Chiral 2D Organic Inorganic Hybrid Perovskite with Circular Dichroism Tunable Over Wide Wavelength Range

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ABSTRACT: The effect of chemical-composition modification on the chiroptical property of chiral organic ammonium cation-containing organic inorganic hybrid perovskite (chiral OIHP) is investigated. Varying the mixing ratio of bromide and iodide anions in S- or R-C6H5CH2(CH3)NH3PbI4-xBrx modifies the band gap of chiral OIHP, leading to a shift of the circular dichroism (CD) signal from 495 to 474 nm. However, it is also found that an abrupt crystalline structure transition occurs, and the CD signal is turned off when iodide-determinant phases are transformed into the bromide-determinant phase. To obtain CD in the wavelength range where the bromide-determinant phase is supposed to exhibit chiroptical activity, that is, 2474 nm, S- or R-C12H7CH2(CH3)NH3 with a larger spacer group can be adopted; thus, the CD signal can be further blue-shifted to 375 nm. Here, we show that chemical-composition modification of chiral OIHP affects the chiroptical properties of chiral OIHP in two ways: (1) tuning the wavelength of CD by modulating the excitonic band structure and (2) switching the CD on and off by inducing a crystalline-structure change. These properties can be utilized for structural engineering of high-performance chiroptical materials for spin-polarized light-emitting devices and polarization-based optoelectronics.

INTRODUCTION

Since organic inorganic hybrid perovskites (OIHPs) were rediscovered as efficient light absorbers,1 they have attracted considerable research attention, leading to impressive improvements in the quantum efficiency of solar cells.2–4 In addition to photovoltaics, other diverse technological possibilities of OIHPs have been investigated, and significant progress has been made in various applications, such as photodetectors,5 light-emitting devices,6,7 spintronic devices,8 memories,9 and X-ray scintillators.10,11 In 2017, our group reported another considerable research attention, leading to impressive improvements in the quantum efficiency of solar cells.2–4 In addition to photovoltaics, other diverse technological possibilities of OIHPs have been investigated, and significant progress has been made in various applications, such as photodetectors,5 light-emitting devices,6,7 spintronic devices,8 memories,9 and X-ray scintillators.10,11 In 2017, our group reported another intriguing application of OIHPs, in which a chiral organic ammonium cation was incorporated into the perovskite lattice.12 The resulting chiral OIHPs showed chiral crystalline phases3,14 and exhibited circular dichroism (CD) corresponding to markedly different absorption of left- and right-handed circularly polarized light (i.e., σ+ and σ−, respectively). Our results triggered additional research on chiral OIHPs whose chirality can be acquired from constituent organic ligands.18 Several research groups subsequently confirmed the chiroptical properties of OIHPs materials.19–21 For example, in a study performed by Long et al., Ruddlesden–Popper-type chiral OIHPs exhibited a circular polarization degree of approximately 3% without an external magnetic field.20 Recently, Ma et al. demonstrated a circular polarization degree of approximately 17% at 77 K in which the chiral OIHPs exhibited circularly polarized photoluminescence (CPL) around 510 nm.22 In other words, enantiomeric chiral OIHPs can radiate light with aligned photon spin. Such a discovery opens up the possibility to develop solution-processable spin-polarized light-emitting diode (spin-LEDs) and other spintronic devices. The strong chiroptical activity of chiral OIHPs is believed to originate from the modulation of the excitonic band structure of the lead halide perovskite framework by chiral ligands.21 This hypothesis is based on the fact that main CD signals appear at the excitonic absorption band, which leads us to question whether the photon energies where chiroptical phenomena (e.g., CD and CPL) occur shift depending on whether the band gap narrows or widens. In this study, we investigated the tunability of the CD signal location via chemical-composition modification in a chiral OIHP to tune the band gap.23–26 Mixing halide anions and precisely controlling the relative amount thereof allowed gradual tuning of the band gap.27 According to previous findings, chiral OIHPs whose halide ions are solely composed of iodide exhibit an absorption edge around 533 nm and corresponding CPL around 510 nm.22 However, to develop polarization-based optoelectronic devices, the wavelength tunability of the chiroptical phenomenon is needed. Replacing iodide with...
bromide is expected to modulate the wavelength where CD peaks appear.

■ EXPERIMENTAL DETAILS

Synthesis of Chiral Organic Ammonium Halide Salts. 1.2 mmol of organic amine (R-MBA (>98%; Sigma-Aldrich, St. Louis, MO), S-MBA (>98%; Sigma-Aldrich), R-NEA (>98%; TCI Chemicals, Tokyo, Japan) or S-NEA (>98%; TCI Chemicals)), and 1.3 mmol of hydrochloric acid in the form of an aqueous solution [hydrochloric acid (48 wt %; Sigma-Aldrich) or hydroiodic acid (57 wt % stabilized with 1.5% hypophosphorous acid; Alfa Aesar, Ward Hill, MA)] were added to 0.5 mL of absolute ethanol (Merck, Darmstadt, Germany). After vigorous stirring for 30 min, the solution was fully evaporated at 120 °C under vacuum to obtain solid precipitates.

Fabrication of Chiral Perovskite Films. To fabricate films, the synthesized chiral organic ammonium cations were dissolved in DMF along with PbI₂ (99.999%; Sigma-Aldrich) or PbBr₂ (99.999%; Sigma-Aldrich) at designated ratios to satisfy the chemical formulas of (R- or S-MBA)₂PbI₄₋ₓBrₓ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0) and (S- or R-NEA)₂PbI₄₋ₓBrₓ (x = 0, 0.3, 0.5, 0.7, 1.0). Here, the mole ratio between the chiral organic ammonium cations and the total amount of lead cations from PbI₂ and PbBr₂ was 2:1. Additionally, dimethyl sulfoxide (DMSO; >99.5%; Sigma-Aldrich) was added to the solutions, such that the ratio of DMSO to the lead cations would be 1:1. Then, DMF was added to the solutions to make the total concentration of solids precursors in the solutions to be 20 wt %.

The resulting solutions were spin-coated onto a glass substrate at 2000 rpm for 30 s. The solution-coated substrate was then annealed on a hot plate at 65 °C for 15 min. After the thermal treatment, the solution-coated substrates were allowed to dry in air, and the spectra were obtained at a scan rate of 100 nm/min, with a data pitch of 1 nm.

Characterizations. An XRD analysis of the chiral OIHP films was performed using SmartLab (Rigaku) with a Cu Kα radiation source (0.154 06 nm). CD data analysis was performed using a CD spectrometer (J-815, JASCO, Easton, MD). The background was subtracted from the CD spectrum before calculating the Cotton effect (CD). CD data and extinction data were collected using a ChiralRaman spectrometer (BioTools Inc.) with a 532 nm wavelength laser having a power of 0.5 mW.

■ RESULTS AND DISCUSSION

To obtain chiral perovskite with varying halide compositions, enantiomers of α-methylbenzylamine (i.e., S-MBA and R-MBA) were reacted with either HBr or HI to obtain the corresponding ammonium halide salts (i.e., S-MBA-HBr, S-MBA-HI, R-MBA-HBr, and R-MBA-HI). Because the extinction and CD spectra were measured for thin films, 20 wt % dimethylformamide (DMF) solutions containing the chiral organic ammonium halide salts and lead halides (PbBr₂ and PbI₂) were prepared, followed by spin-coating on a glass substrate. DMSO was also added into the precursor solution to enhance crystallinity, but it was revealed by thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FT-IR) that residual DMSO is hardly found in resultant films (Figure S2). By controlling the relative amounts of ammonium halide salts and lead halides, we obtained chiral OIHP films with various halide anion compositions, which were denoted as (S-MBA)₂PbI₄₋ₓBrₓ and (R-MBA)₂PbI₄₋ₓBrₓ (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5).

Figure 1 shows the normalized extinction and CD spectra of (S-MBA)₂PbI₄₋ₓBrₓ and (R-MBA)₂PbI₄₋ₓBrₓ films.
the compositions of x = 0.4 and 0.5, where the weak signal intensity made the identification of the blue-shift ambiguous. As a longer light travel path would allow the differentiation of the CD signal, we prepared thicker films from the concentrated precursor solutions (i.e., 40 wt %) for the cases of x = 0.4 and 0.5 to clarify the CD signal. Although the film with the composition of x = 0.5 still exhibited an unclear bisignate CD signal, the films with x = 0.4 exhibited a bisignate CD signal, clearly indicating a blue-shift compared with the case of x = 0.3 (Figure S4, Supporting Information). Despite the unexpectedly weak signals for the film compositions of x = 0.4 and 0.5 (which are discussed below), the series of CD and normalized extinction data supported the notion that the wavelength shift of the CD signal corresponded to the variation of the extinction peaks, as shown in Figure 1a. This observation implies that the band-gap-widening successfully induced a change in the excitonic band structure without excitonic trap state formation below the optical band gap, which was directly correlated with the wavelength change of the CD signals. Although the extinction peaks from (S-MBA)2PbI4−xBrx and (R-MBA)2PbI4−xBrx for x = 0.4 and 0.5 were blue-shifted as expected, the CD signals were abruptly unobservable, in contrast to our expectations. Further inspection of the chiral OIHs films enabled us to understand that this phenomenon was closely related to the phase transition in the crystalline structure. X-ray diffraction (XRD) patterns for the (S-MBA)2Pbi4−xBrx and (R-MBA)2Pbi4−xBrx films are shown in Figure 2a. The peaks at the smallest 2θ angle, representing the interlayer spacing of lead halide layers, did not significantly shift, remaining at ~6.2° for the films in the compositional range of x = 0–0.3 (blue region). In contrast, when the bromide fraction was further increased from x = 0.3 to 0.4, these peaks shifted to 5.7°, and their positions were maintained even when x increased to 1.0 (red region). The halide composition range where significant CD spectra changes occurred coincided with the compositional dependence of the XRD peak shift. Such a coincidence can be visualized by plotting the 2θ values for the smallest-angle peaks with respect to the number of iodine in the chemical formula of OIHs (Figure 2b,c), as well as by a g-factor plot. The g-factor represents the chiral optical asymmetry of the designed OIHs. The local maximum values around the extinction wavelength in g-factor vs full-range wavelength are shown in Figure S5 (Supporting Information). Figure 2b,c clearly reveals abrupt changes in both 2θ and the g-factor when the number of iodine in chemical formula decreased from 3 to 2. These plots indicate that the appearance of the chiroptical property of the chiral OIHs can be ascribed to the phase transition of the crystalline structure due to the modulation of the halide anion mixing ratio.

In a previous study, Yangui et al. investigated the halide anion composition-dependent crystalline-structure change of a 2D layered OIHs, and their findings provide useful information for understanding our results.30 Starting from (C6H11NH3)2PbBr4, when over half of the bromide anions were replaced by iodide ions, dramatic transitions in several crystal structural parameters were observed, and Vegard’s law was not followed. The selective nonrandom distribution of bromide and iodide anions was the fundamental reason for this phenomenon. Because of the ionic-radius difference, iodide is preferentially located in the apical position. The replacement of anions in the apical position alters the hydrogen-bonding force acting between the lead halide octahedral layer and organic ammonium cations.31 This alternation in the hydrogen bonding changes the orientation of organics and causes a tilt in the lead-halide bonding. Thus, when the mixing ratio of halide ions in the apical position exceeds a critical value, the crystalline structure changes dramatically from a (C6H11NH3)2PbBr4-like structure to a (C6H11NH3)2PbI4-like structure.31 As (C6H11NH3)2PbBr4 and (C6H11NH3)2PbI4 are
MBA)\textsubscript{2}PbBr\textsubscript{4} is not elucidated here because such a crystallographic activity. As shown in Figure 4a,b, the characteristic bands at ROA of chiral OIHPs can originate from the chiral space group.\textsuperscript{12} For example, \((\text{S-MBA})_2\text{PbBr}_4\) and \((\text{R-MBA})_2\text{PbI}_4\) are considered to be chiroptical, as they belong to the \(P2_12_12_1\) chiral space group. Although the exact space group of \((\text{S-MBA})_2\text{PbBr}_4\) and \((\text{R-MBA})_2\text{PbI}_4\) is not elucidated here because such a crystallographic analysis is beyond the scope of this communication, it can be assumed that \((\text{S-MBA})_2\text{PbBr}_4\) and \((\text{R-MBA})_2\text{PbI}_4\) did not possess a chiral space group, because they lack the chiroptical property. It is thus reasonable to assume that a sudden transition to the bromide-determinant phase having a nonchiral space group was responsible for the disappearance of the CD signals.

To further elucidate the origin of the chiroptical activity of \((\text{MBA})_2\text{PbI}_4\) and the sudden disappearance of the CD signals upon the bromide-rich phase, the Raman optical activity (ROA) of \((\text{MBA})_2\text{PbI}_4\) and \((\text{MBA})_2\text{PbBr}_4\) was examined (Figure 4). As for other chiral nanostructures,\textsuperscript{32} examining the ROA of chiral OIHPs can confirm the origin of the chiroptical activity. As shown in Figure 4a,b, the characteristic bands at 1430, 1490, and 1520 cm\(^{-1}\) observed for both samples are associated with Raman-active vibration modes of NH\(_3\).

However, only \((\text{MBA})_2\text{PbI}_4\) exhibited ROA peaks of opposite polarity at 1520 cm\(^{-1}\) for carrying opposite organic enantiomers, which corresponds to the asymmetric deformation vibration mode of NH\(_3\) (blue region, Figure 4b).\textsuperscript{33} These results confirm that the replacement of the anions of the OIHPs changed the orientation of organic ammonium cations, thus changing the structural chirality, further confirming our hypothesis of the relation between the crystallographic structure and chiroptical activity.

To broaden the wavelength tunability of the chiroptical phenomenon in the wavelength region below 474 nm, it is necessary to employ spacer materials capable of exhibiting CD signals even in bromide-determinant phases. In the case of 2D layered OIHPs, increasing the spacer size of the organic ammonium cation can lead to a blue-shift of the absorption.\textsuperscript{34} We adopted this strategy to introduce \((\text{S})-1-(2\text{-naphthyl})\text{ethylamine (denoted as S- and R-NEA, respectively possessing a naphthyl group significantly larger than the phenyl group in S- and R-MBA (Figure 5a). In addition to S- and R-NEA, it is expected that the band gap can be further broadened if bromide mixing is accomplished, similar to the cases of S- and R-MBA. Accordingly, we synthesized S-NEA-HBr, S-NEA-HI, R-NEA-HBr, and R-NEA-HI. These precursors were dissolved in DMF, along with either PbBr or PbI at the designated ratios, and the resulting solutions were spin-coated onto glass to obtain \((\text{S-NEA})_2\text{PbBr}_{4(1-y)}\text{Br}_y\) and \((\text{R-NEA})_2\text{PbBr}_{4(1-y)}\text{Br}_y\) films \((y = 0, 0.3, 0.5, 0.7,\) and 1.0).

Figure 5b shows the normalized extinction spectra of the \((\text{S-NEA})_2\text{PbBr}_{4(1-y)}\text{Br}_y\) and \((\text{R-NEA})_2\text{PbBr}_{4(1-y)}\text{Br}_y\) films. Although the extinction peaks of the films composed of pure iodine \((y = 0)\) were broadened without peak sharpness compared with the others, the peaks were located in a shorter-wavelength region compared with those of \((\text{S-MBA})_2\text{PbI}_4\) and \((\text{R-MBA})_2\text{PbI}_4\) (Figure 1b). Moreover, when the ratio of bromide anions increased, the peak shifted further toward the shorter-wavelength region. Notably, \((\text{S-NEA})_2\text{PbBr}_4\) and \((\text{R-NEA})_2\text{PbBr}_4\) exhibited extinction peaks at approximately 382 nm. In the corresponding CD spectra (Figure 5c), the \((\text{S-NEA})_2\text{PbI}_4\) and \((\text{R-NEA})_2\text{PbI}_4\) films \((\text{i.e., } y = 0)\) did not exhibit a strong bisignate CD signal, but when bromide ions replaced iodide ions over \(y = 0.3\), the CD signals became strong and distinctive. As indicated by the XRD patterns of the \((\text{S-NEA})_2\text{PbBr}_{4(1-y)}\text{Br}_y\) and \((\text{R-NEA})_2\text{PbBr}_{4(1-y)}\text{Br}_y\) films (Figure 6), the main peak for the films with \(y = 0\) was located in a different region (blue region) from those for the films with other compositions (red region). Therefore, the transition from the iodide-determinant phase to the bromide-determinant phase occurred between \(y = 0\) and 0.3 when the large naphthyl group was involved, and the iodide-determinant phase exhibited weaker chiroptical properties than the bromide-determinant phase. Above \(y = 0.3\), the CD signals

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Figure 3. Schematic illustration of phase transition while Br ratio increases.

Figure 4. Normalized Raman (top) and ROA backscattering spectra (bottom) with 532 nm excitation of (a) \((\text{R-}\text{S-MBA})_2\text{PbBr}_4\) and (b) \((\text{R-}\text{S-MBA})_2\text{PbI}_4\).
...organic cation and the mixing of halide ions allow effective wide-range tuning of both the band gap and CD signal of the chiral OIHP.

It can be noted that phase transition occurred in lower bromide ratio when it is compared to (S-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$ and (R-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$. As mentioned above, increasing bromide ratio leads to enlargement of interlayer spacing between octahedral layers, and the reason is increased structural instability. It is believed that the bulkier space group of NEA makes (S-NEA)$_{2}$PbI$_{4-x}$Br$_{x}$ and (R-NEA)$_{2}$PbI$_{4-x}$Br$_{x}$ more sensitive to the structural instability. Consequently, in lower bromide ratio, (S, R-NEA)$_{2}$PbI$_{4-x}$Br$_{x}$ can readily initiate the structural change.

Furthermore, more intensive CD signals were observed in NEA perovskite compared to MBA perovskites. The intensity of the CD signal from (S-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$ and (R-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$ was under 40 mdeg, but (S-NEA)$_{2}$PbI$_{4-x}$Br$_{x}$ and (R-NEA)$_{2}$PbI$_{4-x}$Br$_{x}$ can show CD over 60 mdeg when they are composed of chirally active composition. This difference can be explained in terms of high magnetic transition dipole moment of NEA perovskites (see the Supporting Information for a detailed discussion).

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**CONCLUSION**

In conclusion, the spectral position of the CD peaks of chiral OIHPs was tuned by modulating the band gap of the chiral perovskites by controlling the ratio of bromide anions to iodide anions. For (S-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$ and (R-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$ the CD signals were shifted from 495 to 474 nm when $x$ was increased from 0 to 0.3. Additionally, the dramatic crystalline phase change occurring during the halide anion composition change led to the disappearance of CD signals; thus, the CD peaks became weak below 474 nm, e.g., for (S-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$ and (R-MBA)$_{2}$PbI$_{4-x}$Br$_{x}$. To solve this problem, S- and R-MBA were replaced with S- and R-NEA, respectively. This increased the band gap, owing to the larger spacer group, and made it possible to further increase the bromide anion ratio, as the bromide-determinant phases of S- and R-NEA-incorporated OIHPs exhibited higher-intensity CD signals. Thus, the CD signal can be blue-shifted to 375 nm. This tunable chiroptical activity of the chiral OIHP will contribute to the realization of color-tunable CPL-emitting OIHPs. This can eventually lead to full-color spin-LEDs that can overcome the brightness-loss problem of conventional LEDs due to the antiglare filter, hopefully increasing the energy efficiency of LEDs.

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b11453. Photograph, XRD spectra, TGA analysis, FT-IR spectroscopy data, origin of asymmetric CD signal, $g$-factor plot, explanation on CD intensity difference, and stability of chiral perovskite films (PDF)

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Notes

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