## 22.8%-Efficient Single-Crystal Mixed-Cation Inverted Perovskite Solar Cells with a Near-Optimal Bandgap

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## **Materials and Methods**

*Materials:* Methylammonium iodide (MAI) and formamidinium iodide (FAI) were purchased from Greatcell Solar Limited (Australia). Lead(II) iodide (PbI<sub>2</sub>, 99.999%) was purchased from Alfa Aesar.  $\gamma$ -Butyrolactone (GBL, >99%) was purchased from Sigma-Aldrich. All materials were used as received without any further purification.

All the following other than substrate cleaning were carried out in a nitrogen filled environment.

*Substrates Preparation:* 5cm x 5cm ITO substrates were sonicated in soap, DI water, acetone and IPA sequentially, followed by an ultraviolet-ozone (UVO) surface treatment for 15 minutes. Likewise, for polycrystalline devices, patterned ITO/glass substrates were cleaned accordingly. Next, PTAA solution (2 mg/ml in toluene) was spin-coated for 30 s at 4000 rpms, and subsequently annealed at 100 °C for 10 min.

Growth of Single-Crystal Thin Films (Figure S2): 1.9M of FA<sub>0.6</sub>MA<sub>0.4</sub>PbI<sub>3</sub> in GBL was prepared by dissolving an equimolar amount of (0.6 FAI + 0.4MAI) and PbI<sub>2</sub> in GBL at 50 °C by stirring overnight. 60 µl of the solution was placed on a PTAA-coated substrate preheated to the solution temperature and covered with another PTAA-coated substrate. The surface tension and the weight of the top substrate should drive the solution to disperse evenly throughout the entire substrate area. No spacer was used as the surface tension of the thin layer of solution was enough to keep the solution from spilling out. The temperature was then increased to 75°C at a rate of 15°C/hr and then to 120°C at 3°C/hr to induce nucleation and growth. Next, the substrates were separated using a razor blade by placing it at the edge in between the substrates and the remnant solution was quickly cleaned with Kimwipes. Each crystal film preferred to attach on either the top or bottom substrate (not both). The substrates were allowed to cool down slowly to room temperature on the hotplate to ensure good contact between the substrate and single-crystal thin film, after which they were obtained and collected. Crystal sizes ranged from 4-8 mm<sup>2</sup>. MAPbI<sub>3</sub> films were grown in GBL according to our previous study.<sup>1</sup>

*Preparation of Polycrystalline Thin Films:* 1.3M of FAPbI<sub>3</sub> or FA<sub>0.6</sub>MA<sub>0.4</sub>PbI<sub>3</sub> was dissolved in a mixture of DMF and DMSO (9:1 DMF:DMSO by volume). 100 μl of the solution was placed on a PTAA-coated substrate and spincoated at a speed of 4000 r.p.m. for 25 seconds. After 5 seconds elapsed, 150 μl of chlorobenzene was dropped on the spinning substrate. The sample was subsequently annealed for 10 minutes at 150°C for FAPbI<sub>3</sub> or 120°C for FA<sub>0.6</sub>MA<sub>0.4</sub>PbI<sub>3</sub>.

*Device Fabrication:*  $C_{60}$  (20 nm) and BCP (6 nm) were thermally evaporated at a rate of 0.1 Å/s to form the electron transport layer. Then, the edges of the single crystals were masked with Kapton tape to avoid short circuiting between the top electrode (Cu) and ITO. Finally, Cu (80 nm) was

evaporated at a rate of 1 Å/s to complete the device. A photomask was properly placed on each device before photovoltaic testing.

*Solubility Test:* FA<sub>0.6</sub>MA<sub>0.4</sub>PbI<sub>3</sub> or MAPbI<sub>3</sub> crystals were crushed into powder and added gradually (25 mg increments) to 2 ml of GBL preheated to the desired temperature. The addition was stopped when saturation was reached, for e.g., when the solution could no longer completely dissolve the powder within 15 minutes.

Characterization: X-ray diffraction was performed using a Bruker D8 Advance diffractometer employing Cu-Ka radiation. Steady-state absorption was carried out using a LAMBDA 950 PerkinElmer UV/Vis Spectrophotometer with an integrating sphere. Scanning electron microscope (SEM) images were taken under a Teneo VS SEM (Thermo Fisher Scientific). Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded using a Bruker 700 MHz AVANACIII NMR spectrometer equipped with Bruker TCI multinuclear CryoProbe (BrukerBioSpin, Rheinstetten, Germany). The chemical shifts of each 1H spectrum was corrected using TMS signal at 0.0 pp, as internal chemical shift reference. Steady-state photoluminescence (PL) was performed in reflection mode using a WITec Apyron Raman/PL machine with a laser excitation wavelength of 532 nm. Current-Voltage characteristics were tested with a Keithley 2400 Sourcemeter and a Class AAA solar simulator equipped with a 150W Xenon arc lamp (Sun 3000, Abet Technologies) under AM1.5G illumination. The voltage was swept with a speed of 500 mV/s for both forwardand reverse-scans. Prior to measurement, the light intensity was calibrated using a silicon reference cell with a KG5 filter window (ReRa Solutions). The external quantum efficiency (EQE) was measured using a QEX10 Spectral Response Measurement System (PV Measurements, Inc.), calibrated against a reference silicon photodiode.



**Figure S1.** Efficiency progress of single-crystal perovskite solar cells. Abbreviations: ZJU Zhejiang University; UNL University of Nebraska-Lincoln; KAUST King Abdullah University of Science and Technology; SYSU Sun Yat-sen University; STDU Shijiazhuang Tiedao University.



Figure S2. Fabrication scheme of single-crystal thin film growth.



**Figure S3.** Crystallization of FA<sub>0.8</sub>MA<sub>0.2</sub>PbI<sub>3</sub> in GBL at 70 °C resulting in non-perovskite yellow rods and irregular black-shaped crystals.



Figure S4. X-ray Diffraction 2θ patterns of the (a) single-crystal thin films and (b) ground crystal films.



Figure S5. <sup>1</sup>H NMR of the mixed cation single-crystal films.



Figure S6. Normalized photoluminescence spectra of FA<sub>0.6</sub>MA<sub>0.4</sub>PbI<sub>3</sub> and MAPbI<sub>3</sub> single-crystal films.



Figure S7. Absorption spectrum of FA<sub>0.6</sub>MA<sub>0.4</sub>PbI<sub>3</sub> and MAPbI<sub>3</sub> single-crystal films.



Figure S8. Compositional stability of polycrystalline and single-crystal  $FA_{0.6}MA_{0.4}PbI_3$  and  $MAPbI_3$  films at 85 °C and 65% RH.



**Figure S9.** Photo of the rear side of the devices showing a (a) 1-year-stored well-attached single-crystal film and (b) detached single-crystal film after one day at 85 °C in a glovebox.

References:

(1)Chen, Z.; Turedi, B.; Alsalloum, A. Y.; Yang, C.; Zheng, X.; Gereige, I.; AlSaggaf, A.; Mohammed, O. F.; Bakr, O. M. Single-Crystal MAPbI<sub>3</sub> Perovskite Solar Cells Exceeding 21% Power Conversion Efficiency. *ACS Energy Lett.* **2019**, *4*, 1258-1259.