

## Supporting Information

### **Extremely Stable Organic Photovoltaic Incorporated With WO<sub>x</sub> Doped PEDOT:PSS Anode Buffer Layer.**

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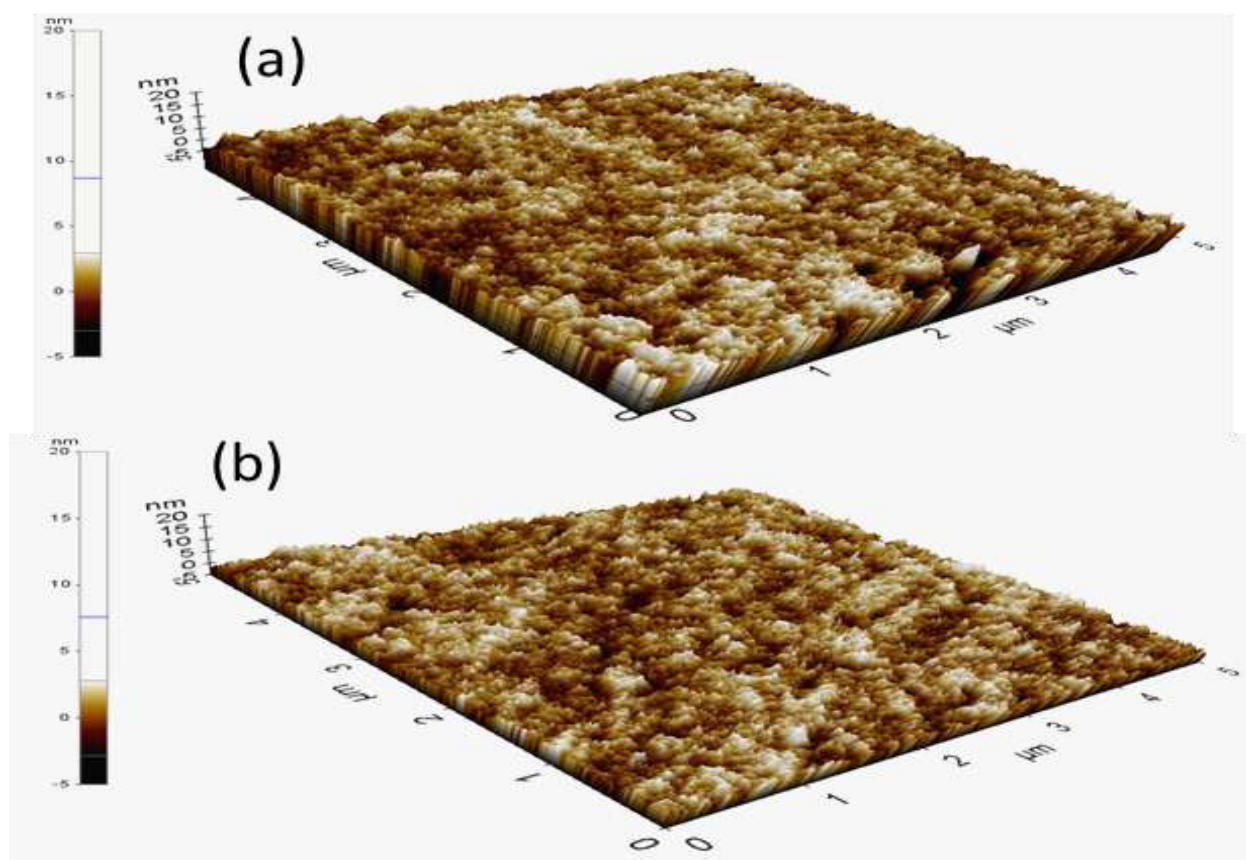
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**A.** Device Performance of OPVs for initial and after 5000 hour with and without WO<sub>x</sub> in PEDOT:PSS.

**Table S1.** The summarized OPV performances for initial and after 5000 h of controlled and WO<sub>x</sub> incorporations devices. The power conversion efficiencies of the inverted OPVs were measured under the illumination of AM1.5G simulated solar light (Oriel Model 91192) at 100 mW/cm<sup>2</sup>. The current density–voltage (*J–V*) characteristics were recorded with a Keithley 2410 source unit. Series and shunt resistance were calculated from the slop of *J–V* plots.

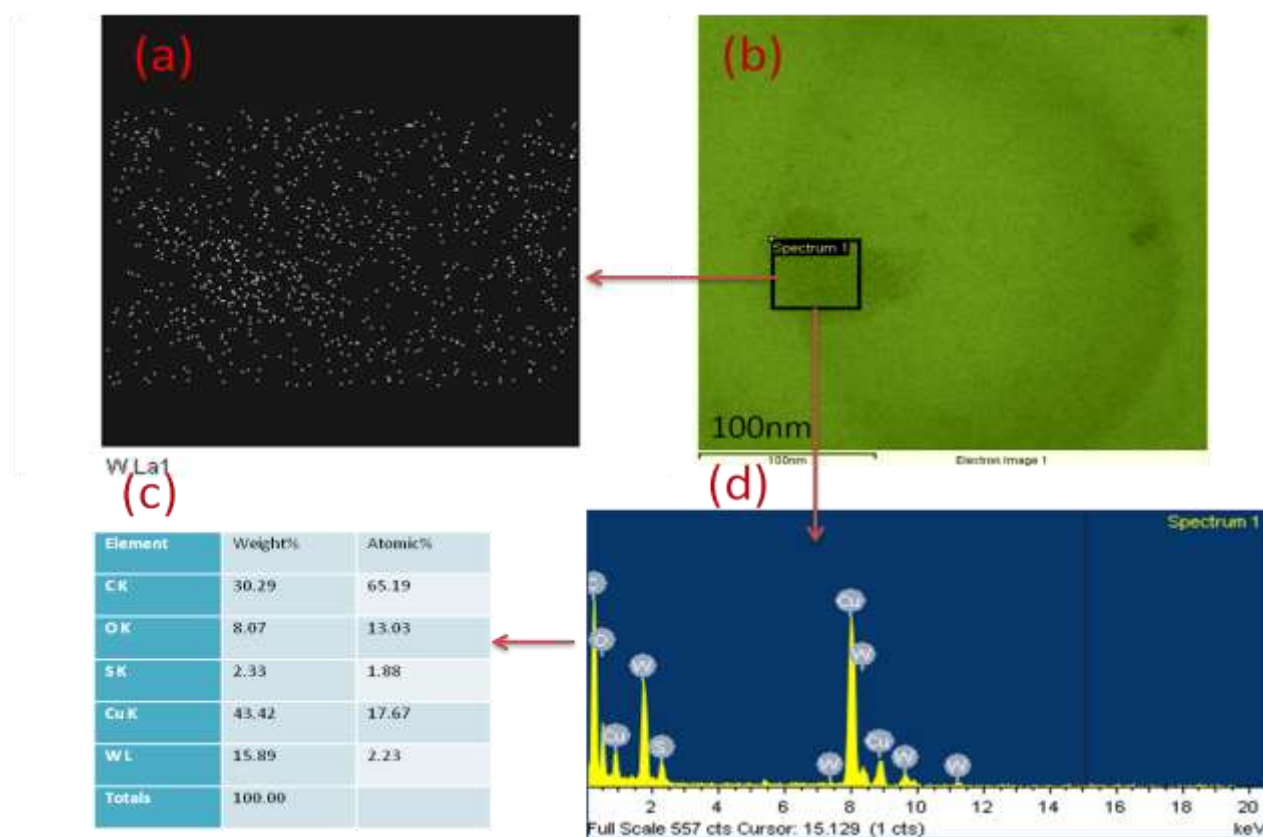
<b>Table S1</b>	PCE(%)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF(%)	R <sub>s</sub> (Ω-cm <sup>2</sup> )	R <sub>sh</sub> (Ω-cm <sup>2</sup> )
<b>PEDOT:PSS (I)</b>	4.08	7.61	0.835	64.3	2.99	2452
<b>PEDOT:PSS:WO<sub>x</sub>(I)</b>	4.63	8.51	0.823	66.1	1.88	3349
<b>PEDOT:PSS (5k)</b>	0.91	7.02	0.411	31.4	4.31	2.24
<b>PEDOT:PSS:WO<sub>x</sub> (5k)</b>	4.38	8.41	0.821	63.4	1.73	2180

**B.** AFM images of PEDOT:PSS and PEDOT:PSS:WO<sub>x</sub> layers. 5 μm x 5 μm scan size was used for characterization.



**Figure S1.** AFM images of (a) PEDOT:PSS, and (b) PEDOT:PSS:WO<sub>x</sub> (1:1). Films were coated on ITO substrate. AFM images were measured in air using Digital Instrument Multimode equipped with a nanoscope IIIa controller. The tapping mode atomic force microscopy (AFM) with 5 μm x 5 μm scan size was carried out for PEDOT:PSS and PEDOT:PSS:WO<sub>x</sub> layers. The films were coated on bare ITO. The root mean square (RMS) roughness of the PEDOT:PSS surface is 1.4 nm. After mixing with WO<sub>x</sub>, the RMS roughness increases to 1.5 nm

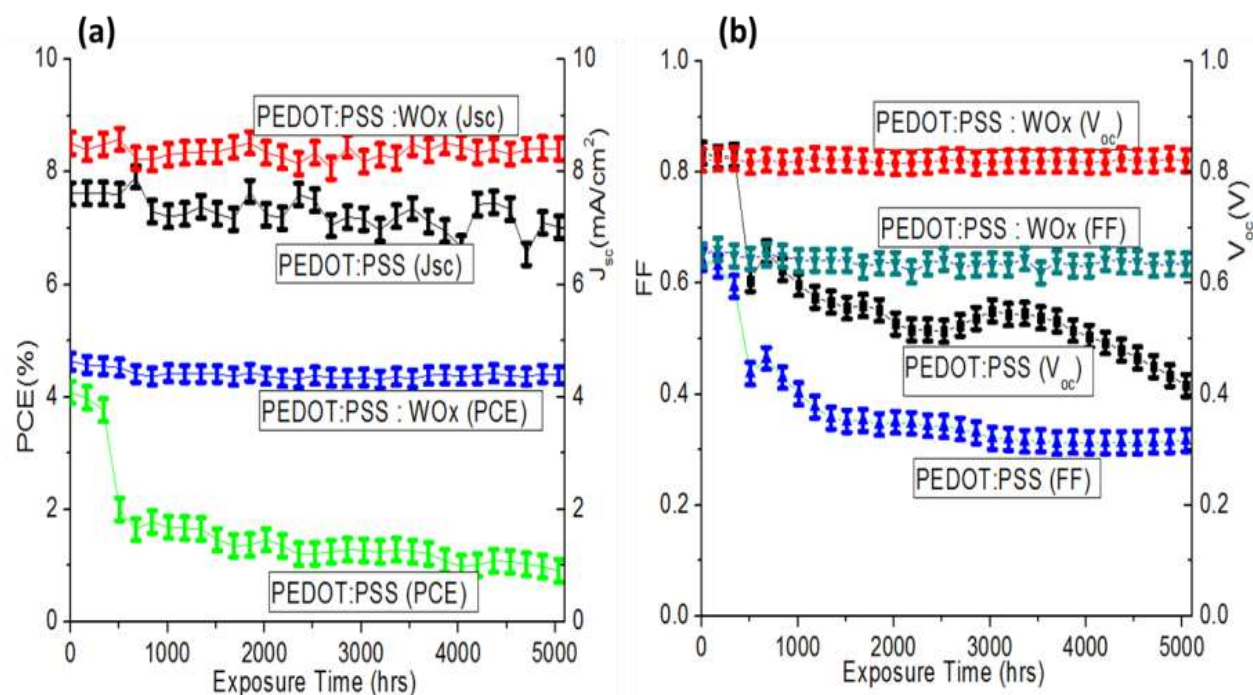
C. Elemental mapping, Energy Dispersive Spectroscopy (EDS), EDS composition of PEDOT:PSS:WO<sub>x</sub> to confirm WO<sub>x</sub> in the film.



**Figure S2.** TEM micrograph of PEDOT:PSS:WO<sub>x</sub> with elemental mapping of (a) chosen area in figure (b) while (c) shows EDS composition and (d) shows EDS peaks.

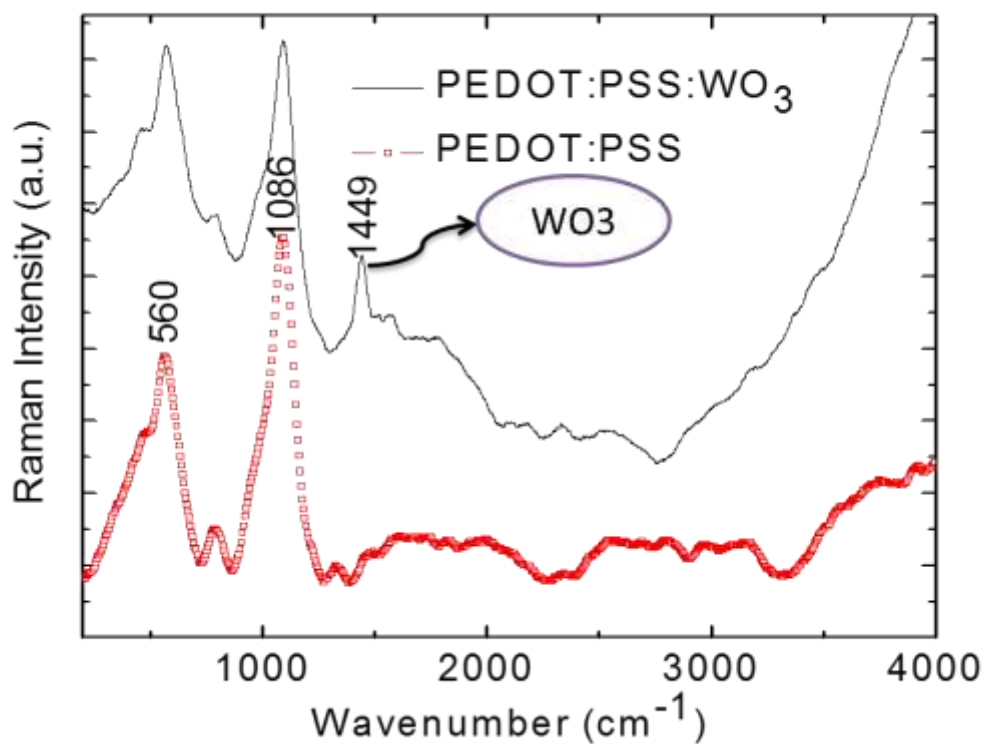
The film of PEDOT:PSS:WO<sub>x</sub> was deposited on carbon coated grid on bare ITO. Then, it was annealed at 130°C for 20 min. TEM, Model no JEM-2100F (JEOL) was used for characterization. The white dots shown in the figure (a) represents WO<sub>x</sub> particle in the film of rectangular area marked in figure (b). The EDS was measured by Oxford INCA with Mn K $\alpha$  source of 136eV. 43.4 % copper concentration shown in the table (c) belongs to grid while other compositions of the film are also noted in the table (c). The selected spectra of the films contains 15.89 wt% W. The peak intensities of all composition are marked in fig (d).

**D.** Long-term stability of the OPVs based on either PEDOT:PSS or PEDOT:PSS:WO<sub>x</sub> interfacial layer. The devices were stored in ambient air.



**Figure S3.** Long-term stability of the OPVs based on either PEDOT:PSS or PEDOT:PSS:WO<sub>x</sub> interfacial layer. The devices were stored in ambient air, (a) PCE and  $J_{sc}$ , (b)  $V_{oc}$  and FF. The main cause of degradation in PEDOT:PSS is drop in open circuit voltage and fill factor in comparison with short circuit current density.

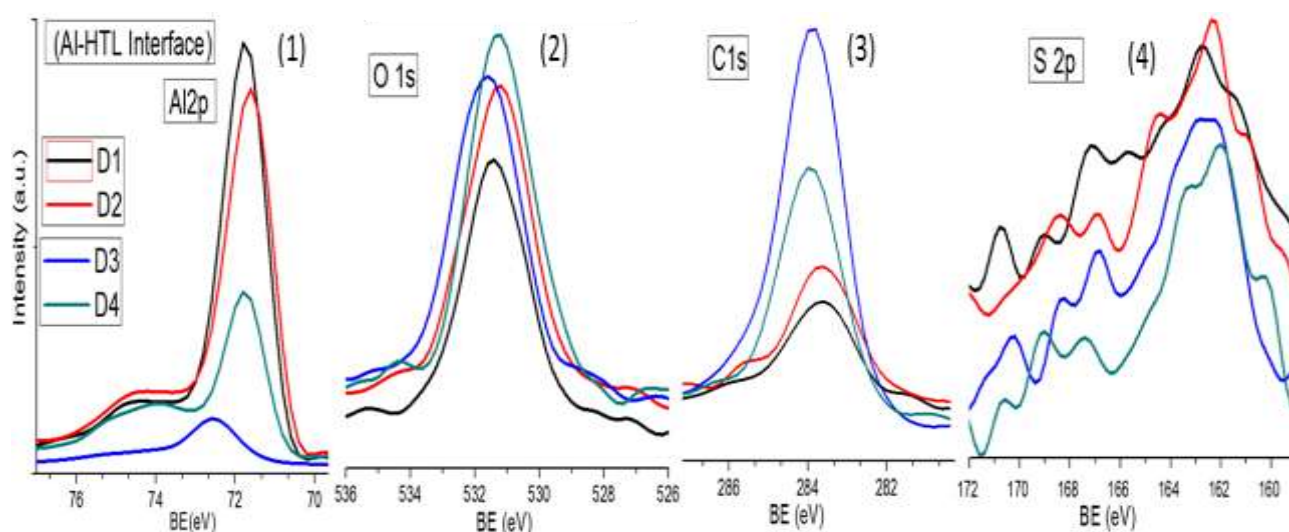
**E.** Raman spectra of PEDOT:PSS and PEDOT:PSS:WO<sub>x</sub> layers coated on ITO substrate.



**Figure S4.** Raman spectra of PEDOT:PSS and PEDOT:PSS:WO<sub>x</sub> layers coated on ITO substrate. Raman scattering experiments were performed at room temperature using a Raman spectrometer (LabRAMHR) with 514.5 nm line of an Ar laser. Additional peak arises at 1449cm<sup>-1</sup> corresponding to WO<sub>3</sub> in PEDOT:PSS.



### F. X-ray photoelectron spectroscopy (XPS) at PEDOT:PSS/PEDOT:PSS:WO<sub>x</sub> – Al interface.



**Figure S5.** X-ray photoelectron spectroscopy (XPS) of the various devices. OPV devices with only PEDOT:PSS buffer layer for Initial and after 5k hrs are represented as D1 and D3 respectively. And, OPV devices with PEDOT:PSS:WO<sub>x</sub> buffer layer for initial and after 5k h are represented as D2 and D4 respectively. Figure S5 represents (1) Al2p, (2) O1s, (3) C1s, (4) S2p at the Al-HTL interfaces for D1, D2, D3 and D4.

XPS measurements were performed in a PHI 5000 VersaProbe (Ulvac-PHI) with background pressure of  $6.7 \times 10^{-8}$  Pa using monochromatized Al K $\alpha$  ( $h\nu = 1486.6$  eV) anode (25 W, 15 kV). The spot size for XPS measurements was  $100 \mu\text{m} \times 100 \mu\text{m}$ . XPS was carried out with the Mg K $\alpha$  line ( $h\nu = 1253.6$  eV) with analyzer pass energy of 10 eV.

Al2p intensity in D3 (neat PEDOT:PSS after 5k h) is reduced due to high oxidation of interface. Sulfur is modified at the interface probably due to interaction with chemical present at the interface or oxidation.

More oxidation at interface leads to failure of OPVs.

**G. Table S2 : XPS peaks of WO<sub>x</sub> and sulfur.**

(a) W4f peaks of WO<sub>x</sub> at Al - PEDOT:PSS:WO<sub>x</sub> interface in eV.

Interface	W(7f/2, 5f/2)	WO <sub>2</sub> (7f/2, 5f/2)	WO <sub>3</sub> (7f/2, 5f/2)
D2 (Initial)	31.2/33.18	32.1/34.2	35.0/36.6
D4 (After 5k)	30.9/33.4	32.23/34.6	36.7/38.3
D6 Initial w/o Al		35.1/36.7	35.5/37.1

(b) W4f peaks of WO<sub>x</sub> in the bulk of PEDOT:PSS:WO<sub>x</sub> film in eV.

Bulk	W(7f/2, 5f/2)	WO <sub>2</sub> (7f/2, 5f/2)	WO <sub>3</sub> (7f/2, 5f/2)
D2 (Initial)	30.30/32.60	31.2/33.12	34.7/36.7
D4 (After 5k)	30.9/33.70	33.2/35.1	34.6/37.0
D6 Initial w/o Al		35.1/36.7	35.5/37.1

(c) S2p peak in PEDOT:PSS and PEDOT:PSS:WO<sub>x</sub> films in eV.

Bulk of HTL (S2p)	S2p in PEDOT	S2p in PSS	S <sub>PEDOT</sub> : S <sub>PSS</sub>
D1(Initial)-PEDOT:PSS(PP)	162.3/163.8	165.5/167.0	90.02 : 9.99
D2(Initial)- PEDOT:PSS:WO <sub>x</sub>	160.9/162.5	164.9	90.6 : 9.4
D3(5k) - PP	161.7/163.0	167.3/168.3	89.1 : 10.9
D4(5k)- PP:WO <sub>x</sub>	161.0/162.6	166.5	98.2 : 1.8
D5 Initial D1 w/o Al	162.8/163.9		
D6 Initial D2 w/o Al	162.8/163.9		



We report the peak intensities of  $\text{WO}_x$  and sulfur. The peaks are in doublet of W4f as we can see in table S2(a) and S2(b). W4f peaks can be noted as  $4f_{7/2}$  and  $4f_{5/2}$ . There were variation in peaks occurred at the interface of HTL-Al and bulk of HTL. It seems that  $\text{WO}_x$  is in much reduced states at interface than the bulk of PEDOT:PSS.

Table S2(c) represents the S2p peaks in the bulk of HTL, again S2p peaks should be in the doublet for PEDOT and PSS. If the doublet is missing then it implies that sulfur is in the charge state which indicates that the bond of sulfur is broken. This phenomenon was observed with  $\text{WO}_x$  doping.  $S_{\text{PEDOT}} : S_{\text{PSS}}$  represents the sulfur concentration in PEDOT and PSS respectively. Initially about 10% of sulfur in PSS was measured in with and without  $\text{WO}_x$  doped devices. But, sulfur in PSS gradually reduced to 1.8% only in  $\text{WO}_x$  devices however in only PEDOT:PSS, sulfur concentration seems to be unchanged.

**H.** TOF SIMS images for negative ion of C and sulfur in initial(I) and after 5000(5k) h devices with PEDOT:PSS and PEDOT:PSS:WO<sub>x</sub> buffer layer

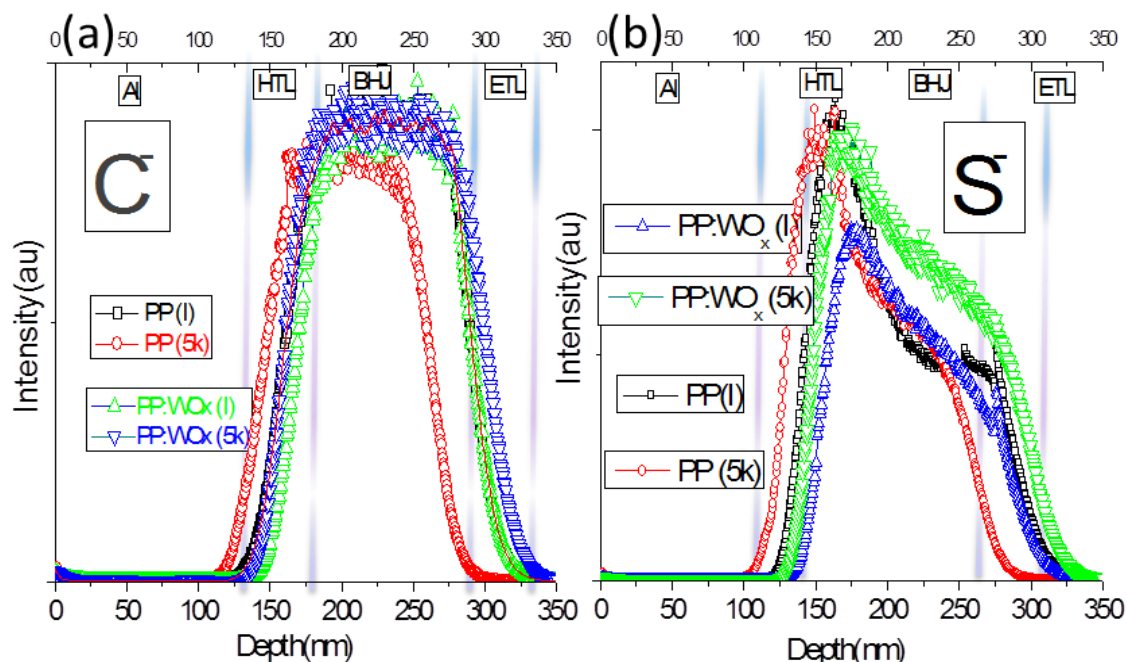


Figure S6 TOF SIMS images of negative ion (a) for C and (b) for sulfur in initial (I) and after 5000(5k) h devices with PEDOT:PSS (PP) and PEDOT:PSS:WO<sub>x</sub> (PP:WO<sub>x</sub>) buffer layer.

TOF-SIM was measured with IONTOF made TOFSIMS5 version. Bi<sup>+</sup> ion gun with 25k eV energy, 1pA current were used as analysis parameters to analysis 0.25 mm<sup>2</sup> areas. Cs<sup>+</sup> ion gun with 3keV energy and 40nA current were used as sputter parameters to analyze 4 mm<sup>2</sup> areas.

The carbon is reduced with aging in PEDOT:PSS (red) probably loss of carbon with time. However, carbon in BHJ shows similar behavior. The variation in sulfur in the whole device especially at the interface can be seen in with and without WO<sub>x</sub>.