Impact of Halide Substitution in the Inorganic Framework on the Optical Activity of Chiral Metal-Halide Perovskites

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Abstract

The combination of chiroptical and semiconducting properties makes chiral hybrid metal-halide perovskites a promising class of materials for optoelectronic and opto-spintronic devices. Still, the detailed connection between material composition and optical activity remains to be fully understood. Here, we study the effect of halogen substitution on optical activity in the chiral hybrid perovskite (R, S, rac)- 3BrMBA₂PbI_{4(1-x)}Br_{4x}. We find that an unusual sign-flip occurs in the circular dichroism (CD) spectrum as the optical gap blueshifts with increasing bromide content. We explain this observation by shifts in the energy level alignment caused by the halide substitution. We also observed an inverse relationship between CD intensity and the microstrain induced in the lattice for mixed-halide compositions, which we attribute to inhomogeneity in chirality transfer across the inorganic framework. Last but not least, transient faraday rotation measurements reveal that the (R/S)-3BrMBA₂PbBr₄ system exhibits a significant spin lifetime even at room temperature, underscoring its potential for spintronic applications.

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Characterized by a structure lacking of symmetry elements such as mirror planes and inversion symmetry, chiral materials display intriguing chiroptical phenomena, such as circular dichroism (CD) and circularly polarized photoluminescence (CPL). These distinctive properties have sparked significant interest across diverse fields including opto-spintronics¹, optoelectronics², optical information processing³, and chiral biosensing⁴. Organic chiral materials are the most common chiral materials in nature. However, they often exhibit limited charge transport due to their structural softness, which leads to a reliance on hopping transport rather than efficient band-like transport. This constrains their practical use in optoelectronics and restricts chiroptical phenomena primarily to the near-UV range⁵. These limitations suggest to search for materials with improved capabilities.

Organic–inorganic hybrid perovskites (OIHPs) possessing properties of both inorganic and organic sub-lattices have emerged as prominent materials for optoelectronic applications due to their exceptional optical properties such as high charge carrier mobility⁶, long carrier diffusion lengths⁷, tunable band gaps^{8,9}, long spin life time¹⁰ and high light-absorption coefficients in the visible range¹¹. Typically, chiral OIHPs have a low-dimensional layered structure with a chemical formula of A'BX₃ for one dimensional (1D) or A'₂BX₄ (2D), where A' is a large organic cation, B is a divalent metal cation, and X is a halide anion. Notably, the structural flexibility and tunability of OIHPs facilitate the integration of chiral organic cations, introducing chirality and therefore breaking the symmetry within the materials.

Through careful material design, chiral OIHPs with different anions and cations combinations can be created, allowing for the precise control of their chiroptical features, such as CD and CPL. Manipulating chiroptical properties involves selecting chiral organic molecules, including different structural isomers^{12,13} and halogen substitutions of the A'-site cation^{14,15} to enhance chirality transfer. Additionally, tuning the composition of the inorganic frameworks (BX₃ or BX₄) and varying B-site metal cations¹⁶ and halide compositions can effectively alter chiroptical responses across the spectrum^{17–19}.

In this study, we aim to develop a deeper insight into the influence of halogen substitution on optical activity of chiral 2D OIHPs. Because of its notable chiral properties¹³, we took (R/ S/ rac)- $3BrMBA_2PbI_4$ [3BrMBA = 1-(3-bromphenyl)-ethylamine] as a control sample and examined its chiroptical behavior when subjected to halogen substitution. Using single-crystal X-ray diffraction (SCXRD) and computational approaches based on density functional theory (DFT), chirality transfer to both single crystals containing iodide and bromide anions has been proved. CD measurements shows CD signals at excitonic absorption position, tunable over wavelength for samples with different ratios of I/Br. In contrast to the study by Ahn et al.¹⁸, where the replacement of bromide with iodide led to abrupt crystal structure transitions and loss of chiroptical properties, our research demonstrates that even when bromide fully replaces iodide, the 2D OIHP still belongs to the chiral space group P2₁, allowing for smooth tuning of the chiroptical wavelength through simple halide substitution. Unlike their work, there is no need to modify the chiral organic ligand to achieve CD signals at lower wavelength. Interestingly, we observed a polarity change in the CD signal at the excitonic peak position when iodide is fully replaced by bromide. Excluding linear dichroism and linear birefringence (LDLB) contributions, we attribute this change to shifts in energy level alignment caused by halide substitution. We also employed transient absorption (TA) spectroscopy and time-correlated single photon counting (TCSPC) to compare the dynamics of

charge carriers in films with different halides, and we found a longer exciton lifetime in variants of our samples with bromide halides. Furthermore, transient faraday rotation measurements show that (R/S)-3BrMBA₂PbBr₄ maintains spin lifetime for hundreds of ps.

We synthesized single crystals and powders of (R)-, (S)-, or racemic-3BrMBA₂PbI_{4(1-x)} Br_{4x} (x = 0 to 1) from hydrothermal synthesis by varying the volume ratios of HI/ HBr solutions (see material section for details). The crystal structures of the single crystals are determined by SCXRD. Detailed crystal structure and refinement data of (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ are shown in Figure 1 and Table S1. Both crystals possess a 2D layered perovskite structure with two layers of chiral organic cations sandwiching the sequential corner-sharing inorganic $[PbX_4]^{2-}$ octahedral layer (Figure 1a, b). Introducing the chiral organic cations reduces the symmetry of inorganic leadhalide octahedra, leading to the non-centrosymmetric monoclinic space group of P21 in both single crystals which belongs to the Sohncke space group. We take this as a demonstration of the successful transfer of chirality from the chiral organic molecule to the metal-halide octahedra. Further, the distortion of the $[PbX_4]^{2-}$ layers from a regular corner-sharing octahedral arrangement is quantified from the bond length distortion index (D) and bond angle variance degree (σ^2) (detailed calculations in Table S2). In comparison with (R)-3BrMBA₂PbI₄ (D = 0.012, σ^2 = 31.91), the octahedra are more distorted in (R)-3BrMBA₂PbBr₄ (D = 0.018, σ^2 = 45.44). Also, the in-plane tilting of PbX₆ octahedra (Pb-X-Pb) in (R)-3BrMBA₂PbBr₄ ($\Delta\beta = 14.1$) is higher compared to (R)- $3BrMBA_2PbI_4$ ($\Delta\beta = 11.9$). Previous work has reported that the in-plane tilting is affected by the organic spacer cation penetration depth into the inorganic slab's axial halogen plane²⁰. The various electrostatic and hydrogen-bonding interactions between PbX₆ octahedra and organic spacer cations act on the geometry of the inorganic layers. Therefore, we calculated the hydrogen-bonding length between the NH₃⁺ groups of the chiral organic spacer and the closest halide atom of the inorganic framework (Table S3). Owing to the higher electronegativity of Br in the inorganic framework of (R)-3BrMBA₂PbBr₄, more robust hydrogen bonds are formed compared to those in (R)-3BrMBA₂PbI₄. The distortion of octahedra in (R)-3BrMBA₂PbBr₄ is also influenced by steric effects due to the smaller size of bromine atoms, allowing the organic molecules to come closer and causing greater steric hindrance. This hindrance forces the PbBr₄ octahedra to adjust their structure, leading to more distortion compared to the PbI4 octahedra in (R)-3BrMBA2PbI4, where larger iodine atoms reduce such effects.

To examine the effect of different anions on the materials' chiroptical properties, we fabricated thin films by spin-coating the DMF solutions containing the synthesized crystals dissolved in DMF onto glass substrates. Subsequently, the films were annealed at 100°C for 10 minutes. XRD spectra of the thin films and the single-crystal XRD spectra obtained by simulating diffraction patterns are compared in Figure1c. The spectra exhibit very similar features, indicating the successful transformation of single-crystal structures into thin films. It is worth noting that the observed discrepancies between the simulated and experimental XRD patterns—such as slight peak shifts and broadening—can be attributed primarily to differences in measurement conditions. Specifically, the SCXRD data were obtained at low temperature, whereas the thin-film XRD measurements were conducted at room temperature. Moreover, thin films are subject to strain effects arising from lattice mismatch with the substrate and differences in thermal expansion coefficients, both of which can significantly influence peak positions and broadening²¹. The well-defined and periodical diffraction peaks correspond to the (001) reflections series of the layered

perovskites, representing the interlayer spacing between the inorganic layers. Figure 1d shows the XRD at the position of the dominant peak. We notice a slight shift to lower degrees upon replacement of iodide ($2\theta = 5.03^\circ$, 5.01°) with bromide in (R)-3BrMBA₂PbI_{4(1-x)}Br_{4x} ($2\theta = 4.97^\circ$, 4.99°) in single crystals and thin films, respectively. This indicates a slightly larger interlayer distance for the bromide-containing film (17.78 Å compared to 17.59 Å for the iodide one). Since the interlayer distance is primarily determined by the orientation of the organic cation, changing the halide ion composition does not significantly alter the (001) peak positions. Nevertheless, the stronger in-plane strain induced by the in-plane compression of PbBr₆ octahedra is in part released by larger expansion along the stacking axis²², subtly influencing the alignment of organic cations and consequently fine-tuning the (001) peak positions.



Figure 1. Structure properties of chiral 2D OIHPs and the influence of the halide substitution. (a,b) Atomic structure of (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ perovskites, respectively. (c) XRD diffraction spectrum of (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ perovskites. (d) Zoom-in to the first dominant diffraction peak. Compared to (R)-3BrMBA₂PbI₄, this XRD peaks shifts towards lower angles for (R)-3BrMBA₂PbBr₄, indicating that the interlayer distance slightly increases in the latter due to a subtle difference in the organic layer packing.

Room temperature steady-state optical studies of racemic and $3BrMBA_2PbI_{4(1-x)}Br_{4x}$ (x=0, 1) thin films are shown in Figure 2. The linear absorption spectra (Figure 2a) reveal a distinct excitonic peak, arising from the confined nature of charge carriers within their layered structure. The peak is followed by an absorption continuum in the band-to-band absorption region. In the case of $3BrMBA_2PbBr_4$, the excitonic peak appears at 387 nm for chiral samples, whereas for racemic ones, it shifts to 395 nm. Similarly, the excitonic peaks for $3BrMBA_2PbI_4$ films are observed at 487 nm for chiral samples and at 499 nm for racemic ones. This blue shift between the chiral and their racemic counterparts (65 meV for $3BrMBA_2PbBr_4$ and 60 meV for $3BrMBA_2PbI_4$) originates from the structural distortion, particularly a greater $\Delta\beta$ in the chiral samples compared to the racemic ones^{23,24}.

The electronic structure of 3BrMBA₂PbBr₄ and 3BrMBA₂PbI₄ was determined from DFT-based first-principles calculations (Figure S2 and S3)¹³. Both compounds show similar features with conduction band minima (CBM) primarily consisting of the lead 6p orbitals, while the valence band maxima (VBM) are mainly made up of lead 6s contributions hybridized with the p orbitals of the halides (i.e., Br 4p or I 5p). In agreement with our optical measurements, the band gap widens when Br 4p replaces I 5p by almost 0.4 eV (Figure S3) as expected because of the lower energy of

the Br 4p orbital with respect to the I 5p one. In addition, both compounds show splitting of the top valence and bottom conduction bands induced by the loss of centrosymmetry in the non-racemic structures. This Rashba-like coupling leads to nearly direct band gaps at the B point of the Brillouin zone. Interestingly, the Rashba parameter α , characterizing the strength of the coupling (Figure S3), is found to be either similar (in conduction bands) or much greater (in valence bands) in the bromide than in the iodide compound. Considering the weaker spin-orbit coupling found in Br with respect to I, the greater α is a signature of the larger distortion found in 3BrMBA₂PbBr₄.



Figure 2. Comparison of optical properties for racemic and chiral films. (a) Linear absorption, (b) CD, and (c, d) linear PL spectra of racemic and chiral 3BrMBA₂PbBr₄ and 3BrMBA₂PbI₄ thin films. 3BrMBA₂PbI₄ exhibit a sharp PL emission from free excitons, whereas in 3BrMBA₂PbI₄ the PL from self-trapped excitons is more dominant. Notably, upon introducing bromide instead of iodide, CD signal at excitonic peak position for same configuration of organic cation (here, R) shows a sign flip.

Next, we collected PL spectra of the thin film samples. The PL spectrum of the iodide-based materials is shown in Figure 2d and exhibits a classic narrow-band emission in the green region (~500 nm) which has been attributed to free exciton (FE) recombination. However, in the case of $3BrMBA_2PbBr_4$ (Figure 2c), we observed a weak and narrow peak at ~400 nm corresponding to FEs, followed by a red-shifted broad-band emission which is attributed to self-trapped excitons (STEs). This spectral shift is induced by lattice deformation and strong exciton—phonon coupling²⁵. Indeed, the stronger the hydrogen bond in (-NH₃)- (PbX₆), the more enhanced exciton—phonon coupling is expected, leading to a known tendency for the formation of STEs²⁶. The chromaticity coordinates of the PL emissions of 3BrMBA₂PbBr₄ are displayed in the CIE 1931 color space in Figure S4, with coordinates of (0.35, 0.46), (0.38, 0.44), and (0.33, 0.45) for the R, rac, and S samples, respectively, demonstrating remarkable white light emission. Via power-dependent PL measurements we confirmed the STE origin of the broad white light emission (BWL) (Figure S5). If the BWL was caused by defects, it would show a sublinear response with increasing excitation

power that finally saturates due to limited defect sites at higher excitation intensities. In contrast, the PL signal of $3BrMBA_2PbBr_4$ exhibits continuous growth with increasing laser power within the range from 5 to 500 µJcm⁻², without showing signs of saturation, suggesting that the BWL is not due to defects. Moreover, no change in the shape of PL emission is observed, indicating constant energy levels of the emissive states, irrespective of variations in excitation intensity. Additionally, we observe a similar wide spectrum in the single crystal which can be expected to show lower levels of defects than thin films (Figure S5).

In comparison to their corresponding absorption spectra, the luminescence of the FEs of all materials shows a Stokes shift with a magnitude of 40 meV for 3BrMBA₂PbI₄ and a larger shift of 100 meV for 3BrMBA₂PbBr₄. The different Stokes shifts could be attributed to varying levels of lattice strain. Between racemic and chiral counterparts, there is a shift in PL spectra, as observed in the absorption spectra, arising from the difference in their in-plane distortion ($\Delta\beta$ angles). Notably, the FE peak of racemic 3BrMBA₂PbBr₄ appears more intense compared to the chiral counterparts, potentially due to a slight indirect transition caused by Rashba band splitting in the chiral perovskites²⁷.



Figure 3. Spectral and spatial analysis of the optical activity in single-halide chiral perovskites. (a, b) CD spectra of thin films of (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄, respectively, under four-scan measurements. $K=0^{\circ}$ and 180° represent front and back side of the thin film, respectively, and θ represent different azimuth angles. (c) The LDLB contribution obtained from four-scan measurements in films containing different halides. (d, e) Optical microscopy images of chiral (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ thin films, respectively, under cross-polarized filters. The higher LDLB term in (R)-3BrMBA₂PbBr₄ can be attributed to its increased local anisotropy and birefringence. (f) Schematic illustration of energy diagram perturbation by chirality leading to CD sign flip.

The CD spectra of chiral compounds containing different halides are shown in Figure 2b and exhibit mirror images for different enantiomers and no CD for racemic films (Figure S6), indicating

efficient transfer of the chirality of the organic cation to the inorganic framework. In chiral films, at their first excitonic band edge, the (R)-3BrMBA₂PbBr₄ shows a derivative-featured CD attributed to the Cotton effect, with a positive peak followed by a negative peak with the cross center at 391 nm. The (R)-3BrMBA₂PbI₄, on the other hand, has a derivative-like peak at 481 nm, with the first peak being negative and the second one being positive. This unexpected change in CD polarity in chiral 2D OIHPs contrasts with the typical scenario where the helicity of the chiral organic spacer (whether it adopts an S- or R-configuration) dictates the polarity of the CD signal. The unexpected CD polarity change has recently been reported in some chiral materials subjected to strain or changes in material compositions while maintaining the handedness of the chiral organic unchanged^{18,28–30}. However, a definitive explanation for this phenomenon is still lacking and warrants further investigation.

It is important to emphasize that the observed reversal of CD signal in isostructural iodide and bromide-based compounds is not due to macroscopic anisotropies typically associated with solid-state samples, as explained in the following discussion. In solid-state thin films with large surface roughness, the intrinsic CD differs from the measured CD. Recalling the basic concept of Mueller matrix analysis, the observed CD can be expressed by three major components²⁹;

$$CD_{obs} \approx CD_{intrinsic} + \frac{1}{2} (LD'.LB-LD.LB') + (-LD \cos 2\theta + LD' \sin 2\theta) \sin \alpha$$
(1)
+ (Px² - Py²) sin 2\alpha (-LB cos 2\theta + LB' sin 2\theta)

where the intrinsic CD is denoted by the first term, the second term accounts for the LDLB effect, in which LD (LD') and LB (LB') stand for the linear dichroism and linear birefringence, in the x y plane (with a +45° shift) and perpendicular to the optical axis z, respectively. The LDLB term is caused by macroscopic anisotropies of the samples and only appears when the primary axes of LB and LD are not aligned with each other. The third and fourth terms are associated with artifacts related to the residual birefringence of the spectrometer's photoelastic modulator PEM (α) and the sample's angular orientation with respect to the optical axis (θ).

To obtain $CD_{intrinsic}$, it is crucial to eliminate the influence of the LDLB effect and the artifact arising from PEM. The cancellation of CD_{LDLB} occurs when measurements are conducted before and after flipping the sample along the incident beam's path (K = 0° and 180°). Regarding the CD signal attributed to the PEM, by averaging two separate measurements—one at $\theta = 0^{\circ}$ and the other with rotating the sample by $\theta = 90^{\circ}$ — the third and fourth terms become zero³¹. Therefore, we applied four-scan measurements on both thin films containing bromide and iodide, as illustrated in Figure 3a, b. In both cases, the CD spectra do not display significant changes upon sample rotation around the azimuth angle (θ), indicating a negligible contribution of PEM imperfection to the CD signal. However, by flipping the sample (K), the CD signal noticeably changes, especially for (R)-3BrMBA₂PbBr₄ which shows a roughly fivefold decrease in intensity. We can separate the CD_{intrinsic} and CD_{LDLB} terms by adding and subtracting the two spectra that were taken with the sample facing forward and backward, as shown in Eq. (2) and Eq. (3), respectively.

$$CD_{intrinsic} = \frac{1}{2} \times (CD_{obs.front} + CD_{obs.back})$$
(2)

$$CD_{LDLB} = \frac{1}{2} \times (CD_{obs.front} - CD_{obs.back})$$
(3)

The CD_{intrinsic} is what is depicted in Figure 2b, while the LDLB contribution is shown in Figure 3c. To highlight the stronger LDLB effect in (R)-3BrMBA₂PbBr₄ film, we further applied optical microscopy images with linearly crossed polarized light (Figure 3d and 3e). If the thin films contain local anisotropy, the presence of nonzero LD and LB would result in localized bright and dark regions when the light polarization is rotated by 90°. We find bright local spots which are in stark contrast with the black background in (R)-3BrMBA₂PbBr₄, suggesting a higher degree of locally anisotropic and linearly birefringent domains compared to (R)-3BrMBA₂PbI₄. This effect explains the higher LDLB signal in (R)-3BrMBA₂PbBr₄. However, it should be noted that the LDLB contribution, which is a significant factor capable of changing the CD sign, is not included in Figure 2b. Since the CD signal presented is the intrinsic CD signal, unaffected by the LDLB contribution.

The observed change in CD signal polarity when excluding the LDLB contribution can be tentatively explained by recent findings on chiral 2D OIHPs. Sercel et al³³ showed that the polarity reversal of the excitonic derivative-like CD peak between two enantiomers directly corresponds to the orientation of the magnetic transition dipole of each fine structure level relative to the respective electric transition dipoles. This effect arises from the inversion of polar distortion between the chiral enantiomers. To further investigate whether this mechanism is responsible for the observed CD reversal in our materials, we calculated the local dipole moment in (R)-3BrMBA₂PbI₄ and (R)-3BrMBA₂PbBr₄ (Table S4). Our calculations reveal that in both cases the local polarization within octahedra is directed along +y axis, parallel to the 2₁ screw axis (Figure S7). This finding confirms that the CD reversal is not driven by a reversal in the relative orientation of magnetic transition dipole moment with respect to the electric transition dipoles. Additionally, an intriguing outcome of this calculation is the difference in local dipole moments experienced by Pb atoms in the two chiral perovskites: the Br-based system exhibits a higher local dipole moment (0.576 Å) compared to the I-based system (0.332 Å). This highlights the influence of halide composition and beneficial effect from bromide substitution on local polarization effects in chiral 2D perovskites.

Additionally, prior studies have linked the magnitude of the CD signal to out-of-plane ionic displacements within the metal-halide lattice—particularly the displacement of axial halide atoms relative to the inorganic framework, denoted as $\Delta_{z-X-ax}^{34,35}$. Notably, they also observed a reversal in CD polarity along the Z-axis when iodide is substituted with bromide. In our systems, the calculated Δ_{z-X-ax} values are 0.025 for the (R)-3BrMBA₂PbBr₄ and -0.008 for the (R)-3BrMBA₂PbI₄ (Figure S8), consistent with the stronger g CD observed in the (R)-3BrMBA₂PbBr₄ compounds as will be shown later. We further observe that the sign of Δ_{z-x-ax} reverses ($\Delta_{z-x_1} - \Delta_{z-x_2}$) upon replacing iodide with bromide, potentially explaining the corresponding inversion in CD polarity. However, this explanation is challenged by the behavior of (R)-3BrMBA₂PbCl₄, which, despite exhibiting a positive Δ_{z-X-ax} value similar to that of (R)-3BrMBA₂PbBr₄, shows a CD signal of opposite sign. This discrepancy implies that Δ_{z-X-ax} does not fully account for the observed sign reversal in CD and additional mechanisms must be considered. In addition, a recent study also demonstrated that the MCD signal in CsPbX₃ (X = Cl, Br, I) changes sign with halide substitution, attributing this behavior to modifications in electronic state mixing and spin polarization³⁶. Therefore, we propose that the CD sign reversal with halide exchange can be rationalized based on a quantum mechanical perspective, but detailed theoretical calculations will be needed to fully reveal the mechanistic origins.

Therefore, we propose that the CD sign reversal with halide exchange can be rationalized based on a quantum mechanical perspective. The total CD spectrum results from the sum of multiple excitonic transitions within the optical spectrum³⁷. A derivative line shape in CD usually indicates that a fundamental transition has split into two bands, with each band being more effectively excited by opposite circular polarizations³⁸. The introduction of chiral molecules can create an asymmetric potential in the inorganic perovskite layers, leading to the splitting of electronic energy levels^{12,28}. This excited state splitting occurs due to the coupling between transition dipole moments that are not aligned. When these split states interact with circularly polarized light, the conservation of angular momentum dictates that transitions occur when the change in the system's angular momentum matches that of the incident light. In chiral iodide-based perovskites, the electronic configuration appears to be such that σ light preferentially excites the higher energy state, while σ^+ light excites the lower energy state, resulting in a positive Cotton effect³⁹. In contrast, in bromide-based chiral 2D HOIP, the substitution of the halide appears to alter the electronic environment, modifying the angular momentum coupling and reversing this interaction, thereby flipping the CD signal (Figure 3f). To confirm our hypothesis, calculations on the exciton energy structure in chiral hybrid perovskites are required, which are beyond the scope of this report and planned in future work.

Next, we investigated the chiroptical properties of mixed halide compositions by studying spincoated (R)-3BrMBA₂PbI_{4(1-x)} Br_{4x} (x=0, 0.3, 0.5, 0.7, 1) films with varying halide ratio, determined using energy-dispersive X-ray spectroscopy (EDX) (Table S5). The structural change caused by the halide mixture is examined with XRD (Figure S9). XRD peak at $2\theta = -10^{\circ}$ is brought here because peak shifts are better resolved at this higher angle, allowing for clearer observation of the changes in the crystalline structure. As mentioned above, the interlayer distance is mainly affected by the organic spacer packing. This suggests that compared to the pure halide, the orientation of the organic layer in the presence of mixed halides is such that it introduces additional strain, leading to a slightly larger interlayer distance. We conducted a Williamson-Hall (W-H) analysis to quantify the microstrain in our samples (Figure S10), revealing that strain levels are lower in pure halide samples but increase in mixed-halide compositions due to lattice distortions caused by the ionic radii mismatch between iodide and bromide⁴⁰. It is worth mentioning that no phase separation is seen over the whole composition range from (R)-3BrMBA₂PbBr₄ to (R)-3BrMBA₂PbI₄, since this would lead to the emergence of broad or multiple diffraction peaks within the intermediate composition range (Figure S9). Figure 4b shows the absorption and PL spectra of films with different halide compositions. All films show an excitonic absorption peak which is gradually blue shifted with increasing bromide ratio, indicating band gap opening, in agreement with calculated band structures from DFT (Figure S3). Additionally, the sharp PL for the iodide sample starts gradually broadening as we increase the bromide ratio. For the pure bromide sample, the sharp free exciton peak nearly disappears, and the PL spectrum is characterized by a weak white-light emission that is indicative of STEs, as discussed above.

To quantify chirality independent of film thickness or optical path length, we calculate the g-factor which is $g_{CD} = \frac{CD_{intrinsic}}{32980^{\times}Exctinction}$ (Figure 4c). The original CD spectra for the mixed-halide samples are provided in the SI (Figure S9). As the bromine concentration increases in the mixed-halide samples, the g_{CD} spectra exhibit spectral blue shifts, consistent with trends observed in both absorption and PL measurements. Figure 4d quantitatively illustrates the relationship between maximum CD intensity (blue), absolute g-factor (red), and microstrain (black) as a function of halide composition in (R)- 3BrMBA₂PbI_{4(1-x)}Br_{4x} films, highlighting the impact of halide-induced

structural distortions on chiroptical properties. The microstrain remains relatively low in the pure halide compositions (x = 0 and x = 1) but reaches its maximum at x \approx 0.5, reflecting significant lattice distortions from the bromide-iodide size mismatch. Interestingly, the variations in microstrain closely align with trends observed in the g_{CD} intensity and g-factor. The g_{CD} intensity follows a non-monotonic trend, decreasing gradually with increasing bromide content and reaching its minimum at x \approx 0.7 before recovering at x = 1. A similar trend is observed for the CD. The suppression of g_{CD} intensity in mixed-halide compositions suggests that microstrain disrupts chirality transfer from the chiral organic spacer to the perovskite framework by creating an inhomogeneous hydrogen bonding environment between the organic moieties and halogens, thereby weakening chiral induction⁴⁰. While the microstrain peaks at x \approx 0.5, the continued decrease in g_{CD} intensity up to x \approx 0.7 suggests that additional factors, such as structural distortions beyond strain, further impact the chiroptical response.

Despite the reduction in g_{CD} intensity at intermediate compositions, a comparison between the pure iodide (x = 0) and pure bromide (x = 1) compositions reveals that the maximum absolute value of g_{CD} increases from 3.69×10^{-4} for (R)-3BrMBA₂PbI₄ to -4.16×10^{-4} for (R)-3BrMBA₂PbBr₄, marking a 12% enhancement. This suggests that bromide incorporation results in a slightly more efficient chirality transfer, possibly due to stronger hydrogen bonding interactions. Overall, we find that manipulation of the optical band gap is possible through the adjustment of bromide-iodide ratios, resulting in color-tunable CD signals. This flexibility in CD properties allows our chiral materials to selectively interact with circularly polarized light across a wide wavelength range, making them suitable materials for circularly polarized detectors^{41,42}.



Figure 4. Structural characteristics and optical properties of mixed-halide chiral hybrid perovskites. (a) X-ray diffraction patterns, (b) Room-temperature absorption (solid lines) and PL (dotted lines), (c) g_{CD} spectra of spin-coated , and (d) Correlation among the absolute value of |CD|, $|g_{CD}|$, and |microstrain| intensity of spin-coated (R)-3BrMBA₂PbI_{4(1-x)} Br_{4x} thin films (x = 0 to 1) as a function of the halide ratio. Changing the ratios between bromide and iodide results in shifts of absorption bands, PL, and CD signals of (R)-3BrMBA₂PbI_{4(1-x)} Br_{4x} films (* indicates the excitonic position).

To explore and compare the charge carrier dynamics of (R)-3BrMBA₂PbI_{4(1-x)}Br_{4x} (x = 0, 1), we used TA spectroscopy. We record TA spectral maps and kinetics for thin films under excitation with pulse energy of 21 μ J/cm² at 300 nm. The TA traces show that the injected hot carriers cool down to the band edge positions, producing noticeable photo-bleaching (PB) peaks marked with positive values centered at 387 and 487 nm for (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄, respectively. These PB signals are accompanied by two photo-induced absorption (PIA) signals on either side (Figure 5a, b, and Figure S11). We extracted the decay kinetics in the PB regions for both samples and plotted them in Figure 5c for comparison. A triexponential decay function was utilized to calculate decay lifetimes (see Table S6 for detailed fit results). We find that (R)-3BrMBA₂PbBr₄ exhibits a longer TA decay than (R)-3BrMBA₂PbI₄.

Additionally, TCSPC was used to examine the PL decay in both (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ films at their FE positions (excitation at 350 nm, ~0.5 μ J/cm²). Since the time resolution of the TCSPC measurement is of the order of 50 ps, it is not sensitive to the ultrafast recombination dynamics observed in TA. PL decay profiles for (R)-3BrMBA₂PbBr₄ indicate a noticeably slower decay compared to (R)-3BrMBA₂PbI₄. To explain the slower PL decay in (R)-3BrMBA₂PbBr₄, we compare the PL decay profile at FE (396 nm) and STE (550 nm) in this sample, as shown in Figure S12. The PL decay curve of FEs reveals that 30% of the population decays rapidly which is attributed to the direct decay from the FE states, while the remaining exhibit a lifetime nearly identical to the PL lifetime of STEs. This suggests that there is some contribution from STEs during the PL decay measurements of FEs.



Figure 5. Photoexcited charge carrier dynamics of hybrid chiral perovskite thin films. (a) Linearly polarized TA map of (R)-3BrMBA₂PbBr₄, (b) time-resolved differential transmission spectra of (R)-3BrMBA₂PbBr₄, (c) recombination kinetics collected in the PB regions, and (d) TCSPC kinetics of (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ thin films obtained at their free exciton wavelengths, respectively. TA and TCSPC measurement are done upon linear excitation at 300 nm (21μ J/cm²) and 350 nm (0.5μ J/cm²), respectively.

Next, we investigated the spin dynamics of photoexcited charge carriers in polycrystalline (R)-3BrMBA₂PbI₄ and (R)-3BrMBA₂PbBr₄ films using pump/probe transient Faraday rotation (FR) pump-probe spectroscopy. Circularly polarized laser pump pulses (345 nm for (R)-3BrMBA₂PbBr₄ and 430 nm for (R)-3BrMBA₂PbI₄, 300 fs duration, 4.5 μ J/cm²) were employed to excite the systems, while linearly polarized probe pulses (410 nm for (R)-3BrMBA₂PbBr₄ and 515 nm for (R)-3BrMBA₂PbI₄,) below the material bandgap were used to studying the FR signal. As shown in Figure 6, we analyzed the kinetics of the normalized transient Faraday angle to investigate how halide substitution in the octahedral framework of 2D chiral perovskites affects spin lifetime. Notably, replacing iodide with bromide resulted in a significant enhancement of spin lifetime,

increasing from 4.8 ps in (R)-3BrMBA₂PbI₄ to 36 ps in (R)-3BrMBA₂PbBr₄ at room temperature (Figure 6a, Table S8). Both R- and S-enantiomers of the studied materials exhibited indistinguishable spin decay kinetics, indicating no enantiomer-dependent variation in spin relaxation behavior (Figure 6c, d). The observed spin lifetime for the bromide variant is substantially longer than previously reported values in polycrystalline perovskite thin films at room temperature. Given that spin scattering from impurities, defects, and grain boundaries typically reduces spin lifetime, prior studies have reported significantly shorter values for polycrystalline hybrid perovskites, such as 0.24 ps for achiral 2D perovskite of PEPI, 3.1 ps for (BA)₂(MA)₃Pb4I₁₃, and ~4 ps for MAPbI₃ perovskites^{43,44}. Furthermore, FR measurements of our samples at 12 K revealed an even greater enhancement for the Br-based perovskite, with spin lifetime extending to 223 ps, whereas the iodide counterpart exhibited only a twofold increase, reaching 9.5 ps (Figure 6b). This substantial difference underscores bromide-based systems as very promising materials for exploiting spin dynamics in chiral perovskites.



Figure 6. Spin dynamics of hybrid chiral perovskite thin films. Comparison of spin dynamics in (R)-3BrMBA₂PbBr₄ and (R)-3BrMBA₂PbI₄ thin films (a) at room temperature and (b) at 12 K. Room temperature spin dynamics of enantiomers of (c) (R/ S)-3BrMBA₂PbBr₄, and (d) (R/ S)-3BrMBA₂PbI₄ thin films. Circularly polarized pump pulses (345 nm for (R/ S)-3BrMBA₂PbBr₄ and 430 nm for (R/ S)-3BrMBA₂PbI₄, 4.5 μ J/cm²) were used for excitation, with linearly polarized probe pulses (410 nm and 515 nm, respectively) below the bandgap probing the FR signals.

In summary, we analyzed and compared the structural, optical, and carrier dynamics properties in 2D chiral perovskites of (R)-3BrMBA₂PbI_{4(1-x)} Br_{4x} under varying halide anions. Through engineering the bandgap by mixing different ratios of halides, we control the wavelength at which the CD signal occurs. Remarkably, we noticed a reversal in CD polarity upon complete replacement

of iodide with bromide, indicating a complex origin of the optical activity in these materials. We attributed this change to the alteration of the electronic environment caused by halide substitution, which affects the angular momentum coupling in the system, rather than the LDLB contribution. Additionally, we observed a negative correlation between the microstrain induced in the lattice—arising from halide mixing—and the CD intensity, which is attributed to nonuniform coupling between the chiral ligand and the inorganic octahedra. The study of spin dynamics in our chiral systems reveals surprisingly long spin lifetimes, particularly in the Br-based compounds, highlighting their strong potential as candidates for spintronic applications.

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The Supporting Information is available free of charge at:

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