

SUPPORTING INFORMATION

Stability and performance of CsPbI₂Br thin films and solar cell devices

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1. Materials and device fabrication, testing and degradation conditions.

Fabrication of CsPbI₂Br and MAPI thin films: the CsPbI₂Br perovskite layer was deposited onto quartz glass in order to study the perovskite layer's properties in isolation. The perovskite precursor solution was prepared by mixing a 40% wt. solution of CsI:PbI₂:PbBr₂ (1:0.5:0.5 molar concentration) in a 9:1 by vol. mix of dimethylformamide (DMF): dimethyl sulfoxide (DMSO), and stirring at 50°C for one hour. After filtration with a 0.22 µl PTFE filter, the solution was dynamically spin coated at 2000 rpm for 25 seconds using a one-step solution method and then annealed under nitrogen for 10 minutes on a hot plate ($150 \leq T \leq 350^\circ\text{C}$, $\Delta T 50^\circ\text{C}$). Fig. S1 presents the SEM pictures of the films, showing an increased crystallinity for the films annealed at higher temperatures; however the uniformity of the films is jeopardised by the abundant presence of pin-holes.

A precursor solution of methylammonium lead iodide (MAPI) was prepared by mixing PbI₂, methylammonium iodide (MAI) and DMSO (1:1:1 molar ratio) in 0.6 ml DMF. The one step precursor solution is then stirred for 30min at room temperature and filtered with a 0.22 µl PTFE filter before being spin-coated. Then, the MAPI films were spin-coated by using 50 µl of the solution and dynamic spin-coating, at 3000 rpm for 35 seconds and then annealed 1 minute at 65°C and 2 minutes at 100°C on a hot plate under nitrogen.

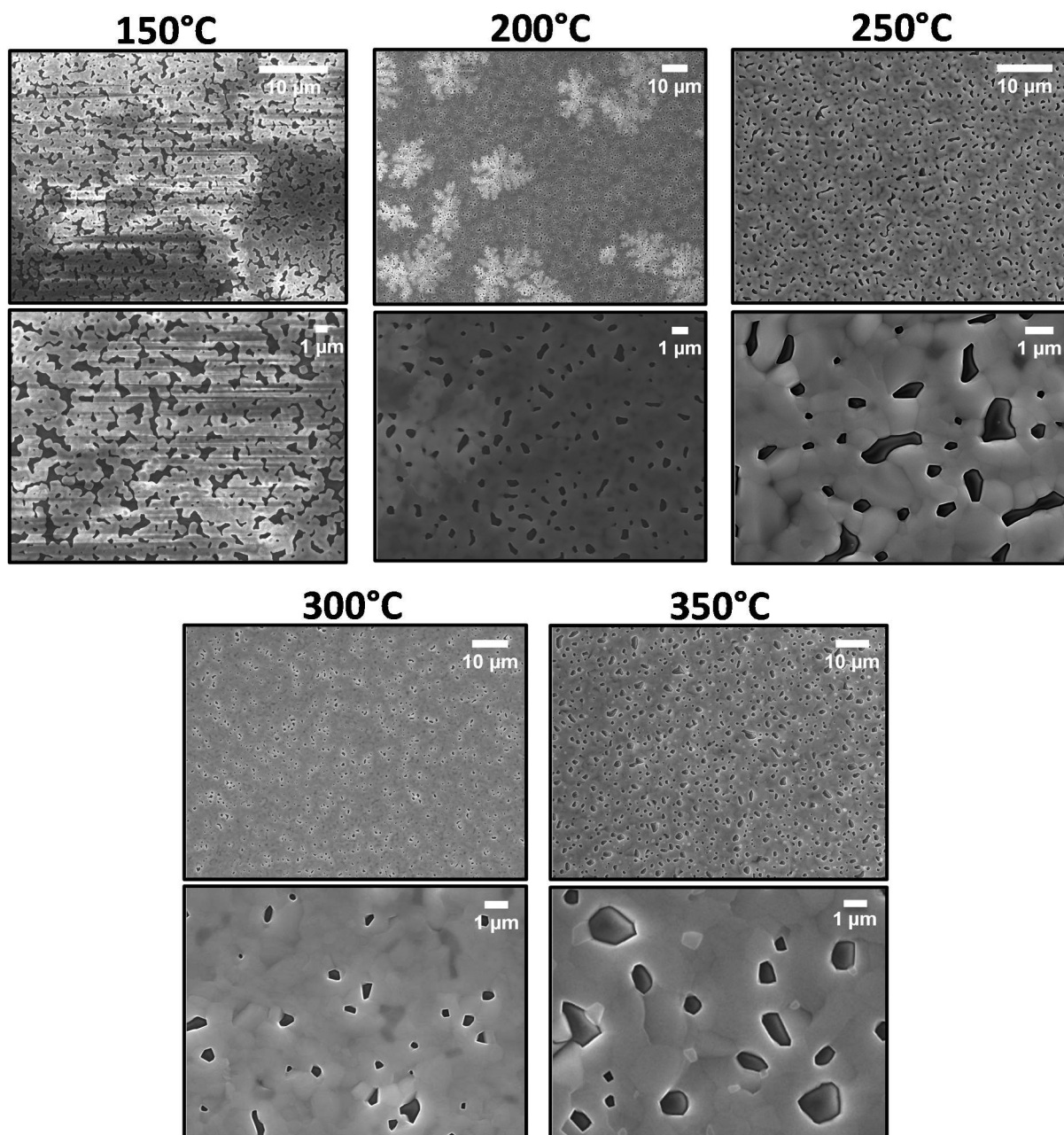


Fig.S1. SEM images of CsPbI₂Br films obtained by annealing at 150, 200, 250, 300 and 350°C. By increasing the temperature an improvement in the crystallinity of the films can be detected which, despite the presence of numerous pin-holes, improves the uniformity of the films. Images of films annealed at 150°C were particularly difficult to take, since their conductivity was not sufficient.

Degradation and recovery conditions: the degradation conditions explored for CsPbI₂Br and MAPI films were as follows:

- N₂/UV - samples were exposed to UV radiation in an inert nitrogen atmosphere (2 × 9W UV lamps on continuously in a glovebox with <10 ppm H₂O).
- Dark/air - samples were covered with metal foil to eliminate sources of illumination, but unsealed and therefore exposed to ambient laboratory conditions (humidity ~40%).

- Desiccator – samples were placed in a sealed box containing silica to absorb ambient moisture and reduce the relative humidity to <15%, but were still exposed to the ambient light present in the lab.
- UV/O₃ - the samples were exposed to a UV-ozone cleaner (Ossila Ltd.) to simulate the effect of UV and oxygen-radicals on the film, replicating one of the proposed causes of degradation in MAPI (see Ref.5, 6 and 7 in main manuscript).

CsPbI₂Br and MAPI film characterisation:

Fresh and degraded films were analysed using an X-ray diffractometer (X'Pert PRO X-ray diffraction system – Philips Analytical, using a Cu X-ray tube) and spectrophotometer (SolidSpec-3700 UV-VIS-NIR Spectrophotometer – Shimadzu).

Bulk powder samples of CsPbI₂Br were prepared for analysis by dripping 1 ml precursor solution onto glass substrates heated at 300°C for 10 minutes in the glovebox. The deposit was scraped off to yield ~16 mg of brown CsPbI₂Br powder. Both this as prepared brown phase and the air-degraded yellow phase were analysed by:

- a) Differential scanning calorimetry – thermo-gravimetric analysis (DSC-TGA, TA Instruments. SDT Q600) using alumina crucible with a heating rate of 10°C/min;
- b) ¹H-NMR in a 400 MHz Bruker NMR spectrometer, with the sample tube being filled under dry argon in dry DMSO-d⁶.

Device fabrication and testing:

A compact titania layer was deposited onto ITO glass (Ossila limited) by spin-coating a solution 0.3M of titanium isopropoxide in ethanol. After a pre-annealing step (110°C for 10 min) the composite was heated at 550°C for 30 min in air. The absorber layer was then deposited by spin coating the CsPbI₂Br solution at 2000 rpm, 25 seconds using a one-step solution method and then annealing under nitrogen for 10 minutes on a hot plate at a range of temperatures ($150 \leq T \leq 350^\circ\text{C}$, $\Delta T 50^\circ\text{C}$). After cooling a layer of doped Spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene) was spin-coated on top to act as the hole transporting material (HTM). Finally, 2 mm diameter gold dots were evaporated on top to form the back contacts. All the procedures were performed inside a nitrogen glovebox (<10 ppm H₂O); however, the cells were kept in a desiccator overnight before measurements were taken in order to oxidise the Spiro-OMeTAD layer.

Devices were examined in an SEM (JEOL JSM-7001F) and tested using a solar simulator (TS Space Systems, calibrated at AM 1.5 – 100 mW/cm² using a scan rate of 0.19 V/s) and in an EQE (Bentham PVE300, operating with a 0.75mm sq slit). Fig. S2 shows the EQE of a device containing CsPbI₂Br annealed at 350°C.

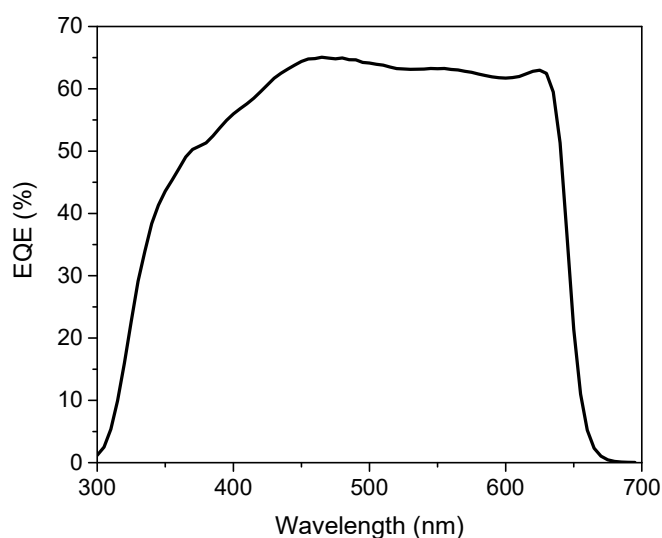


Fig.S2: External quantum efficiency of a device showing 65% photon collection at about 460 nm and a drop at 650 nm, which corresponds to the CsPbI₂Br band-gap. At shorter wavelengths the TiO₂ layer (window layer) absorbs photons, producing a non-squared shaped EQE.

2. CsPbI₂Br - further characterisation of degraded films

Fig. S3 shows the transmittance and reflectance spectra measured from the degraded CsPbI₂Br films and used to calculate the absorption coefficients shown in Figs. 4 b&d (in main manuscript). The spectra compare the films degraded under a variety of environmental conditions with as-grown samples for both one week and one month of degradation (see caption in Fig. S3).

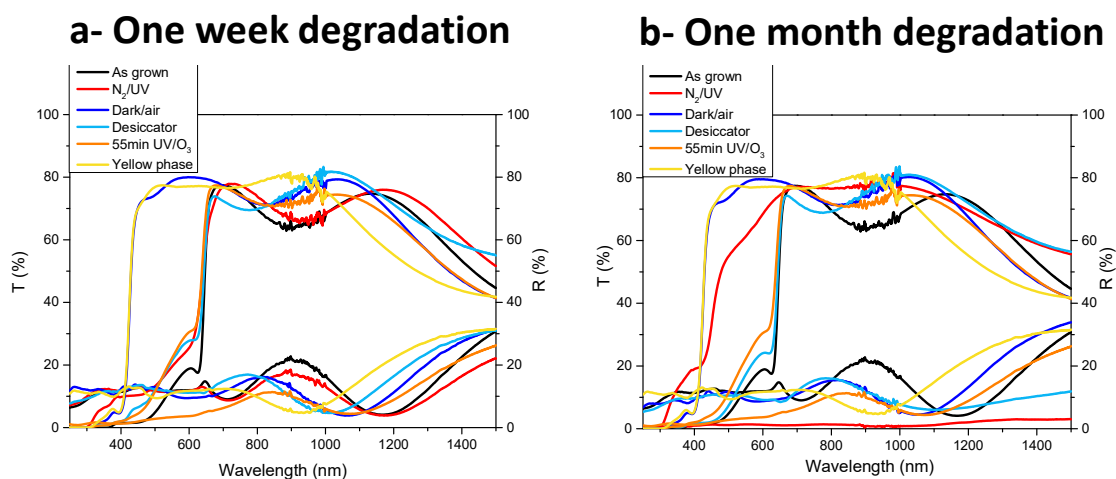


Fig.S3. Optical spectroscopy data exploring the degradation of CsPbI₂Br under different environmental conditions. a) Spectra of samples degraded for up to one week. Control data was obtained from an ‘as-grown’ film and an air aged film that had completely degraded to the ‘yellow phase’. Sample aged in a desiccator, under N₂ with UV and with UV/O₃ (54 mins) did not degrade. Ageing in ambient air in the dark provoked degradation to the yellow phase. b) Spectra for samples degraded for one month. Again, ageing in ambient air has degraded the films as expected but the prolonged exposure to N₂/UV has also begun to cause optical degradation. Results for the other environments are unchanged from (a).

In preparing the Tauc plots we were mindful that the method is prone to systematic error. All absorption coefficients were calculated using thicknesses and taking into account both transmission and reflection. While we recognise that the straight line sections in Fig 1e, we ensured that similar sections of each graph were used in order to guarantee continuity between measurements.

Fig. S4 shows photographs of the degraded CsPbI₂Br layers.

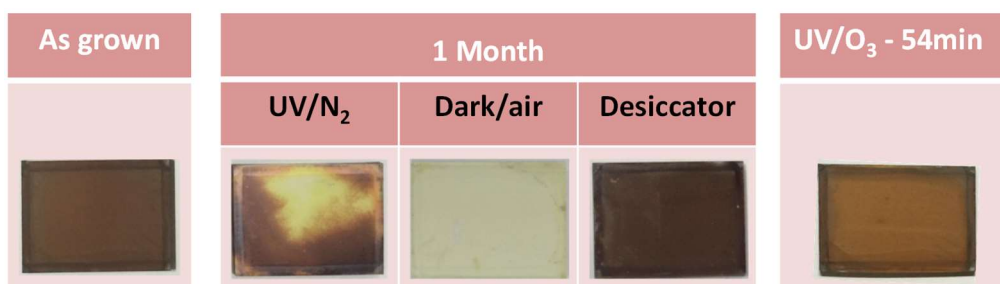


Fig.S4. Photographs of CsPbI₂Br layers taken after one month of degradation, compared with the 'as grown' sample. The photographs confirm the results obtained by transmission and reflectance spectra, shown in Fig. S3.

Fig. S5 compares the experimental XRD from the yellow phase with the records of Cs and Pb halides, however there is no association with the original precursors and other possible compounds containing these elements.

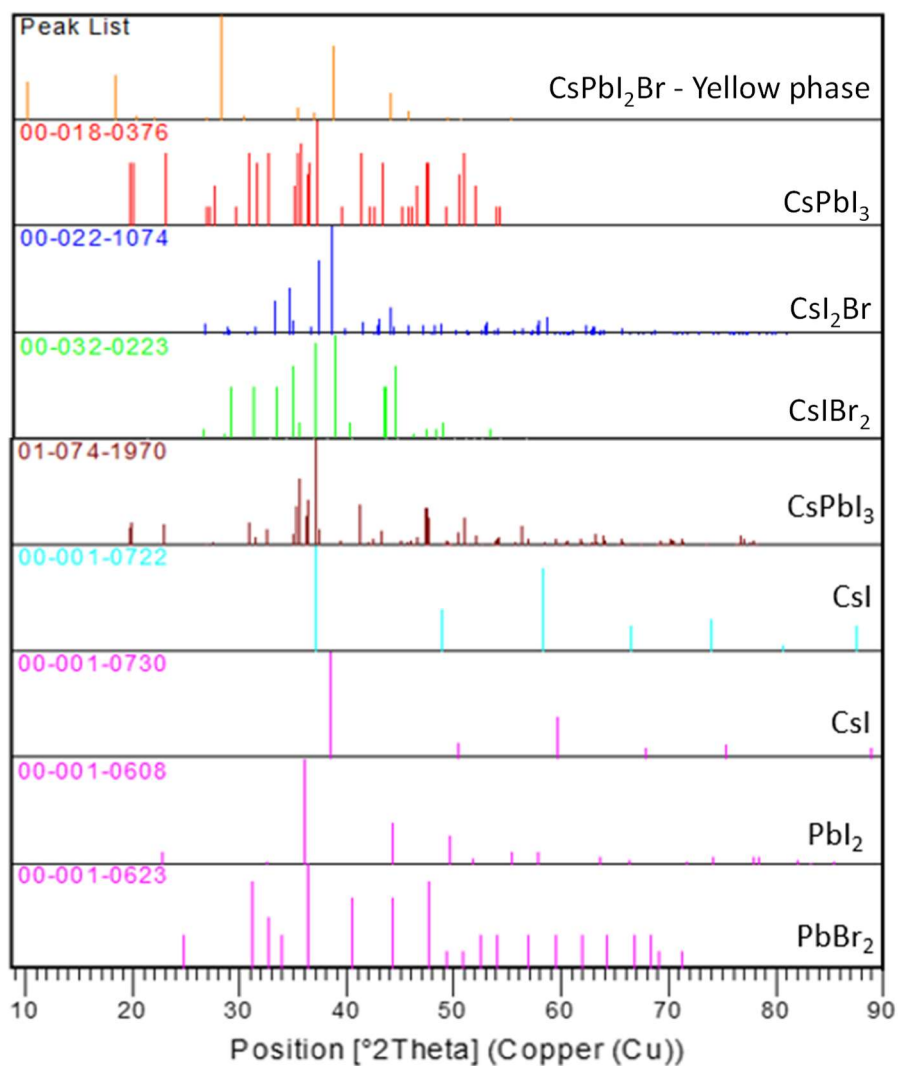


Fig. S5. XRD patterns of CsPbI₂Br yellow phase and comparison with patterns of possible Cs and Pb salts. Each compound is referred to by the X'Pert HighScore PANalytical reference code.

3. Degradation of MAPI and comparison with CsPbI₂Br

Fig. S6 shows a comparative series of photographs of both CsPbI₂Br (a) and MAPI (b) films upon progressive exposure to UV/O₃. It was already established by optical spectroscopy (Fig. S3) that UV/O₃ does not significantly degrade CsPbI₂Br, and this is confirmed by the only very slight change in the visual appearance of this material during exposure for up to 54 minutes. On the other hand, MAPI undergoes a rapid colour change from black to brown/yellow upon exposure to UV/O₃ for as little as 4 minutes: MAPI is significantly more sensitive to UV/O₃ degradation than is CsPbI₂Br.

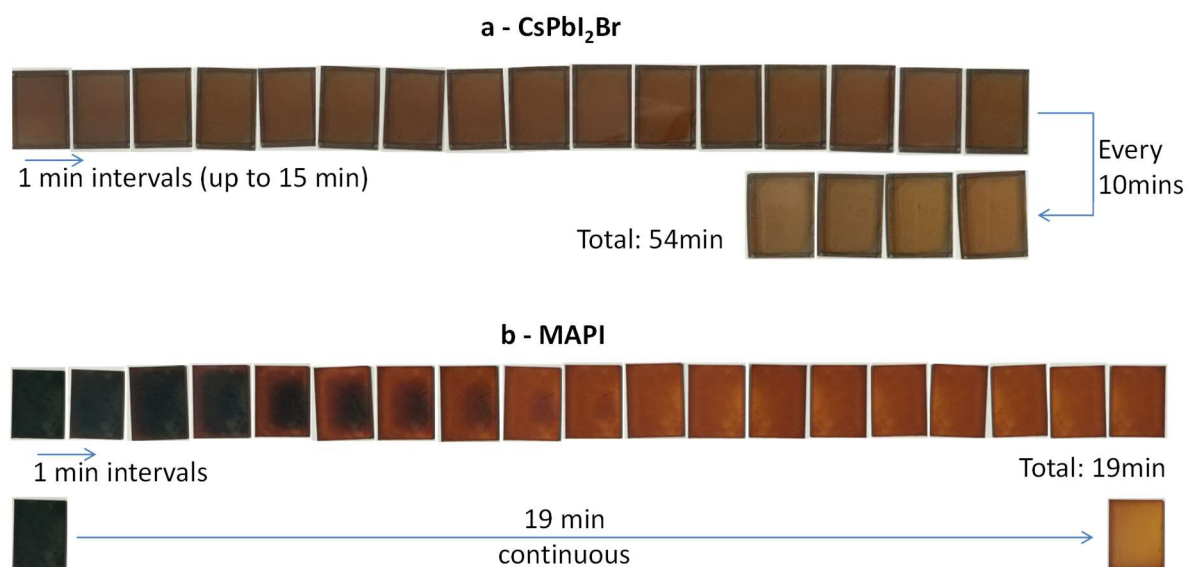


Fig. S6. Photographs comparing the response of films of both CsPbI₂Br and MAPI to UV/O₃ exposure. a) CsPbI₂Br showing negligible colour change for exposure up to 15 min and only very slow changes thereafter up to 54 minutes. b) MAPI showing almost immediate discoloration from black to brown and very profound change to yellow after 19 minutes.

Fig. S7 and Table S1 show the result of a systematic study of the degradation of MAPI under a variety of environmental conditions. This provides data that is directly comparable to that obtained for CsPbI₂Br and shown in Fig. 4, S3 and Table 2. For MAPI the indications of degradation are a) the appearance of XRD peaks for PbI₂ and/or MAI (methylammonium iodide), b) a shift in the band edge from ~790 nm to a lower value, typically 500-600 nm, accompanied by a decrease in absorption coefficient and c) a change in visual appearance from black to yellow or transparent. From the summary in Table S1 it is clear that for MAPI, exposure to light - especially UV light - promotes measurable and visible degradation. This contrasts with CsPbI₂Br, which is transformed from the brown to yellow phase by the action of water vapour.

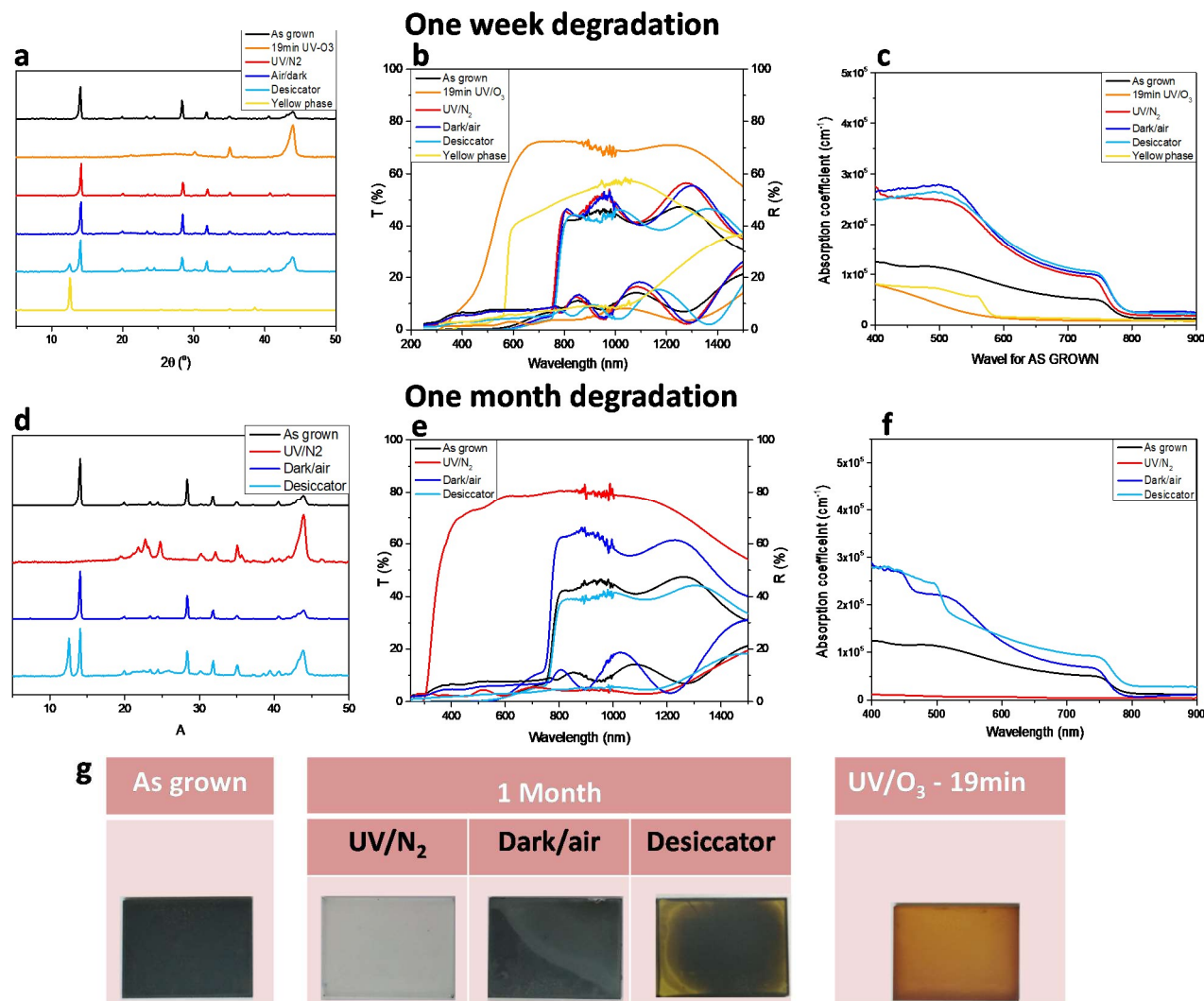


Fig. S7. Degradation data for MAPI films: a-c) XRD, optical spectra and absorption coefficient after one week of degradation (with ‘as-grown’ and a fully degraded ‘yellow phase’ control). d-f) As for a-c but after one month of degradation. g) Photographs of the effects of degradation on MAPI films.

Degradation conditions					Characterisation			
Degradation test	Illumination	Containment	Atmosphere	Duration	Visual	XRD	Optical	Conclusion
N ₂ /UV	UV lamp	glovebox	dry N ₂ ; <10ppm H ₂ O	one week	black, slightly decoloured	unchanged	unchanged	UV-rad for long time produces a fully transformed structure
				one month	white/transparent	changed (MAI peak prevails)	completely changed	
air/dark	dark	none	air with ~40% RH	one week	black (unchanged)	unchanged	unchanged	humidity and oxygen do not provoke changes in the structure
				one month	black (unchanged)	unchanged	changed (Eg shifts slightly)	
dry air/light	lab lighting	desiccator with silica gel	dry air (RH≤15%)	one week	yellow phase starts to appear on corners	slightly changed (MAI peak starts appearing)	unchanged	ambient light and presence of oxygen produce a transformation of the structure
				one month	black centre, yellow corners	PbI ₂ and MAI peak are present	changed (Eg shifts slightly)	
air/O ₂ /UV	UV lamp	inside UV/ozone cleaner	air with ozone	19 min	yellow/orange	changed (MAI peak prevails)	completely changed	UV + O ₂ quickly affects the structure

Table S1. Summary of the response of MAPI films to different degradation conditions selected so as to isolate the causes of degradation. It was concluded that UV and O₂ provoke degradation in contrast to the case of CsPbI₂Br which is optically degraded by humidity.

