

Electronic Supplementary Information

Alkylthienyl substituted asymmetric 2D BDT and DTBT-based polymer solar cells with a power conversion efficiency of 9.2%

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1. Synthesis

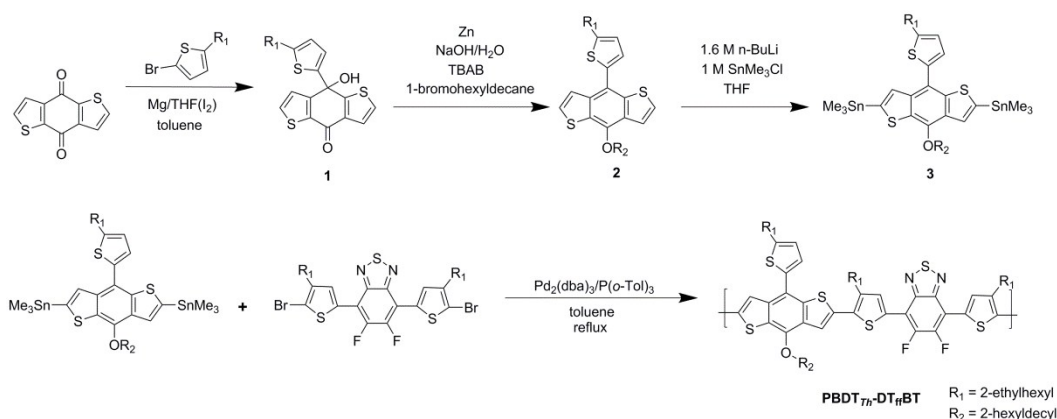


Fig. S1 Synthetic routes of monomer and polymer.

8-hydroxy-8-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen-4-one (1)

To a mixture of magnesium turnings (0.86 g, 36 mmol) and a grain of I_2 in dry THF (10 mL) was added dropwise 2-bromo-5-(2-ethylhexyl)thiophene (8.26 g, 30 mmol) in THF (20 mL) at a rate sufficient to maintain reflux under nitrogen. After addition, the reflux was maintained for 3 h. The Grignard reagent was then added dropwise to a solution of 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-dione (4.40 g, 20 mmol) in toluene (400 mL) in an ice-water bath. Finally, the mixture was stirred for 30 h at room temperature under nitrogen. Then, the mixture was hydrolyzed by careful addition of water followed by 38% aqueous HCl and extracted with diethyl ether. The organic phase was dried over Na_2SO_4 . After removing the solvent under vacuum, residue (5.41 g, 65%) was used for next step without further purification.

4-hexyldecyloxy-8-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (2)

Compound **1** (4.17 g, 10.0 mmol) and zinc powder (1.62 g, 25.0 mmol) were put into a 100 mL flask under nitrogen; then 5.33 g of NaOH in water (50 mL) was added into the mixture. The mixture was well stirred and heated to reflux for 3 h. Then, 1-bromo-2-hexyl-decane (7.63 g, 25.0 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed overnight, the reactant was poured into cold water and extracted by petroleum ether. The organic phase was dried over Na_2SO_4 . After removing the solvent under vacuum, residue was purified by silica column chromatography with petroleum ether to give compound **2** as pale yellow oil (3.63 g, 58%). 1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.58 (d, $J = 5.6$ Hz, 1H), 7.52 (d, $J = 5.6$ Hz, 1H), 7.40 (d, $J = 5.6$ Hz, 1H), 7.37 (d, $J = 5.7$ Hz, 1H), 7.21 (d, $J = 3.5$ Hz, 1H), 6.85

(d, $J = 3.4$ Hz, 1H), 4.25 (d, $J = 5.4$ Hz, 2H), 2.83 (d, $J = 6.8$ Hz, 2H), 1.91 - 1.85 (m, 1H), 1.68 - 1.61 (m, 3H), 1.51 - 1.27 (m, 30H), 0.95 - 0.87 (m, 12H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 148.45, 145.24, 140.48, 138.53, 137.44, 129.99, 128.78, 127.26, 126.94, 126.33, 125.32, 123.60, 120.11, 119.90, 76.44, 41.50, 39.32, 34.29, 32.53, 31.97, 31.95, 31.36, 31.34, 30.12, 29.79, 29.68, 29.41, 28.97, 27.03, 27.00, 26.97, 25.77, 23.07, 22.75, 14.19, 14.18, 10.95.

2,6-bis(trimethyltin)-4-hexyldecyloxy-8-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (3)

To a solution of compound **2** (3.13 g, 5.0 mmol) in THF (60 mL) at -78 °C was added dropwise *n*-BuLi (7.81 mL, 12.5 mmol, 1.6 M in hexane) under nitrogen. The mixture was stirred at -78 °C for 1 h and then warmed to room temperature for 0.5 h. After cooling back to -78 °C again, trimethyltin chloride (13.5 mL, 13.5 mmol, 1 M in hexane) was added in one portion. The mixture was brought to room temperature and stirred overnight. Water was subsequently added to the reaction mixture and extracted by diethyl ether. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was recrystallized by ethanol two times. Compound **3** was obtained as a white solid (2.61 g, 55%). ^1H NMR (600 MHz, CDCl_3): δ (ppm) 7.63 (s, 1H), 7.57 (s, 1H), 7.23 (d, $J = 3.4$ Hz, 1H), 6.87 (d, $J = 3.4$ Hz, 1H), 4.27 (d, $J = 5.3$ Hz, 2H), 2.90 - 2.81 (m, 2H), 1.92 - 1.86 (m, 1H), 1.70 - 1.64 (m, 3H), 1.51 - 1.28 (m, 30H), 0.97 - 0.87 (m, 12H), 0.42 (s, 18H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 147.01, 144.89, 144.81, 141.60, 140.88, 139.68, 138.21, 132.67, 131.21, 131.06, 127.88, 127.05, 125.21, 118.23, 75.97, 41.49, 39.28, 32.53, 31.98, 31.97, 31.43, 30.20, 29.84, 29.74, 29.43, 28.97, 27.23, 25.82, 23.06, 22.75, 22.72, 14.19, 14.17, 14.15, 10.98, -8.33, -8.37.

Synthesis of PBDT_{TH}-DT_{TH}BT

To a 25 mL flask, compound **3** (142.6 mg, 0.15 mmol), 4,7-bis(5-bromo-4-(2-ethylhexyl) -2-thienyl)-2,1,3-benzothiadiazole (102.4 mg, 0.15 mmol), $\text{Pd}_2(\text{dba})_3$ (4.2 mg, 0.0045 mmol), and tri(*o*-tolyl)phosphine (8.4 mg, 0.027 mmol) were added under nitrogen. After the addition of toluene (5 mL), the mixture was heated to 110 °C and maintained at the same temperature for 12 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and purified by column chromatography over silica using chloroform as the eluent. After removing the solvent, the resulting solid was dissolved into a small amount of chloroform and

then poured into methanol again. The product was collected and dried overnight under vacuum at 40 °C with the yield 63% for PBDT_{Th}-DT_{ff}BT as a blue-black solid.

2. TGA

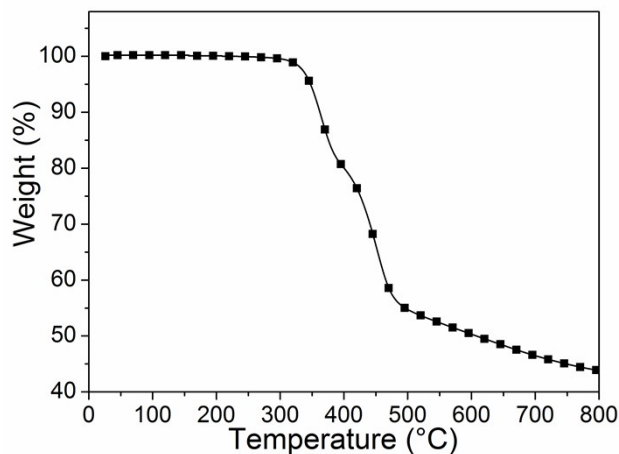


Fig. S2 TGA curve of PBDT_{Th}-DT_{ff}BT with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

3. Detailed device parameters of PSCs

Table S1. PSCs performance with device configuration ITO/PEDOT:PSS/ PBDT_{Th}-DT_{ff}BT:PC₇₁BM/PFN-Br/Al

| Active layer | ratio | spin-coating speed (rpm) | annealing temp. (°C) | DIO (%) | V _{OC} (V) | J _{SC} (mA cm ⁻²) | FF (%) | PCE (%) |
|--|-------|--------------------------|----------------------|---------|---------------------|--|--------|---------|
| PBDT _{Th} -DT _{ff} BT :PC ₇₁ BM | 1:1.5 | 1500 | NO | 0 | 0.91 | 10.02 | 65.5 | 5.97 |
| | 1:1.5 | 1600 | NO | 0 | 0.92 | 11.09 | 68.5 | 6.99 |
| | 1:1.5 | 1700 | NO | 0 | 0.91 | 10.62 | 70.6 | 6.82 |
| | 1:2.5 | 1600 | NO | 0 | 0.90 | 10.97 | 64.7 | 6.39 |
| | 1:2 | 1600 | NO | 0 | 0.91 | 11.92 | 65.8 | 7.14 |
| | 1:2 | 1600 | NO | 0.5 | 0.83 | 12.77 | 66.6 | 7.06 |
| | 1:2 | 1600 | NO | 1.0 | 0.84 | 14.65 | 62.1 | 7.64 |
| | 1:2 | 1600 | NO | 1.5 | 0.83 | 14.67 | 56.6 | 6.89 |
| | 1:2 | 1000 | 100 | 1.0 | 0.85 | 13.61 | 65.7 | 7.60 |
| | 1:2 | 1200 | 100 | 1.0 | 0.85 | 13.07 | 70.1 | 7.79 |
| | 1:2 | 1400 | 100 | 1.0 | 0.87 | 14.12 | 70.6 | 8.67 |
| | 1:2 | 1600 | 100 | 1.0 | 0.87 | 15.06 | 70.4 | 9.22 |
| | 1:2 | 1800 | 100 | 1.0 | 0.87 | 14.57 | 69.5 | 8.81 |
| | 1:2 | 2000 | 100 | 1.0 | 0.87 | 13.55 | 72.1 | 8.48 |

Table S2. PSCs performance with device configuration ITO/PEDOT:PSS/ PBDT_{Th}-DT_{ff}BT:ITIC/PFN-Br/Al

| Active layer | ratio | spin-coating speed (rpm) | annealing temp. (°C) | DIO (%) | V _{OC} (V) | J _{SC} (mA cm ⁻²) | FF (%) | PCE (%) |
|---|-------|--------------------------|----------------------|---------|---------------------|--|--------|---------|
| PBDT _{Th} -DT _{ff} BT :ITIC | 1:0.8 | 1800 | NO | 0 | 0.91 | 12.78 | 50 | 5.81 |
| | 1:1 | 1800 | NO | 0 | 0.92 | 12.81 | 57.7 | 6.80 |
| | 1:1.2 | 1800 | NO | 0 | 0.91 | 12.77 | 59.3 | 6.89 |
| | 1:1 | 1800 | 100 | 0 | 0.91 | 13.46 | 56.0 | 6.86 |
| | 1:1 | 1600 | 130 | 0 | 0.90 | 12.88 | 61.1 | 7.08 |
| | 1:1 | 1800 | 130 | 0 | 0.91 | 13.62 | 63.2 | 7.83 |
| | 1:1 | 2000 | 130 | 0 | 0.91 | 12.96 | 62.3 | 7.35 |
| | 1:1 | 1800 | 150 | 0 | 0.91 | 13.01 | 62.0 | 7.34 |
| | 1:1 | 1800 | 130 | 1.0 | 0.93 | 11.60 | 53.7 | 5.79 |
| | 1:1 | 1800 | 130 | 0.5 | 0.92 | 12.78 | 51.9 | 6.10 |
| | 1:1 | 1800 | 130 | 1.5 | 0.91 | 13.60 | 54.5 | 6.74 |

4. Hole mobility

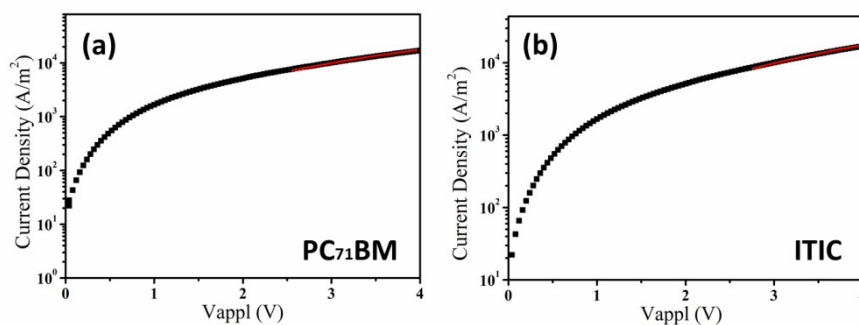


Fig. S3. Current density–voltage (J - V) curves for polymer:PC₇₁BM (a) and polymer:ITIC (b) based device (the symbols are experimental data for transport of hole, and the red line is fitted according to the space-charge-limited-current model). The devices were constructed as ITO/PEDOT:PSS/polymer:PC₇₁BM (or ITIC) (100 nm)/PFN-Br (10 nm)/Al (100 nm).

5. J - V curves of the optimal device based on $\text{PBDT}_{T_h}\text{-DT}_{ff}\text{BT/ITIC}$ under ILP

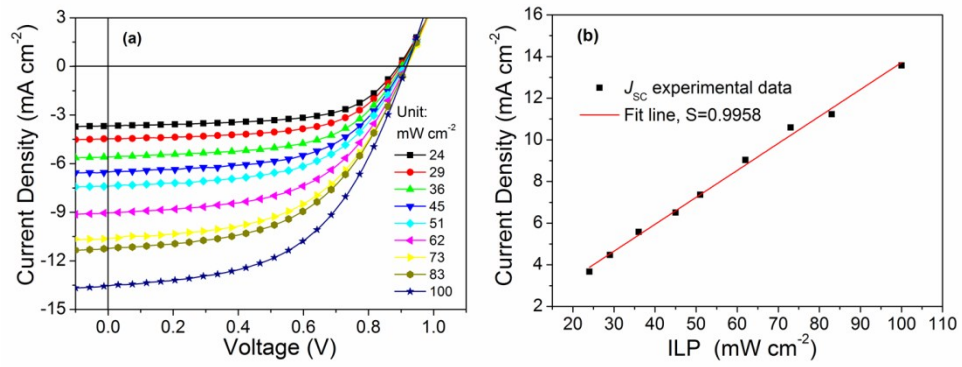


Fig. S4. (a) J - V curves of the optimal device based on $\text{PBDT}_{T_h}\text{-DT}_{ff}\text{BT/PC}_{71}\text{BM}$ under ILP, and (b) J_{sc} versus ILP curves.