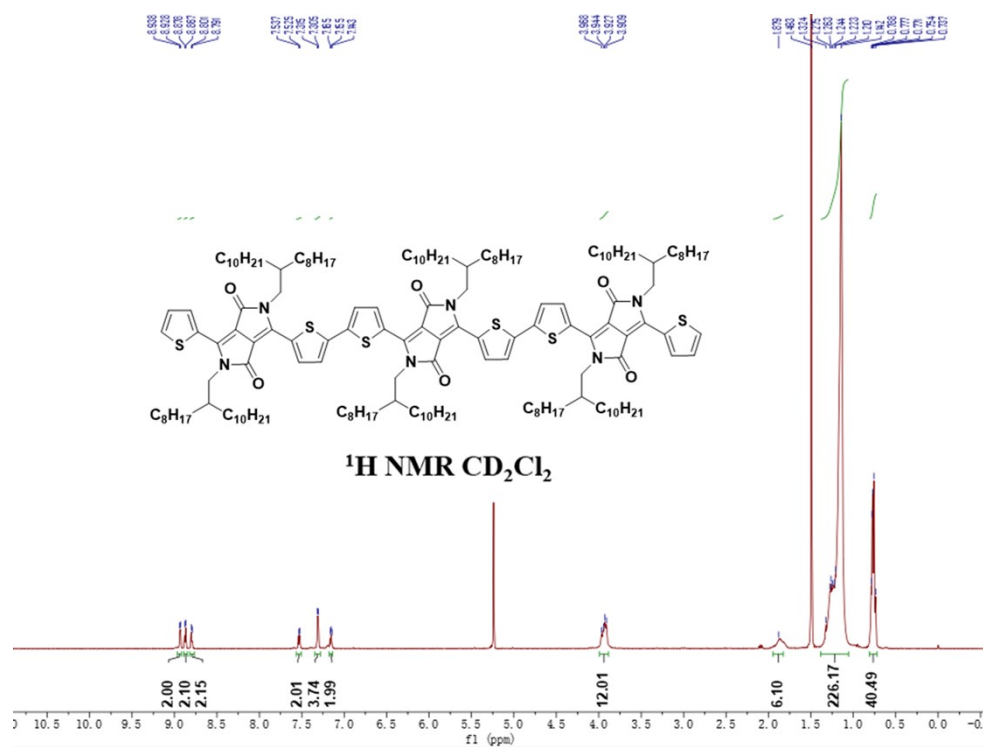
#### 4. Supporting Figures



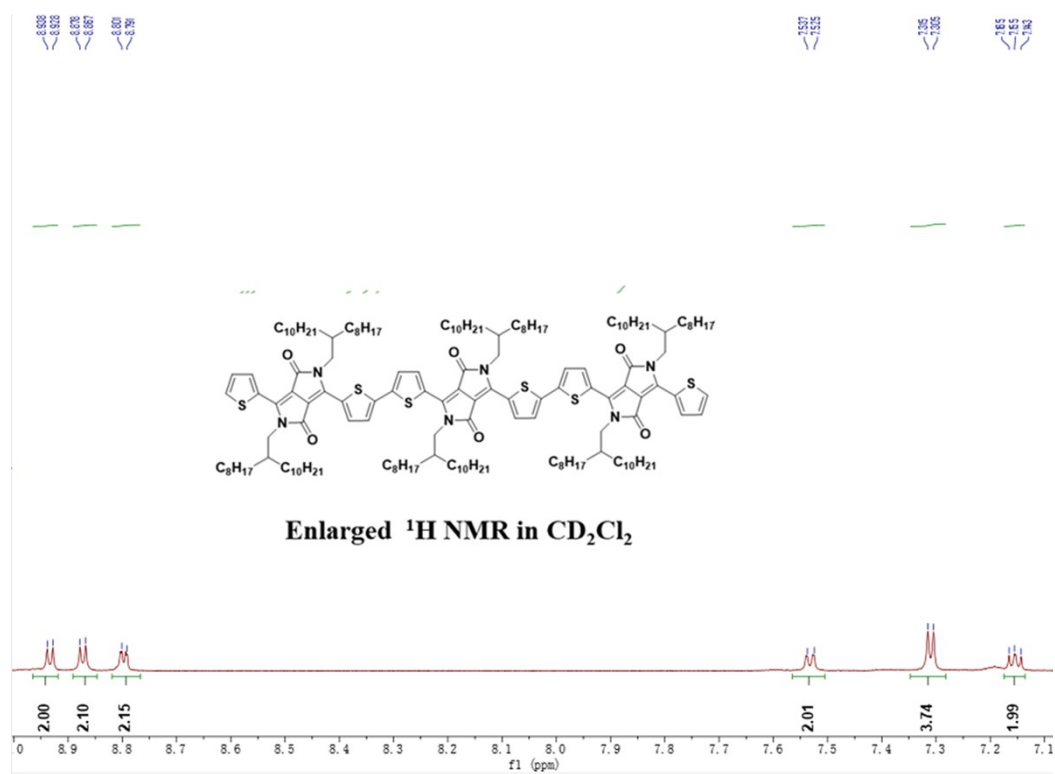
**Figure S1.** TGA curves of **P<sub>n</sub>DPP-BT** (n=1, 2, 3) under the nitrogen flow at the heating rate of 20 °C min<sup>-1</sup>.



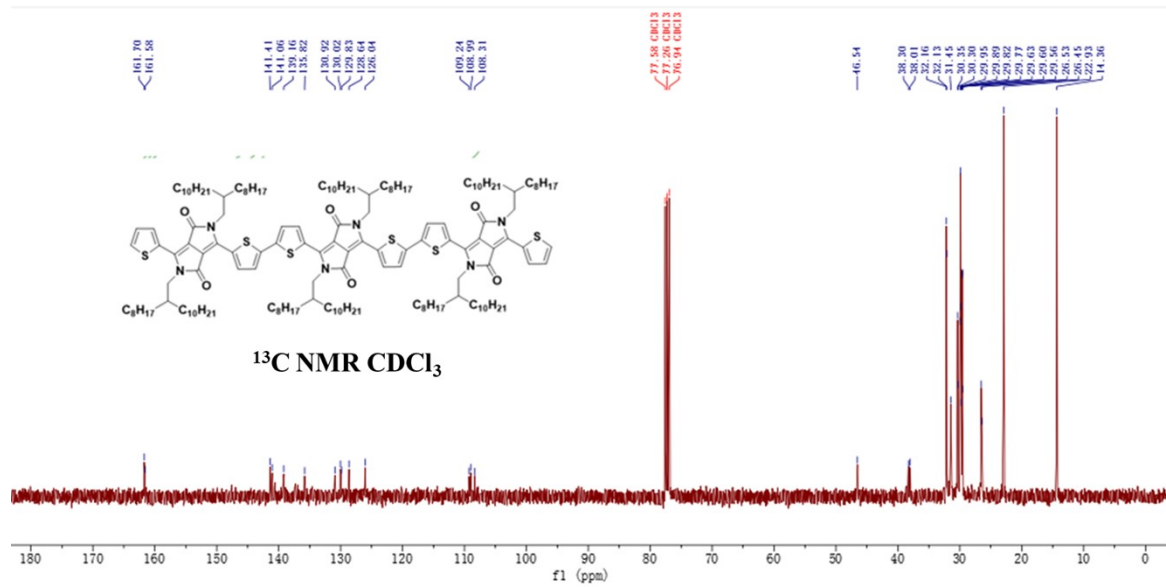
**Figure S2.** DSC curves of **P<sub>n</sub>DPP-BT** (n=1, 2, 3) under the nitrogen flow at the heating (or cooling) rate of 20 °C min<sup>-1</sup>.



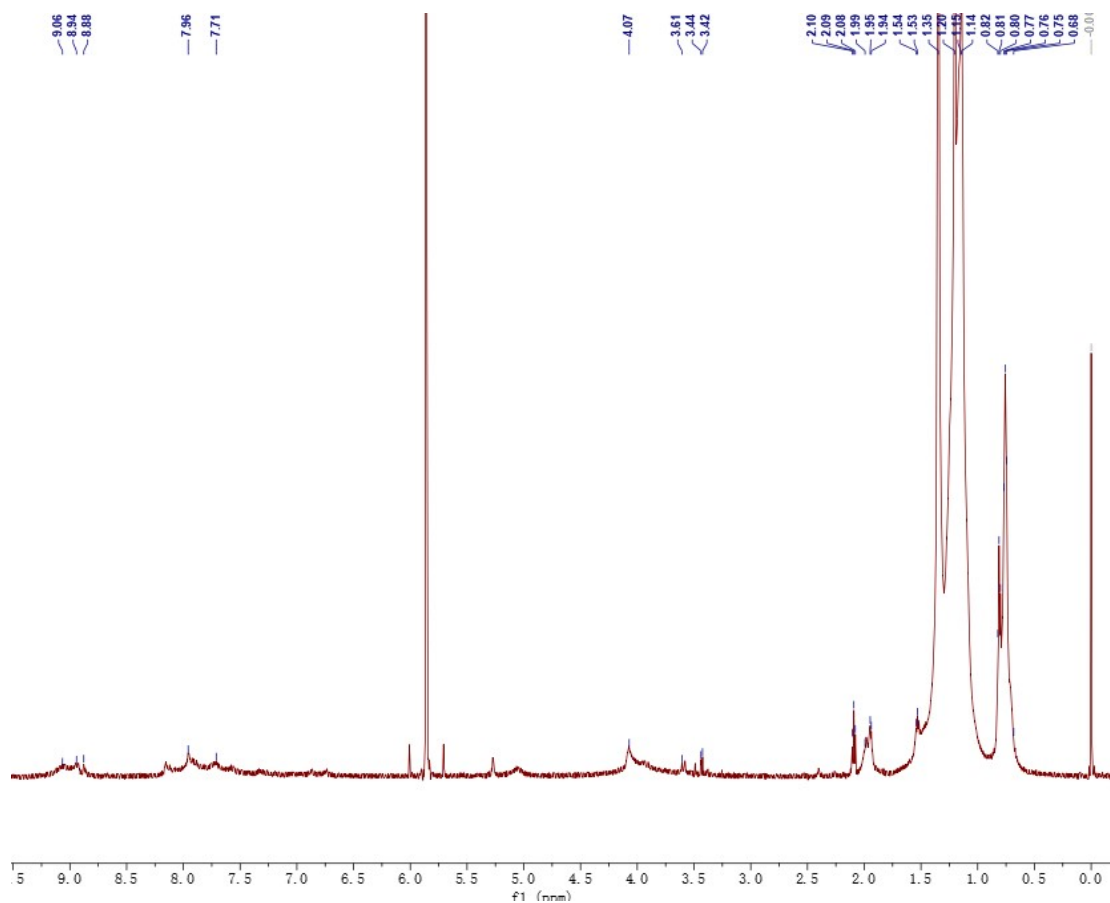
**Figure S3.**  $^1\text{H NMR}$  spectrum (400 Hz) of compound **6** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S4.** Enlarged  $^1\text{H}$  NMR spectrum (400 Hz) of compound **6** in  $\text{CD}_2\text{Cl}_2$  (7.0-9.0 ppm).

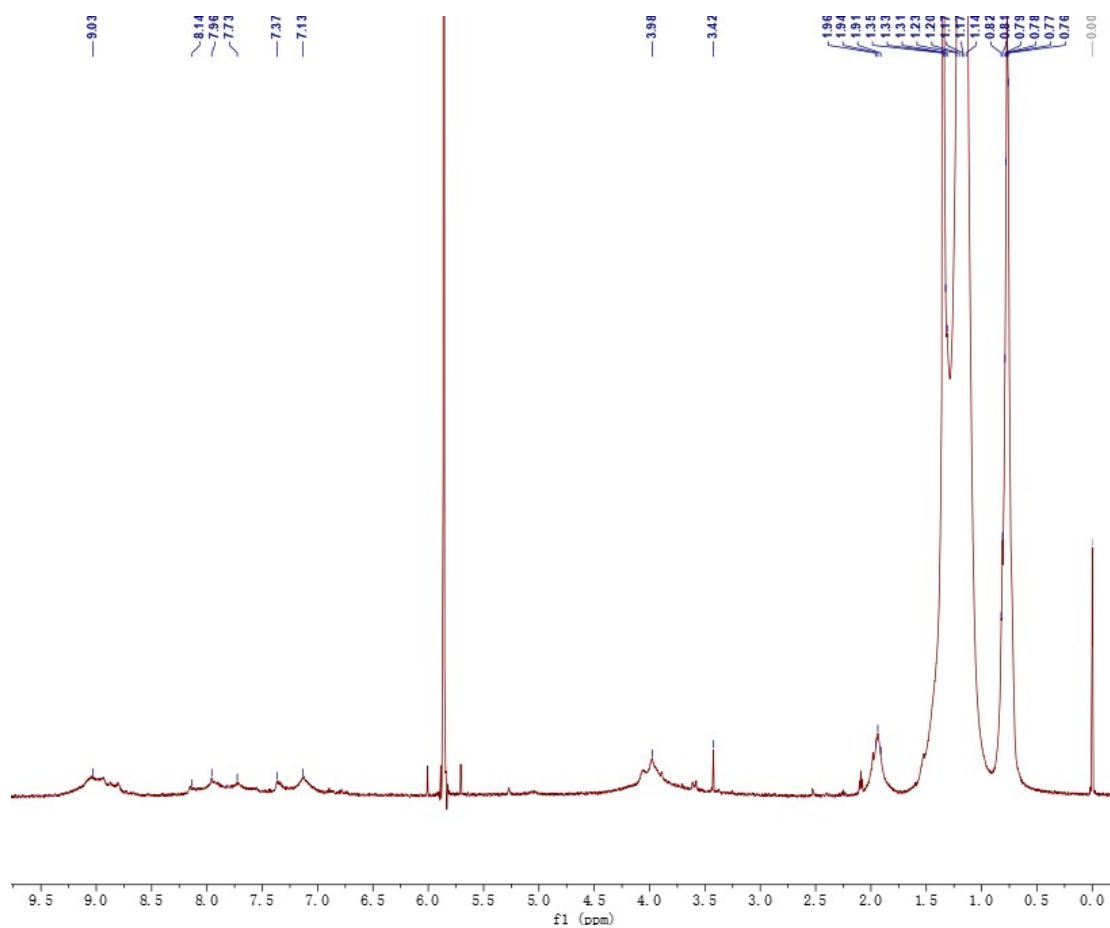


**Figure S5.**  $^{13}\text{C}$  NMR spectrum (100 Hz) of compound **6** in  $\text{CDCl}_3$ .

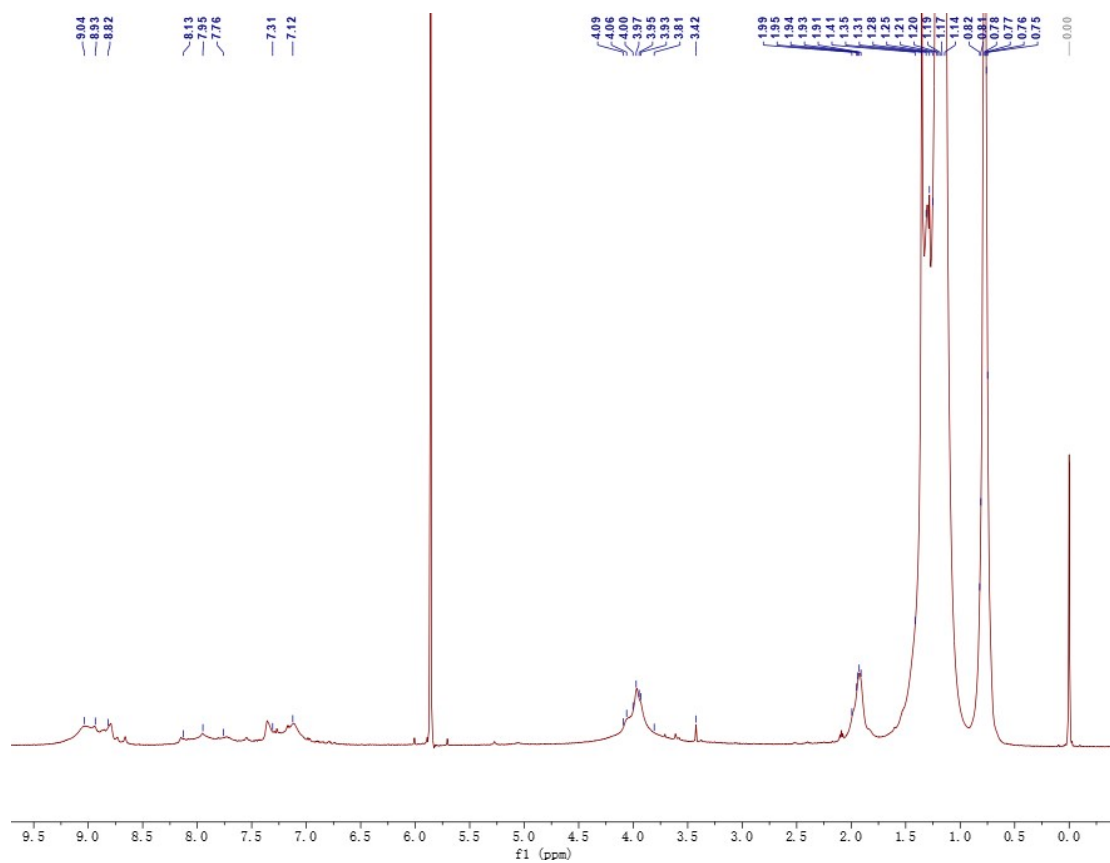


**Figure S6.**  $^1\text{H}$  NMR spectrum (600 Hz) of **P1DPP-BT** in  $\text{C}_2\text{D}_2\text{Cl}_4$  (100 °C).

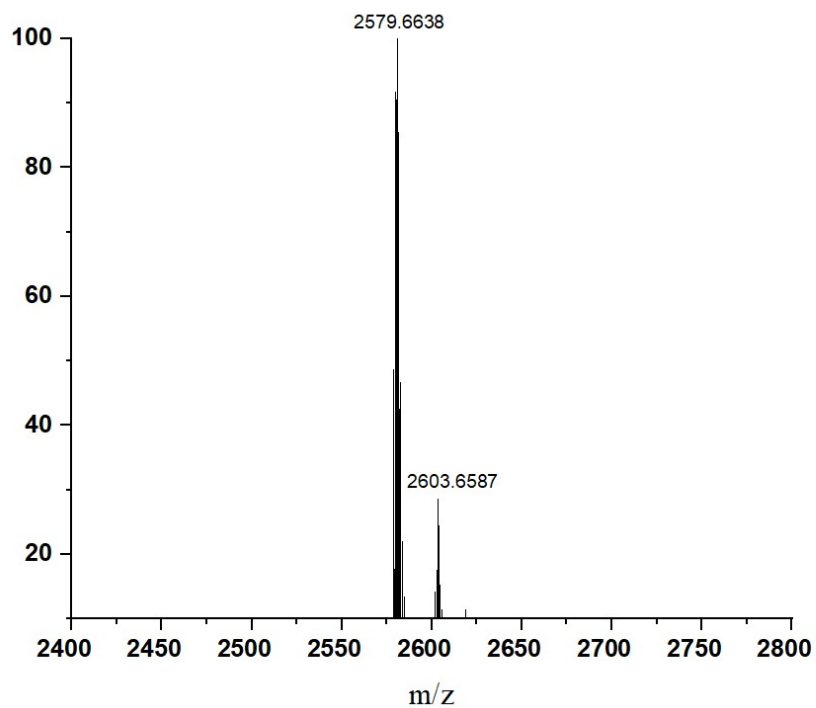




**Figure S7.**  $^1\text{H}$  NMR spectrum (600 Hz) of **P2DPP-BT** in  $\text{C}_2\text{D}_2\text{Cl}_4$  ( $100\text{ }^\circ\text{C}$ ).



**Figure S8.**  $^1\text{H}$  NMR spectrum (600 Hz) of **P3DPP-BT** in  $\text{C}_2\text{D}_2\text{Cl}_4$  (100 °C).



**Figure S9.** MALDI-TOF MS spectrum of compound **6**.

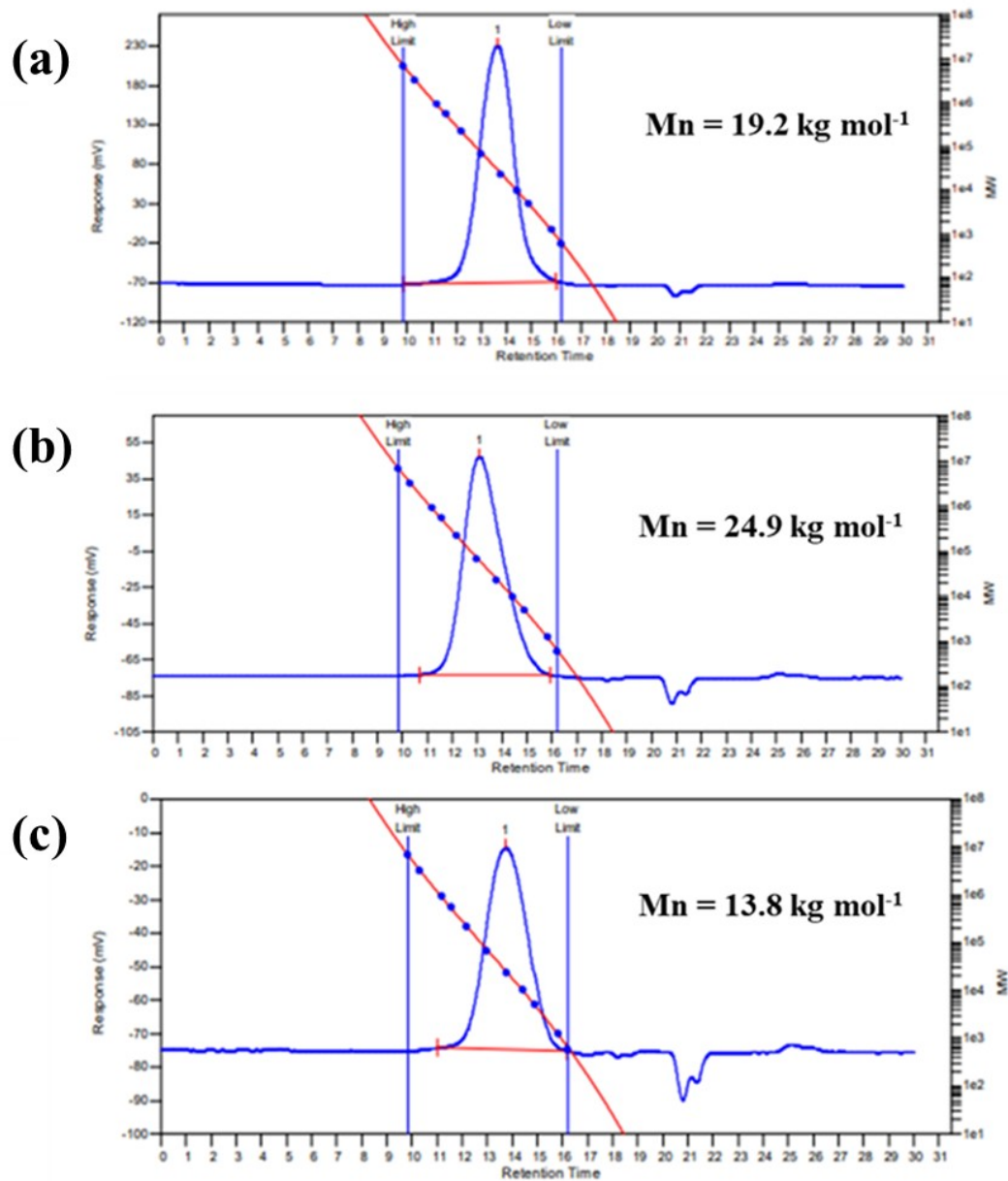


Figure S10. HT-GPC curves of (a) P1DPP-BT, (b) P2DPP-BT, (c) P3DPP-BT.

**Table S1. FWHM and CCL of P1DPP-BT, P2DPP-BT, P3DPP-BT (010) in OOP.**

Polymer	FWHM ( $\text{\AA}^{-1}$ )	CCL ( $\text{\AA}$ )
<b>P1DPP-BT</b>	0.37233	15.18
<b>P2DPP-BT</b>	0.26568	21.27
<b>P3DPP-BT</b>	0.52235	10.82