Electronic Supplementary Information

Blade-coated Highly Efficient Thick Active Layer of Non-fullerene Organic Solar Cells

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Experiment section

Device fabrication:

Organic solar cells were fabricated with a conventional device configuration of ITO/PEDOT:PSS/PM6:IT-4F/ZrAcac/Al. The patterned ITO substrates were cleaned by sonication in detergent water, deionized water, acetone and isopropanol for 20 min of each step. After UVO treatment for 20 min, an hole-transporting layer of PEDOT:PSS (Heraeus Clevios P VP AI 4083) was deposited by spin-coating at 5000 rpm for 30 s, followed by thermal annealing at 150 ^{o}C for 15 min in air. The active layer solution was prepared in chlorobenzene (with 0.25% DIO by volume) at a total concentration of 20 mg mL^{-1} with the D/A ratio of 1:1 by weight, accompanied by string on a hotplate at 50 ^{o}C over 8 h. After the solution cooling to room temperature, an active layer was deposited by blade-coating or spin-coating at ambient environment. The silicon wafer was used as the blade with UVO treatment for 20 min. The velocity was 20~50 mm s^{-1}, and the gap between blade and substrate was 100~600 μm. The film thickness was controlled by changing the gap and velocity. Moreover, the substrate temperature was changed (30 ^{o}C, 50 ^{o}C, 70 ^{o}C) by a controllable heating element. The blade-coating was performed after the dropping of ~10 μL solution at the beginning of the substrate area in air. And then, the residual solution on the back of substrate was erased by cotton swab with chloroform. For spin-coating, the solution was spin-coated on the PEDOT:PSS layer in the air with a various rotate speed to achieve different-thickness films. There are no any other processing treatments (such as thermal annealing or solvent annealing) for all the blade-coated active layer and spin-coated active layer. Then, a thin ZrAcac[1] layer (1.2 mg/mL in ethanol, 3000 rpm for 30 s, about 15 nm) was spin-coated on the active layer in the N_2-filled glovebox. Finally, a 100 nm Al was deposited as anode by vacuum evaporation under vacuum ($<1\times10^{-4}$ Pa). The device configuration of oragnic solar cells for the measurement of long term stability is ITO/ZnO/PM6:IT-4F/MoO_3/Al. ZnO precursor was prepared by dissolving zinc acetate in 2-Methoxyethanol with Ethanolamine. The ZnO layer was deposited by spin-coating a ZnO precursor solution at 4500 rpm for 1 min, followed by thermal annealing at 200 ^{o}C for 1h. The MoO_3 layer was 10 nm prepared by vacuum evaporation.

Characterizations:

The *J-V* characteristics were performed in N_2-filled glovebox under AM 1.5G (100 mW/cm^2) by using a Keithley 2400 source meter unit and an AAA solar simulator (SS-F5-3A, Enli

Technology CO., Ltd.) calibrated by a standard Si photovoltaic cell with a KG5 filter. The *J-V* measurement was made at the sweep speed of 0.02 V s^{-1} and scan direction of -0.5 V to 1.0 V under the room temperature (about 25 ^{o}C). For the device of 4 mm^2 effective area, the *J*-V characteristics was measured without aperture. For large-area device of 90 mm^2 device area, the *J-V* measurement was made with an aperture (or mask) of 56 mm^2. The EQE was measured by a solar cell spectral response measurement system (QE-R3018, Enli Technology CO., Ltd.) with the calibrated light intensity by a standard single-crystal Si photovoltaic cell. The film thickness was measured by a surface profilometer (Dektak XT, Bruker). The UV–Vis absorption spectrum was measured by a Shimadzu UV-3600 Plus Spectrophotometer. TEM characterization was performed by a FEI Talos F200c transmission electron microscope at 200 kV with the film thickness of about 60 nm.

Grazing incidence wide-angle x-ray scattering (GIWAXS) characterization: GIWAXS[2] measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11-0.15°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2 M photon counting detector.

Resonant Soft X-ray Scattering (RSoXS): RSoXS[3, 4] transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source. Samples for RSoXS measurements were prepared on a PEDOT:PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm×1.5 mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm×5 mm, 200 μm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

Hole and electron mobility measurements: The mobilities were measured by using space charge limited current (SCLC) model[5, 6] with the hole-only device of ITO/PEDOT:PSS/PM6:IT-4F/MoO_3/Al and electron-only device of ITO/ZnO/PM6:IT-4F/ZrAcac/Al. Hole mobility and electron mobility were obtained by fitting the current density-voltage curves and calculated by the equation:

$$J=9\varepsilon_0\varepsilon_r\mu(V_{appl}-V_{bi}-V_s)^2/8L^3$$

Where J is current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to 3), μ is hole mobility or electron mobility, V_{appl} is applied voltage, V_{bi} is the buit-in voltage (0 V), V_s is the voltage drop from the substrate's series resistance (V_s=IR) and L is the thickness of film.

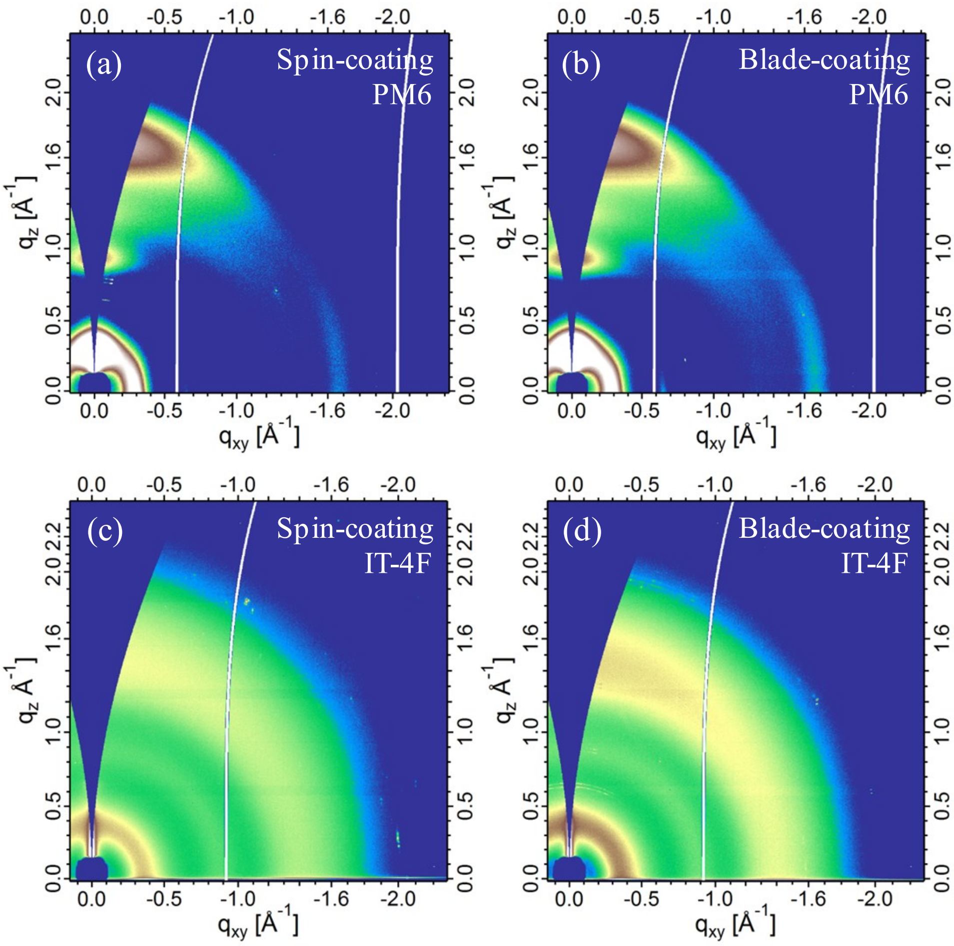

Fig. S1. 2D GIWAXS scattering patterns of PM6 and IT-4F films prepared by spin-coating and blade-coating.

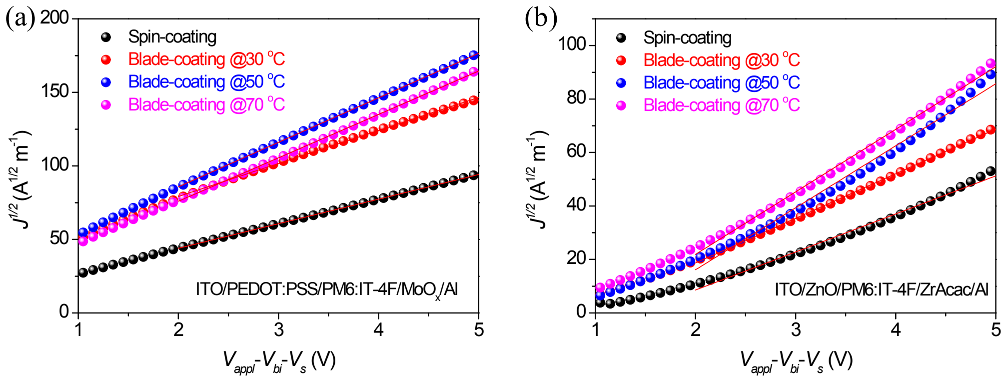

Fig. S2. $J^{1/2}$-V characteristics of (a) hole-only and (b) electron-only devices based on the PM6:IT-4F blends. The lines present linear fitting results.

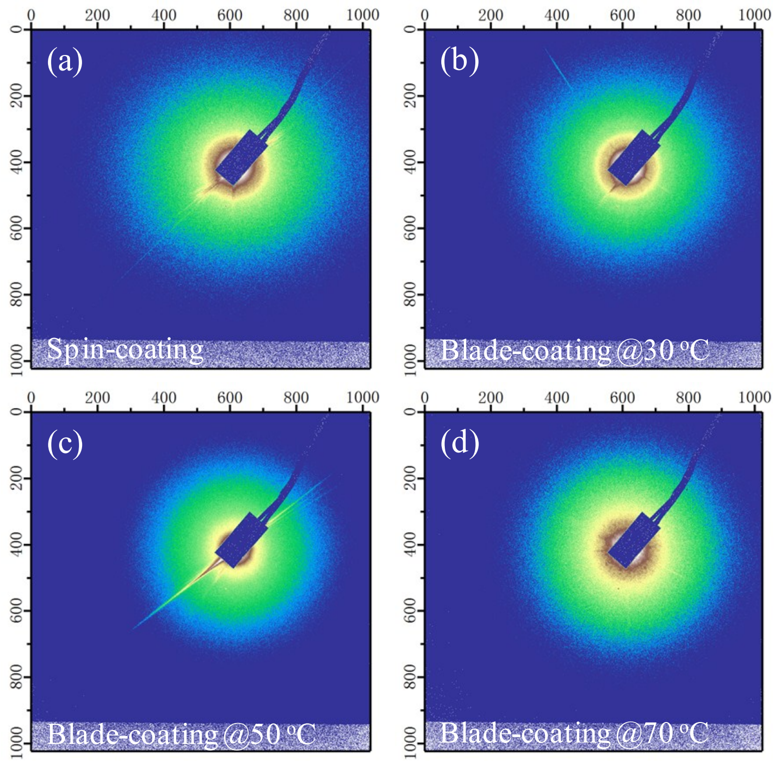

Fig. S3. 2D RSoXS patterns at the X-ray energy of 284.8 eV for the PM6:IT-4F films of spin-coating (a), blade-coating @30 °C (b), blade-coating @50 °C (c) and blade-coating @70 °C (d).

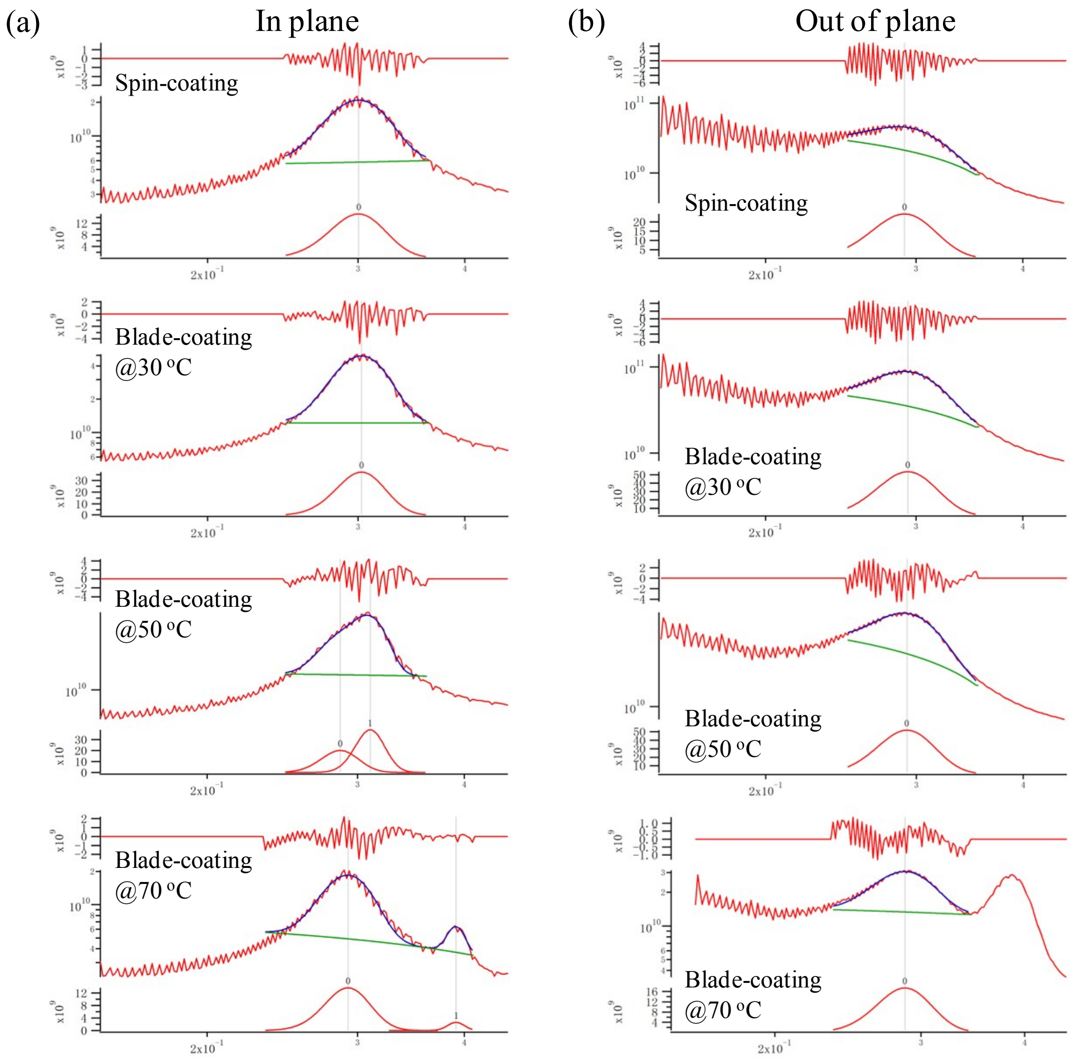

Fig. S4. The fitting results of in plane GIWAXS profiles (a) and out of plane GIWAXS profiles (b) for the PM6:IT-4F films

Table S1. The summarized fitting results of GIWAXS data.

	PM6 (100) in plane		PM6 (100) out of plane		IT-4F (001) in plane		IT-4F (100) in plane	
	q (Å^{-1})	FWHM (Å^{-1})	q (Å^{-1})	FWHM (Å^{-1})	q (Å^{-1})	FWHM (Å^{-1})	q (Å^{-1})	FWHM (Å^{-1})
Spin-coating	0.30	0.053	0.29	0.060	-	-	-	-
Blade-coating @30 ^{o}C	0.30	0.047	0.29	0.057	-	-	-	-
Blade-coating @50 ^{o}C	0.29	0.034	0.29	0.054	0.31	0.029	-	-
Blade-coating @70 ^{o}C	0.29	0.042	0.29	0.052	-	-	0.39	0.021

Table S2. Summarized photovoltaic parameters of PM6:IT-4F devices at different active layer thicknesses under illumination of AM 1.5G, 100 mW cm^{-2}. (The effective device area is 4 mm^2. Average values are obtained from 15 devices)

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	Thickness (nm)
Spin-coating	0.87±0.01	16.02±0.41	70.78±0.52	9.86±0.38 (10.24)	79
	0.88±0.01	18.99±0.52	70.47±0.81	11.78±0.43 (12.21)	103
	0.88±0.01	17.92±0.44	67.96±0.75	10.72±0.36 (11.08)	149
	0.87±0.01	17.68±0.39	64.64±0.70	9.94±0.30 (10.24)	186
	0.85±0.01	17.24±0.46	61.37±0.66	9.27±0.38 (9.65)	233
	0.85±0.01	16.72±0.37	51.35±0.83	7.30±0.28 (7.58)	330
	0.83±0.02	14.63±0.58	48.79±0.78	5.92±0.29 (6.21)	398
	0.83±0.02	12.68±0.55	44.25±0.69	4.52±0.44 (4.96)	480
Blade-coating @30 ^{o}C	0.87±0.01	18.54±0.44	68.01±0.68	10.97±0.33 (11.30)	96
	0.87±0.01	19.89±0.59	68.39±0.62	11.83±0.42 (12.25)	132
	0.87±0.01	18.78±0.41	67.69±0.77	11.06±0.29 (11.35)	178
	0.86±0.01	18.08±0.36	65.09±0.56	10.12±0.31 (10.43)	212
	0.85±0.01	17.62±0.40	61.46±0.58	9.20±0.31 (9.51)	266
	0.84±0.01	16.36±0.52	58.94±0.78	8.10±0.39 (8.49)	325
	0.83±0.02	15.65±0.62	50.54±0.70	6.56±0.37 (6.93)	415
	0.82±0.02	14.43±0.58	44.44±0.72	5.17±0.39 (5.56)	490
Blade-coating @50 ^{o}C	0.88±0.01	19.01±0.46	69.90±0.59	11.69±0.42 (12.11)	98
	0.88±0.01	20.76±0.61	72.00±0.55	13.15±0.49 (13.64)	134
	0.88±0.01	19.87±0.43	70.29±0.71	12.29±0.32 (12.61)	172
	0.87±0.01	19.73±0.32	69.26±0.65	11.89±0.29 (12.18)	216
	0.86±0.01	20.05±0.52	62.29±0.68	10.78±0.33 (11.11)	275
	0.85±0.01	19.60±0.50	58.71±0.51	9.73±0.39 (10.12)	343
	0.85±0.01	18.75±0.45	55.69±0.73	8.78±0.36 (9.14)	401
	0.84±0.02	16.20±0.55	49.42±0.77	6.78±0.41 (7.19)	515
Blade-coating @70 ^{o}C	0.86±0.02	20.26±0.51	68.22±0.60	11.88±0.45 (12.33)	102
	0.87±0.01	20.84±0.63	70.18±0.71	12.74±0.52 (13.24)	141
	0.86±0.01	20.75±0.53	68.00±0.57	12.13±0.38 (12.51)	190
	0.86±0.01	19.60±0.40	68.31±0.62	11.65±0.28 (11.93)	241
	0.86±0.01	19.69±0.47	66.76±0.68	11.30±0.34 (11.64)	270
	0.85±0.01	19.08±0.39	65.99±0.85	10.83±0.33 (11.16)	315
	0.83±0.02	19.40±0.56	58.98±0.77	9.86±0.36 (10.22)	409
	0.82±0.02	18.56±0.65	55.34±0.71	8.85±0.30 (9.15)	502

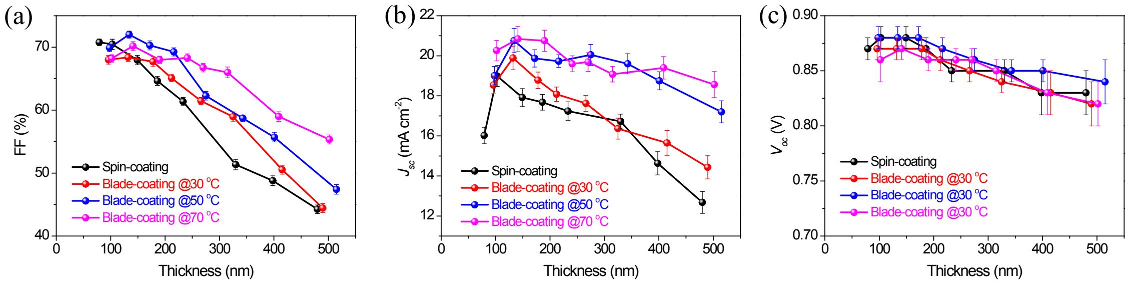

Fig. S5. (a) FF, (b) J_{sc} and (c) V_{oc} values versus the active layer thickness of PM6:IT-4F devices.

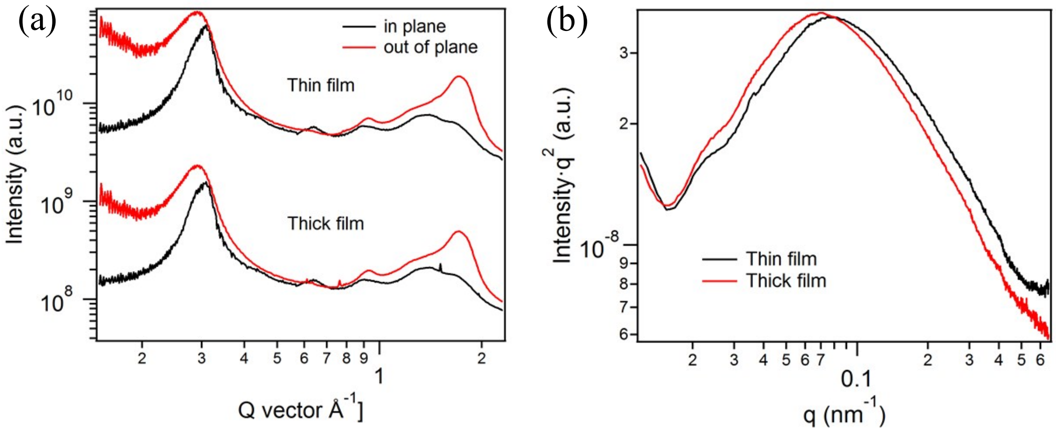

Fig. S6. (a) GIWAXS profiles and (b) RSoXS profiles of blade-coated thin film and thick film.

Table S3. Photovoltaic parameters of blade-coated @70 °C large-area devices with various thickness of active layer under illumination of AM 1.5G, 100 mW cm^{-2}. (The device area is 90 mm^2 and the aperture area is 56 mm^2. Average values are obtained from 15 devices)

Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%) (PCE$_{max}$)
135	0.83±0.01	19.28±0.61	67.56±0.85	10.77±0.62 (11.39)
160	0.83±0.01	19.33±0.63	66.73±0.82	10.56±0.55 (11.11)
171	0.83±0.01	19.44±0.56	66.61±0.77	10.41±0.66 (11.07)
188	0.83±0.01	19.35±0.53	65.99±0.90	10.32±0.61 (10.93)
252	0.83±0.01	18.80±0.32	63.45±0.75	9.70±0.58 (10.28)
306	0.83±0.01	19.69±0.51	57.59±0.71	9.24±0.52 (9.76)

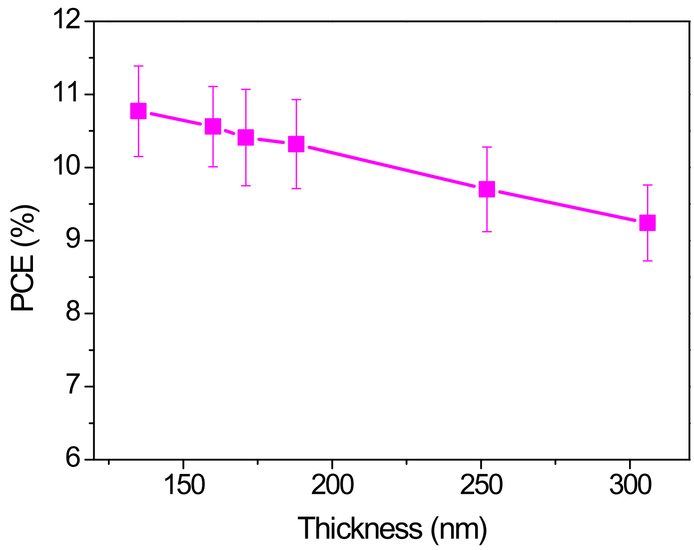

Fig. S7. PCE values versus the thickness of active layer for the blade-coated @70 °C large-area devices. The device area is 90 mm^2 and the aperture area is 56 mm^2.

References

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