

SOLAR CELLS

Stabilizing black-phase formamidinium perovskite formation at room temperature and high humidity

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The stabilization of black-phase formamidinium lead iodide (α -FAPbI₃) perovskite under various environmental conditions is considered necessary for solar cells. However, challenges remain regarding the temperature sensitivity of α -FAPbI₃ and the requirements for strict humidity control in its processing. Here we report the synthesis of stable α -FAPbI₃, regardless of humidity and temperature, based on a vertically aligned lead iodide thin film grown from an ionic liquid, methylamine formate. The vertically grown structure has numerous nanometer-scale ion channels that facilitate the permeation of formamidinium iodide into the lead iodide thin films for fast and robust transformation to α -FAPbI₃. A solar cell with a power-conversion efficiency of 24.1% was achieved. The unencapsulated cells retain 80 and 90% of their initial efficiencies for 500 hours at 85°C and continuous light stress, respectively.

The high power-conversion efficiency (PCE) of lead halide perovskite solar cells (PSCs) is attributed to their high carrier mobility and diffusion length and adjustable band-gap of the active-layer materials (1, 2). Black-phase formamidinium lead iodide (α -FAPbI₃) has the narrowest bandgap (1.45 to 1.51 eV in thin films) (3, 4). This phase easily transforms into a wide-bandgap yellow nonperovskite phase (δ -FAPbI₃) under ambient conditions because the large size of FA⁺ induces lattice distortion (5, 6), so routes have been developed to stabilize α -FAPbI₃ perovskite thin films. Some of these approaches involve mixing alternative cations, anions, or both to form hybrid formamidinium perovskites, such as the FA_xMA_{1-x} double cation (7); the FA_{1-x-y}MA_xCS_y triple cation (8); and even FA⁺, MA⁺, Rb⁺, Cs⁺, SCN⁻, and Br⁻ multiple cation-anion hybrids (5, 9, 10). Although these modifications

improve the stability and enhance PCEs (10, 11), high-quality perovskite and perovskite intermediate thin films must be processed in an inert atmosphere with strict control of both the temperature and relative humidity (RH). These requirements greatly limit production and applications of PSCs (12). The stability issues result from interactions of the precursors in their common solvents and their

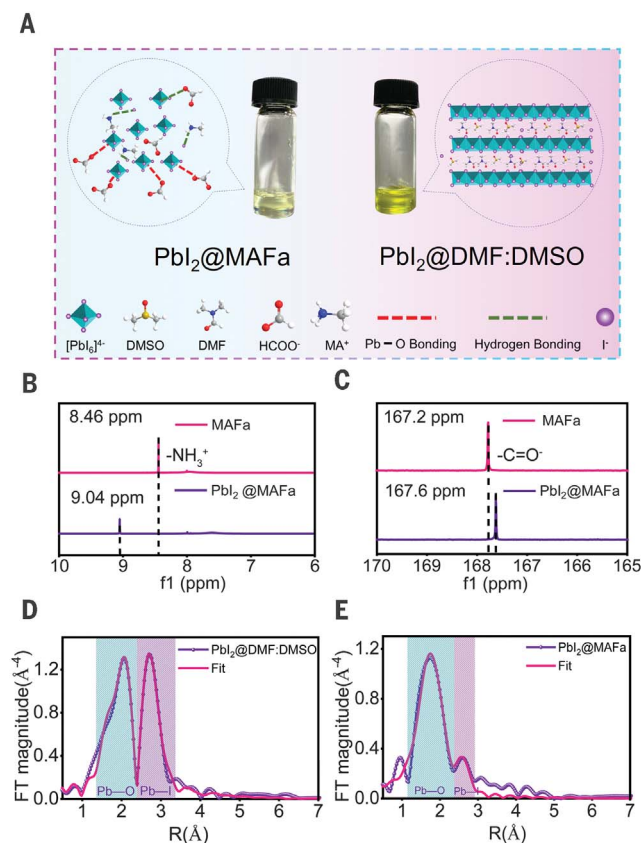
thin films. These interactions control the assembly of perovskite segments and affect the stability and performance of the frameworks (13).

We report a synthesis of stable black-phase α -FAPbI₃ that is insensitive to environmental conditions during its preparation. Vertically aligned thin films of lead iodide (PbI₂) are prepared from the ionic liquid methylamine formate (MAFa). Unlike commonly used solvents, such as *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), strong interactions with PbI₂ through C=O...Pb chelation and N-H...I hydrogen bonds in the MAFa solvent promoted the vertical growth with respect to the substrate. Formamidinium iodide (FAI) could enter the PbI₂ thin films through in situ formation of ion channels, which notably reduced the formation energy barriers. A fast transformation to stable black-phase α -FAPbI₃ was observed irrespective of RH (20 to 90%) and temperature (25° to 100°C). We achieved a PCE of >24% in ambient air, with 93% of the initial efficiency retained up to 5000 hours (under nitrogen-filled glove box), thermal stability for 500 hours (80% of the initial efficiency retained at 85°C), and stability under continuous light stress (90% of the initial efficiency retained over 500 hours of operation at maximum power point).

We dissolved 1.5 M PbI₂ in two different solvents: MAFa (fig. S1) and DMF:DMSO (9:1,

Fig. 1. Chemical environment for precursors in different solvents.

(A) Images of PbI₂@MAFa and PbI₂@DMF:DMSO solutions and schematic diagram of interactions in the solutions. (B) ¹H NMR spectra of the two solutions before and after dissolution of PbI₂. f1, magnetic intensity. (C) ¹³C NMR spectra of the two solutions before and after dissolution of PbI₂. (D and E) Extended x-ray absorption fine structure spectra and fits in R-space at the Pb L₃-edge of PbI₂@DMF:DMSO (D) and PbI₂@MAFa (E). The green area represents the Pb...O bond, and the purple area represents the Pb-I bond. FT, Fourier transform.



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Table 1. Parameters of champion devices based on FAPbI₃@MAFa and FAPbI₃@DMF:DMSO perovskite thin films.

Solvents	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
MAFa	1.17	25.34	81.36	24.1
DMF:DMSO	1.15	24.72	77.85	22.1

v/v) (Fig. 1A). The PbI₂ in DMF:DMSO (PbI₂@DMF:DMSO) solution was a deep yellow, whereas a yellow-green solution formed in the MAFa solvent. Proton nuclear magnetic resonance (¹H NMR) spectra of the two solutions before and after dissolution of PbI₂ (Fig. 1B) (12, 14) showed that the amino hydrogen spectrum in the MAFa solution shifted from 8.46 to 9.04 parts per million (ppm) because of amino hydrogen forming a strong N-H...I hydrogen bond with an I⁻ ion in solution (14–16). However, no similar hydrogen-bond interactions were observed in the PbI₂@DMF:DMSO solution (fig. S2). Moreover, the peak of C=O in the ¹³C NMR spectra moved from 167.2 ppm for pure MAFa to 167.6 ppm for the PbI₂ in MAFa (PbI₂@MAFa) solution (Fig. 1C), which is indicative of a strong interaction of the C=O group in MAFa with Pb²⁺ (15, 17), but no clear

shift was observed before and after the dissolution of PbI₂ in DMF:DMSO (fig. S3).

We used x-ray absorption near-edge structure to determine the coordination environment of the Pb atoms in the two solvents. Both Pb...O and Pb-I bonds were observed in DMF:DMSO (Fig. 1D), which we attributed to the coordination of both S=O in DMSO and C=O in DMF with Pb²⁺ (fig. S4) (13). Strong Pb-I bonds originated from the layered PbI₂ molecules, which indicated relatively weak interactions between the solvent and PbI₂ molecules. By contrast, the PbI₂@MAFa solution had stronger Pb...O coordination and weaker Pb-I bonding (Fig. 1E). Moreover, the length of the Pb...O bond decreased from 2.48 to 2.35 Å (table S1) compared with that of the PbI₂@DMF:DMSO solution. This observation indicated an extremely strong C=O...Pb interaction in the PbI₂@MAFa solu-

tion, which plays an important role in affecting the layered structure of PbI₂ (14, 18).

Free I⁻ formed hydrogen bonds with the amino groups of MAFa that could protect I⁻ in solution from oxidation (12, 14, 19). We exposed the two solutions to the atmosphere (RH > 80%) for 6 hours; the PbI₂@DMF:DMSO solution formed considerable amounts of precipitate (fig. S5) and had absorption characteristics of I³⁻ (fig. S6), whereas a clear solution and no absorption of I³⁻ were observed for the PbI₂@MAFa solution (fig. S7) (14). We attributed the improved solution stability to strong interactions of MAFa and PbI₂ through C=O...Pb chelation and N-H...I hydrogen bonds.

We systematically investigated the PbI₂ thin film formation and crystallization processes from these solutions. The PbI₂@MAFa thin films were prepared in air under ambient humidity, but the PbI₂@DMF:DMSO thin films were prepared in a N₂-filled glove box. A needlelike surface morphology of PbI₂ was observed after spin coating (0 s) from PbI₂@DMF:DMSO solution (Fig. 2A), consistent with previous reports (13, 20). The needlelike initial grains provided multiple nucleation sites, which caused the grains to contract during the growth process and form undesirable pinholes.

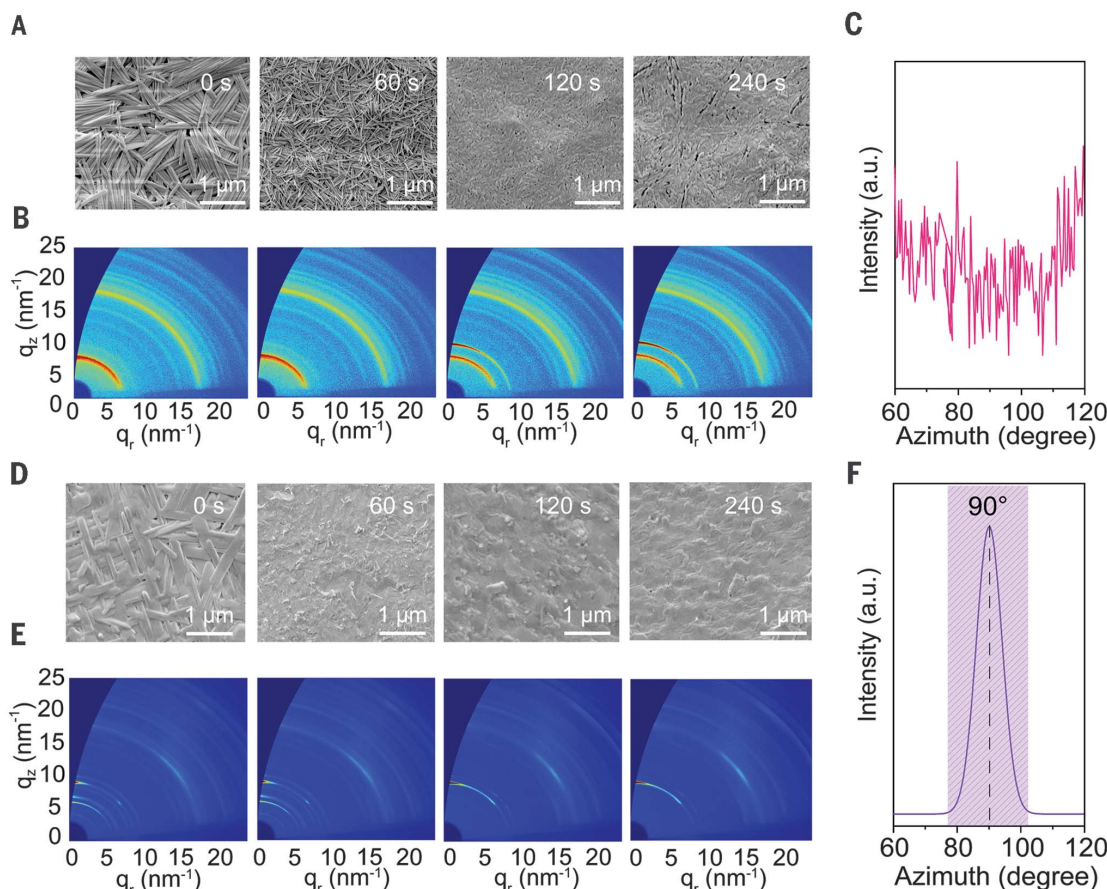


Fig. 2. Morphology and structural characterization of PbI₂@DMF:DMSO and PbI₂@MAFa films.

(A) Scanning electron microscopy (SEM) images of PbI₂@DMF:DMSO films at different annealing times. (B) In situ GIWAXS spectra of PbI₂@DMF:DMSO films at the corresponding annealing time. (C) Azimuth integration at $q \approx 9.25$ nm⁻¹ for PbI₂@DMF:DMSO thin films. a.u., arbitrary units. (D) SEM images of PbI₂@MAFa films at different annealing times. (E) In situ GIWAXS spectra of PbI₂@MAFa films at corresponding annealing times. (F) Azimuth integration at $q \approx 9.25$ nm⁻¹ for PbI₂@MAFa thin films.

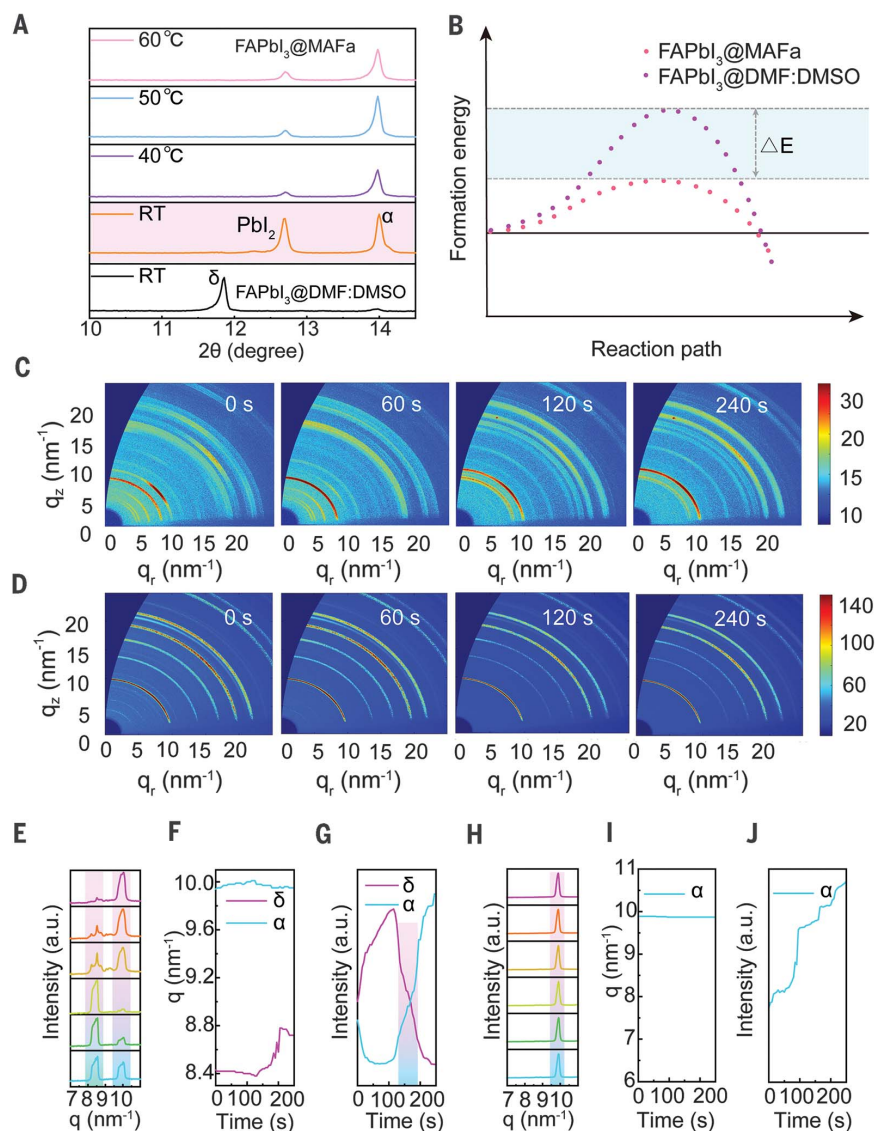


Fig. 3. Structural characterization of FAPbI₃ obtained from PbI₂@DMF:DMSO and PbI₂@MAFa films.

(A) XRD spectra of FAPbI₃ perovskite films prepared from PbI₂@MAFa and PbI₂@DMF:DMSO films at room temperature (RT). The FAPbI₃@MAFa film was prepared under atmospheric conditions and the humidity exceeded 80%, whereas the FAPbI₃@DMF:DMSO film was prepared in a nitrogen glove box because it cannot be prepared under such high humidity conditions. (B) Schematic diagram of perovskite crystallization kinetics of FAPbI₃ film under PbI₂@MAFa (pink) and PbI₂@DMF:DMSO (purple) films, respectively. ΔE , change in energy barrier. (C and D) In situ GIWAXS spectra of FAPbI₃@DMF:DMSO perovskite films (C) and FAPbI₃@MAFa films (D) under different annealing times. (E) 1D GIWAXS integral spectra of FAPbI₃@DMF:DMSO at different annealing times. (F) Variation of the diffraction ring of α -FAPbI₃ and δ -FAPbI₃ with annealing time for the case of PbI₂@DMF:DMSO films. (G) Competition of the integrated intensity of α -FAPbI₃ and δ -FAPbI₃ with annealing time for the case of PbI₂@DMF:DMSO films. (H) 1D GIWAXS integral spectra of FAPbI₃@MAFa at different annealing times. (I) Variation in the diffraction ring of α -FAPbI₃ with annealing time for the case of PbI₂@MAFa films. (J) Evolution of black-phase FAPbI₃@MAFa perovskite with annealing time.

To further understand the crystallization behavior of the PbI₂ thin films, we used in situ grazing-incidence wide-angle x-ray scattering (GIWAXS). The precursor phase (near $q \approx 7 \text{ nm}^{-1}$, where q is the scattering vector) was the main component of the PbI₂@DMF:DMSO thin films in the initial stage of crystallization (Fig. 2B and fig. S8A). As the annealing time was prolonged,

a PbI₂ signal near $q \approx 9.25 \text{ nm}^{-1}$ appeared (27). Although the diffraction intensity of PbI₂ increased as the annealing time was prolonged, most of the precursor structures had a strong signal. The strong Debye-Scherrer ring with an isotropic intensity distribution indicated that the grain orientation was completely random. This result was further confirmed by the disordered

integration lines, as shown by the azimuthal integration of the PbI₂ diffraction ring (Fig. 2C) (8, 22).

In contrast to DMF:DMSO, the use of MAFa as a solvent promoted the formation of uniform and PbI₂ grains larger than 1 μm after spin coating (Fig. 2D). Notably, diffraction from MAPbI₃ was observed given the presence of methylamine ions in the MAFa solution (fig. S9). When the annealing time was prolonged, full coverage of pinhole-free PbI₂ thin films with large grains was achieved. The initial strong diffraction signal of PbI₂ and weak MAPbI₃ signal near $q \approx 10 \text{ nm}^{-1}$ (Fig. 2E and fig. S8B) corresponded to the features in the x-ray diffraction (XRD) spectra. Although a certain precursor structure was produced at the beginning of spin coating, the precursor gradually transformed into a stable PbI₂ phase through a solid-solid conversion during annealing (22).

After the annealing process, the resulting PbI₂ thin films had a strong degree of preferential orientation with respect to the contact, as evident from sharp and discrete Bragg spots (Fig. 2E, 240 s), and the only pole figures of the azimuth angle were at 90° without noticeable peaks along the same rings (Fig. 2F) (23). Moreover, we found the random orientation of PbI₂ domains in the PbI₂@DMF:DMSO thin films from the high-resolution transmission electron microscopy (HRTEM) (fig. S10) (24), whereas the (001)-oriented PbI₂ domains have a high degree of orientation and show a very regular arrangement in the PbI₂@MAFa thin films (fig. S11). This allows the formation of a regular mesoporous structure of ~5 to 10 nm between the oriented domains of PbI₂ with the evaporation of MAFa (fig. S11, A and B) because MAFa remains in the thin films (fig. S12). Moreover, a clear hole was observed in the side view of the PbI₂@MAFa sample (fig. S11C). This structure led to vertically aligned growth of the PbI₂ thin films with formation of nanometer-scale ion channels between the layered PbI₂, which provides a direct reaction channel for cations. This differs from the previously reported pore formation in PbI₂ films (25–27). Most notably, the PbI₂@MAFa thin films were more stable under high humidity than the PbI₂@DMF:DMSO thin films as a result of the strong Pb···O and hydrogen-bond interactions between residual MAFa and the PbI₂ framework (figs. S13 and S14) (14).

We prepared perovskite thin films under ambient conditions in air. The FAPbI₃@DMF:DMSO thin films (prepared from PbI₂@DMF:DMSO thin films at room temperature in a N₂-filled glove box) had a weak α phase at $\sim 13.9^\circ$ with a strong δ -phase signal ($\sim 11.8^\circ$) because of the low formation barrier of the δ phase (Fig. 3A) (3, 21). By contrast, no δ phase was observed in the FAPbI₃@MAFa thin films (prepared by using PbI₂@MAFa thin films at

room temperature in air), but a very strong α -FAPbI₃ perovskite signal was observed together with the PbI₂ peak at $\sim 12.7^\circ$ (2I). This can be attributed to the fact that MAFA prevents the transformation of PbI₂ to δ -phase perovskite by the strong interactions of MAFA and PbI₂ through C=O...Pb chelation and N-H...I hydrogen bonds. The phase transition temperature of α -FAPbI₃ through the PbI₂@MAFA thin films decreased considerably and allowed for the transition to take place at room temperature and in air.

This result was further confirmed by a strong absorption with a band edge at ~ 820 nm and steady-state photoluminescence emission at ~ 820 nm for the FAPbI₃@MAFA film (fig. S15) (2). The PbI₂ peak intensity gradually weakened and crystallization of α -FAPbI₃ was further promoted when the substrate temperature was increased. Moreover, the surface roughness of the perovskite films decreased from 20.5 to 10.3 nm (fig. S16) together with an increase in grain size (fig. S17) (3). The δ phase was suppressed in the FAPbI₃@MAFA thin films because the vertical crystal orientation of the PbI₂ structure provided nanoscale ion channels for rapid entry of FA⁺ and reduced the energy barrier to formation of α -FAPbI₃ (Fig. 3B) (28). The PbI₂@DMF:DMSO thin films had random orientation distributions (Fig. 2C), which limit the diffusion of FA⁺, and this greater energy barrier to form α -FAPbI₃ favored the formation of a low-energy yellow phase (29).

The crystallization process of the FAPbI₃ perovskite thin films was further monitored by in situ GIWAXS measurement in real time. Crystals of the FAPbI₃@DMF:DMSO perovskite thin film grew in the vicinity of 30° through azimuth integration (fig. S18) and had a large δ -FAPbI₃ phase near $q \approx 8.5 \text{ nm}^{-1}$ (Fig. 3C) (2I). Although the thin film eventually transformed into α -FAPbI₃, we could not rule out the possibility of a large amount of δ -FAPbI₃ remaining (Fig. 3C, 240 s, and fig. S19). However, for the FAPbI₃@MAFA perovskite thin films, stable α -FAPbI₃ perovskite thin films formed after the deposition of FAI without annealing (Fig. 3D and fig. S20). A small amount of the intermediates and PbI₂ transformed into α -FAPbI₃ perovskite structures during the annealing process, which is consistent with the XRD analysis.

Moreover, one-dimensional (1D) integration diagrams of 2D GIWAXS images (Fig. 3, E to J) indicated competition between the formation of δ -FAPbI₃ and α -FAPbI₃ phases in the case of the PbI₂@DMF:DMSO thin films (13). The peak position of δ -FAPbI₃ markedly shifted to a high q value upon annealing (Fig. 3F), which we attribute to the structural transformation. This process resulted in the fluctuation of the α -FAPbI₃ peak position over a small range near $q \approx 10 \text{ nm}^{-1}$. The integrated intensity of

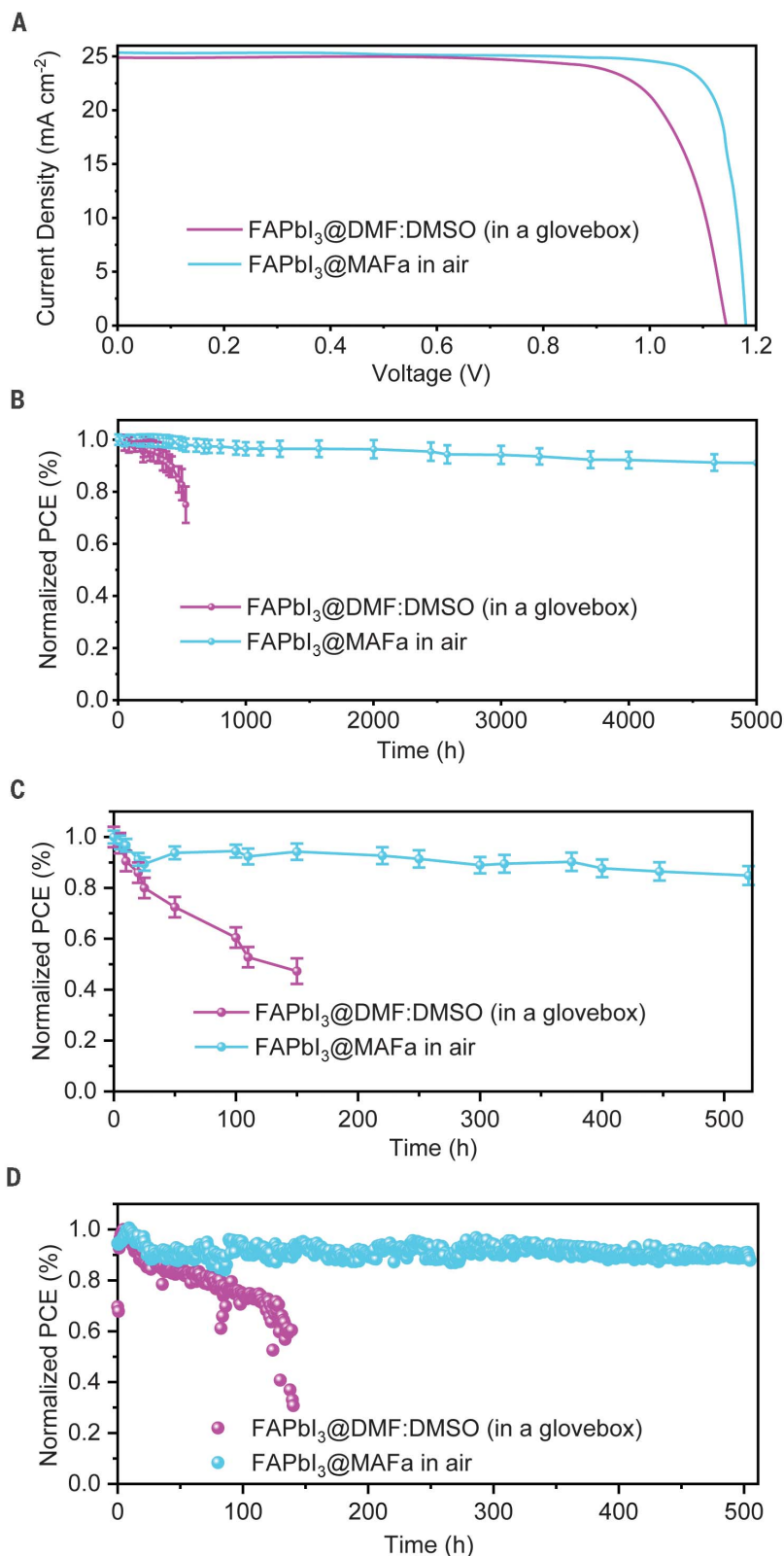


Fig. 4. Photovoltaic device performance. (A) *J*-*V* curves of champion device based on FAPbI₃@MAFA and FAPbI₃@DMF:DMSO films. (B) Stability of unencapsulated devices stored in a N₂-filled glove box in the dark. Error bars indicate the error or uncertainty in the reported measurements. (C) Comparison of the thermal stability of two unencapsulated devices under continuous heating at 85°C in a N₂-filled glove box. Error bars indicate the error or uncertainty in the reported measurements. (D) Operational stability of two unencapsulated devices at maximum power point (0.92 and 0.72 V for FAPbI₃@MAFA and FAPbI₃@DMF devices, respectively) under a white light-emitting diode lamp in a N₂-filled glove box.

δ -FAPbI₃ was markedly higher than that of α -FAPbI₃ in the early stage of crystallization (Fig. 3G); however, δ -FAPbI₃ phases remained inside the final FAPbI₃@DMF:DMSO perovskite thin films (27). By contrast, the FAPbI₃@MAFa perovskite thin films maintained a stable α -FAPbI₃ phase from the initial stage of crystallization (Fig. 3H), and the peak position remained stable (Fig. 3I). This result indicates that the FAPbI₃@MAFa perovskite thin films had excellent crystallinity and a stable structure, as reflected by the increasing trend of the integrated peak intensity (Fig. 3J) (8).

Generally, the I–Pb–I ionic bonds are strong in the layered structure of PbI₂, whereas the van der Waals between adjacent sandwiched layers is weak. This allows a successfully insertion of different guest molecules, bringing about the expansion of interlayer distance along the *c* axis (13, 30). Because of the large size of FA ions, it is difficult to insert them into the layered structure of PbI₂. However, FAI has a high affinity for PbI₂ (31), and it is easy to interact with PbI₂ at the edge of the crystal to form a δ -phase perovskite with a low formation energy barrier (32). The randomly arranged PbI₂ structure formed by the DMF:DMSO solvent could further affect the FAI diffusion process, thus resulting in the easy formation of δ -FAPbI₃ perovskite. In the PbI₂@MAFa thin films, ion channels are constructed that notably improve the diffusion path of FAI in the PbI₂ thin films, providing direct reaction channels for ions and greatly reducing the energy required to transform PbI₂ into α -FAPbI₃ perovskite. In addition, because of the strong chemical effect of MAFa, the structure of PbI₂ changes from the original Pb–I–Pb line structure to a corner-sharing layered structure, which consists of the initial preparation of FAPbI₃ and MAPbI₃ by HPbI₃ (33). This corner-sharing structure prevents the transformation of PbI₂ into δ -FAPbI₃ perovskite but facilitates the transformation of PbI₂ into α -FAPbI₃ perovskite.

Moreover, because of the different growth directions of the PbI₂@DMF:DMSO thin films, the diffraction peak positions of the generated α -FAPbI₃ were located near $q = 9.95 \text{ nm}^{-1}$, compared with the α -FAPbI₃ prepared from PbI₂@MAFa thin films, which were fixed at $q = 9.80 \text{ nm}^{-1}$ (fig. S21). The large FA⁺ anion did not fit well with such a smaller interplanar spacing. This mismatch was not conducive to structural stability of the thin films and contributed to their sensitivity to humidity (figs. S22 and S23) (32, 34, 35). Because the PbI₂@MAFa thin films have excellent vertically oriented crystallization, the FA⁺ quickly enters the interior of the crystal in the second step and immediately reacts with PbI₂ to form a stable α -FAPbI₃ structure. Moreover, the interaction between the perovskite framework and MAFa can probably reduce the elastic

modulus of the perovskite film, which alleviates the lattice strain inside the film and relieves the tensile stress on the surface (fig. S24). These could help to improve the stability of the FAPbI₃ perovskite film under high humidity (movie S1).

We prepared PSCs with a planar structure of indium tin oxide/SnO₂ (20 nm)/perovskite (~950 nm)/spiro-OMeTAD (80 nm)/MoO₃ (5 nm)/Au (100 nm). A device based on FAPbI₃@MAFa perovskite thin films with a champion PCE of 24.1% was achieved, with an open-circuit voltage (V_{oc}) of 1.17 V, a short-circuit current (J_{sc}) of 25.34 mA cm⁻², and a fill factor (FF) up to 81.36% at an RH of 80%, and the PCE was much higher than that for a PSC based on FAPbI₃@DMF:DMSO perovskite thin films under a N₂-filled glove box (22.12%) (Table 1). The steady-state output efficiency had a PCE close to 23.7%, and the steady-state output photocurrent density was 25.23 mA cm⁻² (fig. S25), which is near that obtained from the *J*-*V* curve measurements (Fig. 4A).

We compared the performance of PSCs prepared under an RH of 30, 50, 70, and 90%. Devices based on FAPbI₃@DMF:DMSO perovskite thin films had an efficiency >20% at an RH of 30%, which decreased to 18% at an RH of 50%, and no photovoltaic performance was observed at an RH > 70% (fig. S26 and table S2). However, a PCE of ~23% with negligible hysteresis was achieved by the FAPbI₃@MAFa thin films regardless of RH (figs. S26 to S28 and table S2). Moreover, a high PCE of 20.76% for a large-area device was achieved (1 cm by 1 cm) (fig. S29).

The trap density of the FAPbI₃@MAFa perovskite thin films ($4.74 \times 10^{15} \text{ cm}^{-3}$) was lower than that of FAPbI₃@DMF:DMSO perovskite thin films ($1.36 \times 10^{16} \text{ cm}^{-3}$) (fig. S30), which is also conducive to lower carrier recombination. This result was confirmed by the dependence of the V_{oc} on the light intensity (fig. S31) and the dependence of J_{sc} on the light intensity (fig. S32). Trap-assisted recombination and bimolecular recombination were negligible in the FAPbI₃@MAFa perovskite thin films, which is consistent with its longer carrier lifetime (312.13 ns) than that of the FAPbI₃@DMF:DMSO perovskite thin films (9.82 ns) (fig. S33). Moreover, the FAPbI₃@MAFa thin films had more balanced carrier transport and a prolonged average lifetime owing to their high crystalline quality and low defect state density (figs. S34 and S35 and table S3), which contributed to the improved stability and current density of the devices.

The long-term stability of the PSCs was tested under various conditions without encapsulation. The FAPbI₃@MAFa device retained 93% of its original PCE after storage in the N₂-filled glove box for 5000 hours. This result contrasts with that of the FAPbI₃@DMF:DMSO device, which underwent a 30% PCE loss within only 500 hours (Fig. 4B). More-

over, we conducted the device thermal stability at 85°C in a N₂-filled glove box (Fig. 4C) (36) and found that the average PCE of the FAPbI₃@MAFa device remained at 80% of the initial efficiency for ~500 hours in a N₂-filled glove box, whereas serious PCE decrease was observed in the FAPbI₃@DMF:DMSO device, with 45% left after only ~150 hours. In addition, we performed the stability under operational conditions examined at the maximum power point. As seen in Fig. 4D, the FAPbI₃@DMF:DMSO device degrades rapidly, with 60% decrease of its initial efficiency within 140 hours. By contrast, the FAPbI₃@MAFa device retains 90% of its initial efficiency for 500 hours. We attribute the greater stability of the PbI₂@MAFa thin films to the vertically oriented crystal growth that provides ion channels for the rapid reaction in the second step, which created stable α -FAPbI₃ perovskite thin films. Also, residual MAFa protected the thin films from erosion by water and oxygen and combined with Pb vacancies at grain boundaries to prevent the decomposition of the thin films (fig. S36).

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and H.L. carried out the device fabrication and characterizations. F.X., Q.W., B.L., and Z.S. also contributed to device fabrication. Q.W., G.X., T.N., L.T., W.S., X.R., P.L., and H.Z. conducted the optical spectra measurements. H.L., B.D., and Y.X. synthesized the MAFa. D.L., Y.W., and H.D. carried out the NMR and Fourier transform infrared spectra measurements. S.Z. and J.Z. conducted the x-ray absorption fine structure measurements and analyzed the data. GIWAXS was performed and analyzed by W.Hui, Z.S., C.R., L.S., and X.G., supported by the BL14B beamline of SSRF. W.Hui and L.C. wrote the first draft of the manuscript. Y.C., Y.X., Z.W., and W.Huang participated in data analysis and provided major revisions. All authors discussed the results and commented on the manuscript.

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SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/371/6536/1359/suppl/DC1
Materials and Methods

Figs. S1 to S36

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Movie S1

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Stabilizing black-phase formamidinium perovskite formation at room temperature and high humidity

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Perovskite synthesis out in the open

Although methods have been developed that create the photoactive black perovskite phase of formamidinium lead iodide (#-FAPbI), these routes are temperature and humidity sensitive and less compatible with large-scale solar cell production. Hui *et al.* report an alternative route in which vertically aligned lead iodide thin films are grown from the ionic liquid methylamine formate. Nanoscale channels in the films lower the barrier to permeation of formamidinium iodide and enable transformation to #-FAPbI, even at high humidity and room temperature. Solar cells made with these films have power conversion efficiencies as high as 24.1% that display high stability.

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