Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

A new simple volatile solid additive triggers morphological optimization and performance stabilization in polymer solar cells

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1. Device fabrication

The positive device with ITO/PEDOT:PSS/ PM6:Y6/Phen-NaDPO/Ag was fabricated. The PM6:Y6 organic solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, 15 Ω/sq) patterned on the surface (device area: 0.1cm^2). Substrates were prewashed with isopropanol to remove organic residues before immersing in an ultrasonic bath of soap for 15 min. Samples were rinsed in flowing deionized water for 5 min before being sonicated for 15 min each in successive baths of deionized water, acetone and isopropanol. Next, the samples were dried with pressurized nitrogen before being exposed to a UV-ozone plasma for 15 min. PEDOT: PSS was diluted with the same volume of water, a thin layer of PEDOT: PSS (~20 nm) (Clevios AL4083) was spin-coated onto the UV-treated substrates, the PEDOT-coated substrates were subsequently annealed on a hot plate at 120 °C for 20 min, and the substrates were then transferred into the glovebox for active layer deposition. All solutions were prepared in the glovebox using the donors of PM6 and the acceptor of Y6; The PM6 and Y6 were purchased from organtec. ltd., and the 2,6-Dichloroiodobenzene (DCIB) was purchased from Shanghai Titan Technology Co., Ltd.. Optimized devices were obtained by dissolving PM6 and Y6 in chloroform (CF) using a D/A ratio of 1:1.2 total concentration of 17 mg/mL. Note: The as-prepared solutions were stirred overnight at room temperature before being spin coat on the PEDOT:PSS substrates. The active layers were spin-coated at an optimized speed of 3000 rpm for time period of 30s, resulting in films of 110 to 120 nm in thickness. The active layers were then thermal annealing (TA) for 5 min at 110 °C. The next stage is to coat ETL on active layer, about 40 uL Phen-NaDPO solution (0.5 mg/mL in Isopropyl alcohol) was spin-coated at 2000 rpm for 20s. Finally, the samples were placed in a thermal evaporator for evaporation of a 90 nm-thick layer of Silver (Ag) evaporated at 2 Å🙰s^{-1}; pressure of less than 2x10^{-6} Torr. Following electrode deposition, samples underwent *J-V* testing.

2. Device testing and characterization

The current density-voltage (*J-V*) curves of devices were measured using a Keithley 2400 Source Meter in glove box under AM 1.5G (100 mW cm^{-2}) using a Enlitech solar simulator (purchased from Enli Technology Co., Ltd.). A 2×2 cm^2 monocrystalline silicon reference cell with KG1 filter (purchased from Enli Tech. Co., Ltd., Taiwan). The external quantum efficiency (EQE) was measured by a certified incident photon to electron conversion (IPCE) equipment (QE-R) from Enli Technology Co., Lt. The light intensity at each wavelength was calibrated using a standard monocrystalline Si photovoltaic cell.

For TPV, the measurement was conducted under 1 sun conditions by illuminating the device with a white light-emitting diode, and the champion device is set to the open-circuit condition. For TPC, the champion device is set to the short-circuit condition in dark. The output signal was collected by key sight oscilloscope. The transient photocurrent (TPC) was testing under the short-circuit condition to explore the time-dependent extraction of photogenerated charge carriers. The 10 ns light plus laser were selected to the light source for steady the photogenerated current density. The devices are otherwise kept in the dark between pulses in order to avoid any influence of pulse frequency on the current responses. The transient photovoltage (TPV) was testing under the open-circuit condition to explore the photovoltage decay. The intensity of light is 230 μW/cm^2 and the wavelength of light is 520 nm. The light pulse is 10 ns.

The devices were placed in a nitrogen-filled glove box (O_2< 10 ppm; H_2O < 10 ppm) and performed efficiency tests every two days under a simulated solar light source (a Keithley 2400 source meter and an AAA grade solar simulator (Sirius-SS150A-D, Zolix Ltd.) along with AM 1.5G spectra whose intensity was corrected by a certified standard silicon solar cell (Certificate No.: GXtc2017-1280, NIM) at 1000 W/m^2).

The space-charge-limited current (SCLC) method for testing electron mobility and hole mobility was according to our previous article (*J. Mater. Chem. C*, 2018, ***6***, 11015).

Ultraviolet−visible light (UV-vis) absorption spectra were recorded on a Perkin Elmer Lambda 365 spectrophotometer. Topographic images of the films were obtained on a Bruker Dimension Edge atomic force microscopy (AFM). Transmission electron microscope (TEM) studies were conducted with an FEI Tecnai F20 electron microscope. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO TGA/DSC 1 thermogravimetric analyzer.

The contact angles of the films were performed on a DSA-100 (KRUSS Germany) contact angle meter. Then the surface free energy was calculated by Owens-Wendt method.

$$\gamma_L \times (1 + \cos\theta) = 2 \times \left(\gamma_L^d \cdot \gamma_{sv}^d\right)^{1/2} + 2 \times \left(\gamma_L^p \cdot \gamma_{sv}^p\right)^{1/2} \qquad (1)$$

where γ_L and γ_S are surface free energy of the probe liquid and sample, respectively, θ is the contact angle of the sample. The average contact angles of two liquids (deionized water and formamide) on the various neat films were measured and the results (Test three times separately) in Table S1, and the average contact angles and surface energy parameters are summarized in Table 2 (in Manuscript). Then calculate the Flory-Huggins interaction parameter $\chi_{\text{donor−acceptor}}$ for blend to show the binary miscibility from

$$K\left(\gamma_{donor}^{1/2} - \gamma_{acceptor}^{1/2}\right)^2 \qquad (2)$$

where γ is the surface energy of the material, K is the proportionality constant.

3. Supplemental figures

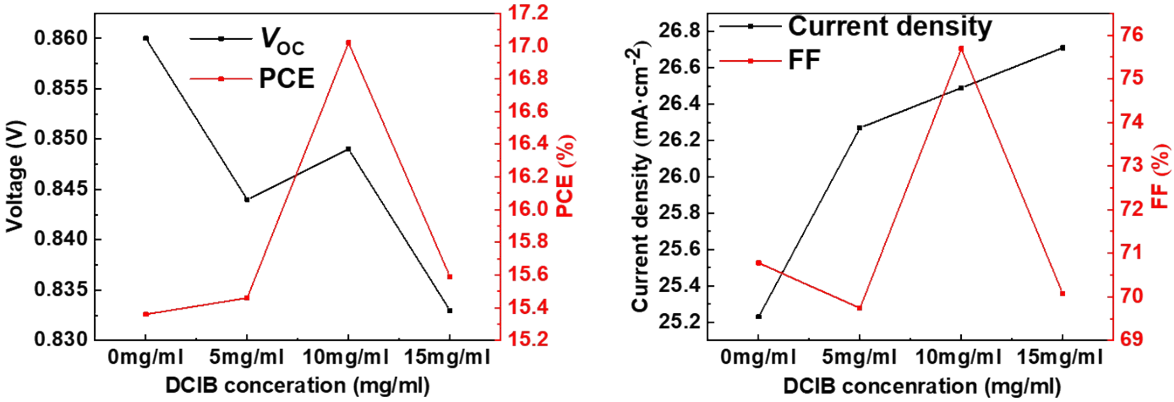

Fig. S1. Photovoltaic performances of PM6:Y6 based OSCs with different concentrations of DCIB.

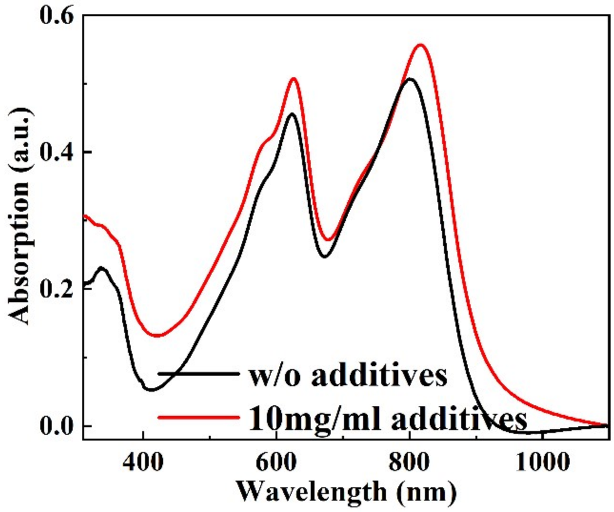

Fig. S2. UV-vis of PM6:Y6 blended films with (red) or with-out (black) DCIB additives.

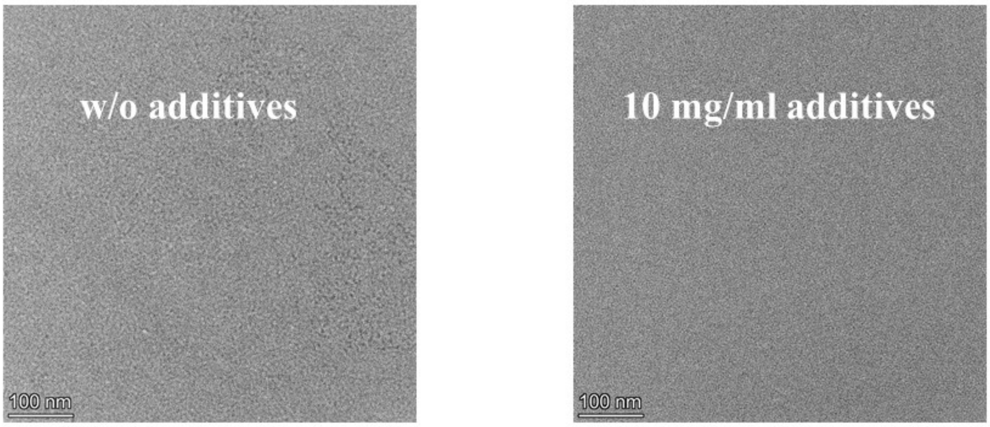

Fig. S3. TEM of PM6:Y6-based OSCs with different concentration of DCIB additive.

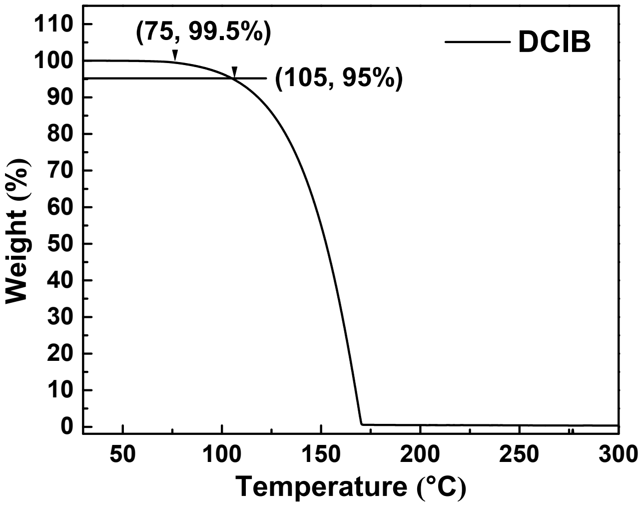

Fig. S4. TGA curve of DCIB additive with thermal balance under the protection of nitrogen at a heating rate of 10 ℃·min^{-1}.

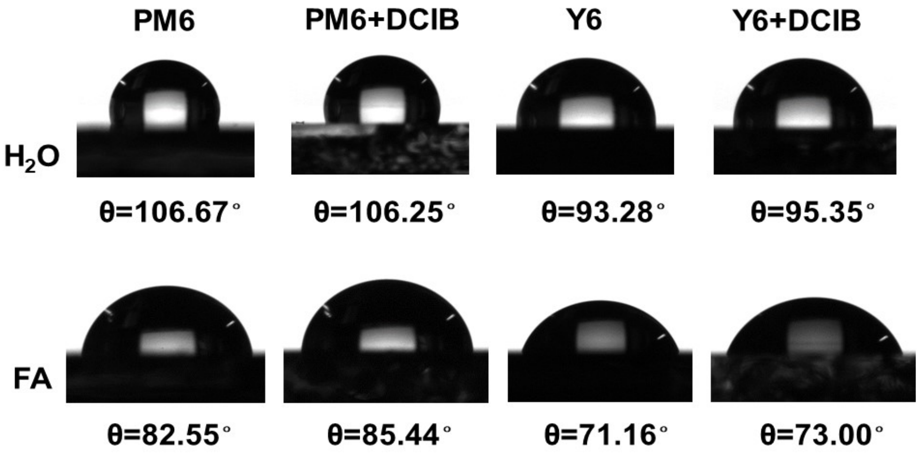

Fig. S5 The contact angles of the pristine and blended materials in deionized water (H_2O) and formamide (FA).

4. Supplemental tables

Table S1. PM6:Y6 based OSC devices with different concentrations of DCIB.

Conditions	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF (%)	$^{(b)}$PCE (%)
$^{(a)}$w/o additives	0.860±0.001	25.23±0.12	70.78±0.32	15.36±0.20
1 mg·mL^{-1} DCIB (TA 110℃ 5 min)	0.844±0.001	26.27±0.20	69.74±0.27	15.46±0.20
10 mg·mL^{-1} DCIB (TA 110℃ 5 min)	0.849±0.001	26.49±0.06	75.69±0.21	17.02±0.14

15 mg·mL^{-1} DCIB (TA 110℃ 5 min)	0.833±0.001	26.71±0.19	70.08±0.33	15.59±0.20
10 mg·mL^{-1} DCIB (TA 110℃ 10 min)	0.834±0.001	25.91±0.20	68.78±0.19	14.86±0.20

(a) Control devices (w/o additives) represent unadulterated additive treatment devices; (b) the average of 12 individual devices.

Table S2. Summarized *J*sat and *P* (E,T) treated under different conditions.

additives	*J*sat (mA·cm^{-2})	*P* (E,T) (%)
w/o	25.86	97.82
10 mg·mL^{-1} DCIB	27.15	96.50

Table S3. Summarized μ_e and μ_h treated under different conditions.

additives	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})	μ_h/μ_e
w/o	3.50×10^{-4} cm^2 V^{-1} s^{-1}	7.32×10^{-4} cm^2 V^{-1} s^{-1}	2.08
10 mg·mL^{-1} DCIB	5.34×10^{-4} cm^2 V^{-1} s^{-1}	8.18×10^{-4} cm^2 V^{-1} s^{-1}	1.53

Table S4. Summarized contact angles of the materials.

Films	**Contact angle (deg)**	
	H_2O	Formamide, FA
PM6	106.72	82.34
	106.70	82.64
	106.58	82.67
PM6+DCIB	106.45	85.00
	106.11	85.80
	106.18	85.51
Y6	93.12	71.18
	93.29	71.20
	93.42	71.10

Y6+DCIB	95.52	72.70
	95.22	72.70
	95.31	73.60