Supporting Information

Simultaneously Enhanced Efficiency and Stability of Polymer Solar Cells by Employing Solvent Additive and Upside-Down Drying Method

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EXPERIMENTAL SECTIONS

Indium tin oxide (ITO) glass substrates with a sheet resistance of 15 Ω square^{-1} were sequentially pre-cleaned in ultrasonic baths containing detergent, deionized water or ethanol, respectively. Then the cleaned ITO substrates were dried with nitrogen-gas and then treated by oxygen plasma to improve work function and clearance. The 80 μl PEDOT:PSS solution (purchased from H. C. Starck Co. Ltd.) was spin-coated onto the ITO substrates at 5000 round per min (RPM) for 40 s, and then annealed at 150 °C for 15 min. The PEDOT:PSS coated ITO substrates were transferred into a high-purity nitrogen-filled glove box. The used donor materials included poly[4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-b:4,5-b']dit-hiophene-co-3-fluor- othieno-[3,4-b]thiophene-2-carboxylate] (PTB7-Th) and 2,6-bis(trimethylstannyl)-4,8-bis(5-(octylthio) -thiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene (PBDT-TS1) (purchased from Organtec Material Inc.), poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-*alt*-(3,3'''-di (2-octyldodecyl)-2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)] (PffBT4T-2OD) (purchased from 1-Material Inc.) and thieno[3,4-b]thiophene/benzodithiophene (PTB7) (purchased from Luminescence Technology Corp.). The used acceptor material [6,6]-phenyl-C71-butyric acid methyl ester (PC$_{71}$BM) was purchased from 1-Material Inc. The mixed solvent of o-dichlorobenzene (DCB)/chlorobenzene (CB) with volume ratio of 1:1 was prepared to use as working solvent. The mixing weight ratio of PTB7-Th:PC$_{71}$BM, PTB7:PC$_{71}$BM or PBDT-TS1:PC$_{71}$BM was 1:1.5 and these blend materials were dissolved in the mixed solvents at a total concentration of 25 mg ml^{-1}, respectively. These solutions were continuously stirred at 80 °C for 12 hours. The blend PffBT4T-2OD:PC$_{71}$BM with weight ratio of 1:1.8 was dissolved in the mixed solvent at a total concentration of 28 mg ml^{-1}, and then the solution was continuously stirred at 110 °C for 12 hours. After that, 3 vol% DIO, 1 vol% AA or 3

vol% NMP was mixed into part of these solutions, respectively. The conjugated polyelectrolyte poly[(9,9-bis(30-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) (purchased from Organtec Materials Inc.) was dissolved in methanol at a concentration of 0.2 mg ml^{-1} with an addition of 0.25 vol% acetic acid. The PTB7-Th:PC$_{71}$BM, PTB7:PC$_{71}$BM or PBDT-TS1:PC$_{71}$BM blend solutions without or with solvent additive (25 °C, 60 μl) were spin-coated onto the top of PEDOT:PSS layer at 1500 RPM for 40 s, respectively. The hot PffBT4T-2OD:PC$_{71}$BM blend solutions without solvent additive (110 °C, 60 μl) were spin-coated onto the top of PEDOT:PSS layer at 800 RPM for 120 s. The pristine blend films were immediately placed in covered glass petri dish to undergo conventional or upside-down drying process, the slow drying process provide enough self-assembly time for active layers. The drying processes of blend films were carried out in high-purity nitrogen-filled glove box under ambient temperature of 25 °C. Here, the conventional drying method was defined as placing the top surface of blend film upward during the slow drying process. The upside-down drying method was defined as placing the top surface of blend film downward during the slow drying process. After that, 100 μl PFN methanol solution was spin-coated onto the top of active layer to prepare solution processed PFN interfacial layer. The cathode of 100 nm aluminum (Al) was deposited by thermal evaporation under 10^{-4} Pa, and the thickness was monitored by a quartz crystal microbalance. The active area of each device is about 3.8 mm^2, which is defined by the vertical overlap of ITO anode and Al cathode.

The current density-voltage (*J-V*) curves of PSCs were measured under 1 sun AM 1.5 G illumination (100 mW cm^{-2}) by using a Keithley 2400 source meter. The AM 1.5 G illumination was provided by an XES-40S2-CE (SAN-EI Electric Co., Ltd.) solar simulator (AAA class, 40 × 40 mm^2 effective irradiated area). All the PSCs were

stored in high-purity nitrogen-filled glove box and dark conditions. The measurement of device stability was also carried out in high-purity nitrogen-filled glove box with the ambient temperature of 25 °C. The external quantum efficiency (EQE) spectra of PSCs were measured by using a Zolix Solar Cell Scan 100. The absorption spectra of blend films were measured by using a Shimadzu UV-3101 PC spectrophotometer. The GIXD and XPS data were obtained at Beijing Synchrotron Radiation Facility (BSRF). A grazing incidence angle of 0.2° was chosen to investigate the crystallinity and orientation that prevailed throughout the blend films. A bent-triangle silicon crystal was used to obtain the X-rays of a wavelength of 1.54 Å. The water contact angle (WCA) images of films were recorded by using a KRÜSS DSA 100 instrument in ambient conditions. The TEM images of blend films were obtained by using a JEOL JEM-1400 transmission electron microscope operated at 80 kV. Prior to the TEM characterization, the blend films were stripped from PEDOT:PSS coated substrates by soaking the samples into deionized water and then transferred onto a holey carbon-coated copper grid. The thickness of the active layers was measured using an Ambios Technology XP-2 stylus Profiler.
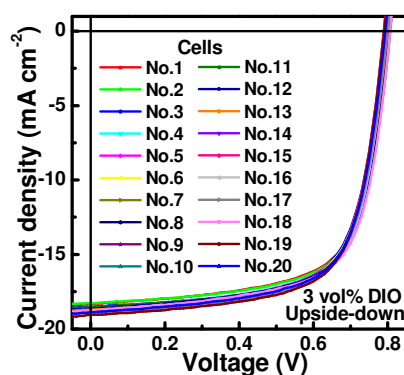

Figure S1. *J-V* curves of 20 optimized PSCs with mixing 3 vol% DIO and employing upside-down drying method.

Table S1. Photovoltaic parameters of 20 optimized PSCs with mixing 3 vol% DIO and employing upside-down drying method.

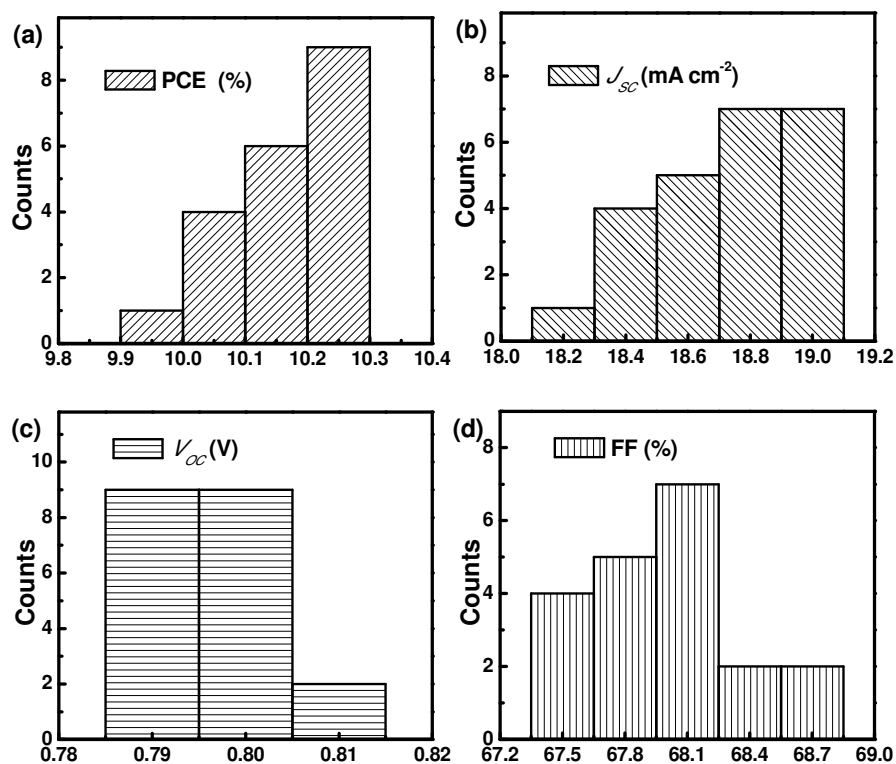| Cells	Jsc (mA cm^{-2})	Voc (V)	FF (%)	PCE (%)	Cells	Jsc (mA cm^{-2})	Voc (V)	FF (%)	PCE (%)
No.1	18.32	0.80	67.98	9.97	No.11	18.53	0.81	67.88	10.19
No.2	18.28	0.80	68.52	10.02	No.12	18.67	0.80	68.27	10.20
No.3	18.52	0.79	68.62	10.05	No.13	18.72	0.80	68.20	10.22
No.4	18.61	0.79	68.45	10.06	No.14	19.02	0.79	68.06	10.23
No.5	18.71	0.80	67.44	10.09	No.15	19.04	0.79	68.07	10.24
No.6	18.80	0.79	68.11	10.12	No.16	18.94	0.80	67.67	10.26
No.7	18.81	0.79	68.40	10.16	No.17	18.90	0.80	67.83	10.26
No.8	19.03	0.79	67.68	10.17	No.18	18.77	0.81	67.53	10.27
No.9	18.74	0.80	67.88	10.18	No.19	19.08	0.79	68.22	10.28
No.10	19.04	0.79	67.72	10.18	No.20	18.87	0.80	68.21	10.30

Figure S2. Statistical histograms of photovoltaic parameters for the 20 PSCs with mixing 3 vol% DIO and employing upside-down drying method: (a) PCE; (b) J_{SC}; (c) V_{OC}; (d) FF.
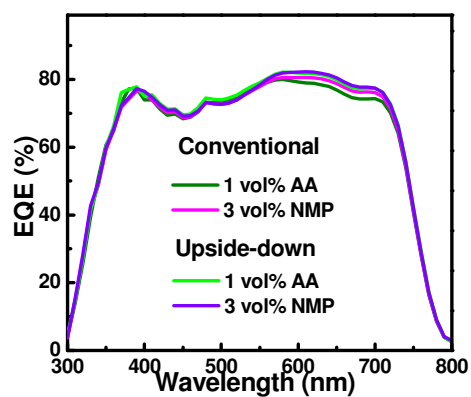
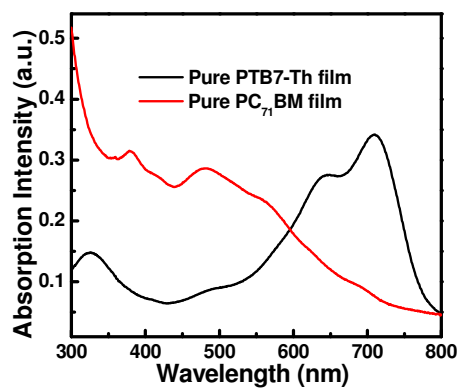**Figure S3.** EQE spectra of PSCs based on PTB7-Th:PC$_{71}$BM with 1 vol% AA or 3 vol% NMP.

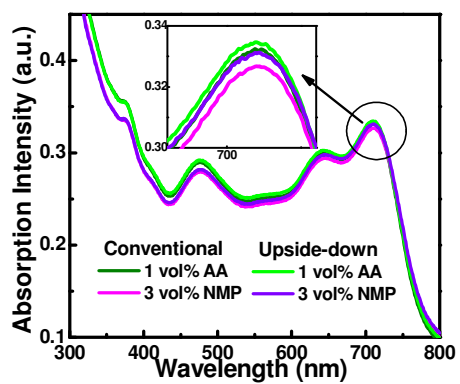**Figure S4.** Absorption spectra of neat PTB7-Th and PC$_{71}$BM films.

Figure S5. Absorption spectra of PTB7-Th:PC$_{71}$BM blend films with 1 vol% AA or 3 vol% NMP (the inset image is partial zoomed-in absorption spectra).
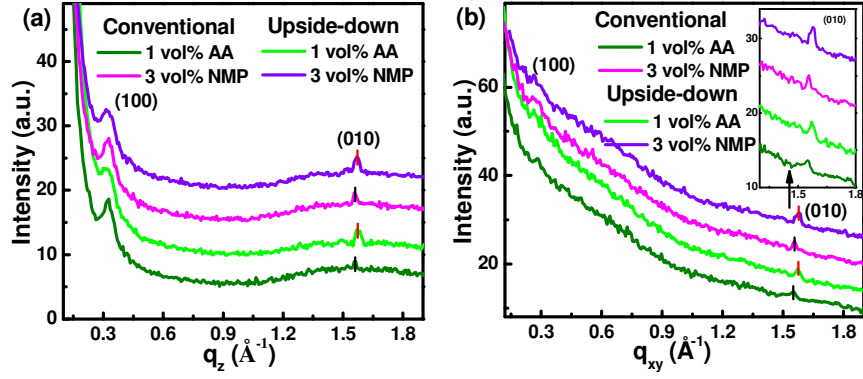
Figure S6. Out-of-plane (a) and in-plane (b) GIXD profiles of PTB7-Th:PC$_{71}$BM blend films with 1 vol% AA or 3 vol% NMP, the inset image is zoomed-in GIXD profiles.

Table S2. Positions of π-π stack peaks and d-spacing distances derived from GIXD profiles.

Drying method	Additive	Out-of-plane direction		In-plane direction	
		q (Å^{-1})	d-spacing	q (Å^{-1})	d-spacing (Å)
Conventional	Without	1.56	4.03	1.54	4.08
	3 vol% DIO	1.56	4.03	1.55	4.05
	1 vol% AA	1.56	4.03	1.55	4.03
	3 vol% NMP	1.56	4.03	1.56	4.00
Upside-down	Without	1.58	3.98	1.56	4.00
	3 vol% DIO	1.58	3.98	1.57	3.97
	1 vol% AA	1.57	4.00	1.57	3.97
	3 vol% NMP	1.57	4.00	1.58	3.95

The mole number ratio of PC$_{71}$BM (C$_{82}$H$_{14}$O$_2$) to PTB7-Th (C$_{49}$H$_{61}$FO$_2$S$_6$) can be calculated by using the following formula:

$$\frac{n_C}{n_S} = \frac{82 \times n_{PC_{71}BM} + 49 \times n_{PTB7-Th}}{6 \times n_{PTB7-Th}} \tag{1}$$

Where $n_{PC_{71}BM}$ and $n_{PTB7-Th}$ are mole number of PC$_{71}$BM and PTB7-Th. The weight ratio of PC$_{71}$BM to PTB7-Th can be determined by using the following formula:

$$\frac{W_{PC_{71}BM}}{W_{PTB7-Th}} = \frac{n_{PC_{71}BM} \times M_{PC_{71}BM}}{n_{PTB7-Th} \times M_{PTB7-Th}} \tag{2}$$

Where $M_{PC_{71}BM}$ and $M_{PTB7-Th}$ are the molar mass of PC$_{71}$BM and repeated unit of PTB7-Th.
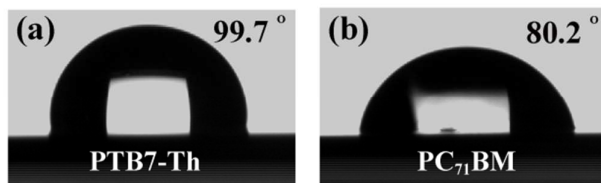
Figure S7. WCA images of neat PTB7-Th film (a) and PC$_{71}$BM film (b).
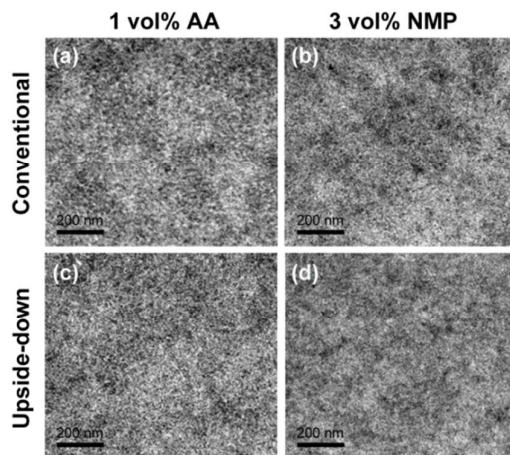

Figure S8. TEM images of PTB7-Th:PC$_{71}$BM blend films with different preparation conditions: (a) with 1 vol% AA and employing conventional drying method; (b) with 3 vol% NMP and employing conventional drying method; (c) with 1 vol% AA and employing upside-down drying method; (d) with 3 vol% NMP and employing upside-down drying method.
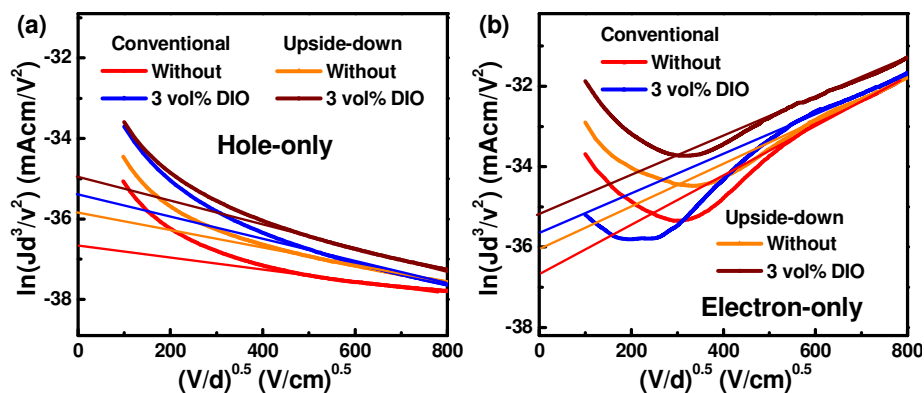

Figure S9. *J-V* curves of (a) hole-only devices and (b) electron-only devices based on PTB7-Th:PC$_{71}$BM without or with 3 vol% DIO and employing different drying methods.

Table S3. Hole and electron mobilities in active layers without or with 3 vol% DIO and employing different drying methods.

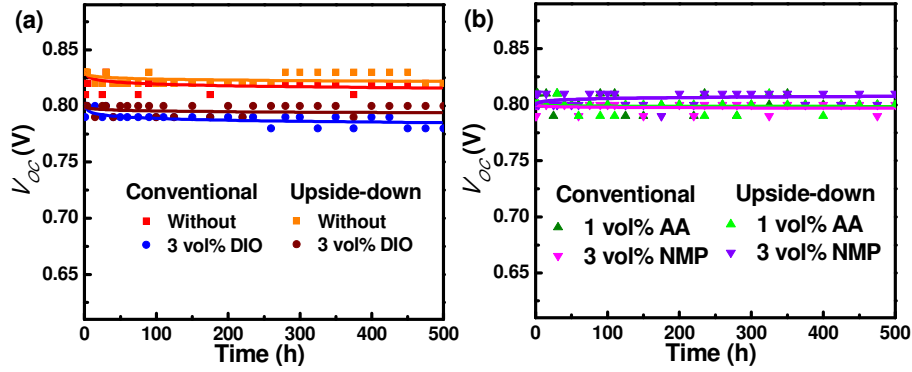| Drying method	Additive	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
Conventional	Without	4.26×10^{-4}	3.49×10^{-4}	1.22
	3 vol% DIO	1.42×10^{-3}	1.05×10^{-3}	1.35
Upside-down	Without	8.58×10^{-4}	7.77×10^{-4}	1.10
	3 vol% DIO	2.11×10^{-3}	1.73×10^{-3}	1.21

Figure S10. V_{OC} degradation characteristics of PSCs based on PTB7-Th:PC$_{71}$BM as a function of storage time (Scatters: measured values; Solid line: fitted curves according to $y = \alpha(1 + t)^\beta$): (a) without solvent additive or with 3 vol% DIO; (b) with 1 vol% AA or with 3 vol% NMP.
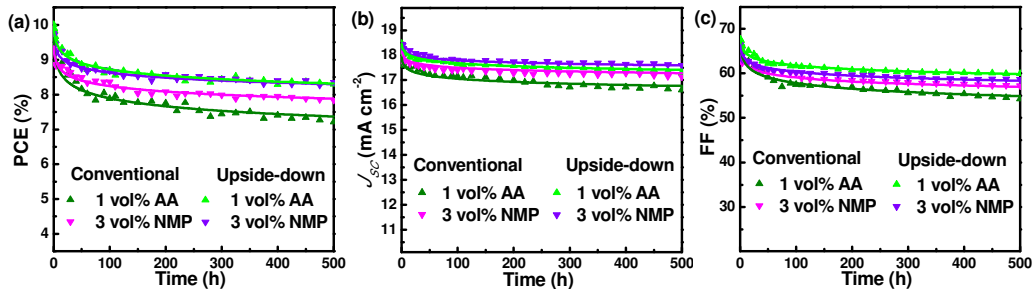

Figure S11. Photovoltaic parameters PCE (a), J_{SC} (b) and V_{OC} (c) as a function of storage time (t) (Scatters: measured values; Solid lines: fitted curves according to the power function $y = \alpha(1 + t)^\beta$).
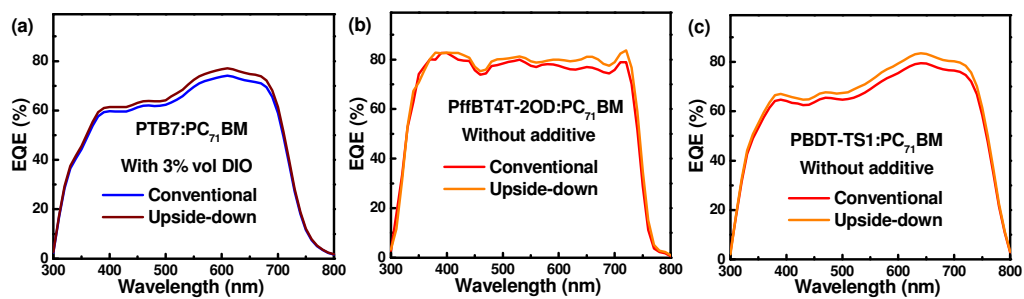
Figure S12. EQE spectra of PSCs with PTB7:PC$_{71}$BM (a), PffBT4T-2OD:PC$_{71}$BM (b) and PBDT-TS1:PC$_{71}$BM (c) as active layer.
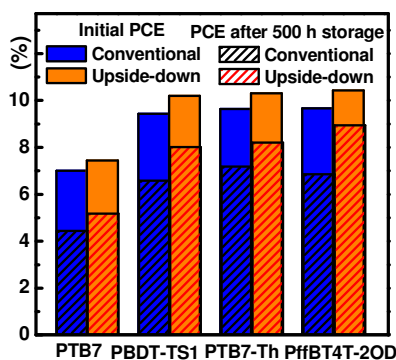

Figure S13. Initial PCEs and preserved PCEs after 500 hours of PSCs with different polymers as donor and PC$_{71}$BM as acceptor.