PEROVSKITES

Bication lead iodide 2D perovskite component to stabilize inorganic α-CsPbI₃ perovskite phase for high-efficiency solar cells

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Among various all-inorganic halide perovskites exhibiting better stability than organic-inorganic halide perovskites, α-CsPbI₃ 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) EDAPbI₄ perovskite containing the ethylenediamine (EDA) cation stabilizes the α-CsPbI₃ to avoid the undesired formation of the nonperovskite δ phase. Moreover, not only the 2D perovskite of EDAPbI₄ facilitate the formation of α-CsPbI₃ perovskite films exhibiting high phase stability at room temperature for months and at 100°C for >150 hours but also the α-CsPbI₃ 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 CH₃NH₃PbI₃ 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 CsPbX₃ perovskite because only the Cs is large enough to occupy the A sites with a suitable tolerance factor to fit the ABX₃ perovskite (B = Pb, X = halide) configuration. The phase-stable CsPbX₃ perovskite is usually based on bromide with a suitable tolerance factor, but the CsPbBr₃ perovskite has a too wide band gap to realize the fabrication of high-efficiency solar cells. Unfortunately, the α-CsPbI₃ 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 δ-CsPbI₃ 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 non-perovskite δ-CsPbI₃ (7–12). Previous reports have suggested that the phase stability of α-CsPbI₃ strongly depends on the crystallite size because stability improves by trimming the dimensions of the α-CsPbI₃ 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 CsPbI₃ crystallites. Recently, α-CsPbI₃ 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 demonstrated as an effective strategy to stabilize the organic-inorganic hybrid perovskite or to increase the thermal stability of CH₃NH₃PbI₃ (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 α-CsPbI₃ PSCs (2). We stabilize the α-CsPbI₃ perovskite films by introducing ethylenediamine cations (EDA⁺) whose terminal NH₃⁺ groups are expected to cross-link the CsPbI₃ perovskite crystal units, rendering them less prone to unwanted phase transition to the δ structure. Stable α-CsPbI₃ films have been deposited by introducing a small amount of bication 2D perovskite EDAPbI₄ into the CsPbI₃ precursor solution. This cross-links the α-CsPbI₃ films without impairing the charge-carrier transport. The resulting α-CsPbI₃ 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 α-CsPbI₃ films showed highly reproducible photoconversion efficiency (PCE) of 11.8%, a record for α-CsPbI₃ devices.

RESULTS

We used a typical one-step method to deposit CsPbI₃ films using a regular precursor containing stoichiometric CsI and PbI₂ 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 non-perovskite δ-CsPbI₃ phase. This is quite expected because the yellow-to-black phase transformation occurs at 350°C (13, 20). Toward the formation of α-CsPbI₃, we develop a low-temperature fabrication method using PbI₂·xHI (x > 1.3) and CsI as precursors. The XRD pattern of PbI₂·xHI is shown in Fig. S1, which exhibits no signature corresponding to the PbI₂ phase and is different from the previous reports on HPbI₃ (21). The brown perovskite CsPbI₃ film was obtained via one-step deposition using the PbI₂·xHI + CsI precursor, followed by the low-temperature annealing at 100° to 150°C. It seems that the HI in the PbI₂·xHI adduct decreases the crystallization energy barrier for the α-CsPbI₃ phase. The as-prepared film shows an absorbance onset at ~718 nm in Fig. 1A,
indicating a band gap of 1.73 eV, consistent with the previous reports on α-CsPbI₃ (13, 22). The XRD pattern (Fig. 1B) obtained from the brown CsPbI₃ film could be indexed to a phase-pure cubic α-CsPbI₃ perovskite structure (12, 13). However, the PSC based on this α-CsPbI₃ film revealed a modest PCE of 5.59% (Fig. 1C), which is comparable to previous reports (10, 13, 23). Unfortunately, this phase-pure α-CsPbI₃ film also suffers from phase instability issues. As shown in Fig. 1D, the brown α-CsPbI₃ film transforms into a yellow δ-CsPbI₃ film within 12 hours.

In organic-inorganic or inorganic lead halide perovskite, the cation usually occupies one A site in either 3D ABX₃ or 2D A₂BX₄ perovskites. Here, the two NH₄⁺ 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 EDAPbI₄ 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 EDAPbI₄ films are consisted of stacks of layer-structured films. Furthermore, an absorption peak around 420 nm observed in the UV-vis spectrum (Fig. 2B) suggested that the EDAPbI₄ 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 EDAPbI₄ sample and the short alkyl chain length of the EDA, we assume that it should be the formation of a (110) layered perovskite structure (s3). We introduce a small amount of EDAPbI₄ into the CsPbI₃ precursor, and these samples are noted as CsPbI₃-xEDAPbI₄. The x-ray photoelectron spectroscopy (XPS) spectra corresponding to an N element acquired from the CsPbI₃-xEDAPbI₄ (x = 0.0125 to 0.05) samples establish the presence of EDA cations in these films (Fig. 4S). XRD patterns and UV-vis spectra of CsPbI₃-xEDAPbI₄ samples are listed in Fig. 2 (C and D). Irrespective of their EDAPbI₄ content (x), all the XRD patterns could be indexed to the standard α-CsPbI₃ perovskite phase. No signature (peaks below 2θ = 10°) corresponding to the EDAPbI₄ phase was found in the CsPbI₃-xEDAPbI₄ samples, which suggests either the absence of the EDAPbI₄ crystal phase or the formation of extremely thin EDAPbI₄ layers or crystallites. Amorphous EDAPbI₄ 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-CsPbI₃ or PbI2, is present. The absence of a PbI2 impurity peak further indicates that ethylenediamine dihydroiodide (EDA(I₂)) is incorporated in the crystal structure. If we add an excess amount (χ) of PbI2 without EDA(I₂) into the precursor, PbI2 crystallizes as a separate phase (Fig. S5). The XRD data indicated that the addition of xEDAPbI₄ in CsPbI₃ does not form a mixture of 2D EDAPbI₄ and 3D CsPbI₃ perovskite. Furthermore, by increasing the content (χ) of EDAPbI₄ (in CsPbI₃-xEDAPbI₄ 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 CsPbI₃-0.05EDAPbI₄ sample. The photoluminescence (PL) spectra of CsPbI₃-xEDAPbI₄ samples (Fig. S6A) also exhibited blueshift when the content of EDAPbI₄ is increased. Moreover, their PL lifetimes also increased with the content of EDAPbI₄ (Fig. S5B). Such a blueshift has been observed in CsPbI₃ 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 CsPbI₃-0.05EDAPbI₄ or to the decrease in crystal size. In the plausible 2D/3D configuration, we hypothesize that the (110) layered 2D EDAPbI₄ component can also function as an interface to separate small CsPbI₃ crystal units, as in the regular 2D/3D perovskite. The 2D EDAPbI₄ might also work as a blocking layer similar to the surfactant, which can eventually reduce the crystallite size of the CsPbI₃-xEDAPbI₄ 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 EDAPbI₄ also helps reduce the pinholes in the deposited CsPbI₃ 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 CsPbI₃–xEDAPbI₄ film increases with its EDAPbI₄ content, suggesting a suppression of recombination. The scanning electron microscopy (SEM) and AFM images (Fig. 3, A and B) show that the grain size of CsPbI₃–xEDAPbI₄ decreases markedly from ~300 nm (x = 0) to ~35 nm (x = 0.025) with increasing EDAPbI₄ content. This is consistent with the XRD peak broadening observed in Fig. 2. Note that the pinholes became much less with the addition of EDAPbI₄, which is favorable for high-performance PSC fabrication.

All these results reveal that the addition of a small content of EDAPbI₄ has strongly affected the properties of CsPbI₃. To rationalize this observation, we first exclude the possibility of Cs⁺ substitution by EDA on a single A site of CsPbI₃ to form a EDA-Cs₁₋₂PbI₃ mixed-cation perovskites on the basis of the large size of EDA (r = 0.31 nm). Moreover, replacing Cs⁺ 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 CsPbI₃–xEDAPbI₄ perovskites. The photovoltaic parameters extracted from the J–V curves (Fig. 4A) are listed in Table 1. We found that CsPbI₃–xEDAPbI₄ (x = 0.0125 to 0.05) devices show a much better performance than those based on the pure CsPbI₃. The enhancement in all the photovoltaic parameters, that is, JSC, VOC, and FF, can be attributed to less pinholes, desired charge-carrier dynamics, and surface passivation by EDAPbI₄. For x ≤ 0.025, the transient photovoltage decay curves (fig. S7) exhibit monotonic increase in the lifetime with the EDAPbI₄ incorporation, which is consistent with the PL decay dynamics (fig. S6B). Furthermore, the 2D EDAPbI₄ in these CsPbI₃–xEDAPbI₄ (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 CsPbI₃–xEA₂PbI₄ perovskite films (18). The best performing cell used the CsPbI₃–0.025EDAPbI₄ perovskite formulation showing a remarkable PCE of 11.8% under reverse scan. To the best of our knowledge, this is a record for α-CsPbI₃ perovskite films if we merely add EA₂I₂ instead of EDAPbI₄. In addition, if the EDA is replaced by the monofunctional ethylamine (EA) in the regular 2D/3D CsPbI₃–xEA₂PbI₄ samples, the perovskite phase of CsPbI₃–xEA₂PbI₄ (x = 0.025) deteriorated as markedly as observed in the pure CsPbI₃. As shown in fig. S11, the typical sample of brown CsPbI₃–0.025EA₂PbI₄ turns into a yellow phase within a day at room temperature. In contrast, the bication EDA with CH₂–CH₂ can effectively assemble the CsPbI₃ crystal units. Furthermore, all the CsPbI₃–xEA₂PbI₄ perovskite film-based solar cells exhibited poor photovoltaic performance, and the best J–V curve obtained from the PSCs based on CsPbI₃–0.025EA₂PbI₄ is listed in fig. S12. The efficiency is only ~4.4%, which is way too low than that of CsPbI₃ PSCs. Such low stability could be due to either the weak reproductibility demonstrated by the CsPbI₃–xEDAPbI₄ solar cells can be ascribed to the better control on the film formation (less pinholes) (36, 37).

The best solar cell based on the CsPbI₃–0.025EDAPbI₄ 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 CsPbI₃–0.025EDAPbI₄ perovskite significantly improves the performance of the devices. Besides the high efficiency, the thermal stability of CsPbI₃–xEDAPbI₄ films markedly improved as compared to the pure CsPbI₃ (fig. S9). The α-CsPbI₃ perovskite phase of the CsPbI₃–0.025EDAPbI₄ sample can be retained for months at room temperature (fig. S10) and after heating the CsPbI₃–0.025EDAPbI₄ film at 100°C for 1 week, as shown in Fig. 5B.

DISCUSSION

All of the above results demonstrate the superior photovoltaic performance of CsPbI₃–xEDAPbI₄ over pure α-CsPbI₃–xEDAPbI₄ films. It appears that the hypothesized EDAPbI₄ 2D perovskite component not only stabilizes the α-CsPbI₃ 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 α-CsPbI₃ perovskite films if we merely add EA₂I₂ instead of EDAPbI₄ and PbI₂ into the CsPbI₃ precursor solution. In addition, if the EDA is replaced by the monofunctional ethylamine (EA) in the regular 2D/3D CsPbI₃–xEA₂PbI₄ samples, the perovskite phase of CsPbI₃–xEA₂PbI₄ (x = 0.025) deteriorated as markedly as observed in the pure CsPbI₃. As shown in fig. S11, the typical sample of brown CsPbI₃–0.025EA₂PbI₄ turns into a yellow phase within a day at room temperature. In contrast, the bication EDA with CH₂–CH₂ can effectively assemble the CsPbI₃ crystal units. Furthermore, all the CsPbI₃–xEA₂PbI₄ perovskite film-based solar cells exhibited poor photovoltaic performance, and the best J–V curve obtained from the PSCs based on CsPbI₃–0.025EA₂PbI₄ is listed in fig. S12. The efficiency is only ~4.4%, which is way too low than that of CsPbI₃ PSCs. Such low stability could be due to either the weak...
Like CsPbI₃·0.025EDAPbI₄, the CsPbI₃·0.025BDAPbI₄ samples are stored time in a dark dry box. (A) PCE of the champion PSC fabricated from CsPbI₃·0.025EDAPbI₄ as a function of storage time in a dark dry box. (B) XRD pattern and images of the CsPbI₃·0.025EDAPbI₄ 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 CsPbI₃·0.025BA₂PbI₄ perovskite. The CsPbI₃·0.025BA₂PbI₄ samples show some improved stability than those of CsPbI₃·0.025EA₂PbI₄ but still far more unstable than the CsPbI₃·0.025EDAPbI₄ 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 CsPbI₃·xEDAPbI₄, we used other two bications, that is, 1,4-diaminobutane (BD) and 2,2′-(ethylenedioxy)bis(ethylammonium) (EDBE₂⁺), which are similar to EDA. The BDAPbI₄ perovskite has been demonstrated to be a (100) layered bication 2D perovskite, whereas the EDBEPbI₄ has been shown to be a (110) layered 2D perovskite (29–31, 33). Like CsPbI₃·0.025BDAPbI₄, the CsPbI₃·0.025EDAPbI₄ samples are composed of smaller perovskite crystallites (fig. S14), exhibiting significantly enhanced thermal stability than pristine CsPbI₃. However, after holding at 100°C for 3 days, the CsPbI₃·0.025EDAPbI₄ film turns into the yellow δ phase, suggesting that its phase stability is lower than that of CsPbI₃·0.025BDAPbI₄ (fig. S15A). The main difference between EDAPbI₄ and BDAPbI₄ 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 CsPbI₃·0.025EDAPbI₄ could be ascribed to the unique (110) layered perovskite structure of EDAPbI₄. The CsPbI₃·0.025EDBE₂PbI₄ sample with the (110) layered EDBEPbI₄ shows enhanced thermal stability than CsPbI₃; however, as compared to CsPbI₃·0.025BDAPbI₄, its thermal stability is even poorer, as shown in fig. S15B. It is found that the CsPbI₃·0.025EDBE₂PbI₄ perovskite sample shows a larger crystal size than CsPbI₃·0.025BDAPbI₄ and CsPbI₃·0.025EDAPbI₄, suggesting that the lower thermal stability of CsPbI₃·0.025EDBE₂PbI₄ 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 α-CsPbI₃. Specifically, we ascribe the enhanced phase stability of CsPbI₃·xEDAPbI₄ to the reduced crystallite size and the EDAPbI₄ component’s unique (110) layered structure.

In summary, we report a phase-stable α-CsPbI₃ film with an EDAPbI₄ 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 EDAPbI₄, the structurally robust α-CsPbI₃ perovskite films were obtained even at temperatures several hundred°C below the phase transition point. The addition of a small amount of EDAPbI₄ stabilizes the α-CsPbI₃. Moreover, these perovskite films can retain the α-CsPbI₃ phase even after annealing at 100°C for >150 hours and are also stable at room temperature for months. The EDAPbI₄ (x = 0 to 0.05) not only enhances the phase stability of α-CsPbI₃ crystallites significantly but also connects them for effective electron transfer and passivates the surface defects. Finally, a champion α-CsPbI₃ PSC based on CsPbI₃·0.025EDAPbI₄ 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

EDA·I₂ 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 (BD·I₂), 2,2′-(ethylenedioxy)bis(ethylammonium) dihydroiodide (EDBE·I₂), ethylammonium iodide (EAI), and butylammonium iodide (BAI) were synthesized following the similar procedure. The PbI₂·xHI sample was synthesized as follows: 1 M PbI₂ 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 PbI₂ 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 CsPbI₃·xEDAPbI₄ precursor solution was prepared by dissolving 1 mmol of PbI₂·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

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| Table 1. Effect of EDAPbI₄ on the metrics of planar CsPbI₃ PSCs (12 to 32 cells for each type). |
|---|---|---|---|---|
| Precursor type | JSC (mA/cm²) | VOC (V) | FF | η (%) |
| Pure CsPbI₃ | 11.33 (11.63 ± 1.55) | 1.04 (0.89 ± 0.09) | 0.65 (0.53 ± 0.06) | 7.66 (5.56 ± 1.16) |
| CsPbI₃·0.025EDAPbI₄ | 13.59 (13.31 ± 0.36) | 1.13 (1.09 ± 0.06) | 0.65 (0.56 ± 0.06) | 9.98 (8.22 ± 1.46) |
| CsPbI₃·0.025EDAPbI₄ | 14.53 (14.05 ± 0.57) | 1.15 (1.13 ± 0.02) | 0.71 (0.64 ± 0.08) | 11.86 (10.42 ± 0.91) |
| CsPbI₃·0.05EDAPbI₄ | 13.97 (13.17 ± 0.88) | 1.08 (1.06 ± 0.03) | 0.65 (0.61 ± 0.02) | 9.81 (8.58 ± 0.66) |

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0.5 M EDAPbI₄ solution. The 0.5 M EDAPbI₄ solution was obtained by dissolving 0.5 mmol of EDAL₃ and 0.5 mmol of PbI₂ into 1 ml of DMF.

Device fabrication
A 20-nm-thick compact TiO₂ layer was first deposited on the patterned fluorene-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 CsPbI₃·diisopropoxide in 1-butanol solution was then spin-coated onto the prewarmed c-TiO₂-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)sulfonylimide lithium salt, and 0.12 M 4-tert-butylpyridine in chlorobenzene/acetoneitrile (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 CsPbI₃·xEDAPbI₄ films were examined by a Shimadzu XRD-6100 diffractometer with Cu Kα radiation. The morphologies of the CsPbI₃·xEDAPbI₄ films were observed by a JSM-7800F Prime SEM and a Bruker Multimode Nanoscope IIIa AFM. The absorption spectra of the EDAPbI₄ and CsPbI₃·xEDAPbI₄ 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 mono-chromatic 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 (805 MHz) at 420 nm under ambient conditions. The average power was kept around 0.05 μW/cm² per pulse. Using a 32-cm focal length monochromator equipped with a nonreflective metal mask with an aperture area of 0.12 cm², the IPCE was measured on a QE-3011 system from Enli-tech. All the J–V and IPCE tests were performed in atmosphere with a relative humidity of 30 to 45%.

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