

Electronic Supplementary Information (ESI) for
**Surface Crystallinity Enhancement in Organic Solar Cells Induced
by Spinodal Demixing of Acceptors and Additives**

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Materials and methods

Materials

Unless stated otherwise, chemicals and solvents were commercially obtained. PBDB-T, ITIC, PM6, Y6, ITTC, ITCC, IT-4Cl, ITIC-Th, ITIC-Th1, PDINO and PEDOT:PSS were purchased from Solmer Materials Inc. All materials were used as received without further modification.

Soft plasma etching for FLAS

The soft plasma etching procedure was performed with N₂ gas pressure < 30 Pa by Diener Femto plasma cleaner. The soft plasma etching is harmless to the beneath layers, especially the optical property. The etching rate is correlated with pressure, in this work, the pressure was controlled at 10 pa and the etching rate is ~10 nm/30 s.

Fabrication of OSC devices

The photovoltaic devices were fabricated with a structure of ITO/PEDOT:PSS/Active layer/PDINO/Al. The patterned ITO glasses were pre-cleaned with ultrasonic in deionized water, acetone and isopropyl alcohol for three times, 5 min each, then dried with N₂ blow. PEDOT:PSS solution was spin-coated onto the ITO glasses with 4000 rpm for 30 s, followed by 10 min thermal annealing of 150 °C in the air to improve the conductivity. The solution of PBDB-T:ITIC, ITTC and ITCC were prepared in CB with the total concentration of 20 mg/ml (D:A = 1:1). The solution of PM6: IT-4Cl and PM6:Y6 were prepared in CF with the total concentration of 16 mg/ml (D: A = 1:1 for IT-4Cl and 1:1.2 for Y6). 0.5% DIO or 0.5% CN was added afterward if needed. The solutions were stirred at RT for several hours and then were spin-coated onto the PEDOT:PSS/ITO glasses to form ~100 nm thick active layers. TA treatment was carried out at 130 °C for ITIC, ITTC, ITCC, IT-4Cl for 5 min and 100 °C for Y6 for 5 min. After that, PDINO solution with 1 mg/ml concentration was spin-coated onto the active layer with 5000 rpm for 10 s to form ~5 nm thick electron transport layer. Finally 100 nm Al electrode was deposited under vacuum (ca. 10⁻⁵ Pa). The active area of the device was 3.8 mm².

The films for absorption, reflection spectra and the real-time measurement were fabricated as same as the device preparation, only changed the substrates to quartz.

Device characterization

The current density-voltage (J - V) curves were measured in the glove box by a Keithly 2400 source meter under AM1.5G (100 mW/cm², Newport simulator). The SCLC method was employed for hole and electron mobility measurement with device structures of ITO/PEDOT:PSS/Active layer/MoO_x/Al for hole-only devices and ITO/ZnO/Active layer/PDINO/Al for electron-only devices. The SCLC mobilities were calculated by MOTT-Gurney equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$. Where J is the current density, ϵ_r is the relative dielectric constant of active layer, here we use a relative constant of 3, ϵ_0 is the permittivity of empty space, L is the film thickness, μ is the hole or electron mobility and V is the internal voltage in the device, and $V = V_{\text{Applied}} - V_{\text{Built-in}}$ ($V_{\text{Built-in}}$ is 0.2 V for hole-only device and 0 for electron-only device), where V_{Applied} is applied voltage and $V_{\text{Built-in}}$ is built-in voltage.

GIWAXS measurement

GIWAXS data of PBDB-T:ITIC blend films were collected at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 1.2398 Å and the incident angle was 0.12°.

NEXAFS measurement

The Near Edge X-ray Absorption Fine Structure (NEXAFS) measurements were carried out at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

This beamline is connected to an undulator and equipped with two gratings that offer soft X-rays from 20 to 600 eV with a typical photon flux of 5×10^{10} photons/s and a resolution ($E/\Delta E$) better than 10^5 at 29 eV. This system is comprised of four ultrahigh vacuum (UHV) chambers including analysis chamber, preparation chamber, molecular beam epitaxy (MBE) chamber, and a radial distribution chamber. The base pressures are 7×10^{-11} , 1×10^{-10} , 5×10^{-10} and 2×10^{-11} mbar, respectively. A sample load-lock system is connected to the sample transfer chamber. The analysis chamber is equipped with a VG Scienta R4000 analyzer, a monochromatic Al $K\alpha$ X-ray source,

a UV light source, low energy electron diffraction (LEED), a flood electron gun, and a manipulator with high precision and five-degree-of-freedom. The preparation chamber comprises an ion gun, a quartz crystal microbalance (QCM), a residual gas analyzer, a manipulator with high precision and four-degree-of-freedom, and several evaporators. The MBE chamber houses a QCM, several evaporators and a manipulator with two-degree-of-freedom. With this radial distribution chamber, the time for each transfer process between two chambers is less than 1 minute.

UPS measurement

UPS measurement was carried out by Thermo Fisher ESCALAB Xi⁺ in an ultra high vacuum chamber (in the order of 10^{-10} mbar). A low-intensity UV light (He I line) with excitation energy of 21.22 eV was used, and the bias voltage of 10 V was applied.

LEIPS measurement

Low-energy inverse photoemission spectroscopy (LEIPS) measurement was performed on a customized ULVAC-PHI LEIPS instrument with Bremsstrahlung isochromatic mode.

Femtosecond time-resolved Transient Absorption (fs-TA) Measurement

Fs-TA spectroscopy was performed to measure the temporal evolution of the absorption changes in the excited states, through which the carrier dynamics in femtosecond to nanosecond regime could be revealed.

The laser beam is supplied by amplified Ti: sapphire laser source (800 nm, Coherent) that provides 100 fs pulses with a repetition rate of 1 kHz. The output was split into two beams, the stronger one of which was frequency doubled to generate a 400 nm pump light, and the other one was focused into a sapphire plate to generate a broadband super-continuum probe light. Using an optical chopper, the repetition rate of the pump pulses was adjusted to 500 Hz, and was focused on the sample with the probe pulse (white light). The TA spectra were obtained by comparing the probe light spectra with and without pump light excitation. The photo-induced absorption change as a function of wavelength was described using optical density (absorbance) changes ($-\Delta T/T$).

Supplementary Figures:

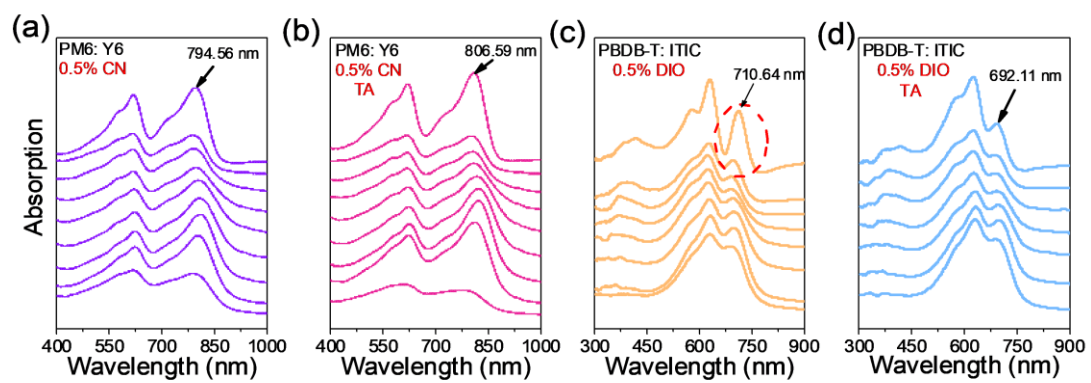


Fig. S1 FLAS of (a, b) PM6:Y6 and (c, d) blend films with different treatment (additives or not, TA treatment or not).

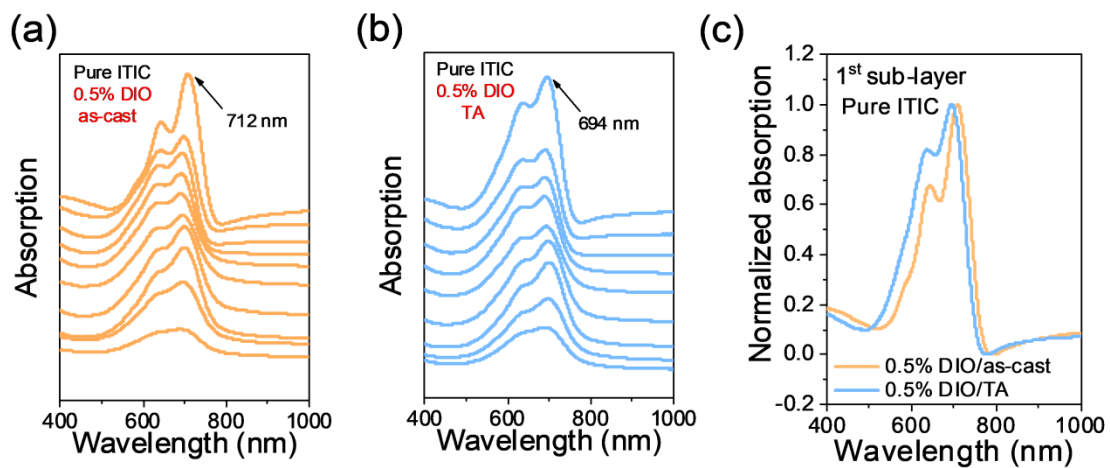


Fig. S2 UV-vis absorption measurement of pure ITIC with 0.5% DIO addition in CB. FLAS results of ITIC pure film with 0.5% DIO addition (a) before and (b) after TA treatment. (c) Absorption spectra of the 1st sub-layer of pure ITIC films with 0.5% DIO added before and after TA treatment.

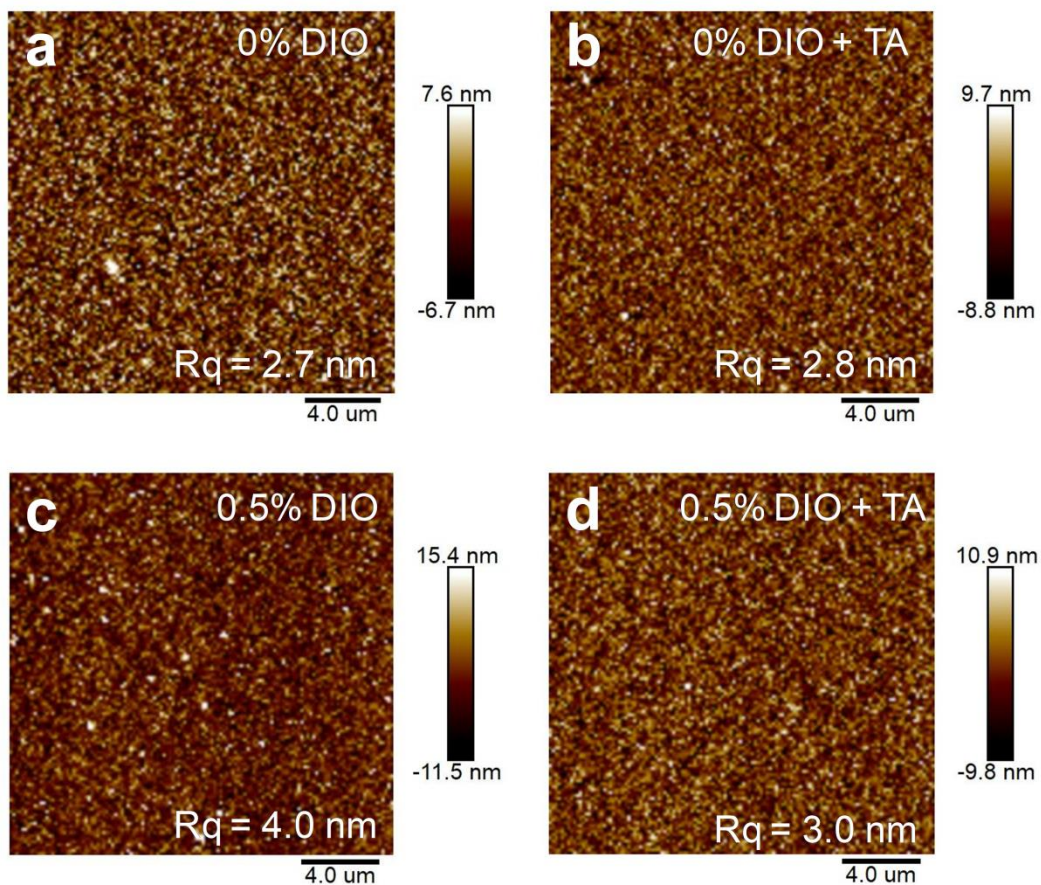


Fig. S3 The AFM images of PBDB-T:ITIC blend films with or without 0.5% DIO before and after TA treatment. (a) 0% DIO, (b) 0.5% DIO after TA treatment, (c) 0.5% DIO, (d) 0.5% DIO after TA treatment.

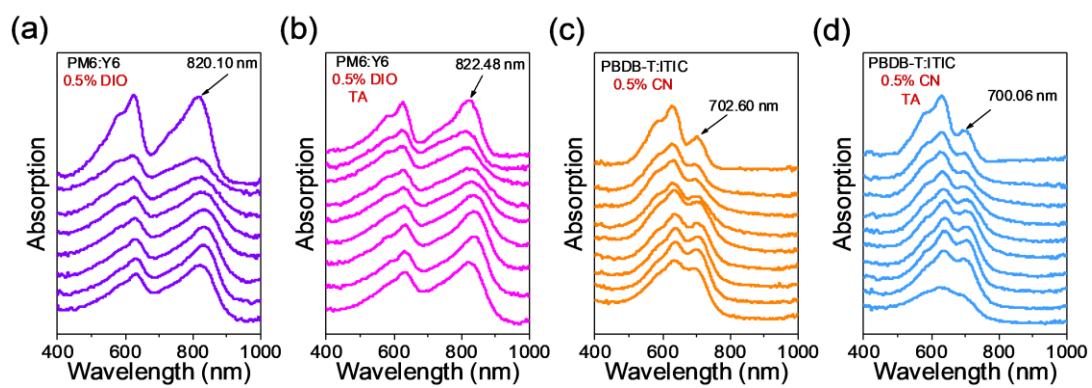


Fig. S4. FLAS of (a, b) PM6:Y6 and (c, d) blend films with exchanged additives. (DIO for PM6:Y6 and CN for PBDB-T:ITIC).

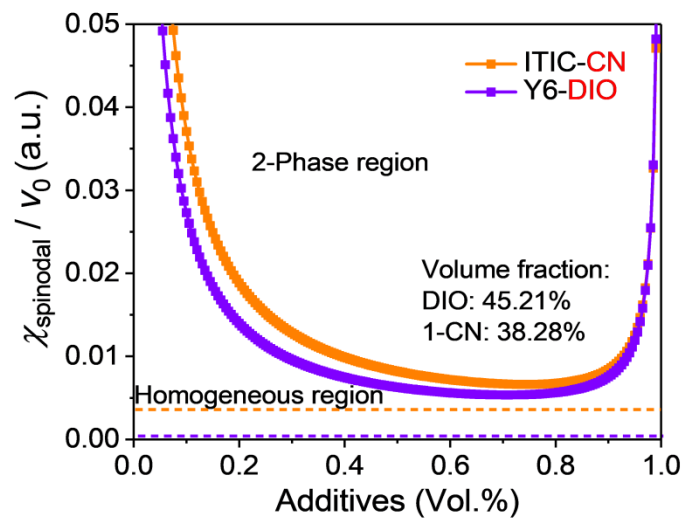


Fig. S5. The additives/acceptors liquid-solid transition diagrams estimated for CN:ITIC and DIO:Y6 as a function of the volume fraction of additives. The dashed lines represent the interaction parameters of additive-acceptor blends ($\chi_{\text{DIO,Y6}}/u_0 = 0.000428$, $\chi_{\text{CN,ITIC}}/u_0 = 0.00368$).

For donor behaviors

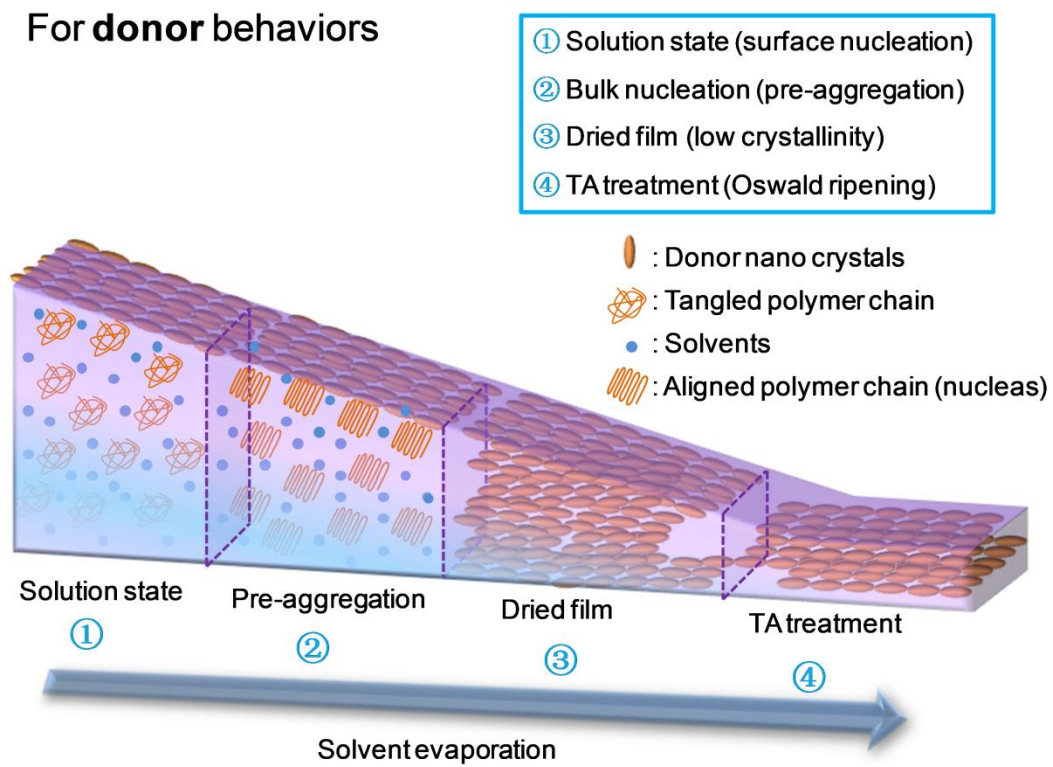


Fig. S6. Schematic diagram of the donor behaviors during film formation process.

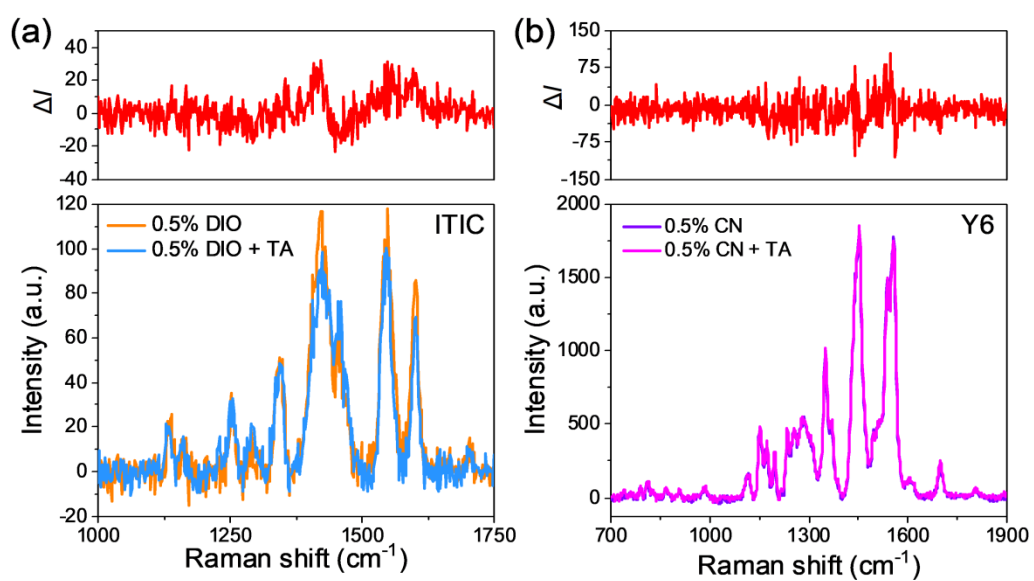


Fig. S7 Raman spectra of (a) ITIC and (b) Y6 neat films with or without 0.5% additives before and after TA treatment. The reduced $\delta_{C=O}$ resonance signal of TA-treated ITIC indicating partial “face-on” to “edge-on” orientation declination.

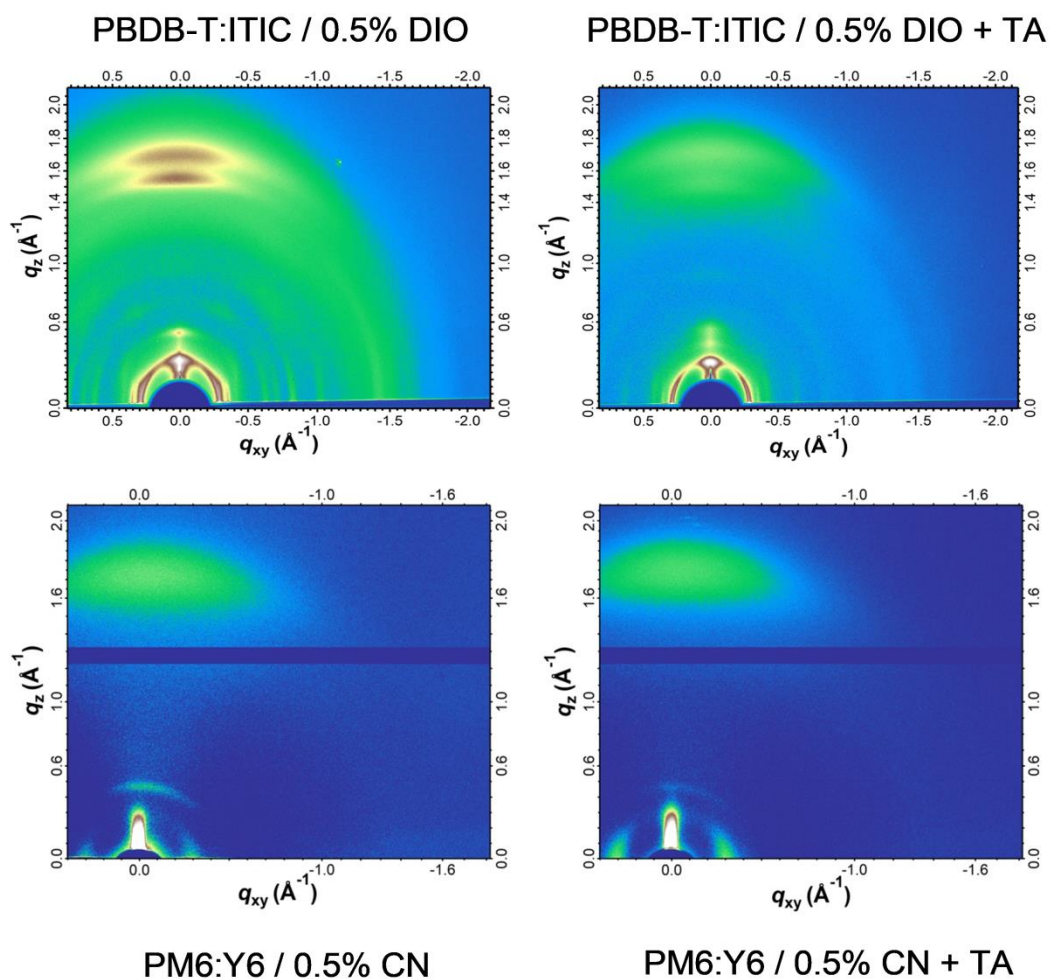


Fig. S8 GIWAXS patterns of PBDB-T:ITIC and PM6:Y6 blend films with 0.5% DIO/CN addition before and after TA treatment. The (010) scattering of the PBDB-T:ITIC film before TA treatment are stronger than that of the film after TA treatment in combination with the disappeared fine structure of scattering after TA treatment, indicating the degraded crystallinity after TA treatment. On the contrary, the crystallinity of PM6:Y6 blend films with 0.5% CN is nearly invariable after TA treatment.

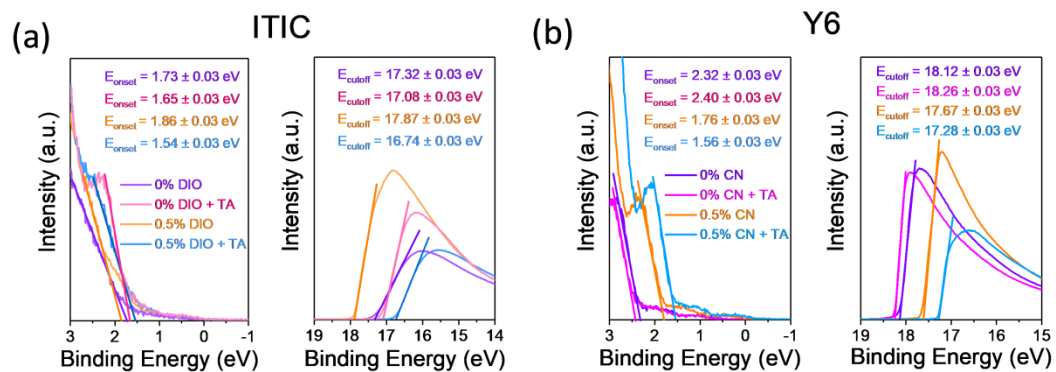


Fig. S9. The UPS profiles of ITIC and Y6 films with different treatments.

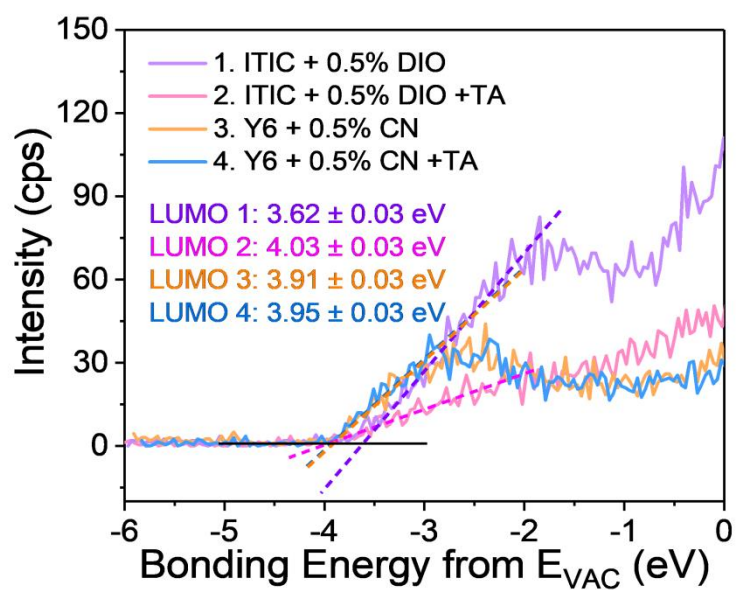


Fig. S10. The LEIPS profiles of ITIC and Y6 films with different treatments.

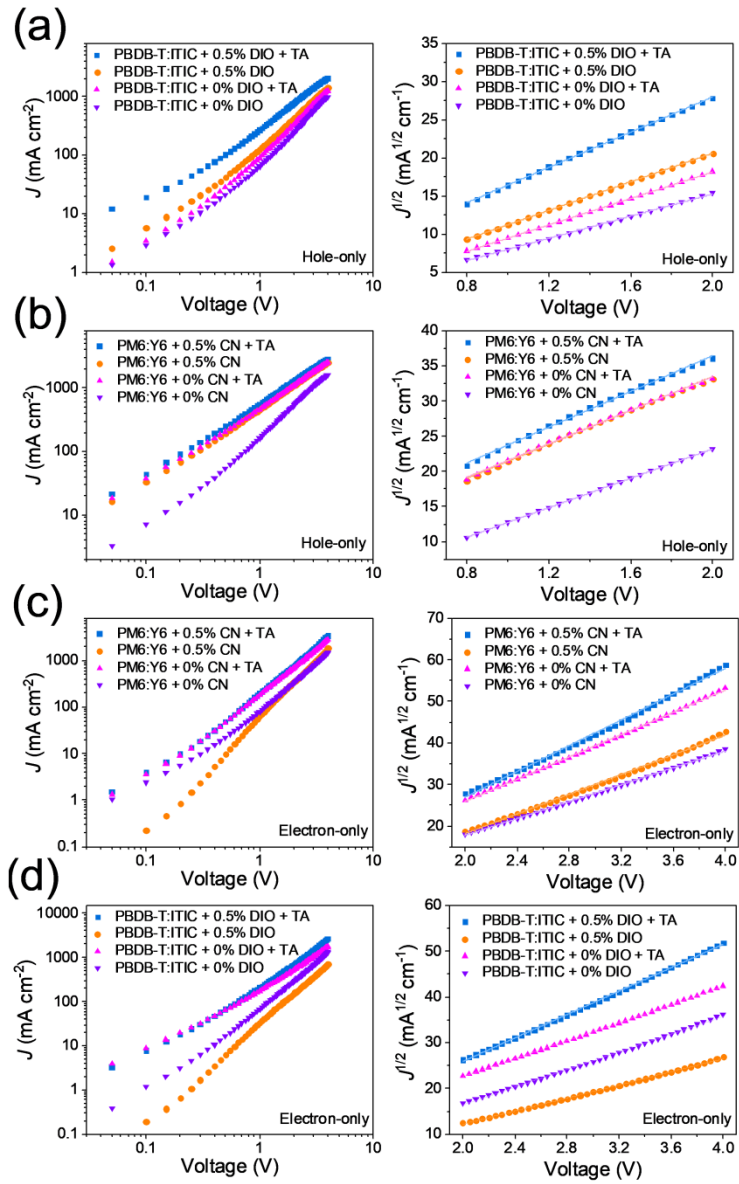


Fig. S11. J - V plots and fitting plots of SCLC measurement. (a) Hole-only devices for PBDB-T:ITIC. (b) Hole-only devices for PM6:Y6. (c) Electron-only devices for PM6:Y6. (d) Electron-only devices for PBDB-T:ITIC.

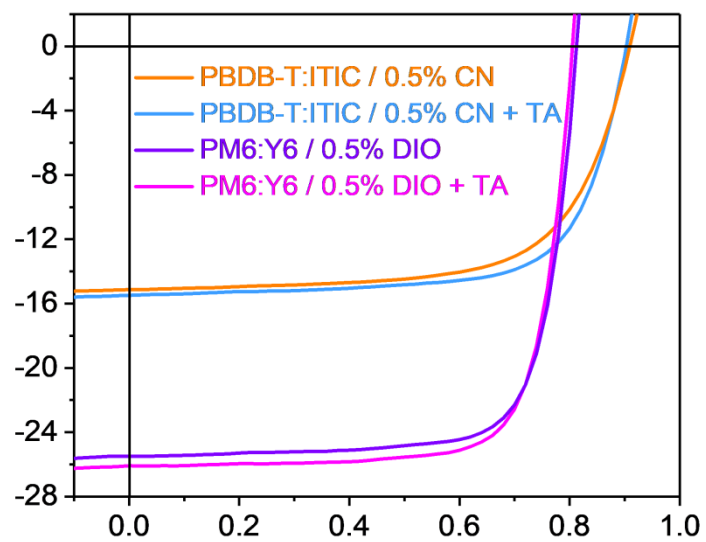


Fig. S12. *J-V* plots of PBDB-T:ITIC and PM6:Y6 blend films with exchanged additives.

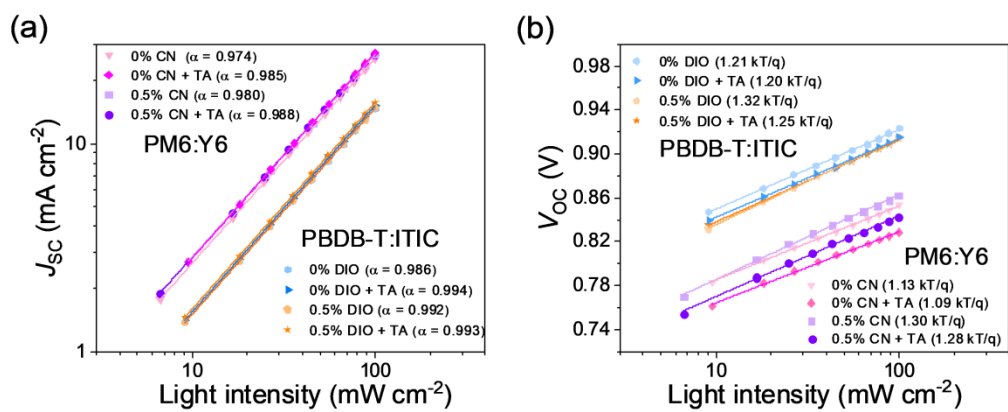


Fig. S13. Dependences of (a) J_{sc} on P_{light} and (b) V_{oc} on P_{light} .

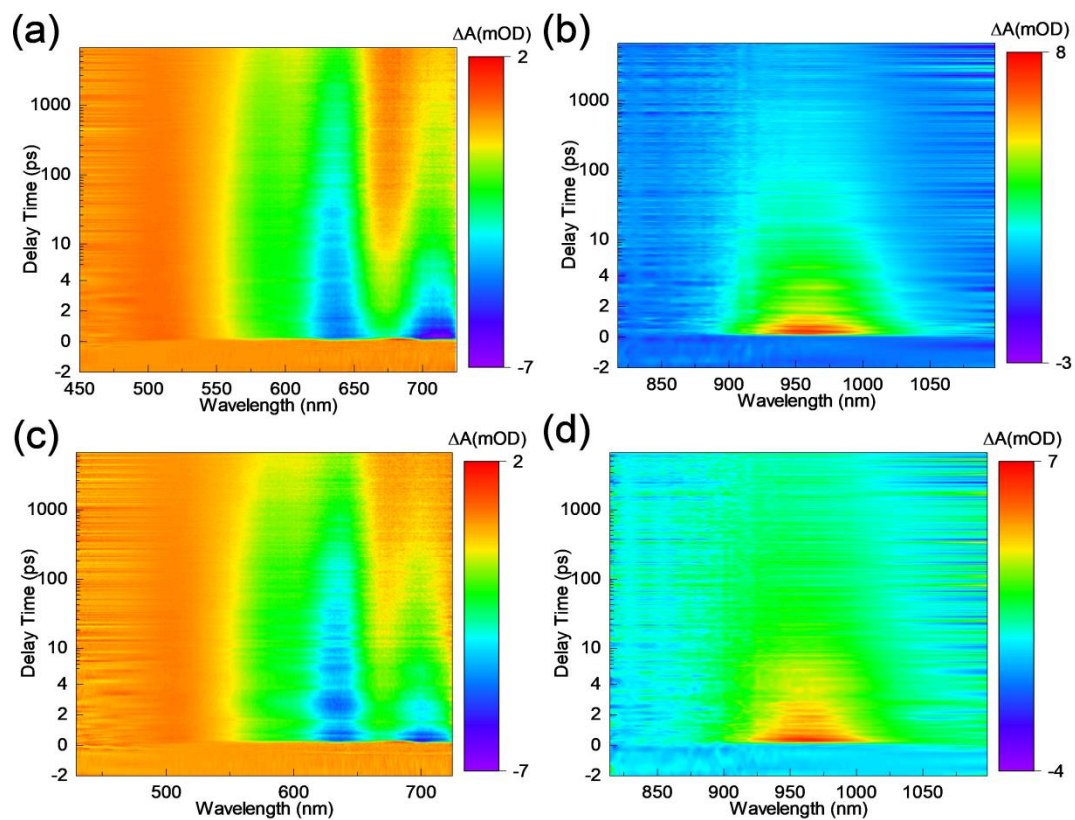


Fig. S14. Contour plots of the fs-TA data of PBDBT:ITIC blend film with 0.5% DIO (a,b) before and (c,d) after TA-treatment.

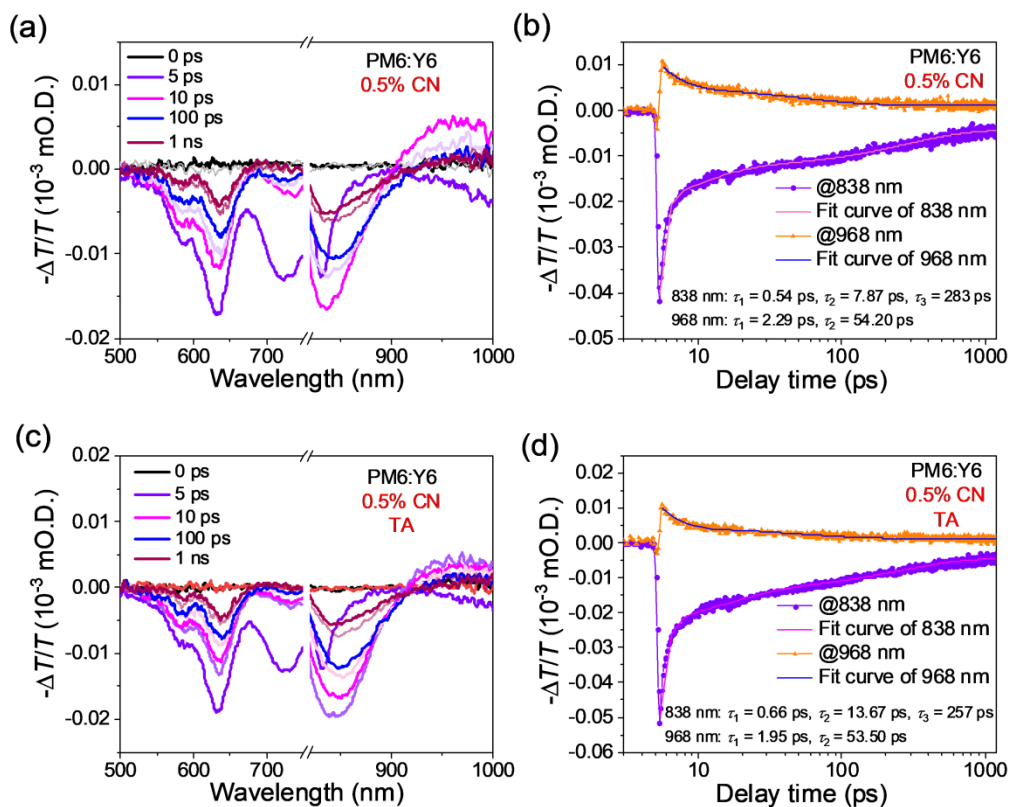


Fig. S15. The fs-TA spectra of PM6:Y6 blend film with 0.5% DIO (a,b) before and (c,d) after TA treatment. (b,d) Kinetic studies: at 838 nm and 968 nm.

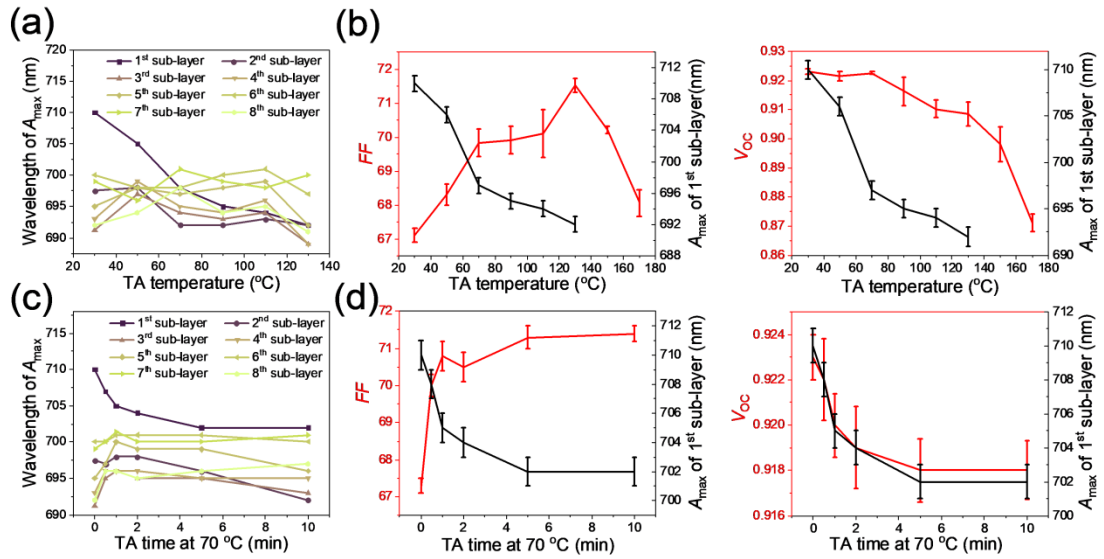


Fig. S16. The relationship between sub-layer absorption peak locations and device performance of PBDB-T:ITIC blend films. (a) Wavelength of A_{\max} of each sub-layer varies with TA temperature. (b) Plots of FF, V_{OC} values and A_{\max} of the 1st sub-layer versus TA temperature. (c) Wavelength of A_{\max} of each sub-layer varies with TA time at 70 $^{\circ}\text{C}$. The choice of 70 $^{\circ}\text{C}$ is owing to the slow transformation that is easier for observation. (d) Plots of FF, V_{OC} values and A_{\max} of the 1st sub-layer versus TA time at 70 $^{\circ}\text{C}$.

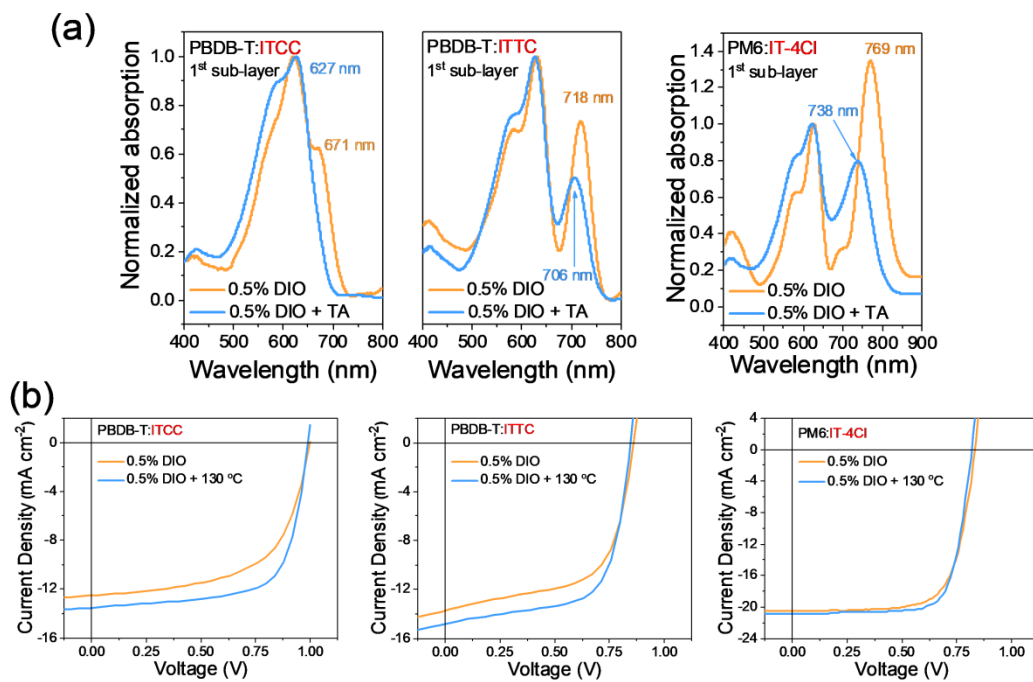


Fig. S17. (a) the absorption spectra of the 1st sub-layers and the (b) *J-V* plots of PBDB-T:ITCC, PBDB-T:ITCC and PM6:IT-4CI before and after TA treatment.

Table S1 Solubility parameter (δ_T), molecular weight (MW) and density (ρ) for materials and solvents.

Materials/ solvents	δ_T (MPa^{1/2})	MW (g/mol)	ρ (g/cm³)
ITIC	24.18	1428	1.24
Y6	19.88	1452	1.32
CB	19.47	112.56	1.11
CF	18.85	119.38	1.49
DIO	18.85	336.02	1.80
CN	21.16	162.62	1.19

Table S2 Summarized device performance parameters of PBDB-T:ITIC and PM6:Y6 blends with exchanged additives.

Device	Treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE ^a (%)
PBDB-T/ITIC	0% CN	0.922	15.17	0.680	9.5 (9.3 \pm 0.1)
PBDB-T/ITIC	0% CN + 130 °C	0.910	15.34	0.706	9.8 (9.6 \pm 0.1)
PBDB-T/ITIC	0.5% CN	0.909	15.12	0.676	9.3 (9.2 \pm 0.1)
PBDB-T/ITIC	0.5% CN + 130°C	0.903	15.48	0.702	9.8 (9.7 \pm 0.1)
PM6/Y6	0% DIO	0.849	24.56	0.689	14.4 (14.2 \pm 0.2)
PM6/Y6	0% DIO + 100°C	0.838	25.22	0.713	15.1 (14.8 \pm 0.2)
PM6/Y6	0.5% DIO	0.812	25.50	0.759	15.7 (15.5 \pm 0.2)
PM6/Y6	0.5% DIO + 100°C	0.805	26.08	0.763	16.0 (15.8 \pm 0.2)

^a All average values with standard deviations were calculated from 10 devices.

Table S3 Summarized device performance parameters of ITIC-derivates based blend films with 0.5% DIO before or after TA treatment.

Device	Treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE^a (%)
PBDB-T/ITCC	0.5% DIO	1.00	12.6	0.596	7.5 (7.2 \pm 0.2)
PBDB-T/ITCC	0.5% DIO 130°C	0.99	13.5	0.685	9.2 (8.9 \pm 0.3)
PBDB-T/ITTC	0.5% DIO	0.86	13.7	0.614	7.2 (7.0 \pm 0.2)
PBDB-T/ITTC	0.5% DIO 130°C	0.85	14.8	0.656	8.2 (7.8 \pm 0.2)
PM6/IT-4Cl	0.5% DIO	0.84	21.7	0.712	12.9 (12.7 \pm 0.2)
PM6/IT-4Cl	0.5% DIO 130°C	0.81	22.7	0.736	13.6 (13.4 \pm 0.1)

^a All average values with standard deviations were calculated from 10 devices.