## Supporting Information

# Controlling the morphology and hole mobility of terpolymers for polymer solar cells

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**1. Synthetic procedures**

**2. NMR**

**3. DSC**

**4. Device optimization**

## 1. Synthesis procedures

*3,6-Bis(4-hexylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione* **(2).** Firstly, potassiumtert-butoxide (5.39 g, 48.10 mmol) and t-amyl alcohol (80 mL) was added to a two-necked 250 mL round- bottom flask with argon protection. Then 4-hexylthiophene-2- carbonitrile (8.00 g, 41.40 mmol) was dropped by a syringe in one portion. The mixture was warmed up to 110 $^{o}$C, and a solution of dimethyl succinate (3.04 g, 20.80 mmol) in t-amyl alcohol (8 mL) was added dropwise. The reaction mixture was kept 110 $^{o}$C for about 7 h. After the mixture was cooled, acetic acid (5 mL) was added to neutralized the remainder sodium tert-butylate. Then the mixture was poured into methanol (100 mL) for 1 h. The suspension was filtered, and washed by methanol and water twice each. The red solid was dried and without further purification (3.25 g, 33.6%).

*2,5-Bis(2-ethylhexyl)-3,6-bis(4-hexylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione* **(3).** 3,6-Bis(4-hexylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2.02 g, 4.30 mmol) and anhydrous potassium carbonate (2.38 g, 17.20 mmol) were added into two-necked 100 mL round-bottom flask. Then *N*,*N*-dimethylformamide (60 mL) was added and heated to 60 $^{o}$C for 1 h, under argon protection. 2-ethylhexyl bromide (2.49 g, 12.90 mmol) was added by a syringe in one portion. After the addition was completed, the reaction mixture was stirred for 15 h at 125 $^{o}$C. After the mixture was cooled to room temperature, the mixture was partitioned between Dichloromethane (DCM) and water. The organic phase was dried by anhydrous $MgSO_4$, and then the solvent was evaporated under vacuum. The crude product was purified by silica gel chromatography with dichloromethane/petroleum ester (1:1) as eluents, giving a purple-black solid (1.50 g, 50.7%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.72 (s, 2H), 7.23 (s, 2H), 4.01–3.87 (d, 4H), 2.72–2.68 (t, 4H), 1.87 (s, 2H), 1.87–1.68 (t, 4H), 1.35–1.24 (m, 28H), 0.89–0.85 (m, 18H). MALDI-TOF MS ($C_{42}H_{64}N_2O_2S_2$) m/z: calcd for 692.441, found 692.499.

*2,5-Bis(2-ethylhexyl)-3,6-bis(5-bromo-4-hexylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione* **(M1).** 2,5-Bis(2-ethylhexyl)-3,6-bis(4-hexylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (1.00 g, 1.44 mmol) was dissolved in $CHCl_3$ (30 mL) and stirred at 0 °C. Protected from light, NBS (513 mg, 2.88 mmol) in $CHCl_3$ (10 mL) was added to the mixture and kept at 0 °C for 2 h. The mixture was partitioned between DCM and water. The organic phase was dried by anhydrous $MgSO_4$, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography on a silica gel (petroleum ester/$CH_2Cl_2$ = 4:1) to afford the title compound as a purple solid (600 mg, 48.9%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.57 (s, 2H), 3.94–3.92 (d, 4H), 2.66–2.63 (t, 4H), 1.84 (s, 2H), 1.66–1.64 (t, 4H), 1.33–1.25 (m, 28H), 0.88–0.86 (m, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$, δ/ppm): 161.41, 143.95, 139.33, 135.57, 129.35, 116.18, 107.91, 45.99, 39.13, 31.59, 30.24, 29.61, 29.48, 28.95, 28.37, 23.70, 23.06, 22.61, 14.05, 13.98, 10.58. MALDI-TOF MS ($C_{42}H_{64}N_2O_2S_2$) m/z: calcd for 848.262, found 848.290.

***Synthesis of PDPPHT-TBT.*** To a 50 mL three-neck round bottom flask, **M1** (102 mg, 0.120 mmol), **M2** (99 mg, 0.120 mmol) and 15 mL of anhydrous toluene were added. The mixture was deoxygenated with nitrogen for 15 min. $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) was added under nitrogen and the mixture was again flushed with nitrogen for 30 min. Then the reaction mixture was stirred at 100 °C for 48 h under nitrogen atmosphere. After cooled to room temperature, the mixture was slowly poured into methanol (150 mL). The precipitate was collected by filtration and then purified by washing with methanol, hexane and chloroform in a Soxhlet extractor for 24 h in sequence. The final product was obtained as a dark green solid (103 mg, 72.1%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.87–8.86 (br, 2H), 7.56–7.55 (br,2H),7.30–7.28 (br, 6H), 4.06–4.04 (br, 8H), 2.94–2.92 (br, 4H), 1.97–1.26 (br, 44H), 1.00–0.90 (br, 30H). Number-average molecular weights ($M_n$) = 20.9 kg mol$^{-1}$, PDI = 1.7.

***Synthesis of PDPPHT-BDTT.*** **PDPPHT-BDTT** was prepared using the similar procedure as **PDPPHT-TBT** with the monomer **M1** (134 mg, 0.158 mmol), **M3** (143 mg, 0.158 mmol). The final product was obtained as a dark blue solid (98.5 mg, 48.3%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.91–8.90 (br, 2H), 7.76–7.34 (br, 4H), 7.12– 6.92 (br, 4H), 4.02–4.00 (br, 4H), 2.96–2.89 (br, 8H), 1.89–1.26 (br, 44H), 0.92–0.91 (br, 30H). $M_n$ = 14.3 kg mol$^{-1}$, PDI = 1.8.

***Synthesis of PDPPHT-TBT-3BDTT.*** **M1** (100 mg, 0.12 mmol), **M2** (24 mg, 0.09 mmol) and **M3** (79 mg, 0.09 mmol) were dissolved into 15 mL of toluene in a 25 mL flask under argon protection. The solution was flushed with argon for 15 min, and then 10 mg of $Pd(PPh_3)_4$ was added into the flask. The solution was flushed with argon for 30 min again, then it was stirred at 100 °C for 72 h under argon atmosphere. After cooled to room temperature, the mixture was added to methanol, and the precipitated solid was collected and purified by Soxhlet extraction with methanol, acetone, petroleum ether and chloroform in sequence. The title polymer was obtained as a dark green solid (114 mg, yield 77.5%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.88−8.87 (br), 7.80 (br), 7.55−7.35 (br), 6.93 (br), 4.05 (br), 2.90−2.88 (br), 1.91−0.91 (br). $M_n$ = 33.6 kg/mol, PDI = 1.4.

***Synthesis of PDPPHT-TBT-BDTT.*** **PDPPHT-TBT-BDTT** was prepared using the similar procedure as **PDPPHT-TBT-3BDTT** with the monomer **M1** (100 mg, 0.112 mmol), **M2** (48 mg, 0.06 mmol) and **M3** (53 mg, 0.06 mmol). The final product was obtained as a dark blue solid (125 mg, 86.3%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.86–8.85 (br,), 7.80–7.34 (br), 6.93 (br), 4.05–4.00 (br), 2.91–2.89 (br), 1.90–0.91 (br). $M_n$ = 32.5 kg $mol^{-1}$, PDI = 1.6.

***Synthesis of PDPPHT-3TBT-BDTT.*** **PDPPHT-3TBT-BDTT** was prepared using the similar procedure as **PDPPHT-TBT-3BDTT, PDPPHT-TBT-BDTT** with the monomer **M1** (100 mg, 0.12 mmol), **M2** (73 mg, 0.09 mmol) and **M3** (27 mg, 0.03 mmol). The final product was obtained as a dark blue solid (127 mg, 89.2%). $^1$H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.88–8.86 (br), 7.80–7.79 (br), 7.57 (br), 7.37–7.25 (br), 4.06–4.05 (br), 2.95–2.90 (br), 1.94–0.91 (br). $M_n$ = 30.3 kg $mol^{-1}$, PDI = 2.1.

## 2. NMR

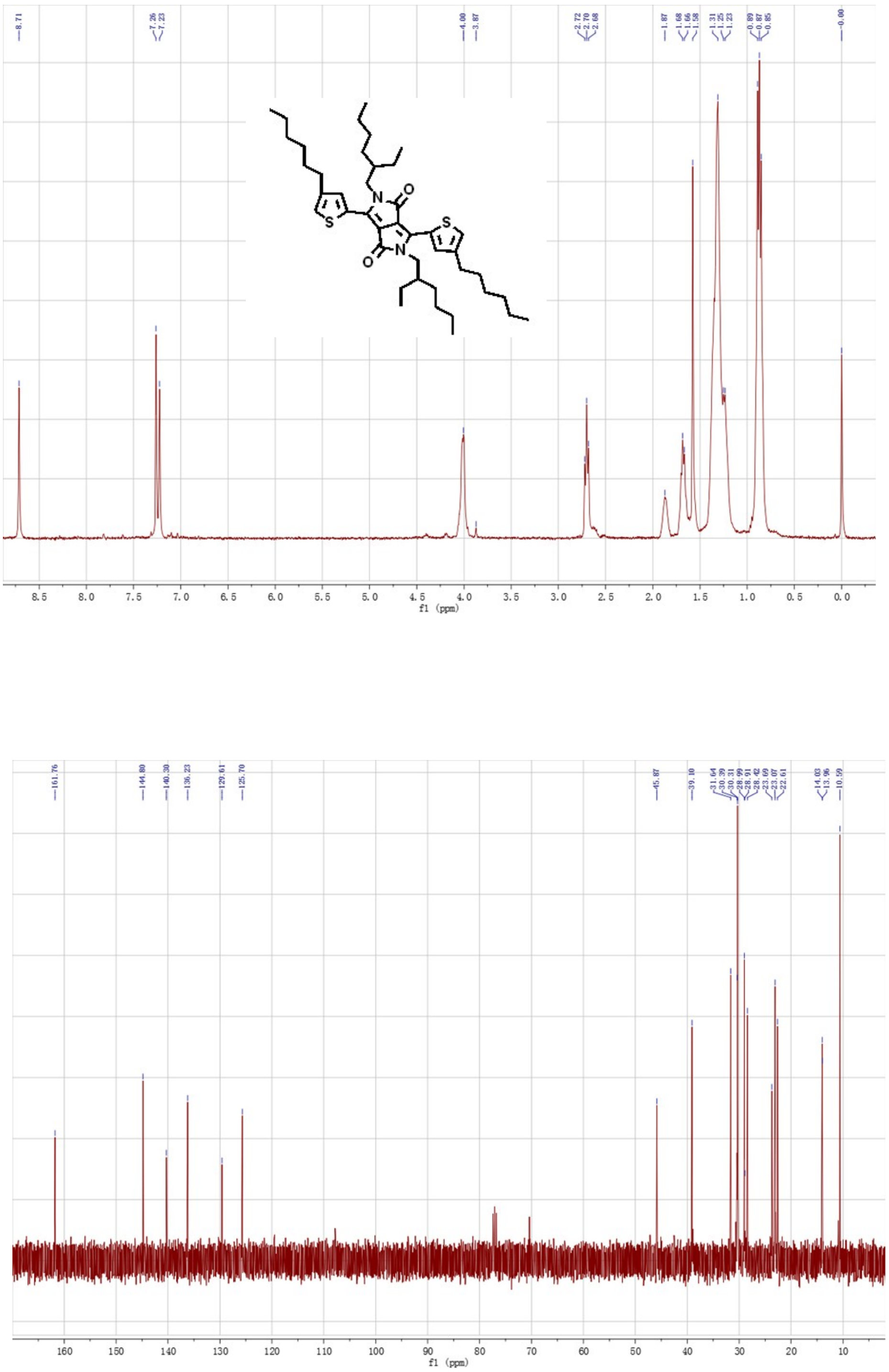

**Figure S1** $^{1}$H NMR and $^{13}$C NMR spectrum of **3**.

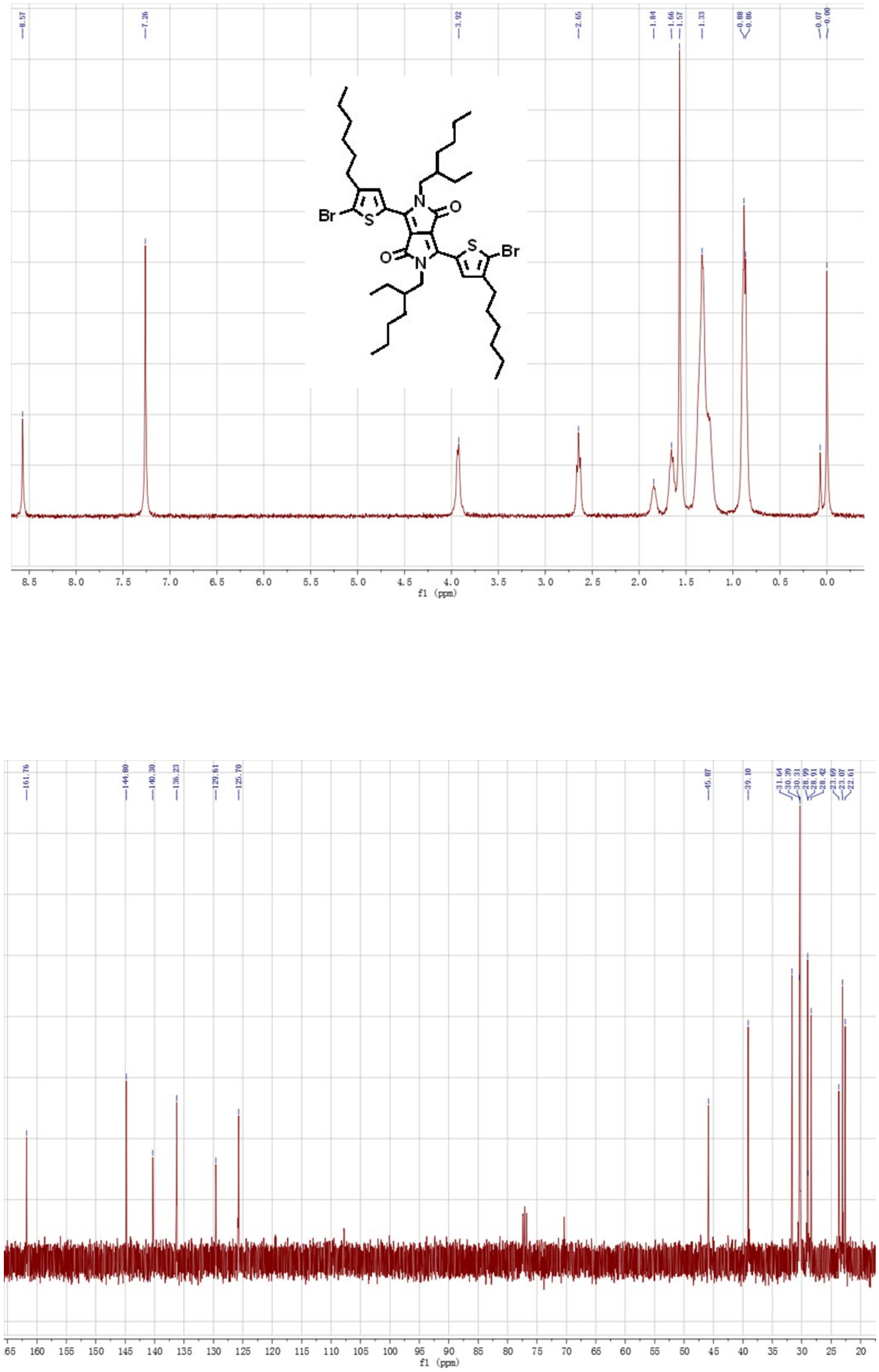

**Figure S2** $^1$H NMR and $^{13}$C NMR spectrum of **M1**.

## 3. DSC

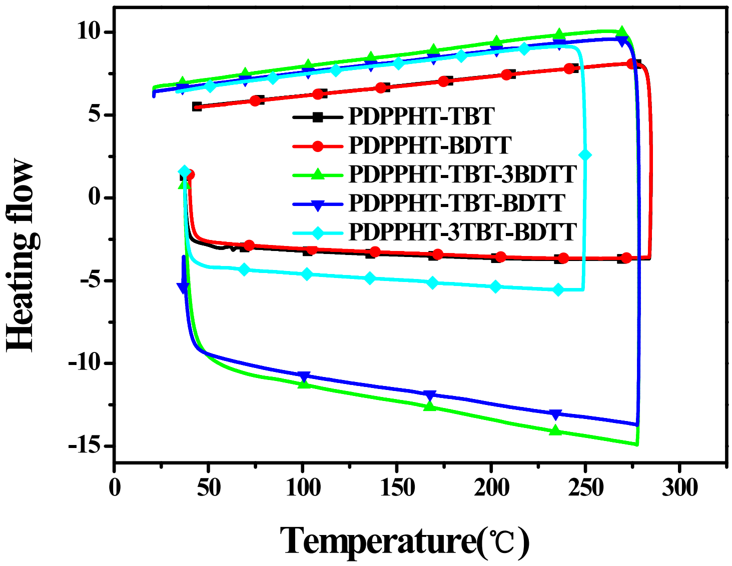

**Figure S3.** Second heating and cooling DSC traces of copolymers with a heating rate of 10 °C min$^{-1}$ and a cooling rate 20 °C min$^{-1}$ under nitrogen.

## 4. Device optimization

**Table S1** Photovoltaic properties of the copolymers and $PCB_{61}M$ (1:2, w/w)

| **Copolymers/$PC_{61}BM$ (1:2, w/w)** | **Solvent** | **$J_{sc}$ ($mA/cm^2$)** | **$V_{oc}$ (V)** | **FF** | **PCE (%)** |
|---|---|---|---|---|---|
| **PDPPHT-TBT** [a] | CB | 11.66 | 0.63 | 0.48 | 3.51 |
| **PDPPHT-TBT** [b] | CB | 7.84 | 0.65 | 0.50 | 2.55 |
| **PDPPHT-BDTT** [a] | CB | 7.26 | 0.77 | 0.44 | 2.46 |
| **PDPPHT-BDTT** [b] | CB | 5.45 | 0.76 | 0.48 | 1.98 |
| **PDPPHT-TBT-3BDTT** [a] | CB | 10.74 | 0.65 | 0.51 | 3.53 |
| **PDPPHT-TBT-3BDTT** [b] | CB | 9.39 | 0.65 | 0.48 | 2.94 |
| **PDPPHT-TBT-3BDTT** [b] | CB:CF=3:1 | 10.39 | 0.70 | 0.50 | 3.64 |
| **PDPPHT-TBT-BDTT** [a] | CB | 10.37 | 0.67 | 0.51 | 3.51 |
| **PDPPHT-TBT-BDTT** [b] | CB | 7.84 | 0.69 | 0.51 | 2.79 |
| **PDPPHT-TBT-BDTT** [b] | CB:CF=3:1 | 10.21 | 0.72 | 0.57 | 4.18 |
| **PDPPHT-3TBT-BDTT** [a] | CB | 9.18 | 0.50 | 0.44 | 2.02 |
| **PDPPHT-3TBT-BDTT** [b] | CB | 8.74 | 0.53 | 0.33 | 1.55 |
| **PDPPHT-3TBT-BDTT** [b] | CB:CF=3:1 | 8.16 | 0.69 | 0.46 | 2.58 |

[a] Processed with DIO 0.25% (v/v). [b] Processed without DIO.