Supporting Information for: Influence of pH-Neutral Lithium Polystyrenesulfonate Polyelectrolyte on the Energy Band Structure and Performance of Organic Solar Cells

Merve Nur Ekmekci,[a] Ju Hwan Kang,[a] Yeasin Khan,[a,b] Jung Hwa Seo[a,*] and Bright Walker[b,*]

[a]*Department of Semiconductors and Chemical Engineering (BK21 FOUR), Dong-A University, Busan, 49315, Republic of Korea*

[b]*Department of Chemistry, Kyung Hee University, Seoul, 02453, Republic of Korea*

seojh@dau.ac.kr and walker@khu.ac.kr

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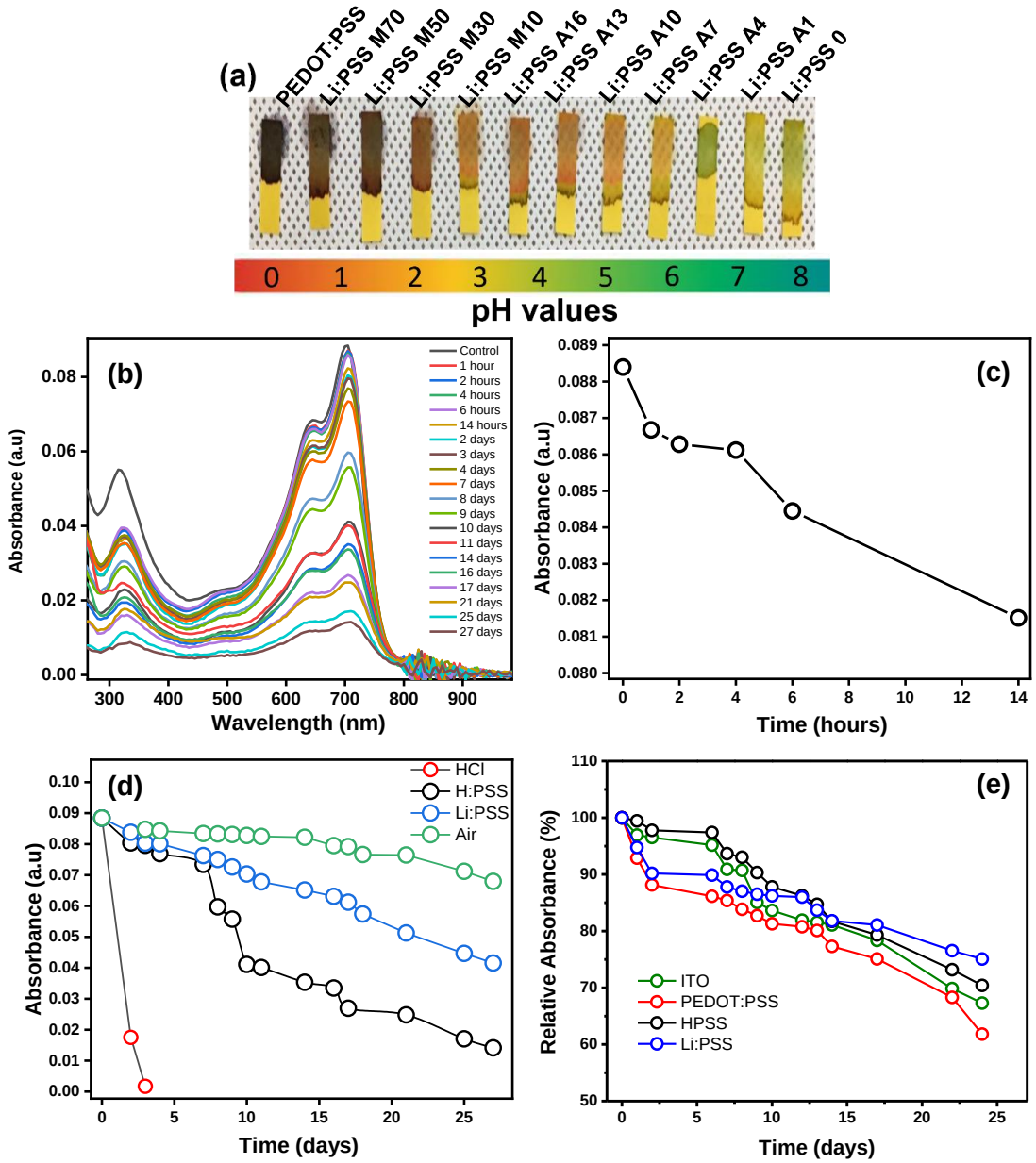

Figure S1. PTB7 Stability in acid. (a) Photograph of pH paper tests for each HTL solution used in the study. (b) Representative absorption spectra of PTB7 films over time during immersion in a 0.1 wt % (5.4 mM) solution of polystyrene sulfonic acid (H:PSS). (c) Absorption at 705 nm of a PTB7 film immersed in a 0.1 wt % (5.4 mM) solution of polystyrene sulfonic acid (H:PSS). (d) Comparison of absorbance at 705 nm vs. time for PTB7 films immersed in 2M HCl solution, 0.1 wt % H:PSS solution, 0.1 wt % Li:PSS solution, and dry PTB7 films in air. (e) Comparison of absorbance at 705 nm vs. time for PTB7 films deposited on ITO, ITO/PEDOT:PSS, ITO/H:PSS and ITO/Li:PSS substrates and exposed to ambient air.

Table S1. Composition of hole transport layers used for PSCs and pH values of Li:PSS and PEDOT:PSS doped films.

Hole Transport Layer	Thickness (nm)	Volume of PEDOT:PSS Soln.[a]	pH[b]
Li:PSS 0	1.62	0 µL	6.36
	2.00	0 µL	6.36
	2.27	0 µL	6.36
	2.54	0 µL	6.36
Li:PSS A1	2	10 µL	4.13
Li:PSS A4	4	40 µL	3.08
Li:PSS A7	6.3	70 µL	2.71
Li:PSS A10	7.3	100 µL	2.59
Li:PSS A13	8	130 µL	2.52
Li:PSS A16	9	160 µL	2.39
		Ratio (Li:PSS) /(PEDOT:PSS)[d]	
Li:PSS M10	20.41	90 /10	2.53
Li:PSS M30	40.36	70 / 30	1.94
Li:PSS M50	43.06	50 / 50	1.68
Li:PSS M70	44	30 / 70	1.50
PEDOT:PSS[e]	43	0 / 100	1.21

a) Volume of commercial PEDOT:PSS solution added to dilute (0.005 wt%) soln of 1 ml Li:PSS in H_2O.
b) SI Analytics / Lab 850.
c) Dilute (0.005 wt%) soln. of Li:PSS in H_2O.
d) Volume ratio of dilute Li:PSS soln to commercial PEDOT:PSS soln.
e) Commercial PEDOT:PSS solution.

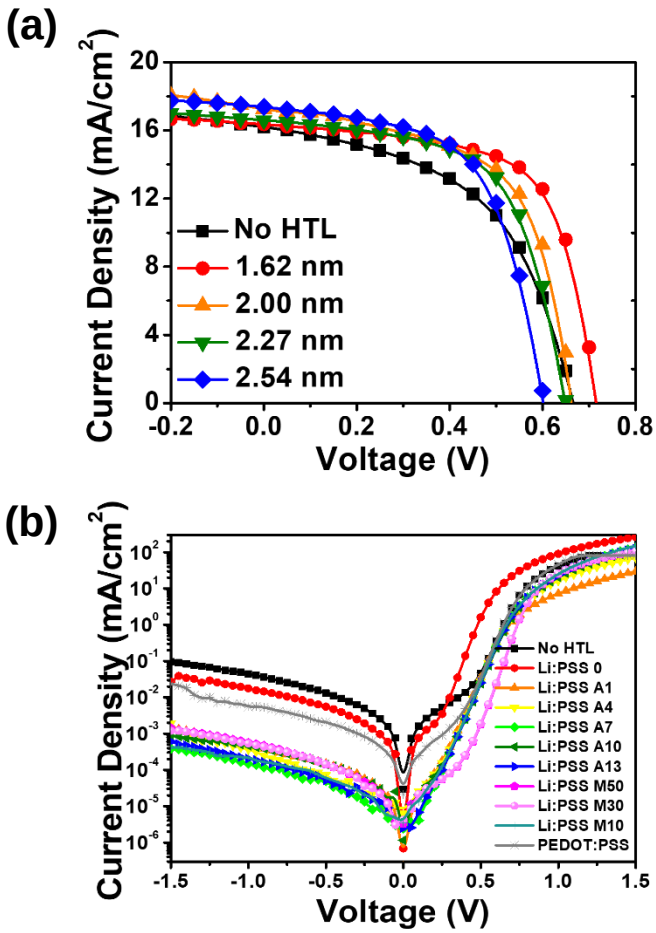

Figure S2. Current density vs. voltage curves of PTB7:$PC_{71}BM$ solar cells measured (a) under simulated AM1.5G solar light and (b) in the dark.

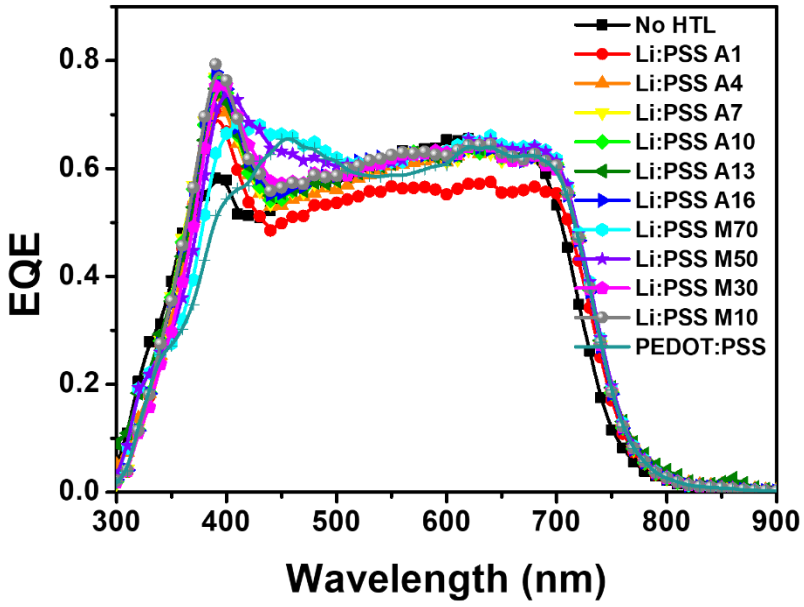

Figure S3. EQE spectra for devices with different HTL formulations.

Table S2. Summary of device parameters for OSCs using different HTL formulations compared to reference devices with no HTL and pure PEDOT:PSS.

HTL	J_{SC} (mA/cm^2)	Spectral J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
No HTL	15.32 ± 1.26	12.57	0.67 ± 0.02	47.76±4.72	4.92 ± 0.85
1.62 nm	16.84 ± 0.62	13.67	0.63 ± 0.05	55.63 ± 1.73	5.93 ± 0.55
2.00 nm	16.71 ± 0.80	13.39	0.63 ± 0.04	52.07 ± 4.69	5.53 ± 0.68
2.27 nm	16.03 ± 1.19	13.53	0.62 ± 0.09	48.12 ± 5.56	4.89 ± 1.23
2.54 nm	13.91 ± 2.70	11.32	0.57 ± 0.18	39.85 ± 8.75	3.47 ± 1.74
Li:PSS A1	16.30 ± 0.68	16.50	0.66 ± 0.06	59.77 ± 5.33	6.48 ± 1.12
Li:PSS A4	16.82 ± 0.74	17.35	0.67 ± 0.04	57.55 ± 5.55	6.58 ± 1.00
Li:PSS A7	16.83 ± 0.78	17.46	0.73 ± 0.03	62.85 ± 4.91	7.73 ± 0.84
Li:PSS A10	17.17 ± 0.76	17.72	0.74 ± 0.01	65.17 ± 2.27	8.32 ± 0.44
Li:PSS A13	17.00 ± 0.96	17.56	0.74 ± 0.01	63.30 ± 2.93	7.98 ± 0.73
Li:PSS A16	16.97 ± 0.93	16.58	0.74 ± 0.01	65.33 ± 2.19	8.23 ± 0.56
Li:PSS M10	17.15 ± 0.66	17.16	0.73 ± 0.01	64.41 ± 3.89	8.17 ± 0.72
Li:PSS M30	17.17 ± 0.82	17.87	0.73 ± 0.01	65.60 ± 2.27	8.33 ± 0.53
Li:PSS M50	17.12 ± 0.86	17.20	0.73 ± 0.01	64.20 ± 4.25	8.10 ± 0.79
Li:PSS M70	16.81 ± 1.24	17.64	0.73 ± 0.01	63.20 ± 6.58	7.82 ± 1.17
PEDOT:PSS	16.99 ± 0.76	14.47	0.73 ± 0.02	64.51 ± 2.85	8.09 ± 0.61

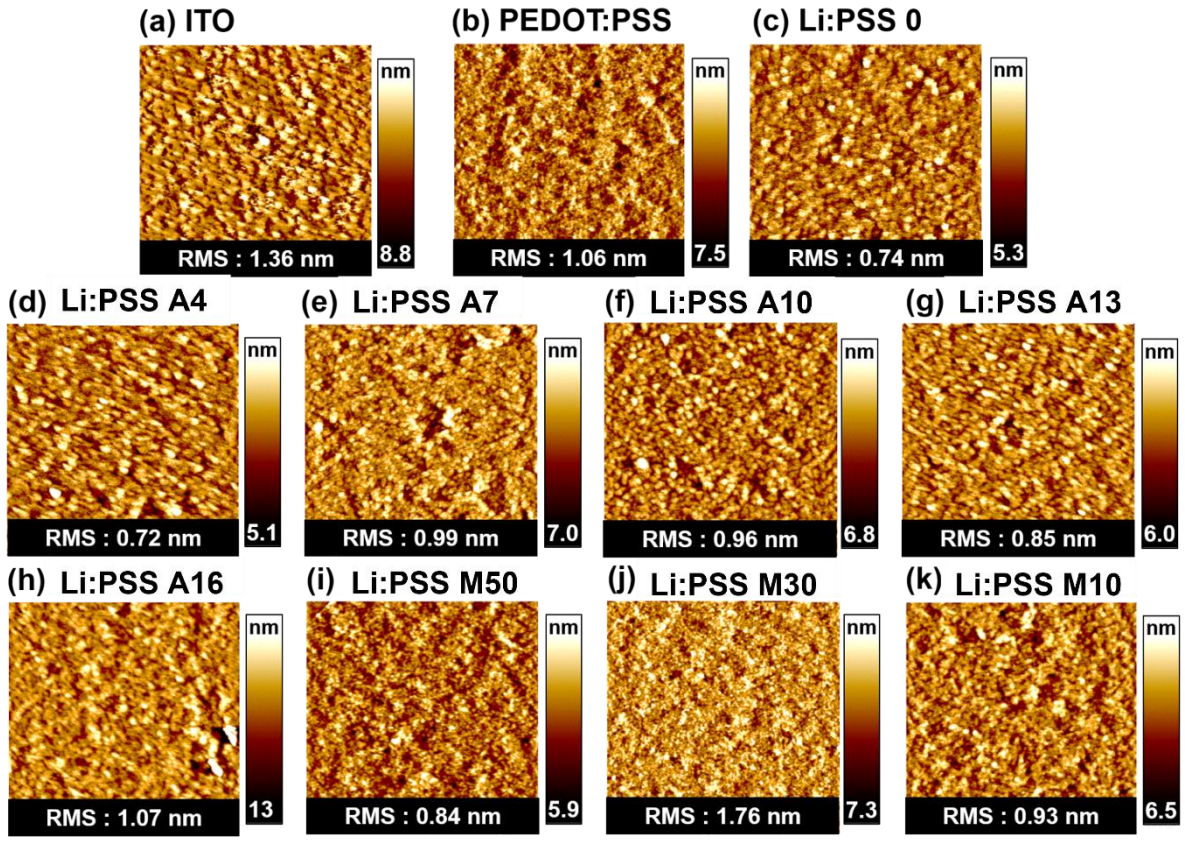

Figure S4. Surface topographic AFM images of (a) ITO, (b) ITO/PEDOT:PSS, (c) ITO/Li:PSS 0, (d) ITO/Li:PSS A4, (e) ITO/Li:PSS A7, (f) ITO/Li:PSS A10, (g) ITO/Li:PSS A13, (h) ITO/Li:PSS A16, (i) ITO/Li:PSS M50, (j) ITO/Li:PSS M30 and (k) ITO/Li:PSS M10 films (size: 5 μm x 5 μm).

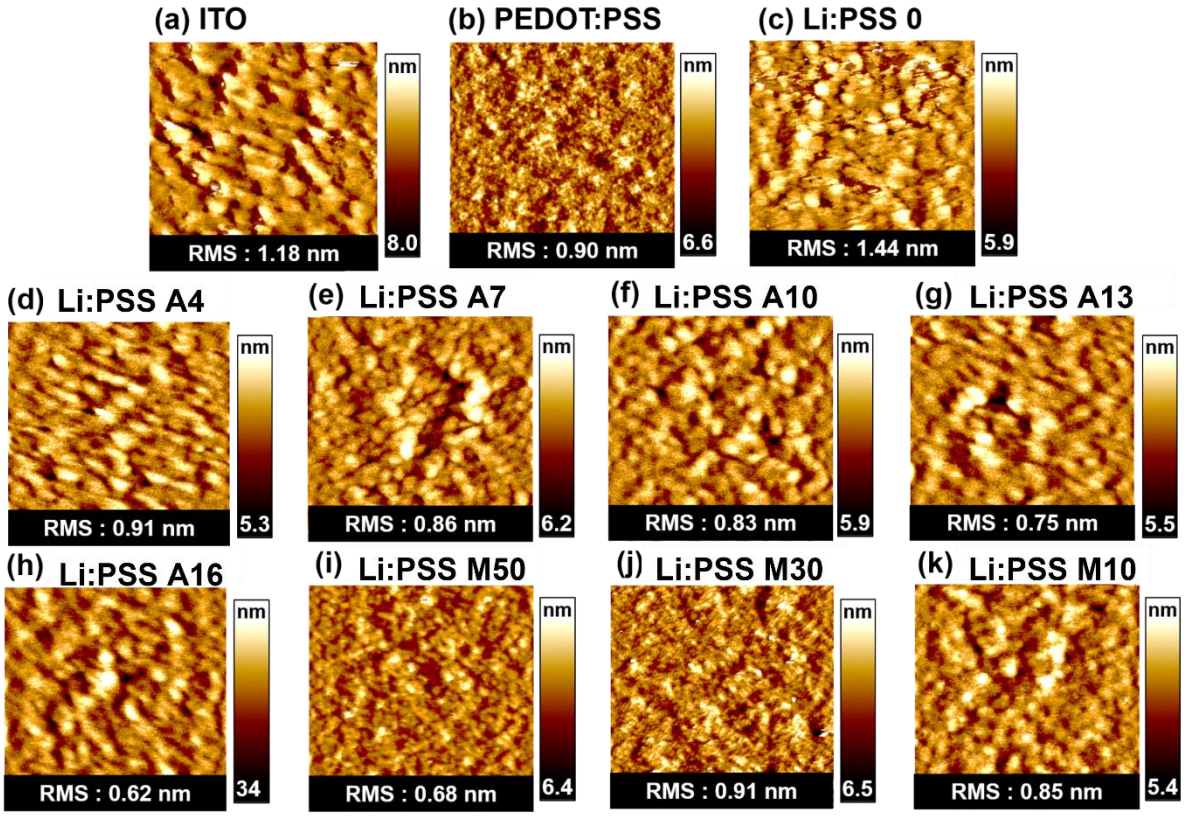

Figure S5. Surface topographic AFM images of (a) ITO, (b) ITO/PEDOT:PSS, (c) ITO/Li:PSS 0, (d) ITO/Li:PSS A4, (e) ITO/Li:PSS A7, (f) ITO/Li:PSS A10, (g) ITO/Li:PSS A13, (h) ITO/Li:PSS A16, (i) ITO/Li:PSS M50, (j) ITO/Li:PSS M30 and (k) ITO/Li:PSS M10 films (size: 2 µm x 2 µm).

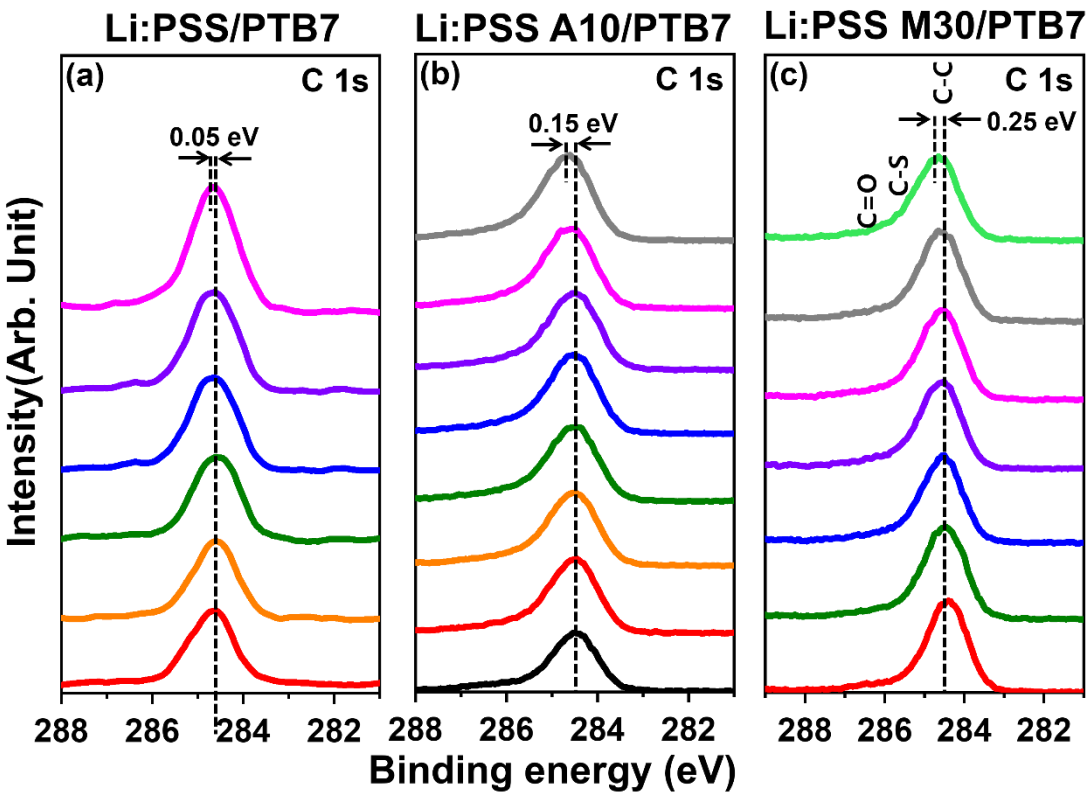

Figure S6. XPS spectra in the C 1s region of (a) Li:PSS 0, (b) Li:PSS A10 and (c) Li:PSS M30 deposited on top of ITO.

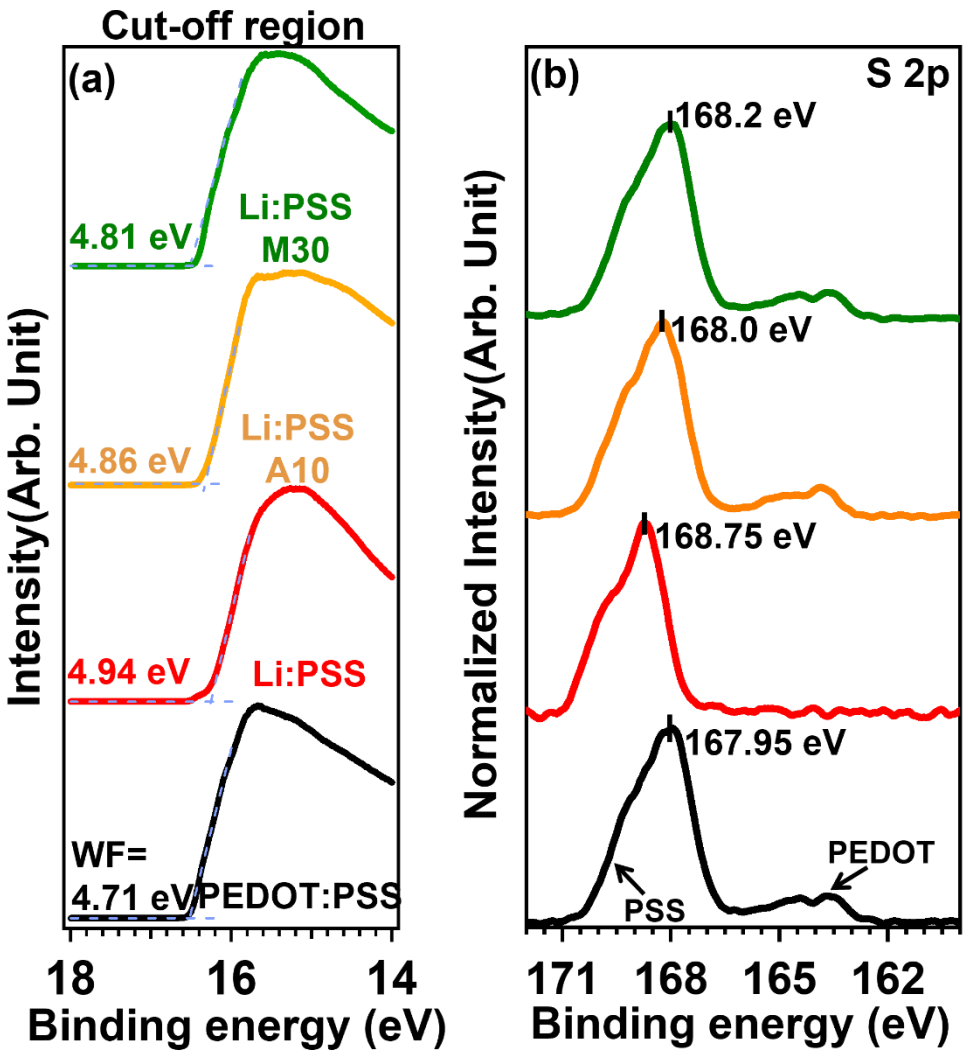

Figure S7. UPS showing the secondary edge (left) and XPS showing S 2p peaks of PEDOT:PSS, Li:PSS 0, Li:PSS A10 and Li:PSS M30 deposited on ITO substrates.

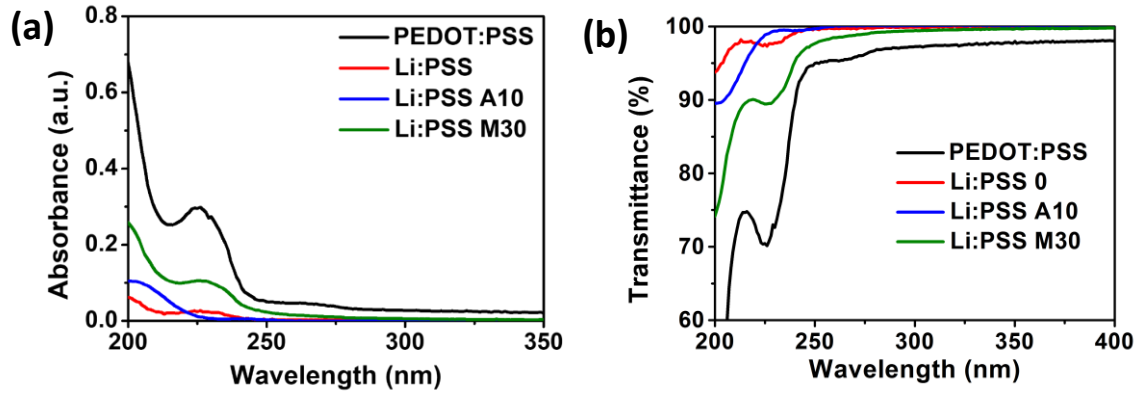

Figure S8. UV-Vis absorbance (a) and transmittance (b) spectra of representative HTLs used in this work.