

Supporting Information

Efficient Ternary Blend Bulk Heterojunction Solar Cells with Tunable Open-Circuit Voltage

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Materials and Methods: All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N₂, unless otherwise noted. All dry reactions were performed with glassware that was oven dried and then flamed under high vacuum and backfilled with N₂. Flash chromatography was performed using a Teledyne CombiFlash R_f instrument in combination with RediSep R_f normal phase disposable columns. Solvents were purchased from VWR and used without further purification except for THF which was dried over sodium/benzophenone before being distilled.

All compounds were characterized by ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) on a Mercury 400. Polymer ¹H NMRs (500 MHz) were obtained on a Varian VNMRS-500. For polymer molecular weight determination, polymer samples were dissolved in HPLC grade *o*-

dichlorobenzene at a concentration of 1 mg/ml, briefly heated and then allowed to return to room temperature prior to filtering through a 0.2 μm PTFE filter. SEC was performed using HPLC grade *o*-dichlorobenzene at a flow rate of 1 ml/min on one 300 \times 7.8 mm TSK-Gel GMH_{H R}-H column (Tosoh Corporation) at 70 °C using a Viscotek GPC Max VE 2001 separation module and a Viscotek TDA 305 RI detector. The instrument was calibrated vs. polystyrene standards (1,050 –3,800,000 g/mol) and data was analyzed using OmniSec 4.6.0 software. MALDI data was obtained using an Applied Biosystems Voyager-DE STR mass spectrometer and 2,5-dihydroxybenzoic acid as matrix.

For thin film measurements solutions were spin-coated onto pre-cleaned glass slides from chlorobenzene solutions at 7 mg/ml for **P3HT**, 20 mg/ml for **PC₆₁BM** and **ICBA** and 10 mg/ml in **P3HT** for **P3HT:PC₆₁BM:ICBA** blends. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. The thickness of the thin films and GIXRD measurements were obtained using Rigaku Diffractometer Ultima IV using Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$) in the reflectivity and grazing incidence X-ray diffraction mode, respectively.

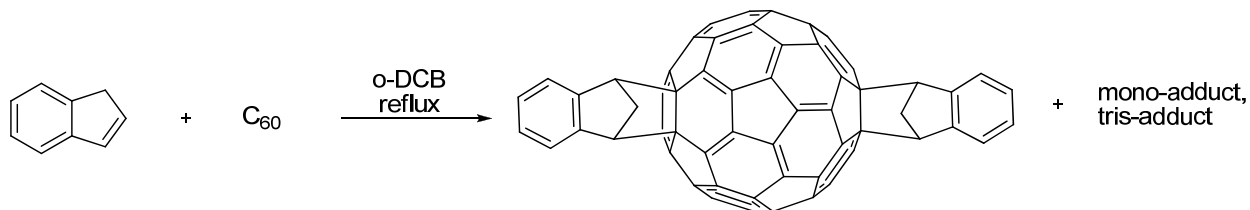
Transmission electron microscopy (TEM) was performed on the JEOL JEM-2100 microscope equipped with the Gatan Orius CCD camera. The accelerating voltage was 200 kV. Films for the TEM measurements were prepared from the chlorobenzene solutions of **P3HT:PC₆₁BM:ICBA** blends at the 1:1:0, 1:0.5:0.5 and 1:0:1 ratios and optimized annealing conditions. Films for TEM were prepared by first spin-casting on KBr plates, which were then placed in de-ionized water

and upon salt dissolution the floated **P3HT:PC₆₁BM:ICBA** films were picked up with the 600 hex mesh copper grid (Electron Microscopy Sciences).

Synthetic Procedures:

Synthetic procedures for the synthesis of **poly(3-hexylthiophene) (P3HT)** were used without modifications as reported in the literature.¹

Scheme S1.



Indene-C₆₀ bisadduct (ICBA) (1):

Modified from the literature.² 200 mg (0.27 mmol) C₆₀ and 0.82 ml (7.02 mmol) indene were combined with 20 ml *o*-DCB and brought to reflux for 22 hours. The reaction mixture was cooled down and poured in methanol. The precipitate was filtered and washed with methanol before being purified with flash chromatography (Hexanes: Toluene, 7:1). 22 mg mono-adduct, 137 mg indene-C₆₀ bisadduct (ICBA) (53 % yield) and 124 mg tris-adduct was obtained. MALDI: 951.41 (calculated for C₇₈H₁₆: 952).

¹H-NMR (**Figure S1**) and ¹³C-NMR (**Figure S2**) of indene-C₆₀ bisadduct (ICBA) in CDCl₃ are identical to those observed in the literature.³

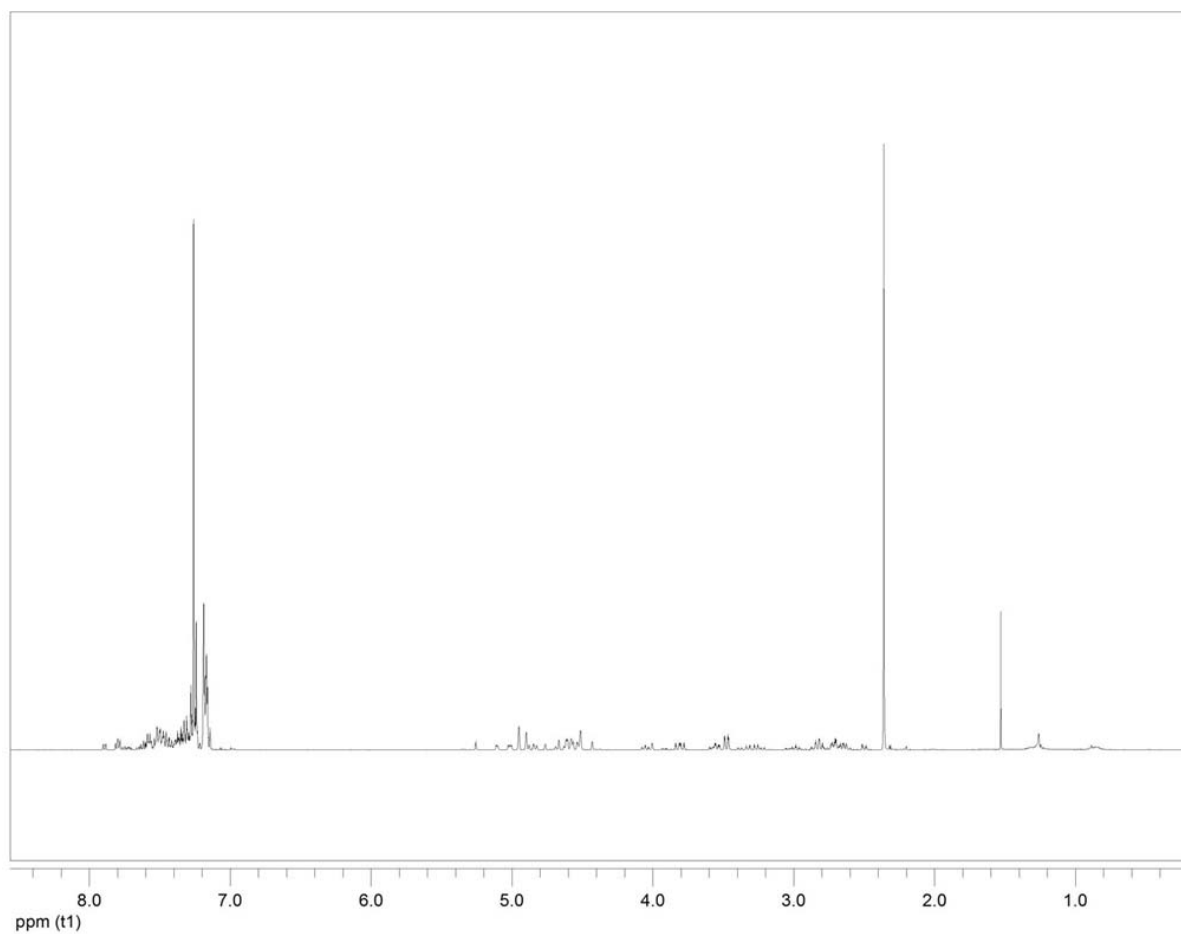


Figure S1. ^1H -NMR of indene- C_{60} bisadduct (ICBA) in CDCl_3 .

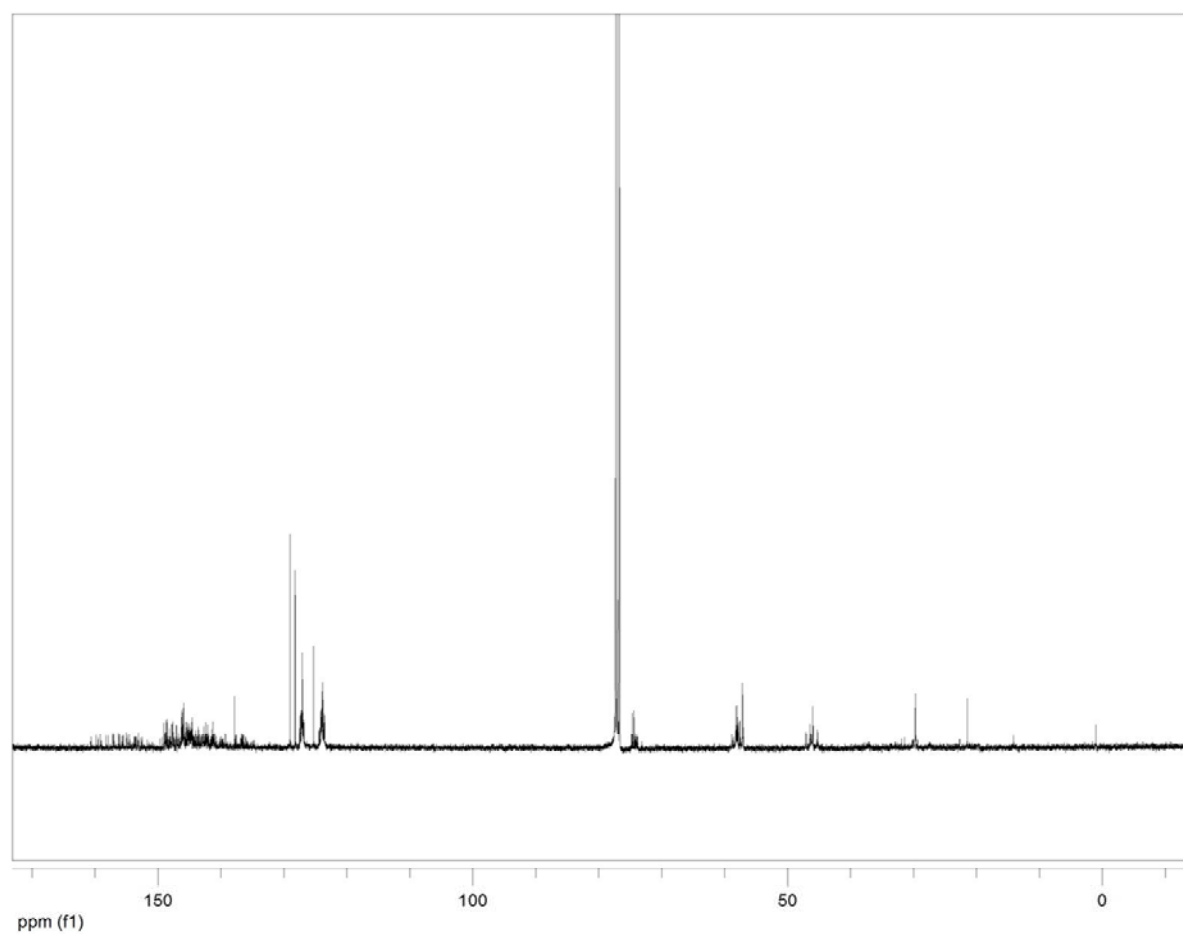


Figure S2. ^{13}C -NMR of indene- C_{60} bisadduct (ICBA) in CDCl_3 .

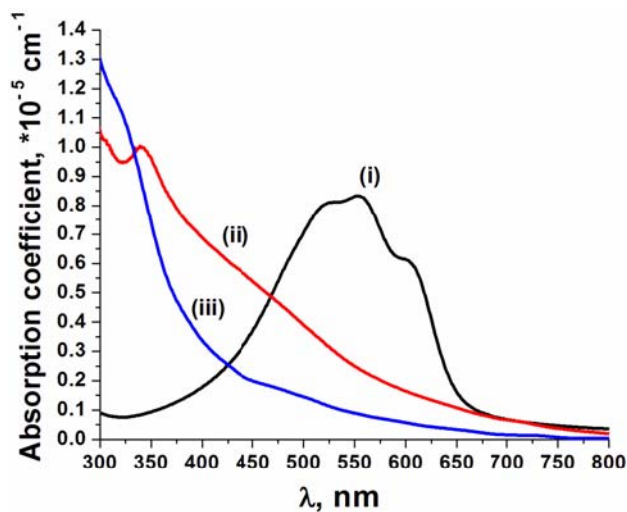


Figure S3. UV-vis absorption spectra of thin films spin-coated from chlorobenzene (CB) and annealed at 150 °C under N₂ for 20 min, where (i) is **P3HT** (black line), (ii) is **PC₆₁BM** (red line) and (iii) is **ICBA** (blue line).

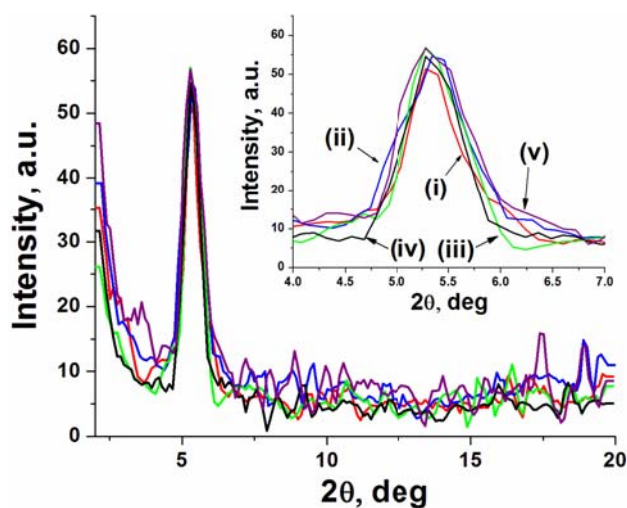


Figure S4. Grazing-incidence X-ray diffraction of thin films of **P3HT:PC₆₁BM:ICBA** spin-coated from chlorobenzene (CB) and annealed at 150 °C under N₂ for 20 min, where (i) is 1:1:0 (red line), (ii) is 1:0.2:0.8 (blue line), (iii) is 1:0.5:0.5 (green line), (iv) is 1:0.8:0.2 (black line) and (v) is 1:0:1 (purple line).

Device fabrication and characterization: All steps of device fabrication and testing were performed in air. ITO-coated glass substrates ($10 \text{ } \Omega/\square$, Thin Film Devices Inc.) were sequentially cleaned by sonication in detergent, de-ionized water, tetrachloroethylene, acetone, and isopropyl alcohol, and dried in a nitrogen stream. A thin layer of PEDOT:PSS (Baytron[®] P VP AI 4083, filtered with a $0.45 \text{ } \mu\text{m}$ PVDF syringe filter – Pall Life Sciences) was first spin-coated on the pre-cleaned ITO-coated glass substrates and baked at $130 \text{ } ^\circ\text{C}$ for 60 minutes under vacuum. Separate solutions of 20 mg/ml **P3HT**, **PC₆₁BM** and **ICBA** each were prepared in chlorobenzene solvent. The solutions were stirred for 24 hrs before they were mixed at the desired ratios and stirred for an additional 24 hrs to form a homogeneous mixture. Subsequently, the **P3HT:PC₆₁BM:ICBA** active layer was spin-coated (with a $0.45 \text{ } \mu\text{m}$ PTFE syringe filter - Whatman) on top of the PEDOT:PSS layer. Upon spin-coating (900 rpm for 60 sec) of **P3HT:PC₆₁BM:ICBA**, at all fullerene ratios (10 mg/ml in P3HT) films formed $95 - 105 \text{ nm}$ thick layers and were directly placed in the vacuum chamber for aluminum deposition. At the final stage, the substrates were pumped down to high vacuum ($< 7 \times 10^{-7} \text{ Torr}$) and aluminum (100 nm) was thermally evaporated at $3 - 4 \text{ } \text{\AA}/\text{sec}$ using a Denton Benchtop Turbo IV Coating System onto the active layer through shadow masks to define the active area of the devices as 4.9 mm^2 . Thermal annealing of **P3HT:PC₆₁BM:ICBA** blends was carried out by directly placing the completed devices in the nitrogen oven at $150 \text{ } ^\circ\text{C}$ for: 10 min for 1:0.3:0.7 and 1:0:1; 20 min for 1:0.9:0.1, 1:0.8:0.2, 1:0.2:0.8 and 1:0.1:0.9; 30 min for 1:0.6:0.4; 40 min 1:0.7:0.3 and 1:0.4:0.6; 50 min 1:0.5:0.5; and 60 min 1:1:0 ternary blend ratios. In case of optimized **P3HT:PC₆₁BM:ICBA** blends at 1:0.5:0.5 and 1:0:1 ratios thicker films of 137 nm (spin-coated from 10 mg/ml in P3HT) (700 rpm for 60 sec) and 174 nm (spin-coated from 13 mg/ml in P3HT) were required (700 rpm for 60 sec). After aluminum deposition films were annealed in the

nitrogen oven at 150 °C for 10 min in both cases. After annealing, the devices were cooled down to room temperature before measurements were carried out.

The current-voltage (I - V) characteristics of the photovoltaic devices were measured under ambient conditions using a Keithley 2400 source-measurement unit. An Oriel® Sol3A class AAA solar simulator with Xenon lamp (450 Watt) and an AM 1.5G filter was used as the solar simulator. An Oriel PV reference cell system 91150V was used as the reference cell. To calibrate the light intensity of the solar simulator (to 100 mW/cm²), the power of the Xenon lamp was adjusted to make the short-circuit current density (J_{sc}) of the reference cell under simulated sun light as high as it was under the calibration condition.

External quantum efficiency measurements were performed using a 300 W Xenon arc lamp (Newport Oriel), chopped and filtered monochromatic light (250 Hz, 10 nm FWHM) from a Conerstone 260 1/4 M double grating monochromator (Newport 74125) together with an EG&G 7220 lock-in amplifier. A silicon photodiode (Hamamatsu S1787-04, 8RA filter) calibrated at the National Renewable Energy Laboratory (NREL) was utilized as the reference cell.

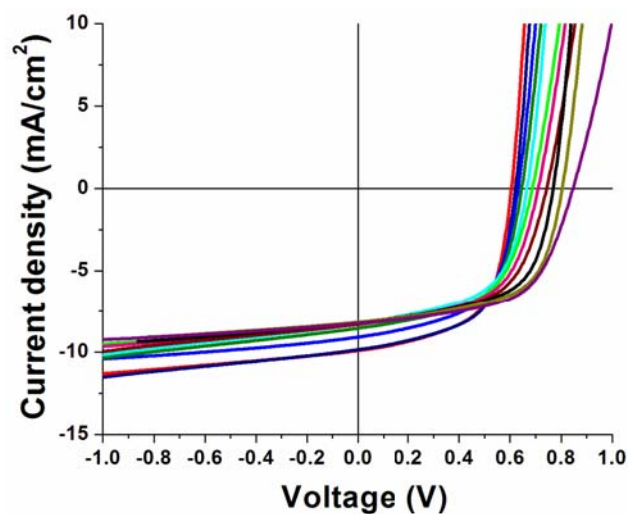


Figure S5. *J-V* curves of the ternary blend BHJ solar cells based on **P3HT:PC₆₁BM:ICBA** at different ratios: 1:1:0 (red line), 1:0.9:0.1 (navy line), 1:0.8:0.2 (blue line), 1:0.7:0.3 (olive line), 1:0.6:0.4 (cyan line), 1:0.5:0.5 (green line), 1:0.4:0.6 (pink line), 1:0.3:0.7 (wine red line), 1:0.2:0.8 (black line), 1:0.1:0.9 (dark yellow line) and 1:0:1 (purple line) under AM 1.5G illumination (100 mW/cm²) at thicknesses 95 – 105 nm presented in **Table 1**.

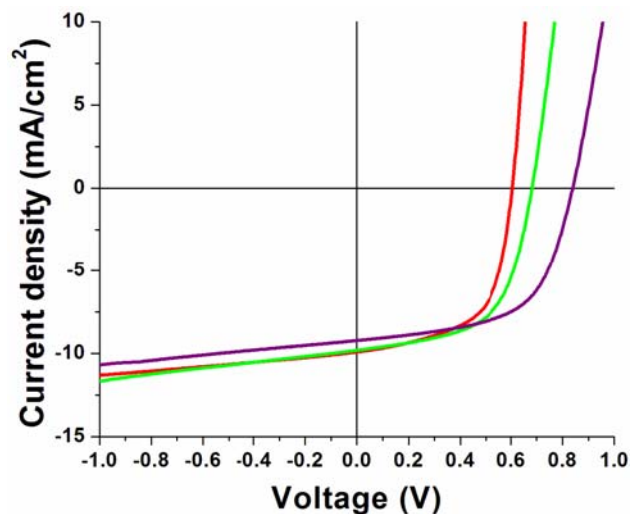


Figure S6. J - V curves of the optimized ternary blend BHJ solar cells based on **P3HT:PC₆₁BM:ICBA** at different ratios: 1:1:0 (red line), 1:0.5:0.5 (green line), 1:0:1 (purple line) under AM 1.5G illumination (100 mW/cm^2) at thicknesses 104 nm, 137 nm and 174 nm, respectively.

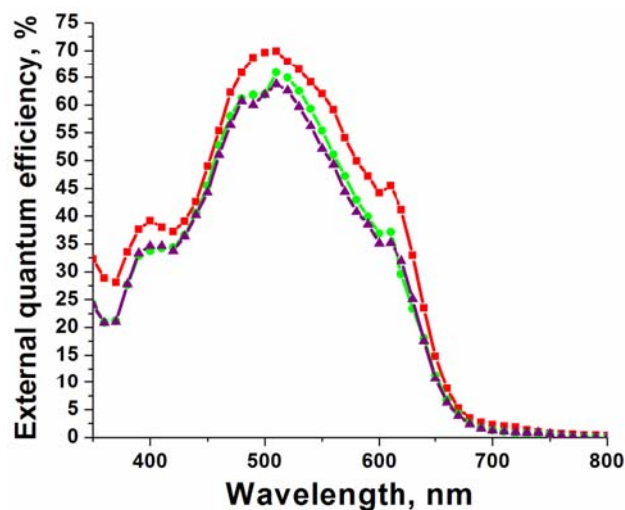


Figure S7. External quantum efficiency of the ternary blend BHJ solar cells based on **P3HT:PC₆₁BM:ICBA** at different ratios: 1:1:0 (red circles), 1:0.5:0.5 (green circles), 1:0:1 (purple circles) at thicknesses 95 – 105 nm presented in **Table 1**.

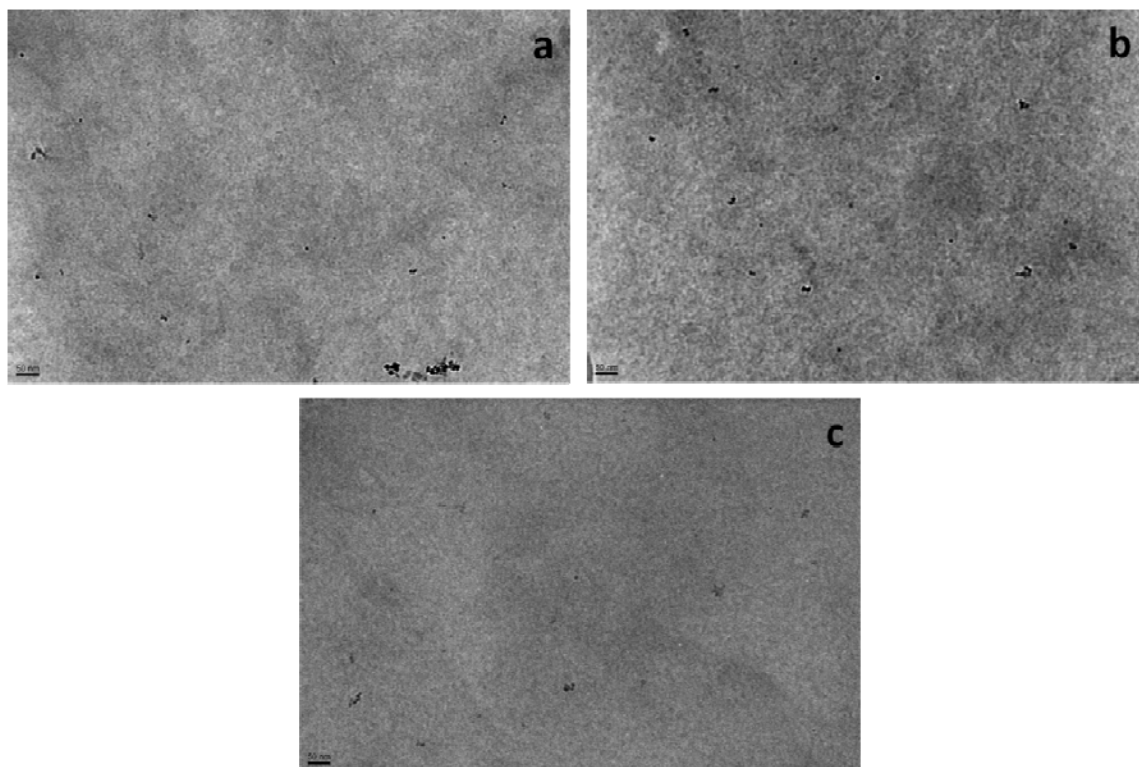


Figure S8. TEM images of **P3HT:PC₆₁BM:ICBA** at (a) 1:1:0, (b) 1:0.5:0.5 and (c) 1:0:1 at thicknesses 95 – 105 nm for BHJ solar cells presented in **Table 1** (scale bar is 50 nm).

References

- (1) Burkhart, B.; Khlyabich, P. P.; Cakir Canak, T.; LaJoie, T. W.; Thompson, B. C. *Macromolecules* **2011**, *44*, 1242-1246.
- (2) Laird, D. W.; Richter, H.; Vejins, V.; Scott, L. T.; Lada, T. A. Organic photovoltaic devices comprising fullerenes and derivatives thereof and improved methods of making fullerene derivatives. World Intellectual Property Organization WO 2009/086210, July 9, **2009**.
- (3) He, Y.; Chen, H.-Y.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 1377-1382.