Supplementary discussion

CLSM images of CH₃NH₃PbI₃ formation in sequential deposition in the dark and under 1 Sun

Here, we further discuss the CLSM images shown in Fig. 1. We observe that samples dipped under illumination (Fig. 1i and 1h) show an increase in the number of non-emissive regions, in correlation with the dipping time. However, SEM images (inserts) show full surface coverage in contrast to samples made in the dark, confirming that the non-emissive regions are not gaps in the film. Instead, they are attributed to perovskite grains with more defects and trap states, as reported by deQuilettes et al. Morphological changes are observed in the perovskite film upon dipping beyond the point of complete conversion (Fig. 1e and 1i). These are partly due to the coarsening process known as Ostwald ripening, as reported in the literature on perovskite films.

Photo-electrochemical experiments characterizing the PbI₂-electrolyte interface

To investigate the mechanism through which absorbed light enhances the nucleation of PbI₂, we performed photo-electrochemical experiments. First, we determined whether a crystalline PbI₂ film, in a 0.38M solution of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm TFSI) in 2-propanol, was photoactive through chopped light chronopotentiometry at zero applied current. Crystalline films were used to improve stability during measurement. We used an ionic liquid solution instead of an MAI solution to avoid perovskite formation during our experiment. This approach is justified since the ionic liquid solution provides a similar ionic environment as MAI. We show that the PbI₂ crystallizes in a solution of the ionic liquid, akin to that in a MAI solution (see Extended Data Fig. 1 for XRD analysis). The photo-voltage measured under 1 Sun is -0.178 V, which confirms that the film is photoactive (Extended Data Fig. 3g). Moreover, the larger negative value under light compared to that in the dark indicates that the PbI₂ film is of n-type. The second aspect of interest is the transient behaviour seen in the potential upon switching from 1 Sun to the dark. The potential is persistent, indicating that some generated charges are very long-lived and recombine slowly, possibly due to trapping or accumulation at the PbI₂-electrolyte interface.

To further characterize the PbI₂-electrolyte interface, we conducted electrochemical impedance spectroscopy (EIS) measurements in the dark (see Extended Data Fig. 3 for experimental setups). The Mott-Schottky plot, shown in Extended Data Fig. 3h, has a positive slope, which confirms that the PbI₂ film is an n-type semiconductor. The flat band potential was determined as -0.46 V vs. Ag/AgCl, KCl (sat’d) (calibrated with ferrocene). We observe that the capacitance becomes independent of potential between +0.2 and +0.6 V vs. Ag/AgCl, KCl (sat’d), indicative of Fermi level pinning at the PbI₂-electrolyte interface. The pinning points to the presence of surface traps, which are located below
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**Photo-electrochemical experiments identifying the carrier trapped in the PbI₂ surface traps**

To determine whether the surface traps in the PbI₂ films are for electrons or holes, we conducted experiments applying an external voltage to a standard (as-deposited) PbI₂ film during dipping in a MAI solution in the dark, but could not induce a high nucleation density. The external voltage we applied (-0.8 V to +0.8 V) manipulates the electron density on the surface of the film, but does not generate holes in PbI₂. This points to the photo-generated holes being the carrier type involved in the nucleation. At a voltage of +0.8 V (reverse bias), the PbI₂ delaminates. This indicates that more positive potentials are not accessible and inversion cannot be achieved, so it is not possible to have holes as majority carriers on the surface. Films dipped under illumination with an external voltage bias, draining the electrons from the film while the photo-generated holes remain trapped at the surface, show high nucleation density (Extended Data Fig. 5). Thus, we conclude that photo-generated holes are indeed involved in lowering the surface tension.

**Crystallization of PbI₂ in an ionic liquid and alternative photo-redox mechanism**

We also studied the crystallization of PbI₂ in different environments. To begin with, pure 2-propanol does not induce nucleation. As already mentioned, we conducted experiments replacing the MAI solution with an ionic liquid solution as a chemically unreactive alternative that does not form perovskite. Through XRD analysis, we show that light-activated nucleation is facilitated by the ionic liquid solution (see Extended Data Fig. 1). At this point, we considered the possibility of an alternative mechanism taking place, namely photo-redox⁴ - i.e., oxidation reactions involving the photo-generated holes. However it is highly unlikely, as the logarithmic dependence of the nucleation density on light intensity, observed in Fig. 2b, cannot be explained. Moreover, since the ionic liquid, whose ions cannot be oxidized or reduced by PbI₂, also enhances the crystallization of PbI₂, we rule it out.

**Supplementary discussion references**