## **Supporting Information**

## Crystal Morphologies of Organolead Trihalide in Mesoscopic/Planar Perovskite Solar Cells

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## **Experimental Procedure**

<u>Raw Chemicals and Precursors Preparation</u>. All reagent grade chemicals were obtained commercially from Sigma-Aldrich, St. Louis, MO, unless noted otherwise. Methylammonium iodide ( $CH_3NH_3I$  or MAI) was prepared in-house. In a typical procedure, 24 ml of 33 wt% methylamine ( $CH_3NH_2$ ) solution in anhydrous ethanol was reacted with 10 ml of 57 wt% hydroiodic acid (HI) in water, in 100 ml of ethanol (excess  $CH_3NH_2$ ) in a dry Ar atmosphere at room temperature. The solvent and the excess  $CH_3NH_2$  were removed using a rotary evaporator, and the resulting MAI powder was harvested.

<u>Preparation of MAPbI<sub>3</sub> Perovskite Thin Films.</u> First, 0.8 M PbI<sub>2</sub> solution in N,N'-dimethylformamide (DMF) was spin-coated at 4000 rpm for 15 s on substrates and then dried at room temperature under blowing air. Second, fresh MAI solution 10 mg.ml<sup>-1</sup> in anhydrous isopropanol was spin-coated onto the as-prepared PbI<sub>2</sub> layer, and it was then annealed at 150 °C for 1 min. This above procedure was then repeated for 3 times to enable the full conversion of PbI<sub>2</sub> into MAPbI<sub>3</sub>.<sup>1</sup> The excess MAI was washed using isopropanol, and the final thin films were annealed at 150 °C for 2 min to obtain a dark-colored MAPbI<sub>3</sub> perovskite films. Two types of substrates are typical used in this study: fluorinated-tin-oxide (FTO)-coated glass with compact TiO<sub>2</sub>, with or without the mesoporous TiO<sub>2</sub> layer.

Fabrication and *J-V* Testing of Perovskite Solar Cells (PSCs). For the fabrication of the planar PSCs, FTO-coated glass was patterned by 25% hydrochloric acid etching with zinc powder, and cleaned by soaking in a base bath (5 wt % NaOH in ethanol) overnight. After washing using deionized water and ethanol, a compact TiO<sub>2</sub> compact layer was deposited on top of the patterned FTO by spray pyrolysis at 450 °C. Perovskite was then deposited following the as-described procedure. This was followed by spin-coating a hole-transporting material (HTM) stock solution, which consisted of 80 mg 2,2',7,7'-tetrakis(N,N-dip-methoxyphenylamine)-9,9'-spirobifluorene, 30  $\mu$ l bis(trifluoromethane) sulfonimide lithium salt stock solution (500 mg Li-TFSI in 1 ml acetonitrile), and 30  $\mu$ l 4-tert-butylpyridine (TBP), and 1 ml chlorobenzene solvent. The HTM spin-coating process was performed in a dry-air atmosphere with humidity below 10%. Finally an Ag layer was deposited using thermal evaporator and a shadow

mask. For mesoscopic-planar hybrid PSCs, before perovskite processing, a layer of mesoporous  $TiO_2$  was deposited by spin-coating a diluted home-made  $TiO_2$  gel followed by 450 °C annealing in air for 30 min.<sup>2</sup>

The current density (J) - voltage (V) characteristics of the cells were obtained using a 2400 SourceMeter (Keithley, Cleveland, OH) under simulated one-sun AM 1.5G illumination (100 mW.cm<sup>-2</sup>) (Oriel Sol3A Class AAA Solar Simulator, Newport Corporation, Irvine, CA). Typical *J*-*V* scans at both forward ( $J_{sc} \rightarrow V_{oc}$ ) and reverse ( $V_{oc} \rightarrow J_{sc}$ ) direction were conducted at the rate of 20 mV s<sup>-1</sup>. A typical active area of 0.12 cm<sup>2</sup> was defined using a non-reflective mask for the *J*-*V* measurements.

<u>Film and Device Structure Characterization.</u> X-ray diffraction (XRD) was performed on a X-ray diffractometer (D8-Advance, Bruker, Germany) using Cu K $\alpha$  radiation using step size/time 0.02°/10 s conditions. The mesoporous sample without capping perovskite was prepared by polishing away the capping layer on a soft paper. For quantitative XRD, LaB<sub>6</sub> reference powder was used to measure the instrumental broadening, which was subtracted before applying the Scherer equation for the quantitative determination of the crystallite size (t). Scherer equation<sup>3</sup>:  $t = (0.9 \lambda)/(B \sin \theta_B)$ , where  $\lambda$  is the X-ray wavelength, B is the full-width at half-maximum (radians), and  $\theta_B$  is the Bragg angle.

Transmission electron microscopy (TEM) was conducted using TEM (2100F, JEOL, Tokyo, Japan) operated at 200 kV accelerating voltage equipped with an energy dispersive spectrometer (EDS; Oxford Instruments, UK) and 2x2 Mb post column CCD camera (GATAN, Pleasanton, CA). Two typical types of specimens are prepared. One set of specimens were prepared based on the cross-sections of the as-fabricated PSCs by focused ion beam (FIB; Helios 600, FEI, Hillisboro, OR) equipped with C and Pt gas injectors and micromanipulator (Omniprobe, Dallas, TX). A Pt layer of 2-3 µm thick was deposited on the surface of the sample prior to the FIB cross-sections preparation. The cross-sections measuring approximately 8x5 µm<sup>2</sup> in area and 0.5 µm in thickness were cut by 30 kV Ga<sup>+</sup> ions with ion beam current 28 nA, removed from the bulk sample, and then attached to the Omniprobe semi-ring. Final thinning was performed with 30 kV Ga<sup>+</sup> ions with ion beam current 2.8 nA followed by cleaning with 2 keV Ga<sup>+</sup> ions with a beam current as low as 10 pA. For some specimens additional Ar<sup>+</sup> ion milling (PIPS, GATAN, Pleasanton, CA) at low glancing angle and energy of 0.1 keV was used at the very final stage. The other set of specimens were prepared by directly solution processing of the perovskite on TEM grids with or without a mesoporous TiO<sub>2</sub> layer. The processing of the mesoporous TiO<sub>2</sub> layer and the perovskite layer was conducted using the procedure as described elsewhere.<sup>2</sup> EDS elemental mapping was performed using an EDS detector (Oxford Instruments, UK) attached to the TEM. The mesoscopic PSC for EDS mapping has a thinner HTM layer compared to the one used for conventional TEM and HRTEM studies. Digital Micrograph (GATAN, Pleasanton, CA) software was used for image and selected area electron diffraction patterns processing.





**Fig. S1.** TEM specimen of planar MAPbI<sub>3</sub> film deposited directly onto a TEM grid (non-FIBed): (A) HRTEM image showing planar defects and (B) corresponding SAEDP showing "streaking" spots.

## **Supplementary References**

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