

Supporting information for

Evidence for surface defect passivation as the origin of the remarkable photostability of unencapsulated perovskite solar cells employing aminovaleric acid as a processing additive

Chieh-Ting Lin^{ab}, Francesca De Rossi^c, Jinhyun Kim^a, Jenny Baker^c, Jonathan Ngiam^b,

Bob Xu^b, Sebastian Pont^a, Nicholas Aristidou^a, Saif A. Haque^a, Trystan Watson^c, Martyn

A McLachlan^{*b}, James R Durrant^{*ac}.

a. Department of Chemistry and Centre for Plastic Electronics, Imperial College

London, Exhibition Road, London SW7 2AZ, U.K

b. Department of Materials and Centre for Plastic Electronics, Imperial College

London, Exhibition Road, London SW7 2AZ, U.K.

c. SPECIFIC IKC, College of Engineering, Swansea University, Bay Campus, Fabian Way,

Swansea SA1 8EN, U.K.

Corresponding author:

Martyn A McLachlan (martyn.mclachlan@imperial.ac.uk)

James R Durrant (j.durrant@imperial.ac.uk)

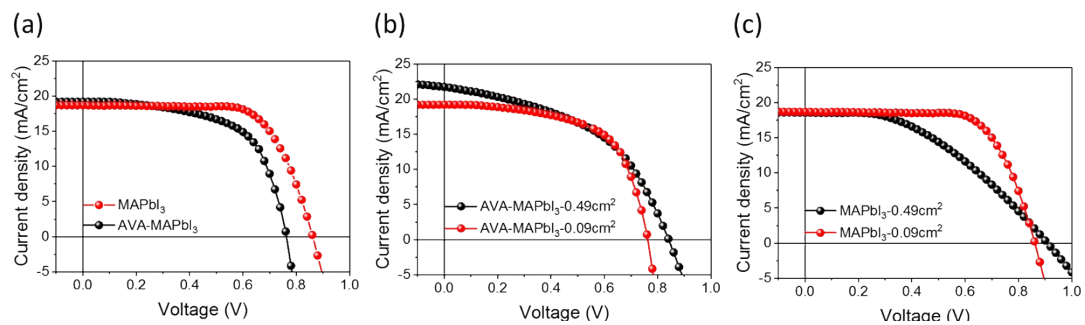


Figure S1. Current voltage characteristic of (a) MAPbI₃ and AVA-MAPbI₃ c-PSCs with 0.09cm² mask, (b) AVA-MAPbI₃ devices with 0.49cm² and 0.09cm² mask and (c) MAPbI₃ devices with 0.49cm² and 0.09cm² mask.

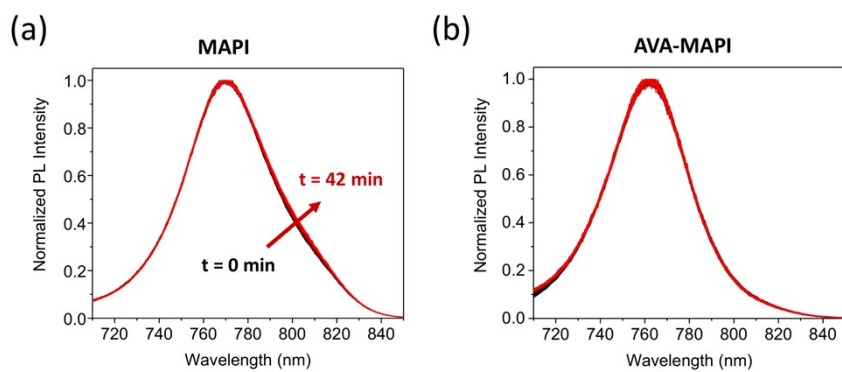


Figure S2. Normalized PL intensity with O₂ exposure of (a) MAPbI₃ and (b) AVA-MAPbI₃

Experimental Section

Device fabrication

Laser patterned FTO glass substrates (XOP, TEC 7) were cleaned using a 5% solution of Hellmanex in water, then rinsed with deionized water, acetone and isopropanol (IPA), dried with nitrogen and plasma cleaned for 10 minutes. A compact TiO₂ layer was deposited by spraying a 0.2 M titanium di-isopropoxide bis(acetylacetonate) solution in IPA onto the substrates kept at 300 °C on a hot plate. 800 nm-thick mesoporous layers of TiO₂ with 1 cm² active area were obtained by screen printing a commercial TiO₂ paste (Dyesol 30-NRD, diluted 1:1 in terpineol) and after firing the samples at 550 °C for 30 minutes. A commercial zirconia ink (Solaronix ZT/SP) was screen printed afterwards and heated at 400 °C for 30 min to obtain a 1.2 μm-thick ZrO₂ layer, followed by the screen printing of the carbon paste (GEM D3) to get a 10 μm-thick top electrode, which was then also annealed at 400 °C for 30 min. The substrates were cooled down and kept at 150 °C until ready for the infiltration of the perovskite solution. All layers were printed in air at ambient conditions. For the MAPbI₃ cells, a solution of PbI₂ (1.2 M in DMF) was drop casted on the cells kept on a hot plate at 70 °C through the carbon and then immersed in a MAI solution in IPA (10 mg/ml) for 30 min, rinsed with IPA and annealed in a fan oven for 10 min at 100 °C. For the AVA-MAPbI₃ cells, an equimolar solution of PbI₂ (TCI Chemicals) and MAI (Dyesol) in γ -butyrolactone (Sigma-Aldrich) was prepared adding 5-AVAI (Dyesol) to obtain a 3% molar ratio of 5-AVAI to MAI and drop casted on the cells through the carbon layer and then annealed in a fan oven for 1 hour at 50 °C. Silver paint was applied on the cells' contacts prior to J-V measurements, carried out using in-house developed software and a Keithley 2400 source meter under AM 1.5 illumination from a class AAA solar simulator (Newport Oriel).

Device stability characterization

Both MAPbI₃ and AVA-MAPbI₃ were masked to 0.49 cm² using black tape and tested in air, at room temperature and relative humidity around 15%, under 1 equivalent sun illumination from white LEDs (72 Oslon PowerFlood, 4000 K), using an in-house stability setup. Cells were placed in a sealed small chamber, endowed with a quartz window and electrical contacts to perform the J-V scans. An in-house developed software allowed to automatically scan the cells every 30 minutes, between 1 V and -0.1 V. Between scans, they were kept at open circuit.

Perovskite thin film fabrication

The MAPbI₃ solution were prepared by dissolving 1.5M MAI and PbI₂ into mixed

solvent (DMF:DMSO=9:1.1). The AVA-MAPbI₃ solution were prepared by adding 3% molar ratio of 5-AVAI to MAPbI₃ solution. The perovskite solution was spinning-coated on cleaned glass substrates at 4000rpm for 30 seconds. At 7 second, 500 μl diethyl ether (Sigma-Aldrich) were dripped on the substrates. The substrates were annealed at 100°C for 30 minutes.

Thin film stability characterization

The optical degradations of perovskite thin films were monitored by averaged RGB output changes in environmental controlled glovebox.

$$\text{Optical degradation} = \frac{|RGB_t - RGB_{deg}|}{|RGB_0 - RGB_{deg}|}$$

The camera recorded the averaged red-green-blue value over time. Here, the RGB₀ refer to the initial RGB value of film, while RGB_t refer to the RGB value at time t. RGB_{deg} is the RGB value of degraded sample. The humidity of glovebox was controlled by humidity sensor and dehumidifier with desiccant column. Light source was provided by 4000 K LED with 1 sun intensity, calibrated by equivalent Jsc produced with MAPbI₃ device measured under AM 1.5 solar simulator.

Low energy ion scattering

For surface analysis, IONTOF Qtac100 was used. 3 keV ⁴He primary beam was used to obtain survey spectra from the 500 to 1400 eV scattering energy range. 5 keV ²⁰Ne primary beam was used to obtain lead and iodine surface peaks with greater energy resolution. Total ion dose density (ions cm⁻²) were restricted to 2 x 10¹³ ions cm⁻² to ensure that original surface conditions were retained and unaltered by beam interactions, *i.e.* “static conditions” were maintained, during measurements. This resulted in the analysis of the outermost atomic layer.

Photoluminescence Spectroscopy and Uv-Vis

Photoluminescence was measured by Horiba Jobin Yvon Fluorolog system. LED light source with 700nm short wavelength pass filter was used as external light source to achieve full sun intensity. For PL stability measurement, the PL was scanned every 26 seconds. The samples were stored in cuvette filled with N₂, and exposed to oxygen at the beginning of stability measurement. Uv-Vis were measured by Shimadazu UV-2600 system, with wavelength range from 450 nm to 850 nm.

Superoxide probing

A stock 31.7 μM solution of the HE probe was prepared by dissolving 10 mg in 10 ml of dry toluene; sonication was used to facilitate miscibility. Films were then added to

10 ml of 0.317 μ M solution created from the stock solution. Photoluminescence spectra were recorded using an excitation wavelength of 520 nm and slit widths of 10 mm on a Horiba Yobin-Ybon Fluorolog-3 spectrofluorometer. Degradation in a moisture free environment was achieved by employing a solution of 10 mL dry toluene to which the films were submerged. Oxygen was continuously gassed through and illumination was provided by a tungsten lamp with a power of approximately 1.5 mWcm⁻²

Scanning electron microscopy:

Gemini LEO 1525 scanning electron microscopy (SEM) was used to obtain the SEM images. Accelerating voltage was 5kv and working distance was kept as low as possible. All samples were coated with 10nm chromium prior to imaging.