Supporting Information

Efficiency exceeding 10% for inverted polymer solar cells with ZnO/ionic liquid combined cathode interfacial layer

*Wei Yu,‡ Linquan Huang,‡ Dong Yang, Ping Fu, Lingyu Zhou, Jian Zhang*and Can Li**

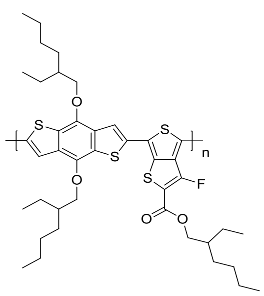
Experimental Section

Materials: The donor polymers, polythieno[3,4-b]thiophene/benzodithiophene (PTB7) and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) were purchased from 1-Material, Inc. The acceptor fullerene derivative, [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) was purchased from Solarmer Materials, Inc. 1-butyl-3-methylimidazolium tetrafluoroborate ($C_8H_{15}N_2BF_4$, [BMIM]BF_4, >99.5%), 1-benzyl-3-methylimidazolium chloride ($C_{11}H_{13}N_2Cl$, [BzMIM]Cl, >99.5%) and all of the solvents, including the solvent additives, were purchased from Sigma-Aldrich. All materials were used as received.

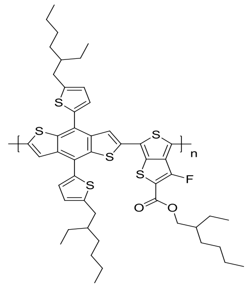
Characterization: A computer-controlled Keithley 2400 source measure unit was used to characterized the *J-V* performance of devices with an AM 1.5G oriel solar simulator at illumination intensity of 100 mW cm^{-2}. The corresponding external quantum efficiency was characterized on the QTest Station 2000ADI system (Crowntech. Inc., USA). The ultraviolet–visible absorption spectra (UV-vis) and optical transmittance spectra were measured on a Varian Cary 5500 spectrometer. Atomic force microscopy (AFM) height images of ZnO, [BzMIM]Cl, [BMIM]BF_4 and ZnO/[BMIM]BF_4 films were obtained using a Bruker Metrology Nanoscope III-D atomic force microscope in tapping mode under atmospheric conditions. The work function of ZnO, [BzMIM]Cl, [BMIM]BF_4 and ZnO/[BMIM]BF_4 were measured in air by scanning Kelvin probe microscopy (SKPM) with a Bruker Metrology Nanoscope III-D atomic force microscope. Conducting AFM tips (SCM-PIT/PtIr, Bruker, USA) were used for this study with a typical spring constant of 2.8 N m^{-1} and a resonance frequency of 75 kHz. XPS measurements were performed using a VG ESCALAB MK2 system with a monochromatized Al Kα under a pressure of 3.75×10^{-9} Torr.

Electron extraction enhancement in ZnO/IL film

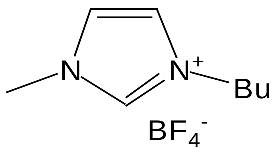
Electrochemical impedance spectra (EIS) are used to investigate the polymer and interface properties of the inverted devices with ZnO and ZnO/IL as interface layers. Fig. 3e shows the Nyquist plots of devices measured at open-circuit voltage based on ZnO and ZnO/IL, with equivalent circuit model displayed in Fig. S3. The fitted equivalent circuit model composes of Rs and three components of R1, R2, and R3 forming a parallel circuit with capacitors (C1, C2, and C3, respectively). The parameters of equivalent circuit are summarized in Table S1. The (R1, C1) and (R3, C3) components are primarily affected by the interface layer between electrodes and active layers. The (R2, C2) component is root in the active layer. The Nyquist plots that follow shows the R1, R2 and R3 of the devices with ZnO as interface layer are 1250, 210.3 and 13.5 Ω, respectively, while the devices based on ZnO/IL decreases to 233.8, 4.41 and 3.59 Ω, respectively. The extracted contact resistance is notable reduced when the devices with ZnO/IL as interface layer. Meanwhile, the C2 decreases from 3.91×10^{-9} to 1.95×10^{-9} F for devices with ZnO/IL. This indicates less carriers exist in active layer based on ZnO/IL and the result is in good agreement with electron mobility measurements that the ZnO/IL has higher electron mobility which insure that the carriers can timely extract from active layer to CILs. The increase of C1 (from 2.67×10^{-9} to 4.58×10^{-8} F) is demonstrated that the process occurs in device. From above all, it is very likely that the carriers can efficient reach to electrode from active layer based on ZnO/IL and thus resulting in the increase of J_{sc} and FF of the PSCs.



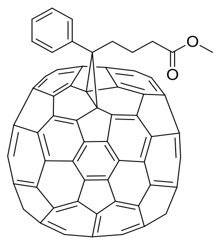
PTB7



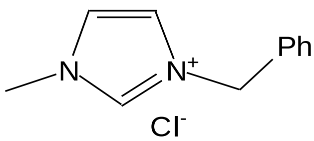
PTB7-Th



[BMIM]BF$_4$



PC$_{71}$BM



[BzMIM]Cl

Fig. S1 Chemical structures of donor polymers and IL used in devices.

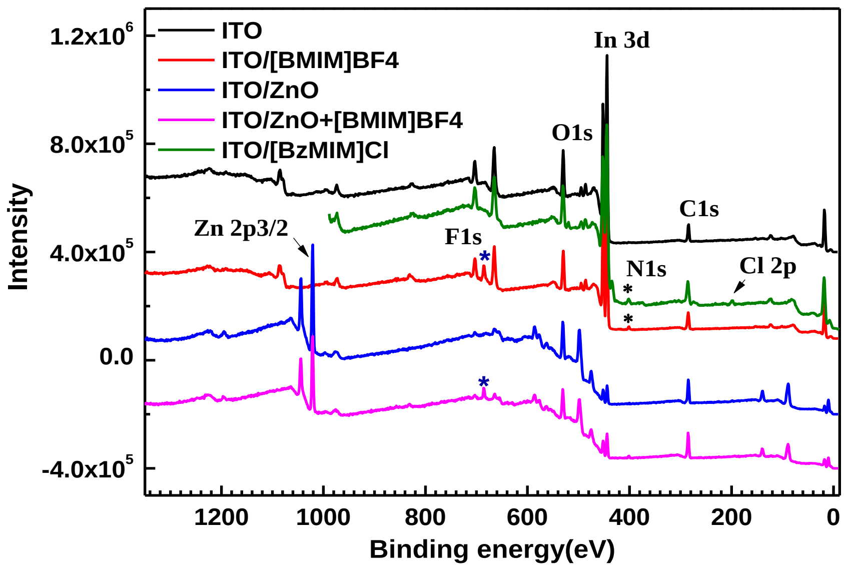
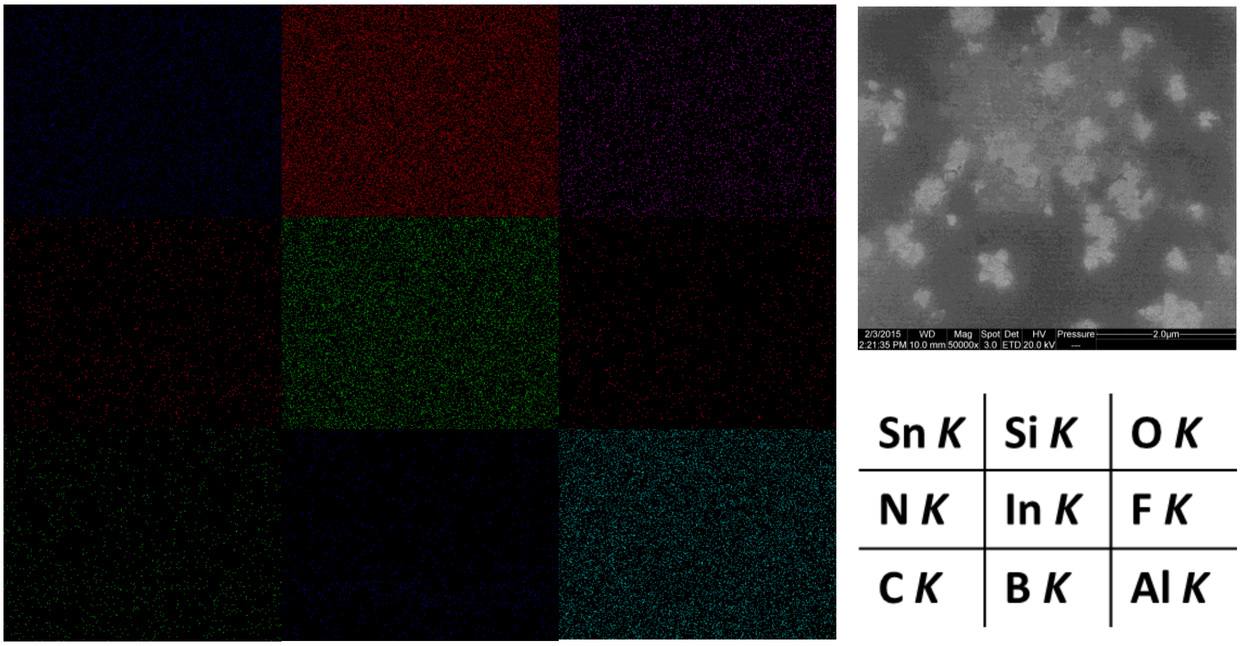


Fig. S2 XPS spectra of ITO/ZnO, ITO/IL and ITO/(ZnO+IL).

(a) 0.1 wt% $[BMIM]BF_4$ on ITO



(b) 0.1 wt% $[BMIM]BF_4$ on ITO/ZnO

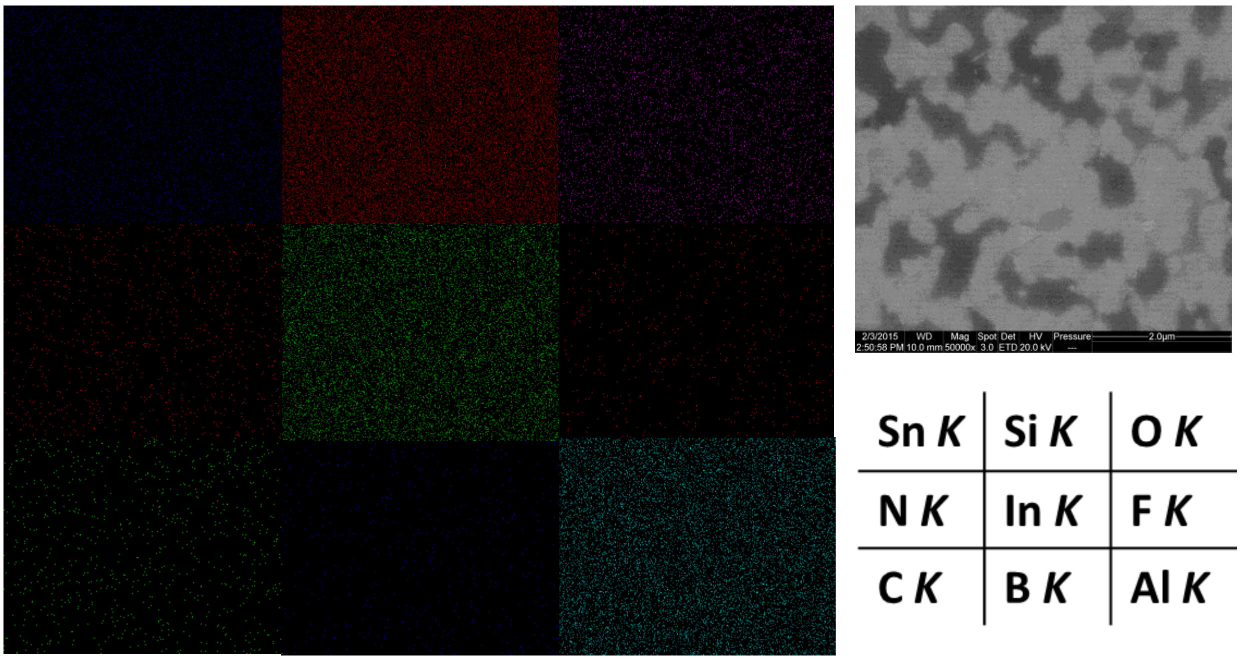


Fig. S3 EDX mapping images of $[BMIM]BF_4$ on (a) ITO and (b) ITO/ZnO substrate.

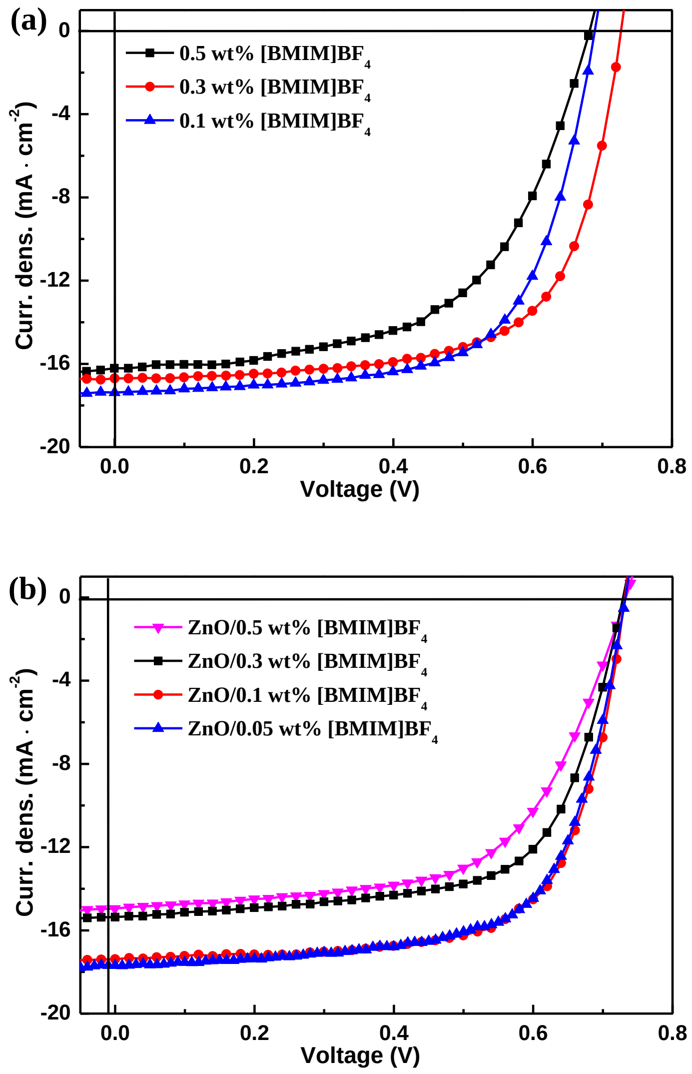


Fig. S4 *J-V* characteristics of the PTB7:$PC_{71}BM$ inverted devices with different concentration of [BMIM]BF_4 on (a) ITO and (b) ITO/ZnO substrate.

Table S1 The parameters of the devices with different concentration of [BMIM]BF_4 on ITO or ZnO substrate

	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
0.5wt% [BMIM]BF_4	16.20	0.68	0.570	6.28
0.3wt% [BMIM]BF_4	16.70	0.72	0.676	8.13
0.1wt% [BMIM]BF_4	17.36	0.68	0.668	7.89
ZnO/0.5wt% [BMIM]BF_4	14.89	0.72	0.617	6.62
ZnO/0.3wt% [BMIM]BF_4	15.36	0.72	0.664	7.34
ZnO/0.1wt% [BMIM]BF_4	17.39	0.72	0.696	8.71
ZnO/0.05wt% [BMIM]BF_4	17.69	0.73	0.674	8.70

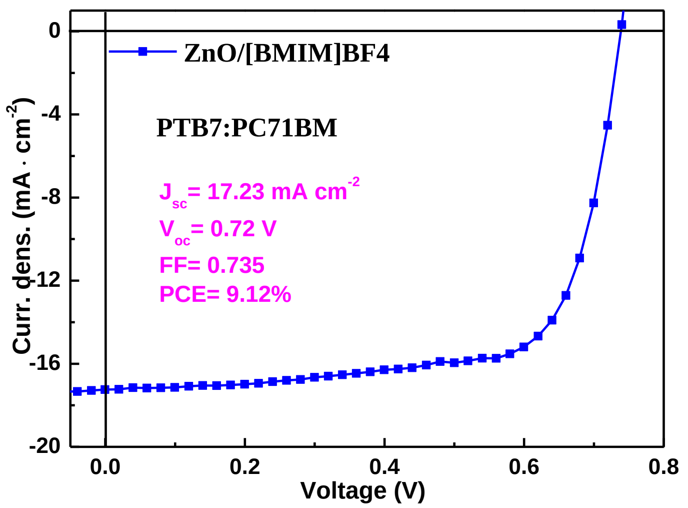


Fig. S5 The *J-V* curve of the best i-PSCs based on PTB7:$PC_{71}BM$ with ZnO/[BMIM]BF_4 as interfacial layer.

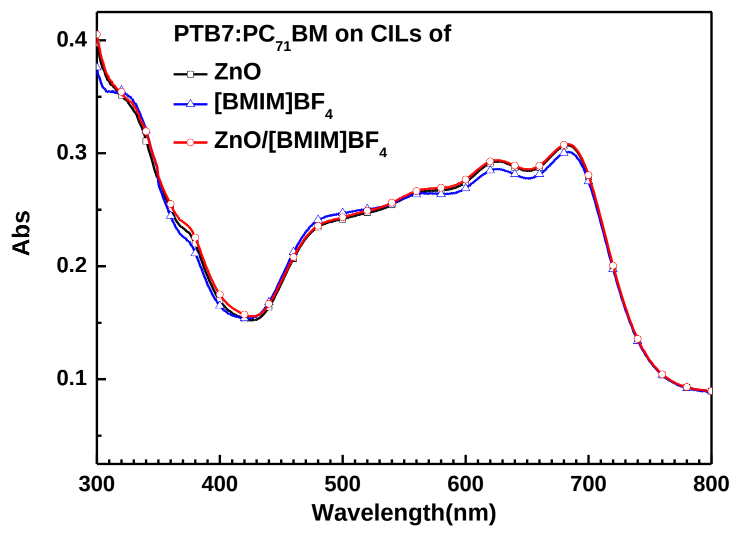


Fig. S6 Absorpiton spectra of PTB7:$PC_{71}BM$ on CILs of ZnO, [BMIM]BF_4 and ZnO/[BMIM]BF_4.

Table S2 Contact Angles of Three Probing Liquids on Various Surfaces at Initial State, And the Calculated Surface Energies (mN m^{-1})

		ITO	**ITO/[BMIM]BF_4**	**ITO/ZnO**	**ITO/ZnO/[BMIM]BF_4**
Contact angle (degree)	**Water**	56±1	41±1	81±1	70±1
	Ethylene Glycol	36±1	26±1	62±1	61±1
	Hexadecane	33±2	33±3	42±2	36±2
Calculated surface energy component (mN m^{-1})	γ	38.9	43.5	26.7	27.2
	γ^{LW}	23.2	23.2	21.0	22.4
	γ^{AB}	15.7	20.2	5.7	4.8
	γ^{+}	2.2	2.3	0.81	0.26
	γ^{-}	28.1	44.5	10.0	22.3

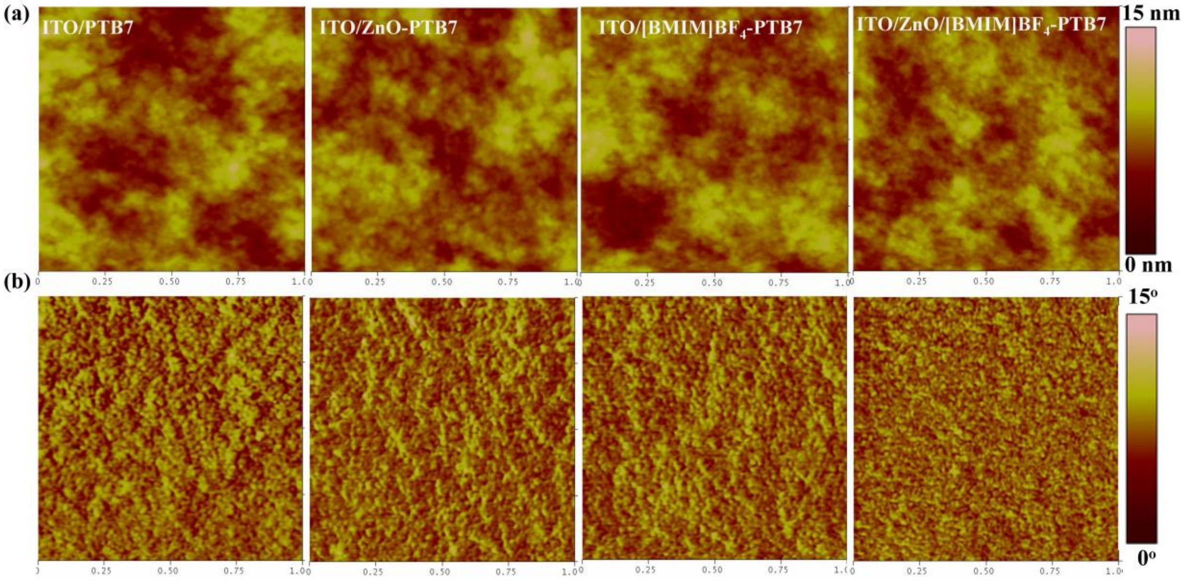


Fig. S7 (a) AFM topography images (1 μm x1 μm) and (b) phase images (1 μm x1 μm) of PTB7:$PC_{71}BM$ on bare ITO and cathode interfacial layers of ZnO, [BMIM]BF_4 and ZnO/[BMIM]BF_4 films (from left to right).

Fig. S8 The equivalent circuit model for i-PSCs in electrochemical impedance spectra.

Table S3. Summarized parameters of the i-PSCs equivalent circuit with ZnO or ZnO/IL as interfacial layers measured at open voltage.

	ZnO/IL	ZnO
Rs (Ω)	31.86	26.89
R1(Ω)	233.80	1250.00
R2(Ω)	4.41	210.30
R3(Ω)	3.59	13.50
C1(F)	4.57E-8	2.67E-9
C2(F)	1.95E-9	3.91E-9
C3(F)	3.29E-9	2.62E-9

Table S4. The calculated R_s and R_{sh} of the i-PSCs with ZnO and ZnO/[BMIM]BF_4 CIL.

Active layer	ITO/interlayer	R_s (Ω cm^2) [a]	R_{sh} (kΩ cm^2) [a]
PTB7:PC_{71}BM	ZnO	10.28	4.53
	ZnO/[BMIM]BF_4	3.46	16.20

[a]The series resistance (R_s) stands for the slope of the *J-V* curve at $J = 0$ for the device and the shunt resistance (R_{sh}) stands for the slope of the *J-V* curve at V = 0 for the device.

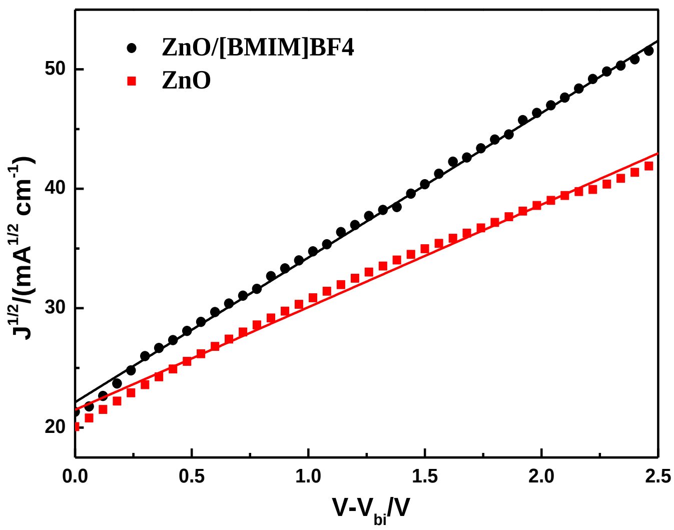


Fig. S9 $J^{1/2}$-*V* characteristics for SCLC fitting of electron only devices with ZnO or ZnO/[BMIM]BF_4 as interfacial layers

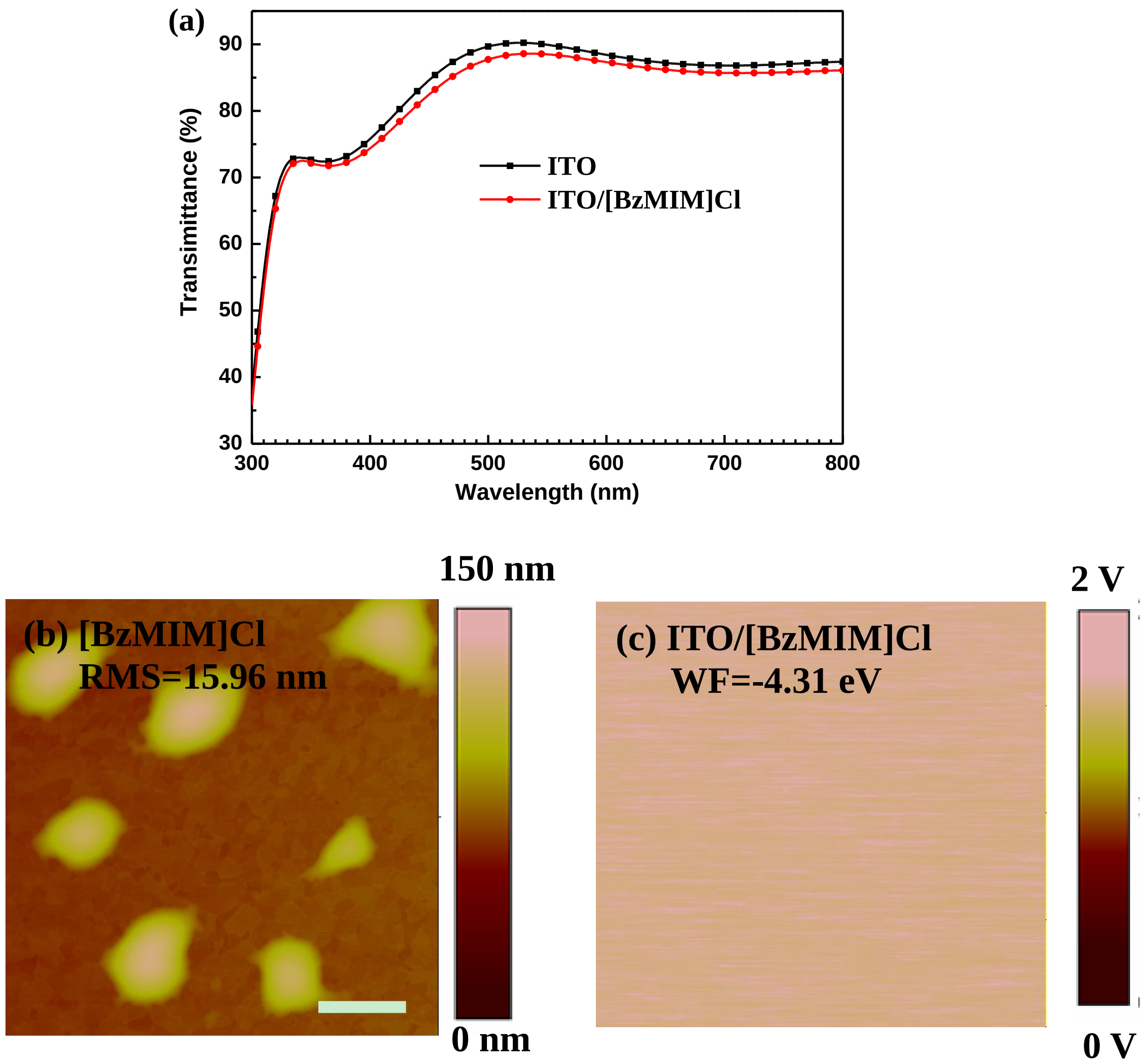


Fig. S10 (a) Optical transmission spectra of bare ITO and ITO/[BzMIM]Cl; (b) AFM images and (c) surface potential images of [BzMIM]Cl on ITO.

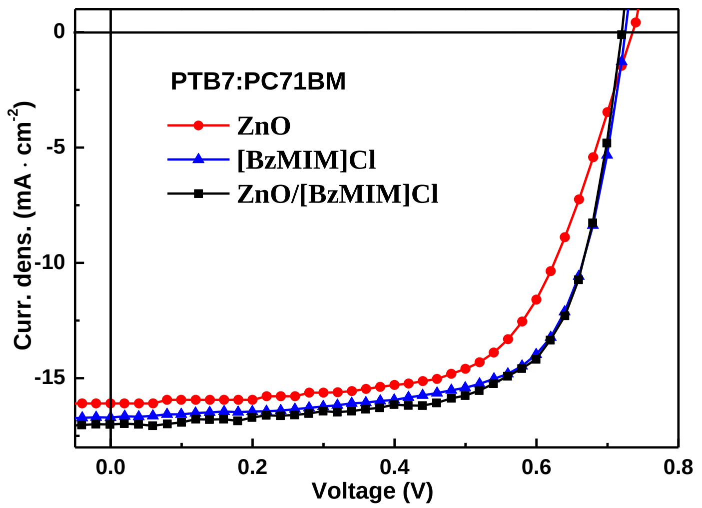


Fig. S11 *J*-*V* characteristics of the PTB7:PC_{71}BM inverted devices with various cathode interface layers (ZnO, [BzMIM]Cl and combined ZnO/[BzMIM]Cl).

References:

[1] F. X. Xie, W. C. H. Choy, W. E. I. Sha, D. Zhang, S. Q. Zhang, X. C. Li, C. W. Leung, J. H. Hou, *Energy Environ. Sci.*, **2013**, *6*, 3372.

[2] N. Baram, Y. Ein-Eli, *J. Phys. Chem. C*, **2010**, *114*, 9781.

[3] F. Fabregat-Santiago, G. Garcia-Belmonte, I. Mora-Sero, J. Bisquert, *Phys. Chem. Chem. Phys.*, **2011**, *13*, 9083.