Supporting Information for:

Effect of counter-ions on the properties and performance of non-conjugated polyelectrolyte interlayers in solar cell and transistor devices

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1. Preparation of Nonconjugated polyelectrolytes

$PEIH^+Br^-$ and $PEIH^+I^-$. A solution of polyethyleneimine PEI in deionized water was made with a concentration of 0.25 g/mL. Aqueous solutions of acid (HI, HBr) were slowly added to the polymer solutions until test aliquots (5 μL of polymer solution diluted in 1 mL water) reached a pH in the range of 5.0 to 5.5. In the case of $PEIH^+Br^-$, 1,800 μL of PEI solution was neutralized with 491 μL of concentrated (48%) HBr. In the case of $PEIH^+I^-$, 1,350 μL of PEI solution was neutralized with 521 μL of concentrated (57%) HI. The solutions were precipitated into isopropanol, re-dissolved in anhydrous methanol, precipitated in diethyl ether, and dried under vacuum yielding gummy solids.

$PEIH^+BIm_4^-$. Was prepared following a previously reported procedure.[1] The structure was confirmed by ^{1}HNMR in D_2O, by comparing the PEI (Figure S1) starting material with the product $PEIH^+BIm_4^-$ (Figure S2) which showed the appearance of 3 distinct resonances at 7.33, 7.06 and 6.88 ppm corresponding to the 3 unique protons on the tetraimidazolyl borate (BIm_4^-) anion.

1. Kim, H.-B.; Yoon, Y. J.; Jeong, J.; Heo, J.; Jang, H.; Seo, J. H.; Walker, B.; Kim, J. Y., Peroptronic devices: perovskite-based light-emitting solar cells. *Energy Environ. Sci.* **2017,** *10* (9), 1950-1957.

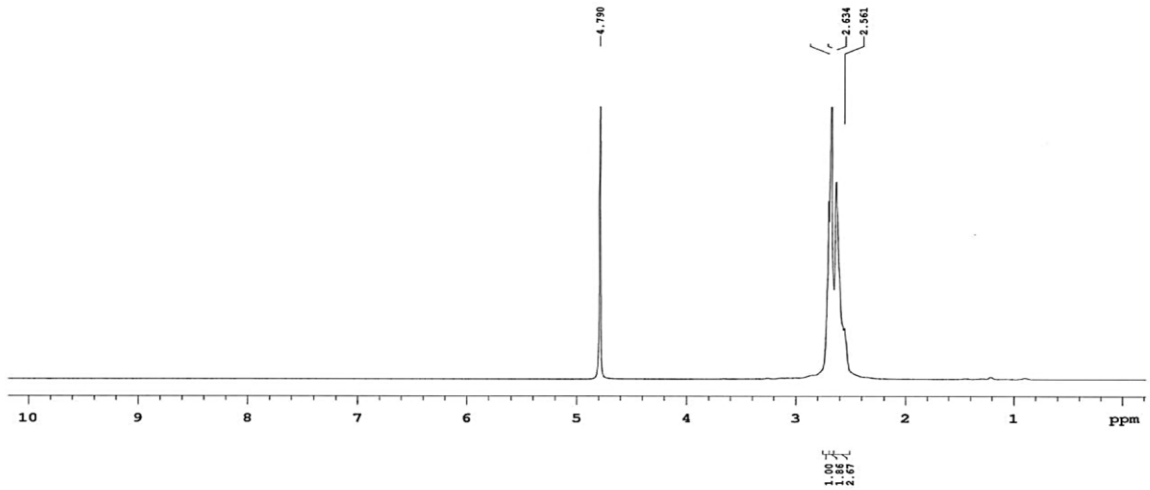

Figure S1. ^{1}HNMR spectrum of PEI polymer in D_2O. The peak at 4.79 ppm corresponds to H_2O.

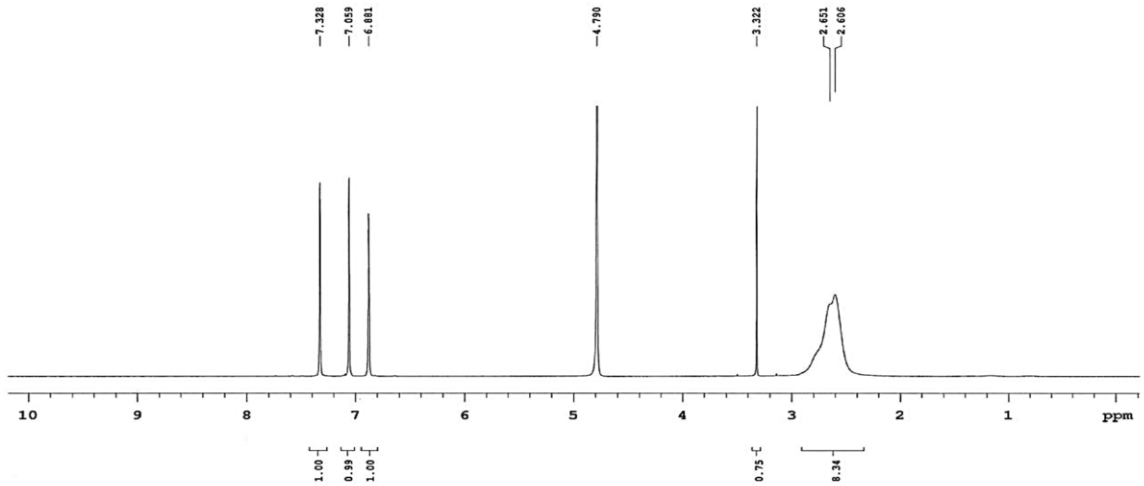

Figure S2. ^{1}HNMR spectrum of $PEIH^{+}BIm_4^{-}$ polymer in D_2O. Peaks at 4.79 and 3.32 ppm correspond to residual H_2O and methanol, respectively.

2. Performance of P3HT:$PC_{61}BM$ solar cells with NPE interlayers

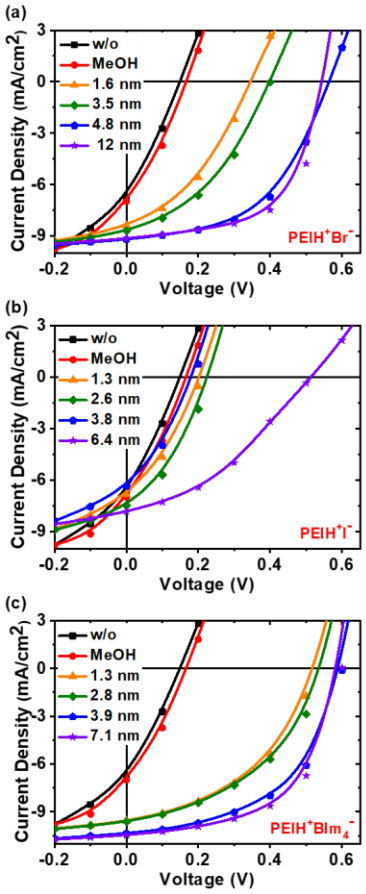

Figure S3. Current Density−Voltage curves of inverted P3HT:$PC_{61}BM$ solar cells with the NPE ETL layers (a) $PEIH^+Br^-$, (b) $PEIH^+I^-$, and (c) $PEIH^+BIm_4^-$.

Table S1. Summary of device characteristics of P3HT:$PC_{61}BM$ solar cells as a function of NPE thicknesses.

	Concentrate (%)	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	
						Average	Best
w/o	-	-	6.774±0.12	0.15±0.012	29.4±1.9	0.24±0.09	0.30
Methanol Treatment	-	-	7.133±0.10	0.17±0.007	33.2±1.5	0.31±0.12	0.39
$PEIH^+Br^-$	0.005	1.6	8.387±0.11	0.32±0.006	46.1±0.2	1.02±0.12	1.23
	0.01	3.5	8.692±0.09	0.43±0.003	46.3±0.6	1.58±0.10	1.74
	0.05	4.8	9.985±0.12	0.58±0.003	53.6±0.5	3.01±0.07	3.12
	0.1	12	9.923±0.08	0.55±0.005	57.5±0.8	2.94±0.05	3.10
$PEIH^+I^-$	0.005	1.3	6.842±0.18	0.21±0.011	32.4±1.8	0.32±0.13	0.46
	0.01	2.6	7.493±0.15	0.22±0.014	33.8±1.7	0.44±0.11	0.55
	0.05	3.8	6.361±0.21	0.19±0.022	41.2±2.1	0.48±0.13	0.50
	0.1	6.4	7.837±0.08	0.54±0.004	32.9±3.2	1.17±0.09	1.38
$PEIH^+BIm_4^-$	0.005	1.3	9.563±0.17	0.57±0.003	57.3±0.5	2.98±0.03	3.12
	0.01	2.8	9.601±0.12	0.59±0.007	56.8±0.8	3.09±0.04	3.22
	0.05	3.9	10.34±0.08	0.61±0.004	60.3±0.3	3.58±0.07	3.80
	0.1	7.1	10.45±0.06	0.60±0.005	62.5±0.6	3.71±0.09	3.89

3. Output characteristics of IZO FETs with different thicknesses of $PEIH^{+}BIm_4^{-}$

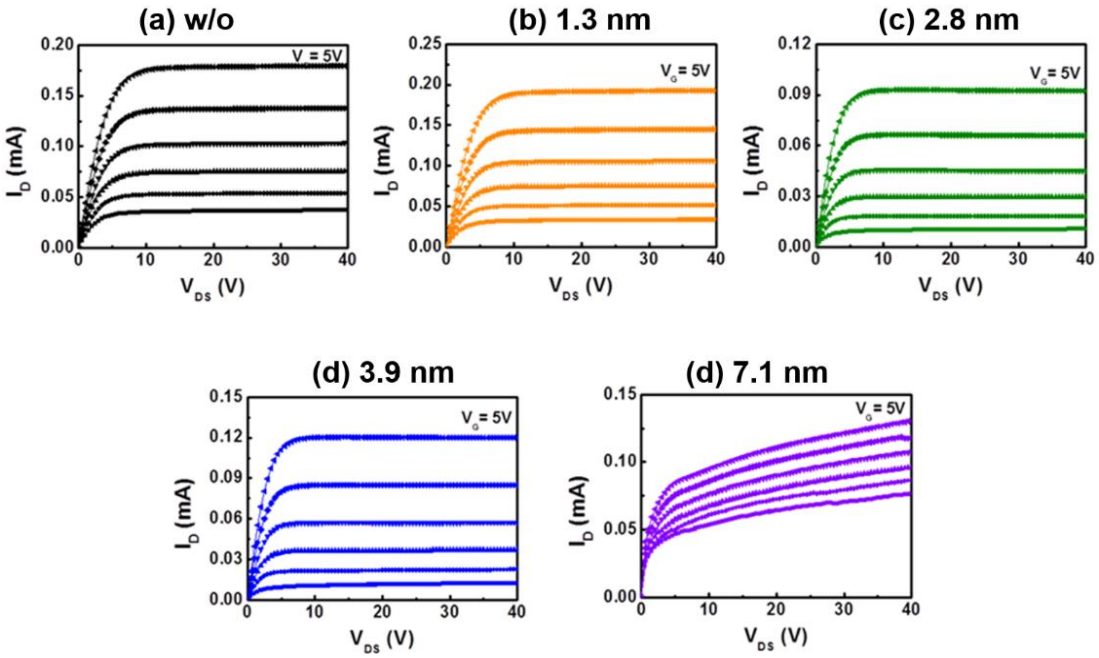

Figure S4. Output characteristics of n-type IZO FETs (a) without and (b)-(e) with $PEIH^{+}BIm_4^{-}$ as a function of the film thicknesses. (1.3, 2.8, 3.9 and 7.1 nm)

4. Au 4f XPS spectra of NPE films

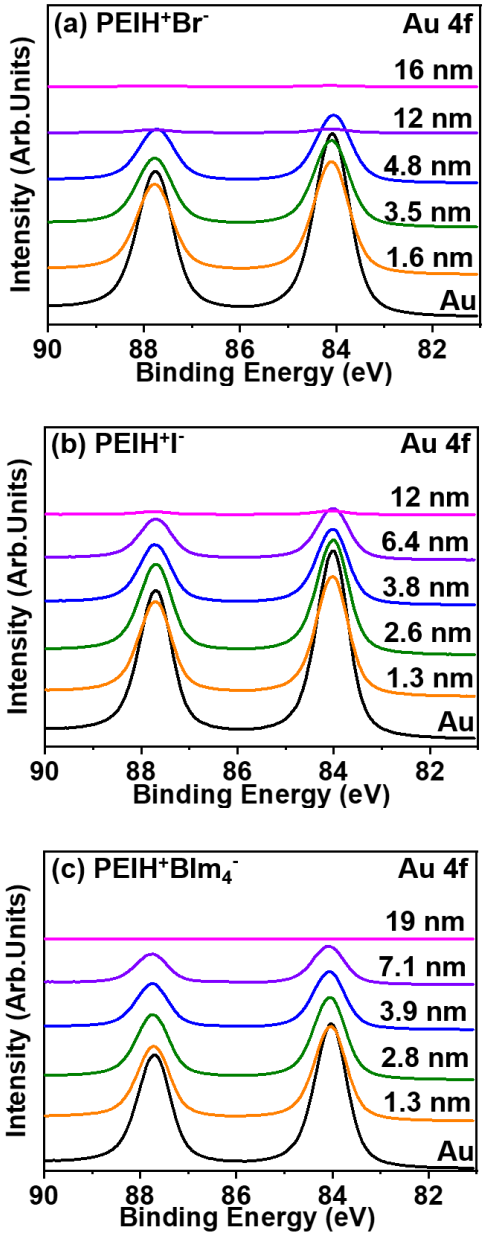

Figure S5. The XPS spectra of Au 4*f* core levels of (a) $PEIH^+Br^-$, (b) $PEIH^+I^-$, and (c) $PEIH^+BIm_4^-$.

It is necessary to know the exact thickness of the NPE layer in order to elucidate the electronic structure at the polymer/metal interface. However the thickness of the spin-coated film is generally have the value in few nanometers so, its hard to measure it accurately. In order to estimate the thickness more precisely, we performed the XPS measurement and calculated it by the attenuation of the Au 4f emission line associated with the substrate . The thickness (*d*) of the each deposited layers is given by, [1-4]

$$d = -l\left[\ln\left(\frac{I}{I_0}\right)\right] \qquad (1)$$

where *l* is the mean free path of the emitted electrons, *I* is the intensity measured on each NPE layer and I_0 is the intensity measured on the bare Au substrate. The ratio I/I_0 was obtained from the Au 4f peak areas. The thicknesses are an average measurement of coverage and the thickness error is approximately ±10% of the last digit.

1. N. Dam, M. Beerbom, J. Braunagel and R. Schlaf, *Journal of applied physics*, 2005, **97**, 024909.
2. W. M. Riggs and M. J. Parker, *Methods of Surface Analysis*, 1975, **1**.
3. J. H. Scofield, *Journal of Electron Spectroscopy and Related Phenomena*, 1976, **8**, 129-137.
4. I. S. Tilinin, A. Jablonski and W. Werner, *Progress in Surface Science*, 1996, **52**, 193-335.

5. AFM images of NPE films

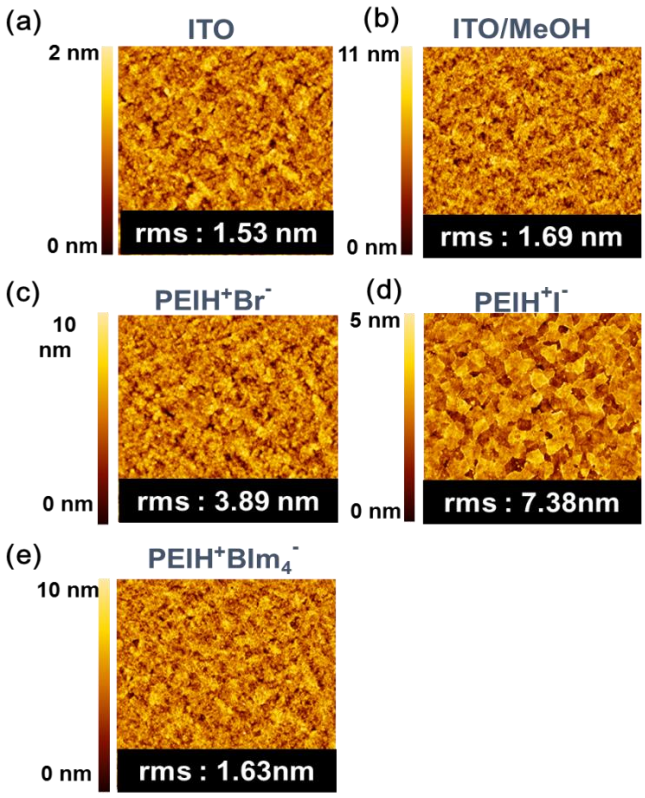

Fig S6. Surface topographic AFM images (size: 5 μm × 5 μm) of (a) ITO, (b) ITO/MeOH treatment, (c) ITO/4.8 nm $PEIH^+Br^-$, (d) ITO/6.4 nm $PEIH^+I^-$ and (e) ITO/7.1 nm $PEIH^+BIm_4^-$ films.

In order to examine the morphological difference of NPEs, we measured NPE surface topography on ITO substrates using AFM. Thicknesses of NPEs are 4.8 nm for $PEIH^+Br^-$, 6.4 nm for $PEIH^+I^-$ and 7.1 nm for $PEIH^+BIm_4^-$, respectively. Root mean square (RMS) from each image was summarized in Figure S5, which is the standard deviation of the surface profile from a mean surface level of zero over large area. Although there is no significant change in the surface topography of the four samples (Fig. S6 (a), (b), (c) and (e)), the RMS values show the $PEIH^+I^-$ exhibit rougher surfaces than that of the $PEIH^+Br^-$ and $PEIH^+BIm_4^-$.

6. Water contact measurements of NPE films

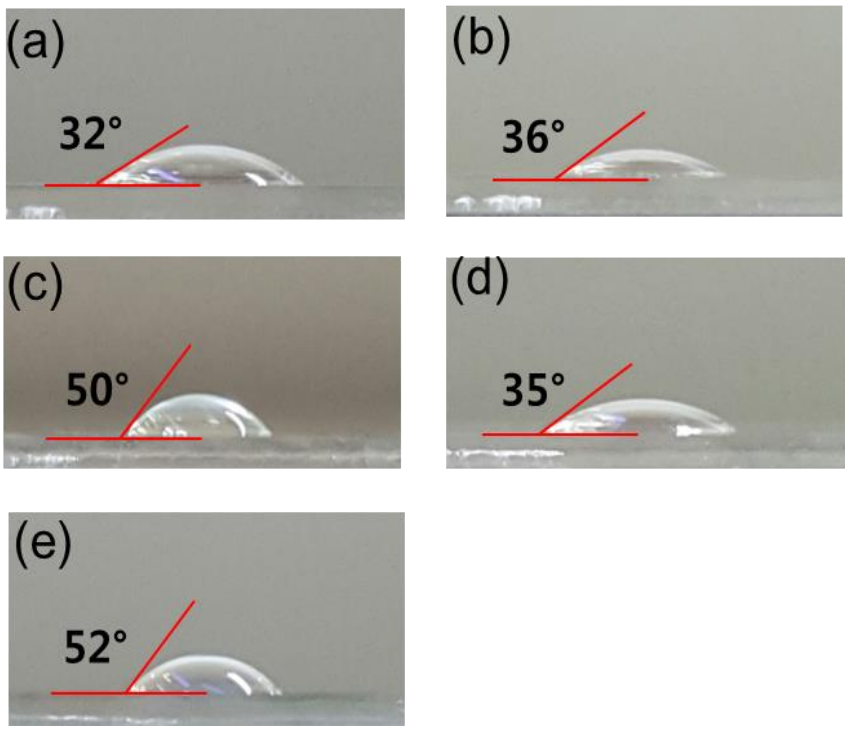

Figure S7. Photographs of water droplets on the surfaces of (a) ITO, (b) methanol, (c) $PEIH^+Br$, (d) $PEIH^+I^-$ and (e) $PEIH^+BIm_4^-$ films deposited on the ITO substrates.