

## PEROVSKITES

Bication lead iodide 2D perovskite component to stabilize inorganic  $\alpha$ -CsPbI<sub>3</sub> perovskite phase for high-efficiency solar cellsTaiyang Zhang,<sup>1</sup> M. Ibrahim Dar,<sup>2</sup> Ge Li,<sup>1</sup> Feng Xu,<sup>1</sup> Nanjie Guo,<sup>1</sup> Michael Grätzel,<sup>2</sup> Yixin Zhao<sup>1\*</sup>

Among various all-inorganic halide perovskites exhibiting better stability than organic-inorganic halide perovskites,  $\alpha$ -CsPbI<sub>3</sub> with the most suitable band gap for tandem solar cell application faces an issue of phase instability under ambient conditions. We discovered that a small amount of two-dimensional (2D) EDAPbI<sub>4</sub> perovskite containing the ethylenediamine (EDA) cation stabilizes the  $\alpha$ -CsPbI<sub>3</sub> to avoid the undesirable formation of the nonperovskite  $\delta$  phase. Moreover, not only the 2D perovskite of EDAPbI<sub>4</sub> facilitate the formation of  $\alpha$ -CsPbI<sub>3</sub> perovskite films exhibiting high phase stability at room temperature for months and at 100°C for >150 hours but also the  $\alpha$ -CsPbI<sub>3</sub> perovskite solar cells (PSCs) display highly reproducible efficiency of 11.8%, a record for all-inorganic lead halide PSCs. Therefore, using the bication EDA presents a novel and promising strategy to design all-inorganic lead halide PSCs with high performance and reliability.

## INTRODUCTION

In past years, the organic-inorganic hybrid lead halide perovskite solar cells (PSCs) have progressed in an impressive manner approaching commercialization (1–5). However, the instability of organic-inorganic hybrid perovskite, such as CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> under thermal stress, might stem from the volatility of the organic cation and has become a challenge for long-term practical deployment. Although organic-inorganic mixed-cation PSCs demonstrating improved efficiency and stabilities have been documented (6–8), all-inorganic lead halide perovskite absorbers are much desired, specifically because the issues related to the release or decomposition of the organic component can be avoided. The most suitable all-inorganic structure could be based on CsPbX<sub>3</sub> perovskite because only the Cs is large enough to occupy the A sites with a suitable tolerance factor to fit the ABX<sub>3</sub> perovskite (B = Pb, X = halide) configuration. The phase-stable CsPbX<sub>3</sub> perovskite is usually based on bromide with a suitable tolerance factor, but the CsPbBr<sub>3</sub> perovskite has a too wide band gap to realize the fabrication of high-efficiency solar cells. Unfortunately, the  $\alpha$ -CsPbI<sub>3</sub> perovskite with a band gap of 1.73 eV, which is suitable for tandem solar cells, is structurally unstable and transforms spontaneously into the unwanted  $\delta$ -CsPbI<sub>3</sub> phase under ambient conditions at room temperature. Currently, cesium has been successfully used as A cation along with formamidinium in high-efficiency PSCs, but at concentrations above 20%, it leads to the formation of nonperovskite  $\delta$ -CsPbI<sub>3</sub> (7–12). Previous reports have suggested that the phase stability of  $\alpha$ -CsPbI<sub>3</sub> strongly depends on the crystallite size because stability improves by trimming the dimensions of the  $\alpha$ -CsPbI<sub>3</sub> grains toward the nanoregime (13, 14). Size-dependent phase or thermal stability has been reported in nanomaterials, especially when surfactants were used as growth-controlling agents (15, 16). However, conventional deposition strategies, which do not involve surfactants, mostly yield large-sized CsPbI<sub>3</sub> crystallites. Recently,  $\alpha$ -CsPbI<sub>3</sub> quantum dots with well-controlled size synthesized by hot injection have been fashioned into stable PSCs exhibiting an efficiency of up to 10% (17). In addition, a two-dimensional (2D) interface has been demon-

strated as an effective strategy to stabilize the organic-inorganic hybrid perovskite or to increase the thermal stability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (18, 19). However, a 2D segment of these structures may impair the electron transport across the device, lowering their efficiency (18). Therefore, it becomes imperative to judiciously design the bication 2D architecture.

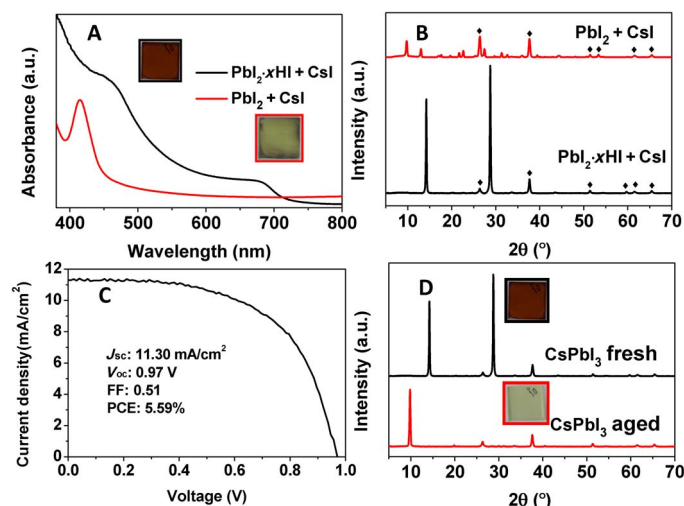
Here, we report a new and facile one-step deposition method to obtain highly efficient and stable  $\alpha$ -CsPbI<sub>3</sub> PSCs (2). We stabilize the  $\alpha$ -CsPbI<sub>3</sub> perovskite films by introducing ethylenediamine cations (EDA<sup>2+</sup>) whose terminal NH<sub>3</sub><sup>+</sup> groups are expected to cross-link the CsPbI<sub>3</sub> perovskite crystal units, rendering them less prone to unwanted phase transition to the  $\delta$  structure. Stable  $\alpha$ -CsPbI<sub>3</sub> films have been deposited by introducing a small amount of bication 2D perovskite of EDAPbI<sub>4</sub> into the CsPbI<sub>3</sub> precursor solution. This cross-links the  $\alpha$ -CsPbI<sub>3</sub> films without impairing the charge-carrier transport. The resulting  $\alpha$ -CsPbI<sub>3</sub> structures are highly robust at room temperature for months and can retain their phase even after annealing at 100°C for a week. In addition to the high stability, PSCs based on the  $\alpha$ -CsPbI<sub>3</sub> films showed highly reproducible photoconversion efficiency (PCE) of 11.8%, a record for  $\alpha$ -CsPbI<sub>3</sub> devices.

## RESULTS

We used a typical one-step method to deposit CsPbI<sub>3</sub> films using a regular precursor containing stoichiometric CsI and PbI<sub>2</sub> dissolved in *N,N'*-dimethylformamide (DMF). A rough yellowish film was obtained after annealing the precursor film at 150°C. As shown in Fig. 1 (A and B), the absorbance peak located at 414 nm and a strong x-ray diffraction (XRD) peak at 9.78° suggest the formation of the unwanted nonperovskite  $\delta$ -CsPbI<sub>3</sub> phase. This is quite expected because the yellow-to-black phase transformation occurs at 350°C (13, 20). Toward the formation of  $\alpha$ -CsPbI<sub>3</sub>, we develop a low-temperature fabrication method using PbI<sub>2</sub>:xHI (*x* > 1.3) and CsI as precursors. The XRD pattern of PbI<sub>2</sub>:xHI is shown in fig. S1, which exhibits no signature corresponding to the PbI<sub>2</sub> phase and is different from the previous reports on HPbI<sub>3</sub> (21). The brown perovskite CsPbI<sub>3</sub> film was obtained via one-step deposition using the PbI<sub>2</sub>:xHI + CsI precursor, followed by the low-temperature annealing at 100° to 150°C. It seems that the HI in the PbI<sub>2</sub>:xHI adduct decreases the crystallization energy barrier for the  $\alpha$ -CsPbI<sub>3</sub> phase. The as-prepared film shows an absorbance onset at ~718 nm in Fig. 1A,

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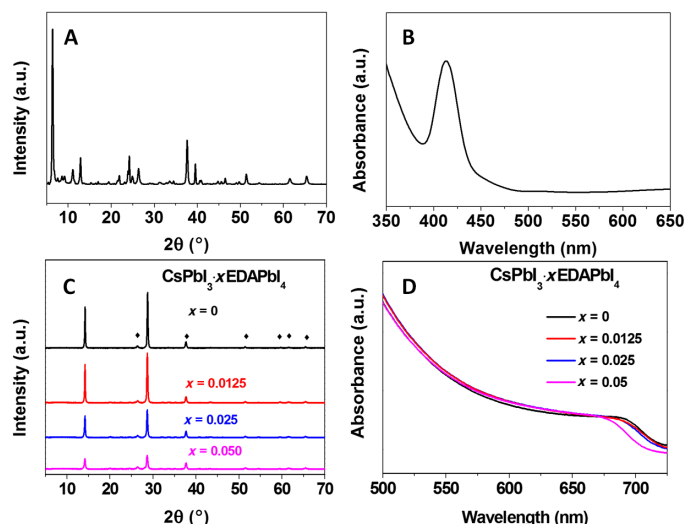
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**Fig. 1. Spectroscopic and structural characterization, photovoltaic performance, and stability test of CsPbI<sub>3</sub> films.** (A) Ultraviolet-visible (UV-vis) spectra of CsPbI<sub>3</sub> films prepared from PbI<sub>2</sub> + CsI and PbI<sub>2</sub>·xHI + CsI. a.u., arbitrary units. (B) XRD patterns of CsPbI<sub>3</sub> films prepared from PbI<sub>2</sub> + CsI and PbI<sub>2</sub>·xHI + CsI. (C) Photocurrent density–voltage (*J*-*V*) curve of α-CsPbI<sub>3</sub>-based PSCs. FF, fill factor. (D) XRD pattern and photos of fresh and aged (within a day) CsPbI<sub>3</sub> films prepared from PbI<sub>2</sub>·xHI + CsI.

indicating a band gap of 1.73 eV, consistent with the previous reports on α-CsPbI<sub>3</sub> (13, 22). The XRD pattern (Fig. 1B) obtained from the brown CsPbI<sub>3</sub> film could be indexed to a phase-pure cubic α-CsPbI<sub>3</sub> perovskite structure (12, 13). However, the PSC based on this α-CsPbI<sub>3</sub> film revealed a modest PCE of 5.59% (Fig. 1C), which is comparable to previous reports (10, 13, 23). Unfortunately, this phase-pure α-CsPbI<sub>3</sub> film also suffers from phase instability issues. As shown in Fig. 1D, the brown α-CsPbI<sub>3</sub> film transforms into a yellow δ-CsPbI<sub>3</sub> film within 12 hours.

In organic-inorganic or inorganic lead halide perovskite, the cation usually occupies one A site in either 3D ABX<sub>3</sub> or 2D A<sub>2</sub>BX<sub>4</sub> perovskites. Here, the two NH<sub>3</sub><sup>+</sup> groups of EDA can occupy two A sites and cross-link these 2D layers. This bication 2D perovskite has been theoretically predicted, and the copper halide perovskite based on EDA has been previously reported (24–26). The EDAPbI<sub>4</sub> perovskite film appears greenish, and its absorption spectrum and XRD pattern are listed in Fig. 2. In the XRD pattern (Fig. 2A), a peak located at 2θ = ~6° is a characteristic feature of 2D perovskites (21, 27). Atomic force microscopy (AFM) images reveal that the EDAPbI<sub>4</sub> films are consisted of stacks of layered structure (fig. S2). Furthermore, an absorption peak around 420 nm observed in the UV-vis spectrum (Fig. 2B) suggested that the EDAPbI<sub>4</sub> is a wider band-gap material (2, 28). Previously, some reports suggested that the bication 2D perovskite can be either a regular (100) layered perovskite or a corrugated (110) layered perovskite (29–33). Given the band-gap value of EDAPbI<sub>4</sub> sample and the short alkyl chain length of the EDA, we assume that it should be the formation of a (110) layered perovskite structure (fig. S3). We introduce a small amount of EDAPbI<sub>4</sub> into the CsPbI<sub>3</sub> precursor, and these samples are noted as CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub>. The x-ray photoelectron spectroscopy (XPS) spectra corresponding to an N element acquired from the CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> (*x* = 0.0125 to 0.05) samples establish the presence of EDA cations in these films (fig. S4). XRD patterns and UV-vis spectra of CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> samples are listed in Fig. 2 (C and D). Irrespective of their EDAPbI<sub>4</sub> content (*x*), all the XRD patterns could



**Fig. 2. Structural characterization and spectroscopic study of EDAPbI<sub>4</sub> and CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> films.** (A) XRD pattern and (B) UV-vis spectrum of EDAPbI<sub>4</sub> films. (C) XRD patterns and (D) UV-vis absorption spectra of CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> (*x* = 0 to 0.05) perovskites.

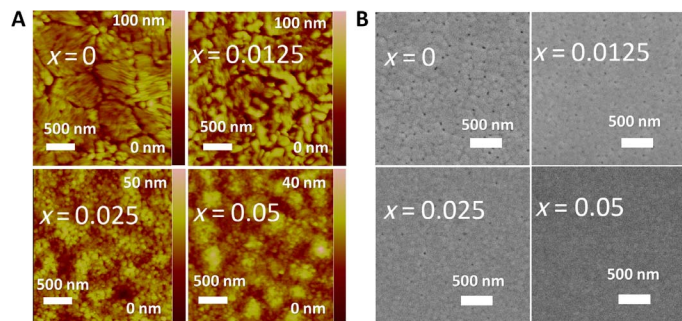
be indexed to the standard α-CsPbI<sub>3</sub> perovskite phase. No signature (peaks below 2θ = 10°) corresponding to the EDAPbI<sub>4</sub> phase was found in the CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> samples, which suggests either the absence of the EDAPbI<sub>4</sub> crystal phase or the formation of extremely thin EDAPbI<sub>4</sub> layers or crystallites. Amorphous EDAPbI<sub>4</sub> could also be present. This matches the behavior of previously reported 2D/3D perovskite formulations (18).

Within the detection limit of XRD, no peak indexable to any impurity phase, such as δ-CsPbI<sub>3</sub> or PbI<sub>2</sub>, is present. The absence of a PbI<sub>2</sub> impurity peak further indicates that ethylenediamine dihydroiodide (EDA<sub>I</sub>) is incorporated in the crystal structure. If we add an excess amount (*x*) of PbI<sub>2</sub> without EDA<sub>I</sub> into the precursor, PbI<sub>2</sub> crystallizes as a separate phase (fig. S5). The XRD data indicated that the addition of xEDAPbI<sub>4</sub> in CsPbI<sub>3</sub> does not form a mixture of 2D EDAPbI<sub>4</sub> and 3D CsPbI<sub>3</sub> perovskite. Furthermore, by increasing the content (*x*) of EDAPbI<sub>4</sub> (in CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> samples), the intensity of the XRD peaks decreases, whereas their peak width broadens, indicating the decrease of crystallite size. Such a confinement effect was further manifested by the blueshift of absorption onset (Fig. 2D), which is quite evident for the CsPbI<sub>3</sub>·0.05EDAPbI<sub>4</sub> sample. The photoluminescence (PL) spectra of CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> samples (fig. S6A) also exhibited blueshift when the content of EDAPbI<sub>4</sub> is increased. Moreover, their PL lifetimes also increased with the content of EDAPbI<sub>4</sub> (fig. S5B). Such a blueshift has been observed in CsPbI<sub>3</sub> quantum dots synthesized using hot-injection solution-based method and other hybrid lead halide perovskite films with the incorporation of 2D perovskite (34). The blueshift in both UV-vis and PL spectra can be ascribed either to the formation of 2D/3D perovskite of CsPbI<sub>3</sub>·0.05EDAPbI<sub>4</sub> or to the decrease in crystal size. In the plausible 2D/3D configuration, we hypothesize that the (110) layered 2D EDAPbI<sub>4</sub> component can also function as an interface to separate small CsPbI<sub>3</sub> crystal units, as in the regular 2D/3D perovskite. The 2D EDAPbI<sub>4</sub> might also work as a blocking layer similar to the surfactant, which can eventually reduce the crystallite size of the CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> perovskite structures. Previous reports have suggested that the reduced crystal size can lead to the blueshift of optical spectrum even when the crystal size is larger than the Bohr radius (35).

Furthermore, the addition of a small amount of EDAPbI<sub>4</sub> also helps reduce the pinholes in the deposited CsPbI<sub>3</sub> perovskite films and passivates their surface, similar to a previously reported regular 2D/3D or cross-linked 2D/3D perovskite (18, 28). Figure S6B shows that the PL lifetime of the CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> film increases with its EDAPbI<sub>4</sub> content, suggesting a suppression of radiation-less recombination. The scanning electron microscopy (SEM) and AFM images (Fig. 3, A and B) show that the grain size of CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> decreases markedly from ~300 nm ( $x = 0$ ) to ~35 nm ( $x = 0.025$ ) with increasing EDAPbI<sub>4</sub> content. This is consistent with the XRD peak broadening observed in Fig. 2. Note that the pinholes became much less with the addition of EDAPbI<sub>4</sub>, which is favorable for high-performance PSC fabrication.

All these results reveal that the addition of a small content of EDAPbI<sub>4</sub> has strongly affected the properties of CsPbI<sub>3</sub>. To rationalize this observation, we first exclude the possibility of Cs<sup>+</sup> substitution by EDA on a single A site of CsPbI<sub>3</sub> to form an EDA<sub>x</sub>Cs<sub>1-2x</sub>PbI<sub>3</sub> mixed-cation perovskites on the basis of the large size of EDA ( $r = 0.31$  nm). Moreover, replacing Cs<sup>+</sup> by larger cations, such as EDA, should narrow the band gap and induce an XRD peak shift, although we observe a widening of the band gap and no shift in the XRD peak position.

We adopted a planar configuration to fabricate PSCs based on these CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> perovskites. The photovoltaic parameters extracted from the  $J$ - $V$  curves (Fig. 4A) are listed in Table 1. We found that CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> ( $x = 0.0125$  to 0.05) devices show a much better performance than those based on the pure CsPbI<sub>3</sub>. The enhancement in all the photovoltaic parameters, that is,  $J_{SC}$ ,  $V_{OC}$ , and FF, can be attributed to less pinholes, desired charge-carrier dynamics, and surface passivation by EDAPbI<sub>4</sub>. For  $x \leq 0.025$ , the transient photovoltage decay curves (fig. S7) exhibit monotonic increase in the lifetime with the EDAPbI<sub>4</sub> incorporation, which is consistent with the PL decay dynamics (fig. S6B). Furthermore, the 2D EDAPbI<sub>4</sub> in these CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> ( $x = 0.0125$  to 0.05) compositions seem to have less impact on the charge transfer because this can be significantly hindered in regular 2D/3D PSCs (18). The best performing cell used the CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> perovskite formulation showing a remarkable PCE of 11.8% under reverse scan. To the best of our knowledge, this is a record for CsPbI<sub>3</sub>-based PSCs. Hysteresis between different scan directions is also found in our planar cell structure (fig. S8), and the scan rate-independent maximum power tracking (Fig. 4B) indicates an efficiency of 10.5%. The integrated  $J_{SC}$  obtained from the incident photon-to-electron conversion efficiency (IPCE) is consistent with the values extracted from the  $J$ - $V$  curves. Note that the IPCE value of the champion cell has reached 86% over a wide wavelength range. Device performance was also highly reproducible, as shown in Fig. 4D. The improved repro-



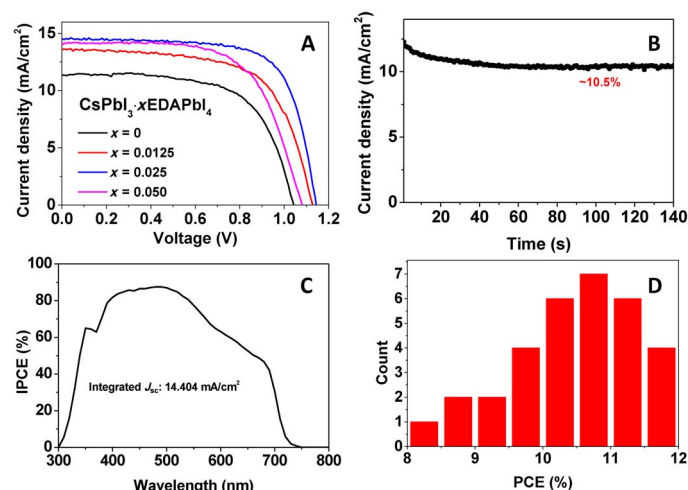
**Fig. 3. Effect of EDAPbI<sub>4</sub> on the evolution of morphology of CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub>.** (A) AFM and (B) SEM images of perovskite films obtained from the CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> additive precursor ( $x = 0, 0.0125, 0.025,$  and  $0.05$ ).

ducibility demonstrated by the CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> solar cells can be ascribed to the better control on the film formation (less pinholes) (36, 37).

The best solar cell based on the CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> perovskite showed good stability because it retained ~10% efficiency after storing in a dark dry box for 1 month without any encapsulation (Fig. 5A). All the above results establish that the formation of CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> perovskite significantly improves the performance of the devices. Besides the high efficiency, the thermal stability of CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> films markedly improved as compared to the pure CsPbI<sub>3</sub> (fig. S9). The  $\alpha$ -CsPbI<sub>3</sub> perovskite phase of the CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> sample can be retained for months at room temperature (fig. S10) and after heating the CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> film at 100°C for 1 week, as shown in Fig. 5B.

## DISCUSSION

All of the above results demonstrate the superior photovoltaic performance of CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> over pure  $\alpha$ -CsPbI<sub>3</sub>-based PSCs. It appears that the hypothesized EDAPbI<sub>4</sub> 2D perovskite component not only stabilizes the  $\alpha$ -CsPbI<sub>3</sub> perovskite phase but also reduces the deterioration of charge-carrier transport across the perovskite film caused by the “insulating” long alkyl spacing layers (18, 38). This improvement in both efficiency and stability is closely related to this unique bifunctional cation perovskite component. We cannot obtain the efficient and stable  $\alpha$ -CsPbI<sub>3</sub> perovskite films if we merely add EDAl<sub>2</sub> + PbI<sub>2</sub> into the CsPbI<sub>3</sub> precursor solution. In addition, if the EDA is replaced by the monofunctional ethylamine (EA) in the regular 2D/3D CsPbI<sub>3</sub>:xEA<sub>2</sub>PbI<sub>4</sub> samples, the perovskite phase of CsPbI<sub>3</sub>:xEA<sub>2</sub>PbI<sub>4</sub> ( $x = 0.025$ ) deteriorated as markedly as observed in the pure CsPbI<sub>3</sub>. As shown in fig. S11, the typical sample of brown CsPbI<sub>3</sub>:0.025EA<sub>2</sub>PbI<sub>4</sub> turns into a yellow phase within a day at room temperature. In contrast, the bication EDA with CH<sub>2</sub>-CH<sub>2</sub> can effectively assemble the CsPbI<sub>3</sub> crystal units. Furthermore, all the CsPbI<sub>3</sub>:xEA<sub>2</sub>PbI<sub>4</sub> perovskite film-based solar cells exhibited poor photovoltaic performance, and the best  $J$ - $V$  curve obtained from the PSCs based on CsPbI<sub>3</sub>:0.025EA<sub>2</sub>PbI<sub>4</sub> is listed in fig. S12. The efficiency is only ~4.4%, which is way too low than that of CsPbI<sub>3</sub> PSCs. Such low stability could be due to either the weak

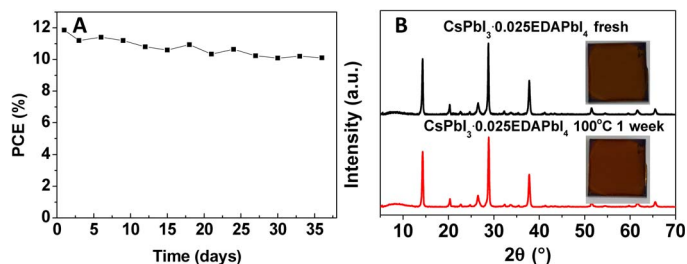


**Fig. 4. Device characteristics for CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> films.** (A) Typical  $J$ - $V$  curves of CsPbI<sub>3</sub>:xEDAPbI<sub>4</sub> PSCs. (B) Stable current output at the maximum point of the champion CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> PSC. (C) IPCE of the best solar cell based on the CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> perovskite. (D) Histogram of device efficiencies of CsPbI<sub>3</sub>:0.025EDAPbI<sub>4</sub> PSCs based on 32 cells from three batches.



**Table 1. Effect of EDAPbI<sub>4</sub> on the metrics of planar CsPbI<sub>3</sub> PSCs (12 to 32 cells for each type).**

Precursor type	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF	$\eta$ (%)
Pure CsPbI <sub>3</sub>	11.33 (11.63 ± 1.55)	1.04 (0.89 ± 0.09)	0.65 (0.53 ± 0.06)	7.66 (5.56 ± 1.16)
CsPbI <sub>3</sub> -0.0125EDAPbI <sub>4</sub>	13.59 (13.31 ± 0.36)	1.13 (1.09 ± 0.06)	0.65 (0.56 ± 0.06)	9.98 (8.22 ± 1.46)
CsPbI <sub>3</sub> -0.025EDAPbI <sub>4</sub>	14.53 (14.05 ± 0.57)	1.15 (1.13 ± 0.02)	0.71 (0.64 ± 0.08)	11.86 (10.42 ± 0.91)
CsPbI <sub>3</sub> -0.05EDAPbI <sub>4</sub>	13.97 (13.17 ± 0.88)	1.08 (1.06 ± 0.03)	0.65 (0.61 ± 0.02)	9.81 (8.58 ± 0.66)

**Fig. 5. Stability test of CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub>-based devices and films. (A)** PCE of the champion PSC fabricated from CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> as a function of storage time in a dark dry box. **(B)** XRD pattern and images of the CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> film heated at 100°C in a dry box for 1 week.

steric effect of short alkyl chain containing the EA cation compared to EDA or the lack of bication effect. Not appropriately, we used a longer-chain alkylamine, such as butylamine (BA), with an even larger size to form the CsPbI<sub>3</sub>-0.025BA<sub>2</sub>PbI<sub>4</sub> perovskite. The CsPbI<sub>3</sub>-0.025BA<sub>2</sub>PbI<sub>4</sub> samples show some improved stability than those of CsPbI<sub>3</sub>-0.025EA<sub>2</sub>PbI<sub>4</sub> but still far more unstable than the CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> samples (fig. S13). This result suggested that both the steric effect and bication in the 2D perovskite improve the phase stability, although the latter might be more important.

To further understand the mechanism behind the high phase stability of CsPbI<sub>3</sub>-xEDAPbI<sub>4</sub>, we used other two bications, that is, 1,4-diaminobutane (BDA<sup>2+</sup>) and 2,2'-(ethylenedioxy)bis(ethylammonium) (EDBE<sup>2+</sup>), which are similar to EDA. The BDAPbI<sub>4</sub> perovskite has been demonstrated to be a (100) layered bication 2D perovskite, whereas the EDBEPbI<sub>4</sub> has been shown to be a (110) layered 2D perovskite (29–31, 33). Like CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub>, the CsPbI<sub>3</sub>-0.025BDAPbI<sub>4</sub> samples are composed of smaller perovskite crystallites (fig. S14), exhibiting significantly enhanced thermal stability than pristine CsPbI<sub>3</sub>. However, after holding at 100°C for 3 days, the CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> film turns into the yellow  $\delta$  phase, suggesting that its phase stability is lower than that of CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> (fig. S15A). The main difference between EDAPbI<sub>4</sub> and BDAPbI<sub>4</sub> is that the former is a (110) layered 2D perovskite, whereas the latter is a (100) layered 2D perovskite. It is likely that the higher phase stability of CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> could be ascribed to the unique (110) layered perovskite structure of EDAPbI<sub>4</sub>. The CsPbI<sub>3</sub>-0.025EDBEPbI<sub>4</sub> sample with the (110) layered EDBEPbI<sub>4</sub> shows enhanced thermal stability than CsPbI<sub>3</sub>; however, as compared to CsPbI<sub>3</sub>-0.025BDAPbI<sub>4</sub>, its thermal stability is even poorer, as shown in fig. S15B. It is found that the CsPbI<sub>3</sub>-0.025EDBEPbI<sub>4</sub> perovskite sample shows a larger crystal size than CsPbI<sub>3</sub>-0.025BDAPbI<sub>4</sub> and CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub>, suggesting that the lower thermal stability of CsPbI<sub>3</sub>-0.025EDBEPbI<sub>4</sub> sample might be due to the presence of large crystallites. All these findings demonstrate

that the confluence of reduced crystal size and the unique (110) layered bication 2D perovskite structure enhance the overall phase stability of  $\alpha$ -CsPbI<sub>3</sub>. Specifically, we ascribe the enhanced phase stability of CsPbI<sub>3</sub>-xEDAPbI<sub>4</sub> to the reduced crystallite size and the EDAPbI<sub>4</sub> component's unique (110) layered structure.

In summary, we report a phase-stable  $\alpha$ -CsPbI<sub>3</sub> film with an EDAPbI<sub>4</sub> 2D perovskite component prepared via a novel and facile single-step method under ambient conditions for high-efficiency all-inorganic PSCs. By introducing the 2D perovskite of EDAPbI<sub>4</sub>, the structurally robust  $\alpha$ -CsPbI<sub>3</sub> perovskite films were obtained even at temperatures several hundred°C below the phase transition point. The addition of a small amount of EDAPbI<sub>4</sub> stabilizes the  $\alpha$ -CsPbI<sub>3</sub>. Moreover, these perovskite films can retain the  $\alpha$ -CsPbI<sub>3</sub> phase even after annealing at 100°C for >150 hours and are also stable at room temperature for months. The EDAPbI<sub>4</sub> ( $x = 0$  to 0.05) not only enhances the phase stability of  $\alpha$ -CsPbI<sub>3</sub> crystallites significantly but also connects them for effective electron transfer and passivates the surface defects. Finally, a champion  $\alpha$ -CsPbI<sub>3</sub> PSC based on CsPbI<sub>3</sub>-0.025EDAPbI<sub>4</sub> perovskite films showing a PCE of 11.8%, a record for all-inorganic PSCs, was realized. Therefore, the concept of using bication presents a novel and promising strategy for designing all-inorganic lead halide PSCs yielding high performance and reliability. Such a bication 2D perovskite with different oriented layer structure concepts could also be extended to balance high performance and high stability in organic-inorganic hybrid lead halide perovskites with the incorporation of a 2D component for their use in optoelectronic applications.

## MATERIALS AND METHODS

### Materials

EDAI<sub>2</sub> was synthesized by reacting EDA and hydroiodic acid with a molar ratio of 1:2.2 in an ice bath for 2 hours. The precipitate was collected by rotary evaporation, washed three times with diethyl ether, and then vacuum-dried. 1,4-Diaminobutane dihydroiodide (BDAl<sub>2</sub>), 2,2'-(ethylenedioxy)bis(ethylammonium) dihydroiodide (EDBEI<sub>2</sub>), ethylammonium iodide (EAI), and butylammonium iodide (BAI) were synthesized following the similar procedure. The PbI<sub>2</sub>-xHI sample was synthesized as follows: 1 M PbI<sub>2</sub> in DMF solution was reacted with 1.5 molar ratio of hydroiodic acid for 1 hour, followed by rotary evaporation, washed three times with diethyl ether, and then vacuum-dried; the concentration of PbI<sub>2</sub> in the final product should be within the range of 62 to 65 weight %. All the other materials were purchased from Sigma-Aldrich and used as received without any purification.

The CsPbI<sub>3</sub>-xEDAPbI<sub>4</sub> precursor solution was prepared by dissolving 1 mmol of PbI<sub>2</sub>-xHI and 1 mmol of CsI (1 mM) in 2 ml of DMF to form a 0.5 M precursor solution mixed with different  $x$  ratios of

0.5 M EDAPbI<sub>4</sub> solution. The 0.5 M EDAPbI<sub>4</sub> solution was obtained by dissolving 0.5 mmol of EDAl<sub>2</sub> and 0.5 mmol of PbI<sub>2</sub> into 1 ml of DMF.

### Device fabrication

A 20-nm-thick compact TiO<sub>2</sub> layer was first deposited on the patterned fluorine-doped tin oxide using 0.2 M Ti(IV) bis(ethyl acetoacetato) diisopropoxide in 1-butanol solution at 450°C, followed by annealing at 450°C for 1 hour. The CsPbI<sub>3</sub>·xEDAl<sub>2</sub> precursor solutions were then spin-coated onto the prewarmed c-TiO<sub>2</sub>-coated substrate (50°C) at 3500 rpm for 30 s, followed by annealing at 150°C for 2 min. After the films were cooled down to room temperature, a layer of hole transport material of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane)sulfonimide lithium salt, and 0.12 M 4-*tert*-butylpyridine in chlorobenzene/ acetonitrile (10:1, v/v) solution was spin-coated at 4000 rpm for 20 s. Finally, a 100-nm-thick Ag contact layer was thermally evaporated as back contact.

### Characterization

The crystal structures of the CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> films were examined by a Shimadzu XRD-6100 diffractometer with Cu K<sub>α</sub> radiation. The morphologies of the CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> films were observed by a JSM-7800F Prime SEM and a Bruker Multimode Nanoscope IIIa AFM. The absorption spectra of the EDAPbI<sub>4</sub> and CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> perovskite films were taken on a Cary 60 UV-vis spectrophotometer. XPS spectra were acquired with a Kratos Axis Ultra DLD spectrometer (Kratos Analytical-A Shimadzu Group Company) using a monochromatic Al K source (1486.6 eV). Time-integrated PL and time-resolved PL experiments were performed by exciting the samples deposited onto a nonconducting glass using the second harmonic of a picosecond mode-locked Ti-sapphire laser (80.5 MHz) at 420 nm under ambient conditions. The average power was kept around 0.05 μJ/cm<sup>2</sup> per pulse. Using a 32-cm focal length monochromator equipped with a charge-coupled device, which has a spectral resolution of >1 meV, and a streak camera with a temporal resolution of >2 ps, the PL data were spectrally and temporally analyzed. The *J-V* curves of the PSCs were measured by a Keithley 2401 SourceMeter under simulated air mass 1.5-global illumination with a scan rate of 0.05 V/S (100 mW/cm<sup>2</sup>) (Enlitech SS-F5-3A Class AAA Solar Simulator; the light intensity was calibrated by a stand Si cell before test), equipped with a nonreflective metal mask with an aperture area of 0.12 cm<sup>2</sup>; the IPCE was measured on a QE-3011 system from Enlitech. All the *J-V* and IPCE tests were processed in atmosphere with a relative humidity of 30 to 45%.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/9/e1700841/DC1>

- fig. S1. Comparative analysis of crystal structures of PbI<sub>2</sub>·xHI and HPbI<sub>3</sub>.
- fig. S2. Morphology of EDAPbI<sub>4</sub> films.
- fig. S3. Schematic structure of (110) layered 2D films.
- fig. S4. The organic compositions of CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> films.
- fig. S5. Characterization of CsPbI<sub>3</sub> + 0.05PbI<sub>2</sub> with or without EDAl<sub>2</sub>.
- fig. S6. Effect of EDAPbI<sub>4</sub> on the optical properties.
- fig. S7. Effect of EDAPbI<sub>4</sub> on the transient photovoltage behavior.
- fig. S8. Hysteresis behavior of CsPbI<sub>3</sub>·0.025EDAPbI<sub>4</sub>-based device.
- fig. S9. Effect of EDAPbI<sub>4</sub> on the phase stability of CsPbI<sub>3</sub>·xEDAPbI<sub>4</sub> perovskite films.
- fig. S10. Phase stability of CsPbI<sub>3</sub>·0.025EDAPbI<sub>4</sub> perovskite film under room temperature.
- fig. S11. Phase stability of CsPbI<sub>3</sub>·0.025EA<sub>2</sub>PbI<sub>4</sub>-based films.
- fig. S12. Device performance of CsPbI<sub>3</sub>·0.025EA<sub>2</sub>PbI<sub>4</sub>-based solar cell.
- fig. S13. Phase stability of CsPbI<sub>3</sub>·0.025BA<sub>2</sub>PbI<sub>4</sub>-based films.
- fig. S14. Effect of CsPbI<sub>3</sub>·0.025BDAPbI<sub>4</sub> and CsPbI<sub>3</sub>·0.025EDBEPbI<sub>4</sub> 2D perovskite component on the evolution of morphology.
- fig. S15. Phase stability of CsPbI<sub>3</sub>·0.025BDAPbI<sub>4</sub> and CsPbI<sub>3</sub>·0.025EDBEPbI<sub>4</sub> films.

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## Bication lead iodide 2D perovskite component to stabilize inorganic $\alpha$ -CsPbI<sub>3</sub> perovskite phase for high-efficiency solar cells

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