Chirality Induced Crystal Structural Difference in Metal Halide Composites

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Incorporating chiral organic compounds into metal halide frames is a common and useful method to introduce chirality in metal halide composites. The structures of resulting racemic and chiral composites are usually considered to be nearly identical owing to similar chemical bonding. In this work, by incorporating chiral MBABr (bromide methylbenzylamine) into an inorganic frame, a significant crystallization difference between the resulting racemic and chiral metal halide composites is observed, as confirmed by both structural and spectroscopic measurements. In addition, the structural transformation in the chiral composites can also be induced by moisture, ascribed to the asymmetric hydrogen bonding in chiral materials. These results provide new insights for the future synthesis of chiral materials and open up new possibilities to advance the materials functionalities.

1. Introduction

Chirality of the materials is usually in the form of chiral molecules with a non-superposable mirror image as enantiomers, which share the same molecular weight, similar structures, and physical properties. Chiral molecules have shown great success in life science, material science, spintronics, and optoelectronic devices.[1-4] Recently, the combination of chiral organic compounds and the metal halide frameworks have attracted increasing research interest, mainly for the following two reasons: 1). It can enable the chirality in new metal halide composites, largely enriching the chiral material family. For instance, the first introduction of left hand-/right hand- methylbenzylamine (R-/S-MBA) in between lead-iodide octahedral layers has been proven success in achieving chiral organic–inorganic hybrid perovskites (HOIPs) with noticeable circular dichroism (CD) in 2017.[7] (2). The optical difference was ascribed to the distortion of weak interactions existing in the perovskite crystal structure such as the hydrogen bonding and van der Waals force.[8]

In conventional cases, the incorporation of (S- or R-) chiral organic ligands will not affect the resulting metal halide composite structure as compared with the incorporation of racemic (mixed equal ratio of S- and R-) organic ligands because of indistinguishable composition, similar chemical bonding and similar tethering group packing characteristics between enantiomers of chiral materials. This is widely demonstrated by near-identical X-ray diffraction (XRD) patterns and photoluminescence (PL) spectra observed for chiral and racemic materials.[9-15] However, Zhao and his co-workers observed different photoluminescent behaviors between chiral and racemic metal halide perovskites. The optical difference was ascribed to the distinction of weak interactions existing in the perovskite crystal structure such as the hydrogen bonding and van der Waals force.[16]

Moreover, recent experimental results by Mitzi and co-workers also demonstrated that the asymmetric hydrogen bonding in the chiral organic ligand (1-(1-naphthyl) ethylammonium) can induce more distorted PbBr$_6$ octahedra than the racemic one (without asymmetric hydrogen bonding), resulting in a difference in the corresponding perovskite XRD patterns.[8,7] These findings point out a new possibility that incorporating chiral ligands in metal halide composites can change the resulting structure, an effect though not been demonstrated previously.

In the present work, by introducing MBA (methylbenzylamine) into manganous bromide frameworks, we discover a significant difference in the crystal structure between chiral and racemic metal halide composites. The XRD patterns indicate that the crystal structure is switched from octahedron of one-dimensional (chain-like) in racemic composites to tetrahedron of one-dimensional (chain-like) in chiral composites. Consistently, significantly different PL results are also observed in these composites. Specifically, the chiral composites exhibit bright green emissions while the racemic composite shows bright red emissions in low-humidity conditions. In addition, the green emission in chiral composite turns red with increasing humidity, suggesting the moisture induced crystal structure transformation. In contrast, the racemic composite shows no moisture response. The different moisture response might result from the difference in hydrogen bonding in these

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adom.202102140.

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DOI: 10.1002/adom.202102140
materials. Our findings reveal chirality induced significant crystal structure difference in lead-free metal halide composites for the first time, providing new possibilities to further enrich chiral materials functionalities.

2. Results and Discussion

We first compare the powder XRD patterns of all the precursors (RAC-MBABr (racemic methylbenzylamine bromide), S-MBABr, R-MBABr, and MnBr₂ (manganese (II) bromide)) in Figure 1a. The corresponding composites crystal structures are also studied through XRD and absorption characterizations. It should be pointed out that the racemic-MBABr exhibits quite different XRD patterns as compared with S- and R-MBABr. The feature peak for RAC-MBABr locates at 9.8° while the feature peak for S-/R-MBABr turns to 10.5°. This significant difference of XRD patterns in MBABr suggests that the intermolecular bonding between chiral and racemic ones are different, providing the precondition to induce a structural difference in the resulting composites. To exclude the possibility of impurities in the S-/R- and RAC-MBABr that causes the XRD difference, the RAC-MBABr is intentionally replaced by mixing the S- and R-MBABr in equal weight (marked as (S+R)-MBA in Figure 1a). It shows nearly identical XRD patterns as compared with the RAC-MBABr, further confirming that the XRD pattern difference originates from the bonding difference between chiral and racemic precursors, rather than impurities.

With the information on precursors, we now look at the corresponding composites structures fabricated with C- and RAC-MBABr. We synthesized single crystals of all three corresponding metal halide composites, as shown in Figure S1, Supporting Information. For simplicity, we name the composites as (S-/R–) Chiral-composite and RAC-composite. The resulting RAC-composites show feature peaks at 5.7° and 6.8° (Figure 1a) in the powder XRD patterns. As determined by single-crystal X-ray diffraction (SCXRD), RAC-composites show a chemical formula of (rac-MBA)[Mn₂Br₅(EtOH)], which possesses a one-dimensional (chain-like) structure with double-layered octahedrons aligned along one direction (Figure 1b) and is also consistent with energy dispersive X-ray spectroscopy (EDS) measurements (Figure S2c, Supporting Information). Specifically, the crystal structure consists of the monoclinic phase and P2₁/c space group, with the lattice parameters of a = 36.2594(17) Å, b = 7.7718(4) Å, and c = 20.8628(10) Å. Two Mn²⁺ ions and four Br⁻ ions form a cuboidal sublattice with a Mn–Br bond distance varying from 2.637(7) Å to 2.819(6) Å; we observe no changes in the oxidation state of manganese. In every two adjacent Mn²⁺ ions, one coordinates with one ethanol molecule with the bond distance of Mn–O 2– = 2.094 Å.

Figure 1. X-ray diffraction (XRD) patterns and composite crystal structures. a) XRD patterns of the precursors (including S-/R-/RAC-/S+R- MBABr and MnBr₂) and respective chiral and racemic composite crystals. b) and c) Crystalline structures of RAC- and (S-/R) Chiral-composites obtained by single-crystal X-ray diffraction data: (b) for RAC-composite with chemical formula of (rac-MBA)[Mn₂Br₅(EtOH)] and c) for (S-/R) Chiral-composite with chemical formula of (R-/S-MBA)₂[MnBr₄]. d) XRD patterns of R-composite, S-composite, RAC-composite, and (S+R)-composite films.
and five Br⁻ ions while the other one possesses six coordination with Br⁻ ions; they together form a one-dimensional (chain-like) continuous cuboidal unit. The angles between two adjacent Br⁻ and Mn²⁺ (Br–Mn–Br) range from 84.15° to 95.57°, and the O-Mn-Br angles range from 83.82° (5) to 97.36° (6), which are within the normal values. In contrast, the S- and R- composites exhibit quite different XRD patterns (Figure 1a), with the feature peaks shifting to 74° and 8.9°. We find that (S–/R–) Chiral-composite (with chemical formula of (R-/S-MBA)₆[MnBr₆] as determined by SCXRD which is consistent with EDS in Figure S2a, Supporting Information) has a zero-dimensional (molecular) crystal structure with tetrahedrons (Figure 1c) and consists of the orthorhombic phase and P2₁2₁2₁ space group, with the lattice parameters of a = 8.0609(5) Å, b = 14.7580(9) Å, and c = 19.2473(12) Å. The isolated tetrahedral [MnX₄]²⁻ is surrounded by large MBA organic molecules. This unique structure enables zero-dimensional (molecular) Mn-based composites to possess a long Mn-Mn distance. The angles between two adjacent Br⁻ and Mn²⁺ (Br–Mn–Br) range from 101.30° to 113.99°. The bond distances between two Br⁻ and Mn²⁺ vary from 2.476(3) Å to 2.549(2) Å, also within the normal reported values. Compared with composites fabricated with RAC-MBABr, C-MBABr induces significantly different crystal structures, which is possibly attributed to the asymmetric hydrogen-bonding interactions. In addition, the measured XRD patterns with corresponding (S–/R–) Chiral- and RAC-composites match well with the simulated results (in Figure S3, Supporting Information).

The thermogravimetric (TG) and derivative thermogravimetric (DTG) results (Figure S4, Supporting Information) further confirm different structures of (S–/R–) Chiral- and RAC-composites. The (S–/R–) Chiral-composites (both S- and R- composite) start to lose weight at 70 °C and ends at 300 °C with a total weight loss of 50%. In contrast, the RAC-composite starts to lose weight at 60 °C and ends at 321 °C with a weight loss of 45%.

We can readily prepare (S–/R–) Chiral-composite and RAC-composite thin films, by dissolving the respective single crystals in ethanol and dropping casting the solutions on glass substrates, followed by annealing at 70 °C. As indicated in Figure 1d, composite thin films show slightly shifted XRD feature peaks as compared with single-crystal samples. Here, the shift towards lower angles for our fabricated thin films is possibly attributed to the influence of ambient moisture.

The overall matched XRD feature peaks of composite thin films indicate that the solution processing method does not affect the crystallization and crystal structure. We further measure the circular dichroism (CD) spectra (Figure S5a, Supporting Information) of the resulting composite films. The distinct CD signals from 240 to 275 nm are observed for (S–/R–) Chiral-composite, indicating the chirality of our composite films fabricated with C-MBA. The peaks in the CD spectra of S- and R- composite exhibit opposite signs, which corresponds to S- and R-polarization. In contrast, RAC-composite exhibits a flat signal, showing no chirality. The absorption spectra are also shown in Figure S5b, Supporting Information to confirm that the chiral absorption region locates within the optical transition of our composites. Our experiments confirm that chirality is incorporated into our composite samples successfully. This result, coupled with different crystal structures of C- and RAC-composites, implies that the incorporation of chiral molecules induces significant crystallization differences in our metal halide composites.

In order to explore whether different structures of (S–/R–) Chiral- and RAC-composites also lead to corresponding changes in optical properties, optical absorption, wavelength-dependent photoluminescence excitation (PLE) and PL spectra were recorded. The absorption spectra (in Figure S6a, Supporting Information) show that the peak absorptions locate at wavelengths of around 280 nm, 370 nm, and 450 nm for both (S–/R–) Chiral- and RAC-composites, which coincide with the electronic transitions between the ground and the excited states of the Mn²⁺ ion. In addition, PLE spectra exhibit similar shapes and features for (S–/R–) Chiral- and RAC-composites (Figure S6b, Supporting Information). (S–/R–) Chiral-composites exhibit similar PLE spectrum under 530 nm and 650 nm (Figure S6c, Supporting Information). However, there are significant differences in PL spectra for these two types of composite films (see Figure 2).

Specifically in a relatively dry environment (with the humidity lower than 7%), the RAC-composite film shows a broad emission ranging from 550 to 800 nm with a peak at around 650 nm, which exhibits bright red PL (see Figure 2a). In the same dry condition, the PL of (S–/R–) Chiral-composite films show a dominant peak at around 530 nm and a shoulder peak at around 650 nm, which exhibits bright green PL. To further reveal the dynamic behaviors of excited states.

**Figure 2.** PL spectra of RAC- and (S–/R–) Chiral-composites films in different conditions. a) PL spectra of R-composite, S-composite, RAC-composite films in a relatively dry environment. b) PL spectra of (S–/R–) Chiral-composite films in a relatively dry and wet environment. c) PL spectra of RAC-composite film in a relatively dry and wet environment. For both (b) and (c), the inset are the photos of composite film under illumination of 254 nm lamp (left and right are in dry and wet conditions, respectively).
in our (S–/R–) Chiral- and RAC-composites, PL lifetime results of all three samples (S-, R-, and RAC-composites) are compared in Figure S7, Supporting Information. We found that the chiral samples (both S- and R-polarized) show a similar lifetime. In contrast, the RAC-composite shows much longer PL lifetime. Interestingly, when the environmental humidity increases to 20%, the luminescent color of (S–/R–) Chiral-composite films changes to red (see Figure 2b). Detailed PL spectra evolution indicates that the positions of two featured PL peaks remain while the relative intensity from the lower-energy peak increases at high humidity. A shoulder in the red region of the (S–/R–) Chiral-composite in the dry environment is caused by the residual moisture inside the (S–/R–) Chiral-composite since we still have moisture in our dry environment (humidity lower than 7%). In contrast, the PL spectrum of RAC-composite film remains unchanged when the humidity is increased (see Figure 2c).

Additional evidence of the moisture induced PL change of our (S–/R–) Chiral-composite comes from the temperature-dependent PL spectra under humid conditions. The temperature changes under humid conditions involve the changes of both temperatures and humidity. We start with the measurements under vacuum conditions, where we observe no obvious changes of the relative intensity between high-energy and low-energy peaks over a wide temperature range in (S–/R–) Chiral-composite (Figure S8, Supporting Information), indicating that temperature does not result in color changes. In contrast, under the humid conditions (humidity kept at 30%), we observe significantly different results when performing the temperature-dependent PL measurements. We take the R-composite as an example, which was heated up from room temperature to 90 °C on a heating platform. Simultaneously, the PL emission image was recorded every 10 s under the illumination of an ultraviolet lamp at 254 nm. As shown in Figure 3a, with increasing heating time, the sample emission color gradually changes from red, to partly green color, and finally turns into green completely. Detailed PL spectra during the heating process are also characterized under the excitation of 405 nm laser diode (Figure 3b). We note that two peaks coexist all the time with the relative intensities of these peaks changing. As the heating time increases, the relative intensity of the emission peak at 530 nm gradually increases while the one at 650 nm gradually decreases. The PL spectra was obtained by normalizing the emission peak at 530 nm, and the emission peak at 650 nm gradually decreases as the heating time increases (Figure 3c). This is a reversible process, where the inverse spectral and color changes are observed (Figure 3a,d,e) during cooling through simply turning off the heater. Similar results are also observed in the S-composite (Figure S9, Supporting Information), while the RAC-composite film shows no color change, with only one single peak at around 650 nm (see Figure S10, Supporting Information).

Under humid conditions, with increasing (decreasing) temperature, the moisture absorbed on the composite also decreases (increases). Since we have excluded the effect of the temperature on the relative intensities of the two PL peaks (Figure S8, Supporting Information), we can safely conclude that the temperature-dependent PL (and emission color) changes under humid conditions for our (S–/R–) Chiral-composites result from the moisture changes.

As such, the PL results of racemic and (S–/R–) Chiral-composite films reveal quite different features and different responses to environmental humidity. Here, we attribute these distinctions to the crystal structure difference based on the following analysis. It is widely recognized that PL emission varies with the manganese environmental conditions where octahedrally coordinated manganese leads to red PL and tetrahedrally coordinated manganese leads to green PL.[24–34] The colors match well with our observed PL results in Figures 2 and 3. Specifically, the red emission of RAC-composite film ((rac-MBA)[Mn2Br5(EtOH)]) originates from the one-dimensional

Figure 3. PL evolution of R-composite film during the heating and cooling processes. a) Time evolutionary photos under illumination of 254 nm lamp during the heating and cooling processes at humid environment. The four top figures are the cases for the heating process by placing the film onto a hotplate (90 °C) and the four bottom figures are the cases for cooling process by turning off the hotplate. b) PL spectra during the heating process. c) Normalized PL spectra during the heating process. d) PL spectra during the cooling process. e) Normalized PL spectra during the cooling process.
(chain-like) manganese octahedrons, while the green emission of (S–/R–) Chiral-composite ((R-/S-MBA)₂[MnBr₄]) originates from the zero-dimensional/ molecular manganese tetrahedral.

Inspired by the color change from green to red for (S–/R–) Chiral-composite in the high-humidity environment, we believe that the tetrahedral structure is transformed into the octahedral structure with the assistance of moisture, where the asymmetric hydrogen bonding of organic components in the chiral composite is the most possible origin. Mitzi and co-workers previously found that the asymmetric hydrogen bonding in the chiral organic ligand (1-(1-naphthyl) ethylammonium) could result in more distorted structure than the racemic perovskite.[8,16] We hypothesize that our case shares a similar mechanism here. The distorted structure of (S–/R–) Chiral-composites under asymmetric hydrogen bonding can be more easily affected, leading to severe structural transformation.

In order to confirm this transformation, we also characterize the structure of the (S–/R–) Chiral-composite single crystal in a high humidity environment (40%). As shown in Figure 4, both crystal structure simulations and the corresponding XRD results of (S–/R–) Chiral-composites in high and low humidity are compared. At low humidity, the (S–/R–) Chiral-composites show zero-dimensional (molecular) tetrahedral structure with asymmetric hydrogen bonding. After placing the composite crystals in a high-humidity atmosphere, significant structural transformation into the single chained octahedral structure is observed (see Figure 4a). As determined by single-crystal X-ray diffraction (SCXRD), the crystal structure of (S–/R–) Chiral-composite-wet (with a chemical formula of (R-/S-MBA)₂[MnBr₃(EtOH)] as determined by SCXRD and consistent with previous reports,[22,23] The measured XRD patterns are in agreement with the simulated results in Figure 4b. The fact confirms our hypothesis that asymmetric hydrogen bonding is responsible for the novel humidity-induced structural change, which is also consistent with our PL results at low and high humidity environments. In contrast, with symmetric hydrogen bonding in the racemic composite, the crystal structure is irrelevant to environmental humidity, which is evidenced by the humidity-independent PL spectra (Figure 2c) and XRD patterns (Figure S11).

According to the detailed crystal structures (Figure 4a), we can see that the Chiral MBA cations are bonded to the tetrahedral through hydrogen bonding asymmetrically in (S–/R–) Chiral-composite. Thus, there is asymmetric hydrogen bonding and unsaturated coordination environment of the manganese atoms within the structure (Figure 4d), making it susceptible to moisture for structural transformation. By contrast, in the RAC-composite, the S- and R-MBA cations are distributed symmetrically around the octahedrons (as shown in Figure 4c). Thus, the hydrogen bonding is exerted in all symmetric directions, leading to the cancellation of each other (Figure 4e). Comparing the (S–/R–) Chiral- and RAC-composite octahedral chain structures, we can find that the octahedral chain structure of (S–/R–) Chiral-composite is more distorted (Figure 4a,c). In this case, the structure of RAC-composite is expected to be stable even in the humid environment.

Based on the humidity response of (S–/R–) Chiral-composite films, we have explored the possibility in the application of humidity sensor. A home-built setup was introduced to control the humidity of the environment. As the humidity increases, the (S–/R–) Chiral-composite film shows that the green light

![Figure 4. a) Crystalline structures of (S–/R–) Chiral-composite under high and low humidity. b) Experimental and simulated powder X-ray diffraction (XRD) patterns of (S–/R–) Chiral composite under high and low humidity. c) Crystal structure of RAC-composite. d) Schematic diagram of asymmetric hydrogen bonding effect of chiral materials. e) Schematic diagram of symmetric hydrogen bonding effect of racemic materials.](https://www.advancedsciencenews.com)
emission decreases and the red-light emission increases (see Figure S12a,c, Supporting Information). It indicates that the (S−/R−) Chiral-composite has the potential to be applied to high-sensitivity water detection.

3. Conclusion

We find that the crystal structures can be significantly different between the racemic and chiral composites, in the case of manganese-based composites incorporated with organic MBABr. One-dimensional (chain-like) octahedral is formed in RAC-composite while zero-dimensional (molecular) tetrahedral is formed in (S−/R−) Chiral-composite. This significant crystallization difference is confirmed by both structural and spectroscopic measurements. RAC-composites show red emission, while (S−/R−) Chiral-composites show green emission in low-humidity conditions. Very interestingly, we also find that in (S−/R−) Chiral-composites, a structural transformation from zero-dimensional (molecular) tetrahedral to one-dimensional (chain-like) octahedral can be induced by moisture. This unique moisture induced structural transformation is ascribed to strong asymmetric hydrogen bonding and unsaturated coordination environment of the manganese atoms of (S−/R−) Chiral-composites, as demonstrated by both XRD simulation results and the PL spectral change in high-humidity conditions. Our results indicate that tuning the asymmetric hydrogen-bonding interactions can utilize the resulting structure distortion of organic–inorganic hybrid composites, which will help guide our future synthesis of chiral materials, enrich our chiral material family and open up new possibilities to advance our materials functionalities.

4. Experimental Section

Materials: (R)-(+)–α-methylbenzylamine (R-MBA, 99%), (S)-(−)–α-methylbenzylamine (S-MBA, 98%), (±)-α-methylbenzylamine (RAC-MBA, 99%), hydrobromic acid (48 wt.% in H2O, ≥99.99%), hydrobromic acid (48 wt.% in H2O, ≥99.99%), Manganese (II) bromide (MnBr2, 99.9%), ethanol (C2H6O, 99.7%). All chemicals were commercially purchased from Sigma-Aldrich and used without further purification.

Synthesis: Fabrication of (R−, S-MBA)2[MnBr4] and (rac-MBA)[Mn2Br5(EtOH)] single crystals. R−, S− and rac-MBA (1 mmol), Manganese (II) bromide (1 mmol), and hydrobromic acid (1 mmol) were dissolved in ethanol solution (30 mL) respectively. By slow evaporation of ethanol at room temperature for about one week, transparent crystals were obtained. After (R−, S-MBA)[MnBr4] absorbs water, it will be converted into (R/S-MBA)[MnBr3(EtOH)]. The yield of all Mn-based organic–inorganic halide materials is about 60%–70% (Scheme 1). The stoichiometric equations for material synthesis are as following:

1. (R−, S-MBA)2[MnBr4] + 2MnBr2 + 4HBr + C2H6O + O2 = 2MBA2MnBr4 + EtOH + 2H2O (1)
2. (R/S-MBA)[MnBr3(EtOH)] + H2O = MBA2MnBr4 + EtOH + MBABr (2)
3. (rac-MBA)[MBAMn2Br5(EtOH)] + 8MnBr2 + 4HBr + 4C2H6O + O2 = 4MBA2MnBr5(EtOH) + 2H2O (3)

Fabrication of (R−, S-MBA)2[MnBr4] and (rac-MBA)[Mn2Br5(EtOH)] thin films. First, 100 mg of (R−, S-MBA)2[MnBr4] and (rac-MBA)[Mn2Br5(EtOH)] crystals were respectively dissolved in 350 μL ethanol solutions. Then, the mixed solutions were heated at 60 °C and stirred for 30 min. Films were obtained by dropping casting the solutions (30 μL) on glass substrates, followed by annealing at 70 °C for 30 min.

Characterization: The XRD patterns of the products were recorded with X’Pert PRO X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å). The Ultraviolet–visible absorption spectra were measured with the PerkinElmer model Lambda 900. Steady-state photoluminescence spectra were recorded with a 405 nm laser as excitation and an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector) as detection. Thermogravimetric (TG) experiments were performed with STA449 F3 thermogravimetric analyzer in the range 30–800 °C at a warming rate of 10 °C min−1 under a nitrogen atmosphere and the crystal samples were placed in an Al2O3 crucible. Room-temperature circular dichroism (CD) spectra were measured for thin films (on glass substrates) of R/S/racemic-NPB using an AVIV 420 CD spectrophotometer with 1 nm s−1 scan speed. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed using a LEO 1550 SEM operated at 18 kV accelerating voltage, with an Oxford Instruments X-Max 80 mm2 SDD detector.

The single-crystal X-ray diffraction data for DP-60 and DP-150 were collected at 298 K by using Cu Kα radiation on a Bruker D8 VENTURE single-crystal X-ray diffractometer (SCXRD) equipped with a kappa geometry goniometer. Data reductions and absorption corrections were

Scheme 1. Chemical reaction progress for (1) (R−, S-MBA)2[MnBr4], (2) (R/S-MBA)[MnBr3(EtOH)] and (3) (rac-MBA)[MBAMn2Br5(EtOH)].
performed with the APEX3 suite. Structures were solved by a direct method using the SHELXL-97 software package.

The crystal structure was refined using full-matrix least-squares based on F2 with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. The details about data collection, structure refinement, and crystallography are summarized in Tables S1, S2, and S3, Supporting Information.

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

Acknowledgements
The authors thank Dr. Weihua Ning for insightful discussions. The authors acknowledge the support from Knut and Alice Wallenberg Foundation (Dnr KAW 2019.0082), and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009-00971). W.C. and T.P. were supported by the China Scholarship Council (CSC). F.G. is a Wallenberg Academy Fellow.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

Keywords
asymmetric hydrogen bonding, chirality, crystal structure difference, lead-free, moisture

Received: October 6, 2021
Revised: April 13, 2022
Published online:

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