Supporting Information

High Performance All-Polymer Solar Cells Enabled with Solvent and Solid Dual Additives

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Experimental Section

Materials

PM6, PY-DT, PY-IT, PYF-T-o, PNDIT:F3N and DCA were acquired from Solarmer Materials. Inc. Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS, clevios PVP Al 4083) were purchased from H.C. Starck Co. Ltd and used as received.

Device Fabrication

Conventional device structure of ITO/PEDOT:PSS/active layers/ PNDIT-F3N/Ag was employed to fabricate the organic solar cells (OSCs). ITO-coated glass substrates were pre-cleaned by a series of ultrasonic treatments in detergent, deionized water, acetone and propanol respectively. Afterwards, wet substrates were blow dried by pure nitrogen gas and then exposed to plasma cleaning for 1 min. Then PEDOT:PSS solution was spin coated on the ITO substrate at 3000 round per minute (RPM) for 20 seconds and baked at 150℃ for 15 minutes. Subsequently, the blend films were spin coated and then thermal annealed at 100 °C for 4 min. PNDIT-F3N solution (1.4 mg/ml in methanol with 0.5 vol% acetic acid) was spin-coated on the active layers at 4200 RPM for 30 seconds. Lastly, Ag (100 nm) was deposited by thermal evaporation at an active area of 4mm^2 under the vacuum condition of 2×10^{-4} Pa.

Fabrication details for the PM6:PY-DT based OSCs

PM6:PY-DT ratio was kept at 1:1.2 (w/w) with the donor's concentration of 6.5 mg/mL in chloroform. The optimal treatments involved were: 1% (v/v) CN; dual additives of 1% CN and 2.5 mgml^{-1} / 5 mgml^{-1} / 7.5 mgml^{-1} / 10 mgml^{-1} of DCA (weight ratio relative to solvent) followed by TA at 100 ℃ for 4 min. The photovoltaic parameters of the PM6:PY-DT based devices processed by various treatments are provided in Table S1.

Sample characterization

DSC measurements were taken using Perkin Diamond DSC instrument at a heating rate of 10 ºC in nitrogen atmosphere.

Rame-Hart Goiniometer was employed in sessile drop mode to carry out the contact angle measurements. The contact angles of neat PM6, PY-DT and DCA films corresponding to water and ethylene glycol (EG) were measured. To calculate the surface energy of neat films, Wu's model was used. Considering the surface energy of neat films, interfacial energy between two different materials in the blend films was evaluated by using following equation:[1,2]

$$\gamma_{X/Y} = \gamma_X + \gamma_Y - \frac{4\gamma_X^d\gamma_Y^d}{\gamma_X^d + \gamma_Y^d} - \frac{4\gamma_X^p\gamma_Y^p}{\gamma_X^p + \gamma_Y^p}$$

Here, $\gamma_{X/Y}$ is the interfacial energy between material X and Y; γ_X and γ_Y are the

surface tension of X and Y, and superscript *d* and *p* represent the dispersion of polar components calculated by using the contact angles.

Fabricated solar cells were characterized in nitrogen atmosphere under the room temperature conditions. The current density–voltage (*J–V*) graphs were obtained using Keithley 2400 source measure unit under 100 mW cm^{-2} simulated illumination and AM1.5G white light source. Next, the EQE spectra was measured with the help of Enlitech QE-R system.

UV-vis absorption spectra were attained using Agilent Cary 60 UV-vis Spectrophotometer by spin coating pure and blended films on quartz glass substrate. GIWAXS measurements were obtained using XEUSS SAXS/WAXS setup. Samples were prepared by spin costing same films on silicon substrates. AFM in the tapping mode is used for the morphology of active layer.

The mobilities of holes and electrons within the active layer of the device were determined using the space charge limited current (SCLC) technique. This involved creating a diode structure with ITO/PEDOT:PSS/active layer/MoO_3/Ag for measuring hole mobility, and ITO/ZnO/active layer/PNDIT-F3N/Ag for electron mobility. Dark current density measurements were conducted across a voltage range from 0 to 5 volts. The Mott-Gurney law was applied to the current density-voltage (*J-V*) curves to deduce the mobilities. According to this law, the space charge limited current (SCLC) can be described by the following equation:

$$J_{SCL} = 9\varepsilon\varepsilon_0\mu V^2/(8L^3)$$

Here, ε represents the dielectric constant of the active layer, ε_0 is the permittivity of free space (8.85419×10^{-12} $CV^{-1}m^{-1}$), μ denotes the zero-field mobility, J is the current density, L is the thickness of the active layer, and V is the voltage applied (V_{app}) to the device minus the built-in potential (V_{bi}). The built-in potential is the result of the work function difference between the anode and the cathode materials.

Supporting Figures

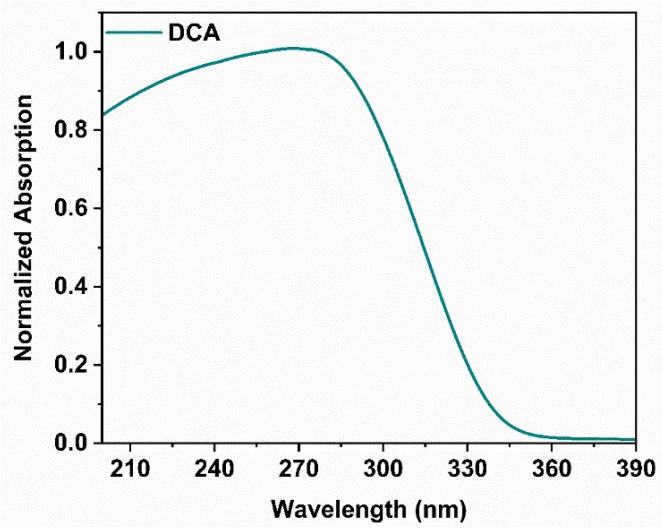

Fig. S1 Normalized absorption of DCA additive.

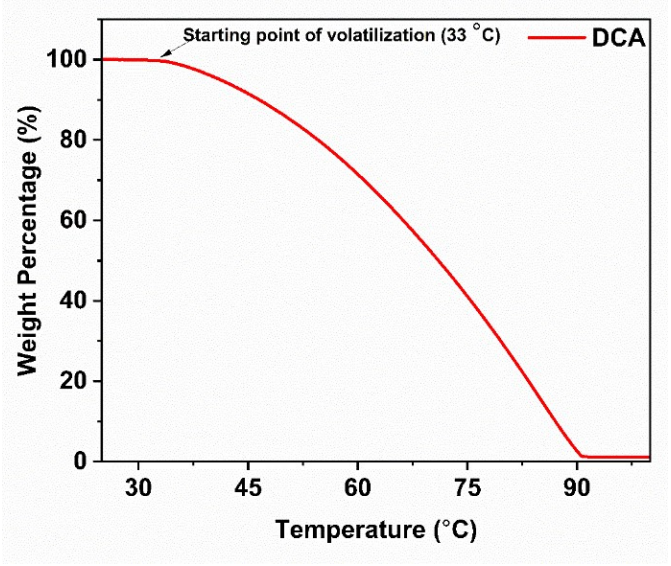

Fig. S2 TGA plot of DCA material at a scan rate of 2 °C min^{-1}.

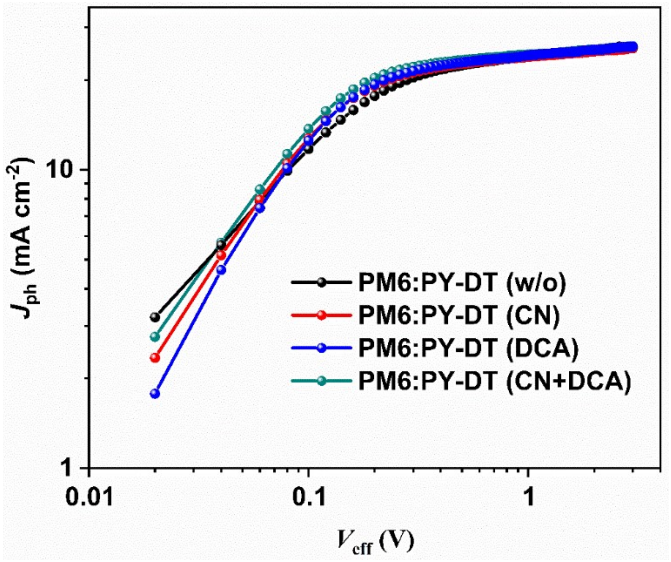

Fig. S3 V_{eff} vs J_{ph} graph of PM6:PY-DT processed under various conditions.

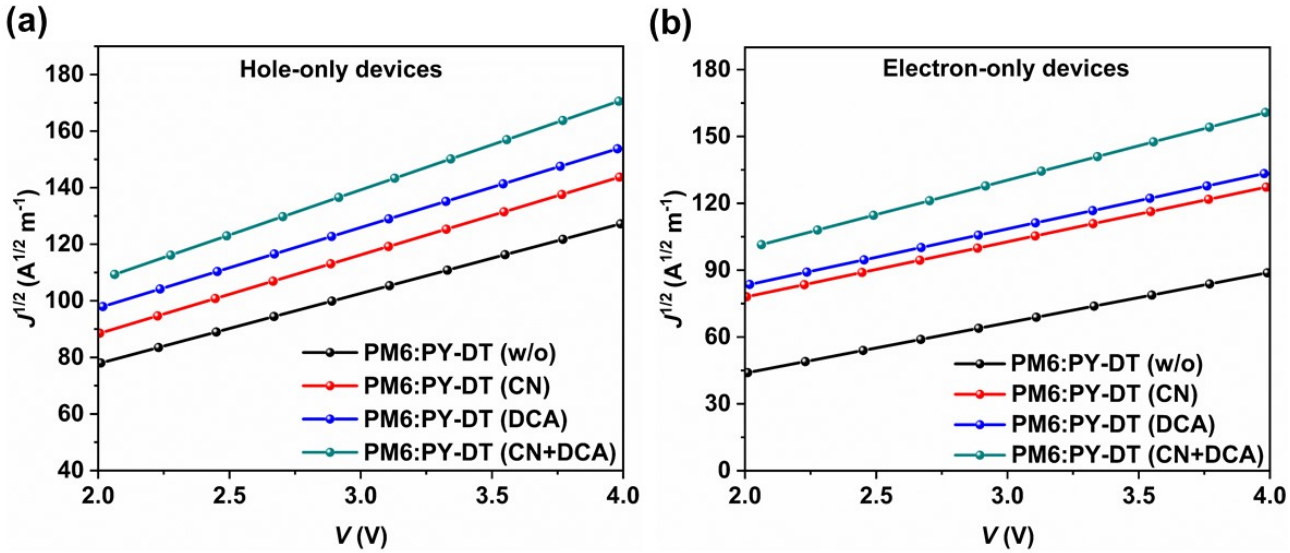

Fig. S4 $J^{1/2}-V$ plots of PM6:PY-DT processed under various conditions for (a) hole-only and b) electron-only devices determined by SCLC method.

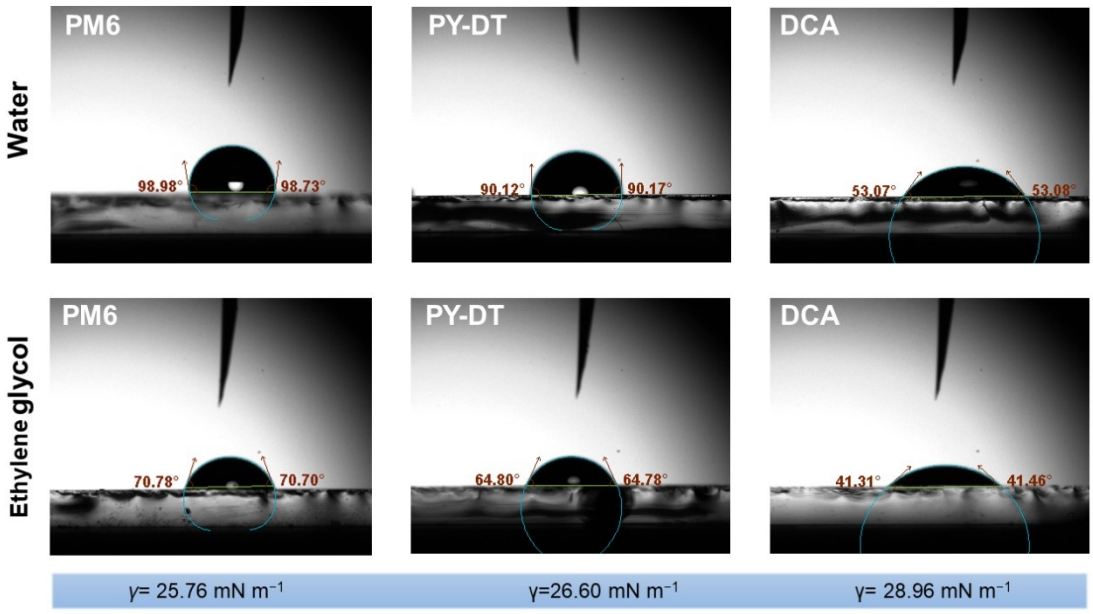

Fig. S5 Contact angle images of neat PM6, PY-DT and DCA films.

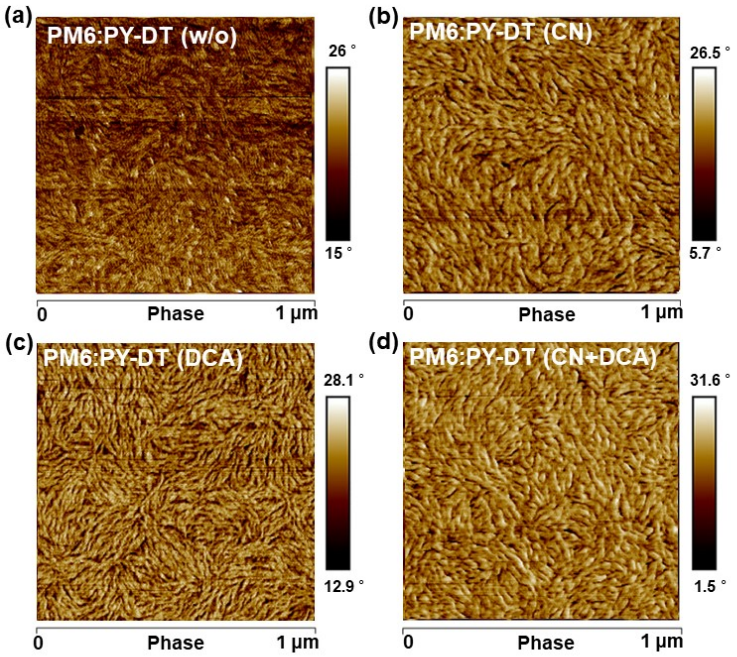

Fig. S6 (a-d) AFM phase images of the PM6:PY-DT blend films fabricated under various conditions.

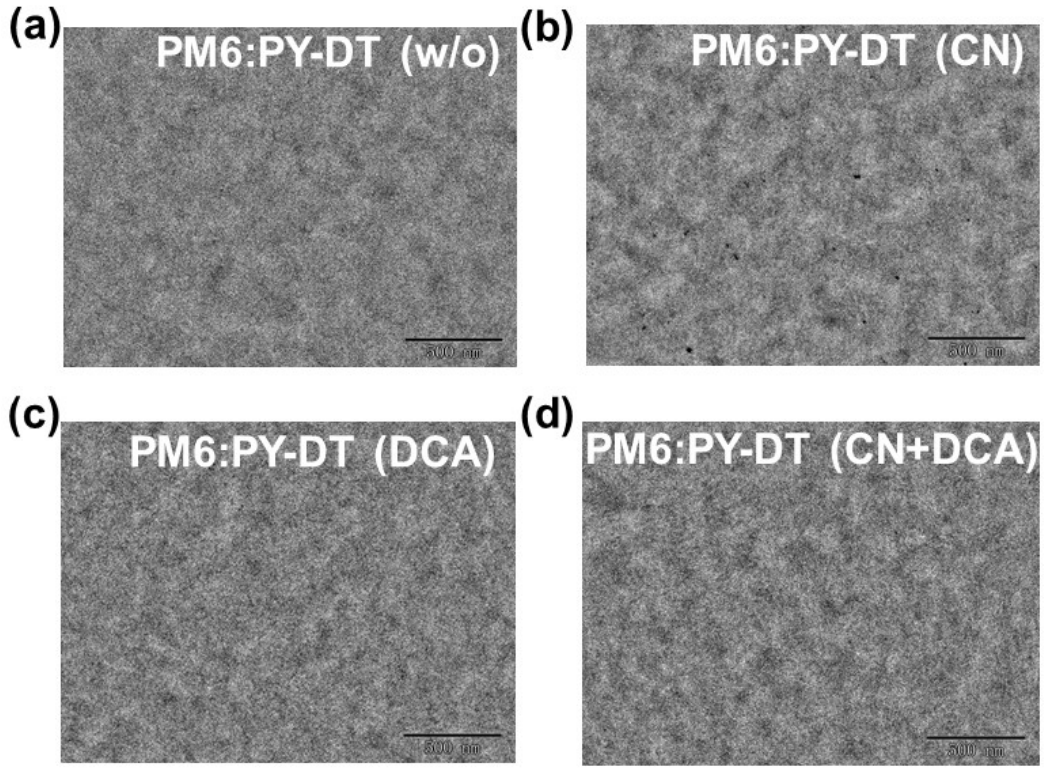

Fig. S7 (a-d) TEM images of the PM6:PY-DT blend films under various conditions.

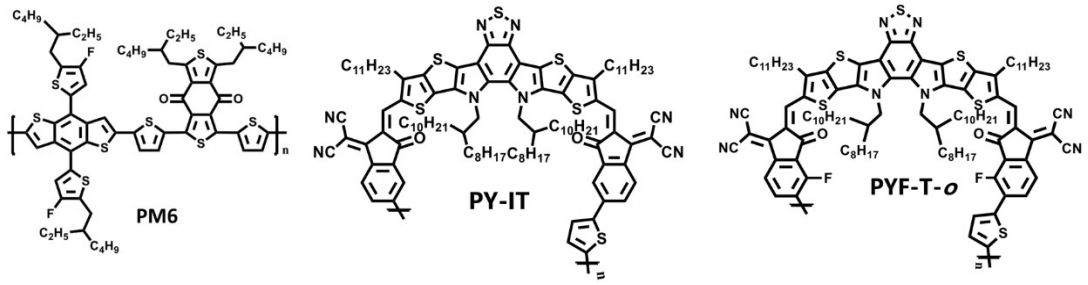

Fig. S8 Chemical structure of PM6, PY-IT and PYF-T-o.

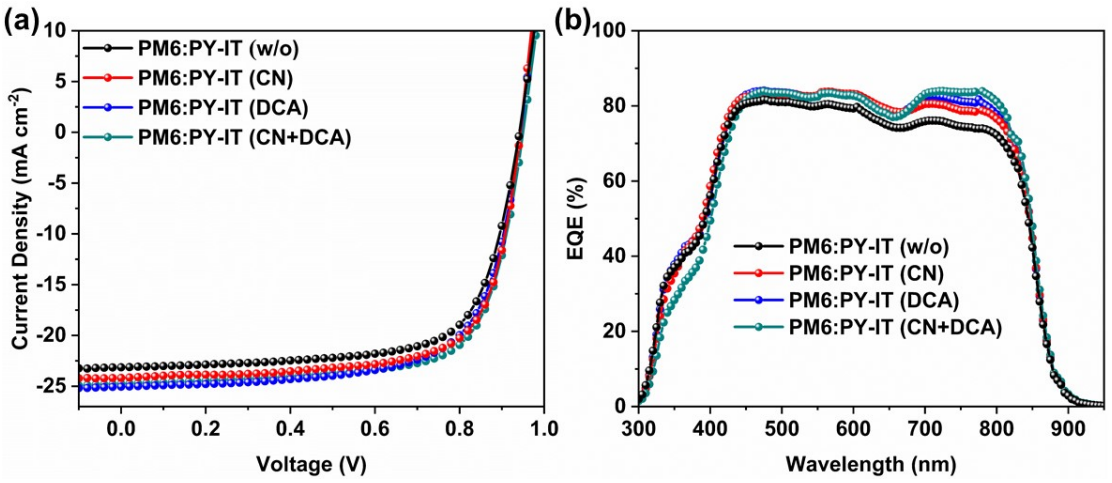

Fig. S9 (a) *J-V* curves and (b) EQE spectra of PM6:PY-IT based OSCs processed under various conditions.

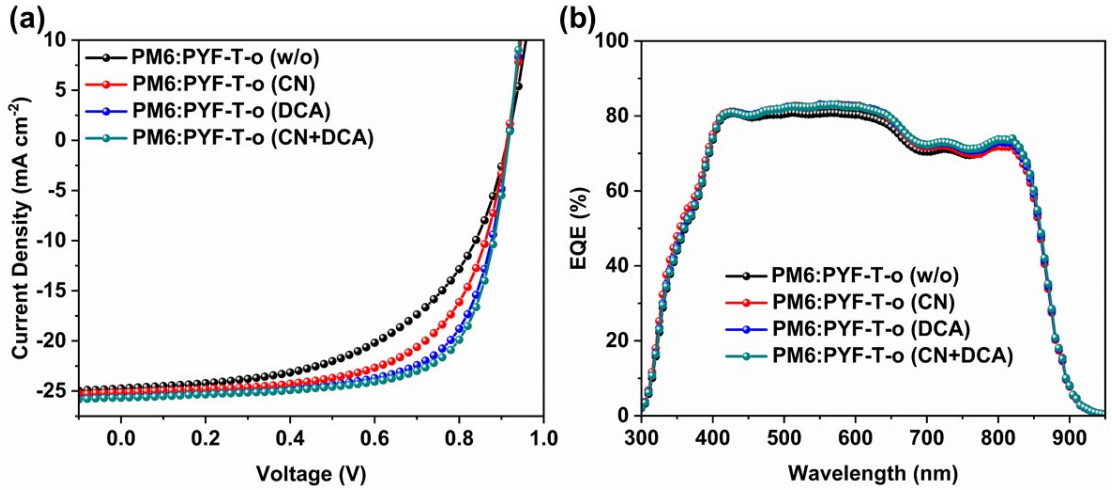

Fig. S10 (a) *J-V* curves and (b) EQE spectra of PM6:PYF-T-o based OSCs processed under various conditions.

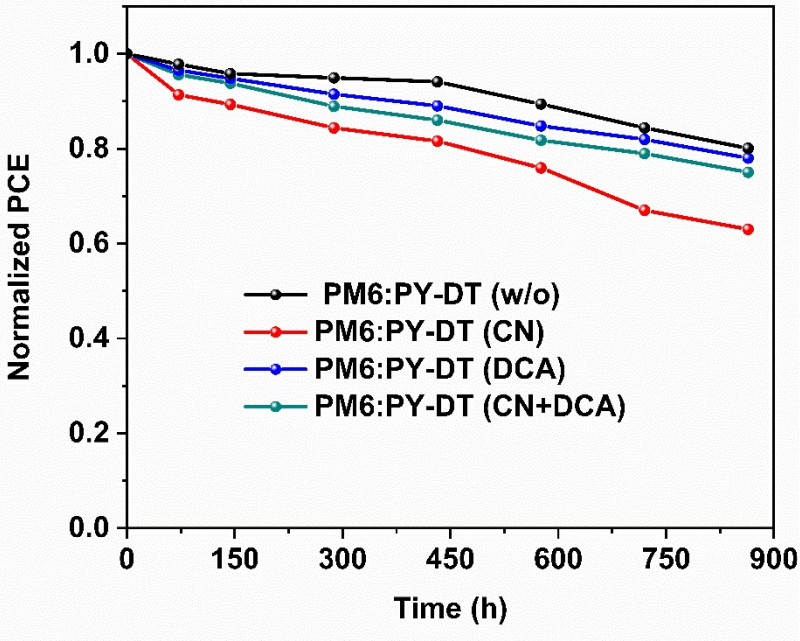

Figure S11. Stability of PM6:PY-DT devices processed under various conditions and kept for 900 h in N_2 atmosphere.

Supporting Tables

Table S1 Photovoltaic parameters of PM6:PY-DT based OSCs with different additive contents.

Additive treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
w/o	0.970	23.86	62.03	14.34
1% CN	0.962	23.96	71.20	16.42
5 mg/ml DCA	0.974	24.48	69.44	16.57
1% CN+ 2.5 mg/ml DCA	0.962	24.20	72.43	16.87
1% CN+ 5 mg/ml DCA	0.977	24.57	72.60	17.42
1% CN+ 7.5 mg/ml DCA	0.973	24.64	71.33	17.12
1% CN+ 10 mg/ml DCA	0.967	24.48	71.79	17.00

Table S2 The hole mobility (μ_h), electron mobility (μ_e) values of the PM6:PY-DT based OSCs processed under various conditions.

Active layer	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
PM6:PY-DT (w/o)	2.07×10^{-4}	1.38×10^{-4}	1.50
PM6:PY-DT (CN)	2.60×10^{-4}	2.01×10^{-4}	1.29
PM6:PY-DT (DCA)	2.71×10^{-4}	2.16×10^{-4}	1.25
PM6:PY-DT (CN+DCA)	3.40×10^{-4}	3.19×10^{-4}	1.06

Table S3 Contact angle, surface tension (γ) of individual materials, and interfacial tension between two materials ($\gamma_{X/Y}$).

Film X	Contact angle H_2O (deg)	Contact angle EG (deg)	γ (mN m^{-1})	γ^d (mN m^{-1})	γ^p (mN m^{-1})	Film Y	$\gamma_{X/Y}$ (mN m^{-1})
PM6	98.85	70.74	25.76	18.60	7.16	DCA	1.79
PY-DT	90.14	64.79	26.60	15.57	11.03	PM6	1.10
DCA	53.07	41.38	28.96	16.13	12.82	PY-DT	0.16

Table S4 Crystal coherence lengths of the (010) peak and the d-spacing for blend films

Active Layer	q (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
PM6:PY-DT (w/o)	1.650	3.80	0.66	9
PM6:PY-DT (CN)	1.652	3.80	0.4032	15.57
PM6:PY-DT (DCA)	1.67	3.76	0.3693	17.0
PM6:PY-DT (CN+DCA)	1.68	3.73	0.28342	22.15

Table S5 Crystal coherence lengths of the (100) peak and the d-spacing for blend films

Active Layer	q (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
PM6:PY-DT (w/o)	0.304	20.65	0.15743	39.89
PM6:PY-DT (CN)	0.311	20.19	0.11704	53.65
PM6:PY-DT (DCA)	0.302	20.78	0.06145	102.16
PM6:PY-DT (CN+DCA)	0.309	20.32	0.05854	107.27

Table S6 Photovoltaic parameters of PM6:PY-IT based OSCs processed under various conditions

Additive treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
w/o	0.941	23.13	70.34	15.27
CN	0.943	24.18	71.11	16.20
DCA	0.943	25.04	68.30	16.13
CN + DCA	0.949	24.76	71.35	16.76

Table S7 Photovoltaic parameters of PM6:PYF-T-o based OSCs processed under

various conditions

Additive treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
w/o	0.914	24.74	54.33	12.24
CN	0.913	25.11	62.89	14.32
DCA	0.916	25.33	68.31	15.75
CN + DCA	0.917	25.66	69.84	16.37

References

1 F. Liu, L. Zhou, W. Liu, Z. Zhou, Q. Yue, W. Zheng, R. Sun, W. Liu, S. Xu, H. Fan, L. Feng, Y. Yi, W. Zhang and X. Zhu, *Adv. Mater.*, 2021, **33**, 2100830.

2 X. Chen, D. Wang, Z. Wang, Y. Li, H. Zhu, X. Lu, W. Chen, H. Qiu and Q. Zhang, *Chem. Eng. J.*, 2021, **424**, 130397.