

Supporting Information

Ultrathin Polymethylmethacrylate Interlayers Boost Performance of Hybrid Tin Halide Perovskite Solar Cells

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Materials and Methods

Materials: Formamidinium iodide (FAI) and phenethylammonium iodide (PEAI) were purchased from Greatcell Solar. Tin(II) iodide (SnI₂, 99.99%) and tin(II) fluoride (SnF₂, 99%) were purchased from Sigma Aldrich. PEDOT:PSS was purchased from Heraeus Clevios. PCBM (99.5%) was purchased from Ossila. All solvents were purchased from Acros Organics.

Substrates preparation: ITO substrates (Psiotec, 1.2 c. x 1.2 cm, 15 Ω/cm²) were first rinsed with acetone and sonicated in soap, deionised water, acetone, and isopropanol sequentially, followed by an ultraviolet-ozone surface treatment for 15 min. PEDOT:PSS was filtered and spin coated on ITO at 5000 rpm with 2000 rpm acceleration for 30s, and subsequently annealed at 140°C for 20 min.

Device Fabrication: Poly(methyl methacrylate) (PMMA) precursor solution (0.1 mg/mL in dry chlorobenzene) was dynamically spin coated onto PEDOT:PSS films at 4000 rpm for 20s, no annealing was needed. The 0.8M (PEA)_{0.2}(FA)_{0.8}SnI₃ perovskite precursor solution was prepared in a glovebox from PEA⁺I⁻, FAI, SnI₂ and SnF₂ powders with a 0.2:0.8:1:0.1 molar ratio in a mixed solvent of 4:1 v/v mixture of DMF and DMSO (both ultradry and bottled with molecular sieves). The precursor solution was stirred and heated at 70°C for 1h before use. The solutions were then filtered (0.2 μm, PTFE) and deposited on the substrate via a two-step spin-coating procedure (1000 rpm for 10 s followed by 5000 rpm/30 s, 800 μL of dry diethyl ether was dropped in the middle of the substrate at 12 seconds), followed by 70°C annealing for 20 minutes. PCBM solution (15 mg/mL in chlorobenzene) was deposited on perovskite films by spin coating at 2000 rpm for 30s. Next, a bathocuproine (BCP) solution in isopropanol (0.5 mg/mL) was dynamically spin coated PC60BM at 5000 rpm for 20 s. 100 nm-thick Ag electrode was then processed via vacuum (10⁻⁶ mbar) thermal evaporation by using a mask leading to a 0.045 cm² device active area.

Film Characterization: UV-Visible spectroscopy measurements were performed with a Shimadzu UV-2600 integrating-sphere spectrophotometer. X-Ray Diffraction was performed with a PANalytical X'Pert Pro MRD diffractometer by using Cu Kα incident radiation (Ni-filtered) at 40 kV and 40 mA. Scanning electron microscopic (SEM) images were collected on a LEO 1525 Field Emission Scanning Electron Microscope operated at 10 kV using an InLens detector. SEM samples were sputtered with chromium (10 nm) before SEM measurement. Steady-state PL spectra and time-resolved PL decays (time-correlated single-photon counting) were measured with a Horiba Deltaflex Modular Fluorescence Lifetime setup fitted with a PPD 900 detector. The excitation wavelength was chosen as 404 nm and applied via a nanoled (Model N-07; repetition rate: 1 MHz; pulse duration < 200 ps). Contact-angle measurements were performed by using a KRUSS Drop Shape Analyzer DSA100 setup and water as the solvent.

Device Characterization: Current-voltage (J-V) characteristics were measured using a Keithley 2400 source meter at a scan rate of 50 mV/s in forward bias. The solar cells were illuminated (100 mW/cm²) using a 150 W Xenon lamp with an AM1.5 filter (ScienceTech), the light intensity was calibrated using an independent calibrated silicon photodiode and checked every hour. Devices were kept under inert conditions during the measurements by loading them in the glovebox in a homemade measuring chamber. External quantum efficiency (EQE) spectra were collected using Bentham Photovoltaic PVE300 system.

Operating stability of the device was measured by biasing the device at the voltage of the maximum power point which was calculated from the J-V curves and recording the current through the device under continuous illumination. Shelf stability of the devices was studied by comparing the J-V curves of the same device immediately after fabrication and after 15 days storage in a glove box filled with nitrogen.

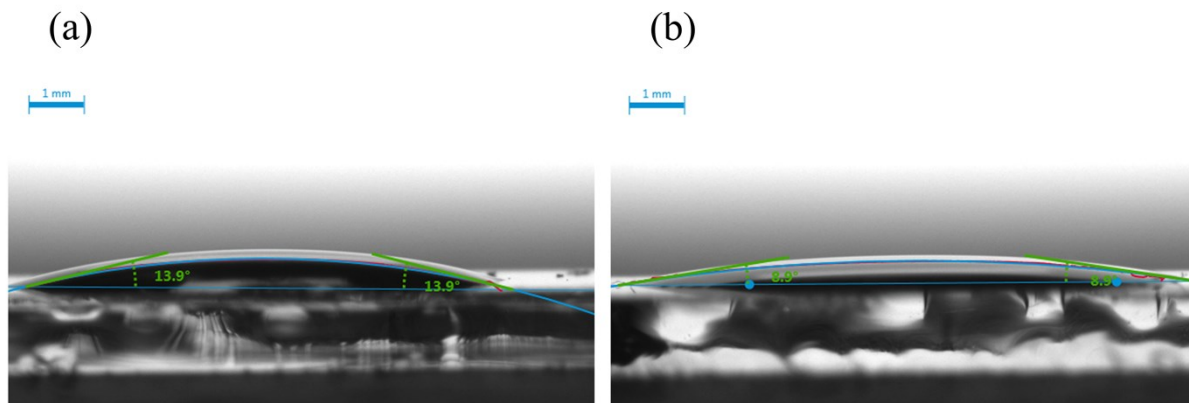


Figure S1. Contact angle measurements of (a) a PEDOT:PSS/PMMA substrate (angle: 13.9°) and (b) a PEDOT:PSS substrate (angle: 8.9°). Water was employed as the solvent and scale bar indicates 1 mm in both cases.

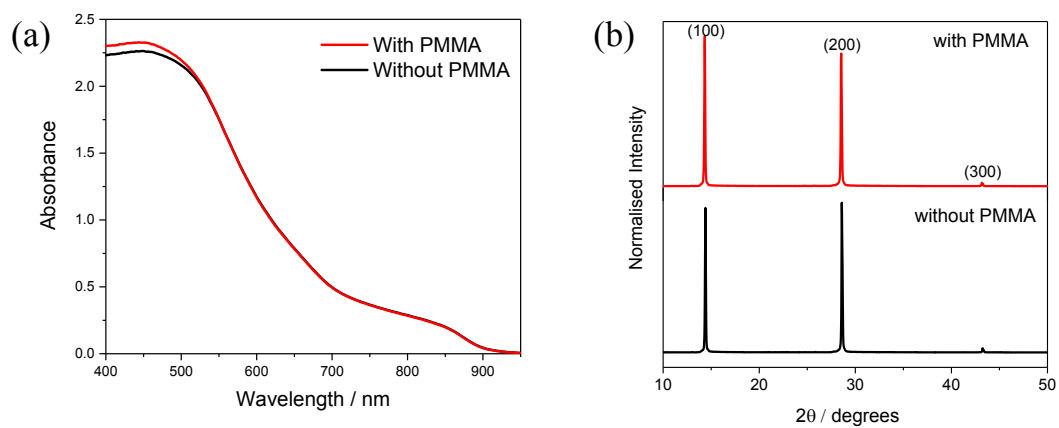


Figure S2. (a) UV-Visible spectra and (b) X-Ray Diffraction (XRD) patterns of $(\text{PEA})_{0.2}(\text{FA})_{0.8}\text{SnI}_3$ films on top of PMMA (red) and glass (black) substrate.

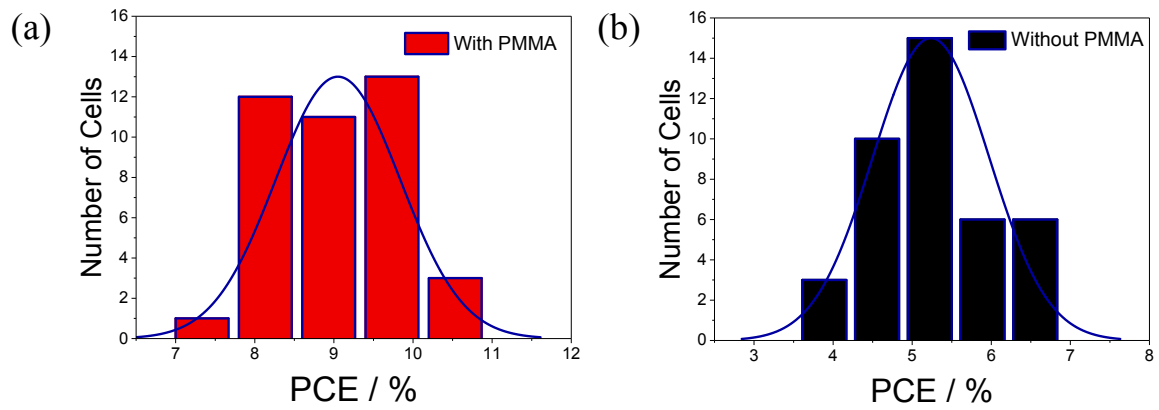


Figure S3. Device statistics for the Sn perovskite solar cells with PMMA (red) and without PMMA interlayer (black).

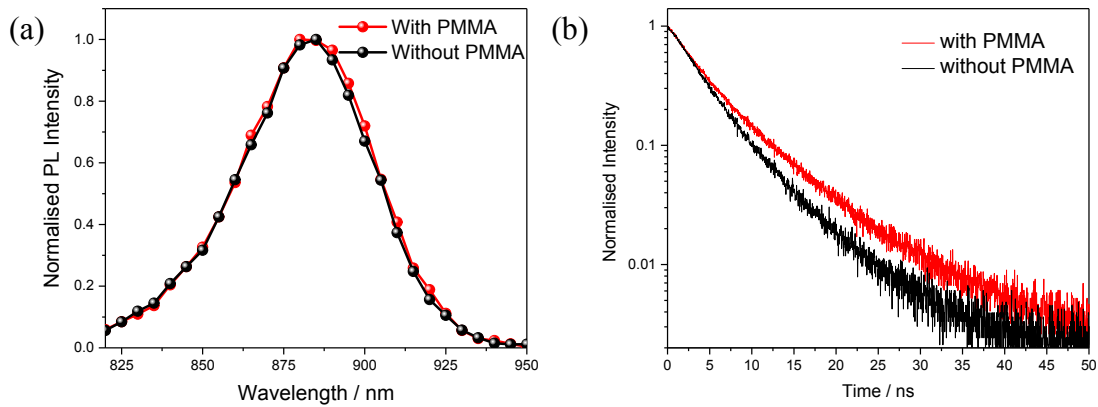


Figure S4. (a) Steady-state PL spectra and (b) time-resolved PL decays acquired at 850 nm with 404 nm excitation of Sn perovskite films deposited on top of glass with PMMA (red) and without PMMA (black) interlayer. Lifetime: with PMMA: $\tau = 4.03$ ns > without PMMA: $\tau = 3.52$ ns.

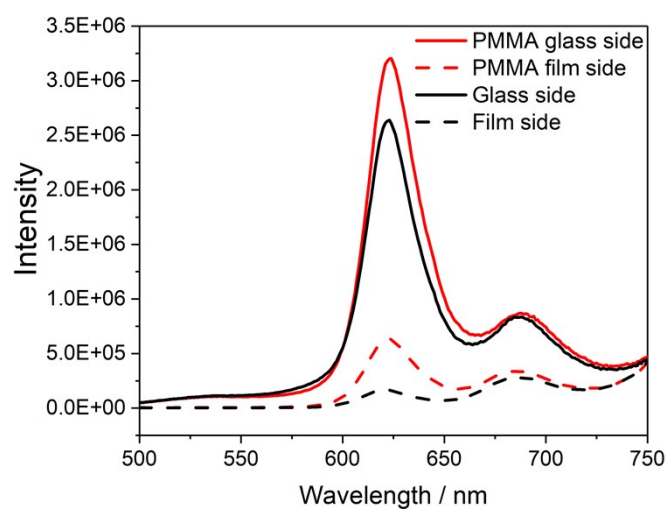


Figure S5. Steady-state PL spectra corresponding to 2D $(\text{PEA})_2(\text{FA})_{n-1}\text{Sn}_n\text{I}_{3n+1}$ Ruddlesden-Popper phases in Sn perovskite films with PMMA (red) and without PMMA (black). Emission peaks at ~ 625 nm and ~ 690 nm are attributed to $(\text{PEA})_2\text{SnI}_4$ ($n = 1$) and $(\text{PEA})_2(\text{FA})\text{Sn}_2\text{I}_7$ ($n = 2$) phases, respectively.

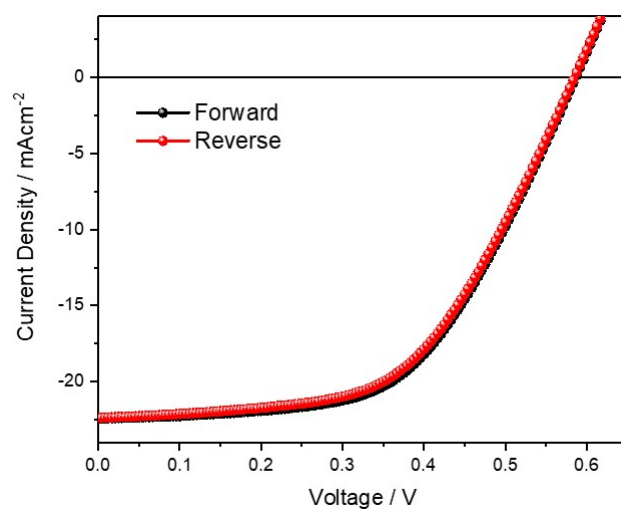


Figure S6. Hysteresis test for PMMA-based Sn perovskite solar cells showing that very little hysteresis exists in Sn-PSCs.

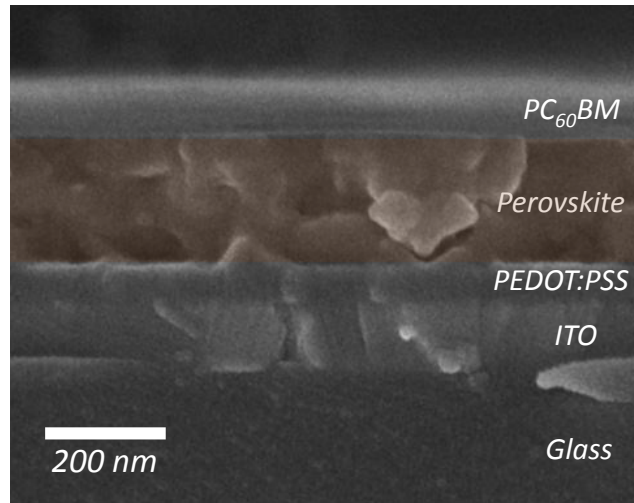


Figure S7. Cross sectional SEM image of a control Sn-based device, scale bar denotes 200 nm.

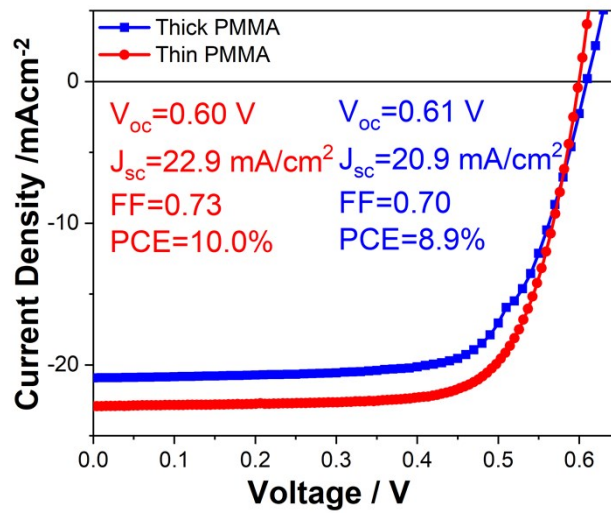


Figure S8. J-V curves of the $(\text{PEA})_{0.2}(\text{FA})_{0.8}\text{SnI}_3$ perovskite solar cells with PMMA layers of different thickness. Thick PMMA layer was made from concentrated precursor solution (0.5 mg/mL) whereas thin PMMA layer was made from standard precursor concentration (0.1 mg/mL).