

## Supporting Information (SI) for

### **A versatile star-shaped organic semiconductor based on benzodithiophene and diketopyrrolopyrrole**

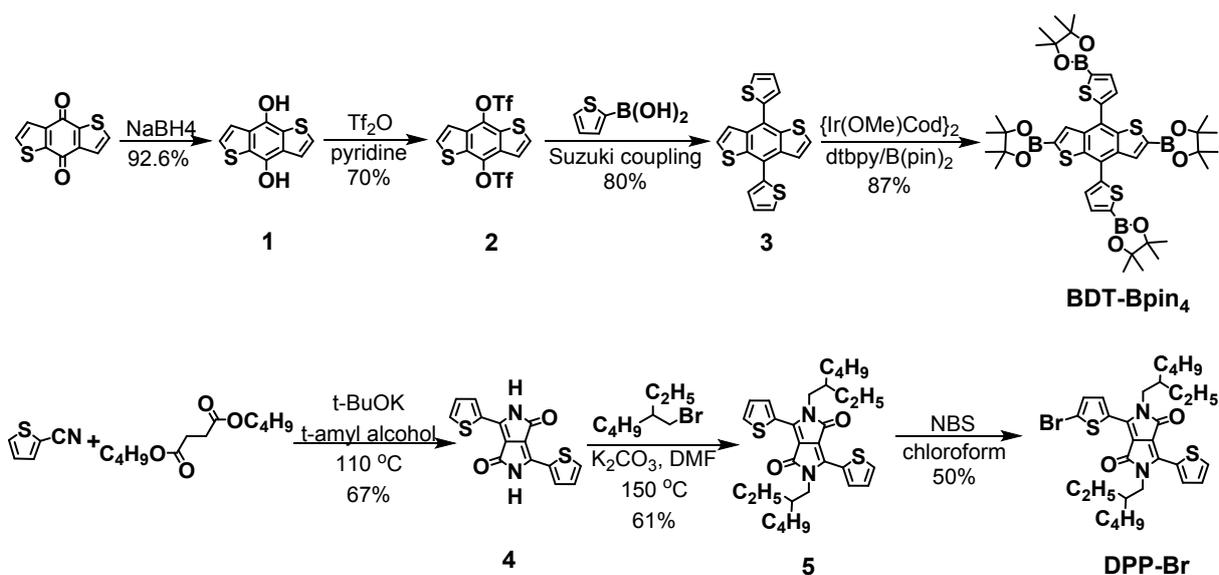
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Scheme S1 Synthetic route to compound BDT-Bpin4 and DPP-Br.

### Synthesis

Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. All reactions were performed under argon unless stated.

#### *Benzo[1,2-b:4,5-b']dithiophene-4,8-diol (1)*

To a stirred suspension of benzo[1,2-b:4,5-b']dithiophene-4,8-dione (2 g, 9.08 mmol) in ethanol (50 mL) was added with NaBH<sub>4</sub> (0.85 g, 21.8 mmol) in one portion under ice/water bath cooling. The reaction mixture was stirred at 90 °C for 12 h before quenching by the addition into aqueous HCl (50 mL, 1 M). The crude product was filtered, washed with water, and dried under vacuum at 70 °C. The compound **1** was obtained as a green solid (1.87 g, yield 92.6%) and used for next step without further purification.

#### *Benzo[1,2-b:4,5-b']dithiophene-4,8-diyl bis(trifluoromethanesulfonate) (2)*

To a suspension of compound **1** (1.8 g, 8.1 mmol) and dry pyridine (2.5 mL) in dichloromethane (50 mL) was slowly added trifluoromethanesulfonic anhydride (4 mL, 24 mmol) at 0 °C. After the mixture was stirred at 0 °C for 12 h, water (30 mL) and hydrochloric

acid (30 mL, 1 M) were added. The resulting mixture was extracted with dichloromethane (3 × 30 mL), and the combined organic layer was dried with MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified with column chromatography on silica gel eluted with petroleum ether/ dichloromethane (1:1) to give pure product as a white solid (1.27 g, yield 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 4 Hz, 2H), 7.57 (d, *J* = 4 Hz, 2H).

*4,8-Di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (3)*

To a degassed mixture of bistriflate compound **2** (1.2 g, 2.47 mmol), thiophene-2-boronic acid (633.5 mg, 4.95 mmol) and palladium[0]-tetrakis(triphenylphosphine) (142 mg, 0.12 mmol) was added tetrahydrofuran (40 mL) and aqueous sodium carbonate (10 mL, 1 M). The mixture was heated at reflux for 24 h then poured into aqueous hydrochloric acid. The mixture was extracted with dichloromethane (3 × 30 mL), washed with water (30 mL), dried with MgSO<sub>4</sub> and evaporated under vacuum. The product was obtained by column chromatography on silica gel using petroleum ether, afforded as a yellow solid (700 mg, 80%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 7.89-7.87 (d, *J* = 8 Hz, 4H), 7.59-7.58 (d, *J* = 4 Hz, 2H), 7.57-7.55 (d, *J* = 8 Hz, 2H), 7.37-7.35 (t, *J* = 8 Hz, 2H). MS (EI, GC-MS) *m/z* = 354.1 (M<sup>+</sup>).

*2,2'-((2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(thiophene-5,2-diyl))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (BDT-Bpin<sub>4</sub>)*

A mixture of compound **3** (425 mg, 1.2 mmol), bis(pinacolato)diboron (1.83 g, 7.2 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (92 mg, 0.34 mmol) and [Ir(OMe)Cod] (45 mg, 0.068 mmol) in anhydrous hexane (20 ml) was heated at 70 °C for 48 hours. The solvent was removed under reduced pressure, and the crude recrystallized from hexane/methanol to afford BDT-Th-4Bpin (900 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.09 (s, 2H), 7.75 (d, *J* = 4 Hz, 2H), 7.57 (d, *J* = 4 Hz, 2H), 1.40 (s, 24H), 1.34 (s, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.54, 142.81,

138.45, 137.77, 133.51, 129.95, 124.84, 84.76, 84.42, 25.01, 24.97. MS (MALDI-TOF)  $m/z = 858.29$  ( $M^+$ ).

*3,6-Di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4)*

A solution of t-amyl alcohol (25 mL) and 2-thiophenecarbonitrile (3.27 g, 30 mmol) was injected in one portion to a flask containing potassium tert-butyrate (4 g, 35.7 mmol). The mixture was heated with stirring to 105 °C and a solution of dibutyl succinate (3.5 g, 15 mmol) in t-amyl alcohol (10 mL) was slowly added over 1 h. When the addition was complete, the reaction was kept at the same temperature for 5 h. Then the mixture was cooled to 65 °C, diluted with methanol (50 mL), and neutralized with acetic acid and refluxed for another 30 min. The resulting suspension was filtered, and the black filter cake was washed by hot methanol (x 2) and water (x 2) and dried in vacuum to get the crude product. This was used directly to next step without further purification (2.03 g, 67%).

*2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5)*

A suspension of compound **4** (1.3 g, 4.33 mmol), anhydrous potassium carbonate (2.4 g, 17.3 mmol) and N,N-dimethylformamide (45 mL) were heated to 145 °C. 2-Ethylhexyl bromide (2.9 g, 15 mmol) was injected one portion by syringe. After reaction for a further 15 h, the solution was cooled to room temperature, poured into ice-water (500 mL), and filtered. The filter cake was washed by water and methanol several times. After drying in vacuum, the crude product was purified by silica gel chromatography using dichloromethane/petroleum ether (1:1) as eluent to obtain a purple-red solid (1.39 g, yield 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.90 (d,  $J = 4$  Hz, 2H), 7.63 (d,  $J = 4$  Hz, 2H), 7.28 (dd,  $J_1 = 4$  Hz,  $J_2 = 4$  Hz, 2H), 4.04-3.97 (m, 4H), 1.95-1.78 (m, 2H), 1.49-1.01 (m, 16H), 0.99-0.53 (m, 12H).

*3-(5-Bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP-Br)*

A solution of **5** (1.05 g, 2 mmol) and N-bromosuccinimide (356 mg, 2 mmol) in chloroform (50 mL) were stirred at room temperature for 24 h in the absence of light. The mixture was poured into methanol (60 mL) and filtered. The filter cake was washed by hot methanol twice. After drying in vacuum, the product was purified by silica gel chromatography using dichloromethane/petroleum ether (1:1.5) as eluent to afford the product as a purple-red solid (604 mg, yield 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.91 (d, *J* = 8 Hz, 1H), 8.63 (d, *J* = 4 Hz, 1H), 7.65 (d, *J* = 8 Hz, 1H), 7.28 (t, *J* = 4 Hz, 1H), 7.23 (d, *J* = 4 Hz, 1H), 4.03-3.93 (m, 4H), 1.85 (s, 2H), 1.46-1.12 (m, 16H), 0.96-0.72 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.87, 161.70, 141.10, 139.16, 135.70, 135.26, 131.58, 131.47, 131.00, 129.96, 128.68, 118.80, 108.40, 108.02, 46.16, 39.34, 39.28, 30.42, 28.56, 23.76, 23.23, 14.19, 10.68. MS (MALDI-TOF) *m/z* = 607.2 (M<sup>+</sup>).

*6,6'-((4,8-Bis(5'-(2,5-bis(2-ethylhexyl)-3,6-dioxo-4-(thiophen-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2'-bithiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(thiophene-5,2-diyl))bis(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (BDT(DPP)<sub>4</sub>)*

Pd<sub>2</sub>(dba)<sub>3</sub> (16 mg, 0.017 mmol) and P(MeOPh)<sub>3</sub> (48 mg, 0.136 mmol) were added to a degassed suspension of **BDT-Bpin<sub>4</sub>** (128.7 mg, 0.15 mmol), **DPP-Br** (380.3 mg, 0.63 mmol), THF (12 mL) and 2M K<sub>2</sub>CO<sub>3</sub> aqueous solution (3 mL) under argon. The reaction was refluxed 16 h, then cooled and precipitated into methanol. The precipitate was filtered and purified by column chromatography (eluent: chloroform/dichloromethane 1:2, followed by further purification by recycling preparative GPC (eluent: chloroform), afforded a purple-black crystal (161 mg, 43.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.95-8.91 (m, 4H), 7.64-7.43 (m, 8H), 7.40-7.28 (b,

4H), 4.05-3.81 (b, 10H), 2.06-0.63 (m, 136H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.24, 141.48, 139.90, 135.48, 135.44, 130.38, 129.91, 129.87, 128.35, 125.22, 108.21, 45.90, 39.22, 30.36, 29.71, 28.58, 28.33, 23.80, 23.11, 14.11, 14.05, 14.03, 10.59, 10.50. MS (MALDI-TOF)  $m/z$  = 2446.0 ( $\text{M}^+$ ). Anal. Calc. for  $\text{C}_{138}\text{H}_{162}\text{N}_8\text{O}_8\text{S}_{12}$ : C, 67.78; H, 6.68; N, 4.58. Found: C, 67.66; H, 6.75; N, 4.72%.

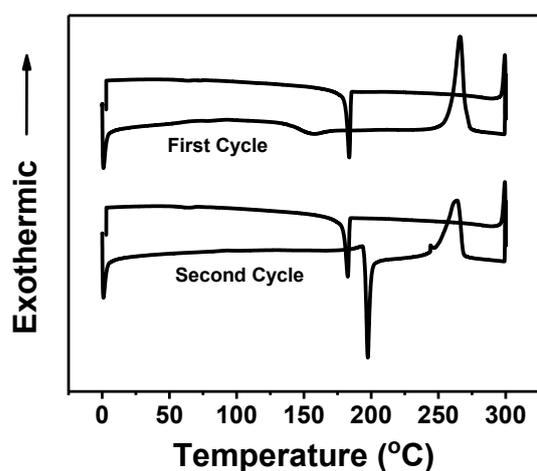


Fig. S1 DSC heating and cooling traces (first and second cycles) of BDT(DPP)<sub>4</sub> at a heating/cooling speed of 10 °C min<sup>-1</sup> under N<sub>2</sub>.

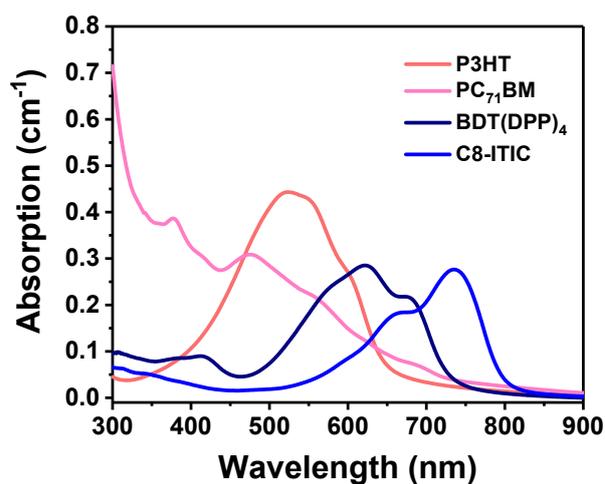


Fig. S2 Absorption spectra of P3HT, BDT(DPP)<sub>4</sub>, PC<sub>71</sub>BM and C8-ITIC as spin-coated films.

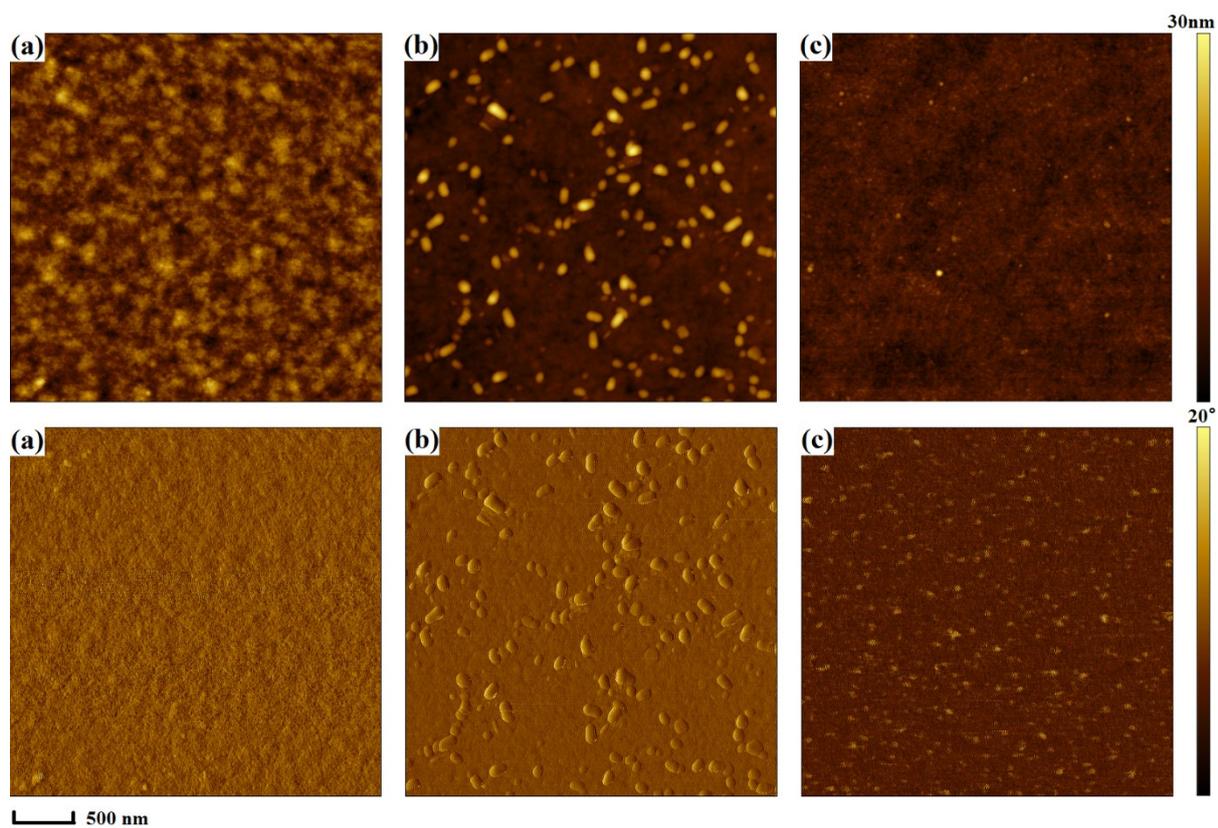


Fig. S3 Active Layer Characterization. AFM height (top) and phase (bottom) images ( $3 \mu\text{m} \times 3 \mu\text{m}$ ) of blended films. (a) P3HT:BDT(DPP)<sub>4</sub> (1:1, w/w); (b) BDT(DPP)<sub>4</sub>:C8-ITIC (1:1, w/w); (c) BDT(DPP)<sub>4</sub>:PC<sub>71</sub>BM (1:2, w/w).

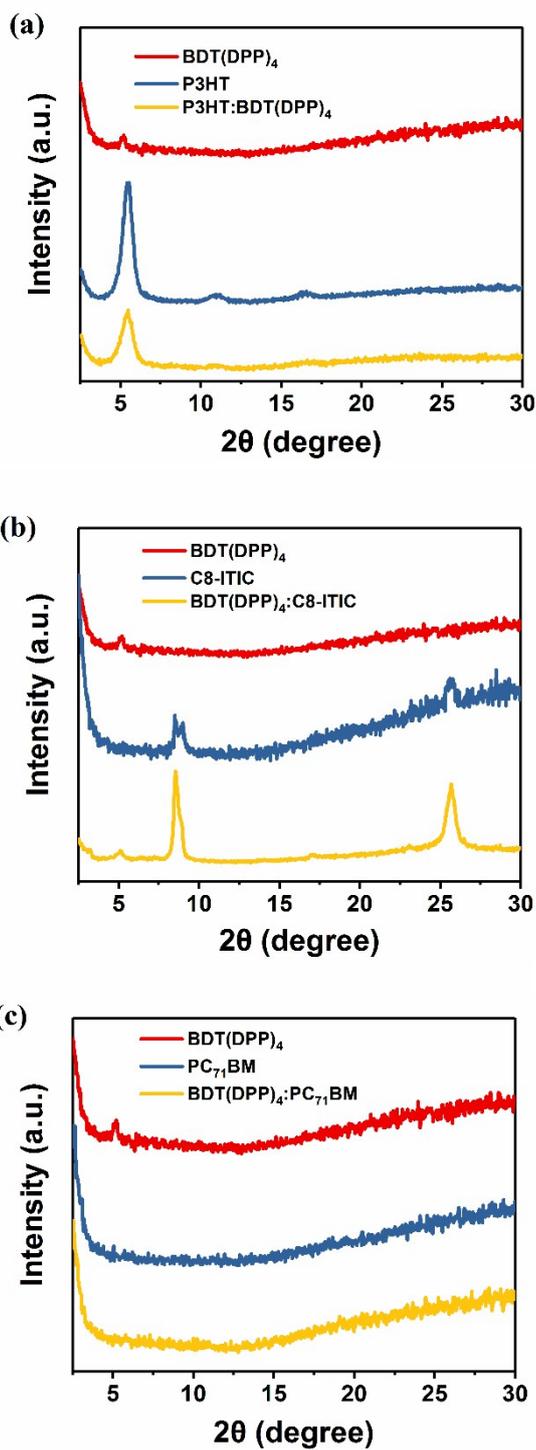


Fig. S4 XRD patterns of P3HT:BDT(DPP)<sub>4</sub> (1:1, w/w), BDT(DPP)<sub>4</sub>:C8-ITIC (1:1, w/w) and BDT(DPP)<sub>4</sub>:PC<sub>71</sub>BM (1:2, w/w) blend films and their neat films on SiO<sub>2</sub>/Si substrate.

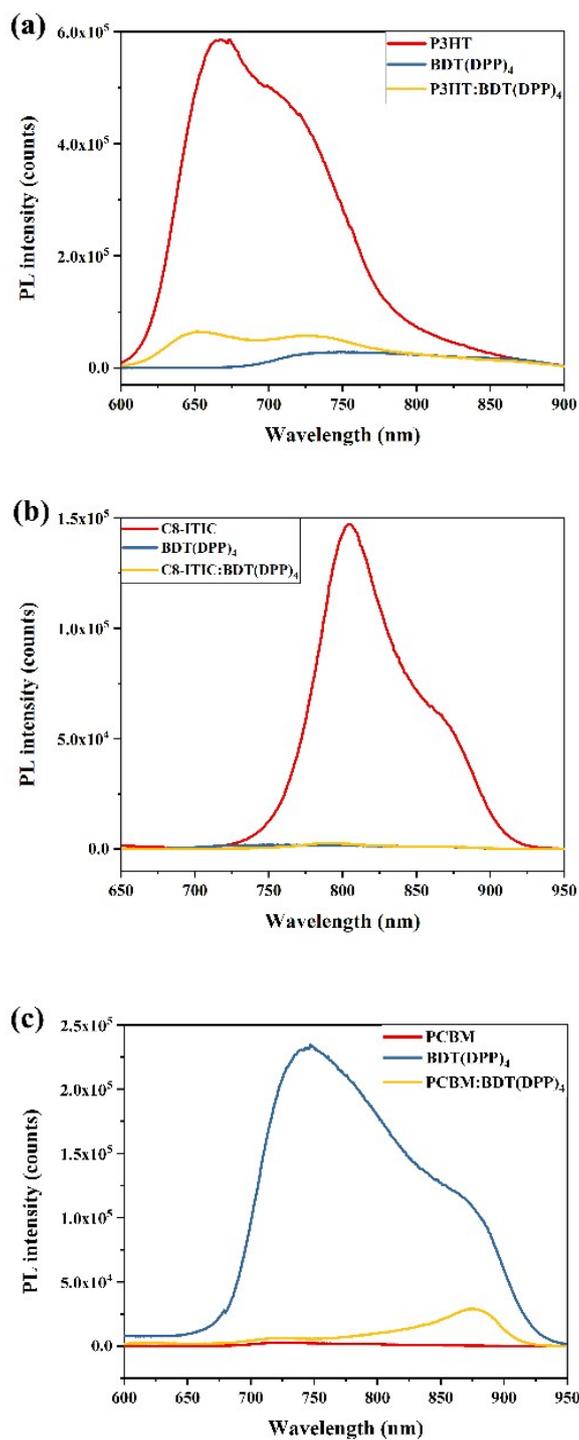


Fig. S5 Photoluminescence spectra of (a) P3HT:BDT(DPP)<sub>4</sub> and its neat films excited at 520 nm; (b) BDT(DPP)<sub>4</sub>:C8-ITIC and its neat films excited at 600 nm; (c) BDT(DPP)<sub>4</sub>:PC<sub>71</sub>BM and its neat films excited at 520 nm.

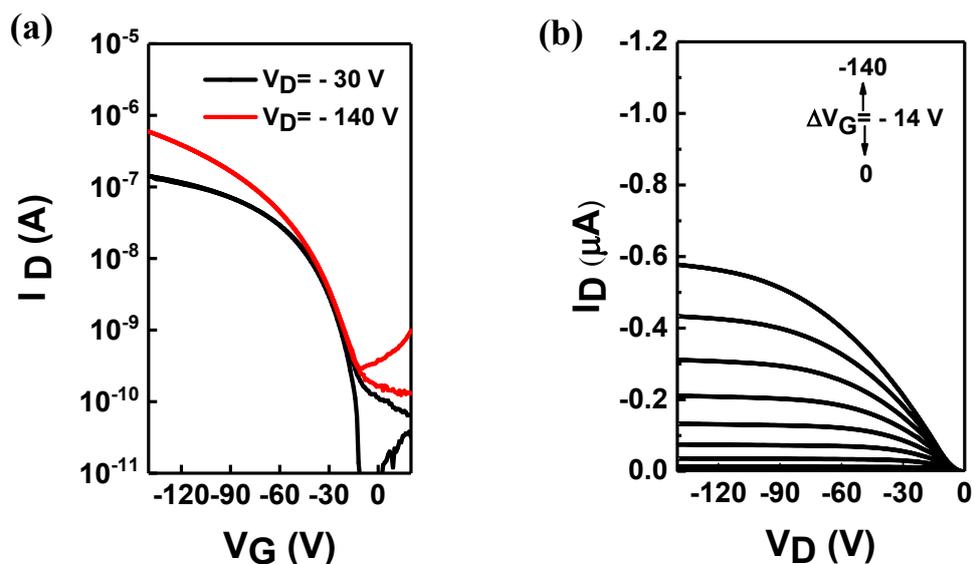


Fig. S6 (a) Typical transfer and (b) output characteristics of BC/TG configuration OFET device for BDT(DPP)<sub>4</sub> with a concentration of 10 mg ml<sup>-1</sup> in chlorobenzene.

Table S1 OSC device Performance of BDT(DPP)<sub>4</sub>

Blends	Post Deposition Treatment	Jsc [mA cm <sup>-2</sup> ]	Voc [V]	FF	PCE [%]
P3HT:BDT(DPP) <sub>4</sub> in CB, 2:1	-	1.44	0.71	0.28	0.28
P3HT:BDT(DPP) <sub>4</sub> in CB, 1:1	-	1.46	0.71	0.42	0.43
	Annealing 130°C, 10min	1.5	0.74	0.42	0.47
	Solvent Annealing	1.46	0.74	0.42	0.45
	DIO (2v %)	1.38	0.71	0.44	0.43
P3HT:BDT(DPP) <sub>4</sub> in CB, 1:2	-	1.35	0.66	0.27	0.24
P3HT:BDT(DPP) <sub>4</sub> in CF, 1:1	-	0.26	0.75	0.30	0.06
	Annealing 130°C, 10min	0.6	0.48	0.31	0.09
	Solvent Annealing	0.23	0.65	0.33	0.05

	DIO (2v %)	0.9	0.82	0.31	0.23
BDT(DPP) <sub>4</sub> :PC <sub>71</sub> BM in CB, 2:1	-	2.43	0.79	0.3	0.57
BDT(DPP) <sub>4</sub> :PC <sub>71</sub> BM in CB, 1:1	-	1.58	0.71	0.3	0.33
BDT(DPP) <sub>4</sub> :PC <sub>71</sub> BM in CB, 1:2	-	8.54	0.75	0.39	2.5
	Annealing 130°C, 10min	8.12	0.78	0.37	2.3
	Solvent Annealing	8.06	0.78	0.33	2.1
	DIO (2V %)	8.11	0.79	0.34	2.2
BDT(DPP) <sub>4</sub> :PC <sub>71</sub> BM in CF, 1:2	-	1.55	0.88	0.36	0.5
	Annealing 130°C, 10min	2.86	0.88	0.38	0.96
	Solvent Annealing	2.2	0.84	0.47	0.87
	DIO (2V %)	1.29	0.82	0.3	0.32
BDT(DPP) <sub>4</sub> :C8-ITIC in CB, 1:1	-	0.9	0.89	0.27	0.22
	Annealing 130°C, 10min	0.4	0.72	0.29	0.08
	Solvent Annealing	0.46	0.6	0.35	0.1
	DIO (2V %)	0.85	0.87	0.27	0.2
BDT(DPP) <sub>4</sub> :C8-ITIC in CF, 2:1	-	6.31	0.75	0.33	1.54
BDT(DPP) <sub>4</sub> :C8-ITIC in CF, 1:1	-	10.1	0.86	0.45	3.9
	Annealing 130°C, 10min	6.84	0.75	0.36	1.84
	Solvent Annealing	9.97	0.87	0.43	3.69
	DIO (2V %)	8.95	0.77	0.35	2.41
BDT(DPP) <sub>4</sub> :C8-ITIC in CF, 1:2	-	6.86	0.66	0.34	1.52

BDT(DPP) <sub>4</sub> :C8-ITIC in DCB, 1:1	-	0.92	0.83	0.27	0.2
BDT(DPP) <sub>4</sub> :C8-ITIC in toluene, 1:1	-	0.15	0.78	0.29	0.03
BDT(DPP) <sub>4</sub> :C8-ITIC in XY, 1:1	-	0.97	0.73	0.26	0.19

Table S2 Device Performance of BDT(DPP)<sub>4</sub> in chlorobenzene

Solvent	V <sub>T</sub> (V)	Linear Mobility (cm <sup>2</sup> /Vs)	Saturation Mobility (cm <sup>2</sup> /Vs)
CB	-35±2	0.0008±0.0002	0.0018±0.0003