Static Rashba Effect by Surface Reconstruction and Photon Recycling of the Dynamic Rashba Gap in Halide Perovskite Single Crystals

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ABSTRACT: Recently, halide perovskites have gained significant attention from the perspective of efficient spintronics owing to Rashba effect. This effect occurs as a consequence of strong spin-orbit coupling under noncentrosymmetric environment, which can be dynamic and/or static. However, there exist intense debates on the origin of broken inversion symmetry since the halide perovskites typically crystallize into a centrosymmetric structure. In order to clarify the issue, we examine both dynamic and static effects in all-inorganic CsPbBr3 and organic-inorganic CH3NH3PbBr3 (MAPbBr3) perovskite single crystals by employing temperature- and polarization-dependent photoluminescence excitation spectroscopy. The perovskite single crystals manifest the dynamic effect by photon recycling of the indirect Rashba gap, causing dual peaks in the photoluminescence. But the effect vanishes in CsPbBr3 at low temperatures (< 90 K), accompanied by a striking color change of the crystal, arising presumably due to lower degrees of freedom for inversion symmetry breaking associated with the thermal motion of the spherical Cs cation, compared with the polar MA cation in MAPbBr3. We also show that static Rashba effect occurs only in MAPbBr3 below 90 K due to surface reconstruction via MA-cation ordering, which likely extends across a few layers from the crystal surface to the interior. We further demonstrate that static Rashba effect can be completely suppressed upon surface treatment with poly methyl methacrylate (PMMA) coating. We believe that our results provide a general consensus on Rashba effect in halide perovskites.

INTRODUCTION

Halide perovskites have emerged as miracle materials for optoelectronic applications because of their superior optical, electronic, and structural properties such as high absorption coefficient,† defect tolerance,‡ bandgap tunability,§ and easy preparation methods.‡ For instance, organic-inorganic halide perovskites (OIPs) have been investigated in the form of thin films for highly efficient light harvesters, as they have a long carrier lifetime and a long diffusion length.‡§ On the other hand, all-inorganic halide perovskites (AIPs) have been prepared into nanocrystals for highly efficient light emitters, as they possess high photoluminescence (PL) quantum yields,‡∥ relatively short PL lifetimes,‡∥ and better stability.‡¶ But these forms are not quite ideal for studying intrinsic properties of halide perovskites because nanocrystals are sensitive to surface defects with a high surface to volume ratio‡∥ and thin films are influenced by substrates and grain boundaries.‡¶ Obviously, a single crystal seems more suitable for analyzing pristine optical properties of these materials with minimal extrinsic effects. Intriguingly, however, the optical behavior of a perovskite single crystal is complicated by an additional feature in the low-energy tail of PL emission arising from cascade of emission and reabsorption in the bulk, namely photon recycling. The resulting dual-peak feature often led to the incorrect concept of above-bandgap-­emission, whereas strong reabsorption renders a typical carrier dynamics unreliable. In fact, there were several attempts to explain nontrivial carrier dynamics in perovskite single crystals by including fast diffusion of carriers into the interior,‡⊥ but there exists a wide variance in dynamic parameters that are strongly model dependent.
Photon recycling requires a subgap state to cause dual emission in halide perovskites. Although typical Urbach tailing can serve as a subgap state, an alternative mechanism was recently proposed to account for dual emission in terms of additional indirect transition allowed by dynamic Rashba effect. When a nonzero electric field is generated by inversion symmetry breaking, the spin of a free charge couples to an effective magnetic field by strong spin-orbit coupling (SOC), causing spin-dependent energy band splitting to form an indirect gap slightly below the direct band edge. Surprisingly, despite the presence of an inversion center, evidences for Rashba splitting have been reported in halide perovskites by computational simulations, circular photo-galvanic effects, spin-polarization dependence, optical Hanle effect and so on. Currently, there are various views on the origin for broken inversion symmetry, which are categorized into dynamic effects (arising from lattice distortion on a 100 fs time scale) and static effects (arising from static inversion symmetry breaking) but the issue still remains controversial.

In this paper, we aim to identify and even control the underlying mechanisms for inversion symmetry breaking that cause both dynamic and static Rashba effects in high-quality single crystals based on a series of precision spectroscopic measurements, which include nonlinear optical multiphoton absorption and harmonic generation. First, we precisely pinpointed the location of the indirect gap by fine-scale photoluminescence excitation (PLE) spectroscopy over a wide temperature range from 10 K to 300 K. The degree of Rashba splitting was assessed by the energy difference between the direct gap and the indirect gap, which shrinks with decreasing temperature. While dynamic Rashba effect persists in MAPbBr₃, we confirmed that it essentially vanishes in CsPbBr₃ below 50 K, which is also evidenced by the recovery of the color purity of the crystal. This in turn causes significant increase in the PL brightness via suppression of photon recycling of the dynamic Rashba gap. We found that dynamic Rashba effect is critically dependent on the type of the A-site cation (Cs or MA) and the origin for dynamic inversion symmetry breaking arises most likely from thermal motion of the cation in the perovskite cage. Then, we showed that static Rashba effect develops only in MAPbBr₃ at low temperatures (< 90 K) based on temperature- and polarization-dependent PL spectroscopy. The degree of circular polarization in MAPbBr₃ increases with lowering temperature and can be as high as ~3% at 10 K. The origin for static inversion symmetry breaking is local reconstruction of surface via MA-cation ordering, which is most significant across a few layers from the crystal surface to the interior as corroborated by nonlinear optical measurements. We further demonstrated that this static effect in the OIHPL can be completely quenched by a simple surface treatment using poly methyl methacrylate (PMMA) coating. We emphasize that our important results do not show any evidence of Rashba splitting by extrinsic effects due to defects or imperfections, and therefore, provide a general consensus for both dynamic and static Rashba effects in this important class of materials in pristine quality. We believe that our fundamental results are important especially considering that halide perovskites have quite recently entered into an emerging field of spin-optoelectronics, which is combination of spintronics and optoelectronics.

**RESULTS AND DISCUSSION**

Our CsPbBr₃ and MAPbBr₃ single crystals were synthesized by Bridgman and inverse temperature crystallization (ITC) methods, respectively. The sample preparation procedure and X-ray diffraction results are detailed in the Supporting Information. Figures 1a and 1d show the absorption (black) and the PL spectra from CsPbBr₃ and MAPbBr₃, respectively, obtained at 300 K under reflection geometry (R mode, blue) and transmission geometry (T mode, red). The corresponding excitation wavelength (λₑₓ) for one-photon absorption (1PA) was 500 nm. The intensity dependence of the PL clearly indicates that it arises from radiative recombination of free carriers at room temperature (Figure S1). The peak position (λₚ) of the blue trace coincides with the absorption edge, which corresponds to the wavelength for the fundamental direct gap of each single crystal; at low temperatures where excitons are dominant, λₚ corresponds to the wavelength for the exciton PL, i.e., the optical gap that is slightly below the direct gap by exciton binding energy (Figure 2).

Under the T mode, however, a completely different PL (red trace) was obtained from each sample in terms of both peak position and brightness. This drastic change in the PL arises from effective reabsorption of the main PL while traveling a macroscopic distance before exiting the sample (thickness ~2 mm). We attribute the origin for this subgap absorption to the indirect Rashba gap arising from dynamic inversion symmetry breaking in accordance with Ref.[16] and as further explained below through its temperature dependence (Figure 2). Hence, the high-energy onset of the red trace was assigned to λ₁ that corresponds to the wavelength for the indirect gap formed slightly below the direct gap. This implies that the single crystal is truly transparent above λ₁ (below the Rashba gap). It is interesting that the dynamic Rashba gap can be measured by time-integrated absorption or PL experiments, because dynamic inversion symmetry breaking is always present throughout random thermal distortion of the perovskite cage. However, we found that this dynamic effect can be discerned by neither circular polarization spectroscopy nor second harmonic generation (SHG) as they have directional dependence, which would be averaged out for the random thermal motion. It is noteworthy that the main PL (blue trace) is spectrally asymmetric because of low-energy tailing, which indeed coincides with the red trace. This dual-peak nature obtained under the R-mode therefore consists of a symmetric band-to-band transition and the additional PL resulting from photon recycling via successive emission and reabsorption of the main PL directed into the interior of the sample. As described later, the low-energy-peak intensity strongly depends on the sample thickness (Figure 5). This indicates that the secondary peak is not simple indirect emission but ambient PL after photon recycling of the dynamic Rashba gap.
In order to determine the precise locations for $\lambda_d$ and $\lambda_i$, we performed fine-scale PLE spectroscopy on our single crystals. Figures 1b and 1e show the series of the PL spectra from CsPbBr$_3$ and MAPbBr$_3$, respectively, plotted on a semi-logarithmic (semi-log) scale when $\lambda_{ex}$ was varied from $\lambda_i$ to $\lambda_d$. The sharp peak on top of each PL spectrum corresponds to the scattered laser light registered as a peak by our detection system, where its intensity was cut down by more than a factor of 100 with orthogonal polarization control. Interestingly, both single crystals yield a weak indirect PL when $\lambda_{ex}$ is resonant with the Rashba gap, i.e., $\lambda_{ex} = \lambda_i$. When $\lambda_{ex}$ was varied from the Rashba onset to the direct gap, the PL intensity steeply increases and its peak position blueshifts towards the direct gap, until the peak position saturates into a constant wavelength, which is $\lambda_d$. In Figures 1c and 1f, we plot the corresponding PL peak position (black squares) and the PL intensity (blue squares) as a function of $\lambda_{ex}$ as determined from Figures 1b and 1e. The values for $\lambda_d$ are 527 nm (~2.35 eV) and 539 nm (~2.30 eV) for CsPbBr$_3$ and MAPbBr$_3$, respectively, at 300 K. These bandgap wavelengths are consistent with values for $\lambda_d$ shown in Figures 1a and 1d. The values for $\lambda_i$ were determined from the onset $\lambda_{ex}$ causing the weak indirect PL, which are 551 nm (2.25 eV) and 567 nm (~2.19 eV) for CsPbBr$_3$ and MAPbBr$_3$, respectively, at 300 K. These indirect-gap wavelengths are consistent with the values for $\lambda_i$ shown in Figures 1a and 1d. This implies that the PL spectra using the R and T modes can be utilized for estimating $\lambda_d$ and $\lambda_i$. Based on the difference between $\lambda_i$ and $\lambda_d$, we conclude that Rashba splitting is about 10% larger for the OHIP single crystal.

In order to study the temperature dependence of dynamic Rashba effect, we measured the PL as a function of temperature from 300 K to 10 K (Figures S2 and S3). For instance, in Figures 2a and 2d, we plot the PL obtained from CsPbBr$_3$ and MAPbBr$_3$, respectively, at 10 K under the R mode (blue) and the T mode (red). At this low temperature, the nature of the PL is essentially excitonic (X) since exciton binding energy is much larger than thermal energy (~0.9 meV). However, we found that MAPbBr$_3$ exhibits a small but measurable free-carrier peak (FC) even at 10 K, which requires further investigation in the future. In both single crystals, the so-called P-band emission (P) is dominant, which occurs near the polariton bottleneck being slightly below the X line as a consequence of inelastic exciton-exciton scattering. Note that the effect of reabsorption is significantly suppressed in CsPbBr$_3$, as indicated by the coincidence between the blue and the red traces across the Rashba gap in Figure 2a. Interestingly, this is accompanied by the striking color change of the crystal from pale orange (300 K) to transparent yellow (10 K) as shown in the inset. The color change arises from the recovery of the true color of the sample without additional absorption of ambient light by the indirect Rashba gap. In contrast, MAPbBr$_3$ does not exhibit a significant color change at 10 K, implying that dynamic Rashba effect persists at this low temperature. Therefore, there exists reabsorption of the PL in MAPbBr$_3$, causing a clear difference in the blue and red traces in Figure 2d. The estimated values for $\lambda_d$ and $\lambda_i$ are 536.9 nm and 537.6 nm in CsPbBr$_3$ and 551.8 nm and 562.1 nm in MAPbBr$_3$, respectively.

In Figures 2b and 2e, we plot $\lambda_d$ (blue squares) and $\lambda_i$ (red squares) of CsPbBr$_3$ and MAPbBr$_3$, respectively, as a function of temperature based on the PL spectra shown in Figures 2a, 2d, S2, and S3.
phase transition\textsuperscript{16} occurs from the tetragonal phase to the orthorhombic phase. A sudden change in $\lambda_i - \lambda_d$ across the dashed line seems to indicate that dynamic inversion symmetry breaking is contingent upon the type of the A-site cation (Cs or MA) and arises most likely from thermal motion of the cation in the perovskite cage. It is also evident that dynamic Rashba effect is more prone to MAPbBr\textsubscript{3} having a polar character in the MA cation, compared with the much more symmetric Cs cation in CsPbBr\textsubscript{3}.

Intriguingly, in our temperature-dependent PL spectra, it was not clear to spectroscopically identify Saha transition from charge carriers to excitons as temperature was lowered from 300 K to 10 K (Figure S4). The PL spectra are also complicated by strong P-band emission. We therefore performed nonlinear optical multiphoton absorption spectroscopy across the boundary between two-photon absorption (2PA) and three-photon absorption (3PA) for the perovskite crystals and examined the excitation power dependences at two representative temperatures of 300 K and 80 K (see for example Figures S5 and S6 for CsPbBr\textsubscript{3}). The purple and cyan dashed lines in Figures 2c and 2f correspond to the 2PA-3PA boundaries for CsPbBr\textsubscript{3} and MAPbBr\textsubscript{3} at 300 K and 80 K, respectively. The purple spheres (300 K) and cyan spheres (80 K) correspond to the power exponents ($\gamma$'s) for the selected excitation wavelengths, indicating that the PL arises from radiative recombination of free carriers as $\gamma$ values are about 4 for 2PA (left side of the dashed lines) and 6 for 3PA (right side of the dashed lines), respectively. We found that a minor deviation from the precise power law is due to the saturation effect of the carriers during the pulse time (30 ps).\textsuperscript{46} We further confirmed that $\gamma$ values near the Saha transition temperature (~60 K) indicate that both free carriers and excitons coexist, i.e., $2 < \gamma < 4$ (2PA) and $3 < \gamma < 6$ (3PA).

Under strong SOC and inversion symmetry breaking, the spin degeneracy of the valence band (VB) and the conduction band (CB) can be removed. In this situation, selective optical excitation of a specific spin band can be realized by using right/left circularly polarized light (RCP/LCP, $\sigma^-/\sigma^+$). Splitting of the VB (CB) is mainly contributed by hybridization of Br 4p and Pb 6s orbitals (Pb 6p orbitals), causing a larger splitting in the CB than the VB as schematically depicted in the inset of Figure 3a.\textsuperscript{33-46} Therefore, the presence of Rashba splitting can be confirmed by measuring the degree of circular polarization (DOCP) given by

![Figure 2](image-url)
Figure 3. (a) Experimental setup for the DOCP measurement using scattering geometry (θ~20°) to remove the polarization dependence of a beam splitter, where M is a mirror, QWP’s are quarter waveplates, and LP’s are linear polarizers. The inset illustrates the schematic of the Rashba-split conduction and valence bands with spin-dependent selective optical transition with circularly polarized light near the bandgap (E_g). Right/left circularly polarized PL(σ−)/PL(σ+) under σ−/σ+ excitation from (b) CsPbBr_3 and (c) MAPbBr_3 at 10 K. Only MAPbBr_3 exhibits a finite DOCP near the direct-gap peak (552 nm). (d) λ_exc-dependent DOCP of MAPbBr_3 by tuning λ_exc being ~10 nm above the exciton PL line.

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\text{DOCP (\%) = \left| \frac{\text{PL}(\sigma^+) - \text{PL}(\sigma^-)}{\text{PL}(\sigma^+) + \text{PL}(\sigma^-)} \right| \times 100}
\]

where PL(σ−) and PL(σ+) are the measured PL intensities under RCP and LCP excitation, respectively. Considering a fast spin relaxation time due to strong SOC in halide perovskites, the DOCP would be most visible when employed to the case for time-resolved excitation, but can be certainly used for our time-integrated PL spectroscopy. However, it should be noted that dynamic Rashba effect would yield DOCP ≈ 0% in the time-integrated regime, since the orientation of spins is random under thermal distortion of the lattice. Therefore, in our experimental configuration, a nonzero DOCP would be a smoking gun for static Rashba effect, where the origin for inversion symmetry breaking is systematic, not thermal.

Figure 3a illustrates our experimental setup for polarization-dependent PL spectroscopy to assess the DOCP of the perovskites using a pair of quarter waveplates (QWP’s) (see the Supporting Information for details). Compared with a typical setup using a beam splitter, we collected the PL signal under scattering geometry (θ~20°) in order to entirely eliminate the beam-splitting efficiency that depends on polarization as well as wavelength. In Figure 3b we plot the PL spectra from CsPbBr_3 using λ_exc = 532 nm being ~10 nm above the exciton PL line at 10 K, where the trace in the upper (lower) panel corresponds to the PL excited by σ+(σ−) polarization and the red (black) trace being the PL detected using σ+(σ−) polarization. In other words, the red (black) PL in the upper panel corresponds to the parallel (orthogonal) polarization scheme and the color code reverses in the lower panel. Ideally, the PL pair with different colors in the upper and lower panels should be a mirror image each other. Throughout careful analyses on the series of the PL data averaged over laser fluctuation we confirmed that the DOCP is zero in our AIHP single crystal over the entire temperature range (Figure S7). Hence, there is no static inversion symmetry breaking in CsPbBr_3. In fact, we did not find any evidence for extrinsic symmetry-breaking sources such as defects or impurities to cause measurable static Rashba effect, thereby signifying the quality of our specimen.

However, our OIHP single crystal exhibits a small but finite DOCP (~2%) near the exciton PL at 10 K as shown in Figure 3c, in which λ_exc was tuned to 542 nm in order to ensure the same excitation condition, i.e., being ~10 nm above the main exciton PL line. We emphasize that DOCP should be assessed at the direct transition, as it is zero for indirect transition involving incoherent phonon scattering. Most importantly, we confirmed that this finite DOCP is always reproducible over any excitation spot on the sample, clearly demonstrating the presence of static Rashba effect. This static effect can be more clearly seen via the PL contrast between the parallel and orthogonal polarization as shown in Figure S8, which plots |PL(σ+) − PL(σ−)|. We also measured DOCP of MAPbBr_3 as a function of λ_exc and temperature as well (Figures S9 and S10). The dots in Figure 3d correspond to the DOCP values at 10 K for several excitation wavelengths, showing that DOCP increases up to nearly 3% when λ_exc was tuned towards the main PL. This effect can
be understood in terms of an available phase space for spin flip and indeed observed in the recent work.  

Figure 3e depicts the DOCP values (dots) of MAPbBr₃ as a function of temperature. DOCP assumes the maximum value of ~3% at the lowest temperature but monotonically decreases with increasing temperature and vanishes at 90 K. Therefore, we conclude that the OIHP exhibits both dynamic and static Rashba effects, where the latter is present at low temperatures < 90 K.

The surface-induced static effect was further evidenced by zero DOCP under resonant 2PA (Figure 4c), which directly generates cold excitons with well-defined spin orientation in the bulk. Note here that resonant excitation to the exciton line would yield the maximum DOCP in accordance with Figure 3d. Therefore, zero DOCP even under resonant 2PA unambiguously demonstrates that the perovskite crystallizes into a centrosymmetric structure inside the OIHP single crystal, and therefore, static inversion symmetry breaking should originate from surface. However, the origin cannot be simply the boundary surface between the sample and ambient, which is present at all temperatures and even in CsPbBr₃. Clearly, our results eliminate the candidates (i), (ii), and (iii). We emphasize that the candidate (ii) is indeed the mechanism for dynamic Rashba effect, which is more prevalent at higher temperatures, whereas static Rashba effect in Figure 4c only occurs at temperatures lower than 90 K. Based on density functional theory calculations, it was recently suggested that surface reconstruction by the MA cation ordering can give rise to static Rashba effect at low temperatures. This localized inversion symmetry breaking is most significant from the boundary surface to a few layers into the interior of the crystal, where the degree of freedom for the MA cation motion is relatively higher than that in the bulk. In order to prove the feasibility of the model, we prepared a single crystal of MAPbBr₃ coated with PMMA. Quite interestingly, we confirmed that the PMMA-coated MAPbBr₃ did not show any static Rashba effect (Figure 4d) in a sharp contrast with the pristine crystal of MAPbBr₃, yielding a finite DOCP value (Figure 3c). We believe that PMMA passivates the surface defects and constrains MA cations by hydrogen bonding between the cations and the capping polymers.  

Our observation therefore indicates that the source for static inversion symmetry breaking at the surface is the candidate (iv), surface reconstruction. In fact, low-temperature surface reconstruction was recently observed in MAPbBr₃ by real-space imaging. Although PMMA coating can passivate surface defects, we can neglect the impact of surface defects on static Rashba effect simply because of the absence of Rashba splitting in CsPbBr₃. In other words, if surface defects are the main mechanism, CsPbBr₃ should also exhibit static Rashba effect as halide vacancy is ubiquitous on the surface of perovskites. The role of surface recombination and its temperature dependence is more discussed in the Supporting Information.

Lastly, we examined the impact of the crystal size on photon recycling of the indirect bandgap. In order to clearly confirm the effect, we carried out polarization-dependent PL spectroscopy on the bulk and powder (~100 µm) samples at 150 K, where static Rashba effect is absent (DOCP = 0). In Figures 5a, 5b, 5c, and 5d, we plot the right/left circularly polarized PL(σ+)/PL(σ−) from (a) bulk CsPbBr₃, (b) CsPbBr₃ powder, (c) bulk MAPbBr₃, and (d) MAPbBr₃ powder, respectively, at 150 K under σ−/σ+ excitation. Our results clearly show that the secondary peak can significantly alter the PL spectrum depending on the degree of photon recycling of the indirect Rashba gap in
Both AIHP and OIHP single crystals. Compared with the bulk counterparts, small-sized powders yield the more pronounced peak below the direct gap due to less efficient photon recycling. This effect is schematically illustrated in Figure 5e.

CONCLUSION

In conclusion, we have thoroughly investigated both dynamic and static Rashba effects in AIHP and OIHP single crystals using precision linear and nonlinear optical spectroscopy as a function of excitation wavelength and polarization over a wide temperature range from 10 K to 300 K. Both perovskite single crystals exhibit dynamic Rashba effect as evidenced by the formation of the indirect gap via thermal distortion of the lattice. While the effect persists in MAPbBr₃, dynamic Rashba splitting in CsPbBr₃ disappears at low temperatures (< 50 K), which is accompanied by the apparent color change of the crystal. Based on circularly polarized PL spectroscopy, we have also examined static Rashba effect and found that only MAPbBr₃ exhibits static Rashba effect with DOCP ~ 3% at 10 K. We further showed that the origin for the static inversion symmetry breaking occurs near the surface, not bulk, by employing nonlinear optical harmonic generation and 2PA. We have identified that the underlying mechanism for static Rashba effect is surface reconstruction of MA cations, which was theoretically predicted and experimentally confirmed recently. Considering the surface nature of the effect and a relatively fast spin decoherence time of ~2 ps in bulk perovskite crystals,¹⁸ we believe that time-integrated DOCP of 3% is a rather large value. We have also demonstrated that static Rashba effect in the OIHP can be actively controlled by a simple surface treatment with PMMA, which suppresses the degree of freedom for MA-cation ordering. Finally, we have shown that the PL spectrum can be significantly affected by photon recycling of the Rashba gap depending on the crystal size. Our results indicate that Rashba effect is less prone to extrinsic defects, thereby providing a general consensus on the controversial topic. We believe that our results are important for furthering the halide perovskites into the emerging field of spin-optoelectronics.

ASSOCIATED CONTENT

Supporting Information

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Notes
The authors declare no competing financial interest. Any additional relevant notes should be placed here.

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REFERENCES

(1) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The Emergence of Perovskite Solar Cells. Nat. Photonics. 2014, 8, 506–514.

(2) Kang, J.; Wang, L. W. High Defect Tolerance inLead Halide Perovskite CsPbBr\text{3}. J. Phys. Chem. Lett. 2017, 8, 489–493.

(3) Protesescu, L.; Yakunin, S.; Bodnarchuk, M.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of CsLead Halide Perovskites (CsPbX\text{3}, X = Cl, Br, I). Novel Optoelectronic Materials Showing Bright Emission withWide Color Gamut. Nano Lett. 2015, 15, 3692–3696.

(4) Byun, H. R.; Park, D. Y.; Oh, H. M.; Namkoong, G.; Jeong, M. S. Light Soaking Phenomena in Organic-Inorganic Mixed Halide Perovskite Single Crystals. ACS Photonics 2017, 4, 2813–2820.

(5) Fang, Y.; Dong, Q.; Shao, Y.; Yuan, Y.; Huang, J. Highly Narrowband Perovskite Single-Crystal Photodetectors Enabled by Surface-Charge Recombination. Nat. Photonics 2015, 9, 679–686.

(6) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovsky, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M. LowTrap State Density and Long Carrier Diffusion inOrganolead Trihalide Perovskite Single Crystals. Science. 2015, 347, 519–522.

(7) Rakita, Y.; Kidem, N.; Gupta, S.; Sadhanala, A.; Kalchenko, V.; Böhm, M. L.; Kulbak, M.; Friend, R. H.; Cahen, D.; Hodes, G. Low-Temperature Solution-Grown CsPbBr\text{3} Single Crystals and Their Characterization. Cryst. Growth Des. 2016, 16, 5777–5775.

(8) Zhang, H.; Liu, X.; Dong, J.; Yu, H.; Zhou, C.; Zhang, B.; Xu, Y.; Jie, W. Centimeter-Sized Inorganic Lead Halide Perovskite CsPbBr\text{3} Crystals Grown by an Improved Solution Method. Cryst. Growth Des. 2017, 17, 6426–6431.

(9) Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J. Electron-Hole Diffusion Lengths > 175 μm inSolutionGrown CH\text{3NH}\text{2PbI}\text{3} Single Crystals. Science. 2015, 347, 967–970.

(10) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcoro, M. P.; Leijten, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in anOrganometal Trihalide Perovskite Absorber. Science. 2013, 342, 341–344.

(11) Pan, J.; Shang, Y.; Yin, J.; De Bastiani, M.; Peng, W.; Dursun, I.; Sinatra, L.; El-Zohry, A. M.; Hedhili, M. N.; Emwas, A. H.; Mohammed, O. F.; Ning, Z.; Bakr, O. M. Bidentate Ligand-Passivated CsPbI\text{3} Perovskite Nanocrystals for Stable Near-Ultrasensitive Photoluminescence Quantum Yield and Efficient Red Light-Emitting Diodes. J. Am. Chem. Soc. 2018, 140, 562–565.

(12) Wang, S.; Bi, C.; Yuan, J.; Zhang, L.; Tian, J. Original Core-Shell Structure ofCubic CsPbBr\text{3}@Amorphous CsPbX\text{3} Perovskite Quantum Dots with a High Blue Photoluminescence Quantum Yield of over 86%. ACS Energy Lett. 2018, 3, 245–251.

(13) Song, J.; Cui, Q.; Li, J.; Xu, J.; Wang, Y.; Xu, L.; Xue, J.; Dong, Y.; Tian, T.; Sun, H.; Zeng, H. Ultralong All-Inorganic Perovskite Bulk Single Crystal for High-Performance Visible-Infrared Dual-Modal Photodetectors. Adv. Opt. Mater. 2017, 5, 1700157.

(14) Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im; J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G. Crystal Growth of the Perovskite Semiconductor CsPbBr\text{3}: A New Material for High-Energy Radiation Detection. Cryst. Growth Des. 2013, 13, 2722–2727.

(15) Wang, Y.; Ren, Y.; Zhang, S.; Wu, J.; Song, J.; Li, X.; Xu, J.; Sow, C. H.; Zeng, H.; Sun, H. Switching Excitonic Recombination and Carrier Trapping inCesium Lead Halide Perovskites by Air. Commun. Phys. 2018, 1, 96.

(16) Zhao, J.; Deng, Y.; Wei, H.; Zheng, X.; Yu, Z.; Shao, Y.; Shield, J. E.; Huang, J. Strained Hybrid Perovskite Thin Films and Their Impact on the Intrinsic Stability of Perovskite Solar Cells. Sci. Adv. 2017, 3, No. eaao5616.

(17) Doherty, T. A. S.; Winchester, A. J.; Macpherson, S.; Johnstone, D. N.; Pareek, V.; Tennyson, E. M.; Kosar, S.; Kosaish, F. U.; Anaya, M.; Abdi-Jalebi, M.; Andaj-Garmaroudi, Z.; Wong, E. L.; Madje, J.; Chiang, Y. H.; Park, J. S.; Jung, Y. K.; Petoukhoff, C. E.; Divitini, G.; Man, M. K. L.; Ducati, C.; Walsh, A.; Midgley, P. A.; Dani, K. M.; Stranks, S. D. Performance-Limiting Nanoscale Trap Clusters at Grain Junctions inHalide Perovskites. Nature 2020, 580, 360–366.

(18) Wu, B.; Yuan, H.; Xu, Q.; Steele, J. A.; Giovanni, D.; Puech, P.; Fu, J.; Ng, Y. F.; Jamaludin, N. F.; Solanki, A.; Mhaisalkar, S.; Mathews, N.; Roelfers, M. B. J.; Grätzel, M.; Hofkens, J.; Sum, T. C. Indirect Tail States Formation by Thermal-Induced Polar Fluctuations inHalide Perovskites. Nat. Commun. 2019, 10, 484.

(19) Murali, B.; Dey, S.; Abdelhady, A. L.; Peng, W.; Alarousu, E.; Kirmani, A. R.; Cho, N.; Sarmah, S. P.; Parida, M. R.; Saidaminov, M. I.; Zhumekonov, A. A.; Sun, J.; Alias, M. S.; Yengel, E.; Ooi, B. S.; Amassian, A.; Bakr, O. M.; Mohammed, O. F. Surface Restructuring of Hybrid Perovskite Crystals. ACS Energy Lett. 2016, 1, 110–116.

(20) Fang, X.; Zhang, K.; Li, Y.; Yao, L.; Zhang, Y.; Wang, Y.; Zhai, W.; Tao, L.; Du, H.; Ran, G. Effect of Excess PbBr\text{3} onPhotoluminescence Spectra ofCH\text{3NH}\text{2PbI}\text{3} Perovskite Particles atRoom Temperature. Appl. Phys. Lett. 2016, 108, 071909.

(21) Schötz, K.; Askar, A. M.; Peng, W.; Seeberger, D.; Gujar, T. P.; Thelakkat, M.; Köhler, A.; Huettner, S.; Bakr, O. M.; Schaner, F.; Panzer, F. Double Peak Emission inCesium Lead Halide Perovskite Single Crystals. Nat. Commun. 2017, 8, 14417.

(22) Saouma, F. O.; Stoumpos, C. C.; Kanatzidis, M. G.; Kim, Y. S.; Jang, J. I. Multiphoton Absorption Order of
Highly Spin-Polarized Carrier Dynamics and Ultralarge Photoinduced Magnetization in CH$_3$NH$_3$PbI$_3$ Perovskite Thin Films. *Nano Lett.*

(50) Chen, X.; Lu, H.; Li, Z.; Zhai, Y.; Ndione, P. F.; Berry, J. J.; Zhu, K.; Yang, Y.; Beard, M. C. Impact of Layer Thickness on the Charge Carrier and Spin Coherence Lifetime in Two-Dimensional Layered Perovskite Single Crystals. *ACS Energy Lett.* **2018**, *3*, 2273-2279.

(51) Che, X.; Traore, B.; Katan, C.; Kepenekian, M.; Even, J. Does Rashba Splitting in CH$_3$NH$_3$PbBr$_3$ Arise from $2 \times 2$ Surface Reconstruction? *Phys. Chem. Chem. Phys.* **2018**, *20*, 9638-9643.

(52) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. Ruddlesden-Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. *Chem. Mater.* **2016**.

(53) Shao, Y.; Xiao, Z.; Bi, C.; Yuan, Y.; Huang, J. Origin and Elimination of Photocurrent Hysteresis by Fullerene Passivation in CH$_3$NH$_3$PbI$_3$ Planar Heterojunction Solar Cells. *Nat. Commun.* **2014**, *5*, 5784.

(54) Masi, S.; Rizzo, A.; Aiello, F.; Balzano, F.; Uccello-Barretta, G.; Listorti, A.; Gigli, G.; Colella, S. Multiscale Morphology Design of Hybrid Halide Perovskites through a Polymeric Template. *Nanoscale* **2015**, *7*, 18956-18963.

(55) Ohmann, R.; Ono, L. K.; Kim, H. S.; Lin, H.; Lee, M. V.; Li, Y.; Park, N. G.; Qi, Y. Real-Space Imaging of the Atomic Structure of Organic-Inorganic Perovskite. *J. Am. Chem. Soc.* **2015**, *137*, 16049-16054.

(56) Oranskaia, A.; Yin, J.; Bakr, O. M.; Brédas, J. L.; Mohammed, O. F. Halogen Migration in Hybrid Perovskites: The Organic Cation Matters. *J. Phys. Chem. Lett.* **2018**, *9*, 5474-5480.