Supplementary Information

Effect of Processing Additive on Morphology and Charge Extraction in Bulk-Heterojunction Solar Cells

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Characterization: ^{1}H and ^{13}C NMR spectra were recorded using a Varian AS400 in deuterated chloroform or acetone solution at 298 K. Chemicals shifts were reported as δ values (ppm) relative to chloroform value of 7.26 ppm. For our size-exclusion chromatography (SEC) measurements, we used a Varian Polymer Laboratories GPC220 equipped with a RI detector, a PL BV400 HT Bridge Viscometer, 2 PLgel Mixed C (300 x 7.5 mm) columns and a PLgel Mixec C Guard column. The temperature of the system was set to 110°C and the 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) flow was set to 1mL/min. The samples (2 mg) were dissolved in 2 mL of TCB in a 5 mL chromatography vial then stirred and heated to 110°C for 1 hour to let aggregates completely dissolve. Then, a filtration through a .45 μm cellulose fiber film in a 5 mL chromatography vial lead to a homogenous polymeric solution. The sample was injected though a loop of 200 μL with a Varian Polymer Laboratories PL-SP 260VC sample preparation system. Calibration was set with narrow polystyrene standards. UV-vis-NIR absorption spectra were recorded using a Varian Cary 500 UV-vis-NIR spectrophotometer using 1 cm path length quartz cells. A polymeric solution was spin-coated on untreated glass substrate in order to perform the solid-state measurement. The optical bandgap was calculated from the onset of the absorption band. Cyclic

voltamogramms were recorded from a Solartron 1287 Potentiostat using a three-electrode set-up; a working and counter electrodes in platinum and an Ag/Ag^+ (0.1 M of $AgNO_3$ in anhydrous acetonitrile) reference electrode. The scan rate was 50 mVs^{-1} and the electrolyte was an anhydrous argon saturated solution of 0.1 M of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4). Thin films were made by casting a diluted solution of a copolymer on the working electrode, dried under ambient conditions. For each measurement, a new film was cast. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets, assuming an SCE electrode to be at -4.7 eV from vacuum.

Table S1. Information of synthesized polymer of PBnDT-FTAZ.

Polymer	Mn (kDa)	Mw (kDa)	PDI	Yield (%)	HOMO (eV)	LUMO (eV)	E_g^{CV}	E_g^{Opt}
PBnDt-FTAZ	73	146	2.0	91	-5.32	-3.38	1.94	1.91

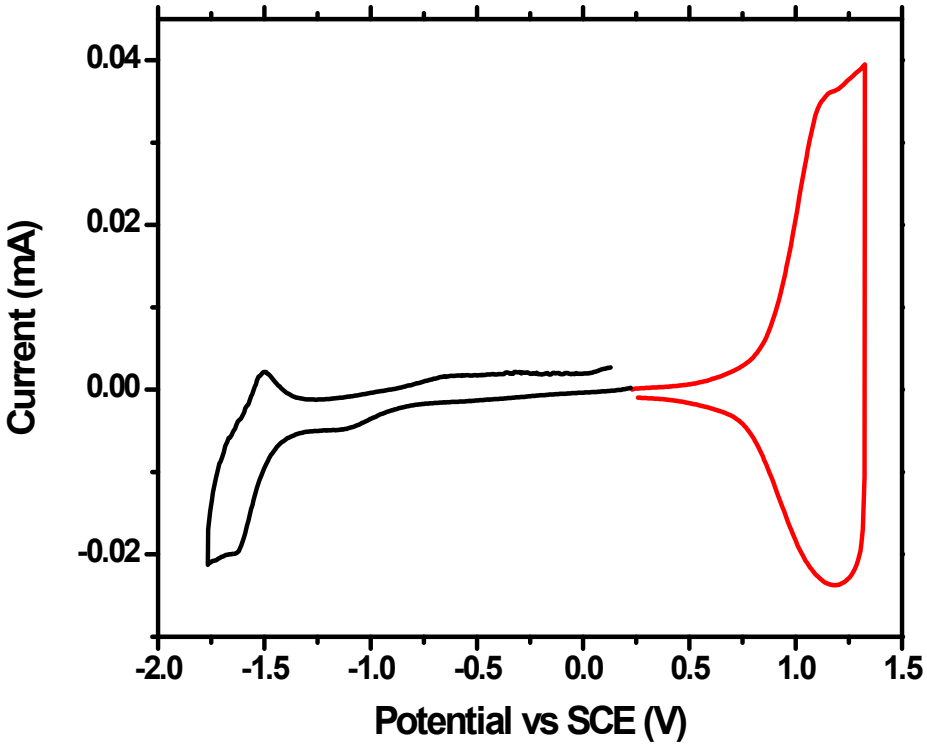


Figure S1. Cyclic voltammetry (black line: reducetion and red line: oxidation) of PBnDT-FTAZ. The HOMO and LUMO level of PBnDT-FTAZ shows -5.32 eV and -3.38 eV, respectively.

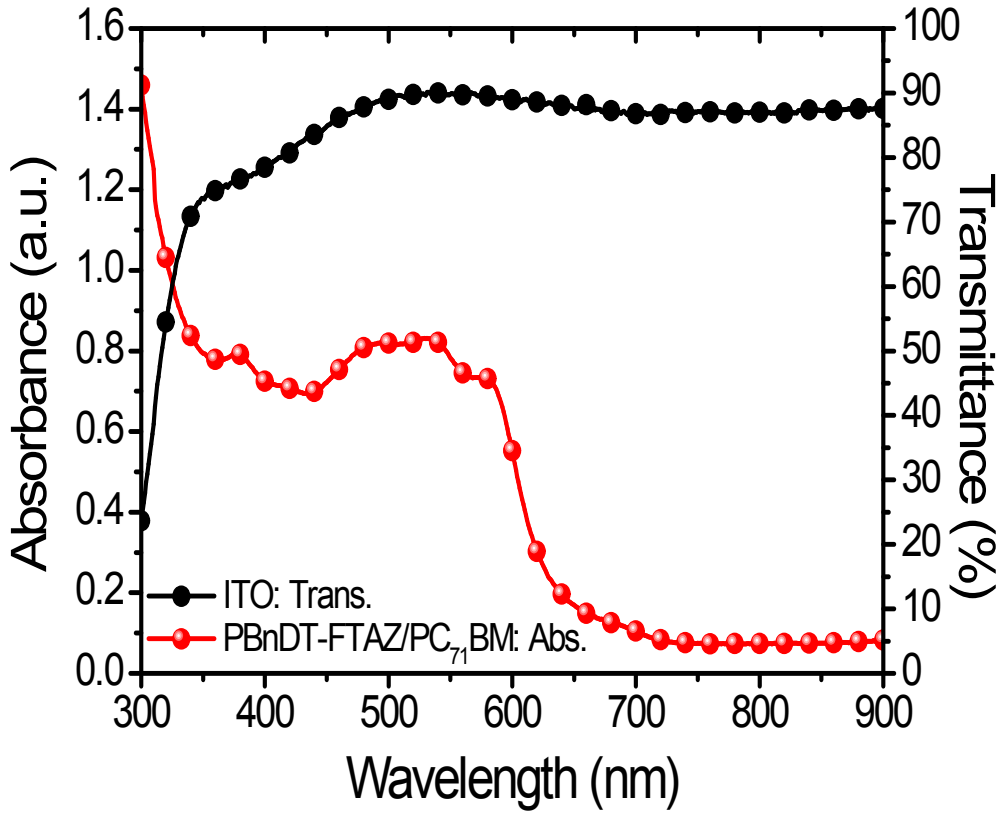
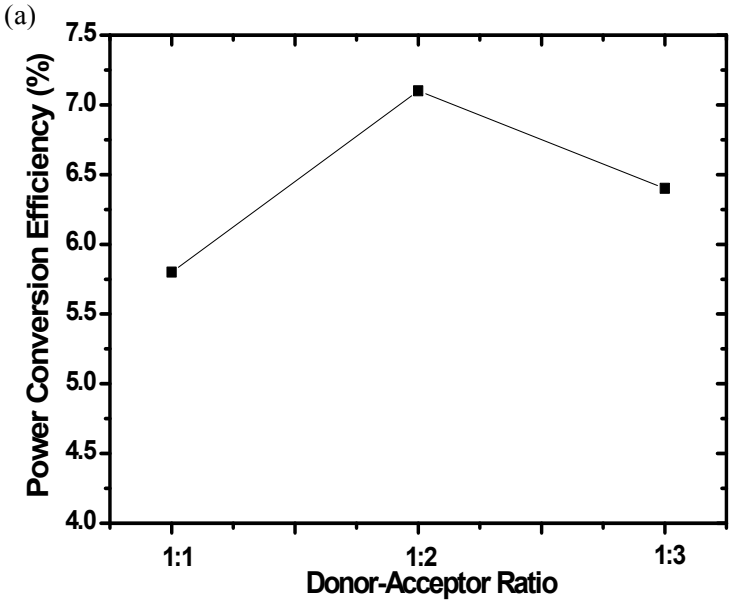
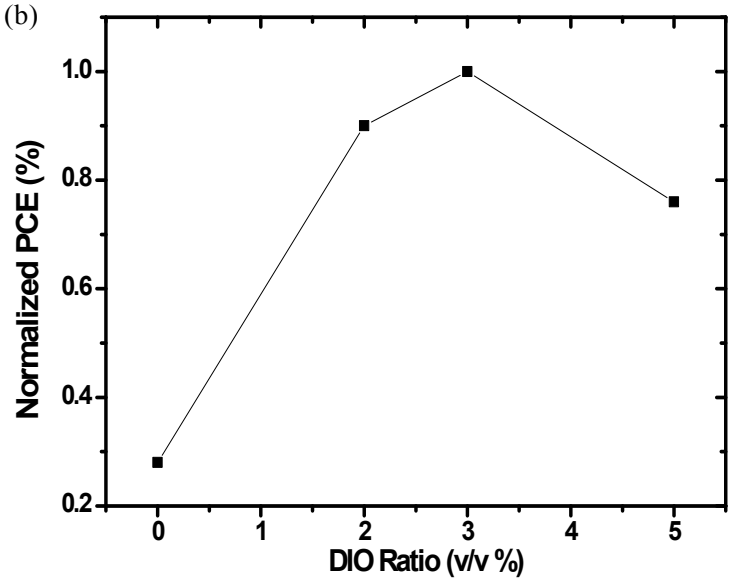


Figure S2. Normalized UV-vis absorption spectra of PBnDT-FTAZ:$PC_{70}BM$ BHJ film (red curve) and transmittance of the ITO substrate (black curve).

(a)


Power Conversion Efficiency (%)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
1:1
1:2
1:3
Donor-Acceptor Ratio

(b)


Normalized PCE (%)
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
DIO Ratio (v/v %)

(c)

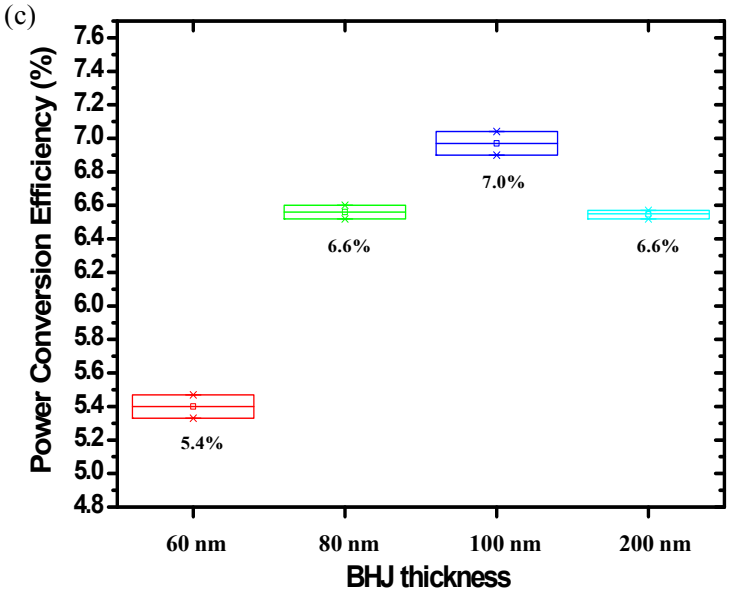

Power Conversion Efficiency (%)
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
7.0%
6.6%
6.6%
5.4%
60 nm
80 nm
100 nm
200 nm
BHJ thickness

Figure S3. PCE ranges of the PBnDT-FTAZ:$PC_{70}BM$ BHJ device fabricated with (a) donor:acceptor ratio from 1:1 to 1:3, (b) Normalized PCE of DIO ratio from 0% to 5%, and (c) Average PCE depending on BHJ thicknesses from 60 nm to 200 nm (DIO 3%).

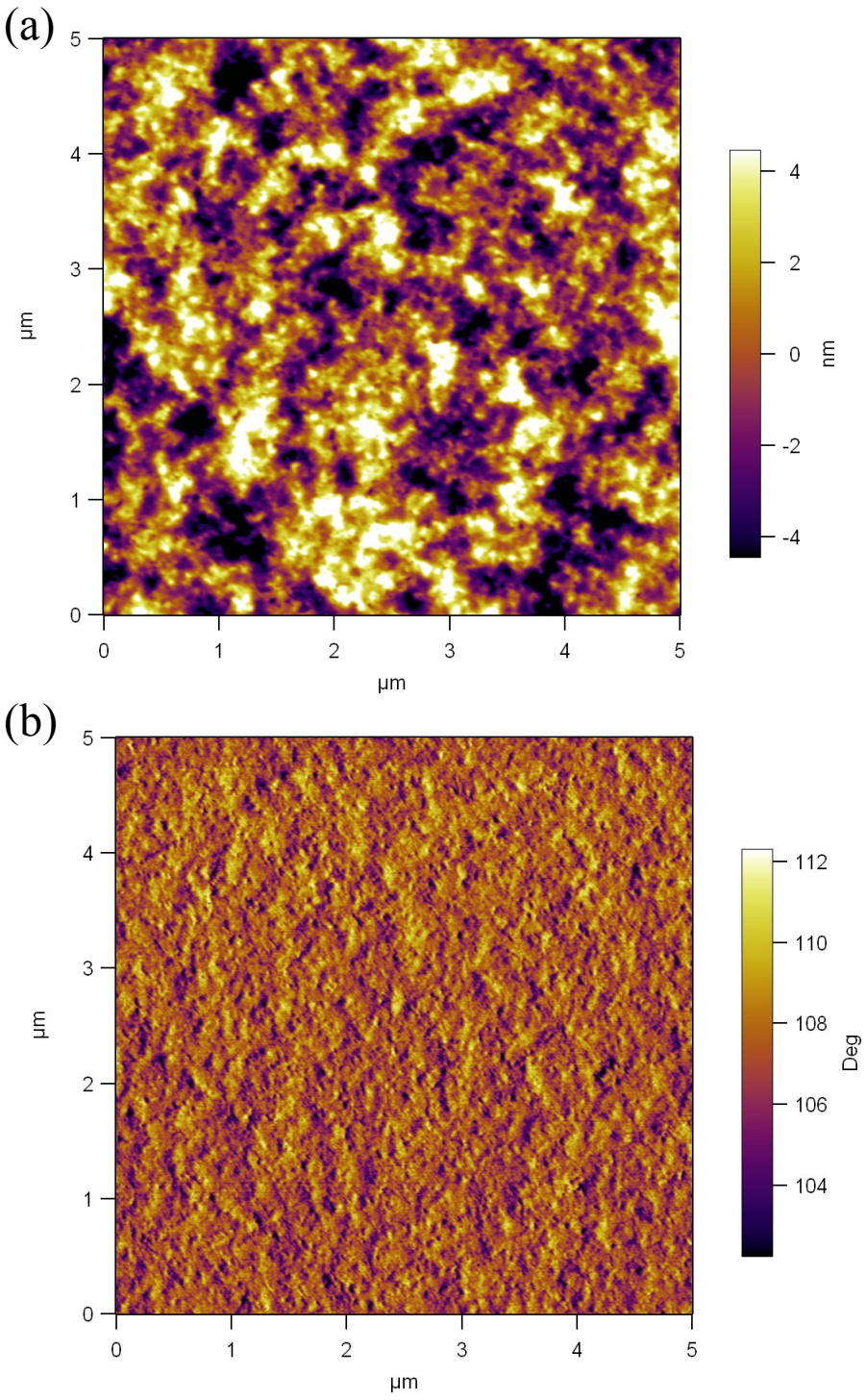


Figure S4. AFM two dimensional images of PBnDT-FTAZ:$PC_{70}BM$ BHJ fabricated with DIO (3%); height images (a) and phase images (b). The D-A ratio of BHJ is 1:2.