

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/172332/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Lim, Jihoo, Kim, Jaehui, Davies-Jones, Josh, Danaie, Mohsen, Choi, Eunyoung, Shim, Hongjae, Chen, Liang, Kim, Jincheol, Kim, Judy S., Davies, Philip R. , Seidel, Jan, Green, Martin A., Stranks, Samuel D., Il Seok, Sang and Yun, Jae Sung 2024. Benign methylformamidine byproduct induced by cation heterogeneity inhibits local formation of δ -phase perovskites. *Energy & Environmental Science* 17 (23) , pp. 9134-9143. 10.1039/D4EE03058C

Publishers page: <http://dx.doi.org/10.1039/D4EE03058C>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



Benign methylformamidinium byproduct induced by cation heterogeneity inhibits local formation of d-phase perovskites†

Jihoo Lim,^{‡a} Jaehui Kim,^{‡b} Josh Davies-Jones,^{ic} Mohsen Danaie,^{id} Eunyoung Choi,^{de} Hongjae Shim,^a Liang Chen,^b Jincheol Kim,^{id} Judy S. Kim,^{ig} Philip R. Davies,^{id} Jan Seidel,^{id} Martin A. Green,^a Samuel D. Stranks,^{id} Sang Il Seok^{id,*b} and Jae Sung Yun^{id,j}

Efforts to enhance the efficiency and stability of formamidinium lead triiodide (FAPbI₃) perovskite solar cells (PSCs) have primarily focused on employing methylammonium chloride (MACl) as an effective additive. MACl significantly improves the crystallinity and lowers the d-to-a phase transition temperature of FAPbI₃, thereby contributing to the remarkable efficiency of these solar cells. However, upon evaporation with deprotonation of MACl during annealing, the highly reactive methylamine leads to the formation of N-methylformamidinium (MFA⁺) cations. Despite their potential for significant influence on the properties of FAPbI₃ perovskites, the chemical and optoelectronic characteristics of MFA⁺ in FAPbI₃ remain poorly understood. This study investigates the unexplored role of MFA⁺ in FAPbI₃ perovskite with MACl incorporation through advanced nanoscale characterization techniques, including photo-induced force microscopy (PiFM), four-dimensional scanning transmission electron microscopy (4D-STEM), and wavelength-dependent Kelvin probe force microscopy (KPFM). We reveal that MACl induces compositional heterogeneities, particularly formamidinium (FA⁺) and MFA⁺ cation inhomogeneities. Surprisingly, MACl selectively promotes the formation of MFAPbI₃ at grain boundaries (GBs) and as clusters near GBs. Additionally, we confirm that MFAPbI₃ is a wide bandgap, and charge carriers are effectively separated at GBs and clusters enriched with MFAPbI₃. This is particularly interesting because MFAPbI₃, despite its crystal structural similarity to yellow phase d-FAPbI₃, displays a high surface photovoltage, and does not deteriorate the solar cell performance. This study not only provides insights into the byproduct formation of MFA⁺ induced by local cation heterogeneity after employing MACl, but also guides a crucial perspective for optimizing formamidinium-based PSC design and performance.

Broader context

Formamidinium lead triiodide (FAPbI₃) based perovskite solar cells (PSCs) have demonstrated significant advancements, nearly reaching the maximum theoretical efficiency of single-junction solar cells. However, they are known to be metastable and undergo a phase transition from corner-sharing FAPbI₃ perovskite to the undesirable wide-bandgap face-sharing d-FAPbI₃ perovskite. To address this challenge, methylammonium chloride (MACl) has been widely

^a Australian Centre for Advanced Photovoltaics (ACAP), School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, NSW 2052, Australia. E-mail: j.yun@surrey.ac.uk

^b Department of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-Gil, Eonyang-eup, Ulju-gun, Ulsan 44919, Republic of Korea. E-mail: seoksi@unist.ac.kr

^c Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK

^d Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK

^e Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge, CB3 0AS, UK

^f Sustainable Energy Research Centre, School of Engineering, Macquarie University, Sydney, NSW 2109, Australia

^g Department of Materials, University of Oxford, Oxford, OX1 3PH, UK

^h School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

ⁱ ARC Centre of Excellence in Future Low-Energy Electronics Technologies (FLEET), University of New South Wales, Sydney, NSW 2052, Australia

^j Department of Electrical and Electronic Engineering, Advanced Technology Institute (ATI), University of Surrey, Guildford, GU2 7XH, UK

employed as a universal additive to enhance the performance of FA-based PSCs. However, upon evaporation with deprotonation of MACl during annealing, the highly reactive methylamine leads to the formation of N-methylformamidinium (MFA^+) cations. Despite the potential for significant impact of MFA^+ on the properties of FAPbI₃ perovskites, the chemical and optoelectronic characteristics of MFA^+ in FAPbI₃ remain poorly understood. In this work, we elucidate that the incorporation of MACl additive in FAPbI₃ perovskite induces the heterogeneous distribution of FA^+ cations, promoting the selective formation of MFA^+ -complexes primarily at grain boundaries (GBs) or in cluster formations, while concurrently suppressing the unwanted formation of d-phase perovskites near GBs. Furthermore, we demonstrate that the MFA^+ -byproduct, despite its crystal structural similarity to the yellow phase d-FAPbI₃, exhibits benign characteristics, displaying a high surface photovoltage, and not serving as non-radiative recombination sites.

Introduction

Tremendous efforts have been devoted to the study of solution-processed perovskite solar cells (PSCs), which have reached power conversion efficiencies (PCE) surpassing 26%.¹ Until now, formamidinium lead triiodide (FAPbI₃) based PSCs have been the predominant materials employed as highly efficient PSCs that report record-efficiencies.^{2,3} However, they are known to be metastable and undergo a phase transition from the corner sharing FAPbI₃ perovskite into the undesired wide-bandgap face sharing d-FAPbI₃ perovskite. In this context, methylammonium chloride (MACl) has been widely incorporated as a universal additive for enhancing the performance of FA-based PSCs, including those high-efficiency PSCs.^{2–9} MACl effectively inhibits the unwanted phase conversion of FA-based perovskite, fosters grain growth, and improves crystallinity, consequently enhancing device performance.^{10,11}

It has been reported that most MACl additives evaporate during the annealing process,^{10,12,13} resulting from deprotonation. This deprotonation process results in the formation of volatile methylamine (MA^0), which subsequently reacts with FA^+ cations, ultimately producing N-methyl formamidinium iodide (MFAI).^{14–18} Recently, Seok's group first demonstrated MACl additives in single crystal FAPbI₃ perovskite led to the predominance of cis-MFAI as the resulting species, ultimately forming cis-MFAPbI₃ perovskite following a reaction with lead iodide (PbI_2). However, the role of MFAPbI₃ within the final FAPbI₃ film after MACl incorporation and its effect on the device performance remain unknown.

Additionally, it is noteworthy that the incorporation of additives in a precursor solution often results in compositional heterogeneities across multiple orders of magnitude in size.¹⁹ The existence of nanoscale halide inhomogeneities and segregation have been intensively reported.^{20–25} However, only a handful of studies have reported the cation inhomogeneities in perovskites^{26–28} despite their potential significance in determining the performance of PSCs. Surprisingly, even though there is widespread utilization of MACl additive to achieve highly efficient FA-based PSCs, there has not been a thorough investigation of how the MACl additive contributes to local cation inhomogeneities or the principal locations where MFA^+ byproducts are generated.

Here, we reveal that MACl additive in FAPbI₃ perovskite leads to the heterogeneous FA^+ distribution across the surface and in the bulk and facilitates the selective formation of MFAPbI₃ mainly at the grain boundaries (GBs) rather than in the neighbouring grains. Also, FA^+ deficient and MFAPbI₃ rich

clusters with a size of 400–600 nm are formed near GBs. Through photo-induced force microscopy (PiFM), we confirm the presence of FA^+ -deficient clusters, with GBs emerging as primary sites for MFA^+ formation. Our four-dimensional scan-ning transmission electron microscopy (4D-STEM) results indicated the crystal structure of MFAPbI₃ exhibits d-FAPbI₃ perovskite-like diffraction pattern. Moreover, our investigation into the electrical properties of MFA^+ -rich regions, utilizing wavelength-dependent Kelvin probe force microscopy (KPFM), uncovered an intriguing enhancement in charge separation within FA^+ -deficient clusters and GBs, suggesting a beneficial role for selective formation of MFA^+ -complexes, instead of undesired d-phase FAPbI₃ perovskites near GBs, resulting in improving device performance.

To investigate the nanoscale chemical heterogeneity in pure FAPbI₃ perovskites, we conducted PiFM measurement. A schematic of the PiFM measurement setup is shown in Fig. 1(a). PiFM is a technique for spectral imaging that enables the mapping of AFM topography and broadband infrared (IR) response of a sample surface simultaneously, with high spatial resolution at the nanoscale.^{29,30} By using the contrast in morphology and IR broadband intensity from the PiFM images, analysis of the IR spectrum at specific locations of interest can be performed. For instance, the distinct chemical compositions of individual, different grains and GBs can be investigated precisely as represented in Fig. 1(b). The two different modes utilized in PiFM modulation are shown in Fig. S1 (ESI†). The direct mode involves the excitation of cantilever vibration at the initial resonance frequency (f_1) while tuning the repetition rate of the laser excitation to the second resonance frequency (f_2). This allows simultaneous extraction of topography and PiFM signals at the two frequencies, thereby enabling the study of bulk properties (B250 nm depth). The sideband mode uses frequency mixing ($f_1 f_2$ or $f_1 + f_2$) to generate a difference with frequency at the cantilever resonance, which leads to a response that is confined to the surface (B20 nm depth) at the interface of the tip and the sample.^{31,32}

As shown in Fig. 1(c and d), we first obtained PiFM images for pure FAPbI₃, at 1713 cm^{-1} , well-established IR peak for CQN symmetric stretching of FA^+ cation,³³ using two different scanning modes to investigate the surface and bulk region, respectively. Corresponding topography images can be found in Fig. S2 (ESI†). Interestingly, the pure FAPbI₃ perovskite exhibits a heterogeneous and random distribution of FA^+ , both at the surface and in the bulk. The point spectra recorded in Fig. 1(e) indicate that the nominally pure FAPbI₃ perovskite exhibits a weak IR peak at 1355 cm^{-1} , compared to 1713 cm^{-1} at both the

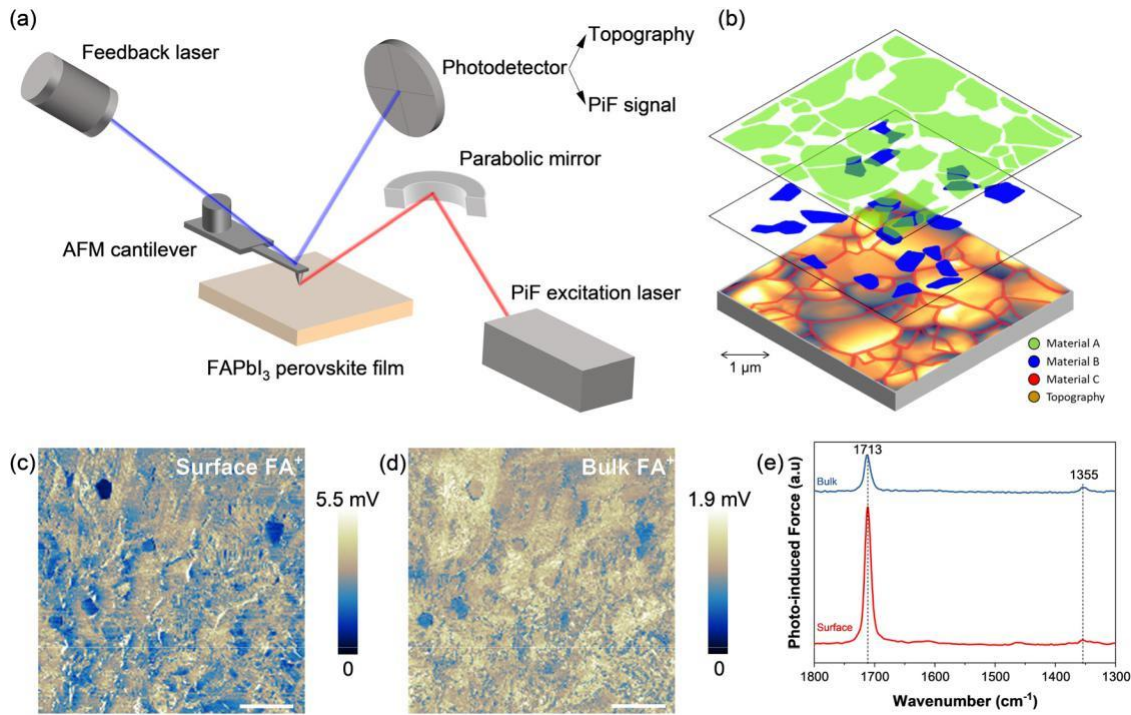


Fig. 1 Photo-induced force microscopy (PiFM) measurement. (a) Schematic of PiFM setup, (b) perovskite film with different chemical compositions for grains and grain boundaries, (c) and (d) PiFM images at 1713 cm^{-1} at the surface and in the bulk of FAPbI₃ perovskite without MACl incorporation (the scale bar represents $1\text{ }\mu\text{m}$, and the colour scale indicates the strength of the PiFM signal, effectively the strength of the 1713 cm^{-1} band), and (e) corresponding IR spectra of pure FAPbI₃ perovskite.

surface and in the bulk of the film. This can be attributed to the presence of the d-FAPbI₃ phase,³⁴ showing some degree of unwanted phase impurities. Further information can be gained by comparing the relative IR peak intensities at 1713 cm^{-1} and 1355 cm^{-1} in the surface and bulk IR spectra, where the 1355 cm^{-1} peak is relatively stronger in the bulk spectrum, suggesting more phase transition in the bulk than in the surface region.

To explore how the different amounts of MACl in the precursor solution affect the heterogeneous distribution of FA⁺ in the resulting FAPbI₃ perovskite films shown in Fig. 1(c and d), we employ PiFM measurements probing the surface and bulk regions. The topography images can be seen in Fig. 2(a–c). As widely reported, the incorporation of MACl promotes the enlarged grain size.¹³ Fig. 2(d–f) shows the surface PiFM images at 1713 cm^{-1} (FA⁺) of FAPbI₃ perovskites with 15, 50, and 80 mol% of MACl. As the amount of MACl increases in the FAPbI₃ perovskite, the selectivity of FA⁺ with certain grains near GBs, referred to as ‘clusters’, still exists and increases until 50 mol%, yet the distribution becomes less heterogeneous for the FAPbI₃ perovskite with 80 mol%. Recently, it was reported that enhanced dynamical freedom of FA⁺ cations within FA⁺-rich regions could potentially serve as a significant driving force for clustering MA⁺ and FA⁺ cations in FAMA mixed-cation perovskites.³⁵

Notably, the FAPbI₃ perovskite with 50 mol% exhibits the most distinguished contrast between the GBs and neighbouring grains, along with FA⁺-deficient clusters marked with white

arrows. We then obtained bulk PiFM images, as shown in Fig. 2(g–i). From Fig. S3 (ESI†), we can clearly see the highest degree of heterogeneity with the FAPbI₃ perovskite with 50 mol% in surface region, and a relatively less heterogeneous distribution of FA⁺ in bulk, regardless of the amount of MACl. We then calculate the surface-to-bulk ratio of FA⁺, as shown in Fig. S4 (ESI†). The FAPbI₃ perovskites with 50 mol% of MACl exhibit the highest and the lowest surface-to-bulk ratio of FA⁺ at GBs and clusters, respectively, representing the greatest contrast between GBs and clusters at the surface region. To correlate this chemical heterogeneity to optoelectronic performance, we fabricate the FAPbI₃ PSCs with the corresponding compositions, and the results are summarised in Fig. S5 (ESI†). The FAPbI₃ perovskite device with 50 mol% of MACl shows the highest PCE of 24.2%, while exhibiting the least hysteresis as shown in Fig. S6 (ESI†). However, the role of nanoscale selectivity of FA⁺ at the GBs of FAPbI₃ perovskite with 50 mol% of MACl should be further investigated.

We then investigated the surface and bulk IR spectra of FAPbI₃ perovskites with varying amounts of MACl, as shown in Fig. 3(a and b). IR spectra were obtained by averaging measurements from three different locations: grains, FA⁺-deficient grains and GBs. This approach accounts for intensity variations of FA⁺ within both grains and GBs, as shown in Fig. S7 (ESI†). For the surface region, all FAPbI₃ perovskites with MACl additives exhibit IR peaks at 1713 cm^{-1} , and 1355 cm^{-1} , which indicate FA⁺, and d-FAPbI₃ phase, respectively. From Fig. 3(a), because of excessive MACl addition, only FAPbI₃ perovskite

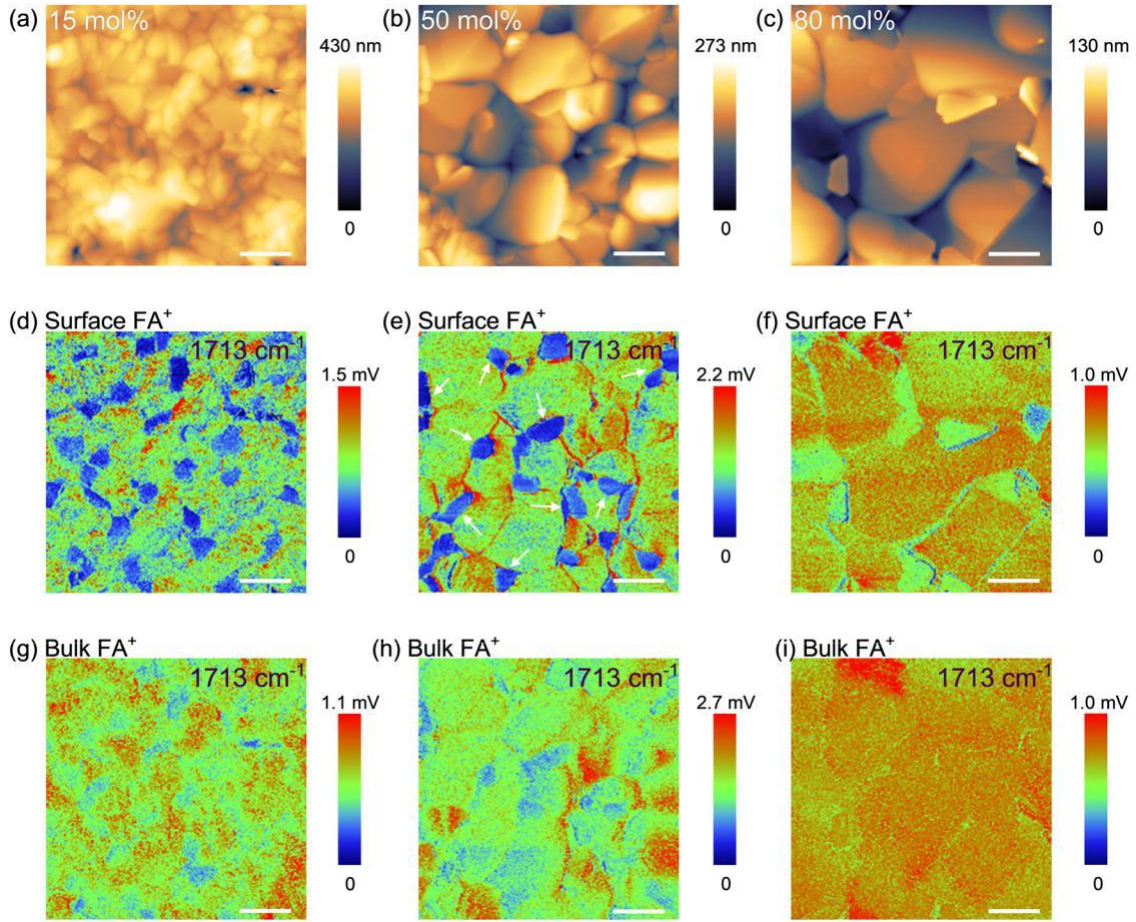


Fig. 2 (a)–(c) Topography images of FAPbI₃ perovskites with increasing amounts of MACl in the precursor solution, (d)–(f) PiFM images at 1713 cm⁻¹ in the surface region, and (g)–(i) in the bulk region. The scale bar represents 1 μm.

with 80 mol% of MACl exhibits a strong peak at 1465 cm⁻¹ in the surface region, which indicates symmetric NH₃⁺ bending of MA⁺ cation.³³ As a result of the evaporation of most MACl after the annealing process,^{10,12} the peak signal for MA⁺ is significantly weak compared to that of FA⁺ peak at 1713 cm⁻¹ in IR spectra for both FAPbI₃ perovskites with 15 and 50 mol% of MACl. Despite the weaker signal in IR spectra, PiFM images at 1465 cm⁻¹ for MA⁺ shown in Fig. S8 (ESI†) represents a slightly stronger contrast variation at GBs for both surface and bulk regions, exclusively for FAPbI₃ perovskite film with 50 mol% of MACl incorporation.

Interestingly, all MACl-incorporated FAPbI₃ (15–80 mol%) exhibit significant peak broadening at around 1355 cm⁻¹, which is highlighted as region ‘A’ in Fig. 3(a) and similarly from Fig. 3(b), this is also observed in bulk IR spectra. Fig. 3(c–e) shows magnified IR spectra of each of the three perovskite films at around 1355 cm⁻¹, which were deconvoluted using the Gaussian function to identify the precise components. All three spectra show two components, wherein the first peak at 1355 cm⁻¹ indicates d-FAPbI₃ phase, and the second peak at around 1346 cm⁻¹ indicates partial CQN for MFA⁺ cation,³⁴ attributed from MACl incorporation into FAPbI₃ perovskite. FAPbI₃ perovskite with the optimal amount of MACl

(50 mol%) exhibits B4 times higher peak intensity of MFA⁺ compared to other films, and the ratio of MFA⁺ is B1.8 and B2.5 times higher than that of FAPbI₃ perovskite with 15 and 80 mol% of MACl additive, respectively. This is consistent with the recent work from Stranks and his colleagues showing that the presence of MA⁺ induces octahedral tilt, suppressing the undesired formation of polytypes.²⁵ Moreover, Seok’s group recently reported that MFAPbI₃ has a similar crystal structure to d-FAPbI₃ phase.³⁴ Thus, in order to precisely differentiate between d-FAPbI₃ and MFAPbI₃, we obtained PiFM image at 1610 cm⁻¹. This peak also indicates partial CQN bonding of MFA⁺ cation,³⁴ along with 1346 cm⁻¹, as presented in Fig. 3(f and g), since 1346 cm⁻¹ is too close to the peak indicating d-FAPbI₃ phase (1355 cm⁻¹).

In the PiFM image at 1610 cm⁻¹, a more homogeneous signal within neighbouring grains is evident, along with a pronounced contrast between GBs and grains. This observation suggests the selective formation of MFA⁺ primarily at FA⁺-rich GBs (marked in red) and clusters of FA⁺-deficient clusters (presented in blue, marked with white arrows) shown in Fig. 2(e), which is notably absent in the bulk region, owing to the highly specific distribution of FA⁺ in the surface region. This can also be seen in Fig. 3(h), which shows the overlaid two

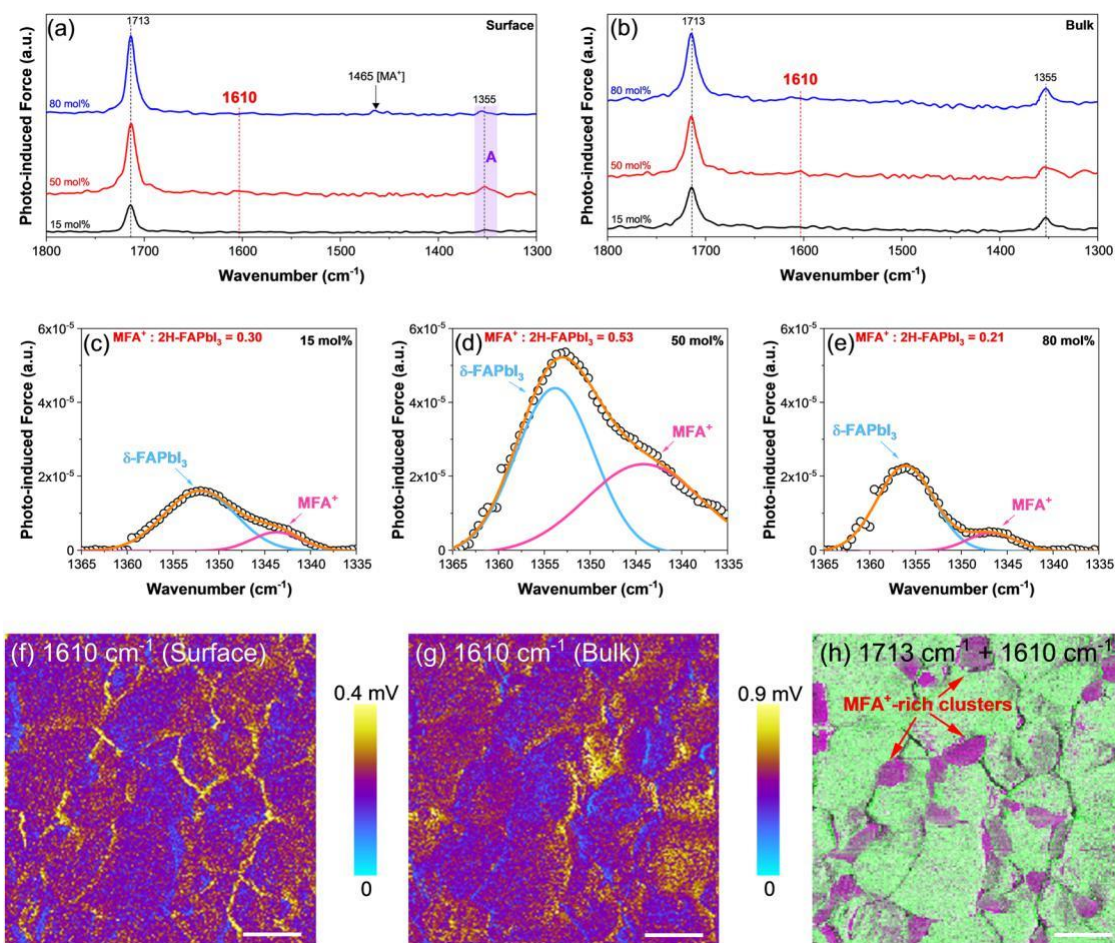


Fig. 3 Selective formation of MFA^+ at GBs of FAPbI_3 perovskite with optimal amount of MACl . (a) and (b) Surface and bulk IR spectra obtained from PiFM for FAPbI_3 perovskites with varying amounts of MACl , (c)–(e) deconvolution of peaks from the highlighted region ‘A’ in figure (a), (f) and (g) surface and bulk PiFM image at 1610 cm^{-1} , and (h) overlaid two PiFM images of FA^+ (green) and MFA^+ (purple) in the surface region of FAPbI_3 perovskite with optimal amount of MACl . The scale bar represents $1\text{ }\mu\text{m}$.

PiFM images of FA^+ and MFA^+ cations, colored in green and purple, respectively. As opposed to heterogeneous $\delta\text{-FAPbI}_3$ phase grains (in dark navy) of pure FAPbI_3 perovskite shown in Fig. 1(c and d), it can be concluded that FAPbI_3 perovskite with the optimal amount of MACl exhibits the heterogeneous MFA^+ -rich GBs and clusters near the GBs.

To identify the formation of MFA^+ after MACl incorporation into FAPbI_3 perovskites, we first compared $^1\text{H-NMR}$ measurement of FAPbI_3 perovskite solutions and films with different amounts of MACl as shown in Fig. S9 (ESI†). Previous reports indicated that MFA^+ can form during perovskite solution aging.^{36–38} To determine if the MFA^+ formation occurs during the preparation of the perovskite precursor solution, we included $^1\text{H-NMR}$ measurements of freshly prepared FAPbI_3 perovskite solutions with varying amounts of MACl (0, 15, 50, and 80 mol%). The $^1\text{H-NMR}$ spectrum of pure FAPbI_3 (without any MACl additive) precursor solution and perovskite film both exhibit three peaks at 2.50, 3.32, and 7.85 ppm, which indicate DMSO , H_2O , and FA^+ , respectively. Interestingly, a new peak at 2.37 ppm (MA^+) arises in the precursor solutions after MACl incorporation. However, for final MACl -incorporated FAPbI_3

perovskite films, no MA^+ peak is observed, regardless of the amount added due to the evaporation of most of the MACl additive during the annealing process.^{17,39} However, the magnified $^1\text{H-NMR}$ spectra in Fig. S10 (ESI†) show that two new peaks appeared at 2.81 and 7.96 ppm for MACl incorporated FAPbI_3 perovskites, which are only evident in the film $^1\text{H-NMR}$ results, indicating that the deprotonation of MACl occurs during the fabrication of the perovskite film. These peaks are attributed to MFA^+ , as the hydrogens of the methyl functional group ($-\text{CH}_3$), and the hydrogens in the carbon of amidines ($-\text{CH}$), respectively.³⁴ In addition, the calculated molar fractions of A-site cations for increasing the amount of MACl from 0 to 80 mol% from $^1\text{H-NMR}$ measurement of perovskite films are shown in Table S1 (ESI†). It is noticeable that the MFA^+ content for FAPbI_3 with 50 mol% MACl additive is the highest among others and is higher than that of MA^+ . Therefore, we can confirm that the byproduct MFA^+ , rather than $\delta\text{-FAPbI}_3$ is formed at both the GBs and those FA^+ -deficient (MFA^+ -rich) clusters near the GBs as shown in Fig. 3(h).

To investigate structural change after introducing the MACl additive further, scanning electron diffraction (SED)

measurements were conducted for the FAPbI₃ perovskite with the optimal amount of MACl incorporation, as this analysis can provide nanoscale orientation and phase mapping information. We used the open-source software py4DSTEM for analysing the SEND data, as presented in Fig. S11 (ESI†). As shown in Fig. S12 and S13 (ESI†), the majority of the FAPbI₃ perovskite with 50% mol of MACl could be indexed as pseudo-cubic (close to cubic) FAPbI₃ phase. We note that previous works have demonstrated that FA-rich mixed-cation perovskites exhibit tetragonal structure with octahedral tilting induced by cation alloying,^{40,41} resulted from frustrating the transformation from photoactive a-FAPbI₃ to performance-limiting d-phases. However, this is not resolved as the fraction of FAPbI₃ is increased.⁴⁰ Fig. 4(a) compares the Bragg peaks identified in one example dataset with powder pattern simulations of simplified FAPbI₃ (top)⁴² and MFAPbI₃ (bottom)³⁴ phases, which were adapted from the recent work.³⁴ By forming virtual annular dark-field (ADF) images from the non-overlapping Bragg reflections at the lowest scattering angles ($0.156 \text{ \AA}^{-1}$ for pseudo-cubic FAPbI₃ and $0.13 \text{ \AA}^{-1}$ for MFAPbI₃ phase – also presented as blue arrows in Fig. 4(a)), we could locate the minority MFAPbI₃ phase (see Fig. S11, ESI†).

Though this method underestimates the coverage of the MFAPbI₃ phase in the sample, it was adopted to ensure we avoid regions where these two phases were both sampled through the thickness of the film. The applied masks in real space (squares in Fig. 4(b)) indicate the regions identified as each phase where the blue and green squares are identified as pseudo-cubic FAPbI₃ and the red square as the MFAPbI₃ phase, as shown in Fig. 4(c and e), respectively. These results intuitively demonstrate the possible formation of MFAPbI₃ phases in addition to the formation of pseudo-cubic FAPbI₃ phases, when the optimised quantity of MACl is introduced into FAPbI₃ perovskites.

In addition, the phase in contrast to pseudo-cubic FAPbI₃ could be identified even through the smallest Bragg peak of MFAPbI₃ shown in Fig. 4(a). By using the strongest Bragg peak, which can be clearly distinguished as the MFAPbI₃ phase, we further investigated where these phases are mainly formed. We are using the reflection at $0.288 \text{ \AA}^{-1}$ of this phase instead (see highlighted Bragg peak with a blue rectangle in Fig. 4(a)). In the virtual images constructed shown in Fig. 4(g and h), although we see some of the pseudo-cubic FAPbI₃ phases with overlapping reflection also appearing, we observe several cases of what we identify to be the MFAPbI₃ phases around the GB regions, which are shaded in yellow, in Fig. 4(b and h). Moreover, we identified a peak at $0.23 \text{ \AA}^{-1}$, corresponding to the 2H-FAPbI₃ phase (highlighted with a green rectangle – please see Fig. S14, ESI†), which allows us to show that some of the regions overlap with those identified at $0.13 \text{ \AA}^{-1}$ for the MFAPbI₃ phase as shown in Fig. S15 (ESI†). It is indeed challenging and necessitates further investigation to clearly distinguish between the two different phases. This difficulty aligns with the previously reported similarity in crystal structures between the MFAPbI₃ and 2H-FAPbI₃ phases.³⁴ Nevertheless, this result coincides with the selective formation of

MFA⁺ at both the GBs and those clusters near the GBs after incorporating the optimal amount of MACl into the FAPbI₃ perovskite, which are shown in red arrows in Fig. 4(g and h), and as we discussed above (see Fig. 3(h)).

To gain further insight into the electrical properties of the selective formation of the MFAPbI₃ at the GBs and those clusters that resulted from the addition of MACl, we performed wavelength-dependent Kelvin probe force microscopy (KPFM). Considering the wide-bandgap characteristic of MFAPbI₃, similar to 2H-FAPbI₃ perovskite,³⁴ we employed two different wavelengths (400 and 800 nm), which allowed us to differentiate the high and low bandgap regions, respectively (see Fig. S16, ESI†). We calibrated the intensity of the laser excitation for different wavelengths, and the detailed information can be found in the Experimental section.

We first compared FAPbI₃ perovskite film labeled as “Target” containing the optimal amount of MACl with its counterpart referred to as “Control”, pure FAPbI₃ perovskite film, representing without any incorporation of MACl. Fig. 5(a and c) shows topography images, and Fig. 5(b and d) represents contact potential difference (CPD) spatial maps obtained in the dark condition of Control and Target film, respectively. This shows inhomogeneous CPD distribution between grain to grain due to a variation in work function. Based on the PiFM measurement results shown in Fig. 1(c) and 3(f), we suspect that such inhomogeneity can be related to cation heterogeneity and the existence of 2H-FAPbI₃. To precisely identify the electronic properties, we measured CPD under illumination using two different wavelengths to investigate high and low bandgap regions. CPD is obtained by calculating the difference in the work function of the sample surface and the tip, which has a known work function.

The dark CPD distribution curves for each sample are shown in Fig. S17 (ESI†), and we found that the peak position of Control film is 0.271 V and 0.133 V for Target film. We calculated the work function of each sample by subtracting the CPD at the peak position from the work function of the tip, which is 4.93 eV. As can be seen, the work function of the Target perovskite surface has increased than that of Control film. This increase in work function could be attributed to the shift of the Fermi energy level towards the valence band, indicating that the material has become more p-type by passivation of the perovskite surface⁴³ with the reduced density of shallow traps such as halide vacancy defects at GBs induced by the MACl incorporation.⁴⁴

Subsequently, the surface photovoltage (SPV) maps were obtained by subtracting the CPD maps measured under laser illumination (Fig. S18, ESI†) from the CPD obtained in dark condition (Fig. 5(c and d)) as represented in Fig. 5(e and h). As shown in Fig. 5(e and f), the heterogeneous clusters of Control film exhibit brighter contrast and higher SPV than that of neighbouring grains and GBs under 400 nm illumination and higher SPV for normal grains compared to those clusters and GBs under 800 nm illumination. This identifies that such inhomogeneity originates from the 2H-FAPbI₃ phase due to its wide bandgap characteristic and is well-matched with the

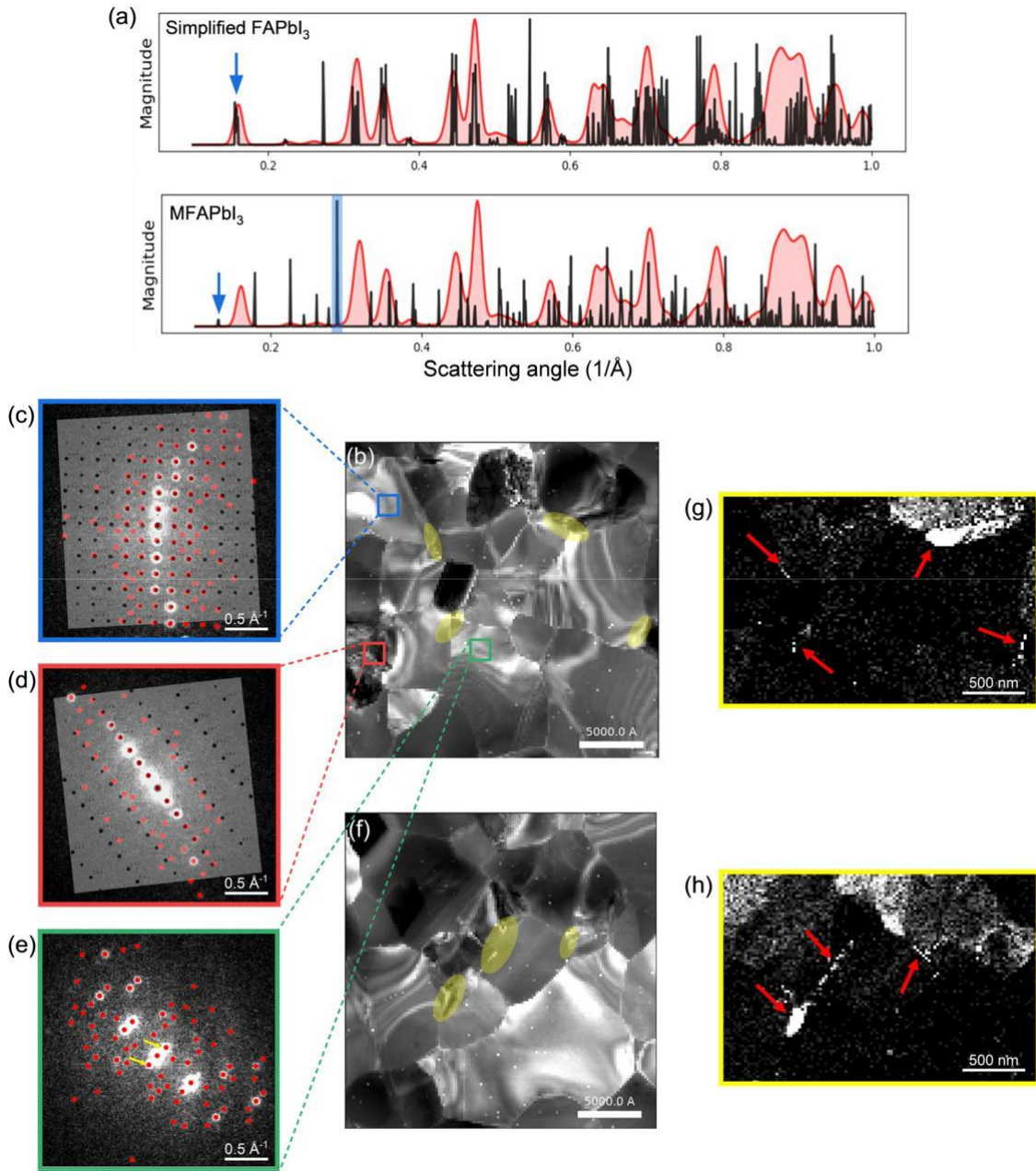


Fig. 4 (a) Comparison of the identified peaks in SEND data (in red) with the simulated power diffraction patterns of simplified FAPbI₃ phase (top) and MFAPbI₃ (bottom), which are in black lines. The majority of the peaks can be seen to correspond to pseudo-cubic FAPbI₃ phase. The peaks labelled with a blue arrow were used to form virtual images as one of the two routes to identify the MFAPbI₃ regions. (b) VADF image of example SED data, regions marked with squares are used to obtain sum diffraction patterns, (c) sum diffraction pattern and overlaid simulated patterns as a pseudo-cubic FAPbI₃ phase close to [010] zone axis (blue square), (d) close to [012] zone axis (green square). The region in (e) is identified as MFAPbI₃ with yellow arrows marking $0.13 \text{ \AA}^{-1}$ reflections. (f) VADF image of another example SED data, and (g) and (h) corresponding virtual images using the peak highlighted with a blue rectangle in figure (a) for the MFAPbI₃ phase at $0.288 \text{ \AA}^{-1}$ reflections, marked with red arrows.

existence of 2H-FAPbI₃ from our PiFM results shown in Fig. 1. On the other hand, the MFAPbI₃-rich grains and GBs of Target film exhibit brighter contrast and higher SPV compared to that of neighbouring grains under both 400 and 800 nm illumination, as can be seen in Fig. 5(g and h). To differentiate inhomogeneous clusters in Control from the ones in Target film, calculated SPV values of Control and Target film at two

different wavelengths for GBs, grains, and heterogeneous clusters (2H-FAPbI₃- or MFAPbI₃-phases) are shown in Fig. 5(i and j), respectively.

Using 400 and 800 nm wavelengths excitation not only can differentiate the bandgap, but also can identify the surface and bulk characteristics. For Control film, SPV of 2H-FAPbI₃ phase is higher and lower than that of normal grains and GBs under

illumination using 400 nm, and 800 nm, respectively, indicating that 2H-FAPbI₃-phase grains are high-bandgap material, and behave as recombination centres,^{25,45} which confirms that those clusters are 2H-FAPbI₃ phase. Moreover, overall SPV values of 800 nm are higher than those of 400 nm, which is attributed to defects at the surface induced by 2H-FAPbI₃ phase. In contrast, the SPV of MFAPbI₃-phase grains and GBs are higher for Target film under 400 nm excitation than that of

800 nm, indicating MFAPbI₃-phase clusters and GBs are high bandgap materials but with reduced surface defects compared to Control film. This indicates the improved charge separation on the surface and in the bulk at MFAPbI₃-phase clusters and GBs. Therefore, we can confirm the existence of MFAPbI₃-phases at both the GBs and those clusters near the GBs, instead of 2H-FAPbI₃-phases for Target perovskite film.

Considering that MFAPbI₃ is chemically formed by the interaction of FA⁺ with MA⁰ after MACl incorporation,³⁴ the segregated formation of MFAPbI₃ at GBs and inhomogeneous

grains near GBs are attributed to effective passivation at GBs^{46,47} and accelerates byproduct formation of MFA⁺. Fig. 5(k and l) represents two distinct energy level schematics with 2H-FAPbI₃ or MFAPbI₃ located at GBs for Control and Target perovskite films, respectively, based on UPS measurements shown in Fig. S19 (ESI[†]). 2H-FAPbI₃-phases at GBs for Control film induces clusters of deep trap sites, leading to non-radiative recombination,^{25,45} as can also be seen from the steady-state spectral photoluminescence (PL) measurement shown in Fig. S20 (ESI[†]). On the other hand, MFAPbI₃ at GBs for Target film, due to the higher bandgap of MFAPbI₃-complexes than that of FA⁺-ones,³⁴ the segregated formation of large bandgap MFAPbI₃-phases at the GBs and clusters near GBs leads to forming gradient in the bandgap and suppressing charge recombination^{48,49} between GBs and neighbouring grains. This results in efficient hole and electron extraction toward the GBs and neighbouring grains. Therefore, the optimal amount of MACl results in improved device performance of

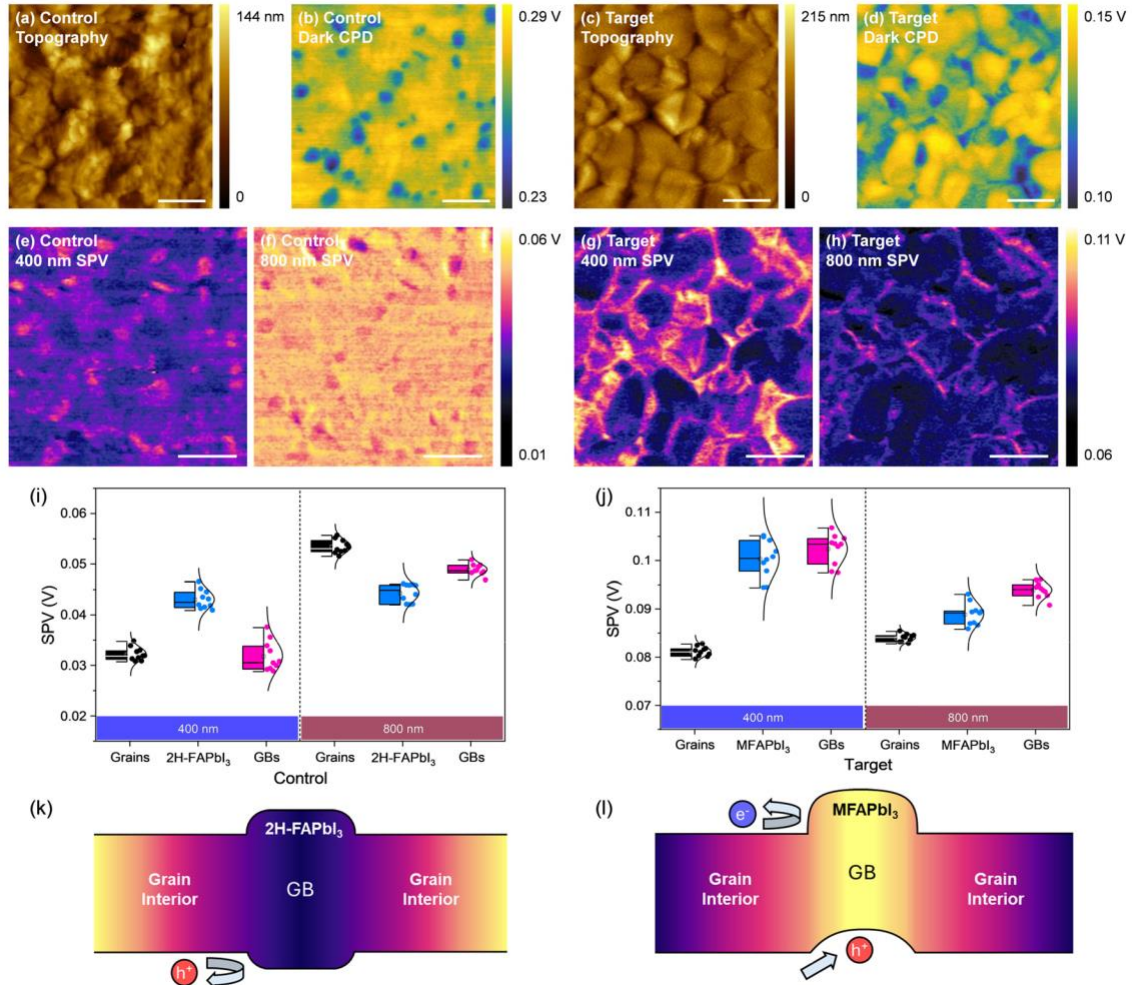


Fig. 5 Wavelength-dependent Kelvin probe force microscopy (KPFM) measurement. (a) Topography image, (b) CPD spatial map in dark condition of Control, (c) topography image, (d) CPD spatial map in dark condition of Target perovskite film, (e) and (f) SPV map at 400 and 800 nm of Control film, (g) and (h) SPV map at 400 and 800 nm of Target film, (i) and (j) SPV plot at 400 and 800 nm of Control and Target film, (k) energy level schematics of Control and 2H-FAPbI₃-phase, and (l) Target and MFAPbI₃-phase. All scale bars represent 1 μ m.

FAPbI₃ perovskites with the PCE of 24.2%, induced by the byproduct formation of MFAPbI₃-phases at both the GBs and as clusters near the GB regions.

Conclusion

In summary, our nanoscale characterization, involving PiFM, 4D-STEM, and wavelength-dependent KPFM measurements, demonstrates that the incorporation of MACl induces FA⁺ cation heterogeneity in FAPbI₃ perovskites. This results in benign MFA⁺ byproduct formation, suppressing the unwanted local formation of 2H-FAPbI₃. Our results indicate that such selective formation of structurally 2H-FAPbI₃ phase-like MFAPbI₃ that exists mainly at the GBs region leads to a PCE of over 24%, while an excessive amount reduces PCE slightly. Moreover, this study not only contributes to a thorough understanding of the effect of byproduct formation of the MFAPbI₃-phases induced by MACl incorporation on local cation inhomogeneities but also underscores its role in improving the performance of FAPbI₃ PSCs, where MACl is widely employed as a universal additive. These insights provide a foundation for optimizing additive engineering strategies when employing MACl and advancing the design of stable and efficient FA-based PSCs.

Data availability

All data supporting the findings of this study are available within the main text and the ESI.† All relevant data are available from the corresponding authors upon reasonable request.

Conflicts of interest

S.D.S. is a co-founder of Swift Solar Inc.

Acknowledgements

We acknowledge Diamond Light Source for access in the use of JEOL ARM300CF E02 at the Electron Physical Science Imaging Centre (ePSIC) (proposal number: MG34931-2). We thank the developers of the open-source package py4DSTEM, especially Dr Colin Ophus, for providing advice on data analysis. J. K., L. C., and S. I. S. acknowledge financial support from the Basic Science Research Program (NRF-2018R1A3B1052820) and STEAM research program (No. RS-2024-00418209) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (MSIP). J. S. Y. acknowledges the Royal Society research grant (RGS/R1/221369) and the support from the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (RS-2023-00257494 and 2022H1D3A2A01082324). PiFM data was acquired on an instrument funded by EPSRC grant EP/V05399X/1. S. D. S. thanks the Royal Society and Tata Group (UF150033). E. C. and S. D. S. acknowledge the Leverhulme Trust for funding.

References

- 1 Best Research-Cell Efficiency Chart. NREL, <https://www.nrel.gov/pv/cell-efficiency.html>.
- 2 H. Min, D. Y. Lee, J. Kim, G. Kim, K. S. Lee, J. Kim, M. J. Paik, Y. K. Kim, K. S. Kim, M. G. Kim, T. J. Shin and S. Il Seok, *Nature*, 2021, 598, 444–450.
- 3 J. Park, J. Kim, H.-S. Yun, M. J. Paik, E. Noh, H. J. Mun, M. G. Kim, T. J. Shin and S. Il Seok, *Nature*, 2023, 616, 724–730.
- 4 J. Jeong, M. Kim, J. Seo, H. Lu, P. Ahlawat, A. Mishra, Y. Yang, M. A. Hope, F. T. Eickemeyer, M. Kim, Y. J. Yoon, I. W. Choi, B. P. Darwich, S. J. Choi, Y. Jo, J. H. Lee, B. Walker, S. M. Zakeeruddin, L. Emsley, U. Rothlisberger, A. Hagfeldt, D. S. Kim, M. Graetzel and J. Y. Kim, *Nature*, 2021, 592, 381–385.
- 5 Q. Tan, Z. Li, G. Luo, X. Zhang, B. Che, G. Chen, H. Gao, D. He, G. Ma, J. Wang, J. Xiu, H. Yi, T. Chen and Z. He, *Nature*, 2023, 620, 545–551.
- 6 Y. Miao, M. Ren, Y. Chen, H. Wang, H. Chen, X. Liu, T. Wang and Y. Zhao, *Nat. Sustainability*, 2023, 6, 1465–1473.
- 7 W. Peng, K. Mao, F. Cai, H. Meng, Z. Zhu, T. Li, S. Yuan, Z. Xu, X. Feng, J. Xu, M. D. McGehee and J. Xu, *Science*, 2023, 379, 683–690.
- 8 S. M. Park, M. Wei, J. Xu, H. R. Atapattu, F. T. Eickemeyer, K. Darabi, L. Grater, Y. Yang, C. Liu, S. Teale, B. Chen, H. Chen, T. Wang, L. Zeng, A. Maxwell, Z. Wang, K. R. Rao, Z. Cai, S. M. Zakeeruddin, J. T. Pham, C. M. Risko, A. Amassian, M. G. Kanatzidis, K. R. Graham, M. Graetzel and E. H. Sargent, *Science*, 2023, 381, 209–215.
- 9 S. M. Park, M. Wei, N. Lempeis, W. Yu, T. Hossain, L. Agosta, V. Carnevali, H. R. Atapattu, P. Serles, F. T. Eickemeyer, H. Shin, M. Vafaie, D. Choi, K. Darabi, E. D. Jung, Y. Yang, D. Bin Kim, S. M. Zakeeruddin, B. Chen, A. Amassian, T. Filleter, M. G. Kanatzidis, K. R. Graham, L. Xiao, U. Rothlisberger, M. Graetzel and E. H. Sargent, *Nature*, 2023, 624, 289–294.
- 10 M. Kim, G.-H. Kim, T. K. Lee, I. W. Choi, H. W. Choi, Y. Jo, Y. J. Yoon, J. W. Kim, J. Lee, D. Huh, H. Lee, S. K. Kwak, J. Y. Kim and D. S. Kim, *Joule*, 2019, 3, 2179–2192.
- 11 K. Odysseas Kosmatos, L. Theofylaktos, E. Giannakaki, D. Deligiannis, M. Konstantakou and T. Stergiopoulos, *Energy Environ. Mater.*, 2019, 2, 79–92.
- 12 Y. Zhao and K. Zhu, *J. Phys. Chem. C*, 2014, 118, 9412–9418.
- 13 J.-W. Lee, S. Tan, S. Il Seok, Y. Yang and N.-G. Park, *Science*, 2024, 375, eabj1186.
- 14 V. Valenzano, A. Cesari, F. Balzano, A. Milella, F. Fracassi, A. Listorti, G. Gigli, A. Rizzo, G. Uccello-Barretta and S. Colella, *Cell Rep. Phys. Sci.*, 2021, 2, 100432.
- 15 Y. Zhang, Z. Xing, B. Fan, Z. Ni, F. Wang, X. Hu and Y. Chen, *Angew. Chem., Int. Ed.*, 2023, 62, e202215799.
- 16 J. Zhao, S. O. Fuerrer, D. P. McMeekin, Q. Lin, P. Lv, J. Ma, W. L. Tan, C. Wang, B. Tan, A. S. R. Chesman, H. Yin, A. D. Scully, C. R. McNeill, W. Mao, J. Lu, Y.-B. Cheng and U. Bach, *Energy Environ. Sci.*, 2023, 16, 138–147.

- 17 D. Zheng, F. Chen, M.-N. Rager, L. Gollino, B. Zhang and T. Pauporte', *Adv. Mater. Interfaces*, 2022, 9, 2201436.
- 18 X. Wang, Y. Fan, L. Wang, C. Chen, Z. Li, R. Liu, H. Meng, Z. Shao, X. Du, H. Zhang, G. Cui and S. Pang, *Chem*, 2020, 6, 1369–1378.
- 19 E. M. Tennyson, T. A. S. Doherty and S. D. Stranks, *Nat. Rev. Mater.*, 2019, 4, 573–587.
- 20 D. W. deQuilettes, W. Zhang, V. M. Burlakov, D. J. Graham, T. Leijtens, A. Osherov, V. Bulovic', H. J. Snaith, D. S. Ginger and S. D. Stranks, *Nat. Commun.*, 2016, 7, 11683.
- 21 T. W. Jones, A. Osherov, M. Alsari, M. Sponseller, B. C. Duck, Y.-K. Jung, C. Settens, F. Niroui, R. Brenes, C. V. Stan, Y. Li, M. Abdi-Jalebi, N. Tamura, J. E. Macdonald, M. Burghammer, R. H. Friend, V. Bulovic', A. Walsh, G. J. Wilson, S. Lilliu and S. D. Stranks, *Energy Environ. Sci.*, 2019, 12, 596–606.
- 22 A. J. Knight, J. Borchert, R. D. J. Oliver, J. B. Patel, P. G. Radaelli, H. J. Snaith, M. B. Johnston and L. M. Herz, *ACS Energy Lett.*, 2021, 6, 799–808.
- 23 S. Wiegbold, J. Tresback, J.-P. Correa-Baena, N. T. P. Hartono, S. Sun, Z. Liu, M. Layurova, Z. A. VanOrman, A. S. Bieber, J. Thapa, B. Lai, Z. Cai, L. Nienhaus and T. Buonassisi, *Chem. Mater.*, 2019, 31, 3712–3721.
- 24 K. Frohna, M. Anaya, S. Macpherson, J. Sung, T. A. S. Doherty, Y.-H. Chiang, A. J. Winchester, K. W. P. Orr, J. E. Parker, P. D. Quinn, K. M. Dani, A. Rao and S. D. Stranks, *Nat. Nanotechnol.*, 2022, 17, 190–196.
- 25 T. A. S. Doherty, S. Nagane, D. J. Kubicki, Y.-K. Jung, D. N. Johnstone, A. N. Iqbal, D. Guo, K. Frohna, M. Danaie, E. M. Tennyson, S. Macpherson, A. Abfalterer, M. Anaya, Y.-H. Chiang, P. Crout, F. S. Ruggeri, S. Collins, C. P. Grey, A. Walsh, P. A. Midgley and S. D. Stranks, *Science*, 2021, 374, 1598–1605.
- 26 J.-P. Correa-Baena, Y. Luo, T. M. Brenner, J. Snider, S. Sun, X. Li, M. A. Jensen, N. T. P. Hartono, L. Nienhaus, S. Wiegbold, J. R. Poindexter, S. Wang, Y. S. Meng, T. Wang, B. Lai, M. V. Holt, Z. Cai, M. G. Bawendi, L. Huang, T. Buonassisi and D. P. Fenning, *Science*, 2019, 363, 627–631.
- 27 S. Jariwala, R. E. Kumar, G. E. Eperon, Y. Shi, D. P. Fenning and D. S. Ginger, *ACS Energy Lett.*, 2022, 7, 204–210.
- 28 Z. Liang, Y. Zhang, H. Xu, W. Chen, B. Liu, J. Zhang, H. Zhang, Z. Wang, D.-H. Kang, J. Zeng, X. Gao, Q. Wang, H. Hu, H. Zhou, X. Cai, X. Tian, P. Reiss, B. Xu, T. Kirchartz, Z. Xiao, S. Dai, N.-G. Park, J. Ye and X. Pan, *Nature*, 2023, 624, 557–563.
- 29 J. A. Davies-Jones and P. R. Davies, *Mater. Chem. Front.*, 2022, 6, 1552–1573.
- 30 A. A. Sifat, J. Jahng and E. O. Potma, *Chem. Soc. Rev.*, 2022, 51, 4208–4222.
- 31 G. E. Sommargren, *Appl. Opt.*, 1981, 20, 610–618.
- 32 M. T. Cuberes, H. E. Assender, G. A. D. Briggs and O. V. Kolosov, *J. Phys. D: Appl. Phys.*, 2000, 33, 2347.
- 33 R. Szostak, J. C. Silva, S.-H. Turren-Cruz, M. M. Soares, R. O. Freitas, A. Hagfeldt, H. C. N. Tolentino and A. F. Nogueira, *Sci. Adv.*, 2024, 5, eaaw6619.
- 34 L. Chen, M. Hu, S. Lee, J. Kim, Z.-Y. Zhao, S.-P. Han, M. S. Lah and S. Il Seok, *J. Am. Chem. Soc.*, 2023, 145, 27900–27910.
- 35 H. Gru'ninger, M. Bokdam, N. Leupold, P. Tinnemans, R. Moos, G. A. De Wijs, F. Panzer and A. P. M. Kentgens, *J. Phys. Chem. C*, 2021, 125, 1742–1753.
- 36 G. Bravetti, N. Taurisano, A. Moliterni, J. M. Vicent-Luna, D. Altamura, F. Aiello, N. Vanni, A.-L. Capodilupo, S. Carallo, G. Gigli, G. Uccello-Barretta, F. Balzano, C. Giannini, S. Tao, S. Colella and A. Rizzo, *Chem. Mater.*, 2024, 36, 3150–3163.
- 37 X. Wang, Y. Fan, L. Wang, C. Chen, Z. Li, R. Liu, H. Meng, Z. Shao, X. Du, H. Zhang, G. Cui and S. Pang, *Chem*, 2020, 6, 1369–1378.
- 38 V. Valenzano, A. Cesari, F. Balzano, A. Milella, F. Fracassi, A. Listorti, G. Gigli, A. Rizzo, G. Uccello-Barretta and S. Colella, *Cell Rep. Phys. Sci.*, 2021, 2, 100432.
- 39 T. Zhu, D. Zheng, M.-N. Rager and T. Pauporte', *Sol. RRL*, 2020, 4, 2000348.
- 40 A. N. Iqbal, K. W. P. Orr, S. Nagane, J. Ferrer Orri, T. A. S. Doherty, Y.-K. Jung, Y.-H. Chiang, T. A. Selby, Y. Lu, A. J. Mirabelli, A. Baldwin, Z. Y. Ooi, Q. Gu, M. Anaya and S. D. Stranks, *Adv. Mater.*, 2024, 2307508.
- 41 T. A. S. Doherty, S. Nagane, D. J. Kubicki, Y.-K. Jung, D. N. Johnstone, A. N. Iqbal, D. Guo, K. Frohna, M. Danaie, E. M. Tennyson, S. Macpherson, A. Abfalterer, M. Anaya, Y.-H. Chiang, P. Crout, F. S. Ruggeri, S. Collins, C. P. Grey, A. Walsh, P. A. Midgley and S. D. Stranks, *Science*, 2021, 374, 1598–1605.
- 42 WMD-group/hybrid-perovskites, https://github.com/WMD-group/hybrid-perovskites/tree/master/2014_cubic_halides_PBEsol.
- 43 J. Kim, B. Park, J. Baek, J. S. Yun, H.-W. Kwon, J. Seidel, H. Min, S. Coelho, S. Lim, S. Huang, K. Gaus, M. A. Green, T. J. Shin, A. W. Y. Ho-baillie, M. G. Kim and S. Il Seok, *J. Am. Chem. Soc.*, 2020, 142, 6251–6260.
- 44 B. Chen, Z. Yu, K. Liu, X. Zheng, Y. Liu, J. Shi, D. Spronk, P. N. Rudd, Z. Holman and J. Huang, *Joule*, 2019, 3, 177–190.
- 45 T. A. S. Doherty, A. J. Winchester, S. Macpherson, D. N. Johnstone, V. Pareek, E. M. Tennyson, S. Kosar, F. U. Kosasih, M. Anaya, M. Abdi-Jalebi, Z. Andaji-Garmaroudi, E. L. Wong, J. Made'o, Y.-H. Chiang, J.-S. Park, Y.-K. Jung, C. E. Petoukhoff, G. Divitini, M. K. L. Man, C. Ducati, A. Walsh, P. A. Midgley, K. M. Dani and S. D. Stranks, *Nature*, 2020, 580, 360–366.
- 46 H. Fan, F. Li, P. Wang, Z. Gu, J.-H. Huang, K.-J. Jiang, B. Guan, L.-M. Yang, X. Zhou and Y. Song, *Nat. Commun.*, 2020, 11, 5402.
- 47 H. Fan, J.-H. Huang, L. Chen, Y. Zhang, Y. Wang, C. Gao, P. Wang, X. Zhou, K.-J. Jiang and Y. Song, *J. Mater. Chem. A*, 2021, 9, 7625–7630.
- 48 X. Chen, Y. Xia, Z. Zheng, X. Xiao, C. Ling, M. Xia, Y. Hu, A. Mei, R. Checharoen, Y. Rong and H. Han, *Chem. Mater.*, 2022, 34, 728–735.
- 49 J. Zhang, X. Jiang, X. Liu, X. Guo and C. Li, *Adv. Funct. Mater.*, 2022, 32, 2204642.