# Supporting information for:

# Optimizing domain size and phase purity in all-polymer solar

# cells by solution order aggregation and confinement effect of

# the acceptor

Qiang Zhang, <sup>a,b</sup> Zhenyu Chen, <sup>c</sup> Wei Ma, <sup>\*c</sup> Zhiyuan Xie, <sup>a</sup> and Yanchun Han<sup>\*a</sup>

<sup>a</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of

Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun

130022, P. R. China

<sup>b</sup>University of the Chinese Academy of Sciences, No.19A Yuquan Road, Beijing

100049, China

<sup>c</sup>State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University,

Xi'an 710049, P. R. China

# **Corresponding Author**

Email: ychan@ciac.ac.cn (Yanchun Han)

Email: msewma@mail.xjtu.edu.cn (Wei Ma)

## 1. Experiment section:

## 1.1 Materials and solvents:

Polymeric donor J51 (Mn=13.3k, PDI=1.9) and polymeric acceptor N2200 (Mn=37.9k, PDI=2.4) were purchased from Solarmer Materials, Inc. and Polyera Corporation., respectively. All polymers were used as received without further treatment. Chloroform was obtained from Beijing Chemical Works, it was purified before use. Mesitylene and anhydrous solvent cyclopentyl methyl ether (CPME) containing 50 ppm BHT as inhibitor were purchased from Sigma-Aldrich.

## **1.2 Solution Characterization:**

UV-bis absorption spectra of solutions (filled in quartz cuvettes) were collected at room temperature using AvaSpec UV–vis spectrophotometer (Avantes Corporation) with halogen lamp source. The solution PL spectra were recorded with Fluorescence Spectrometer (Ocean Optics Corporation). A face-on geometry and thin 1 mm cuvettes were used. Solution phase WAXS was collected at the Beijing Synchrotron Radiation Light Source (SSRL) at beamline 4–2. Transmission WAXS was conducted on 3 mg/mL solutions for the J51 and N2200. The sample was contained in a 1mm diameter quartz capillary tube, and the background was subtracted using the scattering generated by a capillary filled with a neat solvent.

## **1.3 Solubility Measurement:**

The solubilities of J51 and N2200 were determined by dissolving the materials in CF, Mes and CPME three solvents over the solubility limit. For calibration, absorption spectra of both polymers were obtained with different given low concentration polymer solutions, so the absorption intensities of polymers were varied linearly on the concentrations to calculate the molar absorption coefficient. The saturated solutions of polymers in each solvent were filtered and then diluted to reasonable low concentration, followed by measuring UV absorptions. According to Beer-Lambert law, the solution concentration was calculated.

#### 1.4 Fabrication and Characterization of All-PSCs:

The all-PSCs were fabricated with a configuration of ITO/PEDOT:PSS/active

layer/PFN-Br/Ag. The indium-tin oxide (ITO)-coated glass substrate was cleaned with deionized water, acetone, and isopropanol in an ultrasonic bath for 15 min successively. The substrates were dried by nitrogen flow, then ultraviolet-ozone treated for 25 min. Next, 40 nm layer of poly(3,4а ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Heraeus Materials, 4083) was spin coated onto the ITO. After annealing for 30 min at 140 °C, all PEDOT:PSS coated glass substrates were transferred to a nitrogen-filled glovebox. The active layer was prepared by spin-coating the blend solutions onto the PEDOT:PSS layer and then treated by thermal annealing at 150  $^\circ\!\mathrm{C}$  for 10 min. The PFN-Br interlayer material was dissolved in methanol (concentration, 0.5 mg mL<sup>-1</sup>), a 5 nm PFN-Br was spin-coated on top of blend films. Then, the device fabrications were completed after a 90 nm Ag metal electrode was thermally deposited on the blend films under high vacuum (about 8.0×10<sup>-5</sup> Pa). The active layer area of the device was 0.072  $\text{cm}^2$  defined by a shadow mask.

For all J51:N2200 devices, active layers were prepared in weight ratios of 2:1 in chloroform (CF), mesitylene (Mes), cyclopentyl methyl ether (CPME) solvents. For the CF-processed samples, the concentration of the blend solution was 14 mg ml<sup>-1</sup>. After spin-coating the solution at 2000 rpm for 30 s, the film with a thickness of about 95 nm was obtained. When the processing solvent was Mes, the concentration of the blend solution was 18 mg ml<sup>-1</sup>. The film is obtained by spin-coating at 1200 rpm for 60 s with a film thickness of about 100 nm. For devices processed from CPME, the concentration of blend solution was 12 mg ml<sup>-1</sup>. The CF solution was stirred overnight, whereas the Mes and CPME solutions were heated to

100 °C and 120 °C, respectively.

The current-voltage characteristics of all J51:N2200 devices were measured under illumination of 100 mW cm<sup>-2</sup> AM 1.5 G simulated solar light and recorded by a computer-controlled Keithley 2400 source meter in the high purity nitrogen filled glovebox. EQEs were detected with QE-R 3011 equipment (Enli Tech. Co.) in ambient air.

#### **1.5 SCLC device fabrication and measurement:**

The hole and electron mobilities of J51/N2200 blend films processed from different solvents were measured via the SCLC method. The hole–only and electron–only device structures are ITO/PEDOT:PSS (40 nm)/active layer/MoO<sub>3</sub> (10 nm)/Al (100 nm) and ITO/ZnO (30 nm)/active layer/PFN-Br (5 nm)/Ag (100 nm), respectively. The current density–voltage (*J*–*V*) characteristics in the range of 0–8 V of hole- and electron-only devices were recorded with a Keithley 2400 source meter under dark in an N<sub>2</sub> atmosphere, the charge mobility was determined by fitting a space-charge limited function (1):

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_n \mu \frac{V^2}{L^3} exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right)$$
(1)

Where J is the current density,  $\varepsilon_0$  is the permittivity of free space (8.85×10<sup>-14</sup> F/cm),  $\varepsilon_r$  is relative permittivity of the material (assumed as 3 for organic materials),  $\mu$  is the zero-filed mobility, V is the effective voltage (V =  $V_{applied} - V_{bi} - V_{series}$ ) and  $\beta$  is the field–activation factor.

#### 1.6 Thin Film Characterization:

Absorption profiles were recorded with AvaSpec UV–vis spectrophotometer (Avantes Corporation.) with a halogen lamp source. AFM measurements were performed with an SPA-300HV instrument with a SPI3800N controller (Seiko Instruments Inc., Japan) in tapping mode. Silicon microcantilevers from Olympus Japan were used for scanning. TEM images were obtained using a JEOL JEM-1011 instrument operated at an acceleration voltage of 100 kV. The active layer thin films for TEM were floated from the substrates immersed in deionized water and then transferred onto a copper grid. Samples for AFM and TEM measurements were prepared from films under the same conditions as devices on substrates with 40 nm PEDOT:PSS transport layer. GIWAXS characterization was carried out at the Advanced Light Source (ALS) on beam 7.3.3. Samples were prepared with identical blend solutions under the same conditions as devices on Si substrates. The sample was irradiated at 10 keV X-ray beam with a grazing angle of 0.12°–0.16°, which optimized signal-to-background ratio. The scattering was recorded on a Dectris

Pilatus 1M photon counting detector from the sample. R-SoXS characterization was performed at beamline 11.0.1.2 at the Advanced Light Source (ALS) in transmission geometry under vacuum. For sample preparation, glass substrates were modified with PEDOT:PSS, and then the solutions desired for devices was spin-coated on the PEDOT:PSS-coated glass substrates. The active layer thin films were floated off in deionized water and picked up onto 1.5 mm × 1.5 mm, 100 nm thick Si<sub>3</sub>N<sub>4</sub> membrane supported by a 5 mm × 5 mm, 200  $\mu$ m thick Si frame (Norcada Inc.) 2D scattering patterns were obtained on an in-vacuum CCD camera (Princeton Instrument PI-MTE).

## **Supporting Figures**



Fig. S1 Chemical structures of J51 (left) and N2200 (right).



Fig. S2 Chemical structures of processing solvents with their boiling points.



**Fig. S3** (a) UV-vis absorption spectra on different concentrations of J51 and (b) calibration plots of J51 absorbance at 545 nm. (c) UV-vis absorption spectra on different concentrations of N2200 and (b) calibration plots of N2200 absorbance at 710 nm.



**Fig. S4** Temperature-dependent normalized UV-vis absorption spectra of (a), (c), (e) J51 and (b), (d), (f) N2200 in varied solvents. The concentration was 0.1 mg mL<sup>-1</sup>.



**Fig. S5** Normalized UV-visible absorption spectra for (a) J51 and (b) N2200 films processed from different solvents.



**Fig. S6** *J-V* curves of the J51:N2200 cast from different solvents (a) CF, (b) Mes, and (c) CPME under AM 1.5 G illumination with different light intensity.



**Fig. S7** Space–charge–limited *J–V* characteristics in dark for hole and electron mobility of the J51:N2200-based OSCs from different solvents (a) (d) CF, (b) (e) Mes and (c) (f) CPME.

## **Supporting Tables**

	Chloroform		Cyclopentyl methyl ether	
J51	220.1	206.8	93.2	
N2200	150.9	75.2	3.2	
Solubility ratio	1.5	2.8	29.1	

Table S1. Solubilities of J51 and N2200 in Each Solvent (mg/mL).

**Table S2.** Key parameters of optimized all-PSCs processed from different solvents.

J51:N2200	J <sub>sat</sub> [mA cm <sup>-2</sup> ]	J <sub>ph</sub> [mA cm <sup>-2</sup> ]	J <sub>ph</sub> /J <sub>sat</sub> [%]	G <sub>max</sub> [10 <sup>28</sup> m <sup>-3</sup> s <sup>-1</sup> ]
CF	11.91	11.11	93.28	0.74
Mes	13.31	12.53	94.14	0.83
СРМЕ	14.19	13.61	95.51	0.88

Device $\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_h$	$\mu_e$	$\mu_h/\mu_e$
J51:N2200 blend from CF	9.13×10 <sup>-5</sup>	$1.64\times10^{-5}$	5.57
J51:N2200 blend from Mes	$1.46  imes 10^{-4}$	$3.76\times10^{-5}$	3.88
J51:N2200 blend from CPME	$3.45 \times 10^{-4}$	$7.14\times10^{-5}$	4.83

**Table S3.** Values of  $\mu$  determined from dark *J*–*V* curves for the hole and electrondominated carrier devices for J51:N2200 blend films cast from different solvents.