Title: Vapor-assisted deposition of highly-efficient, stable black phase $FAPbI_3$ perovskite solar cells

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Abstract: Mixtures of cations or halides with $FAPbI_3$ (where FA is formamidinium) lead to high-efficiency in perovskite solar cells (PSCs) but lead to blue-shifted absorption and long-term stability issues caused by loss of volatile methylammonium and phase segregation. We report a deposition method using methylammonium thiocyanate (MASCN) vapor treatment to convert yellow δ-$FAPbI_3$ perovskite films to the desired pure α-phase. Molecular dynamics simulations show that the SCN^- anions promote the formation and stabilization of α-$FAPbI_3$ below the thermodynamic phase-transition temperature. We used these low-defect density α-$FAPbI_3$ films to make PSCs with > 23% power conversion efficiency with long-term operational and thermal stability, as well as a low (330 mV) open-circuit voltage loss and a low (0.75 V) turn-on voltage of electroluminescence.

One Sentence Summary: Methylammonium thiocynate vapor promotes the formation and stabilization of α-$FAPbI_3$ from yellow δ-phase.

Main Text: Metal halide perovskites are being widely investigated in many fields, including solar cells (*1-10*), light-emitting diodes (LEDs) (*11-15*), lasers (*16*) and photodetectors (*17, 18*). Within a decade, power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have been increasing from 3.8% (*19*) to 25.2% (*20*) exceeding other thin film solar cells and the market leader polycrystalline silicon. Since 2015, formamidinium (FA) has been used as the preferred cation in almost all high efficiency PSCs, because these formulations are thermally more stable than perovskites containing methylammonium (MA) and its narrower bandgap is closer to the Shockley-Queisser optimum (*4*). Our previous molecular dynamics studies showed that FA

reorientation was faster than that of MA on the A cation site of the perovskite, which led to enhanced stabilization and slower charge carrier recombination (*21, 22*). Also, $FAPbI_3$ has a Goldschmidt tolerance factor of 0.99 (*2*), which suggests a perfect crystalline perovskite structure with minimum distortions. Thus, $FAPbI_3$ perovskite could be an ideal candidate for efficient, and stable PSCs.

Unfortunately, a photoinactive δ form of $FAPbI_3$ is the most stable phase at room temperature, and the crystallinity of $FAPbI_3$ film is normally poor even after high temperature annealing. To avoid formation of the δ-phase and improve the crystallinity, various complex perovskite compositions have been developed. For example, a combination of MA, Cs, or Br are commonly mixed with $FAPbI_3$, especially for the record high efficiency PSCs (*2, 3, 5, 6*). However, these mixed perovskite compositions show an unwanted blue-shift in their light absorption. Moreover, the mixed perovskite precursor solutions can easily form precipitates when they are used for scale-up fabrications. Furthermore, MA is thermally unstable (*4, 23*), whereas Br/I mixtures suffer from severe ion segregations under long-term light illuminations (*24*). Thus, a mixing strategy may be unfavorable regarding long-term operational stability. Our previous work showed that mixing Cs and Rb with $FAPbI_3$ could be an alternative way to improve the operational stability (*4*), however, the resulting PCE was still less than that reported for most efficient PSCs. Hence obtaining efficient, phase pure and stable $FAPbI_3$ perovskite layers is of vital importance for the perovskite research field.

In contrast to the previous mixing strategies, manipulation of surface energy has been reported to stabilize the perovskite phases and modify the gain growth orientations (*25-29*). For example, templated growth of oriented layered perovskites has been demonstrated for 2D perovskites (*28*), and epitaxial growth and stabilization of α-$FAPbI_3$ has been reported recently (*29*). Swarnkar *et al*. showed that α-$CsPbI_3$ can be stabilized in the form of colloidal quantum dots because of a large contribution of surface energy (*26*). Fu *et al*. reported that functionalizing the surface of $FAPbI_3$ with large organic molecules could lower the formation energy to stabilize the α-$FAPbI_3$ at room temperature (*27*). However, the performance, stability, or both of these systems are still poor comparing with those of mixed-cation-halide PSCs (*25*).

Motivated by these promising strategies of surface-energy manipulations and our recent work using polyiodide vapor for scalable perovskites (*30*), we developed a methylammonium thiocyanate (MASCN) vapor treatment method for preparing efficient and stable α-$FAPbI_3$ PSCs. Figure 1A illustrates the steps of this vapor treatment process. Yellow-color δ-$FAPbI_3$ film was obtained by spin-coating a precursor solution of equal molar FAI and PbI_2 mixture. The as-fabricated δ-$FAPbI_3$ film was annealed at 100 °C for 1 min. Then, the annealed film was put in a MASCN vapor environment for ~5 s until the yellow color changed to black. This vapor treatment was done under normal pressure as MASCN has a sublimation point < 100 °C, which rendered the entire treatment process low-cost and of practical interest for industrial scale-up applications.

Figure. 1B shows x-ray diffraction (XRD) data of $FAPbI_3$ perovskite films before and after exposure to MASCN vapor, confirming a structural transformation from yellow δ-phase to pure black α-phase. XRD data of $FAPbI_3$ films fabricated with conventional method (reference $FAPbI_3$) is also shown for comparison. Our results demonstrated that the reference $FAPbI_3$ films contained the yellow δ-phase. However, for the vapor-treated $FAPbI_3$ films, the δ-phase was effectively

suppressed, and the full-width at half-maxima of the reflection peaks were decreased accordingly because of the increased XRD intensities indicating an increase in film crystallinity. Time-resolved XRD data of $FAPbI_3$ perovskite films under MASCN vapor treatment (fig. S1) showed that δ-phase vanished after vapor treatment for only ~5 s. In particular, the preferred orientation along the (001) plane in Fig. 1B reflected a change of surface energy during the crystallization processes (*31*). Synchrotron-based two-dimensional grazing-incidence XRD (2D-GIXRD) for $FAPbI_3$ films with and without MASCN vapor treatment (fig. S2) performed at incident angles of 0.05°, 0.10° and 0.40° confirmed that the preferred orientation was along the (001) plane from the near surface to the bulk region of the vapor-treated $FAPbI_3$ films.

Figure. 1C illustrates the ultraviolet-visible (UV-vis) absorption and the photoluminescence (PL) spectra of the reference and vapor-treated $FAPbI_3$ films. It shows identical absorption onsets as well as PL peaks at 812 nm, which implies that the vapor treatment did not induce a bandgap change. However, vapor-treated $FAPbI_3$ films showed stronger absorption over all wavelengths compared to the reference sample, which was in accord with the enhanced phase purity and crystallinity apparent from the XRD results. Unlike this work, other recent studies that used MACl as an additive (*5, 32, 33*), a considerable amount of MA was doped inside the bulk $FAPbI_3$. Our UV-vis absorption and PL emission matched the features of pure $FAPbI_3$, unlike the results in (*5*) and (*32*), where the features were blue-shifted. Also, the XRD peaks of the vapor-treated $FAPbI_3$ were identical to those of the reference pure $FAPbI_3$ (fig. S2).

From the scanning electron microscopy (SEM) top-view images, shown in Fig. 1, D and E, the grain size of $FAPbI_3$ films increased to ~1μm after vapor treatment. Atomic-force microscopy (AFM) images of the reference and vapor-treated $FAPbI_3$ films showed that the surface roughness was ~ 15 nm (fig. S3, a and b). The SEM images of the δ-phase $FAPbI_3$ films, shown in fig. S3, c and d, demonstrated that the average grain size was ~100 nm before the vapor treatment. Figure. 1, F and G, illustrate cross-sectional SEM images, showing that the irregular reference $FAPbI_3$ perovskite crystals converted to monolithic grains from the top to the bottom after the vapor treatment. In summary, our XRD data as well as SEM images showed that the vapor treatment with MASCN induced a yellow δ to black α-phase transformation below the phase transition temperature together with a recrystallization of the $FAPbI_3$ films.

We performed solid-state nuclear magnetic resonance (ssNMR) spectroscopy measurements to unravel the role of MASCN during the vapor treatment. Recently, we and others have shown that ssNMR can identify cation incorporation (*22, 34-36*), halide-mixing (*37*), cation dynamics (*21*) and atomic-level interface interactions (*38*) in PSCs. We first performed ^{14}N magic angle spinning (MAS) NMR measurements to investigate the effect of atomic-level interaction from the MASCN presence on the intrinsic crystallographic symmetry of the parent $FAPbI_3$ lattice. The ^{14}N MAS NMR spectra of $FAPbI_3$ featured a ^{14}N spinning sideband (SSB) pattern, which corresponds to FA cation reorientation on the picosecond timescale (*21*).

Figure. 2, A and B indicate that the SSB width was altered by the MASCN surface treatment. The width of the ^{14}N SSB manifold was correlated with the symmetry of the cuboctahedra cavity in which FA cation reorientation took place, whereby a narrower manifold indicated a symmetry closer to cubic (*21, 22, 35*). MASCN-treated $FAPbI_3$ thin film featured three to four orders of SSB less in ^{14}N spectrum compared to the reference $FAPbI_3$, indicative that FA was in a more symmetric

environment. Note that, for both the reference and the vapor-treated $FAPbI_3$, the central peak of the ^{14}N MAS NMR spectra had an identical shift. We concluded that MASCN was most likely interacting with the surface of the $FAPbI_3$ films (*39*). During the annealing process, MA was doped into the surface of $FAPbI_3$ films, which was confirmed by the time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements (fig. S4). The concentration of both MA^+ and SCN^- ions of the vapor-treated $FAPbI_3$ film decreased by a factor of > 30 over a distance of ~20 nm from the surface to the bulk. The bulk of the vapor-treated $FAPbI_3$ film showed negligible MASCN content, which was close to that of the reference $FAPbI_3$ film, in agreement with the 2D-GIXRD measurements.

We performed ^1H MAS ssNMR experiments to assess the amount of MA cation that was present in $FAPbI_3$ after the MASCN treatment. Figure. 2C shows the ^1H spectrum of MASCN powder which identified two distinct ^1H environments corresponding to CH_3 at 3.05 and NH_3^+ at 7.45 ppm. $MAPbI_3$ and reference $FAPbI_3$ perovskites yielded signals at 3.5 and 6.5 ppm corresponding to MA (Fig. 2D) and at 7.5 and 8.2 ppm corresponding to FA (Fig. 2E). Figure. 2F shows the ^1H spectrum of vapor-treated $FAPbI_3$ perovskites, which was identical to that of the reference $FAPbI_3$. When the signal was enhanced 8 times, small additional peaks at 3.5 and 6.3 ppm confirmed that MA is present at very low concentrations in a $MA_xFA_{1-x}PbI_3$ environment, and not present as MASCN or any other form of MA. This agreed with two-dimensional ^1H-^1H spin diffusion measurements, where the appearance of the cross-peak (fig. S5) between MA and FA suggested that MA and FA moieties were with 10 Å of each other. We performed quantitative solid-state one-dimensional measurements where the integral over the peak showed up to 1.8% of MA in this vapor-treated $FAPbI_3$ film (supplementary note 1).

We performed molecular dynamics (MD) simulations to gain insights into the vapor treatment process (fig. S6). Simulation details as well as movies of the MD trajectories are given in SI. The SCN^- ions on the surface of δ-$FAPbI_3$ do not diffuse inside the face-sharing structure of δ-$FAPbI_3$ but remain at the surface (supplementary movie 1). Because of their strong affinity to Pb^{2+} ions, SCN^- anions coordinate to Pb^{2+} on the surface of δ-$FAPbI_3$ (supplementary movies 2 and 3). In particular, Pb^{2+} ions are coordinated with the sulfur atoms of SCN^- (fig. S7) strong enough that the SCN^- ions displace the iodides. This process disintegrates the top layer of face-sharing octahedra and induces the transition to the corner-sharing architecture of α-$FAPbI_3$. Furthermore, the disruption of the topmost surface layer with SCN^- ions also helps the penetration of monovalent cations (MA^+) into the PbI_6 chains of δ-$FAPbI_3$, which further helps the growth of α-$FAPbI_3$ (supplementary movie 4), in agreement with our ssNMR analysis above.

We investigated the re-arrangement of ions at the surface of δ-$FAPbI_3$. Some parts of face-sharing octahedra on the interface start to form corner-sharing Pb-I-SCN structures (fig. S8). With the addition of extra SCN^- ions, corner-sharing structures, which contain mixtures of SCN^- ions and iodides, are formed and stabilized (fig. S9). The atomic view of this whole transformation from face-sharing to corner-sharing octahedra is shown in Fig. 3 and supplementary movies 5 and 6. Further analysis reveals that the conversion of the face-sharing structure proceeds via formation of edge-sharing intermediates. This results mainly from the step by step addition of SCN^- ions around the Pb^{2+} ions as seen in supplementary movies 5 and 6. Our previous studies have also shown formation of such intermediate structures before conversion to perovskites (*40*). Some

particular domains of the mixed corner and face-sharing structures formed during the simulation, we find that SCN^- ions can also induce the formation of polytypes at the interface.

We observe the formation of localized structures similar to the well-known 4H polytypes of $FAPbI_3$ (supplementary movies 6 and 7, and fig. S10). We also generate a model of a periodic structure of 4H polytype with iodides replaced by SCN^- and find this structure remains stable after DFT optimization (SI). We conclude that SCN^- ions drive and stabilize the formation of corner-sharing structures upon contact formation with MASCN, which in turn trigger the conversion to α-$FAPbI_3$. Strikingly, this process can occur below the thermodynamic phase-transition temperature. A further illustration of the δ to α-phase transition by SCN^- ions from the surface to the bulk is shown in fig. S11.

In order to confirm the role of SCN^-, we used FASCN instead of MASCN for the vapor treatment of the δ-phase $FAPbI_3$. This treatment formed pure α-$FAPbI_3$ even at an annealing temperature of only 100 °C (fig. S12), far below the thermodynamic phase-transition temperature. In the absence of FASCN, the reference $FAPbI_3$ films annealed at 100 °C mainly formed the δ-phase. Thus, the complete transformation from the δ to α-$FAPbI_3$ also occurred in the absence of MA^+ ions, which agreed well with our MD simulations. We note that the α-phase $FAPbI_3$ remained kinetically stable; once the pure α-phase $FAPbI_3$ formed, its transition back to δ-phase was restrained by a high potential energy barrier (fig. S13).

After the successful preparation of pure α-$FAPbI_3$ with ordered and monolithic grains, we further investigated the performance of the corresponding PSCs. All PSCs were fabricated using an ITO/SnO_2/$FAPbI_3$/Spiro-MeOTAD/Au (ITO, indium tin oxide; Spiro-MeOTAD, 2,2′,7,7′-tetrakis[*N*,*N*-bis(*p*-methoxyphenyl)amino]-9,9′-spirobifluorene) configuration (Fig. 4A). A cross-sectional SEM image of the full device structure is given in fig. S14. Figure. 4B demonstrates a PCE of 23.1% for one of our champion $FAPbI_3$ PSCs with a short-circuit current density (J_{sc}) of 24.4 mA/cm^2, open-circuit voltage (V_{oc}) of 1.165 V and fill factor (FF) of 81.3%. It also exhibited negligible hysteresis under both forward and reverse scans between 0 and 1.2 V. Details on the reproducibility of this vapor treatment technique are provided in fig. S15.

We validated the performance of our PSCs at the Photovoltaic Laboratory of the Institute of Micro Technique (IMT), Neuchâtel, Switzerland. The Wacom high-precision class AAA solar simulator available at the IMT PV-lab closely mimics the solar spectrum in the absorption range of the PSCs in the range of 350 to 850 nm, avoiding any substantial spectral mismatch between the simulated and true AM 1.5G solar light source. The solar spectrum of Wacom lamp is given by the insert in fig. S16a. An efficiency of 22.4% was confirmed under maximum power point (MPP) condition in IMT, which is near the measured 22.8% in our lab (fig. S16). As a comparison, the current density-voltage (J-V) curves of the reference PSCs are given in fig. S17, which shows a relatively poor performance and large hysteresis. Figure. 4C shows the corresponding incident photon-to-electron conversion efficiency (IPCE) curve and a projected J_{sc} of 24.3 mA/cm^2, obtained by integrating the IPCE over the AM 1.5G standard spectrum. This value matched well the J_{sc} of 24.4 mA/cm^2, measured under the solar simulator. Steady-state power output at MPP under 1 sun light-soaking conditions is shown in fig. S18. The rapid response and stable output indicated efficient charge extraction and negligible charge accumulation.

Once efficient carrier collection is achieved, the V_{oc} becomes the main limiting factor for the device efficiency. Figure. 4D illustrates a V_{oc} of 1.19 V obtained for one of the vapor-treated $FAPbI_3$ PSCs. The J-V curves for this device were measured under a cooling air flow at 20.1 °C. The detailed determination of the measured V_{oc} is shown in supplementary note 2. The temporal evolution of the V_{oc} measured for 5 mins under 0.9 Sun is shown in fig. S19. Over this time period the V_{oc} reached a stable plateau. From the emission spectra (Fig. 4E), we determined an Urbach energy of 14 meV (fig. S20). Using these data, the IPCE and the reciprocity relation (*41*), we determined the theoretical radiative limit V_{oc} to be ~1.255 V (see SI for details of this calculation and the influence of temperature (fig. S21)). Thus, our measured V_{oc} is only 65 mV below the radiative limit and the voltage loss compared to the bandgap is only 330 mV. We derived a band gap of 1.52 eV for $FAPbI_3$ using the Tauc plot (fig. S22), which is somewhat larger than reported values (*42*). To the best of our knowledge, our $FAPbI_3$ devices have the smallest V_{oc} loss reported so far for PSCs, outperforming silicon solar cells, and closely approaching that of GaAs photovoltaics (*43*). The V_{oc} value is related to density of defect of the perovskite layer acting as centers for non-radiative recombination of photo-generated charge carriers. To check on this loss channel, we measured the time-resolved photoluminescence (TRPL) of the reference and vapor-treated $FAPbI_3$ films. Figure. S23 shows that the lifetime of the vapor-treated $FAPbI_3$ is 299.3 ns, which is 3.7 times longer that of the reference film.

A solar cell's photovoltage is directly related to the ability to extract its internal luminescence, as derived by Ross (*44*):

$$V_{oc} = V_{oc,rad} + \frac{kT}{q}\ln(\eta_{ext})$$

where $V_{oc,rad}$ is the radiative limit of open-circuit voltage, k is the Boltzmann constant, T is the temperature, q is the electronic charge and η_{ext} is the external luminescence quantum efficiency. For any solar cell technology to approach the radiative limit, efficient external electroluminescence (EL) is a necessity (*45*). Because we obtained a V_{oc} approaching the radiative limit $V_{oc,rad}$, we expected a high EQE_{EL} from our $FAPbI_3$-based PSCs. Figure. 4E shows the EL spectra of $FAPbI_3$-based PSCs, which were measured under different bias voltages in ambient conditions. It shows a EL peak position at 810 nm, consistent with the above PL results. We detected EL emission even under a low bias voltage of 0.75 V. Thermal activation can contribute to reduce the turn-on voltage below the bandgap/q of the active/emissive semiconductor. To the best of our knowledge, 0.75 V is the lowest reported turn-on voltage value for perovskite-based devices, which suggests low leakage currents, low energy loss, or both, as well as almost perfectly balanced carrier injection and low nonradiative recombination. Figure. 4F shows an EQE_{EL} of 6.5% for an injection current density of 25 mA/cm^2 (corresponding to the J_{sc} measured under 1 sun illumination). This result translated into a non-radiative loss as low as 70 mV (see supplementary note 2), which surpasses the reported values in the literature and even light emission from the best silicon solar cells.

The measured EQE_{EL} was actually underestimated, as we have substantial emission losses from glass sheets, which could partially explain the 5-mV difference between the measured and predicted non-radiative loss. An even higher 8.6% EQE_{EL} was achieved with an injected current density < 100 mA/cm^2. These EQE_{EL} values are among the highest ones reported in the literature. Compared to the results published recently (*5, 45*), our driving voltage was substantially smaller, resulting in an exceptional high peak wall-plug efficiency of 7.5% with a low bias voltage of 1.55 V (fig. S24). Importantly, our devices exhibited a low roll-off under injected current densities up

to 300 mA/cm^2 (fig. S25). These results contrast with the difficulties to reach high efficiency at high current densities, which has been a challenge for the other reported perovskite devices (*5, 46*), as well as organic LEDs (*13*). Hence, our $FAPbI_3$-based PSCs compare favorably with the state-of-the-art perovskite-based LEDs, and even other organic LEDs.

We investigated the operational stability of our $FAPbI_3$-based PSCs as stability issues remain the main obstacle toward the commercialization of PSCs. Reports of long-term stability under MPP tracking conditions (operational stability) is still scarce for PSCs with a PCE exceeding 22% (*3, 5*). Surprisingly, the reported operational stability of some high-efficiency PSCs, where 2D structures, Cs, or both have been used to improve the device stability remains low (*25, 47, 48*). Recently, Seo *et al.* improved the stability using poly(3-hexylthiophene) as the hole-transporting material (HTM) (*6*). However, the stability of their reference cell with standard Spiro-MeOTAD lagged far behind.

We checked the phase stability of the MASCN vapor-treated $FAPbI_3$ films under long-term heat stress at 85 °C in an inert N_2 environment because $FAPbI_3$ undergoes a transition to a yellow phase below 150 °C. Figure. S26a shows the XRD data of the vapor-treated $FAPbI_3$ films annealed up to 500 hours. The black α-phase for all vapor-treated $FAPbI_3$ perovskite films persisted even after 500 hours of annealing at 85 °C. On the contrary, the reference $FAPbI_3$ films degraded severely during the heat test and formed mainly the PbI_2 (fig. S26b). We also checked the shelf life of our vapor-treated $FAPbI_3$-based PSCs (fig. S27). After 2500 hours storage in a dry box, the PCE remained at 97.8% of its initial value.

We performed long-term operational stability tests for 500 hours with MPP tracking under continuous 1 sun illumination for our $FAPbI_3$ PSCs. Figure. 5A shows that the PCE of our $FAPbI_3$ PSCs remains around 90% of the initial value (21.4%) after 500 hours MPP measurements. The PCE partially recovered to 20.2%, which is 94.4% of the initial value after 12 hours of rest in open circuit conditions in the dark, consistent with our previous reports (*49*). PV metrics derived from the J-V curves, including V_{oc}, J_{sc}, FF and the hysteresis factor (P_{for}/P_{rev}), are shown in Fig. 5, B to E. The V_{oc} and J_{sc} remained constant during 500 hours MPP tracking and hysteresis factor remained near unity, suggesting minimal electronic charge trapping at interfaces.

The main degradation of our PSCs is the FF decline from 0.77 to 0.70 over the light soaking period. However, the FF largely recovered when the cell was left in the dark for a few hours as shown by the final red point in Fig. 5D. Thus, the FF decrease was a reversible phenomenon and did not indicate permanent degradation of the device. During the long-term light soaking, the PSC was subjected to an electric field originating from the voltage difference across the device at MPP. This electric filed in turn caused migration of Li^+ ions across the film and de-doping of the hole conductor. As a result, the hole transport resistance increased, explaining the observed decline of FF. In the dark, the internal field vanished, and the hole conductor recuperated most of the Li^+ ions, which led to the recovery of FF. Our devices did not exhibit appreciable hysteresis, which ruled out the decrease of the FF arising from ion movement within the perovskite layer and their trapping at charge defects present at the interface of the perovskite film with the electron or hole selective contact material. However, apart from the outflow of Li^+, inflow of iodide could de-dope the hole conductor and increase the series resistance, which would lead to the observed decrease of the FF (9).

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Supplementary Materials:

Materials and Methods

Supplementary Text

Figures S1-S27

Movies S1-S7

References (*50-66*)

Fig. 1. $FAPbI_3$ perovskite film characterization. (**A**) Simplified scheme presenting the MASCN vapor treatment process for pure black phase $FAPbI_3$ perovskite films. (**B**) XRD patterns of $FAPbI_3$ perovskite films before (yellow color) and after (red color) vapor treatments, as well as the reference $FAPbI_3$ perovskite films fabricated with conventional method, ♦ indicates PbI_2 species. (**C**) UV-vis absorption and PL spectra of vapor-treated and reference $FAPbI_3$ perovskite films. Top-view SEM images of (**D**) the reference $FAPbI_3$ perovskite films and (**E**) vapor-treated $FAPbI_3$ perovskite films. Cross-sectional SEM images of (**F**) the reference $FAPbI_3$ perovskite films and (**G**) vapor-treated $FAPbI_3$ perovskite films. Scale bar is 1 μm.

Fig. 2. ^{14}N and ^{1}H ssNMR spectroscopy measurements. ^{14}N solid state MAS NMR spectra at 21.1 T, 298 K and 5 kHz MAS of **(A)** reference $FAPbI_3$ perovskites, and **(B)** vapor-treated $FAPbI_3$ perovskites. ^{1}H MAS NMR spectra at 21.1 T, 298 K and 20 kHz MAS of **(C)** MASCN powder, **(D)** bulk-mechanochemical $MAPbI_3$, **(E)** reference $FAPbI_3$ perovskites, and **(F)** vapor-treated $FAPbI_3$ perovskites.

Fig. 3. MD simulations showing a structural conversion. Representative snapshot from the MD simulations showing a structural conversion of (**A**) the initial face-sharing octahedra and (**B**) the corner-sharing octahedra. Pb-I octahedra are shown with green color with iodide as orange balls on corners. To highlight the structural transformation, red color is chosen for octahedra on the interface. FA^+ and MA^+ ions are not shown for clarity. Selected SCN^- ions are shown with ball and sticks representation: sulfur with yellow, carbon with light blue and nitrogen with dark blue (the other SCN^- ions are not shown for the sake of clarity).

Fig. 4. Vapor-treated $FAPbI_3$-based PSC characterization. (**A**) A simplified graph of planar-structure $FAPbI_3$ PSC. (**B**) J-V curves under both reverse and forward scan directions, and power outputs under different bias voltages. (**C**) IPCE curve of $FAPbI_3$ PSC over 300 nm to 900 nm wavelengths, and integrated J_{sc} over AM 1.5G standard spectrum. (**D**) J-V curve of $FAPbI_3$ PSC with a V_{oc} of 1.19 V (measured at T = 20.1 °C). (**E**) EL spectra of $FAPbI_3$ PSC under different bias voltages from 0.75 V to 1 V. (**F**) EQE_{EL} and current density of $FAPbI_3$ PSC under bias voltages from 0 to 1.8 V, a photograph of the luminescence of $FAPbI_3$ PSC under 1.45 V bias voltage is inserted.

Fig. 5. Operational stability test of the vapor-treated $FAPbI_3$-based PSCs. Tests were performed under 500 hours MPP tracking conditions for (**A**) PCE, (**B**) J_{sc}, (**C**) V_{oc} , (**D**) FF, and (**E**) hysteresis factor (P_{for}/P_{rev}).