

## Supporting Information

### **Thermal Stability and Performance Enhancement of Perovskite Solar Cells Through Oxalic Acid-Induced Perovskite Formation**

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## MATERIALS AND METHODS

### Materials

Fluorine-doped tin oxide (FTO) substrates (sheet resistance:  $15 \Omega/\square$ , size:  $1.5 \times 1.5 \text{ cm}^2$ , thickness: 2.2 mm) were purchased from Hartford Glass Co, USA. Lead (II) iodide ( $\text{PbI}_2$ , 99%) was acquired from Acros Organics. Methylammonium iodide (MAI or  $\text{CH}_3\text{NH}_3\text{I}$ ) was obtained from GreatCell Solar. Anhydrous Oxalic Acid ( $(\text{COOH})_2$ ) was purchased from Spectrum Chemical Mfg. Corp. PEDOT: PSS (Clevios P VP AI 4083) was obtained from Heraeus. PCBM (99.5%) was received from Nano-C, and Rhodamine 101 dye was procured from Sigma-Aldrich. All the solvents used were anhydrous and obtained from commercial sources.

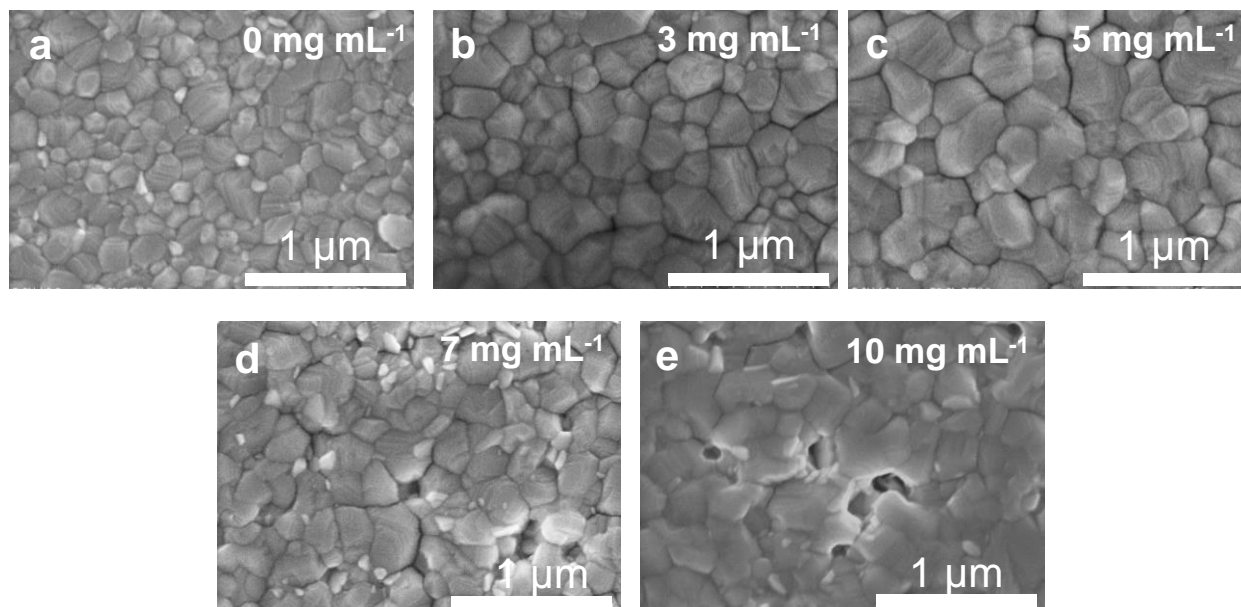
### Device Fabrication

On a pre-cleaned FTO substrate, the PEDOT: PSS layer was first spin coated at 4500 rpm for 60 s followed by baking at  $140^\circ\text{C}$  for 10 min. The PEDOT: PSS coated substrates, after cooling down to room temperature, were transferred to a glove box filled with nitrogen. Perovskite precursor solutions were prepared by mixing 209 mg of MAI, 581 mg of  $\text{PbI}_2$ , and different amount of oxalic acid (0, 3, 5, 7, & 10 mg) in a mixed solvent (300  $\mu\text{L}$  of DMSO and 700  $\mu\text{L}$  of  $\gamma$ -butyrolactone). Sixty microliters of these precursor solutions were spin coated on top of the PEDOT:PSS films at 750 rpm for 20 s followed by 4000 rpm for 60 s. During the second step of spin coating, 40 s before the end, 160  $\mu\text{L}$  of anhydrous toluene was dripped over the precursor film. The substrates were then annealed on a hotplate at  $80^\circ\text{C}$  for 10 min. After cooling down to room temperature, a 20  $\text{mg mL}^{-1}$  solution of PCBM in chlorobenzene was spun at 2000 rpm for 40 s over the perovskite film and annealed at  $80^\circ\text{C}$  for 5 min. A very thin layer of rhodamine was then spin coated from a 0.5  $\text{mg mL}^{-1}$  solution in IPA at a spin speed of 4000 rpm for 40 s. Finally,  $\sim 100 \text{ nm}$  of silver was evaporated using a shadow mask under a vacuum in the order of  $10^{-6} \text{ mbar}$  to achieve an active area of  $0.16 \text{ cm}^2$ .

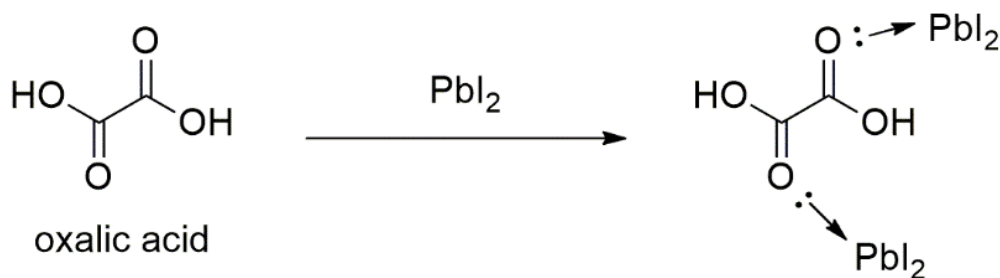
### Characterization Methods

Fourier transform infrared (FTIR, Perkin-Elmer-Spectrum) spectroscopy was used to study the interaction of OA and perovskite. The morphology of perovskite samples were examined on a scanning electron microscope (SEM, Hitachi S-4800). Perovskite grain orientation was measured using X-ray diffraction (XRD, Rigaku SmartLab system, 2.2 kW,  $\text{Cu-K}\alpha = 1.54 \text{ \AA}$ ). Optical and Photoluminescence spectra were recorded using an UV-vis spectrometer (Hitachi, U-3010) and a fluorescence spectrophotometer (HORIBA Jobin Yvon, fluoromax-4 with a 405 nm laser excitation) respectively. An Ametek VERSASTAT3-200 Potentiostat was used in the frequency range 1 Hz–1 MHz with amplitude of 20 mV in dark condition at MPP to perform EIS analysis. Photocurrent density-voltage ( $J$ - $V$ ) performance of the PSCs was measured in ambient environment without encapsulation using a Xenon arc lamp with a filter under AM 1.5 conditions, which were calibrated using a standardized silicon solar cell from NREL (S1133-14). External quantum efficiency measurements were done using the Newport monochromator, Model 74125

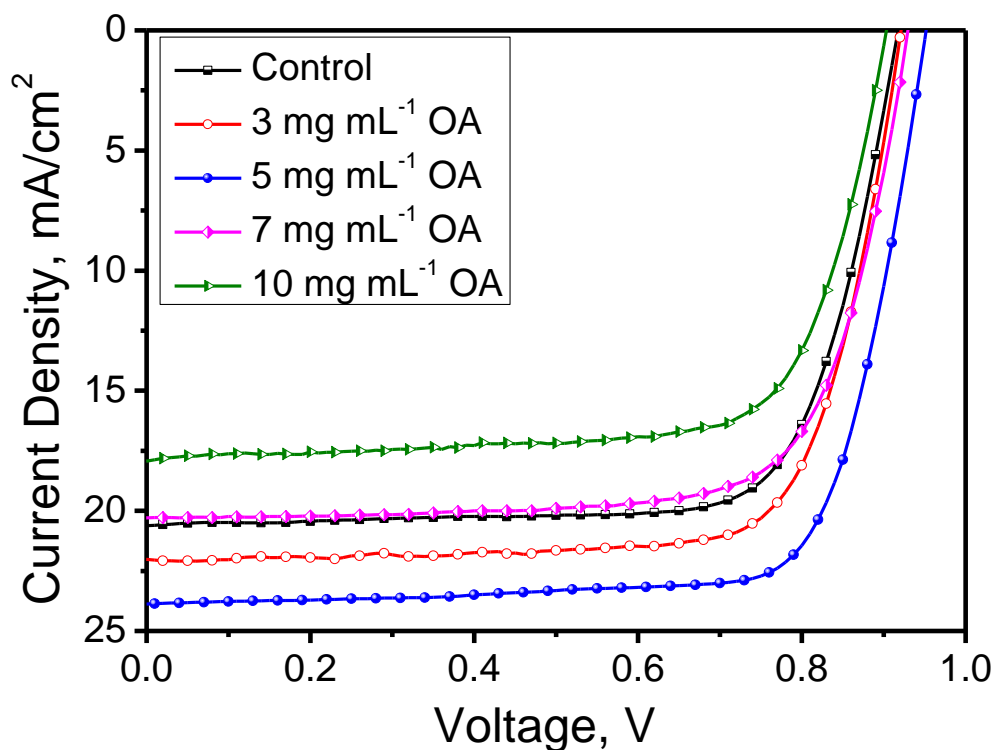
and the Xenon lamp (Newport, Model 67005). The transient photocurrent and photovoltage investigations were made utilizing nitrogen laser pulse (OBB's Model OL-4300) at 377 nm to pump a dye laser (model 1011) for generating a short pulse. This pulsed laser worked as a source of excitation with  $<1$  ns pulse duration and  $\sim 4$  Hz frequency. The dynamics curves of TPC and TPV measurements were recorded on a digital oscilloscope in open condition at around  $1\text{ M}\Omega$  resistor for TPV and in short-circuit condition at  $50\text{-}\Omega$  resistor for TPC. Operational stability of perovskite solar cells was estimated by storing the devices in a temperature and humidity chamber (ESPEC SH-240) at  $85\text{ }^{\circ}\text{C}$  and RH of  $60 \pm 5\%$ .



**Figure S1.** FESEM images of  $\text{MAPbI}_3$  perovskite films (a) without and (b-e) with different amount of OA additive



**Figure S2.** Structure of OA additive and schematic of the probable reaction between OA and  $\text{Pb}^{2+}$ .



**Figure S3.** Photocurrent density vs voltage ( $J$ - $V$ ) curves of PSCs fabricated without and with different amount of OA additive.

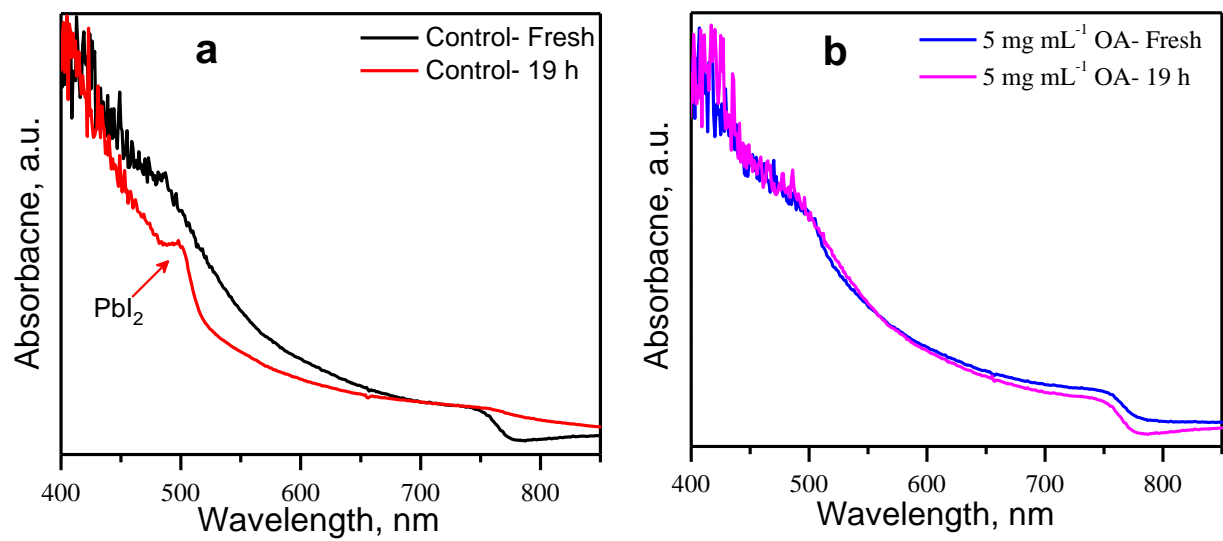
**Table S1.** Photovoltaic performance parameters of the PSCs fabricated without and with different amount of OA additive.

Device	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	$V_{oc}$ (V)	FF	PCE, Best (Average) (%)
Control	20.58	0.92	0.74	14.06 (13.34 $\pm$ 0.35) <sup>a</sup>
3 mg mL <sup>-1</sup> OA	22.09	0.93	0.74	15.23 (14.61 $\pm$ 0.44) <sup>b</sup>
5 mg mL <sup>-1</sup> OA	23.89	0.96	0.75	17.12 (16.46 $\pm$ 0.48) <sup>a</sup>
7 mg mL <sup>-1</sup> OA	20.29	0.93	0.73	13.79 (12.97 $\pm$ 0.48) <sup>b</sup>
10 mg mL <sup>-1</sup> OA	17.93	0.91	0.72	11.68 (11.15 $\pm$ 0.59) <sup>b</sup>

<sup>a</sup> Average of 50 devices. <sup>b</sup> Average of 15 devices

**Table S2.** Parameters extracted from EIS curve

Device	$R_s$ (ohm)	$R_{ct}$ (ohm)	CPE (nF)
control	7.57	3590	36.29
5 mg mL <sup>-1</sup> OA	7.15	16108	22.59



**Figure S4.** UV visible absorption spectra of perovskite film (a) without and (b) with 5 mg mL<sup>-1</sup> OA additive stored in a temperature and humidity chamber at 85 °C and RH of 60 ± 5%.