

Composition-Dependent Antiferromagnetism in Low-Dimensional Hybrid Organic Cobalt-Halide Semiconductors

Shangpu Liu,[#] Jonathan Zerhoch,[#] Stanislav Bodnar, Julia A. Gessner, Luca Bischof, Jan Arneth, Franz Bodenmüller, Joachim Ballmann, Frank Rominger, Rüdiger Klingeler, and Felix Deschler*



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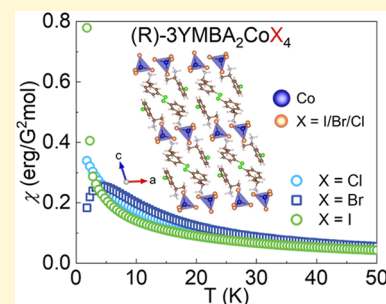


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ABSTRACT: Low-dimensional magnets exhibit complex magnetic phases for studying fundamental spin ordering phenomena, while semiconducting variants of these materials are explored for all-optical control and readout of magnetic states. Thus, the discovery of systems with compositional tuning of optical and magnetic properties unlocks emerging functionalities and fundamental investigations. Here, we report the synthesis of low-dimensional (canted-)antiferromagnets (R)-3YMBA₂CoX₄ (Y, X = halide; MBA = methylbenzylamine) and study their magnetic and optical properties. Structural characterization confirms distorted Co-halide tetrahedra separated by organic groups, forming chiral crystal structures. Magnetic measurements reveal composition-dependent (canted) antiferromagnetism at high cryogenic temperatures. While (R)-3ClMBA₂CoBr₄ was identified as an easy-plane-type antiferromagnet, (R)-3BrMBA₂CoI₄ was found to exhibit canted antiferromagnetism showing a 50 times higher spontaneous magnetic moment than that of reported hybrid metal halides. Using optical measurements, we find an optically active metal–ligand charge-transfer state involving cobalt atoms that participate in the magnetic ordering. Using photoexcitation of the metal–ligand transfer state for optical spin-alignment in ultrafast magneto-optical measurements, we find a spin dephasing time of 60 ps in our hybrid cobalt compounds, exceeding spin lifetimes of related low-dimensional hybrid metal halides. Our report introduces a promising material platform for symmetry-mediated spin control, paving the way for hybrid quantum materials with optical spin manipulation capabilities.



INTRODUCTION

Low-dimensional magnetic semiconductors show unique properties such as (electro-)optical control of magnetic and spin states,¹ complex quantum magnetic properties,² and fabrication of nanoscale spintronic devices,^{3–5} which makes them promising materials in the field of opto-spintronics. Antiferromagnetic variants show especially advantageous properties such as a lack of stray fields⁶ and potential THz spin control.⁷ Additionally, low-dimensional antiferromagnets show quantum phenomena such as a strong excitonic confinement and exotic many-body phenomena,^{8,9} while complex quantum magnetic phenomena have been reported recently in the frustrated 2D (two-dimensional) cobalt-halide triangular antiferromagnet Cs₂CoBr₄, e.g., the existence of a spin density wave phase.^{10,11}

A less explored direction of low-dimensional semiconductor magnets is spin-selective effects originating from the distortion of their material structure. In the related material class of low-dimensional hybrid organic–inorganic lead halide perovskites (HOIPs), distortion in the crystal structure has been shown to produce a diverse array of magneto-optic properties,^{12–15} arising from the HOIP's lattice softness and tunability of organic groups. The asymmetric nature of these materials has led to the demonstration of unique processes, such as chirality-induced spin-selectivity (CISS), spin memory, circular

dichroism (CD), and circularly polarized photoluminescence (CPL).^{15–18} Thus, materials that combine distorted structure features with magnetic properties are poised for complex magnetic ordering and opening up different directions for spin-state manipulation.^{19,20} Motivated by these reports, and our work on low-dimensional hybrid organic-metal-halide frameworks,^{13,21,22} we have now synthesized chiral hybrid variants of Cs₂CoBr₄, in which the Cs-atoms were replaced by chiral organic groups, and report the formation of unusual magnetic phases, unique to the materials' crystal structure.

We for the first time find clear signatures of the predominant antiferromagnetic nature in a series of 0D hybrid organic–inorganic tetrahedral Co-halide compounds. We report the single-crystal synthesis of four hybrid organic–inorganic cobalt-halide compounds (R)-3BrMBA₂CoI₄, (R)-3ClMBA₂CoBr₄, (R)-3BrMBA₂CoCl₄, and PEA₂CoI₄. We employ single-crystal X-ray diffraction (SCXRD) to resolve the crystal structure of the compounds and magnetometry to

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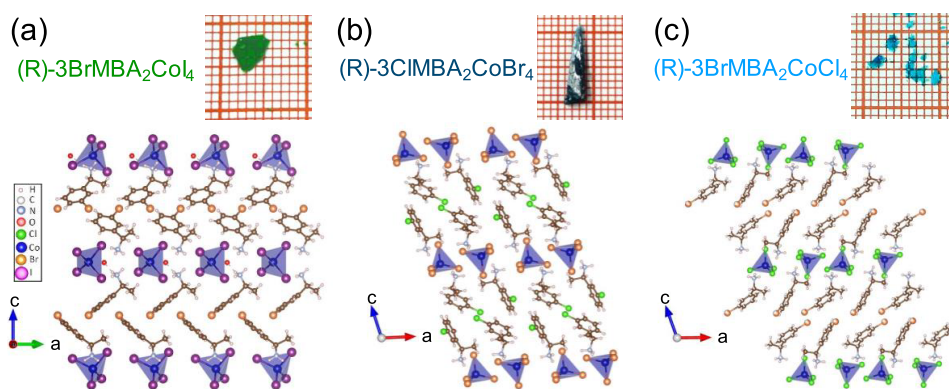


Figure 1. Images and crystal structures derived from SCXRD measurements of (R)-3BrMBA₂CoI₄ (a), (R)-3CIMBA₂CoBr₄ (b), and (R)-3BrMBA₂CoCl₄ (c). For simplicity and clarity in (c), there is only one of two possible organic group orientation modifications shown.

study magnetic material properties in dependence of crystal structure and chemical composition. Selected compounds with promising magneto-optic properties are investigated with ultrafast polarization-resolved pump–probe spectroscopy. This work unveils a pioneering class of hybrid low-dimensional materials where tunable crystal structures provide a powerful design knob to coengineer canted antiferromagnetism and strong magneto-optical responses, opening pathways for future spintronics and magneto-optic applications.

MATERIALS AND METHODS

Materials

Cobalt acetate (Co(Ac)₂), enantiopure (R)-3BrMBA (3BrMBA = 1-(3-bromophenyl)-ethylamine), methylammonium bromide (MABr), phenethylammonium iodide (PEAI), hydrochloric acid (HCl, 37%), hydrobromic acid (HBr, 48%), hydroiodic acid (HI, 57%), ethanol, toluene, and *N,N*-dimethylformamide (DMF) were ordered from Sigma-Aldrich. Enantiopure (R)-3CIMBA (3CIMBA represents 1-(3-chlorophenyl)ethylamine) was purchased from BLDpharm. All of the chemicals were used directly without further purification.

Growth of Hybrid Organic–Inorganic Cobalt Halides Single Crystals (R)-3BrMBA₂CoX (X = Cl, Br, and I)42

(R)-3BrMBA₂CoX₄ single crystals were prepared by sequentially adding 0.177 g of Co(Ac)₂, 2 mL of HX (X = Cl, Br, and I), and 302 μ L of (R)-3BrMBA into 20 mL of ethanol in an ice bath. After continuously stirring the solution at 80 °C for ~1 h, the fully dissolved solution was kept at room temperature for a few days until large crystals showed up. The crystals were cleaned three times with toluene, dried under vacuum overnight, and stored inside a glovebox for further usage.

(R)-3CIMBA₂CoBr₄

(R)-3CIMBA₂CoBr₄ single crystals were prepared by the same solution- evaporation method as above, except putting 278 μ L of (R)-3CIMBA replacing 302 μ L of (R)-3BrMBA inside precursor solutions.

(PEA)₂CoI₄ and MA₂CoBr₄

Both (PEA)₂CoI₄ and MA₂CoBr₄ single crystals were prepared by a hydrothermal synthesis method. For a general process, 89 mg of Co(Ac)₂ and 249 mg of PEA or 112 mg of MABr were dissolved in 2 mL of HI or HBr solutions at 95 °C. The fully dissolved solutions were transferred to 25 mL autoclaves and kept at the same temperature (95 °C) inside the oven for 24 h. After slowly decreasing the temperature to room temperature at a rate of 1 °C/h, large single crystals appeared at the bottom of the autoclaves. Toluene was used here to clean the obtained crystals three times, which were then dried under vacuum conditions. The crystals were stored inside a N₂-filled glovebox before usage.

Fabrication of Hybrid Organic–Inorganic Cobalt Halide Thin Films

For optical characterization, we prepared hybrid organic–inorganic cobalt halide thin films by spin-coating methods. The thin-film fabrication process was performed inside a glovebox under an inert gas. The stock solution was prepared by adding single-crystal samples (80 mg) to a 200 μ L of DMF solution. After fully dissolving at 100 °C for 30 min, 100 μ L of the solution was spin-coated on 20 $\times$ 20 mm glass substrates (4000 rpm, 35 s). The substrates were precleaned by a UV-ozone cleaner for 30 min. The obtained films were then annealed at 100 °C for 30 min and stored in a glovebox before characterization.

General Structural and Optical Measurements

Single-crystal XRD measurements were performed on a Bruker D8 Venture system with a Helios optic monochromator and Mo radiation (λ = 0.71073 Å). The measurement temperatures for each crystal are listed in Table S1. Absorption and CD measurements were performed on a commercial CD spectrometer (JASCO J-1700). During CD measurements, to exclude additional artifacts, we rotated and flipped all samples at different orientations to ensure that the obtained CD signal was not due to linear dichroism or birefringence.

TA Spectroscopy Measurements

Room-temperature TA measurements were performed by a commercial TA setup (Ultrafast Systems, HELIOS).

Faraday Rotation Measurements

The transient Faraday rotation measurements were conducted in a home-built setup where the sample is located inside a closed-cycle helium magneto-optical cryostat (Montana Instruments). The pump–probe experiments were performed at a laser (Pharos + Orpheus + Hiro + Lyra by Light Conversion) repetition rate of 16.667 kHz. Before the sample, the pump beam was circularly polarized by an achromatic quarter wave plate (B-Halle) while the probe beam was kept linearly polarized. After the sample, the probe beam was guided through a Wollaston prism and onto an amplified balanced detector (PDB210A by Thorlabs). The differential signal was analyzed by a Lock-In amplifier (MFLI by Zurich Instruments) as a function of pump and probe time delay.

Magnetic Measurements

The direct current (dc) and alternating current (ac) magnetization were studied in the temperature range 1.8–300 K and in magnetic fields up/down to ± 7 T by means of a Magnetic Properties Measurement System (MPMS3, Quantum Design). Measurements were restricted to $T < 300$ K to avoid thermal degradation of the materials. For dc measurements down to 400 mK, the MPMS3 instrument was equipped with the iQuantum ³He probe.

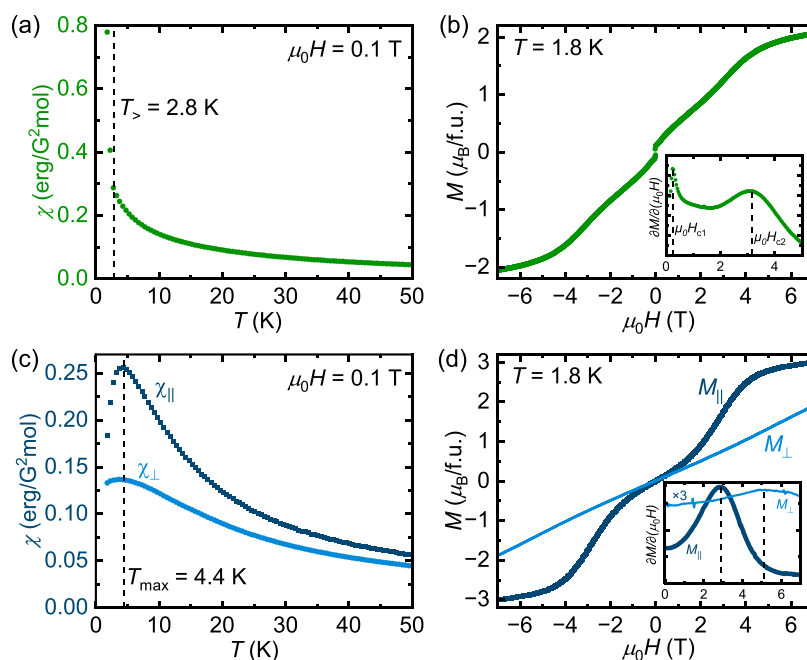


Figure 2. Magnetic characterization of (R)-3BrMBA₂CoI₄ (a, b) and (R)-3ClMBA₂CoBr₄ (c, d). (a) Static magnetic susceptibility $\chi = M/(\mu_0 H)$ as a function of the temperature T in the presence of an external magnetic field $\mu_0 H = 0.1$ T measured after zero field cooling. (b) Magnetization M as a function of the external magnetic field $\mu_0 H$ at $T = 1.8$ K. Bottom right inset shows the differential magnetic susceptibility $\partial M/\partial(\mu_0 H)$. The vertical dashed lines located at the peaks of the derivative indicate the critical field $\mu_0 H_{c1}$ and the spin-reorientation field $\mu_0 H_{c2}$. (c) Static magnetic susceptibility χ along two different directions with 90° in between, respectively ($\chi_{||}$ square symbols and $\chi_{\perp}$ dots) as a function of the temperature T in the presence of an external magnetic field $\mu_0 H = 0.1$ T measured after zero field cooling. (d) Magnetization $M_{||}$ and $M_{\perp}$ as a function of the external magnetic field $\mu_0 H$ at $T = 1.8$ K. The inset shows the differential magnetic susceptibility $\partial M/\partial(\mu_0 H)$. The vertical dashed lines located at the peaks of the derivatives indicate the spin-reorientation fields.

RESULTS AND DISCUSSION

Single-Crystal Structures of Hybrid Organic Cobalt-Halide Compounds

We synthesize a series of hybrid organic–inorganic cobalt halide single crystals using two solution-processing methods, which have a strong dependence on the precursor concentration and solubility.²³ We slowly evaporated the ethanol solutions containing the large distorted organic molecules (R)-3BrMBA or (R)-3ClMBA, cobalt acetate (Co(Ac)₂), and HX (X = Cl, Br, I) mixtures to produce (R)-3BrMBA₂CoX₄ or (R)-3ClMBA₂CoBr₄ single crystals (see details in the [Materials and Methods](#) section). PEA₂CoI₄ and MA₂CoBr₄ single crystals with symmetrical organic cations were synthesized for comparison by a hydrothermal method, wherein large crystals formed by controlling the cooling rate (1 °C/h) of highly concentrated precursor solutions.

We used SCXRD measurements to identify the crystal structures of the synthesized hybrid cobalt-halide compounds (detailed crystal information is listed in [Table S1](#) in the SI). The three Co-based samples (R)-3ClMBA₂CoBr₄, (R)-3BrMBA₂CoI₄, and (R)-3BrMBA₂CoCl₄ show a zero-dimensional (0D) crystal structure, consisting of disconnected distorted cobalt-halide tetrahedra with surrounding large organic molecules ([Figure 1](#)). The compounds (R)-3ClMBA₂CoBr₄ and (R)-3BrMBA₂CoCl₄ crystallize in a monoclinic $P2_1$ space group, while (R)-3BrMBA₂CoI₄ shows a hexagonal $P6_1$ space group, which is a chiral space group. Both space groups belong to the Sohncke space groups, confirming the formation of distorted crystal structures due to structure modeling from large asymmetric organic molecules.²⁴ We further included the Flack parameters for all non-

centrosymmetric structures in [Table S1](#). For (R)-3ClMBA₂CoBr₄ and (R)-3BrMBA₂CoCl₄ (space group $P2_1$), the Flack parameters refine to values near zero with reasonable standard uncertainties, confirming the correct absolute structure assignment. For (R)-3BrMBA₂CoI₄ (space group $P6_1$), the Flack parameter was refined to 0.27, indicating that the major domain constitutes 73% of the major twin crystal volume and 27% of the minor twin crystal volume. This twinning likely arises from a displacive phase transition during the crystallization process, where a higher-symmetry parent phase transforms to the low-temperature chiral $P6_1$ phase upon cooling. Such symmetry reduction further gives rise to multiple equivalent orientation variants. Similar behavior is also reported in many systems such as quartz, metal oxides, and chiral metal-halide compounds,^{25–28} where symmetry-lowering transitions generate twin domains. Incorporation of symmetrical groups, like PEA and MA ([Figure S1](#)), also yields 0D cobalt halide tetrahedral structures in PEA₂CoI₄, and in the previously reported MA₂CoBr₄,²⁹ which both crystallize in a $P2_1/c$ space group with inversion symmetry.

A main difference between the five synthesized hybrid cobalt-halide samples is the average distance between the Co atoms, analyzed by evaluating the distance between the next neighbor lattice planes of Co atoms ([Table S2](#)). By tuning the size of organic cations or halide compositions, the average distance of the lattice planes formed by Co-halide tetrahedra, i.e., in direction perpendicular to the “2D planes”, decreases from 15.1 Å (001) in (R)-3BrMBA₂CoCl₄ to 14.43 Å (001) in (R)-3ClMBA₂CoBr₄ to 13.30 Å in PEA₂CoI₄ (010) to 12.13 Å (001) in (R)-3BrMBA₂CoI₄ and finally to 6.5 Å (010) in MA₂CoBr₄. The fact that MA₂CoBr₄ exhibits the smallest interplanar distance agrees with the smaller size of the MA

compared to the other organic groups. Along the other two crystal directions, the average distance of the Co planes varies between a minimum distance of 3.59 Å (100) in PEA_2CoI_4 and a maximum distance of 5.60 Å (001) in MA_2CoBr_4 . Interestingly, (R)-3BrMBA₂CoI₄ is the only compound which shows the same distances along *a* and *b* directions. Furthermore, we analyze the H-bond distance and angle, which has been reported as an important structure factor.³⁰ We notice that, compared to the substitution of the organic cations, different halide compositions result in the different H bond acceptor atoms from Cl to Br and to I, which have a larger impact on the formed H bond. Both (R)-3BrMBA₂CoI₄ and PEA_2CoI_4 show a similar H–I distance (~ 2.7 Å, see details in Table S2), while 3ClMBA₂CoBr₄ and MA_2CoBr_4 show a shorter H–Br distance (~ 2.5 Å), indicating stronger H bond connections. The shortest H-halide distance is found in the Cl-based compound (R)-3BrMBA₂CoCl₄ with ~ 2.35 Å. Opposite trends were observed in H bond angles, in which we found that (R)-3BrMBA₂CoCl₄ shows a largest N–H–Cl angle ($\sim 178^\circ$), while the smallest N–H–I angles were observed in (R)-3BrMBA₂CoI₄ and PEA_2CoI_4 samples ($\sim 140^\circ$).

In summary, we demonstrated that the crystal structure and symmetry of hybrid organic cobalt-based semiconductors can be controlled by cation and halide engineering, tuning the lattice distance, and H-bond strength.

Compositional Tunability of Magnetism in Hybrid Organic–Inorganic Cobalt Halides

While the fully inorganic compounds Cs_2CoBr_4 , Cs_2CoCl_4 , and the related Cs_2CuBr_4 and Cs_2CuCl_4 are known to be very interesting 2D frustrated quantum triangular-lattice antiferromagnets,^{10,11,31–34} hybrid organic–inorganic Co-halide compounds with tetrahedrally coordinated Co^{2+} ions were reported to only show paramagnetic behavior^{33,35} and signs of cooperative magnetism were only found in higher-dimensional versions based on Mn or Cu.^{36–39} Interestingly, we find signatures of cooperative magnetism of predominantly antiferromagnetic nature in all of our presented materials (Figures 2 and S2). Our data suggest that both magnetic interaction and magnetic anisotropy depend on the organic group and halide composition, as summarized in Table S3.

The magnetization data of Co compounds (R)-3BrMBA₂CoI₄ and (R)-3ClMBA₂CoBr₄ are shown in Figure 2. Starting with the powder sample of compound (R)-3BrMBA₂CoI₄, we find a sizable spontaneous magnetic moment below $T_s = 2.8$ K, which can be seen in the rapid increase of magnetization in Figure 2(a) and the remnant magnetization of nearly $M_R = 0.1 \mu_B/\text{f.u.}$ at 0 T in Figure 2(b). The magnetic susceptibility data were fitted using the modified Curie–Weiss law.⁴⁰ The Curie–Weiss-like fit, adapted in the temperature range from 200 to 300 K (solid black line in Figure S3(a)),

$$\chi = \frac{C}{T - \theta_W} + \chi_0 \quad (1)$$

with the Curie constant *C*, the Weiss temperature θ_W , and the temperature-independent contribution χ_0 , reveals $C = 2.31(10)$ ergK/(G² mol) and a negligible Weiss temperature. The Curie constant yields the effective moment $p_{\text{eff}} = 4.30(9) \mu_B$, i.e., $g \approx 2.22(5)$, when considering $J = 3/2$, which is in agreement with typical values for tetrahedrally coordinated Co^{2+} and reflects the contribution of unquenched orbital angular momentum.⁴¹

The small spontaneous magnetic moment observed in the isothermal magnetization curve, compared to the expected fully saturated magnetization, suggests that the observed spontaneous magnetization may result from a canted antiferromagnetic ground state spin configuration. Given the expected saturation moment of $M_S = gJ = 3.33(7) \mu_B$ suggested by the Curie–Weiss analysis, the size of the measured net magnetic moment M_R implies the canting angle $\varphi = \tan^{-1}(M_R/M_S) \approx 1.7^\circ$. To precisely determine the long-range magnetic ordering temperature T_{CA} of the material, we performed additional magnetization measurements down to 400 mK, shown in Figure S4, revealing $T_{\text{CA}} = 2.2$ K as read off from the minimum in the temperature derivative of the static magnetic susceptibility.

The apparent high-field saturation in the isothermal magnetization at 7 T indicates a plateau-like behavior at around $2M_S/3$, as the full saturation of the magnetization $M_S = 3.4 \mu_B$ is not reached in the accessible field range. The derivative $\partial M/\partial(\mu_0 H)$ shown in the inset of Figure 2(b) unveils the existence of two critical fields $\mu_0 H_{c1}$ and $\mu_0 H_{c2}$ indicated by a sharp peak and a broad hump in $\partial M/\partial(\mu_0 H)$, respectively. The former anomaly is associated with a discontinuous increase in magnetization of about $0.06 \mu_B/\text{f.u.}$ We attribute $\mu_0 H_{c2}$ to a field-driven spin reorientation.

The temperature and frequency dependencies of the real and imaginary parts of the AC susceptibility χ' and χ'' , shown in Figure S5, demonstrate the increase of the real part of χ' around the long-range ordering temperature T_{CA} , but also show that it is associated with slow spin dynamics as it is suppressed at high frequencies. At 1.8 K, a maximum in the imaginary part of χ'' centered around 5 Hz reveals a long magnetic relaxation time of $\tau \approx 0.03$ s, which was determined from $\tau = 1/2\pi f_{\text{peak}}$ assuming Debye relaxation. Similar slow relaxation just below the transition temperature has been also observed in the canted antiferromagnetic ground state of Co(II)-tetrazolate-carboxylate with quasi-two-dimensional magnetic interaction.⁴² While the slow relaxation observed in ac susceptibility is reminiscent of single-molecule magnet behavior (Figure S5), it occurs just below the long-range ordering temperature T_{CA} . This points to dynamics associated with the domain state of a bulk canted antiferromagnet rather than isolated molecular behavior, similar to observations in related quasi-2D canted antiferromagnets.⁴² To definitively exclude SMM (single-molecule magnets) behavior, magnetic dilution experiments would be necessary; however, the clear signatures of cooperative antiferromagnetic ordering (Figure 2) indicate that the slow dynamics arise from bulk magnetic correlations rather than molecular anisotropy.

In the case of (R)-3ClMBA₂CoBr₄, we are able to synthesize single crystals of sufficient size, shape, and physical stability to allow magnetization measurements. The growth process results in thin platelet-shaped single crystals (see Figure 1), which typically exhibit the *c*-axis perpendicular to the platelet layers. Hence, magnetic measurements were performed for magnetic fields applied either in parallel to the layers ($\chi_{\parallel}$) or perpendicular to them ($\chi_{\perp}$), which we attribute to the in-plane (B_{llab}-plane) and out-of-plane (B_{llc}) magnetization, respectively. Compared to (R)-3BrMBA₂CoI₄, the compound (R)-3ClMBA₂CoBr₄ does not show a detectable spontaneous magnetic moment down to 1.8 K. It displays clear antiferromagnetic characteristics, evidenced by the decreasing susceptibility at low temperatures that peaks at approximately $T_{\text{max}} = 4.4$ K in Figure 2(c). An attempt to fit the experimental

data using a Curie–Weiss-like model (eq 1) yields slightly different Curie constants for the two measured directions (Figure S3(b)), the average of which is consistent with the iodide compound (R)-3BrMBA₂CoI₄, discussed above. It further suggests a very small positive Weiss temperature, which might result from competing ferro- and antiferromagnetic interactions (magnetic frustration) yielding the overall antiferromagnetic characteristics.⁴³ At low temperatures, the static magnetic susceptibility measurements (Figure 2(c)) along the two orthogonal directions reveal magnetic anisotropy and show an easier and harder magnetic response in the measured susceptibilities $\chi_{||}$ and $\chi_{\perp}$, respectively. This is supported by the crystal orientation dependence of the isothermal magnetization in Figure 2(d) and the resulting dependence of the spin reorientation fields, which are denoted by the vertical lines in the inset. The data suggest an easy-plane-type antiferromagnet, similar to what is observed in (CH₃CH₂NH₃)₂CuCl₄.⁸⁷

Comparison of Co-halide compounds with symmetric (e.g., PEA-based shown in Figure S2) and nonsymmetric organic groups (MBA-based) suggests that the geometry of the distorted tetrahedra and the lack of inversion symmetry in organic compounds favor canting of spins and further reduce transition temperatures overall. This can also be connected to different Co–Co distances due to the different sizes and arrangements of the organic groups (see Table S2). Taniguchi et al. reported the Dzyaloshinskii–Moriya interaction (DMI) to be responsible for the canted antiferromagnetism which they observed in hybrid organic 1D Mn–Cl perovskite derivatives.³⁹ Here, we show a 50 times higher spontaneous magnetic moment ($\sim 0.1 \mu\text{B}/\text{f.u.}$) in (R)-3BrMBA₂CoI₄ than reported recently ($\sim 0.002 \mu\text{B}/\text{f.u.}$),³⁹ which we also attribute to DMI. It may be related to the larger spin–orbit coupling of Co²⁺ in (R)-3BrMBA₂CoI₄ and the smaller interatomic distance between Co atoms (Table S2). Spin canting is often promoted by the interplay between isotropic Heisenberg exchange and the antisymmetric DMI.^{44,45} In (R)-3BrMBA₂CoI₄, the chiral crystal structure breaks spatial inversion symmetry, making DMI a likely origin of the observed spin canting,^{46–49} which is underlined by the comparison to the centrosymmetric arrangement of Co-iodide tetrahedra in the material PEA₂CoI₄ (Figure S2(a),(b)), that does not show spin canting. Detailed investigations of the magnetic phase diagram are planned to elucidate this behavior further. Such strong DMI together with previously observed easy-plane-type antiferromagnetism further places the hybrid organic cobalt-halide semiconductors on the list of potential solution-processable layered materials for spintronic applications.^{15,24,50}

The anisotropy within the Co-halide tetrahedra is another important aspect governing the magnetic order. From the SCXRD results, we find that the Co–Br tetrahedra exhibit minimal distortion, with averaged angular deviations from the ideal bond angle of 109.5° of 1.45° for (R)-3ClMBA₂CoBr₄ and 1.55° for MA₂CoBr₄. This distortion increases for the Co–Cl tetrahedra, reaching 1.73° in (R)-3BrMBA₂CoCl₄, and culminates in the Co–I tetrahedra, where the distortion is 1.99° for PEA₂CoI₄ and peaks at 3.51° for (R)-3BrMBA₂CoI₄, which exhibits the highest magnetic susceptibility. The distortion of the tetrahedra lifts the degeneracy of the e and t₂ orbitals,⁵¹ modifying the orbital angular momentum contribution to the magnetic moment and influencing the magnetic anisotropy—an effect well-documented in tetrahedral CoX₄^{2–} systems.⁵² The increasing distortion from Br- to I-

based compounds correlates with the emergence of canted antiferromagnetism, suggesting a strong link among the ligand field strength, spin–orbit coupling, and the antisymmetric exchange interactions. While variable-temperature structural studies are beyond the scope of the current work, the continuous nature of the magnetic susceptibility curves suggests that no major structural phase transitions occur across the measured temperature range. Future temperature-dependent diffraction experiments would provide direct confirmation of the structural stability.

Ultrafast Transient Magneto-Optical Photophysics

Next, we investigate the optical features of the synthesized cobalt halides. Like for hybrid metal-halide perovskite materials,¹³ we obtained color-tunable single crystals (R)-3Br/ClMBA₂CoX₄ from blue (X = Cl) to dark blue (X = Br) and to green (X = I) by changing the halide compositions (Figure 1(a–c)), indicating energy shifts in their optical transitions. To study the origin of this behavior, we dissolved as-synthesized single crystals in *N,N*-dimethylformamide (DMF) solvent to fabricate spin-coated thin films (details in the Materials and Methods section). Steady-state absorption spectroscopy measurements show that (R)-3Br/ClMBA₂CoX₄ (X = Cl, Br, or I) films have a dominant broad absorption feature in the range 600 to 850 nm (Figure S6), which we attribute to cobalt d–d transitions. These d–d transitions are highly sensitive to the local coordination environment of Co²⁺, and the presence of sharp, well-defined features confirms that the CoX₄^{2–} tetrahedra remain intact and are properly coordinated in the films. Further, all film preparation and measurements were performed under a strict inert atmosphere (N₂-filled glovebox), and the UV–vis spectra showed no additional features that would indicate decomposition or formation of secondary phases. We found these optical transitions shift spectrally with halide composition, moving increasingly toward longer wavelengths from Cl to Br to I. Additionally, the relative intensities of the different d–d transitions change with the halide composition. Both observations can be rationalized by the impact of ligand field strengths, which depend on the metal-halide tetrahedral geometry. Differently sized halides result in variations of the tetrahedral distortion which lead to relative shifts in the electronic structure of the e and t₂ sets of orbitals.⁵¹ More importantly, we find high-energy optical transitions at ~ 400 nm for (R)-3BrMBA₂CoI₄, and at ~ 320 nm for (R)-3ClMBA₂CoBr₄ films. For the (R)-3BrMBA₂CoCl₄ samples, the position of these optical transitions is further moved to <290 nm, beyond our detection limit. These systematic blue-shifts with changing halide composition (I to Br to Cl) follow the trend expected for increasing ligand field strength and widening band gaps, consistent with typical semiconductor behavior in metal-halide materials. The observed transitions can be interpreted as signatures of the fundamental band-to-band transitions or charge-transfer excitations that define the semiconducting gap. Previous reports have attributed such high-energy features in related cobalt halide systems to band transitions arising from more delocalized “bandlike” states extending across multiple tetrahedral units, rather than being confined to individual metal centers.^{53,54} These assignments are supported by computational studies on analogous hybrid metal-halide systems, where the conduction band minimum typically derives from metal orbitals with some halide contribution, while the valence band maximum is dominated

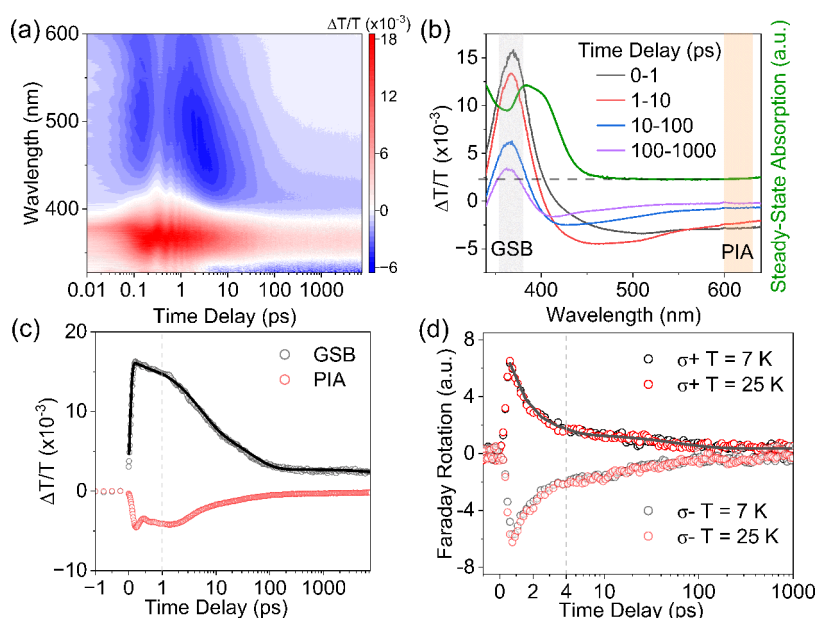


Figure 3. Time-resolved magneto-optical properties of (R)-3BrMBA₂CoI₄. Transient absorption (TA) spectroscopy color maps (a), spectra (b), and kinetics (c) of (R)-3BrMBA₂CoI₄ thin films. TA measurements were performed under 300 nm excitations with a fluence of $\sim 70 \mu\text{J}/\text{cm}^2$. Transient Faraday rotation measurement of (R)-3BrMBA₂CoI₄ at $T = 7 \text{ K}$ and $T = 25 \text{ K}$ (d), pumped at 343 nm and probed at 700 nm for the two opposite helicities of the pump denoted by $\sigma+$ and $\sigma-$.

by halide p-orbitals hybridized with metal d-states. While detailed band structure calculations (e.g., DFT) are beyond the scope of the current experimental work, the systematic optical data presented here provide strong evidence of the semiconducting nature of these hybrid cobalt-halide compounds and establish a foundation for future theoretical investigations.

Circular dichroism (CD) measurements (Figure S6(b)) on (R)-3Br/CIMBA₂CoX₄ ($X = \text{Cl}, \text{Br}, \text{or I}$) thin films show Gaussian-shaped optical activity with obvious Cotton effect near the wavelengths of the high-energy “bandlike” transitions, while no CD signals are observed at the d–d transition regions. This suggests that the chirality transfer happens from the chiral organic cations to delocalized states across hybrid cobalt halide tetrahedra rather than to the cobalt d–d orbitals. From previous reported work,^{12,13,20,24} we know the pure organic cations (MBA-based) exhibit CD signals only below 300 nm, with no detectable optical activity in the region above 300 nm where our hybrid cobalt halide samples absorb. Thus, the observed CD signals must originate from the hybrid cobalt halide framework itself and not from the organic cations alone.

To study the photophysics of the hybrid organic–inorganic cobalt halide samples, we focus our investigation on (R)-3BrMBA₂CoI₄ films, which show metal-to-ligand charge-transfer (MLCT) states in the spectral range of our optical setup. We investigate the photoexcited state population dynamics with broad-band TA spectroscopy. Using femto-second pulses at a wavelength of 300 nm with a fluence of $\sim 70 \mu\text{J}/\text{cm}^2$ for excitation, we probe the ensuing optical TA response in (R)-3BrMBA₂CoI₄ films with broad-band white-light probe pulses. We observe a ground state bleach (GSB) signal located at $\sim 370 \text{ nm}$ (Figure 3 (a)) and a broad photoinduced absorption (PIA) signal (400–600 nm). The GSB is close to the optical transitions that we have detected in steady-state absorption (Figure 3(b)). We find that the dominant GSB signal quickly decays and levels out within the first $\sim 100 \text{ ps}$ (Figure 3(b),(c)). Within this regime, the signal can be qualitatively fitted with a biexponential decay

function with corresponding lifetimes of $\tau_1 \approx 5 \text{ ps}$, and $\tau_2 \approx 44 \text{ ps}$. Beyond a time delay of 100 ps, the signal shows no further detectable evolution up to the end of our probe range, indicating nano- to microsecond decay kinetics. The PIA signal shows an initial peak, which could stem from hot carriers, followed by a rise up to 1.5 ps, suggesting the fast population of a photoinduced state from the initially photoexcited levels.

To probe the excited-state spin dynamics, we performed transient Faraday rotation measurements at cryogenic temperatures. Control measurements at room temperature show a negligible signal. Although the material’s ordering temperature $T_{\text{CA}} = 2.2 \text{ K}$ lies below the base temperature of our magneto-optical cryostat (around 7 K), cooperative magnetic interactions, evident from deviations from Curie–Weiss behavior, emerge already around 25 K, prompting measurements at both 7 and 25 K to explore potential coupling between developing magnetic order and spins of photoexcited states. As shown in Figure 3d, the transient Faraday response for opposite pump helicities is mirrored and no significant differences are observed between the two temperatures. Importantly, the Faraday decay curves last longer than 1 ns, indicating the ultralong spin lifetime in our hybrid cobalt compounds. We further fit the decay dynamics by a biexponential model, with components $\tau_1 \approx 1 \text{ ps}$ and $\tau_2 \approx 60 \text{ ps}$. Thus, the spin lifetime observed in our hybrid cobalt compounds far exceeds typical spin lifetimes of related low-dimensional hybrid metal-halide materials,^{55–57} suggesting that moderate Co-induced spin–orbit coupling, which acts directly on the magnetically active d-orbitals,^{58–60} enables efficient optical spin injection while rapid spin relaxation is suppressed. In future work, accessing temperatures below T_{CA} will be essential to elucidate the expected interactions between fully ordered localized spins in magnetic phases and photoexcited spins.

CONCLUSION

In summary, we synthesized and characterized a series of hybrid organic–inorganic cobalt halide semiconductor magnets. Magnetic characterization reveals cooperative antiferromagnetic ordering across all compounds, with (R)-3BrMBA₂CoI₄ exhibiting sizable spontaneous magnetization in the canted antiferromagnetic ground state. Our findings underscore the potential of hybrid cobalt halides as model systems for investigating the interplay among structures, low-dimensional magnetism, and optically accessible spin-polarized states. The easy-plane-type antiferromagnetism and possible strong DMI furthermore suggest their potential for spintronics applications. Further investigation, particularly comparing the chiral enantiomers and racemic mixtures, neutron scattering, and advanced theoretical modeling, will be essential to fully elucidate the effects of structural distortion, the rich spin textures, and anisotropies present. More broadly, our work highlights the promise of hybrid organic–inorganic systems for exploring emergent phenomena at the nexus of structure symmetry, quantum magnetism, and excited-state spin physics and motivates future studies leveraging optical and magnetic probes at ultralow temperatures in these tunable platforms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.6c00755>.

Experimental details of synthesis and characterization, crystallographic data, structure distortion calculation, magnetic characterization, and absorption and CD spectra (PDF)

Accession Codes

Deposition Numbers 2481379–2481382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe [Access Structures service](#).

AUTHOR INFORMATION

Corresponding Author

Felix Deschler – *Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*; Email: deschler@uni-heidelberg.de

Authors

Shangpu Liu – *Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*; *Walter Schottky Institut and Physics Department, TUM School of Natural Sciences, Technische Universität München, 85748 Garching, Germany*; orcid.org/0000-0001-9067-7098

Jonathan Zerhoch – *Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*; *Walter Schottky Institut and Physics Department, TUM School of Natural Sciences, Technische Universität München, 85748 Garching, Germany*; orcid.org/0000-0003-4336-8828

Stanislav Bodnar – *Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*; *Walter Schottky Institut and Physics Department, TUM School of Natural Sciences, Technische Universität München, 85748 Garching, Germany*

Julia A. Gessner – *Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*

Luca Bischof – *Kirchhoff Institut für Physik, Universität Heidelberg, 69120 Heidelberg, Germany*

Jan Arneith – *Kirchhoff Institut für Physik, Universität Heidelberg, 69120 Heidelberg, Germany*; orcid.org/0000-0002-1527-8449

Franz Bodenmüller – *Physikalisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*

Joachim Ballmann – *Anorganisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*; orcid.org/0000-0001-6431-4197

Frank Rominger – *Organisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany*

Rüdiger Klingeler – *Kirchhoff Institut für Physik, Universität Heidelberg, 69120 Heidelberg, Germany*

Complete contact information is available at:

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Author Contributions

*S.L. and J.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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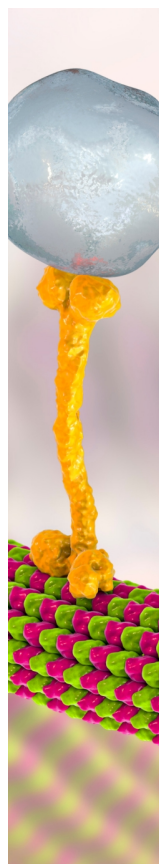
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