Impact of the Solvation State of Lead Iodide on its Two-Step Conversion to MAPbI₃: An

***In Situ* Investigation**

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Abstract

The two-step process to produce hybrid organic-inorganic perovskite MAPbI₃ has been successfully and widely used; however, producing high efficient solar cells without high-temperature processing and use of additives still remains a challenge. Here, we investigate the two-step solution processing of MAPbI₃ from PbI₂ films exhibiting different solvation states in DMF. *In situ* grazing incidence wide-angle X-ray scattering (GIWAXS) measurements reveals an elaborate sol-gel process involving three PbI₂-DMF solvate complexes—including disordered (P₀) and ordered ones (P₁, P₂)—prior to PbI₂ formation. We show that exposure of the appropriate solvated state of PbI₂ to MAI can lead to rapid and complete room temperature conversion into MAPbI₃ and yield higher quality films with improved solar cell performance. Complementary *in situ* optical reflectance, absorbance and quartz crystal microbalance with dissipation (QCM-D) measurements are used to monitor the two-step process. These measurements show that dry PbI₂ can take up only one third of the MAI take up by the solvated crystalline P₂ phase of PbI₂, requiring additional annealing and yet still underperforming. The perovskite solar cells fabricated from the ordered P₂ precursor show much higher power conversion efficiency (PCE) and reproducibility than devices fabricated using the conventional annealed PbI₂ film or the other precursor phases. The average PCE of the fabricated solar cells is greatly improved from 13.2(±0.53)% (from the annealed PbI₂) to 15.7(±0.35)% (from P₂) with the champion device reaching up to 16.2%. This work demonstrates the importance of controlling the solvation of PbI₂ as an effective strategy for the growth of high-quality perovskite films and their application in high efficiency and reproducible solar cells.

Introduction

Due to their low-cost fabrication, the use of abundant materials and their high efficiency reaching a power conversion efficiency (PCE) of 23.3%, perovskite solar cells (PSCs) have attracted tremendous attention lately as a prime alternative to current thin film semiconductors.^[1–9] The unique photovoltaic properties of perovskite absorbers such as large light absorption coefficient, long electron and hole diffusion lengths, high carrier mobility, and easily tunable band gap have contributed to the high efficiency of perovskite solar cells.^[10–14] AMX_3 is the structure representing the organic-inorganic hybrid perovskite compounds, where A is an organic cation, most often methylammonium ($CH_3NH_3^+$, MA^+), or formamidinium ($HC(NH_2)_2^+$, FA^+), M is a metal cation typically (Sn^{2+} or Pb^{2+}) and X is a monovalent anion such as (halide ion I^- , Br^- , or Cl^-).^[15–17] To achieve high-performance PSCs, significant effort has been made toward improving the quality of the polycrystalline perovskite films in terms of their phase, crystallinity, morphology, and coverage. Several processing techniques have been developed to achieve high-quality perovskite layers, including solution-based spin coating (two-step sequential deposition and one-step deposition) and blade coating, as well as vapor deposition, among others.^[18–23]

Even though one-step spin coating process is the most popular procedure to date for fabricating high-quality hybrid perovskite thin films, the two-step sequential deposition method continues to overcome some of the challenges faced during one-step solution processing, such as uncontrolled precipitation of perovskite crystals, formation of pinholes requiring large volumes of antisolvent dripping, large surface undulations and low coverage, all of which can influence defects and trap state densities, and impact the optoelectronics properties of the semiconductor.^[24]

The critical step in the sequential deposition process is the intercalation reaction of methylammonium iodide (MAI) with the pre-deposited PbI_2 film to form $MAPbI_3$.^[18] According to Liu et al.^[25], if the PbI_2 film is well crystallized and compact, it might cause an

incomplete conversion to perovskite phase once the film is exposed to MAI solution in isopropanol (IPA) for a short duration. On the other hand, longer exposure time has been linked to abnormal growth of perovskite crystals, and/or the dissolution or delamination of the converted perovskite films. These drawbacks have made it difficult to fabricate highly efficient and stable PSCs by a sequential deposition method. Consequently, important efforts have been made to achieve optimal conversion either by increasing reaction temperature,^[26] IPA pre-wetting,^[3] by employing strong coordinative solvents, such as dimethyl sulfoxide,^[2,27] additional film treatment steps,^[28] or by incorporating additives.^[19,29,30] Gong et al.^[31] showed the importance of fabricating mesoporous PbI_2 films instead of dense and compact films, claiming this facilitates the diffusion and intercalation of MAI.

Since the presence of PbI_2 in the final perovskite films has been shown to affect the quality of the formed layers and the resulting solar cell efficiencies,^[32] another step consisting of IPA wash was performed to further control the PbI_2 content in the film. It has been shown by Shiratori *et al.*^[33] that the IPA wash step improves the uniformity and quality of perovskite layer as it allows the dried MAI present at the surface to diffuse into the film leading to higher degree of conversion to MAPbI_3 . It removes the excess MAI since it can selectively dissolve unreacted MAI byproducts without affecting the MAPbI_3 phase.^[34] It also prevents the degradation of MAPbI_3 back to PbI_2 phase by decreasing the vapor reactions resulting in the presence of ambient air/water vapor condensing on the surface and increasing the IPA relative humidity in the surrounding gas during the drying phase.^[35]

However, further progress in the implementation of two-step conversion requires a deeper understanding of the conversion process to perovskite, requiring the use of *in situ* characterization methods which can be sensitive to temporal changes in the phase, composition and microstructure, optical properties as well as mass uptake. Toward this end, techniques such as grazing incidence wide-angle X-ray scattering (GIWAXS),^[36–42] UV–vis transmission/reflection,^[36,38,43] and quartz crystal microbalance with dissipation (QCM-

D),^[37,44–47] are especially powerful as they can be combined with commonly-used solution-casting techniques to monitor *in situ* the ink-to-solid phase transformation in organic and hybrid semiconductors.^[48]

QCM-D measures changes in mass and rigidity and has been used, among other things, to monitor mass deposition at the solid-liquid interface during solution-casting, to measure solvent vapor uptake by an organic film and to detect its dissolution, and to monitor rapid mass change during solid-state ligand exchange of a colloidal quantum dot film.^[37,44,46] Grätzel et al. used the QCM-D technique to monitor the conversion of PbI_2 to perovskite.^[49] They quantified the completion of the conversion process and correlated the dissipation variations to changes in the perovskite film morphology. *In situ* GIWAXS has recently emerged as a powerful diagnostics tool for solution-cast hybrid perovskites. It has revealed the formation of intermediate solvated phases during the evolution from precursor ink to solid-state during solution-casting of 3D and reduced dimensional perovskites.^[15,18,22,50–54] The one-step process was shown to proceed via the formation of disordered colloids which can subsequently form intermediate precursor-solvent co-crystal phases or directly crystallize into the perovskite phase, depending on the choice of halide, strongly dictating the microstructure and morphology of the hybrid perovskite film.^[15,55,56] The crucial role of antisolvent drip has also been revealed using *in situ* GIWAXS.^[50,51,57–59] Previously, we were able to investigate the formation of the metal halide PbI_2 from a DMF solution.^[18] The latter work demonstrated that PbI_2 deposition proceeds via a sol-gel process whereby a disordered precursor solvate crystallizes into metastable PbI_2 -DMF co-crystal phases which spontaneously convert to PbI_2 at room temperature. The observation that as-cast PbI_2 films exhibit a complex and time-dependent solvated states provides interesting opportunities to convert from solvent-expanded and metastable precursors into the perovskite phase and thus access improved conversion and high quality perovskite films.^[31,36,60]

Here, we build on this understanding of the state of solvation of as-cast PbI_2 films to propose a new low-temperature conversion route that increases the quality and optoelectronic properties

of perovskite films and achieves improved reproducibility of the two-step processes. *In situ* measurements reveal that PbI₂ in DMF inks forms, over time, three different solvated precursor phases (P₀, P₁, and P₂) exhibiting different structural characteristics. We have compared the conversion process of these intermediate solvated phases of PbI₂ to conversion from the dry PbI₂ film obtained after thermal annealing. The precise timing of the process, including the duration of the first step and the start of the conversion step determine the state of the precursor at the moment of conversion and are shown to matter to the overall conversion process. Our study identifies the precursor phase P₂ as the optimum state for conversion into hybrid perovskites because of the direct molecular substitution reaction of weakly coordinating DMF with MAI into the expanded lattice of crystalline solvated PbI₂. We observed a considerable enhancement of the average PCEs (of 15 devices) from $13.2 \pm 0.53\%$ (from annealed PbI₂) to $15.7 \pm 0.35\%$ (from P₂) with the champion device reaching up to 16.2%. The improved PCEs is achieved due to the completed conversion from solvated crystalline phase P₂ of PbI₂ and DMF to perovskite phase at room temperature leading to greater absorbance and better film morphology along with lower trap state densities and recombination losses.

Results and Discussion

Solvated precursor states of PbI₂ in DMF

We monitored the PbI₂ ink drying and film formation during spin coating from a DMF solution by performing *in situ* GIWAXS and *in situ* UV–vis absorbance measurements.^[18] The time-evolution of the GIWAXS scattering features (after integration for each time slice) is plotted in a 2D intensity map with respect to time (abscissa; $7 < t < 600$ s; logarithmic) and q (ordinate; $2 < q < 10 \text{ nm}^{-1}$) in **Figure 1a**. The measurements reveal an elaborate sol-gel process involving three PbI₂–DMF solvate complexes, including disordered (P₀) and ordered ones (P₁, P₂) forming sequentially before the PbI₂ formation, which initiates after 5 min. The ordered solvates are shown to be highly metastable and eventually disappear, leading to the formation of the PbI₂

phase at room temperature without requiring thermal annealing. Evidence of solvent retention by the as-cast film can also be seen when monitoring the dynamical thinning behavior of the PbI_2 solution in DMF in comparison with the blank solvent (**Figure 1b**). The thinning behavior of the PbI_2 solution deviates from the blank solvent indicating slower drying thanks to solvent retention. The film thickness plateaus at $t \approx 13$ s to a floor of ≈ 0.5 μm , which decreases to the expected thickness of 0.34 μm after thermal annealing. The *ex situ* GIWAXS measurement in **Figure 1c** confirms that thermal annealing produces a PbI_2 film without any other phases present. **Figure 1d** shows a 2D map of the temporal evolution of the UV-vis absorbance spectra. Selected spectra corresponding to the solvated PbI_2 phases P_0 (~ 10 s), P_1 (~ 30 s) and P_2 (~ 80 s) and to nearly formed PbI_2 (~ 600 s) are shown in **Figure 1e**.

The solvated phases of PbI_2 are clearly swollen with DMF molecules and unstable at room temperature, given their transformation into PbI_2 within minutes of casting. Therefore, it is reasonable to expect the solvated PbI_2 layer will convert more easily to the perovskite phase than the dry PbI_2 film. Moreover, the state of the solvated PbI_2 phase is expected to dictate the ease and completion of the conversion, as well as the microstructure of the converted perovskite film. If correct, then the precise timing of the two-step deposition protocol implemented during the conversion process is expected to play a critical role.

Conversion of dry and solvated PbI_2 to perovskite

We study the impact of all four different PbI_2 precursor states, namely, P_0 , P_1 , P_2 , and dry PbI_2 , on the conversion to the perovskite phase using *in situ* GIWAXS measurements. The perovskite layers were prepared following the two-step sequential deposition protocol as shown in **Figure 2a**, which involved (i) PbI_2 spin-coating from DMF solution for different durations (10 s, 30 s, 80 s), followed immediately by (ii) casting the MAI solution loading for 30 s and spinning the residual solution for 30 s at 3000 rpm, (iii) IPA wash by casting and spinning residual IPA for 30 s at 3000 rpm, and (iv) thermal annealing. One exception was the case of dry PbI_2 , which

was annealed at 100°C for 10 min. The sample was cooled prior to exposure to MAI solution and subjected to the same IPA wash and thermal annealing steps.

Figure 2b shows a series of 2D GIWAXS snapshots measured *in situ* for each of the four sample types (columns from left to right: P₀, P₁, P₂, dry PbI₂), for casting and conversion experiments performed directly at the beam line. The snapshots presented correspond to the state of each sample immediately after the different steps of conversion are completed (rows from top to bottom: PbI₂ spin-coating, MAI loading and spinning, IPA washing and spinning, thermal annealing). The state of the as-cast PbI₂ film at the end of spin coating and just prior to MAI loading (1st row) confirms that P₀ is in the disordered colloidal state, whereas P₁ ($q \approx 8.1, 6.7, 6.4$ and 4.2 nm^{-1}) and P₂ ($q \approx 7.0, 6.7, 6.1 \text{ nm}^{-1}$) exhibit crystalline order. P₂ appears to be far more textured than P₁, indicating the solvated PbI₂ crystalline phase transition from 3D-like to 2D-like powder texture.^[18] The thermally annealed PbI₂ layer also exhibits a 2D-like powder texture. Immediately after the MAI solution loading and spin-off (2nd row), the GIWAXS measurements reveal the formation of 3D powder rings associated to PbI₂ (001) and to the (110) reflection of the perovskite α phase at $q \approx 10 \text{ nm}^{-1}$, indicating that in all cases the perovskite phase is formed. However, substantial unconverted PbI₂ remains in films that were in the P₀ and P₁ states prior to MAI loading, as well as in the dry PbI₂ case in addition to the remaining unconverted MAI powder associated to the formation of a ring at $q \approx 7.1 \text{ nm}^{-1}$, with $q \approx 5.0 \text{ nm}^{-1}$ corresponding to the kapton tape covering the spin coater (removed in the case of annealed P₀ and P₁). Importantly, we note that the sample exposed to MAI in the P₂ state is converted completely immediately after MAI loading and spin-off, in contrast to the other samples. The additional step of IPA washing (3rd row) is meant to re-dissolve any unconverted MAI remaining in the sample. GIWAXS measurements performed immediately after IPA washing reveal its contribution to further perovskite conversion. The integrated intensity vs. q (**Figure S1**) indicates the overall perovskite scattering intensity increases and PbI₂ scattering decreases after IPA wash for conversions from P₂ and dry PbI₂. **Figure S2** shows the time-evolution of

the integrated intensity of the diffraction features related to the perovskite phase α ($q = 10 \text{ nm}^{-1}$) and the PbI_2 phase ($q = 9.1 \text{ nm}^{-1}$) during MAI spinning and subsequent IPA washing for conversion experiments based on P_2 and dry states of PbI_2 . Both data sets reveal a rapid increase of the perovskite intensity immediately upon MAI casting, followed by a slow increase (decrease) of the perovskite (PbI_2) intensity. The perovskite (PbI_2) intensity increases (decreases) further upon IPA washing, resulting in higher intensity for P_2 as compared to dry PbI_2 . **Figure S3a** and **Table S1** summarize the *ex situ* XRD patterns, the full width at half maxima (FWHM) and crystallite size distribution of the samples just after completion of the MAI loading and IPA washing steps, and confirms the *in situ* GIWAXS observations. All four samples exhibit the perovskite phase (14.18°). However, for films converted from P_0 and dry PbI_2 states we found a large amount of residual crystalline PbI_2 (12.68°), indicating only partial conversion. **Figures S1a** and **S1b** show that further thermal annealing of the perovskite films eliminates any remaining PbI_2 residues while enhancing the intensity of the perovskite scattering even further. These observations are consistent with the findings of Shiratori *et al.*^[33] that IPA washing step improves the uniformity and quality of perovskite layers as it allows the dried MAI present at the surface to re-dissolve and diffuse into the film leading to higher degree of conversion to MAPbI_3 . The increase of perovskite intensity with IPA wash is also consistent with the claim that IPA washing removes excess MAI by re-dissolving unreacted MAI without damaging the MAPbI_3 phase.^[34] partial conversion of dry PbI_2 is consistent with the fact that dense and compact films must undergo significant volume expansion, which limits the ability of the conversion reaction to occur at room temperature.^[2,61] Indeed, the complete conversion of P_1 and P_2 could be explained by the fact that the weak coordinating ligand DMF in the precursor phases can be easily replaced by a direct molecular substitution reaction with MAI to form MAPbI_3 at low temperature; therefore, increasing the conversion rate and improving the perovskite crystal growth.^[62] The expanded lattice of solvated PbI_2 (P_1 and P_2) and the presence

of weakly bound Pb-DMF complexes considerably increase the conversion rate of PbI_2 to MAPbI_3 . We note that conversion from P_1 was complete when experiments were performed in a N_2 glove box, but not when performed in air, which was the case for *in situ* GIWAXS measurements. The incomplete conversion of P_0 solvated state of PbI_2 may be due to the large amount of liquid phase solvent present in the wet film. The MAI loading and spin-off may simply not provide sufficient time for the solvent exchange to occur and MAI to be supplied uniformly to the wet film.

Steady-state UV-vis absorbance measurements of the converted and annealed samples reveal a broad absorption with band edge around 756 nm (**Figure S3b**). The thickness of the perovskite layers does not differ significantly, being in all cases $532(\pm 46)$ nm, as measured by cross-sectional SEM. Importantly, we note that P_0 exhibits significantly weaker absorbance than the other samples, while perovskite layers prepared from P_2 exhibit enhanced absorbance in the visible region. We attribute the higher absorbance of the perovskite layer converted from P_2 to its complete conversion and high degree of crystalline order of the final film.

Dynamics of conversion of dry and solvated PbI_2

So far, our study has shown that the majority of the conversion from PbI_2 to perovskite occurs during the MAI loading stage. However, *in situ* GIWAXS measurements could not be easily performed during the loading stage as the sample is buried under a bulk solution and the incident and scattered X-rays are absorbed by the solvent. Consequently, we have little information about the dynamics of conversion during MAI loading until the MAI solution is spun-off. We have instead performed *in situ* UV-vis absorbance measurements to monitor the conversion behavior of PbI_2 to perovskite. **Figures 3a** and **3b** show the time-evolution of spectra absorbance from the initial P_2 and dry states of PbI_2 , respectively, to perovskite phase formation. The increase of absorbance and its red-shift from those of P_2 or PbI_2 toward that of MAPbI_3 can be clearly seen in both instances. However, the conversion is much faster in the

case of P_2 , happened during the first 20 s and at a very rapid rate in comparison with PbI_2 , which needs more than 100 s and does not reach the same absorbance. The differences in the kinetics of conversion explain why the conversion from dry PbI_2 after a loading time of 30 s was incomplete, as confirmed by *in situ* GIWAXS and XRD measurements, whereas the same loading time is more than sufficient to completely convert P_2 at room temperature.

We provide further insight into the conversion process using the QCM-D technique. This method can be used to monitor the mass uptake of MAI by the PbI_2 film during MAI loading for PbI_2 films in the solvated P_2 and dry states. QCM-D is sensitive only to the addition or loss of mechanically bound mass and to the viscoelastic properties of the material bound at the solid-liquid interface. Changes in the resonance frequency (Δf) of the AT-cut quartz crystal are associated to mass uptake for $\Delta F < 0$ or mass loss for $\Delta F > 0$. The energy dissipation (ΔD) is related to the viscoelastic properties of the adsorbed mass, with $\Delta D \approx 0$ when the film is mechanically rigid and $\Delta D > 0$ if the film is soft or is solubilized.^[63,64] To recreate the conditions of MAI loading on PbI_2 films, we spin-cast PbI_2 films on SiO_2 -coated quartz sensors prior to mounting them into the instrument. However, we have noticed that the mounting and stabilization times exceed the lifetime of the P_0 , P_1 and P_2 solvated states of the film. Indeed, the pale yellow color associated to the solvated PbI_2 changes to a bright yellow color associated with dry PbI_2 .^[65] We have therefore recreated the solvated state of PbI_2 by enclosing the QCM-D chamber and exposing it to DMF solvent vapor. Opening the enclosure removes the solvent vapor environment and makes it possible to perform MAI loading experiment on a solvated PbI_2 film. In **Figure S4a**, we plot the evolutions of ΔF and ΔD during this solvent vapor uptake experiment for 4800 s. Initially, ΔF decreases by nearly 1.4 kHz while ΔD remains negligible, corresponding to solid-state uptake of DMF by the PbI_2 film. The uptake stabilizes up until 1500 s, at which point we detect significant softening of the now solvated PbI_2 film with further uptake of DMF. At $t = 4800$ s, the enclosure is opened, allowing the solvent to evaporate. The ΔD returns to low value instantaneously and is accompanied by rapid loss of the wet solvent

mass. However the ΔF recovers very slowly over a period of several thousand seconds as the solvent is released from the solvated but rigid PbI_2 film. We have performed the same experiment using *in situ* UV-Vis absorbance (**Figure S4b**) and found that the vapor-solvated PbI_2 has identical absorbance after 30 minutes as P_2 from as-cast films. This proves that the solvated P_2 phase can be recreated for the purpose of *in situ* QCM-D experiments.

The MAI loading experiments were recreated by casting the MAI solution on the surface of a quartz sensor coated with dry or P_2 states of PbI_2 . The experiments were performed in an open configuration to allow IPA to dry but were performed without subsequent spin-off or IPA washing. In **Figure 3c**, we plot the changes of ΔF when the MAI solution is cast on the surfaces of PbI_2 films in the dry and P_2 solvated states. In both cases, the data has been corrected for baseline changes of ΔF when blank IPA is cast over the same sensors (**Figure S5a**). In both cases, we detect a decrease of ΔF attributed to the uptake of MAI by the films. In the case of P_2 , we observe a more sustained mass uptake for the 30 s duration of loading, whereas for dry PbI_2 the uptake appears to slow down after 5 s and proceeds slowly thereafter, consistent with the time-evolution of *in situ* UV-vis absorbance measurements. Using the Sauerbrey equation^[66], we have estimated the mass change due to MAI uptake in P_2 to be ~3-4 times higher than in PbI_2 , as shown in **Figure S5b**.

We have sought to further quantify the amount of MAI uptake in PbI_2 films in the dry and solvated states from the above QCM-D data. **Figure S5c** represents the changes in frequency of the sensor before and after coating with PbI_2 films. One of the samples is further vapor solvated to the P_2 state following the procedure described above to assess its mass difference. This allows us to estimate the DMF solvent retained in the P_2 film. We note from the QCM-D measurements that in the case of dry PbI_2 the frequency shift is approximately -6900 Hz, which corresponds to a change in Sauerbrey mass of $+122.13 \times 10^{-6} \text{ g cm}^{-2}$. On the other hand, in the case of P_2 , the frequency shift is approximately -16000 Hz, which corresponds to a change in Sauerbrey mass of $+283.2 \times 10^{-6} \text{ g cm}^{-2}$, yielding a differential mass of $161.07 \times 10^{-6} \text{ g cm}^{-2}$,

which we attribute to DMF. Furthermore, using the molar mass of DMF (73.09 g/mol), we obtained a molar area concentration of 2.2×10^{-6} mol cm⁻² of DMF incorporated in P₂. On the other hand, using the dry mass of PbI₂ $+122.13 \times 10^{-6}$ g cm⁻² and its molar mass (461 g/mol), the amount of PbI₂ in the films is found to be 0.26×10^{-6} mol cm⁻². The data collected from **Figure 3** and **Figure S5b** thus allow us to calculate the amount of MAI incorporated during the conversion to perovskite. The dry MAI mass in PbI₂ case is $+2.74 \times 10^{-6}$ g cm⁻² and its mass in the case of P₂ is $+8.37 \times 10^{-6}$ g cm⁻². Using the molar mass of MAI (159 g/mol), we achieved 0.017×10^{-6} mol cm⁻² and 0.05×10^{-6} mol cm⁻² of MAI in perovskite films converted from PbI₂ and P₂, respectively. We therefore conclude that the amount of MAI incorporated during the MAI loading stage is nearly three times higher in P₂ than in dry PbI₂, in agreement with the qualitative observations made above.

Optoelectronic properties and morphology

We further evaluated the influences of the PbI₂ solvation state on the solid state properties of MAPbI₃. In **Figure 4a** we present the steady-state photoluminescence (PL) spectra for the four types of samples. The PL peak stays at 768(±2) nm for all films, with a slight shift to shorter wavelength for the P₂ sample, indicating a lower trap state density. The time-resolved PL (TRPL) analysis performed for the four samples on glass confirms this. The correlated parameters were fitted using a bi-exponential equation (**Figure 4b**)^[67,68]:

$$f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + B \quad (1)$$

where τ_1 and τ_2 are the slow and fast decay time constants, respectively, A_1 and A_2 are their corresponding amplitudes and B is a constant. The average carrier lifetimes evaluated are 5.6 ns, 6.1 ns, 16.7 ns and 7.4 ns for the perovskite films converted from P₀, P₁, P₂ and dry PbI₂, respectively. We observe significantly longer lifetime for the P₂-based film in contrast to other three cases, despite the fact these lifetime values are somewhat lower than those measured for MAPbI₃ films grown using anti-solvent engineering.^[51] This observation implies that P₂-based

perovskite films should exhibit smaller recombination losses than the other films. The suppression of the charge recombination losses is expected to benefit charge collection, the fill factor (FF) and open circuit voltage (V_{OC}) of solar cells.

In **Figure 4c** we compare the plan-view scanning electronic microscopy (SEM) images for the four films. We observe relatively smooth surfaces for all films with more evidence of pin holes in films prepared from P_0 and P_1 , while the smallest grain size is seen in films converted from dry PbI_2 . Further analysis of the solid film morphology was performed using atomic force microscopy (AFM). The topographic images and the corresponding root-mean-square roughness (RMS) for each sample are presented in **Figure 4d**, while **Figure 4e** plots the statistical distribution of surface height for the perovskite layers prepared by the different methods. In case of P_0 the surface exhibit significant roughness with the maximum height features (z_{max}) reaching values up to 600 nm, consistent with the presence of deep pin holes and open grain boundaries. On the other hand, even though the PbI_2 -based film seems smoother (lower surface RMS and narrower height distribution) than all other layers, the mean height at which the distribution peak appears (≈ 270 nm) indicates the presence of deep cracks/pinholes that penetrate through the layer. The tail of the height distribution reaching well below the surface also points to the presence of open grain boundaries. By contrast, the height distributions associated to P_1 and P_2 are the shallowest, indicating the inability of the AFM tip to penetrate deep into the film through pinholes or grain boundaries. The continuity of this film is therefore compromised compared to P_1 and P_2 , which could cause a decrease in the V_{OC} due to recombination losses. Based on the structural, morphological and optical absorbance measurements, we anticipate the most efficient light harvesting and charge collection in P_2 -based perovskite solar cells.

Photovoltaic performance

We incorporated the four types of $MAPbI_3$ films into planar heterojunction n-i-p devices

consisting of glass/FTO/c-TiO₂/MAPbI₃/Spiro-OMeTAD/Au (**Figure 5a**) as shown in their corresponding cross-sectional SEM images (**Figure S6**). The PCE distribution of a total of 60 devices is illustrated in **Figure 5b** for all films. The standard deviation and average values are presented in **Table 1**. The average PCEs vary from 12.2(± 0.72)% to 12.0(± 0.76)%, 15.7(± 0.35)% and 13.2(± 0.53)% for the P₀, P₁, P₂ and PbI₂ based devices, respectively. Note that the P₂ based cells exhibit smaller deviation in contrast to the other three cases, indicating better reproducibility (**Figure S7a**). We observed improvements in all figures of merit of photovoltaic parameters for the P₂ based cells as compared to all other ones, highlighting the importance of suppression of charge recombination losses within the perovskite layer. We achieved a champion cell with PCE of 16.2% for a P₂ based cell (**Figure 5c**), with V_{OC} of 1.07 V, short circuit voltage (J_{SC}) of 21.99 mA cm⁻² and FF of 68.5%. This PCE value significantly surpasses the dry PbI₂ based cell (16.2% vs. 14.04%). The external quantum efficiency (EQE) of all devices is shown in **Figure 5d**. All cells exhibit good photocurrent generation in the visible region with a band edge near 790 nm, while the integrated J_{sc} matches the value obtained from the J - V curves measured under simulated illumination. Notably, in the region 500-750 nm, the devices based on P₀ and P₁ show lower EQE than that based on PbI₂ and P₂, which is consistent with the trend of J_{SC} . We note that the FF for the P₂-based cell is significantly higher than that of other cells (**Figure S7b**), which can be ascribed to reduced charge recombination rate. A stable output photocurrent density and PCE of the four champion cells were measured under ambient conditions (25 °C; relative humidity of 40%) and continuous AM 1.5-G, 1-sun illumination at a fixed maximum power point (MPP) voltage for 200s (**Figure S8a,b**). We achieved a stabilized PCE of 16.16% for the P₂ based devices, higher than the P₀ (13.07%), P₁ (13.05%), and PbI₂ (13.84%) based ones. **Figure S8c** shows the PCE degradation of non-encapsulated champion cells before and after 100 hours ambient exposure (humidity and temperature of ~30-40% RH and 25 °C, respectively) in the dark. All the four devices exhibit a

good ambient stability with only 3-5% degradation.

Conclusion

We have shown that the PbI_2 to MAPbI_3 conversion and resulting thin film morphology, trap state density and light harvesting can be dramatically influenced by the solvation state of PbI_2 in the two-step growth process. The improved solar cell efficiency seen in MAPbI_3 films converted from the P_2 crystalline solvated state was attributed to the improved overall conversion, greater absorbance and more compact film morphology, which significantly reduced the trap state densities, recombination losses and enhanced light harvesting. With the aid of complementary *in situ* measurements, we showed that the solvated crystalline phase P_2 of PbI_2 and DMF can readily, rapidly and completely convert to the perovskite phase at room temperature. Comparing the amount of MAI uptake by dry PbI_2 and solvated P_2 phase we found a three-fold increase of MAI content during the MAI loading step. The unstable P_2 phase is expanded by the presence of solvent and spontaneously converts to MAPbI_3 through direct substitution/intercalation of DMF with MAI molecules which possess larger affinity than DMF to Pb^{2+} .

Solar cells made with MAPbI_3 converted from the solvated P_2 state showed significant improvement in the average PCE [$15.7(\pm 0.35)$ %] with the champion device reaching a PCE value of up to 16.2%. Devices prepared from the other three PbI_2 states showed significantly lower PCE values, achieving 13.1%, 13.1%, and 14.0%, for cells grown from P_0 , P_1 and dry PbI_2 precursor states, respectively. This work is the first of its kind and provides key new insights into the conversion dynamics of PbI_2 into MAPbI_3 via the two-step synthesis process and the key role that the solvation state of the metal halide plays with far-reaching implications on low-temperature processing of perovskites and its technological applications.

Experimental Section

Solution preparation and device fabrication

Materials preparation: Lead iodide ultra-dry beads (PbI_2 , 99.999%), anhydrous N,N-dimethylformamide (DMF, 99.8%) and anhydrous isopropanol solvent (IPA) were purchased from Sigma-Aldrich. Methylammonium iodide (MAI, 99.5%) was purchased from Ossila. All chemicals were used as received without further purification.

Solution preparation: The precursor solution preparation was conducted under inert atmosphere inside a nitrogen glove box. To prepare PbI_2 solution (1 M), 460 mg of PbI_2 were dissolved in 1 mL DMF. The solution was stirred overnight at 80 °C. The MAI solution was prepared by dissolving 40 mg MAI in 1 mL isopropanol. The Spiro-OMeTAD solution was prepared by dissolving 90 mg 2,2',7,7'-tetrakis-(N,N-di-pmethoxyphenylamine) 9,9'-spirobifluorene (spiro-OMeTAD), 22 μL lithium bis(trifluoromethanesulfonyl) imide (99%, Acros Organics, 520 mg mL^{-1}) in acetonitrile (99.7+%, Alfa Aesar) and 36 μL 4-tert-butylpyridine (96%, Aldrich) in 1 mL chlorobenzene(99.8%, Aldrich).

Device fabrication: Glass substrates were cleaned by sequential sonication in acetone, isopropanol and ethanol for 30, 30, and 20 minutes, separately, and then dried under N_2 flow. Subsequently, the substrates were treated with UV-Ozone for 10 min.

All the GIWAXS experiments were conducted on TiO_2 coated glass substrate. The TiO_2 layer was prepared by chemical bath deposition with the cleaned glass immersed in TiCl_4 (CP, Sinopharm Chemical Reagent Co., Ltd) aqueous solution with the volume ratio of TiCl_4 : H_2O equal to 0.0225 : 1 at 70 °C for 1 hour. The substrates were dried under N_2 flow and then exposed to ultraviolet and ozone for 15 minutes before solution-casting. The spin-coating was accomplished under inert atmosphere inside a nitrogen glove box.

For solar cell devices, glass was replaced by FTO-coated glass (2.5 cm $\times$ 2.5 cm) substrates, and residue procedure is kept the same.

The PbI₂ layer was prepared by dropping 50 μ L PbI₂ solution and spin-coating at 1000 r.p.m. for 5s and 2000 r.p.m. for 5s, 25s and 75s separately without delay. 200 μ L MAI solution was then introduced on the PbI₂ precursor layer and spin-cast at 3000 r.p.m. for 30s with a delay for 30s (MAI Loading time). Pure IPA solvent was dropped on the substrates and spin coated for 30s before thermal annealing at 100 °C for 10 minutes for crystallization. The hole-transporting layer (HTM) was deposited by spin-coating Spiro-OMeTAD solution at 5000 r.p.m. for 30s, followed by evaporation of 80 nm gold electrode on Spiro-OMeTAD/MAPbI₃/TiO₂/FTO substrate.

Characterization

Grazing incidence wide-angle X-ray scattering (GIWAXS): GIWAXS measurements were performed at the D1 beam line at the Cornell High Energy Synchrotron Source (CHESS). These results were collected during spin coating using a custom-built spin coater covered with a Kapton to avoid solution splashes. The spin coater can also be computer-controlled from outside the hutch. An exposure time of 0.2 s was used to balance between time resolution and signal quality along with an incidence angle of 0.25° (above the estimated critical angle of 0.22°) with respect to the substrate plane. The scattering signal was collected with a Pilatus 200k pixel array detector (100 frames per second), and the wavelength of the X-rays was 1.17 Å (10.5 keV). In situ experiments were conducted in an ambient environment with relative humidity of ~20-25%. There is an estimation of 15s delay between the solution dropping and the beginning of the spin coating along with the measurements collection.

In situ UV-vis transmittance/reflectance measurements: These were performed using an F20-UVX spectrometer with a tungsten halogen light source (Filmetrics, Inc.) with an integration time of 0.1 s and a repetition rate of 10 Hz for each spectrum during spin coating or loading experiments. These measurements were performed under moisture/O₂ levels below 0.1 ppm inside a N₂ glove box.

Quartz crystal microbalance with dissipation monitoring (QCM-D): QCM-D was performed in the open module accessory of the E4 instrument (QCM-D, Q-sense, Biolin Scientific) using the quartz sensors coated with silicon dioxide (100 nm) to characterize the conversion of PbI₂ to MAPbI₃ during MAI solution loading time. A drop of 200 μ L MAI-IPA solution was cast into the open module loaded with a previously coated quartz sensor with a PbI₂ film (following the same procedure as for other substrates). Vapor solvation of PbI₂ was monitored in the open module by using an enclosure to prevent the solvent from drying prematurely. All measurements were performed at 25 °C. Changes in frequency of the third overtone ($n = 3$) are presented herein.

Morphology: The surface morphology and structure of the perovskite films were characterized by scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The SEM images were acquired using Hitachi SU-8020 Cold Field Emission Scanning Microscopy. The surface topography and root mean squared (RMS) roughness were measured in semi-contact mode on 10 x 10 μ m² areas using Icon atomic force microscope from Bruker Nano Surfaces Division. The measurements were performed with a scanning speed of 1 Hz in ambient air, at room temperature, with relative humidity in the 40-60% range.

X-ray diffraction (XRD): XRD measurements were carried out in a θ -2 θ configuration using Bruker D8 ADVANCE diffractometer (X-ray Source: Cu K α ; $\lambda = 1.54$ Å).

Optical metrology: UV-Visible absorbance spectra were acquired on a Cary 5000 UV-Vis-NIR spectrophotometer instrument. Steady-state PL (excitation at 532 nm) as well as time-resolved photoluminescence (TRPL) (excitation at 510 nm and emission at 760 nm) were measured with a PicoQuant FT-300.

Solar cell characterization: The J - V performance of the perovskite solar cells was analyzed using Keithley 2400 source under an ambient condition at room temperature, and the illumination intensity was 100 mW cm⁻² (AM 1.5 G Oriel solar simulator). The scan rate was 0.3 V s⁻¹. The delay time was 10 ms, and the scan step was 0.02 V. The power output of the

lamp was calibrated by an NREL-traceable KG5 filtered silicon reference cell. The device area of 0.09 cm^2 was defined by a metal aperture to avoid light scattering from the metal electrode into the device during the measurement. The EQE was characterized on a QTest Station 2000ADI system (Crowntech. Inc., USA), and the light source was a 300 W xenon lamp. The monochromatic light intensity for the EQE measurement was calibrated with a reference silicon photodiode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Author contribution

D.B. and P.C. contributed equally to this work. A.A. conceived the project. A.A., K.Z. and T.D.A. supervised the work. D.B. and P.C. performed all of the experiments. M.T., K.W., H.D. and D.-M.S. helped to acquire the GIWAXS measurements. S.(F.)L. helped with useful discussions of device fabrication. All the authors contribute to the writing of the Manuscript.

Notes

The authors declare no competing financial interest.

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Figure 1. (a) Time-evolution of 2D GIWAXS intensity map of the spin-coating process of PbI_2 in DMF solution showing the disordered colloidal phase P_0 , the first ordered solvated phase P_1 , the second ordered solvated phase P_2 and the onset of PbI_2 formation. (b) Thinning behaviors of blank DMF solvent and PbI_2 solution in DMF showing evidence of solvent uptake in as-cast films and significant solvent release after annealing. (c) GIWAXS snapshot taken obtained after annealing a PbI_2 film at 100°C for 10 minutes. Diffraction at $q_z = 9.1 \text{ nm}^{-1}$ corresponds to the (100) reflection of PbI_2 . (d) 2D color maps showing the spectral evolution of the UV-vis absorbance of the PbI_2 solution in DMF during spin coating. (e) Selected *in situ* UV-Vis spectra corresponding to P_0 (10s), P_1 (30s), P_2 (80s), and PbI_2 (600s).

Figure 2. (a) Schematic representation of the sample fabrication procedure used during the *in situ* GIWAXS measurements. (b) GIWAXS snapshots obtained during *in situ* measurements of PbI₂ conversion to MAPbI₃. Rows from top to bottom: PbI₂ spin-coating, MAI loading and spinning, IPA washing and spinning, thermal annealing. Scattering features associated with the disordered and ordered precursor solvates are identified as the diffraction of PbI₂ and the diffraction of MAPbI₃ (α). The circular dashed lines in delineate the integration area for generating the time-evolution of 2D GIWAXS intensity map.

Figure 3. 2D color maps showing the spectral evolution of the UV–vis absorption during MAI loading on (a) the PbI₂ film in its precursor phase P₂ and (b) annealed PbI₂ film. (c) Quartz-crystal microbalance dissipation (QCM-D) measurements of frequency changes (Δf) after the drop-casting of MAI solution over the annealed PbI₂ film, and the film at its precursor phase P₂ deposited over a SiO₂-coated quartz sensor.

Figure 4. (a) Steady-state PL and (b) time-resolved (TRPL) spectra of perovskite films fabricated from four different PbI₂ phases. (c) Plan-view scanning electronic microscopy (SEM) images (d) Atomic force microscopy (AFM) topographic images (10 μm × 10 μm) showing root-mean-square roughness (RMS) and (e) height histograms of the perovskite films converted from different PbI₂ phase.

Figure 5. (a) Solar cell architecture of FTO/TiO₂/perovskite/Spiro-OMeTAD/Au. (b) The PCE distribution of a total of 60 cells for perovskite solar cells fabricated from four different PbI₂ phases. (c) Current density-voltage curves measured at reverse scan (from V_{OC} to J_{SC}) for four champion cells. (d) External quantum efficiency (EQE) for the four different champion cells.

Table 1. The average photovoltaic parameters and the highest PCE of perovskite solar cells fabricated from four different PbI₂ phases.

Sample	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE_{ave} (%)	PCE_{max} (%)
MAPbI ₃ (PbI ₂)	1.03 ± 0.01	20.5 ± 0.57	62.6 ± 0.8	13.2 ± 0.53	14.04
MAPbI ₃ (P ₂)	1.06 ± 0.01	21.4 ± 0.46	68.3 ± 1.04	15.7 ± 0.35	16.20
MAPbI ₃ (P ₁)	1.01 ± 0.01	18.5 ± 1.34	65.1 ± 1.67	12.0 ± 0.76	13.14
MAPbI ₃ (P ₀)	1.01 ± 0.02	18.4 ± 1.32	64.4 ± 1.51	12.2 ± 0.72	13.10

The table of contents entry:

Solution-cast lead iodide films can exhibit different metastable solvated states in the presence DMF. Using in situ diagnostics, we show that conversion of PbI_2 to MAPbI_3 from its crystalline solvated state can occur spontaneously at room temperature and lead to high quality perovskite films with reduced trap state density and a high power conversion efficiency.

Keywords: hybrid perovskite solar cells, two-step conversion, in situ grazing incidence wide angle x-ray scattering, high performance, solution processing

Impact of the Solvation State of Lead Iodide on its Two-Step Conversion to MAPbI_3 : An *In Situ* Investigation

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Supporting Information

Impact of the Solvation State of Lead Iodide on its Two-Step Conversion to MAPbI₃: An *In Situ* Investigation

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Figure S1. Scattering vector q versus intensity distribution of the PbI_2 films and their conversion to perovskite inks at (a) precursor phase P_2 and (b) annealed PbI_2 at 100°C during different steps: after MAI loading and spinning, after IPA washing and after annealing.

Figure S2. Time evolution of the diffraction intensity related to perovskite phase α ($q = 10 \text{ nm}^{-1}$), and the PbI_2 phase ($q = 9.1 \text{ nm}^{-1}$) for the different perovskite inks from the annealed PbI_2 film and from precursor phase P_2 during MAI spinning and IPA washing.

Figure S3. (a) X-ray diffraction spectra of as-cast perovskite films. (b) UV-Vis spectra of the annealed perovskites films.

Table S1. XRD parameters of the as-cast perovskite films, FWHM and crystallite size distribution of the perovskite peak α at 14.18° .

	PbI_2 Peak (°)	α Peak (°)	FWHM (nm)	t_c (nm)
$\text{MAPbI}_3 (\text{PbI}_2)$	12.68	14.18	0.23852	35.07
$\text{MAPbI}_3 (\text{P}_2)$	---	14.18	0.23438	35.69
$\text{MAPbI}_3 (\text{P}_1)$	---	14.18	0.23496	35.6
$\text{MAPbI}_3 (\text{P}_0)$	12.68	14.18	0.24431	34.24

Figure S4. (a) Change of frequency (Δf) and dissipation (ΔD) as the DMF vapor flow over the annealed PbI_2 film coated on SiO_2 -coated quartz sensor and when the module is uncovered and (b) UV-Vis spectra of PbI_2 -DMF.

the solvent is left to dry. (b) UV-Vis spectra of the annealed PbI_2 film, PbI_2 at its precursor phase P_2 and the film obtained from the exposure of the annealed PbI_2 film to DMF vapor resulting on a reversible formation of ordered precursor phases.

Figure S5. Quartz-crystal microbalance (QCM-D) measurements of (a) frequency changes (Δf) after the drop-casting of IPA solvent over the annealed PbI_2 film, and the film at its precursor phase P_2 , both deposited over a SiO_2 -coated quartz sensor (b) of mass changes after the drop-casting of MAI solution over the annealed PbI_2 film, and the film at its precursor phase P_2 deposited (c) frequency changes (Δf) after the PbI_2 film at its different precursor phases is deposited on the bare SiO_2 -coated quartz sensor.

Figure S6. Cross-sectional SEM images of the perovskite films.

Figure S7. (a) Statistics of 15 devices for the perovskite solar cells (b) Photovoltaic parameters of solar cells devices based on the champion perovskite films converted from different precursor phases.

Figure S8. A stable output (a) photocurrent density and (b) PCEs and of the four champion cells measured under ambient conditions (25 °C; relative humidity of 40%) and continuous AM 1.5-G, 1-sun illumination at a fixed maximum power point (MPP) voltage for 200s. (c) The PCE degradation of non-encapsulated champion cells before and after 100 hours ambient exposure (humidity and temperature of ~30-40% RH and 25 °C, respectively) in the dark.