

Electronic Supplementary Information (ESI)

Parallel Bulk Heterojunction Photovoltaics Based on All-Conjugated Block Copolymer

Additives

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Organic solar cells fabrication and measurement:

PCBM (C60PXBM, p/n PCBM61-X01) was obtained from Nano-C. The ZnO precursor solution was prepared by dissolving 1 g of zinc acetate dihydrate ($\geq 98\%$, Sigma-Aldrich) in 10 mL of 2-methoxyethanol ($\geq 99.0\%$, 50ppm BHT as stabilizer, Sigma-Aldrich) with 0.28 g of ethanolamine ($\geq 99\%$, Alfa Aesar) as a surfactant. The solution was stirred overnight before use. The PEDOT:PSS solution was prepared by diluting 1 mL of PEDOT:PSS Clevios P VP AI4083 (Heraeus) in 10 mL of isopropyl alcohol.

ITO glass substrate was cleaned in sequential 15-minute ultrasonic baths using deionized soap water (0.5% Hellmanex III, Helma), deionized water, acetone, and isopropyl alcohol, and dried in an oven at 100°C for 1 hour. The ITO glass substrate then received 15 minutes of UV-ozone treatment before coating the ZnO precursor. The ZnO precursor solution was spin-coated onto the ITO glass at 2000 rpm for 60 s and thermally annealed at 200°C on a hot plate in air for 1 h. After air-cooling to room temperature, the substrate was rinsed with acetone and isopropyl alcohol and subsequently dried in an oven at 100°C for 1 hour.

The glass/ITO/ ZnO substrate was then transferred into a nitrogen-filled glove box for coating the active layer and the PEDOT:PSS. The active layer blend consists of a blend of 1:1.75 by mass ratio between PTB7 and PCBM. The concentration of PTB7-PNDI or PNDI was varied between 0% and 15%. The total concentration was kept constant at 28 mg/mL of solution of chlorobenzene (97%) and diiodooctane (3%).

The active layer solution was spin-coated at 800 rpm for 2 minutes and thermally annealed at 100°C on a hot plate for 10 minutes, yielding an active layer thickness ~ 70 nm. After allowing the substrate to cool to room temperature, the PEDOT:PSS solution was spin-coated at 5000 rpm

for 90 s and allowed to dry for 1 h inside the glovebox. A 200 nm Ag anode layer was evaporated through a shadow mask using thermal vacuum deposition to give 10 pixels, each with an active area of 4 mm² (0.2 cm x 0.2 cm). The photovoltaic cells were tested under AM 1.5 G solar illumination at 100 mW cm⁻².

Table S1. Device characteristics of PTB7/PCBM₆₀ OPVs, averaged over 10 cells. Active layer thickness: 70 nm.

Additive	Additive Conc. (wt %)	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)
No additive	0	2.5 ± 0.1	0.68 ± 0.02	9.4 ± 0.5	40.7 ± 1.9
PTB7- <i>b</i> -PNDI	1	3.4 ± 0.2	0.77 ± 0.01	10.7 ± 0.6	41.6 ± 1.8
	2	4.4 ± 0.2	0.81 ± 0.00	10.8 ± 0.4	50.9 ± 0.9
	3	4.2 ± 0.2	0.79 ± 0.01	11.2 ± 0.5	47.5 ± 1.4
	10	2.9 ± 0.1	0.80 ± 0.01	9.4 ± 0.1	39.3 ± 1.2
	15	1.9 ± 0.1	0.78 ± 0.15	7.8 ± 0.4	31.5 ± 0.8
PNDI	2	4.5 ± 0.2	0.74 ± 0.01	14.2 ± 0.5	41.7 ± 0.4
	3	3.9 ± 0.2	0.74 ± 0.02	13.3 ± 0.5	40.14 ± 0.7
	5	2.5 ± 0.1	0.76 ± 0.01	8.1 ± 0.4	40.9 ± 0.4
	10	2.6 ± 0.0	0.80 ± 0.00	8.9 ± 0.2	36.1 ± 0.5
	15	2.6 ± 0.0	0.81 ± 0.01	9.1 ± 0.2	35.6 ± 0.9

PCE: power conversion efficiency; J_{sc} : short circuit current; V_{OC} : the open-circuit voltage; FF: fill factor.

Size-exclusion chromatography (SEC): Polymer molecular weights and polydispersity indices (PDIs) were obtained by size-exclusion chromatography (SEC) using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10,000 Å pore sizes), an Agilent variable wavelength UV–visible detector, a Wyatt Technology HELEOS II multiangle laser light scattering (MALLS) detector ($\lambda = 658$ nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV–VIS (SEC-UV–VIS), and MALLS (SEC-MALLS) detection. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 mL min⁻¹ at 40 °C. Weight average molecular weights (M_w) and

PDI were determined using SEC-RI calibrated with a set of monodisperse polystyrene standards (Astra Software Version 5.3.4).

Nuclear Magnetic Resonance Spectroscopy (NMR): Measurements were carried out with a Bruker 400 MHz. Samples were prepared with concentrations about 10 mg/mL in deuterated chloroform. Solvents contain 0.05 % TMS as standard.

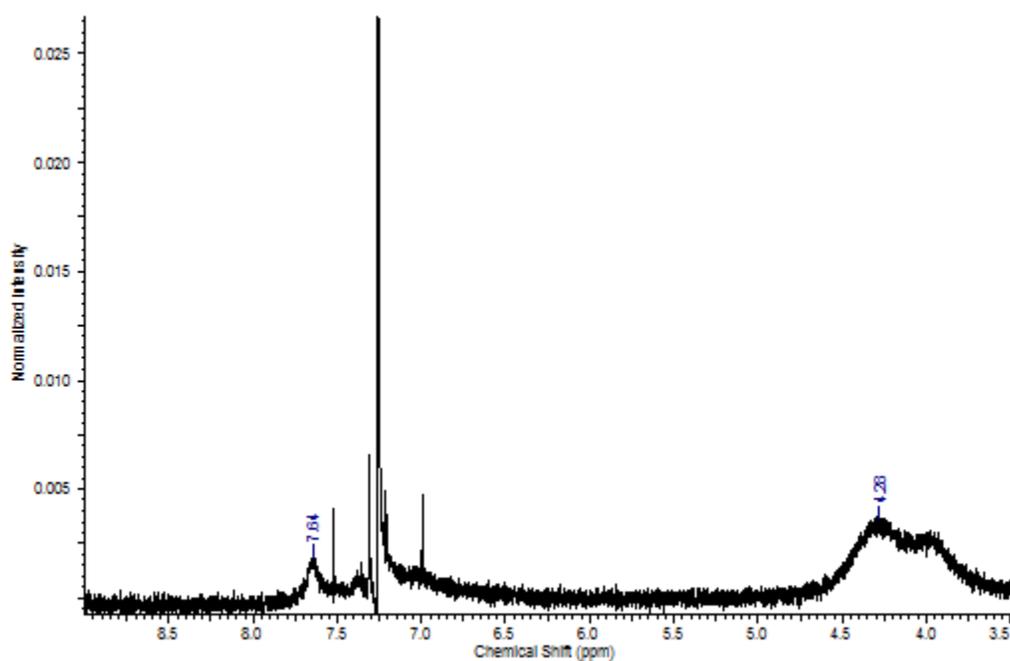


Figure S1. PTB7 ¹H NMR spectrum.

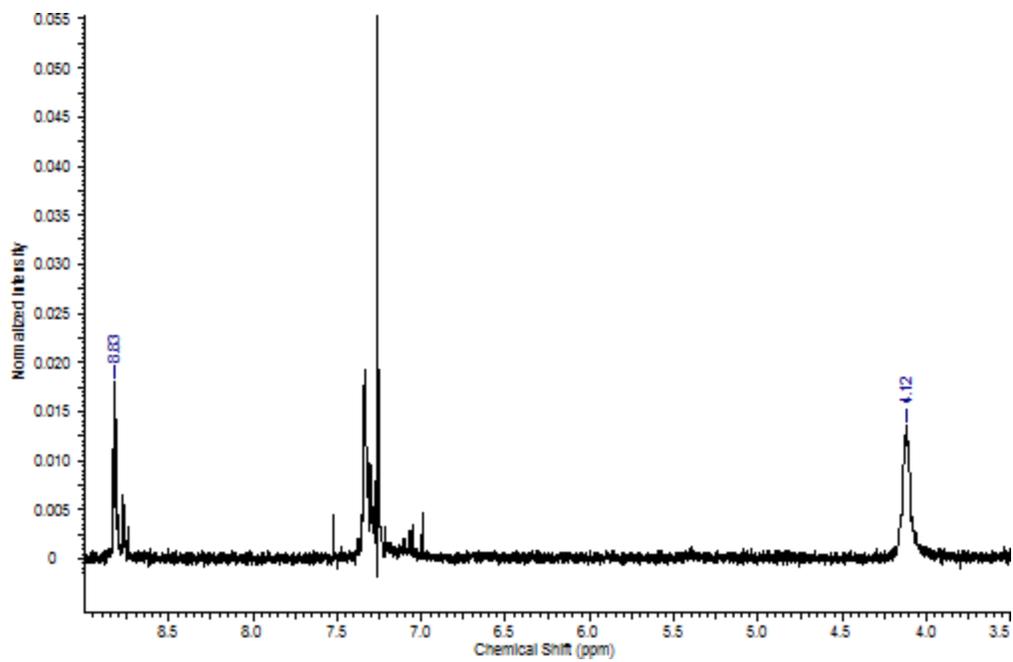


Figure S2. PNDI ^1H NMR spectrum.

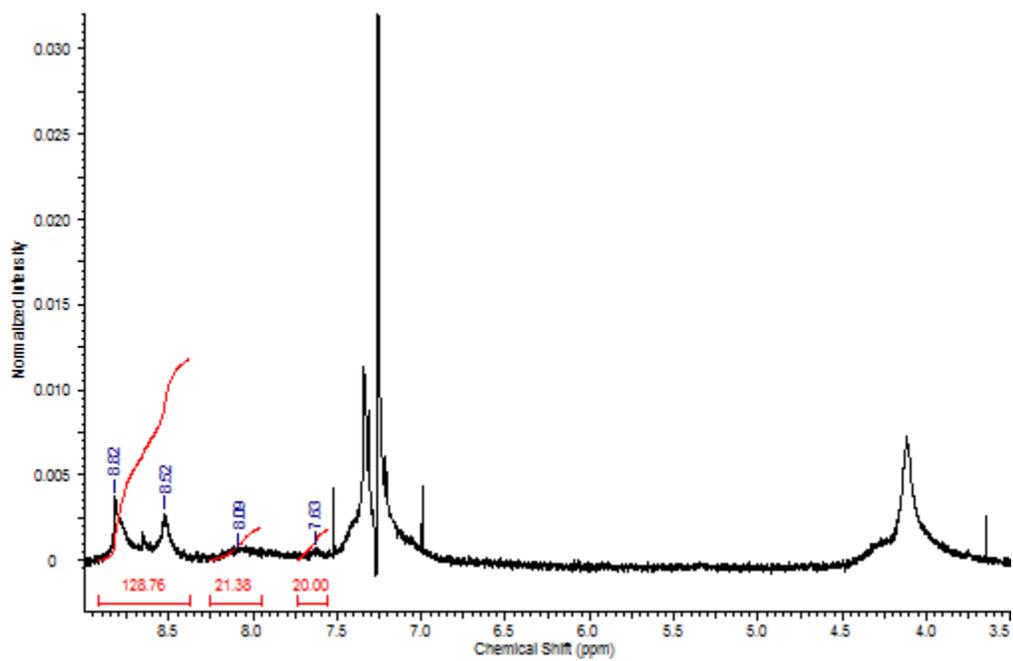


Figure S3. PTB7-*b*-PNDI ^1H NMR spectrum.

Steady-state UV-Vis absorption: The polymers were dissolved in tetrahydrofuran (0.01 mg/ml) and the UV-Vis absorbance was measured using a Shimadzu UV-3101PC spectrophotometer

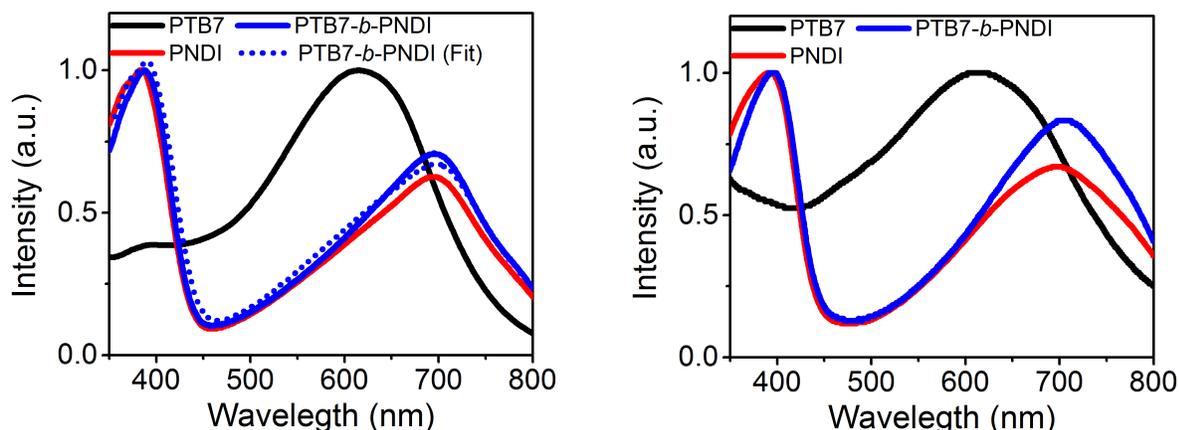


Figure S4. (Left) UV-Vis absorption of PTB7, PNDI and PTB7-*b*-PNDI in tetrahydrofuran and PTB7-*b*-PNDI fit. (Right) Thin film UV-Vis absorption of PTB7, PNDI and PTB7-*b*-PNDI casted from chlorobenzene (Concentration = 10 mg/mL)

Determining PTB7-*b*-PNDI composition: The block copolymer composition can be determined by ^1H NMR, SEC UV-Vis and steady state UV-Vis analysis.

Method 1, ^1H NMR: The block copolymer composition was estimated by integrating the peaks for PTB7 (8.1 ppm and 7.6 ppm) and for PNDI (8.4 – 9.0 ppm), see **ESI Figure S3**. The estimated composition by ^1H NMR is 9.7 wt% of PTB7 and 90.3 wt% of PNDI.

Method 2, size exclusion chromatography UV-Vis (SEC UV-Vis): Detailed procedure is reported by Smith et al.¹ Briefly, a solution of PTB7-*b*-PNDI was injected to a SEC coupled to a UV-Vis detector at 380 nm and 630 nm wavelength. SEC UV-Vis traces are shown in **Figure 1b**. The block copolymer composition was determined by integrating the 380 nm and 630 nm

traces and comparing to corresponding integrated areas for PRB7 and PNDI homopolymer. The estimated composition by SEC UV-Vis is 9.9 wt% of PTB7 and 90.1wt% of PNDI.

Method 3, steady state UV-Vis absorption: The block copolymer composition was determined by analyzing the steady-state UV-Vis absorption spectrum and comparing with the separate PTB7 and PNDI homopolymers. A linear combination of UV-Vis absorbance traces for PTB7 and PNDI homopolymer reproduces that for the block copolymer, giving an estimated composition of 9.5 wt% of PTB7 and 90.5 wt% of PNDI.

Time of flight secondary ion mass spectroscopy (TOF-SIMS): Bilayer films were prepared by spin-casting a 1:1 blend of PTB7:d-PCBM or PNDI:d-PCBM (dissolved in chlorobenzene after stirring for 24 hours at 70 °C) onto a 1 X 1 cm Si wafer. The second layer (either PTB7 or PNDI homopolymer) was spin cast (chlorobenzene) onto a 1 X 1 cm Si wafer coated with PEDOT:PSS.

The pure polymer film was then lifted off the wafer by submerging in DI water, and the film was subsequently carefully deposited on the first layer, resulting in a film of a pure polymer on top of a polymer:PCBM₆₁ blend. Bilayers were dried overnight under vacuum. Bilayers were annealed at 100 °C, 200 °C and 250 °C for 10 minutes prior measurement. PTB7, PNDI and d-PCBM depth profile was probed by tracking chemical fragments of CF⁻, C₂N⁻ and ²H⁻, respectively.

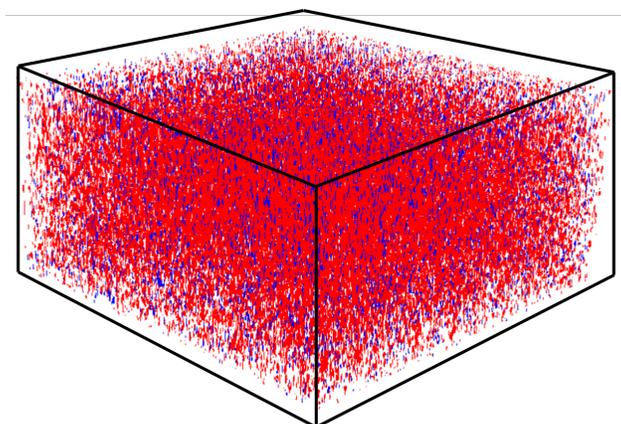


Figure S5. 3D reconstruction of TOF-SIMS depth profile of PTB7-*b*-PNDI thin film (dimensions: 200 μm x 200 μm x 140 nm . PTB7 (blue) was tracked by CF^- fragments and PNDI (red) was tracked by C_2N^- fragments.

Cyclic Voltammetry (CV): measurements were performed using a CH Electrochemical Analyzer by CH instruments. Samples were prepared by dissolving trace amounts of the polymers in 0.1 M tetrabutylammonium perchlorate (TBAP) in tetrahydrofuran solution. A solution of trace amounts of ferrocene in 0.1M TBAP in tetrahydrofuran was used as calibration.

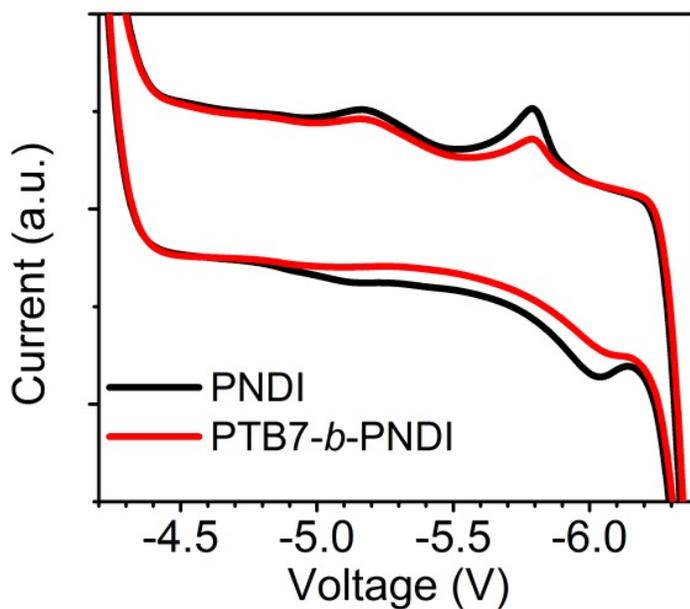


Figure S6. CV measurements on PTB7-*b*-PNDI and PNDI. Ferrocene/Ferrocenium (Fe/Fe⁺) was used for calibration.

Parallel bilayer OPV Fabrication and Testing.

A procedure as reported by Nakano et al. was employed to fabricate bilayer OPVs.² These devices were subsequently tested independently and in parallel for comparison with bulk-heterojunction devices. Briefly, ITO glass substrates and pre-cut glass slides (1 in x 1 in) were cleaned sequentially (15 minutes each step) in aqueous soap solution (0.5% Hellmanex III, Helma), deionized water, acetone, and isopropyl alcohol, and then dried in an oven at 100°C for

1 hour. The ITO glass substrate was then treated with UV-ozone for 15 minutes before coating with ZnO. The ZnO precursor solution was spin-coated onto the ITO glass at 2000 rpm for 60 s and thermally annealed at 200 °C on a hot plate in air for 1 h. After air-cooling to room temperature, the substrate was rinsed with acetone and isopropyl alcohol and subsequently dried in an oven at 100°C for 1 hour. The glass/ITO/ ZnO substrate was then transferred into a nitrogen-filled glove box for coating of layer of PCBM₆₁ or PNDI, at a concentration 10 mg/mL and 8 mg/ml in chlorobenzene, respectively. A separate clean glass slide then received 1 hour of UV-ozone treatment before coating with poly(sodium 4-styrenesulfonate) (PSS, 30 mg/mL in water). The PSS coated glass slides were transferred to a glovebox, where a layer of PTB7 (8 mg/mL in chlorobenzene) was spun cast.

Both ITO/ZnO/PCBM and glass/PSS/PTB7 substrates were transferred back out of the glovebox. The glass/PSS/PTB7 was placed on top of the ITO/ZnO/PCBM layer, and a few drops of water were added to the edge of the glass/PSS/PTB7. After few seconds, the water dissolved the PSS layer and the PTB7 thin film detached and transferred to the top of ITO/ZnO/PCBM. A similar procedure was applied to deposit PTB7 on top of ITO/ZnO/PNDI. Excess PSS was removed by rinsing substrate with DI waters. The ITO/ZnO/PCBM//PTB7 was then transferred to the glovebox, annealed at 100 °C for 5 minutes before a PEDOT:PSS in IPA solution was deposited. Finally, a 200 nm Ag anode layer was evaporated through a shadow mask using thermal vacuum deposition to give 10 pixels, each with an active area of 4 mm² (0.2 cm x 0.2 cm). The photovoltaic cells were tested under AM 1.5 G solar illumination at 100 mW cm⁻². ITO/ZnO/PCBM₆₁//PTB7/PEDOT:PSS/Ag and ITO/ZnO/PNDI//PTB7/PEDOT:PSS/Ag devices were tested separately and in parallel, and the device characteristics are reported in **ESI Table S2** and **Figure S6**.

Table S2. Device characteristics of PTB7//PCBM₆₁, PTB7//PNDI and PTB7//PCBM₆₁ + PTB7//PNDI in parallel

Device bilayer	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)
PTB7//PCBM	1.21	0.72	3.69	45.6
PTB7//PNDI	0.32	0.80	0.84	48.9
PTB7//PCBM + PTB7//PNDI (in parallel)	0.77	0.74	2.20	46.9

PCE: power conversion efficiency; J_{sc} : short circuit current; V_{OC} : the open-circuit voltage; FF: fill factor.

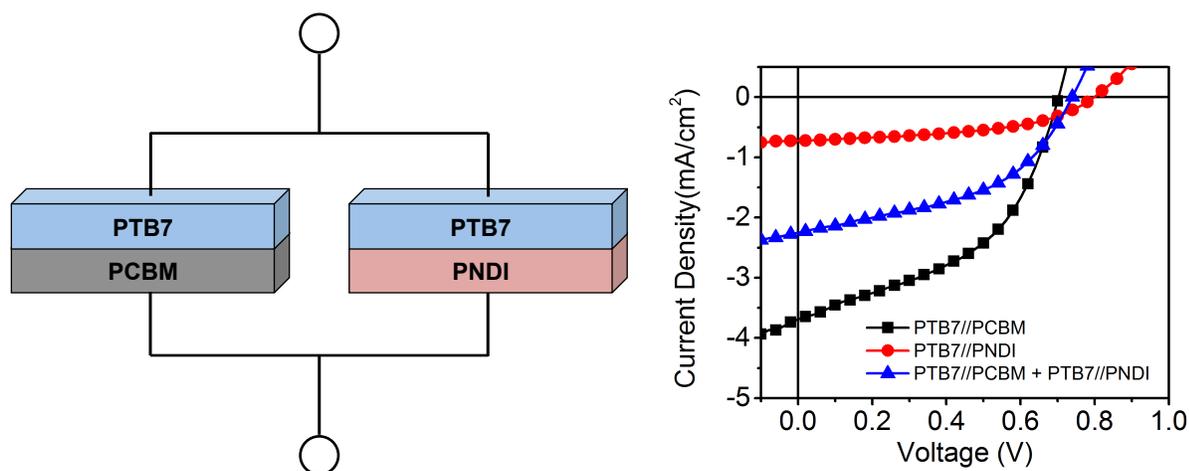


Figure S7. Schematic for parallel bilayer OPV device (left) and J - V curves for bilayer OPV devices illuminated at AM 1.5 and 100 mW cm⁻² (right).

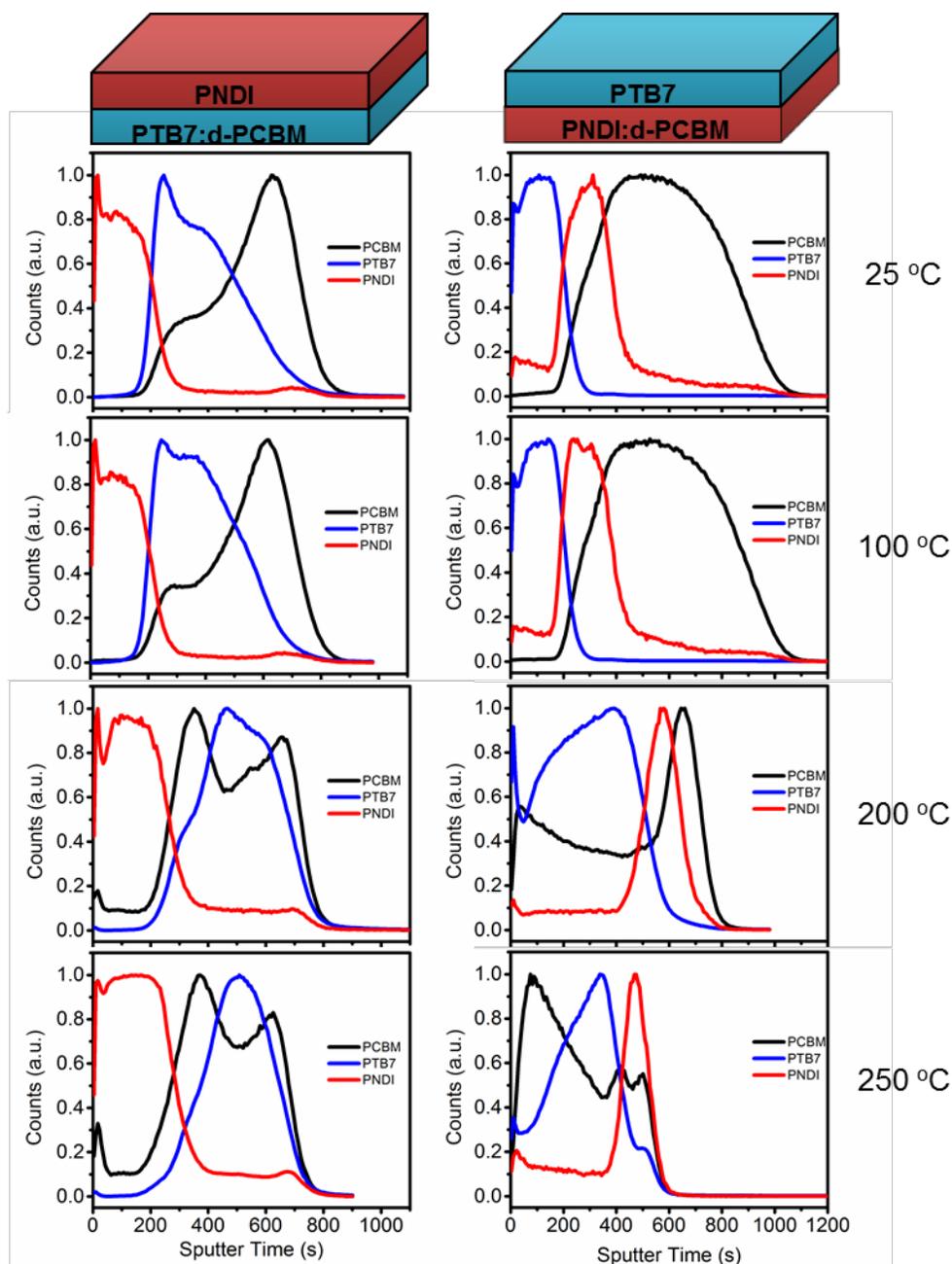


Figure S8. TOF-SIMS depth profiles of PTB7 (CF^-), PNDI (C_2N^-) and d-PCBM ($^2\text{H}^-$) for bilayers of (left) PNDI/PTB7:d-PCBM and (right) PTB7/PNDI:d-PCBM annealed at 100 °C, 200 °C and 250 °C for 10 minutes. Overall bilayer thickness was 140 nm, measured by profilometry. In all of these cases, the PCBM re-distributes during annealing but the PNDI and PTB7 remain segregated.

Transmission Electron Microscopy (TEM): PTB7/PCBM/Additive blends thin films were coated on top of PEDOT:PSS coated silicon substrates and processed under similar conditions of devices. Subsequently lifted in a pool of DI water and transferred to TEM grids and further dried under vacuum overnight. Samples were analyzed in a JEOL 1230 High Contrast Transmission Electron Microscope.

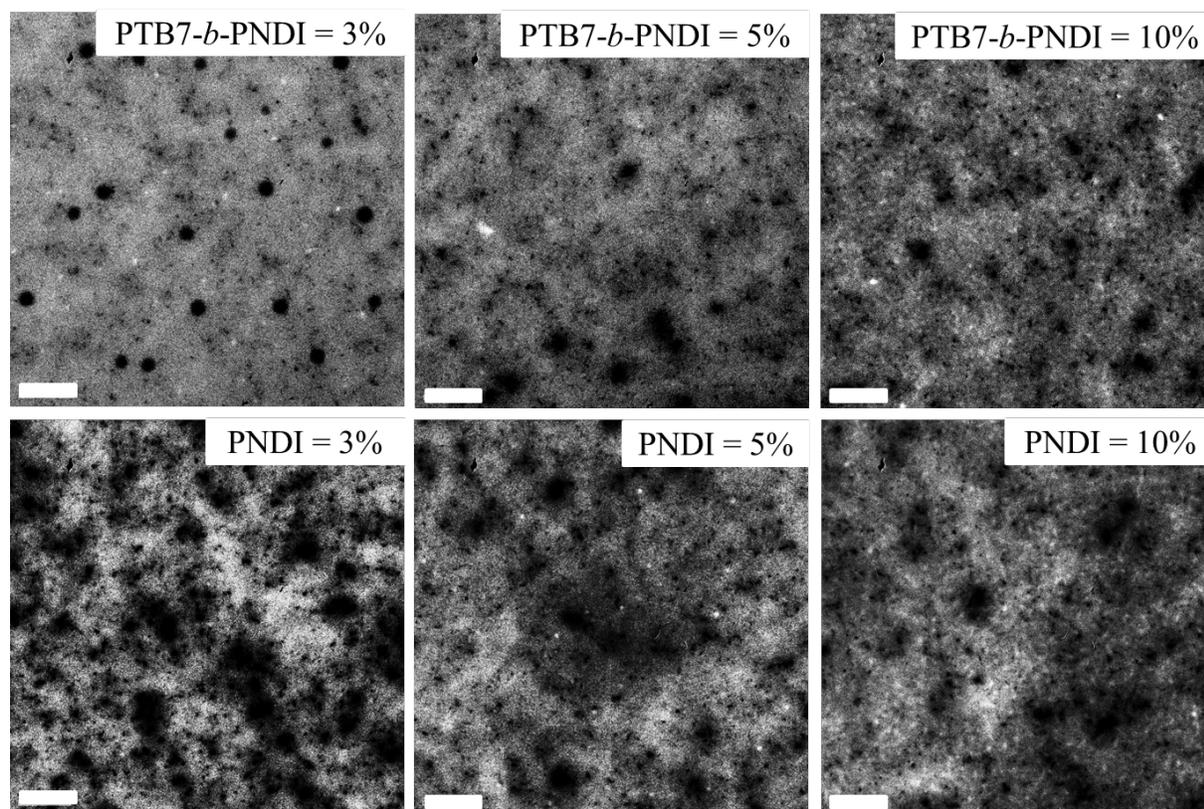


Figure S9. TEM images of PTB7/PCBM blends with PTB7-*b*-PNDI and PNDI as additive. Scale bar = 1 μm.

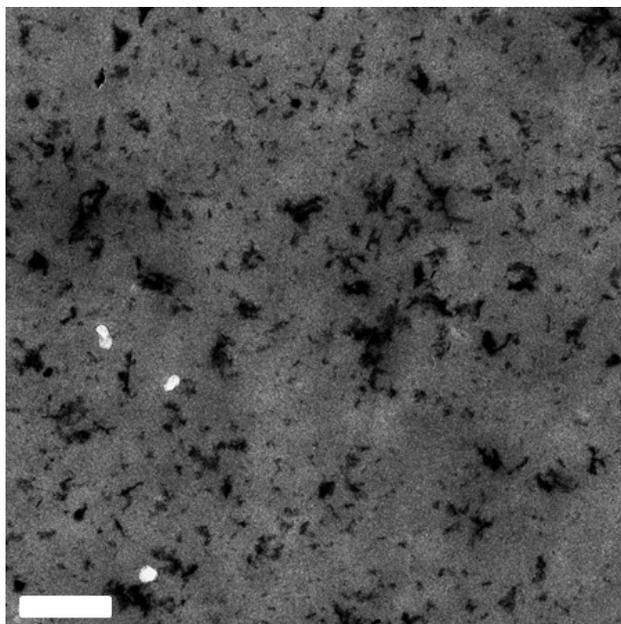


Figure S10. TEM image of pristine PTB7/PCBM₆₁ blend. Scale bar = 200 nm.

Grazing incidence wide-angle and small-angle X-ray scattering (GIWAXS and GISAXS):³

Grazing incidence small- and wide-angle X-ray scattering measurements were carried out on the 8-ID-E beamline at the Advanced Photon Source, Argonne National Laboratory, with photon energy 7.35 keV and wavelength $\lambda = 1.6868 \text{ \AA}$. The specimen-detector distance for GIWAXS measurements was 208 mm and the typical incident angle was 0.20° . Samples were prepared by spin coating blends of PTB7/PCBM/Additive on silicon substrates and treating them under similar conditions of devices.

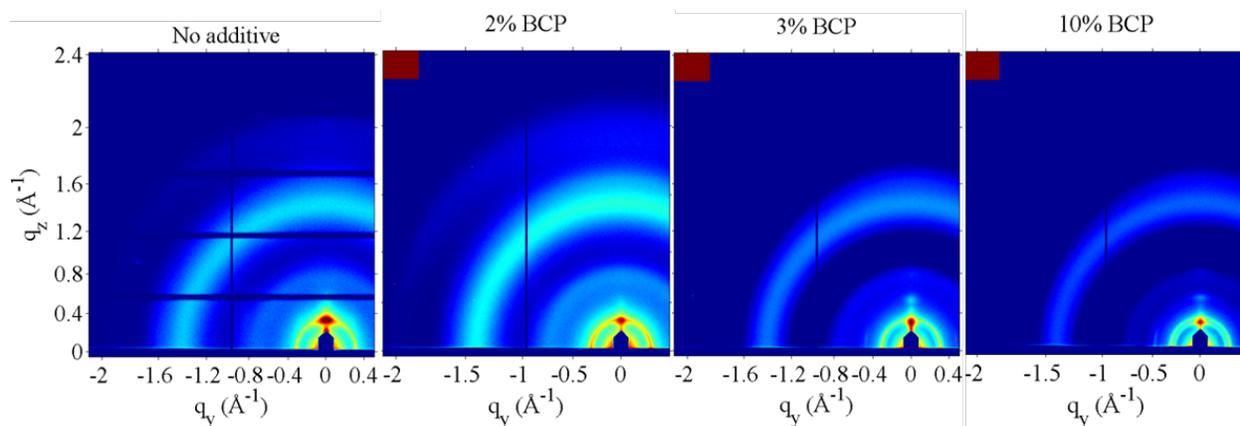


Figure S11. Grazing Incidence Wide Angle X-ray scattering profile of PTB7/PCBM + PTB7-*b*-PNDI blends

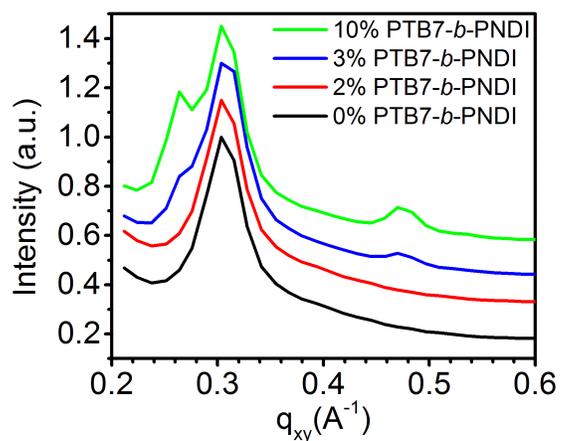


Figure S12. Linecuts of Grazing Incidence Wide Angle X-Ray scattering profile of PTB7/PCBM + PTB7-*b*-PNDI (BCP) blends. Zoom from 0.2 \AA^{-1} to 0.6 \AA^{-1}

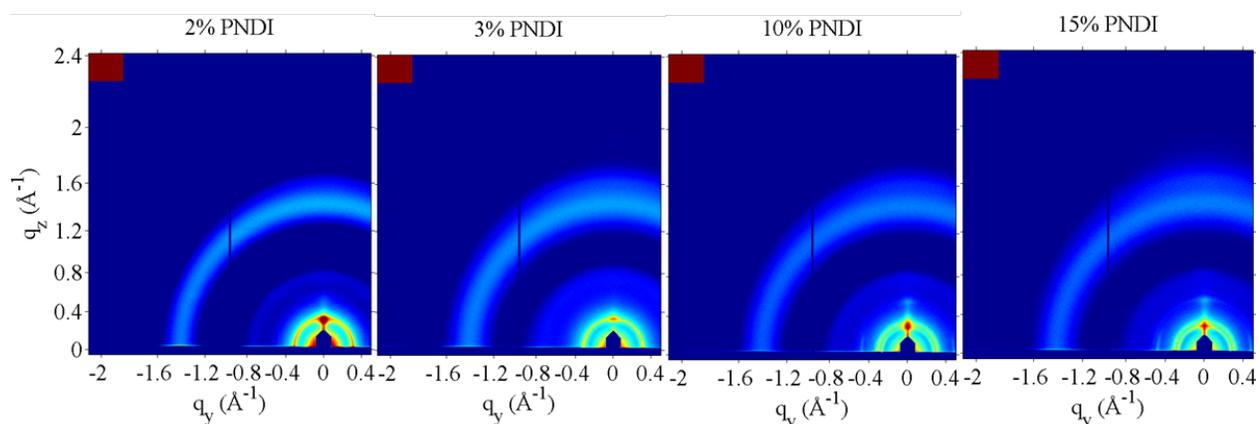


Figure S13. Grazing Incidence Wide Angle X-ray scattering profile of PTB7/PCBM + PNDI blends.

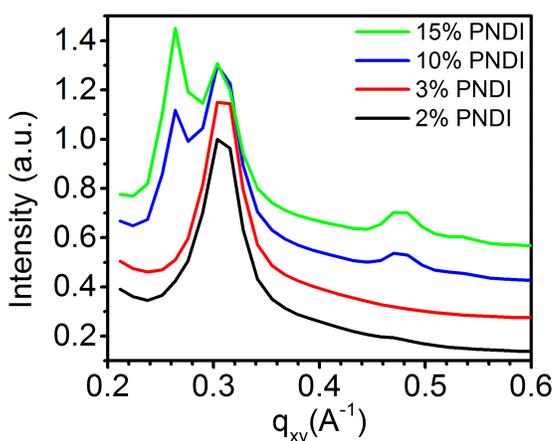


Figure S14 Linecuts of Grazing Incidence Wide Angle X-Ray scattering profile of PTB7/PCBM + PNDI blends. Zoom from 0.2 \AA^{-1} to 0.6 \AA^{-1}

REFERENCES

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3. Zhang Jiang, Xuefa Li, Joseph Strzalka, Michael Sprung, Tao Sun, Alec R. Sandy, Suresh Narayanan, Dong Ryeol Lee, Jin Wang, *J. Synchrotron Rad.* **19**, 627 (2012).