Supporting Information

Correlating High Power Conversion Efficiency of PTB7:$PC_{71}BM$ Inverted Organic Solar Cells to Nanoscale Structure

Sanjib Das,[a] Jong K. Keum,[*b,c] James F. Browning,[c] Gong Gu,[a] Bin Yang,[b] Ondrej Dyck,[d] Changwoo Do,[c] Wei Chen,[e,f] Jihua Chen,[b] Ilia N. Ivanov,[b] Kunlun Hong,[b] Adam J. Rondinone,[b] Pooran C. Joshi,[g] David B. Geohegan,[b] Gerd Duscher,[d] Kai Xiao[*b]

[a]Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN 37996, USA.
[b]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.
[c]Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.
[d]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA.
[e]Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA.
[f]Institute for Molecular Engineering, The University of Chicago, Chicago, IL 60637, USA.
[g]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

Experimental Section

Device Fabrication:

PTB7 and PFN were purchased from 1-Material, and $PC_{71}BM$ was purchased from Lumtec, and used as received. 1,8-diiodooctane was purchased from Sigma Aldrich. The casting solution was prepared by dissolving PTB7 and $PC_{71}BM$ (with 1:1.5 weight ratio and 25 mg ml^{-1} total concentration) in dichlorobenzene with or without 3% DIO additive, and heating at 70 °C for couple of hours under stirring. ITO substrates were first cleaned using detergent and subsequently by sonication in DI water, acetone, and isopropyl alcohol (IPA) followed by baking at 80 °C for one hour.For i-OSC fabrication, the PFN solution was prepared by dissolving PFN in methanol (2 mg ml^{-1}) in the presence of a small amount of acetic acid (2 µl

ml^{-1}), and the solution was spun-cast onto UV-treated ITO substrates at 2000 rpm. The PTB7:$PC_{71}BM$ active layers were then spun-cast on top of PFN-coated ITO at 1000 rpm for 90 s, followed by drying for 30 minutes in inert ambient. Finally, devices were completed by thermally depositing 8 nm-thick MoO_3 and 100 nm-thick Ag layers under a vacuum level of 5 × 10^{-6} mbar. For c-OSCs, PEDOT:PSSsolution was spun-cast onto UV-treated ITO substrates, followed by baking at 135 °C for 30 minutes. The active layer was spun-cast using same recipe as in i-OSCs, and devices were completed by thermally depositing 15 nm-thick Ca and 85 nm-thick Al layers. The device area of 23.7 mm^2 was calculated by a high-resolution optical microscope.

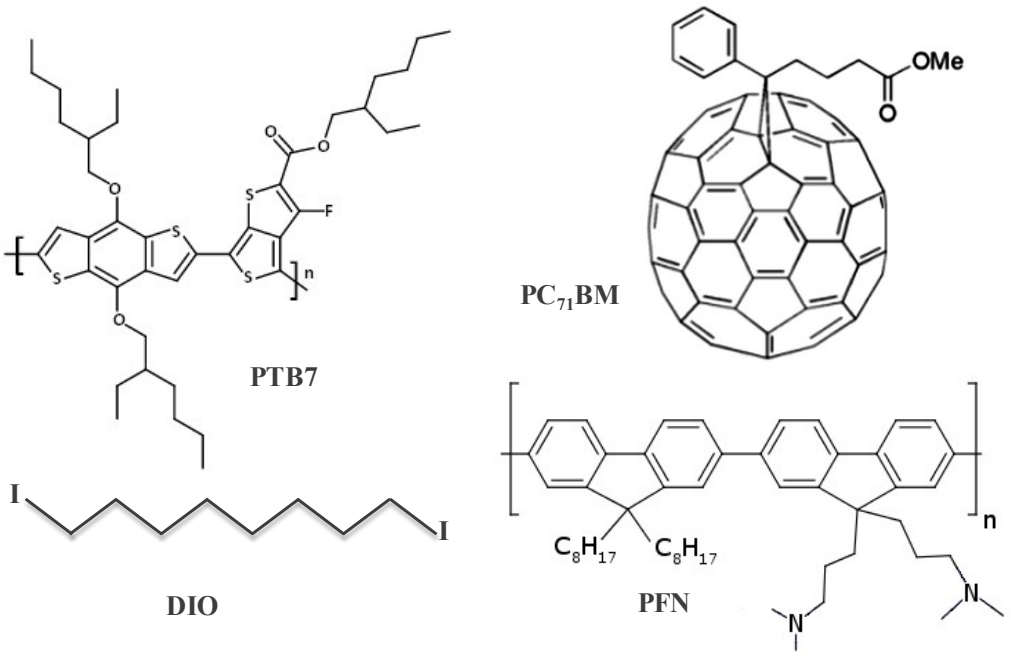
Device, Solution, and Thin Film Characterization:

The current density-voltage (*J-V*) curves of the fabricated solar cells were recorded using a source meter (Keithley 2400, USA) and a solar simulator (Radiant Source Technology, 300 W, Class A) under the AM 1.5G (100 mW cm^{-2}) conditions. The intensity of the solar simulator was calibrated by a NIST-certified Newport Si reference cell. The EQE spectra were measured in air using a Newport QE measurement kit under short circuit conditions.The reflective absorption spectra were recorded by measuring in diffuse mode with an integration sphere using a Varian Cary UV-Vis-NIR spectrophotometer. In this case, the incident light through the ITO electrode was reflected from the metal electrode back into the active layer for secondary absorption. Films for neutron reflectometry, cross-section transmission electron microscopy, and grazing-incidence wide-angle X-ray scattering were prepared on PFN-coated or bare Si-substrates. SANS measurements for the solutions were conducted at the EQ-SANS beamlinein the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). 10 mg ml^{-1} PTB7/DCBand PTB7/DCB:DIO, and 15 mg ml^{-1} $PC_{71}BM$/DCB and $PC_{71}BM$/DCB:DIO solutions were loaded into 1mm-thick quartz cells, and the scattered beams were collected at each SANS configuration. The raw 2D SANS data were corrected for detector response, dark current, and scattering from background, before being azimuthally

averaged to producethe 1D SANS profiles, i.e., $I(q)$ versus q profile. The datawere placed on an absolute scale (cm^{-1}) by the useof measured direct beam. In the SANS measurements, scattered neutrons were collected using a 2D position sensitive He detector with 1×1 m^2 active area, composed of tube detectors providing 256×192 pixels.

Neutron reflectometry (NR) data were collected on the Liquids Reflectometer at the SNS, ORNL using a neutron beam with a bandwidth of 3.5 Å (2.5 Å<λ<6.0 Å), where λ is the wavelength of incident neutron. The reduced data were in the format of absolute neutron reflectometry (R) vs. Out-of-plane neutron momentum transfer (q_z), where $q_z=(4\pi/\lambda)\sin\alpha_i$ with α_i being the incidence angle of neutron beam. In order to account for the instrumental smearing of NR data, the instrumental resolution provided at the beamline was convolved with the calculated NR curves. GIWAXS patterns were measured on the beamline 8ID-E at Advanced Photon Source (APS), Argonne National Laboratory (ANL). In the GIWAXS measurements, the used wave length of the X-ray beam was 1.6868 Å, and the grazing incidence angle was 0.2°.

Samples for cross-section TEM measurements were prepared by a focused ion beam (FIB) milling in a Zeiss Auriga dual beam SEM FIB. TEM imaging was performed using a Zeiss Libra 200 MC operated at 200 kV. For EF-TEM imaging, an energy slit width of 8 eV was used, centered at 19 and 30 eV, to generate contrast between the PTB7 and $PC_{71}BM$. The contrast in the images was adjusted to maximize the intensity variations within the PTB7:$PC_{71}BM$ layer. The two complementary images were artificially colored blue and yellow, and superimposed to clearly show the morphological structure within the bulk-heterojunction.



Scheme S1. Chemical structures of PTB7,$PC_{71}BM$, PFN, and DIO.

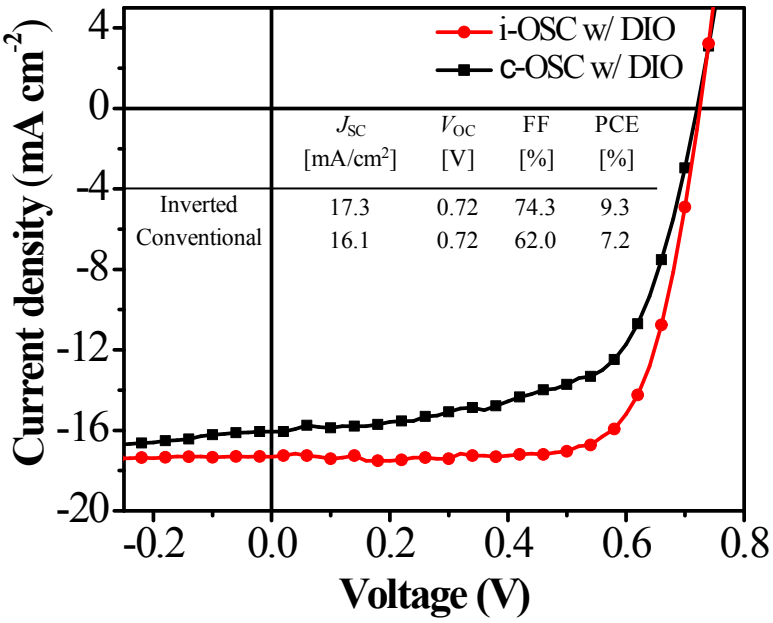


Figure S1. *J-V* curves for the champion i-OSC and c-OSC, measured under AM 1.5G (100 mW cm^{-2}) illumination.

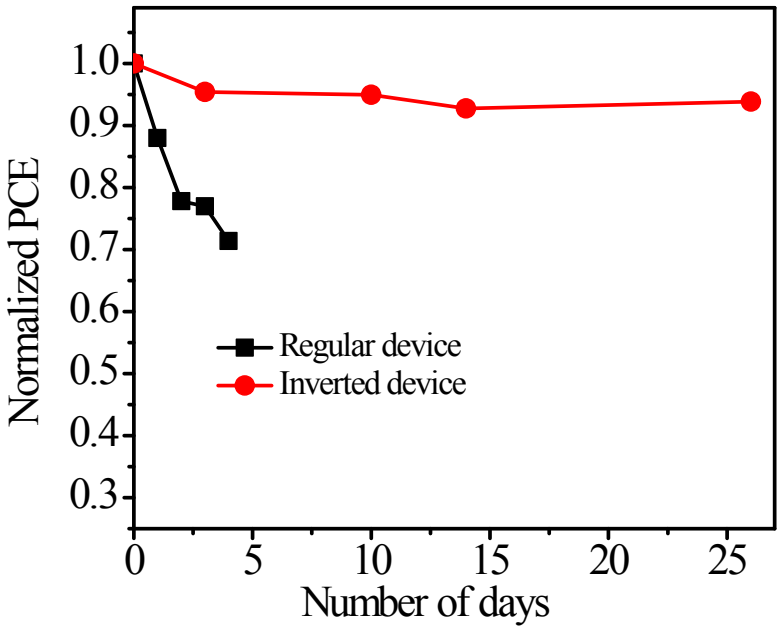


Figure S2. Stability comparison of c-OSCs and i-OSCs stored in air without encapsulation- the normalized PCE as a function of time.

The volume fraction of $PC_{71}BM$, V_{PC71BM} of i^{th} layer in PTB7:$PC_{71}BM$ layer is defined as,

$$V_{PC71BM} = (\rho_i - \rho_{PTB7})/(\rho_{PC71BM} - \rho_{PTB7}) \quad \text{(S1)}$$

where, $V_{PC71BM,i}$ is equal to 1-$V_{PTB7,i}$ (volume fraction of PTB7 in i^{th} layer) and varies from 0 to 1 depending on the composition of components. ρ_i is the SLD of i^{th} layer in film, and $\rho_{PTB7}$and $\rho_{PC71BM}$are the SLDs of pristine PTB7 and $PC_{71}BM$, respectively. The SLDs of PTB7 and $PC_{71}BM$ are obtained by fitting the NR curves for the pristine PTB7 and $PC_{71}BM$ films, which are 1.26×10^{-6} Å^{-2} and 4.34×10^{-6} Å^{-2}, respectively, as shown in Figure S3 and S4. Similarly, V_{PC71BM} in PFN layer is calculated as,

$$V_{PC71BM} = (\rho_i - \rho_{PFN})/(\rho_{PC71BM} - \rho_{PFN}) \quad \text{(S2)}$$

where, ρ_{PFN} is the SLDs of pristine PFN, in which the SLD is obtained by fitting the NR curves for the pristine PFN film. In the case of PFN film two layers exist, where the layer

adjacent to the substrate is enriched by poly(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene) block and the air interfacial layer is enriched by poly(9,9–dioctylfluorene), which are0.83×10^{-6} Å^{-2} and 1.14×10^{-6} Å^{-2}, respectively, as seen in Figure 4b.

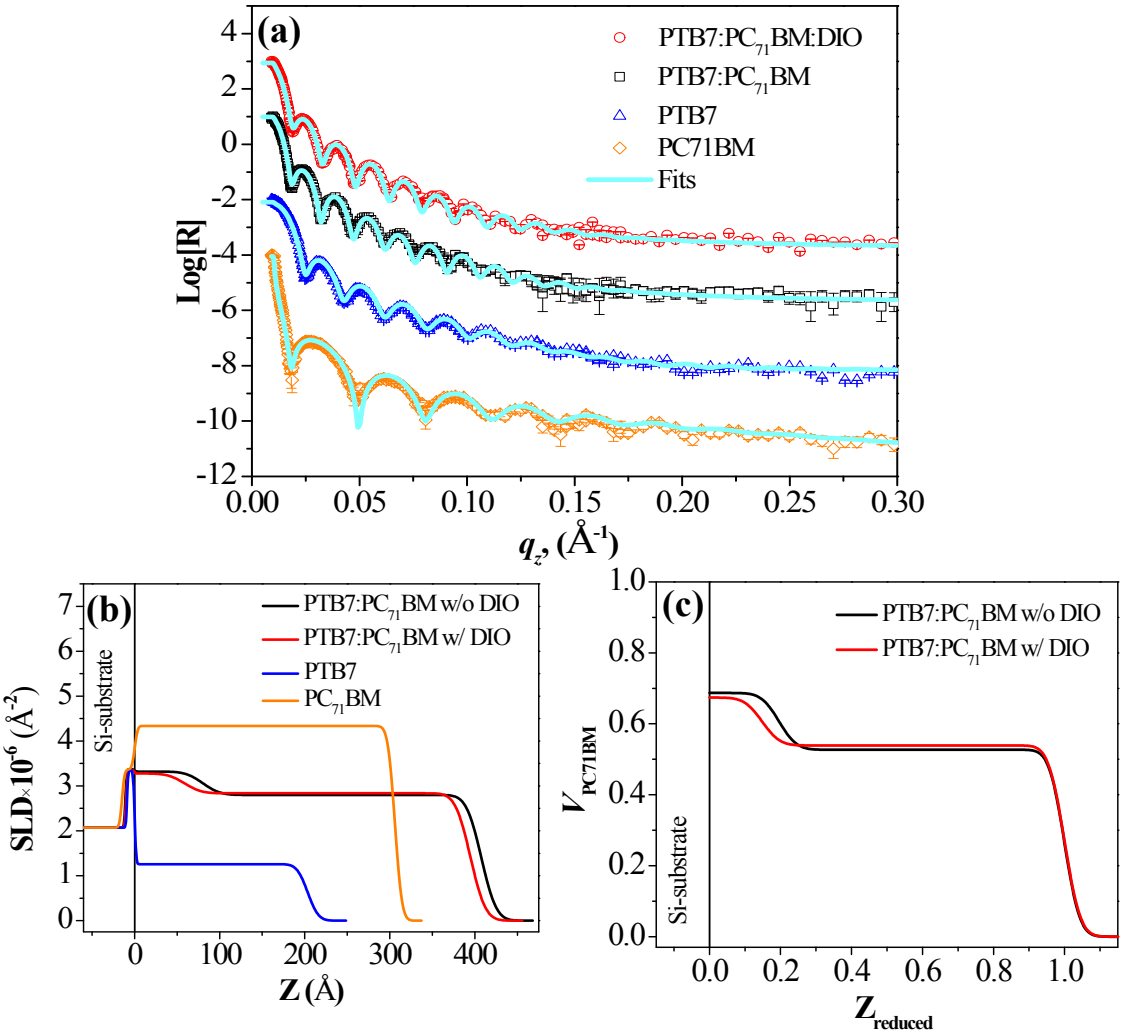


Figure S3. (a) Experimental and fit neutron reflectivity curves for PTB7:$PC_{71}BM$ films with and without DIO, pristine PTB7, and $PC_{71}BM$ films spun-cast onto Si-substrates. (b) Neutron SLD distributions obtained from the model-fit in (a). (c) Volume fraction of $PC_{71}BM$ vs. reduced distance from the substrate, $Z_{reduced}$ profiles calculated from the SLD profiles shown in (b).

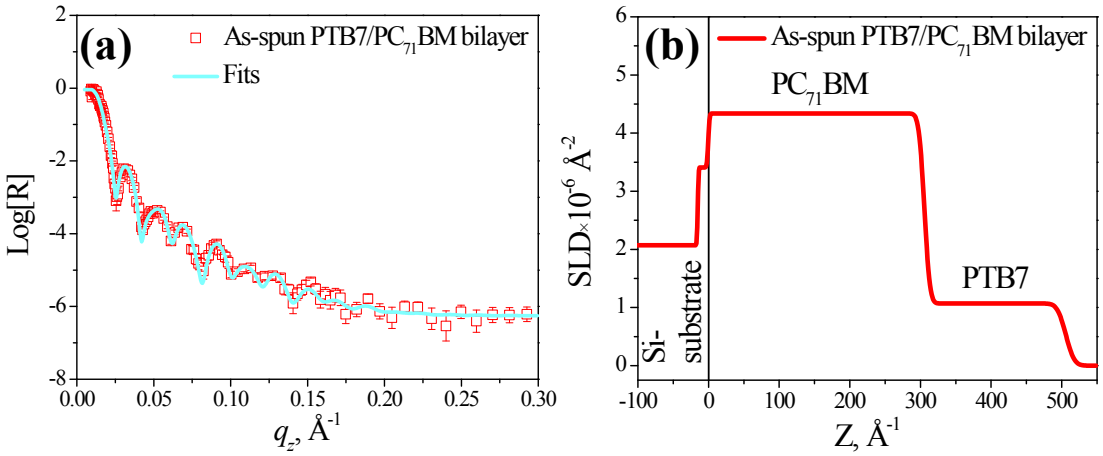


Figure S4. (a) Experimental and fit neutron reflectivity curves for PTB7:$PC_{71}BM$ bilayer film. (b) SLD distribution obtained from the model-fit in (a).