Supporting Information

Influence of Binary Processing Additives on the Performance of Polymer Solar Cells

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1. Fabrication and Characterization of PSCs

PSCs were fabricated using the conventional structure of ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/Al. The fabrication steps are as follows: patterned ITO substrates were sequentially cleaned in ultrasonic bath of detergent, de-ionized water, acetone, and isopropanol. Subsequently, ITO substrates were dried in oven overnight before treatment by UV-ozone for 20 minutes. The PTB7:$PC_{71}BM$ (PTB7:$PC_{71}BM$= 1:1.5 by weight) BHJ composite was spin-coated onto ITO substrates from (a) pristine *o*-DCB; (b) *o*-DCB mixed with 3% CN solution; (c) \ *o*-DCB mixed with 3% ODT solution; (d) *o*-DCB mixed with 3% CN and 3% ODT solution. The device fabrication was completed by thermal evaporation of 100 nm Al as the cathode under vacuum at the base pressure of 2×10^{-6} mbar. The device area was 0.045 cm^2.

PSCs were characterized under an AM 1.5 G calibrated solar simulator (Newport model 91160-1000) with the light intensity of 100 mW/cm^2, which was calibrated by utilizing a mono-silicon detector (with KG-5 visible color filter) of National Renewable Energy Laboratory (NREL) to

reduce spectral mismatch. The *J-V* characteristics were recorded using a Keithley 2400 source meter. The EQE was measured through the EQE measurement setup in use at ESTI for cells and mini-modules. A 300 W steady-state xenon lamp provides the source light. Up to 64 filters (8 to 20 nm width, range from 300 to 1200 nm) are available on four filter-wheels to produce the monochromatic input, which is chopped at 75 Hz, superimposed on the bias light, and measured via the usual lock-in technique. Bias light is necessary to put the device under examination close the operating irradiance condition. After collecting the EQE data, the software also integrates the date with the AM1.5G spectrum and gives the calculated J_{SC} value, which is helpful for checking the accuracy of the measurement.

1. **Characterization of PTB7:$PC_{71}BM$ Thin Film**

Thin film surface morphology was studied by AFM (NanoScope NS3A system. For AFM measurements, four sets of samples were prepared by spin-coating PTB7:$PC_{71}BM$ BHJ composites from 10 mg/mL *o*-DCB solution onto PEDOT:PSS coated ITO glass (thickness is ca.100 nm). Phase distribution was explored by TEM (FEI-Philips scanning transmission electron microscope: Model Tecnai T12T/STEM). For TEM measurement, samples were prepared by coating PTB7:$PC_{71}BM$ BHJ composites from 10 mg/mL *o*-DCB solution onto copper grid (thickness is less than 100 nm). One-dimensional WAXD powder experiments (reflection mode of a Rigaku 12 kW rotatinganode X-ray Cu Ka radiation generator coupled to a diffractometer) were conducted to measure the crystalline order of BHJ thin films. The specimen was prepared by two steps: first the polymer thin film was spin-coated from 1% *o*-DCB onto PEDOT:PSS coated ITO, and then the sample was rinsed with DI-water. After PEDOT:PSS dissolved, the polymer thin film will float and the thin film can be conducted to WAXD measurement after being dried.

2. **Transition Spectroscopies**

Transient absorption measurements were conducted with a Ti-Sapphire femtosecond laser system with a wavelength of 790nm a pulse width of 120 fs. The pulses were split into pump and probe paths. The pump pulse frequency was doubled to 395 nm and focused onto the sample with pulse energies of 8 $\mu J/cm^2$. This pump intensity is chosen to gain enough transient absorption signal while keeping the initial photo-excited charge carrier density not too far away from PSC device operating conditions ($\sim 10^{16}$ cm^{-3}). The pump pulse was put through a delay stage to achieve time resolution. The probe pulse was focused into a sapphire disk in order to generate the white light continuum used to measure visible and near-IR spectra. The probe pulse was split before reaching the sample to provide a reference path to correct intensity fluctuations. In addition, synchronous chopping of the probe enabled the subtraction of an accurate dark count reading, which tends to drift over time. All spectra were manually corrected for the temporal chirp present in the white light continuum. The polarization angle between pump and probe beams was $54° \pm 1°$.

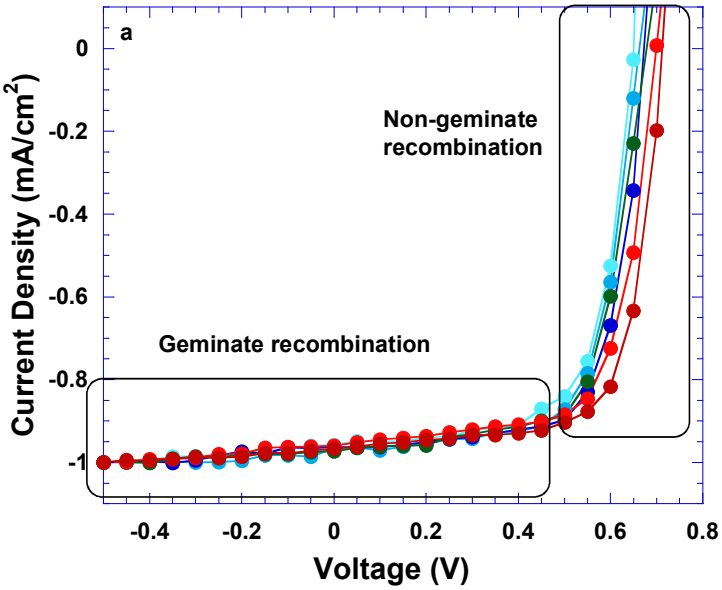
3. **Impedance Spectroscopy**

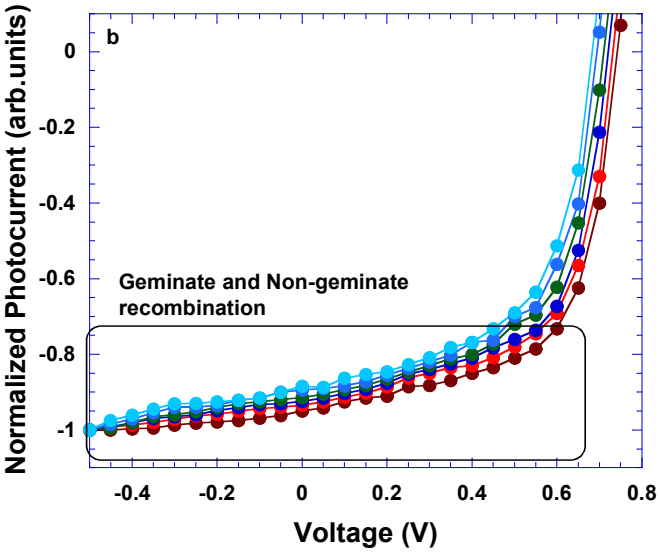
The IS is obtained using a HP 4194A Impedance/gain phase analyzer. All the devices are measured under 100 mW/cm^2 AM 1.5 G illumination with an oscillating voltage of 10 mV and frequency of 1 Hz to 1 MHz. All PSCs are held at their respective open circuit potentials obtained from the J-V measurements, while the IS spectra are recorded.

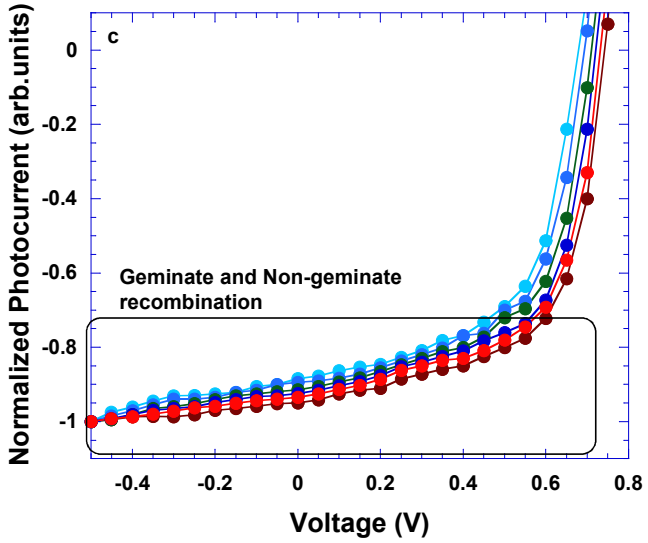
4. **Investigation of geminate and nongeminate recombination**

PSCs were characterized under an AM 1.5 G calibrated solar simulator (Newport model 91160-1000) with the light intensity ranging from 0 sun to 1 sun (100 mW/cm^2), which was calibrated by utilizing a mono-silicon detector (with KG-5 visible color filter) of National Renewable

Energy Laboratory (NREL) to reduce spectral mismatch. The *J-V* characteristics were recorded using a Keithley 2400 source meter, as shown in Figure S1. We can observe that the Pc (I,V) remains almost the same in CN+ODT-PSCs (as shown in Figure S1a), and the Pc (I,V) is independent on the light intensities from -0.5V to 0.65V (near MPP). It reveals that the efficiency loss in CN+ODT-PSCs was dominated by geminate recombination in the range from short circuit to MPP.[1] As clear contrast, strong dependencies of Pc (I,V) on the light intensities were observed in the other three PSCs, indicating a much larger amount of non-geminate recombination than that of (CN+ODT)-PSCs in the regime from short circuit to MPP.[2]




b
Normalized Photocurrent (arb.units)
0
-0.2
-0.4
-0.6
-0.8
-1
Geminate and Non-geminate
recombination
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Voltage (V)


c
Normalized Photocurrent (arb.units)
0
-0.2
-0.4
-0.6
-0.8
-1
Geminate and Non-geminate
recombination
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Voltage (V)

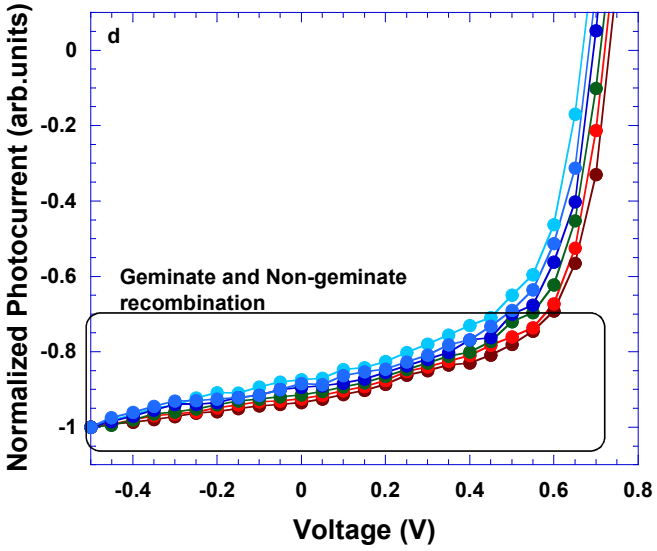

d
Normalized Photocurrent (arb.units)
0
-0.2
-0.4
-0.6
-0.8
-1
Geminate and Non-geminate
recombination
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Voltage (V)

Figure S1. *J-V* characteristics are investigated under different illumination intensities (0~1 sun), as shown in a (CN+ODT-PSCs) b (CN-PSCs), c (ODT-PSCs), d (pristine-PSCs).

5. **Hole and electron mobilities of BHJ thin films**

Hole and electron mobilities of BHJ thin films were estimated by SCLC method based on *J-V* characterization from hole-only or electron-only diode with a structure of ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/MoO_3/Ag or ITO/Al/PTB7:$PC_{71}BM$/Al. The mobility is determined by fitting the dark current observed from the hole-only and electron-only diode saccording to the model of a single carrier SCLC. The *J-V* curves and fitting lines of diodes made by BHJ thin film in the range from 0 to 4 V are shown in Figures S2a and S2b. The hole/electron mobility was obtained by equation: $J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$

where ε_0 is the dielectric constant of free space, ε_r is the dielectric constant of the polymer, V is the voltage drop across the device, and d is the thickness of BHJ thin film. The dielectric constant, ε_r is assumed to be 3 in our analysis,[2] which is a typical value for conjugated polymers. The estimated electron and hole for the four BHJ systems are summarized in Table S2. A balanced hole and electron mobility was observed from BHJ composites, which indicates that the space charge effects are not responsible for the decreasing of α; thus, nongeminate recombination can be assumed as the only limitation in PSCs.[3]

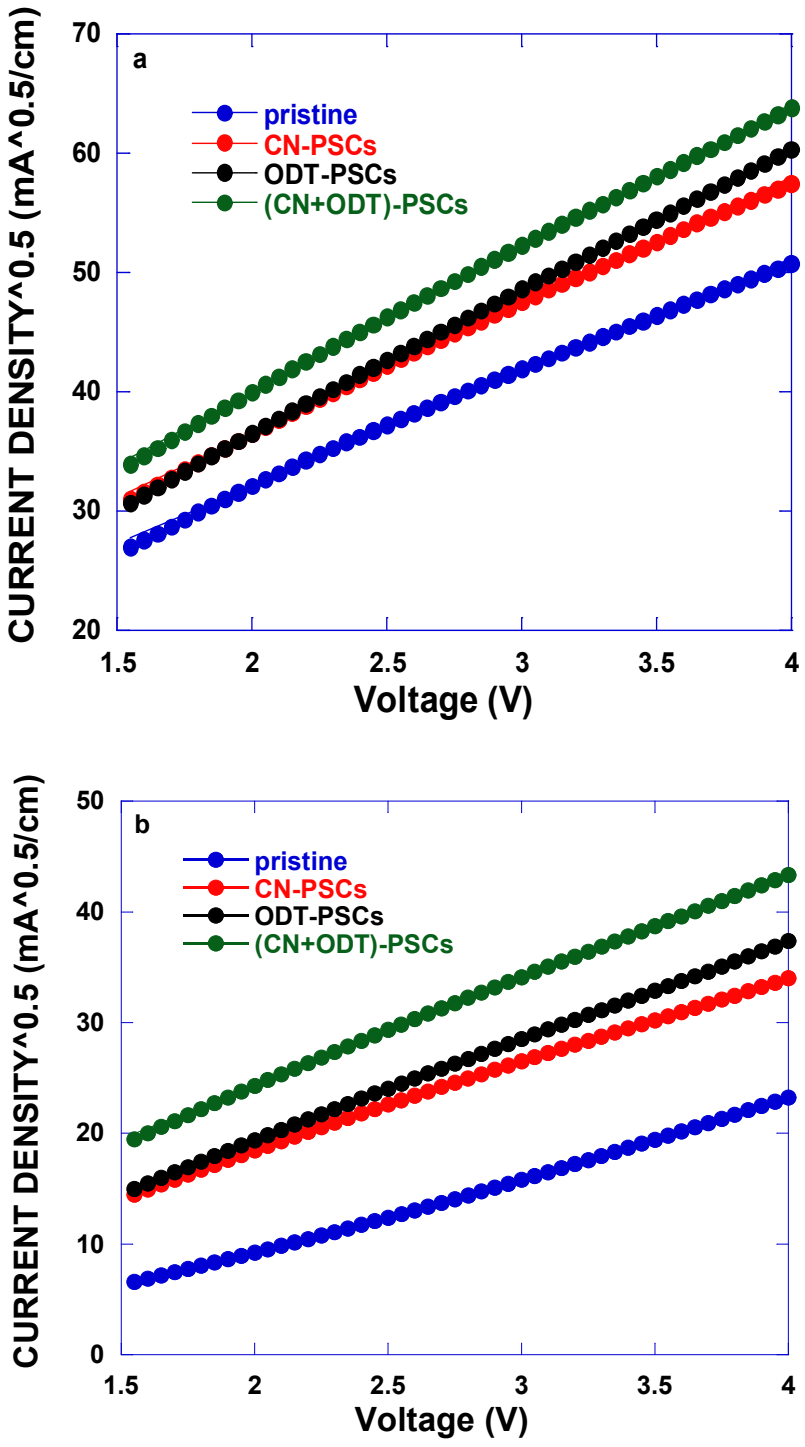


Figure S2. (a) Hole-only diodes with a structure of ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/MoO_3/Al;

(e) electron-only diodes with a structure of ITO/Al/PTB7:$PC_{71}BM$/Al.

	Electron mobility (cm^2/Vs)	Hole mobility (cm^2/Vs)
Pristine	8.0×10^{-5}	2.8×10^{-4}
CN-PSCs	1.6×10^{-4}	4.7×10^{-4}
ODT-PSCs	1.8×10^{-4}	4.6×10^{-4}
(CN+ODT)-PSCs	2.9×10^{-4}	6.8×10^{-4}

Table S1. Hole and electron mobility of PSCs.

References

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3 M. Lenes, M. Morana, C. J. Brabec and P. W. M. Blom, *Adv. Funct. Mater.,* **2009**, *19*, 1106-1111.