

Supporting Information

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

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Table S1. Crystallographic data for (R)-3ClMBA₂CoBr₄, (R)-3BrMBA₂CoI₄, (R)-3BrMBA₂CoCl₄ and PEA₂CoI₄.

	(R)-3ClMBA ₂ CoBr ₄	(R)-3BrMBA ₂ CoI ₄	(R)-3BrMBA ₂ CoCl ₄	PEA ₂ CoI ₄
Empirical Formula	C ₁₆ H ₂₂ Br ₄ Cl ₂ CoN ₂	C ₁₆ H ₂₂ Br ₂ CoI ₄ N ₂ O	C ₁₆ H ₂₂ Cl ₄ Br ₂ CoN ₂	C ₁₆ H ₂₄ CoI ₄ N ₂
Temperature, K	200	200	120	200
Formula Weight, g/mol	691.82	984.70	602.89	809.89
Crystal System	monoclinic	hexagonal	monoclinic	monoclinic
Space group	P2 ₁	P6 ₁	P2 ₁	P2 ₁ /c
a, Å	10.9869(8)	8.0853(3)	10.6376(3)	8.1363(2)
b, Å	7.7466(6)	8.0853(3)	7.2514(2)	26.6813(6)
c, Å	14.4257(11)	72.775(5)	15.9487(4)	10.7773(2)
α, °	90	90	90	90
β, °	105.2165(16)	90	109.160(3)	90.1601(12)
γ, °	90	120	90	90
Volume, Å ³	1184.74(16)	4120.1(4)	1162.09(6)	2339.60(9)
Z	2	6	2	4
Density (calculated), g/cm ³	1.94	2.38	1.72	2.30
Absorption coefficient, mm ⁻¹	7.70	43.67	14.07	6.01
F(000)	664	2694	594	1492
Radiation	MoK _α (λ = 0.71073)	MoK _α (λ = 0.71073)	CuK _α (λ = 1.54184)	MoK _α (λ = 0.71073)
2θ range for data collection, °	1.5 to 29.3	3.6 to 68.7	8.8 to 142.716	2.0 to 27.5

Reflections collected	23012	23067	16317	26171
Independent reflections	5919 [$R_{\text{int}} = 0.0779$]	4904 [$R_{\text{int}} = 0.1265$]	4445	5396 [$R_{\text{int}} = 0.0505$]
Data/restraints/parameters	5919/1/238	4904/290/211	4445/408/369	5396/0/216
Goodness of fit on F^2	0.98	1.84	1.026	1.05
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.043$, $wR_2 = 0.056$	$R_1 = 0.112$, $wR_2 = 0.289$	$R_1 = 0.0409$, $wR_2 = 0.1054$	$R_1 = 0.037$, $wR_2 = 0.070$
Flack parameter	0.015	0.73	-0.040	/
CCDC number	2481379	2481380	2481382	2481381

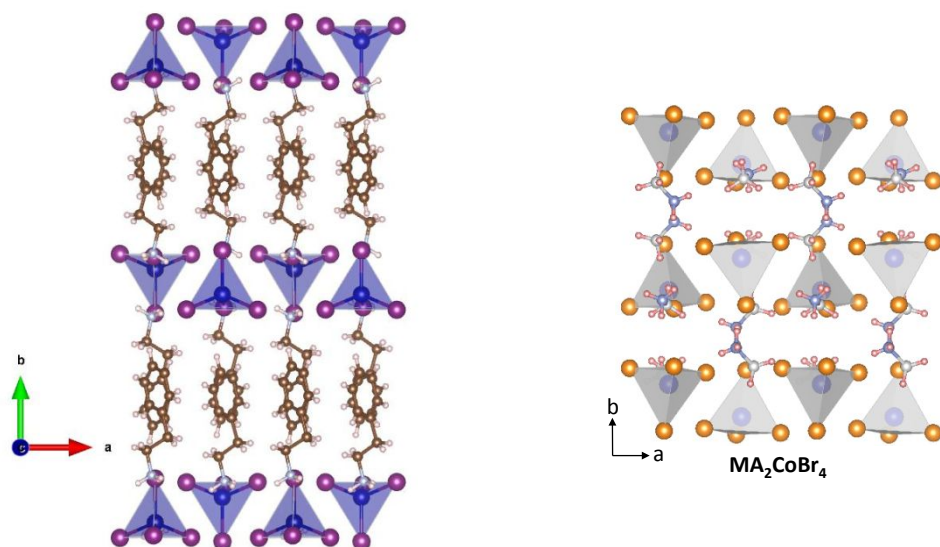


Fig. S1. crystal structures derived from SCXRD measurements of PEA₂CoI₄ (a) and MA₂CoBr₄ (b). Crystal structure of (b) was taken from.¹

Table S2. Average Co lattice distance, H bond angle and distance values in (R)-3BrMBA₂CoI₄, PEA₂CoI₄, (R)-3ClMBA₂CoBr₄, (R)-3BrMBA₂CoCl₄ and MA₂CoBr₄. The data are collected from single-crystal XRD measurement results.

Hybrid cobalt halide materials	Average lattice distance (Å)			N-H-X Angle (X = Cl, Br, I)	N-H-X bond length (Å) (X = Cl, Br, I)
(R)-3BrMBA ₂ CoI ₄	12.13	4.05	4.05	137°, 151°	2.76(12),
	(001)	(100)	(010)	162°, 171°	2.71(10)
PEA ₂ CoI ₄	13.30	5.40	3.59	143°, 173°	2.74(6),
	(010)	(001)	(100)		2.72(5)
(R)-3ClMBA ₂ CoBr ₄	14.43	5.50	3.87	151°, 161°	2.48(4),
	(001)	(100)	(010)	175°, 177°	2.45(4)
(R)-3BrMBA ₂ CoCl ₄	15.10	5.05	3.60	154°, 159°	2.32(18),
	(001)	(100)	(010)	164°, 178°	2.38(19)
MA ₂ CoBr ₄	6.50	5.60	3.98	148°, 173°	2.54(10),
	(010)	(001)	(100)		2.58(11)

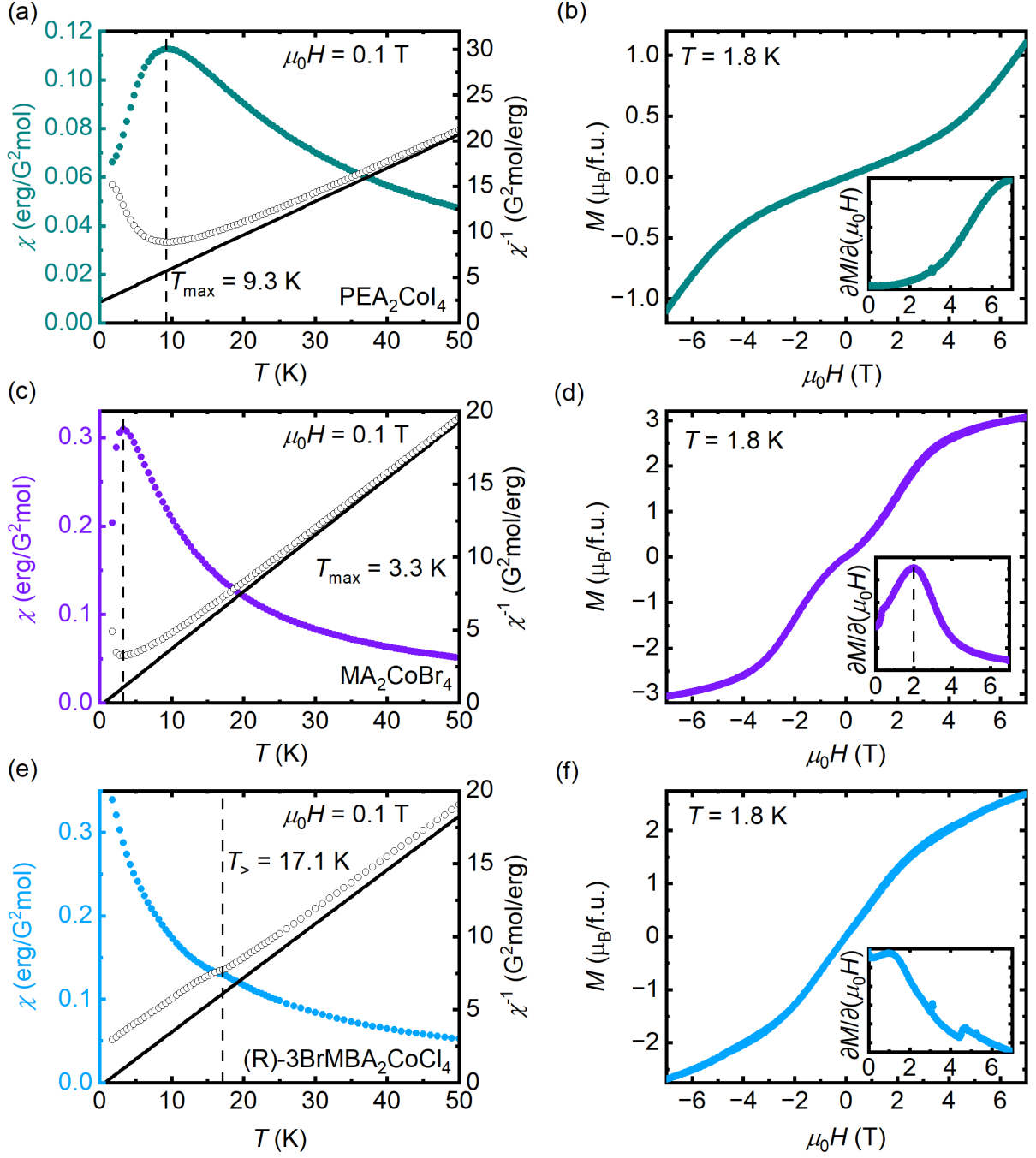


Fig. S2. Magnetic characterization of PEA_2CoI_4 (a, b), MA_2CoBr_4 (c, d) and $(\text{R})\text{-3BrMBA}_2\text{CoCl}_4$ (e, f). (a, c, e) Static magnetic susceptibility $\chi = M/(\mu_0 H)$ (coloured dots and left axis) as a function of the temperature T in presence of an external magnetic field $\mu_0 H = 0.1$ T measured after cooling in zero magnetic field, and its inverse χ^{-1} with a Curie-Weiss-like model (right axis) fitted in the temperature ranges (a) 230 K to 300 K and (c,e) 200 K to 300 K, respectively. (b, d, f) Magnetization M as a function of the external magnetic field $\mu_0 H$ at $T = 1.8$ K. Bottom right insets show the differential magnetic susceptibility $\partial M / \partial (\mu_0 H)$.

Table S3. Summarized magnetic properties of (R)-3BrMBA₂CoI₄, PEA₂CoI₄, (R)-3ClMBA₂CoBr₄, (R)-3BrMBA₂CoCl₄ and MA₂CoBr₄. Results of Curie-Weiss-like fits in the temperature range 200 K to 300 K (230 K to 300 K for PEA₂CoI₄) and positions of characteristic anomalies in temperature-dependent susceptibility and isothermal magnetization are collected. Errors given for θ_W denote the statistical uncertainty of the fits but do not include the effect of a varied temperature range for fitting, which significantly affects the fit result for θ_W .

Hybrid Cobalt Halide Materials	Curie-Weiss Fit	Characteristic	Critical
	C (ergK/G ² mol), θ_W (K), $ \chi_0 $ (erg/G ² mol)	Temperature (K)	Field (T)
(R)-3BrMBA ₂ CoI ₄	2.31(10), -1.3(6), $< 4 \times 10^{-4}$	$T_{cA} = 2.2$	0.25, 3.1
PEA ₂ CoI ₄	2.7(1), -6(2), $< 3 \times 10^{-4}$	$T_{\max} = 9.3$	> 7
(R)-3ClMBA ₂ CoBr ₄	$\perp$: 2.3(2), 3(2), $< 1 \times 10^{-4}$ $\parallel$: 2.5(2), 3.3(12), $< 6 \times 10^{-3}$	$T_{\max} = 4.4$	2.9 5
(R)-3BrMBA ₂ CoCl ₄	2.7(1), 1(1), $< 5 \times 10^{-4}$	$T_{\gamma} = 17.1$	1, 4.7
MA ₂ CoBr ₄	2.54(4), 0.6(3), $< 6 \times 10^{-4}$	$T_{\max} = 3.3$	2

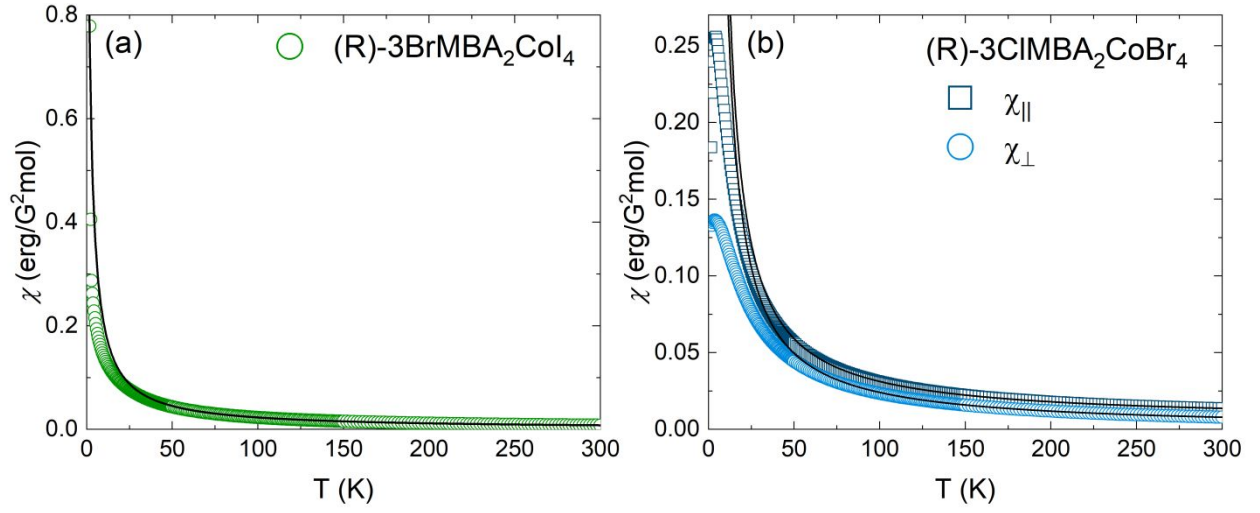


Fig. S3. Magnetic susceptibility at $\mu_0 H = 0.1$ T and Curie-Weiss like fit of (a) (R)-3BrMBA₂CoI₄ and (b) (R)-3ClMBA₂CoBr₄. The fits were performed in the temperature range from 200 K to 300 K.

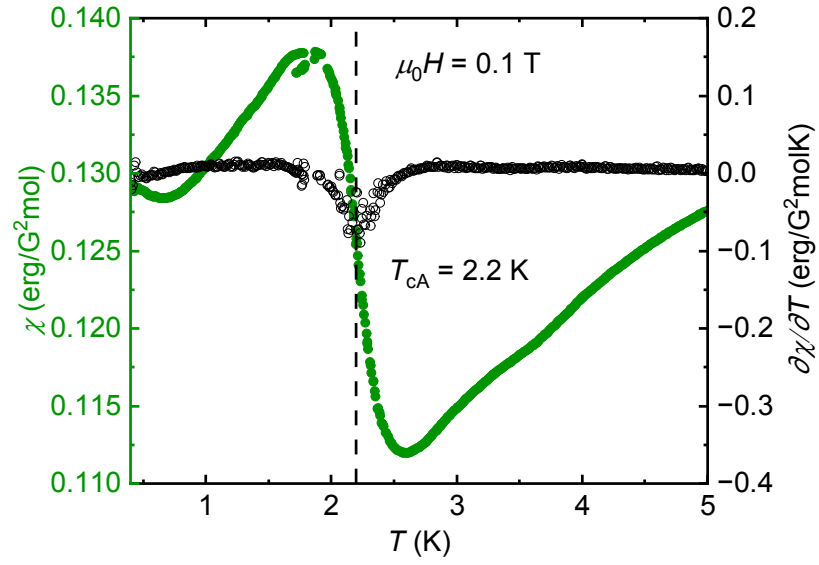


Fig. S4. Static magnetic susceptibility χ of (R)-3BrMBA₂CoI₄ at low temperatures in presence of an external magnetic field $\mu_0 H = 0.1$ T. The measurement was performed after field-cooling to $T = 400$ mK. Quantitatively this data does not match the data presented in Figure 2 of the main text which can be explained by temperature cycling induced degradation of the sample. This effect was observed in consecutive measurements on the same sample that was going through temperature cycles. Nevertheless, the sudden increase of the magnetization which was discussed in the main text can here be qualitatively observed, too. This allows us to determine the ordering temperature to $T_{\text{cA}} = 2.2$ K.

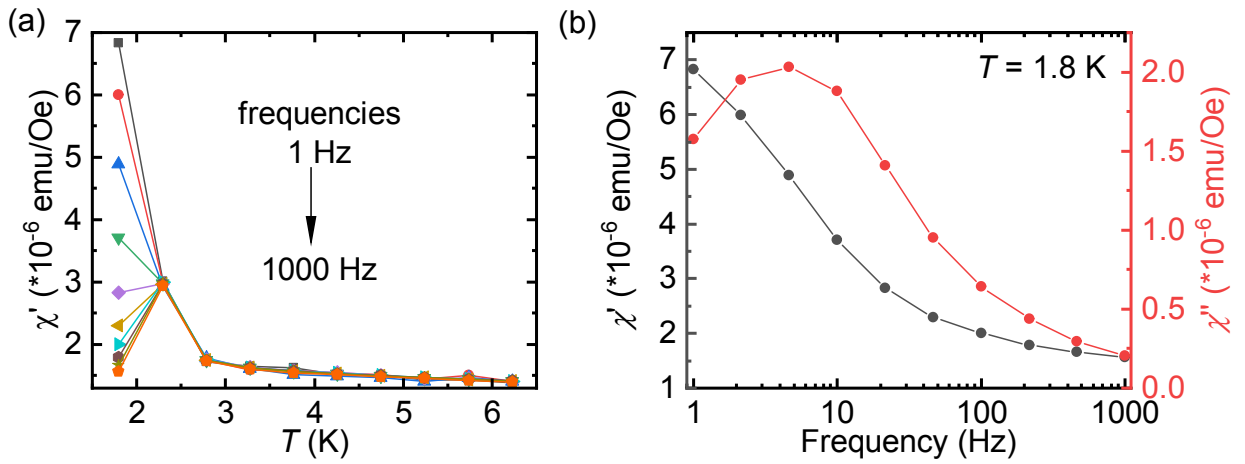


Fig. S5. AC susceptibility data of (R)-3BrMBA₂CoI₄. (a) In-phase χ' component of the AC susceptibility as a function of temperature at zero DC field, $H_{ac} = 1$ Oe, and for ten AC field frequencies ranging from 1 Hz to 1000 Hz in logarithmically equidistant steps. (b) In-phase χ' and out-of-phase χ'' component of the AC susceptibility as a function of the frequency of the AC field at $T = 1.8$ K.

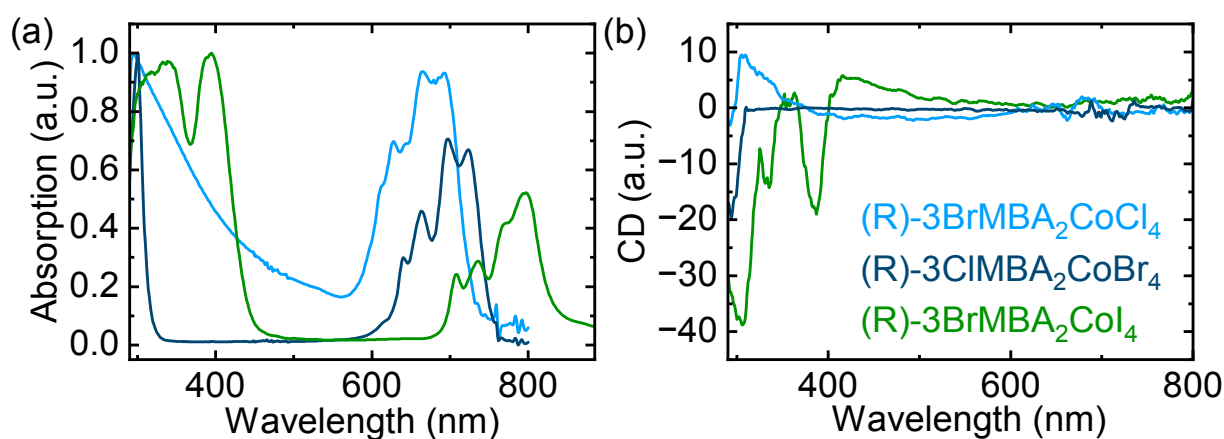


Fig. S6. Steady-state room temperature UV-Vis Absorption (a) and CD measurements of spin-coated films of (R)-3BrMBA₂CoI₄, (R)-3ClMBA₂CoBr₄ and (R)-3BrMBA₂CoCl₄.

References

- (1) Babu, R.; Vardhaman, A. K.; Dhavale, V. M.; Giribabu, L.; Singh, S. P. MA₂CoBr₄: Lead-Free Cobalt-Based Perovskite for Electrochemical Conversion of Water to Oxygen. *Chem. Commun.* **2019**, 55 (47), 6779–6782. <https://doi.org/10.1039/c9cc00878k>.