Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Formation Criteria of High Efficiency Perovskite Solar Cells in Ambient Conditions

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Coordination Chemistry of the Precursor Solution

During formation of the perovskite layer using the one step deposition method the correct stoichiometry (1:1:1) of the intermediate complex PbI_2:MAI:DMSO needs to be generated. It is well established that water and DMSO are two highly polar molecules with similar coordinating properties. Then, it is clear that during device preparation in an ambient atmosphere both molecules will be competing to coordinate the Pb atom. We have recently shown that there is a direct competition between iodide ions and the solvents used in the precursor solution, clearly impacting the structural defects present in the films.[1] Scheme SI1 shows some representative equilibrium reactions that generate several multiiodide plumbate ions where all iodide ions, solvent/additive molecules (S) or other Pb atoms can coordinate to the lead and will be competing to fill the octahedral coordination sphere.

$$Pb(S)_6^{2+} \underset{-S}{\overset{+I^-}{\rightleftharpoons}} PbI(S)_5^{+} \underset{-S}{\overset{+I^-}{\rightleftharpoons}} PbI_2(S)_4 \underset{-S}{\overset{+I^-}{\rightleftharpoons}} PbI_3(S)_3^{-} \underset{-S}{\overset{+I^-}{\rightleftharpoons}} \cdots \quad \text{(Eq. 1)}$$

i.e. S=H_2O, DMSO or DMF

$$PbI_3(DMF)_3^{-} \underset{-I^-}{\overset{+DMSO}{\rightleftharpoons}} PbI_2(DMF)_3(DMSO) \quad \text{(Eq. 2)}$$

Scheme SI1: Example of competitive reactions between different solvents and additives to coordinate the lead atom.

Absorption spectra of PbI_2 dissolved in pure solvents shown (Figure SI1) confirm the equilibrium proposed in Scheme 1. Assignment of the bands that correspond to the species present under diluted conditions is provided in Figure 1 as reported previously: $PbIS_5^+$ (λ_{max}=286 nm), PbI_2S_4 (λ_{max} = 325 nm) and $PbI_3S_3^-$ (λ_{max} = 370).[1] Partially supporting this assignment the work by Kamat *el al.* described the photophysics of $PbI_3S_3^-$ and $PbI_4S_2^{2-}$ species.[2] Interestingly, the use of highly coordinating solvents like H_2O leads to increased formation of species with a low number of iodide ions such as $PbIS_5^+$, PbI_2S_4 and possibly PbS_6^{2+} as highlighted by the increased intensity of bands in the high energy region. Alternatively, more discreetly coordinating molecules like DMF will not be so effective at displacing iodide ions from the lead coordinating sphere and species containing more iodide will be obtained (i.e. PbI_2S_4 or some $PbI_3S_3^-$).

Furthermore, in order to study the effect of water/additive in the presence of MAI absorption measurements of solutions containing PbI_2:MAI in DMF (1 mM, 1:1 mol-ratio) are carried out. Very small amounts of either DMSO or H_2O are added to the solution which after solvent evaporation should lead to a perfect stoichiometry of the PbI_2:MAI:Additive complex (1:1:1). It is important to note that at these highly diluted conditions lead atoms are mostly surrounded by DMF molecules with a DMF/Additive mol-ratio of 25:1. However, the better coordinating ability of DMSO as opposed to DMF is evidenced by the reduction of the $PbI_3S_3^-$ absorption band intensity which indicates that DMSO will displace some Iodide ions that DMF molecules were unable to shift. This type of solvent displacement reactions is shown in Eq. 2 in Scheme SI1.

Alternatively, water molecules are the most coordinating molecules in the series of solvents and if present in the precursor solution we expect a similar displacement as that shown for DMSO. Very interestingly, when H_2O is added no changes in absorption bands intensity are observed. It is well known that water molecules and DMF interact very strongly through hydrogen bonds being DMF able to breakdown the water structure by generation of DMF·H_2O dimers and aggregates ($(DMF)_m \cdot (H_2O)_n$).[3] Therefore, it is expected that at this small water concentration no H_2O molecules will be free to coordinate to the Pb atom. Unfortunately, at high water concentration the PbI_2 precipitates from solution and no representative data for devices can be obtained. However, a very different scenario is expected during spin coating of the precursor solution where the effect of water will be more prominent at the end of the drying process, when most of the DMF has been evaporated. Indeed, it is observed that the time of antisolvent addition will depend very much on relative humidity (R.H.) conditions. Shiny and scattering-free films will be obtain only if antisolvent is added at the correct waiting time. Whilst at high R.H. long waiting times are required at low R.H. addition of diethyl ether will need to be fast and this is a direct consequence of the different kinetics to coordinate Pb by H_2O and DMSO molecules.

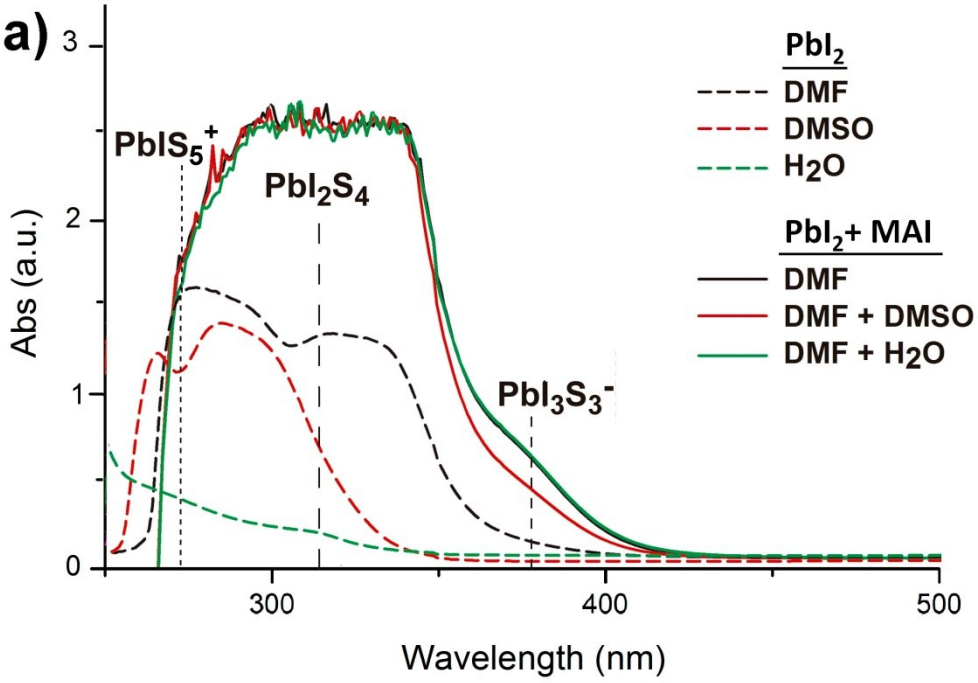

Figure SI1: Absorbance spectra of solutions containing PbI_2 (1mM) in different pure solvents (dashed line) and PbI_2 + MAI (1mM, 1:1 mol) mixtures in DMF (solid lines) either pure or with a small amount of additive (DMSO or H_2O). The proportion of additive is calculated to provide a PbI_2:MAI:DMSO ratio of 1:1:1. λ_{max} for representative multiiodide plumbate ions are represented as vertical lines where S= solvent/additives.

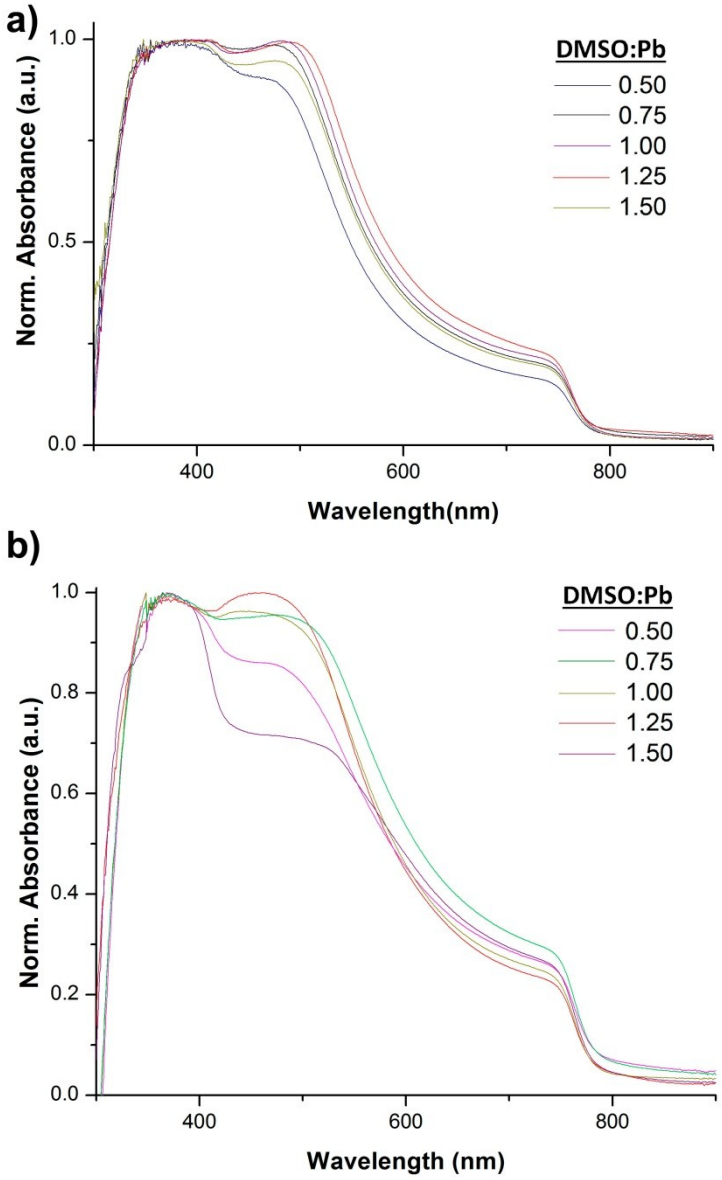

Figure SI2: a) Absorption spectra of $MAPbI_3$ films measured as a function of the DMSO:Pb ratio used under different R.H. conditions: a) R.H.= 30 % and b) R.H.= 60 %.

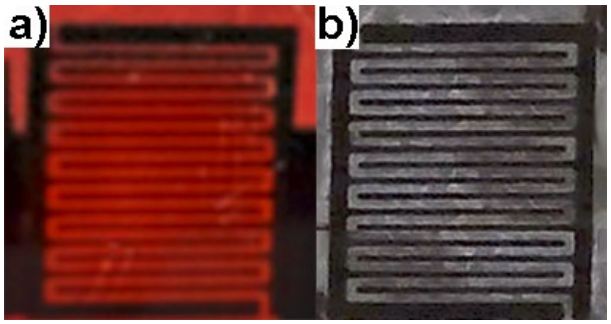

Figure SI3: Optical images of interdigitated electrodes a) fresh b) degraded by exposure to moisture using a climatic chamber at R.H.=80 % and 60 °C during 60 min.

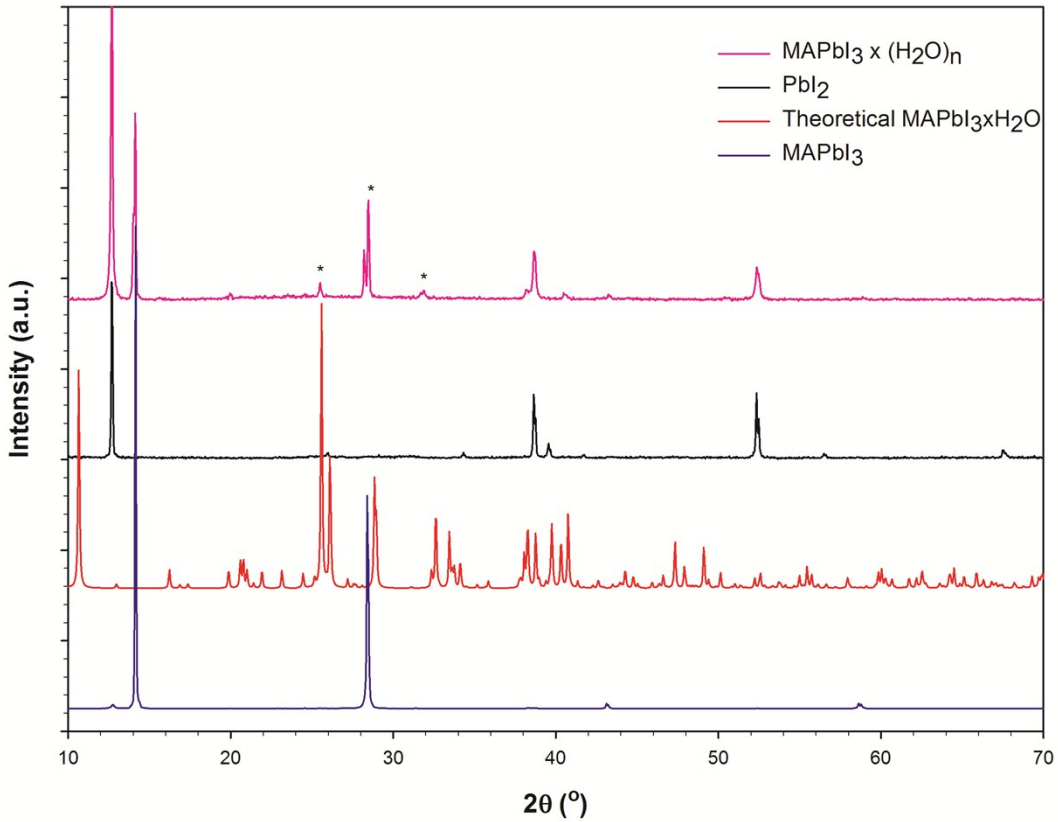

Figure SI4: Comparison of XRD difraction patterns of pure $MAPbI_3$ and PbI_2 with the theoretical powder of monohydrate $MAPbI_3 \cdot H_2O$ and the reaction product of $MAPbI_3$ in a climatic chamber at R.H.=80 % and 60 °C during 60 min. Signals marked with asterisc may arise from the monohydrate complex.

References

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