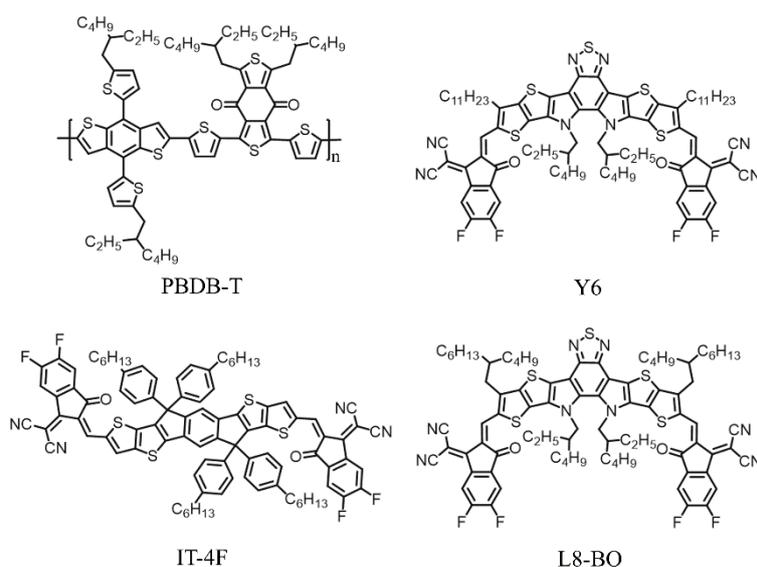


Supporting information

1 General characterization

UV-vis absorption spectra were measured on a UV-2600 UV-vis spectrophotometer (Shimadzu, Japan). Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted on an Xenocs-SAXS/WAXS system with an X-ray wavelength of 1.5418 Å and 0.2° as an incidence angle. Pilatus 300 K was used as a 2D detector. AFM was performed on a Bruker Dimension icon using tapping mode. The J - V curves were measured by using a Keithley 2450 SourceMeter in the nitrogen-filled glove box along the forward scan direction from -0.2 V to 1 V at room temperature. The scan speed and dwell time were fixed at 0.02 V per step and 0 ms, respectively. The photocurrent was measured under AM 1.5G illumination at 100 mW/cm² by using a 3 A solar simulator (LSS-55, Lightsky Technology Co., Ltd.). Light intensity was calibrated with a standard photovoltaic cell equipped with a KG2 filter (certificated by the National Institute of Metrology). The EQE measurement was carried out in the air with a solar cell spectral response measurement system (LST-QE, Lightsky Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell. Transient photocurrent (TPC) and Transient photovoltage (TPV) measurements were conducted on an all-in-one characterization platform, Paios(Fluxim AG, Switzerland). In the TPV measurement, the light intensities are 0.10%, 0.23%, 0.53%, 1.23%, 2.83%, 6.52%, 15.0%, 34.6% and 80.0%, respectively, relative intensity is 20.0% and settling time is 30.0 ms, pulse length is 5.0 ms, and the follow-up time is 30.0 μs.

2 Chemical structure



Scheme S1 Chemical structures of PBDB-T, Y6, IT-4F and L8-BO

3 GIWAXS

Table S1 The d -spacing and corresponding crystal coherence length (CCL) of π - π and lamellar stacking of PM6, PM6+, PM6:BTP-eC9 and PM6:BTP-eC9+ thin films

Film	$q_z/\text{\AA}^{-1}$	d -spacing/ \AA	$\text{FWHM}_{\pi-\pi}/\text{\AA}^{-1}$	$\text{CCL}_{\pi-\pi}/\text{\AA}$	$q_{xy}/\text{\AA}^{-1}$	d -spacing/ \AA	$\text{FWHM}_{\text{lam}}/\text{\AA}^{-1}$	$\text{CCL}_{\text{lam}}/\text{\AA}$
PM6	1.68	3.74	0.41	14	0.29	21.67	0.097	58
PM6+	1.68	3.74	0.39	15	0.30	20.94	0.092	62
PM6:BTP-eC9	1.73	3.63	0.26	22	0.29	21.67	0.081	70
PM6:BTP-eC9+	1.73	3.63	0.23	25	0.30	20.94	0.078	73

4 AFM

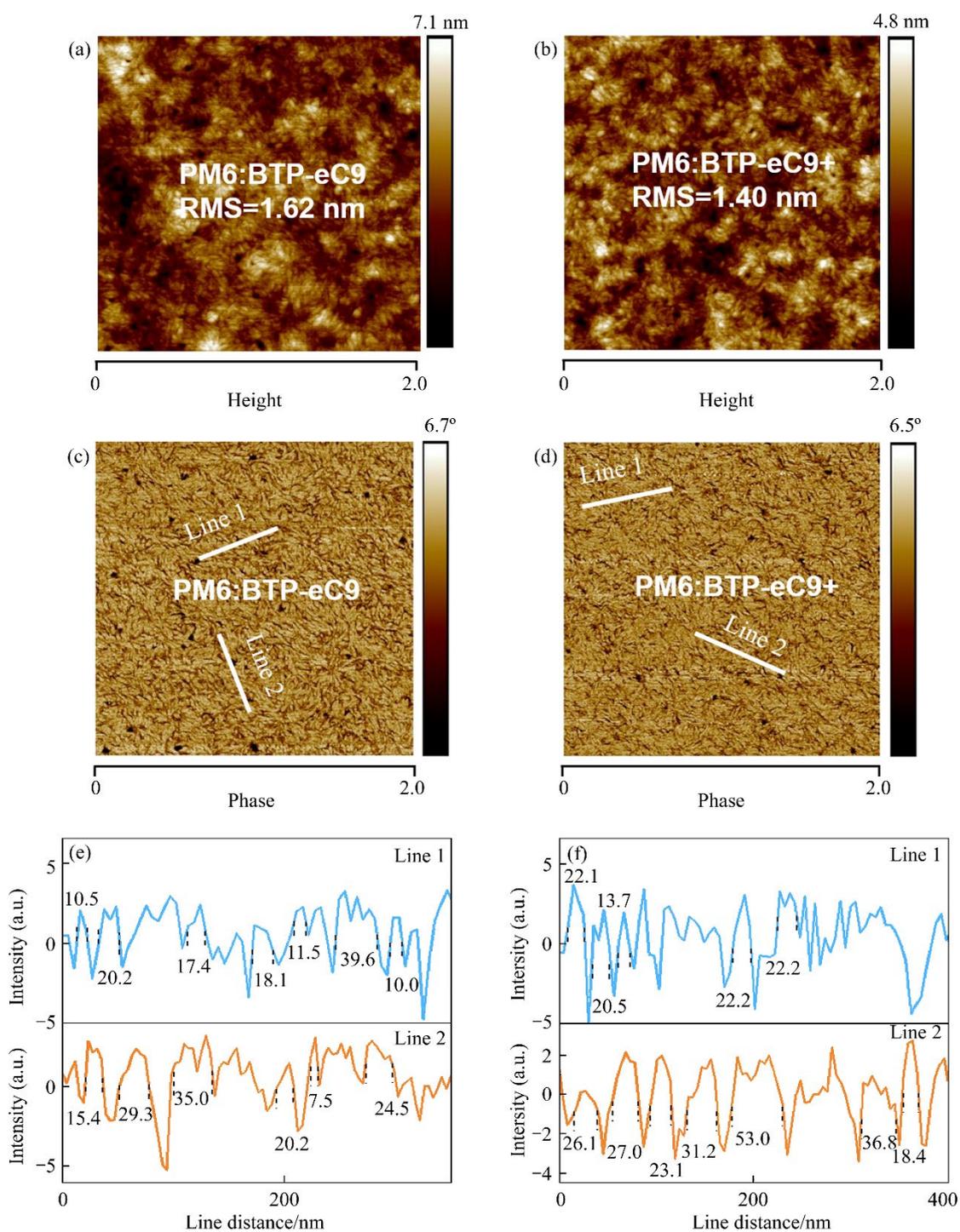


Figure S1 AFM height images of (a) PM6:BTP-eC9 and (b) PM6:BTP-eC9+ blend films; AFM phase images of (c) PM6:BTP-eC9 and (d) PM6:BTP-eC9+ blend films; The line profiles along the white lines to obtain the nano-grain size of (e) PM6:BTP-eC9 and (f) PM6:BTP-eC9+ blend films (The nano-grain size is obtained from the average FWHMs (the distance between two adjacent dashed lines in the graph))

5 Impedance spectra

Table S2 Components of the equivalent circuit as extracted by fitting the Nyquist plot data of PM6:BTP-eC9 and PM6:BTP-eC9+ based devices

Device	R_s/Ω	R_{sh}/Ω	Impedance frequency/Hz	$\tau/\mu\text{s}$
PM6:BTP-eC9	43.48	2487	4.64×10^4	21.6
PM6:BTP-eC9+	13.77	7308	1.47×10^4	68.0

6 SCLC

Charge carrier mobility was obtained by using the SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which can be described as:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \quad (\text{S1})$$

where J is the current density; μ is the zero-field mobility of electron (μ_e) or hole (μ_h); ε_0 is the permittivity of the vacuum; ε_r is the relative permittivity of the material; d is the thickness of the blend film; and V is the effective voltage, $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by the electrode work function difference.

6.1 Electron-only devices

The structure of electron-only devices is ITO/ZnO/active layer/Ca/Al. The ZnO precursor was spin-coated onto the ITO glass and annealed under 200 °C in air for 30 min. The PM6:BTP-eC9 blend in chlorobenzene (D:A ratio=1:1.2 (w/w)) with/without AN, was deposited onto the ZnO layer via spin-coating with 1200 r/min for 60 s. Then the film was annealed under 100 °C in N₂ for 10 min. Ca (~15 nm) and Al (~60 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10⁻⁴ Pa).

6.2 Hole-only devices

The structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Ag. A ~30 nm thick PEDOT:PSS layer was made via spin-coating an aqueous dispersion of PEDOT:PSS onto the ITO glass with 4000 r/min for 30 s. The PEDOT:PSS substrate was dried at 150 °C for 10 min. The PM6:BTP-eC9 blend in chlorobenzene (D:A ratio=1:1.2 (w/w)) with/without AN, was deposited onto the PEDOT:PSS layer via spin-coating with 3000 r/min for 30 s in N₂. Then the film was annealed under 100 °C for 10 min in N₂. Finally, MoO₃ (~3 nm) and Al (~100 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. 10⁻⁴ Pa).

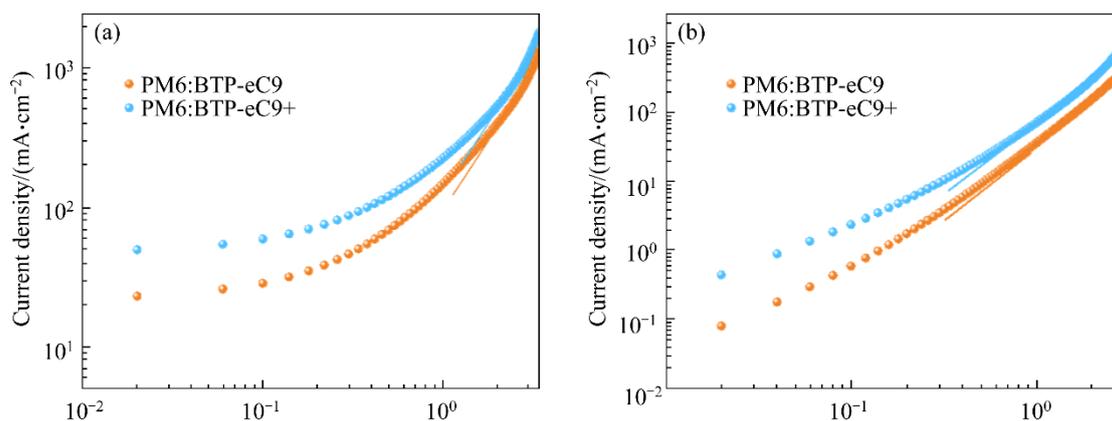


Figure S2 Typical current density-applied voltage log plots for (a) electron-only devices and (b) hole-only devices based on PM6:BTP-eC9 and PM6:BTP-eC9+ blend films under dark. The measured data are shown as symbols, while the solid lines are the best fits to the SCLC model. Mobilities were extracted from the fitting

Table S3 Charge carrier mobilities of devices based on PM6:BTP-eC9 and PM6:BTP-eC9+ blend films

Blend film	$\mu_e/(10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})$	$\mu_h/(10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})$
PM6:BTP-eC9	9.80	4.97
PM6:BTP-eC9+	13.22	9.70

7 Photovoltaic performance of OSCs

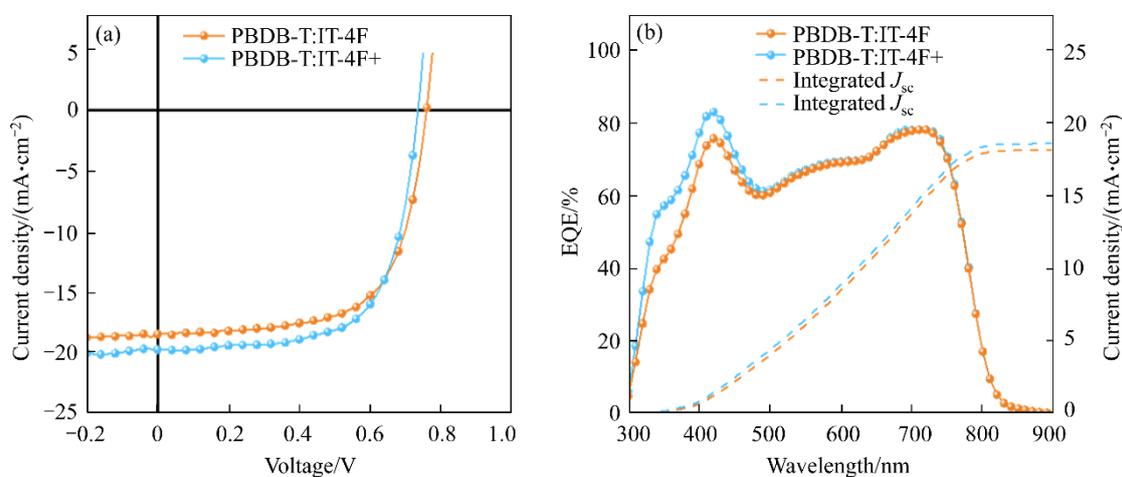


Figure S3 J - V curves and EQE spectra of PBDB-T:IT-4F and PBDB-T:IT-4F+ based OSCs

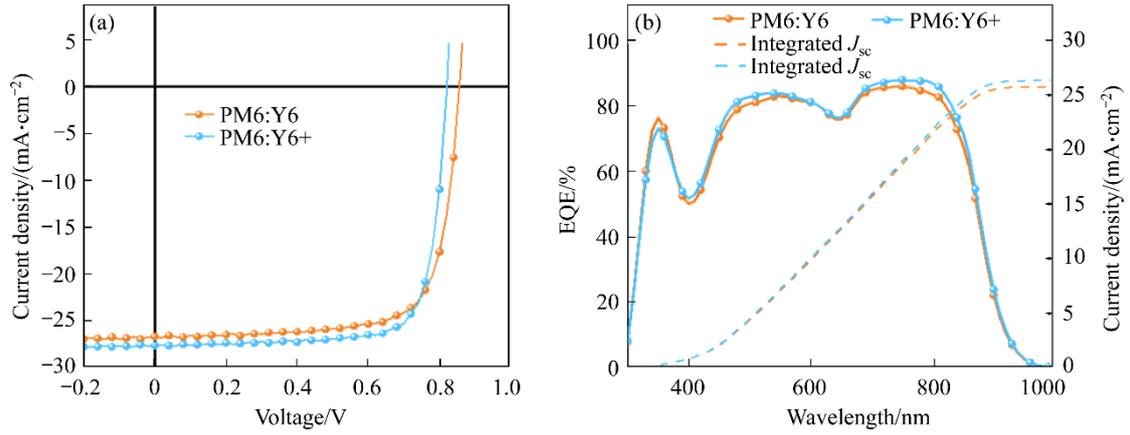


Figure S4 J - V curves and EQE spectra of PM6:Y6 and PM6:Y6+ based OSCs

Table S4 Photovoltaic parameters of OSCs based on PBDB-T:IT-4F, PBDB-T:IT-4F+, PM6:Y6 and PM6:Y6+ blend films

Blend film	V_{oc}/V	$J_{sc}/(\text{mA}\cdot\text{cm}^{-2})$	$FF/\%$	$PCE/\%$	$J_{EQE}/(\text{mA}\cdot\text{cm}^{-2})$
PBDB-T:IT-4F	0.759	18.50	65.17	9.15	18.12
	(0.748±0.005)	(18.47±0.39)	(63.76±0.98)	(8.80±0.17)	
PBDB-T:IT-4F+	0.734	19.72	66.79	9.67	18.56
	(0.732±0.003)	(19.56±0.25)	(66.29±0.75)	(9.49±0.12)	
PM6:Y6	0.856	26.76	74.33	17.02	25.75
	(0.850±0.008)	(26.61±0.31)	(74.25±0.59)	(16.80±0.19)	
PM6:Y6+	0.821	27.66	77.95	17.70	26.35
	(0.816±0.002)	(27.44±0.25)	(77.71±0.45)	(17.40±0.17)	

Note: The average values and standard deviations of 10 devices are in parentheses.

8 Exciton dissociation

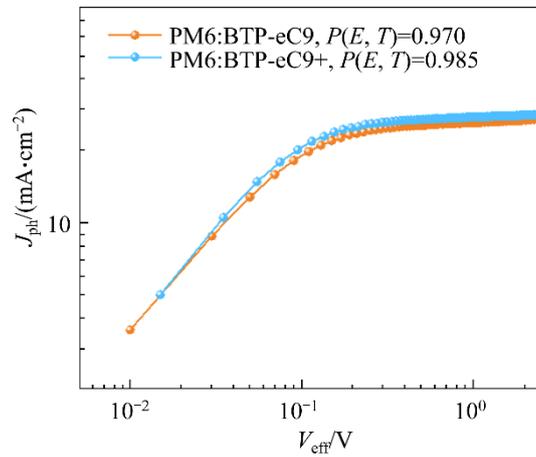


Figure S5 Photocurrent density versus effective voltage curves of PM6:BTP-eC9 and PM6:BTP-eC9+ based OSCs

9 Monomolecular recombination

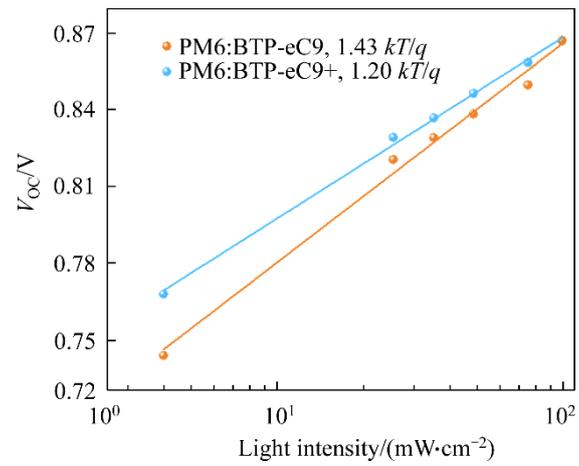


Figure S6 Dependence of V_{OC} on incident light intensity of PM6:BTP-eC9 and PM6:BTP-eC9+ based OSCs