Additive-induced intermolecular interaction enhancement enable highly efficient organic solar cells

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Experimental Section

1. Materials

All reagents and solvents, unless otherwise specified, were purchased from Energy Chemical, Tansoole, Suna Tech, Aldrich, and JiangSu GE-Chem Biotech., Ltd. and were used without further purification. All materials are provided by commercial suppliers: PM6, Y6, eC9, PNDIT-F3N, PFN-Br was purchased from Solarmer Energy Inc. CB and CB was purchased from Macklin. PEDOT:PSS (Clevios P VP AI. 4083) was purchased from Heraeus.

2. Device Fabrication and characterizations

The device structures were ITO / PEDOT: PSS / Active layer / PFN-Br / Ag. ITO-coated glass substrates underwent a sequential ultrasonic bath cleansing with detergent water, deionized water, acetone, and isopropyl alcohol, each for a duration of 15 minutes. Following the drying process with high-pressure nitrogen, the glass sheet underwent UV irradiation in a UV-ozone chamber for 15 minutes. PEDOT: PSS was precisely spin-coated onto the substrate for 20 seconds at 4000rpm, and subsequently, it was subjected to a 150℃ bake for 10 minutes before being transferred to a nitrogen-filled glove box for subsequent processing. The substrates were then transferred into a nitrogen-filled glove box. The PM6:Y6, PM6:eC9, PM6:N3 concentration was 16.4 mg/ml chloroform solution with D:A ratio of 1:1.2 (w/w) and PDCI 6 mg/mL in CF containing 0.4% (v / v) solvent additive (CB, PDC). The solution was stirred at room temperature for 2 hours, following which the mixed solution was spin-coated onto the upper layer of PEDOT: PSS. Subsequently, PFN-Br was spin-coated at 3000rpm in an isopropanol solution for 30 seconds. Finally, in the thermal evaporator, transferred from the substrate, the Ag electrode was evaporated at a pressure of 2×10^{-5}Pa.

The EQE measurements of organic solar cells were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with WDG3 mono-chromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. The *J*–V curves were measured under AM 1.5 G (100 mW/cm^2) (Enli Technology Co., Ltd. SS-X50R).

3. Density Functional Theory Computation

The molecular geometry optimizations of Y6 and two additives are performed by Gaussian 16 at B3LYP/6-31G* level, where the long alkyl side chains are simplified to methyl groups to save computational cost. Conformational searches of the complex (Y6 and additives) are performed to find the low-energy conformers. 500 conformers are generated and optimized by semi-empirical extended tight-binding method GFN2-xTB as implemented in xtb program. The conformers with the lowest energy are further optimized by Gaussian 16, where the 6-311G** basis set in conjunction with the D3BJ dispersion correction are used to calculate Gibbs free energy. The binding energy is determined by $\Delta E_b = E_{com} - (E_{M1} + E_{M2})$, where E_{M1}, E_{M2} and E_{com} are the Gibbs free energy of molecule 1, molecule 2 and their complex.

4.Atomic force microscopy (AFM)

Topographic images of the films were acquired through a Bruker atomic force microscopy (AFM), employing the Dimension Edge system equipped with Scan AsystTM, operating in tapping mode. This process utilized an etched silicon cantilever under a nominal load of approximately 2nN. The scanning rate for an image size of 2 μm × 2 μm was set at 1.5 Hz.

5.GIWAXS/GISAXS

GIWAXS measurements were carried out with a Xeuss 2.0 SAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°.

GISAXS measurements were carried out with a Xeuss 2.0 SAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°.

6.Space-charge-limited current (SCLC)

The carrier mobility (hole and electron mobility) of photoactive layer was determined by fitting the dark current of hole/electron-only diodes to the space-charge-limited current (SCLC) model. Hole-only diode configuration: Glass/ITO/PEDOT:PSS/active layer/MoO_3/Ag; Electron-only diode configuration: Glass/ITO/ZnO/PFN-Br/active layer/PFN-Br/Ag. V_{bi} = 0 was used for both fittings. The active layer thickness was determined by a Tencor surface profilometer. The electric-field dependent SCLC mobility was estimated using the following equation:

$$J(V) = \frac{9}{8} e_0 e_r m_0 exp\left(0.89b \sqrt{\frac{V - V_{bi}}{L}}\right) \frac{(V - V_{bi})^2}{L^3}$$

Supplementary Figures

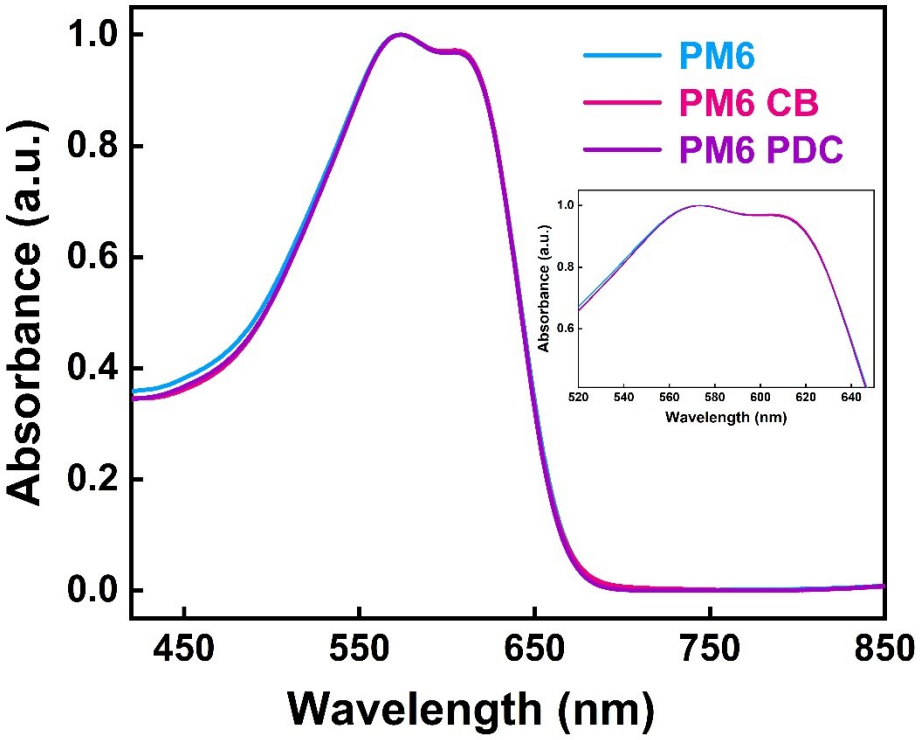

Figure S1.UV-vis absorption of Y6 film without and with CB, PDC solvent additives.

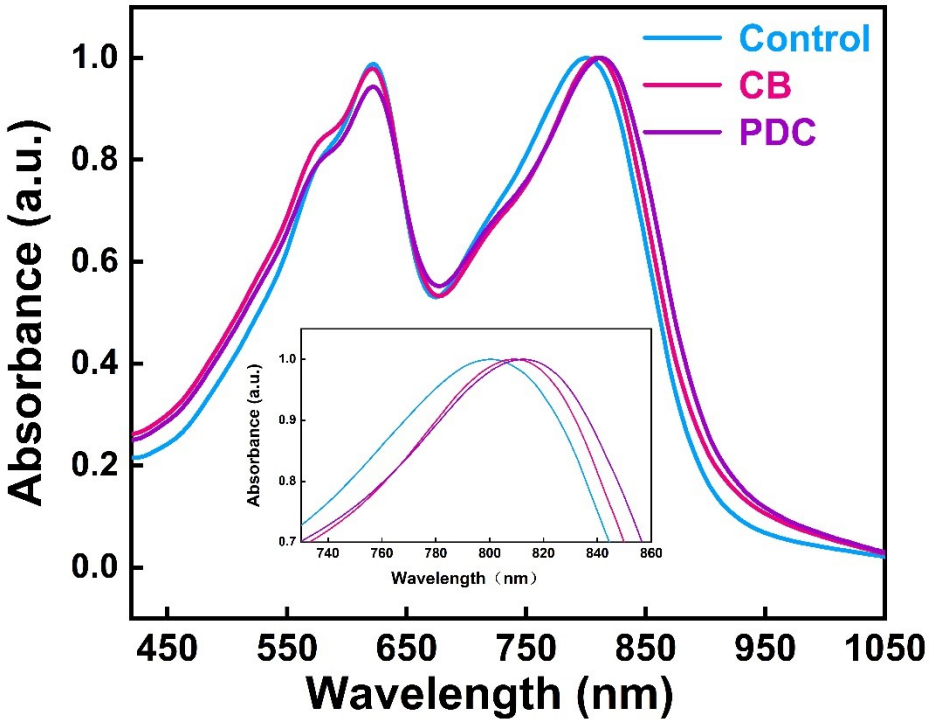

Figure S2. UV-vis absorption of PM6:Y6 film without and with CB, PDC solvent additives.

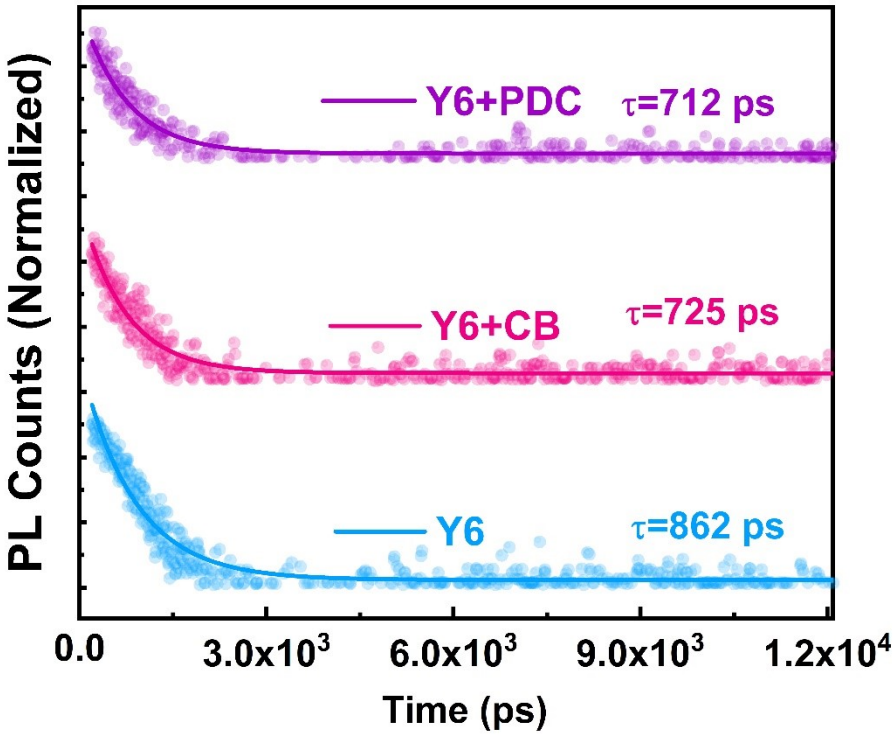

Figure S3. TRPL kinetics of Y6 and fits to the experimental data using a bi-exponential decay (solid line).

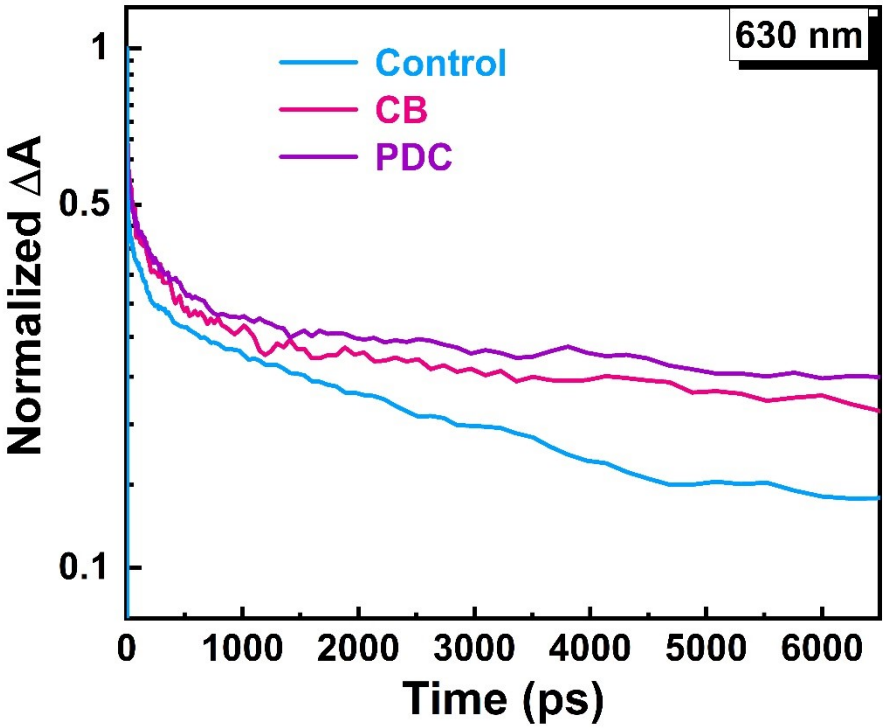

Figure S4. Carrier transfer kinetics analysis of 630nm.

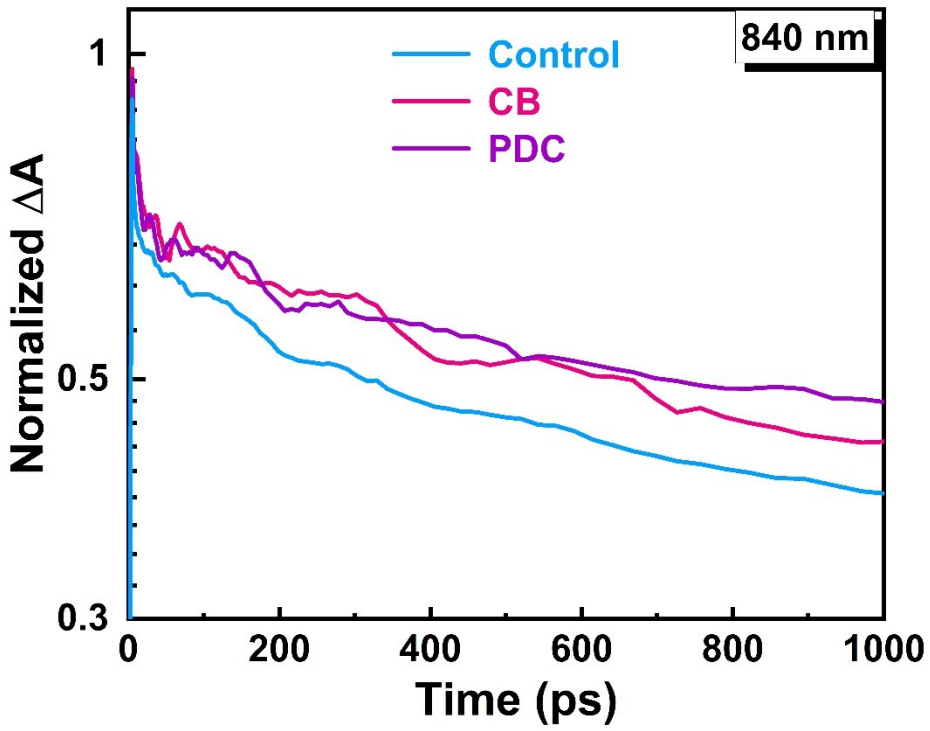

Figure S5. Carrier transfer kinetics analysis of 840 nm.

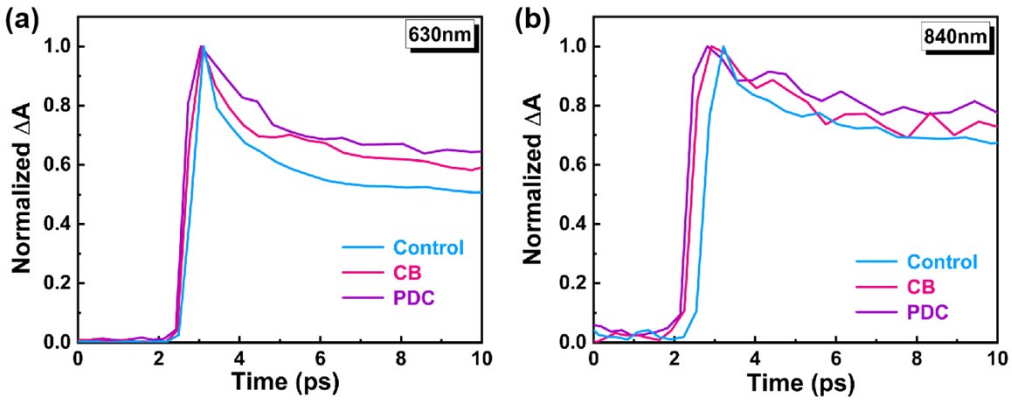

Figure S6. Free charge recombination analysis of a) 630nm and b)840nm

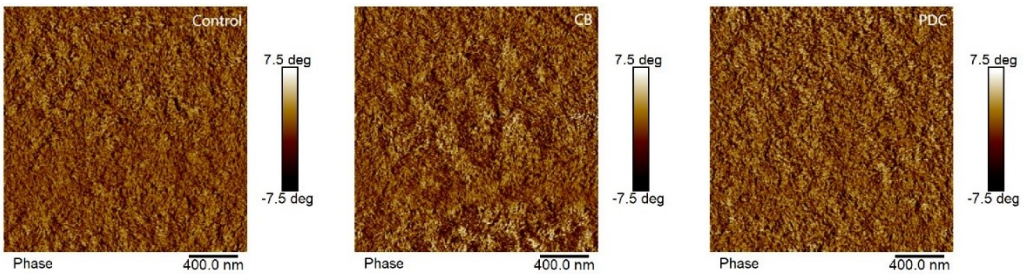

Figure S7. AFM phase images with the x-axis and y-axis scales of 2 μm of PM6:Y6 blend films processed without/with different additives.

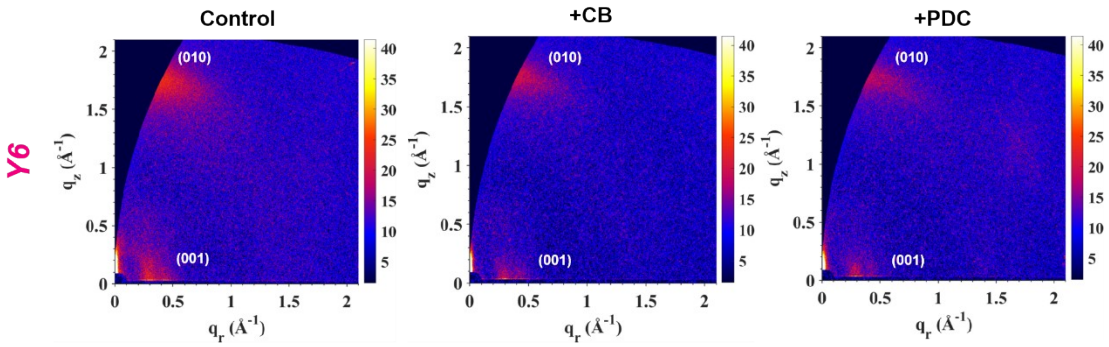

Figure S8. Y6 films without/with different additive processes.

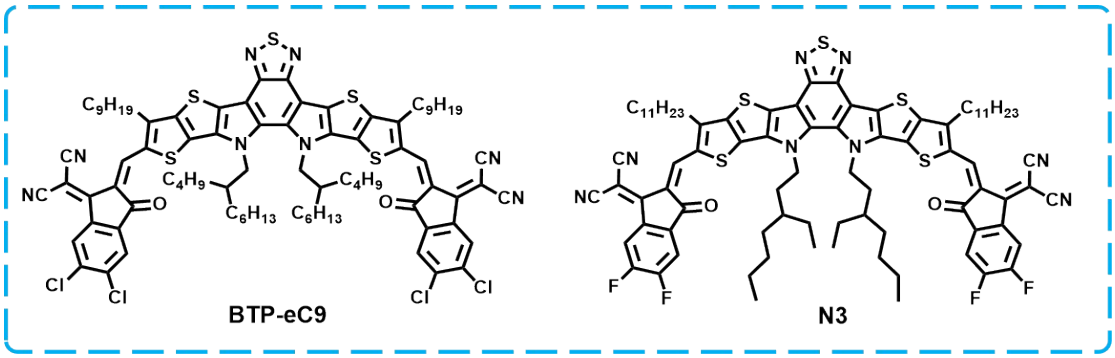

Figure S9. Chemical structure of BTP-eC9 and N3.

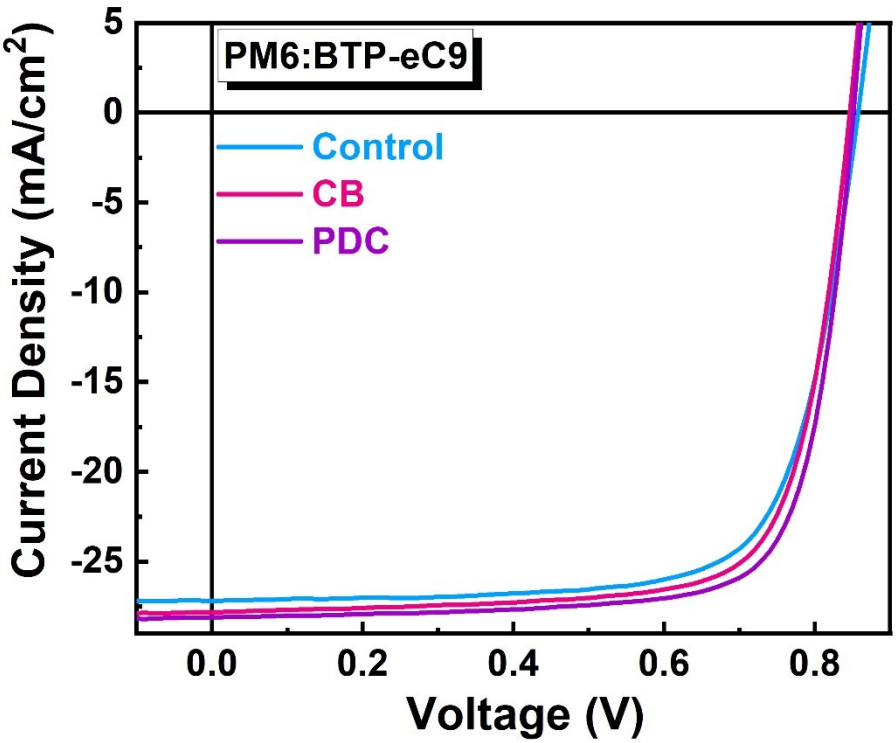

Figure S10. *J*-V of PM6:BTP-eC9 film without and with CB, PDC solvent additives.

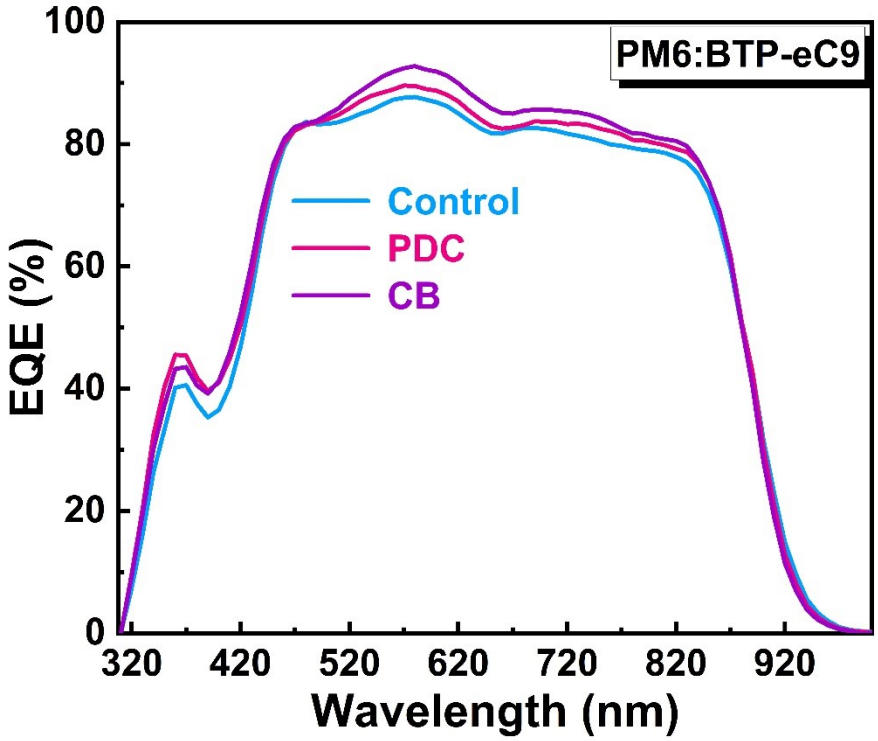

Figure S11. EQE of PM6:BTP-eC9 film without and with CB, PDC solvent additives.

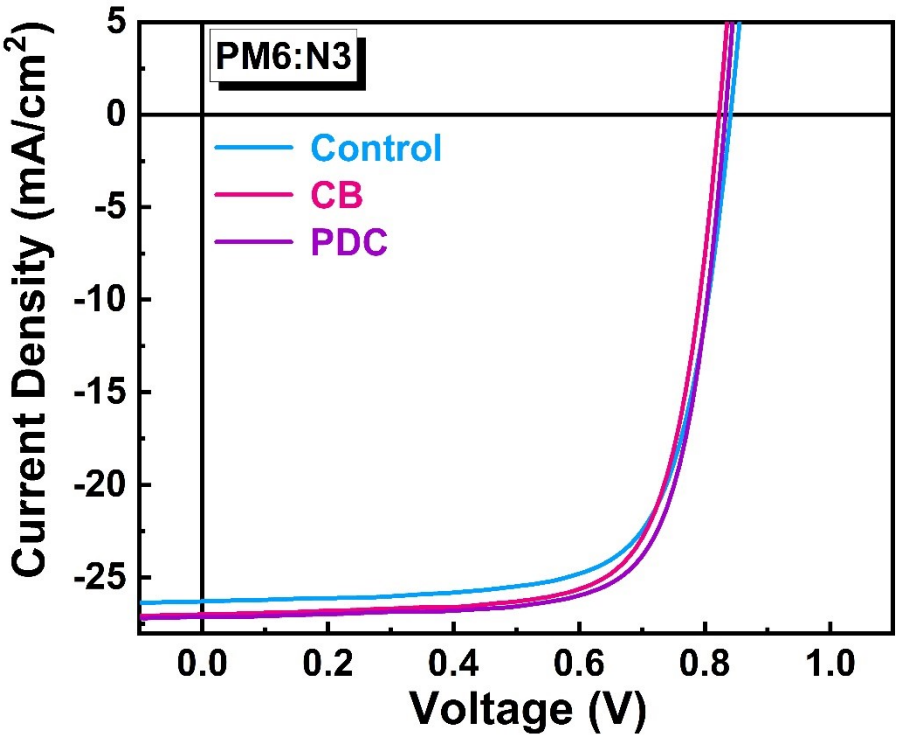

Figure S12. *J*-V of PM6:N3 film without and with CB, PDC solvent additives.

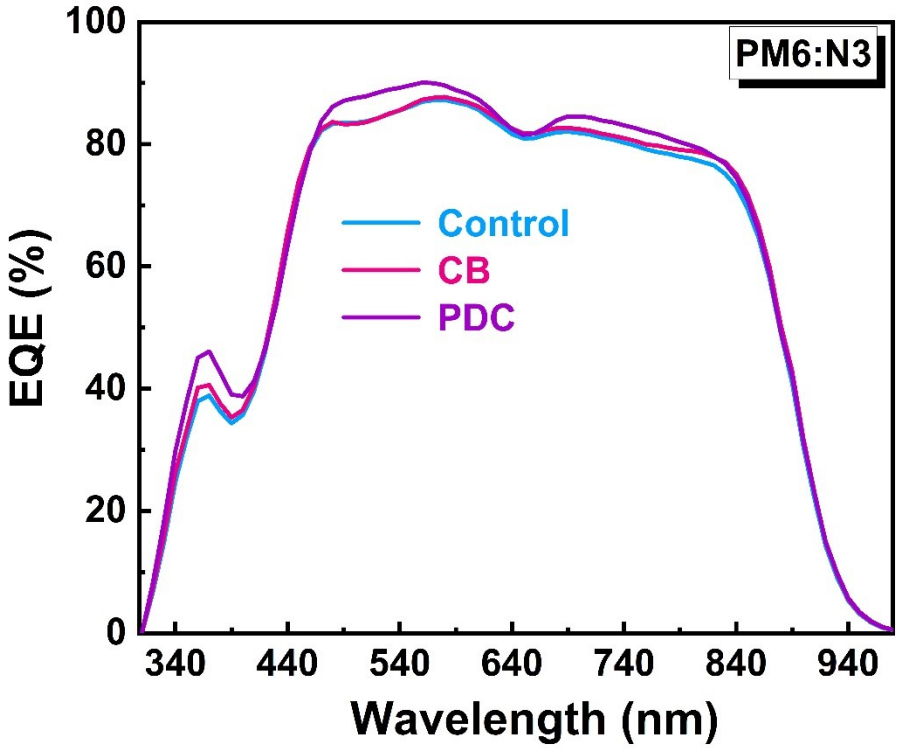

Figure S13. EQE of PM6:N3 film without and with CB, PDC solvent additives.

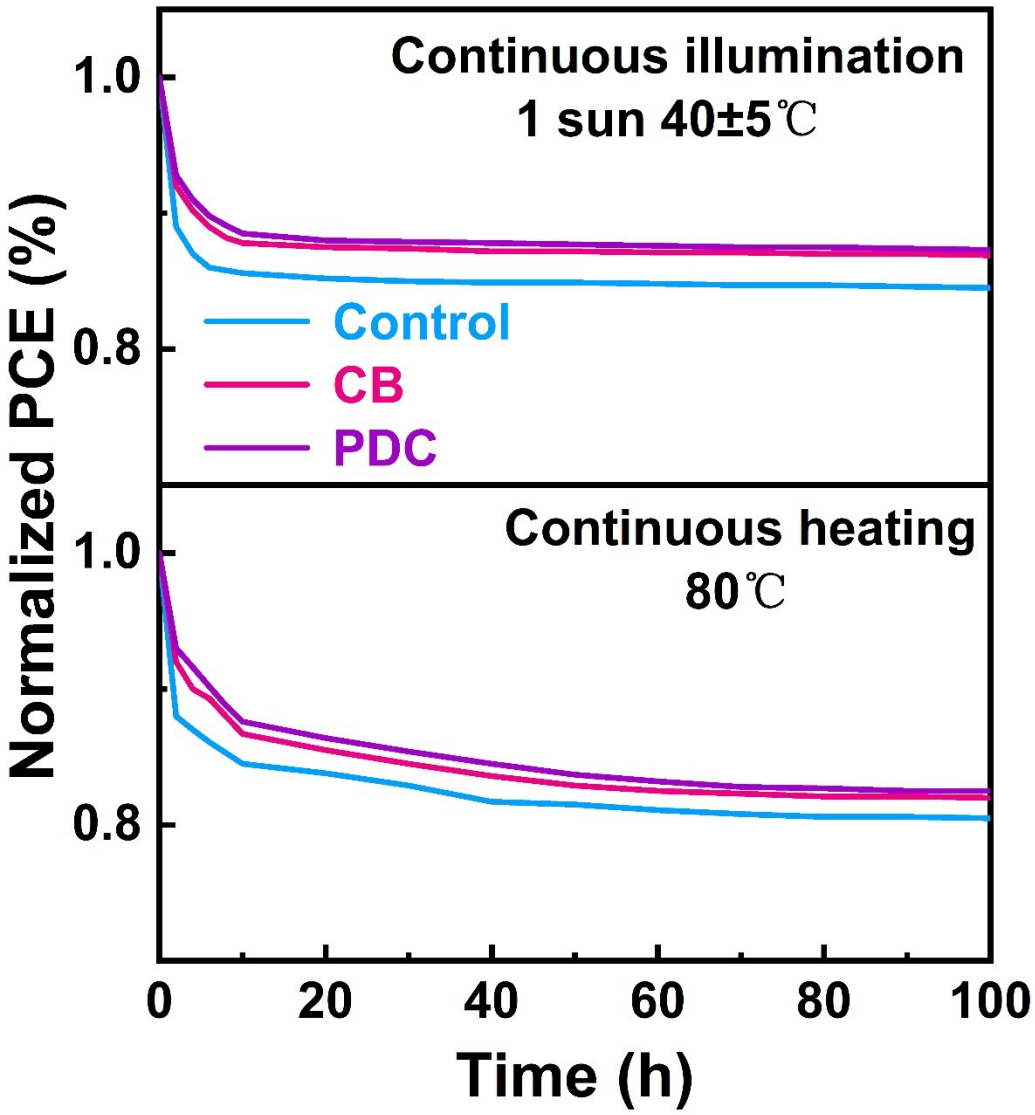

Figure S14. The stability of control, CB and PDC-treated devices under continuous heating at 80°C and 1 sun illumination.

Supplementary Tables

Table S1. Summary of photovoltaic operating parameters for different OSCs.

Device Condition	V_{OC}(mV)	J_{SC} (mA/cm^2)	J_{EQE}(mA/cm^2)[a)]	*FF* (%)	*PCE* (%)[b)]
PM6:eC9, control	857.4	27.17	25.98	72.93	16.99 (16.72±0.23)
PM6:eC9, CB	846.3	27.80	26.48	74.72	17.58 (17.38±0.21)
PM6:eC9, PDC	851.1	28.09	26.93	76.27	18.24 (18.01±0.18)
PM6:N3, control	841.3	26.28	25.67	71.53	15.82 (15.64±0.19)
PM6:N3, control	823.0	26.98	26.16	73.09	16.23 (16.00±0.25)
PM6:N3, PDC	832.9	27.11	26.41	74.10	16.73 (16.43±0.17)

[a)] The integrated J_{EQE} values were calculated from the EQE spectra;

[b)] The average PCEs with standard deviation were calculated from at least 10 devices.

Table S2. Summary of exciton dissociation rate and exciton collection rate for control and optimized devices with Control, CB and PDC.

J (mA/cm^2)	Control	CB	PDC
J_{sc}	26.87	27.25	27.82
J_{sat}	27.44	27.60	28.15
$J_{maxpower}$	24.00	24.78	25.61

Table S3. Electron and hole mobility of control, CB and PDC devices.

BHJ	μ_h (×10^{-4} cm^2 V^{-1} s^{-1})	μ_e (×10^{-4} cm^2 V^{-1} s^{-1})	μ_h/μ_e
Control	4.12	2.47	1.67
With CB	7.39	6.39	1.16
With PDC	8.11	7.53	1.08

Table S4. Analysis data of the two-dimensional GIWAXS results in out-of-plane direction (OOP) of Y6.

Pure film	Lattice plane	Peak location ($Å^{-1}$)	d-spacing (Å)	Coherence length (Å)	CCL/d
		q_z	q_z	q_z	q_z
Y6	010	1.78	3.54	19.14	5.41
CB	010	1.800	3.50	20.50	5.86
PDC	010	1.79	3.51	21.20	6.04

Table S5. Analysis data of the two-dimensional GIWAXS results in out-of-plane direction (OOP) of PM6:Y6.

Blend film	Lattice plane	Peak location ($Å^{-1}$)	d-spacing (Å)	Coherence length (Å)	CCL/d
		qz	qz	qz	qz
PM6:Y6	010	1.77	3.55	18.66	5.26
PM6:Y6+ CB	010	1.76	3.57	19.28	5.41
PM6:Y6+ PDC	010	1.77	3.54	19.66	5.55