Myths and reality of HPbI₃ in halide perovskite solar cells

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All-inorganic perovskites have a special place in halide perovskite family because of their potential for better stability. However, the representative cesium lead iodide (CsPbI₃) is metastable and spontaneously converts to the non-perovskite structure at room temperature. Here, we demonstrate that what appears to be all-inorganic CsPbI₃ stabilized in its perovskite form using the purported intermediate known as hydrogen lead iodide (HPbI₃) is, in fact, the hybrid perovskite cesium dimethylammonium lead iodide (Cs₁₋ₓDMAₓPbI₃, x = 0.2 to 0.5). Thus, many of the reported all-inorganic perovskites are actually still hybrid organic-inorganic perovskites, as strongly evidenced by a wide battery of experimental techniques presented here. Solar cells based on the representative composition Cs₀.₇DMA₀.₃PbI₃ can achieve an average power conversion efficiency of 9.27 ± 1.28% (max 12.62%). These results provide an alternative angle to look at previous results pertaining all-inorganic CsPbI₃ while the DMA cation is now revealed as an alternative A site cation.
Halide perovskites have unique properties such as tunable band gaps, long diffusion lengths, high optical absorption coefficients, and low exciton binding energies. Halide perovskite solar cells have achieved a record power conversion efficiency (PCE) of 22.7%, which are great candidates for the next generation of photovoltaics. High-performance perovskite solar cells typically employ organic-inorganic hybrid Pb-based perovskites as light absorbers such as methylammonium lead iodide (MAPbI₃), formamidinium lead iodide (FAPbI₃), and their mixtures, due to their excellent optical and electrical properties. However, the intrinsic thermal and light instabilities of organic cations of MA and FA present serious hurdles in the further development and commercialization of long-term operating devices. The all-inorganic perovskite analog cesium lead iodide (CsPbI₃) could present an important way forward, since it possesses a relatively wider band gap with large band widths and especially a significantly better thermal stability compared with the organic cations-based perovskites. However, the black CsPbI₃ perovskite is metastable and it spontaneously converts to the undesired yellow polytype (δ-phase, NH₄CdCl₃ structure-type) at room temperature. Yellow δ-CsPbI₃ has a wide band gap of Eᵥ = 2.82 eV and has poor transport properties. By contrast, black CsPbI₃ has a narrow band gap of around 1.7 eV and it is suitable for solar cell applications. Therefore, much effort has been devoted to improving the phase-stability of the black-phase CsPbI₃ perovskites so that highly efficient all-inorganic solar cells can be made. In one approach, researchers used pre-synthesized CsPbI₃ nanocrystals to make solar cells. For example, Protesescu et al. demonstrated that colloidal CsPbI₃ quantum dots synthesized by a hot-injection method can be phase-stable for several months in ambient air and the solar cells achieved a PCE as high as 13.4%. In another approach, You et al. used dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) solvent followed by high-temperature annealing process to obtain the black α-CsPbI₃. These solar cells yielded a record PCE of 15.7% and showed a good light-soaking stability under the protection of N₂-filled glovebox. Much more commonly, the use of hydriodic acid (HI) or the so-called hydrogen lead iodide (HPbI₃) precursor, produced by HI treatment, are the most used approaches to stabilize the black α-CsPbI₃. The use of HPbI₃ was first reported as an intermediate in the synthesis of FAPbI₃ solar cells and was prepared by mixing PbI₂ and HI in DMF. Eperon et al. subsequently reported that HI can be used directly as an additive in DMF solutions of CsPbI₃ to stabilize the black α-CsPbI₃ films at room temperature. The planar device made from this black CsPbI₃ film achieved a PCE of 2.9%. Recently, Zhang et al. reported the formation of black CsPbI₃ by a low-temperature deposition using the pre-synthesized PbI₂-xHI, which was also made from DMF, PbI₂, and HI. Combined with the use of larger ethylenediammonium (en) cation, the champion α-CsPbI₃ solar cell yielded a PCE of 11.8% with enhanced stability and good reproducibility. More recently, Jiang et al. also used HPbIₓ (x = 1, Br) as a precursor together with phenylethylammonium (PEA) cation to fabricate low-dimensional α-CsPbI₃ and the solar cells achieved a high PCE of 12.4%. Despite the apparent success of the HPbI₃ methodology, the mechanism of the stabilization of the black CsPbI₃ by HI and HPbI₃ remains unclear. The claim alone that HPbI₃ even exists is extraordinary and there is no structural or spectroscopic validation for the existence of this compound. From the chemistry point of view, HPbI₃ would be a solid acid with HI fragment in it and intuitively is unlikely to exist. This is because the HI molecule itself is not known to engage in binding to metals and it is likely that cannot form a stable structure and will readily dissociate to PbI₂ and HI. Thus, the claim that HPbI₃ is a real compound deserves closer attention and we set out to investigate it in the context of the present manuscript.

Here, we report that HPbI₃ does not exist and instead what was believed to be it is in fact a compound of DMAPbI₃ (DMA = dimethylammonium, (CH₃)₂NH₂⁻), where DMA is a decomposition product of the acidic hydrolysis of DMF catalyzed by HI. We demonstrate that the black CsPbI₃ films deposited from DMF containing HI/HPbI₃ and reported to be all-inorganic black phase of CsPbI₃ are not. Instead, they are the mixed-cation perovskite phase of cesium dimethylammonium lead iodide (CsₓDMAₓPbI₃, x = 0.2 to 0.5). The α-CsₓDMAₓPbI₃ perovskite films have similar characteristics with the black γ-CsPbI₃ films arising from HI addition but they exhibit better charge transport due to the superior band structure characteristics (larger bandwidth, smaller band gap) of the cubic phase. Our best-performing solar cell based on α-Cs₀.₇DMA₀.₃PbI₃ perovskite absorber achieve a remarkable PCE of 12.62%. Our results reveal the existence of α-Cs₀.₇DMA₀.₃PbI₃, a black 3D perovskite which is a great absorber for the fabrication of high efficiency solar cells.

Results

Phase diversity of CsPbI₃. The structure of halide perovskites which have a general formula of AMX₃ can be only stabilized by limited cations, according to the rule of tolerance factor, n₃⁹,⁴⁰. Where A, M, and X represent a nonbonding univalent cation, an octahedrally coordinated bivalent metal ion, and a monoanionic halide ion, respectively. A cubic structure of perovskite materials typically has a suitable t value ranged from 0.9 to 1.0, which is defined by the equation of t = (rₐ + rₓ)/2(rₐ + rₓ). rₐ, rₓ, and rₓ represent the ionic sizes of A, B, and X, respectively. Different A cations have different ionic sizes, only cubic MAPbI₃ can stabilize at room temperature. Both FAPbI₃ and CsPbI₃ normally adopt the yellow phase at room temperature, due to the too large too small size of A cations, respectively. Specifically, CsPbI₃ can adopt two structures: the NH₄CdCl₃-type yellow phase (δ-phase) stable at room temperature (Fig. 1a) and the black cubic CaTiO₃-type (α-phase) structure stable above 300 °C (Fig. 1b). The perovskite structure can be kinetically stabilized at room temperature, where it adopts the black orthorhombic γ-phase (bandgap of around 1.73 eV) but it converts within hours to the δ-phase. Thus, CsPbI₃ is typically stabilized by adjusting the t via formation of solid solutions such as partial replacement of I with smaller Br anions to form CsPbI₃-xBr compositions, which exhibit a wider band gap or by substituting the A-site with larger organic cations such as FA to form CsₓFAₓPbI₃ solid solutions. The perovskite due to the too large size of DMA which leads to a prohibitively large t, even at elevated temperatures. On the other hand, the effective radius of Cs cation is only 1.88 Å and pure CsPbI₃ has a low tolerance factor of t = 0.851 which is below the ideal range of cubic structure (Fig. 1d). However, mixing Cs with DMA, i.e., CsₓDMAₓPbI₃, can on average bring the effective tolerance factor within the desirable region, thus enabling the stabilization of a black perovskite phase, namely...
Cs$_{1-x}$DMA$_x$PbI$_3$ ($x = 0.2$ to $0.5$), having a $t = 0.904$ ($x = 0.3$) that allows it to adopt the cubic $\alpha$-phase (Fig. 1d), similarly to Cs$_{1-x}$FA$_x$PbI$_3$.

Cs$_{1-x}$DMA$_x$PbI$_3$ film properties. This has indeed turned out to be the case in our thin films, where the nominal Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ composition is able to adopt the perovskite phase. As shown in Fig. 2a, the Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ film without HI addition shows a black color, indicating the successful fabrication of black-phase perovskite structure with lattice constant $a = 6.272$ Å and $Pm\text{3}m$ space group. On the contrary, the pristine CsPbI$_3$ and DMAPbI$_3$ films deposited on FTO/PEDOT substrates are yellow and pale-yellow color (Fig. 2a), respectively, because they are non-perovskite NH$_4$CdCl$_3$ structure-type. For comparison, we also fabricated CsPbI$_3$ film with HI addition (see details in Methods). Similar to the previously reported results, the CsPbI$_3$ film prepared with HI addition also shows a black color and a shiny surface (Fig. 2a), indicative of the formation of the similar black-phase perovskite structure. The color of the films is in good agreement with the band gaps of the respective compounds as determined by optical absorption measurements. Fig. 2b shows that the Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ film has an absorbance onset at around 730 nm, indicating a band gap of 1.7 eV. The CsPbI$_3$ film with HI addition shows a similar absorption but slightly blue-shifted from 730 nm to 710 nm. As expected, the pure CsPbI$_3$ and DMAPbI$_3$ films only show an absorption at around 440 nm and 390 nm, respectively, due to the wide band gaps of these yellow phases.

Photoluminescence (PL) measurements reveal the same trend. As shown in Fig. 2c, the Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ film has a PL emission at around 724 nm. The black CsPbI$_3$ film with HI addition shows a blue-shift PL peak at around 704 nm, consistent with the trend of UV-vis absorption spectra. Both CsPbI$_3$ and DMAPbI$_3$ films only show negligible PL emission, due to the indirect nature of the band gaps.

X-ray diffraction (XRD) patterns on the thin-films confirm the structure description discussed above. As shown in Fig. 2d, the main peaks of the neat yellow CsPbI$_3$ film locates at 9.9°, 13.2°, 22.8° etc. are assigned to the orthorhombic ($Pnma$) yellow $\delta$-phase (Supplementary Fig. 1). The XRD pattern of the DMAPbI$_3$ film only shows two main reflections at $2\theta = 11.8^\circ$ and 20.4° (Fig. 2d), due to the preferred orientation, corresponding to the hexagonal ($P6_3/mmc$) yellow phase (Supplementary Fig. 2). The Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ film shows peaks at $2\theta = 14.4^\circ$, 20.2°, 28.9°, and 40.9° etc., which can be indexed to the (100), (110), (200), and (220) reflections of cubic CsPbI$_3$, showing some orientation of the perovskite in both (100) and (110) directions of the cubic ($Pm\text{3}m$) $\alpha$-phase (Supplementary Fig. 3). While the CsPbI$_3$ film with HI additive exhibits similar peaks, it has no preferred orientation showing reflections that correspond to the black orthorhombic ($Pbnm$) perovskite $\gamma$-phase (Supplementary Figs. 4–5). In addition, the CsPbI$_3$ film with HI also reveals a weak reflection at $2\theta = 9.9^\circ$, which corresponds to the yellow $\delta$-phase, indicating that the conversion to the black phase is incomplete.

To further prove that DMA cation is actually present in the black CsPbI$_3$ films, we measured the proton nuclear magnetic resonance ($^1$H NMR) spectrum of the powder obtained from scratching away the Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ films and dissolving it in dimethyl sulfoxide-d$_6$ (DMSO-d$_6$) (Fig. 2e). The signals of $-\text{NH}_2^+$– (singlet) and $-\text{CH}_3$ (doublet) protons are located at

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**Fig. 1** Crystal and molecular structures. a Crystal structure of CsPbI$_3$ with non-perovskite yellow orthorhombic (6) phase. b Crystal structure of CsPbI$_3$ with perovskite black cubic (α) phase. c Molecular structures of FA (top) and DMA (bottom) cations. d Tolerance factors of CsPbI$_3$, DMAPbI$_3$, and Cs$_{0.7}$DMA$_{0.3}$PbI$_3$.
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\delta = 8.17 \text{ ppm and } \delta = 2.55 \text{ ppm, respectively. The ratio integrated from the signals of } -\text{NH}_2^+ \text{ and } -\text{CH}_3 \text{ is } 1:3, \text{ indicating that DMA is protonated. The NMR spectrum of the pure DMAI powder confirms the peak position (Supplementary Fig. 6), thus demonstrating DMA is incorporated in the CsPbI}_3 \text{ structure as would be expected by the Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ composition. Remarkably, the NMR spectrum of the DMSO-d}_6 \text{ solution of DMAI from the reaction of DMF and HI directly (see Methods). As Fig. 2e illustrate, DMAI can indeed be readily formed by the reaction between DMF and HI with } ^1\text{H-NMR spectra and XRD patterns confirming its identity in comparison with the commercial DMAI compound (Supplementary Figs. 6 and 8). Note that the two peaks at } \delta = 7.22 \text{ ppm and } \delta = 6.18 \text{ ppm shown in Fig. 2e are assigned to the –PH}_2– \text{ protons of hypophosphorous acid (H}_3\text{PO}_2 \text{) which presents as a stabilizer in concentrated HI aqueous solutions. Therefore, this is the reason why } ^1\text{H-NMR spectra of Cs}_0.7\text{DMA}_0.3\text{PbI}_3, \text{CsPbI}_3 \text{ with HI, DMAI, and DMF + HI samples are identical. Most importantly, it explains why the UV-vis absorption, PL, XRD, and } ^1\text{H-NMR results between the intentionally made Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ film and the DMF derived CsPbI}_3 \text{ with HI, DMAI, and DMF + HI samples are so similar. Note that the red shift (around 20 nm) of PL and UV-vis spectra of Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ with respect to the CsPbI}_3 \text{ sample with HI is because the former (which contains significant amounts of DMA) adopts the cubic } \alpha-\text{CsPbI}_3 \text{ phase, whereas the latter (containing only small amounts of DMA) stabilizes the orthorhombic } \gamma-\text{phase (as would be expected by the effective tolerance factor discussed above).}
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The hydrolysis of DMF in the presence of acid such as HI as a film fabrication tool has great implications in the fabrication of perovskite films and solar cells. Since HI addition has been reported to alter the phase transition temperature and improve the film morphology of MAPbI\(_3\), and also was identified as the critical reagent for stabilizing the perovskite phase of CsPbI\(_3\), the nature and exact composition of these crystalline films will need to be re-examined. In addition, HPbI\(_3\), obtained from the DMAI from the reaction of DMF and HI directly (see Methods). As Fig. 2e illustrate, DMAI can indeed be readily formed by the reaction between DMF and HI with \(^1\text{H-NMR spectra and XRD patterns confirming its identity in comparison with the commercial DMAI compound (Supplementary Figs. 6 and 8). Note that the two peaks at } \delta = 7.22 \text{ ppm and } \delta = 6.18 \text{ ppm shown in Fig. 2e are assigned to the –PH}_2– \text{ protons of hypophosphorous acid (H}_3\text{PO}_2 \text{) which presents as a stabilizer in concentrated HI aqueous solutions. Therefore, this is the reason why } ^1\text{H-NMR spectra of Cs}_0.7\text{DMA}_0.3\text{PbI}_3, \text{CsPbI}_3 \text{ with HI, DMAI, and DMF + HI samples are identical. Most importantly, it explains why the UV-vis absorption, PL, XRD, and } ^1\text{H-NMR results between the intentionally made Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ film and the DMF derived CsPbI}_3 \text{ with HI, DMAI, and DMF + HI samples are so similar. Note that the red shift (around 20 nm) of PL and UV-vis spectra of Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ with respect to the CsPbI}_3 \text{ sample with HI is because the former (which contains significant amounts of DMA) adopts the cubic } \alpha-\text{CsPbI}_3 \text{ phase, whereas the latter (containing only small amounts of DMA) stabilizes the orthorhombic } \gamma-\text{phase (as would be expected by the effective tolerance factor discussed above).}
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In order to further demonstrate this reaction, we synthesized the DMAI from the reaction of DMF and HI directly (see Methods). As Fig. 2e illustrate, DMAI can indeed be readily formed by the reaction between DMF and HI with \(^1\text{H-NMR spectra and XRD patterns confirming its identity in comparison with the commercial DMAI compound (Supplementary Figs. 6 and 8). Note that the two peaks at } \delta = 7.22 \text{ ppm and } \delta = 6.18 \text{ ppm shown in Fig. 2e are assigned to the –PH}_2– \text{ protons of hypophosphorous acid (H}_3\text{PO}_2 \text{) which presents as a stabilizer in concentrated HI aqueous solutions. Therefore, this is the reason why } ^1\text{H-NMR spectra of Cs}_0.7\text{DMA}_0.3\text{PbI}_3, \text{CsPbI}_3 \text{ with HI, DMAI, and DMF + HI samples are identical. Most importantly, it explains why the UV-vis absorption, PL, XRD, and } ^1\text{H-NMR results between the intentionally made Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ film and the DMF derived CsPbI}_3 \text{ with HI, DMAI, and DMF + HI samples are so similar. Note that the red shift (around 20 nm) of PL and UV-vis spectra of Cs}_0.7\text{DMA}_0.3\text{PbI}_3 \text{ with respect to the CsPbI}_3 \text{ sample with HI is because the former (which contains significant amounts of DMA) adopts the cubic } \alpha-\text{CsPbI}_3 \text{ phase, whereas the latter (containing only small amounts of DMA) stabilizes the orthorhombic } \gamma-\text{phase (as would be expected by the effective tolerance factor discussed above).}
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the reaction of HI, DMF, and PbI₂, has been widely used for making stable FAPbI₃, CsPbI₃, MAPbI₃ solar cells, which actually does not exist and should be reformulated to DMAPbI₃. It is confirmed by the XRD patterns of our DMAPbI₃ film (Fig. 2d and Supplementary Fig. 2) and the reported HPbI₃, showing the exact same reflections. Given that the use of HPbI₃ is in a serendipitous manner, these systems also need to be revisited and studied carefully under the understanding of the DMF hydrolysis mechanism. It is important to re-evaluate these systems counting the time as a synthetic parameter since the preparation will significantly vary over time as different amounts of DMA are produced at different times of the reactions and therefore the composition of the films will vary accordingly.

In a previous report, we demonstrated that HI addition can alter the MAPbI₃ phase transition temperature. A room temperature phase transition from tetragonal to cubic was observed for MAPbI₃ films treated with high HX (X = Cl, Br, I) concentrations. In our original hypothesis, we and others speculated that the reduction of the crystallite size induced by the acid were responsible for this phase transition. HI can improve the perovskite film morphology and eliminate the hysteresis of MAPbI₃ solar cells. However, in light of the results reported here, we can now revise our original concept and ascribe the compositional phase transition to the presence of DMA, induced by the presence of acid. Note that the concept of the role of acid expands beyond the HX acids, as other acids such as H₂PO₂ appear to have a similar effect. Therefore, based on the above results, all those compositionally-induced phase transitions may be attributed to the introduction of the in-situ forming DMA cation in the perovskite lattice and it applies equally well in the MAPbI₃ and CsPbI₃ systems. Note that FAPbI₃ is excluded since FA is already too large to stabilize the perovskite structure.

Now that we have established that the so-called all-inorganic CsPbI₃ films processed with HI and HPbI₃ are in fact Cs₁₋ₓDMAₓPbI₃, films, we return to the study of the latter and their behavior and performance in complete solar cells. The CsPbI₃ film with HI addition was prepared by a conventional one-step method and using DMF as solvent, actually is unintentionally-made Cs₁₋ₓDMAₓPbI₃ but we still referred it as HI-treated CsPbI₃ in the following discussion. A small amount of HI aqueous solution was added into the CsPbI₃ precursor after all materials were dissolved in DMF solvent. All other intentionally-made Cs₁₋ₓDMAₓPbI₃ (x = 0 to 0.5) films were fabricated by CsI, PbI₂, and pre-synthesized DMAI using a solvent-engineering method with a mixture of DMF and DMSO as the solvent. Scanning electron microscopy (SEM) images show that the yellow-phase CsPbI₃ film has a rough surface with big grains and pin-holes, Fig. 3a. The morphology of the so-called black Cs₁₋ₓDMAₓPbI₃ film is even worse, showing some large and big cracks (Fig. 3b). Fig. 3c shows the one-step method-prepared CsPbI₃ film treated with HI which clearly has much smoother surface, still containing some pin holes. The best film quality was obtained from the CsPbI₃ film with DMA cation i.e., Cs₀.₇DMA₀.₃PbI₃. As shown in Fig. 3d, the Cs₀.₇DMA₀.₃PbI₃ film has a smooth surface, big grains and few pinholes. The average grain size of the Cs₀.₇DMA₀.₃PbI₃ film is around 500 nm, which is comparable with the film thickness. This is desirable since big grains facilitate charge transfer and reduce the recombination at grain boundaries. Fig. 3e shows a cross-sectional SEM of a complete device based on the Cs₀.₇DMA₀.₃PbI₃ absorber. The 380 nm thick Cs₀.₇DMA₀.₃PbI₃ film is sandwiched between a thin poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) hole transporting layer and a thin fullerene (C₆₀) electron transporting layer. The ultra-smooth Cs₀.₇DMA₀.₃PbI₃ film enables the fabrication of solar cells with an inverted planar structure.

Effects of DMA cation on solar cell performance. We then investigated the effects of various absorbers on device performance. Fig. 4a shows the photocurrent density-voltage (J–V) curves of the representative solar cells based on the yellow CsPbI₃, the pale-yellow DMAPbI₃, the black HI-treated CsPbI₃, and the black Cs₀.₇DMA₀.₃PbI₃ absorbers, measured under a reverse voltage scan. The performance of the solar cells based on different absorbers shows huge difference. As expected, the solar cells with yellow CsPbI₃ and DMAPbI₃ absorbers show very poor efficiencies. As shown in Fig. 4a, the solar cell employed the yellow CsPbI₃ film achieved a very low PCE of 0.002% with an open-circuit voltage (Vₒ.c) of 0.05 V, a short-circuit current density (Jₒ) of 0.21 mA cm⁻², a fill factor (FF) of 22.63%. A similarly low PCE of 0.001% with a Vₒ.c of 0.03 V, a Jₒ of 0.30 mA cm⁻², and an FF of 14.23% was obtained for the solar cell employing the yellow DMAPbI₃ film. Both CsPbI₃ and DMAPbI₃ devices were almost short-circuited, due to the poor film quality, non-perovskite structure, and limited light absorption due to their wide band gaps. The device performance of the so-called black CsPbI₃ was significantly enhanced after adding HI into the perovskite precursor. The HI-treated CsPbI₃ solar cell achieved a Vₒ.c of 0.82 V, a Jₒ of 9.56 mA cm⁻², an FF of 61.56%, and a PCE of 4.84%, which is comparable with other reports. The enhanced performance can be mainly attributed to the better morphology and the unintended incorporation of DMA cation which can stabilize the Cs₁₋ₓDMAₓPbI₃ perovskite as a black phase. Nevertheless, adding HI into the perovskite precursor makes it difficult to control the amount of DMA in the final film in a consistent manner, so after realizing the role of HI in the film formation the major focus was given in the easily reproducible fabrication of devices containing controlled amounts of DMA. As expected, the solar cells based on the designed Cs₀.₇DMA₀.₃PbI₃ absorber showed much better performance. A significantly enhanced PCE of 10.39% with a high Vₒ.c of 1.03 V, a Jₒ of 15.43 mA cm⁻², an FF of 65.61% was achieved for an optimized device, with both the high-quality of the films and narrow band gap contributing to the decent performance of the Cs₀.₇DMA₀.₃PbI₃ solar cells.

We find that the amount of DMA cation incorporated in the perovskite structure of CsPbI₃ has a huge effect on the material properties. Unlike the HI addition to DMF which results in the uncontrollable generation of DMA, it is easy to fabricate Cs₁₋ₓDMAₓPbI₃ films using precise DMA ratios. First, the film morphology was affected by different amounts of DMA. As shown in Supplementary Fig. 9, Cs₀.₇DMA₀.₃PbI₃, Cs₀.₆DMA₀.₄PbI₃, Cs₀.₅DMA₀.₅PbI₃, and Cs₀.₄DMA₀.₆PbI₃ films show different morphology. All films are compact and have smooth surface with Cs₀.₇DMA₀.₃PbI₃ film having the biggest grains. The Cs₀.₆DMA₀.₄PbI₃, and Cs₀.₅DMA₀.₅PbI₃ films are compact and have smaller grains. In addition, these films show similar band baps and PL peaks but different absorption intensities (Supplementary Fig. 10). In particular, the Cs₀.₇DMA₀.₃PbI₃ film shows the strongest absorption at long wavelength range. Supplementary Fig. 11 shows that the different films also have different XRD results. The diffraction intensities of the cubic Cs₀.₇DMA₀.₃PbI₃ and Cs₀.₅DMA₀.₅PbI₃ films are weaker while the extra peak at 2θ = 11.8° indicates that DMAPbI₃ is present as a second phase, suggesting that the substitution of DMA for Cs is limited. Cs₀.₇DMA₀.₃PbI₃ and Cs₀.₅DMA₀.₅PbI₃ show the exclusive formation of the black α-CsPbI₃ phase along with the former orienting preferentially along both (100) and (110) planes and the latter exclusively along the (110) planes. From the combined data, around 30% of DMA seems to be the optimum amount to make high-quality perovskite film. This is also reflected in the device performance of the corresponding solar cells based on the CsPbI₃ absorbers with various amounts of DMA. Supplementary Fig. 12 shows the J–V curves of the solar cells.
cells using the Cs$_{0.8}$DMA$_{0.2}$PbI$_3$, Cs$_{0.7}$DMA$_{0.3}$PbI$_3$, Cs$_{0.6}$DMA$_{0.4}$PbI$_3$, and Cs$_{0.5}$DMA$_{0.5}$PbI$_3$ absorbers. The device performance first increases and then decreases as the DMA amount increases. As expected, the solar cell derived from the best-quality Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ film achieved the highest performance (Supplementary Table 1).

Figure 4b shows the $J$–$V$ curves of the best-performing Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ solar cell measured under different voltage scan directions. This solar cell achieved a $V_{oc}$ of 0.99 V, a $J_{sc}$ of 16.65 mA cm$^{-2}$, an FF of 76.49%, and therefore a high PCE of 12.62% when measured under the reverse voltage scan. A similar PCE of 12.31% with a $V_{oc}$ of 0.99 V, a $J_{sc}$ of 16.44 mA cm$^{-2}$, and an FF of 75.71% was achieved for the solar cell measured under the forward voltage scan, suggesting small hysteresis behavior of our devices. External quantum efficiency (EQE) measurement was taken to confirm the high $J_{sc}$ obtained from the $J$–$V$ curves. The EQE spectrum of the solar cell based on the Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ absorber is shown in Fig. 4c. The cell shows...
high average value in the whole visible wavelength range. The $J_{SC}$ integrated from the EQE curve is about 15.95 mA cm$^{-2}$, which is very close to the $J_{SC}$ measured from the $J-V$ curves. To check the reproducibility of the device performance, we then made 40 solar cells based on the Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ absorbers. The histograms of the 40 solar cells achieved an average PCE of 9.27% ± 1.28% with a $V_{OC}$ of 1.01 ± 0.03 V, a $J_{SC}$ of 15.45 ± 1.80 mA cm$^{-2}$, and an FF of 59.40 ± 4.01%.

Furthermore, we also added the DMA cation into solutions of CsPbI$_3$Br and CsPbBr$_2$ perovskites. Supplementary Fig. 13a-b shows UV-vis absorption and XRD pattern of a Cs$_{0.7}$DMA$_{0.3}$PbI$_3$Br film coated on a FTO/PEDOT:PSS substrate. The Cs$_{0.7}$DMA$_{0.3}$PbI$_3$Br film shows an absorption onset at around 685 nm, according to a band gap of around 1.8 eV (Supplementary Fig. 13a). The Cs$_{0.7}$DMA$_{0.3}$PbI$_3$Br film has good crystalline quality and shows peaks at 14.7°, 20.5°, 29.5°, and 41.6° (Supplementary Fig. 13b), which can be indexed to the (100), (110), (200), and (220) planes. Supplementary Fig. 13c shows the $J-V$ curve of a solar cell based on the Cs$_{0.7}$DMA$_{0.3}$Br absorber. The Cs$_{0.7}$DMA$_{0.3}$I$_{2}$Br solar cell achieved a PCE of 5.24%, a $V_{OC}$ of 1.02 V, a $J_{SC}$ of 12.39 mA cm$^{-2}$, and an FF of 41.67%. The lower $J_{SC}$ is consistent with the wider band gap compared to Cs$_{0.7}$DMA$_{0.3}$PbI$_3$. The Cs$_{0.7}$DMA$_{0.3}$PbI$_2$Br film has a more blue-shifted absorption onset at around 620 nm, according to a wider band gap of around 2.0 eV, Supplementary Fig. 14a. The Cs$_{0.7}$DMA$_{0.3}$PbI$_2$Br solar cell achieved a PCE of 2.80%, a $V_{OC}$ of 1.11 V, a $J_{SC}$ of 8.55 mA cm$^{-2}$, and an FF of 29.57% (Supplementary Fig. 14c). A much lower $J_{SC}$ is obtained from the Cs$_{0.7}$DMA$_{0.3}$PbI$_2$Br cell because of the much wider band gap. Higher performance for the Cs$_{1-x}$DMA$_{x}$PbI$_3$Br and Cs$_{1-x}$DMA$_{x}$PbI$_2$Br cells is anticipated after further device optimization.

**Discussion**

We have demonstrated that small cation DMA can be formed in suite by the HI induced decomposition of DMF and can subsequently stabilize the black perovskite phase of CsPbI$_3$. However, the films are not really the all-inorganic CsPbI$_3$ phase but the Cs$_{1-x}$DMA$_{x}$PbI$_2$Br and Cs$_{1-x}$DMA$_{x}$PbI$_2$Br cells is anticipated after further device optimization.

**Methods**

**Device fabrication.** For the DMAI synthesis, DMF was slowly added into the HI solution with continuous stirring at 0 °C for 30 min. Water and excess DMF in solution was removed by low-vacuum rotary evaporation and then a white polycrystalline powder (DMAI powder) was obtained. Pre-cleaned FTO substrates were treated with UV-Ozone for 30 min. PEDOT:PSS films were coated on the FTO substrates with a spin-rate of 4000 rpm for 30 s and then annealing for 30 min at 150 °C. Perovskite films were deposited on FTO/PEDOT:PSS substrates in a N$_{2}$-filled glovebox. Neat CsPbI$_3$, neat DMAPbI$_3$, and Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ (X = I, Br) films were prepared by a solvent-engineering method$^{15}$ at a spin rate of 4000 rpm for 60 s. 0.7 ml of diethyl ether was quickly dropped onto the rotating substrates during the spin-coating process. CsPbI$_3$ films with HI addition were prepared by a one-step method at a spin rate of 2000 rpm for 60 s.$^{18}$ The neat CsPbI$_3$ precursor was prepared by dissolving 260 mg of CsI (99.999%, Sigma-Aldrich) and 461 mg of PbI$_2$ (beads, 99.999%, Sigma-Aldrich) in 0.8 ml of DMF (anhydrous, 99.8%, Sigma-Aldrich) and 0.2 ml of DMSO (anhydrous, 99.9%, Sigma-Aldrich). The neat DMAI precursor was prepared by dissolving 173 mg of DMAI and 461 mg of PbI$_2$ in 0.8 ml of DMF and 0.2 ml of DMSO. The Cs$_{0.7}$DMA$_{0.3}$PbI$_3$ precursor was prepared by dissolving (1-x) x 260 mg of CsI, x 173 mg of DMAI, and 461 mg of PbI$_2$ in 0.8 ml of DMF and then adding 3.3vol% HI (57 wt% in H$_2$O, 99.95%, Sigma-Aldrich) into the dissolved solution. All the films were annealed for 2 min at 60 °C and then 5 min at 100 °C on a hot plate. To complete the devices, a thin Cs$_{0.7}$DMA$_{0.3}$I$_2$Br (20 nm), a thin 2.9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (5 nm), and a Ag (80 nm) films were sequentially thermal evaporated on top of the absorber layers using a metal mask. The active area of the solar cells was 0.09 cm$^2$.

**Film and device characterization.** 1H-NMR spectra were measured with Bruker Avance III 600 MHz system with BBI probe. The morphology of the films and devices was examined on a high-resolution field emission SEM (Hitachi SU8030). XRD patterns of the films were characterized by a Rigaku Miniflex600 xPDR (Cu Kα radiation, λ = 1.5406 Å) operating at 40 kV/15 mA with a Kα filter. UV−vis absorption spectra of the films were measured with a Shimadzu UV−3600 UV−vis NIR spectrometer operating in the 200−2000 nm region at room temperature. EQE spectrum was obtained on an Oriel model QE−PV−SI instrument equipped with a NIST−certified Si diode. J−V curves were recorded using a Keithley model 2400 instrument under AM1.5 G simulated irradiation with a standard solar simulator (Abet Technologies). J−V curves were measured from 1.5 V to −0.2 V (reverse) or from −0.2 V to 1.5 V (forward) with an integration time of 16.67 ms and a voltage step of 11.4 mV. The light intensity of the solar simulator was calibrated by a NREL-certified monocrystalline silicon solar cell.

**Data availability**

The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information. Extra data are available from the authors upon request.

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Author contributions

W.K., C.C.S., and M.G.K. conceived the idea, designed the experiments, and wrote the manuscript. I.S. performed the NMR measurements and analyzed the data. W.K. carried out film and device fabrication and characterization. All authors discussed the results and commented on the manuscript. M.G.K. supervised the project.

Additional information

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