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Supplementary Information

Energy Level Alignment of Polythiophene/ZnO Hybrid Solar Cells

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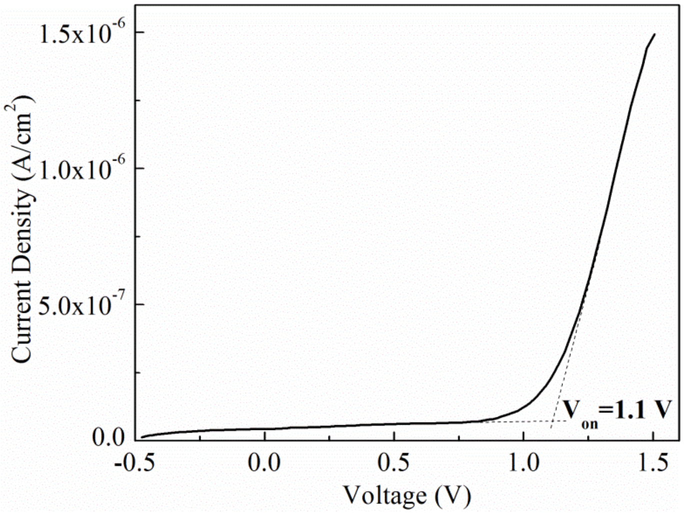
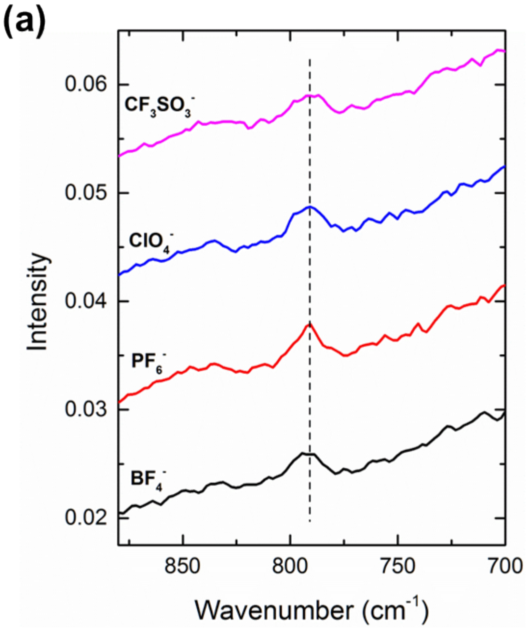


Fig. S1 Dark *J-V* curve of Ag/e-PT/ITO. The turn-on voltage (V_{on}) is determined by the intersection of the two tangent (dashed) lines. This *J-V* curve shows a typical diode effect for semiconducting materials. In a parallel experiment, we measured a sample consisting of graphite electrode/e-PT/Au, and it yielded similar results with a turn-on voltage of an identical value at ~1.1 V.



(b)

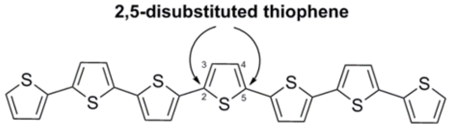
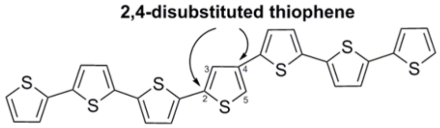
linkage	structure	wavenumber (cm^{-1})	presence in e-PT films
α-linkage		791	Yes
β-linkage		730, 820	No

Fig. S2 (a) FTIR-ATR spectra for on the four undoped polymer films grown on ZnO for a fixed polymerization charge of 50 mC. (b) The corresponding structure, wavenumber and presence in e-PT films of α- and β-linkages.[2]

Table S1. XPS C 1s peak energy (in eV) table for neutral polymers grown in the electrolyte solution containing the following anions: BF_4^-, PF_6^-, ClO_4^- and $CF_3SO_3^-$.

	BF_4^-	PF_6^-	ClO_4^-	$CF_3SO_3^-$
α carbon	284.3	284.2	284.3	284.3
β carbon	285.0	285.0	285.0	285.0
C-COO	286.4	286.5	286.1	286.5
C-O	287.7	287.9	287.6	287.8
C=O	288.9	289.6	289.0	289.5
O-**C**=O	290.4	290.7	290.4	290.5

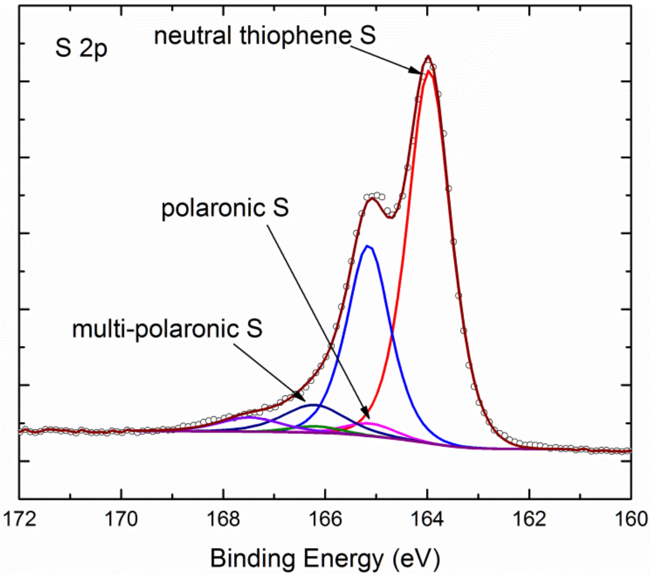
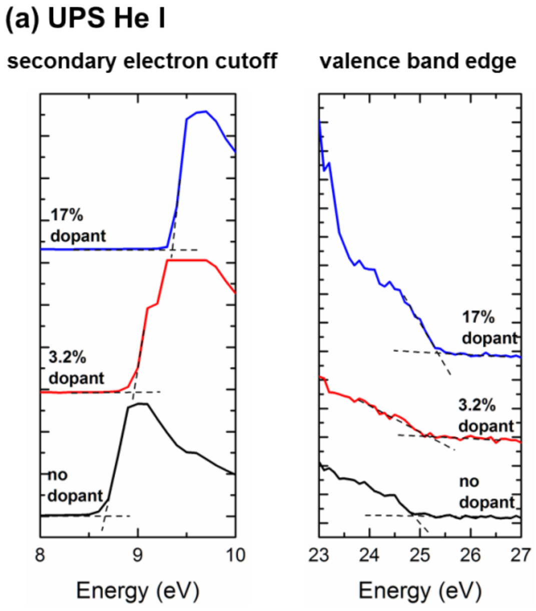


Fig. S3 XPS S 2p core level spectra of a heavily anion (ClO_4^-)-doped polythiophene on Au, with three spin-orbit doublets corresponding to sulfur from neutral thiophene, polaronic and multi-polaronic state.



(b) Summary of UPS He I Data

	He I		
	E_{SEC}	E_{VBE}	IP
no dopant	8.7	24.9	5.0
3.2% dopant	9.0	25.2	5.0
17% dopant	9.4	25.4	5.2

Fig. S4 (a) UPS He I spectra of the secondary electron cutoff and valence band edge of various ClO_4^- dopant level polythiophene films on Au. (b) Summarized Table for E_{SEC}, E_{VBE} and IP (in eV).

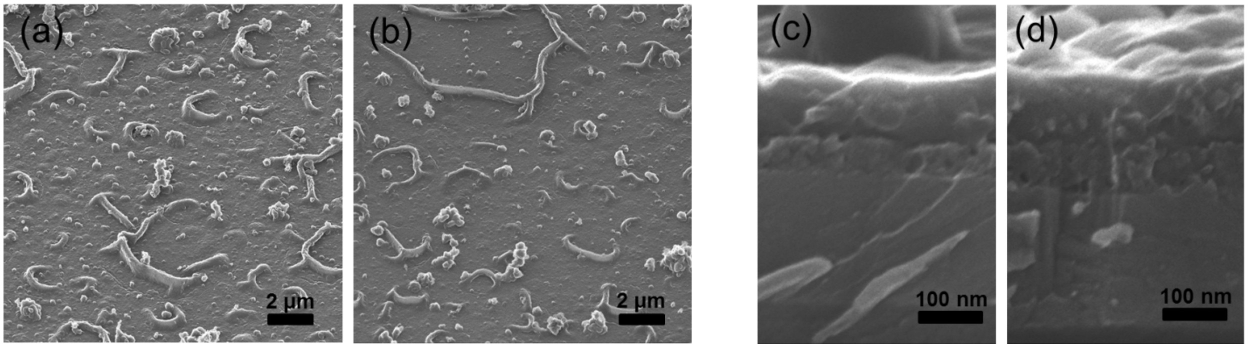


Fig. S5 45° tilt angle helium ion microscope (HIM) image of (a) doped e-PT film and (b) dedoped e-PT film; cross sectional HIM image of (c) doped e-PT film and (d) dedoped e-PT film. All e-PT films were deposited on ZnO film substrate with ClO_4^- as electrolyte anion. Both films are ~80 nm thick.

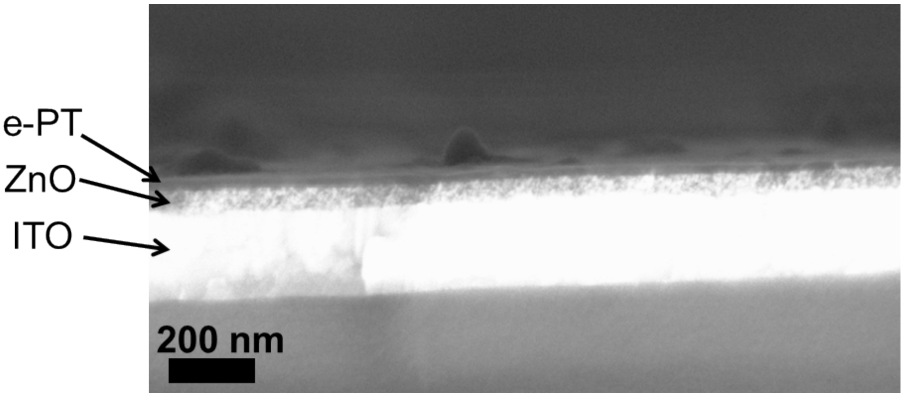


Fig. S6 Cross sectional SEM image of a thin polymer film (BF_4^-) deposited on ZnO film with a fixed charge of 5 mC. The thin e-PT film is ~10-20 nm.

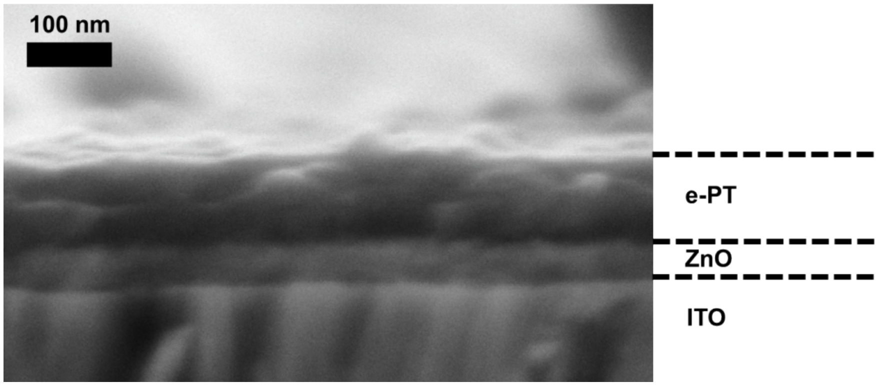


Fig. S7 Cross sectional SEM image of a thick polymer film ($CF_3SO_3^-$) deposited on ZnO film with a fixed charge of 50 mC. The thick e-PT film is ~80 nm.

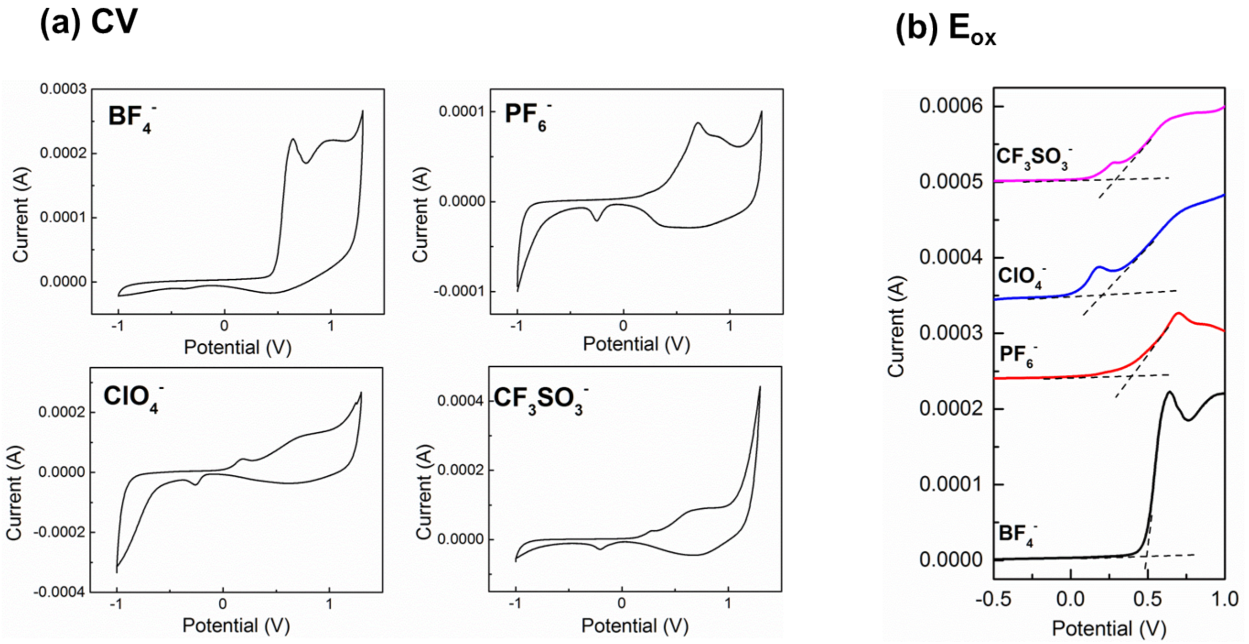


Fig. S8 (a) Cyclic voltammograms for polymers grown in electrolyte solutions containing the following anions: BF$_4^-$, PF$_6^-$, ClO$_4^-$ and CF$_3$SO$_3^-$. (b) Magnified view of the potential region between -0.5 V to 1.0 V and corresponding E_{ox} values (0.5, 0.4, 0.2, 0.3 V) by extrapolation of leading edges. From IP = e(E_{ox} + 4.9 V), E_{ox} is thus converted to corresponding IP values of 5.4, 5.3, 5.1, 5.2 eV for BF$_4^-$, PF$_6^-$, ClO$_4^-$, CF$_3$SO$_3^-$ polymers, respectively. Note: The 0.19 V peak has been attributed to the presence of more regioregular polymer domains.[1] The ClO$_4^-$ polymer, with the most prominent 0.19 V peak, appears to have the highest fraction of regioregular domains and exhibits higher order within the polymer chains. This finding was also reflected in our XPS studies in the paper.

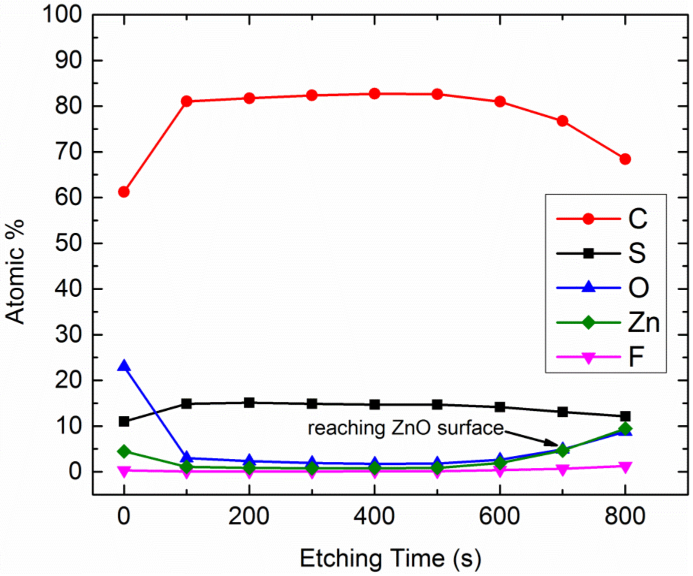


Fig. S9 XPS depth profile of a thick polymer film (BF$_4^-$) deposited on ZnO film with a fixed charge of 50 mC. At etching time ~700 s, Zn and O intensity (from ZnO film) increased significantly, indicating that the sputtering has reached the e-PT/ZnO interface. The F intensity from the dopant anion remained extremely low throughout the bulk of the e-PT film to the interface of e-PT/ZnO.

References

1. E. L. Ratcliff, J. L. Jenkins, K. Nebesny and N. R. Armstrong, Chem. Mater., 2008, **20**, 5796-5806.
2. T. Yamamoto, K.-I. Sanechika and A. Yamamoto, Bull. Chem. Soc. Jpn., 1983, **56**, 1497-1502.