# Supplementary Information

for

# Dedoping Induced Interfacial instability of Poly(ethylene imine)s treated PEDOT:PSS as Low-Work-Function Electrodes

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Figure S1. (a) Work function of PH1000 film with rinsing and modification by PEIx, (b)
Typical J-V characteristic of slot die printed devices with cathode of PH1000 modified by PEIx,
rinsing: before modification, PH1000 has been rinsed by IPA; WO rinsing: before modification,
PH1000 layer has not been rinsed. (c) The JV characteristic of devices based on PEDOT:
PSS/PEI electrode, exposure time refer to the duration time before the active layer deposition,
the corresponding performance parameters were summarized in the table 1.

The extracted and accumulated PSS can be removed through IPA rinsing. Clearly, removing free PSS has effects on the work function of PEDOT: PSS electrodes. As shown in Figure S1, the

unwashed PEDOT: PSS has a WF of 5.01 eV. After removal of free PSS with IPA, the WF decreased to 4.93 eV. It has been suggested that PSS can functions as a dipole layer on the PEDOT: PSS surface<sup>1</sup>, which increase the WF comparing to the bulk. The decrease in WF after rinsing can therefore be understood as the removal of PSS on the surface, which reduces the dipole effect. Figure S 1(b) shows two typical JV curve of device with rinsing and without rinsing. The devices fabricated with PEDOT:PSS electrode film without rinsing shows a lower Voc, which is only 0.3V, and a higher reverse injection current compared to the device based on the PEDOT:PSS film with rinsing. This results indicates a big injection barrier in the device, which is consistent with work function measurement results.

#### The IRRAS method

In the infrared reflection-absorption (IRRAS) method, the IR beam passes twice through the sample, at an angle of incidence (as measured from the surface normal) of typically over  $85^\circ$ , see Figure S2a. The 180° phase shift of the s-component of the incident wave cancels the s-component near the metal surface, whereas a shift near 90° for the p-component causes constructive interference, and acts to amplify the component. This has a consequence, that only vibrational modes with a component of the transition dipole moment parallel to the surface normal can be excited by the incident field. This is known as the "surface selection rule". A polarization modulation (PM) technique is employed to mitigate the spectral disturbances caused by H<sub>2</sub>O and CO<sub>2</sub>, and the setup is shown in Figure S2b.



**Figure S2**. (a) Schematic of the infrared reflection-absorption spectroscopy configuration (IRRAS). (b) Schematic of a PM-IRRAS setup. (c) PCA score plot for IR data in the range 1300 to 1100 cm<sup>-1</sup> of PEDOT: PSS films coated with different PEIx thicknesses (obtained by PCA analysis of the data in Figure 2 in the main text). PC1 = 61.9%, PC2 = 27.2%. (d) PCA score plot for IR data in the range 1600 to 1450 cm<sup>-1</sup>, PC1 = 62.7%, PC2 = 21.1%.



Figure S3 Absorbance for (a) PH1000 film and (b) 4083 film with a top layer of PEI from 0.1wt.% and 0.5wt.%, both is spin-coated at 2000 rpm



**Figure S4**. Conductivity and Seebeck coefficient for PH1000 film with a top layer of PEIx from varying concentrations. The dots represent regarding properties of a 5 wt.% PEIx layer on the bottom of PH1000 film.



**Figure S5.** Secondary-electron cut-off region in UPS spectra of pristine, half reduced and fully reduced PEDOT:tosylate, and work function is listed along with the spectrum respectively.

#### PEIx effects on the doped and dedoped PEDOT:Tos

Tosylate can be easily removed and re-introduced,<sup>2</sup> which makes this material suitable for oxidation state studies. As shown in Figure 4 (a), pristine, i.e., oxidized PEDOT:tos, shows an increasing absorption from visible to near IR (NIR) wavelength range, where the absorption around 900 nm and 1200 nm is attributed to the formation of polarons and bipolarons on the charged PEDOT chain, respectively.<sup>3-4</sup>As shown in Figure 4a of the main text, the chemical reduction of PEDOT:tos is reversible. After being immersed in *p*-toluenesulfonic acid solution, the characteristic absorption of doped PEDOT was restored. The de-doping has immediate effects on the conductivity. The conductivity of pristine PEDOT: tos is around 600 S/cm. Dedoped PEDOT has a reduced conductivity of 6 S/cm. With decreased concentration of SO<sub>3</sub><sup>-</sup> groups in the film, coating of PEIx on PEDOT:tos shows even more pronounced color shifting effects. Figure S6 shows an example of 20 nm PEIx coating turning the sky-blue film into purple. The absorption increase around 600 nm and decrease around 800 nm strongly suggest that PEIx caused dedoping of PEDOT:tos.



Pristine +10 nm peie x2

**Figure S6.** Left film is a pristine PEDOT:tosylate film, right film: PEDOT:tosylate coated with PEIE and annealing under 160° C.



**Figure S7**. The molecular structure of the active layer materials, they are (poly[[2,3-bis(3-octyloxyphenyl)-5,8-quinoxalinediyl]-2,5-thiophenediyl])(TQ1 )and PC<sub>61</sub>BM. TQ1 is firstly reported in ref (Adv. Mater., 2010, 22, 5240–5244.)

Figure S8 shows the surface potential of PH1000 with PEIx coating after exposure to ambient conditions. PEIx induces a surface potential decrease on PH1000, which is consistent with our results in Figure 4 and Figure S1. When the films are exposed in the ambient, both potential decreases. The faster decrease was observed on PH1000/PEIx. We conclude that long term exposure to ambient conditions are detrimental to the surface potential of both films, which may be due to the hydrophilic property of PSS in PH1000, and/or to the unstable deduced state of PH1000.



Figure S8. The stability of surface potential of PH1000 and PH1000/PEIx.

Figure S9 shows the JV characteristic of devices with PEIx modified PEDOT:PSS electrodes, using a lamination technique. We carried out all the processes in the ambient condition at room temperature. The PEDOT:PSS electrodes are first coated with PEIx layer. This PEIx modified electrodes were dried at 60  $^{\circ}$ C for from 0 to 30 minutes. The corresponding performance parameters are summarized in Table S1.



**Figure S9.** The JV characteristic of devices with PEIx modified PEDOT:PSS electrodes, and this electrodes were dried at 60  $^{\circ}$ C for from 0 to 30 minutes in air.

Performances of device based on PEDOT/PEDOT electrodes

As discussed in the experimental part, the OPVs in Table 1 are fabricated using a lamination technique, which was reported in Reference [5]. All the fabrication processes were finished manually under the ambient conditions. Due to this, the size and geometry of the active area is not strictly defined. We therefore note that the  $J_{SC}$  reported in Table 1 does not accurately represent the device performance, and the variation should be treated with caution, hence the PCE.

Table S1 Performance parameters of devices based on PEDOT: PSS/PEI electrode, exposure time refer to the duration time before the active layer deposition (this active layer is TQ1:PC<sub>61</sub>BM). PEDOT: PSS/PEI layer are kept in heating under 60°C before active layer coating. All process steps were carried out in air.

Exposure time	$V_{OC}(V)$	$J_{SC}(mA/cm^2)$	PCE (%)	FF
reference	0.739	7.4	1.70	0.31
10 mins	0.71	4.73	1.11	0.33
30 mins	0.615	4.96	0.80	0.26

**Table S2.** Performance parameters of devices based on PEDOT: PSS/PEI electrode, exposure

 time refer to the duration time before the active layer deposition. The active layer is

PTB7:PC<sub>61</sub>BM. Top electrode is  $MoO_3/Ag$  with a defined area of 0.04 cm<sup>2</sup>. The performance

Exposure time	V <sub>OC</sub> (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	PCE (%)	FF
reference	0.70	14.13	2.95	0.30
15 mins	0.68	13.11	3.33	0.34
30 mins	0.64	13.00	1.87	0.23

parameters are average value based on four cells.

PEDOT: PSS	Conductivity	Transmittance at 500 nm(%)	Thickness (nm)
PH1000	~300 S/cm	~90	~200 nm
PH 1000R	~300 S/cm	~90	~200 nm
4083	0.0001 S/cm	~98	~40nm

Table S3. The conductivity, transmittance and thickness of the all three kinds of PEDOT: PSS

## Conductivity of 4083 + PEI.

Due to the low conductivity of 4083, resistance is difficultly measured with lateral device structure. Therefore, device structure is constructed to be ITO/4083/PEI/Ag. PEI was spin-coated from its 0.1 wt.% solution. The resistances were obtained by fitting the J-V curve of devices with Ohm's Law from -0.5 V to 0.5 V.

Table S4. The			conductivity of
4083 coated with	Film	Conductivity (mS/cm)	PEI or not
	Without PEI	4.45	
	With ~5 nm PEI	4.98	
	0.1 wt.% 2000rpm		
	With ~40 nm PEI	1.78	-
	0.1 wt.% 500rpm		
_	With ~10 nm PEI	2.78	
_	0.5 wt.% 2000rpm		



**Figure S10.** The JV characteristic of devices of ITO/4083/PEI/Ag from -0.5 V to 0.5 V, with the fitting curves

## References:

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