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Supporting Information

Self-doped Conjugated Polyelectrolyte with Tunable Work Function for Efficient Hole Transport in Polymer Solar Cells

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PEDOT-S synthesis and purification

PEDOT-S was synthesized according to the procedure developed by Roger H. Karlsson et al.[28]

The synthesis of PEDOTS is based on an oxidative polymerization of EDOTS (Heraeus) in water using as oxidants a catalytic amount of iron (III) chloride and sodium peroxosulfate (both were purchased from Sigma Aldrich) ([M/O] = 0.5) at room temperature for 4 hours. Instantaneously upon addition of the oxidants the EDOTS solution turns to deep blue.

After 4h the reaction is quenched and a Dowex (Sigma Aldrich) ion exchange resin, that behaves like an acid without counter ions, is used to remove the left iron. Finally, the obtained product is dialyzed against deionized water for 48 hours using a 3000 g/mol cutoff membrane and freeze-dried.

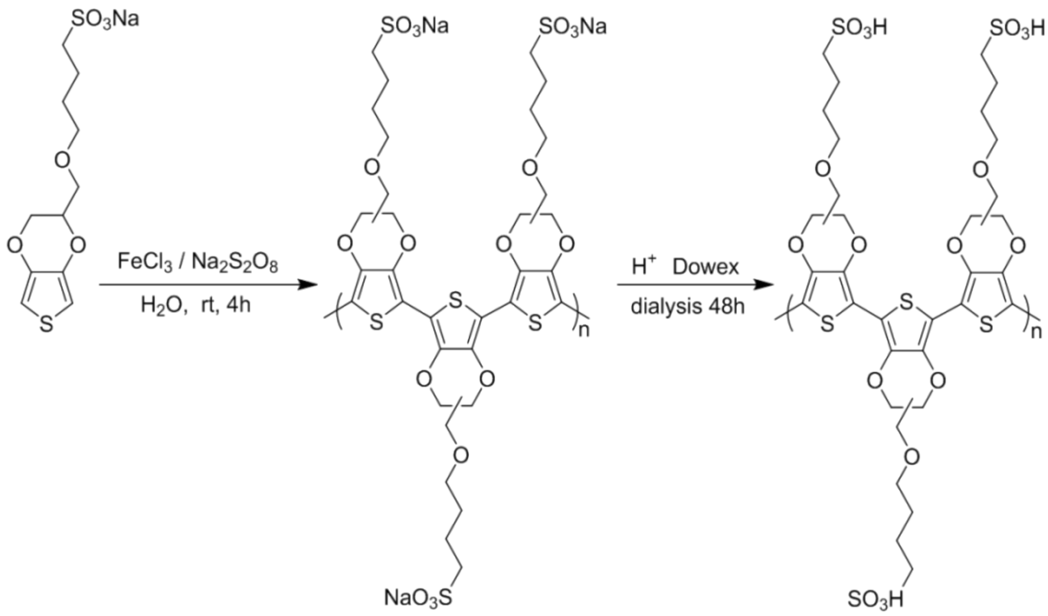

Figure S1. Synthesis route of PEDOT-S

Table S1. Performance parameters of the devices base on P3TI:$PC_{71}BM$ under $100mW\cdot cm^{-2}$ AM1.5G solar simulation light. The parameters are average of 6 devices' data.

HTL	Jsc($mA\cdot cm^{-2}$)	Voc(V)	PCE(%)	FF(%)
PEDOT-S	12.80±0.08	0.73±0.00	6.7±0.0	72±2
PEDOT:PSS 4083	12.68±0.29	0.73±0.00	5.5±0.2	59±3

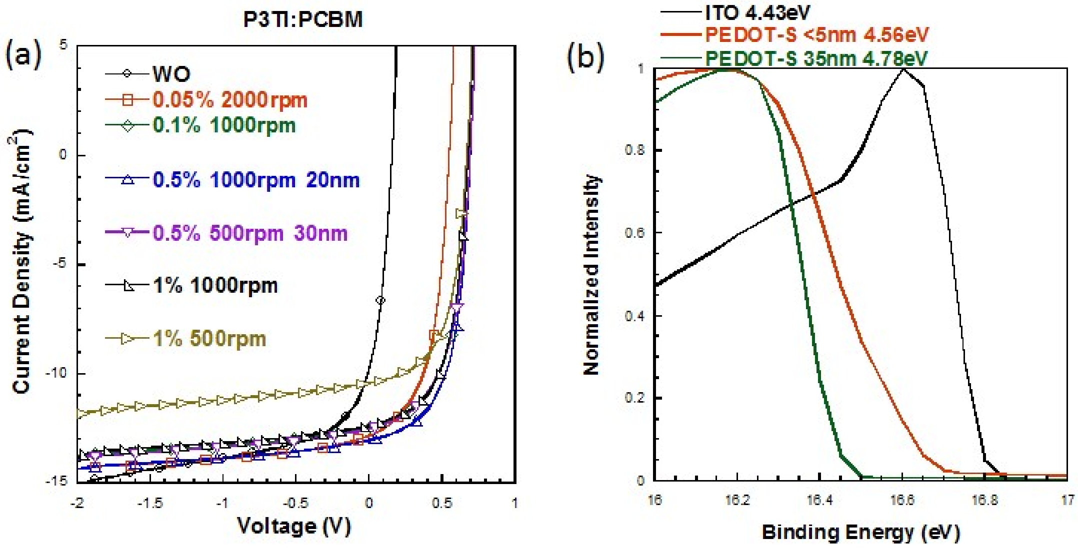

Figure S2. (a) JV-Curves for P3TI:$PC_{71}BM$ device with different thickness of PEDOT-S, under 100mW·cm^{-2} AM1.5G solar simulation light (b) UPS spectra showing the the secondary electron cutoff energy onset of bare ITO, with ~5nm and ~30nm thick PEDOT-S film.

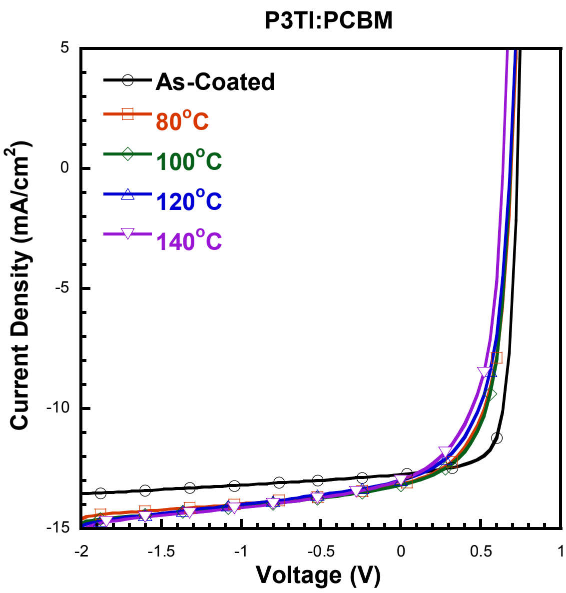

Figure S3. JV-Curves for P3TI:$PC_{71}BM$ device with 25nm thick PEDOT-S, the PEDOT-S films are heated at different temperatures for 10mins in air.

Table S2. Performance parameters extracted from the JV curves in figure S3.

Condition	Jsc(mA·cm^{-2})	Voc(V)	PCE(%)	FF(%)
As-Coated	**12.74**	**0.73**	**6.73**	**0.73**
80℃	**13.16**	**0.69**	**5.22**	**0.57**
100℃	**13.18**	**0.69**	**5.36**	**0.59**
120℃	**12.99**	**0.68**	**4.90**	**0.55**
140℃	**12.99**	**0.64**	**4.52**	**0.54**

Geometry induced decrease of Voc

Our device geometry is the widely used "figure" geometry, whose active area is defined by the overlapping of ITO and the aluminum electrodes, shown in Figure S3 (a), which is 0.046cm^2. We utilize a photocurrent imaging technique to map the real active area, and find that the PEDOT-S device has additional active area, shown in figure (c), more than PEDOT:PSS, in figure (d) as reference. The PEDOT-S can serve as electrode on ITO to a certain degree. In order to characterize an accurate photocurrent density, we fixed light exposure area to be a rectangle with area of 0. 046cm^2, thus the additional active area A2 was covered.

In a simple equivalent circuit simulation for PEDOT-S device, as the device active are is separated into two parts A1 and A2, A1 is with same size of PEDOT:PSS device, and A2 is additional active area marked in Figure S3 (a). The equivalent circuit is shown in Figure S3(c), I_L is the current through the A1, I_D is the current through the additional active area A2, which is covered and unexposed to the light. Iph is the current generated in A1. I is the output current, and Rs is the series resistance in device. The simulated J-V characterization give decreased Voc and Jsc when the ratio A2/A1 increases. When the PEDOT-S thickness increase, the sheet resistance will decrease, as the result, the additional active area will be larger. This is the reason why the Voc and Jsc decrease when the HTL thickness increases.

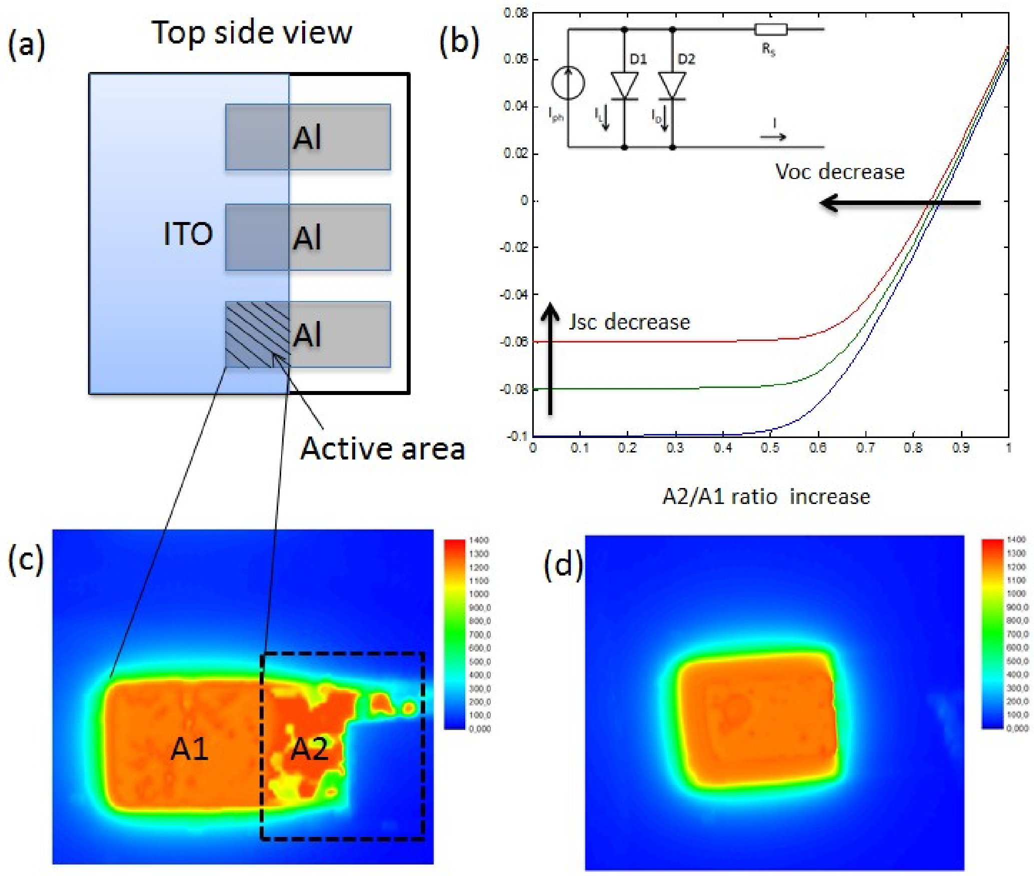

Figure S4. (a) Device geometry. (b) The equivalent circuit and simulated J-V characterization. Photocurrent image (scale: 6000× 6000um^2) of (c) PEDOT-S device and (d) PEDOT:PSS device,

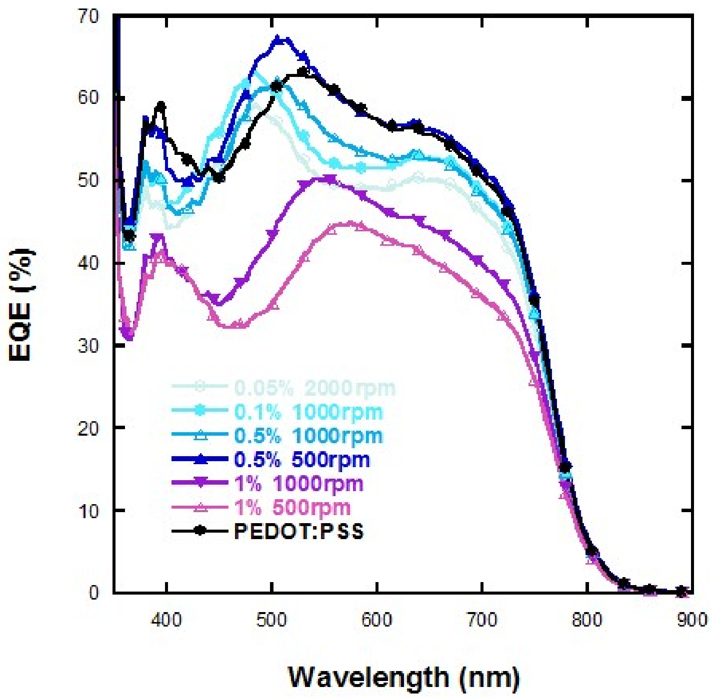

Figure S5. EQE spectra of the devices based on P3TI:$PC_{71}BM$ with different thickness of PEDOT-S

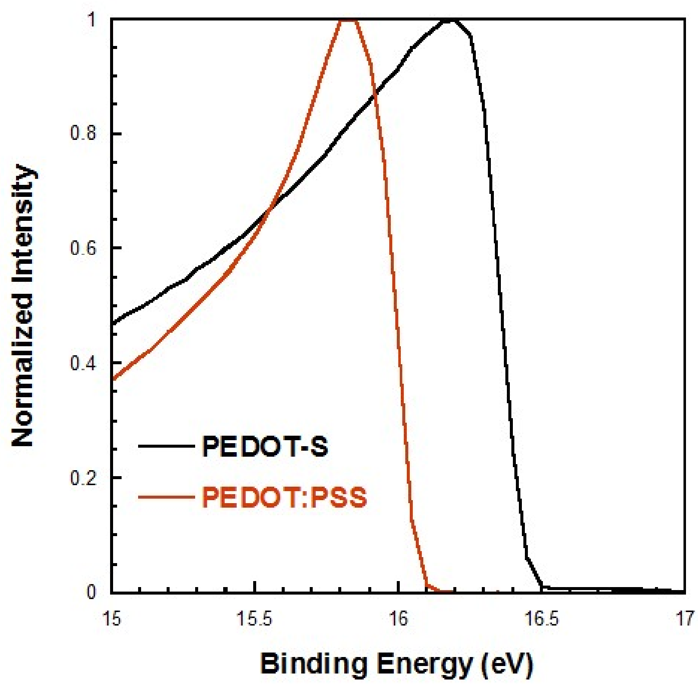

Figure S6. UPS spectra of ~35nm PEDOT-S and ~40nm PEDOT:PSS, their work functions are calculated to be -4.78eV and -5.15eV.

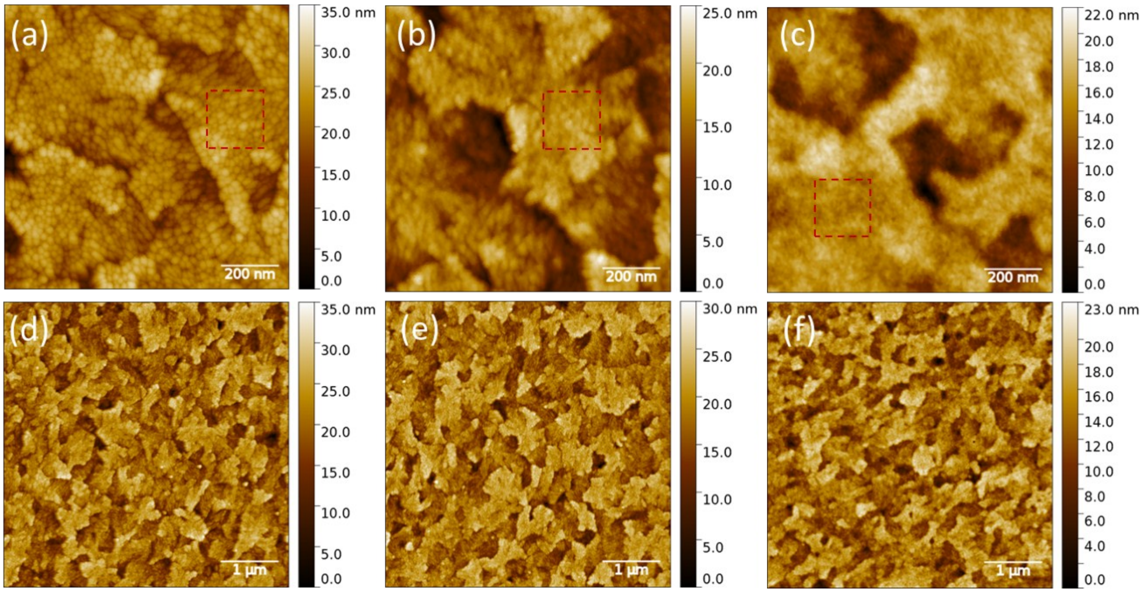

Figure S7. Tapping-mode AFM images of (a, d) bare ITO, (b, e) ~10 nm and (c, f) ~35 nm thin PEDOT-S films. The red squares in (a-c) mark the regions where the roughness measurements reported in Table S2 have been performed.

Table S3. Root mean square roughness (R_{RMS}) of the films of Figure S7, measured on delarge (5x5 μm^2) and small (200x200 nm^2) areas.

Area	R_{RMS}		
	ITO	PEDOT-S 10 nm on ITO	PEDOT-S 35 nm on ITO
5x5 μm^2	4.21 nm	3.69 nm	3.53 nm
200x200 nm^2	1.85 nm	1.41 nm	1.11 nm

Table S4. In-plane conductivity for PEDOT-S film with different temperature annealing.

Annealing Temperature and Time	Conductivity ($S \cdot cm^{-1}$)
As-deposited	0.69
80°C for 10mins	0.87
100°C for 10mins	1.02
120°C for 10mins	1.07
120°C for 30mins	1.06
140°C for 10mins	1.03