Supporting Information for

To enhance the molecular aggregation and decrease the optical gap by the dual-additive to reduce the energy loss of all-polymer organic solar cells

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1. Device Characterization

The current density–voltage (*J-V*) characteristics were tested under AM 1.5G irradiation (100 mW cm^{-2}) using a Keithley 2400 source meter. A QE-R 3011 was employed to give EQE data. EQE_{EL} measurements were performed by applying external voltage/current sources through the devices (REPS, Enlitech). The FTPS-EQE measurement was carried out on an Enlitech FTPS PECT-600 instrument.

2. Device performance:*J-V* Measurement

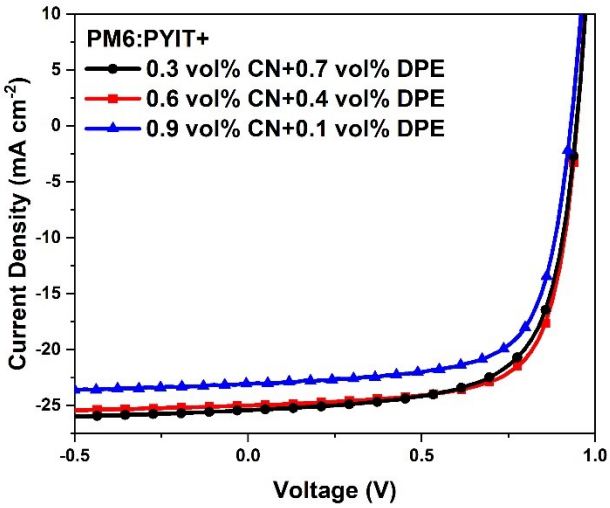

Figure S1. *J-V* curves of the optimal binary OSCs with different additives under the illumination of AM 1.5G, 100 mW cm^{-2}.

3. Stability Test

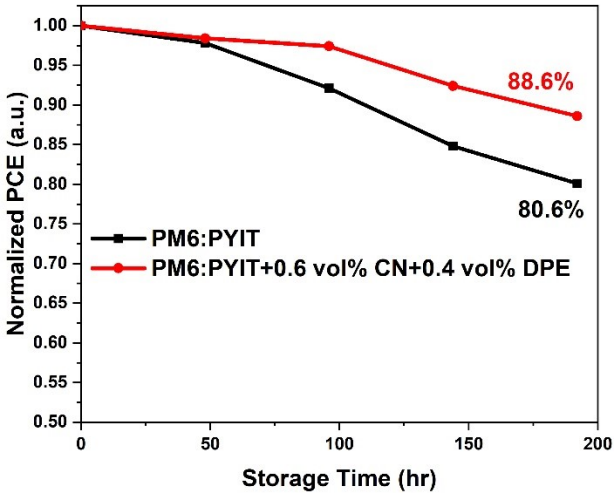

Figure S2. Storage stability in a nitrogen-filled glove of the un-encapsulated PM6:PYIT devices with no additive treatment and dual-additive treatment.

4. Testing for E_g

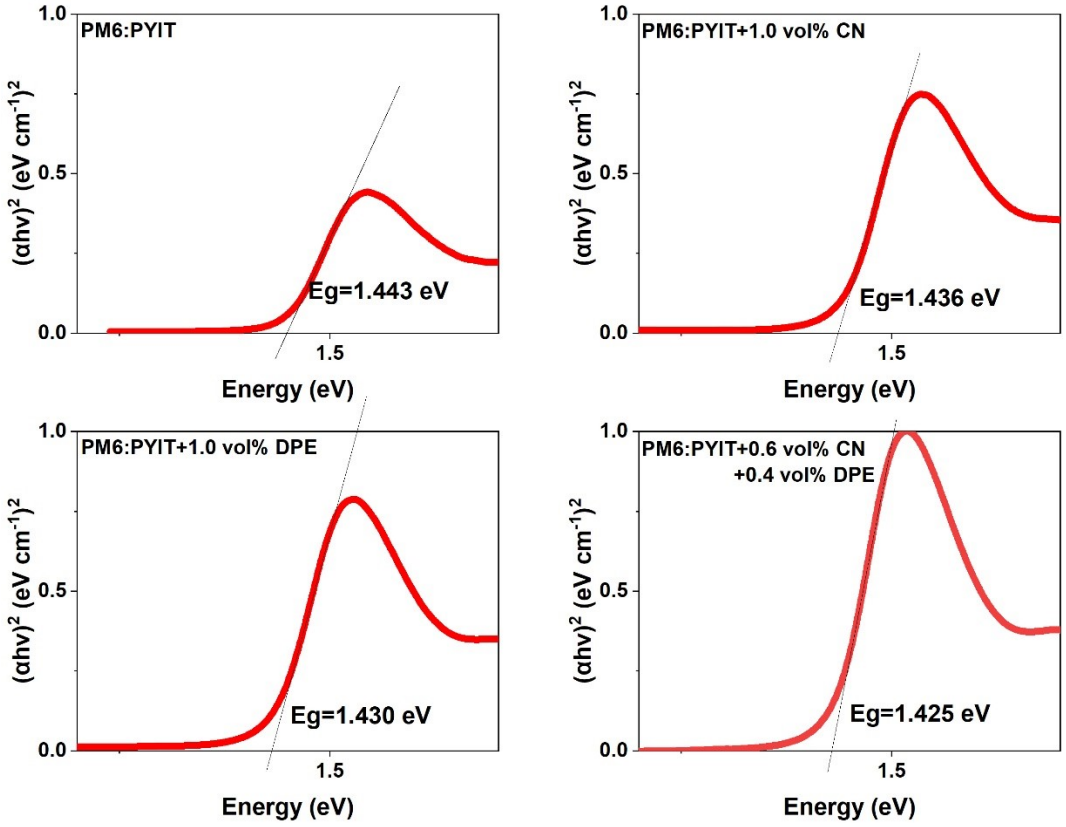

Figure S3. Changes in E_g of devices treated with different additives.

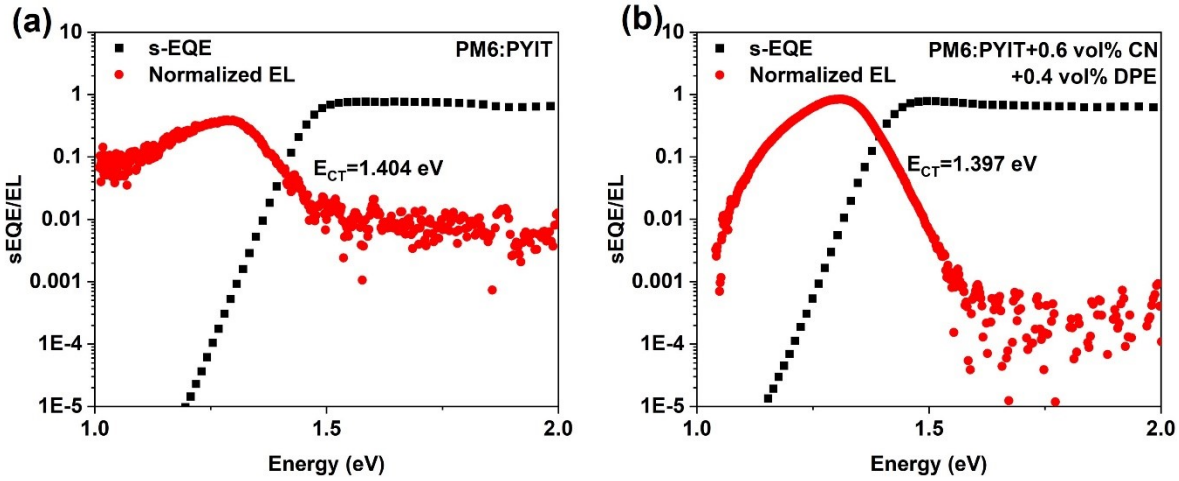

Figure S4. sEQE and EL spectra of devices treated with no additive and dual-additive.

5. AFM Measurement

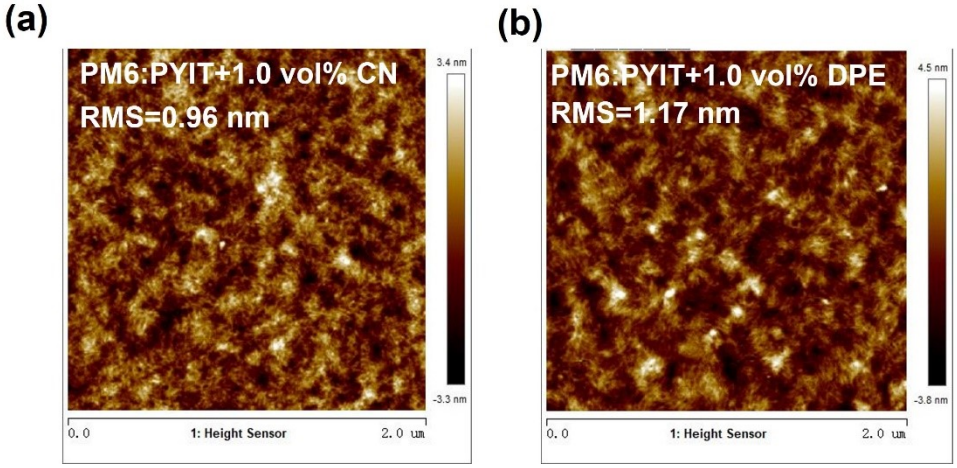

Figure S5. The AFM height images of PM6:PYIT active layers (a) with CN (b) with DPE.

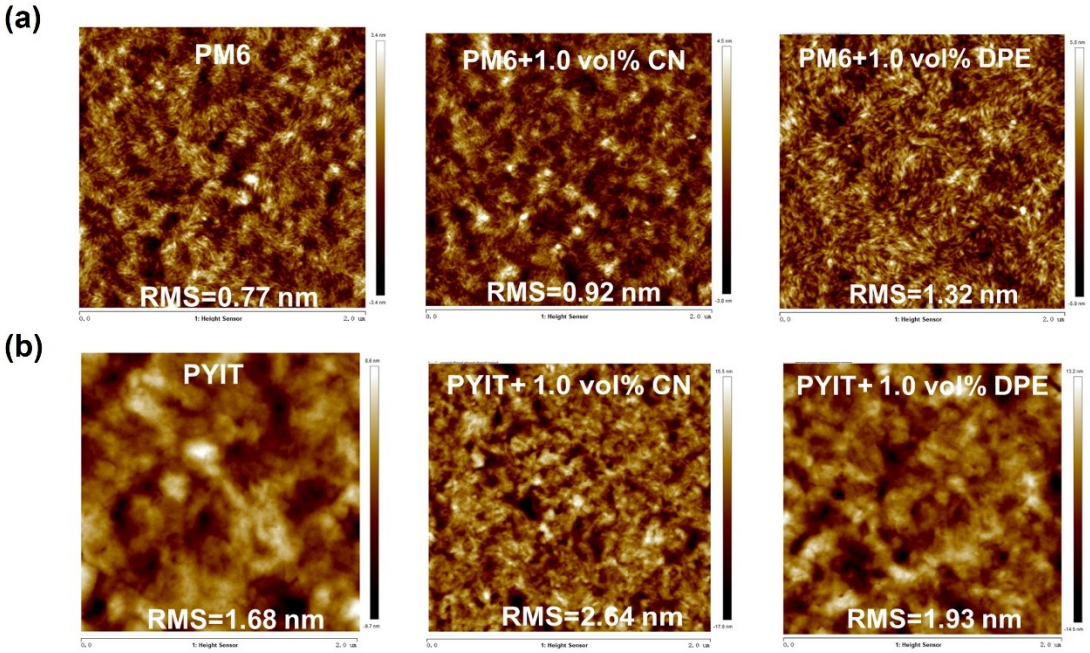

Figure S6. The AFM images of (a) PM6 pure films with different additives; (b) PYIT pure films with different additives.

6. Film-Depth-Dependent Light Absorption Spectroscopy

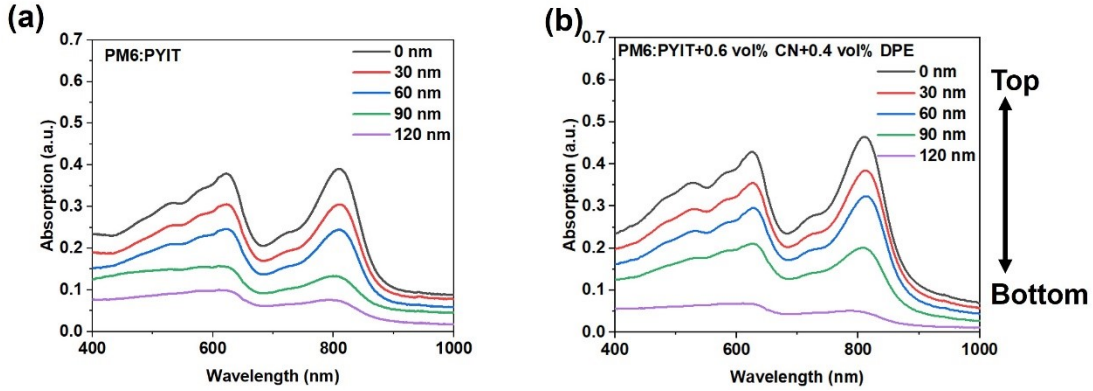

Figure S7. Film-depth-dependent-light absorption spectroscopy of (a) no additive and (b) dual-additive treated PM6:PYIT blend films.

7. Contact angle measurement.

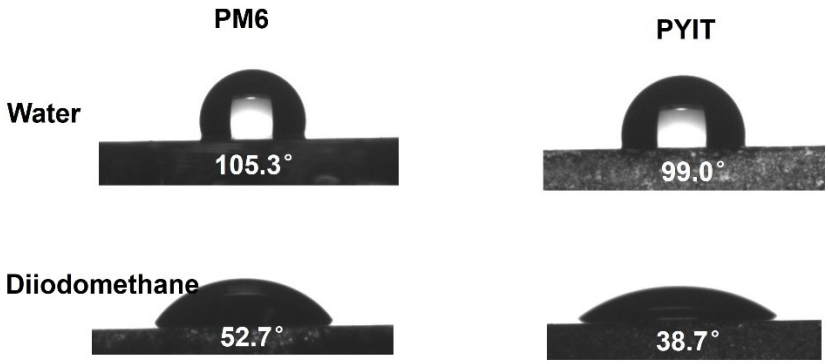

Figure S8. Contact angle images of neat PM6 and PYIT films.

8. UV-vis Absorption Spectroscopy

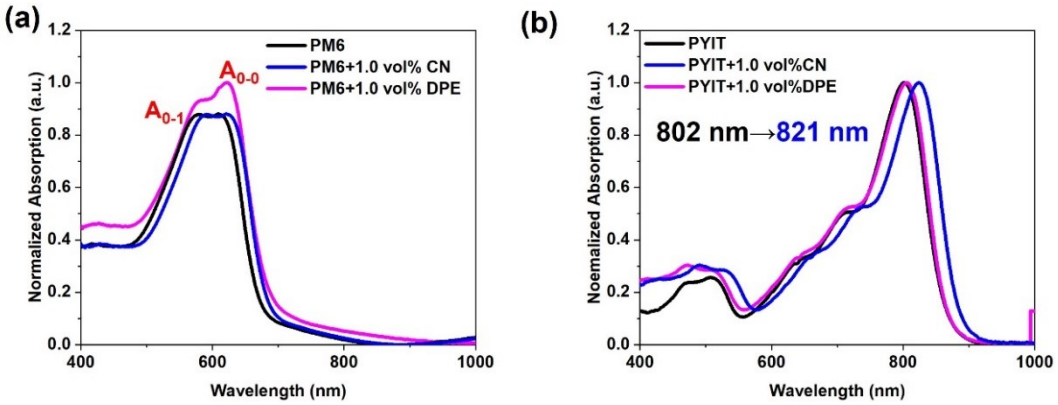

Figure S9. Normalized UV-vis absorption spectrum: (a) PM6 pure films with different additives; (b) PYIT pure films with different additives.

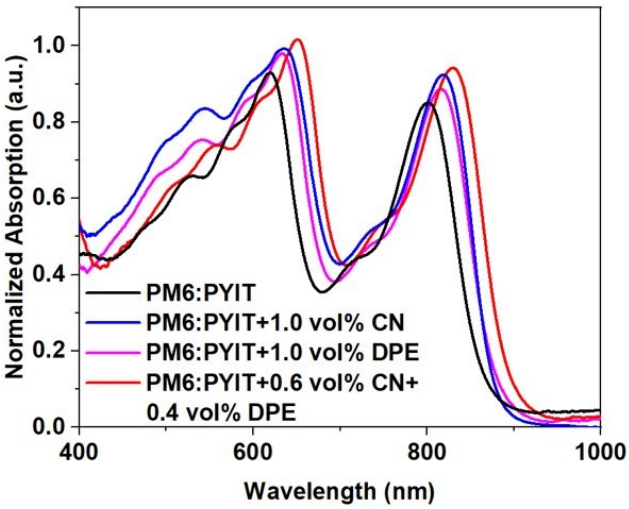

Figure S10. The Normalized absorption spectra of the PM6:PYIT BHJ active layer prepared under different processing conditions.

9. GIWAXS Measurement

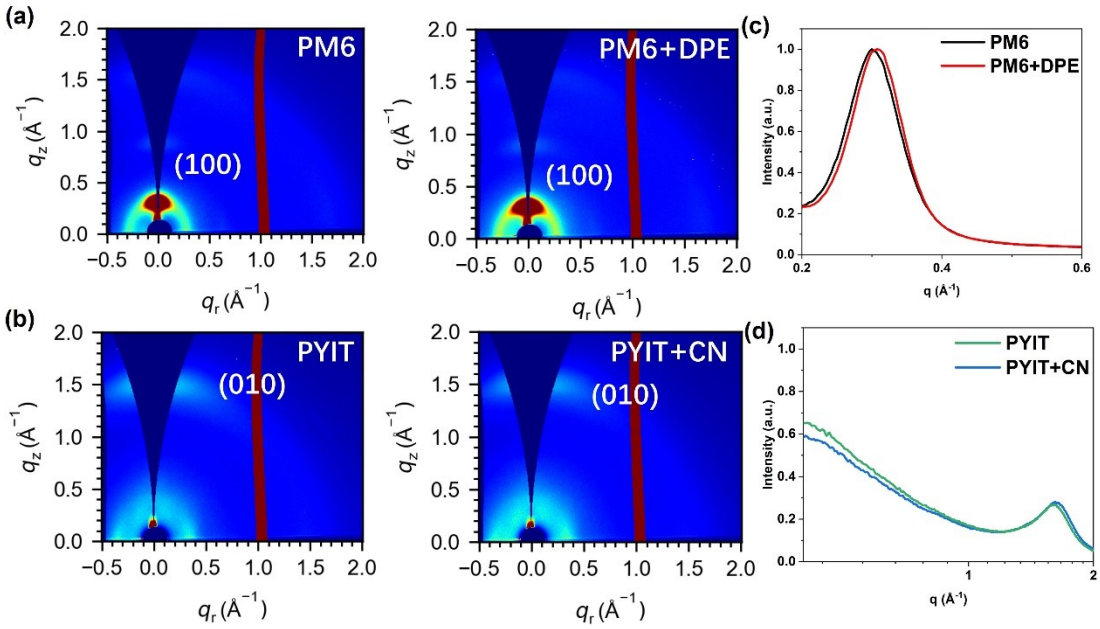

Figure S11. 2D GIWAXS images of (a) PM6 and (b) PYIT neat films before and after adding additives; The one-dimensional integrated signal of the (c) PM6 (100) peak and the (d) PYIT (010) peak in the out-of-plane direction.

10. Auxiliary Table

Table S1. Photovoltaic performance parameters of the OSCs based on PM6:PYIT with different additives.

Additive condition	J_{SC} (mA/cm^2)	V_{OC}(V)	FF(%)	PCE(%)
0.3 vol% CN+0.7 vol% DPE	25.39 (25.01±0.31)	0.948 (0.947±0.001)	66.72 (66.43±1.39)	16.06 (15.77±0.46)
0.6 vol% CN+0.4 vol% DPE	24.99 (24.82±0.18)	0.949 (0.946±0.002)	70.26 (70.27±0.42)	16.67 (16.50±0.14)
0.9 vol% CN+0.1 vol% DPE	22.35 (21.98±0.33)	0.939 (0.937±0.002)	71.17 (71.15±0.15)	14.94 (14.65±0.28)

Table S2. Specific numerical changes of BHJ PM6: PYIT absorption peak under different processing conditions.

Devices	(PM6)$A_{0\text{-}0}/A_{0\text{-}1}$	PM6 peak position	PYIT peak position
PM6:PYIT	1.14	618 nm	801 nm
PM6:PYIT+1.0 vol% CN	1.06	630 nm	817 nm
PM6:PYIT+1.0 vol% DPE	1.17	634 nm	813 nm
PM6:PYIT+0.6 vol% CN+0.4 vol% DPE	1.19	647 nm	825 nm

Table S3. Parameters related to (010) diffraction peaks in the out-of-plane direction of

PM6:PYIT thin films.

Samples	q(Å^{-1})	d-spacing (Å)	FMHW(Å^{-1})	CCL(Å)
Control	1.58	3.97	0.389	14.36
+CN	1.60	3.92	0.359	15.56
+DPE	1.60	3.92	0.362	15.43
Dual Additive	1.64	3.82	0.258	21.66

Table S4. GIWAXS Parameters of the out-of-plane (100) peak in the blend films.

Samples	q(Å^{-1})	d-spacing (Å)	FMHW(Å^{-1})	CCL(Å)

Control	0.31	20.25	0.085	65.75
+CN	0.32	19.62	0.081	69.01
+DPE	0.31	20.25	0.065	85.98
Dual Additive	0.34	18.47	0.063	88.71