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## **Supplementary Information**

Improving the device performance of organic solar cells with immiscible solid additives

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## **Materials and Methods**

**Instruments.** UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. FT-IR Topographic absorption spectra were recorded on a BRUKER FT-IR spectrophotometer. images of the films were obtained on a VeecoMultiMode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of  $\sim$ 2 nN, and the scanning rate for a 1  $\mu$ m×1  $\mu$ m image size was 1.5 Hz.

**Materials.** All reagents and solvents, unless otherwise specified, were purchased from commercial sources and were used without further purification. PM6, Y6, ITIC, IT4F, and  $PC_{71}BM$  were purchased from Solarmer Inc. 2-hydroxy-4-methoxybenzophenone was purchased from Rhawn Inc.

**GISAXS Measurements.** GISAXS measurements were performed at beamline BL19U2 of National Facility for Protein Science Shanghai (NFPS) at Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray radiation was set as 1.01 Å and the incident angle was 0.15 degree. Scattered X-ray signals were collected using a Pilatus 1M detector (DECTRIS Ltd).

**Surface Tension Measurements.** Contact angle measurements were performed using water and diiodomethane by sessile drop analysis. The surface tension values of films were calculated through Fowkes approximation.

**Device Fabrication and Characterization.** Organic solar cell (OSC) devices were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) with the conventional structure of ITO/PEDOT:PSS/Active Layer/PFN-Br/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively

for 20 min in each step, and then treated in an ultraviolet ozone generator for 20 min before being spin-coated 4500 with layer of 20 nm thick poly(3,4at rpm a ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P AI4083). After baking the PEDOT:PSS layer in air at 150 °C for 20 min, the substrates were transferred to a glovebox. For PM6:Y6 based devices, the active layer was spin coated from 16 mg/mL chloroform solution (D:A = 1:1.2 by wt., 0.5% v/v CN, 25% w/w uv-9, uv-9 was previously dissolved in chloroform at a concentration of 200 mg/mL) at 2400 rpm for 25 s to form an active layer of around 100 nm. Then an extra pre-annealing at 100 °C for 10 min was performed for devices. For PM6:PC71BM based devices, the active layer was spin coated from 20 mg/mL chlorobenzene solution (D:A = 1:1.5 by wt., 0.5% v/v DIO, 25% w/w uv-9) at 2500 rpm for 25 s to form an active layer. Then an extra pre-annealing at 100 °C for 10 min was performed for devices. For PM6:ITIC or PM6:IT4F based devices, the active layer was spin coated from 17 mg/mL chloroform solution (D:A = 1:1.2 by wt., 0.5% v/v CN for PM6:ITIC based devices, 0.5% v/v DIO for PM6:ITIC based devices, 25% w/w uv-9) at 2400 rpm for 25 s to form an active layer. Then an extra preannealing at 100 °C for 10 min was performed for devices. The time for adding DIO, CN and uv-9 is different. DIO and CN is generally added 5-10 minutes before spin coating, while uv-9 needs to be added 30-40 minutes before spin coating. After that, a 5 nm thick poly9,9-bis6-(N,N,N-trimethylammonium)hexylfluorene-alt-co- phenylenebromide (PFN-Br) film was deposited as the cathode buffer layer by the spin-coating of a solution of 0.5 mg/mL PFN-Br in methanol. Finally, the Ag (100 nm) electrode was deposited by thermal evaporation to complete the device with an active area of 9.25 mm<sup>2</sup>, then a mask with an area of 5.979 mm<sup>2</sup> (certified by National Institute of Metrology (NIM), China) was used to measure the efficiency.

The *J-V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV/cm<sup>2</sup>. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (RE-R, Enlitech).

The photo stability of the OSCs was tested under simulated solar illumination (SS-F5-3A, Enlitech) along with AM 1.5G spectrum whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV/cm<sup>2</sup> in a dry nitrogen glove box.

The charge carrier mobilities of the films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/Active Layer/MoO<sub>3</sub>/Ag, electron-only devices were fabricated in a structure of ITO/ZnO/Active Layer/PFN-Br/Ag. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law.

$$J = \frac{9}{8} \varepsilon_{\rm r} \varepsilon_0 \mu \frac{{\rm V}^2}{{\rm L}^3}$$

Here,  $\varepsilon_r \approx 3$  is the average dielectric constant of the blend film,  $\varepsilon_0$  is the permittivity of the free space,  $\mu$  is the carrier mobility, *L* is the thickness of the film, and *V* is the applied voltage.



Fig. S1 FF statistic histogram of OSCs without or with different additives.



Fig. S2  $V_{OC}$  statistic histogram of OSCs without or with different additives.



Fig. S3 Normalized UV-vis absorption spectra of PM6 films with and without additive.



Fig. S4 Normalized UV-vis absorption spectrum of uv-9 in Film

Table S1	Charge carrier	mobility in the	corresponding active	e layers of devices.
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Active layer	AD	$\mu_h~(\times 10^{-4}cm^{-2}V^{-1}s^{-1})$	$\mu_{e}~(\times 10^{-4}cm^{-2}V^{-1}s^{-1})$	$\mu_e/\mu_h$
PM6:Y6	none	4.12	6.25	1.51
PM6:Y6	CN	4.52	5.17	1.14
PM6:Y6	uv-9	6.14	9.12	1.48

AD	$V_{OC}(V)$	Eg (eV)	Voc loss (eV)
none	0.838	1.41	0.572
CN	0.839	1.42	0.581
uv-9	0.813	1.38	0.567

**Table S2.** The band gap of OSC devices with and without uv-9 additive treatment calculated from EQE results and the corresponding  $V_{OC}$  loss.



Fig. S5 FT-IR absorption spectra of Y6 film and Y6+uv-9 films before and after thermal annealing.



Fig. S6 The photo stability of OSC devices with and without uv-9 additive treatment under simulated solar illumination in a dry nitrogen glove box.



Fig. S7 Normalized UV-vis absorption spectra of Y6+uv-9 films with different

thermal annealing time at 100 °C.



Fig. S8 Normalized UV-vis absorption spectra of Y6 and uv-9 blend films with different mass

ratios.



Fig. S9 Contact angles of (a) PM6, (b) Y6, (c) Y6:uv-9 (1:0.417 by wt.), and (d) uv-9 films.

Blend film	χ
PM6:Y6	0.27
PM6:Y6+uv-9	0.29
PM6:uv-9	5.784
Y6:uv-9	3.557

Table S3Flory-Huggins interaction parameters of the blend films.



Fig. S10 Photo images of Y6:uv-9 blend solvants with different mass ratios (uv-9:chloroform)at room temperature and 55°C.



Fig. S11 Chemical structures of PCBM, IT-4F, and ITIC

Table S4Summary of photovoltaic parameters of PM6/PC71BM, PM6/IT4F, and PM6/ITIC<br/>based devices without additive, with CN/DIO or uv-9 as active additive.

Active layer	Additive	$V_{OC}(V)$	Jsc (mA/cm <sup>2</sup> )	FF (%)	PCE(%)
PM6:PC71B	w/o	0.939±0.002	13.12±0.05	61.39±1.80	7.72(7.25)
	0.5%DIO	0.902±0.003	13.65±0.24	67.40±0.91	8.45(8.31)
	25%uv-9	0.926±0.002	13.78±0.23	68.33±1.00	9.01(8.71)
PM6:IT4F	w/o	0.883±0.002	19.03±0.10	68.47±0.56	11.77(11.51)
	0.3%DIO	$0.847 \pm 0.004$	20.54±0.24	70.95±0.93	12.76(12.35)
	25%uv-9	$0.645 \pm 0.004$	20.72±0.15	70.62±1.15	12.52(12.37)
PM6:ITIC	w/o	0.995±0.004	15.67±0.12	59.72±0.70	9.56(9.30)
	0.5%CN	$0.991 \pm 0.004$	15.44±0.13	61.99±0.58	9.60(9.48)
	25%uv-9	0.975±0.003	17.24±0.14	64.45±0.32	10.99(10.82)