Electronic Supplementary Information

Polyelectrolyte interlayers with a broad processing window for high efficiency inverted organic solar cells, towards mass production

Chen Wang,[a] Chang Li,[a] Roderick C. I. MacKenzie,[b] Shanpeng Wen,*[a] Yang Liu,[c] Pengfei Ma,[a] Ge Wang,[a] Wenjing Tian[c] and Shengping Ruan[a]

a) State Key Laboratory on Integrated Optoelectronics and College of Electronic Science & Engineering, Jilin University, Changchun 130012, P. R. China

b) Faculty of Engineering, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

c) State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China

Corresponding authors: sp_wen@jlu.edu.cn

Device fabrication and characterization

The basic device structure is ITO/ZnO/Active layers/MoO$_3$/Ag, and then we modified the ZnO surface by PEI and subsequent DMF washing. The patterned ITO glass substrates (15 ohm/square) were pre-cleaned by ultrasonic baths in detergent, deionized water, acetone and isopropyl alcohol sequentially. Sol-gel-derived ZnO films were prepared according to the reference[1] with modification: using zinc acetate in 2-methoxyethanol:2-aminoethanol as a precursor solution by spin-coating method onto the ITO substrate followed by thermal treatment at 150 °C for 60 min. The thickness of ZnO film is approximately 30 nm, determined by a profilometer. Then the substrates were immediately transferred into a nitrogen-filled glove box for subsequent film deposition. PEI was dissolved in 2-methoxyethanol to different weight concentration from 0.05 wt% to 1.6 wt%. The PEI solutions were spin coated on the ZnO surface at 5000 rpm for 60s and thermal annealed at

100°C for 10 min, resulting in different thickness of PEI layer. For the DMF washing based device, after PEI solution spin coating, 200 μL DMF at 70 °C was pipetted onto the PEI-coated substrate and spun off immediately, then the substrate was thermal annealed at 100°C for 10 min. The PDTS-DTffBT based photoactive layer was prepared by spin coating PDTS-DTffBT:PC$_{71}$BM (1:2 polymer concentration 10 mg mL^{-1}) blend solution, using chlorobenzene/1, 8-diiodooctane (97:3 v/v) as solvent, then thermal annealed at 120°C for 5 min.[2] The P3HT based photoactive blend layer was prepared by spin coating (1000 rpm) the 1,2-dichlorobenzene solution of P3HT and IC$_{60}$BA (1:1 w/w, polymer concentration of 20 mg mL^{-1}) on the modified ITO/ZnO electrode and thermal annealed at 150°C for 10 min, resulting 186 nm active layer thickness. The PTB7 and PTB7-Th based photoactive layers were prepared by spin coating corresponding blend solutions. PTB7 or PTB7-Th and PC$_{71}$BM were dissolved in chlorobenzene/1, 8-diiodooctane mixed solvent (97:3 v/v) with the D/A weight ratio of 1:1.5 and the polymer concentration of 10 mg mL^{-1}. The PDTS-DTffBT, PTB7 and PTB7-Th based active layers thicknesses were all around 90 ~ 100 nm, which was measured by the Veeco DEKTAK 150 surface profilometer. The devices were finally completed by thermal evaporation of a 6 nm thick molybdenum trioxide (MoO$_3$) and 90 nm thick silver (Ag) anode in vacuum (vacuum degree ≈ 5×10^{-4} Pa) with a shadow mask (device active area of about 0.064 cm^2). Solar cell performance was tested under Air Mass 1.5 Global (AM 1.5 G) solar illuminations with an Oriel 300 W solar simulator at an intensity of 100 mW/cm2. The light intensity was measured by a photometer (International light, IL1400) and corrected by a standard silicon solar cell. The EQE spectra were conducted using Q-Test Station 1000 AD (Crowntech Inc. USA) with a standard silicon photovoltaic cell traced to the American

National Standards Institute. The surface morphologies were characterized with atomic force microscopy (AFM, Veeco Dimension 3100). Ultraviolet photoemission spectroscopy (UPS) experiments were carried out using a VG Scienta R3000 spectrometer in an ultrahigh vacuum at a base pressure of 2×10^{-10} mbar. The measurement chamber was equipped with monochromatized He (Ia) radiation at 21.2 eV.

TPC, TPV and Photo-CELIV measurements

For TPC measurement, the samples were irradiated through the ITO side by one 10 ns 532 nm laser pulse (Continuum Minilete TM Nd:YAG) with the energy flux of 96.8 $\mu J/cm^2$, the photocurrent was recorded on an oscilloscope (Tektronix MSO 4054) by measuring the voltage drop over a 50 ohm sensing resistor in series with the solar cell. For TPV measurement, the solar cells were placed understand open circuit condition and monitored the change in open circuit voltage after the laser pulse. In photo-CELIV measurement, the devices were irradiated through the ITO side by one 10 ns 532 nm laser pulse with the energy flux of 96.8 $\mu J/cm^2$. After a variable t_{delay}, a linear extraction ramp was applied via a function generator. The ramp was 100 μs long and 2 V in amplitude. The active layer thicknesses for the devices used in the CELIV measurements were 95nm ± 3nm. These were measured with a Veeco DEKTAK 150 surface profilometer. The equation,[3]
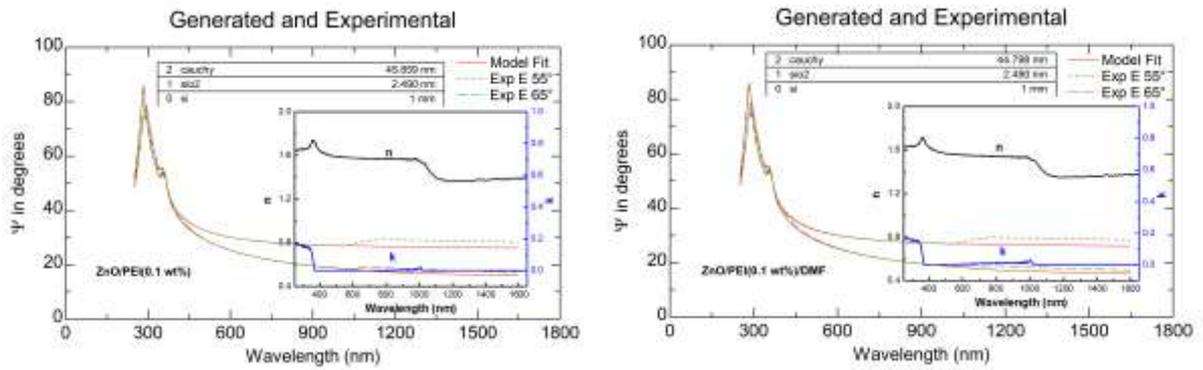
$$\mu = \frac{2d^2}{3At_{max}^2 \left[1 + 0.36 \frac{\Delta j}{j(0)}\right]} if \Delta j \leq j(0)$$

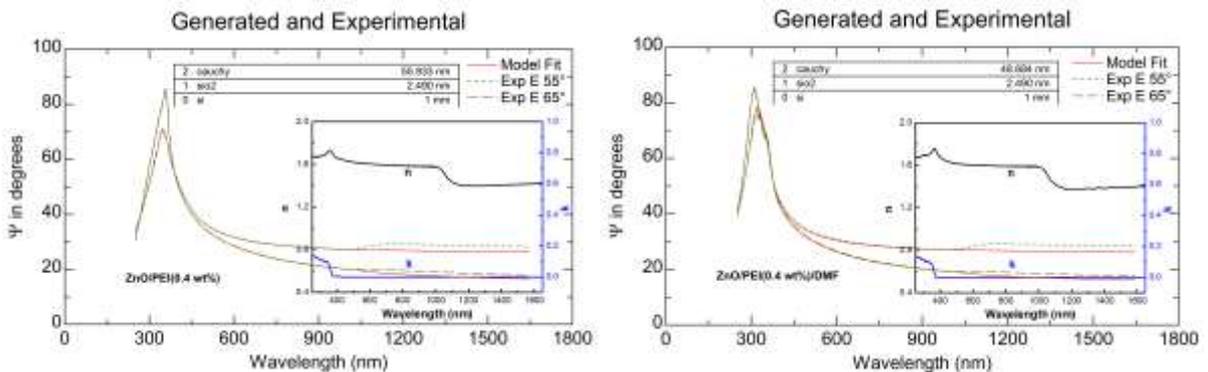is then applied to the transient to extract an estimation of the average charge carrier mobility.

*Part of the Ψ fitting in Ellipsometry analysis*
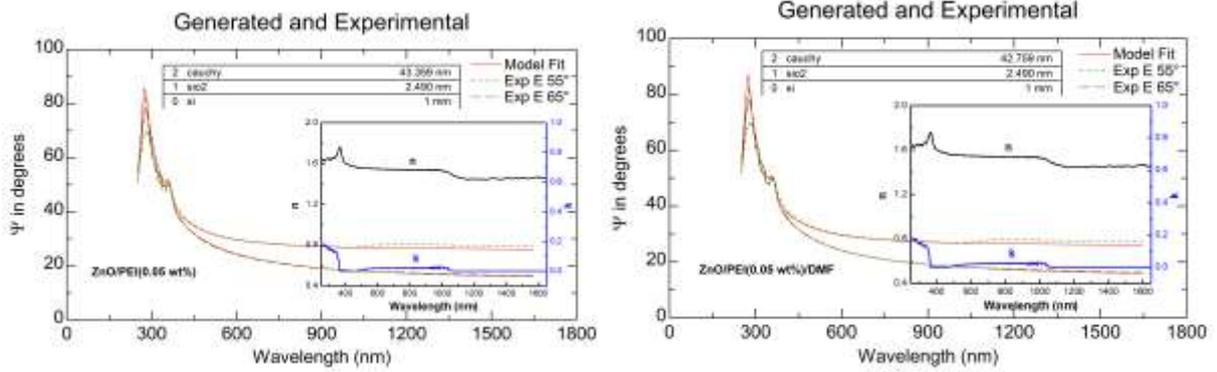
Figure S1a Fitting results based on PEI(0.05 wt%) case in which the fitted ZnO thickness was

41.59 nm.

Figure S1b Fitting results based on PEI(0.1 wt%) case in which the fitted ZnO thickness was

43.14 nm.

Figure S1c Fitting results based on PEI(0.4 wt%) case in which the fitted ZnO thickness was

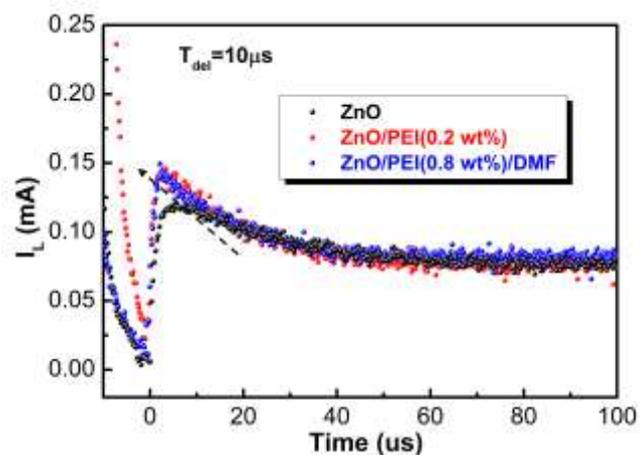48.41 nm for left figure and 42.69 nm for right figure.
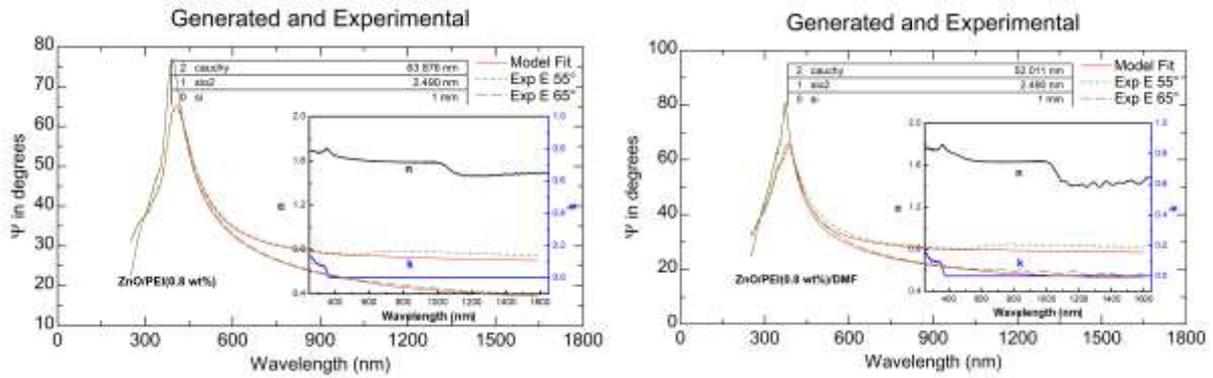
Figure S1d Fitting results based on PEI(0.8 wt%) case in which the fitted ZnO thickness was

50.47 nm for left figure and 42.58 nm for right figure.
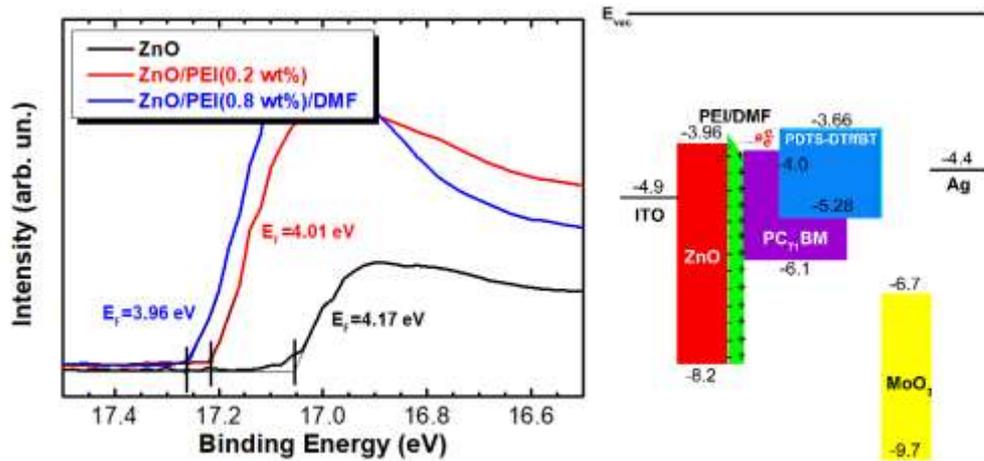
Figure S2. a). The PL and UPS results based on different sample (ZnO, ZnO/PEI,

ZnO/PEI/DMF). b). The flat energy band diagram of devices with PEI modification and DMF

treatment.

Figure S3. The CELIV-transients of devices based on ZnO, ZnO/PEI and ZnO/PEI/DMF.
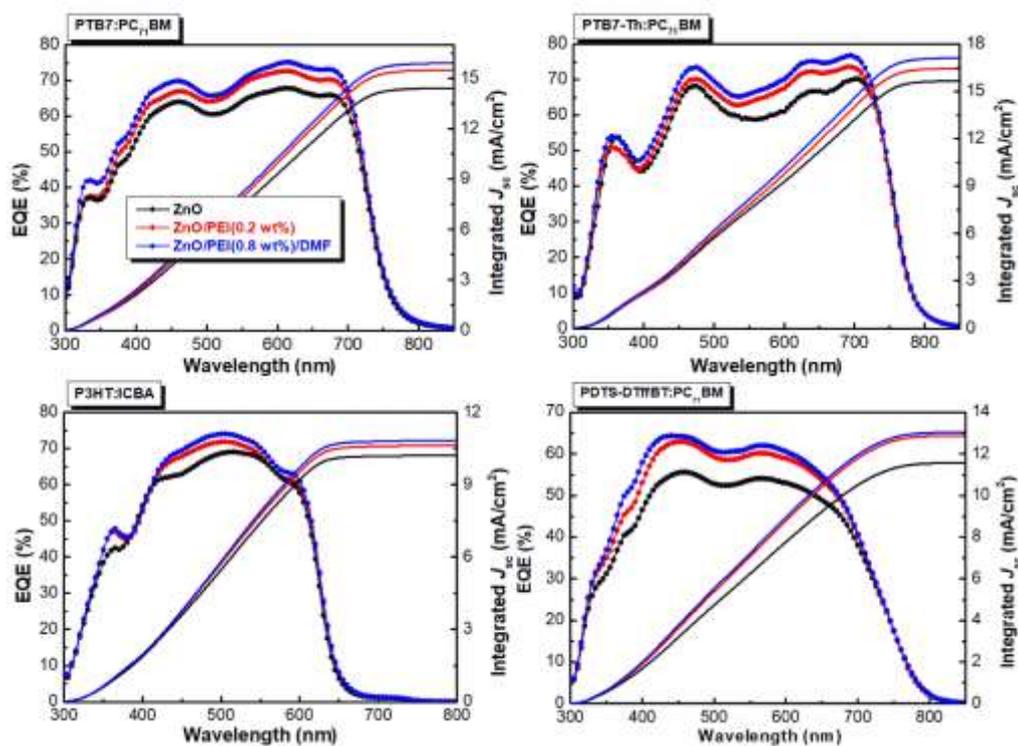
Figure S4 The EQE spectra and corresponding integrated J_{sc} curves based on different active layer system.

Figure S5 AFM height images of PDTS-DTffBT based active layer on different substrates.

Figure S6. PEI thickness variation trend on Si and Si/ZnO substrate

Table S1. PEI thickness values determined by Ellipsometry.

	0.05 wt%		0.1 wt%		0.2 wt%		0.4 wt%		0.8 wt%		1.6 wt%	
DMF	w/o	with	w/o	with	w/o	with	w/o	with	w/o	with	w/o	with
Si	1.54	1.38	2.54	2.22	4.56	4.05	6.89	5.37	9.47	7.12	11.62	9.77
Si/ZnO	1.77	1.17	2.72	1.66	3.01	2.20	7.50	5.99	13.41	9.43	22.08	11.97
AFM scratch	1.1± 0.2	1.0± 0.3	2.0± 0.2	1.8± 0.1	3.2± 0.1	2.3± 0.2	5.6± 0.4	4.1± 0.2	7.8± 0.2	5.3± 0.2	9.4± 0.3	6.6± 0.2

Reference

[1]Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, Adv. Mater., 2011, 23, 1679.

[2]S. P. Wen, C. Wang, P. F. Ma, Y.-X. Zhao, C. Li and S. P. Ruan, *J. Mater. Chem. A*, 2015, **3**, 13794.

[3] A. Pivrikas, N. S. Sariciftci, G. Juška, R. Österbacka, Progr. Photovoltaics Res. Appl. 2007, 15, 677.