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# Strong Magneto-Chiroptical Effects through Introducing Chiral Transition-Metal Complex Cations to Lead Halide

Haolin Lu, Fenglian Qi, Hebin Wang, Tengfei He, Bing Sun, Xiaoqing Gao, Andrew H. Comstock, Sehrish Gull, Yunxin Zhang, Tianjiao Qiao, Tianyin Shao, You-Xuan Zheng, Dali Sun, Yongsheng Chen, Hao-Li Zhang,\* Zhiyong Tang,\* and Guankui Long\*

Abstract: The interplay between chirality with magnetism can break both the space and time inversion symmetry and have wide applications in information storage, photodetectors, multiferroics and spintronics. Herein, we report the chiral transition-metal complex cation-based lead halide, *R*-CDPB and *S*-CDPB. In contrast with the traditional chiral metal halides with organic cations, a novel strategy for chirality transfer from the transition-metal complex cation to the lead halide framework is developed. The chiral complex cations directly participate the band structure and introduce the *d*-*d* transitions and tunable magneto-chiroptical effects in both the ultraviolet and full visible range into *R*-CDPB and *S*-CDPB. Most importantly, the coupling between magnetic moment of the complex cation and chiroptical properties is confirmed by the magneto-chiral dichroism. For the band-edge transition, the unprecedented modulation of +514 % for *S*-CDPB and -474 % for *R*-CDPB was achieved at -1.3 Tesla. Our findings demonstrate a novel strategy to combine chirality with magnetic moment, and provide a versatile material platform towards magneto-chiroptical and chiropspintronic applications.

## 1. Introduction

Hybrid organic–inorganic metal halides (HOIMHs) are regarded as a wondrous platform for the designing of novel chiral materials since they can exhibit superior chiroptical and chiro-spintronic properties such as circular dichroism (CD),<sup>[1]</sup> circularly polarized luminescence (CPL),<sup>[2]</sup> nonlinear chiroptical effect,<sup>[3]</sup> chiral-induced spin selectivity (CISS),<sup>[4]</sup> chiral-phonon-activated spin Seebeck effect,<sup>[5]</sup> etc. The A- site chiral organic cations play a vital role in the designing and constructing of chiral HOIMHs. By introducing different chiral organic cations, the chirality can be successfully transferred from the A-site cation to the inorganic framework.<sup>[6]</sup> This general strategy has brought about remarkable progress but also has some limitations. For example, magnetism cannot be achieved through this traditional A-site engineering.

<ul> <li>[*] H. Lu, H. Wang, T. He, S. Gull, Y. Zhar Prof. G. Long Tianjin Key Lab for Rare Earth Materials able Energy Conversion and Storage Ce Sensing Interdisciplinary Science Cente Science and Engineering, National Insti Nankai University Tianjin 300350 China E-mail: longgk09@nankai.edu.cn F. Qi, Prof. Z. Tang Chinese Academy of Science (CAS) Key and Hierarchy Fabrication, CAS Center f science National Center for Nanoscience Beijing 100190 China E-mail: zytang@nanoctr.cn T. He, Prof. Y. Chen The Centre of Nanoscale Science and Te Laboratory of Functional Polymer Mater Chemistry, Renewable Energy Conversion (RECAST), College of Chemistry Nankai University</li> </ul>	ng, T. Qiao, T. Shao, s and Applications, Renew- nter (RECAST), Smart r, School of Materials itute for Advanced Materials Laboratory of Nanosystem for Excellence in Nano- te and Technology echnology and Key rials, Institute of Polymer on and Storage Center	<ul> <li>B. Sun, Prof. HL. Zhang</li> <li>State Key Laboratory of Applied Organic Chemistry (SKLAOC), Key</li> <li>Laboratory of Special Function Materials and Structure Design (MOE), College of Chemistry and Chemical Engineering</li> <li>Lanzhou University</li> <li>Lanzhou 730000 China</li> <li>E-mail: haoli.zhang@lzu.edu.cn</li> <li>Prof. X. Gao</li> <li>Wenzhou Institute</li> <li>University of Chinese Academy of Sciences</li> <li>Wenzhou 325000 China</li> <li>A. H. Comstock, Prof. D. Sun</li> <li>Department of Physics</li> <li>North Carolina State University</li> <li>Raleigh NC 27695–8202 USA</li> <li>Prof. YX. Zheng</li> <li>State Key Laboratory of Coordination Chemistry, Collaborative</li> <li>Innovation Center of Advanced Microstructures, Jiangsu Key</li> <li>Laboratory of Advanced Organic Materials, School of Chemistry</li> <li>and Chemical Engineering</li> <li>Nanjing University</li> </ul>
Nankai University Tianjin 300350 China		Nanjing University Nanjing 210023 China
Laboratory of Functional Polymer Materials, Institute of Po Chemistry, Renewable Energy Conversion and Storage Cer (RECAST), College of Chemistry Nankai University Tianjin 300350 China	rials, Institute of Polymer on and Storage Center	Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering Nanjing University Nanjing 210023 China

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Currently, the common approach to construct magnetic HOIMHs is still based on introducing the magnetic atom as B-site,<sup>[7]</sup> such as  $Cu^{2+,[8]} Fe^{2+,[9]} Mn^{2+,[10]}$  and  $Ce^{3+,[11]}$  etc. However, the requirement of simultaneous engineering of the A-site and B-site creates a major obstacle for the synthesis of magnetic chiral HOIMHs. A novel strategy that could introduce both chirality and magnetism more flexibly is still highly needed.

Transition-metal complex cations bring the opportunity to achieve both magnetism and chirality through A-site engineering. The positive charge at the A-site is provided by the metal cation,<sup>[12]</sup> which promotes the inclusion of nonamino organic molecules into HOIMHs, thus extending the ligand database to sulfinyl,<sup>[13]</sup> cyclopentadiene,<sup>[14]</sup> and carboxyl groups,<sup>[15]</sup> etc. Most importantly, the combination of chiral ligands with magnetic transition-metal coordination centers offers a substantial platform for the integration of chirality with magnetism. On the other hand, compared with the traditional organic cations, transition-metal complex cations could introduce characteristic magnetic, spintronic and optical properties of coordination complexes, such as magnetic moment, magneto-optical effect, metal-to-ligand charge transfer (MLCT),<sup>[16]</sup> d-d transition,<sup>[17]</sup> and heavy atom effect,<sup>[18]</sup> which could construct the multi-functional chiral HOIMHs (as shown in Figure 1a). However, chiral HOIMH based on the chiral transition-metal complex cation has not been reported up to today.

In this work, we employed the inorganic chiral transition-metal complex cation,  $Cu(1R,2R-DACH)_2^{2+}$  and  $Cu-(1S,2S-DACH)_2^{2+}$  (DACH=diaminocyclohexane) to construct the magnetic chiral metal halide. Since there exists an unpaired electron of  $Cu^{2+}$  ( $d^9$  electron configuration), the spin density is mainly located on the Cu ion and the coordinated amino group, as confirmed by the unrestricted density functional theory calculation (as shown in Figure 1b). Here, we reported the synthesis of the chiral transition-metal complex cation-based lead halide, [Cu- $(1R,2R-DACH)_2]_3(PbBr_5)_2 \bullet 3DMSO$ and [Cu(1S,2S-DACH)<sub>2</sub>]<sub>3</sub>(PbBr<sub>5</sub>)<sub>2</sub>•3DMSO (*R*-CDPB and *S*-CDPB) where both the chirality and the magnetism are derived from the chiral transition-metal complex cations (as shown in Figure 1c). Besides, the influence of chiral transition-metal complex cations on the chiroptical and magnetic properties of R-CDPB and S-CDPB was systematically investigated by superconducting quantum interference device (SQUID), vibrational circular dichroism (VCD), natural circular dichroism (NCD), magnetic circular dichroism (MCD), magneto-chiral dichroism (MChD) and theoretical calculations. It is found that the chiral transition-metal complex cations directly contribute to the band structure and exhibit d-d transitions in R-CDPB and S-CDPB, and tunable magneto-chiroptical effects in both the ultraviolet and full visible range. The strong coupling between the magnetic moment of the complex cation and chiroptical properties is confirmed by the MChD, and the apparent CD (CD\_tot) of *R*-CDPB and *S*-CDPB can be tuned by both the magnitude and direction of the external magnetic field. For the CD\_tot of band-to-band transition at 298 nm, a modulation of +290% for S-CDPB and -62% for R-CDPB at -1.3 Tesla can be reached, while for band-edge transition at 335 nm, we find a modulation of +514% for S-CDPB and -474%for R-CDPB. Our work provides a novel strategy for breaking both space inversion symmetry and time reversal symmetry in HOIMHs and reveals the potential of these HOIMHs with chiral transition-metal complex cations



*Figure 1.* The strategy of constructing the magnetic chiral lead halide by introducing transition metal complex cations. (a) The advantage of A-site with transition-metal complex cations  $ML_x^{m+}$  (M represents transition metal, L represents ligand). (b) The spin density of  $Cu(1R,2R-DACH)_2^{2+}$  and  $Cu(1S,2S-DACH)_2^{2+}$ . (c) The chemical structure of the organic chiral ligand, inorganic transition-metal complex-based chiral cation and the corresponding magnetic chiral metal halide.

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towards magneto-chiroptical and chiro-spintronic applications.

## 2. Results and Discussion

### 2.1. Crystal Structure

The *R*-CDPB and *S*-CDPB single crystals were directly synthesized by the antisolvent method. The crystal structures and refinement data are provided in Figure 2a, 2b, Figure S1 and Table S1, respectively. The powder X-ray diffraction (PXRD) matches well with the simulated result based on their single crystal structures (Figure S2). The strongest diffraction peak at  $7.3^{\circ}$  is assigned to the (002) crystal plane parallel to the 2D Pb-Br-Cu plane. The crystals exhibit strong oxygen and humidity stability since there is no obvious displacement or attenuation of the PXRD peaks after they were exposed to air for 4 months (Figure S3). Besides, thermogravimetric analysis (TGA) measurements indicate that both of the *R*-CDPB and *S*-CDPB possess high thermal stability, with identical decomposition temperatures above 166 °C (Figure S4).

As shown in Figure 2c, the distorted  $Cu(DACH)_2Br_2$ Jahn–Teller octahedrons and  $[PbBr_5X]^{3-}$  (X=O or S) octahedrons in *R*-CDPB and *S*-CDPB are connected in the clockwise and anticlockwise twisted form due to the chirality transfer. This kind of 2D chiral Pb-Br-Cu plane is essentially a derivative of 0D HOIMH, in which the complex cation acts as a structural substitute for A-site organic ammonium, and the Jahn–Teller interactions in *R-/S*-CDPB replace the hydrogen bonds in traditional 0D HOIMH (Figure S5). Both *R*-CDPB and *S*-CDPB crystallize into the  $P2_12_12_1$ Sohncke space group, which further confirms their chiral nature (Figure S6 to S8).<sup>[19]</sup>

VCD and the corresponding infrared (IR) absorption spectra (Figure S9 and S10) further confirm the chirality of A-site complex cations is successfully transferred to the inorganic lead halide framework. The IR peaks at 1446 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> are assigned to the  $-CH_2-$  and  $-NH_2$  bending vibrations of DACH, while the IR peak at 1120 cm<sup>-1</sup> is assigned to the C–N stretching vibrations of DACH. Compared with the IR peak of pure DACH molecule at 1082 cm<sup>-1</sup>, the blue-shift should be ascribed to the coordination, which further proves the formation of the complex ions.

The lead halide single crystal based on the racemic ligands is also synthesized. As shown in Figure S11, each Cu ion coordinates with one 1R,2R-DACH ligand and one 1S,2S-DACH ligand to form a mesomeric complex cation,  $[Cu(1R,2R-DACH)(1S,2S-DACH)]^{2+}$ , further forming a 3D network through bridging one dimensional (1D)  $[PbBr_4]^{2-}$  octahedron chains extending along the *c*-axis (as shown in Figure S13). Therefore, the mesomeric complex cation-based lead halide  $[Cu(1R,2R-DACH)(1S,2S-DACH)]PbBr_4$  (*meso*-CDPB) exhibits a totally different crystal structure with *R*-CDPB and *S*-CDPB, and crystallizes into the centrosymmetric space group of *R*-3, which is also consistent with its achiral nature.



Figure 2. Crystal structures of *R*-/*S*-CDPB. (a, b) The crystal structures of *R*-CDPB (a) and *S*-CDPB (b), H atoms are ignored for clarity. (c) The spiral connection between the Pb and Cu octahedrons in *R*-CDPB and *S*-CDPB.

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#### 2.2. Magnetic Properties

First, we investigated the magnetic characteristics of *R-/S*-CDPB before systematically studying their chiroptical properties. The magnetic susceptibilities of *R*-CDPB and *S*-CDPB were measured under a constant magnetic field of 1000 Oe over the temperature range of 2–300 K (as shown in Figure 3a). The obtained  $\chi_m$ -*T* data is fitted by Curie–Weiss law based on Equation 1,

$$\chi_m = \frac{C}{T - T_c} + \chi_0 \tag{1}$$

where  $\chi_m$  is the magnetic susceptibility, *C* represents the Curie constant, *T* is the temperature,  $T_c$  is the Curie temperature and  $\chi_0$  is the diamagnetic coefficient. The effective magnetic moments ( $\mu_{eff}$ ) of *R*-CDPB and *S*-CDPB are further calculated by Equation 2,

$$\mu_{\rm eff} = \sqrt{\frac{3k_{\rm B}C}{N_{\rm A}}}\mu_{\rm B} \tag{2}$$

Where  $k_{\rm B}$  is the Boltzmann constant,  $N_{\rm A}$  is the Avogadro constant and  $\mu_{\rm B}$  is the Bohr magneton. The fitted  $\mu_{\rm eff}$  of *R*-CDPB and *S*-CDPB are 1.817  $\mu_{\rm B}$  and 1.824  $\mu_{\rm B}$ , respectively. As shown in Table S2, both *R*-CDPB and *S*-CDPB exhibit paramagnetic behavior with the fitted Curie temperatures close to 0. Similar paramagnetic characteristic of *meso*-CDPB is also shown in Figure S14. The lack of magnetic coupling between the isolated Cu octahedrons is the origin of the paramagnetism. The  $\mu_{\rm eff}$  of *meso*-CDPB is 1.739  $\mu_{\rm B}$ , which matches very well with the expected theoretical value of 1.732  $\mu_{\rm B}$ .



**Figure 3.** Magnetic properties and optical properties under zero magnetic field. (a) The plot of  $\chi_m$  vs. *T* of *R*-CDPB and *S*-CDPB from 2 K to 300 K under a magnetic field of 1000 Oe, and related Curie–Weiss fitting curves. (b) PL and PLE spectra of *R*-CDPB and *S*-CDPB powders. (c) UV/Vis absorption spectra of *R*-CDPB and *S*-CDPB powders, which are obtained by transforming the diffuse reflectance spectra by Kubelka–Munk function. (d) NCD of *R*-CDPB and *S*-CDPB powders.

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#### 2.3. Chiroptical and Magneto-Optical Properties

The absorption coefficient of left- or right-handed circularly polarized light ( $\varepsilon_+$  and  $\varepsilon_-$ ) of a chiral material under magnetic field is described based on Equation 3,<sup>[20]</sup>

$$\varepsilon_{\pm} = \varepsilon_0 \pm \alpha_{\rm NCD}^{R/S} \boldsymbol{k} \pm \beta_{\rm MCD}^{R/S} \boldsymbol{B} + \gamma_{\rm MChD}^{R/S} \boldsymbol{k} \boldsymbol{B}$$
(3)

where k is the wavevector, B is the magnetic field,  $\varepsilon_0$  is the normal zero-field absorption, and  $\alpha_{\text{NCD}}$ ,  $\beta_{\text{MCD}}$ ,  $\gamma_{\text{MChD}}$  are the optical activities of NCD, MCD and MChD, respectively. For natural circular dichroism and magneto-chiral dichroism, both  $\alpha_{\text{NCD}}^R$  and  $\gamma_{\text{MChD}}^R$  are opposite to their chiral counterparts,  $\alpha_{\text{NCD}}^S$  and  $\gamma_{\text{MChD}}^S$ , while for magnetic circular dichroism,  $\beta_{\text{MCD}}^R$  is equal to  $\beta_{\text{MCD}}^S$  (Equation S6). This indicates that natural circular dichroism and magneto-chiral dichroism are the chiroptical properties relying on their chirality, while magnetic circular dichroism is independent of the chirality. Therefore, for chiral materials, the CD\_tot under magnetic field and the natural circular dichroism can be described by Equations 4 and 5, while the contribution of MCD after excluding the contribution of NCD from CD\_ tot, and the MChD, are defined by Equations 6 and 7.

$$CD\_tot_{R/S,\pm B} \propto \alpha_{NCD}^{R/S} \boldsymbol{k} \pm \beta_{MCD}^{R/S} \boldsymbol{B}$$
(4)

$$\mathrm{NCD}_{R/S} \propto a_{\mathrm{NCD}}^{R/S} \boldsymbol{k}$$
 (5)

$$\mathrm{MCD}_{R/S} \propto \beta_{\mathrm{MCD}}^{R/S} \boldsymbol{B}$$
(6)

$$MChD_{R/S} \propto 2\gamma_{MChD}^{R/S} kB$$
(7)

Therefore, the simplest expression of CD\_tot, NCD, MCD, and MChD of R-, S- and meso-CDPB is summarized in Table S3, which were systematically investigated and discussed as shown below.

#### 2.3.1. Natural Circular Dichroism

The ultraviolet-visible (UV/Vis) absorption and NCD spectra of R-/S-CDPB are measured and shown in Figures 3c and 3d. The band gap of both R-CDPB and S-CDPB is estimated to be 3.45 eV by fitting the absorption edges. All the absorption peaks have their respective NCD response.<sup>[21]</sup> The clear and opposite NCD signals in wide range further confirm that the chirality is successfully transferred to R-CDPB and S-CDPB, by comparing with the NCD signals of Cu(1R,2R-/1S,2S-DACH)Br<sub>2</sub> which only appear before 300 nm (Figure S15). The peak at 540 nm in both UV/Vis and NCD spectra should be attributed to the d-d transition of the Cu ion. The photoluminescence (PL) and PL excitation (PLE) spectra of these lead halides are further measured, and a blue emission at 440 nm (Figure 3b) is observed, while the PLE peaks at 350 nm match well with the absorption edges.

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We further performed theoretical calculations to investigate the electronic structures of these chiral lead halides. As shown in Figure S16, the magnetic moments of the transition-metal complex cations are successfully introduced into R-CDPB and S-CDPB. The band structures and projected density of states (PDOS) of all elements are shown in Figure S17. The band structures exhibit fairly nondispersive character, which further demonstrates the alternative arrangement of Cu and Pb octahedrons.<sup>[22]</sup> The valence band maximum (VBM) consists of Cu 3d, Pb 6s and Br 4p orbitals, while the conduction band minimum (CBM) is mainly composed of Pb 6p orbital. Compared with the VBMs which only consisted of Pb 6s-Br 4p antibonding orbits in most HOIMHs,<sup>[23]</sup> the chiral transition-metal complex cations directly participated in the formation of the VBMs of R-/S-CDPB. In R-/S-CDPB, there are twelve isolated energy levels above and below the Fermi level, consisting of the unpaired 3d electrons of twelve Cu ions in the unit cell.<sup>[24]</sup> The orbital hybridization is confirmed by the strong coupling between N 2p orbits and Cu 3d orbits (as shown in Figure S17c and S17f), which may result in the strong *d*-*d* transitions. The calculated absorption spectra are shown in Figure S18, the peaks at ca. 3.59 eV match well with the band-edge of the experimental absorption spectra. By comparing the DOS of the crystal with the natural transition orbitals (NTO) of the complex cation (as shown in Figure S19), it is further confirmed the absorption peak centered at 540 nm should be attributed to the d-d transition.

The PL, PLE, and UV/Vis absorption spectra of *meso*-CDPB are also measured and shown in Figures S20 and S21, which exhibit the same peaks with a slightly red-shifted absorption edge compared with those of *R*-CDPB and *S*-CDPB. The decrease of the band gap should be attributed to the edge-shared connections between Pb octahedrons of *meso*-CDPB, which is also consistent with the theoretical calculated results (as shown in Figure S22 to S28).

#### 2.3.2. Magnetic Circular Dichroism

The CD\_tot spectra of R- and S-CDPB were further measured under external magnetic field varying from 0.4 T, 0.7 T, 1.0 T to 1.3 T in exploring the influence of magnetic field on the different dichroic contributions, which originated from both magneto-optical and chiroptical effects. Owing to the intrinsic structural chirality of R-/S-CDPB, asymmetric chiroptical characteristics of CD\_tot signals are observed under both positive and negative magnetic fields. The magnitude of CD tot can be further enhanced, reduced, or even reversed by applying the external magnetic fields. However, since the positive and negative magnetic fields have opposite influences on MCD, the CD\_tot signal of R-CDPB under the positive magnetic field is approximately mirror-symmetric with that of S-CDPB under the negative magnetic field if the same magnitude of magnetic field is applied (as shown in Figure 4a to 4d).

To distinguish the intrinsic NCD signal of *R-/S*-CDPB and the influence of external magnetic field on CD, the NCD and MCD are obtained from the CD\_tot signals based on Equations 8 and 9.<sup>[25]</sup>



Figure 4. MCD measurements of *R*-/*S*-CDPB. (a, d) The CD\_tot spectra of *R*-CDPB under positive (a) and negative (d) magnetic fields. (b, c) The CD\_tot spectra of *S*-CDPB under positive (c) and negative (b) magnetic fields. The positive and negative magnetic fields are defined as the magnetic fields with directions parallel and antiparallel to the incident light, respectively. (e, f) MCD of *R*-CDPB (e) and *S*-CDPB (f).

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$$NCD = \frac{[CD\_tot_{+B} + CD\_tot_{-B}]}{2}$$
(8)

$$MCD = \frac{[CD\_tot_{+B} - CD\_tot_{-B}]}{2}$$
(9)

In contrast with NCD, MCD peaks only appear near the absorption edge as shown in Figure 4e and 4f, which is also consistent with the mechanism of MCD generation (as shown in Figures S29). At the external magnetic field of -1.3 T, the CD\_tot intensity at 298 nm achieves a maximum modulation of about +290 % for S-CDPB, which can reach to -62 % for *R*-CDPB. While for the apparent circular dichroism at 335 nm, the modulation can reach +514 % for S-CDPB and -474 % for *R*-CDPB (as shown in Table S4).

The origin of strong MCD can be addressed by Equation S9. As the preliminary analysis, near-band edge absorption dominates the MCD spectra, but the near-band edge absorption between 290 nm (4.28 eV) and 360 nm (3.44 eV) is not dominated by a single peak. The joint participation of Cu element in the valence band may lead to the absorption near band edges not entirely originated from the Pb-based octahedra. Therefore, a global fitting with Gaussian lines was performed on the absorption spectra. As shown in Figure 5a, the fitted curve is in good agreement with the

experimental curve. The magnetic field-normalized MCD obviously depend on the 1st derivative of peak 2 and the absorption peak 1 and peak 3 themselves, as shown in Figure 5d. This characteristic is related to the two components in *R-/S*-CDPB, which contribute to MCD as two functional modules.

- 1. Diamagnetic lead halide octahedra often contribute to the derivative-shaped MCD spectra through *A*-term.<sup>[26]</sup>
- 2. For paramagnetic molecules, *C*-term dominates MCD spectra.<sup>[27]</sup> But distinguishable *A*-term signal often appears together with the *C*-term signal.<sup>[28]</sup>

As shown in Figure 5b and 5c, the MCD spectra is consistent with the 1st derivative of peak 2 (which should be attributed to the *A*-terms of the lead halide octahedra), and peak 1 and peak 3 (which should be attributed to the *C*-terms of the complex cations). The *C*-term peaks at the same wavelength as the *A*-term peak have the same signs as the *A*-term peak, which enhanced the signals and broaden the response range of MCD spectra. Figure 5e and 5f show in detail the parts of the signal corresponding to *A*-, *B*- and *C*-term from each peak. We also calculated the  $g_{MCD}$  of each fitted peaks, as shown in Table S5, the g-factors of peak 3 are even larger than the apparent total  $g_{MCD}$  (Figure S30),  $g_{NCD}$  (Figure S31), and even  $g_{CD_{-tot}}$  (Figure S32).

The MCD measurements under the same conditions are also applied to *meso*-CDPB (Figure S33 and S34). The NCD



*Figure 5.* Analysis of the origin of MCD. (a) The experimental and fitting absorption spectra. (b, c) The experimental and fitting magnetic fieldnormalized MCD spectra of *R*-CDPB (b) and *S*-CDPB (c). (d) The comparison of the shape of the magnetic field-normalized MCD spectra and the shape of the fitted absorption peaks and the 1st derivative of them. (e, f) The contribution of different Faraday terms in the response of each absorption peaks to the magnetic field-normalized MCD of *R*-CDPB (e) and *S*-CDPB (f).

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of *meso*-CDPB (Figure S35) shows a zero signal as expected, and the MCD shows weak peaks at 300 nm and 350 nm derived from absorption edge splitting (Figure S36–37).

#### 2.4. Magneto-Chiral Dichroism

Magneto-Chiral dichroism represents a fascinating manifestation of light-matter interaction in which the absorption of unpolarized light depends on the relative orientation of the magnetic field (**B**), the direction of light propagation, and the absolute configuration of the system, as described by Equation 7. MChD is the inner product of the light wavevector and the magnetic vector, exhibiting an intrinsic interplay between magnetic moment and chirality which is distinct from the traditional magneto-optical activity such as  $MCD.^{[29]}$  The introduction of the magnetic moment could break the time-reversal symmetry, thus MChD effect is the most straightforward and sufficient evidence of coupling magnetic moment and chiroptical properties.<sup>[30]</sup>

By switching the direction of the magnetic field parallel or antiparallel to k, the difference between the absorption spectra is the MChD.<sup>[31]</sup> As shown in Figure 6a, the MChD spectra of R-CDPB and S-CDPB are opposite. Due to the Jahn-Teller effect, the symmetry of the Cu<sup>2+</sup> ion is decreased. With the distortion of the octahedral field, the  $Cu^{2+}$  ion gets closer to the Br atom at one side (solid line) and weakens the interaction at the other (dashed line, as shown in Figure 6b), but they are both weaker than the strong coordination between Cu and N atoms. The  ${}^{2}E_{g}$  state of  $Cu^{2+}$  is split into the  $d_{x^2-y^2}$  and  $d_{z^2}$  states with different energies, while the  ${}^{2}T_{2g}$  state is split into  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ states. The MChD bands at ca. 763 nm and 543 nm correspond to the  $d_{x^2-y^2} \rightarrow d_{xy}$  and  $d_{x^2-y^2} \rightarrow d_{z^2}$  transitions, respectively, while the MChD peak located in the near ultraviolet region originates from the transitions between  $d_{x^2-y^2}$  and the nearly degenerate  $d_{yz}$  and  $d_{xz}$  orbitals. Therefore, the optical transitions of MChD are different from that of NCD and MCD, which are only determined by the intraatomic *d*-*d* transitions of Cu<sup>2+</sup> ions (Table S6).<sup>[8a]</sup> Therefore, as revealed by CD, MCD and MChD, tunable magnetochiroptical effects in both the ultraviolet and full visible range are observed in R-CDPB and S-CDPB (Figure S38).



**Figure 6.** The MChD effect of *R*-/S-CDPB. (a) The MChD spectra of *R*-CDPB and S-CDPB at 2 K. (b) The energy level diagram of the *d*-orbitals for  $Cu^{2+}$ -based complex cations in *R*-CDPB and S-CDPB.

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# 3. Conclusions

In summary, the chiral lead halide with chiral transitionmetal complex cations was reported, and both the chirality and the magnetic moment were successfully infused by Asite cations. It is found that the chiral transition-metal complex cations directly contribute to the band structure, and exhibit the *d-d* transitions, and tunable magnetochiroptical effects in both the ultraviolet and full visible range in the HOIMHs. The strong coupling between magnetic moment of transition-metal complex cation and chiroptical properties is confirmed by the magneto-chiral dichroism, and both the magnitude and direction of CD\_tot of R-CDPB and S-CDPB is successfully tuned by the external magnetic field. For CD\_tot of the band-edge transition at 335 nm, the modulation reaches +514 % for S-CDPB and -474% for R-CDPB. The MCD spectra originate from the joint contribution of the A-term of diamagnetic lead halides and the C-term of paramagnetic complex cations. Considering that chiral transition-metal complex cation could introduce the characteristic magnetic, spintronic and optical properties of coordination complexes, such as magnetic moment, magneto-optical effect, metal-toligand charge transfer, *d-d* transition and heavy atom effect, a novel strategy to construct the multi-functional chiral HOIMHs is developed in this work. Our results suggest that these materials hold great potential towards magnetochiroptical and chiro-spintronic applications.

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# **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 Supporting Information of this article.

**Keywords:** chiral lead halide · complex ion · chiroptical effect · magneto-chiral dichroism · A-site engineering

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# **Research Article**

# **Research Article**

## **Complex Cations**

H. Lu, F. Qi, H. Wang, T. He, B. Sun,
X. Gao, A. H. Comstock, S. Gull, Y. Zhang,
T. Qiao, T. Shao, Y.-X. Zheng, D. Sun,
Y. Chen, H.-L. Zhang,\* Z. Tang,\*
G. Long\* \_\_\_\_\_\_\_\_\_ e202415363

Strong Magneto-Chiroptical Effects through Introducing Chiral Transition-Metal Complex Cations to Lead Halide



The chiral metal halide based on A-site chiral complex cation is synthesized, which provides a new strategy to construct the magnetic chiral metal halide. The influence of complex cation on the chiroptical and magnetic properties is systematically investigated. An ultrahigh modulation of over 500% of apparent circular dichroism is achieved under 1.3 T magnetic field. The coupling between magnetic moment and chiroptical activity is confirmed by the magnetochiral dichroism.

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