

Atmospheric Humidity Underlies Irreproducibility of Formamidinium Lead Iodide Perovskites

Keonwoo Park, Shaun Tan, Tim Kodalle, Do-Kyoung Lee, Maged Abdelsamie, Ji-Sang Park, Joo-Hong Lee, Sung-Kwang Jung, Jeong Hoon Ko, Nam-Gyu Park, Carolin M. Sutter-Fella,* Yang Yang,* and Jin-Wook Lee*

Metal halide perovskite solar cells (PSCs) are infamous for their batch-to-batch and lab-to-lab irreproducibility in terms of stability and performance. Reproducible fabrication of PSCs is a critical requirement for market viability and practical commercialization. PSC irreproducibility plagues all levels of the community; from institutional research laboratories, start-up companies, to large established corporations. In this work, the critical function of atmospheric humidity to regulate the crystallization and stabilization of formamidinium lead triiodide (FAPbI₃) perovskites is unraveled. It is demonstrated that the humidity content during processing induces profound variations in perovskite stoichiometry, thermodynamic stability, and optoelectronic quality. Almost counterintuitively, it is shown that the presence of humidity is perhaps indispensable to reproduce phase-stable and efficient FAPbI₃-based PSCs.

overlooked, but negatively impacts institutional research laboratories, start-up companies, and large established corporations all alike. From a commercial standpoint, PSC irreproducibility detrimentally impedes quality control and reduces production yield and thus overall profit margins. Identifying and controlling process variability is thus a crucial consideration for PSCs to become market viable.

Since 2018, nearly all record-breaking, high-performance PSCs (single junction) have been based on formamidinium lead triiodide (FAPbI₃) as main component of the absorber layer, often incorporated with excess methylammonium chloride (MAcI) which is added for

crystallization control.^[1,2] Browsing through the literature, it becomes obvious that many variations exist in the optoelectronic quality, performance, and operational stability of these PSCs reported by different labs (Table S1, Supporting Information).^[3–17] For example, the reported bandgaps show a spread between ≈ 1.48 and 1.55 eV for the supposedly identical FAPbI₃ composition.^[1,3–7,18] Simultaneously, different groups have reported perovskite fabrication and processing protocols

1. Introduction

For metal halide perovskite solar cells (PSCs), their subpar operational durability, module scalability, and material toxicity (lead-containing) are challenges often brought up as the major barriers hindering practical commercialization and widespread adoption. The poor reproducibility of PSCs has been relatively

K. Park, J.-S. Park, J.-H. Lee, S.-K. Jung, J.-W. Lee
Department of Nano Engineering and Department of Nano Science and Technology, SKKU Advanced Institute of Nanotechnology (SAINT)
Sungkyunkwan University
Suwon 16419, Republic of Korea
E-mail: jw.lee@skku.edu
S. Tan, Y. Yang
Department of Material Science and Engineering
University of California Los Angeles
Los Angeles, CA 90095, USA
E-mail: yangy@ucla.edu
T. Kodalle, C. M. Sutter-Fella
Molecular Foundry
Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA
E-mail: csutterfella@lbl.gov

D.-K. Lee, N.-G. Park
School of Chemical Engineering
Sungkyunkwan University
Suwon 16419, Republic of Korea
M. Abdelsamie
Materials Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA
J. H. Ko
Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125, USA
J.-W. Lee
SKKU Institute of Energy Science & Technology (SIEST)
Sungkyunkwan University
Suwon 16419, Republic of Korea

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202307265>

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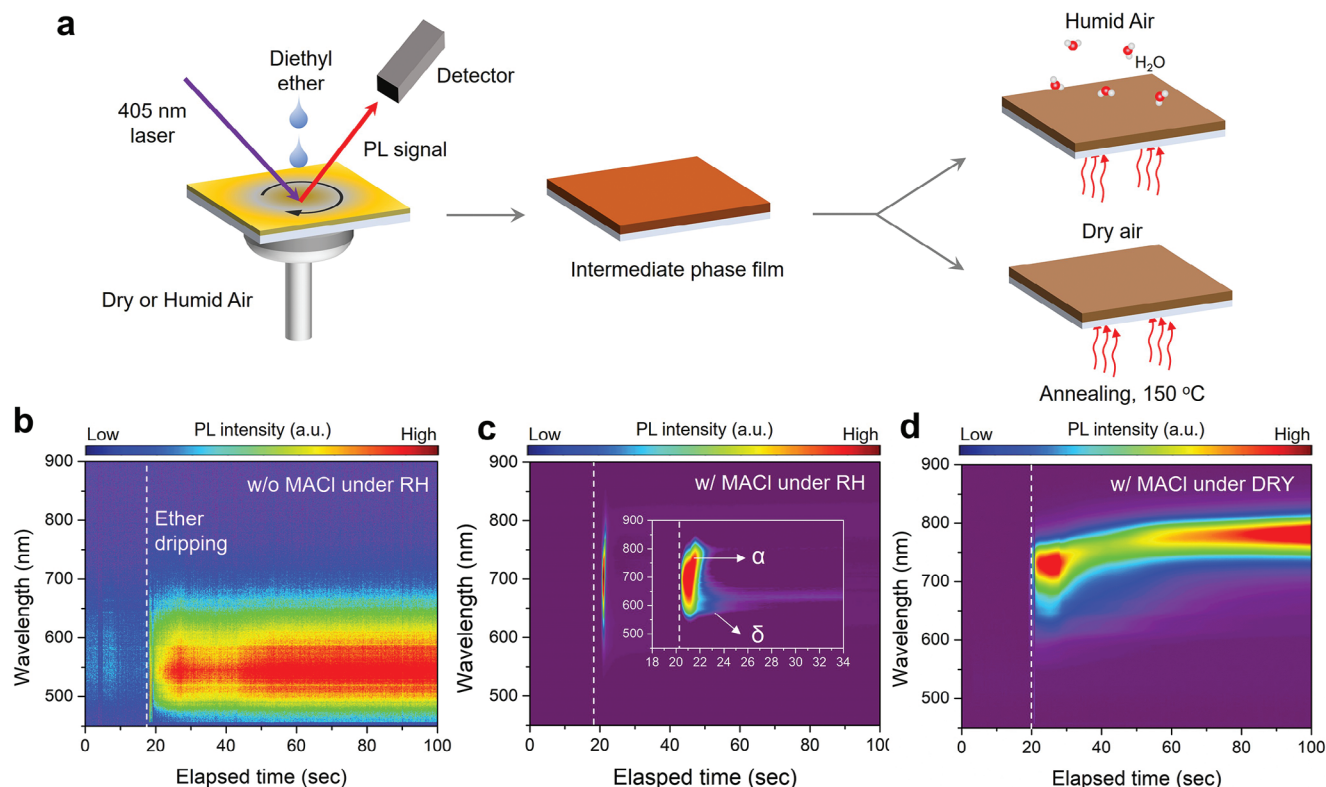


Figure 1. In situ investigation on formation of FAPbI₃ films. a) Schematic illustration of the FAPbI₃ thin film fabrication process under different atmospheric conditions. b–d) In situ photoluminescence (PL) spectra measured during the nucleation process from solution under 50% $\pm$ 5% relative humidity (RH) of the b) pristine film and c,d) films with the addition of 40 mol% excess MACI measured under c) 50 $\pm$ 5% RH or d) dry atmosphere with 0% RH. The in-set PL spectra in (c) illustrate the rapid dissipation of the formed α -FAPbI₃ nuclei within short time duration of spin-coating.

under different atmospheric conditions (Table S1, Supporting Information).

Owing to the hygroscopic nature of the polar aprotic solvents and the ionicity of the component precursors, the perovskite crystallization may intrinsically be affected by the atmospheric humidity content. Previous studies have shown that the presence of water and fabrication under controlled humidity conditions may confer benefits for both the prototype methylammonium lead triiodide (MAPbI₃)^[19–23] and FAPbI₃ perovskites.^[11,24–26] While these studies have analyzed the beneficial effects of humidity on perovskites and often concluded with “defect-healing effects”,^[23,25] their observations have been largely limited to the optoelectronic quality of perovskites and have relied predominantly on theoretical assumptions. As such, the impact of humidity on FAPbI₃ formation and its potential implications for the reproducibility of high-performance PSCs remains a relatively unexplored area of research within the perovskite community.^[27] Moreover, the crystallization thermodynamics and kinetics of FAPbI₃ are known to be distinct from other perovskites. Most critically, the photo-active α -FAPbI₃ perovskite phase is thermodynamically metastable at room temperature, and thus, an effective stabilizer such as MACI is essential to fabricate a phase-pure and stable α -FAPbI₃ film. Nevertheless, the effect of humidity (if any) on FAPbI₃ formation with such a stabilizer, and how this links back to the reproduction of current high-performance PSCs, has largely been unexplored in the community.

Herein, we utilized in situ capabilities to monitor the perovskite formation and crystallization dynamics under controlled atmospheric environments. We report on the crucial roles of the atmospheric humidity content to affect the stoichiometry, thermodynamic stability, and optoelectronic quality of FAPbI₃ perovskites. Thermogravimetry coupled with differential thermal analysis and mass spectroscopy (TG-DTA/MS) provides insights into the physical mechanisms underlying the variations. We show that the presence of atmospheric humidity is perhaps indispensable during processing, and fundamentally underlies the reproducibility of phase stable and high performance FAPbI₃ PSCs. This work paves the way for understanding processing control to fabricate reproducible PSCs, a critical hurdle that must be resolved before commercialization of the technology.

2. Results and Discussion

2.1. Initial Nucleation from Solution

Figure 1a illustrates the FAPbI₃ film fabrication process. We first investigated the perovskite crystallization dynamics from solution during spin-coating at room temperature in different atmospheres using in situ photoluminescence (PL) (Figure 1b–d). Upon antisolvent (diethyl ether) application at $\approx$ 20 s, strong PL signals emerged owing to the formation of the perovskite and/or intermediate phases. For FAPbI₃ without MACI (hereafter denoted as the pristine film) fabricated under a humid

atmosphere ($50 \pm 5\%$ RH, Figure 1b), a broad PL peak spanning from 450 to 650 nm can likely be ascribed to the formation of the non-perovskite δ -FAPbI₃ “yellow” phase and/or solvent complex phases (selected individual spectra are given in Figure S1, Supporting Information),^[28] as verified by the X-ray diffraction (XRD) patterns of the as-spun films (Figure S2, Supporting Information). For FAPbI₃ with MACl added (40 mol% unless otherwise stated^[6]), a strong initial broad asymmetric peak around 700 nm immediately appears after antisolvent application (Figure 1c and Figure S5d, Supporting Information), but rapidly decreases in intensity and almost completely disappears within a short time. This PL peak is possibly related to the metastable formation of the initial nuclei of the α -FAPbI₃ “black” phase,^[29] indicating that MACl incorporation enabled the initial formation of the perovskite phase at room temperature even without annealing treatment. However, the peak emission originating from the δ -FAPbI₃ phase becomes dominant, while the α -FAPbI₃ phase can be seen to be thermodynamically unstable at this stage (Figure S3 and Note S1, Supporting Information). The more rapid dissipation kinetics of the initial nuclei of α -FAPbI₃ are observed to occur with increasing humidity, as evidenced by the additional in situ PL data set obtained at various controlled humidity levels (Figures S4 and S5, Supporting Information). In contrast, for the film of FAPbI₃ with MACl excess fabricated under a dry atmosphere (N₂ atmosphere, <0.1 ppm for H₂O and O₂ unless otherwise stated) (Figure 1d), an intense and asymmetric PL peak appeared around 740 nm immediately upon antisolvent application, and without any trace of a δ -FAPbI₃ phase emission at lower wavelength. The PL peak red-shifted and intensified with time, implying that the α -FAPbI₃ phase can be formed and remained stable under a dry atmosphere, even at room temperature. This is further evidenced by comparing the XRD patterns of the films (Figure S2, Supporting Information). The PL peak red-shifting with time is probably associated with the growth of the α -FAPbI₃ phase beginning from quantum-confined nanocrystalline nuclei owing to a lowered critical Gibbs free energy under a dry atmosphere (see Note S1 and Figure S3, Supporting Information).^[29–32] Highly luminescent but amorphous precursor clusters cannot be excluded as an alternative explanation. Additional observations indicate that the PL signal from both the α -phase and δ -phase emerged during the spin-coating process of pristine FAPbI₃ (without MACl) under dry atmospheric conditions, indicating that the perovskite α -phase cannot be fully stabilized under a dry atmosphere without MACl (Figure S1, Supporting Information). All films were subsequently annealed at 150 °C under a dry atmosphere to trigger the full phase conversion to the α -FAPbI₃ perovskite phase (Figure S2b, Supporting Information). The film spin-coated fabricated under a dry atmosphere demonstrated the highest crystallinity with dominant (001) and (002) peaks ascribed to the cubic α -FAPbI₃ phase. Scanning electron microscopy (SEM) also indicates that the surface grain size distribution was most enhanced for the film spin-coated under a dry atmosphere (Figure S6, Supporting Information). Furthermore, we have fabricated devices based on the provided spin coating environments to compare the performance to confirm the detrimental effects of humidity (Figure S7, Supporting Information). Devices with perovskite spin coated under humidity environment exhibited lower J_{sc} and poor device efficiency compared to the devices spin coated under dry atmosphere, which is

consistent with our observation on the grain size and crystallinity tendency (Figures S2 and S6, Supporting Information).

2.2. Phase Stability and Optoelectronic Quality of FAPbI₃

We further investigated the effect of humidity during the film thermal annealing process. Based on our observations discussed in Figure 1, our subsequent studies focused only on the FAPbI₃ film with MACl spin-coated under a dry atmosphere. We now varied the thermal annealing atmosphere, under either a dry atmosphere (N₂ atmosphere, H₂O and O₂ < 0.1 ppm, hereafter denoted as FAPbI₃-DRY); or humid atmosphere at $30 \pm 5\%$ RH (hereafter denoted as FAPbI₃-RH). We first compared the ambient environmental stability of the films in Figure 2a,b. In striking contrast, the FAPbI₃-DRY film was nearly bleached completely after just 24 h storage under ambient conditions (Figure 2a), while the FAPbI₃-RH film remained barely changed (Figure 2b). This is consistent with the XRD patterns of the corresponding films in Figure 2c, where the FAPbI₃-DRY film can be seen to have mostly phase degraded into the δ -phase after 24 h in ambient. The relatively poor phase stability of the FAPbI₃-DRY film was also observed when the film was stored in a N₂-filled (<0.1 ppm H₂O) glovebox for 3 weeks, implying that the FAPbI₃-DRY film intrinsically experiences more severe phase instability (Figure S8a,b, Supporting Information). Accelerated degradation of the FAPbI₃-DRY film under ambient air can be attributed to ingress of humidity into FAPbI₃^[33,34] which further decreases the activation energy for catalyzing the phase degradation process (Figure S9, Supporting Information).

Steady-state and time-resolved PL spectroscopy (Figure 2d,e) show that the PL intensity of the FAPbI₃-RH film (9.7×10^6) was over two orders of magnitude higher than that of the FAPbI₃-DRY film (8.8×10^4). Moreover, the different emission peak positions (806 nm for FAPbI₃-RH, 798 nm for FAPbI₃-DRY) provided the first evidence that the film compositions were different as a result of the annealing atmosphere (vide infra). The time-resolved PL decay profiles of the films were fitted to a double exponential decay model. The fitted parameters are summarized in Table S2, Supporting Information. The relatively smaller proportion and longer fast decay (τ_1) time constant for the FAPbI₃-RH film imply a lesser degree of trap-mediated non-radiative recombination of charge carriers, compared to the FAPbI₃-DRY film.^[35–37] Furthermore, the slow decay (τ_2) time constant for the FAPbI₃-RH film (1076.6 ns) was significantly enhanced as compared to the FAPbI₃-DRY film (359.1 ns). Resultingly, the average PL lifetime (τ_{ave}) for the FAPbI₃-RH film (1072.1 ns) was more than 156.6% prolonged relative to that of FAPbI₃-DRY film (417.7 ns).

Space-charge-limited current (SCLC) measurements were conducted to investigate the trap density (N_t) in the films (Figure 2f). The FAPbI₃-RH film had a lower trap-filling voltage (V_{TFL} , 0.218 V) than that of the FAPbI₃-DRY film (0.284 V). The calculated N_t value significantly reduced from 3.22×10^{15} cm⁻³ (FAPbI₃-DRY film) to 1.28×10^{15} cm⁻³ (FAPbI₃-RH film), consistent with the higher PL intensity and longer carrier lifetime of the FAPbI₃-RH film. In Figure S10 and Table S3, Supporting Information, the photovoltaic parameters of the proof-of-concept PSC devices based on the FAPbI₃-DRY and FAPbI₃-RH

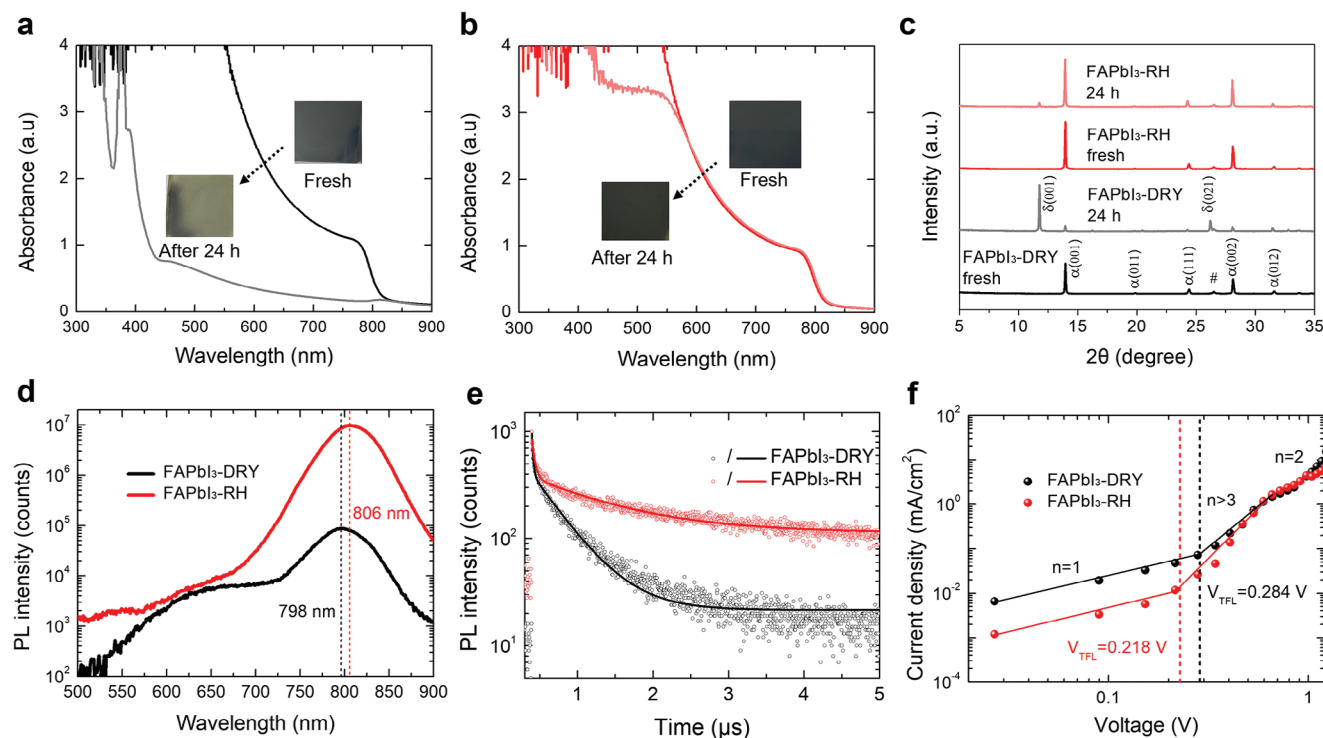


Figure 2. Phase stability and optoelectronic properties of α -FAPbI₃ films. a,b) UV-visible absorption spectra of fresh and aged FAPbI₃ films annealed under a) a dry atmosphere (RH 0%, H₂O < 1 ppm) or b) a humid atmosphere (RH 30 $\pm$ 5%) for 10 min. The films were aged in ambient for 24 h (RH 30 $\pm$ 5%). c) X-ray diffraction (XRD) patterns of the corresponding fresh and aged films. d) Steady-state photoluminescence (PL) spectra, e) time-resolved PL decay profiles, and f) space-charge-limited current measurements of the FAPbI₃ films annealed under a dry or humid atmosphere (RH30 $\pm$ 5%) for 30 min.

films are presented. The photovoltaic parameters of the FAPbI₃-RH devices can all be seen to be higher. In particular, the average open-circuit voltage (V_{OC}) of the FAPbI₃-RH devices (1.12 $\pm$ 0.01 V for reverse scan) was improved by 13.1% relative to that of FAPbI₃-DRY devices (0.99 $\pm$ 0.01 V for reverse scan). Current density–voltage (J – V) curves and stabilized power output (SPO) data for the best-performing devices are demonstrated in Figure S10b,c, Supporting Information. The SPO of the FAPbI₃-RH device was 21.34%, which is improved by 19% relative to that of the FAPbI₃-DRY device (17.93%, note that no surface treatment or additive has been applied for all devices just discussed). Figure S11, Supporting Information, further shows the external quantum efficiency (EQE) spectra of the devices. The improved integrated short-circuit current density (J_{SC}) of the FAPbI₃-RH device (23.12 mA cm^{−2}) compared to the FAPbI₃-DRY device (22.20 mA cm^{−2}) was well correlated with the J_{SC} s measured from the J – V measurements (<5% discrepancy). From the normalized EQE spectra (Figure S11b, Supporting Information), a slightly red-shifted absorption edge of the FAPbI₃-RH device is in line with the observations from the PL peak position measurements. The best-performing FAPbI₃-RH device with surface passivation demonstrated PCE of 23.81% under reverse scan (22.80% under forward scan, Figure S12, Supporting Information). To check if this observation is applicable to different processes and compositions, we further fabricated devices by the anti-solvent free, scalable D-bar coating process. We also used a different composition of (FAPbI₃)_{0.95}(CsPbBr₃)_{0.05} with 30 mol% MACl excess.^[12] We

employed an air-knife assisted D-bar coater as shown in Figure S13a, Supporting Information (details in the Experimental Section). Notably, the device fabricated using the D-bar coating process exhibited consistent improvements across all photovoltaic parameters when annealed under a humid environment compared to a dry atmosphere (Figure S13 and Table S4, Supporting Information). Altogether, we supposed that humidity during the film annealing process has beneficial effects on the optoelectronic quality of the perovskite films.

2.3. Perovskite Crystallization and Grain Growth during Thermal Annealing

To understand the implied composition difference between the films, we subsequently monitored the absorption of the FAPbI₃-DRY and FAPbI₃-RH films in situ during the thermal annealing process (Figure 3a–d). A home-built chamber with atmosphere and humidity control was used for the measurements (Figure S14, Supporting Information). Obvious differences in the absorbance evolution can be observed for the films, particularly around the 600 nm to 800 nm range. From Figure 3e, the FAPbI₃ with 40 mol% excess MACl compared to the pristine FAPbI₃ film (without MACl) experienced a blue-shifted absorption edge in addition to reduced absorbance between 600 and 800 nm, before prolonged annealing, probably due to formation of the FA_{1−x}MA_xPbI_{3−y}Cl_y intermediate phase ($x > y$, Note S2,

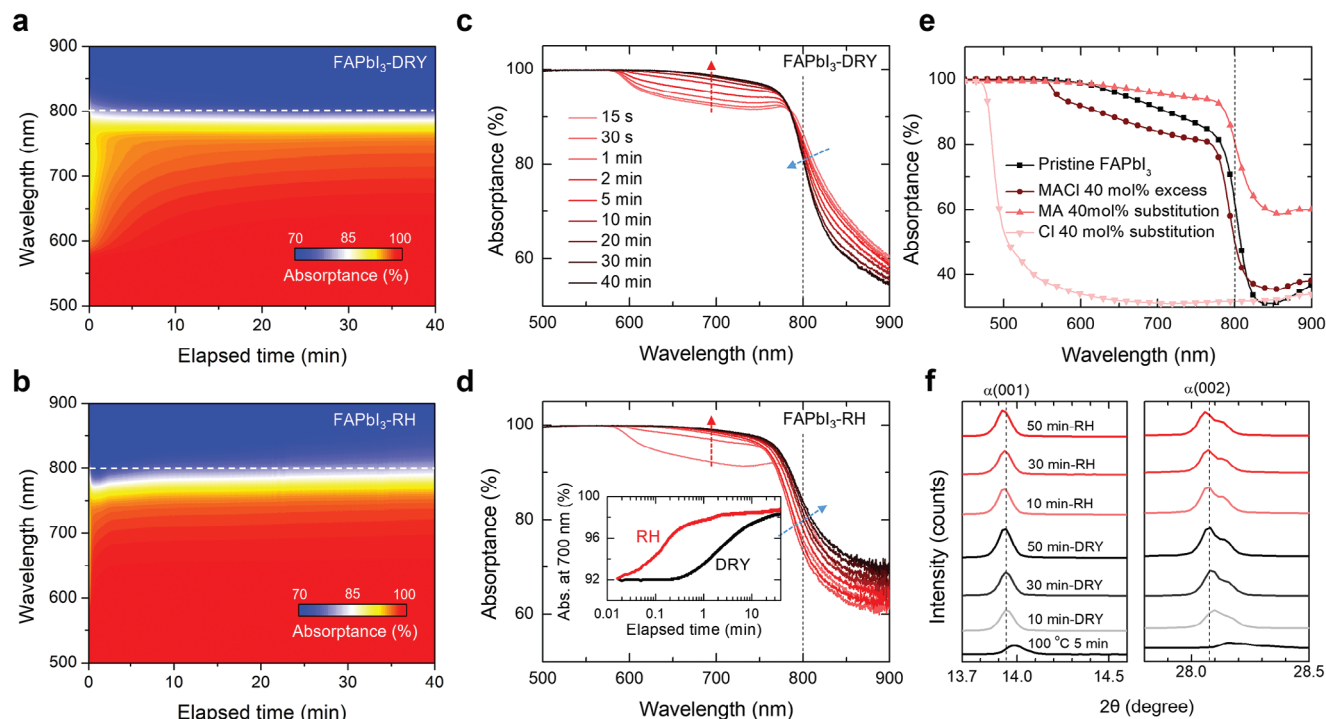


Figure 3. In situ absorbance and XRD of FAPbI₃ during thermal annealing. a,b) In situ absorbance spectra of the FAPbI₃ films annealed under a) dry atmosphere or b) 30 ± 5% relative humidity (RH). c,d), Selected absorbance spectra of the films annealed under a c) dry atmosphere or d) 30 ± 5% RH. The color coding for the time legends for (c) and (d) are the same. Inset in (d) shows the absorbance evolution at 700 nm. e) Absorbance spectra of the pristine FAPbI₃ film and FAPbI₃ with different substituents, after annealing at 150 °C for 30 s. f) X-ray diffraction (XRD) patterns of films at different annealing times under a dry atmosphere or 30 ± 5% RH.

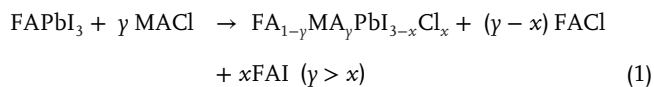
Supporting Information).^[6] Therefore, we postulate that the progressive absorbance enhancement with time between 600 and 800 nm (red arrows in Figure 3c,d) is associated with MACl vaporization during thermal annealing. For the FAPbI₃-RH film, the absorbance in this wavelength region rapidly saturated in a few tenths of seconds, whereas that of the FAPbI₃-DRY film exhibited a significantly delayed absorbance evolution (inset of Figure 3d). In addition, an obvious red-shifting of the absorption edge simultaneously occurred during thermal annealing for the FAPbI₃-RH film (Figure 3d), whereas a slight blue-shift of the absorption edge was observed for the FAPbI₃-DRY film. For the FAPbI₃-RH film, the vaporization of MACl should induce conversion of the intermediate FA_{1-x}MA_xPbI_{3-x}Cl_x to FAPbI₃, resulting in a red shift of the absorption edge. On the contrary, such a reaction is relatively not active for the FAPbI₃-DRY film, and thus incorporation of MACl into the lattice (particularly MA⁺, i.e., $x < y$) might induce the observed slight blue shift in absorption edge. Based on this, we conjecture that humidity beneficially facilitates the vaporization of MACl during the thermal annealing of FAPbI₃. This is also consistently supported by subsequent in situ absorbance measurements under different atmospheric humidity contents, where a higher humidity content progressively promoted the absorbance enhancement and the red-shifting of the absorption edge toward longer wavelengths (Figure S15 and S16, Supporting Information). Regardless of different humidity levels, Humidity-assisted annealing consistently resulted in higher device performance, particularly in terms of V_{OC} and J_{SC} , across all humidity levels, where the most notable improvement

was observed at a humidity level of RH 30% (Figure S17 and Table S5, Supporting Information). The steady-state and time-resolved PL data were correlated with observed trends in device performance with different humidity levels (Figure S18 and Table S6, Supporting Information). At this stage, we speculate that the more effective vaporization of MACl additive with higher RH might facilitate formation of less defective FAPbI₃ films. However, too high humidity (RH 50%) might damage the perovskite film. Indeed, exceptional absorbance change with the RH 50% was observed in Figure S16, Supporting Information. Still, it is important to note that the optimal humidity level for perovskite fabrication may vary depending on the choice of precursor composition and fabrication parameters (e.g., solvent, composition, additives, annealing temperature and time, etc). Importantly, for pristine FAPbI₃ without MACl, such dynamic evolution of the absorbance and red-shifting were not observed regardless of the atmospheric humidity levels, indicating that the observed absorbance evolution may be primarily due to MACl vaporization (Figure S19, Supporting Information).

We also monitored the XRD patterns of the films with annealing time (Figure 3f and Figure S20, Supporting Information). During the annealing process, the α (001) and α (002) peaks gradually shifted toward lower 2θ angles, indicating expansion of the α -FAPbI₃ lattice. In consideration of the smaller ionic radii of MA⁺ and Cl⁻ as compared to FA⁺ and I⁻, respectively, the gradual peak shifts toward lower 2θ can be associated with the vaporization of MACl from FA_{1-x}MA_xPbI_{3-x}Cl_x, accompanied by the incorporation of FA⁺ and I⁻.^[6] Particularly, comparing the same

annealing times, the FAPbI₃-RH film experienced larger 2θ shifts toward lower angles (Figure 3f, Figure S21 and Table S7, Supporting Information), complementing the in situ absorbance results that the volatilization of MAI is accelerated by humidity. As shown in the surface SEM images in Figure S22, Supporting Information, the grain sizes of the films were comparable regardless of the different annealing atmospheres, implying that the observed difference in phase stability and optoelectronic properties is due to inherent differences in the film composition associated with the volatilization of MAI.

Linking back to the observed aggravated phase instability (Figure 2a,b), we investigated perovskite films with compositions FA_{1-x}MA_xPbI₃ and FAPb(I_{1-y}Cl_y)₃ (Figure S23, Supporting Information). For FA_{1-x}MA_xPbI₃, a single perovskite phase can be formed even up to *x* = 0.40, whereas for FAPb(I_{1-y}Cl_y)₃, PbI₂ and δ-FAPbI₃ emerged even for incorporation levels as low as *y* = 0.02. This observation can likely be explained using tolerance factor considerations;^[1,38,39] while MA⁺ beneficially reduces the tolerance factor of FAPbI₃ to stabilize the α-phase, Cl⁻ incorporation adversely increases the tolerance factor and facilitates defect generation to aggravate the phase instability of α-FAPbI₃ (Figure S24 and Notes S2, S3, Supporting Information). Therefore, most of the added MA⁺ substitute for FA⁺ in the lattice, while only a small fraction of Cl⁻, if any at all, can be incorporated into the cubic perovskite lattice, resulting in a precipitation of excess FAcI and formamidinium iodide (FAI) as follows.



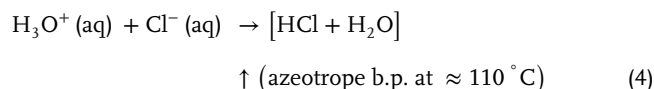
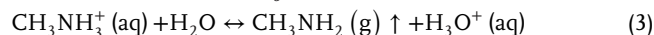
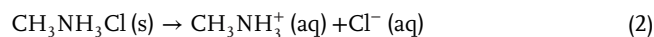
We thus hypothesize that the excess FAcI and/or FAI generated in the film is responsible for the phase instability and poor optoelectronic quality of the FAPbI₃-DRY film. Subsequent experiments to incorporate excess FAI or FAcI into pristine FAPbI₃ (without MAI) were performed to verify this hypothesis (Figure S25, Supporting Information). Notably, we observed that a phase-pure α-FAPbI₃ cannot exist solely with the addition of >10 mol% of excess FAcI. After storage under ambient conditions for 24 h, the films with excess FAI or FAcI underwent nearly complete phase degradation to the δ-phase. Their observed phase stability was even inferior to that of the pristine FAPbI₃ film. In our previous study, we showed that excess I⁻ can generate iodine interstitial defects to accelerate the phase degradation of α-FAPbI₃.^[40] Similarly, the presence of excess FA⁺, MA⁺, I⁻ and/or Cl⁻ likely resulted in the formation of interstitial defects, which may have contributed to the observed deterioration of perovskite phase stability.^[41] We noted that FA_i+I_i, FA_i+Cl_i, MA_i+Cl_i, and MA_i+I_i split interstitial defect complexes have formation energies of 0.562 eV, 0.300 eV, 0.480 eV, and 0.449 eV, respectively, which are higher than that of halide Frenkel pairs (Figures S26 and S27, Supporting Information) but comparable to other intrinsic point defects.^[41] Notably, the defect complex consisting of FA_i and Cl_i exhibited the lowest formation energy, consistent with compositional studies involving excess FAI and FAcI in FAPbI₃ (Figure S25, Supporting Information), where the films with excess FAcI showed much worse α-phase instability compared to the film with the same amount of excess FAI. Not only does the intrinsic phase stability degrade, but the interac-

tion of the defect with surrounding humidity should further degrade the phase stability of the FAPbI₃-DRY film under ambient atmosphere.^[42,43]

2.4. Humidity-Catalyzed Volatilization of MAI

In Figure 4a, time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis of the FAPbI₃-DRY and FAPbI₃-RH films was conducted to investigate the residual Cl⁻ content in the films. The TOF-SIMS 3D image confirmed a lower residual Cl⁻ content in the FAPbI₃ film annealed under a humid atmosphere (line profiles are shown in Figure S28, Supporting Information). It was noted that the intensity of the Cl⁻ in the film's bulk region is comparable to that on the top and bottom surfaces, implying incorporation of Cl⁻ at interstitial and/or lattice sites. The relatively lower Cl⁻ content observed from the FAPbI₃-RH films is consistent with energy-dispersive X-ray (EDX) analysis of the films. Specifically, the EDX analysis revealed negligible Cl⁻ content in the FAPbI₃-RH films, whereas FAPbI₃-DRY showed a noticeable amount of Cl⁻ residues, with a concentration of 3.9 mol% (Figure S29 and Table S8, Supporting Information). As discussed above, we note that FAPbI₃ film showed much-accelerated phase conversion from α to δ phase even with 1 mol% excess of FAI or FAcI in Figure S25, Supporting Information.

To investigate possible mechanisms, we performed TG-DTA/MS on pure MAI powder in Figure 4b–e. We compared the TG-DTA/MS of the completely dry MAI (Figure 4b,d) versus MAI exposed to humidity (Figure 4c,e). The MS peaks corresponding to MAI were assigned as summarized in Table S9, Supporting Information.^[44–50] Even before TG-DTA/MS, we observed that the initially solid MAI powder liquified when exposed to humidity (inset of Figure 4c), demonstrating the highly hygroscopic nature of MAI. For the case of the dry MAI powder, the weight loss began at ≈234.4 °C (endothermic peak in DTA) with simultaneous detection of gaseous fragments such as NH₂⁺, NH₄⁺, CH₂N⁺ and H³⁵Cl⁺ (MS for the other fragments are included in Figure S30, Supporting Information). On the other hand, the MAI powder exposed to humidity showed a noticeable initial weight loss starting from ≈50 °C, with a broad endothermic peak at ≈113.2 °C. The weight loss can be primarily attributed to the vaporization of water, but notably, MAI also vaporizes simultaneously, as directly evidenced by the detection of the NH₂⁺, NH₄⁺, CH₂N⁺, and H³⁵Cl⁺ fragments between 50 and 250 °C. Moreover, the additional weight loss and endothermic peaks at higher temperatures occurred at lower temperatures for the MAI powder exposed to humidity (232.0 and 326.8 °C; versus 234.4 and 334.4 °C for the dry MAI powder). We attributed the simultaneous vaporization of water and MAI to a solvation effect by water to generate volatile species as follows:



First, solid-state MAI absorbs moisture from the atmosphere and dissolves in it. Next, the solvated MA⁺ cation is a weak acid,

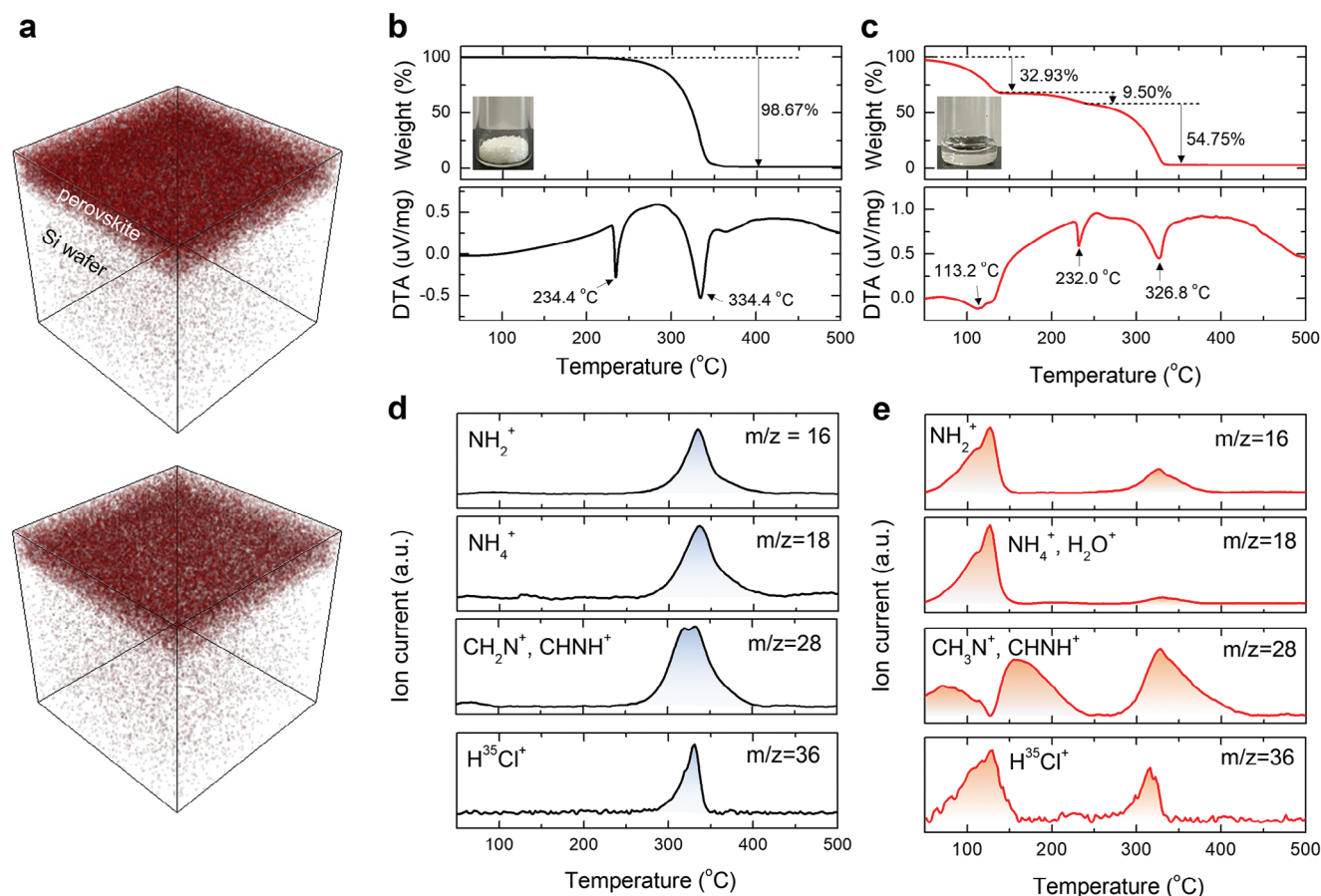


Figure 4. Investigation of residual Cl and its origin. a) Time-of-flight secondary ion mass spectrometry of Cl anion in FAPbI₃ films with 40 mol% excess MACl annealed under dry air (upper panel) and 30% relative humidity (lower panel). Measured area is 40 μm by 40 μm . b,c) Thermogravimetry coupled with differential thermal analysis and mass spectroscopy (TG-DTA/MS) analysis of b) dry MACl powder and c) MACl powder exposed to humidity for 24 h. The arrows in the DTA curves indicate inflection points of the spectra. The heating rate was 5 $^{\circ}\text{C min}^{-1}$, and the measurements were carried out under an Ar atmosphere. d,e) Temperature-dependent MS data of the d) dry MACl powder and e) MACl powder exposed to humidity measured during heating. The mass-to-charge ratios (m/z) and corresponding fragments are labeled in each plot.

and thus it can transfer a proton to a water molecule to generate an H_3O^+ ion. Although the equilibrium favors the reverse reaction due to the higher basicity of the amine, the proton exchange occurs rapidly and allows some methylamine to evaporate either by itself or together with other neutral water molecules. Finally, H_3O^+ can associate with solvated Cl^- to form HCl, whose boiling point is dependent on composition, but significant evaporation is expected during thermal annealing of the perovskite film at 150 $^{\circ}\text{C}$. The loss of MA^+ (in the form of methylamine) and Cl^- (in the form of hydrochloric acid) is consistent with our TG-DTA/MS results (Figure 4 and Figure S30, Supporting Information).

3. Conclusions

In summary, we performed systematic studies coupled with theoretical calculations to investigate the profound roles of atmospheric humidity to influence the stoichiometry, thermodynamic stability, and optoelectronic quality of FAPbI₃ perovskite films with the addition of MACl. We show that humidity destabilizes the initial desirable α -phase perovskite nuclei formation during the spin-coating process. On the other hand, atmospheric hu-

midity content beneficially assists in stabilizing the α -phase perovskite by promoting the vaporization of hygroscopic MACl during the thermal annealing process. Our work demonstrates that careful consideration of the PSC fabrication environment is vital to prevent irreproducibility, and detailed information regarding the fabrication environment needs to be provided to foster the realization of perovskite commercialization.

4. Experimental Section

Materials: *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), *N*-methyl-2-Pyrrolidone (NMP, anhydrous, 99.9%), diethyl ether (>99.7%), chlorobenzene (CB, 99.8%), lithium bis (trifluoromethane sulfonyl)imide (LiTFSI, 99.8%), 4-tert-butyl pyridine (tBP, 98%), acetonitrile (ACN, 99.9%), formamidinium acetate (FAAc, 99%), Lead (II) bromide (PbBr_2 , >99.999%), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, >98%), and titanium diisopropoxide bis(acetylacetonate) (TiO_2 , 75 wt% in isopropanol) were purchased from Sigma Aldrich. Aqueous colloidal tin (IV) oxide solution (SnO_2 , 15 wt% in H_2O) was purchased from Alfa Aesar. 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD) was purchased from Lumtec. Lead (II)

iodide (PbI_2 , 99.99%) was purchased from TCI. Hydrochloric acid (HCl , 35.0–37.0%) was purchased from Samchun Chemicals. FAI, and MACI were purchased from Greater Solar. Formamidinium chloride (FACl) was synthesized according to previously reported methods.^[51] FTO glass (Pilkington, TEC-8, $8 \Omega \text{ sq}^{-1}$) was used as the conductive substrate.

Perovskite Precursor Solution Preparation: The FAPbI_3 perovskite solution was prepared by mixing 461 mg lead iodide (PbI_2 , TCI) and 172 mg FA iodide (FAI, Greatcell solar), and 1 mol of NMP in 500 μL of DMF. For the additive engineering of MACI, 40 mol% (27 mg) MACI was added to the FAPbI_3 perovskite solution. The Spiro-MeOTAD solution was prepared by mixing 86.8 mg Spiro-MeOTAD, 34 μL TBP, and 20 μL LiTFSI solution (520 mg Li-TFSI dissolved in 1 mL ACN).

Small-Area Device Fabrication: FTO glass was cleaned with detergent, acetone, deionized water, and ethanol for 15 min by ultrasonication. The cleaned FTO glass was then dried with nitrogen gas. The dried FTO glass was further treated with ultraviolet ozone (UVO) for 1 h. A SnO_2 layer was deposited on the FTO substrate by spin-coating the diluted SnO_2 solution at 4000 rpm for 20 s, which was annealed at 185 $^\circ\text{C}$ for 30 min. The SnO_2 -coated FTO substrate was then treated again with UVO for 30 min prior to coating the perovskite layer. The perovskite solutions were spin-coated onto the SnO_2 -coated FTO substrate at 4000 rpm for 20 s. Diethyl ether (0.15 mL) was dripped after 10 s during the 20 s rotation. The perovskite films were annealed at 100 $^\circ\text{C}$ for 5 min and then annealed at 150 $^\circ\text{C}$ for different times under a dry and humid environment. For the best-performing device, octylammonium tosylate surface passivation was applied as described in the previous study.^[52] The hole-transporting layer was deposited on the perovskite film by spin-coating the 30 μL Spiro-MeOTAD solution at 3000 rpm for 25 s. A 100 nm Ag electrode was deposited on the Spiro-MeOTAD layer using a thermal evaporator at an evaporation rate of $0.1\text{--}0.9 \text{ \AA s}^{-1}$.

Device Fabrication Based on D-Bar Coating: Fluorine-doped tin oxide (FTO)-coated substrates (4.8 cm x 9.6 cm) were cleaned by sonication for 30 min with isopropanol. Before depositing TiO_2 and SnO_2 layers, the substrates were treated with UV/ozone cleaner for 60 min. Compact TiO_2 layer was first coated on FTO substrates, and then SnO_2 layer was deposited on FTO/ TiO_2 substrates. 0.1 M titanium diisopropoxide bis(acetylacetonate) solution diluted in 1-butanol was spin-coated at 4000 rpm for 30 s and then annealed at 125 $^\circ\text{C}$ for 15 min on the hot-plate and 450 $^\circ\text{C}$ for 30 min in the furnace. For forming SnO_2 layer, the diluted colloidal SnO_2 solution (1:3 volume ratio with deionized water) was spin-coated at 3000 rpm for 30 s and then annealed at 180 $^\circ\text{C}$ for 20 min on the hot-plate. 20 mM potassium chloride solution dissolved in deionized water was treated on FTO/ TiO_2 / SnO_2 substrates by the spin coating process at 3000 rpm for 30 s and then heated at 150 $^\circ\text{C}$ for 30 min. Before coating perovskite layers, the substrates were treated with UV/ozone for 30 min. 1.43 M perovskite precursor solution was prepared by dissolving 163.4 mg FAI, 437.9 mg PbI_2 , 10.6 mg CsBr, 18.4 mg PbBr_2 , and 20.3 mg MACI in 639.5 μL DMF and 60.5 μL DMPU. The precursor solution was filtered with 0.2 μm pore size of PTFE-H filter prior to use. To form large-area perovskite layers, the D-bar & air-knife coating process was used. 54 μL perovskite precursor solution was loaded on the substrate and then coated with 3 mm^{-1} s coating velocity. Argon gas blowing by air-knife with 2.0 MPa blow pressure was supplied to the wet film. The as-coated films were annealed at 150 $^\circ\text{C}$ at different times on the hot-plate under N_2 inert and ambient conditions. Spiro-MeOTAD layer was spin-coated on the perovskite film at 3000 rpm for 30 s, where the spiro-MeOTAD solution was prepared by dissolving 90.9 mg spiro-MeOTAD, 39 μL TBP and 23 μL Li-TFSI solution (520 mg mL^{-1} in ACN) in 1 mL chlorobenzene. Au counter electrode was deposited by thermal evaporation with $0.3 \text{ \AA s}^{-1}$ evaporation rate.

Device Characterization: Photocurrent density–voltage (J – V) curves were obtained under AM 1.5 G 1 sun (100 mW cm^{-2}) illumination using a solar simulator (Oriel Sol 3A, class AAA) equipped with a 450 W xenon lamp (Newport 6280NS) and Keithley 2400 source meter. The J – V curves of the PSCs were obtained with a scan rate of 0.1 V s^{-1} from -0.1 to 1.2 V (forward scan) or 1.2 to -0.1 V (reverse scan). The light intensity was adjusted using an NREL-calibrated silicon reference solar cell. Pre-conditioning, such as applied bias voltage and light-soaking, was not per-

formed prior to the measurement. The PSCs were measured with a metal mask (aperture area 0.125 cm^2) under ambient environment (temperature $\approx 25 \text{ }^\circ\text{C}$, relative humidity $\approx 30\%$). For the best performance PSCs (Figure S12, Supporting Information), 150 nm thick MgF_2 anti-reflection layer was deposited on the glass side of the FTO substrate. The SPO measurements were performed by measuring photocurrent density at a constant bias voltage 0.935 and 0.802 V for FAPbI_3 -RH and FAPbI_3 -Dry, respectively. The EQE spectra were obtained using an IPCE system equipped with a 75 W Xenon lamp (USHIO) as a white light source, where the monochromatic beam was generated under DC mode conditions. SEM images were obtained using a field-emission SEM (JSM-7401F).

Material Characterization: XRD patterns were obtained using a Rigaku SmartLab SE X-ray diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan rate of 4° min^{-1} . UV-absorption spectra were recorded using a UV-vis spectrometer (Lambda 45, PerkinElmer). Steady-state PL and time-resolved PL decay profiles were measured using a Quantarus-Tau compact fluorescence lifetime spectrometer (Quantaarus-Tau C11367, Hamamatsu) with excitation by a 464 nm laser (PLP-10, Hamamatsu). For SCLC measurement, the device with structure of ITO/Perovskite/Au was used. The N_t was calculated using the equation $V_{\text{TFL}} = N_t e L^2 / 2 \epsilon_0 \epsilon_r$ (e = electric charge, L = thickness of the absorber film (FAPbI_3 -DRY $\approx 700 \text{ nm}$, FAPbI_3 -RH $\approx 680 \text{ nm}$), ϵ_0 = vacuum permittivity, and ϵ_r = dielectric constants). TG-DTA/MS was conducted using a simultaneous thermal analyzer at a scan rate of $5 \text{ }^\circ\text{C min}^{-1}$, heated from 35 to 550 $^\circ\text{C}$ under argon flow.

In Situ Measurements: In situ PL measurements were acquired during spin-coating and post-annealing on a hot plate. Measurements were performed under controlled atmosphere with a home-built setup as described in previous works^[31,53] using a 405 nm laser diode, a plano-convex lens above the substrate, a 450 nm long-pass filter, and a fiber-coupled Ocean Optics spectrometer (Flame) calibrated by the manufacturer. A maximum power density of $\approx 100 \text{ mW cm}^{-2}$ was used during the in situ PL measurements. Spectra were continuously acquired every 100 ms. PL emission spectra were fitted using single Gaussian peak fitting after background counts were accounted for by the spectrometer and Jacobian transformation to the energy scale.^[54] Transmission measurements were collected using a fiber-coupled with an Ocean Optics spectrometer (Flame) with an integration time of 0.1 s per transmission spectrum. The equation $[A_\lambda = -\log_{10}(T_\lambda)]$ was used to calculate the UV-visible absorption spectra from the transmission spectra, where A_λ is the absorbance at a certain wavelength (λ) and T_λ is the corresponding transmitted radiation. The in situ UV-visible absorption measurements during spin-coating were performed using a setup described in a previous study.^[55] The in situ UV-visible absorption measurements during thermal annealing were performed using a custom-built heating stage with a hole that allowed transmission measurements.^[56] The heating stage was placed in a custom-built chamber with controlled humidity.

Density Functional Theory Calculation: Density functional theory calculation was performed using the PBEsol exchange-correlation functional^[57] and the projector augmented wave pseudo-potential,^[58] as implemented in the Vienna ab-initio Simulation Package code.^[59] The energy cutoff for the plane waves was set to 400 eV, and the atomic structures were fully optimized until the residual forces became less than $0.03 \text{ eV \AA}^{-1}$. Defects were investigated by employing a 192-atoms supercell, and a $2 \times 2 \times 3$ k-point mesh was used for the Brillouin zone integration.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

K.P., S.T., and T.K. contributed equally to this work. J.-W.L. conceptualized the idea and designed the experiments. K.P. conducted most of the experiments under supervision of J.-W.L., Y.Y., and C.M.S.-F. K.P., S.T., and S.-K.J. fabricated the PSCs for characterization of perovskite films under controlled atmospheric humidity. D.-K.L. fabricated the large-area PSCs utilizing an air-knife assisted D-bar coater and measured PSCs under supervision of N.-G.P. J.-H.L. measured XRD of perovskite films. S.T., T.K., M.A., and K.P. carried out in situ experiments of perovskite films under supervision of C.M.S.-F. J.-S.P. did modeling and interpretation of DFT calculations. J.-W.L. and J.-H.K. assisted with the data analysis of TG-DTA/MS. K.P., S.T., and J.-W.L. wrote the manuscript, with all corresponding authors supervising and editing the manuscript. All authors contributed feedback and comments on the manuscript.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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crystallizations, halide perovskites, humidity, in situ studies, reproducibility, scalability, solar cells, stability

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