Electronic Supplementary Information

Design, synthesis and photovoltaic properties of two π-bridged cyclopentadithiophene-based polymers

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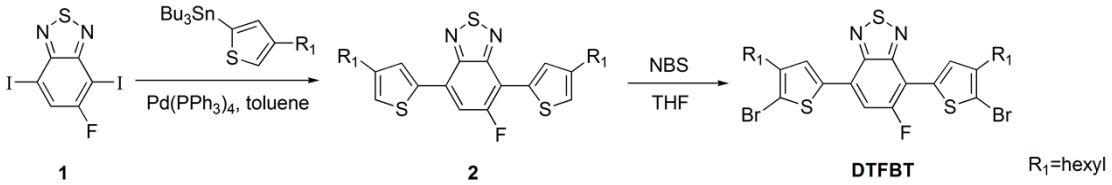
1. Synthesis of DTFBT



4,7-bis(4-hexylthienyl)-5-fluoro-2,1,3-benzothiadiazole (2)

In a 250 mL flame-dried 2-neck round-bottom flask with a condenser, 5-fluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (**1**) (1.22 g, 3.0 mmol), excess of (4-(2 -hexyl)thiophen-2-yl)tributylstannane (3.66 g, 8.0 mmol) and dry toluene 20 mL were added. The mixture was purged with argon for 15 min. Then $Pd(PPh_3)_4$ (30 mg) was added and the reaction mixture was heated to reflux for 24 h. The reaction mixture was then cooled to room temperature and the solvent was evaporated. The crude orange product was purified by column chromatography with hexane/dichloromethane (50:1 v/v) as eluent. The solvent was evaporated and the product was recrystallized from ethanol as orange solid. Yield: 1.02 g (70%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.10 (s, 1H), 7.99 (d, J = 1.0 Hz, 1H), 7.74 (d, J = 12.9 Hz, 1H), 7.15 (s, 1H), 7.09 (s, 1H), 2.74 – 2.67 (m, 4H), 1.77 – 1.63 (m, 4H), 1.44 – 1.23 (m, 12H), 0.90 (t, J = 6.8 Hz, 6H).

4,7-bis(5-bromo-4-hexylthienyl)-5-fluoro-2,1,3-benzothiadiazole (DTFBT)

Under nitrogen, to a solution of **2** (1.02 g, 2.1 mmol) in THF was added N-bromosuccinimide (NBS) (0.75 g, 4.2 mmol) in the dark. The reaction mixture was stirred at a room temperature for 8 h, and then the reaction mixture was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under a

reduced pressure. The product as an orange solid was obtained by recrystallization from iso-propanol. Yield: 1.15 g (85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.96 (s, 1H), 7.77 (s, 1H), 7.67 (d, J = 13.0 Hz, 1H), 2.69 – 2.60 (m, 4H), 1.67 (m, 4H), 1.43 – 1.31 (m, 12H), 0.90 (m, 6H).

2. X-ray Diffraction

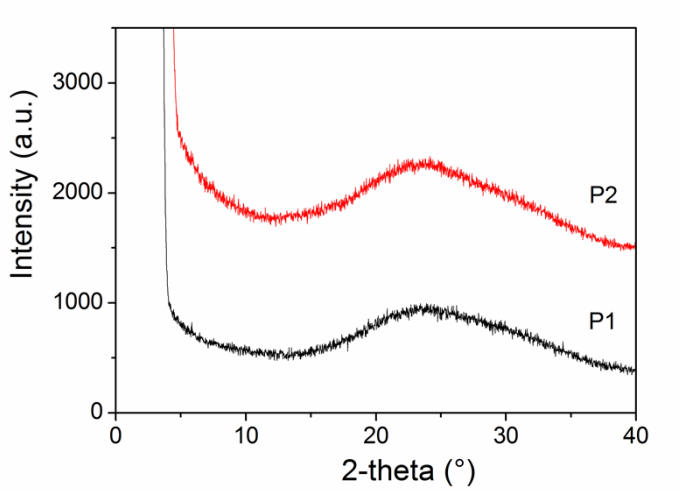


Fig. S1. Out-of-plane XRD patterns of **P1** and **P2** films. Curves are offset for clarity.

3. Detailed device parameters of PSCs

Table S1. PSCs performance with devices configuration ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al

Active layer	ratio	DIO (%)	spin-coating speed (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	PCE (%)
P1:$PC_{71}BM$	5:4	0	1250	0.75	7.68	40.2	2.32
P1:$PC_{71}BM$	5:4	1	1250	0.70	9.58	53.1	3.56
P1:$PC_{71}BM$	5:4	2	1250	0.67	10.88	64.6	4.71
P1:$PC_{71}BM$	5:4	3	1250	0.68	8.69	64.8	3.83
P1:$PC_{71}BM$	5:4	2	1000	0.68	9.29	64.2	4.06
P1:$PC_{71}BM$	5:4	2	1500	0.68	10.20	64.5	4.47
P1:$PC_{71}BM$	3:2	2	1250	0.70	9.50	65.1	4.33
P1:$PC_{71}BM$	1:1	2	1250	0.71	9.91	62.6	4.40

P1:$PC_{71}BM$	1:2	2	1250	0.70	6.62	63.8	2.96
P2:$PC_{71}BM$	5:4	0	1250	0.79	4.17	36.2	1.19
P2:$PC_{71}BM$	5:4	1	1250	0.64	8.06	48.3	2.49
P2:$PC_{71}BM$	5:4	2	1250	0.70	13.58	61.6	5.85
P2:$PC_{71}BM$	5:4	3	1250	0.68	12.92	64.4	5.66
P2:$PC_{71}BM$	5:4	2	1000	0.69	12.95	62.5	5.58
P2:$PC_{71}BM$	5:4	2	1500	0.70	13.04	62.1	5.67
P2:$PC_{71}BM$	3:2	2	1250	0.70	12.59	57.7	5.08
P2:$PC_{71}BM$	1:1	2	1250	0.69	13.20	63.1	5.75
P2:$PC_{71}BM$	1:1.5	2	1250	0.68	12.28	64.6	5.40
P2:$PC_{71}BM$	1:2	2	1250	0.69	9.78	62.6	4.22

4. Hole mobility

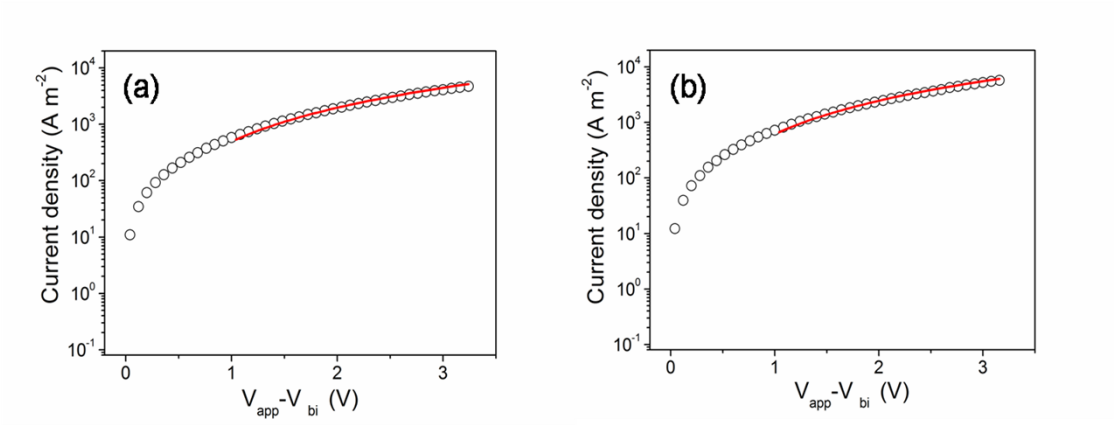


Fig. S2. Current density–voltage (*J-V*) curves for **P1**:$PC_{71}BM$ based device (a) and **P2**:$PC_{71}BM$ based device (b) (the symbols are experimental data for transport of hole, and the red line is fitted according to the space-charge-limited-current model). The devices were constructed as ITO/PEDOT:PSS (40 nm)/Polymer:$PC_{71}BM$ (130 nm)/MoO_3 (10 nm)/Al (100 nm).