Supplementary Material

Fabrication of ultrathin PEG-modified PEDOT:PSS HTL for high-efficiency Sn-Pb perovskite solar cells by eco-friendly solvent etching technique

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Characterization; Figure S1 to S14; Table S1 to S6.

1. Characterizations

The date of current-voltage (J-V) curves were measured by Keithley 2400 source meter under a solar simulator. Light intensity was adjusted to AM 1.5G (100 mW·cm^{-2}) by a calibrated Si solar cell. The voltage test range was +0.9 to -0.2 V (reverse scan, R) or -0.2 to +0.9 V (forward scan, F), and the step was set to 0.02 V. External quantum efficiency (EQE) was tested using xenon lamp (Newport, 69920) as light source. The photocurrents from the device or the calibrated silicon detector were measured by a lock-in amplifier (Stanford Research Systems, SR-830) to calculate the light intensity and then the EQE. The electrochemical impedance spectroscopy (EIS) was measured with an electrochemical workstation (model CHI660D, Shanghai Chen Hua Instrument Co., Ltd.) in the frequency range of 3 Hz-100 kHz. The bias potential was 0.3 V with amplitude of 0.02 V under AM 1.5G simulated light. Ultraviolet–visible (UV-Vis) absorption spectra were obtained by a UV-Vis spectrometer (Shimadzu UV-21011C). The contact angle goniometer (YIKE-360A, Chengde Precision Test Instrument Factory, China) was employed to test the contact angle (CA). The X-ray diffraction patterns were carried out by an XRD-7000 X-ray diffractometer (SHIMADZU). The surface and cross-sectional morphology of perovskite films were measured by field-emission scanning electron microscopy (FESEM, JSM-6700F). The steady-state photoluminescence (PL) and the time-resolved photoluminescence (TRPL) spectra were taken on steady state/transient fluorescence spectrometer (FLS 920 and FLS 980). The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were used to analyze different films (Thermo Fisher ESCALAB 250Xi). The surface roughness, morphology and local conduction signal of the HTL was obtained using atomic force

microscopy (AFM CSPM 5500). The thickness of perovskite films was measured by a step profiler (KOSAKA, ET-150). Transient photovoltage (TPV) and transient photocurrent (TPC) of devices were measured by laser pulses (532 nm, 6 ns width from an Nd:YAG laser) with input impedance of 1 MΩ and 50 Ω, respectively.

1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The solid powder can be directly mixed and ground with potassium bromide powder. Generally, 1-2 mg sample was added to 100-200 mg potassium bromide, which was then ground into fine powder in an agate mortar. When grinding, we continuously use small stainless-steel spatula to scrape the sample to the center of the mortar to grind finer. The solid sample was generally ground for 5-15 min, and can be pressed after fully drying under the infrared lamp. The pressure of the hydraulic press was 8000 kg·cm^{-2}, and the pressing time was kept for at least 1 min to obtain transparent tablets. The Fourier transform infrared (FTIR) spectroscopy were then recorded with a Nicolet iS50 Infrared Fourier transform microscope (Thermo Fisher Nicolet 6700).

1.2 Fabrication of Space Charge Limited Current (SCLC) device

The structure of the device was ITO/HTL/Sn-Pb/MoO_3/Au. The process of the bottom few layers of the SCLC samples was the same as the normal PSCs. Thermal evaporation was performed by physical vapor deposition (PVD) to sequentially deposit 10 nm MoO_3 (~0.4 nm·min^{-1}) and 80 nm Au (~3 nm·min^{-1}). The vacuum pressure was less than 2×10^{-5} Pa.

The trap density (N_t) of the device was calculated according to the formula:

$$N_t = \frac{2 \times V_{TFL} \times \varepsilon_r \times \varepsilon_0}{e \times L^2}$$

where ε_r was the relative permittivity of the perovskite (ε_r=35 [1]), ε_0 was the

vacuum permittivity, e was the elementary charge, and L was the perovskite film thickness.

Figures

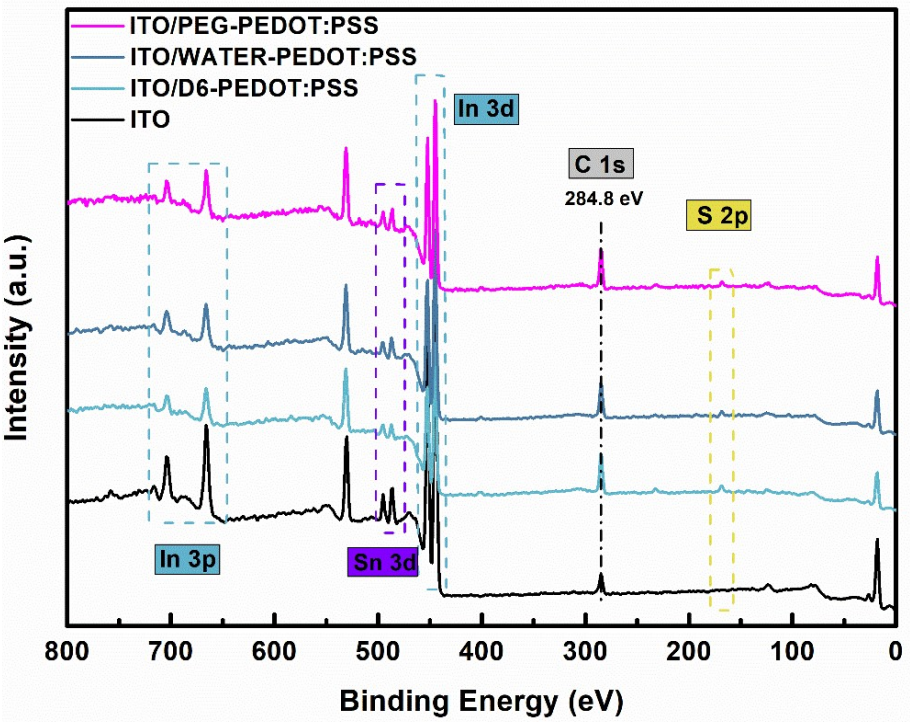

Figure S1 Survey of the XPS spectra of the four samples.

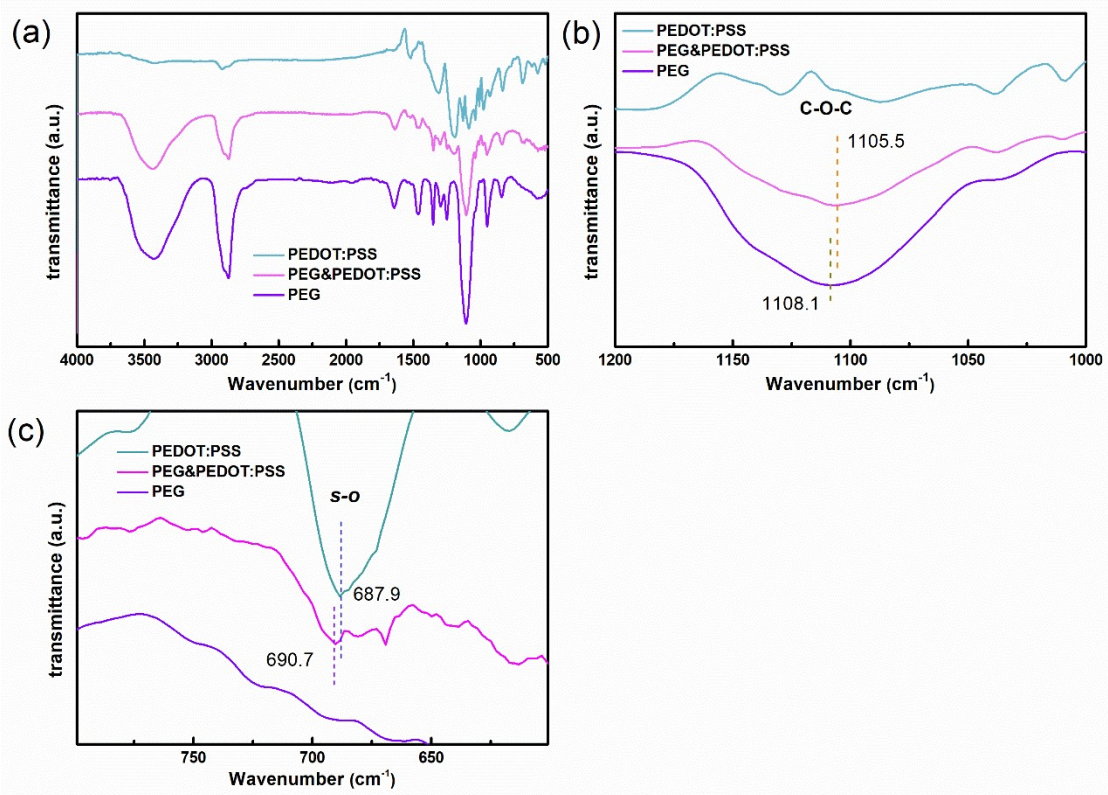

Figure S2 (a) FTIR spectra of PEDOT:PSS, PEG and PEG&PEDOT:PSS mixture. (b) and (c) partial enlargements of (a). The peak shift demonstrates the interaction of PEG with PSS sulfonic acid groups.

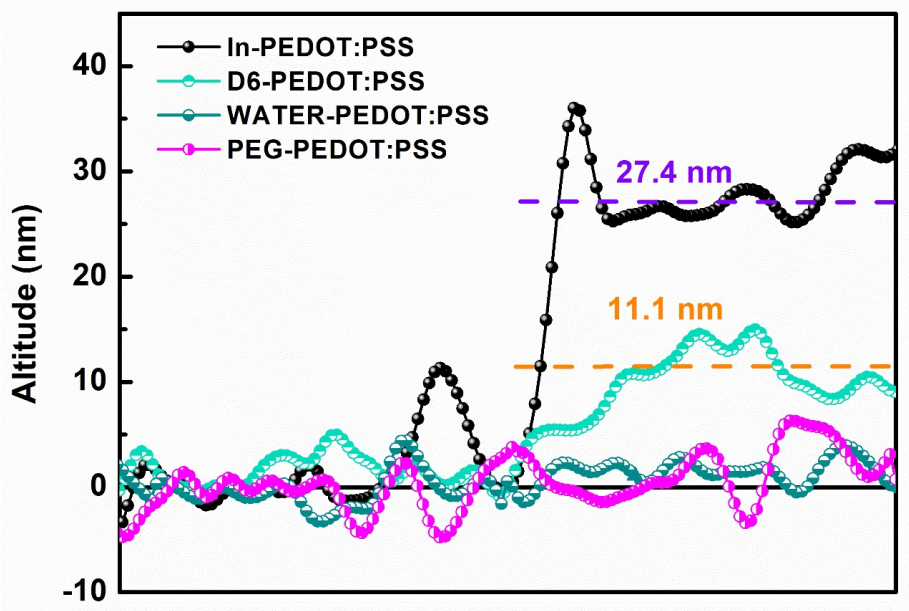

Figure S3 AFM contour lines of different PEDOT:PSS layers profile for estimating film thickness. In-PEDOT:PSS was obtained by spin-coating commercial PEDOT:PSS solution. The thickness of the WATER-PEDOT:PSS and PEG-PEDOT:PSS films cannot be distinguished because its thickness is lower than the roughness of the substrate.

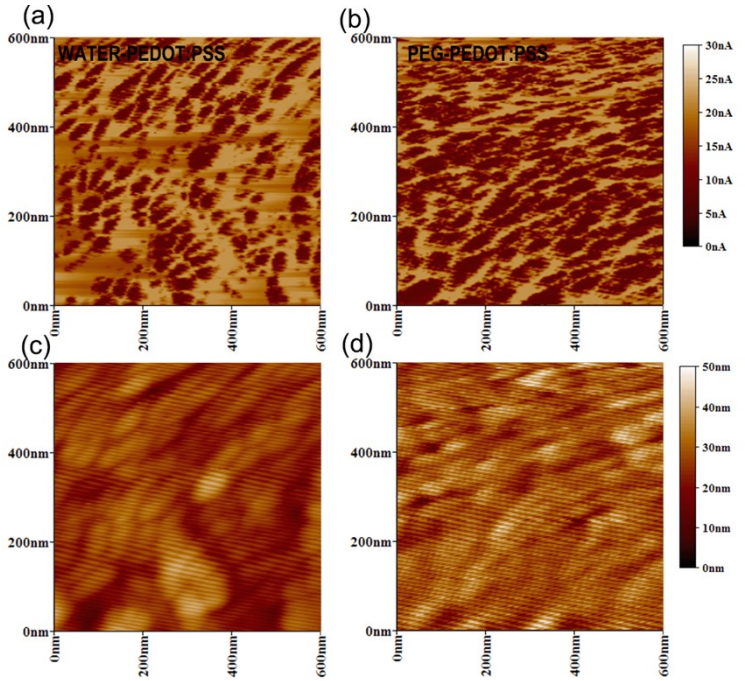

Figure S4 C-AFM micro-zone conductivity (bias voltage of 0.1 V) images of (a) WATER-PEDOT:PSS and (b) PEG-PEDOT:PSS films. AFM images of (c) WATER-PEDOT:PSS and (d)PEG-PEDOT:PSS films.

Commentary: Due to the ITO topography of **Figure S4**c-d, the conductive current is slightly different, but the conduction of both is uniform and there is no current mutation point in both of them, indicating a compact film without pinholes. This is one of the evidences that solvent etching technology has successfully obtained complete PEDOT:PSS HTL.

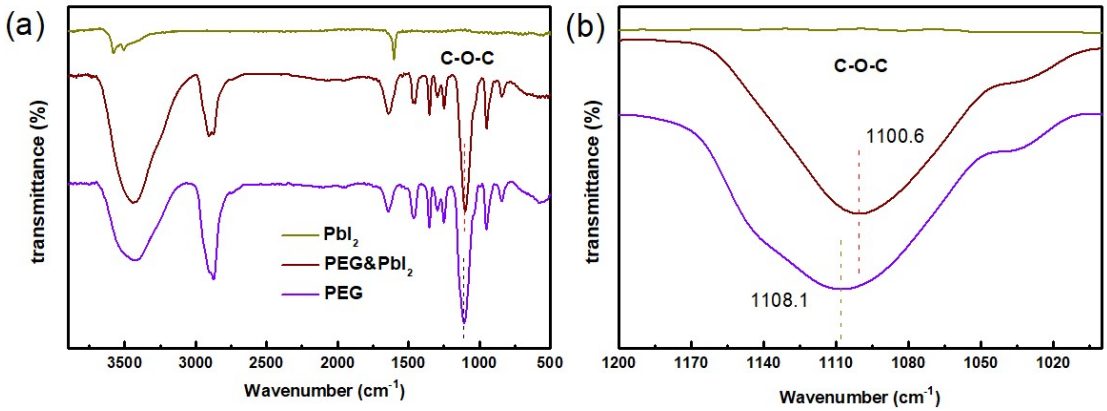

Figure S5 (a) FTIR spectra of PbI_2, PEG and PEG&PbI_2 mixture. (b) Partial enlargements of (a), which reveal interaction between PEG and PbI_2.

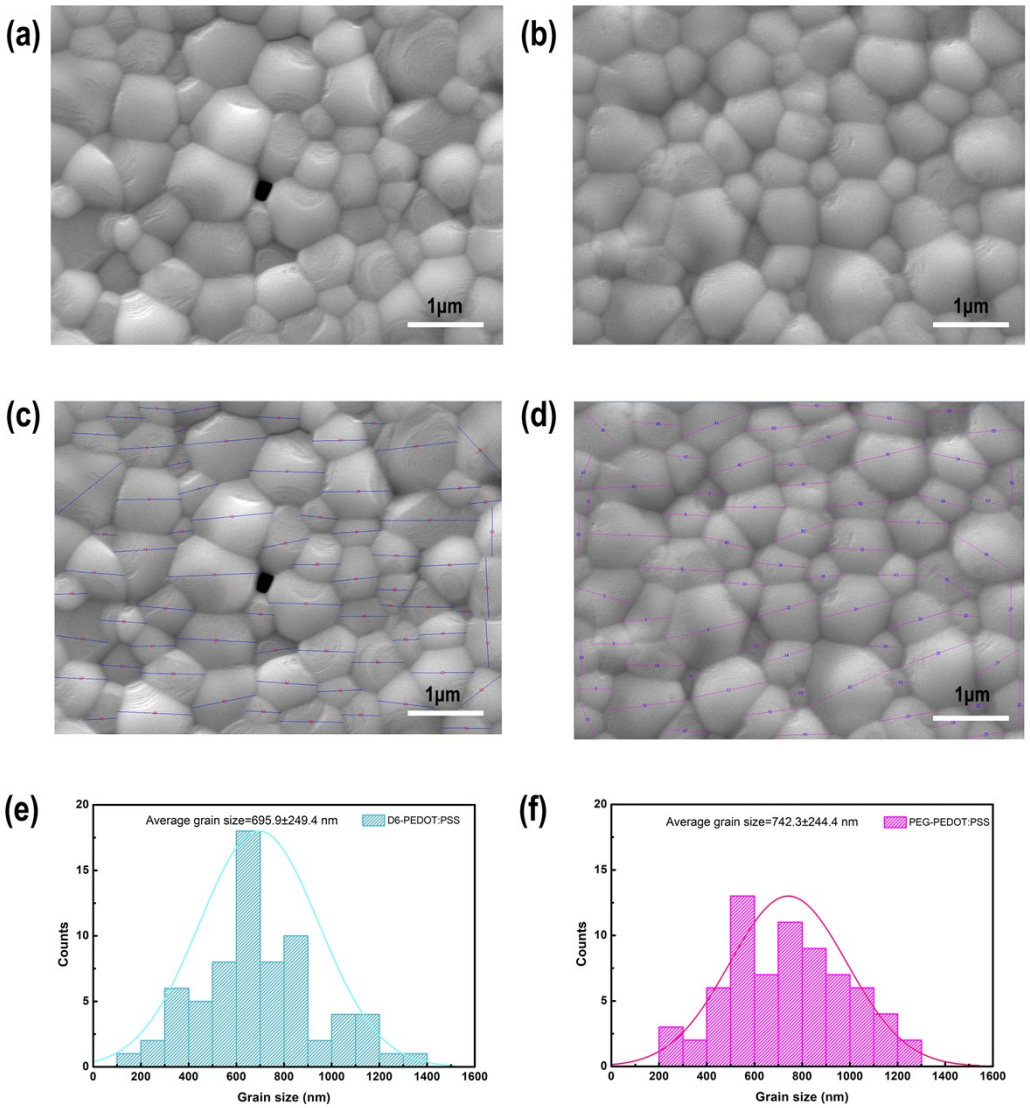

Figure S6 FESEM and grain size statistics of perovskite grown on different films. (a), (c) and (e) D6-PEDOT:PSS; (b), (d) and (f) PEG-PEDOT:PSS.

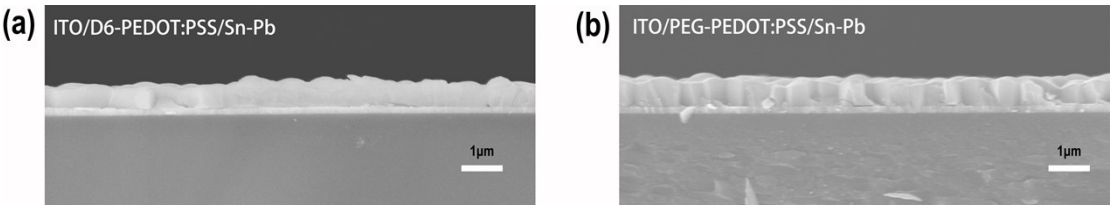

Figure S7 Cross-sectional view of perovskite grown on different substrates. (a) D6-PEDOT:PSS, (b) PEG-PEDOT:PSS.

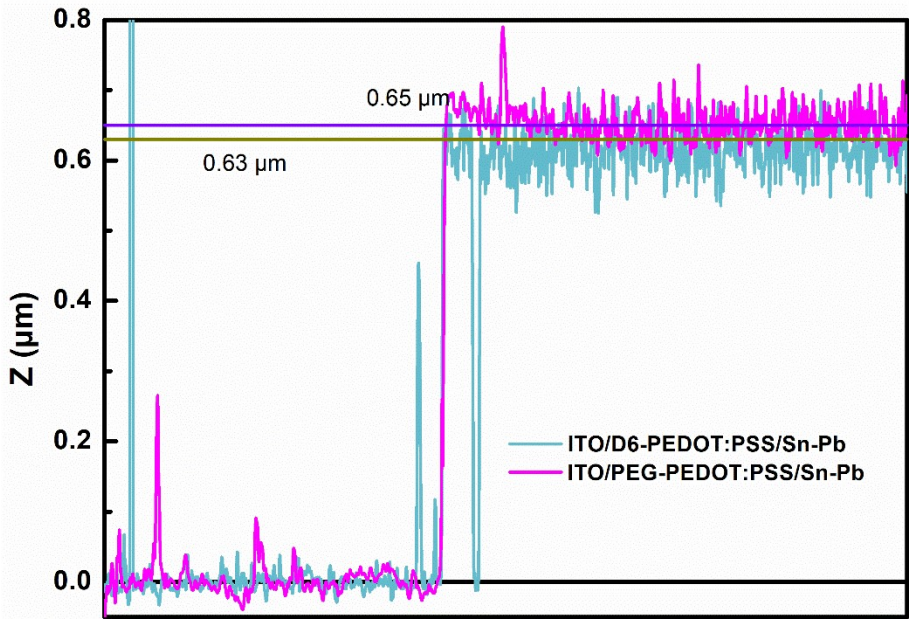

Figure S8 The thicknesses of perovskite layers grown on D6-PEDOT:PSS and PEG-PEDOT:PSS films measured by step profiler.

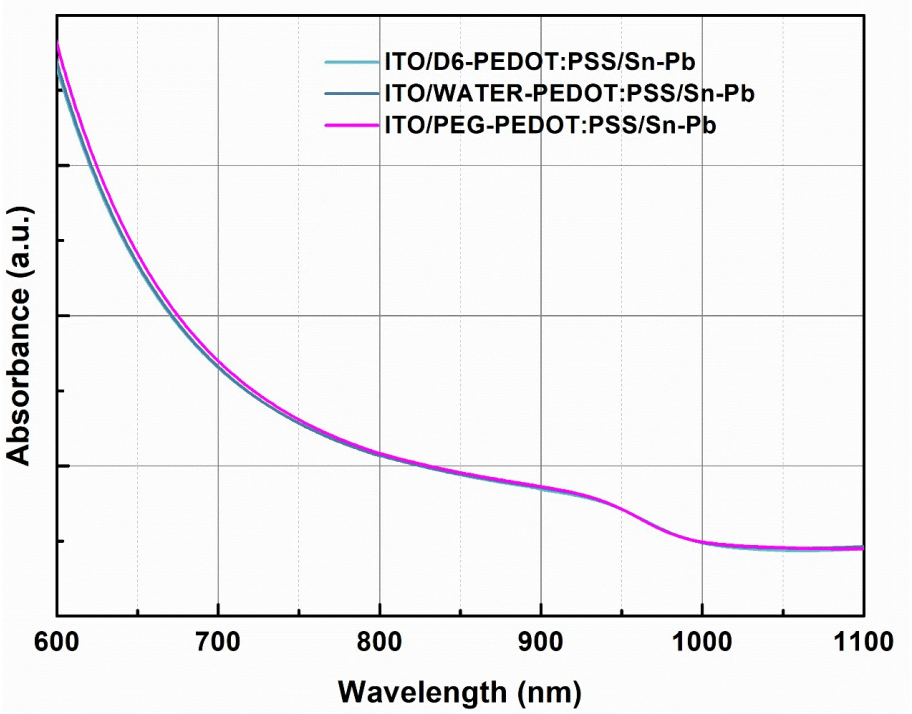

Figure S9 Absorbance of perovskites grown on D6-PEDOT:PSS, WATER-PEDOT:PSS and PEG-PEDOT:PSS films.

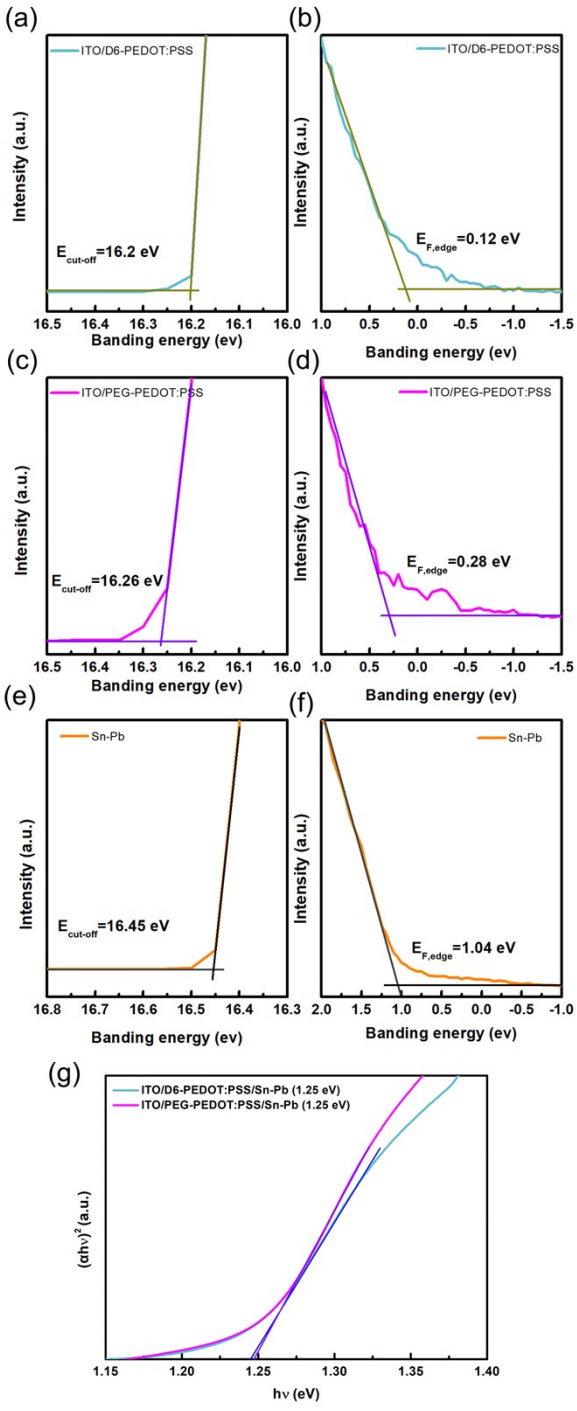

Figure S10 The UPS spectra of (a) and (b) D6-PEDOT:PSS film; (c) and (d) PEG-PEDOT:PSS film; (e) and (f) Sn-Pb perovskite film. (g) Optical band gap of perovskite grown on different films.

Energy Band Calculation of HTL and Perovskite Layer

The UPS measurement results in **Figure S10**a-e show that, according to the formula $E_F = E_{cut\text{-}off}$-21.22 eV, Fermi levels (E_F) of D6-PEDOT:PSS and PEG-PEDOT:PSS are -5.02 and -4.96 eV, respectively, where $E_{cut\text{-}off}$ is the cut-off binding energy. The Fermi edge ($E_{F,\ edge}$) is estimated to be 0.12 eV for D6-PEDOT:PSS film and 0.28 eV for PEG-PEDOT:PSS film. Then, the maximum of valence band (E_{VB}) of D6-PEDOT:PSS and PEG-PEDOT:PSS films are calculated to be -5.14 and -5.24 eV using the formula $E_{VB} = E_F$-$E_{F,\ edge}$. Likewise, the calculated E_F and E_{VB} of the perovskite film are -4.77 and -5.81 eV. The minimum of conduction band (E_{CB}) of Sn-Pb perovskite is calculated to be -4.56 eV based on the measured optical band gap value of 1.25 eV (**Figure S10**g). **Fig. 4**f is energy level alignment diagram of the device based on these data.

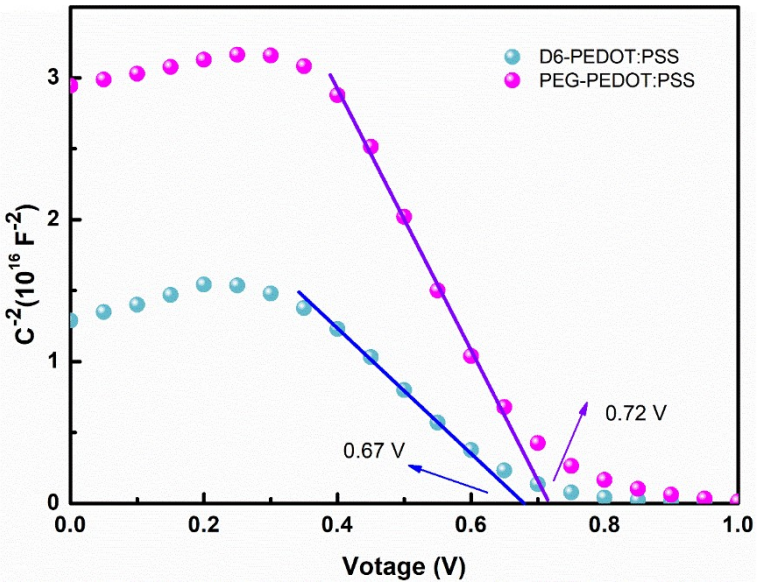

Figure S11 C-V measurements of D6-PEDOT:PSS and PEG-PEDOT:PSS devices. The built-in voltage increases from 0.67 V of the reference to 0.72 V of the device using PEG-PEDOT:PSS.

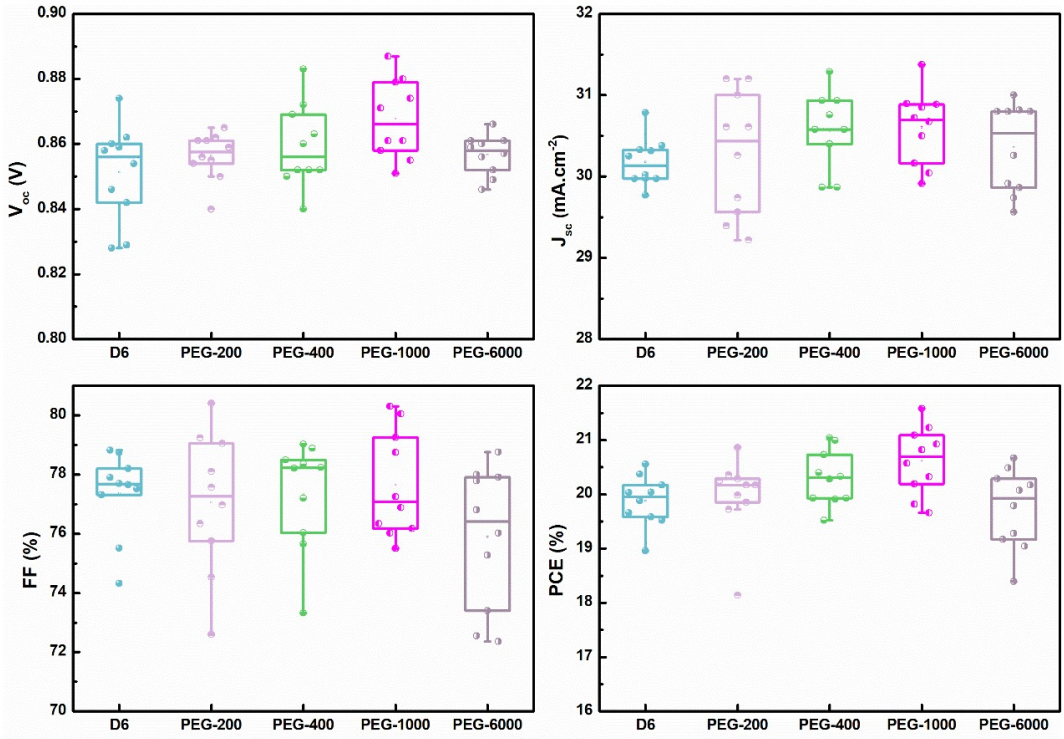

Figure S12 Statistical results of devices based on 0.75 mg·mL^{-1} PEG with different molecular weights using solvent etching process. The best device is the one with PEG molecular weight of 1000.

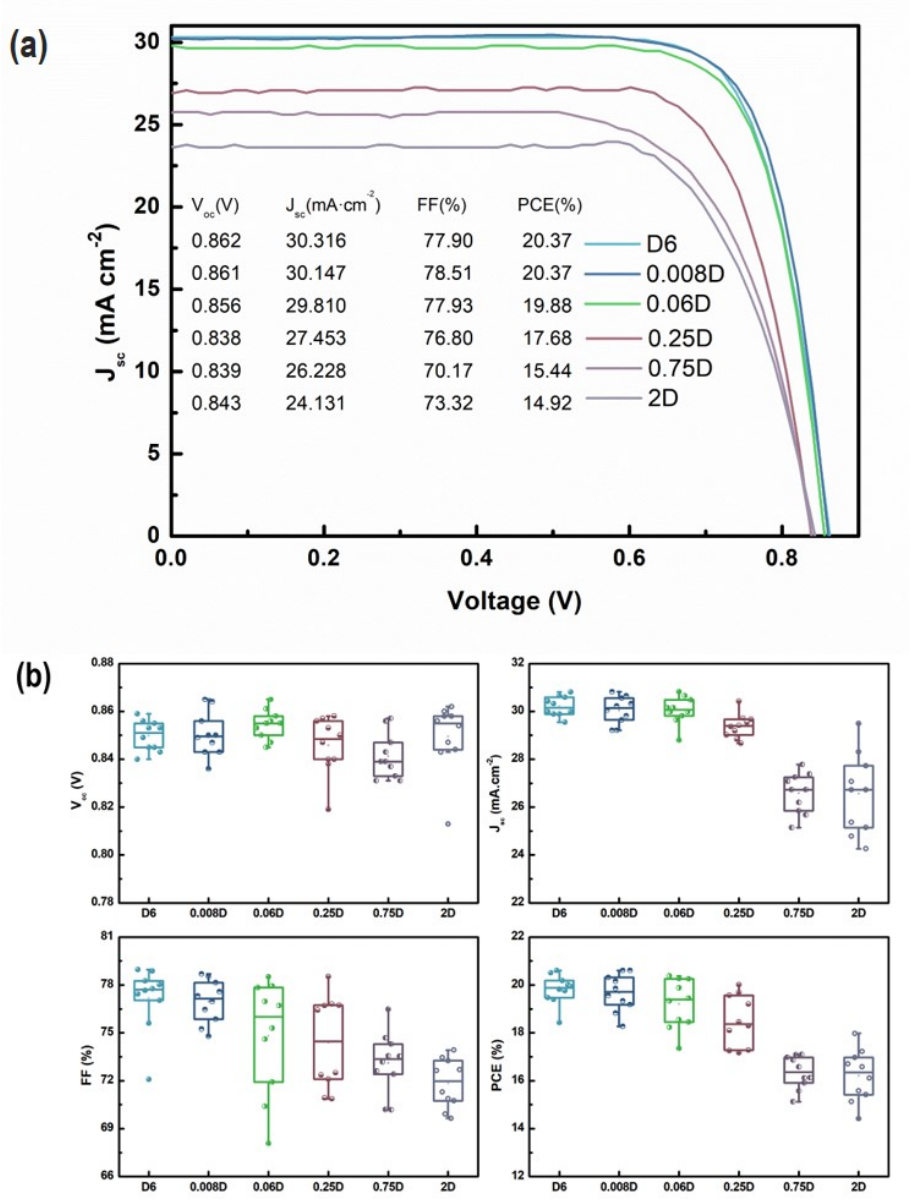

Figure S13 (a) J-V curve parameters of devices doped with different concentrations of PEG. (b) V_{oc}, J_{sc}, FF and PCE photovoltaic parameters statistics box of PEG doped devices with different concentrations. 0.008D, 0.06D, 0.25D, 0.75D, 2D correspond to 0.008, 0.06, 0.25, 0.75, and 2 mg·mL^{-1} PEG doped into the perovskite precursor. The trace PEG doping has little effect on the performance of device.

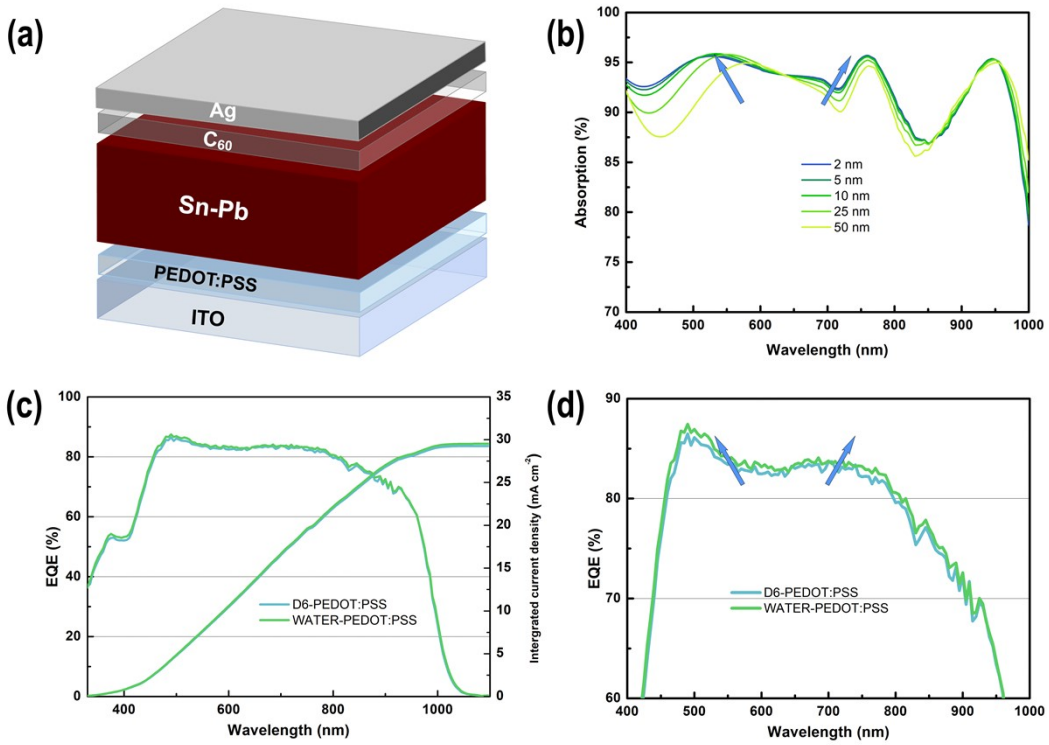

Figure S14 (a) The device structure and materials used in the simulation. (b) The absorption of devices with different thicknesses of PEDOT:PSS is calculated by simulation. (c) EQE spectra of the devices using D6-PEDOT:PSS and WATER-PEDOT:PSS HTLs. The integrated photocurrents calculated from the EQE spectra are also shown. (d) Partial enlargements of (c). The actual value has the same trend as absorption of simulation, which indeed indicates the thinning HTL after solvent etching process.

Optical simulation and detail parameters

An open-source program based on the Python programming language, which is available on the Web site (numpy.scipy.org), was used for optical simulation. We are based on the material in the P-I-N structure (**Figure. S14**a). The optical parameters of

each layer of the device, including refractive index (n) and extinction coefficient (k), were obtained from the reports [2-4]. The thickness parameters for each layer were chosen as follows: glass 7,000,00 nm (Incoherent), ITO 135 nm, perovskite 650 nm, C_{60} 30 nm and Ag 120 nm, respectively. The theoretical calculation of **Fig. 3**e is also based on this program.

Tables

Table S1. XRD data of perovskite films grown on different substrates.

Samples	2θ (deg)	Crystal orientation	Area	Height	FWHM
Glass/ITO/D6-PEDOT:PSS/Sn-Pb	13.7	(110)	357.1	2970.1	0.096
	24.2	(113)	36.7	179.4	0.163
	28.0	(220)	413.6	2702.8	0.123
	31.4	(122)	46.2	251.0	0.147
	40.2	(222)	18.7	107.0	0.159
	42.7	(330)	22.9	106.2	0.172
Glass/ITO/PEG-PEDOT:PSS/Sn-Pb	13.7	(110)	378.1	3194.5	0.094
	24.2	(113)	32.9	165.5	0.158
	28.0	(220)	472.3	3063.4	0.121
	31.4	(122)	47.3	255.5	0.145
	40.2	(222)	18.1	90.1	0.155
	42.7	(330)	24.8	115.3	0.170

Table S2. The TRPL spectra fitting results of perovskite films deposited on different substrates.

Samples	τ_1 (ns)	A_1(%)	τ_2 (ns)	A_2(%)	τ_{ave} (ns)
ITO/D6-PEDOT:PSS/Sn-Pb	27.88	27.9	141.85	71.7	133.97
ITO/PEG-PEDOT:PSS/Sn-Pb	15.73	37.2	119.33	62.6	111.88

Table S3. Performance statistics of 10 independent devices with D6-PEDOT:PSS (D6), WATER-PEDOT:PSS (WATER) and PEG-PEDOT:PSS HTL of different PEG-1000 concentrations etching (concentration).

Device		V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
D6	Average	0.851±0.014	30.18±0.28	77.37±1.34	19.88±0.44
	Champion	0.860	30.45	78.32	20.52
WATER	Average	0.853±0.008	30.22±0.55	77.51±1.55	19.98±0.56
	Champion	0.865	30.67	78.45	20.81
0.25 mg·mL^{-1}	Average	0.861±0.011	30.27±0.52	77.78±1.55	20.27±0.79
	Champion	0.872	30.78	78.60	21.09
0.5 mg·mL^{-1}	Average	0.863±0.009	30.38±0.72	77.46±1.58	20.32±0.76
	Champion	0.875	30.85	78.52	21.19
0.75 mg·mL^{-1}	Average	0.868±0.012	30.61±0.43	77.65±1.68	20.62±0.59
	Champion	0.874	31.37	78.75	21.58
1 mg·mL^{-1}	Average	0.863±0.009	29.73±0.91	75.80±1.64	19.46±0.92
	Champion	0.878	30.78	76.16	20.58
2 mg·mL^{-1}	Average	0.860±0.009	28.23±0.79	75.17±1.71	18.25±0.79
	Champion	0.866	29.57	76.49	19.59

The devices were measured with an aperture area of 0.0625 cm^2 under full AM1.5G illumination.

Table S4. Photovoltaic parameters and hysteresis index (HI) of devices with perovskite films deposited on different substrates.

Devices	Scan	V_{oc}(V)	J_{sc} (mA·cm^{-2})	FF(%)	PCE(%)	HI
D6-PEDOT:PSS	F	0.856	29.78	77.58	19.76	0.024
	R	0.857	29.78	79.3	20.23	
PEG-PEDOT:PSS	F	0.889	30.88	75.66	20.65	0.016
	R	0.887	30.88	76.34	20.92	

Table S5. Decay constants of TPC and TPV for different devices.

	Devices	τ (μs)
TPC	D6-PEDOT:PSS	1.18
	PEG-PEDOT:PSS	0.85
TPV	D6-PEDOT:PSS	8.69
	PEG-PEDOT:PSS	18.29

Table S6. The fitted EIS parameters of the devices

Devices	R_s (Ω)	R_{tc} (Ω)	R_{rec} (Ω)
D6-PEDOT:PSS	36.72	1057	5513
PEG-PEDOT:PSS	23.36	974.9	7870

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