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1 **Oriented nucleation in formamidinium perovskite for photovoltaics**

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29

30 **Abstract**

31 Black-phase formamidinium lead iodide perovskite (FAPbI₃), whilst the most
32 promising species for efficient perovskite photovoltaics, is energetically unfavored at
33 room temperature, and is thus always accompanied by undesirable yellow phases
34 during crystallization^{1,2,3,4}. The challenge to formulate the fast crystallization process
35 of perovskite has limited the community in deriving unified guidelines for governing
36 the formation of black-phase FAPbI₃^{5,6}. Here, through in-situ monitoring of the
37 perovskite crystallization process, we report an oriented nucleation mechanism that
38 acted as the key to avoid undesirable phases. This concept was applicable to improving
39 the photovoltaic device performance under different film-processing scenarios. The
40 small-area device demonstrated a power conversion efficiency of 25.4% (certified
41 25.0%), and the module (27.83 cm²) achieved a champion aperture efficiency of 21.4%
42 (certified).

43

44 **Main**

45 Formamidinium lead iodide perovskite (FAPbI₃) features desirable bandgap and
46 thermal resistance, and has thus emerged as the most promising candidate among the
47 perovskite family for highly efficient photovoltaic devices^{1,2,3,7,8}. However, the
48 photoactive black-phase FAPbI₃ is not energetically favorable at room temperature^{4,9,10}.
49 Polytype formation and other intermediate non-photoactive phases can readily occur,
50 which undermines the photovoltaic performance. A few approaches have been
51 developed to promote the formation of black-phase FAPbI₃ at room temperature, such
52 as adduct formation with PbI₂ and solvent engineering using ionic liquids^{11,12}.
53 Unfortunately, the fast crystallization kinetics of FAPbI₃ perovskites precludes in-depth
54 investigations on its film formation processes^{5,6}. The microscale phase evolution
55 mechanism of its crystallization has yet to be unambiguously defined^{13,14}. This has
56 hampered more rational and targeted design of film processing methods for efficient
57 FAPbI₃ perovskite absorbers, particularly when it comes to different scenarios, e.g. one-
58 step and two-step film deposition protocols, small- and large-area devices¹⁵⁻¹⁸. A
59 strategy to promote the formation of black-phase FAPbI₃ in one processing scenario
60 usually fails when applied to other situations. Here, we observed an oriented nucleation
61 mechanism that originated from reduced surface energy of a specific crystallographic
62 plane, and thus sidestepped yellow-phase FAPbI₃ and governed the formation of black-
63 phase FAPbI₃. This mechanism was verified in different film deposition methods and
64 was applicable to improve the performance of both small-area devices and solar
65 modules.

66 In a two-step deposition protocol of perovskite films, where the PbI₂ and organo-halide
67 precursors were sequentially deposited, intermediate non-photoactive phases were
68 always observed at room temperature. The x-ray diffraction (XRD) patterns of the as-
69 deposited perovskite film at room temperature showed diffraction peaks corresponding
70 to (100) planes of the black phase, accompanied with the diffraction peaks of 2H and
71 6H phases (**Fig. 1a**). Upon incorporating PAd in the precursor of organic cations, the

72 intermediate phases were eliminated. Density-functional theory (DFT) calculations and
73 Fourier transform infrared (FTIR) spectroscopy were used to investigate the interaction
74 of PAd with the Pb-I framework. As modelled in **Fig. 1b**, the positively charged
75 amidinium head of PAd was able to anchor into the octahedral cavity of the black-phase
76 perovskite via electrostatic and H-bonding interactions. Peak shifts of the C=N and N-
77 H vibration are observed in the FTIR spectra of PAd after mixing with PbI₂, confirming
78 the strong interaction between PAd and the Pb-I framework through the amidinium unit
79 (**Extended Data Fig. 1**). This interaction exposed the hydrophobic alkyl chain of PAd
80 such that it was stacked in an ordered manner on the black-phase perovskite (100) plane.
81 As a result, compared to other planes, the surface energy of the perovskite (100) plane
82 was the most significantly reduced (dropped by 64%, from 3.16 to 1.14 eV) when the
83 plane was terminated by PAd (see calculation details and the variations in surface
84 energies of different crystallographic planes in **Supplementary Note 1**). This
85 interaction configuration was corroborated by the formation of a two-dimensional
86 perovskite phase characterised by XRD of the perovskite film fabricated with PAd
87 (**Supplementary Fig. 1**). The reduced dimension of perovskite phase evidenced the
88 dominantly low surface energy of the (100) plane. Such a thermodynamic driving
89 force led to the preferential formation of the (100) orientation of the black-phase
90 perovskite, which finally determined the crystallization texture and promoted the
91 formation of black-phase perovskite crystals. In contrast, a relatively even energy
92 profile of the phase transformation process for the case without PAd resulted in the co-
93 existence of several phases and orientations (**Fig. 1c**).

94 Synchrotron-based multimodal in-situ probes were employed to scrutinize the
95 crystallization of perovskites from the precursors and verify the orientated nucleation
96 mechanism. The details of the measurements and film processing procedures were
97 provided in **Supplementary Note 2**. In-situ grazing-incidence x-ray diffraction
98 (GIXRD) measurements revealed that the perovskite nucleated (N₀ step) upon dropping
99 the FAI solution onto pre-deposited PbI₂ as evidenced by the emergence of the
100 perovskite (100) diffraction peak (**Fig. 2a**). During the spin-coating process, the peak
101 intensity of the (100) plane gradually increased, which we described as a nucleation
102 stage (N_s step) where the vanishing, formation and growth of the nuclei take place
103 concurrently. The subsequent annealing step led to a rapid rise in the intensity of the
104 (100) peak, indicating a fast crystal growth process (G step). During the nucleation
105 stage, the control perovskite film showed diffraction peaks corresponding to multiple
106 intermediate phases, whereas the film with PAd featured a clean (100) diffraction
107 pattern of black-phase perovskite. This indicated the incorporation of PAd suppressed
108 the formation of yellow phases right from the beginning of the nucleation process.
109 Notably, the control film showed a faster increase in the (100) peak intensity during the
110 nucleation stage as compared to that with PAd, suggesting retarded nucleation kinetics
111 with PAd. The retarded nucleation kinetics may be attributed to the strong interaction
112 of PAd with the Pb-I framework, i.e. FA had to compete with PAd to interact with the
113 Pb-I, slowing down the reaction kinetics. The in-situ azimuth angle mapping was
114 extracted from the GIXRD patterns of the perovskite (100) plane during the nucleation
115 stage (**Fig. 2b**). The azimuth angle showed a broad distribution ranging approximately

116 from 60 to 120°, indicating a relatively random crystallographic orientation of the
117 control sample. However, a sharp peak centered at the azimuth angle of 90° was
118 observed with PAd incorporation, the half-peak width of which remained as small as
119 ~8° with time. This verified a nucleation stage with a preferred out-of-plane orientation
120 along the (100) facet, which we described as an oriented nucleation mechanism.

121 The proposed mechanism was studied further by varying the length of the alkyl chain
122 attached to the organic amidinium cation, thus modulating the impact on the surface
123 energy. Butylamidinium (BAd) and propylamidinium (PRd), which contain shorter
124 alkyl chains than PAd, were investigated. DFT calculations revealed an increase in the
125 surface energy of the perovskite (100) plane as the alkyl chain became shorter
126 (**Extended Data Fig. 2**). The (100) plane terminated with PRd, BAd, and PAd, which
127 featured increasingly elongated organic tail exposed and thus the increased
128 hydrophobicity, showed a calculated surface energy of 1.57, 1.20, and 1.14 eV/nm²,
129 respectively. In-situ GIXRD measurements revealed that both BAd and PRd suppressed
130 the formation of intermediate photo-inactive phases during the nucleation stage
131 (**Extended Data Fig. 3**). However, the in-situ azimuth angle mapping during the
132 nucleation stage demonstrated different levels of oriented nucleation as the surface
133 energy varied (**Extended Data Fig. 4**). Since the application of PAd afforded the lowest
134 surface energy of the perovskite (100) plane, it induced the most oriented nucleation
135 among the three additives. Despite the ability of BAd and PRd to induce more oriented
136 nucleation than the control sample, they resulted in broader azimuth angle distributions
137 than that of PAd. These observations further proved that the oriented nucleation and the
138 promoted formation of black-phase perovskite were governed by the surface energy of
139 perovskite (100) plane.

140 The sluggish nucleation kinetics was further verified by in-situ photoluminescence (PL)
141 measurements. **Fig. 2c** showed the evolution of PL spectra of the perovskite films
142 during the nucleation stage. Without PAd, a PL peak at 770 nm rose rapidly, which we
143 attributed to the photoactive perovskite phase. With PAd in the precursor solution, the
144 PL peak appeared at 760 nm with delayed kinetics. The slight blue-shift in the PL peak
145 could be attributed to the smaller sizes of the nuclei, which could either lead to
146 compressive lattice strain or induce stronger quantum confinement (**Extended Data**
147 **Fig. 5**). This in turn evidenced the slower nucleation kinetics in perovskite films with
148 PAd. Sluggish nucleation kinetics was also observed for BAd and PRd (**Extended Data**
149 **Fig. 6**), but to a lesser extent than PAd, which further confirmed the important role of
150 the surface energy in regulating the crystallization. The strong interaction between the
151 perovskite inorganic framework and the PAd cation lowered the surface energy of the
152 (100) plane, leading to retarded nucleation kinetics with preferred crystallographic
153 orientation. This oriented nucleation mechanism governed the subsequent crystal
154 growth step, which also followed the preferred orientation along the (100) facet
155 (**Supplementary Fig. 2**)¹⁹. The resulting perovskite film exhibited higher crystallinity
156 and conductivity as indicated by the increased intensity of the XRD patterns and
157 conductive atomic force microscopy (c-AFM) measurements, respectively
158 (**Supplementary Figs. 3 and 4**). The film also had larger grain sizes as a result of the

159 retarded nucleation (**Supplementary Fig. 5**). The enhanced PL intensity and prolonged
160 PL lifetime of the PAd-based perovskite film indicated that there were fewer
161 nonradiative recombination sites (**Extended Data Fig. 7**).

162 PAd incorporation in a one-step deposition protocol was also investigated and
163 elimination of the yellow-phase was observed. As revealed by the in situ XRD
164 measurements, a mixture of intermediate phases arose with the black-phase perovskite
165 during the crystallization in the absence of PAd (**Fig. 3a**). In contrast, incorporation of
166 PAd eliminated all the intermediate phases, leading to a single diffraction feature
167 apparent from the (100) plane of black-phase perovskite (**Fig. 3b**). In situ PL
168 measurements on the perovskite films with and without PAd were performed
169 (**Supplementary Note 3**). The evolution profiles of PL peak positions and PL intensity
170 with time are shown in **Fig. 3c** and **Fig. 3d**, respectively. In the control sample, we
171 observed a turning point (red dotted circle) in the evolution profile of the PL peak
172 position, which coincide with PL intensity fluctuations. In general, PL peak position
173 changes may be related with lattice or structural changes. Therefore, this turning point
174 might indicate the emergence of intermediate phases during the crystallization in
175 addition to the target black phase. The perovskite film with PAd, instead, exhibited a
176 smooth PL evolution profile of both the peak position and peak intensity, further
177 verifying the direct conversion into the black phase. The perovskite film with PAd
178 exhibited considerably enhanced PL intensity and PL lifetime (**Fig. 3e** and **Fig. 3f**),
179 indicative of pure black-phase perovskite with reduced nonradiative recombination
180 sites in the film.

181 We subsequently evaluated the photovoltaic performance of the as-fabricated solar cell
182 devices. In the two-step deposition protocol (**Extended Data Fig. 8**), the device with
183 PAd showed a champion PCE of 24.0%, whereas the best control device showed a PCE
184 of only 22.9%, primarily owing to the increased fill factor (FF) and open circuit voltage
185 (V_{oc}) with PAd (**Fig. 4a**). This was attributed to the reduced nonradiative recombination
186 in the device with PAd as further evidenced by a slower transient photovoltage decay
187 (**Supplementary Fig. 6**). The device short circuit currents (J_{sc}) were marginally
188 enhanced, reflective of the marginally faster transient photocurrent decay of the device
189 with PAd (**Supplementary Fig. 7**)^{20,21}. A similar trend in device performance was
190 observed for the one-step method (**Fig. 4b**, **Extended Data Fig. 9**). The device with
191 PAd demonstrated an improved PCE of up to 25.4% (certified 25.0%). The histogram
192 of PCEs for 36 devices is shown in **Fig. 4c** (the detailed parameters are shown in
193 Supplementary Table 1), which confirms good reproducibility of the performance
194 improvement with PAd (5.6% improvement in an average PCE from $23.7 \pm 0.4\%$ to
195 $25.0 \pm 0.4\%$ with the incorporation of the PAd). We further extended the application of
196 PAd to the fabrication of solar modules to verify its compatibility with upscaled devices.
197 A high aperture efficiency of 21.4% (certified) was achieved in the PAd-based
198 perovskite module with an area of 27.83 cm² (**Fig. 4d**). The module showed an average
199 PCE of 20.4%, whereas the control module has an average PCE of only 18.9%, further
200 demonstrating the universality of the approach (**Extended Data Fig. 10**). The as-
201 fabricated devices also demonstrated considerably improved operational stability.

202 When tracked at the maximum power point (MPP) under constant illumination at
203 30 ± 3 °C, the PCE of the control device dropped by 30%, whereas the device fabricated
204 with PAd maintained 95% of its initial PCE after over 1000 h (**Fig. 4e**). In an
205 accelerated aging test at 65 ± 3 °C and $85\pm 5\%$ relative humidity, the device with PAd
206 kept more than 82% of its initial PCE after over 500 h when held at the MPP under
207 constant illumination, whereas the PCE of the control device dropped by around 37%
208 (**Supplementary Fig. 8**). The enhanced stability could be attributed to the higher
209 crystallinity, reduced defect density and the reduced surface energy caused by PAd
210 (**Supplementary Fig. 9**)^{8,22,23}.

211

212 **Methods**

213 **Materials**

214 Solvents and chemicals used in two step method were obtained commercially and used
215 without further purification. N, N-dimethylformamide (DMF) (anhydrous, 99.8%),
216 dimethyl sulfoxide (DMSO) (anhydrous, $\geq 99.9\%$), chlorobenzene (CB) (anhydrous,
217 99.8%), isopropanol (IPA) (anhydrous, 99.5%), 2-methoxyethanol (2-MeO, anhydrous,
218 99.8%), water (ACS reagent), t-BP (99%), Li-TFSI (99.95% trace metals basis), PbI₂
219 (99.999%, perovskite grade), Cesium Iodide (CsI, 99.999%), silver (Ag) and gold (Au)
220 were obtained from Sigma-Aldrich Inc. MACl (99%) and FAI was obtained from Great
221 Cell. FK209 and Spiro-OMeTAD (99.8%) were obtained from Xi'an Polymer Light
222 Technology Corp. Pentylamidinium hydrochloride, butylamidinium hydrochloride and
223 propionamidinium hydrochloride were obtained from Bldpharm. Tin Oxide (SnO₂)
224 nanoparticle (15 wt% in water) was obtained from Alfa-Aesar Inc. The materials used
225 in the experiments of one step method included: lead(II) iodide (PbI₂; 99.99%, TCI),
226 tin(II) chloride dihydrate (SnCl₂·2H₂O; 98%, Acros), tin(IV) chloride (TiCl₄; 99%,
227 Sigma-Aldrich), hydrochloric acid (HCl; 37 wt% in H₂O, Sigma-Aldrich),
228 methylammonium chloride (MACl, 99.99%, Greatcell solar), formamidinium iodide
229 (FAI; 99.99%, Greatcell solar) N,N-dimethylformamide (DMF; 99.8%, Sigma-
230 Aldrich), dimethyl sulfoxide (DMSO; 99.9%, Sigma-Aldrich), 2-propanol (99.5%,
231 Sigma-Aldrich), chlorobenzene (99.8%, Sigma-Aldrich), Spiro-OMeTAD (Boron
232 Tech.), 4-tert-butylpyridine (tBP; Sigma-Aldrich), bis(trifluoromethane)sulfonimide
233 lithium salt (Li-TFSI; 99.95%, Sigma-Aldrich), FK209 Co(III) TFSI salt (Sigma-
234 Aldrich, acetonitrile (ACN; 99.8%, Sigma-Aldrich).

235 **Device Fabrication**

236 **(1) Fabrication of perovskite solar cells by two-step method.** For the perovskite layer
237 made by two-step method, perovskite solar cells were fabricated with the following
238 structure: indium tin oxide (ITO)/SnO₂/FA_{0.95}Cs_{0.05}PbI₃/Spiro-OMeTAD/Ag or Au.
239 The ITO glass was pre-cleaned in an ultrasonic bath of acetone and isopropanol and
240 treated in ultraviolet-ozone for 20 min before use. A thin layer (ca. 30 nm) of SnO₂ was
241 spin-coated onto the ITO glass and baked at 165 °C for 35 min. SnO₂ solution was
242 diluted in water ($V_{\text{SnO}_2}:V_{\text{H}_2\text{O}}=1:4$) before spin-coating. After cooled down to room

243 temperature, the glass/ITO/SnO₂ substrates were transferred into a nitrogen glove box.
244 The PbI₂ solution was prepared by dissolving 1.4 M PbI₂ and 0.07 M CsI into 1 mL
245 DMF/DMSO (v/v 94/6). The FAI solution for the control film was prepared by
246 dissolving 80 mg FAI and 13 mg MAI in 1 mL IPA. For the preparation of precursors
247 with PAd, BAd or PRd, 2.05 mg PAd, 1.84 mg BAd or 1.63 mg PRd were added to the
248 FAI solution in IPA. The solutions should be stirred overnight before use. To fabricate
249 the perovskite layer, the PbI₂ solution was spin-coated on the substrate at 1500 rpm for
250 40 s, and then, the FAI/PAd, FAI/BAd or FAI/PRd solution was spin-coated on the PbI₂
251 film at 1800 rpm for 40 s, followed by pre-annealing inside the glove box at 90 °C for
252 1 min and annealing outside the glove box at 150 °C for 10 min with 30%-40%
253 humidity (the first-step and the second-step precursor was denoted as PbI₂ solution and
254 FAI solution respectively for simplification, and the exact composition followed the
255 descriptions above). The Spiro-OMeTAD solution [60mg Spiro-OMeTAD in 700 μL
256 CB with 25.5 μL t-BP, 15.5 μL Li-TFSI (520 mg/mL in ACN) and 12.5 μL FK209
257 (375 mg/mL in ACN)], was spun onto the perovskite film as a hole conductor. The
258 devices were completed by evaporating 100 nm gold or silver in a vacuum chamber
259 (base pressure, 5×10^{-4} Pa) and the aperture area of the device is 0.1 cm², designated
260 by the shadow mask.

261 **(2) Fabrication of perovskite solar cells by one-step method.** The device with an
262 architecture of FTO glass/compact TiO₂ layer (c-TiO₂) /compact SnO₂ layer, (c-
263 SnO₂)/Cs_{0.05}MA_{0.05}FA_{0.9}PbI₃ (PVK)/spiro-OMeTAD (HTM)/Au structure was
264 fabricated. The patterned FTO substrate (Asahi FTO glass, 12-13 Ω cm⁻²) was
265 sequentially cleaned with detergent (5% Hellmanex in water), deionized water, acetone,
266 and isopropanol in the ultrasonic bath for 30 min, respectively. The FTO substrate was
267 then further cleaned with Ultraviolet-Ozone surface treatment for 15 min. The compact
268 TiO₂ layer (c-TiO₂) and SnO₂ layer were sequentially deposited on the clean FTO
269 substrate by chemical bath deposition (CBD) method. The substrate was annealed on a
270 hotplate at 190 °C for 60 min. The perovskite precursor solution (1.4 M) was prepared
271 by adding 645.4 mg of PbI₂, 216.7 mg of formamidium iodide (FAI), 11.1 mg of
272 methylammonium iodide (MAI), and 11.8 mg of CsCl into 200 μL of N, N'-
273 dimethylsulfoxide (DMSO) and 800 μL of dimethylformamide (DMF) mixture. The
274 solution was then stirred for 2 h at 60 °C. 2.09 mg of PAd was dissolved into 1.0 mL
275 of DMSO to make a stock solution (concentration around 0.52 M). After UV-ozone
276 treatment of the substrates for 15 min, the perovskite precursor solution was spin-coated
277 onto the surface of the FTO/c-TiO₂/c-SnO₂ substrate at 1000 rpm for 10 s, accelerated
278 to 5000 rpm for 5s and maintained at this speed for 20 s. This process was carried out
279 in an N₂ filled glove box. Then, the substrate was placed in a home-made rapid vacuum
280 drying equipment. After pumping for 20 s, a brown, transparent perovskite film with a
281 mirror-like surface was obtained. The fresh perovskite layer was annealed at 100 °C for
282 1 h and then at 150 °C for 10 min. Afterwards, 60 μL of PEAI solution (5 mg/mL in
283 isopropanol) was spin-coated on the perovskite film at 5000 rpm for 30 s. A hole
284 transport layer was deposited on the perovskite film by depositing a doped spiro-
285 OMeTAD solution at 3000 rpm for 30 s. The doped spiro-OMeTAD solution was
286 prepared by dissolving 105 mg of spiro-OMeTAD and 41 μL of 4-tert-butylpyridine in

287 1343 μL of chlorobenzene with additional 25 μL of bis(trifluoromethane)sulfonimide
288 lithium salt solution (517 mg/mL in acetonitrile) and 19 μL of cobalt-complex solution
289 (376 mg/mL in acetonitrile). Finally, a ~ 70 nm-thick gold layer was evaporated on the
290 spiro-OMeTAD layer as the back electrode and the aperture area of the certified device
291 is 0.06 cm^2 .

292 **(3) Fabrication of perovskite modules.** Perovskite solar modules, with 8 sub-cells
293 connected in series, were fabricated on FTO glass substrates with a size of $6.5 \times 7.0\text{ cm}^2$.
294 The series interconnection of the module was realized by P1, P2, and P3 lines, which
295 were patterned using a laser scribing system with a 1064 nm and a power of 20 W
296 (Trotec). The FTO substrate was pre-patterned for P1 (a width of 50 μm) by means of
297 60% laser power under a speed of 300 mm/s with a frequency of 65 kHz and pulse
298 width of 120 ns. The subsequent processes for the preparation of c-TiO₂/c-SnO₂
299 substrates are the same with the small-area device procedures. Besides, the perovskite
300 precursor deposition and fabrication procedures were also similar to that of the small-
301 size solar cells except for the concentration of perovskite precursor. 1.2 M of perovskite
302 precursor was employed to do the perovskite layer by using spin-coated method and
303 custom-made gas-induced pump method. The perovskite precursor was spin-coated on
304 the c-TiO₂/c-SnO₂ substrates, which are similar with those of the small-size devices.
305 The perovskite films were annealed at 100 °C for 1 h and 150 °C for 10 min. After
306 cooling down to room temperature, the Spiro-OMeTAD layer are similar with those of
307 the small-size devices. The P2 lines (a width of 150 μm) were patterned before the Au
308 evaporation process step with an average laser power of 15% under a speed of 1000
309 mm/s and frequency of 65kHz for pulse duration of 120 ns. When a 70 nm-thick Au
310 layer was deposited, the P3 line (a width of 100 μm) was fabricated under the same
311 scribing condition as the P2 line. The distance between P1 and P3 was around 400 μm ,
312 and the geometric fill factor (GFF) was around 0.93.

313 For perovskite solar modules prepared by the blade-coating method (Coatmaster 510),
314 perovskite solar modules with 9 sub-cells connected in series were fabricated on FTO
315 glass substrates with a size of $6.5 \times 7.0\text{ cm}^2$. The processes for the preparation of c-
316 TiO₂/c-SnO₂ substrates and the fabrication of spiro-OMeTAD as well as gold electrode
317 are the same with the gas-pump method. The perovskite precursor solution (1.2 M) was
318 prepared by dissolving 580.9 mg of PbI₂, 185.7 mg of FAI, 9.5 mg of MAI, and 10.8
319 mg of CsCl into 1.0 mL 2-methoxyethanol. The precursor solution was blade-coated
320 onto the c-TiO₂/c-SnO₂ substrates with a gap of 260 μm at a movement speed of 21
321 mm/s in the N₂ glovebox. The N₂ knife was operated at 30 psi during blade-coating,
322 and the as-obtained were annealed at 100 °C for 1 h and 150 °C for 10 min. The laser
323 scribing procedures are also the same with gas-pump method, but the GFF was 0.91.

324 **Stability Test**

325 The devices for stability test were fabricated using the method as mentioned above. The
326 devices were encapsulated by a glass-glass encapsulation technology combined with an
327 edge seal (UV Curing Sealant, Three bond 3035B) to seal the device under UV light
328 illumination (LED flood lamp, DELOLUX 20). First, the edge of the device was cleared

329 by laser. An indium solder was soldered on the FTO and Au electrodes on the edge of
330 the 15×25 mm² substrate. Then, a glass with a size of 13×23 mm² was put on the top of
331 the Au layer of the device. A light-curing sealant was deposited on the edges of the
332 glass to fully cover the gap between the top glass and device. Finally, a UV light was
333 employed to induce the cross-linking in sealant with a glass under a 25% maximum
334 power for 120 s in the glove box. For the stability test at ambient condition (30±3°C),
335 unencapsulated devices were evaluated. For the accelerated degradation test, the
336 encapsulated devices were kept in a thermo-hygrostat (GP/TH-150, SH Guangpin test
337 equipment manufacturing Co., Ltd) which was set under 85±5% relative humidity at
338 65±3°C. The devices were measured by an electronic system using a 22-bit delta-sigma
339 analog-to-digital converter. A reference Si photodiode was placed in the neighbor of
340 devices to record the light intensity. The long-term stability tests were measured at the
341 maximum power point (MPP) condition using a MPP tracking algorithm under 1 Sun
342 illumination according to ISOS-L-3 protocol.

343 **Device Characterization**

344 *J–V* characteristics of photovoltaic cells were taken using a Keithley 2400 source
345 measure unit under a simulated AM 1.5G spectrum, with an Oriel 9600 solar simulator.
346 Typically, the small-size devices were measured in reverse scan (1.20 → 0 V, step 0.01
347 V for one-step devices, and 1.25 → 0 V, step 0.02 V for two-step devices). The modules
348 were measured in reverse scan (from 9.45 to 0 V) under a constant scan speed of 100
349 mV/s with a step of 50 mV. For the measurement of high-efficiency devices, an
350 antireflection film was applied on the surface of devices. All the devices were measured
351 without pre-conditioning such as light-soaking and applied a bias voltage. Steady-state
352 power conversion efficiency was calculated by measuring stabilized photocurrent
353 density under a constant bias voltage. External quantum efficiencies (EQEs) were
354 measured using an integrated system (Enlitech) and a lock-in amplifier with a current
355 preamplifier under short-circuits' condition.

356 **Materials Characterization and Spectroscopic Investigation**

357 UV-vis absorption spectra of the perovskite films were obtained using a Shimadzu UV-
358 VIS-NIR (UV3600Plus+UV2700) equipped with integrating sphere, in which
359 monochromatic light was incident to the substrate side. For TRPL measurement, the
360 sample was excited with a picosecond pulsed diode laser (Pico-quant LDH 450), with
361 a ~ 70 ps pulse width and 20 or 10 MHz repetition rate, focused on sample with a 100x
362 objective (NA=0.90). The PL signal was acquired through the TCSPC strobelock
363 system. The total instrument response function (IRF) for the PL decay was less than
364 200 ps, and the temporal resolution was less than 30 ps. XRD experiments performed
365 on sealed-tube Cu X-ray source, equipped with 1D LynxEye detector. The in-situ
366 experiment was performed on High-brilliance rotational point-focused Cu X-ray
367 source, equipped with DUO detectors of Scintillation counter and LynxEye. The in-situ
368 chamber of TC DOME creates robust heating environment and the measurement was
369 initiated with a temperature increasing from room temperature to 450 K in the air, and

370 followed by XRD data collection. TPV and TPC were conducted by Photo-
371 Electrochemical measurement system. Conductive atomic force microscope was
372 measured by Environmental Atomic Force Microscopy. X-ray photoelectron
373 spectroscopy (XPS) measurements were carried out on a XPS (ThermoFisher
374 ESCALAB Xi+). Al K α radiation (1486.6 eV) was used as the excitation source.
375 Transmission Fourier transform infrared (FTIR) spectroscopy was obtained using
376 FT/IR-6100 (Jasco). PAd was mixed with PbI₂ using a molar ratio of 1:1 for the FTIR
377 measurements. UPS measurements were carried out to determine the work function and
378 the position of valence band maximum of materials. A He discharge lamp, emitting
379 ultraviolet energy at 21.2 eV, was used for excitation. All UPS measurements were
380 performed using standard procedures with a -10 V bias applied between the samples
381 and detectors. Clean gold was used as a reference.

382

383 **Data availability**

384 The data that support the findings of this study are available from the corresponding
385 authors upon reasonable request.

386

387 **References and Notes:**

- 388 1. T. A. S. Doherty et al. Stabilized tilted-octahedra halide perovskites inhibit local
389 formation of performance-limiting phases. *Science*. **374**, 1598–1605 (2021).
- 390 2. J.-W. Lee, D.-J. Seol, A. N. Cho and N.-G. Park. High-Efficiency Perovskite
391 Solar Cells Based on the Black Polymorph of HC(NH₂)₂PbI₃. *Adv. Mater.* **26**,
392 4991–4998 (2014).
- 393 3. S. H. Turren-Cruz, A. Hagfeldt and M. Saliba. Methylammonium-free, high-
394 performance, and stable perovskite solar cells on a planar architecture. *Science*.
395 **362**, 449–453 (2018).
- 396 4. J. Xue et al. Surface Ligand Management for Stable FAPbI₃ Perovskite
397 Quantum Dot Solar Cells. *Joule*. **2**, 1866–1878 (2018).
- 398 5. M. Yang et al. Facile fabrication of large-grain CH₃NH₃PbI_{3-x}Br_x films for high-
399 efficiency solar cells via CH₃NH₃Br-selective Ostwald ripening. *Nat. Commun.*
400 **7**, 1–9 (2016).
- 401 6. S. Sánchez, L. Pfeifer, N. Vlachopoulos and A. Hagfeldt. Rapid hybrid
402 perovskite film crystallization from solution. *Chem. Soc. Rev.* **50**, 7108–7131
403 (2021).
- 404 7. G. E. Eperon et al. Formamidinium lead trihalide: a broadly tunable perovskite
405 for efficient planar heterojunction solar cells. *Energy Environ. Sci.* **7**, 982–988
406 (2014).

- 407 8. Q. Jiang et al. Surface passivation of perovskite film for efficient solar cells. *Nat.*
408 *Photonics*. **13**, 460–466 (2019).
- 409 9. Z. Qiu, N. Li and Z. Huang, Q. Chen. and H.P. Zhou et al. Recent Advances in
410 Improving Phase Stability of Perovskite Solar Cells. *Small Methods*. **4**, 1900877
411 (2020).
- 412 10. Y. Zhang et al. Propylammonium Chloride Additive for Efficient and Stable
413 FAPbI₃ Perovskite Solar Cells. *Adv. Energy Mater.* **11**, 2102538 (2021).
- 414 11. T. Bu et al. Lead halide-templated crystallization of methylamine-free perovskite
415 for efficient photovoltaic modules. *Science*. **372**, 1327–1332 (2021).
- 416 12. W. Hui et al. Stabilizing black-phase formamidinium perovskite formation at
417 room temperature and high humidity. *Science*. **371**, 1359–1364 (2021).
- 418 13. Z. A. Nan et al. Revealing phase evolution mechanism for stabilizing
419 formamidinium-based lead halide perovskites by a key intermediate phase.
420 *Chem*. **7**, 2513–2526 (2021).
- 421 14. M. Qin, P. F. Chan and X. Lu. A Systematic Review of Metal Halide Perovskite
422 Crystallization and Film Formation Mechanism Unveiled by In Situ GIWAXS.
423 *Adv. Mater.*, 2105290 (2021).
- 424 15. Z. Li et al. Scalable fabrication of perovskite solar cells. *Nat. Rev. Mater.* **3**
425 (2018), pp. 1–20.
- 426 16. Y. M. Xie, Q. Xue and H. L. Yip. Metal-Halide Perovskite Crystallization
427 Kinetics: A Review of Experimental and Theoretical Studies. *Adv. Energy*
428 *Mater.* **11**, 2100784 (2021).
- 429 17. J. W. Lee, D. K. Lee, D. N. Jeong and N.-G. Park et al. Control of Crystal Growth
430 toward Scalable Fabrication of Perovskite Solar Cells. *Adv. Funct. Mater.* **29**,
431 1807047 (2019).
- 432 18. A. Dubey et al. A strategic review on processing routes towards highly efficient
433 perovskite solar cells. *J. Mater. Chem. A*. **6**, 2406–2431 (2018).
- 434 19. O. Engler, H. E. Vatne and E. Nes. The roles of oriented nucleation and oriented
435 growth on recrystallization textures in commercial purity aluminium. *Mater. Sci.*
436 *Eng. A*. **205**, 187–198 (1996).
- 437 20. H. Tan et al. Efficient and stable solution-processed planar perovskite solar cells
438 via contact passivation. *Science*. **355**, 722–726 (2017).
- 439 21. R. Lin et al. Monolithic all-perovskite tandem solar cells with 24.8% efficiency
440 exploiting comproportionation to suppress Sn(ii) oxidation in precursor ink. *Nat.*
441 *Energy*. **4**, 864–873 (2019).
- 442 22. J. W. Lee et al. Solid-phase hetero epitaxial growth of α -phase formamidinium
443 perovskite. *Nat. Commun.* **11**, 1–11 (2020).

444 23. F. Wang et al. Phenylalkylamine Passivation of Organolead Halide Perovskites
445 Enabling High-Efficiency and Air-Stable Photovoltaic Cells. *Adv. Mater.* **28**,
446 9986–9992 (2016).

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470 fabrication of perovskite films and devices, and did the data analysis under the
471 supervision of J.X. and R.W.. Y.D. and B.D. did the one-step fabrication of the small-
472 area perovskite devices and fabricated the modules under the supervision of M.N.. Q.Y.
473 and S.T. did the in situ characterizations under the supervision of Y.Y. and C.M.S.-F..
474 C.M.S.-F., J.L.S., and T.K. designed the in situ PL, in situ multimodal diffraction
475 monitoring system at the ALS, and facilitated the in situ measurements. I.Y. and C.Y.
476 carried out the theoretical calculations. W.F., J.Z, Y.T., D.G., X.Z. K.Z. and L.Y.
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481

482 **Fig. 1 | Direct conversion to black-phase FAPbI₃ at room temperature and the**
483 **driving force. a**, X-ray diffraction (XRD) patterns of perovskite films after spin-
484 coating the precursors at the room temperature. **b**, Theoretical models of perovskite

485 (100) plane with and without PAd. **c**, Schematic illustration of the thermodynamic
486 driving force and the kinetics of the oriented nucleation of perovskite films.

487

488 **Fig. 2 | In situ multimodal monitoring of the crystallization process of perovskite**
489 **films fabricated using the two-step method.** **a**, In-situ grazing-incidence x-ray
490 diffraction (GIXRD) measurements of perovskite films fabricated with and without
491 PAd, where N_0 denotes the start of the nucleation, N_s denotes the nucleation stage, and
492 G denotes the growth stage. **b**, The evolution of the azimuth angle during the nucleation
493 stage of perovskite films with and without PAd. **c**, The evolution of the
494 photoluminescence spectra during the nucleation stage of perovskite films with and
495 without PAd.

496

497 **Fig. 3 | Crystallization process and optical properties of perovskite films fabricated**
498 **using the one-step method.** In-situ x-ray diffraction (XRD) measurements of
499 perovskite films fabricated **a**, with and **b**, without PAd, showing a mixture of
500 intermediate phases in the control sample, but not in the sample with PAd during the
501 annealing process. **c**, Evolution of the photoluminescence (PL) peak position and **d**,
502 evolution of the PL intensity of the perovskite films during the annealing process with
503 and without PAd. Comparison of **e**, the steady-state PL spectra and **f**, the time-resolved
504 PL of the perovskite films with and without PAd, demonstrating an increased PL
505 lifetime from 0.19 to 4 μ s in the film with PAd.

506

507 **Fig. 4 | Photovoltaic device performance.** Current density-voltage (J - V) curves of the
508 perovskite photovoltaic devices fabricated using **a**, two-step and **b**, one-step deposition
509 methods with and without PAd. **c**, PCE distribution of perovskite solar cells with and
510 without PAd. **d**, Certified device performance of the perovskite modules of an aperture
511 area of 27.83 cm^2 fabricated with PAd. The insert shows a photograph of the module.
512 **e**, Maximum power point (MPP) tracking of the perovskite devices fabricated with and
513 without PAd under ambient conditions (30 ± 3 $^\circ\text{C}$).

514

515 **Extended Data Fig. 1 | FTIR measurements for investigating the interaction**
516 **between PAd and Pb-I framework.** FTIR spectra of PAd, PbI_2 and PAd mixed with
517 PbI_2 .

518

519 **Extended Data Fig. 2 | DFT slabs of FA-based perovskite lattice with different**
520 **surface termination.** The slab of **a**, bare FA-based perovskite and the ones terminated
521 with **b**, PRd, **c**, BAd, **d**, PAd, and the surface energies of the (100) planes.

522

523 **Extended Data Fig. 3 | In-situ GIXRD patterns of perovskite films.** In-situ GIXRD
524 patterns of **a**, the control perovskite film and the ones fabricated with **b**, PRd, **c**, BAd,
525 **d**, PAd.

526

527 **Extended Data Fig. 4 | Evolutions of the azimuth angles during the nucleation stage**
528 **of perovskite films.** Evolution of the azimuth angle during the nucleation of **a**, the
529 control perovskite film and the films fabricated with **b**, PRd, **c**, BAd and **d**, PAd.
530

531 **Extended Data Fig. 5 | In-situ GIXRD monitoring of the initial nucleation stage of**
532 **perovskite films.** In-situ GIXRD monitoring of the initial nucleation stage of
533 perovskite films fabricated **a**, with and **b**, without PAd. The control perovskite nuclei
534 contained a diffraction peak at around 14° , whereas the one with PAd showed a
535 diffraction peak at around 14.4° , indicating compressive strain within the lattice of the
536 perovskite nuclei.

537 **Extended Data Fig. 6 | Evolution of the PL spectra during the perovskite**
538 **nucleation stage.** Evolution of the PL spectra during the nucleation stage of **a**, the
539 control perovskite film and the ones with **b**, PRd, **c**, BAd and **d**, PAd.
540

541 **Extended Data Fig. 7 | Optical properties of perovskite films a**, TRPL plots of the
542 perovskite film with PAd and the control. The PL lifetime was fitted to be $4.89 \mu\text{s}$ and
543 $0.5 \mu\text{s}$ for the perovskite film with PAd and the control, respectively. **b**, PL spectra of
544 the perovskite film with PAd and the control. The above-mentioned perovskite films
545 were deposited by two-step method on glass substrates for measurements.
546

547 **Extended Data Fig. 8 | Photovoltaic parameters of perovskite devices made by two-**
548 **step method.** Box plots showing the distribution of the **a**, PCE, **b**, FF, **c**, V_{oc} , and **d**, J_{sc}
549 for the control and the PAd devices made by two-step method. Centre line, median; box
550 limits, 25th and 75th percentiles; curve, normal distribution curve; whiskers, outliers.
551

552 **Extended Data Fig. 9 | Photovoltaic parameters of perovskite devices made by one-**
553 **step method.** Box plots showing the distribution of the **a**, FF, **b**, V_{oc} , and **c**, J_{sc} for the
554 control and PAd devices made by one-step method. Centre line, median; box limits,
555 25th and 75th percentiles; curve, normal distribution curve; whiskers, outliers.
556

557 **Extended Data Fig. 10 | Photovoltaic parameters of perovskite modules.** Box plots
558 showing the distribution of the **a**, PCE, **b**, FF, **c**, V_{oc} , **d**, I_{sc} for the control and the PAd-
559 based perovskite modules with an aperture area of 30.86 cm^2 . Centre line, median; box
560 limits, 25th and 75th percentiles; curve, normal distribution curve; whiskers, outliers. In
561 this case, the width of P2 lines and P3 lines was $200 \mu\text{m}$ and $100 \mu\text{m}$ respectively and
562 the geometric fill factor (GFF) is around 0.90.
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