

Pseudo-halide Anion Engineering for α -FAPbI₃ perovskite solar cells

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Abstract

Metal halide perovskites of the general formula ABX₃ where A is a monovalent cation such as caesium, methylammonium or formamidinium, B stands for divalent lead, tin or germanium and X is a halide anion, have shown great potential as light harvesters for thin film photovoltaics. (1-5) Amongst a large number of compositions investigated, the cubic α -phase of formamidinium lead triiodide (FAPbI₃) has emerged as the most promising semiconductor for highly-efficient and stable perovskite solar cells (PSCs) (6-9). Maximizing the performance of α -FAPbI₃ has therefore become of vital importance for the perovskite research community. Here, we introduce a new anion engineering concept that employs the pseudo-halide formate (HCOO⁻) to suppress anion vacancy electric defects present at grain-boundaries and the surface of the perovskite films and to augment their crystallinity, enabling PSCs to attain a record power conversion efficiency of 25.6 % (certified 25.2%), long-term operational stability and

1 intense electroluminescence with external quantum efficiencies over 10%. Our findings open
2 up a direct route to eliminate the most abundant and deleterious lattice defects present in metal
3 halide perovskites providing a facile access to solution processable films with unprecedented
4 opto-electronic performance.

5 6 **Main text**

7
8 Perovskite solar cells (PSCs) have attracted much attention since their first demonstration in
9 2009 (1-5). There has been a rapid expansion of research on PSCs, driven by the low-cost
10 solution processing and attractive optoelectronic properties, such as tuneable bandgap (6), high
11 absorption coefficient (10), low recombination rate (11) and high mobility of charge carriers
12 (12). Within a decade, the power conversion efficiency (PCE) of single junction PSCs
13 progressed from 3% to a certified value of 25.5% (13), the highest for thin-film photovoltaics.
14 Moreover, the long-term operational stability of PSCs exceeds now 1000 hours in full sunlight
15 using additive and interface engineering strategies (14,15). Thus, PSCs show great promise for
16 deployment as the next generation of photovoltaics.

17
18 Compositional engineering plays a key role in achieving highly-efficient and stable PSCs. In
19 particular, mixtures of methylammonium lead triiodide (MAPbI₃) with formamidinium lead
20 triiodide (FAPbI₃) have been extensively studied (5,7). Compared to MAPbI₃, FAPbI₃ is
21 thermally more stable and has a bandgap closer to the Shockley-Queisser limit (6), rendering
22 FAPbI₃ the most attractive perovskite layer for single junction PSCs. Unfortunately, thin
23 FAPbI₃ films undergo a phase-transition from the black α -phase to a photoinactive yellow δ -
24 phase below a temperature of 150 °C. Previous approaches to overcome this problem include
25 mixing FAPbI₃ with a combination of MA⁺, Cs⁺ and Br⁻ ions, at the cost of blue-shifted
26 absorbance and phase segregation under operational conditions (7-9,16).

27
28 Nevertheless, α -FAPbI₃ has recently emerged as the candidate of choice for highly-efficient
29 and stable PSCs (9,17,18). We prepared α -FAPbI₃ by spin coating a precursor solution of
30 FAPbI₃ mixed with excess MAI and achieved a certified efficiency of 23.48% for the
31 mesoporous-structure FAPbI₃ PSC (17). Later, Min *et al.* reported that FAPbI₃ PSCs could be
32 further stabilized with methylenediammonium dichloride (MDACl₂), resulting in a certified
33 efficiency of 23.73% (18). By fully exploiting the absorption spectrum of FAPbI₃ together with
34 proper light management, the short-circuit current density (J_{sc}) reached 26.7 mA/cm²,
35 approaching the theoretical maximum (18). However, the open-circuit voltage (V_{oc}) of ~1.15
36 V for FAPbI₃ PSCs still lags behind the radiative limit (9,18), implying that more work is
37 needed to further reduce the defect density in the FAPbI₃ perovskite films to suppress non-
38 radiative recombination of charge carriers.

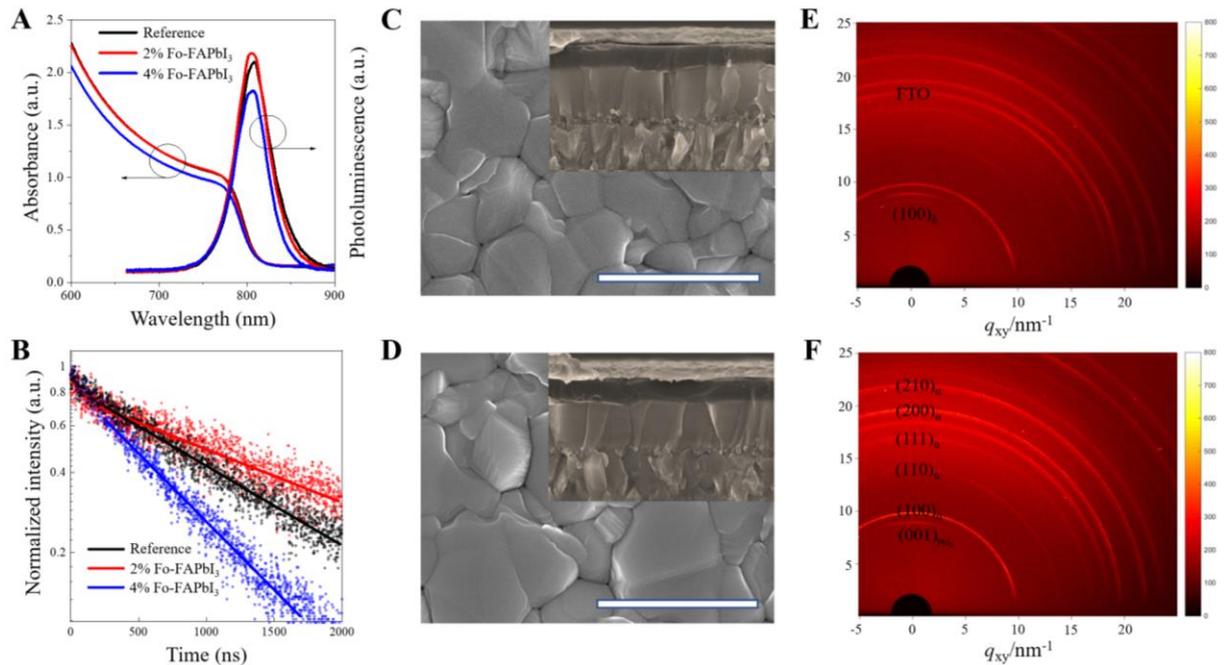
39
40 Br⁻, Cl⁻, and thiocyanate (SCN⁻) anions, have been commonly used to improve the crystallinity
41 and stability of perovskite films (8,9,11,17-22). Another pseudo-halide anion, formate
42 (HCOO⁻), has been investigated in connection with MAPbI₃ based PSCs (23-26). T. Moore *et al.*
43 (23) and Seo *et al.* (24) reported that methylammonium formate, an ionic liquid, improves
44 the quality of MAPbI₃ films by controlling the perovskite crystal growth, while K. Nayak *et al.*
45 (25) reported that formic acid accelerates the crystallisation of MA cation-based perovskites
46 by dissolving the perovskite colloids in the precursor solution. Similar findings were published
47 by Meng *et al.* (26). Thus, the previous work mainly dealt with the effect of formate on the
48 morphology, nucleation and growth of MAPbI₃. Recently, Khan *et al.* (27) reported highly
49 fluorescent methylammonium lead bromide/formate mixture in water, but a fundamental
50 understanding is missing.

1 Here, we uncover the key role of HCOO^- anions in removing the halide vacancies, which are
 2 the predominant lattice defects in FAPbI_3 perovskite films. This enables the PCE of the PSC
 3 to pass over 25% combined with a high operational stability and external quantum efficiency
 4 (EQE) of electroluminescence exceeding 10%. Iodide vacancies are also the principle cause
 5 for the unwanted ionic conductivity of metal halide perovskites which exerts a deleterious
 6 effect on their operational stability. We provide new insight into the mode of formate
 7 intervention. Based on its size effect, formate is small enough to fit in the iodide vacancy (22),
 8 eliminating a prevalent and notorious defect in the metal halide perovskite that accelerates the
 9 nonradiative recombination of photogenerated charge carriers decreasing both the fill factor
 10 (FF) and V_{oc} of a solar cell. In addition, FAPbI_3 perovskite films with improved crystallinity
 11 and larger grain size were achieved by introducing 2% FAHCOO into the precursor solution.
 12 The defect passivation and the improved crystallinity are essential to attain the record
 13 efficiency and excellent stability demonstrated by our FAPbI_3 -based PSCs.

14

15 The reference FAPbI_3 film, hereafter noted as “reference”, was prepared as previously reported
 16 using a precursor solution containing a mixture of FAPbI_3 powder with 35 mol% additional
 17 MAI (17). For the formate doped FAPbI_3 (Fo- FAPbI_3) film, x mol% ($x \leq 4$) FAHCOO was
 18 added to the reference precursor solution. Experimental details are included in the
 19 supplementary materials (SM). In the later discussion, we quantify the amount of MA in the
 20 resulting perovskite composition to be 5%, but for simplicity, we will still refer to the sample
 21 as FAPbI_3 in the following text. Figure 1A shows the ultraviolet-visible (UV-Vis) absorption
 22 and photoluminescence (PL) spectra of the FAPbI_3 perovskite films. Identical absorption
 23 threshold and PL peak position were observed for all films, but there was an obvious decrease
 24 of the absorbance when 4% FAHCOO was added. Figure 1B shows the time-resolved
 25 photoluminescence (TRPL) of the FAPbI_3 perovskite films. The 2% Fo- FAPbI_3 perovskite film
 26 showed a slower PL decay than the reference which indicates a reduced non-radiative
 27 recombination rate due to a reduction of trap-mediated bulk or surface recombination. In
 28 contrast, the 4% Fo- FAPbI_3 perovskite film showed a faster PL decay than the reference. A
 29 full PL decay up to 4 μs is shown in fig. S1. A quantitative analysis of the TRPL is presented
 30 in Note 1 in the SM.

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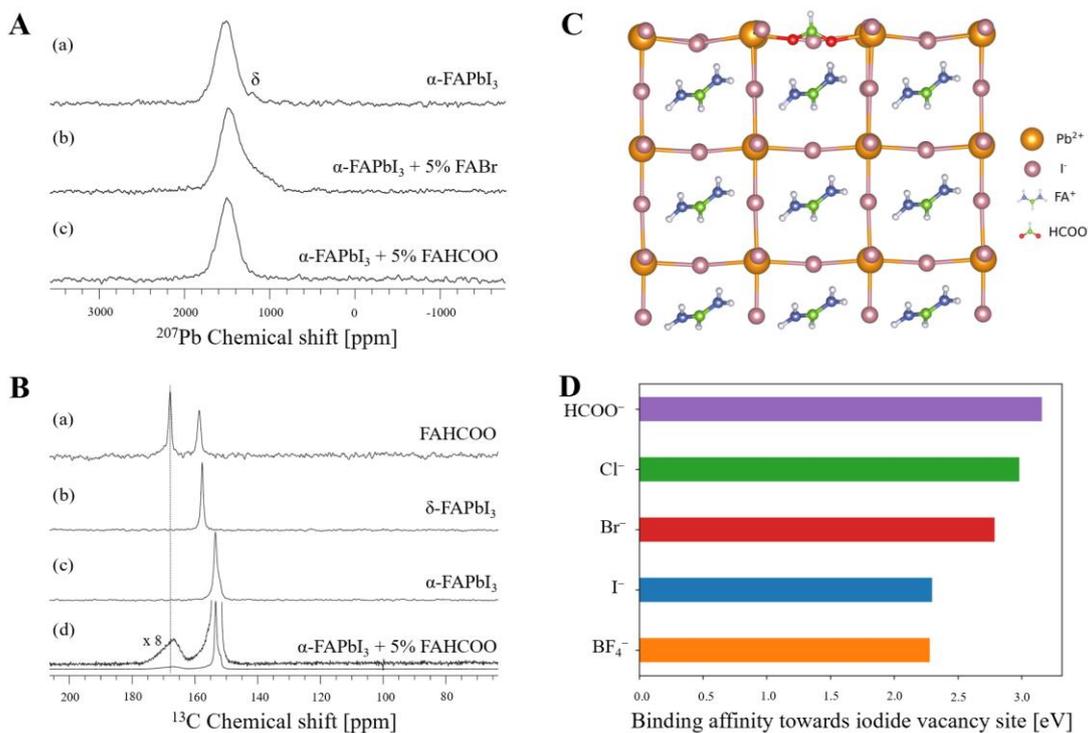
1 **Figure 1.** Characterisation of the FAPbI₃ films. (A) UV-Vis absorption and PL spectra of the
2 FAPbI₃ films. (B) TRPL of the FAPbI₃ films. SEM images of the reference FAPbI₃ (C) and 2%
3 Fo-FAPbI₃ (D) films (Scale bar is 2 μm, cross-sectional SEM images are inserted). 2D-GIXRD
4 patterns of the reference (E) and 2% Fo-FAPbI₃ (F) films.

5
6 Scanning electron microscopy (SEM) measurements were performed to investigate the
7 perovskite film morphology. Compared to the reference film (Fig. 1C), the 2% Fo-FAPbI₃ film
8 (Fig. 1D) had a larger grain size of up to 2 μm. The inset pictures in Fig. 1, C and D, are the
9 cross-sectional SEM images of the corresponding perovskite films. Both the reference and 2%
10 Fo-FAPbI₃ films showed monolithic grains from the top to the bottom. Figure S2 shows the
11 irregular and small grain size for the 4% Fo-FAPbI₃ films. Atomic force microscopy (AFM)
12 measurements (fig. S3) showed a surface roughness of 41.66 and 57.47 nm for the reference
13 and 2% Fo-FAPbI₃ films, respectively. The slightly increased surface roughness of the 2% Fo-
14 FAPbI₃ film is mostly like due to the increased grain size.

15
16 X-ray diffraction (XRD) measurements (fig. S4) showed that the reference and Fo-FAPbI₃
17 perovskite films had identical peak positions at around 13.95 ° and 27.85 °, corresponding to
18 the α-phase of FAPbI₃. However, the XRD pattern of the 4% Fo-FAPbI₃ film showed additional
19 peaks which are assigned to fluorine doped tin oxide (FTO) substrates and different orientations
20 of α-FAPbI₃. The broader and lower intensity diffraction peaks (resulting in higher relative
21 noise level) indicate a poor crystallinity, which is consistent with the poor optical
22 measurements of the 4% Fo-FAPbI₃ film above. Synchrotron-based two-dimensional grazing-
23 incidence XRD (2D-GIXRD) measurements were also performed for the FAPbI₃ films at a
24 relative humidity (RH) of ~100% at 30 °C in ambient air. Figure 1E clearly shows the presence
25 of the δ-phase for the reference, while the δ-phase was absent in the 2% Fo-FAPbI₃ film (Fig.
26 1F). This provides strong evidence that the FAHCOO stabilizes the α-phase of FAPbI₃ against
27 humidity. In addition, the full width at half maximum of the α-phase peak was decreased for
28 the 2% Fo-FAPbI₃, hereafter noted as “target”. The integrated 1D diffraction intensity is shown
29 in fig. S5. We infer from these data that including FAHCOO in the synthesis of the FAPbI₃
30 films strongly enhances their crystallinity.

31
32 We performed solid state nuclear magnetic resonance (NMR) spectroscopy measurements in
33 order to unravel the molecular mechanism of the improvements afforded by the HCOO⁻ anions.
34 We prepared the samples by mixing FAI and PbI₂ powders with 5 mol% extra FAHCOO using
35 a mechano-synthesis method. MAI was not added to avoid broadening of resonances,
36 affording greater resolution and therefore sensitivity to the local environments (details are
37 given in the SM). The ²⁰⁷Pb spectrum is sensitive to the nature of the anions coordinated to
38 Pb²⁺ in the perovskite (28); Figure 2A shows the ²⁰⁷Pb spectrum of α-FAPbI₃ which resonances
39 at 1543 ppm. The addition of 5% FABr results in a notable shoulder on the low-frequency side
40 of the ²⁰⁷Pb resonance, as shown in Fig. 2A (b). Since FAPbBr₃ resonates at 510 ppm (28), the
41 new ²⁰⁷Pb environment has a slightly lower frequency than α-FAPbI₃. However, the ²⁰⁷Pb
42 resonance of the α-FAPbI₃ remained the same after adding 5% FAHCOO in the synthesis,
43 which is strong evidence that HCOO⁻ does not substitute for iodide anions on the α-FAPbI₃
44 lattice. This is also supported by the density functional theory (DFT) calculations of the
45 formation energy shown in Note 2 in the SM.

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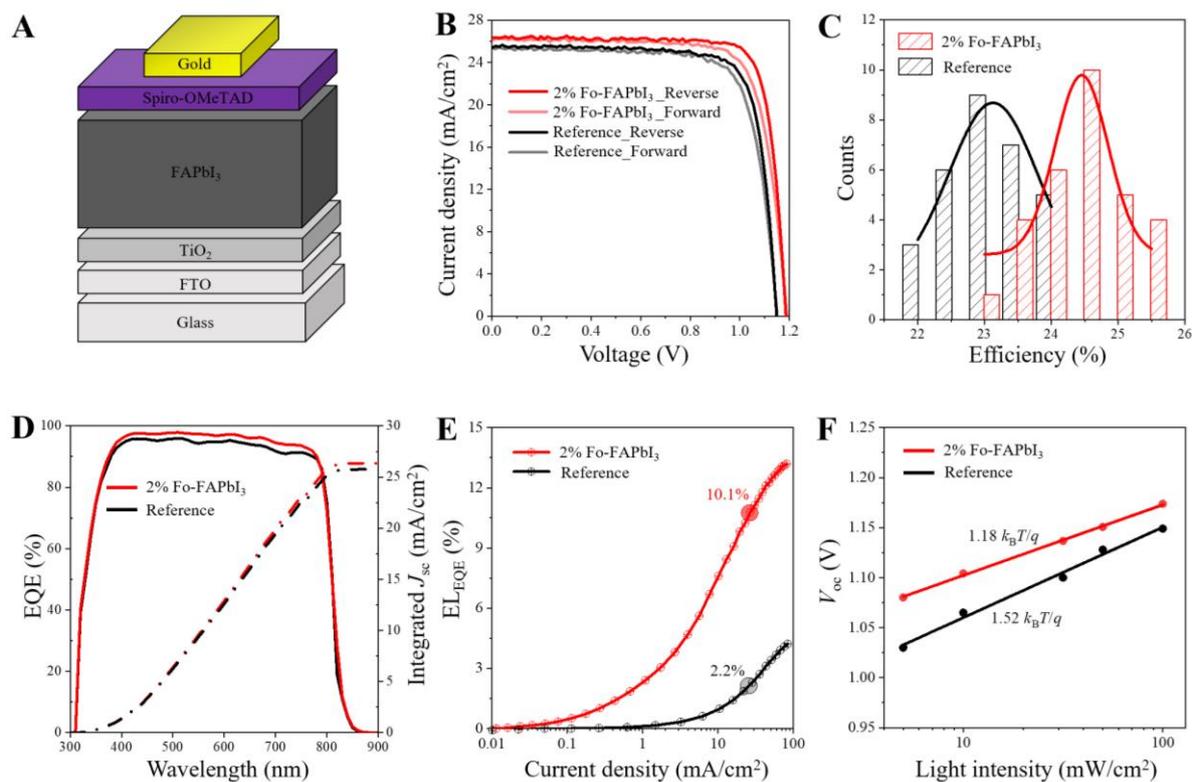


1
2
3 **Figure 2.** Solid-state NMR and MD simulations. (A) ^{207}Pb ssNMR measurements at 15 kHz
4 MAS and 298 K for (a) $\alpha\text{-FAPbI}_3$, (b) $\alpha\text{-FAPbI}_3 + 5\% \text{FABr}$, (c) $\alpha\text{-FAPbI}_3 + 5\% \text{FAHCOO}$. In
5 (a) a small amount of the δ phase can be seen, but this is distinct from the shoulder seen in (b),
6 and in any case is not seen in (c). (B) ^{13}C ssNMR measurements at 12 kHz MAS and 100K for
7 (a) FAHCOO, (b) $\delta\text{-FAPbI}_3$, (c) $\alpha\text{-FAPbI}_3$, (d) $\alpha\text{-FAPbI}_3 + 5\% \text{FAHCOO}$ (the upper trace is
8 an 8-fold magnification). (C) Calculated structure showing passivation of an I^- vacancy at the
9 FAPbI₃ surface by a HCOO^- anion. All chemical species are shown with the balls and sticks
10 representation. Pb^{2+} ions are shown with large yellow coloured spheres, I^- ions with light pink,
11 oxygen atoms with red, carbon atoms with green, nitrogen atoms with blue and hydrogen atoms
12 with white. (D) The binding affinities of different anions to the I^- vacancy at the surface.

13
14 To explore the local environment of the HCOO^- anions in the Fo-FAPbI₃ perovskite, $^1\text{H} \rightarrow ^{13}\text{C}$
15 cross-polarization (CP) experiments were performed at 100 K (29). Figure 2B(a) shows ^{13}C
16 resonance signals at 167.8 ppm and 158.5 ppm for the HCOO^- and FA^+ environments in
17 FAHCOO. Figure 2B, (b) and (c) show the $\delta\text{-FAPbI}_3$ and $\alpha\text{-FAPbI}_3$ and ^{13}C resonances at 157.6
18 ppm and 153.4 ppm, respectively. Upon mixing 5 mol% FAHCOO with FAPbI₃, the ^{13}C signal
19 of $\alpha\text{-FAPbI}_3$ remained unchanged, at 153.4 ppm, shown in Fig. 2B(d), which further
20 corroborates the lack of substitution of iodide by HCOO^- inside the FAPbI₃ lattice. The HCOO^-
21 peak, however, exhibited significant broadening, indicative of a distribution of local
22 environments which we attribute to the interaction of the HCOO^- anion with undercoordinated
23 Pb^{2+} via insertion in iodide vacancies present at the surface or grain boundaries of the
24 perovskite, in contrast to the well-defined environment in crystalline FAHCOO. For the spin-
25 coated 2% Fo-FAPbI₃ thin films, the formate ^{13}C signal is less intense, appearing as a shoulder
26 on the peak of $\alpha\text{-FAPbI}_3$ (fig. S6). This is due to a combination of the lower initial formate
27 concentration and potentially greater evaporation of formate during annealing in the thin films
28 compared to powders since the exposed area is greater, although the CP spectra are not
29 quantitative. The presence of FAHCOO in the $\alpha\text{-FAPbI}_3$ films is also supported by the time-
30 of-flight secondary ion mass spectrometry (TOF-SIMS) measurements shown in fig. S7. We
31 further quantified the composition of the spin-coated 2% Fo-FAPbI₃ films using directly-

1 detected ^{13}C NMR at 100 K (fig. S8). Integration of the FA^+ and MA^+ resonances in the
 2 quantitative ^{13}C spectrum yields 5.1% of the MA^+ ion in the final perovskite films (see Note 3
 3 in the SM).

4
 5 To explore in more detail the unique role of HCOO^- anions, we performed *ab-initio* molecular
 6 dynamics (MD) simulations of a homogeneous mixture of different ions in the precursor
 7 solution (see Note 4 and fig. S9), comprising Pb^{2+} , I^- , HCOO^- , and FA^+ , and found that the
 8 HCOO^- anions coordinate strongly with the Pb^{2+} cations (Supplementary movie 1). This strong
 9 coordination might help in slowing down the growth process, resulting in larger stacked grains
 10 of the perovskite film, which is validated by the *in-situ* images of the perovskite films without
 11 annealing (fig. S10). Compared to the reference film, 2% Fo-FAPbI₃ film had a slower color
 12 change from brown to black. We also performed MD simulations to understand the surface
 13 passivation effects of HCOO^- anions. Figure S11 shows a super cell of a α -FAPbI₃ perovskite
 14 slab with surface iodides replaced by formate anions. We found that HCOO^- anions can form
 15 a nexus of hydrogen bonding with FA^+ ions (shown in fig. S11C and supplementary movie 2),
 16 in agreement with the hydrogen bonding in the FAHCOO crystal structures (30). In addition,
 17 HCOO^- anions can also form a bonding network on the Pb^{2+} ion terminated surface because of
 18 their strong affinity towards lead (shown in fig. S11B and supplementary movie 3). Figure 2C
 19 shows a HCOO^- anion passivating an I^- vacancy at the FAPbI₃ surface. We then calculated the
 20 binding affinity of the HCOO^- anions to the I^- vacancies at the surface (figs. S12, S13 and S14
 21 in the SM). I^- vacancy defects are the most deleterious defects for the stability of halide
 22 perovskites. The energies in Fig. 2D show that the HCOO^- has the highest binding energy to
 23 I^- vacant sites at the interface compared to other anions including Cl^- , Br^- , I^- and BF_4^- .
 24 Furthermore, we have also calculated the bonding energies of formamidinium at the interface
 25 with formate anions and with other anions (see Note 5 in the SM and figs. S15 and S16). We
 26 found that FA^+ cations at the interface form a stronger bonding with HCOO^- than with the
 27 other anions. One can conclude that the HCOO^- anion acts as a passivating agent against the
 28 formation of vacancy defects (such as I^- and FA^+).



30

1
2 **Figure 3.** PV performance characterisation of the FAPbI₃ PSCs. (A) The configuration of a
3 typical FAPbI₃ PSC device. (B) J - V curves of the reference and target PSCs under both reverse
4 and forward scans. (C) The statistical distribution of the PCE of the reference and target PSCs.
5 (D) EQE and the integrated J_{sc} of the reference and target PSCs. (E) EQE_{EEL} measurements of
6 the reference and target PSCs under a current density from 0.01 to 100 mA/cm². (F) The
7 relationship between the measured V_{oc} and light intensity for the reference and target PSCs.

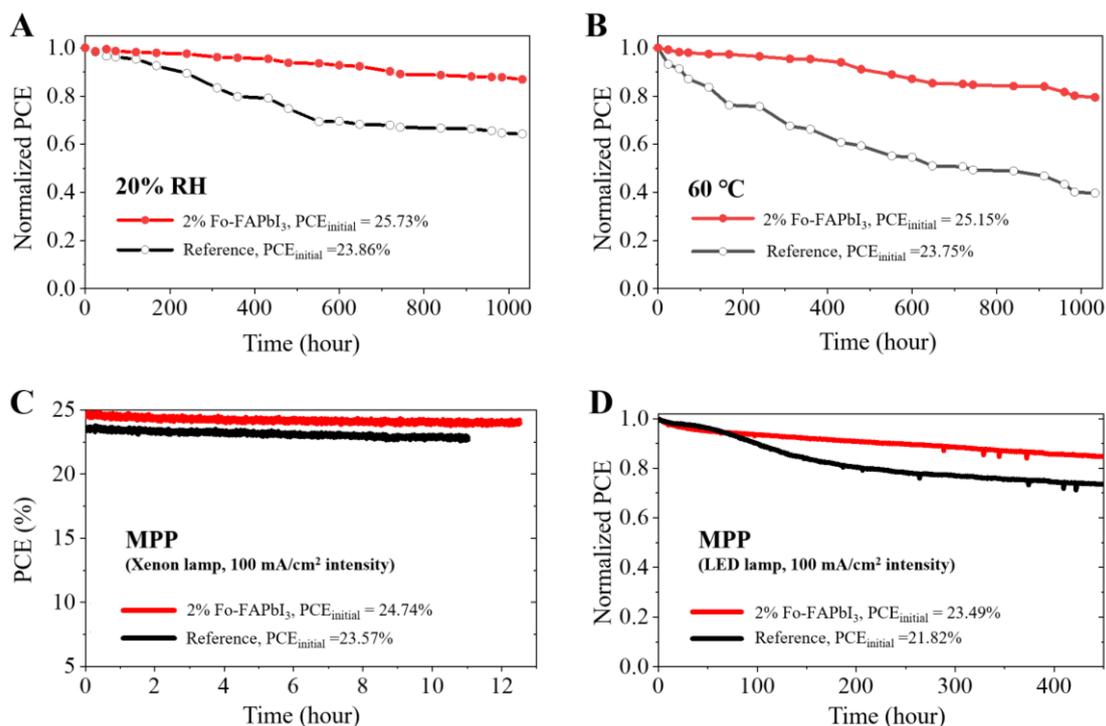
8
9 We further explored the photovoltaic (PV) performance of the reference and Fo-FAPbI₃ based
10 PSCs. FAPbI₃ PSCs were fabricated using a FTO/TiO₂/FAPbI₃/Spiro-MeOTAD/Au (FTO,
11 fluorine doped tin oxide; c-TiO₂; Spiro-MeOTAD, 2,2',7,7'-tetrakis[*N,N*-bis(*p*-
12 methoxyphenyl)amino]-9,9'-spirobifluorene) configuration as illustrated in Fig. 3A. Figure 3B
13 shows J - V curves of the reference and target PSCs under both forward and reverse scans. The
14 reference cell had a maximum PCE of 23.92% with a J_{sc} of 25.72 mA/cm², V_{oc} of 1.153 V and
15 FF of 80.69%. The target PSC had a maximum PCE of 25.59% with a J_{sc} of 26.35 mA/cm²,
16 V_{oc} of 1.189 V and fill factor (FF) of 81.7%. The detailed parameters are summarized in Table
17 1 in the SM. The statistical distribution of the measured PCE of the reference and target PSCs
18 are shown in Fig. 3C. It shows an average PCE of 23.2% and 24.4% for the reference and target
19 PSCs, respectively. To verify the efficiency, we sent one of our best target PSCs to an
20 accredited PV test laboratory (Newport, USA) for certification. Figures S17 and S18 represent
21 a certified quasi-steady-state efficiency of 25.21% with a V_{oc} of 1.174 V, J_{sc} of 26.25 mA/cm²
22 and FF of 81.8%.

23
24 EQE measurements (Fig. 3D) of the FAPbI₃ PSCs were performed to verify the measured J_{sc}
25 above. The EQE of the target PSC was higher than that of the reference cell during the whole
26 visible light absorption region. By integrating the EQE over the AM 1.5G standard spectrum,
27 the projected J_{sc} of the reference and target PSCs are 25.75 and 26.35 mA/cm² respectively,
28 which matches well with the measured J_{sc} under the solar simulator. Figure 3E shows the EQE
29 of the electroluminescence (EQE_{EEL}) of the reference and target PSCs. We know that a solar
30 cell's photovoltage is directly related to the ability to extract its internal luminescence (31).
31 EQE_{EEL} has been successfully used to predict the V_{oc} of PSCs (32). The reference cell had an
32 EQE_{EEL} of 2.2%, while the target cell had an EQE_{EEL} of 10.1% for an injection current density
33 of 25.5 and 26.5 mA/cm² (corresponding to the J_{sc} measured under 1 sun illumination),
34 respectively. Hence, the formate treatment reduces the non-radiative recombination rate 5 times.
35 We derived a bandgap of 1.53 eV for the target film using the Tauc plot (fig. S19). The obtained
36 V_{oc} of 1.21 V (shown in fig. S20) of the target cell shows a record 96.8% of the Shockley-
37 Queisser limit V_{oc} (1.25 V) for an absorption threshold of 1.53 eV (32,33). To further confirm
38 the role of formate, we also provided the PV performance of the devices fabricated using
39 formamidinium acetate additive (fig. S21), which unfortunately showed a negative effect. For
40 the devices fabricated without using MACl additives or passivation layers, formate containing
41 devices still showed an advantage (fig. S22).

42
43 Figure S23, A and B present the J - V responses of the reference and target PSCs under different
44 light intensities. Figure S23C shows a linear relationship (a slope of ~0.95) between J_{sc} and
45 light intensity for both the reference and target PSCs, indicating good charge transport and
46 negligible bimolecular recombination. Figure 3F shows the linear relationship between V_{oc} and
47 the logarithm of light intensities of the FAPbI₃ PSCs. We fitted the data points with a slope of
48 $n_{id}k_B T/q$, where n_{id} is the ideality factor, k_B is the Boltzmann constant, T is temperature, and q
49 is the electric charge. The reference cell had an n_{id} of 1.52, while the target cell had an n_{id} of
50 1.18, which is lower than the previously reported 1.27 by Jiang. *et al* (33). A summary of the

1 detailed PV parameters is given in Table S2 in the SM. The reduced n_{id} indicates a reduced
 2 trap-assisted recombination (34, 35), which is further supported by the space-charge limited
 3 current (SCLC) measurements (fig. S24). We know that for a solar cell where the shunt and
 4 series resistance are negligible, the FF depends only on the V_{oc} divided by $n_{id}k_B T/q$ (36). The
 5 reduced n_{id} in our case also contributes to the increased measured FF of the target PSCs.

6
 7 To assess the stability of our PSCs, we measured first their shelf life by storing unencapsulated
 8 devices in the dark at 25 °C and 20% relative humidity. Figure 4A shows that the PCE of the
 9 reference cell decreased by about 35%, while there was only a 10% degradation for the 2% Fo-
 10 FAPbI₃ cell after 1000-hour aging. A heat stability test was also performed by annealing the
 11 unencapsulated PSC devices at 60 °C under 20% relative humidity. Figure 4B shows that the
 12 2% Fo-FAPbI₃ solar cell retained about 80% of the initial efficiency after 1000-hour aging,
 13 while the reference cell retained only about 40%.



14
 15 **Figure 4.** Stability test of the FAPbI₃ PSCs. (A) The shelf stability of the reference and 2% Fo-
 16 FAPbI₃ PSCs. (B) The heat stability of the reference and 2% Fo-FAPbI₃ PSCs. (C) The
 17 operational stability of the reference and one top performance 2% Fo-FAPbI₃ PSCs. (D) The
 18 long-term operational stability of the reference and 2% Fo-FAPbI₃ PSCs.

19
 20 We further investigated the operational stability of the PSCs by aging the unencapsulated
 21 devices under nitrogen atmosphere at maximum power point (MPP) tracking condition under
 22 simulated one sun illumination. Figure 4C shows the PCE of the PSCs (top performance) under
 23 continuous light soaking using a Xenon lamp. The PCE of the 2% Fo-FAPbI₃ solar cell
 24 remained over 24% after 10-hour MPP tracking, while the PCE of the reference solar cell
 25 decreased down to 22.8%. Figure 4D shows the long-term operational stability of the PSCs.
 26 The PCE of the reference cell decreased by about 30%, while the 2% Fo-FAPbI₃ solar cell only
 27 lost about 15% of its initial efficiency. Note that in this study the temperature of the PSCs was
 28 measured to be around 35°C, as we did not cool the cells during illumination. We recorded the
 29 PV metrics of the devices every 30 mins. Compared to the 2% Fo-FAPbI₃ PSC, the reference
 30 cell had a significant decrease for J_{sc} and FF over the 450-hour MPP tracking test (fig. S25),
 31 suggesting less stable reference perovskite layer. The decline of FF resembles our previous

1 observation (9), where we attributed the decline in FF to a de-doping of the hole conductor due
2 to Li ion migration from the Spiro-MeOTAD to the perovskite layer under illumination (37).

3
4 The relatively better thermal and operational stability of the target cell should be assigned to
5 the improved crystallinity and reduced halide defects of the 2% Fo-FAPbI₃ perovskite films.
6 We know that crystallinity is crucial for the stability of the perovskites as the main degradation
7 process starts from defects near the grain boundaries. The high crystallinity and large grain size
8 of the formate containing perovskite films (validated by the SEM and XRD measurements)
9 suggest fewer grain boundaries, which will contribute to greater stability and performance.
10 Importantly, our simulations and calculations suggest that formate anions have the highest
11 binding affinity to iodide vacancy sites among all halides/pseudo halides thus are the best
12 candidates to eliminate the most abundant and deleterious lattice defects present in halide
13 perovskite films resulting in a dramatic reduction of the trap concentration (validated by SCLC,
14 TRPL and EQE_{EL} measurements). The low level of halide vacancies benefits the stability of
15 the solar cells, as halide vacancies could also act as a main degradation pathway due to photo-
16 induced iodine loss, especially under light illumination.

17 18 **References**

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20 (1) Kojima, A. et al. Organometal halide perovskites as visible-light sensitizer for photovoltaic
21 cells. *J. Am. Chem. Soc.* **131**, 6050-6051 (2009).
22 (2) Grätzel, M. et al. The light and shade of perovskite solar cells. *Nature Materials* **13**, 838-
23 842 (2014).
24 (3) Park, N.-G. et al. Towards stable and commercially available perovskite solar cells. *Nature*
25 *Energy* **1**, 16152 (2016).
26 (4) Correa-Baen, J.-P. et al. Promises and challenges of perovskite solar cells. *Science* **358**,
27 739-744 (2017).
28 (5) Lu, H. et al. Compositional and interface engineering of organic-inorganic lead halide
29 perovskite solar cells. *iScience* **23**, 101359 (2020).
30 (6) Eperon, G. E. et al. Formamidinium lead trihalide: a broadly tunable perovskite for efficient
31 planar heterojunction solar cells. *Energy Environ. Sci.* **7**, 982-988 (2014).
32 (7) Pellet, N. et al. Mixed-organic-cation perovskite photovoltaics for enhanced solar-light
33 harvesting. *Angew. Chem. Int. Ed.* **53**, 3151-3157 (2014).
34 (8) Jeon, N. J. et al. Compositional engineering of perovskite materials for high-performance
35 solar cells. *Nature* **517**, 476-480 (2015).
36 (9) Lu, H. et al. Vapor-assisted deposition of highly-efficient, stable black phase FAPbI₃
37 perovskite solar cells. *Science* **370**, eabb8985 (2020).
38 (10) De Wolf, S. et al. Organometal halide perovskites: sharp optical absorption edge and its
39 relation to photovoltaic performance. *J. Phys. Chem. Lett.* **5**, 1035-1039 (2014).
40 (11) Stranks, S. D. et al. Electron-hole diffusion lengths exceeding 1 micrometer in an
41 organometal trihalide perovskite absorber. *Science* **342**, 341-344 (2013).
42 (12) M. Herz, L. et al. Charge-carrier mobilities in metal halide perovskites: fundamental
43 mechanisms and limits. *ACS Energy Lett.* **2**, 1539-1548 (2017).
44 (13) www.nrel.gov/pv/cell-efficiency.html.
45 (14) Zheng, X. et al. Managing grains and interfaces via ligand anchoring enables 22.3%-
46 efficiency inverted perovskite solar cells. *Nature Energy* **5**, 131-140 (2020).
47 (15) Liu, Z. et al. A holistic approach to interface stabilization for efficient perovskite solar
48 modules with over 2000-hour operational stability. *Nature Energy* **5**, 596-604 (2020).
49 (16) Saliba, M. et al. Cesium-containing triple cation perovskite solar cells: improved stability,
50 reproducibility and high efficiency. *Energy. Environ. Sci.* **9**, 1989-1997 (2016).

- 1 (17) Kim, M. et al. Methylammonium chloride induces intermediate phase stabilization for
2 efficient perovskite solar cells. *Joule* **3**, 1-14 (2019).
- 3 (18) Min, H. et al. Efficient, stable solar cells by using inherent bandgap of α -phase
4 formamidinium lead iodide. *Science* **366**, 749-753 (2019).
- 5 (19) Yang, S. et al. Thiocyanate assisted performance enhancement of formamidinium based
6 planar perovskite solar cells through a single one-step solution process. *J. Mater. Chem. A* **4**,
7 9430-9436 (2016).
- 8 (20) Kim, D. H. et al. Bimolecular additives improve wide-band-gap perovskites for efficient
9 tandem solar cells with CIGS. *Joule* **3**, 1734-1745 (2019).
- 10 (21) Kim, D. et al. Efficient, stable silicon tandem cells enabled by anion-engineered wide-
11 bandgap perovskites. *Science* eaba3433 (2020).
- 12 (22) Walker, B. et al. Pseudohalides in lead-based perovskite semiconductors. *Adv. Mater.* **31**,
13 1807029 (2019).
- 14 (23) T. Moore, D. et al. Direct crystallization route to methylammonium lead iodide perovskite
15 from an ionic liquid. *Chem. Mater.* **27**, 3197-3199 (2015).
- 16 (24) Seo, J. et al. Ionic liquid control crystal growth to enhance planar perovskite solar cells
17 efficiency. *Adv. Energy Mater.* **6**, 1600767 (2016).
- 18 (25) K. Nayak, P. et al. Mechanism for rapid growth of organic-inorganic halide perovskite
19 crystals. *Nat Commun.* **7**, 13303 (2016).
- 20 (26) Meng, L. et al. Improved perovskite solar cell efficiency by tuning the colloidal size and
21 free ion concentration in precursor solution using formic acid additive. *Journal of Energy*
22 *Chemistry.* **41**, 43-51 (2020).
- 23 (27) Khan, Y. et al. Waterproof perovskites: high fluorescence quantum yield and stability from
24 a methylammonium lead bromide/formate mixture in water. *J. Mater. Chem. C* **8**, 5873-5881
25 (2020).
- 26 (28) Askar, A. et al. Composition-tunable formamidinium lead mixed halide perovskites via
27 solvent-free mechanochemical synthesis: decoding the Pb environments using solid-state NMR
28 spectroscopy. *J. Phys. Chem. Lett.* **9**, 2671-2677 (2018).
- 29 (29) J. Kubicki, D. et al. Cation Dynamics in Mixed-Cation (MA)_x(FA)_{1-x}PbI₃ Hybrid
30 Perovskites from Solid-State NMR. *J. Am. Chem. Soc.* **139**, 10055-10061 (2017).
- 31 (30) Zhou, Z. et al. Synthesis, microwave spectra, x-ray structure, and high-level theoretical
32 calculations for formamidinium formate. *J. Chem. Phys.* **150**, 094305 (2019).
- 33 (31) Ross, R. et al. Some Thermodynamics of Photochemical Systems. *J. Chem. Phys.* **46**,
34 4590-4593 (1967).
- 35 (32) Tress, W. et al. Predicting the open-circuit voltage of CH₃NH₃PbI₃ perovskite solar cells
36 using electroluminescence and photovoltaic quantum efficiency spectra: the role of radiative
37 and non-radiative recombination. *Adv. Energy Mater.* **5**, 1400812 (2015).
- 38 (33) Jiang, Q. et al. Surface passivation of perovskite film for efficient solar cells. *Nat. Photonics*
39 **13**, 460-466 (2019).
- 40 (34) Yang, D. et al. Surface optimization to eliminate hysteresis for record efficiency planar
41 perovskite solar cells. *Energy Environ. Sci.* **9**, 3071-3078 (2016).
- 42 (35) Kuik, M. et al. Trap-assisted recombination in disordered organic semiconductors. *Phys.*
43 *Rev. Lett.* **107**, 256805 (2011).
- 44 (36) Green, M. Accuracy of analytical expressions for solar cell fill factors. *Solar cells.* **7**, 337-
45 340 (1982).
- 46 (37) Wang, Y. et al. Stabilizing heterostructures of soft perovskite semiconductors. *Science*
47 **365**, 687-691 (2019).

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49 **Data availability:** The data that support the findings of this study are available from the
50 corresponding author upon reasonable request.

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Code availability: The code used for this study are available from the corresponding author upon reasonable request.

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