Electronic supplementary information

Influence of 2,2-bithiophene and thieno[3,2-b] thiophene units on the photovoltaic performance of benzodithiophene-based wide-bandgap polymers

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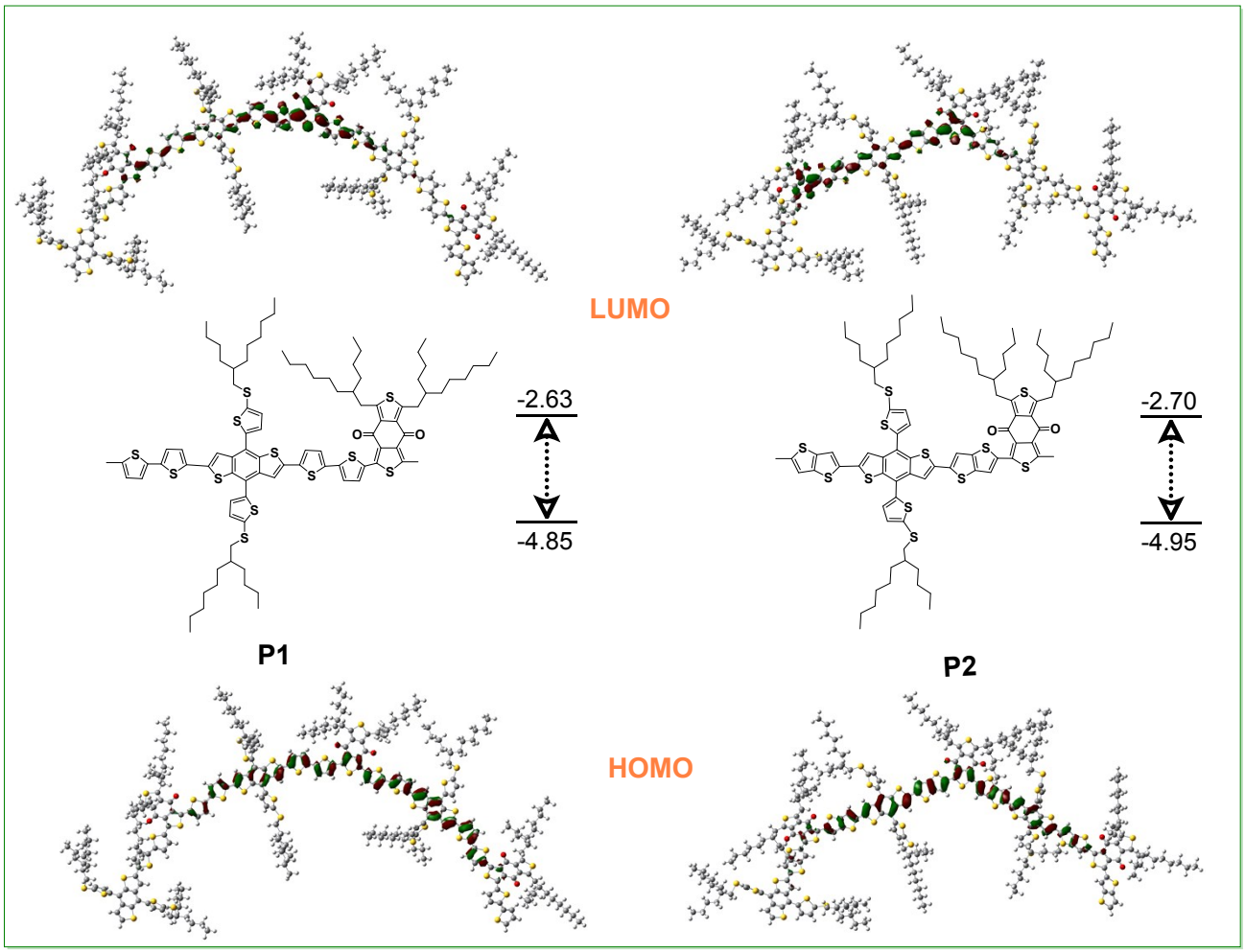

Figure S1. Theory calculated HOMO and LUMO electron density distributions for **P1** and **P2** by the DFT calculation at B3LYP/6-31G level

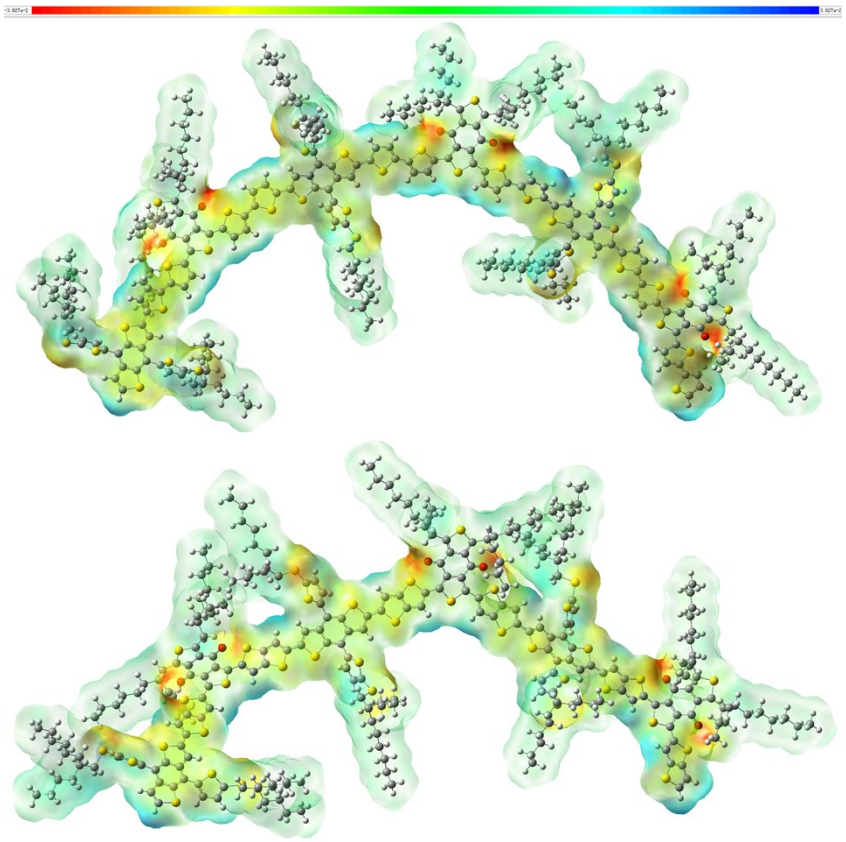

Figure S2. Map of the DFT electrostatic potential (ESP) surfaces of **P1** (up) and **P2** (down), dark color indicates greater negative charge, while white and grey colors indicate positive charges.

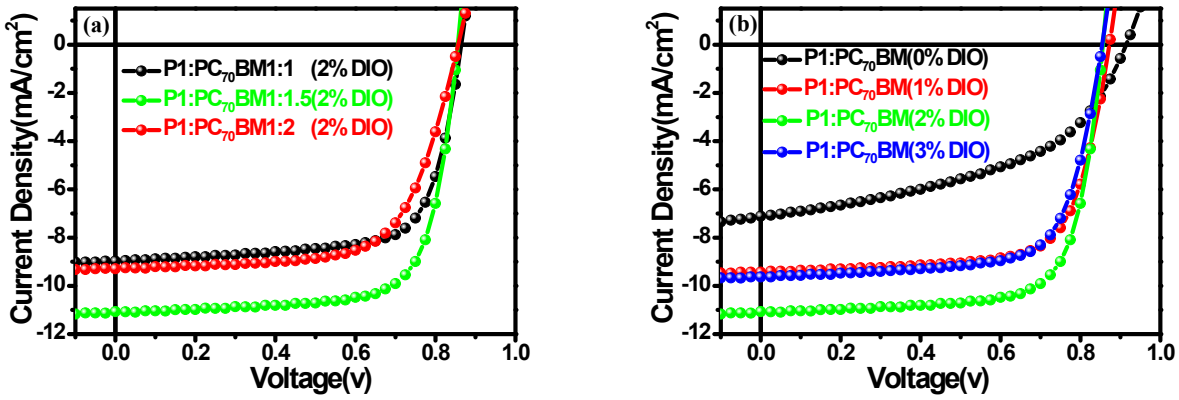

Figure S3. *J-V* curves of **P1**:$PC_{70}BM$ active layer a) different blend ratios (DIO 2%) and b) different concentration of DIO(**P1**:$PC_{70}BM$=1:1.5).

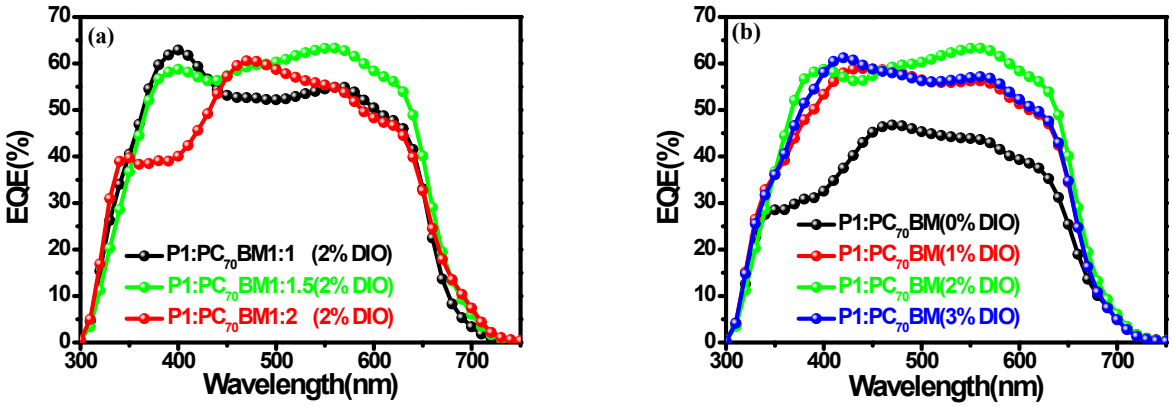

Figure S4. EQE curves of **P1**:$PC_{70}BM$ active layer a) different blend ratios (DIO 2%) and b) different concentration of DIO (**P1**:$PC_{70}BM$ =1:1.5).

Table S1. Photovoltaic parameters of PSCs with **P1**:$PC_{70}BM$ active layer in different blend ratios and different concentration of DIO

Ratio of D:A (w/w)	DIO (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE_{ave} (%)	PCE_{max} (%)
1:1	2	0.87	8.97±0.01	70.8±0.00	5.49±0.02	5.51
1:1.5		0.86	11.00±0.06	72.9±0.00	6.86±0.07	6.93
1:2		0.86	9.27±0.01	66.1±0.01	5.26±0.04	5.30
1:1.5	0	0.92	7.09±0.03	47.2±0.01	3.06±0.05	3.11
	1	0.87	9.43±0.01	70.4±0.00	5.79±0.05	5.84
	2	0.86	11.00±0.06	72.9±0.00	6.86±0.07	6.93
	3	0.85	9.57±0.05	70.4±0.00	5.75±0.05	5.80

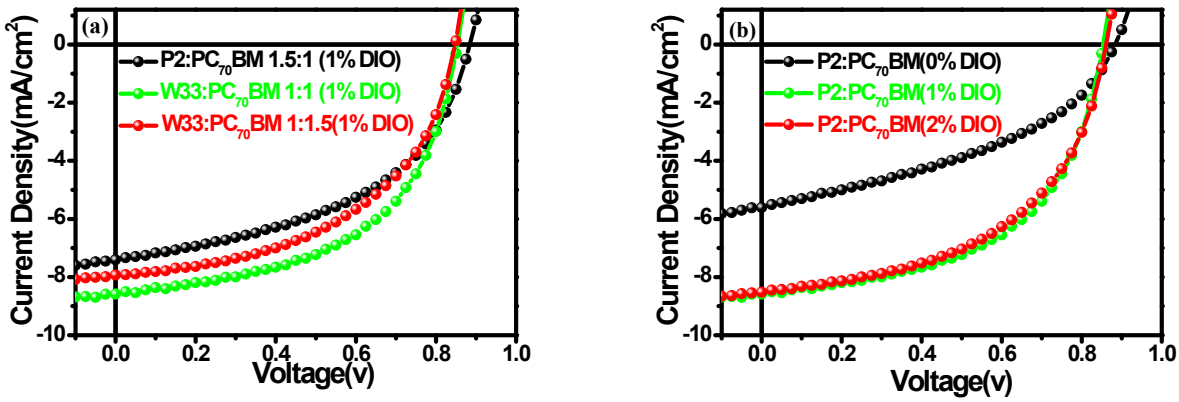

Figure S5. *J-V* curves of **P2**:$PC_{70}BM$ active layer a) different blend ratios (DIO 1%) and b) different concentration of DIO (**P2**:$PC_{70}BM$=1:1).

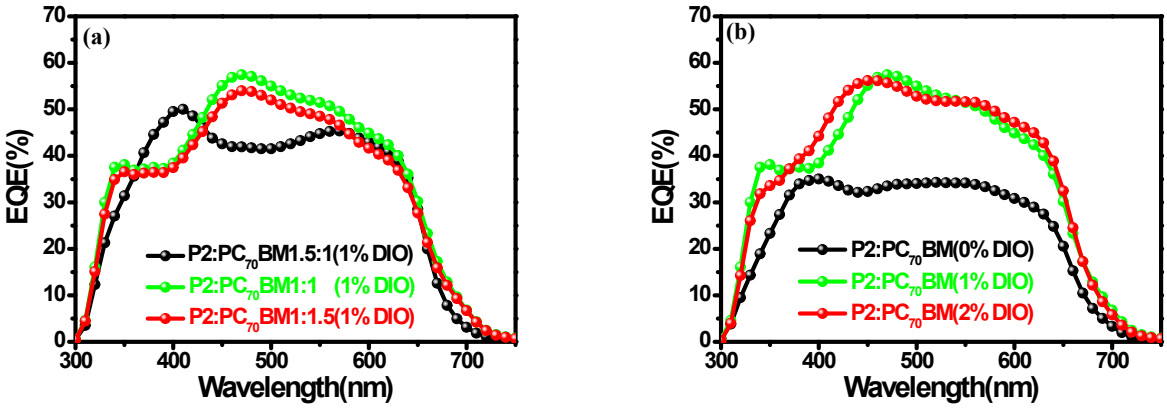

Figure S6. EQE curves of **P2**:$PC_{70}BM$ active layer a) different blend ratios (DIO 1%) and b) different concentration of DIO (**P2**:$PC_{70}BM$ =1:1).

Table S2. Photovoltaic parameters of PSCs with **P2**:$PC_{70}BM$ active layer in different blend ratios and different concentration of DIO

Ratio of D:A (w/w)	DIO (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE_{ave} (%)	PCE_{max} (%)
1.5:1		0.88	7.37±0.03	48.2±0.01	3.14±0.04	3.18
1:1	1	0.85	8.55±0.04	53.1±0.01	3.87±0.05	3.92
1:1.5		0.85	7.91±0.01	50.3±0.00	3.37±0.03	3.40
	0	0.88	5.60±0.01	40.5±0.00	2.00±0.02	2.02
1:1	1	0.85	8.55±0.04	53.1±0.01	3.87±0.05	3.92
	2	0.86	8.51±0.01	51.1±0.00	3.74±0.03	3.77

Table S3. The hole mobilities of **P1** and **P2** for pristine and blend films

sample	Hole moobilities(cm^2 V^{-1} s^{-1})
P1	1.62×10^{-3}
P2	1.17×10^{-3}
P1:$PC_{70}BM$ (1:1.5)	9.86×10^{-4}
P2:$PC_{70}BM$ (1:1)	6.82×10^{-4}
P1:$PC_{70}BM$ (1:1.5, 2%DIO)	1.22×10^{-3}
P2:$PC_{70}BM$ (1:1, 1%DIO)	8.60×10^{-4}

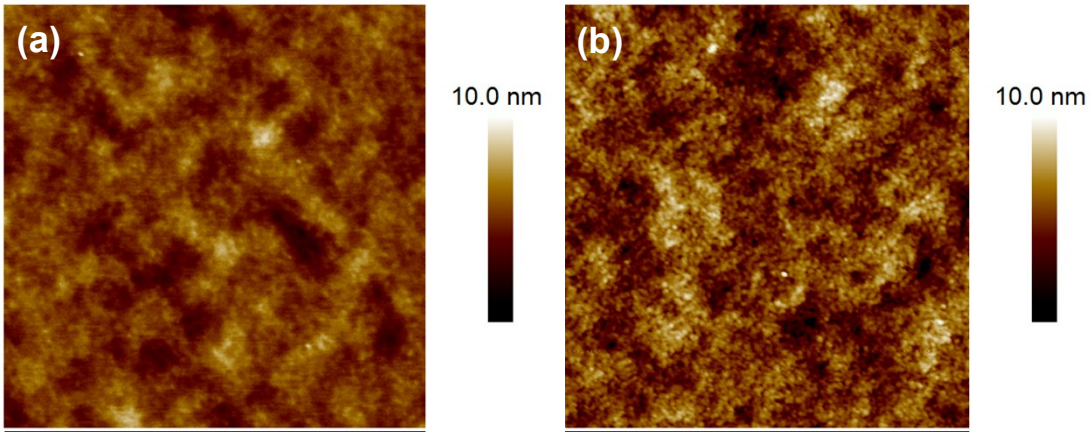

Figure S7. AFM height images of **P1** neat film, and b) **P2** neat film.

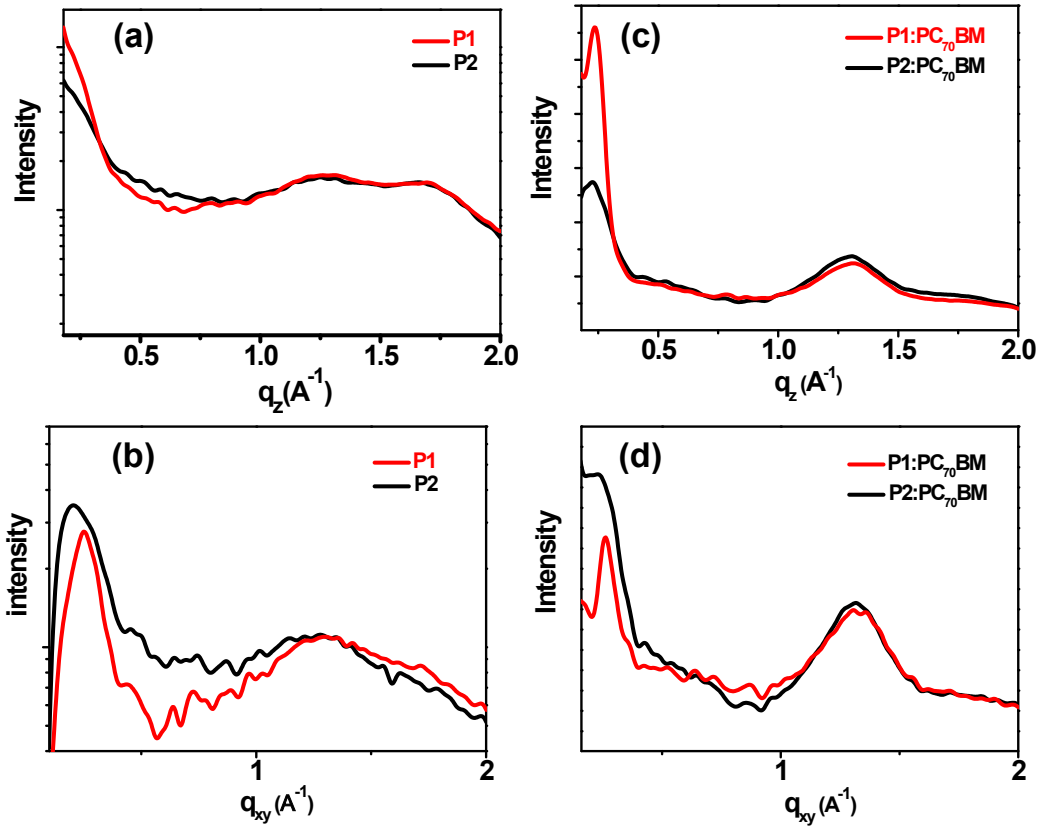

Figure S8. GIWAXS patterns of neat polymer and blend films. Out-of-plane linecut profiles of pristine films (a) and blend films (c) and In-plane linecut profiles of pristine films (b) and blend films (d).