

Elastic Lattice and Excess Charge Carrier Manipulation in 1D–3D Perovskite Solar Cells for Exceptionally Long-Term Operational Stability

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3D organic-inorganic hybrid halide perovskite solar cells (pero-SCs) inherently face severe instability issue due to ion migration under operational conditions. This ion migration inevitably results from the decomposition of ionic bonds under lattice strain and is accelerated by the existence of excess charge carriers. In this study, a 1D-3D mixed-dimensional perovskite material is explored by adding an organic salt with a bulk benzimidazole cation (Bn⁺). The Bn⁺ can induce 3D perovskite crystalline growth with the preferred orientation and form a 1D BnPbI3 perovskite spatially distributed in the 3D perovskite film. For the first time, the electro-strictive response, which has a significant influence on the lattice strain under an electric field, is observed in polycrystalline perovskite. The 1D-3D perovskite can effectively suppress electro-strictive responses and unbalanced charge carrier extraction, providing an intrinsically stable lattice with enhanced ionic bonds and fewer excess charge carriers. As a result, the ion migration behavior of the p-i-n 1D-3D based pero-SC is dramatically suppressed under operational conditions, showing ultra-long-term stability that retains 95.3% of its initial power conversion efficiency (PCE) under operation for 3072 h, and simultaneously achieving an excellent PCE with a hysteresis-free photovoltaic behavior.

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1. Introduction

3D perovskite solar cells (pero-SCs) based on organic-inorganic halide perovskites have attracted considerable interest due to their great potential as a new generation photovoltaic technology that boasts low costs, large-scale processing, and high efficiencies.^[1] Despite the many great achievements that have been obtained with pero-SCs, the problems with its long-term stability, particularly under maximum power point (MPP) operational conditions, still hinder the commercialization of pero-SCs.^[2,3] This is because the ion migration induced by the lattice deformation of 3D perovskite in operational conditions can overflow the entire device due to the intrinsically low formation energy and soft nature of the perovskite lattice.^[4]

Recently, low-dimensional perovskites, such as those 0D, 1D, and 2D, have attracted much attention due to their unique advantages in improving sta-

bility.^[5] The characteristics of intrinsically ultralow self-doping and high lattice formation energies can efficiently mitigate ionic migration through the suppression of the occurrence of Schottky/Frenkel defects.^[6] In addition, the hydrophobic and large-sized organic spacer cations inserted into low-dimensional perovskites can not only prevent the penetration of water molecules into the perovskite lattice but also hinder ion motion in the perovskite film by incorporating A-site cations with higher escaping energies from the lattice than that of methylammonium (MA⁺) or formamidinium (FA⁺).^[] Unfortunately, in photovoltaic applications, these low-dimensional perovskites usually have intrinsic inferior characteristics such as natural quantum wells with a much higher exciton binding energy,^[7] a wide optical bandgap,^[8] and low film quality.^[9] Therefore, mixed-dimensional perovskites are proposed by combining the advantages of 3D perovskites with high-efficiencies and low-dimensional perovskites with high stability. Bulky organic spacer cations such as 2-thiophenemethylammonium,^[10] 4-carboxybutan-1-aminium,^[3] phenylethylammonium,^[11] and guanidinopropionic,^[12] all of which present high steric hindrance effects, were used to dope a 3D perovskite precursor solution to reduce the dimension. The resultant 2D/3D-perovskitebased devices exhibit suppressed lattice deformation by strain



compensation, resulting in low defect density and ion migration and an efficient improvement in operational stability. However, in 2D perovskites, these organic spacing layers with insulating properties tend to grow parallel to the substance restricting out-of-plane charge transport;^[13] a large interlayer distance separated by the long chains of adjacent bulky cations may allow MA⁺ and iodide (I⁻) ions to enter the 2D perovskite, and the lattice can be further expanded, deteriorating the device performance.^[14] Instead, 1D perovskite with improved carrier transport characteristics and structural flexibility has gradually been attracting considerable attention.^[15,16] Recently, an ultrathin 1D perovskite layer was used to modulate the interfacial strain of 3D perovskite, in which the resultant perovskite film could release residual tensile strain to stabilize lattice at the interface, demonstrating a substantial contribution to the operational stability at the MPP.^[17] Even though, intrinsic problems such as ion migration and carrier dynamics in bulk 3D perovskite, which may play determined roles in operational stability, are still not resolved.^[2]

It was found that the mechanical properties existing in 3D perovskite have a substantial influence on lattice deformation and carrier dynamics. In particular, 3D polycrystalline perovskite films show compressive strain in the out-of-plane direction and tensile strain in the in-plane direction during the thermal annealing process due to mismatched thermal expansion. This can reduce the activation energy of ion migration and accelerate perovskite decomposition.^[18] Although short-term light illumination demonstrated to enable relaxation of the local lattice strain and contribute to the increased power conversion efficiency (PCE) and stability of the devices,^[19] long-term illumination still induces halide segregation for mixed-halide perovskites, further degrading device performance. Interestingly, an electro-strictive response was found in a 3D single-crystal perovskite when applying an electric field due to its soft lattice characteristic with a low Young's modulus (Ym) of 14.8 GPa. This is likely to induce lattice deformation, reducing ion escaping energies to create more Schottky/Frenkel defects, which may also result in more severe ion migration.^[20] As for the pero-SCs with polycrystalline perovskite and a sandwiched capacitance structure between electrodes, there is a built-in electric field $(1.5-1.9 \text{ V} \mu \text{m}^{-1})$, and the calculated electro-strictive strain in the range of 0.16-0.26% usually occurs under operational conditions.^[20] Meanwhile, polycrystalline perovskite has more dangling bonds at the grain boundaries (GBs) compared with its single-crystal counterpart.^[21,22] This can render ion dislocation easily under an electric field, leading to a non-healing electrostrictive response. However, the role of this behavior in the operational stability of pero-SCs has never been demonstrated. In addition, excess photoexcited carriers could prevail upon illumination, easily filling the ion vacancy and weaken the binding force between the ion and perovskite vacancy, leading to the acceleration of ion migration.^[23,24] Although the excess charge carriers could be suppressed by improving the carrier extraction efficiency of the interface layer, the spatial defects localized in bulk 3D perovskite with an inhomogeneous composition inevitably generate unbalanced extraction.^[25] To realize the long-term operational stability of pero-SCs, it is highly desirable to explore the role of the electro-strictive strain and synergistically suppress excess charge carriers under operational conditions.

In this work, we propose a 1D-3D mixed-dimensional perovskite approach to address the bottleneck issue of ion migration that limits the operational stability of pero-SCs. An organic salt of benzimidazole iodide (BnI) blended with the perovskite precursor effectively induces 1D perovskite formation and polycrystalline 3D perovskite film growth with the preferred orientation and with compact grains. The 1D perovskite was found to show an enriched distribution at the bottom in the 3D perovskite by anchoring onto the GBs. In addition, the 1D perovskite can also compensate for the dangling bonds and passivate the defects. The well-regulated 1D-3D spatial composition and defects in the perovskite facilitate the balanced extraction of carriers to reduce the accumulation of excess charge carriers, decreasing the activation energy of ion migration. In addition, upon using a derivative atomic force microscopy (AFM) technology, we observed for the first time the electro-strictive strain that occurs in the polycrystalline perovskite, which could be suppressed by incorporating 1D perovskite to increase the Ym of the 3D perovskite. The reduced electro-strictive strain effectively weakened the lattice deformation, resulting in an attenuated ion migration. As a result, the p-i-n planar pero-SCs based on this 1D-3D perovskite exhibit excellent operational stability through limiting ion migration, retaining 95.3% of their initial efficiency at approaching MPP under light-emitting diode (LED) irradiation for 3072 h at 45 °C. Moreover, this mixed-dimensional approach does not sacrifice the power conversion efficiency (PCE) and an impressive PCE of 21.17% was achieved.

2. Results and Discussion

Organic salt BnI was simply synthesized through one-step ionization reaction, and the structure was confirmed as shown in Figure S1, Supporting Information. Then, BnI was added to the Lead(II) iodide (PbI₂) solution with varied ratios of PbI₂/BnI (0:1, 1:0, 1:1, and 1:2) to investigate their coordination capacity. Figure 1a shows photographs of the precursor solutions and their derivative films. The pure PbI₂ film shows a yellow color, which changes both in the solutions and films when BnI is incorporated. This indicates that the Bn⁺ acts as a Lewis base to form an adduct with PbI2 in the precursor due to the lone electron pairs of the nitrogen atoms in the imidazole group. As expected, the perovskite films prepared according to the different stoichiometric ratios (PbI₂:BnI = 1:1 and 1:2) showed X-ray diffraction (XRD) patterns agreeing well with the standard characteristic peaks of 1D BnPbI3 and 2D Bn2PbI4 perovskites (Figure S2, Supporting Information).^[26] It should be noted that there is still a trace amount of 1D BnPbI₃ in the perovskite film prepared from the stoichiometric ratio of 1:2. Ultravioletvisible spectroscopy (UV-vis) absorption spectra (Figure S3, Supporting Information) reveals that both 1D BnPbI₃ and 2D Bn₂PbI₄ perovskites present clear and strong exciton absorption peaks with an absorption edge at 442 and 590 nm, respectively. These results demonstrate that the dimensions of the perovskites can be easily tuned by changing the stoichiometric ratio of BnI and PbI₂. Figure 1b shows the electrostatic potential surface images of Bn⁺ calculated using a density functional theory method. Bn⁺ shows an inhomogeneous electron density distribution, in which the positive charge (blue region) and







Figure 1. a) Photographs of the precursor solutions and films with varied molar ratios of Pbl₂/Bnl (0:1, 1:0, 1:1, and 1:2). b) The electrostatic potential distributions of Bn⁺. c) The schematic diagram of dimensional perovskite regulation based on the stoichiometric ratio of Bnl.

negative charge are concentrated around the N⁺ and N atom, respectively. This suggests that the organic salt BnI can coordinate with the under-coordinated Pb²⁺ in the perovskite through the N atom, which well indicates that the incorporation of organic salt BnI can trigger different crystal behaviors, such as those found in 1D BnPbI₃ and 2D Bn₂PbI₄, as shown in the schematic diagram of Figure 1c.

To synthesize mixed-dimensional perovskite and retain the low-bandgap nature of 3D Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45} perovskite, we added a small amount of BnI ranging from 0 to 2 wt% in the 3D perovskite precursor based on the total weight of the precursor solution, and the optimized content is 0.2 wt%. XRD measurements were performed to investigate the role of Bn⁺ cation in crystal growth and dimension tuning of perovskite films. As shown in Figure 2a, the 3D perovskite without BnI showed distinct characteristic diffraction peaks at 14.08°, 19.97°, 24.50°, 28.35°, 31.77°, and 34.93°, ascribed to the (100), (110), (111), (200), (210), and (211) lattice planes of cubic 3D perovskite films, respectively.^[27] After adding BnI, the intensities of the characteristic diffraction peaks increased, and the diffraction peaks at 12.67° corresponding to PbI₂ was dramatically suppressed, suggesting that BnI can not only facilitate 3D perovskite crystallization but also enable a more completed PbI₂ transformation. And we speculated this phenomenon ascribe to the existence of intermediate phase adduct between the BnI and PbI₂ due to the nature of Lewis base of the imidazole group in the Bn⁺.^[10,28] And BnI can react with excess lead iodide forming ID BnPbI₃ perovskite thus enable a more completed PbI₂ transformation. We also observed that the peak intensity ratios of (100)/(110) and (100)/(111) increased when adding BnI, indicating a preferred orientation along the (100) direction. We then conducted the 2D grazing-incidence wide-angle X-ray scattering measurements (Figure S5, Supporting Information) to further investigate the crystal orientation by azimuthally integrating scattering intensity along the ring at q = 1.00 Å⁻¹ ascribed to the (100) lattice plane, as shown in Figure S5c, Supporting Information. The 1D-3D films exhibit remarkably enhanced intensities of (100) plane diffraction peaks at the azimuth angles in the range of 20°-60° and 120°-160° but slightly increased intensities at the angle of 90° compared to those of 3D perovskite. Accordingly, it is visualized that the (100) lattice plane shows preferred orientation mainly along the azimuth angles of 20° - 60° and 120°-160°.^[29] The new peak appeared at 8.1° is attributed to the 1D BnPbI₃ perovskite,^[26] the intensity of which could be enhanced with the increase in BnI up to 2 wt%. No diffraction peaks stemming from the BnI aggregates were observed (Figure S4, Supporting Information). We also checked the XRD patterns of the perovskite film with higher BnI concentration (4, 7, and 10 wt%), as shown in Figure S6, Supporting Information. Notably, all of those films exhibit a typical 1D characteristic diffraction peak at 8.1°. And there is no shift on the characteristic diffraction peaks of 3D perovskite with the BnI content increased from 0 to 10 wt%, indicating that the excessive Bn⁺ just forms 1D BnPbI₃ but could not enter the 3D perovskite lattice.







Figure 2. a) Left: X-ray diffraction patterns of pristine 3D perovskite, 1D–3D perovskite with 0.2 wt% BnI, 1D–3D perovskite with 2 wt% BnI, and pristine 1D BnPbl₃ perovskite; right: magnification of the marked peak. b) Left: FTIR spectra for BnI, 1D BnPbl₃ perovskite, 3D perovskite, and 1D–3D perovskite; right: magnification of the characteristic peaks. c) XPS of Pb 4f peaks of 3D perovskite and 1D–3D perovskite with 0.2 wt% BnI. d) Schematic diagram of the interaction between 1D BnPbl₃ and 3D in 1D–3D perovskite film with 0.2 wt% BnI. e) Top-view SEM images of 3D and 1D–3D perovskite films. f) UV–vis absorption spectra of 3D and 1D–3D perovskite films.

To detect the state of Bn⁺ in the 1D–3D perovskite with 0.2 wt% BnI, Fourier-transform infrared spectroscopy (FTIR) measurements were conducted. As shown in Figure 2b, the out-of-plane deformation vibration of the benzene ring skeleton in Bn arising at 751 cm⁻¹ can be found in the BnI sample, 1D perovskite sample, and 1D–3D perovskite sample, indicating

that BnI was successfully incorporated into the perovskite film. Interestingly, an N–H stretching vibration peak at 3119 cm⁻¹ in the BnI sample completely shifted to a higher wavelength number (3136 cm⁻¹) in both the 1D and 1D–3D perovskite samples, indicating that there is no Bn⁺ residue, instead, a hydrogen bond interaction between H of N–H and the perovskite







Figure 3. a–c) TEM images of the 1D–3D perovskite. The highlighted area (1) and (2) were investigated in (b) and (c), respectively. Inset pictures show fast Fourier transform (FFT) analysis of two representative areas: (1-1) and outer (2-1) region within boxes, respectively. d,g) The morphology maps $(1.0 \times 1.0 \ \mu\text{m}^2)$ of 3D and 1D–3D perovskite samples. e,h) The spatial CPD maps $(1.0 \times 1.0 \ \mu\text{m}^2)$ of 3D and 1D–3D perovskite samples. f,i) The relative V_{CPD} line-scan spectra of the 3D and 1D–3D perovskite films extracted from the corresponding maps.

framework appears.^[26,30] We also observed a -C-N- stretching vibration peak at 1260 cm⁻¹ in both the BnI and 1D perovskite samples but none in the 3D perovskite sample. Interestingly, this -C-N- stretching vibration reappeared in 1D-3D perovskite shifted to 1254 cm⁻¹, which suggests that the Lewis-base N atoms of the imidazole in the 1D BnPbI₃ lattice can coordinate with uncoordinated Pb2+. This assumption was further confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2c, the binding energies of Pb $4f_{7/2}$ and Pb $4f_{5/2}$ in 1D-3D perovskite shifted from 138.6 to 138.3 eV and from 143.5 to 143.2 eV, respectively, compared with those of 3D perovskite. These results demonstrate that the 1D BnPbI₃ in 1D-3D perovskite has an interaction with the 3D perovskite bridging by the coordination of N-Pb and hydrogen bond interaction, as shown in the schematic diagram of Figure 2d. Furthermore, we explored the role of BnI in perovskite film morphology. As seen from the top-view scanning electron microscopy (SEM) images of 3D and 1D-3D perovskite films (Figure 2e), there are brightwhite grains widely distributed on the 3D perovskite film surface, whereas no grains are observed on the 1D-3D perovskite film. This suggests that the bright-white grains are attributed to unreacted PbI₂ residues, which can transform into 1D BnPbI₃ upon reacting with BnI in bulk 3D perovskite through the strong coordination capacity of BnI.^[31] This behavior is in agreement with the above mentioned XRD results. We also found that the 1D–3D perovskite film becomes more compact and has a larger average grain size than that of 3D perovskite film. The trace amount of 1D perovskite in the 1D–3D perovskite exhibits a negligible influence on the absorption compared with that of 3D perovskite as evidenced from the nearly equivalent UV–vis absorption spectra in terms of shape and intensity (Figure 2f).

To probe the composition distribution of 1D perovskite throughout the film, we perform time-of-flight secondary-ion mass spectrometry (TOF-SIMS). In the 1D–3D perovskite film, the Bn⁺ is gradiently distributed in the bulk perovskite, mainly enriched at the buried interface (Figure S7, Supporting Information). The structures of the 1D–3D perovskite thin films were further investigated using high-resolution transmission electron microscopy (HR-TEM). The representative HR-TEM images, and the selected areas shown by the yellow solidline frame, are displayed in **Figure 3**a. Region (1) and region (2) denote the grain interior and grain boundary, respectively,





which are magnified and analyzed by Fast Fourier transform (FFT), as shown in Figure 3b and 3c. The inter-planar spacing of 6.5 Å in Figure 3b and 8.1 Å in Figure 3c is well-matched with the (200) reflection of cubic 3D perovskite^[32] and the characteristic reflection of 1D BnPbI₃^[26]. The above results support the presence of 1D perovskite which is distributed at GBs of 3D perovskite. In order to explore the mechanism of 1D-3D perovskite formation, we prepared the perovskite films using standard stoichiometric perovskite precursor with the different content of BnI (0, 0.2, and 0.5 wt%). All of those films show no 1D BnPbI₃ characteristics peak (Figure S8, Supporting Information), indicating the priority of 3D perovskite film formation. Considering the downward grain growth behavior of perovskite polycrystalline film^[33] and the bottom enriched 1D BnPbI₃ in 1D-3D perovskite, the 3D and 1D perovskites are likely to successively form in the order of formation energies, where the 1D BnPbI₃ grows under the assistance of excess PbI₂.

To further investigate the effect of 1D BnPbI₃ incorporation on morphology and the electrical properties of variation between grain interiors and GBs, Kelvin probe force microscopy was performed on the same test structures whereby the perovskite surface is directly accessible by the AFM probe, as shown in the Figure 3d–i. 3D perovskite exhibits a relatively uniform contact potential difference (V_{CPD}) map, but there is still a V_{CPD} difference (ΔV_{CPD}) of ~18 mV between the GBs and adjacent grain interior (Figure 3f), in which the local GBs show a relatively low potential (indicated by the green circles). This implies that the charge carriers are likely trapped at the GBs, increasing the leakage current of the device.^[34] As for the 1D–3D perovskite, the V_{CPD} along the GBs significantly increases to be much higher than that of the adjacent grain interior,

rendering a ΔV_{CPD} of 33 mV (Figure 3i). This suggests that 1D perovskite is mainly distributed in the GBs through their interaction which is in accordance with the HR-TEM results. And the reverse ΔV_{CPD} may facilitate charge transport and passivate the defect state.^[22] Photoluminescence (PL) mappings of the perovskite films (Figure S9, Supporting Information) reveal that the 1D-3D perovskite film has a more homogeneous PL intensity and reduced difference of PL intensity between GBs and grains compared to those of 3D perovskite film. It indicates the defect density at the GBs of the 1D-3D perovskite were reduced. Notably, the overall improved V_{CPD} of the 1D–3D perovskite resulted in a lower surface potential (SP) compared with 3D perovskite (26.7 mV for 1D-3D perovskite compare with 51.8 mV for 3D perovskite), indicating a more N-type nature that can contribute to carrier extraction and transport in the p-i-n devices.^[35] This behavior was also confirmed by UV photoelectron spectroscopy, where the Fermi level was pushed toward the conduction band after incorporating 1D perovskite (Figure S10, Supporting Information).

Next, to systematically explore the passivation mechanism of the ID–3D perovskite film, time-resolved PL (TRPL) measurements were conducted. The charge carrier lifetime of pristine 3D perovskite illuminated from top side is slightly longer than that from bottom side, while the 1D–3D perovskite shows a slightly shorter lifetime (**Figure 4**a,b; Table S1, Supporting Information). We also noted that 1D–3D perovskite illuminated from bottom side exhibits a much longer charge carrier lifetime (86.26 ns) than that of 3D perovskite from top side (58.49 ns). The significantly prolonged lifetime is probably caused by the bottom enriched 1D BnPbI₃ in 1D–3D perovskite that enables to more efficiently compensate the dangling bonds and



Figure 4. TRPL spectra of 3D and 1D–3D perovskite films and their PTAA and C_{60} heterojunction on glass plates: a) the sample was illuminated from the bottom side; b) the sample was illuminated from the top side. c) Current–voltage curves of hole-only devices for 3D and 1D–3D perovskites. d) Mott–Schottky plots of the 3D and 1D–3D devices. e) Schematic diagram of spatially distributed 1D perovskite incorporating polycrystalline 3D perovskite film at the GBs, and the regulating carrier transport behavior to limit the accumulation of excess charge carriers.





passivate the defects of 3D perovskite. When combining with poly(triarylamines) (PTAA) or fullerene (C_{60}), the lifetimes of PTAA/3D illuminated from bottom side and 3D/C₆₀ illuminated from top side quenched to 21.18 and 5.07 ns, respectively. While, the PTAA/1D-3D and $1D-3D/C_{60}$ greatly decreased to 7.11 and 5.89 ns. It is noted that in the 3D perovskite sample, there exists a relatively poor hole extraction capacity compared with that of electrons, which may be caused by the inhomogeneous composition of 3D perovskite, thus inducing a higher defect density near the PTAA interface.^[25] The balanced hole/ electron extraction capacity in the 1D-3D perovskite can sufficiently suppress the accumulation of excess charge carriers to increase the ion migration activation energy under operational conditions.^[23] We speculate the spatial regulation of carriers dynamic is ascribe to the gradient distribution of 1D perovskite in the 1D-3D perovskite film. In addition, spacecharge-limited current and Mott-Schottky plot measurements were performed, showing increased carrier concentration (from 5.15×10^{16} to 5.6×10^{16} cm⁻³) and reduced hole trap densities (from 9.3×10^{15} to 5.3×10^{15} cm⁻³) compared with the 3D perovskite film (Figure 4c,d; Table S2, Supporting Information). Notably, the exact trap density may be underestimated by several orders of magnitude due to the mixed ionic and electronic nature of perovskite.^[36] This result was further confirmed by PL measurements in which the films were illuminated from the glass side and perovskite side. The 3D perovskite film shows a 4-nm shift in the PL peak when illuminated from both sides, whereas the 1D-3D perovskite film shows negligible dependence on the incident light direction with a consistent peak at 762 nm (Figure S11, Supporting Information), suggesting that the 1D-3D perovskite film demonstrates a more homogenous/

balanced ambipolar nature typical of perovskite. Therefore, the gradient enriched 1D $BnPbI_3$ in the 1D–3D perovskite film can effectively suppress the accumulation of excess charge carriers by regulating hole defects to enhance hole extraction, as Figure 4e depicts.

Besides the defect passivation mechanism, the mechanical properties of 1D-3D perovskite under the electric field were explored. A derivative AFM technology was carried out to detect the influence of the electric field on the lattice strain of the perovskite by employing cantilever displacement devices with point-surface capacitor characteristic, as illustrated in Figure S12, Supporting Information.^[37] The observed oscillation signals for detecting the strain of the film are converted from the deflection of probe bending under the electric field. Under an alternating current (A.C.) electric field of 2 V μ m⁻¹ with a frequency of 10 Hz, the 3D polycrystalline perovskite film shows a surface oscillation proportional to the square of the electric field (indicated in the box). This implies that an electro-strictive behavior occurred in the 3D polycrystalline perovskite film (Figure 5a). We further applied a constant electric field of 2 V μ m⁻¹ (direct current (D.C.) bias pulse mode) to in situ monitor the lattice creep, demonstrating that the surface thickness of the film gradually compresses under a continuous electric field (indicated by the yellow line), and the oscillations stop when the electric field is removed, as shown in Figure 5b. Next, XRD characteristics were used to investigate the possible lattice deformation of perovskite induced by electro-strictive response, where the samples were aged under a constant electric field of 2 V μ m⁻¹ in N₂ atmosphere without light. As shown in Figure 5c and Figure S13, Supporting Information, both the diffraction peaks of (100) and (200) planes of



Figure 5. a,b) Electro-strictive strain of the 3D perovskite film under an A.C. bias at 10 Hz and alternating electric fields. c) The XRD spectra patterns of the (200) plane of the 3D perovskite film with and without aging for 14 h under an electric field of 2 V μ m⁻¹. d,e) Electro-strictive strain of the 1D–3D perovskite film under an A.C. bias at 10 Hz and alternating electric fields. f) The XRD spectra patterns of the (200) plane of the 1D–3D perovskite film with and without aging for 2 V μ m⁻¹.



aged 3D perovskite shifted to larger angles compared with fresh 3D perovskite, indicating that lattice compression occurs when the electric field is applied along the out-of-plane direction and that the deformation is not self-healing. In comparison, the aged 1D–3D perovskite film shows much weaker oscillations and in the opposite direction of the electric field (Figure 5d). A similar reduced electro-strictive behavior was observed under a D.C. bias pulse mode (Figure 5e). These results suggest that the incorporated 1D perovskite can effectively suppress lattice deformation in 3D perovskite by compensating the dangling bonds in the GBs. XRD was conducted to verify this speculation.

aged 1D-3D perovskite film shows much weaker oscillations and in the opposite direction of the electric field (Figure 5d). A similar reduced electro-strictive behavior was observed under a D.C. bias pulse mode (Figure 5e). These results suggest that the incorporated 1D perovskite can effectively suppress lattice deformation in 3D perovskite by compensating the dangling bonds in the GBs. XRD was conducted to verify this speculation. Contrary to what occurs in the 3D perovskite film, there is no shifting of the (100) and the (200) planes for 1D-3D perovskite (Figure 5f; Figure S14, Supporting Information), indicating a suppressed lattice compression. It has been reported the lattice strain could be heavily affected by the mechanical property of the perovskite materials.^[16] Therefore, the nanoindentation test was conducted to explore the mechanical property of the 3D and1D-3D perovskite, as shown in Figure S15, Supporting Information. The 1D-3D perovskite possesses an increased Ym of 51.2 GPa compared with that of 3D perovskite (38.9 GPa). We speculate that the increased mechanical strength could be owing to the change of the crystal structure in the 1D–3D perovskite through the compensated dangling bonds, leading to a suppressed electro-strictive strain in the 1D–3D perovskite. It needs to be noted that the reduced electro-strictive response is related to the suppressed defect formation, which may increase activation energy of ion migration of the pero-SCs.

To explore how electro-strictive response affects the ion migration behavior, we first employed the measurements of activation energy (E_a) .^[38] E_a enables to quantitatively characterize how easily ion migrates from the dependence of conductivity on the temperature in perovskite films. The device with lateral structure (Figure 6a) was used to weaken the electrons conduction and thus highlight the ion conduction proportion in total current.^[39] The ion migration rate (σ) in perovskite film is determined by E_a according to Nernst-Einstein equation: $\sigma(T) = \sigma_0 \exp(E_a/kT)$, where k is the Boltzmann constant and σ_0 is a constant. E_a can be calculated from the slope of $\ln(\sigma T)$ -1/kT. During this measurement, a small electric field is adapted to trigger the electro-strictive strain. Figure 6b shows the conductivity of perovskite films under different temperatures. The fitted E_a increased from 0.08 eV of 3D perovskite to 0.15 eV of the 1D-3D perovskite, indicating ion migration behavior



Figure 6. a,b) Device structure used in activation energy measurement; the temperature-dependent conductivity of 3D and 1D–3D perovskite films. c,d) Device structure used in galvanostatic characterization; polarization curve in Au/perovskite/Au device measured in air by applying a constant current of 2 nA. The voltage response with time is recorded using Keithley 4200-SCS. Inset shows the equivalent circuit mimicking the galvanostatic characterization (R_{eon} electronic resistance, R_{ion} ionic resistance, and C^{δ} chemical capacitance). e) The schematic diagram of ion migration and lattice distortion deformation induced by the electro-strictive strain for the polycrystalline 3D and 1D–3D perovskite films.





becomes more difficult in 1D-3D perovskite film. Then, the ion conductivity of perovskite films was measured using galvanostatic characterization with lateral structure,^[39] as shown in Figure 6c,d. The ion conductivity (σ_{ion}) of 3D and 1D–3D perovskites were calculated to be 0.36×10^{-9} and 0.26×10^{-9} S cm⁻¹, respectively, as listed in Table S3, Supporting Information. The 28%-decreasement σ_{ion} of 1D–3D perovskite film further confirms that the alleviated electro-strictive strain of 1D-3D perovskite can effectively suppress the ion migration. Therefore, as Figure 6e depicted, the 1D species effectively compensated the dangling bonds at the GBs of 3D perovskite, which inhibits the formation of the iodine Frenkel pairs. When applying electric field, the reduced iodine Frenkel pairs in 1D-3D perovskite can effectively weaken electro-strictive response, thus suppressing ion migration.^[40] The reduction of the iodine vacancies may further alleviate the activation energy of the ion migration and ultimately benefit the operational stability of the film.

To gain insight into the influence of 1D-3D mixed-dimensional perovskite on the photovoltaic performance, p-i-n planar pero-SCs with a configuration of indium tin oxide (ITO)/PTAA/ perovskite/C₆₀/BCP/silver (Ag) were fabricated and the corresponding cross-sectional SEM image of the device is shown in Figure 7a,b. The current density-voltage (I-V) curves of the champion 3D and 1D-3D devices are shown in Figure 7c, along with detailed photovoltaic parameters listed in the inset. The 3D pero-SC under a reverse scan shows a PCE of 18.60% with an open-circuit voltage (V_{oc}) of 1.07 V, a short-circuit current density (I_{sc}) of 22.60 mA cm⁻², and a fill factor (FF) of 76.92%. The 1D–3D device exhibited an overall improved V_{oc} of 1.13 V, a $J_{\rm sc}$ of 23.72 mA cm⁻², and an FF of 78.99%, resulting in an impressive PCE of 21.17%. The detailed photovoltaic parameters of the 3D and 1D-3D pero-SCs under reverse and forward scanning are summarized in Figure S16 and Table S4, Supporting Information and show a negligible discrepancy in



Figure 7. a) Schematic illustration of layer-stacking in the pero-SC with a structure of ITO/PTAA/perovskite/C₆₀/BCP/Ag. b) Corresponding crosssectional SEM image of the pero-SC. c) J-V curves of champion devices of the 3D and 1D–3D devices, inset: photovoltaic parameters of the devices. d) EQE spectra and integrated current of the corresponding devices. e) The stabilized PCEs at MPP for the 3D and 1D–3D devices. f) Statistics of the PCEs for the 3D and 1D–3D devices.





the J-V behavior. To understand the mechanism behind the enhanced $V_{\rm oc}$ and FF for the 1D–3D device, we performed light intensity dependence of *I-V* characteristics measurements (Figure S17, Supporting Information). The $V_{\rm oc}$ versus the logarithm of the light intensity presented a linear relationship with a slope of 1.27 kT/q for the 1D–3D device, which is smaller than that of 1.45 kT/q for the 3D device, suggesting suppressed trapassisted recombination,^[32] thus leading to the improved V_{oc} .^[41] We speculate the increased J_{sc} value could be attributed to the preferred orientation along the (100) direction and better balanced hole/electron extraction capacity in the 1D-3D perovskite film, which facilitate charge transport in the corresponding devices. The integrated J_{sc} from the external quantum efficiency (EQE) spectra (Figure 7d) is 22.48 mA cm⁻² for the 3D device and 23.02 mA cm⁻² for the 1D-3D device, which agrees well with the I_{sc} values obtained from the I-V curves with only a 3% deviation. We further evaluated these values by recording the MPP tracking tests corresponding to the PCEs of 18.51% and 20.85% for the 3D and 1D-3D pero-SCs, respectively, as shown in Figure 7e. The detailed statistical photovoltaic performance parameters from 30 devices reveal an improved reproducibility when incorporating 1D-3D perovskite as evidenced from a lower standard deviation of 0.36 for the 1D-3D-based pero-SCs compared with that of the 3D-based devices (0.45) (Figure 7f; Figure S18, Supporting Information).

The long-term operational stability of the pero-SCs was evaluated by approaching MPP tracking on unencapsulated devices under continuous 1 Sun equivalent illumination in an N₂-filled glovebox (white LED, 100 mW cm⁻²). The fixed resistance is selected according to the calculated values from the maximum power (P_{max}) of initial *J*–*V* curve (Figure S19, Supporting Information), so that all the devices can work at an approaching MPP. The PCE for the 3D device dramatically decreased to

53.4% of its initial PCE within 792 h. In contrast, the operational stability was intrinsically improved for 1D-3D pero-SCs, in which 95.3% of its initial efficiency could be retained even after 3072 h of aging, as shown in Figure 8a. And the detailed PV parameters are shown in Figure S20, Supporting Information. To the best of our knowledge, this is the first reported ultra-long-term operating stability achievement of the pero-SCs without any interface modification. As aforementioned, the 1D-3D perovskite shows a reduction of excess PbI₂ compared with that of 3D perovskite. To evaluate the effect of reduced excess PbI₂ on the high MPP stability,^[42] we then performed the MPP stability test based on the 3D perovskite derived from the stoichiometric precursor without any BnI additive. As shown in Figure S21, Supporting Information, the PCE can retain 90% of its initial efficiency within 192 h aging, which is slightly higher than the 3D (3% excess PbI₂) device (84%). And it is worth noting that there is nearly no efficiency dropping in the 1D-3D pero-SCs after 1000 h of MPP stability test(Figure 8a). Therefore, we can conclude that the reduction of excess PbI₂ is not the main reason for the enhanced MPP lifetime. In addition, the 1D-3D pero-SCs also showed better stability toward humidity and heating (Figure S22, Supporting Information). The enhanced humidity stability of the device could be owing to the increased contact angles of 1D-3D perovskite (Figure S23, Supporting Information).

To determine the mechanisms behind the significant breakthrough in operational stability, we observed the photographs of the 3D and 1D–3D devices after aging 500 h under operational conditions (Figure 8b; Figure S24, Supporting Information). Interestingly, the color of the top Ag electrode of the 3D device changed from silver to gray in the region that overlaps with the ITO bottom, and the opaque color of the entire device became transparent. This behavior suggests that the Ag



Figure 8. a) Long-term stability of 3D and 1D–3D pero-SCs at a fixed resistance under continuous light soaking (100 mW cm⁻²) in N₂ at a temperature of \approx 45–55 °C. b) Photographs of the fresh and 500 h-aged 3D and 1D–3D devices. c,d) Morphology and element distribution via cross-sectional SEM of 3D and 1D–3D pero-SCs with a structure of ITO/PTAA/perovskite/C₆₀/BCP/Ag for an aging period of 500 h under operational conditions.



electrode may react with perovskite or its composition, causing a degradation of the electronic contacts. As previously reported, severe ion migration usually occurs under operational conditions, and ions such as iodine present a high reactivity with Ag electrode.^[15] A cross-sectional SEM with energy dispersive X-ray analysis was conducted to demonstrate the above hypothesis by investigating the element distribution in the aged pero-SCs (operational condition in an N₂ atmosphere for 500 h). As shown in Figure 8c, the iodide ions diffused onto the top Ag electrode and partially aggregated on it in the 3D device, confirming the morphology change phenomenon of the aged device, in which the Ag diffusion can be clearly observed. In contrast, in the 1D-3D pero-SC, the Ag electrode diffusion and iodide ion migration were significantly suppressed (Figure 8d). The TOF-SIMS measurement was used to further confirm this result. As shown in Figure S25, Supporting Information iodine ions diffused into the Ag electrode then accumulated in it of the aged 3D pero-SCs. In contrast, few iodine ions were observed in the Ag electrode of the 1D–3D pero-SCs.

3. Conclusion

We successfully prepared a 1D-3D mixed-dimensional perovskite by simply incorporating Bn⁺ spacer cations with strong coordination capacity to uncoordinated Pb2+. The created 1D perovskite could induce the crystalline growth and preferred orientation of 3D perovskite, and bridged with 3D perovskite through bonding interaction to compensate the dangling bonds at the GBs. For the first time, we directly observed that the mixed-dimensional 1D-3D perovskite can effectively suppress the intrinsic electro-strictive response in organic-inorganic hybrid metal-halide perovskite. The weakened electro-strictive response was demonstrated to enable lattice compression strain restriction under an electric field to intrinsically improve the ion migration problem. The bottom enriched 1D perovskite in 3D perovskite can provide the homogenous/balanced ambipolar nature of perovskite to suppress the accumulation of excess charge carriers to increase the activation energy of ion migration. The p-i-n pero-SCs based on this 1D-3D perovskite not only achieve a promising PCE of 21.17% but also exhibit an exceptional long-term operational stability by suppressing ion migration, where the device can retain 95.3% of its initial PCE at a fixed resistance under operational conditions even after aging for 3072 h. As far as we know, this is the first example to realize the ultra-long operational stability by exploring intrinsically stable 1D-3D perovskite, paving a new path toward highly stable and efficient solar cells for further industrial applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

electro-strictive strain, excess charge carriers, ion migration, long-term operational stability, mixed-dimensional perovskite solar cells

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- a) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, J. Am. Chem. Soc.
 2009, 131, 6050; b) J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, Nature 2013, 499, 316; c) M. Liu, M. B. Johnston, H. J. Snaith, Nature 2013, 501, 395; d) N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, Nature 2015, 517, 476; e) H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. G. De Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang, Y. Zhao, Science 2017, 355, 722; f) E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T.-Y. Yang, J. H. Noh, J. Seo, Nature 2019, 567, 511; g) R. Xue, M. Zhang, D. Luo, W. Chen, R. Zhu, Y. M. Yang, Y. Li, Y. Li, Sci. China Chem. 2020, 63, 987.
- [2] a) L. Meng, J. You, Y. Yang, *Nat. Commun.* 2018, *9*, 5265; b) S. Bai,
 P. Da, C. Li, Z. Wang, Z. Yuan, F. Fu, M. Kawecki, X. Liu, N. Sakai,
 J. T.-W. Wang, S. Huettner, S. Buecheler, M. Fahlman, F. Gao,
 H. J. Snaith, *Nature* 2019, *571*, 245.
- [3] G. Grancini, C. Roldan-Carmona, I. Zimmermann, E. Mosconi, X. Lee, D. Martineau, S. Narbey, F. Oswald, F. De Angelis, M. Graetzel, M. K. Nazeeruddin, *Nat. Commun.* 2017, *8*, 15684.
- [4] Y. Wang, T. Wu, J. Barbaud, W. Kong, D. Cui, H. Chen, X. Yang, L. Han, *Science* **2019**, *365*, 687.
- [5] a) L. Gao, F. Zhang, X. Chen, C. Xiao, B. W. Larson, S. P. Dunfield, J. J. Berry, K. Zhu, *Angew. Chem.* 2019, *131*, 11863; b) Y. Chen, Y. Sun, J. Peng, J. Tang, K. Zheng, Z. Liang, *Adv. Mater.* 2018, *30*, 1703487; c) F. Zhang, H. P. Lu, J. H. Tong, J. J. Berry, M. C. Beard, K. Zhu, *Energy Environ. Sci.* 2020, *13*, 1154; d) E. Bi, W. Tang, H. Chen, Y. Wang, J. Barbaud, T. Wu, W. Kong, P. Tu, H. Zhu, X. Zeng, *Joule* 2019, *3*, 2748; e) D. Yu, Y. Hu, J. Shi, H. Tang, W. Zhang, Q. Meng, H. Han, Z. Ning, H. Tian, *Sci. China Chem.* 2019, *62*, 684.
- [6] Y. Yuan, J. Huang, Acc. Chem. Res. 2016, 49, 286.
- [7] R. Yang, R. Li, Y. Cao, Y. Wei, Y. Miao, W. L. Tan, X. Jiao, H. Chen, L. Zhang, Q. Chen, H. Zhang, W. Zou, Y. Wang, M. Yang, C. Yi, N. Wang, F. Gao, C. R. McNeill, T. Qin, J. Wang, W. Huang, *Adv. Mater.* 2018, *30*, 1804771.

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- [8] T. M. Koh, V. Shanmugam, J. Schlipf, L. Oesinghaus, P. Müller-Buschbaum, N. Ramakrishnan, V. Swamy, N. Mathews, P. P. Boix, S. G. Mhaisalkar, *Adv. Mater.* **2016**, *28*, 3653.
- [9] H. Tsai, W. Nie, J. C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P. M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis, *Nature* **2016**, *536*, 312.
- [10] T. Zhou, H. Lai, T. Liu, D. Lu, X. Wan, X. Zhang, Y. Liu, Y. Chen, Adv. Mater. 2019, 31, 1901242.
- [11] J. W. Lee, Z. Dai, T. H. Han, C. Choi, S. Y. Chang, S. J. Lee, N. De Marco, H. Zhao, P. Sun, Y. Huang, Y. Yang, *Nat. Commun.* **2018**, *9*, 3021.
- [12] Q. Yao, Q. Xue, Z. Li, K. Zhang, T. Zhang, N. Li, S. Yang, C. J. Brabec, H. L. Yip, Y. Cao, *Adv. Mater.* **2020**, *32*, 2000571.
- [13] A. Krishna, S. Gottis, M. K. Nazeeruddin, F. Sauvage, Adv. Funct. Mater. 2019, 29, 1806482.
- [14] C. Zhang, S. Wu, L. Tao, G. M. Arumugam, C. Liu, Z. Wang, S. Zhu, Y. Yang, J. Lin, X. Liu, R. E. I. Schropp, Y. Mai, *Adv. Energy Mater.* 2020, *10*, 2002004.
- [15] J. Fan, Y. Ma, C. Zhang, C. Liu, W. Li, R. E. I. Schropp, Y. Mai, Adv. Energy Mater. 2018, 8, 1703421.
- [16] H. Wang, C. Zhu, L. Liu, S. Ma, P. Liu, J. Wu, C. Shi, Q. Du, Y. Hao, S. Xiang, H. Chen, P. Chen, Y. Bai, H. Zhou, Y. Li, Q. Chen, *Adv. Mater.* **2019**, *31*, 1904408.
- [17] N. Yang, C. Zhu, Y. Chen, H. Zai, C. Wang, X. Wang, H. Wang, S. Ma, Z. Gao, X. Wang, *Energy Environ. Sci.* **2020**, *13*, 4344.
- [18] J. Zhao, Y. Deng, H. Wei, X. Zheng, Z. Yu, Y. Shao, J. E. Shield, J. Huang, *Sci. Adv.* 2017, *3*, eaao5616.
- [19] H. Tsai, R. Asadpour, J.-C. Blancon, C. C. Stoumpos, O. Durand, J. W. Strzalka, B. Chen, R. Verduzco, P. M. Ajayan, S. Tretiak, J. Even, M. A. Alam, M. G. Kanatzidis, W. Nie, A. D. Mohite, *Science* 2018, 360, 67.
- [20] B. Chen, T. Li, Q. Dong, E. Mosconi, J. Song, Z. Chen, Y. Deng, Y. Liu, S. Ducharme, A. Gruverman, F. Angelis, J. Huang, Nat. Mater. 2018, 17, 1020.
- [21] Q. Chen, H. Zhou, T.-B. Song, S. Luo, Z. Hong, H.-S. Duan, L. Dou, Y. Liu, Y. Yang, Nano Lett. 2014, 14, 4158.
- [22] J. S. Yun, A. Ho-Baillie, S. Huang, S. H. Woo, Y. Heo, J. Seidel, F. Huang, Y. B. Cheng, M. A. Green, J. Phys. Chem. Lett. 2015, 6, 875.
- [23] Y. Lin, B. Chen, Y. Fang, J. Zhao, C. Bao, Z. Yu, Y. Deng, P. N. Rudd, Y. Yan, Y. Yuan, J. Huang, *Nat. Commun.* **2018**, *9*, 4981.
- [24] B. Chen, J. Song, X. Dai, Y. Liu, P. N. Rudd, X. Hong, J. Huang, Adv. Mater. 2019, 31, 1902413.
- [25] a) Z. Ni, C. Bao, Y. Liu, Q. Jiang, W.-Q. Wu, S. Chen, X. Dai, B. Chen, B. Hartweg, Z. Yu, *Science* **2020**, *367*, 1352 b) C. Wu, D. Wang, Y. Zhang, F. Gu, G. Liu, N. Zhu, W. Luo, D. Han, X. Guo, B. Qu, *Adv. Funct. Mater.* **2019**, *29*, 1902974.
- [26] C. Lermer, S. P. Harm, S. T. Birkhold, J. A. Jaser, C. M. Kutz, P. Mayer, L. Schmidt-Mende, B. V. Lotsch, Z. Anorg. Allg. Chem. 2016, 642, 1369.

- [27] X. P. Zheng, Y. Hou, C. X. Bao, J. Yin, F. L. Yuan, Z. R. Huang, K. P. Song, J. K. Liu, J. Troughton, N. Gasparini, C. Zhou, Y. B. Lin, D. J. Xue, B. Chen, A. K. Johnston, N. Wei, M. N. Hedhili, M. Y. Wei, A. Y. Alsalloum, P. Maity, B. Turedi, C. Yang, D. Baran, T. D. Anthopoulos, Y. Han, Z. H. Lu, O. F. Mohammed, F. Gao, E. H. Sargent, O. M. Bakr, *Nat. Energy* **2020**, *5*, 131.
- [28] Y. Zhao, P. Zhu, M. Wang, S. Huang, Z. Zhao, S. Tan, T. H. Han, J. W. Lee, T. Huang, R. Wang, J. Xue, D. Meng, Y. Huang, J. Marian, J. Zhu, Y. Yang, *Adv. Mater.* **2020**, *32*, 1907769.
- [29] a) G. Zheng, C. Zhu, J. Ma, X. Zhang, G. Tang, R. Li, Y. Chen, L. Li, J. Hu, J. Hong, Q. Chen, X. Gao, H. Zhou, *Nat. Commun.* 2018, 9, 2793 b) F. Li, J. Yuan, X. Ling, L. Huang, N. Rujisamphan, Y. Li, L. Chi, W. Ma, ACS Appl. Mater. Interfaces 2018, 10, 42397.
- [30] S.-C. Yun, S. Ma, H.-C. Kwon, K. Kim, G. Jang, H. Yang, J. Moon, Nano Energy 2019, 59, 481.
- [31] Y. Liu, S. Akin, L. Pan, R. Uchida, N. Arora, J. V. Milić, A. Hinderhofer, F. Schreiber, A. R. Uhl, S. M. Zakeeruddin, *Sci. Adv.* 2019, *5*, 2543.
- [32] H. Lai, D. Lu, Z. Xu, N. Zheng, Z. Xie, Y. Liu, Adv. Mater. 2020, 32, 2001470.
- [33] S. Chen, X. Xiao, B. Chen, L. L. Kelly, J. Zhao, Y. Lin, M. F. Toney, J. Huang, *Sci. Adv.* **2021**, *7*, eabb2412.
- [34] H. Kim, J. W. Lee, G. R. Han, S. K. Kim, J. H. Oh, Adv. Funct. Mater. 2020, 31, 2008801.
- [35] H. Chen, Y. Zhan, G. Xu, W. Chen, S. Wang, M. Zhang, Y. Li, Y. Li, Adv. Funct. Mater. 2020, 30, 2001788.
- [36] W. Lee, J. W. Han, Y. Chen, Z. Cai, B. Yildiz, J. Am. Chem. Soc. 2013, 135, 7909.
- [37] N. Rolston, R. Bennett-Kennett, L. T. Schelhas, J. M. Luther, J. A. Christians, J. J. Berry, R. H. Dauskardt, *Science* 2020, 368, eaay8691.
- [38] S. Yang, S. Chen, E. Mosconi, Y. Fang, X. Xiao, C. Wang, Y. Zhou, Z. Yu, J. Zhao, Y. Gao, *Science* **2019**, *365*, 473.
- [39] X. Li, W. Zhang, Y. C. Wang, W. Zhang, H. Q. Wang, J. Fang, Nat. Commun. 2018, 9, 3806.
- [40] B. Chen, T. Li, Q. Dong, E. Mosconi, J. Song, Z. Chen, Y. Deng, Y. Liu, S. Ducharme, A. Gruverman, F. D. Angelis, J. Huang, Nat. Mater. 2018, 17, 1020.
- [41] T. S. Su, F. T. Eickemeyer, M. A. Hope, F. Jahanbakhshi, M. Mladenovic, J. Li, Z. Zhou, A. Mishra, J. H. Yum, D. Ren, A. Krishna, O. Ouellette, T. C. Wei, H. Zhou, H. H. Huang, M. D. Mensi, K. Sivula, S. M. Zakeeruddin, J. V. Milic, A. Hagfeldt, U. Rothlisberger, L. Emsley, H. Zhang, M. Gratzel, J. Am. Chem. Soc. 2020, 142, 19980.
- [42] a) S. H. Cho, J. Byeon, K. Jeong, J. Hwang, H. Lee, J. Jang, J. Lee, T. Kim, K. Kim, M. Choi, Y. S. Lee, *Adv. Energy Mater.* **2021**, *11*, 2100555; b) G. Tumen-Ulzii, C. Qin, D. Klotz, M. R. Leyden, P. Wang, M. Auffray, T. Fujihara, T. Matsushima, J.-W. Lee, S.-J. Lee, Y. Yang, C. Adachi, *Adv. Mater.* **2020**, *32*, 1905035.