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Supporting Information

Tailoring buried interface with self-assembled 2-chloroethylphosphonic acid for defect reduction and improved performance of tin-based perovskite solar cells

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Experimental section

Materials: Formamidinium iodide (FAI, 99.9%) and methylamium iodide (MAI, 99.9%) were purchased from Xi'an Polymer Light Technology Corp. CEPA was received from Aladdin Co., Ltd. PEDOT:PSS (AI 4083) was acquired from Heraeus Materials Technology Co., Ltd. Chlorobenzene (CB, 99.8%), DMF (99.8%), DMSO (99.9%), tin (II) iodide (SnI_2, 99.99%), and tin (II) fluoride (SnF_2, 99%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Device Fabrication: The ITO substrates were sequentially ultrasonic cleaned with deionized water, acetone, and ethanol for 15 min each time. After drying with high purity N_2 and vacuum drying in an oven, the ITO substrates were treated with UV-ozone for 20 min. The PEDOT:PSS solution was spin-coated onto ITO and spun at 4000 rpm for 30 seconds, then annealed at 140°C for 30 minutes and quickly transferred to a nitrogen-filled glove box. For the preparation of CEPA-modified PEDOT:PSS, different concentrations of CEPA were dissolved in DMSO and spin-coated onto PEDOT:PSS film and annealed at 120°C for 10 min. To prepare the perovskite precursor solution, 1 mmol of SnI_2, 0.75 mmol of FAI, 0.25 mmol of MAI and 0.1 mmol of SnF_2 were dissolved in 1 mL of mixed solvent (DMF/DMSO = 4/1) and an additional 10% GAI was added as an additive to improve the quality of the Sn perovskite films. The perovskite solution was then spin-coated at 6000 rpm for 60 seconds on PEDOT:PSS, and the CB was dropped on the perovskite film at the 12th second. The resulting films were annealed at 100°C for 10 min. Finally, C60 (30 nm), BCP (8 nm) and Ag (80 nm) electrodes were sequentially prepared by vacuum

thermal deposition.

Characterization: The *J-V* characteristics were carried out using Keithley 2400 under AM 1.5 G illumination (100 mW cm^{-2}) from a solar simulator (Oriel Sol3A Class Solar Simulator). The IPCE curves were measured by a QTest Station 500AD Solar Cell Quantum Efficiency System (CROWNTECH, INC.). The SEM images were obtained by using a Hitachi S-4800 field-emission scanning electron microscopy. The instrument for testing AFM images were icon/Dimension icon from Bruker Instrument Co., Ltd. X-ray diffraction patterns were examined by a Bruker D8 ADVANCE XRD equipment. The nuclear magnetic resonance (NMR) spectra were obtained using Bruker DELL PC1 equipment. The optical absorption spectra were carried out by a Shimadzu UV-vis 3600 spectrophotometer (UV-3600). PL was measured with a pulse laser at 510 nm (EI, FLS920). EIS were studied by the Zahner electrochemical workstation under dark condition. The XPS and UPS spectra of perovskite films were recorded by PHI Quantera SXM (ULVAC-PHI).

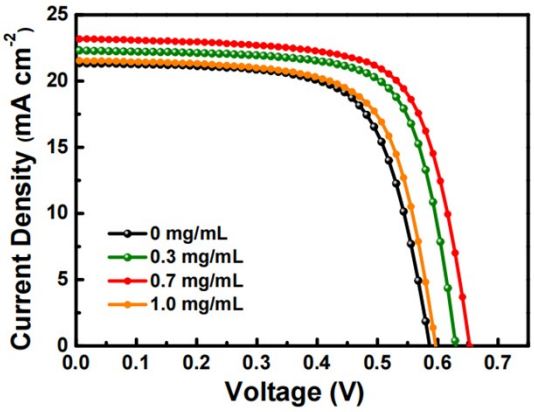

Figure S1. The *J-V* curves of Sn-PSCs based on PEDOT:PSS film modified with different CEPA concentrations.

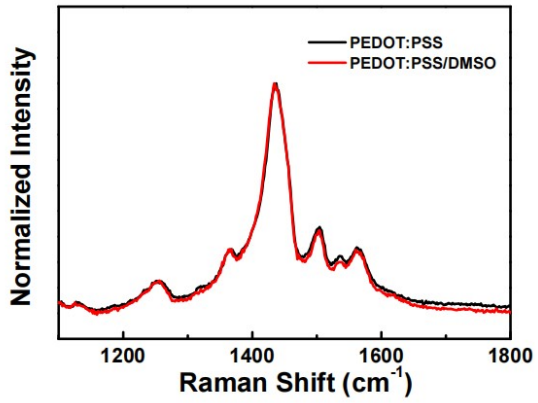

Figure S2. Raman spectra of the pristine PEDOT:PSS film and the film post-treated with anhydrous DMSO.

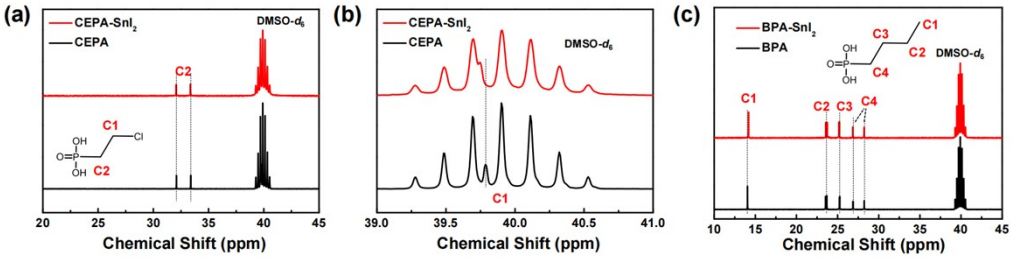

Figure S3. (a) The ^{13}C NMR spectra of CEPA and CEPA-SnI_2 mixtures in DMSO-d_6 solution. (b) Enlargement of the ^{13}C NMR spectral regions. (c) The ^{13}C spectra of BPA and BPA-SnI_2 mixtures in DMSO-d_6 solution.

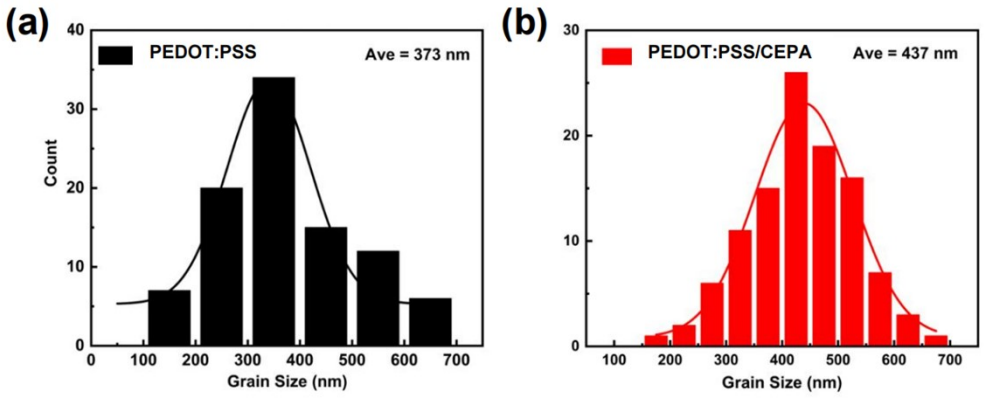

Figure S4. Grain size distribution of Sn perovskite deposited on (a) PEDOT: PSS and (b) CEPA-modified PEDOT: PSS films.

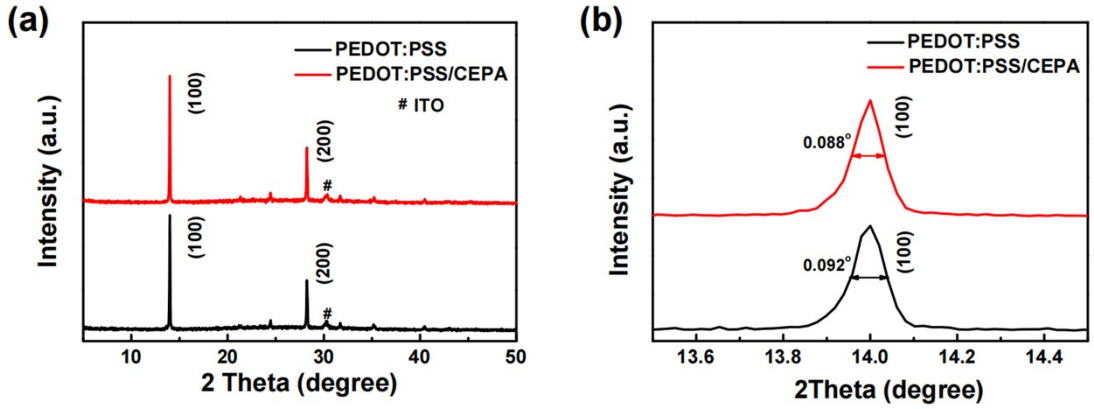

Figure S5. (a) XRD patterns of Sn perovskite films deposited on PEDOT: PSS with and without CEPA modification. (b) the corresponding FWHM values of (100) peak.

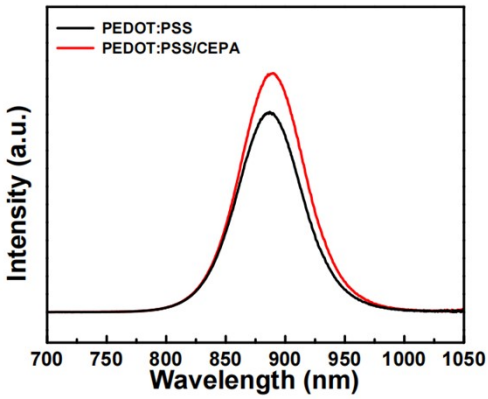

Figure S6. PL spectra of Sn perovskite films deposited on PEDOT: PSS with and without CEPA modification.

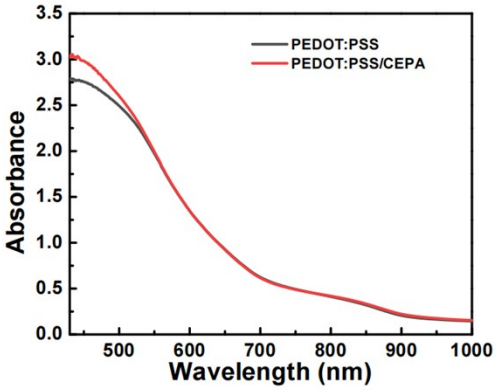

Figure S7. Absorption spectra of Sn perovskite films deposited on PEDOT: PSS with and without CEPA modification.

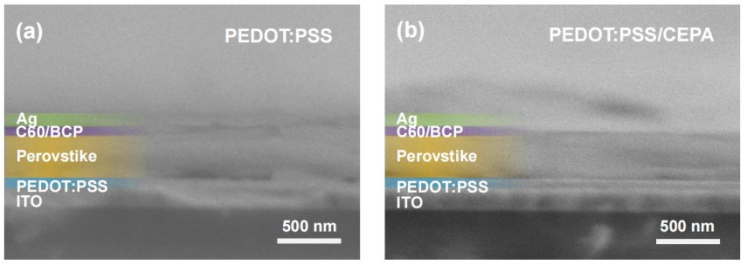

Figure S8. Cross-section SEM images of the Sn-PSCs based on PEDOT:PSS and PEDOT:PSS/CEPA films.

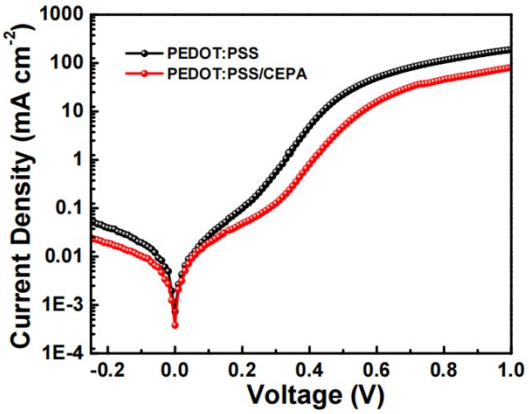

Figure S9. The dark *J-V* curves of devices with PEDOT: PSS and CEPA-modified PEDOT: PSS as the HTLs.

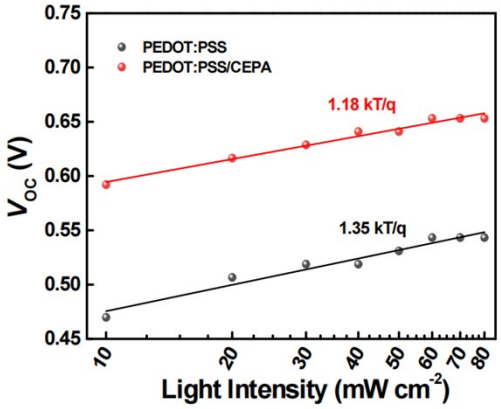

Figure S10. Linear relationship of V_{OC} to the light intensity.

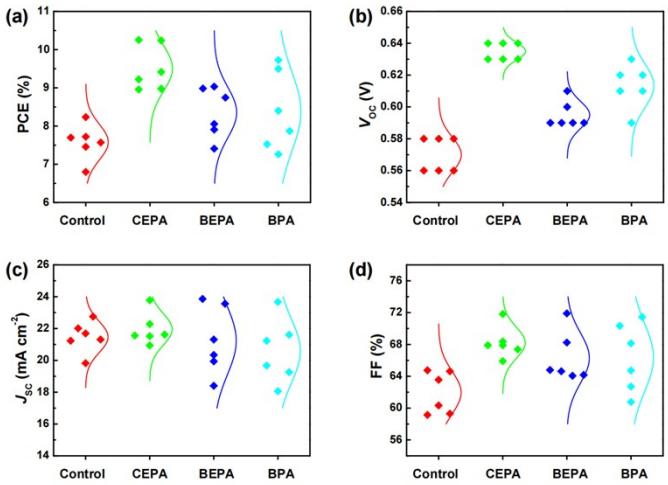

Figure S11. The statistical evaluation of PCE, V_{OC}, J_{SC}, and FF of Sn-PSCs with pristine PEDOT:PSS and the modified-PEDOT:PSS films with chloroethylphosphoric acid (CEPA), bromoethylphosphonic acid (BEPA), and butylphosphonic acid (BPA), respectively.

Table S1. Photovoltaic parameters of devices with PEDOT: PSS and CEPA-modified PEDOT: PSS as the HTLs. For each architecture, 16 devices were recorded to get an average value.

CEPA (mg/mL)		V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0	champion	0.58	21.34	69.24	8.57
	average	0.57 ± 0.01	19.25 ± 1.47	69.06 ± 3.57	7.58 ± 0.57
0.3	champion	0.63	22.31	71.85	10.10
	average	0.61 ± 0.01	21.85 ± 1.01	71.62 ± 1.19	9.58 ± 0.55
0.7	champion	0.64	23.17	71.81	10.65
	average	0.63 ± 0.01	22.45 ± 0.73	70.16 ± 2.68	9.96 ± 0.48
1.0	champion	0.59	21.54	69.56	8.84
	average	0.59 ± 0.02	19.59 ± 1.63	66.98 ± 3.34	7.78 ± 0.74