Origin of unusual bandgap shift and dual emission in organic-inorganic lead halide perovskites

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Emission characteristics of metal halide perovskites play a key role in the current widespread investigations into their potential uses in optoelectronics and photonics. However, a fundamental understanding of the molecular origin of the unusual blueshift of the bandgap and dual emission in perovskites is still lacking. In this direction, we investigated the extraordinary photoluminescence behavior of three representatives of this important class of photonic materials, that is, CH3NH3PbI3, CH3NH3PbBr3, and CH(NH2)2PbBr3, which emerged from our thorough studies of the effects of temperature on their bandgap and emission decay dynamics using time-integrated and time-resolved photoluminescence spectroscopy. The low-temperature (<100 K) photoluminescence of CH3NH3PbI3 and CH3NH3PbBr3 reveals two distinct emission peaks, whereas that of CH(NH2)2PbBr3 shows a single emission peak. Furthermore, irrespective of perovskite composition, the bandgap exhibits an unusual blueshift by raising the temperature from 15 to 300 K. Density functional theory and classical molecular dynamics simulations allow for assigning the additional photoluminescence peak to the presence of molecularly dispersed orthorhombic domains and also rationalize that the unusual blueshift of the bandgap with increasing temperature is due to the stabilization of the valence band maximum. Our findings provide new insights into the salient emission properties of perovskite materials, which define their performance in solar cells and light-emitting devices.

INTRODUCTION

Advancement in the performance of organic-inorganic metal halide perovskite solar cells and light-emitting devices has been remarkable over the last few years; however, an understanding of the fundamental properties of these perovskite materials is still evolving (1). In a light-harnessing or light-emitting device, bandgap, absorption coefficient, and excitonic properties of the light absorber or emitter play critical roles in determining its performance (2, 3). Arguably, the perovskite materials exhibit all the desired properties that make them potential candidates for the fields of photovoltaics, light-emitting devices, field effect transistors, and lasers (4–7). Bandgap modulation, spontaneous dissociation of excitons, and long-range balanced electron- and hole-diffusion lengths in the perovskite materials are among the main distinctive properties that have led to an unprecedented evolution of efficient perovskite solar cells (8, 9).

To gain deeper insight into the photophysical processes occurring in the perovskite materials (10–14), it is worth exploring them at low temperatures where the additional complexity induced by thermal effects is minimized. Although in the literature different perovskite materials have been studied using various kinds of spectroscopies, there have been only a few exhaustive reports regarding temperature-dependent photoluminescence (PL) studies (15, 16). Investigating the temperature-dependent optoelectronic properties of hybrid organic-inorganic perovskites could be of interest for the identification of their potential for particular technological applications, such as space power applications. Therefore, exploring emission characteristics of a perovskite absorber across a wide temperature range, particularly at low temperatures, can provide important clues regarding the performance of a light-emitting device and solar cell based on perovskites (17). Previous studies reported the temperature dependence of PL and an additional emission peak in CH3NH3PbI3 at low temperature (7, 18–20). However, a fundamental understanding of the molecular origin of the unusual blueshift of the bandgap and dual emission in perovskites is still evolving (21–23).

Here, we systematically explored the temperature dependence of the bandgap and decay kinetics of emission in CH3NH3PbI3, CH3NH3PbBr3, and CH(NH2)2PbBr3 using time-integrated and time-resolved PL spectroscopy. The low-temperature (<100 K) time-integrated PL studies of CH3NH3PbI3 and CH3NH3PbBr3 highlighted the presence of a well-defined second emission peak, whereas CH(NH2)2PbBr3 exhibited a single emission peak. The emission dynamics demonstrated the transfer of charge carriers from the high-energy emission peak to the low-energy emission peak. In addition to the lack of comprehensive experimental results regarding temperature-dependent PL studies of perovskites, there is no unequivocal theoretical interpretation of the existing data. To bridge this gap, we have carried out density functional theory (DFT) calculations and classical molecular dynamics (MD) simulations to identify the molecular origin of the experimentally observed temperature- and composition-dependent emission characteristics of perovskites. Our in-depth investigation provides new fundamental insights into the emission characteristics of this important class of photonic materials—the lead halide perovskites.

RESULTS

Organic-inorganic metal halide perovskites exhibit the general formula ABX3 (where A is a monovalent organic cation, B is Pb2+ or Sn2+, and X is a halide anion) (24). To obtain CH3NH3PbI3, CH3NH3PbBr3, and CH(NH2)2PbBr3 films, we used solution-based...
deposition methods (see Materials and Methods) (25, 26). X-ray diffraction (XRD) (fig. S1) and field emission scanning electron microscopy (fig. S2) established the formation of phase-pure and homogenous perovskite films, respectively (27).

Emission characteristics of CH$_3$NH$_3$PbI$_3$

The structural characterization based on XRD (fig. S1) confirmed the formation of the tetragonal phase of CH$_3$NH$_3$PbI$_3$, which is thermodynamically the most stable phase at room temperature (28). Below 160 K, the tetragonal phase transforms into an orthorhombic phase, whereas above 330 K, CH$_3$NH$_3$PbI$_3$ stabilizes into a cubic phase (29, 30). Furthermore, using time-integrated and time-resolved PL spectroscopy, we have explored in detail the temperature dependence of the bandgap and the dynamics of emission in CH$_3$NH$_3$PbI$_3$ perovskite films deposited on mesoporous Al$_2$O$_3$.

Temperature-dependent PL

Exploring the PL of hybrid organic-inorganic perovskites over a wide range of temperature is not only of fundamental interest but also aims to identify the practical applications of the devices based on these perovskites. Figure 1A shows the time-integrated PL of the CH$_3$NH$_3$PbI$_3$ film recorded at 15 K, which highlights the presence of two emission peaks located at 1.574 and 1.649 eV (Fig. 1B). While increasing the temperature to 80 K, the low-energy emission peak experienced a blueshift of 15 meV (from 1.574 to 1.589 eV). Likewise, the central energy of the high-energy emission peak attributable to the orthorhombic phase of CH$_3$NH$_3$PbI$_3$ exhibits a blueshift of 25 meV (from 1.649 to 1.674 eV) before disappearing above 120 K (Fig. 1B). This widening of the bandgap is in apparent discord with the usual Varshni behavior of standard tetrahedral semiconductors in which the bandgap experiences a redshift with the increase in temperature (31). Furthermore, while raising the temperature from 15 to 75 K, the linewidth or full width at half maximum (FWHM) of the low-energy emission peak unusually decreases by 7 meV (from 77 to 70 meV), whereas the FWHM of the high-energy emission peak increases from 39 to 43 meV (Fig. 1C). At 75 K, the low-energy emission peak commences to redshift from 1.589 to 1.569 eV up to 150 K, which is also followed by a decrease in the linewidth from 70 to 56 meV (Fig. 1B). From 150 to 300 K, the single emission peak attributed to the tetragonal phase reveals a systematic blueshift of 32 meV (from 1.569 eV at 150 K to 1.601 eV at 300 K) (Fig. 1B), with concurrent enhancement in the linewidth from 56 to 87 meV (Fig. 1C).

The evolution of the FWHM of emission peaks that correspond to the orthorhombic and tetragonal phases (Fig. 1C) can be fitted by taking into account the temperature-independent inhomogeneous broadening ($\Gamma_0$) and the interaction between charge carriers and LO-phonons, described by the Fröhlich Hamiltonian (32, 33). The extracted fitting values [$\Gamma_0 = 39$ meV; charge carrier LO-phonon coupling strength ($\gamma_{cLO}$) = 40 meV; and energy of LO-phonon ($E_{LO}$) = 15 meV] agree with the literature (Fig. 1C) (33). The intensity of emission peaks corresponding to the orthorhombic (high-energy peak below 120 K) and tetragonal phases (above 150 K) (Fig. 1D) continuously

![Fig. 1. Temperature-dependent emission characteristics of CH$_3$NH$_3$PbI$_3$ (fluence = 2 $\mu$J/cm$^2$).](image-url)
diminishes with increasing temperature, which could arguably be attributed to the activation of nonradiative recombination centers. The PL intensity is maximal around 150 K (Fig. 1D), which implies that CH$_3$NH$_3$PbI$_3$ could be a strong emitter around 140 to 160 K (7). The intensity and linewidth of the low-energy emission peak (Fig. 1D) do not follow the trend exhibited by the orthorhombic (high-energy peak below 120 K) and tetragonal (above 150 K) phases. The emission from the low-energy peak increases considerably from 75 to 150 K.

### Fluence-dependent PL

It is well known that the accumulation of charges during photoexcitation increases the inherent bandgap of the CH$_3$NH$_3$PbI$_3$ (34). Therefore, to further understand the dependence of the position and intensity of the three PL peaks on the excitation energy densities, we investigated the emission characteristics of CH$_3$NH$_3$PbI$_3$ at 15 and 300 K using different laser fluences (Fig. 2). With increasing fluence, a continuous blueshift of the low-energy emission peak from 1.436 eV at 0.1 nJ/cm$^2$ up to 1.536 eV at 4.5 μJ/cm$^2$ was observed at 15 K (Fig. 2, A and B), which could be attributed to the band filling effect (34). On the other hand, the high-energy emission peak exhibits a blueshift only at higher fluences (>0.2 μJ/cm$^2$). This suggests that the charge transfer from the orthorhombic phase of CH$_3$NH$_3$PbI$_3$ to the low-energy emission peak occurs at lower fluences (<0.2 μJ/cm$^2$), whereas at higher fluences (>0.2 μJ/cm$^2$) the band filling effect predominates over a dynamic charge transfer. At 300 K, no noticeable shift in the position of the single PL peak assigned to the tetragonal phase of CH$_3$NH$_3$PbI$_3$ was observed over a range of excitation intensities (Fig. 2, D and E). Figure 2 (C and F) displays the dependence of PL intensity on the fluence recorded at 15 and 300 K. At 15 K, we observe a perfectly linear relationship between the fluence (<0.2 μJ/cm$^2$) and the integrated PL intensity over more than five orders of magnitude for both the high-energy and low-energy emission peaks, which confirms the absence of nonradiative recombination at low temperature. In contrast, at 300 K, the integrated PL intensity of the tetragonal phase of CH$_3$NH$_3$PbI$_3$ shows an overlinear dependence on the fluence. At higher fluences, an enhancement in the carrier density leads to the saturation of nonradiative recombination centers, which improves the effective internal quantum efficiency. No signature of reduction in effective internal quantum efficiency was observed for the tetragonal phase of CH$_3$NH$_3$PbI$_3$, which suggests that Auger recombination plays a minimal role under this fluence.

### Temperature- and fluence-dependent time-resolved PL

From the fluence-dependent emission studies of CH$_3$NH$_3$PbI$_3$, we observed the transfer of charge carriers from the high-energy (orthorhombic phase) to the low-energy emission peak at 15 K. To further unravel the charge transfer process and to understand the effect of temperature and fluence on charge carrier dynamics in CH$_3$NH$_3$PbI$_3$, we explored time-resolved PL.

With increasing fluence, the charge carrier lifetime ($\tau_{10}$, time at which the maximum PL intensity reduces by a factor of 10) continuously decreases in the low-energy emission peak (15 K) (Fig. 3, A and B) as well as in the tetragonal phase (300 K) of CH$_3$NH$_3$PbI$_3$ (Fig. 3, E and F). For a given fluence at 15 K, the charge carriers are relatively long-lasting in the low-energy emission peak (Fig. 3A), as compared to those in the high-energy emission peak (orthorhombic phase) (Fig. 3C).

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**Fig. 2.** Fluence-dependent emission characteristics of CH$_3$NH$_3$PbI$_3$ recorded at 15 and 300 K. (A) PL spectra of the low- and high-energy emission peaks as a function of fluence recorded at 15 K. (B) Position of the low- and high-energy emission peaks as a function of fluence recorded at 15 K. (C) Intensity of the low- and high-energy emission peaks as a function of fluence recorded at 15 K. (D) PL spectra of the tetragonal phase as a function of fluence recorded at 300 K. (E) Position of the tetragonal emission peak as a function of fluence recorded at 300 K. (F) Intensity of the tetragonal emission peak as a function of fluence recorded at 300 K.
The recombination dynamics in the orthorhombic phase at 15 K unusually relaxes (Fig. 3, C and D) within a nanosecond range at higher fluences, which implies that relaxation occurs through processes other than pure charge carrier recombination. We envisage that this strange behavior of carrier dynamics involves the charge transfer from the orthorhombic phase into the low-energy emission peak, in addition to the recombination of the carriers (see Discussion). When carrier lifetime exceeds ~0.5 ns, the decay dynamics shows a normal trend, that is, the higher the fluence, the faster the recombination dynamics.

At 300 K, the lifetime ($\tau_{10}$) decreases with increasing fluence in the tetragonal phase, which can be explained by evoking the bimolecular recombination mechanism (the charges predominantly exist as free carriers) (Fig. 3, E and F). However, because of the concurrent non-radiative recombination of charge carriers, the bimolecular recombination rate and fluence do not follow the linear trend, which agrees with the overlinear dependence of PL intensity on fluence, observed at 300 K (Fig. 2F). Overall, the charge carrier lifetime increases while raising the temperature from 15 to 300 K (fig. S6), which indicates that the charge carrier dynamics involves bimolecular recombination.

**Temperature-dependent emission characteristics of CH$_3$NH$_3$PbBr$_3$**

The thorough analysis of emission characteristics established that CH$_3$NH$_3$PbI$_3$ exhibits a dual emission at low temperature and widening of the bandgap with the increase in temperature. To substantiate these unusual spectral features, we examined CH$_3$NH$_3$PbBr$_3$, another representative of the organic-inorganic lead halide perovskite family. CH$_3$NH$_3$PbBr$_3$ crystallizes in the cubic phase at room temperature (fig. S1) (35). By replacing the iodide with bromide, the bandgap increases from 1.61 eV in CH$_3$NH$_3$PbI$_3$ to 2.36 eV in CH$_3$NH$_3$PbBr$_3$ at 300 K (36). The PL spectrum of CH$_3$NH$_3$PbBr$_3$ also displays two emission peaks located at 2.28 and 2.36 eV at 15 K (Fig. 4A), which
confirms that the origin of dual emission is not associated with the nature of the halide ion in methylammonium (MA; CH$_3$NH$_3^+$)–based perovskites. The nature of the halide ion has negligible impact on the difference in the positions of two emission peaks, which is ~75 to 80 meV for both CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$. Below 175 K, the FWHM of the high-energy emission peak does not show any temperature dependence and remains constant around 65 meV (Fig. 4B). On the contrary, the linewidth of the low-energy emission peak increases from 40 meV at 75 K to 130 meV at 300 K. With increased temperature, the high-energy emission peak showed a maximal shift of 45 meV before disappearing above 175 K, whereas the low-energy emission peak revealed a continuous blueshift of 74 meV (from 2.285 eV at 15 K to 2.359 eV at 300 K) up to 300 K (Fig. 4C).

**Temperature-dependent emission characteristics of CH(NH$_2$)$_2$PbBr$_3$**

Thus far, we observed that the presence of the additional emission peak remains unaffected when replacing iodide with bromide in MA-based perovskites. To get further insight into the origin of dual emission at low temperature, we replaced MA with a formamidinium [FA; CH(NH$_2$)$_2$]$^+$ cation in bromide-based perovskite. Surprisingly, this replacement led to the disappearance of the distinct second emission peak (Fig. 4D), which implies that the origin of the dual emission is associated with the nature of the organic cation (37). As compared to CH$_3$NH$_3$PbBr$_3$ perovskite, the CH(NH$_2$)$_2$PbBr$_3$ sample exhibits a narrower linewidth at both low and high temperatures (Fig. 4E), which indicates that peak broadening is also associated with the nature of organic cations. Furthermore, the energy of the single emission peak increases with temperature from 2.20 eV at 25 K to 2.22 eV at 150 K, and between 150 and 175 K, the position of the PL peak shifts by 9 meV (Fig. 4F), which could possibly be attributed to a phase transition. The emission peak exhibited a continuous blueshift of 54 meV when the temperature was raised to 300 K.

**Theoretical study**

To identify the origin of peculiar emission characteristics, such as the widening of the bandgap and the dependence of dual emission on the nature of the organic cation, we performed classical MD on large systems (~25,000 atoms) in combination with DFT calculations. Previously, it has been established that in the tetragonal phase of CH$_3$NH$_3$PbI$_3$ ($T > 160$ K; Fig. 5), MA cations reorient on a picosecond time scale, resulting in a dynamical molecular disorder (29, 30, 38–40), whereas in the orthorhombic phase of CH$_3$NH$_3$PbI$_3$, MA cations tend to align because of the constraints imposed by the PbI$_3$ framework (fig. S9) (38–40). However, classical MD simulations show that upon the cooling of a large tetragonal structure below the transition temperature, it is possible to kinetically trap MA in disordered configurations, leading to the formation of MA-disordered domains in an otherwise ordered orthorhombic phase of CH$_3$NH$_3$PbI$_3$ (Fig. 5A) (41). It is worth emphasizing that the disordered domains are not...
tetragonal inclusions but rather orthorhombic domains with a molecular disorder, which is further confirmed by comparing the Pb-I partial pair correlation function, \(g_{\text{PbI}}(r)\), of the disordered and ordered orthorhombic domains with the tetragonal phase (fig. S10A) and the existing literature (41). DFT band structure calculations show (Fig. 5B) that the MA-ordered domains [Fig. 5A (a)] have an \(-85\) meV larger bandgap \(E_g\) than the MA-disordered ones [Fig. 5A (d)], in agreement with the experimental results recorded at low temperature (Fig. 1). This supports the hypothesis that the two PL peaks are associated with MA-ordered and MA-disordered domains in CH₃NH₃PbI₃. In the ordered domains, the alignment of MA cations produces a strong local electric field, which eventually increases the \(E_g\) of MA-ordered orthorhombic domains (Stark-like effect) (42). Furthermore, after MA cations were removed (and Pb²⁺ and I⁻ were kept fixed at their original positions), the computational study reveals the reduction of the \(\Delta E_g\) between ordered and disordered domains by \(-65\) meV, establishing the fact that MA alignment majorly splits the peaks \(\sim 85\) meV with the Stark-like effect.

To investigate the origin of the effect on temperature on the PL peak position, we computed the \(E_g\) of the various systems as a function of the pseudocubic lattice parameter, \(a = \sqrt[3]{V}\). Figure 5B shows that \(E_g\) grows with \(a\), suggesting that the blueshift of the PL peaks with temperature is due to the thermal expansion of the CH₃NH₃PbI₃ lattice. Consequently, this expansion reduces the overlap between Pb-6s and I-5p antibonding atomic orbitals, forming the valence band maximum (VBM; fig. S11), which increases the overall bandgap of CH₃NH₃PbI₃ (43, 44). Between 120 and 150 K, that is, below the orthorhombic to tetragonal phase transition temperature of CH₃NH₃PbI₃ (<160 K), the experiments show two phenomena: (i) the high-energy PL peak disappears, and (ii) the low-energy peak smoothly shifts toward lower energies. Fundamentally, the disappearance of the high-energy emission peak is associated with the rotational mobility of the MA cations in the tetragonal phase of CH₃NH₃PbI₃ (38-40, 42, 45). Concerning the evolution of the low-energy emission peak, the mobility of MA cations in disordered orthorhombic domains gradually increases with temperature and eventually leads to a smooth transition into a regular tetragonal phase. This is further illustrated by a smooth change of the second set of peaks in the \(g_{\text{PbI}}(r)\) of the disordered domains in temperatures ranging from 100 to 150 K (fig. S10C), which reduces \(E_g\) by \(-20\) meV (Fig. 5B), in excellent agreement with the redshift observed experimentally (Figs. 1A and 4A).

**DISCUSSION**

The existence of a dual emission peak at low temperature in CH₃NH₃PbI₃ perovskite agrees with previous studies; however, its origin has remained inconclusive so far (18). Xing et al. (7) assigned three emission peaks to two bound-exciton emissions (815 and 782 nm) and a free-exciton emission (higher energy), whereas Kong et al. (19) attributed them to a donor-acceptor pair (low energy) and free-exciton transitions. Fang et al. (20) ascribed the low- and high-energy emission peaks to free and bound excitons, respectively. Wehrenfennig et al. (46) and Panzer et al. (47) concluded the presence of tetragonal inclusions in the orthorhombic phase at low temperature (46, 47). These hypotheses have not been confirmed theoretically and are insufficient to explain the complete phenomenology presented in this work (Figs. 1 to 4). For example, tetragonal inclusions are not possible in CH₃NH₃PbBr₃, which exists in the cubic phase at room temperature and thus cannot explain why the well-distinct additional emission peak disappears in the CH(NH₂)₂PbBr₃ perovskite. Here, we propose a theoretical model supported by simulation results, which can explain all the observed trends of the PL spectra over the entire temperature range (15 to 300 K) for all perovskite systems.

Our calculations suggest that the difference in \(E_g\) between the ordered and disordered domains arises from the relatively higher energy of VBM in the latter domains (fig. S12). Therefore, the migration of photogenerated carriers from the ordered domains to the disordered ones becomes energetically feasible (Fig. 2A). At low fluence, the charge carriers from the wide bandgap (ordered) domains are transferred to the low bandgap (disordered) domains (fig. S13A),
and the recombination of charge carriers predominantly occurs in the latter domains (black spectrum, fig. S13D). Because of the absorption of more photons at intermediate fluences and the transfer of carriers from the ordered domains (high-energy emission peak) to the disordered domains (low-energy emission peak) (fig. S13B), the accumulation of the charges shifts the emission peak toward higher energy (band filling effect) (red spectrum, fig. S13D). At fluences greater than 0.2 mJ/cm², the band filling effect predominates over the charge transfer process (fig. S13C); thus, both the emission peaks corresponding to the ordered and disordered orthorhombic domains become prominent (green spectrum, fig. S13D).

Replacing iodide with bromide does not induce any significant qualitative difference, that is, ordered and disordered domains with a ΔEₖ of ~85 meV still exist through the Stark-like effect, corroborating the experimental results (~80 meV) (fig. 4). However, when MA is replaced with a less polar monovalent cation [for example, FA (fig. S14), which exhibits a smaller dipole moment (μₐ = 0.2 D versus μₐ = 2.3 D) (48)], the intensity of the Stark-like effect diminishes, and the calculated peak splitting in the CH(NH₂)₂PbBr₃ (<10 to 20 meV) becomes smaller than the linewidth. Even if ordered and disordered domains form in CH(NH₂)₂PbBr₃ perovskite, it will be difficult to resolve their emission features under these conditions.

The unconventional temperature effects on the intensity and linewidth of the emission peak ascribed to the disordered orthorhombic domains of CH₃NH₃PbI₃ demand more attention because possible insights could further help in unfolding the promising emission characteristics of perovskites. The unusual broadening observed at low temperature could be explained by evoking the thermally activated microstructure evolution of the material and the dynamics of MA cations within the inorganic framework. The MD reveals that the disordered phase is composed of zones with different degrees of local alignment of MA cations. Eventually, different local molecular dipoles result in slightly different energies, which translate into a broad emission peak. Above 50 K, the temperature progressively activates the evolution of microstructure with molecular rearrangements and reduces the disordered phase (and thus the linewidth), whereas the energy of the low-energy emission peak tends to reach the energy of the tetragonal phase.

In conclusion, we demonstrated the temperature dependence of decay dynamics of emissions in CH₃NH₃PbI₃, CH₃NH₃PbBr₃, and CH(NH₂)₂PbBr₃. We have rationally addressed the unusual blueshift of the bandgap with temperature and the dual emission at low temperature (<100 K). With the help of MD and first-principles calculations, the blueshift in the bandgap could be attributed to the stabilization of the VBM, and the presence of the well-defined two emission peaks revealed by MA-based perovskites at low temperature is caused by the coexistence of MA-ordered and MA-disordered orthorhombic domains. CH(NH₂)₂PbBr₃ exhibits only a single emission feature at low temperature because the difference between ordered and disordered domains is much smaller (<10 to 20 meV in CH(NH₂)₂PbBr₃ versus ~80 to 90 meV in MA-perovskites) than the linewidth. Overall, our in-depth study presents intriguing results into the temperature-dependent emission properties and bandgap modulation of lead halide perovskites.

**Photoanode preparation**

A 250-nm-thick Al₂O₃ mesoporous layer was deposited on a precleaned nonconductive glass substrate. Before the deposition of the Al₂O₃ mesoporous layer, the glass substrate was cleaned with a detergent, rinsed with deionized water and ethanol, and then treated in an ultraviolet/O₃ cleaner for 10 min. Subsequently diluted [1:3.5 (w/w) ratio] Al₂O₃ mesoporous paste containing 30 nm of Al₂O₃ nanoparticles (homemade) was spin-coated (5000 rpm, acceleration of 2000 rpm for 30 s) onto the glass substrate. After sintering by following a series of steps (325°C for 5 min with a 15-min ramp time, 375°C for 5 min with a 5-min ramp time, 450°C for 15 min with a 5-min ramp time, and 500°C for 15 min with a 5-min ramp time), mesoporous Al₂O₃ films were obtained.

**Preparation of perovskite samples**

Synthesis of the CH₃NH₃PbI₃ and CH(NH₂)₂PbBr₃ samples involved a sequential deposition method with some modifications. One molar solutions of PbI₂ (TCI, 99.99%) and PbBr₂ (TCI, 99%) were prepared, respectively, in N,N'-dimethylformamide (DMF) and DMF-dimethylsulfoxide (DMSO) [1:1 (v/v)] solvent mixture by constant stirring at 100°C for 10 min. Mesoporous Al₂O₃ photoanode films were coated with PbI₂ or PbBr₂ by spin-coating the corresponding precursor solutions (1 M) at 6500 rpm for 30 s, and the films were dried at 70°C for 15 min. After the lead halide films were cooled to room temperature, a 200-μl solution of CH₃NH₃I (Dyesol) in 2-propanol (8 mg/ml) was spin-coated on the PbI₂ film with a delay of 120 s for 30 s, whereas the PbBr₂ films were dipped into 50 mM solutions of CH₃NH₃I (Dyesol) in 2-propanol for 15 min. For the preparation of CH₃NH₃PbBr₃, a single-step methodology was used. Typically, 50 μl of a reaction mixture containing 1 mol of each PbBr₂ and CH₃NH₃Br (Dyesol) dissolved in 1 ml of DMF-DMSO [1:1 (v/v)] solvent mixture was deposited onto mesoporous photoanode films by spin-coating at 2000 rpm for 30 s. All the resulting perovskite films were annealed at 110°C for 15 min.

**Structural and morphological characterization**

XRD data acquired from perovskite films were collected on a Bruker Advance D8 x-ray diffractometer with a graphite monochromator, using Cu-Kα radiation, at a scanning rate of 1 deg/min. A field-emission scanning electron microscope (Merlin) was used to examine the surface morphology of the perovskite films. An electron beam accelerated to 3 kV was used with an in-lens detector.

**Spectroscopic characterization**

Different perovskite samples were analyzed using time-integrated and time-resolved PL spectroscopy as a function of the temperature. All samples were excited from the perovskite side with the second harmonic (~425 nm) of a picosecond mode-locked Ti:sapphire laser (80.5 MHz). The excitation beam was focused on the sample by means of a 90-mm focal that allows for an excitation spot diameter of around 100 μm. The collected PL spectra were spectrally and temporally analyzed 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 ~20 ps.

**Computational section**

Classical MD simulations were performed by the DL_POLY package (49) by using a force field recently developed by Mattoni et al. (39). We considered computational samples of several sizes, ranging from ~900 to ~25,000 atoms. Periodic boundary conditions were applied along the

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**MATERIALS AND METHODS**

**Materials**

All materials were purchased from Sigma-Aldrich and used as received unless stated otherwise.

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XRD data acquired from perovskite films were collected on a Bruker Advance D8 x-ray diffractometer with a graphite monochromator, using Cu-Kα radiation, at a scanning rate of 1 deg/min. A field-emission scanning electron microscope (Merlin) was used to examine the surface morphology of the perovskite films. An electron beam accelerated to 3 kV was used with an in-lens detector.

**Spectroscopic characterization**

Different perovskite samples were analyzed using time-integrated and time-resolved PL spectroscopy as a function of the temperature. All samples were excited from the perovskite side with the second harmonic (~425 nm) of a picosecond mode-locked Ti:sapphire laser (80.5 MHz). The excitation beam was focused on the sample by means of a 90-mm focal that allows for an excitation spot diameter of around 100 μm. The collected PL spectra were spectrally and temporally analyzed 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 ~20 ps.

**Computational section**

Classical MD simulations were performed by the DL_POLY package (49) by using a force field recently developed by Mattoni et al. (39). We considered computational samples of several sizes, ranging from ~900 to ~25,000 atoms. Periodic boundary conditions were applied along the
three directions. Samples were first equilibrated at 300 K and 1 bar by NPT (constant number of atoms, pressure, and temperature) MD and then quenched and aged at several temperatures (100, 150, 200, and 300 K), still allowing the volume to change according to the temperature and pressure. The smooth transition was investigated by a 10-ns-long classical MD at 10 K intervals ranging from 100 to 150 K.

First-principles calculations were performed within the framework of the generalized gradient approximation to DFT. In particular, we used the Perdew-Burke-Ernzerhof exchange and correlation functional of the generalized gradient approximation to DFT. In particular, we calculated for the optimized structure.

The experimental value. Then, the geometries and the cells were optimized over a range of ~1.5% of the pseudocubic lattice parameter, \( a = \sqrt{3} \) (V, volume per stoichiometric unit). At each given value of the lattice, the geometry of the system was relaxed, and the \( E_g \) was computed on the relaxed structure. \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) samples were prepared starting from the corresponding \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) ones by shrinking the lattice to match the experimental value. Then, the geometries and the cells were optimized, and the \( E_g \) values were computed. In the case of \( \text{CH}(\text{NH}_2)_2\text{PbBr}_3 \), we started from the experimental structure of \( \text{CH}(\text{NH}_2)_2\text{PbI}_3 \) (54), replaced I with Br, and let the geometry and cell relax. The orientation of the FA cations was changed to produce a configuration that is analogous to that of ordered and disordered \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) and \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \), with the C–H pointing along the same direction as the C–N bonds. The geometry and cell were then optimized, and the bandgap was calculated for the optimized structure.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/10/e1601156/DC1

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