

Electronic Supplementary Information For:

Binary additives synergistically boost the efficiency of all-polymer solar cells up to 3.45%

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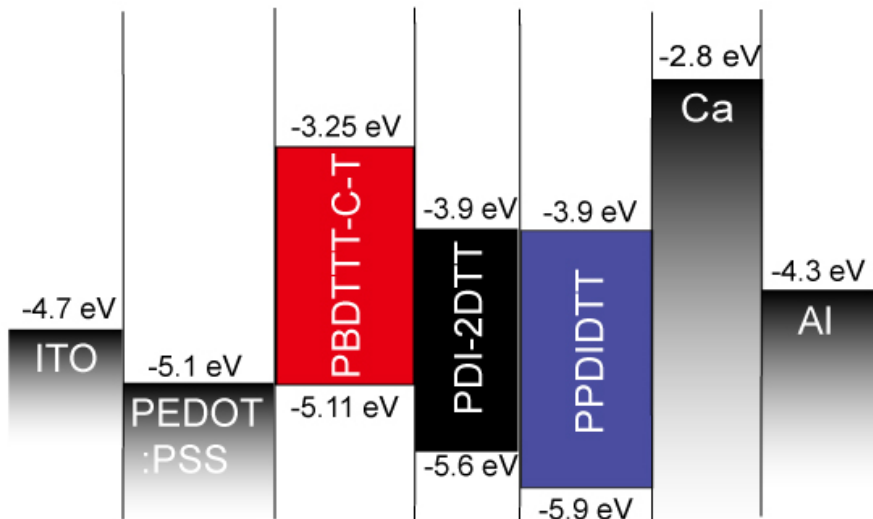


Fig. S1. Schematic energy level diagram for all-PSCs based on PBDTTT-C-T: PPDIDTT blend.

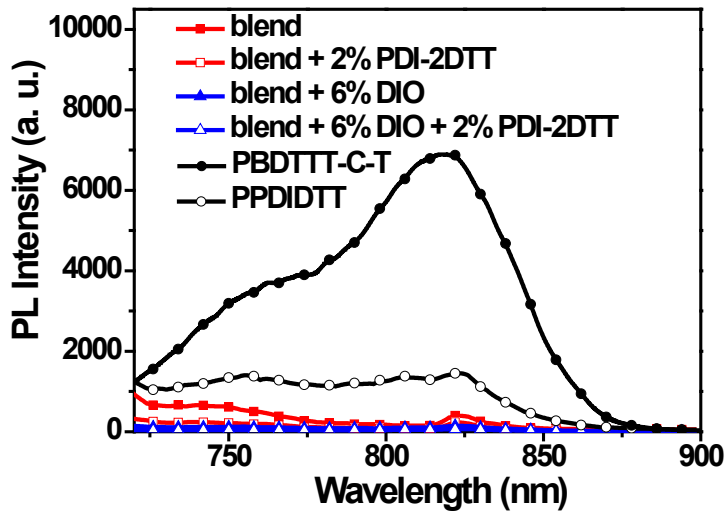


Fig. S2. Emission spectra of PBDTTT-C-T, PPDIDTT, PBDTTT-C-T: PPDIDTT (1:1, w/w) blend films without or with additives.

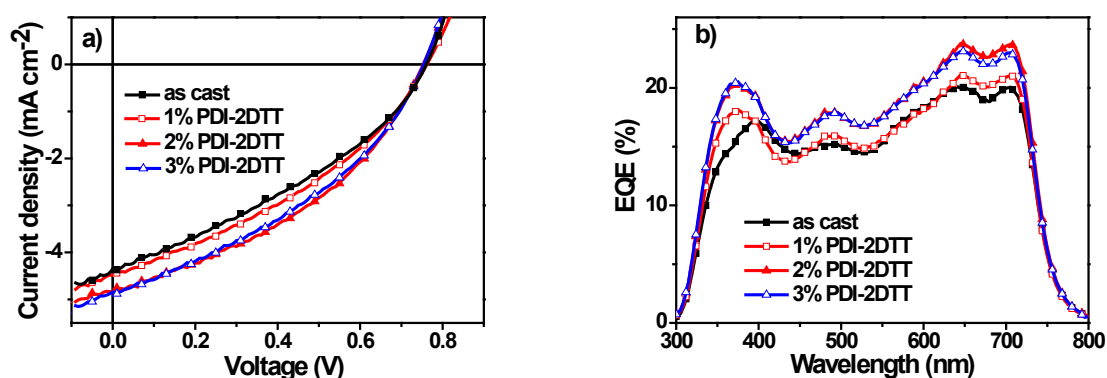


Fig. S3. a) J - V curves and b) EQE spectra of devices with the structure ITO/PEDOT: PSS/PBDTTT-C-T: PPDIDTT (1:1 w/w)/Ca/Al with different amount of nonvolatile additive PDI-2DTT under the illumination of an AM 1.5G solar simulator, 100 mW cm^{-2} .

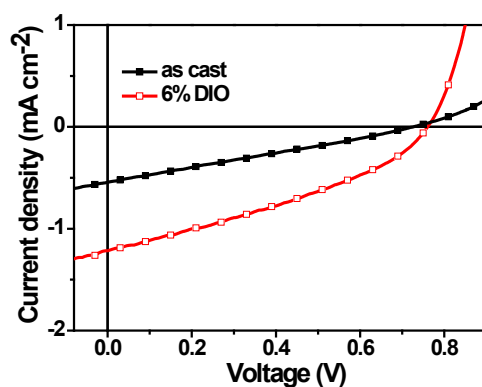


Fig. S4. J - V curves of devices with the structure ITO/PEDOT: PSS/PBDTTT-C-T: PDI-2DTT (1:1, w/w)/Ca/Al without or with solvent additive DIO under the illumination of an AM 1.5G solar simulator, 100 mW cm^{-2} .

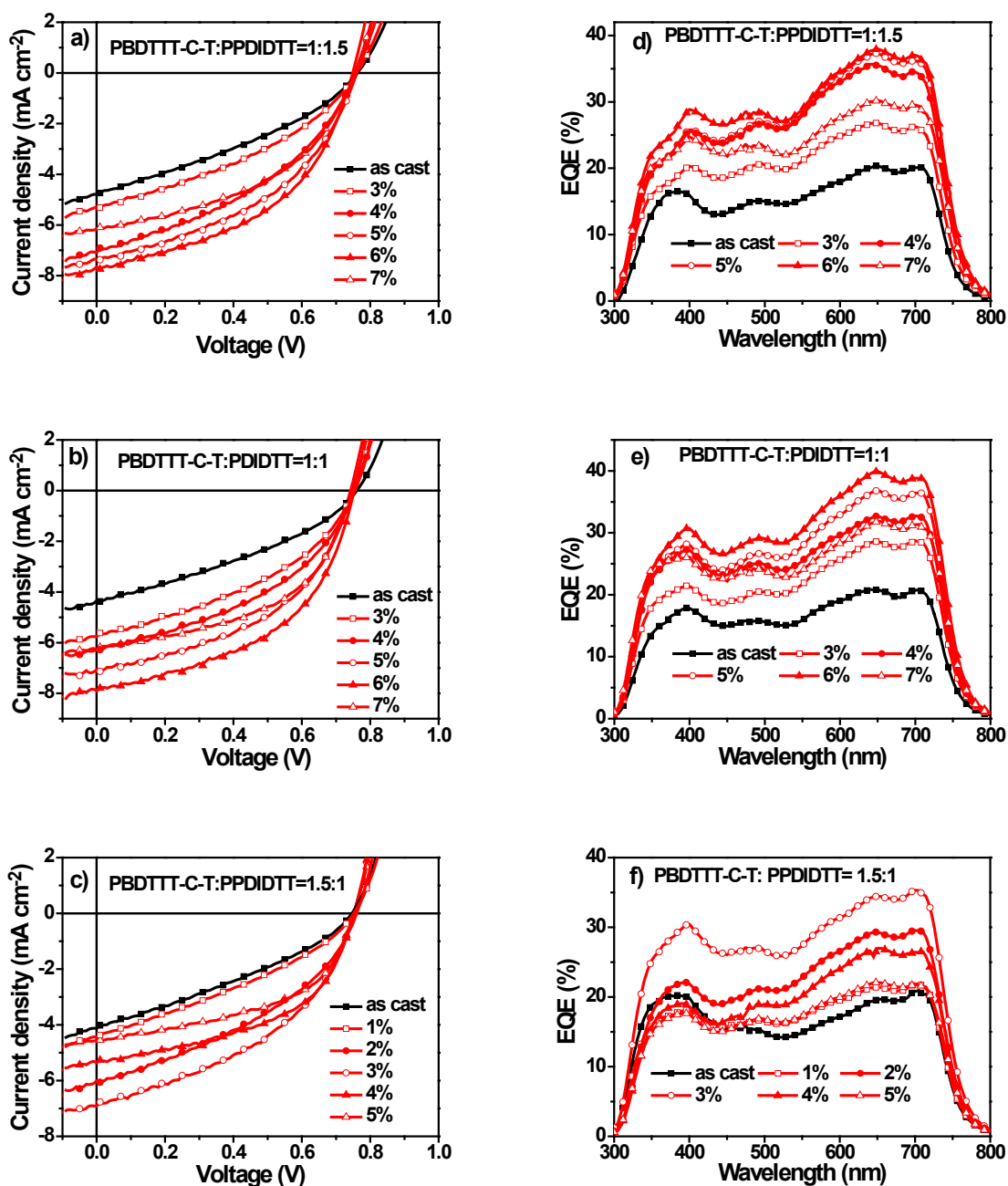


Fig. S5. a-c) $J-V$ curves and d-f) EQE spectra of devices with the structure ITO/PEDOT: PSS/PBDTTT-C-T: PPDIDTT/Ca/Al in different ratio of donor/acceptor with different amount of solvent additive DIO under the illumination of an AM 1.5G solar simulator, 100 mW cm^{-2} .

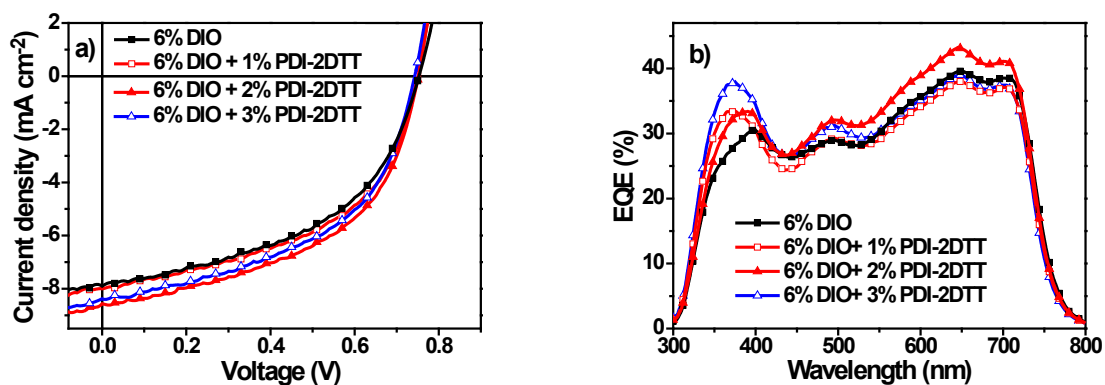


Fig. S6. a) J - V curves and b) EQE spectra of devices with the structure ITO/PEDOT: PSS/PBDTTT-C-T: PPDIDTT(1:1, w/w, 6% DIO)/Ca/Al with different amount of nonvolatile additive under the illumination of an AM 1.5G solar simulator, 100 mW cm⁻².

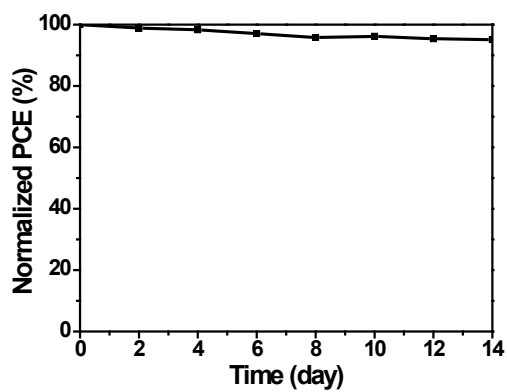


Fig. S7. Long-term stability of All-PSCs.

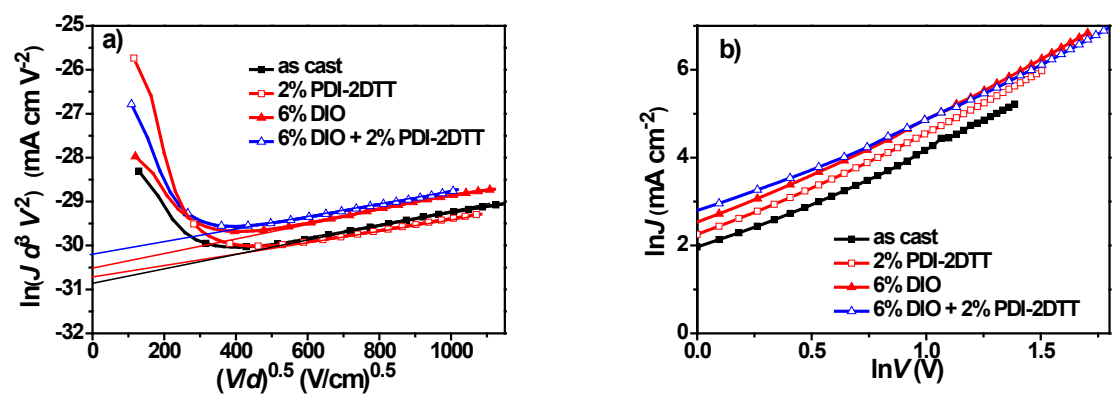


Fig. S8. J - V characteristics under dark for a) hole-only and b) electron-only devices based on blend films of PBDTTT-C-T: PPDIDTT (1:1, w/w) without or with additives.

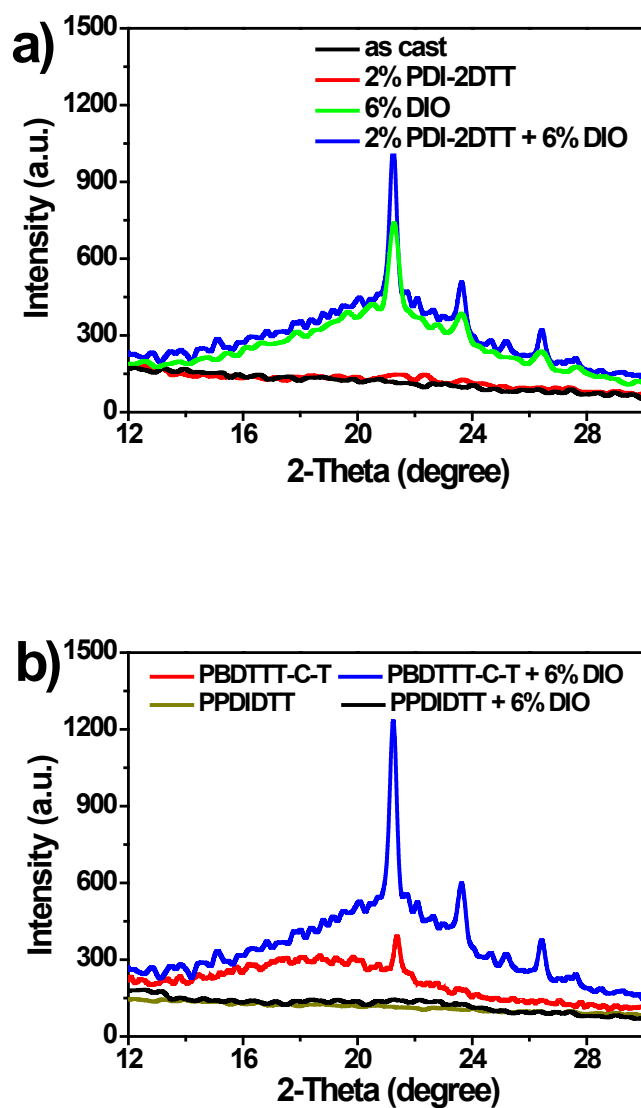


Fig. S9. XRD patterns of a) PBDTTT-C-T: PPDIDTT (1:1, w/w) blend films without or with additives and b) PBDTTT-C-T and PPDIDTT without or with DIO.

Table S1. Average and best device data in different ratio of donor/acceptor with different amount of solvent additive DIO

PBDTTT-C-T:PPDIDTT	DIO (v/v, %)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)	PCE (%)	
							average	best
1:1.5	None	0.764	4.73	0.337	49.0	257.5	1.22	1.27
1:1.5	3	0.761	5.29	0.372	47.1	277.9	1.50	1.55
1:1.5	4	0.760	6.93	0.394	31.4	282.2	2.08	2.13
1:1.5	5	0.761	7.37	0.445	24.1	287.5	2.50	2.57
1:1.5	6	0.751	7.65	0.456	19.9	320.7	2.62	2.68
1:1.5	7	0.755	6.17	0.470	27.1	445.4	2.19	2.28
1:1	None	0.761	4.34	0.350	50.4	248.3	1.16	1.18
1:1	3	0.751	5.65	0.398	30.5	273.7	1.69	1.78
1:1	4	0.756	6.28	0.419	29.8	282.2	1.99	2.13
1:1	5	0.750	7.06	0.472	20.8	293.1	2.50	2.62
1:1	6	0.753	7.92	0.489	17.5	327.4	2.92	3.04
1:1	7	0.743	6.24	0.509	21.6	477.6	2.36	2.45
1.5:1	None	0.747	4.11	0.319	56.8	260.0	0.98	1.03
1.5:1	1	0.752	4.31	0.328	47.8	272.3	1.06	1.10
1.5:1	2	0.761	5.97	0.389	28.5	281.8	1.77	1.78
1.5:1	3	0.753	6.85	0.434	23.6	335.5	2.24	2.31
1.5:1	4	0.753	5.30	0.496	25.1	481.1	1.98	2.18
1.5:1	5	0.753	4.53	0.503	26.4	627.7	1.72	1.73