Electronic Supplementary Information For

Effect of heteroatomic benzothienothiophenedione acceptor on

properties of a series of wide-bandgap photovoltaic polymers

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Figure S1. TGA thermograms of the copolymers of PBDT-O1, PBDT-S1 and PBDT-Se1 with a heating rate of 10°C min⁻¹ under nitrogen atmosphere



Figure S2. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT-O1:PC₇₀BM solar cells with different weight ratios.



Figure S3. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT-O1:PC₇₀BM solar cells with different DIO concentration at the blend ratio of 1:1.



Figure S4. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT-S1:PC₇₀BM solar cells with different weight ratios.



Figure S5. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT-S1:PC₇₀BM solar cells with different DIO concentration at the blend ratio of 1:1.



Figure S6. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT-Se1:PC₇₀BM solar cells with different weight ratios.



Figure S7. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT-Se1:PC₇₀BM solar cells with different DIO concentration at the blend ratio of 1:1.

Table S1. Photovoltaic performance of solar cells based on different weight ratios of PBDT-X1: $PC_{70}BM$ in a conventional structure under the illumination of AM1.5G, 100 mW/cm².

Active layer	Weight ratios (w/w)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDT-O1:PC ₇₀ BM	1:1.5	0.84	9.4	55.7	4.4
	1:1	0.86	9.3	63.3	5.1
	1.5:1	0.87	6.9	55.3	3.3
PBDT-S1:PC ₇₀ BM	1:1.5	0.89	12.6	68.8	7.7
	1:1	0.89	13.4	74.2	8.9
	1.5:1	0.91	11.5	69.3	7.2
PBDT-Se1:PC ₇₀ BM	1:1.5	0.84	11.7	71.6	7.1
	1:1	0.85	12.9	73.6	8.1
	1.5:1	0.90	11.6	50.7	5.3



Figure S8. AFM phase images. (a) PBDT-O1:PC₇₀BM blend film, (b) PBDT-O1:PC₇₀BM blend film with 0.5% DIO, (c) PBDT-S1:PC₇₀BM blend film, (d) PBDT-S1:PC₇₀BM blend film with 0.5% DIO, (e) PBDT-Se1:PC₇₀BM blend film, (f) PBDT-Se1:PC70BM blend film with 0.5% DIO