

Supporting Information

Comparative Study of Thermal Stability, Morphology and Performance of All-Polymer, Fullerene-Polymer, and Ternary Blend Solar Cells Based on the Same Polymer Donor

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Methods

Materials: Unless stated otherwise, solvents and chemicals were obtained commercially and used without further purification. The monomers (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane), 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, and 4,9-dibromo-2,7-bis(2-hexyldecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone were purchased from Sunatech Incorporation. PCBM was purchased from Solarmer Materials Incorporation. Commercial PEDOT:PSS in water (PH 500, Clevios) was used. The monomer 2,5-bis(trimethylstannyl)thiophene, and other materials and solvents were purchased from Sigma-Aldrich.

Synthesis and Characterization of polymers: Both polymer donor PBDTTTPD and polymer acceptor P(NDI2HD-T) were synthesized and characterized according to previously reported procedures.¹

Thermal analysis: Standard differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MTDSC) methods were conducted on a TA instruments Discovery DSC 25 with an RCS 90 cooling module. Sapphire was used to calibrate heat capacity measurements. All samples were gathered from drop casted films on the slide glass and the solvent was completely removed.

Conditions for the T_g measurements of PBDTTTPD: (i) heating from 35 °C to 320 °C at 100 °C/min, (ii) cooling to 35 °C at 20 °C/min, and (iii) reheating from 35 °C to 320 °C at 100 °C/min). The second heating cycle is shown in **Figure S1**.

MTDSC methods^{2,3} were used for the T_g measurements of P(NDI2HD-T) and PCBM. The

modulation amplitude was 1 °C/min with a period of 60 s. The samples were heated from -60 °C to 310 °C at 3 °C/min and held at 310 °C for 5 min before cooling to -60 °C. The samples were then re-heated to 310 °C at 3 °C/min to observe the glass transition.

Fabrication and Characterization of PSCs: Conventional devices were fabricated with a device architecture of ITO/PEDOT:PSS/active layer/LiF/Al. ITO glass substrates were washed sequentially with acetone, deionized water, and isopropyl alcohol for 20 min each in an ultrasonicator. The ITO substrates were then treated with O₂ plasma prior to PEDOT:PSS deposition. PEDOT:PSS films were spin-coated on the ITO substrates at 3,000 rpm for 40 s and then annealed at 150 °C for 20 min in ambient conditions. Donor:acceptor blend solutions were spin-coated onto the PEDOT:PSS layer in a N₂ glovebox. The PBDTTTPD:PCBM blend solution was prepared by dissolving PBDTTTPD:PCBM in chloroform at a ratio of 1:1.5 (w/w) and a total concentration of 25 mg mL⁻¹. For the PBDTTTPD:P(NDI2HD-T) system, the blend solution was prepared in chloroform with a PBDTTTPD:P(NDI2HD-T) ratio of 1.3:1 (w/w) and a total concentration of 12.5 mg mL⁻¹. The ternary blend solution composed of PBDTTTPD:P(NDI2HD-T):PCBM was prepared using the same conditions as for the binary blends of all-PSCs except that a D:A ratio of 1.3:x:1-x (w/w/w) was used, where x = 0-1.0. The final thicknesses of active layers were 80-120 nm for the all-PSCs and ternary-PSCs. The LiF layer and Al electrode were deposited in an evaporation chamber under high vacuum (< 10⁻⁶ Torr), with thicknesses of approximately 0.9 nm and 100 nm, respectively. The configuration of the shadow mask produced four independent devices on each substrate. The active area of the fabricated device was 0.09 cm², which was measured by optical microscopy. The photovoltaic characteristics were measured under AM 1.5G solar irradiation (100 mW cm⁻², Peccell: PEC-L01) in ambient conditions using a Keithley 2400 Source Measure Unit (SMU). This solar simulator system satisfies the Class AAB, ASTM

Standards. The light intensity was calibrated with a standard Si diode with a KG-5 visible color filter.

Morphology characterization: Unless stated otherwise, all active layers were spin-coated on glass/PEDOT:PSS substrates. The blend morphologies of the PCBM and all-polymer blend films were characterized by OM (Nikon, Eclipse 80i), AFM (Veeco Dimension 3100 instrument in tapping mode) and TEM (JEM-3011 HR) measurements. RSoXS measurements were performed at BL 11.0.1.2 in the Advanced Light Source (USA). RSoXS and TEM samples were prepared using the following procedure: the active layer films were first deposited on glass/ polystyrene sulfonate (PSS) substrates, and then floated onto the air/water interface, and collected on a 1.0 mm × 1.0 mm, 100 nm-thick Si₃N₄ membrane supported by a 5 mm × 5 mm, 200 μm-thick Si frame (Norcada Inc.) or a TEM grid. GIXS measurements were performed at beamline 3C in Pohang Accelerator Laboratory (South Korea). The active layers were prepared on Si/PEDOT:PSS substrates. Incidence angles (0.12° - 0.14°) were selected to allow for complete penetration of X-rays (wavelength= 1.1179 Å) into the film.

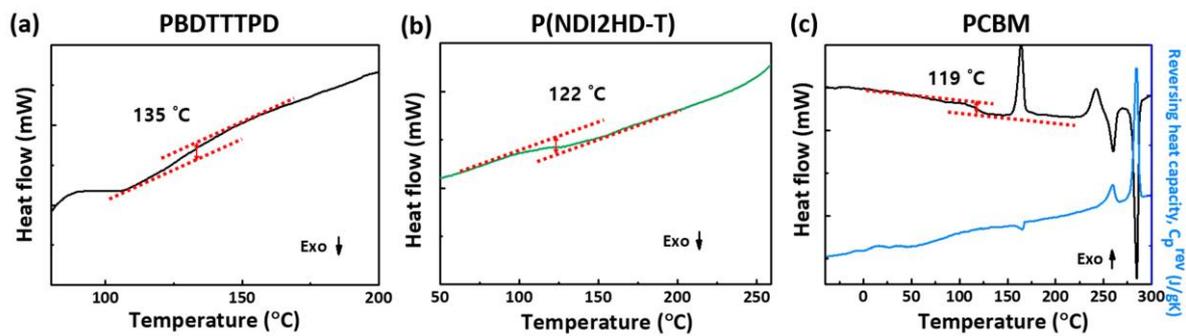


Figure S1. Heating DSC thermograms for (a) PBDTTTPD, (b) P(NDI2HD-T) and (c) PCBM.

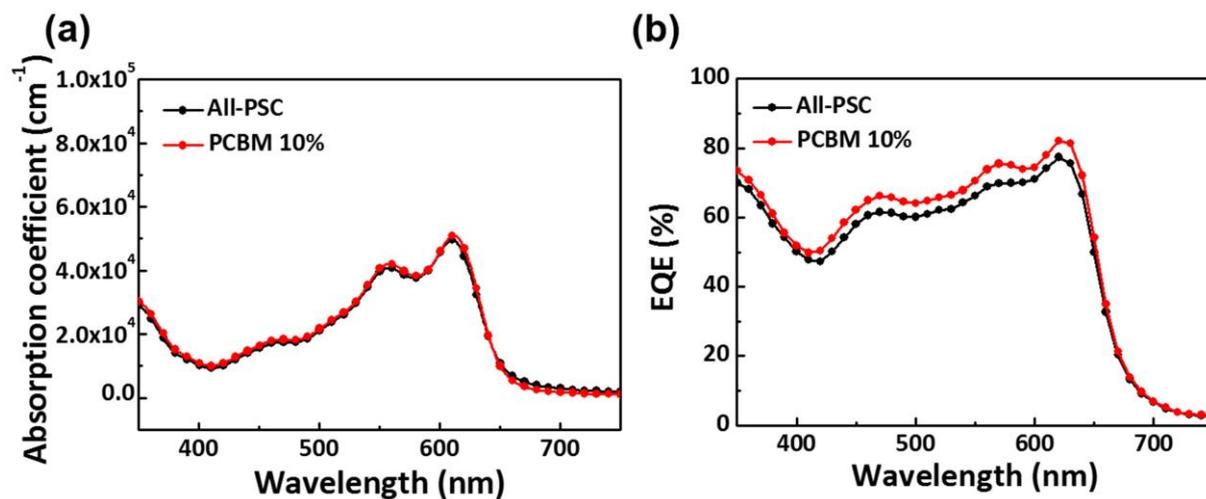


Figure S2. (a) UV-vis absorption spectra and (b) EQE characteristics of PBDTTTPD:P(NDI2HD-T):PCBM films containing 0 and 10% PCBM acceptor.

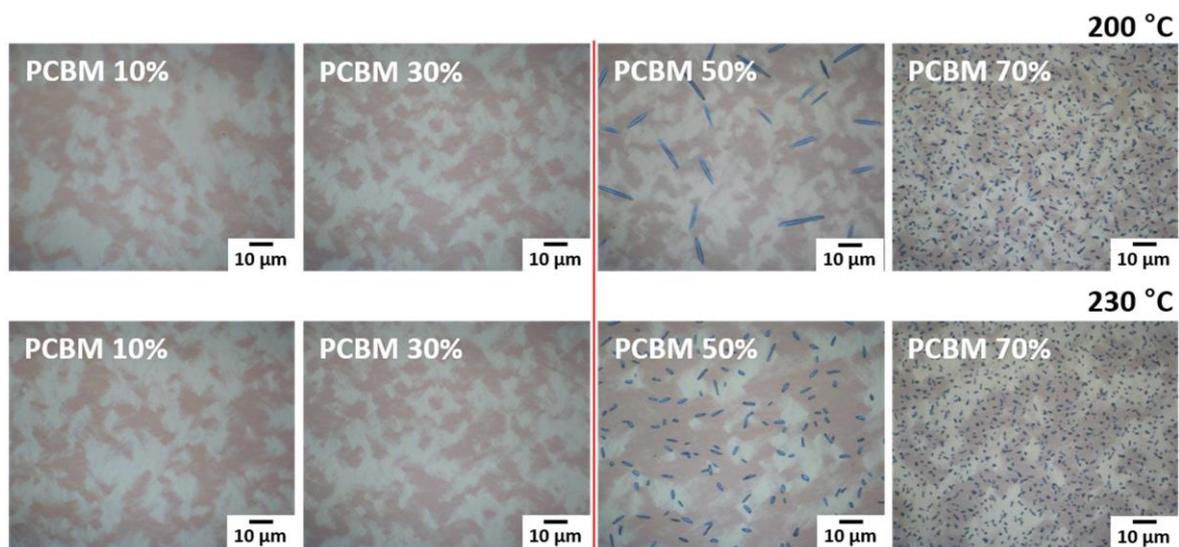


Figure S3. OM images showing morphology changes in the active layer of the ternary blend films annealed for 18 h at 200 °C and 230 °C.

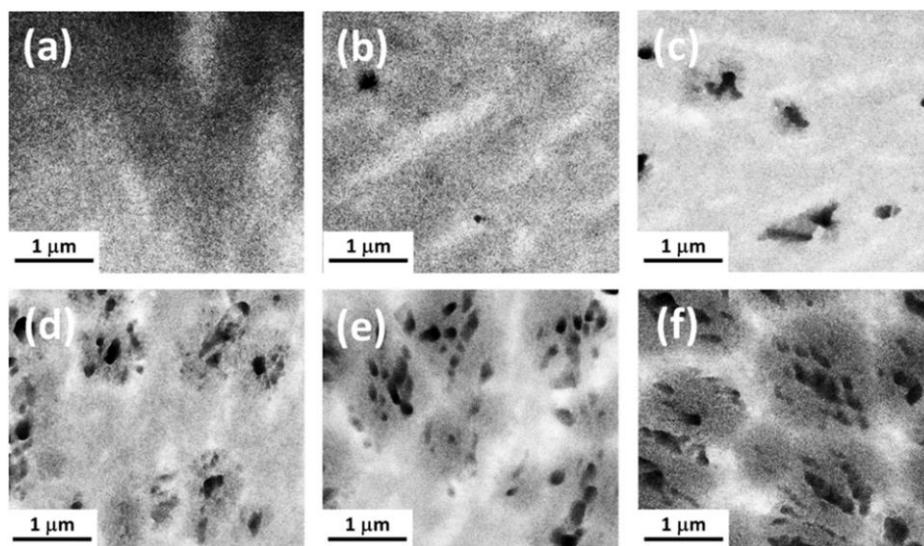


Figure S4. High-magnification TEM images showing morphological changes in the optimized active layer PBDTTTPD:PCBM blend films annealed at 150 °C for (a) 0, (b) 1, (c) 2, (d) 3, (e) 6 and (f) 12 h.

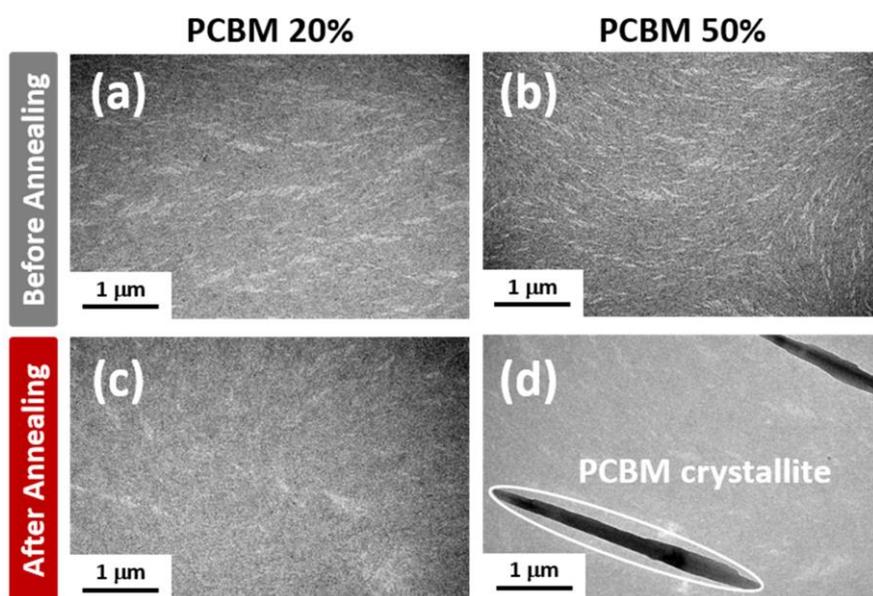


Figure S5. TEM images showing active layer morphology of PBDTTTPD:P(NDI2HD-T) devices with 20 and 50% PCBM acceptor before and after annealing at 150 °C.

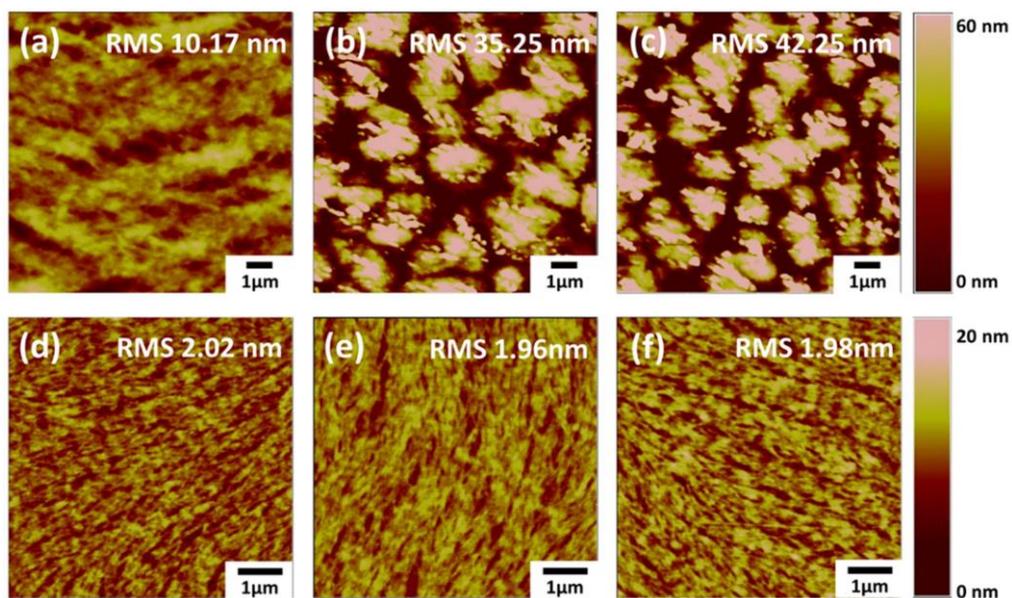


Figure S6. AFM height images of optimized PBDTTTPD:PCBM and PBDTTTPD:P(NDI2HD)-T blend films annealed at 150 °C for 0 (**a** and **d**), 6 (**b** and **e**) and 12 h (**c** and **f**).

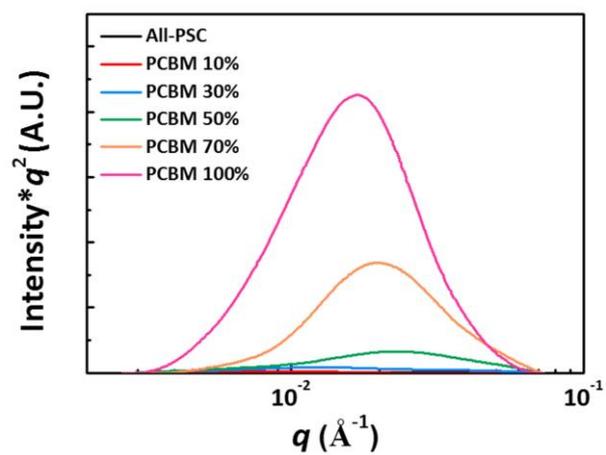


Figure S7. RSoXS profiles with the overall q -range of the as-cast PBDTTTTPD:P(NDI2HD-T):PCBM blend films with different PCBM contents. The baseline of the RSoXS profiles was subtracted by line fits.

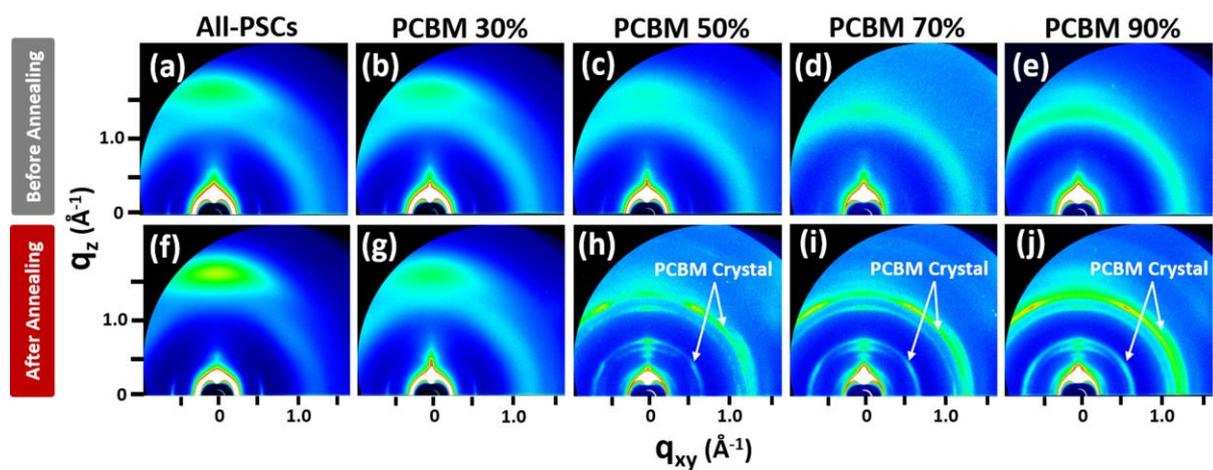
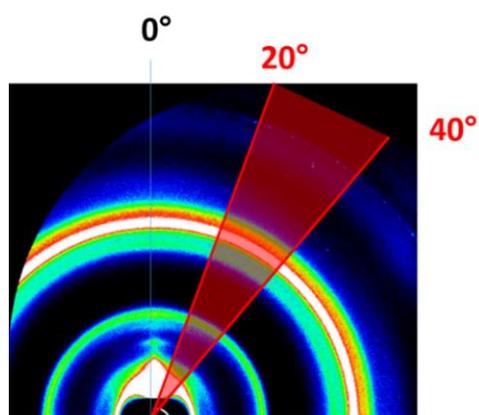


Figure S8. 2D GIXS images of all-PSCs and ternary-PSCs with 30, 50, 70% and 90% PCBM contents (a-e) before and (f-j) after annealing 12 hr at 150 °C.



PCBM-PSC

Figure S9. Example for cake segments (20-40°) through 2D-GIXS images.

References

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- (2) Trinh Tung, N.; Duc Nghia, N.; Van Tuyen, N. Glass transition of PCBM, P3HT and their blends in quenched state. *Adv. Nat. Sci: Nanosci. Nanotechnol.* **2012**, *3*, 045001.
- (3) Bruner, C.; Novoa, F.; Dupont, S.; Dauskardt, R. Decohesion Kinetics in Polymer Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 21474-21483.