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Supplementary Methods:

Insights into the increased degradation rate of $CH_3NH_3PbI_3$ solar cells in combined water and O_2 environments

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All the chemicals were used as received, including 99% of PbI_2 (Sigma-Aldrich), HI (57% in water, Sigma-Aldrich), CH_3NH_2 (52%wt in absolute ethanol, Sigma-Aldrich), Titanium diisopropoxide bis(acetylacetonate) 97%wt in isopropanol (IPA) (Aldrich), spiro- OMeTAD (Lumtec), Bis(triluoromethane)-sulfonimide lithium salt (Li-TFSI, Aldrich), 4- tert-butylpyridine (TBP), 97%wt Titanium (IV) chloride tetrahydro-furan complex (Sigma- Aldrich), diethyl ether, acetone, ethanol, isopropanol, ethanolamine, 2-methoxyethanol, chlorobenzene, γ-butyrolactone (GBL), TiO_2 paste (Dyesol DSL 30 NR-D 30nm), Terpineol, hydroethidine, toluene, Dimethyl sulfoxide (DMSO), acetonitrile.

Synthesis of CH_3NH_3I (MAI): The MAI was made by reacting 24 ml of CH_3NH_2 and 10 ml of HI in a 500 ml round-bottom flask in a cold bath (0°C) for approximately 2 hours while mixing. The solution with precipitate was then filtered using a rotary evaporator through carefully removing the solvent at 50°C. The product was re-dissolved in 80 ml absolute ethanol and re-precipitated with additional 300 ml diethyl ether. After this procedure was repeated 2 times, the final MAI was dried and collected at 60°C in vacuum after it was warmed overnight (24 hours). $CH_3NH_3PbI_3$ Film Fabrication: All films were deposited onto clean glass substrates of ca. 1 cm^2 in size. The glass substrates were washed sequentially in acetone, water and isopropyl alcohol (IPA) under sonication for 10 minutes during each washing cycle. A Laurell Technologies WS-650MZ-23NPP Spin Coater was used to fabricate the films. a) $CH_3NH_3PbI_3$: A 1 M solution of $CH_3NH_3PbI_3$ was formed by adding PbI_2 in a 1:1 molar ratio with methylammonium iodide in a solvent mixture of 4:1 γ-butyrolactone (GBL) to DMSO. This solution was then spin-coated onto the substrates using a consecutive two-step spin program under a nitrogen atmosphere in a glove box. The first spinning cycle was performed at 1000 rpm for 10 s followed by 5000 rpm for 20 s. During the second phase, the substrate was treated with toluene (350 mL) drop-casting. The films were then annealed at 100◦C for 10 minutes.

Perovskite films for transient absorption spectroscopy were prepared as above with the addition of a hole transporting layer. The Spiro-OMeTAD hole conductor layer was spin coated from a solution of 72.5 mg/mL of 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) containing lithium bis(trifluoromethane) sulfonimide lithium salt (Li-TFSl) and 4-tert-butylpyridine (tBP) additives in anhydrous chlorobenzene.

Ageing conditions: All samples were sealed in a controlled environment, where dry air was gassed through, from a dry compressed air cylinder (<2ppm of water) for the duration of the degradation and Illumination was provided by a tungsten lamp of approximately 1.5 mW/cm power or by a Lamp with power of 25 mW/cm2. Controlled Humidity environments: Samples soaked in humid environments were generated via creating a controlled humidity in a small controlled environment. To generate the desired humidities specific Glycerol-Water solutions were prepared, nitrogen gas was then bubbled through this solution acting as an inert gas carrier for the moisture. This allowed a moisture environment to be transported into a separate inert chamber holding pristine dry perovskite films. For the 85% relative humidity environment a 40% Glycerol (w/w) solution was used and for the 25% environment a 90% Glycerol (w/w) solution was employed. All films were soaked for two hours, after which the chambers were sealed and samples were taken immediately for testing.

UV/VIS: UV-Vis measurements were carried out using a UV-Vis spectrometer (PerkinElmer) in a wavelength range from 400 to 900 nm with a scan speed of 480 nm per minute with 1 nm data intervals and cycle times of 1 second. Its slit width was set at 1.0 nm.

TAS: measurements were performed with a 567 nm dye and a GL-301 dye laser (Photon Technology International, TSI) through an oscilloscope (TG330 Function generator with 3 MHz-Generator, 120 MHz counter/sweep). The frequency of the laser pulse was 4 Hz. The pulse was generated with a light source (Bentham IL 1 illuminator) and a voltage of approximately 12.3 V (Bentham 605). The signal size was filtered with a long pass filter monochromator (Thorlabs) and an optical shielding filter. Each measurement was measured at 10 ms time scales for 64 averages for 10 times with a pulse power of 25 μJ/cm^2.

ToF-SIMS: Data was obtained using an IONTOF TOF.SIMS-Qtac LEIS spectrometer employing an Argon sputter gun for D2O detection. The D2O was introduced by substituting water in the water/glycerol mixes used to create the humid environments. Superoxide Probe Measurements: i) Standard superoxide probe testing was achieved by dissolving 10 ml of stock solution (31.7 μM) of the hydroethidine (HE) probe in 10 ml dry toluene. Sonication was used to facilitate miscibility. Perovskite films were submerged into this solution. Photoluminescence spectra were recorded with excitation wavelength of 520 nm and slit width of 10 mm on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer. The film was illuminated by the visible light through a 400 nm long pass optical filter thoughout the experiment. The illumination was provided by a tungsten halogen lamp. The light intensity was approximately 1.5 mW/cm2. ii) Superoxide measurements conducted with water present in solution, were carried out using the same system setup as described above. However, the moisture was introduced by generating a moisture loaded Toluene solution via liquid-liquid extraction. Combining the water containing Toluene with the dry Toluene in the desired ratios then made the corresponding samples of 25% and 85% water solutions. iii) To generate the Nitrobenzoic acid and benzoic acid containing toluene solutions the respective acid was taken and dissolved into the toluene solution to yield a concentration of 1×10−4M. The solutions were then used as in the standard protocol and the superoxide yields measured.

XRD: X-ray diffraction patterns were obtained from a PANalytical X’Pert ProMRD diffractometer using Ni filtered Cu KÎś radiation at 40 keV and 40 mA. SEM-EDX measurements were performed on a JEOL 6400 scanning electron microscope operated at 20 kV. SEM images were acquired on a LEO 1525 Field Emission Scanning Microscope operated at 5 kV using an In Lens detector.

Supplementary figures:

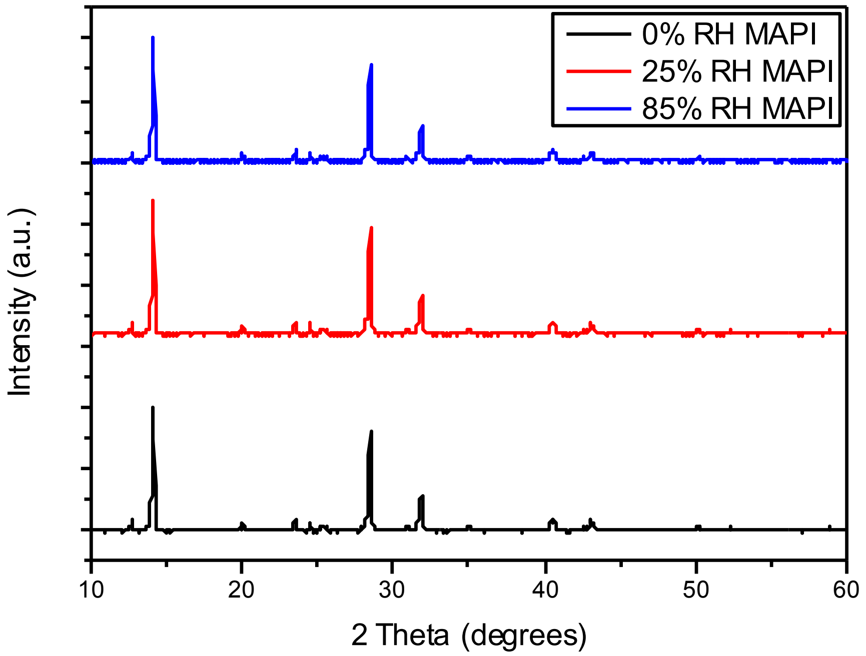


Figure S1. X-Ray diffraction patterns of Methylammonium lead iodide after synthesis and exposure to: i) no moisture (Black trace) ii) 25% RH (Red trace) and iii) 85% RH (Blue trace).

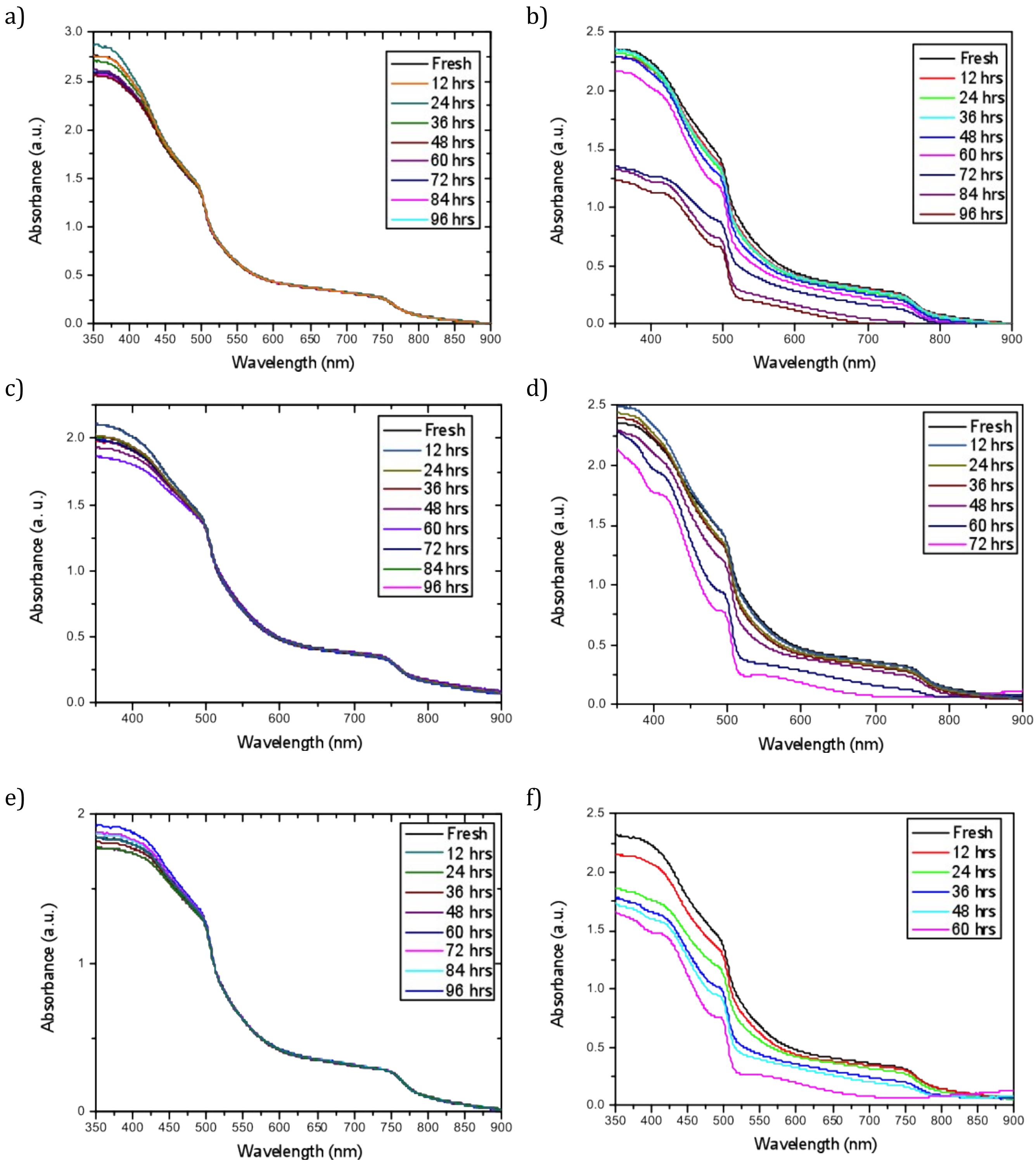
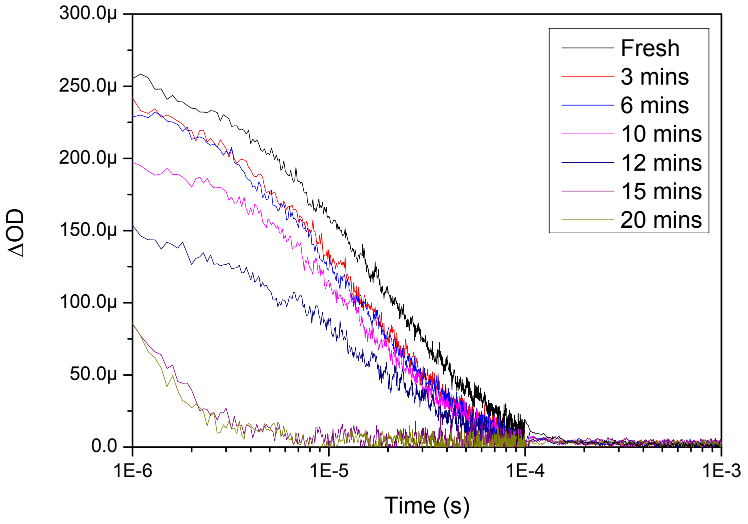


Figure S2. Raw absorbance data collected of Methylammonium lead Iodide, showing the degradation effects upon exposure to the following conditions a) N_2, light and no moisture b) O_2, light and no moisture c) N_2, light and 25% RH moisture d) O_2, light and 25% RH moisture e) N_2, light and 85% RH moisture f) O_2, light and 85% RH moisture.

a)



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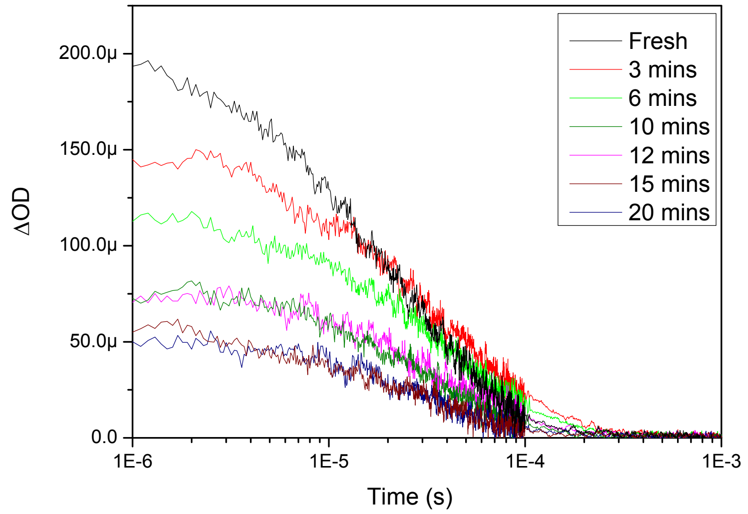

c)

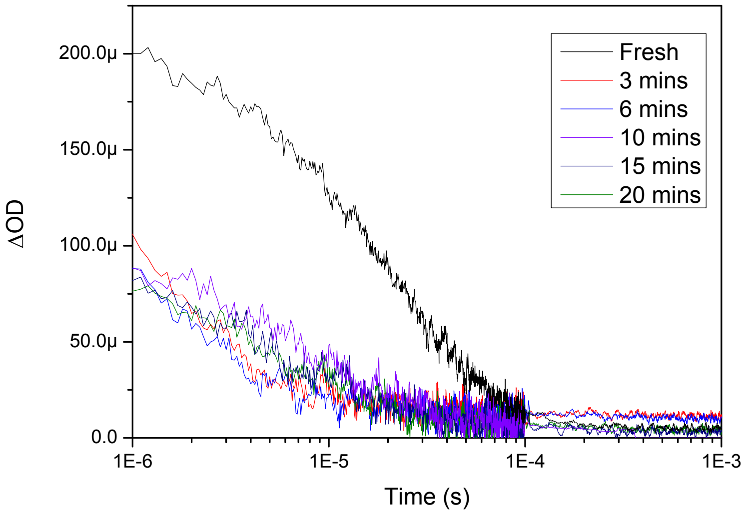

Figure S3. Transient absorption spectra at 1600nm for $CH_3NH_3PbI_3$/Spiro-OMeTAD films upon exposure to oxygen and light with a) no moisture treatment, b) 25% RH moisture treatment and c) 85% RH moisture treatment.