

## Supporting Information for

### Light and oxygen induced degradation limits the operational stability of methylammonium lead triiodide perovskite Solar Cells

#### Experimental

##### Device Manufacture

Cells were manufactured following a previously reported procedure.[1] In short and FTO coated glass substrate was coated with a compact TiO<sub>2</sub> layer by spray pyrolysis, of a 20 mM titanium diisopropoxide bis(acetylacetonate) solution (Aldrich) at 475 °C. In instances where a mesoporous TiO<sub>2</sub> layer was used, a commercially available paste (18-nrt, dyesol) was first diluted 1:9wt with ethanol before spin coating deposition at 4500rpm for 45 seconds and sintering at 500 °C. In instances where a mesoporous Al<sub>2</sub>O<sub>3</sub> layer was used, a 4%wt. suspension of Al<sub>2</sub>O<sub>3</sub> nanoparticles in 2-propanol (Aldrich) was spin coated at 4500rpm and dried at 150 °C. Next a perovskite precursor solution was made by mixing a stoichiometric ratio of PbI<sub>2</sub> and methylammonium iodide was dissolved in a mix of DMSO and GBL (7:3) and stirred for 10 minutes. This perovskite precursor solution was coated using a spin coating procedure using two speeds where toluene was dripped onto the surface during the second step and then dried at 100°C post deposition. A solution of 8% wt. 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, Borun Chemical) in chlorobenzene was next spin-coated onto the perovskite films. The spiro-OMeTAD solution contained additives including 19mM bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI), 7mM 4-*tert*-butylpyridine (tBP). V<sub>2</sub>O<sub>5</sub> powder (99.99%, Aldrich) was also added to the spiro-OMeTAD solution in the quantity of 2.5%wt with respect to the spiro-OMeTAD powder. Finally a 50nm Au contact was evaporated onto the cell under vacuum leaving an active area of 0.045cm<sup>2</sup>.

##### Current-Voltage (JV) Measurements

Initial *JV* characteristics were measured using a Xenon lamp at AM1.5 solar illumination (Oriel Instruments) calibrated to a silicon reference cell with a Keithley 2,400 source meter. Calibration was performed with a silicon photodiode before measurements. Scans were performed at a rate of 0.125 V/s either in a direction from forward bias (FB)/ open circuit to reverse bias (RB)/ short circuit (denoted FB-RB) or in the opposite direction (RB-FB). Cells displayed varying amounts of hysteresis in these initial measurements depending on the architecture used which has been displayed in Figure S1a for reference. In ageing measurements a slow (0.005 V/s) scan rate was used with the aim to negate hysteresis effects encountered during the *JV* scan. Cells were unmasked during measurements, using the area created by the overlap of the metallic contact and the FTO substrate as the defined active area.

##### JV Measurements as a Function of Ageing

Samples were sealed in glass fronted chambers, initially under N<sub>2</sub>, which allowed electrical contact to be made and devices to be illuminated. Devices were exposed to varying environmental

conditions via a valve system on the chamber using pressureised clean dry air (CDA) or nitrogen with and without moisture. Clean dry air (CDA) and N<sub>2</sub> were provided in cylinders from BOC UK as previously (O'Mahony et al. *J. Materials Chemistry A*. 2015, 3, 7219-7223). CDA contains less than or equal to 20% oxygen and greater than or equal to 80% Nitrogen, both are quoted as containing (<2 vpm) however the gases were still passed over silica desiccant before the devices were exposed to them. Light exposure was performed at equivalent 1 sun white light illumination provided by an array of white LEDs, calibrated to the device performance as measured under AM1.5 with the ultraviolet portion removed by filtering and a Keithley 2,400 source meter. The PCE was first allowed to stabilise under initial exposure to illumination and once stabilised this point is defined as time 0s. JV measurements were performed periodically with dwell time of 200ms per 1mV step to try and negate hysteresis effects using the same LED light array described previously. Devices in 'dark' conditions were exposed to light only during JV scans. 10 devices per data set were used to give an accurate representation of performance. The same Keithley 2,400 source meter was used to vary the conditions from open circuit to short circuit by applying a voltage bias to the devices. A fan was used to keep the sample chambers (and the devices inside) at a constant 30°C during measurements.

#### Photoluminescence Measurements

Photoluminescence spectra of were measured on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer.

#### Time Resolved Photoluminescent Measurements (TRPL)

As excitation source for TRPL a pulsed laser diode (PicoQuant) emitting at 485nm with a repetition rate of 10MHz was used. PL is collected using a 0.5m focal length spectrometer and a GaAs photomultiplier tube (PMT) for the detection (PMC-100-20, Becker & Hickl). For CW measurements a mechanical light modulator and a lock-in amplifier was used, whereas for time resolved measurements, the signal of the PMT is sent to a correlation card (Becker & Hickl), giving a time resolution of 0.3ns.

#### Superoxide detection measurements

These studies were conducted following our previously published method [2]

Table S1: Shows FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub>/MAPbI<sub>3</sub>/spiro-OMeTAD/Au solar cell device performance characteristics obtained from JV scans done at 0.01 V/s under equivalent 1 sun white LED illumination at 0hrs and after exposure to a range of different environmental conditions. CDA refers to clean dry air and RH refers to relative humidity.

| <b>0hrs</b>                    | <b>Light/N2 (dry)</b> | <b>Dark/CDA</b> | <b>Dark/N2 (dry)</b> | <b>Light/N2 (85% RH)</b> | <b>Light/CDA</b> | <b>Light/CDA (85% RH)</b> |
|--------------------------------|-----------------------|-----------------|----------------------|--------------------------|------------------|---------------------------|
| <b>Jsc (mAcm<sup>-2</sup>)</b> | 19.76 ±1.68           | 19.86 ±1.19     | 19.11 ±1.18          | 19.27 ±0.73              | 19.76 ±1.68      | 19.16 ±0.7                |
| <b>Voc (V)</b>                 | 1.00 ±0.01            | 0.98 ±0.03      | 0.99 ±0.02           | 1.00 ±0.03               | 1.00 ±0.01       | 1.00 ±0.03                |
| <b>Fill Factor</b>             | 0.47 ±0.03            | 0.48 ±0.06      | 0.45 ±0.02           | 0.45 ±0.04               | 0.47 ±0.03       | 0.45±0.04                 |
| <b>PCE (%)</b>                 | 9.30 ±1.25            | 9.42 ±1.04      | 8.48 ±0.59           | 8.70 ±1.06               | 9.30 ±1.25       | 8.54 ±1.00                |
| <b>12hrs</b>                   |                       |                 |                      |                          |                  |                           |
| <b>Jsc (mAcm<sup>-2</sup>)</b> | 20.51 ±0.45           | 20.52 ±0.35     | 20.36 ±0.49          | 18.51 ±0.58              | 1.35 ±0.47       | 1.17 ±0.52                |
| <b>Voc (V)</b>                 | 1.02 ±0.01            | 1.00 ±0.03      | 0.98 ±0.02           | 0.84 ±0.04               | 0.71 ±0.19       | 0.58 ±0.14                |
| <b>Fill Factor</b>             | 0.47 ±0.03            | 0.49 ±0.03      | 0.43 ±0.06           | 0.48 ±0.04               | 0.36 ±0.10       | 0.29 ±0.07                |
| <b>PCE (%)</b>                 | 9.81 ±0.71            | 10.12 ±0.43     | 8.62 ±1.28           | 7.37 ±0.53               | 0.36 ±0.18       | 0.19 ±0.14                |

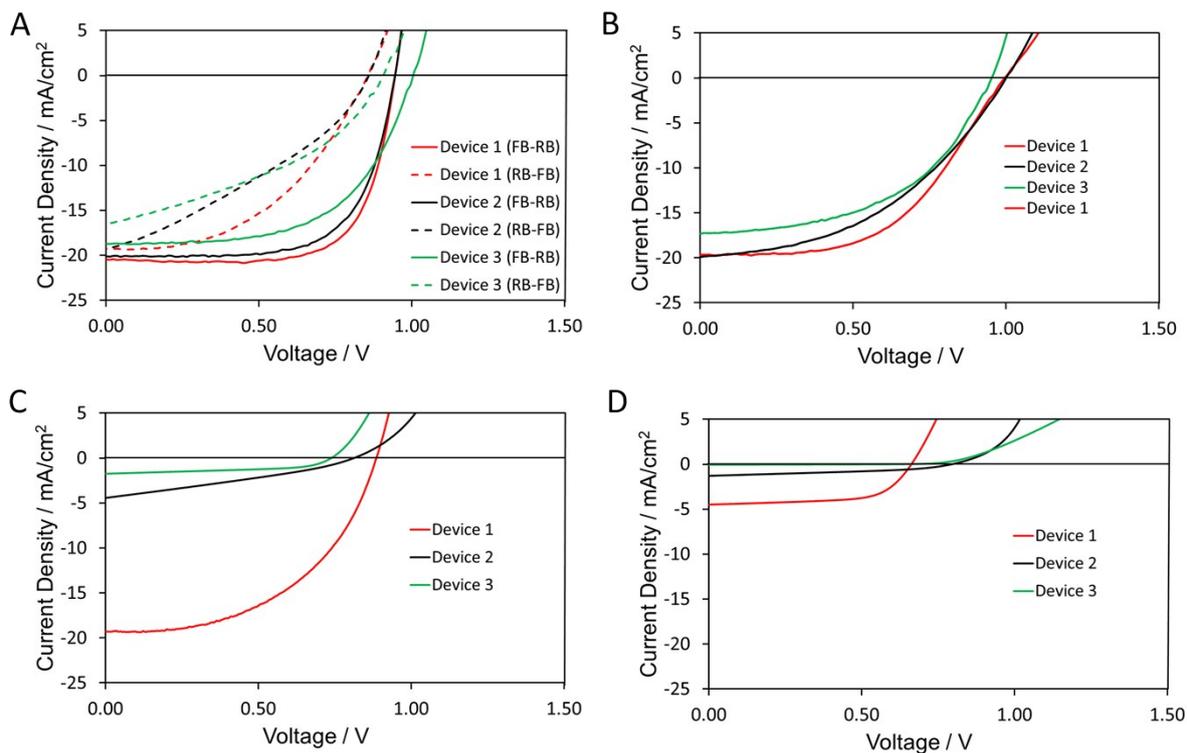


Figure S1. Shows the current voltage characteristics for three different  $\text{MAPbI}_3$  solar cells; Device 1 comprises:  $\text{FTO}/\text{c-TiO}_2/\text{m-TiO}_2/\text{MAPbI}_3/\text{spiro-OMeTAD}/\text{Au}$  (red line); Device 2 comprises:  $\text{FTO}/\text{c-TiO}_2/\text{MAPbI}_3/\text{spiro-OMeTAD}/\text{Au}$  (black line) and Device 3 comprises:  $\text{FTO}/\text{c-TiO}_2/\text{m-Al}_2\text{O}_3/\text{MAPbI}_3/\text{spiro-OMeTAD}/\text{Au}$  (green line). Measured A) prior to exposure to oxygen with a xenon lamp AM1.5 simulated sunlight at a scan rate of 0.125 V/s in FB-RB and RB-FB directions. B) prior to exposure to oxygen with a white light LED array 1 sun equivalent at a scan rate of 0.005 V/s RB-FB direction C) same as B however after a 1 hour exposure to CDA and 1 sun equivalent white light from an LED array D) same as C however after 5 hours exposure..

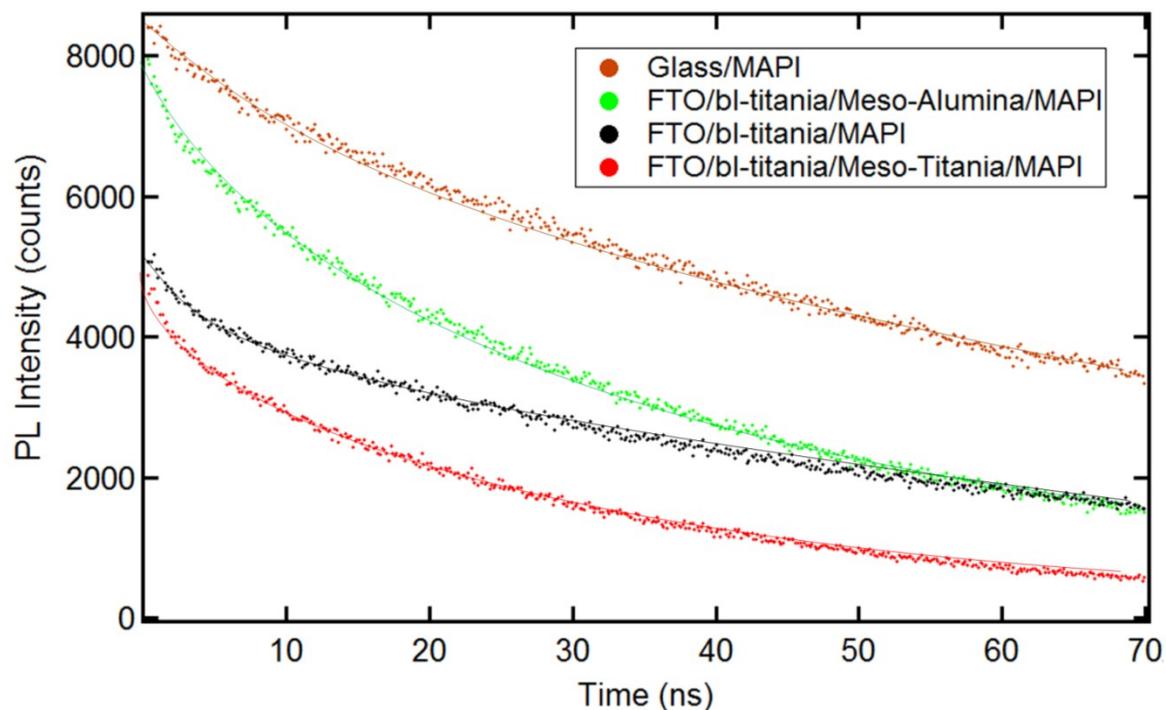


Figure S3. Time-resolved PL measurements taken at the peak emission wavelength of the MAPI perovskite devices incorporating a FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub>/MAPbI<sub>3</sub>/spiro-OMeTAD/Au (red dots), FTO/c-TiO<sub>2</sub>/MAPbI<sub>3</sub>/spiro-OMeTAD/Au (black dots), FTO/c-TiO<sub>2</sub>/m-Al<sub>2</sub>O<sub>3</sub>/MAPbI<sub>3</sub>/spiro-OMeTAD/Au (green dots) and a Glass/MAPbI<sub>3</sub> (brown dots) without a hole transport layer. Excitation at 485 nm of a 3 nJ/cm<sup>2</sup> pulse onto the MAPI film side with an instrument response time of 0.3ns.

[1] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. I. Seok, *Nat. Mater.* 2014, 13, 897.

[2] N. Aristidou, I. Sanchez-Molina, T. Chotchuangchutchaval, M. Brown, L. Martinez, T. Rath, S. A. Haque, *Angew. Chem. Int. Ed.* 2015, 54, 8208.