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Supporting Information

Annealing Effects on the Photovoltaic Performance of All-Conjugated Poly(3-alkylthiophene) Diblock Copolymer-Based Bulk Heterojunction Solar Cells

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Experimental

ITO-coated glass substrate was cleaned sequentially by ultrasonication in acetone, methanol and iso-propanol, followed by O_2-plasma exposure for 5 min. PEDOT:PSS aqueous solution was purified with a 0.45 μm PTFE filter, and then spin-coated on the ITO substrate at 4000 rpm for 60 s and dried in a vacuum oven at 120°C for 1 h. The thickness of PEDOT:PSS layer was approximately 40 nm. All devices were fabricated in the glove box filled with argon. 50 mg/ml $PC_{71}BM$ ODCB solution was prepared by ultrasonic mixing for 1 h, and purified with a 0.45 μm PTFE filter prior to use. P3BHT21 was dissolved in ODCB at 90°C to yield a 20 mg/ml P3BHT21 ODCB solution. The hot solution was quickly purified with a 0.45 μm PTFE filter before cooling down to room temperature. Subsequently, the P3BHT21 and $PC_{71}BM$ ODCB solutions at the 1:0.75 wt/wt ratio was thoroughly mixed, and spin-coated on the PEDOT : PSS surface at 1100 rpm for 40 s. Thermal annealing was performed at 140°C for 20 min, and solvent annealing was performed under $CHCl_3$

vapor in a petri dish for 12 h, respectively. A cathode was prepared by sequentially depositing a 50 nm Ca and a 100 nm Al through a shadow mask onto the P3BHT21/$PC_{71}BM$ active layer with a thermal evaporator at a vacuum of 2×10^{-6} torr.

Photovoltaic devices with an area of 0.10 ± 0.01 cm^2 were tested under simulated AM 1.5 G irradiation (100 $mWcm^{-2}$, calibrated with Daystar Meter) using a SoLux Solar Simulator, and the current~voltage (*I*~*V*) curves were measured using a Keithley 2400 multisource meter. X-ray diffraction (XRD) data were collected by a Scintag XDS 2000 X-ray diffractometer using Cu Kα1 radiation (λ= 1.541 Å) operated at 30 kV and 40 mA. UV-Vis absorption spectra were recorded with a Newport OSM-100-UV/vis optical spectrometer. AFM measurements were prepared in an identical manner as those of photovoltaic devices, but with no Ca/Al deposited on the top.

Figure S1

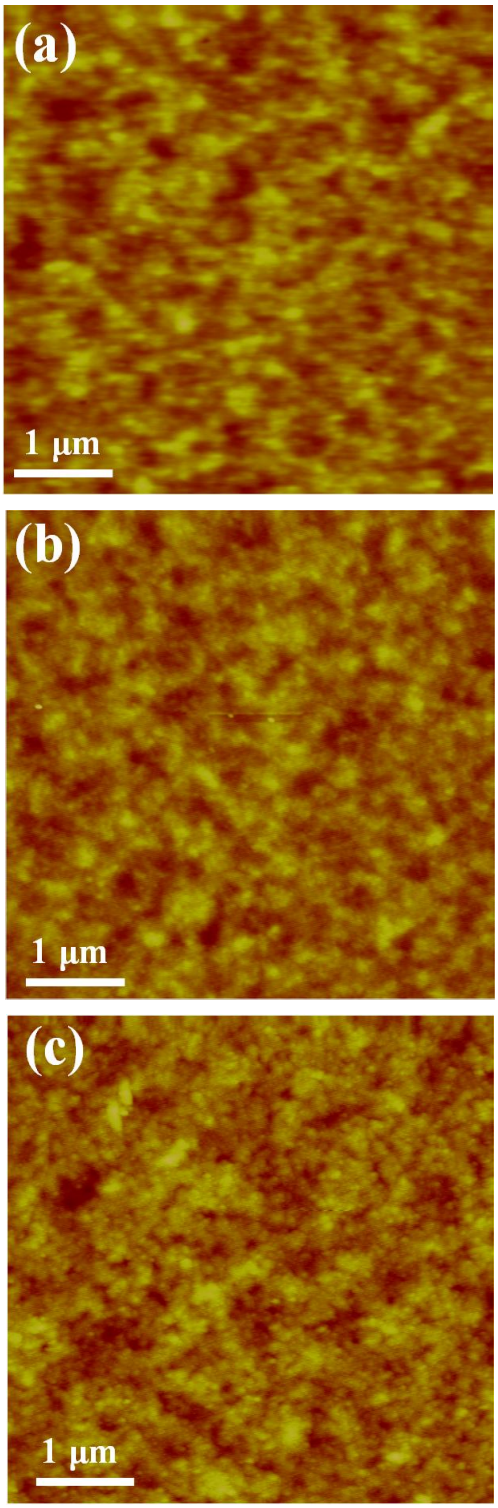

Figure S1. AFM height images of the blend films. (a) without annealing treatment, the root mean square (*rms*) roughness is 4.0 nm; (b) with thermal annealing at 140°C for 20 min, the *rms* roughness is 3.8 nm; and (c) with chloroform vapor annealing for 12 h, the *rms* roughness is 4.3 nm. Scanning size = 5 × 5 μm^2 for all images.