Luminescent Intermediates and Humidity-Dependent Room-Temperature Conversion of the MAPbI₃ Perovskite Precursor

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Supporting Information

ABSTRACT: Preparation of metal-halide perovskites under room temperature attracts attention because of energy saving by removing thermal annealing. Room-temperature transformation of spin-cast wet films consisting of methylammonium (MA) iodide, PbI₂, and dimethylformamide toward solid MAPbI₃ perovskite proceeds via several intermediate crystalline states and is strongly dependent on ambient humidity. Light transmission and photoluminescence (PL) microscopy and spectroscopy were used to monitor the growth of crystals and transformation of their properties in time under nitrogen atmosphere at room temperature. Under low humidity, a highly luminescent intermediate phase with low absorption in the visible range appears, with the PL spectra composed of several bands in the range from 600 to 760 nm. We assign these bands to low-dimensional (nanocrystals and two-dimensional inclusions) MAPbI₃ intermediates, where the exciton confinement shifts the spectrum to higher energies in comparison with the bulk MAPbI₃. The intermediate levels of ambient humidity (10−50%) appear to catalyze the conversion of the intermediate phase to MAPbI₃. At a high ambient humidity (>80%), the initially formed MAPbI₃ is quickly transformed to the transparent hydrate phase of MAPbI₃. The role of ambient water catalyzing the material transformation by competing for Pb coordination with the solvent molecules is discussed.

1. INTRODUCTION

As a typical representative of organic–inorganic hybrid perovskite semiconductors, methylammonium lead trihalide perovskite (CH₃NH₃PbI₃ or MAPbI₃) has attracted lots of attention in the material science community because of its high performance as an active material for solar cells and light-emitting diodes.¹⁻⁵ One of the biggest advantages with MAPbI₃ and other similar perovskites is that they can be solution-processed. MAPbI₃ thin films can be prepared using many different techniques including one-step⁶⁻⁹ and two-step deposition,¹⁰⁻¹³ as well as more complicated methods like, for example, chemical vapor deposition.¹⁴⁻¹⁷ However, thermal annealing of the film is usually required for most of the existing techniques today as the final synthesis step to remove solvent molecules from the structure. To reduce the energy cost of the preparation process, much attention has been given to the preparation of the perovskite film at room temperature by the solvent–solvent extraction or solid–gas interaction process, which has been proven to yield high-performance solar cells.¹⁸⁻²¹ Another key factor for the preparation of the perovskite film is the humidity of the environment, which is often considered detrimental for the stability of perovskite films.²²⁻²⁵ For this reason, film preparation inside a glovebox is always required to minimize the side effects of H₂O in the atmosphere. However, it was shown that even without a glovebox, if the humidity is well-controlled within the range of 30−50%, it is possible to prepare high-quality films with a large grain size of perovskite crystals.²⁶⁻²⁸ The synthesis of MAPbI₃ under higher controlled ambient humidity was shown to exhibit less favorable morphology, yet higher photoluminescence (PL) quantum yield.²⁹ It was also demonstrated that water vapor annealing at room temperature can help to achieve high-performance perovskite solar cells.³⁰ To summarize, there are many factors influencing the material quality and hence the optoelectronic properties during synthesis. However, the influence of most of the factors is just empirical knowledge lacking real understanding. The interaction between water and perovskite materials is a good example for this general situation.

It is known that during drying and annealing, a precursor film transforms via several intermediate stages (from amorphous to crystalline) into a bulk perovskite film. Obviously, during these intermediate stages, the sample can contain amorphous and/or crystalline complexes of MA, Pb, and I with solvent molecules or water. The transformation of this phase was found to depend on the sample preparation conditions and was studied by structure-resolving techniques such as X-ray diffraction.³¹⁻³⁹ Although in situ PL spectroscopy has been used to monitor the thermal annealing of perovskite solar cells,⁴⁰ the luminescence spectral properties of...
the solid pre-perovskite material have, to the best of our knowledge, not been investigated.

In this contribution, we studied the room-temperature transformation process of the film prepared by spin-casting of the dimethylformamide (DMF) precursor solution using optical transmission microscopy, PL microscopy, and spectroscopy. We observed film crystallization and, depending on the humidity of the environment, slow transformation from the transparent crystals to black crystals, which possessed absorption and PL spectra comparable to those of MAPbI₃. The time evolution of the PL spectra and real-time optical transmission images were recorded. We found that a partially converted material can possess PL anywhere between 600 and 760 nm. This blue-shifted emission with high-energy bands was assigned to small nanoinclusions and clusters of low-dimensional MAPbI₃ (nanosized crystals, two-dimensional (2D) layers, etc.) in the matrix of a nonconverted precursor phase. We observed that at a moderate level of humidity (20–60%), the film almost completely converts to the perovskite phase within an hour of maturing at room temperature without any annealing. A very high humidity (above 80%) accelerated the initial conversion; however, in the end, it led to a transparent phase presumably consisting of hydrate phases and PbI₂. We propose that water plays a critical role in catalyzing the transformation of the solvate precursor phases to MAPbI₃.

2. RESULTS AND DISCUSSION

2.1. Room-Temperature Crystallization of the Precursor Film and Its Light Transmission. The time evolution of the transmission image of the precursor films under different humidity levels is presented in Figure 1a (see also Video S1 in the Supporting Information for the sample in dry N₂). During the first minute after spin-casting, the precursor films looked uniform and transparent. This means that the films were amorphous, containing a large fraction of the solvent. Then, after a short time of drying, the precursor films started to crystallize, as illustrated in Video S1. The shape of the transparent crystals was different, depending on the ambient humidity conditions: from a leaf-like in dry environment to a needle-like in humid environment (Figures 1 and S2).

Depending on the ambient humidity in the sample chamber, the further evolution of the film was different (Figure 1a), as also shown in Video S2 and Figure S2 in the Supporting Information. In dry N₂, the film stayed predominantly transparent (observed in the wavelength range from 530 to 800 nm) for more than 1 h. At elevated humidity, the transformation of the crystals from transparent to black was observed within 1 h. No change in the geometrical shape of the crystals was noticed during this transformation.

At humidity >80%, the transparent crystals started to locally change from being transparent to black already after 10 min of exposure to the humid atmosphere. We observed the initial formation of several black regions that were expanding with time and finally occupying the whole sample area. However, after about 35 min, the black regions were consumed by the emergence of a transparent phase, and finally the whole sample became predominantly transparent. A closer look at Video S2 shows that the black crystals started to convert to transparent crystals of a different shape and different orientation of the crystal growth in comparison with the black crystals formed initially. If the initial crystals were growing in a horizontal fashion (as shown in Figure 1a with the yellow line), the new transparent crystals were growing mostly in the vertical direction in the center of the image (as shown in Figure 1a with the green line).

2.2. Analysis of the Absorption Spectra. As seen from Figure 1a, the sample in dry N₂ remained highly transparent during the whole observation time, meaning that the full conversion to MAPbI₃ did not occur. This becomes obvious by comparing the absorption spectra measured after 3 and 60 min in dry N₂ with the absorption spectrum of the reference (REF) MAPbI₃, as shown in Figure 1b. Drying for 3 min led to almost no absorption in the visible range, whereas after 1 h, some absorption was observed over the whole range of the typical
MAPbI₃ absorption, but still much weaker than that for the thermally annealed REF sample. However, the absorption edge at about 750 nm clearly shows that a small fraction of the material was indeed converted to MAPbI₃. In addition, we can see that there is a small absorption feature at 450 nm in the sample matured in dry N₂ for 3 and 60 min, which means that the sample might also contain some lead-halide-solvent complexes.³¹

2.3. Time Evolution of PL Spectra from Precursor(s) to MAPbI₃ at Different Humidity Levels. The PL spectra of the samples evolved at different humidity levels in N₂ (0, 35, 63, and 83%) at room temperature for selected time durations of exposure to the environment (0, 5, 30 and 60 min) are presented in Figure 2. For a particular sample, the area excited by the laser was located at the center of the image, where there were almost no crystals grown in the sample measured in 50% humidity. That is why the PL spectra for this sample are not shown. The full dataset can be found in the Supporting Information.

PL was absent when the film in the amorphous state was just transferred to the controlled humidity setup, as shown in Video S1 in the Supporting Information. Moreover, crystalization did not immediately lead to a PL signal. It took several minutes until a detectable PL signal started to appear. From the results presented in Figure 2, it is evident that the spectral features emerging during the sample maturing strongly depend on the level of ambient humidity. The initial PL spectrum in dry N₂ showed a complex multiband shape covering the region from 600 to 750 nm. Over time, the PL spectrum was continuously evolving from the multiband appearance to a spectrum with the dominant band shifting from 715 to 760 nm, whereas the high-energy bands from 600 to 740 nm remain unchanged. The persistence of these bands may suggest the presence of possibly lead-halide-solvent intermediate species that remain intact in the absence of ambient water.

During 1 h of measurement, the low-energy bands showed a significant PL intensity increase (Figure 3c) and red shift with time (Figure 3a). The final maximum wavelength at about 760 nm was still shorter compared with the REF sample (773 nm, Figure 3a). These results suggest that the precursor film converts at room temperature in dry N₂ to a material containing inclusions of crystal structures, the spectral features of which are very similar to that of MAPbI₃. It is quite remarkable that a strong PL signal was detected from the sample having a very low absorption at the excitation wavelength (514 nm). This means that this precursor or intermediate phase must possess quite a high PL yield. It appears that the presence of humidity triggers the conversion of this intermediate phase to MAPbI₃, At 35% humidity, the film transparency after 1 h reduced substantially, and the final PL band after 1 h ended up at 765 nm, which is very close to the PL maximum position of the REF sample shown in Figure 3a,b. The high-energy bands related to the intermediate phase almost disappeared after 1 h of the film maturing. For example, the band around 600 nm which...
remained persistent in the sample measured under dry N\textsubscript{2} disappears after 5 min of measuring under 35% humidity. This indicates that the intermediate species related to the blue-shifted electronic transition are consumed in the presence of humidity. The PL intensity of the MAPbI\textsubscript{3}-related bands increased to the maximum value within the first 15 min after which it remained unchanged.

At the humidity levels from 35 to 63%, the high-energy bands in the range from 600 to 740 nm were either negligible or only temporally present in the PL spectra during 1 h of maturing in the humid environment. The slight progressive drift of the PL spectra to red indicates that samples crystallizing at high ambient humidity are probably directly converted into MAPbI\textsubscript{3}, as the final PL band maximum was very close to MAPbI\textsubscript{3}. Note that in spite of a seemingly direct conversion to MAPbI\textsubscript{3}, the PL intensity in this case was much lower compared with the sample in the intermediate phase formed at low humidity (compare Figure 3c,d).

When the samples appear black under the microscope, it means that the visible light (including the excitation wavelength of 514 nm) is mostly absorbed by them. For such highly absorbing samples, the PL intensity is proportional to the PL quantum yield when excited with the same excitation power. Therefore, when we observed a lower PL intensity of the perovskite luminescence (for the samples matured in humid conditions) in comparison with the PL intensity of the intermediate phase obtained in dry N\textsubscript{2}, it means that the former possesses a lower PL quantum yield than the latter (Figure 3d). This can be due to the formation of nonradiative recombination centers related to the presence of water in the structure.

When humidity was 80% or higher, a rapid formation of the black phase occurred, with the PL maximum wavelength close to that of the REF MAPbI\textsubscript{3} sample (Figure 3a,b). The PL intensity, however, was much lower than that of all other samples (Figure 3c,d). The drastic difference compared to the other samples was that the amount of the black phase (perovskite) reached its maximum after 20–30 min and then decreased, making a part of the sample transparent again (Figures 1a, S2, and Video S2 in the Supporting Information). This affected the PL maximum causing it to shift to blue (Figure 3a,b) and finally led to the disappearance of PL completely after 1 h (Figure 3a,b). We assign this transformation of the perovskite crystals to another nonemissive transparent phase that must be related to the interaction with water, as will be discussed in detail below.

These results can be summarized as follows:

i) In dry N\textsubscript{2} atmosphere, the precursor film cannot be fully converted to MAPbI\textsubscript{3} under room temperature (approximately 23 °C), and possesses a quasi-stable intermediate phase with low absorption in the region from 530 to 800 nm, broad PL spectra with several PL bands in the range from 600 to 750 nm, and a relatively appreciable PL quantum yield.

ii) The higher the humidity (if less than 80%), the faster the formation of the perovskite phase without a change in the visible geometrical shape of the crystals is and the lower the PL yield of the final material.

iii) Extreme humid conditions (>80%) lead to a rapid formation of MAPbI\textsubscript{3} with low PL intensity, which then converts to another transparent crystal solid with a different visual geometry.

### 2.4. Origin of the Blue-Shifted PL.

It is natural to test the hypothesis that the formation of bulk MAPbI\textsubscript{3} is preceded by the growth of small inclusions of the perovskite material in the precursor matrix. These inclusions then unite and form larger crystallites and finally the bulk phase. This process is called Ostwald ripening and is a common route of aggregation and crystallization. Small inclusions, if nanosized, indeed exhibit the excitonic confinement effect, leading to a higher energy of the band gap than the bulk material. That is why we propose that the PL in the region from 600 to 740 nm originates from the small nanoinclusions of low-dimensional perovskite clusters including 2D structures.

At first glance, this hypothesis may look unsubstantiated; however, the very fact of observing strong PL of the intermediate phase gives it a very strong support. This is because, to the best of our knowledge, low-dimensional perovskite is the only material consisting of the available components (Pb, I, MA, DMF, and water), which is documented to show strong PL in the spectral range between 600 and 750 nm. Indeed, it is known that MAPbI\textsubscript{3} quantum dots possess PL emission in the range from 650 to 740 nm for the sizes ranging from 6.5 to 7.4 nm, as shown in Table S1 in the Supporting Information. Smaller crystals should have an even larger blue shift of PL. The evolution/shift of the PL bands between 650 and 760 nm shown for the 0 and 35% ambient humidity experiments would hence be consistent with the crystal growth by Ostwald ripening.

The other possible candidates of the blue-shifted emitters are the 2D-layered MAPbI\textsubscript{3} nanosheets. The 2D MAPbI\textsubscript{3} nanosheets having different number of layers can generate PL covering the range from 514 to 763 nm according to the literature (see Table S2 in the Supporting Information). The 2D-layered perovskite nanosheets might be formed during the partial conversion process, and the different PL wavelengths correspond to different thicknesses of the layers. With an increasing layer thickness of the 2D structures or the size of the nanocrystals, the PL position shifts toward red, becoming more similar to the emission of the bulk perovskite material. In addition, potentially, some of the blue-shifted PL might come from the lead-halide-solvent complexes present in an intermediate phase. Although the crystal structures of several solvate intermediate phases have been identified, nothing is known about the absorption or luminescence properties of these intermediates and whether they can possess any substantial luminescence at all. Identifying the spectra of the crystalline intermediate phases requires more in-depth and detailed investigations.

### 2.5. Analysis of the Multiband PL Spectra.

To separate several species contributing to PL, we applied multiband fitting of the PL spectra, in which each band was fitted with the pseudo-Voigt model (linear combination of Gaussian and Lorentzian profiles). As the multiband structure was the most visible in the sample prepared in dry N\textsubscript{2} (Figure 2a), fitting this spectrum was used as a starting point to identify the positions and widths of the bands. The minimum number of bands required to fit the whole spectrum with good accuracy was five, and the approximate positions of the bands were 600, 640, 680, 720, and 740 nm (see Figure 4a). The justification of the necessity of five bands for fitting is given in the Supporting Information.

The PL band at 740 nm (marked band 1) is very close to the MAPbI\textsubscript{3} PL maximum and becomes more and more close to it in the course of film conversion. It is known that the band gap...
energy in the bulk perovskite is related to the angle of Pb−I−Pb bond in PbI₆⁴⁻ octahedra, which is close to 170° for pristine MAPbI₃ at room temperature. If the angle is smaller, the band gap increases. Therefore, we assign the experimentally observed red shift of band 1 with time to the increase of the Pb−I−Pb angle during the transformation of the material into a more ordered bulk perovskite structure.

It is important to note that we were able to apply the five-band model with the same starting parameters to fit all the PL spectra obtained in experiments with different humidity levels. During the fitting, the width of each band was fixed, whereas the position was allowed to shift by at most 20 nm relative to the positions obtained for the sample measured in dry N₂ (see the Supporting Information for details). The fitted spectra and the evolution of the number of bands and their positions are presented in Figures 4, 5 and S6−S9. The main difference between the spectra measured at different ambient humidity levels was in the relative intensity of the bands. The presence of clearly defined bands at 600, 640, 680, and 720 nm allows us to hypothesize that they correspond to specific nanosized, low-dimensional perovskite structures, which are more readily formed in the intermediate phase than others. The experimentally observed width variation of each band is probably related to the distribution of crystal sizes (2D layer thickness) and great variety of the dielectric properties of the environment in the highly disordered solid. At the moment, we are not in a position to tell with confidence what these stable nanostructures are.

In general, the higher the humidity of the environment, the lower the contribution of the high-energy PL bands to the total PL. At high humidity, band 5 and band 4 were not observed at all. If band 3 and band 2 existed from the beginning, they disappeared after several minutes of exposure to the humid environment, leaving the perovskite PL (band 1) only (Figure 4ef).

2.6. Possible Chemical Transformations of the Precursor Film. Our results show that MAPbI₃ perovskite can be readily formed at room temperature from the precursor film with an appropriate amount of water in the environment. If the humidity is low, an intermediate phase with a weak absorption and broad PL forms instead of the bulk perovskite structure.

As known from the literature, during the standard thermal annealing procedure, the solvent is removed quickly, allowing the MA⁺ ions and PbI₆⁴⁻ octahedra to form the perovskite structure. In this structure, MA⁺ is located in the space between the corner-shared PbI₆⁴⁻ octahedra as shown in the scheme of bulk MAPbI₃ in Figure 6. Heating is needed because of the high boiling point of the commonly used solvents (153 °C for DMF).

When the precursor film is left to mature at room temperature in dry N₂, the solvent molecules do not leave the film so easily. It is not only because of the high boiling point, but also because the DMF molecules coordinate to lead and form hydrogen bonds with MA⁺, which retain the solvent in the film. As the size of the MA−DMF complex is larger than that of MA⁺, PbI₆⁴⁻ cannot be assembled in the corner-sharing perovskite structure. Instead, the PbI₆⁴⁻ octahedral adapt face-sharing structures (see the schematic of MAPbI₃−DMF in Figure 6), leading to low absorption in the visible

Figure 4. Pseudo-Voigt fitting of PL spectra measured after 5 min (left column) and 60 min (right column) during the sample evolution under different humidity levels at room temperature (the data are indicated at the top of each spectrum): (a,b) dry N₂, (c,d) 35% humidity, and (e,f) 63% humidity.

Figure 5. Time evolution of the maxima of the individual PL bands extracted from the five-band fitting procedure applied to the experimental data at different humidity levels (indicated in each plot): (a) dry nitrogen, (b) 35% humidity, and (c) 63% humidity. The band shift is much smaller than the distance between the bands.
The absorption feature at 450 nm from the sample in dry N2 after 3 and 60 min also indicates that there might be a complex having similar face-sharing PbI$_6^{4−}$ octahedral arrangement as that of lead–iodide compounds. Judging from the final absorption in comparison to that of the REF sample, we conclude that most of the DMF molecules remained in the structure. However, the emergence of the perovskite-like absorption and PL means that even in dry atmosphere in some local regions, DMF could evaporate out leaving MA$^+$ ions to form perovskite unit cells surrounded by the PbI$_6^{4−}$ octahedra.

Our understanding of the whole process of ripening of the precursor films and transformation through several intermediate stages is illustrated in Figure 6. It contains low-dimensional perovskite structures (giving a strong PL with maxima at 600, 640, 680, and 720 nm) surrounded by the nonemissive transparent structure. The disordered bulk perovskite phase, which dominated the final PL spectra in dry N$_2$, must also be the result of growing and joining together of low-dimensional perovskite clusters via the Ostwald ripening process. When such intermediate structures were further thermally annealed, the DMF molecules evaporated completely, leading to the formation of perovskite structure in the whole film.

When water was added to the atmosphere, even in small amounts, intermediate structures with blue-shifted PL were formed after a very short time, as revealed by the appearance of the multiband PL spectra. In this case, water probably works as a catalyst helping to remove the DMF molecules from the structure by either forming hydrogen bonds with DMF or replacing DMF in the lead-halide-solvent structure because of the stronger coordination to lead. Upon the progress of crystallization, the high-energy PL bands disappear and low-energy PL bands red-shift toward 760 nm, as shown in Figures 2, 4, and 5. The clear formation of black nontransparent crystals shows that the presence of water leads to a high extent of conversion of the precursor film to MAPbI$_3$. Visually, the optical density of the resulting samples was similar to that of the REF film prepared by thermal annealing. Note that the geometrical shape of the crystals was determined in the very beginning, at the initial crystallization of the precursor film, into transparent crystals, and it did not change during further transformation of the material to MAPbI$_3$ under moderate humidity. This reaffirms the strong effect of the formation of crystalline intermediates on the morphology of the MAPbI$_3$ thin films.

Increasing the humidity led to faster precursor film conversion, however, with a lower PL yield of the resulting perovskite. We assign this to a combination of formation of nonradiative recombination channels because of the interaction with water and a better charge carrier transport in fully converted films in comparison with the partially converted ones that allow the excitations to reach the nonradiative recombination centers.

When the humidity was very high (>80%), the perovskite structure was quickly formed (Figure 1a). However, the reaction obviously did not stop. On the basis of the literature, we propose that a further interaction of water with MAPbI$_3$ might make a complex between MA$^+$ and H$_2$O (the hydrogen bond MA$^-$H$_2$O), as shown in Figure 6. As the size of MA$^-$H$_2$O is larger than that of MA$, the perovskite crystal was converted to a hydrated perovskite crystal, for example, the monohydrate MAPbI$_3$$\cdot$H$_2$O phase, or dihydrate MA$_4$PbI$_6$$\cdot$2H$_2$O phase, as described in refs 26,51, in which the PbI$_6^{4−}$ octahedral reorganized again from corner-sharing to face-sharing crystal structures. During the conversion process, some PbI$_2$ might be formed at the same time. On the basis of this understanding, we assume that the newly formed transparent phase might contain the hydrated perovskite and PbI$_2$ phases, and it possesses low absorption in the visible range, thus appearing transparent in the microscope. Video S2 nicely shows how black crystals transform to transparent crystals.

Figure 6. Cartoon illustrating our view on the room-temperature transformation of the perovskite precursor and final material at different conditions. It is based on the experimental observation of the film’s transparency, PL intensity and spectra, visible film crystallinity, literature data about the intermediate stages, and the origin of the blue-shifted PL as luminescence of low-dimensional perovskite inclusions proposed here.
(hydrated phase) with different crystal growth directions, as also marked in Figure 1a.

3. CONCLUSIONS

The room-temperature transformation of the perovskite DMF precursor film prepared from PbI₂ and CH₃NH₃I was studied by PL micro-spectroscopy and light transmission imaging as a function of ambient humidity. We found that the amorphous film, within 1 h, spontaneously converts at room temperature in dry nitrogen atmosphere to the MAPbI₃ intermediate phase. This phase possesses an appreciable PL with a broad multiband spectrum ranging from 600 to 760 nm. We propose that the blue-shifted emission comes from the presence of perovskite nanocrystals and other low-dimensional perovskite structures of different sizes. It is remarkable that the PL maxima of several high-energy bands (from 600 to 720 nm) were reproducible from sample to sample, which may indicate that certain sizes/geometries of low-dimensional perovskite structures are more stable than others. We found that adding water to the environment drastically increases the conversion reaction leading to the formation of a strongly absorbing perovskite film within 1 h, although having a low PL yield. The shape of the crystals was found to depend on the humidity of the environment in which the film was placed for drying. We propose that water works as a catalyst helping to remove the residual solvent from the film. However, a prolonged exposure to water at high humidity (>80%) conditions leads to the recrystallization of the initially formed perovskite film to the transparent hydrated perovskite phase.

4. EXPERIMENTAL SECTION

We used a single-step synthesis method to prepare the perovskite samples. The CH₃NH₃PbI₃ (MAPbI₃, MA = CH₃NH₃⁺) precursor solutions were prepared by dissolving 461 mg of PbI₂ (Sigma-Aldrich, 99%) and 159 mg of methylammonium iodide (Sigma-Aldrich, 98%) in 1.25 mL of DMF (Sigma-Aldrich, anhydrous). The solution was stirred for 2 h at 60 °C. A 100 μL of the precursor solution was dropped on a microscope coverslip (22 mm × 22 mm × 0.17 mm) at ambient conditions (∼50% humidity). It was followed by spin-casting at low speed (650 rpm) to keep the liquid film on the substrate. Within 2 min after spin-casting, the sample was placed in a microscope sample chamber with controlled atmosphere for observations. The REF sample was prepared in the same way, but spin-cast at 1460 rpm and annealed at 80 °C over 1 h in ambient conditions (∼50% humidity in the air).

The nitrogen (N₂) atmosphere, with a required humidity, was prepared by bubbling dry N₂ gas through water, as shown in Figure S1 in the Supporting Information. The humidity was measured using a commercial hygrometer with absolute accuracy ±10%. The sample was placed in a microscope chamber, which was constantly flushed with N₂ of the desired humidity. We used a home-built wide-field epifluorescence microscope based on Olympus IX71 with a 40× objective lens (Olympus LUCPlanFL, NA = 0.6) (see Figure S1). The Argon-ion laser (514 nm, CW) was used for the excitation of PL. The excitation spot of approximately 40 μm in diameter at the sample plane was located in the center of the image. The power density was approximately 3.6 W/cm². The PL spectra of the samples as a function of time were recorded by a charge-coupled device camera (ProEM S12B, Princeton Instruments) with a slit and a transmission diffraction grating placed in the optical path. The real-time transmission images and videos of the crystallization process in the precursor film were recorded by a Nikon DS100 digital camera using a 530 nm long-pass filter. The image and PL spectra were recorded every 5 min with <5 s exposure of the sample to light, whereas for the rest of the time the sample was kept in dark to avoid photoinduced effects. The absorption spectra were measured by a UV–vis spectrometer (PerkinElmer: Lambda 1050) using an integrating sphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01799.

Experimental setup, optical transmission images of all samples, time evolution of PL spectra of all the precursor films, literature data on PL of low-dimensional MAPbI₃, fitting of the PL spectra by multiband models, and time evolution of the relative intensity of the PL bands obtained from the fitting (PDF)

Time evolution of light transmission micrographs of the precursor films exposed to nitrogen gas of different humidity levels at room temperature (AVI)

Transmission images of the precursor film sample taken after different times of the sample maturing in different humidity conditions in nitrogen (AVI)

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Notes
The authors declare no competing financial interest.

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