

Supporting Information

Disassembly of Micelles to Impart Donor and Acceptor Gradation to Enhance Organic Solar Cell Efficiency

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1. Solar cell device fabrication procedure

Polymer bulk heterojunction solar cells were fabricated by the following procedure. The ITO substrate was cleaned with detergent, acetone and i-propyl alcohol for 10min and subsequently dried in an oven for 12hrs. Highly conducting Poly (3,4 ethylenedioxy thiophene):Polystyrene sulfonate (PEDOT:PSS) hole transport layer for controlled devices, SDS disassembled oxidized PEDOT films were used as HTL for other devices. The HTL layers were heat treated for removing residual solvents and transferred into the Glove box. On top of these HTL layers the active layer (P3HT:PCBM) blend was spin coated at 800rpm with various blend ratios. Before spinning the photoactive layers, few drops of acetonitrile were dropped on top of the PEDOT-SDS layer. The active layer was then annealed at 130°C for 10min and subsequently the substrates were pumped inside the thermal evaporating unit (1×10^{-6} mbar) for evaporating Al top electrode. The active area of the devices were found to be 0.08cm².

2. Transistor device fabrication procedure

The bottom gate bottom contact field effect transistors (FET) substrates were procured from Fraunhofer microelectronic institute. Substrates consists SiO₂ dielectrics with doped Si as a gate with gold source, drain electrodes. The devices were cleaned with acetone and i-propyl alcohol and then dried. As such cleaned substrates were used as a controlled devices for hydrophilic surface, on the other hand, Octadecyl trichloro silane (OTS) modified devices were used as a hydrophobic surface. OTS treatment was done inside the Glove box using 2wt% chloroform solution of OTS for 30min. Then the substrates were washed in chloroform to remove poorly adsorbed silanes and then annealed for 10min at 120°C. On top of these hydrophilic and hydrophobic FET substrates, the P3HT:PCBM blend solutions were spun at 800rpm and the output and transfer characteristics were measured using Keithley 4200 SCS Parameter Analyzer.

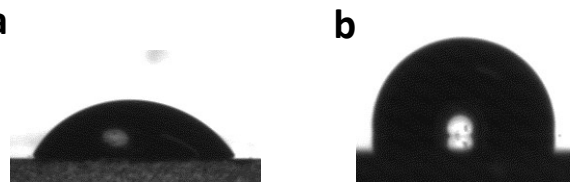


Figure S1. Water drop contact angle for PEDOT:PSS (a) and P3HT (b) films.

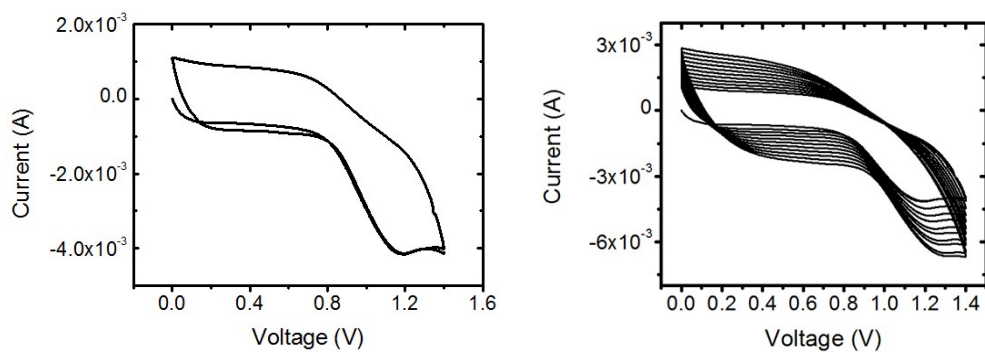


Figure S2. Cyclic voltammogram for EDOT electro polymerization.

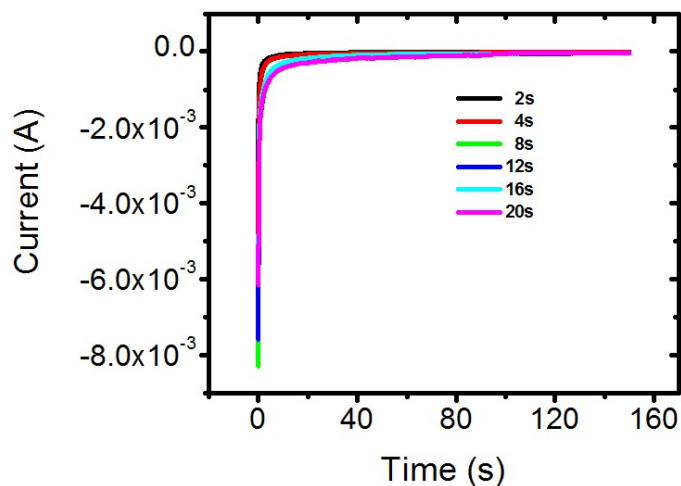


Figure S3. Chronoamperometry growth of PEDOT polymer at constant potential with different time.

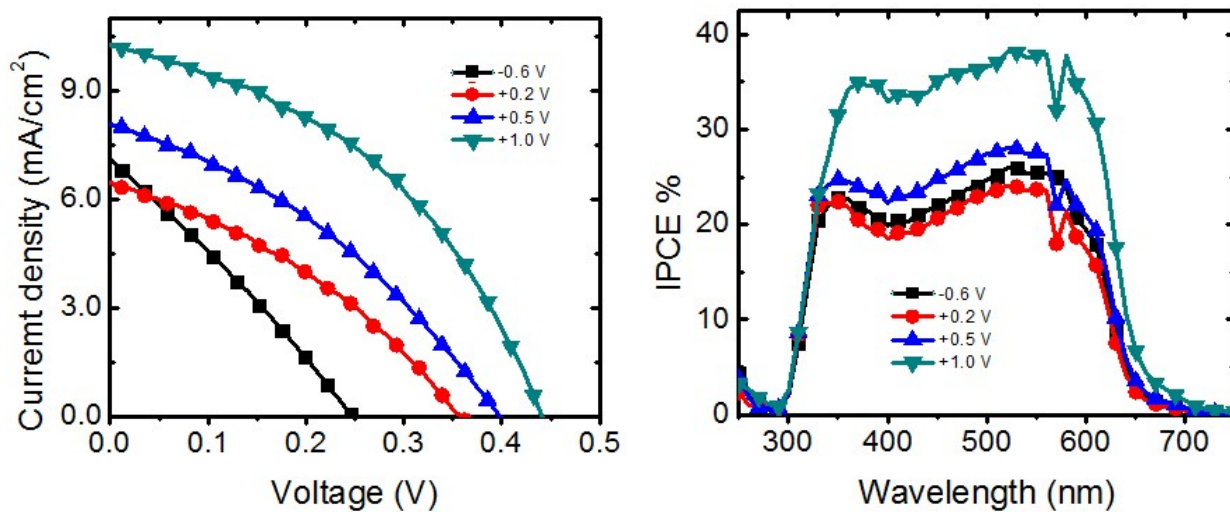


Figure S4. J-V characteristics and corresponding IPCE spectrum for SDS treated PEDOT (PEDOT:SDS) HTL films with different oxidation potentials.

Table S1. Characteristics of P3HT:PCBM solar cells with PEDOT:SDS HTL films with different applied potential.

S.No	PEDOT Ox. Potential (V)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF %	IPCE %	Eff. %
1	-0.6	0.25	7.1	25.5	25.1	0.48
2	+0.2	0.35	6.4	35.5	24.3	0.80
3	+0.5	0.41	8.7	34.2	27.1	1.20
4	+1.0	0.43	10.3	43.2	38.2	2.30

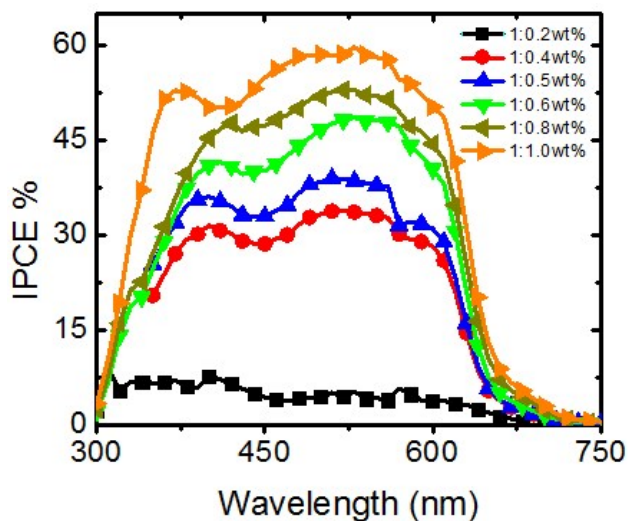
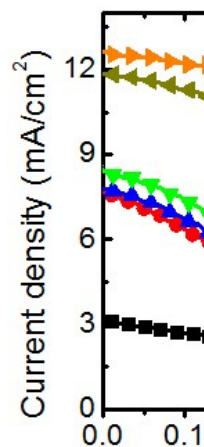


Figure S5. J-V characteristics and corresponding IPCE spectrum of PEDOT:PSS HTL films with different ratio of P3HT:PCBM.

Table S2. Characteristics of P3HT:PCBM solar cells with PEDOT:PSS HTL films with different ratio of P3HT:PCBM.

S. No	P3HT:PCBM weight ratio (wt%)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF %	IPCE %	η %
1	1.0:0.2	0.32	3.2	42.0	4.0	0.44
2	1.0:0.4	0.34	7.6	35.0	32.0	0.88
3	1.0:0.5	0.34	7.9	37.0	36.0	0.93
4	1.0:0.6	0.33	8.4	44.0	46.0	1.05
5	1.0:0.8	0.42	11.9	48.0	50.0	2.64
6	1.0:1.0	0.54	12.2	52.0	59.0	3.66

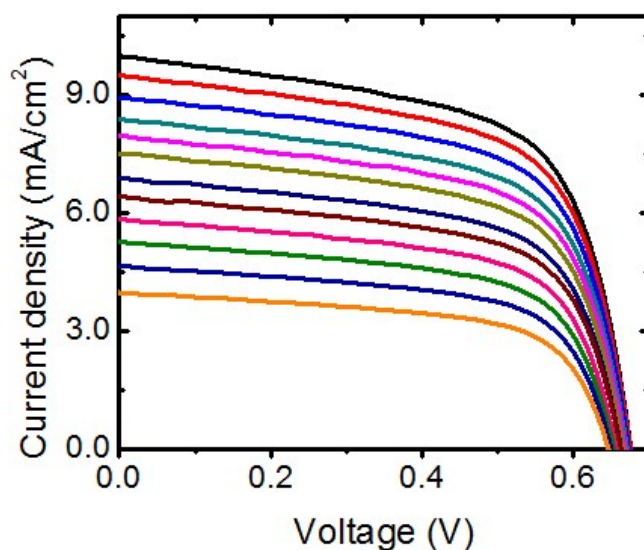


Figure S6. J-V characteristics and corresponding IPCE spectrum of PEDOT:SDS HTL films with light intensity (50mW/cm² to 100Mw/cm²).

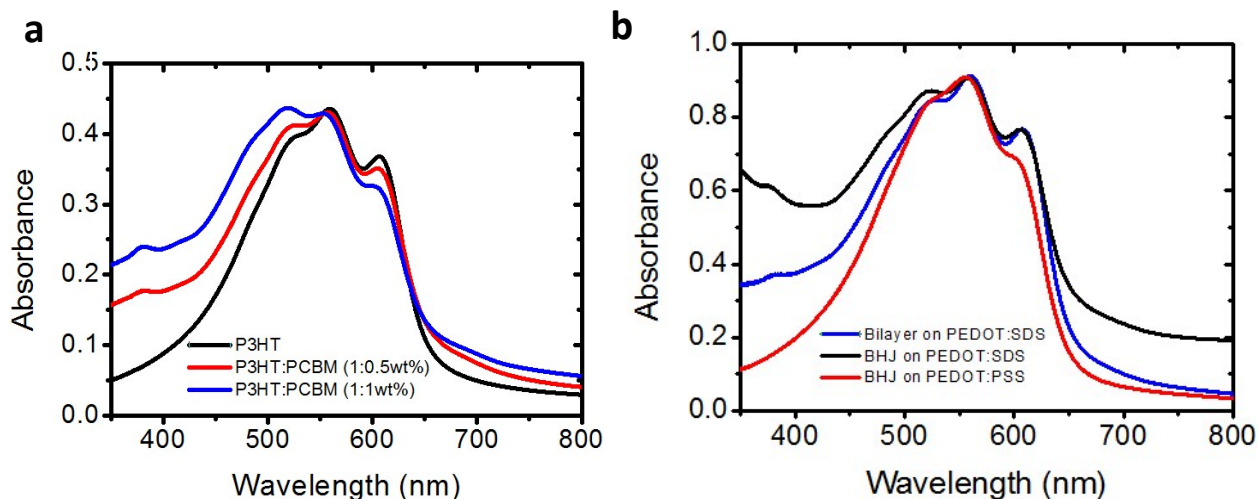


Figure S7. UV-Visible spectrum shows the band at 610nm for different ratio of P3HT:PCBM (a) and on various HTL surfaces (b).

XRD and XPS analysis:

Thin film XRD was used to study the packing distance between the P3HT interlayers in the BHJ layer. For P3HT alone, the distance between interlayers is 1.52 nm, which is in agreement with the reported values (Figure 3a).^[1] The distance increased to 1.55 nm for P3HT:PCBM (wt% 1:1), which further increased to 1.62 nm for P3HT:PCBM (wt% 1:0.5) (Figure S8-a and S8-b). At higher concentration of PCBM, highly intermixed P3HT:PCBM phases originate. The intermixing of phases doesn't facilitate charge transport properties.^[2, 3] Although, the interlayer distance is smaller in case of increased PCBM concentration, the charge transport properties are not improved due to this intermixing. This result in the decreased PCE for cells fabricated with P3HT-PCBM (wt% 1:1). However, despite the increased interlayer distance in case of P3HT:PCBM (wt% 1:0.5), the charge transport is better due to the non intermixing of P3HT:PCBM phases. The increased charge transport improves the FF and the PCE. X-ray Photoelectron Spectroscopy is a useful technique to understand the locations of molecules with different atoms. In the current experiments, the donor polymer has sulfur atom, which is not present in

the acceptor PCBM.^[4, 5] Similarly, the PCBM has very high percentage of carbon compared to other elements. Therefore, by monitoring sulfur and carbon, the gradation of P3HT and PCBM can be studied. On PEDOT-SDS surface, P3HT:PCBM blend film was prepared by strictly following the procedure used for the preparation of BHJ cells. The top surface (the surface farther from the PEDOT-SDS) was probed using XPS.

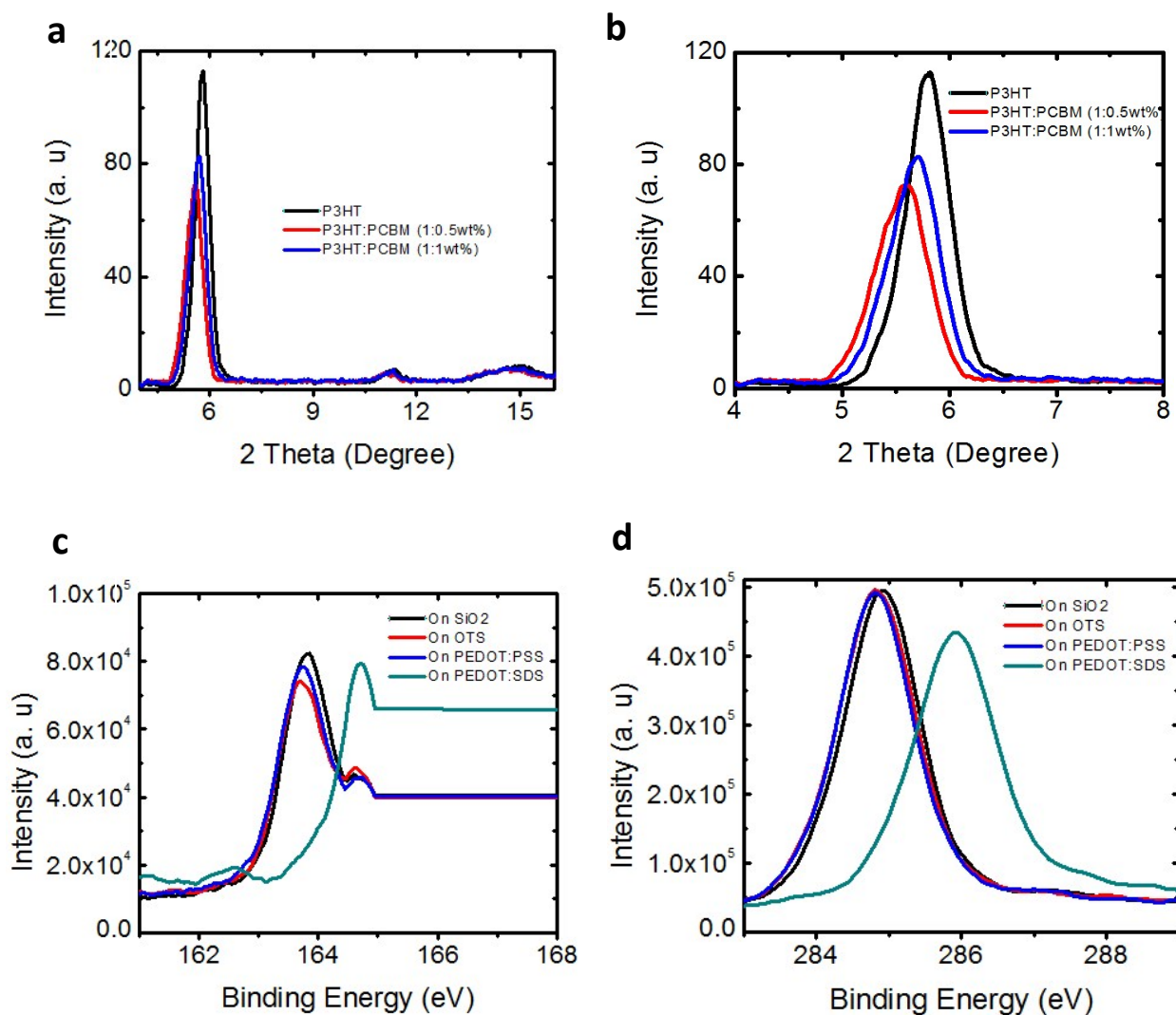


Figure S8. Powder XRD pattern of P3HT and its blends (a and b). XPS spectra of P3HT-PCBM (1:0.5%) films prepared on top of hydrophilic and hydrophobic substrates (c and d).

Peaks are observed at 164.5 eV and 286 eV for sulfur and carbon, respectively (Figure S8-c and S8-d). The ratio of the intensity of these two peaks provides information about the presence of PCBM on the surface. The ratio was found to be 0.09. This indicates the increased presence of carbon (PCBM) on the top surface. This is likely due to preferential crystallization of P3HT near the PEDOT-SDS surface due to the presence of alkyl chain of SDS. On the other hand, the ratio was found to be 0.148 for films prepared using P3HT:PCBM on top of PEDOT-PSS HTL layer. This indicates the presence of significantly higher amount of P3HT farther from the HTL layer. While fabricating the BHJ cell, aluminum is evaporated on top of the active layer. In such a device architecture, the higher quantity of PCBM will be in touch with aluminum while using PEDOT- SDS as HTL layer. This results in improved charge injection to the aluminum electrode. On the other hand, the P3HT is also in contact with aluminum while using PEDOT-PSS as HTL layer. This leads to undesirable charge injection that decreases the FF as well as PCE. The experiments so far have clearly indicated that the gradation of P3HT and PCBM occur if the PEDOT-SDS is used as HTL layer. In our experiments, the long alkyl chain of SDS protrudes from the PEDOT surface and imparts hydrophobicity and surface energy variation that is desired

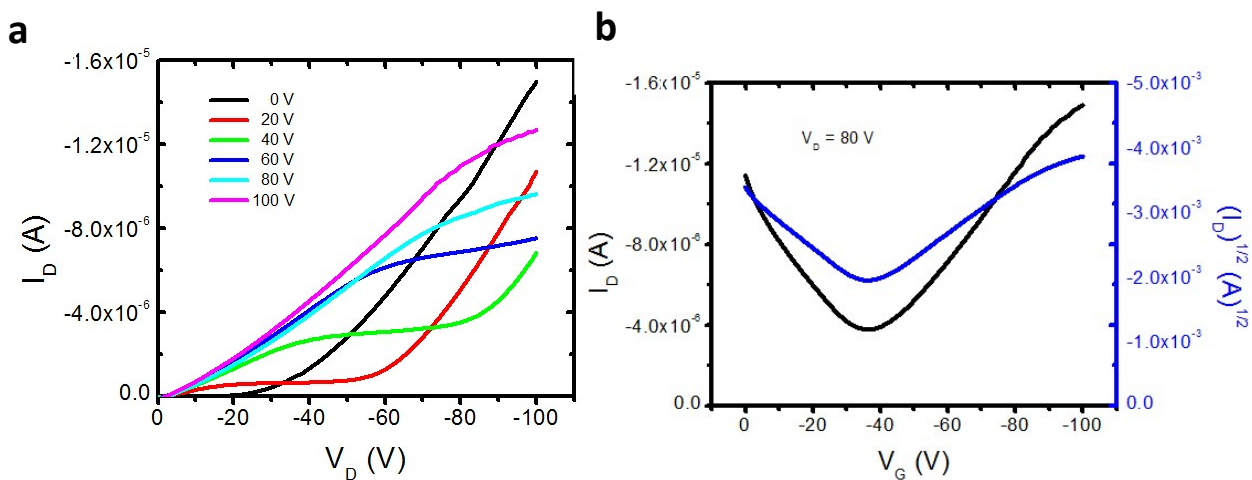


Figure S9. Output characteristics (a) and transfer characteristics (b) of P3HT:PCBM blend with SiO_2 hydrophilic surface (p mode).

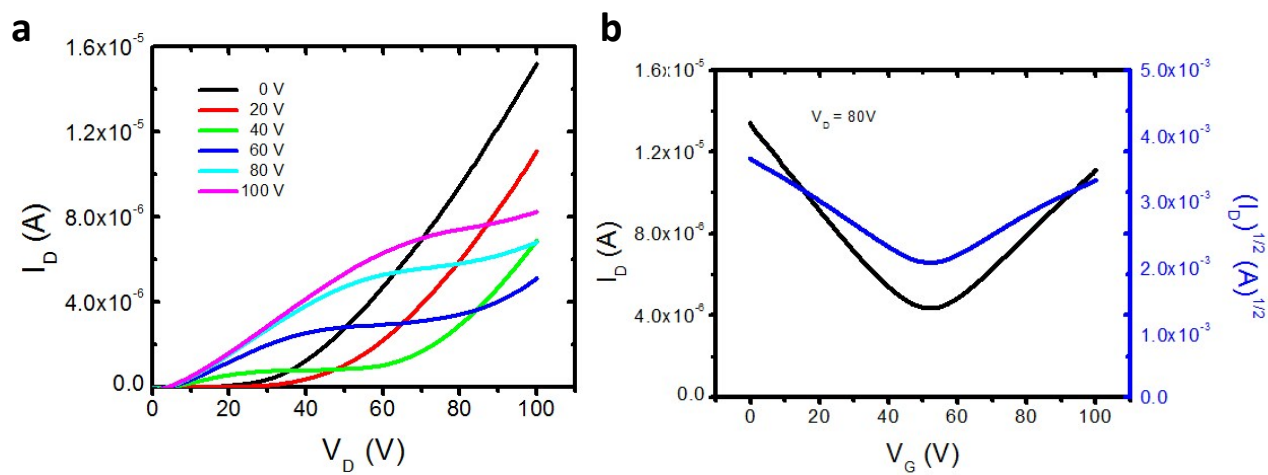


Figure S10. Output characteristics (a) and transfer characteristics (b) of P3HT:PCBM blend with SiO_2 dielectric surface (n mode).

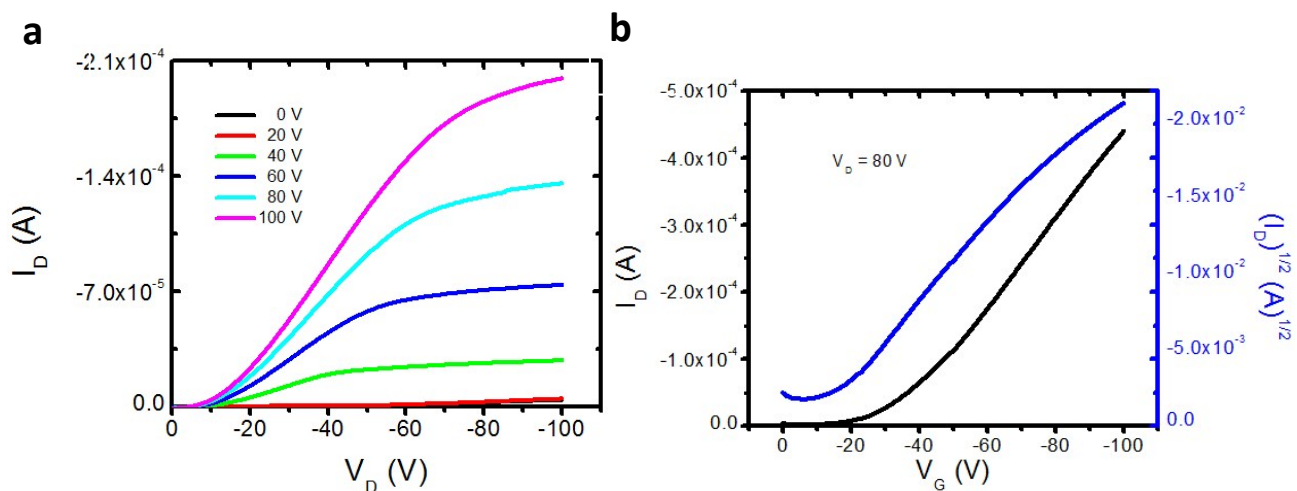


Figure S11. Output characteristics (a) and transfer characteristics (b) of P3HT:PCBM blend with OTS modified hydrophobic surface (p mode)

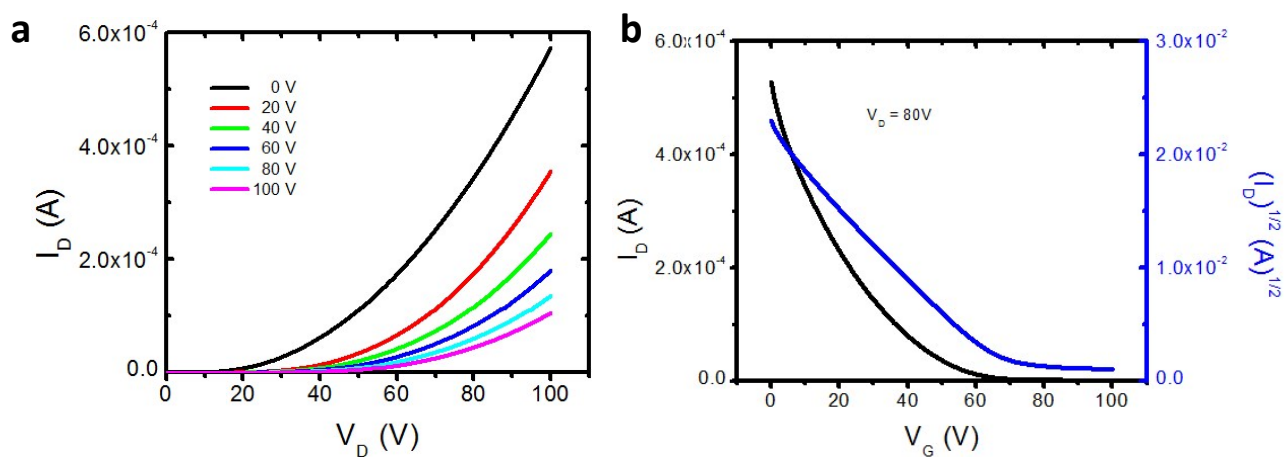


Figure S12. Output characteristics (a) and transfer characteristics (b) of P3HT:PCBM blend with OTS modified hydrophobic surface (n mode).

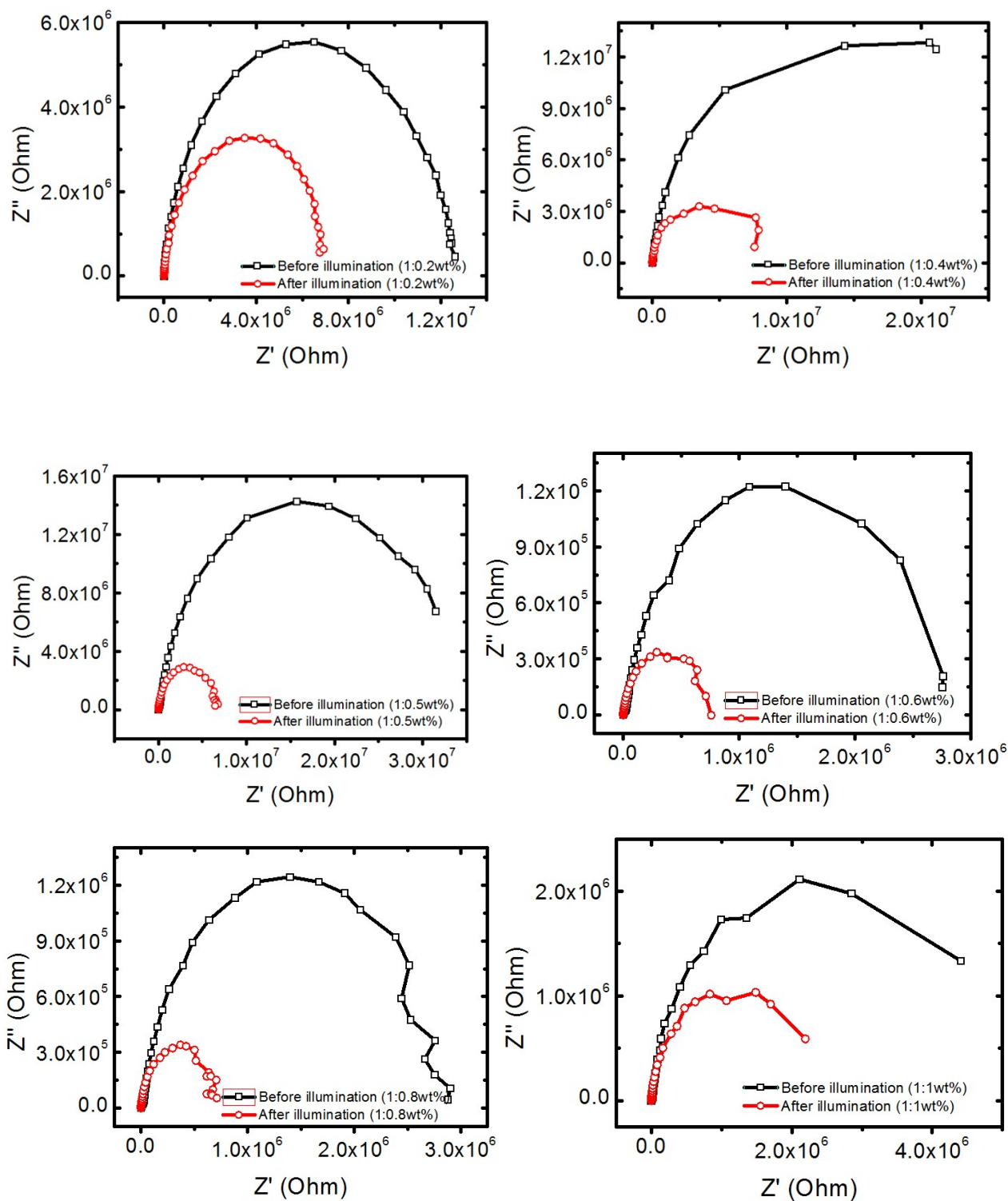


Figure S13. Electrochemical Impedance Spectroscopic study of P3HT:PCBM solar cells with different ratios of active layer blend on PEDOT:PSS HTL layers.

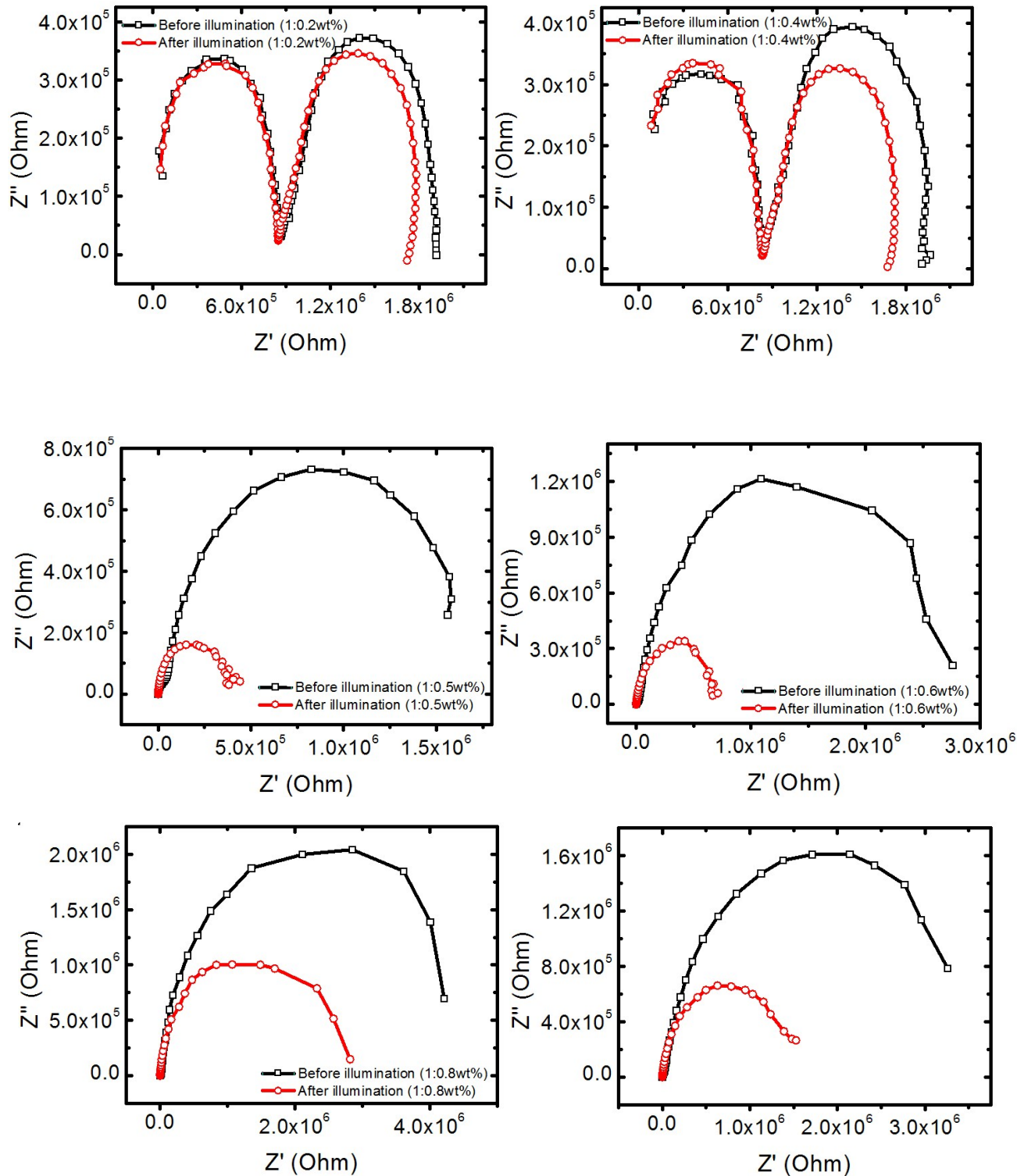


Figure S14. Electrochemical Impedance Spectroscopic study of P3HT:PCBM solar cells with different ratios of active layer blend on PEDOT:SDS HTL layers.

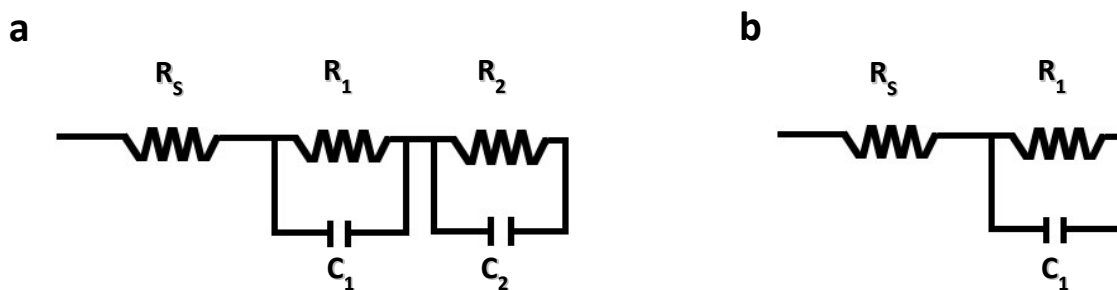


Figure S15. Equivalent circuit model used for fitting Electrochemical impedance spectrum of cells before (a) and after (b) illumination.

	Device name	VOC	JSC	FF	EFF
1	09012015-PEDOTPSS-5	0.61	9.81	58.02	3.46
2	09012015-PEDOTPSS-10	0.6	9.99	57.9	3.51
3	10122013Arul-1_25D	0.59	10.06	52.3	3.35
4	10122013Arul-1_28D	0.57	10.3	52.38	3.11
5	10122013Arul-1_29D	0.59	10.27	50.64	3.1
6	16122014aRUL-1_2D	0.59	11.96	51.27	3.64
7	16122014aRUL-1_3D	0.58	12.41	52.76	3.78
8	16122014aRUL-1_4D	0.59	11.95	51.2	3.63
9	16122014aRUL-1_5D	0.59	11.77	51.6	3.56
10	16122014aRUL-1_6D	0.56	11.34	50.1	3.1
11	16122014aRUL-1_8D	0.58	11.38	52.7	3.51
12	16122014aRUL-1_9D	0.58	12.32	52.2	3.75
13	16122014aRUL-1_10D	0.58	11.36	53.2	3.5
14	16122014aRUL-1_11D	0.58	12.2	53.2	3.8
15	16122014aRUL-1_12D	0.58	11.43	53.3	3.44
16	16122014aRUL-1_20D	0.58	11.2	54.5	3.45
17	16122014aRUL-1_21D	0.57	11.42	53.1	3.4
18	16122014aRUL-1_22D	0.57	11.8	53.3	3.53
19	16122014aRUL-1_23D	0.58	12.52	53.2	4.1
20	16122014aRUL-1_25D	0.58	12.1	52.5	3.78
21	16122014aRUL-1_26D	0.57	11.07	53.2	3.33
22	NOV23-800RPPM-1_2	0.56	10.5	55.5	3.6
	Mean (x-bar)	0.580909091	11.32545455	53.09409091	3.519545455

Table S3. Mean calculation (V_{OC} , J_{SC} , FF and efficiency) for PEDOT:PSS with 1:1 P3HT:PCBM devices (22 numbers).

	$(V-V(\bar{V}))^2$	$(J-J(\bar{J}))^2$	$(FF-FF(\bar{FF}))^2$	$(EFF-EFF(\bar{EFF}))^2$
	0.00086436	2.29643716	24.265476	0.00354025
	0.00037636	1.78329316	23.097636	9.025E-05
	8.836E-05	1.60123716	0.630436	0.02873025
	0.00011236	1.05144516	0.509796	0.16769025
	8.836E-05	1.11386916	6.022116	0.17598025
	8.836E-05	0.40271716	3.326976	0.01452025
	3.6E-07	1.17635716	0.111556	0.06786025
	8.836E-05	0.39012516	3.587236	0.01221025
	8.836E-05	0.19766916	2.232036	0.00164025
	0.00042436	0.00021316	8.964036	0.17598025
	3.6E-07	0.00298116	0.155236	9.025E-05
	3.6E-07	0.98922916	0.799236	0.05313025
	3.6E-07	0.00119716	0.011236	0.00038025
	3.6E-07	0.76492516	0.011236	0.07868025
	3.6E-07	0.01094116	0.042436	0.00632025
	3.6E-07	0.01572516	1.976836	0.00483025
	0.00011236	0.00894916	3.6E-05	0.01428025
	0.00011236	0.22524516	0.042436	0.00011025
	3.6E-07	1.42706916	0.011236	0.33698025
	3.6E-07	0.60000516	0.352836	0.06786025
	0.00011236	0.06522916	0.011236	0.03591025
	0.00042436	0.68128516	5.788836	0.00648025
Mean	0.000135633	0.673006615	3.725006	0.056967977
STD. DEVIATION	0.011646146	0.820369804	1.930027461	0.238679654
Final deviation	V_{OC}	J_{SC}	FF	EFF
Avg ± Std. Deviation	0.58 ± 0.01	11.32 ± 0.82	53.0 ± 1.93	3.52 ± 0.24
			or	
			0.53 ± 0.02	

Table S4. Standard deviation calculation (V_{OC} , J_{SC} , FF and efficiency) for PEDOT:PSS with 1:1 P3HT:PCBM devices (22 numbers).

	Device name	VOC	JSC	FF	EFF
1	Compiled 1-1	0.76	8.52	60.3	3.89
2	Compiled 1-2	0.75	8.83	60.75	3.98
3	Compiled 1-3	0.74	8.95	61.1	4.02
4	Compiled 2-1	0.725	8.59	61.5	3.8
5	Compiled 2-2	0.755	8.42	61	3.85
6	Compiled 2-3	0.737	8.57	60.85	3.84
7	1-0-5_8D	0.81	7.2	71.4	4.11
8	1-0-5_8	0.84	8	70.1	4.6
9	1-0-5_9	0.83	7.2	71.1	4.13
10	1-0-5_9D	0.83	7.3	71.8	4.15
11	1-0-5_10D	0.83	8.1	69.5	4.55
12	1-0-5_11	0.82	7.2	69.6	4.11
13	1-0-5_11D	0.83	7.2	69.3	4.2
14	1-0-5_12	0.84	7.3	70.25	4.3
15	16122014aRUL-1_12D	0.81	7.4	70.3	4.3
	Mean (x-bar)	0.7938	7.918666667	66.59	4.122

Table S5. Mean calculation (V_{OC} , J_{SC} , FF and efficiency) for PEDOT:SDS with 1:0.5 P3HT:PCBM devices (15 numbers).

	$(V-V(\bar{V}))^2$	$(J-J(\bar{J}))^2$	$(FF-FF(\bar{FF}))^2$	$(EFF-EFF(\bar{EFF}))^2$
	0.00114244	0.36	39.69	0.053824
	0.00191844	0.8281	34.2225	0.020164
	0.00289444	1.0609	30.25	0.010404
	0.00473344	0.4489	26.01	0.103684
	0.00150544	0.25	31.36	0.073984
	0.00322624	0.4225	33.0625	0.079524
	0.00026244	0.5184	23.04	0.000144
	0.00213444	0.0064	12.25	0.228484
	0.00131044	0.5184	20.25	6.4E-05
	0.00131044	0.3844	27.04	0.000784
	0.00131044	0.0324	8.41	0.183184
	0.00068644	0.5184	9	0.000144
	0.00131044	0.5184	7.29	0.006084
	0.00213444	0.3844	13.3225	0.031684
	0.00026244	0.2704	13.69	0.031684
Mean	0.001742827	0.4348	21.92583333	0.054922667
STD. DEVIATION	0.041747176	0.659393661	4.682502892	0.234355855
Final deviation	V_{OC}	J_{SC}	FF	EFF
Avg ± Std. Deviation	0.794 ± 0.042	7.92 ± 0.659	66.59 ± 4.68	4.12 ± 0.234
			or	
			0.67 ± 0.047	

Table S6. Standard deviation calculation (V_{OC} , J_{SC} , FF and efficiency) for PEDOT:SDS with 1:0.5 P3HT:PCBM devices (15 numbers).

PEDOT:SDS Devices (1:0.5)			
Number of devices	N	15	
Avg efficiency in Batch B (1:0.5)	η_1	4.12	
Avg efficiency in Batch A (1:1)	η_0	3.52	
Std deviation	σ	0.234	
		Z	$Z = [\text{Sqrt}(N) \times \eta_1 - \eta_0] / \sigma$
			9.93073
		p	≈ 0

Table S7. Z factor determination for PEDOT-SDS devices (1:0.5 P3HT:PCBM) with PEDOT-PSS (1:1 P3HT:PCBM) devices.

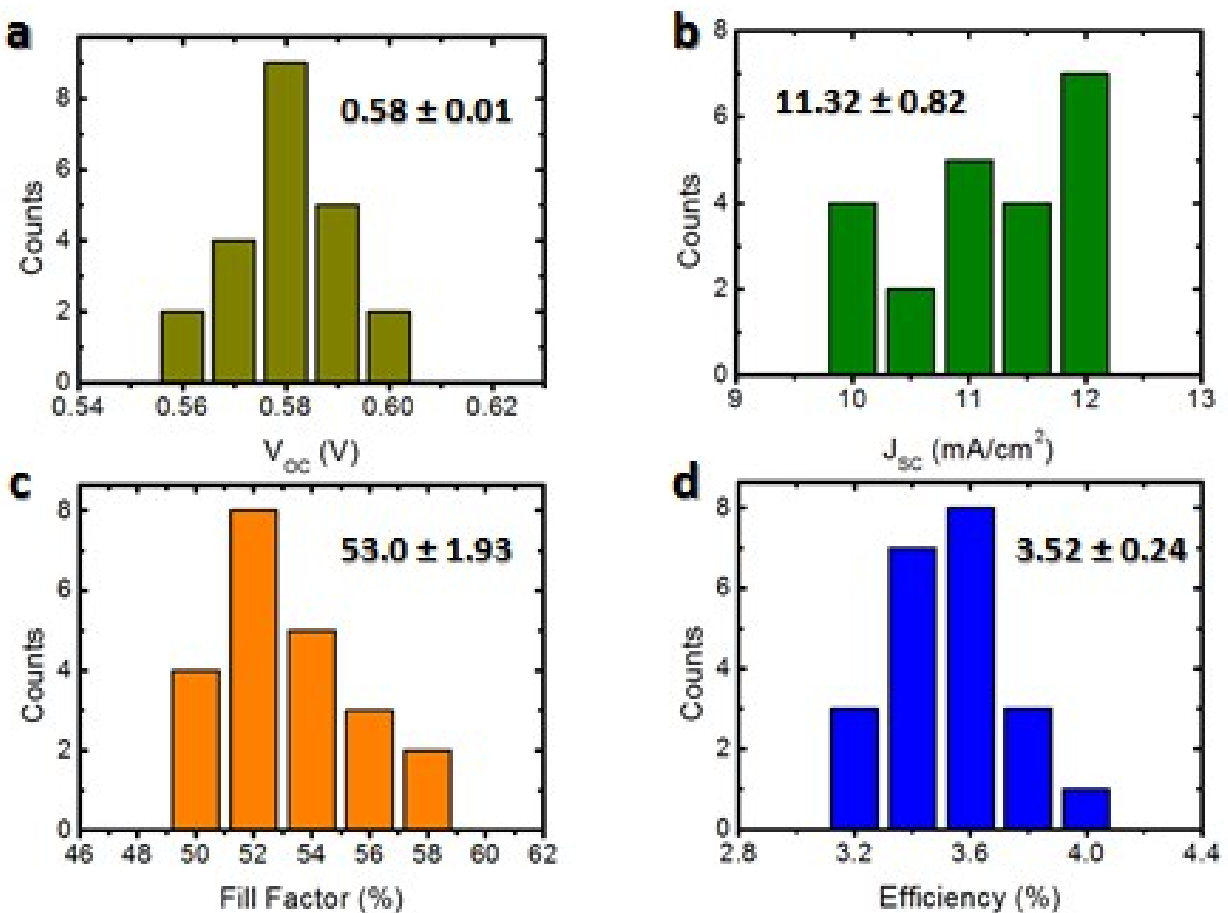


Figure S16. Standard deviation in V_{oc} , J_{sc} , FF and efficiency for P3HT:PCBM (1:1) devices with PEDOT:PSS Hole transport layers (22 numbers)..

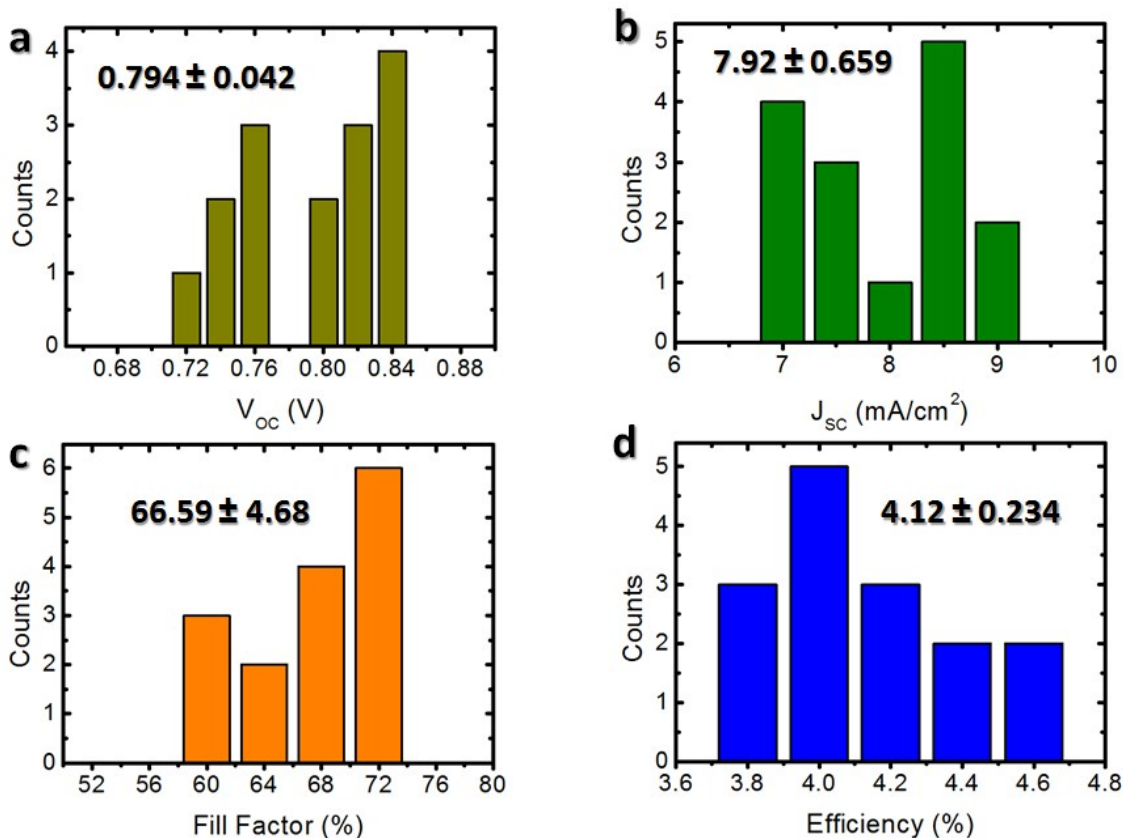


Figure S17. Standard deviation in V_{OC} , J_{SC} , FF and efficiency for P3HT:PCBM (1:0.5) devices with PEDOT:SDS Hole transport layers (15 numbers).

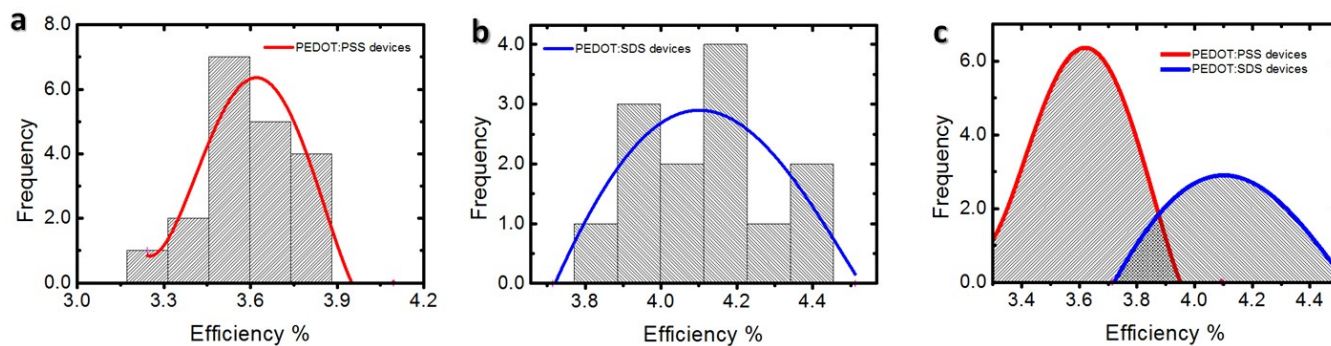


Figure S18. Histogram plot for PEDOT:PSS (a) and PEDOT:SDS (b) devices.

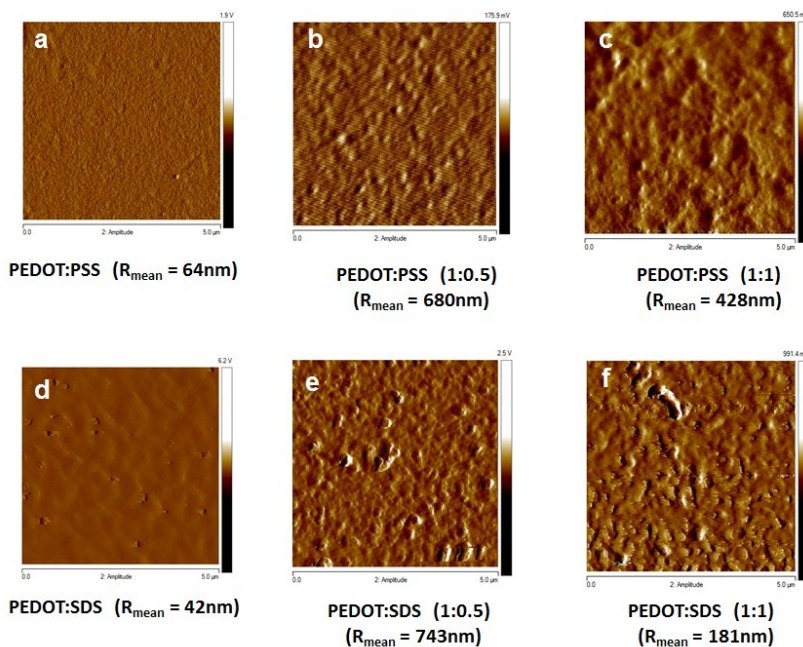


Figure S19. AFM image of PEDOT:PSS HTL (a), P3HT:PCBM with 1:0.5% (b) and 1:1% (c) active layer blends spin coated on PEDOT:PSS HTL. AFM image of PEDOT:SDS HTL (d), P3HT:PCBM with 1:0.5% (e) and 1:1% (f) active layer blends spin coated on PEDOT:SDS HTL layer.

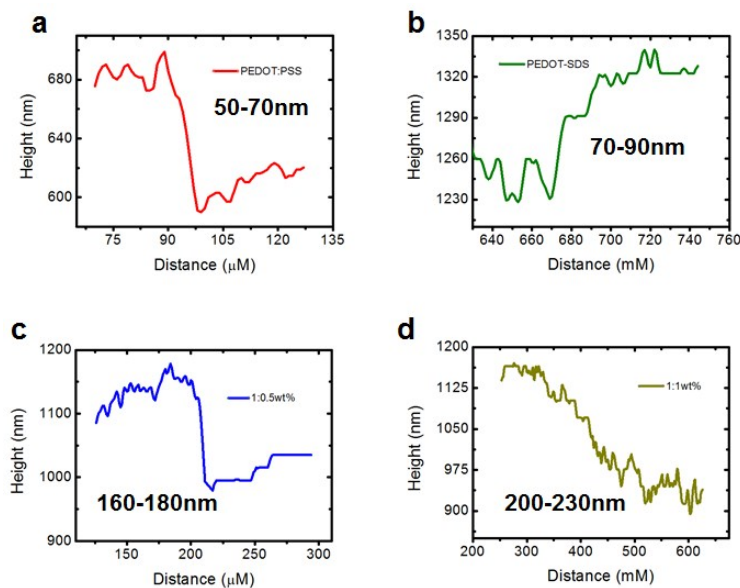


Figure S20. Height profile for PEDOT:PSS (a), PEDOT:SDS (b), P3HT:PCBM 1:0.5% (c) and P3HT:PCBM 1:1% (d).

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