

## **Synergistic effect of processing solvent and additive for the production of efficient all-polymer solar cells**

Xiaohui Liu,<sup>a</sup> Xiaodong Li,<sup>b</sup> Lei Wang,<sup>a</sup> Junfeng Fang,<sup>\*,b</sup> and Chuluo Yang<sup>\*,a,c</sup>

<sup>a</sup>Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China.

<sup>b</sup>School of Physics and Materials Science, Ministry of Education Nanophotonics & Advanced Instrument Engineering Research Center, East China Normal University, Shanghai 200062, China.

<sup>c</sup>Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan 430072, China.

Corresponding Authors

\* E-mail: jffang@phy.ecnu.edu.cn.; clyang@whu.edu.cn

## Experimental Section

### *Materials and Reagents:*

Patterned ITO glass substrates ( $R_s \leq 15 \Omega \text{ sq}^{-1}$ ) were purchased from Shenzhen huayulianhe Technology Co.. Photoactive donor J71 was bought from Solar mer Materials Inc. (China). Acceptor N2200 ( $M_n$  of 75.6 kg/mol, PDI of 1.75) and PEDOT:PSS were obtained from Shanghai vzchem. All the available solvents reagents were used as received without any further purification unless otherwise specified.

### *Device Fabrication:*

The regular all-PSCs were fabricated using the device configuration of ITO/PEDOT:PSS/active layer/AZO/Al. Patterned ITO substrates were sequentially ultrasonicated in detergent, deionized water, acetone, and isopropanol, and then were treated with  $O_2$ -plasma for 8 min. PEDOT:PSS (Baytron, Clevious 4083) was spin-coated onto the ITO surface at 4000 rpm for 60 s, followed by annealing at 150 °C for 10 min in air. Photoactive blends of J71:N2200 with a fixed D:A ratio of 2:1 were dissolved in CB or CF with the total concentration of 15 mg/mL or 10 mg/mL, respectively. Then the blends solutions with varied amount of DIO additive were deposited onto the PEDOT:PSS layer and then annealed at 100 °C for 10 min. The thickness of photoactive layers spin-coated from all of the solvent/additive systems were around 100-110 nm by controlling the blends concentration and spinning condition. Then the AZO solution (8 mg/mL in TFE) was spin-coated onto the active layer at 4000 rpm for 60 s, followed by deposition of Al (100 nm) top electrode in an evaporation chamber under high vacuum ( $< 2 \times 10^{-4}$  Pa). The effective device area was defined to be  $\approx 0.09 \text{ cm}^2$  controlled with a shadow mask.

### *Characterizations and Measurements:*

UV-vis absorption spectra were performed on a GS54T UV-vis-NIR absorption spectrophotometer. The thickness of the active layer was determined by a surface profiler

(Veeco, Dektak 150). Tapping-mode atomic force microscopy (AFM) images were conducted by using a scanning probe microscope (Dimension 3100 V, Veeco). Transmission electron microscopy (TEM) images of blend films were tested by FEI Tecnai F20 TEM. The  $J$ - $V$  characteristics were measured with a Keithley 2400 source meter by using a So13A solar simulator (Newport Inc.) with an AM 1.5G irradiation intensity ( $100 \text{ mW cm}^{-2}$ ). The EQE measurements were performed with a Newport quantum efficiency measurement system (ORIEL IQE 200TM) with a lock-in amplifier in ambient atmosphere. The light intensity at each wavelength was calibrated with a standard Si/Ge solar cell. And the apparent hole/electron mobility ( $\mu$ ) was calculated with the Mott-Gurney law, given by equation:  $J = 9\epsilon_0\epsilon_r\mu V^2 / (8L^3)$ , where  $J$  stands for the current density,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity of the medium,  $\mu$  is the mobility of hole or electron,  $V$  is the effective voltage, and  $L$  is the thickness of the active layer. The hole and electron mobility can be calculated from the slope of the  $J^{0.5}$ - $V$  curves.

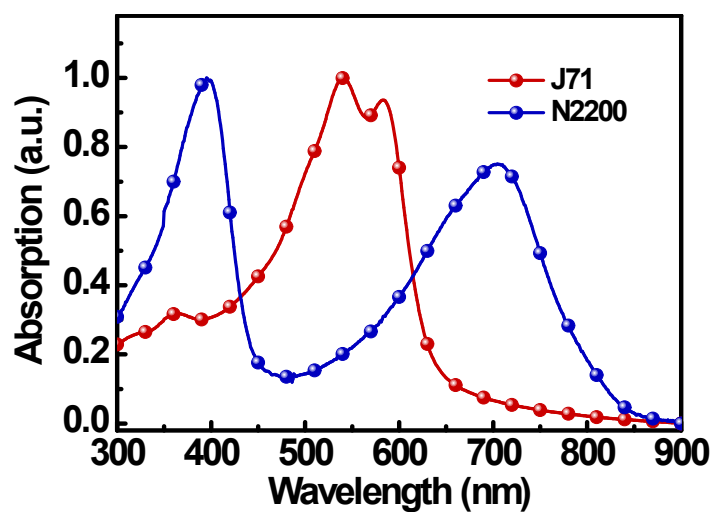


Fig. S1 Normalized absorption spectra of J71 and N2200 solid films.

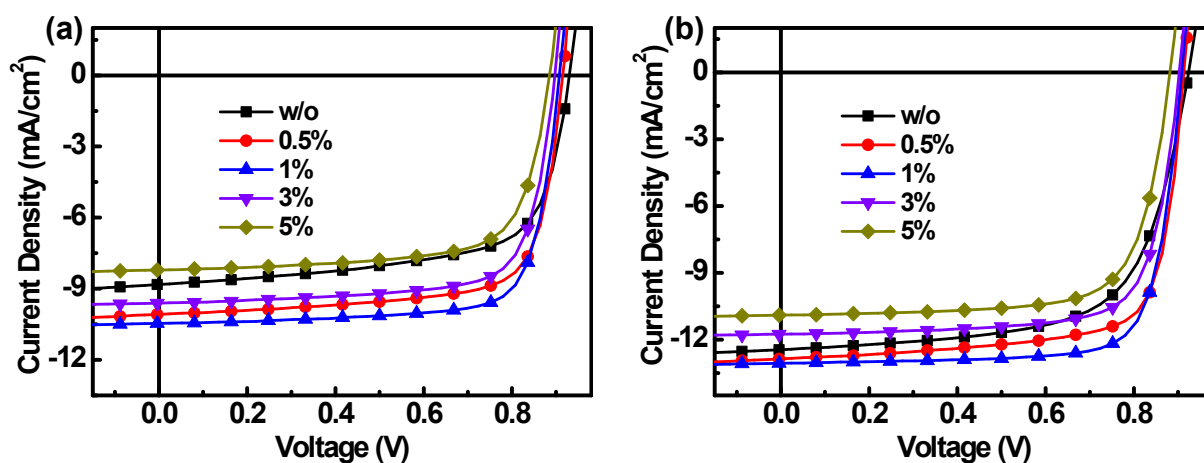
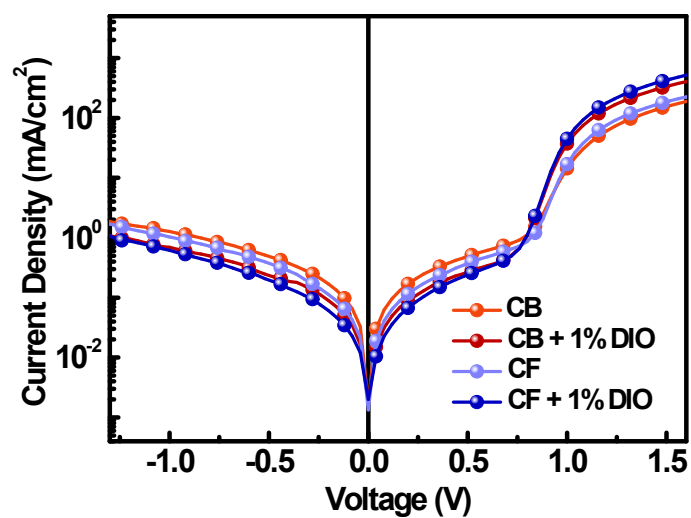


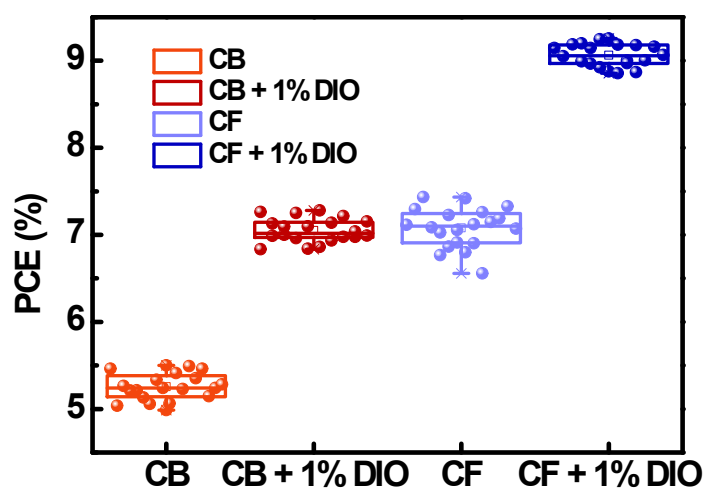
Fig. S2  $J-V$  curves of J71:N2200 all-PSCs processed with (a) CB, and (b) CF based on various DIO contents (w/o, 0.5%, 1%, 3% and 5%).

**Table S1** Summary of the photovoltaic performances J71:N2200 all-PSCs processed with CB, and CF based on various DIO contents (w/o, 0.5%, 1%, 3% and 5%).

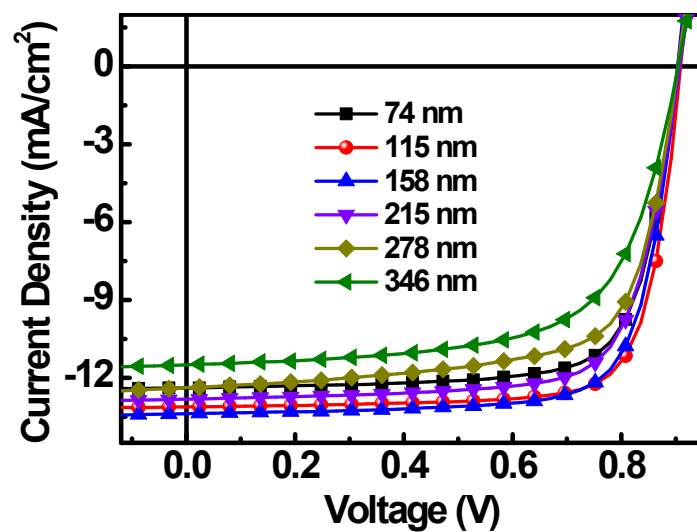
| Solvent | DIO (%) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm <sup>2</sup> ) | FF (%) | PCE (%) | $R_s$ ( $\Omega \cdot \text{cm}^2$ ) |
|---------|---------|--------------|--------------------------------|--------|---------|--------------------------------------|
| CB      | w/o     | 0.929        | 8.82                           | 66.76  | 5.47    | 8.84                                 |
|         | 0.5     | 0.915        | 10.08                          | 73.27  | 6.76    | 6.92                                 |
|         | 1       | 0.907        | 10.46                          | 76.68  | 7.27    | 5.56                                 |
|         | 3       | 0.897        | 9.60                           | 74.18  | 6.39    | 6.38                                 |
|         | 5       | 0.885        | 8.21                           | 71.63  | 5.21    | 9.03                                 |
| CF      | w/o     | 0.926        | 12.21                          | 65.68  | 7.43    | 7.72                                 |
|         | 0.5     | 0.914        | 12.86                          | 74.30  | 8.73    | 6.99                                 |
|         | 1       | 0.908        | 13.14                          | 77.75  | 9.28    | 5.25                                 |
|         | 3       | 0.902        | 11.71                          | 74.63  | 7.88    | 6.76                                 |
|         | 5       | 0.880        | 10.82                          | 72.21  | 6.88    | 7.87                                 |



**Fig. S3** Dark  $J-V$  curves of J71:N2200 all-PSCs processed with various treatments (CB, CB + 1% DIO, CF, CF + 1% DIO).



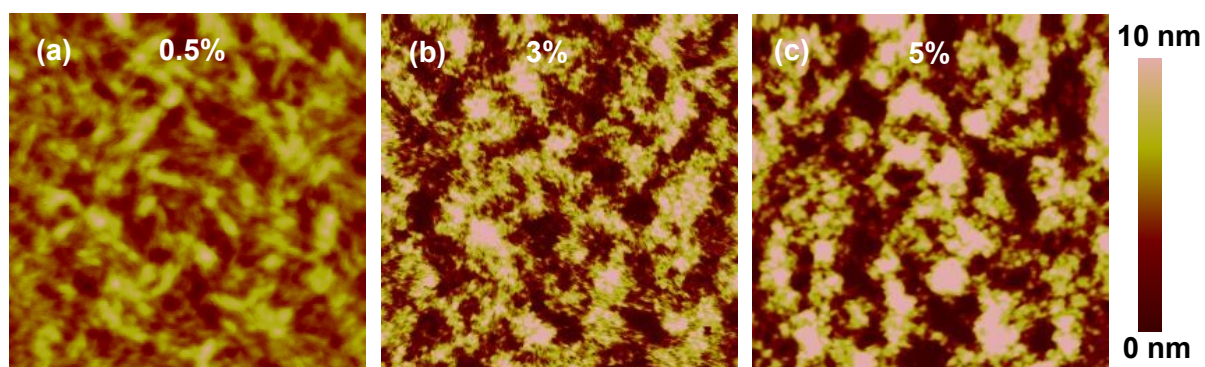
**Fig. S4** The box chart of PCEs of J71:N2200 all-PSCs processed with various treatments (CB, CB + 1% DIO, CF, CF + 1% DIO).



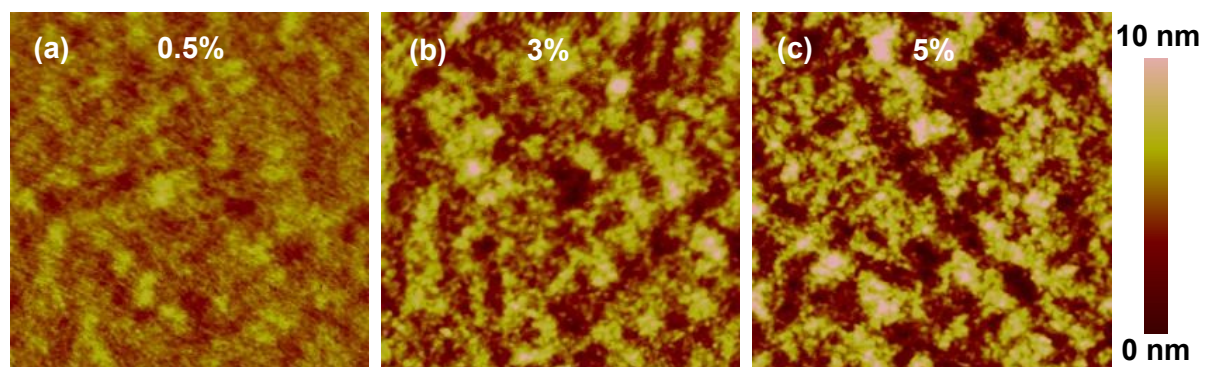
**Fig. S5**  $J$ - $V$  curves of J71:N2200 all-PSCs based on different active layer thickness prepared from CF + 1% DIO processing.

**Table S2** Summary of photovoltaic parameters of J71:N2200 all-PSCs based on different active layer thickness prepared from CF + 1% DIO processing.

| Active layer | Thickness (nm) | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF (%) | PCE (%) |
|--------------|----------------|--------------|---------------------------------|--------|---------|
| J71:N2200    | 74             | 0.905        | 12.37                           | 75.23  | 8.42    |
|              | 115            | 0.909        | 13.14                           | 77.75  | 9.29    |
|              | 158            | 0.905        | 13.38                           | 75.84  | 9.18    |
|              | 215            | 0.907        | 12.81                           | 73.62  | 8.55    |
|              | 278            | 0.904        | 12.39                           | 68.85  | 7.71    |
|              | 346            | 0.903        | 11.48                           | 64.59  | 6.70    |

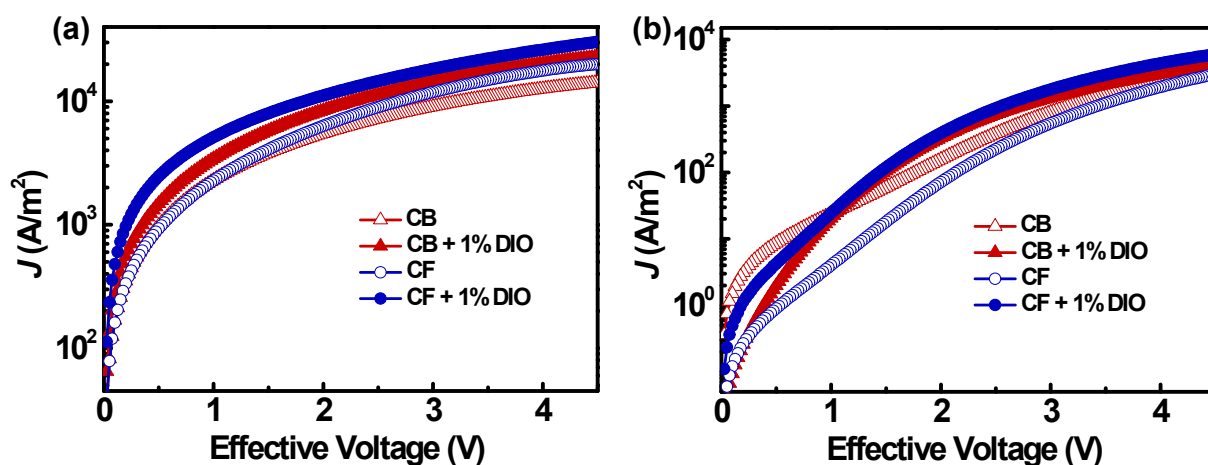


**Fig. S6** AFM topography images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of the J71:N2200 films processed with CB based on various DIO contents.



**Fig. S7** AFM topography images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of the J71:N2200 films processed with CF based on various DIO contents.





**Fig. S8**  $J$ - $V$  characteristics of (a) hole-only and (b) electron-only devices based on various treatments (CB, CB + 1% DIO, CF, CF + 1% DIO).

**Table S3** Hole and electron mobilities of J71:N2200 devices processed with various treatments (CB, CB + 1% DIO, CF, CF + 1% DIO).

| Solvent & Additive | $\mu_h$ (( $\text{cm}^2 / (\text{V s})$ )) | $\mu_e$ (( $\text{cm}^2 / (\text{V s})$ )) | $\mu_h / \mu_e$ |
|--------------------|--|--|-----------------|
| CB                 | $0.81 \times 10^{-4}$                      | $0.39 \times 10^{-4}$                      | 2.08            |
| CB + 1% DIO        | $1.40 \times 10^{-4}$                      | $1.18 \times 10^{-4}$                      | 1.19            |
| CF                 | $1.59 \times 10^{-4}$                      | $0.96 \times 10^{-4}$                      | 1.66            |
| CF + 1% DIO        | $2.03 \times 10^{-4}$                      | $1.85 \times 10^{-4}$                      | 1.09            |