Electronic Supplementary Material (ESI) for Materials Horizons.

Simultaneous Spin-Coating and Solvent Annealing: Manipulating the Active Layer Morphology to a Power Conversion Efficiency of 9.6% in Polymer Solar Cells

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Experiment Details:

Fabrication of the Polymer Solar Cells. Electron donor material PTB7 (batch # SX6-037P, Mw=138K, PDI=2.99) and electron acceptor $PC_{71}BM$ were purchased from 1-material Inc. (St-Laurent, Quebec, Canada) and Aldrich, respectively, and used as received. The inverted device structure was ITO/PFN/PTB7:$PC_{71}BM$ (1:1.5 by weight)/MoO_3/ Ag. The PFN interlayer material was dissolved in methanol under the presence of small amount of acetic acid (2 µl/ml) and its solution (with a concentration of 2 mg/ml) was spin coated on the top of the pre-cleaned ITO substrate, which is treated by oxygen plasma cleaning for 4 min. The conventional PTB7:$PC_{71}BM$ active blend layer, with thickness around ~100 nm, was prepared by spin-coating the mixed solvent of 1,2-dichlorobenzene/1,8-diiodoctane (97%:3% by volume) solution (with a concentration of 25 mg/ml) at 1000 rpm. Novel spin coating was performance in a closed chamber and coated at 800-1000 rpm for 1 minute, which was then remained in this environment for a few minutes (~5 min). A 10 nm MoO_3 layer and a 100 nm Ag layer were subsequently was evaporated through a shadow mask to define the active area of the devices (2×8 mm^2) and form top anode.

Characterization and measurements. The PCE was determined from *J*–*V* curve measurement (using a Keithley 2400 source meter) under 1 sun, AM 1.5G (air mass 1.5 global) spectrum from a solar simulator (Oriel model 91192) (1000 W m^{-2}). Masks made from laser beam cutting technology with well-defined area size of 3.14, or 16.0 mm^2 are attached to define the effective area for accurate

measurement. All of the masked and unmasked tests give consistent results with relative errors within in 5%. Solar simulator illumination intensity was determined by a mono-crystal silicon reference cell (Hamamatsu S1133, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). Theoretical J_{SC} obtained by integrating the product of the EQE with the AM 1.5G solar spectrum perfectly agreed with the measured value to within 3%. The spectral mismatch factors (M) were calculated according to standard procedure, and M value of 1.03 were used to obtain correct photocurrent and efficiency for the PTB7 devices.

Small-angle Neutron Scattering(SANS) experiments were performed at the High Flux Isotope Reactor neutron scattering facility at Oak Ridge National Laboratories (ORNL) (CG-2 SANS). Deuterated1,2-dichlorobenzene was obtained from Sigma-Aldrich, which was used as the solvent to dissolve PTB7 polymer. A 10 mg/ml solution was prepared and stirred at 60 ^{o}C overnight before testing. A peltier device was used to control the temperature during the measurement. In experiment, three different sample-to-stage distance and neutron energies are used to cover the required q regions and standard data reduction were performed using SPICE SANS Reduction and KCL SAS Analysis Macros in Igor software package. NCNR Analysis Macros in Igor software package was used to fit the data.

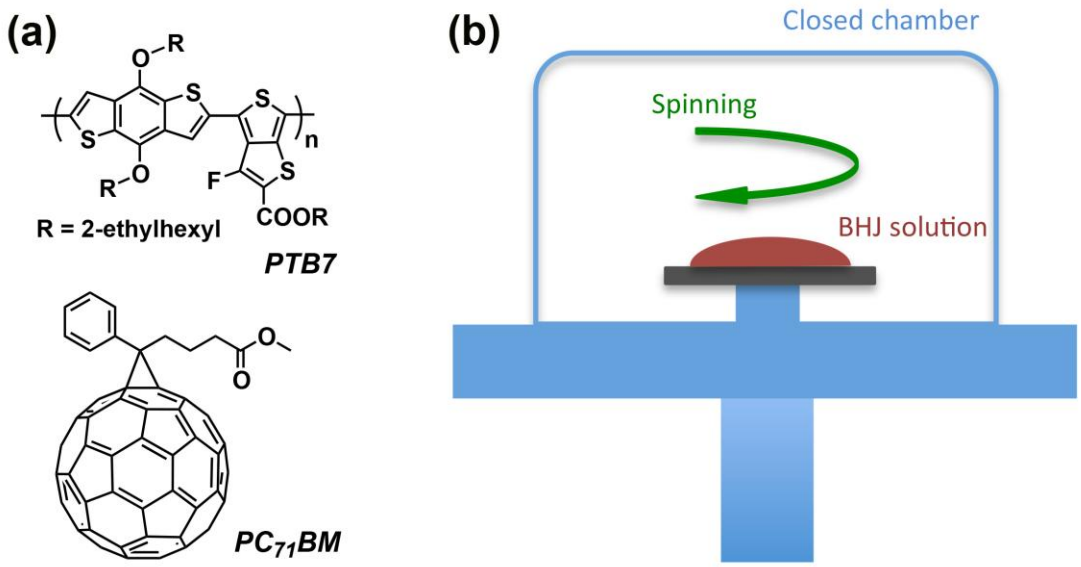
Near edge x-ray absorption fine structure (NEXAFS) measurements were performed on the wiggler beam line 10-1 at Stanford Synchrotron Radiation

Laboratory, using ~80% linearly polarized light and an energy resolution of ~ 60 meV at the carbon K-edge. A cylindrical mirror analyzer was used to monitor the Carbon KLL Auger electrons and a picoamp meter was used to detect the sample current. A highly transmissive gold grid (~85%) was used to normalize to the incoming flux. The resulting Auger Electron Yield (AEY) and Total Electron Yield (TEY) was furthermore normalized by subtracting a linear pre-edge background and scaling such that the edge jump far above the K-edge was constant, i.e. normalized to the number of C atoms. Monochromator drifts were calibrated by the structure in the monitored incoming photon flux around 284.7 eV.

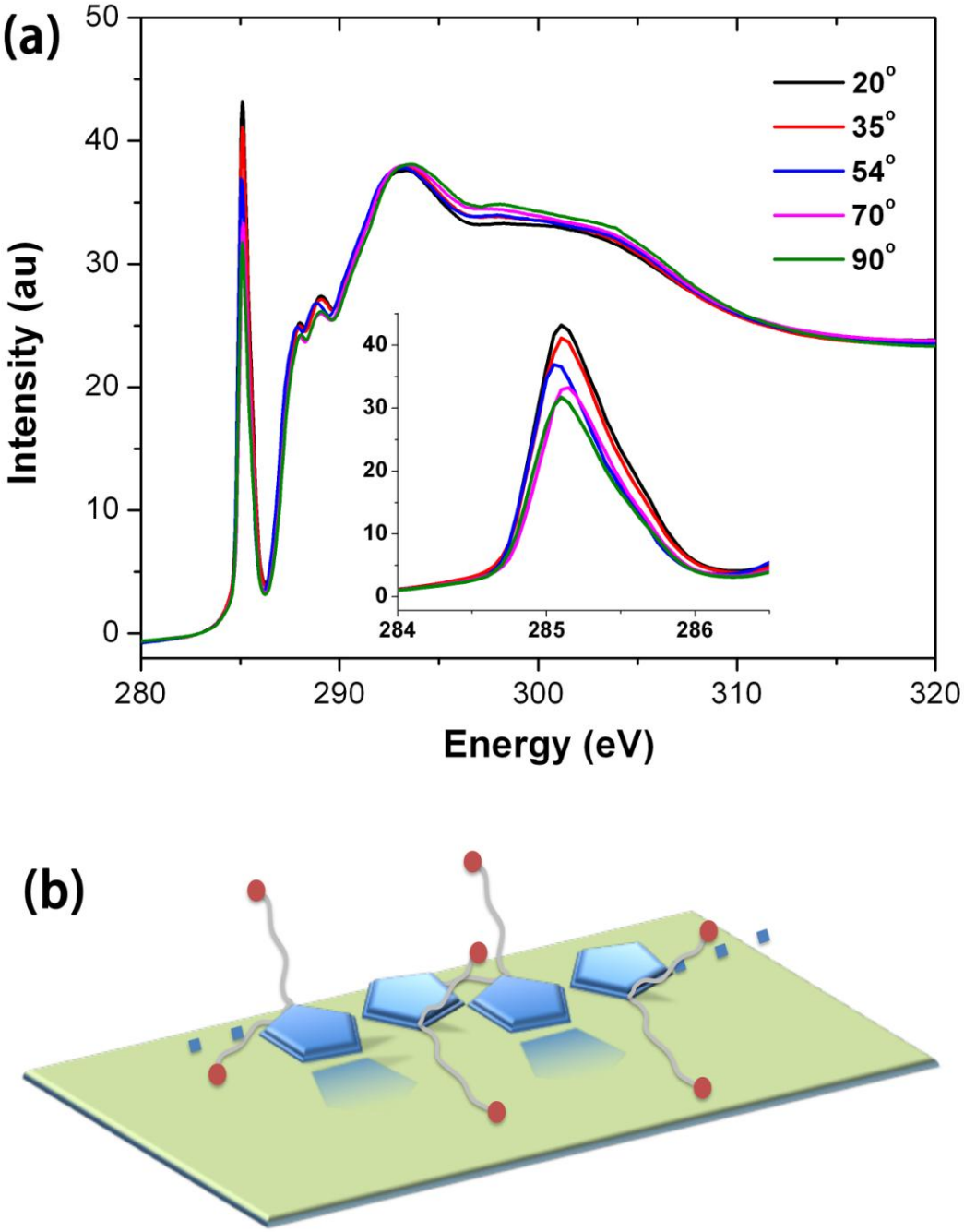
Grazing incidence x-ray diffraction (GIXD) measurements were performed on Beamline 7.3.3 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The experimental set-up and sample cell were designed for the surface studies on thin films. Thin film samples were coated onto silicon wafer substrate as used in device fabrication. In measurement, samples were loaded in helium chamber to suppress air scattering. An X-ray beam of 10 keV photon energy impinged onto the sample at a grazing angle above and below the critical angle of the polymer film but below the critical angle of the silicon substrate. Scattering data were recorded in Pilatus two-dimensional detector with pixel size of 0.172 mm^2. Same incidence angle and exposure time were used in measurement. Data were processed and line-cut profiles were generated using Nika package in Igor software package.

Resonant Soft x-ray scattering （**RSoXS)** were performed on Beamline 11.0.1.2 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. Beamline energies at around carbon k-edge (284.2 eV) were used in experiment. The scattering was done in transmission geometry, using silicon nitride widow as support for organic thin films. BHJ thin films were prepared in the same fashion as in device, onto silicon oxide wafers. Thin films were then floated using HF dilute solution and transferred onto silicon nitride window. Scattering experiment was done in high vacuum (~10^{-7}torr.) and a two-dimensional CCD detector was used to record signal. The data is reduced and analyzed using Nika package and home developed macros interfaces.

Transmission electron microscopy (TEM). Bright field TEM studies were conducted with a JEOL 2000 FX TEM operating at an accelerating voltage of 200 kV. Energy filtered TEM experiments were performed with an in-line Omega (energy) filter in a Zeiss Libra 120 at 120kV. An emission current as low as 3μA and minimal exposure times were used to minimize electron-beam-induced morphological changes, along with frequent sample film monitoring before and after energy filtered mapping. Thickness maps were obtained along with 0eV images and low eV plasmon maps by calculating the intensity ratio of filtered and unfiltered images, yielding t/λ values pixel by pixel. (The sample thickness t is in nanometer, and λ is the mean free path of electrons in the sample film.)



SchemeS1.(a)ChemicalstructureofPTB7and$PC_{71}BM$;(b) illustration of spin coating with solvent annealing.



FigureS2.(a)NEXAFS of PFN on ITO substrate; (b)scheme of chain orientation of PFN on ITO substrate.

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CNAS 检 测 L0260

TEST REPORT

No.: 2013DMWA00030

Product Name	Polymer solar cells
Model/type	Glass substrate
Customer	South China University of Technology

CPVT®
国家光伏质检中心

National Center of Supervision & Inspection on Solar Photovoltaic Products Quality

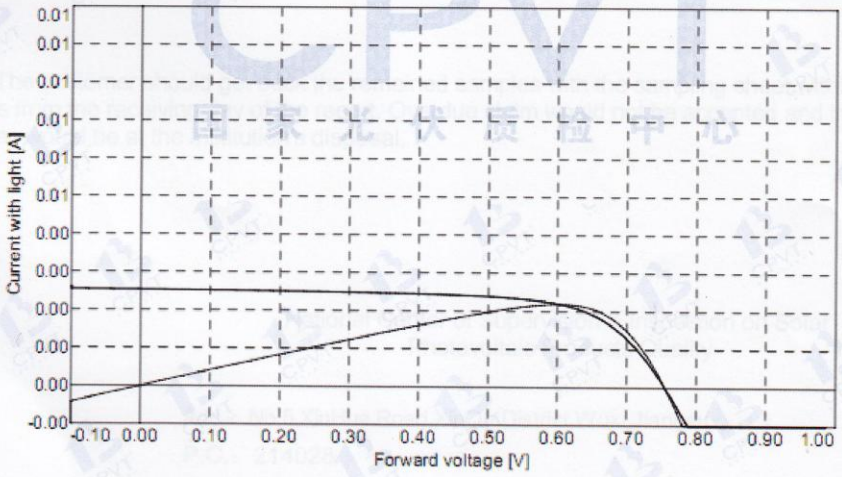
检验专用章 (1)

№：2013DMWA00030

Test Results

Clause	Test item(s)	Unit	Technical requirements	Results	Verdict (Pass/Fail)
1	Current-voltage characteristic measurement	---	At STC (module temperature: 25 ℃, irradiance: 1000W·m^{-2}, standard solar spectral irradiance distribution corresponds to IEC60904-3), measure the current-voltage characteristics of the cell with the variation of load	------	---
1.1	Open-circuit voltage, Voc	V	------	0.7553	---
1.2	Short-circuit current, Isc	A	------	0.002539	---
1.3	Maximun-power, Pmax	W	------	0.001323	---
1.4	Maximun-power voltage, Vmp	V	------	0.6034	---
1.5	Maximun-power current, Imp	A	------	0.002193	---
1.6	Fill factor, F.F. (%)	---	------	69.02	---
1.7	Conversion efficiency,η (%)	---	$\eta = \frac{P_{max}}{1000W/m^2 \times S} \times 100\%$	9.611	---

Current-voltage characteristic at STC



Remark： Sample area (S) is determined by sample surface outer range，S=13.77cm^2.

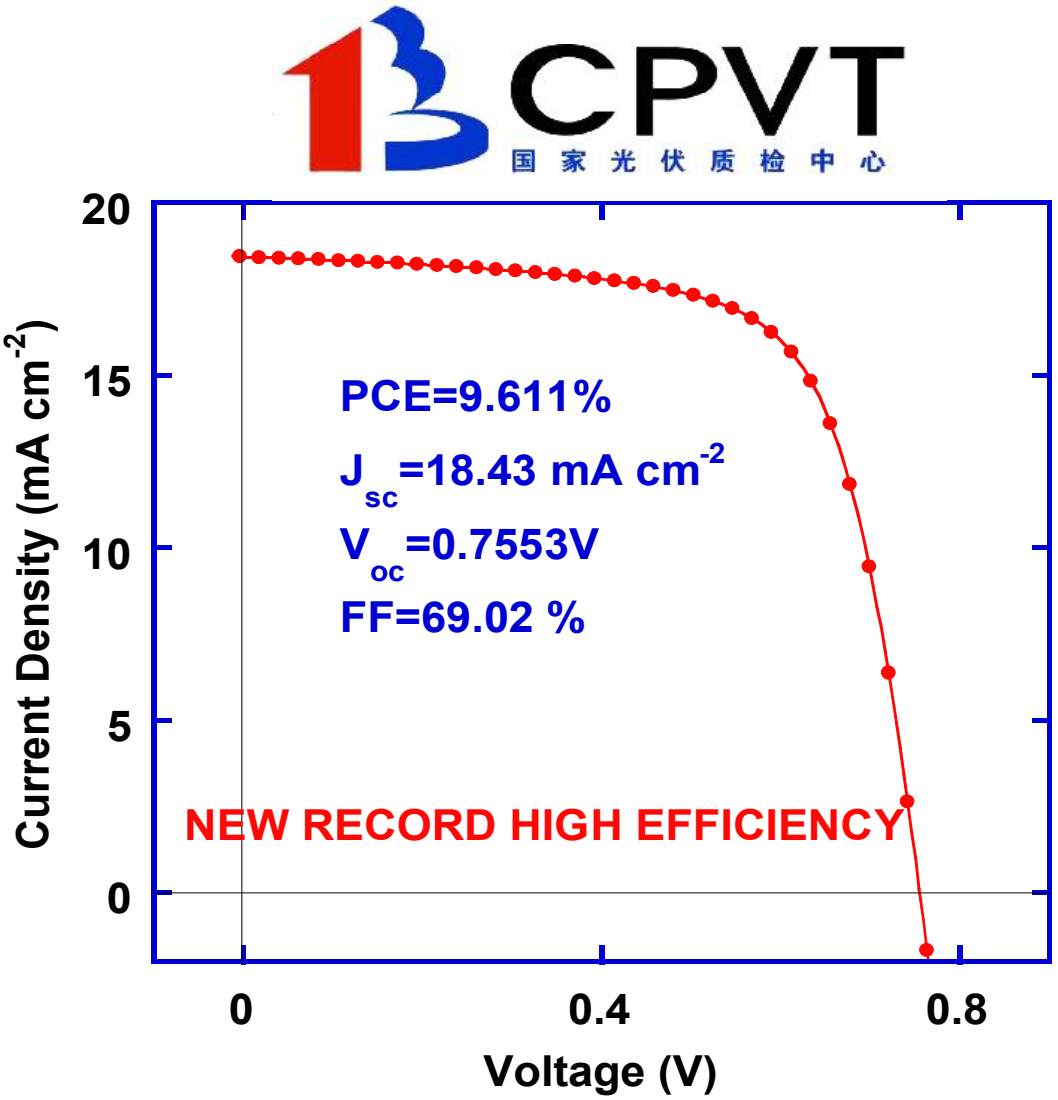
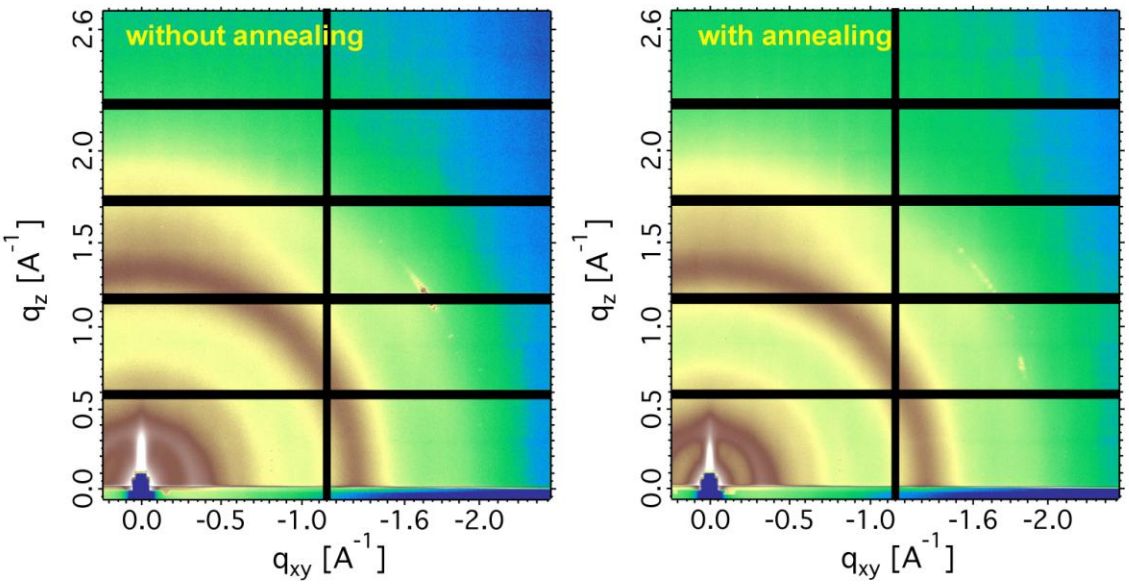
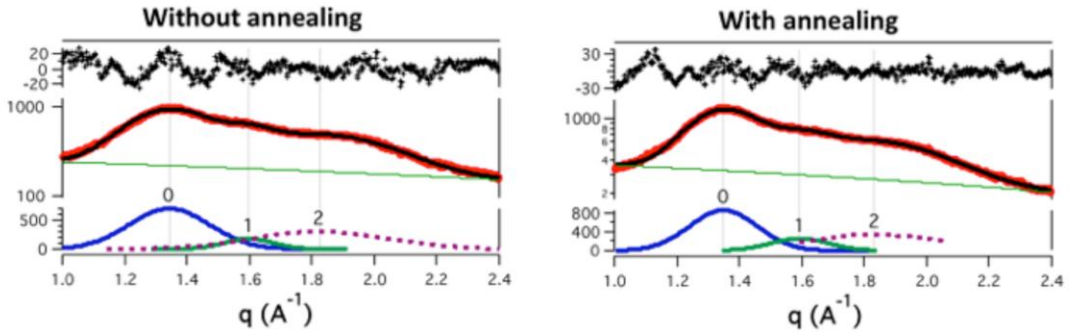


Figure S3. Certification of the polymer solar cells.





Peak 0 Type: Gauss

Location =	1.3437	+/-	0.00075966
Height =	688.33	+/-	2.978
Area =	219.49	+/-	1.5436
FWHM =	0.29956	+/-	0.0016511

Peak 1 Type: Gauss

Location =	1.5974	+/-	0.0017808
Height =	175.01	+/-	7.1057
Area =	33.958	+/-	2.2422
FWHM =	0.18229	+/-	0.0053359

Peak 2 Type: Gauss

Location =	1.8264	+/-	0.0045381
Height =	297.99	+/-	2.1291
Area =	157.94	+/-	3.3373
FWHM =	0.49793	+/-	0.007947

Peak 0 Type: Gauss

Location =	1.3497	+/-	0.0009219
Height =	847.99	+/-	3.9163
Area =	229.43	+/-	2.3079
FWHM =	0.25417	+/-	0.0018929

Peak 1 Type: Gauss

Location =	1.5929	+/-	0.0026236
Height =	249.7	+/-	15.11
Area =	58.768	+/-	5.4992
FWHM =	0.2211	+/-	0.0079537

Peak 2 Type: Gauss

Location =	1.831	+/-	0.0072154
Height =	339.56	+/-	5.0137
Area =	176.6	+/-	7.1176
FWHM =	0.48857	+/-	0.013096

Figure S4. GIXD scattering images and multi-peak fitting analysis.

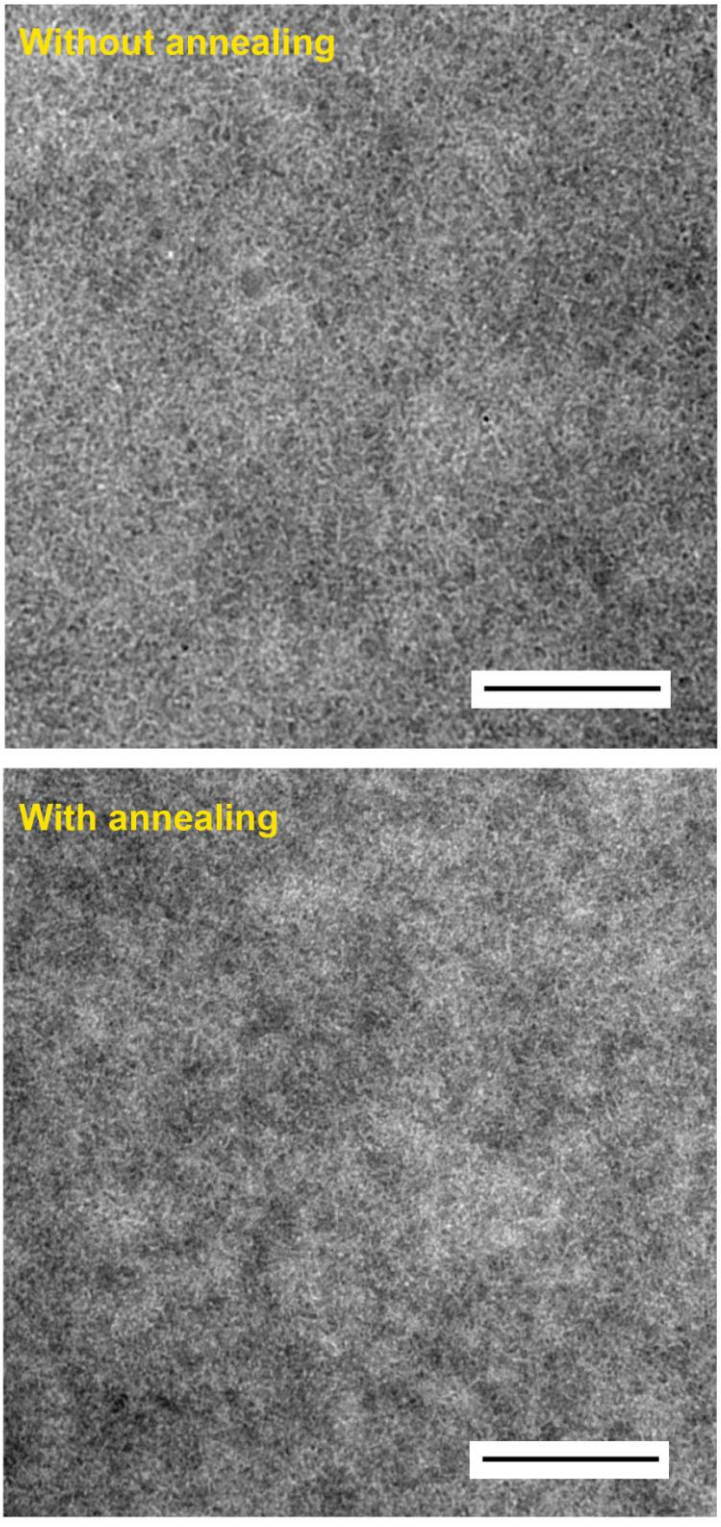


Figure S5. Bright field TEM (scale bar = 500nm).

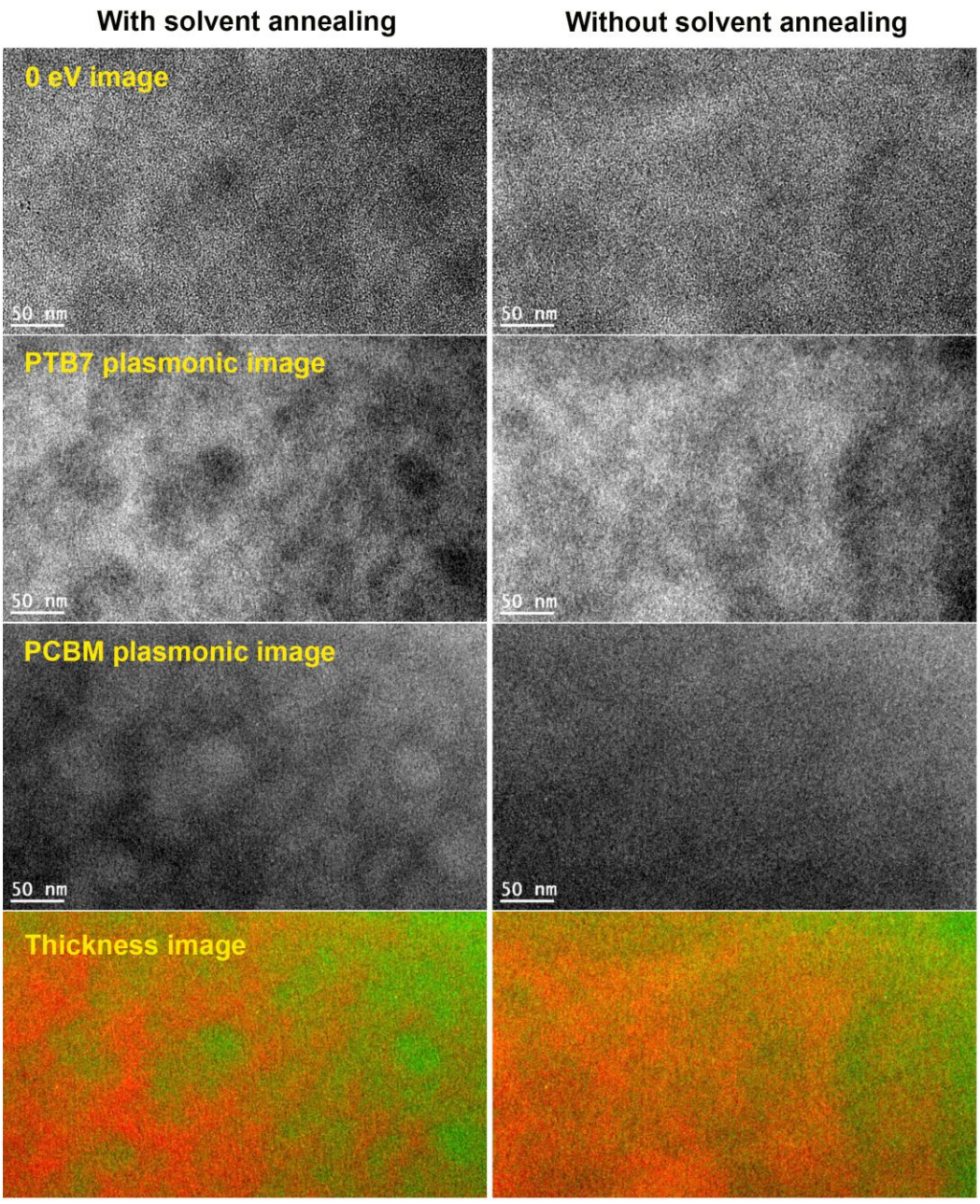


Figure S6. Energy filtered TEM images. The thickness map in color had the same size and scale bar with 19 eV and 30 eV TEM images.

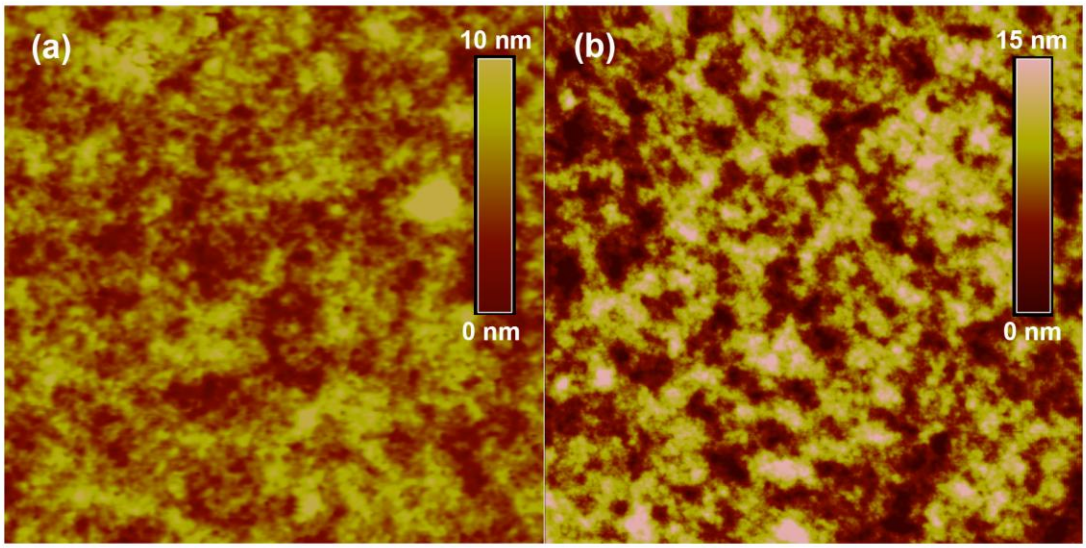


Figure S7. AFM characterization of BHJ thin films casted using conventional spin-coating (a) and spin-coating with solvent annealing (b).

Table S1 Device performance of a few devices with a separated chlorobenzene (CB) solvent annealing process after spin coating, as measured under 100 mW cm^{-2} AM 1.5G illumination.

	Voc[V]	Jsc[mA/cm^2]	FF[%]	PCE[%]
C15-A	0.724	17.9	69.4	8.97
C03-A	0.71	18.2	66.2	8.56
C33-A	**0.724**	**17.8**	**70**	**9.02**
C33-B	0.724	17.8	69.3	8.93
C06-A	0.724	17.7	69.2	8.92

Table S2. Device performance of series individual devices fabricated by the method reported in this study, as measured under 100 mW cm^{-2} AM 1.5G illumination.

ID	Voc[V]	Jsc[mA/cm^2]	FF[%]	PCE[%]
C09-A	0.735	18.0	72.7	9.54
C09-B	0.735	18.1	73.1	9.61
C09-C	0.740	17.9	73.2	9.59
C09-D	0.740	18.0	71.8	9.61
C10-A	**0.752**	**17.9**	**72.5**	**9.76**
C10-B	0.740	18.0	72.8	9.69
C10-C	0.730	18.1	72.4	9.56
C13-A	0.730	17.8	71.1	9.24
C13-B	0.730	17.8	71.3	9.26
C14-A	0.742	17.8	70.7	9.34
C14-B	0.740	17.8	70.0	9.25
C16-A	**0.730**	**18.2**	**73.3**	**9.74**
C16-B	0.740	17.6	73.4	9.6
C16-C	0.745	17.9	71.6	9.54
C16-D	0.735	17.9	71.3	9.38
C17-A	0.742	17.8	70.1	9.35
C17-B	0.742	17.8	69.9	9.27
C05-A	0.735	17.9	73.0	9.53
Average	0.738	17.9	71.9	9.49
STD	0.006	0.143	1.2	0.17