Supporting Information for

Achieving 20% Efficiency for Binary Organic Solar Cells with Suppressed

Non-radiative Recombination via Triphenylamine Halides

Junjie Zhang,^{ab} Xiaopeng Duan, ^{*ab} Xiaoming Li,^b Guangkuo Dai,^b Jiawei Deng,^b Xunchang Wang,^c Jiawei Qiao,^d Hanzhi Wu,^d Liming Liu,^e Haodong Huang,^f Sha Liu,^f Jun Yan,^e Huotian Zhang,^g Xiaotao Hao,^d Renqiang Yang, ^{*c} Feng Gao,^g and Yanming Sun^{*ab}

Experimental Section

Materials and Methods

All purchased materials were used without further purification. PM6 and L8-BO were purchased from Solarmer Materials Inc. The number-average molecular weight (Mn) and PDI of PM6 are 41 kDa and 2.39, respectively. FPA and IPA were purchased from Shanghai Haohong Scientific Co., Ltd. ClPA and BrPA were synthesized in our group. Chloroform (CF) was purchased from Energy Chemical. The silver for electrodes were purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd.

Device Fabrication

All OSCs were fabricated with a device structure of ITO/2PACz/active layer/PNDIT-F3N/Ag. The ITO-coated substrates were sequentially cleaned by detergent, deionized water, acetone, and isopropyl alcohol for 20 min in an ultrasonic cleaning machine. The cleaned ITO-coated substrates were dried in an oven at 100 °C overnight. Before used, the ITO-coated substrates were pretreated by a plasma cleaner for 1 min under a vacuum condition below 100 Pa. Then a monolayer of 2PACz (0.3 mg/ml in ethanol) was firstly deposited on the top of the ITO substrates at a rate of 3000 rpm for 30 s, followed by thermal annealing at 100 °C for 10 min under ambient conditions. The active materials were dissolved in the CF with a D/A weight ratio of 1:1.2 and a total concentration of 17 mg ml⁻¹. All the optimal contents of additives FPA, CIPA, BrPA and IPA are 20% to the weight of PM6. The CF solutions were stirred at room temperature (25 °C) for 4 h before used. The active layers were prepared by spin-coating the CF solutions on the top of 2PACz layer with an optimal thickness of 100 nm in a nitrogen glove box. Then, the active layers were thermally annealed at 80 °C for 8 min. Subsequently, a thin layer of PNDIT-F3N (1.2 mg ml⁻¹ in methanol with 1 vol% acetic acid) was spin-coated onto the active layer at a rate of 4200 rpm for 30 s. Finally, a 100 nm-thick silver layer was thermally deposited under a vacuum condition of 2×10⁻⁴ Pa. The active area of devices is 5.12 mm².

Device characterization

The devices were tested through a mask with an area of 3.15 mm^2 . The device performance was measured by using a 510 Air Mass 1.5 Global (AM1.5G) solar simulator (SS-F5-3A, Enlitech) with an irradiation intensity of 100 mW cm⁻², which was determined by using a calibrated silicon solar cell (SRC2020, Enlitech). The *J-V* characteristics were measured by using a Keithley 2400 Source

Measure Unit. EQE spectra were performed by using a QE-R3011 Solar Cell EQE measurement system (Enlitech).

Ultraviolet-visible (UV-vis) spectroscopy measurements

UV-vis absorption spectra of the pristine and blend films were acquired with a UV-vis spectrophotometer (Shimadzu UV-3700).

Space-charge-limited current (SCLC) measurements

SCLC method was used to study the charge transport properties of neat film and blend films. The hole-only and electron-only devices were fabricated with a structure of ITO/2PACz/Active Layer/MoO₃/Ag and ITO/ZnO/ Active Layer /PNDIT-F3N/Ag, respectively. The charge carrier mobility was determined by fitting the corresponding *J*-*V* characteristics by using the equation of $J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where *J* is the current density, ε_0 is the permittivity of free space, ε_r is the permittivity of the active layer, μ is the charge carrier mobility (μ_h and μ_e), *V* is the effective voltage ($V=V_{appl}-V_{bi}$, in which V_{appl} is the applied voltage, V_{bi} is the built-in potential) and *L* is the film thickness of the neat film or blend film.

Voltage loss characterization

The EL spectra were measured using a Shamrock SR-303i spectrometer from Andor Tech with a Newton EM-CCD Si and an iDus InGaAs array detector at -60 °C. EQE_{EL} measurements were done using a home-built setup using a Keithley 2400 to inject current to the solar cells. Emission photon-flux from the solar cells was recorded using a Si detector (Hamamatsu s1337-1010BQ) and a Keithley 6482 picoammeter.

Photo-induced force microscope (PiFM)

A VistaScope microscope from Molecular Vista Inc. was coupled to a LaserTune QCL product with a wave number resolution of 0.5 cm⁻¹ and a tuning range from 800 to 1800 cm⁻¹ from Block Engineering. The microscope was performed in dynamic mode, with NCH-Au 300 kHz noncontact cantilevers from Nanosensors.

In-situ absorption measurements

The in-situ absorption measurements were detected by Spectrum Microvision DU-200. The detection range of the instrument is 186-1026 nm with a spectral resolution of 0.01 nm and a time resolution of

1 ms.

Atomic force microscopy (AFM)

AFM images were performed on a Dimension Icon AFM (Bruker) in a tapping mode.

Two-dimensional grazing incidence X-ray diffraction (2D-GIXRD)

2D-GIXRD measurement was performed by detector Pilatus3R 1M, Dectris (X-ray Source: MetalJet-D2, Excillum).

Femtosecond transient absorption spectroscopy (TAS)

Femtosecond transient absorption spectroscopy measurements were performed on an Ultrafast Helios pump-probe system in collaboration with a regenerative amplified laser system from Coherent. An 800 nm pulse with a repetition rate of 1kHz, a length of 100 fs, and an energy of 7 mJ/pluse, was generated by an Ti:sapphire amplifier (Astrella, Coherent). The time delay between pump and probe was controlled by a motorized optical delay line with a maximum delay time of 8 ns. The samples films were spin-coated onto the 1 mm-thick quartz plates and are encapsulated by epoxy resin in nitrogen-filled glove box to resist water and oxygen in the air. The pump pulse is chopped by a mechanical chopper with 500 Hz and then focused on to the mounted sample with probe beams. The probe beam was collimated and focused into a fiber-coupled multichannel spectrometer with CCD sensor. The energy of pump pulse was measured and calibrated by a power meter (PM400, Thorlabs).charge transport properties of the blend film were investigated by a space-charge-limited current method. The hole-only devices were fabricated with a configuration of ITO/2PACz /active layer/MoO₃/Ag, and the electron-only devices were fabricated with a structure of ITO/ZnO/ active layer /PNDIT-F3N-Br/Ag. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by: $J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the current density, μ is the zero-field mobility of holes (μ_h) or electrons (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, L is the thickness of the blend film, and V is the effective voltage (V = V_{appl} - V_{bi} , where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, $V_{\rm bi} = 0.1$ V for hole-only devices, $V_{\rm bi} = 0$ V for electron-only devices. The mobility was calculated from the slope of $J^{1/2}$ -V plots.

Photoluminescence Quantum Yield Measurements (PLQY)

PLQY measurement was conducted using the N-M01 integrating sphere from Edinburgh Instruments, with the optical system calibrated by a standard halogen light source (AvaLight HAL-S-Mini). The film samples were spin-coated onto glass substrates at a concentration of 12 mg/mL and a rotation speed of 1800 rpm. The solution samples were prepared by dissolving 2.4 μ g/mL of the substance in chloroform and stored in quartz cuvettes. The excitation sources consisted of continuous-wave (CW) lasers: the CPS532 (532 nm) and CPS780S (780 nm) from Thorlabs, with laser intensity monitored using a power meter. For PLQY measurements, a 550 nm long-pass filter with an optical density of 4.0 was used to attenuate the 532 nm excitation light. The film samples were tested for both "direct" and "indirect" excitation to eliminate the interference of indirect excitation. Due to the wavelength limitations of the silicon detector and the presence of the second-order laser at 1064 nm, the initial PLQY calculation covers only the PL range up to 1000 nm. The InGaAs detector was employed to measure the full PL spectrum under 780 nm excitation, with the ratio of the PL integral to the full PL integral below 1000 nm serving as the correction factor.

Figures and Tables



Figure S1. FT-IR spectra of annealed PM6:L8-BO films without or with TPA halide additives.



Figure S2. FT-IR spectra of different TPA halides and the annealed PM6:L8-BO blends without or with TPA halide additives.



Figure S3. *J-V* characteristics of (a) PM6:L8-BO-X, (b) D18:L8-BO, (c) PM6:BTP-eC9 and (d) PM6:L8-BO-C4 devices processed under different conditions. EQE spectra and the integrated J_{sc} s of (e) PM6:L8-BO-X, (f) D18:L8-BO, (g) PM6:BTP-eC9 and (h) PM6:L8-BO-C4 devices processed with different conditions.



Figure S4. Certification report of ClPA-processed D18:L8-BO device by National Institute of Metrology (NIM), China.



Figure S5. The thermal stability of PM6:L8-BO OSCs processed with different conditions.



Figure S6. J-V characteristics of the large-area PM6:L8-BO OSCs (1 cm²) processed with different conditions.



Figure S7. Normalized sEQE, normalized EL and calculated EL (dashed lines) as a function of energy for OSCs treated with (a) FPA, (b) BrPA and (c) IPA. The product of sEQE and Φ_{BB} is used to calculate the EL, where Φ_{BB} represent the room-temperature black body photon flux.



Figure S8. Normalized absorption and PL spectra of PM6:L8-BO without or with TPA halides.



Figure S9. Plots of the PCE *vs.* ΔE_{nr} of the binary OSCs reported in the literature.



Figure S10. Measured and fitted temperature-dependent PL spectra of L8-BO thin films treated without additives. All measurements were performed in a cryostat at six different temperatures: 80 K, 120 K, 160 K, 200 K, 240 K, and 300 K.



Figure S11. Measured and fitted temperature-dependent PL spectra of L8-BO thin films treated with FPA. All measurements were performed in a cryostat at six different temperatures: 80 K, 120 K, 160 K, 200 K, 240 K, and 300 K.



Figure S12. Measured and fitted temperature-dependent PL spectra of L8-BO thin films treated with CIPA. Allmeasurements were performed in a cryostat at six different temperatures: 80 K, 120 K, 160 K, 200 K, 240 K,and300K.



Figure S13. Measured and fitted temperature-dependent PL spectra of L8-BO thin films treated with BrPA. All measurements were performed in a cryostat at six different temperatures: 80 K, 120 K, 160 K, 200 K, 240 K, and 300 K.



Figure S14. Measured and fitted temperature-dependent PL spectra of L8-BO thin films treated with IPA. All measurements were performed in a cryostat at six different temperatures: 80 K, 120 K, 160 K, 200 K, 240 K,

and 300 K.



Figure S15. (a) Energy levels of L8-BO processed with different conditions measured in thin films using cyclic voltammetry. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potential and the onset reduction potential using the equation: HOMO/LUMO= - (E_{ox}/E_{red} + 4.37) eV. (b) Static energetic distribution of local excitonic state for L8-BO thin films processed with different conditions. σ_s indicates the size of static energetic disorder assuming Gaussian type DOS. The gray shaded area denotes the exciton occupation under optical excitation assuming quasi-thermal equilibrium.



Figure 16. Cyclic voltammetry curves of (a) PM6 films and (b-f) L8-BO films processed with different conditions.



Figure S17. *J-V* characteristics of (a) electron-only devices and (b) hole-only devices based on PM6:L8-BO devices without and with different TPA halides.



Figure S18. FT-IR spectra of the PM6 and L8-BO.



Figure S19. Combined PiFM images of PM6:L8-BO blend films without or with TPA halides.



Figure S20. PiFM images at the wavenumber of (a) 1648 cm⁻¹ (representing PM6, green) and (c) 1270 cm⁻¹ (representing L8-BO, red), and (b,d) the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO blend processed without additives.



Figure S21. PiFM images at the wavenumber of (a) 1648 cm⁻¹ (representing PM6, green) and (c) 1270 cm⁻¹ (representing L8-BO, red), and (b,d) the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO blend processed with FPA.



Figure S22. PiFM images at the wavenumber of (a) 1648 cm⁻¹ (representing PM6, green) and (c) 1270 cm⁻¹ (representing L8-BO, red), and (b,d) the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO blend processed with CIPA.



Figure S23. PiFM images at the wavenumber of (a) 1648 cm⁻¹ (representing PM6, green) and (c) 1270 cm⁻¹ (representing L8-BO, red), and (b,d) the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO blend processed with BrPA.



Figure S24. PiFM images at the wavenumber of (a) 1648 cm⁻¹ (representing PM6, green) and (c) 1270 cm⁻¹ (representing L8-BO, red), and (b,d) the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO blend processed with IPA.



Figure S25. AFM height images of PM6:L8-BO blends processed with different conditions.



Figure S26. (a) 2D GIWAXS patterns and (b) the corresponding OOP and IP line cuts of neat PM6 films without or with different TPA halides.



Figure S27. (a) 2D GIWAXS patterns and (b) the corresponding OOP and IP line cuts of neat L8-BO filmswithoutorwithdifferentTPAhalides.

 $J_{\rm sc}{}^{\rm cal}$ FF PCE a) $V_{\rm oc}$ $J_{\rm sc}$ Active layer $(mA cm^{-2})$ (V) $(mA cm^{-2})$ (%) (%) 0.880 26.53 77.0 17.98 PM6:L8-BO-X (w/o) 25.80 (0.878 ± 0.003) (26.24 ± 0.31) (75.8 ± 1.1) (17.70 ± 0.32) 0.896 27.65 79.7 19.74 PM6:L8-BO-X (ClPA) 26.67 (0.895 ± 0.003) (27.40 ± 0.27) (78.8 ± 1.1) (19.50 ± 0.25) 0.917 26.10 78.0 18.67 D18:L8-BO (w/o) 25.46 (0.914 ± 0.004) (25.82 ± 0.30) (76.8 ± 1.3) (18.44 ± 0.27) 0.925 27.11 80.0 20.06 D18:L8-BO (ClPA) 26.20 (0.923 ± 0.003) (26.82 ± 0.30) (79.9 ± 1.5) (19.82 ± 0.26) 0.864 27.29 77.7 18.32 PM6:BTP-eC9 (w/o) 27.00 (0.860 ± 0.003) (26.99 ± 0.33) (76.9 ± 1.3) (18.01 ± 0.33) 0.876 28.48 79.4 19.81 PM6:BTP-eC9 (ClPA) 27.62 (0.875 ± 0.002) (28.20 ± 0.28) (78.5 ± 1.0) (19.53 ± 0.28) 0.886 26.38 78.0 18.23 PM6:L8-BO-C4 (w/o) 25.46 (0.884 ± 0.004) (26.11 ± 0.29) (77.1 ± 0.9) (17.98 ± 0.25) 0.894 27.22 80.2 19.52 PM6:L8-BO-C4 (ClPA) 26.30 (0.892 ± 0.003) (27.00 ± 0.25) (79.2 ± 1.1) (19.24 ± 0.28) D18:L8-BO (ClPA) b) 0.920 26.13 81.34 19.54

Table S1. Detailed photovoltaic parameters of PM6:L8-BO-X, D18:L8-BO, PM6:BTP-eC9, and PM6:L8-BO-C4 devices processed with different conditions.

^{a)} Average values obtained from 10 devices.

^{b)} Certified efficiency by the National Institute of Metrology (NIM), China.

Table S2. Detailed photovoltaic parameters of the large-area PM6:L8-BO OSCs (1 cm²) processed with different conditions.

Active layer	$V_{\rm oc}$ (V)	$J_{\rm sc}~({ m mA~cm^{-2}})$	FF (%)	PCE (%) ^{a)}	
PM6:L8-BO (w/o)	0.893	25.91	68.0	15.73	
	(0.891 ± 0.003)	(25.62 ± 0.36)	(67.2 ± 0.9)	(15.57 ± 0.23)	
PM6:L8-BO (CIPA)	0.914	26.93	75.1	18.48	
	(0.911 ± 0.003)	(26.65 ± 0.33)	(74.3 ± 0.9)	(18.27 ± 0.20)	

^{a)} Average values obtained from 10 devices.

Active layer	${\mu_{\rm h}}^{ m a)}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_{ m e}^{ m a)}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_{ m h}/\mu_{ m e}$
PM6:L8-BO (w/o)	9.44×10 ⁻⁴	6.10×10 ⁻⁴	1.55
PM6:L8-BO (FPA)	1.06×10 ⁻³	8.08×10 ⁻⁴	1.31
PM6:L8-BO (CIPA)	1.41×10 ⁻³	1.27×10 ⁻³	1.10
PM6:L8-BO (BrPA)	1.19×10 ⁻³	1.07×10 ⁻³	1.12
PM6:L8-BO (IPA)	9.50×10 ⁻⁴	6.91×10 ⁻⁴	1.38

Table S3. The hole mobilities and electron mobilities of varied PM6:L8-BO devices.

^{a)} Average values obtained from 20 devices.

	100 (IP)			010 (OOP)				
Blend films	q	<i>d</i> -spacing ^{a)}	FWHM	CCL ^{b)}	q	<i>d</i> -spacing ^{a)}	FWHM	CCL ^{b)}
	(Å-1)	(Å-1)	(Å-1)	(Å)	(Å-1)	(Å-1)	(Å-1)	(Å)
PM6:L8-BO (w/o)	0.306	20.52	0.117	47.93	1.596	3.93	0.371	15.05
PM6:L8-BO (FPA)	0.307	20.46	0.111	50.58	1.607	3.91	0.361	15.49
PM6:L8-BO (ClPA)	0.310	20.26	0.110	51.04	1.61	3.90	0.348	16.04
PM6:L8-BO (BrPA)	0.309	20.32	0.110	50.81	1.608	3.91	0.353	15.82
PM6:L8-BO (IPA)	0.309	20.32	0.110	50.81	1.614	3.89	0.369	15.15

Table S4. Crystal coherence length and the *d*-spacing of (100) peaks in IP direction and (010) peaks in OOP direction of the PM6:L8-BO blend films.

^{a)} Obtained by the equation of $d=2\pi/q$, in which q is the corresponding x-coordinate of diffraction peak;

^{b)} Calculated using the equation: CCL= $2\pi K$ /FWHM, in which FWHM is the full width at half maxima and *K* is a form factor (0.89 here).

	100 (IP)				010 (OOP)			
Neat films	q	<i>d</i> -spacing ^{a)}	FWHM	CCL ^{b)}	q	<i>d</i> -spacing ^{a)}	FWHM	CCL ^{b)}
	(Å-1)	(Å-1)	(Å-1)	(Å)	(Å-1)	(Å-1)	(Å-1)	(Å)
PM6 (w/o)	0.287	21.88	0.113	49.68	1.571	4.00	0.375	14.90
PM6 (FPA)	0.287	21.88	0.105	53.49	1.571	4.00	0.372	15.02
PM6 (ClPA)	0.287	21.88	0.103	54.32	1.581	3.97	0.369	15.16
PM6 (BrPA)	0.287	21.88	0.104	53.85	1.581	3.97	0.371	15.05
PM6 (IPA)	0.287	21.88	0.105	53.08	1.571	4.00	0.374	14.96
L8-BO (w/o)	0.379	16.57	0.170	32.80	1.603	3.92	0.385	14.529
L8-BO (FPA)	0.403	15.58	0.172	32.55	1.618	3.88	0.374	14.948
L8-BO (ClPA)	0.414	15.18	0.163	34.33	1.629	3.85	0.363	15.414
L8-BO (BrPA)	0.400	15.70	0.171	32.67	1.626	3.86	0.374	14.956
L8-BO (IPA)	0.396	15.84	0.173	32.40	1.614	3.89	0.377	14.810

Table S5. Crystal coherence length and the *d*-spacing of (100) peaks in IP direction and (010) peaks in OOP direction of the neat films.

^{a)} Obtained by the equation of $d=2\pi/q$, in which q is the corresponding x-coordinate of diffraction peak;

^{b)}Calculated using the equation: CCL= $2\pi K$ /FWHM, in which FWHM is the full width at half maxima and *K* is a form factor (0.89 here).