



Structural and Physical Properties of Two Distinct 2D Lead Halides with Intercalated Cu(II)

Journal:	<i>Journal of Materials Chemistry C</i>
Manuscript ID	TC-ART-04-2024-001322.R1
Article Type:	Paper
Date Submitted by the Author:	28-May-2024
Complete List of Authors:	Parashar, Kanika; University of Oklahoma, Department of Chemistry & Biochemistry Zhang, Zheng; Tulane University, Chemistry Buturlim, Volodymyr; Idaho National Laboratory, Glenn T. Seaborg Institute Jiang, Jie; Air Force Research Laboratory, Materials & Manufacturing Directorate Roseborough, Alexander; Oregon State University Nyman, May; Oregon State University, Chemistry Gofryk, Krzysztof; Idaho National Laboratory Pachter, Ruth; Air Force Research Laboratory, Materials & Manufacturing Directorate Saparov, Bayram; University of Oklahoma, Department of Chemistry & Biochemistry

Structural and Physical Properties of Two Distinct 2D Lead Halides with Intercalated Cu(II)

Kanika Parashar^a, Zheng Zhang^b, Volodymyr Buturlim^c, Jie Jiang^d, Alexander Roseborough^e, May Nyman^e, Krzysztof Gofryk^c, Ruth Pachter^d, Bayram Saparov^{a*}

^aDepartment of Chemistry & Biochemistry, The University of Oklahoma, Norman, Oklahoma 73019-5251, United States

^bDepartment of Chemistry, Tulane University, New Orleans, Louisiana 70118, United States

^cGlenn T. Seaborg Institute, Idaho National Laboratory, Idaho Falls, ID 83415, USA

^dMaterials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433, USA

^eDepartment of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA

*Author to whom correspondence should be addressed: saparov@ou.edu

Abstract: Transition metal cation intercalation between the layers of two-dimensional (2D) metal halides is an underexplored research area. In this work we focus on the synthesis and physical property characterizations of two layered hybrid lead halides: a new compound $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and the previously reported $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. These compounds exhibit 2D layered crystal structures with incorporated Cu^{2+} between the metal halide layers, which is achieved by combining Cu(II) and lead bromide with suitable amino acid precursors. The resultant $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ adopts a 2D layered perovskite structure, whereas the new compound $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ crystallizes with a new structure type based on edge-sharing dodecahedral PbBr_5O_3 building blocks. $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ is a semiconductor with a bandgap of 3.25 eV. It shows anisotropic charge transport properties with a semiconductor resistivity of $1.44 \times 10^{10} \Omega \cdot \text{cm}$ (measured along the *a*-axis) and $2.17 \times 10^{10} \Omega \cdot \text{cm}$ (along the *bc*-plane), respectively. The fabricated prototype detector based on this material showed response to soft low-energy X-rays at 8 keV with a detector sensitivity of $1462.7 \mu\text{CGy}^{-1}\text{cm}^{-2}$, indicating its potential application for ionizing radiation detection. These encouraging results are discussed together with the results from density functional theory calculations, optical, magnetic, and thermal property characterization experiments.

Keywords: Halide perovskites, semiconductor, copper(II) halide, lead(II) halide, X-ray detection, 2D layered materials

1. Introduction

Hybrid organic-inorganic metal halides have been developed as novel functional materials that possess excellent structural versatility and outstanding optoelectronic properties enabling their use in solar energy harvesting,¹ light emitting diodes (LEDs)² and radiation detection.³ Through the selection of suitable organic cations and metal halide anions, crystalline ionically-bonded hybrid materials can be obtained with varied structures other than the commonly known ABX₃ perovskites. These hybrid materials with different and unique structures show interesting new properties that offers great potential for practical applications.⁴

Recent scientific research aims to controllably alter the structures of hybrid metal halides from 3D structures (e.g., for halide perovskites) to lower dimensional (0-2D) structures at both morphological and molecular levels. Among these, due to the enhanced stability of 2D and quasi-2D metal halide perovskites and closeness to their 3D parents, there has been a continued interest in 2D perovskites research.⁵ Various studies have shown that the characteristics of incorporated organic cations such as sizes, shapes, electronic properties, and dielectric constants,^{6, 7} can significantly impact the overall properties of layered hybrid materials. Another possible strategy to expand the chemistry of 2D layered perovskites is through the intercalation of transition metal ions in between the layers. Beyond discovery of new materials systems, this strategy could provide some additional benefits, e.g., intercalation could result in the formation of covalent network between the layers stitching one layer to the adjacent one, thereby enhancing their structural stability (due to presence of stronger covalent bonds) and charge transport properties (due to the quasi-3D structures of the intercalated materials). However, there are very few reports of successful intercalation of transition metals into layered halide structures. For example, a compound [Cu(O₂C-(CH₂)₃-NH₃)₂]₂PbBr₄ featuring intercalated Cu²⁺ ions has been reported.⁸ In this case 4-aminobutyric acid was used to enable the Cu²⁺ intercalation; zwitterionic amino based molecules are bifunctional entities and can serve as anchors for the metal halide layer through their cationic amino functional group, whereas their anionic segment can form metal complexes with the incorporated metal ion.⁹ A recent study¹⁰ suggests that [Cu(O₂C-(CH₂)₃-NH₃)₂]₂PbBr₄ is a candidate for sensitive and stable X-ray detectors, which indicates exciting new possibilities made possible through the expansion of 2D metal halide family. However, transition metal intercalation strategy has not yet been expanded beyond this sole example.

This work reports the preparation, crystal and electronic structures and physical properties of a new compound [Cu(O₂C-CH₂-NH₂)₂]₂Pb₂Br₄ featuring intercalated Cu²⁺ ions. The new compound contains non-perovskite layers sandwiched by a glycine-based layer containing the Cu²⁺ ions. The obtained characterization results for [Cu(O₂C-CH₂-NH₂)₂]₂Pb₂Br₄ are compared to that of [Cu(O₂C-(CH₂)₃-NH₃)₂]₂PbBr₄.

2. Experimental Section

2.1. Materials

All chemicals were obtained commercially and were used as received without any further purification: Copper(II) bromide (>99%, Alfa Aesar), lead(II) bromide (99.98%, Alfa Aesar), glycine (≥98.5%, Sigma Aldrich), 4-aminobutyric acid (>99%, TCI America) and HBr (48 wt% in water, Sigma Aldrich). Unless specified otherwise, all synthesis procedures were carried out in a fume hood under ambient air conditions.

2.2. Synthesis of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$

2.2.1. Single crystal growth via slow evaporation method

Glycine (0.0491g) and CuBr_2 (0.0730g) were added to form 10mL of clear blue aqueous solution. In the next step, a small amount of PbBr_2 (0.01137g) and 20 μL of HBr acid were added, resulting in the complete dissolution of reactants. The precursor solution was left for slow evaporation at room temperature for a period of 20 days till the complete evaporation of solvent. After the complete evaporation, air-stable dark blue crystals ($\sim 1 \times 1 \times 1 \text{ mm}^3$) were formed and were collected for further use. Additional reactions were conducted with controlled pH to reach the isoelectronic point of glycine, aiming to promote the presence of only the zwitterionic form. In all cases, dark blue crystals of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ were obtained.

2.2.2. Single crystal growth via evaporation on heating

PbBr_2 (0.01137g) was mixed into a 10 mL aqueous solution of glycine (0.0491g) and CuBr_2 (0.0730g) under ambient air conditions. Then, 20 μL of concentrated HBr was further added, producing a clear solution. The clear precursor solution was then subjected to evaporation at 40°C over a period of one week. Following the complete evaporation, air-stable dark blue crystals of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ measuring approximately $1 \times 1 \times 1 \text{ mm}^3$ were obtained. These crystals were collected and subsequently washed with acetonitrile.

2.2.3. Single crystal growth via vapor diffusion

Stoichiometric amounts of glycine (0.0491g) and CuBr_2 (0.0730g) were dissolved in 10mL of water at room temperature. Subsequently, 20 μL of concentrated HBr was added together with PbBr_2 (0.01137g) to produce a clear solution. For crystal growth, 2mL of precursor solution was placed in a sealed container, and 1.5 mL of diethyl ether was diffused into it in a period of one week at room temperature. This procedure produced dark blue crystals ($< 1 \text{ mm}$ on all sides). These crystals were washed with acetonitrile and dried at room temperature. For further characterizations, the crystals were stored under ambient conditions.

2.2.4. Single crystal growth via slow cooling

Glycine (0.0491g) and CuBr_2 (0.0730g) were added in 3mL of water to form a saturated solution. 6 μL of concentrated HBr was added to this solution under a continuous flow of N_2 . A small amount of PbBr_2 (0.01137g) was then dissolved while stirring and keeping the solution at 80°C . The clear precursor solution was then allowed to cool to room temperature over a period of 48 hours. The resultant dark blue crystals of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ of approximately $1 \times 1 \times 1 \text{ mm}^3$ dimensions were collected and stored for further use.

2.2.5. Single crystal growth via liquid-liquid diffusion

A clear precursor solution was prepared at room temperature by using stoichiometric amounts of glycine (0.0491g) and CuBr_2 (0.0730g) in 10mL of water. A small amount of concentrated HBr (20 μL) and PbBr_2 (0.01137g) were then added in the solution. In the next step, the clear precursor solution was divided into four separate vials to facilitate the crystal growth. In each vial, 2mL of precursor solution and 1mL of a secondary solvent (isopropanol, diethyl ether, acetonitrile, and methanol) were added. The added solvents diffused into the solution over a period of one week. This method yielded air-stable blue

crystals, measuring up to $(2 \times 1 \times 0.2)$ mm³ in size. These crystals were collected and stored under the ambient air for further use.

2.3. Synthesis of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_2)_2]\text{PbBr}_4$

2.3.1. Single crystal growth via slow evaporation method

4-amino butyric acid (0.0675g) and CuBr_2 (0.0730g) were added in 10 mL of water to prepare a light blue solution. A small amount of concentrated HBr (20 μL) was added to maintain the zwitterionic state of 4-amino butyric acid ($^-\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3^+$). Then, 0.01137g of PbBr_2 was further added, leading to clear blue solution. The resultant solution was then left for slow evaporation at room temperature for a period of 20 days. Air-stable blue-green crystals of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ were collected and stored for further utilization.

2.3.2. Single crystal growth via evaporation on heating

A 10mL aqueous solution containing 4-amino butyric acid (0.0675g), CuBr_2 (0.0730g) and PbBr_2 (0.01137g) was prepared at room temperature. After addition of 20 μL of concentrated HBr, a clear blue solution was obtained which was left for evaporation at 40 °C over a period of one week. Following the complete evaporation of solvent, plate like blue-green crystals of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ with approximate dimensions of $(2 \times 1 \times 0.5)$ mm³ were obtained. The obtained crystals were washed with acetonitrile and stored under room temperature for further use.

2.3.3. Single crystal growth via slow cooling

A saturated solution of 4-amino butyric acid (0.0675g) and CuBr_2 (0.0730g) was prepared in 3mL of water. Then, 6 μL of concentrated HBr was added to the solution under a continuous flow of N_2 gas. A small amount of PbBr_2 (0.01137g) was added to the solution with continuous stirring by keeping it at a temperature of 80 °C for a complete dissolution. The resultant solution was allowed to cool down to room temperature over a period of 48 hours, resulting in the formation of blue-green crystals with approximate dimensions of $(1 \times 3 \times 1)$ mm³. These crystals were filtered and stored under ambient conditions for further use.

2.4. Synthesis of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ single crystals

For the synthesis of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ single crystals, 36.7mg of PbBr_2 and 40.42 mg of as synthesized $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{Br}$ were added into 0.2mL of HBr acid (48 wt% in water). The mixture was heated and was held at 120°C until complete dissolution of all solids. Subsequently, the solution was left for overnight cooling resulting in the precipitation of small white plate-like crystals of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$. These crystals were then collected, rinsed with ethanol, and subjected to overnight drying in a vacuum oven at 60 °C.

2.5. Powder X-ray diffraction (PXRD) measurements

For powder X-ray diffraction (PXRD) measurements, the obtained single crystals were carefully ground in air. PXRD measurements were done using a Rigaku MiniFlex600 system equipped with Cu K α radiation source. PXRD scans were performed in the 3 - 90° (2 θ) range, with a step size of 0.02°. The obtained PXRD patterns were analyzed using the PDXL2 software.

To assess the air-stability of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, their polycrystalline powder samples were placed on a laboratory bench under ambient air conditions (room

temperature of 20 °C and relative humidity of 60%). Then regular PXRD measurements were performed for a period of three months to monitor any changes.

2.6. Single Crystal X-ray diffraction (SCXRD) measurements

For single crystal X-ray diffraction (SCXRD) measurements, a Bruker D8 Quest Kappa-geometry diffractometer equipped with an Incoatec Iμs microfocus Mo Kα X-ray source and a Photon II area detector was utilized. For absorption, the data were corrected using a semi-empirical method based on equivalent reflections. Crystal structures were then determined through intrinsic phasing methods incorporated in the APEX3 v2015.5-2 program. The site occupancy factors were examined by allowing the occupancies of each unique crystallographic position to vary. Table S1 shows the detailed information about the data collection as well as crystallographic parameters for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. Atomic coordinates, equivalent isotropic displacement parameters, selected interatomic distances and bond angles are provided in Tables S2-S5. The Crystallographic Information Files (CIFs) for compounds $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ have been deposited in the Cambridge Crystallographic Data Centre (CCDC) database under deposition numbers 2314262 and 2314263, respectively.

2.7. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements

The TGA and DSC measurements were conducted simultaneously on approximately 10mg samples of compounds $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ by using a TA Instrument SDT 650 thermal analyzer system. The crystalline samples were subjected to heating from 25 °C to 475 °C at a heating rate of 5 °C/min under the continuous flow of N₂ gas at a flow rate of 100 mL/min.

2.8. UV-vis spectroscopy

Finely ground powder samples of corresponding compounds were used for UV-vis diffuse reflectance measurements. The data were obtained using a PerkinElmer Lambda 750 UV-vis-NIR spectrometer equipped with a 100 mm Spectralon InGaAs integrating sphere, covering a range of 250–1100 nm. The obtained diffuse reflectance data were converted to pseudo-absorption spectra using the Kubelka-Munk function $F(R) = \alpha/S = (1-R)^2/2R$, where α represents the absorption coefficient, S is the scattering coefficient, and R denotes the reflectance.

2.9. Density Functional Theory (DFT) calculations

DFT calculations were carried out with the Vienna ab initio simulation package VASP 5.4.^{11, 12} The Kohn-Sham equations are solved using a plane wave basis set with an energy cutoff of 550 eV, and the projector augmented-wave (PAW) potential was applied.¹² A 4×3×3 k -point sampling was used for the unit cells. The crystal structures were optimized using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,¹³ including the D3 correction of Grimme,¹⁴ as inclusion of London dispersion for treating halide perovskites was emphasized,¹⁵ and previously applied.¹⁶ Geometries were fully relaxed regarding lattice parameters and interatomic distances until forces were less than 0.01 eV/Å. Band structures were performed with the hybrid range-separated HSE06 functional.¹⁷

2.10. Electrical and thermodynamic characterizations and X-ray response measurements

For electronic characterizations and X-ray radiation response measurements, a $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ single crystal was selected. High-quality fast drying silver paste (purchased from Ted Pella,

Inc.) was then brushed onto the two opposite sides of the single crystal. Electrical measurements, including current-voltage (I-V) and space-charge-limited-current (SCLC) measurements, were conducted using a Keithley 6487 pico-ammeter (Fig. S1, ESI). The voltage scan for both I-V and SCLC measurements was performed with a step size of 2 V. For X-ray response measurement, the fabricated prototype single crystal-based detector was exposed to 8 keV soft X-rays produced from a Rigaku Micromax 007HF microfocus X-ray generator equipped with a Cu target. The X-ray radiation dose rate was carefully calibrated using a commercial dosimeter. Magnetization and heat capacity were measured using a Quantum Design setup (DynaColl-14) and VSM and HCP options.

2.11. Optical Absorption measurements

A high-resolution PerkinElmer LAMBDA 750 UV-Vis-NIR spectrometer equipped with a 2D detector module was used to collect the UV-Vis absorption spectra of as prepared solutions used for crystal growth. The optical absorption measurements were conducted beyond the UV-vis cutoff of 300 nm for water and HBr mixture.

2.12. Small-Angle X-Ray Scattering (SAXS) studies

Scattering data were collected on an Anton Paar SAXSess instrument using Cu K α radiation (1.54 Å) and line collimation. The instrument was equipped with a 2-D image plate for data collection in the $q = 0.018\text{--}2.5\text{ Å}^{-1}$ range. The low q range was limited to 0.018 Å^{-1} by the beam attenuator. Scattering data of neat water was collected for background subtraction. The sample solutions were concentrated over a steam bath until crystals appeared, then 200 μL of the saturated solutions were syringe filtered and sealed in 1.5 mm glass capillaries (Hampton Research). Scattering data were collected for 30 minutes. SAXSQUANT was used for data collection and treatment (normalization, primary beam removal, background subtraction, desmearing, and smoothing to remove extra noise created by the desmearing routine). SolX was used to simulate scattering data based on the crystal structure.¹⁸

2.13. Electrospray Ionization Mass Spectrometry (ESI-MS) measurements

Mass spectra were collected on an Agilent 6230 time-of-flight (TOF) mass spectrometer coupled to an electrospray ionizer. The capillary, skimmer, RF octopole, and fragmentor voltages were set to 3500, 65, 750, and 200V respectively. Both solutions were diluted with neat water to 0.1mM [Pb] and syringe filtered. The solutions were injected into the ESI-MS system at 0.1mL/min using a syringe pump and then nebulized with the aid of heated N₂ (325°C, 35psi, 8L/min). The data were collected in both the positive (+) and negative (-) modes. Agilent Mass Hunter was used for data collection and processing.

3. Results and Discussion

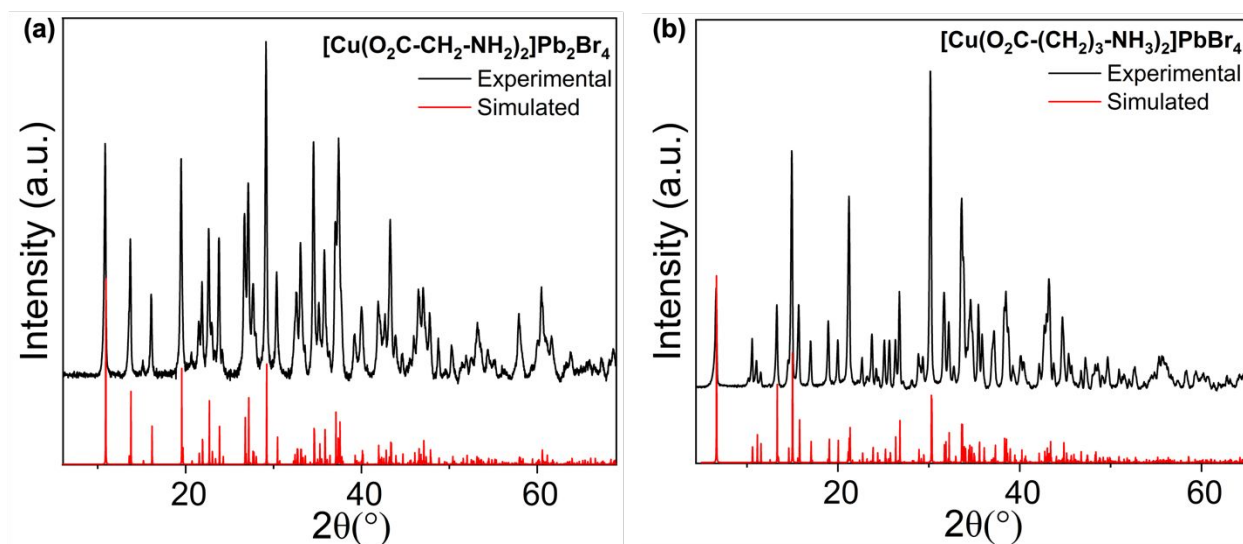


Fig. 1 Powder X-ray diffraction (PXRD) patterns of (a) $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and (b) $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ synthesized via slow evaporation method.

Single crystals of compound $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ can be synthesized through a variety of crystal growth methods: slow evaporation, vapor diffusion, liquid diffusion, evaporation on heating and slow cooling of concentrated solutions (Fig. S2-S3, ESI). In each case, the purity of crystalline products was confirmed through PXRD measurements. The close match observed between the experimental and simulated PXRD confirms the sample purity (Fig. 1). For liquid-liquid diffusion method, a range of four different solvents, isopropanol, acetonitrile, diethyl ether and methanol, were used for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ (Fig. S3, ESI). On the other hand, three distinct solution synthesis methods were used for the crystal growth of compound $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$: slow evaporation, slow cooling of concentrated solutions and evaporation on heating (Fig. S4, ESI). The convenience of using multiple different synthetic approaches could be advantageous for the practical applications of these layered halides (Fig. S5, ESI). The slow evaporation crystal growth method yielded the highest quality crystals (Fig. S6, ESI), all subsequent characterization studies were conducted using the crystals produced by this method.

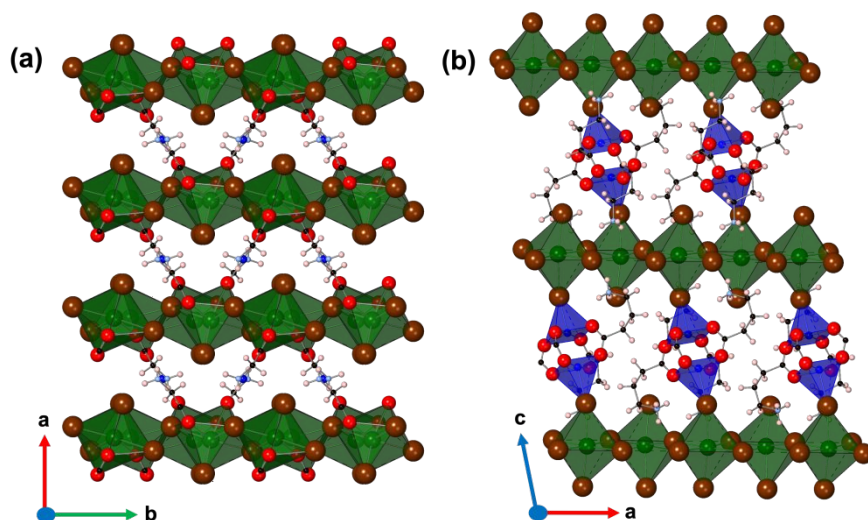


Fig. 2 Crystal structures of (a) $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and (b) $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are depicted. Copper is represented by blue, lead by green, bromine by brown, oxygen by red, nitrogen by cyan, carbon by black and hydrogen by peach spheres.

Both $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ crystallize in the monoclinic crystal system in the centrosymmetric space groups $P2_1/c$ and $P2_1/n$ respectively (Table S1, ESI). The results of SCXRD measurements for these two compounds are summarized in Table S1-S5 (ESI). The obtained crystal data for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ agree with the reported structure.⁸ Remarkably, $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ exhibit distinct crystal structures from the well-known class of 2D lead halide perovskites (Fig. 2). In the case of Ruddlesden–Popper 2D lead bromide perovskites such as $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ ¹⁹ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ ²⁰, the perovskite interlayer space is occupied by a bilayer of organic cations. The structure of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ can be derived from the typical layered perovskite structure through the incorporation of Cu(II), which is enabled by employing the amino acids. The incorporated Cu(II) tethers to the inorganic layer through Cu–Br bonds on each side of the PbBr_4^{2-} perovskite layer. The coordination environment of Cu(II) is further completed by the carboxylate groups of the zwitterions in the form of $\text{Cu}_2(\text{CO}_2)_4$ “paddle-wheel” clusters (Fig. 3), which are commonly found in compounds like hydrated copper acetate, and have been extensively investigated in various copper carboxylate compounds.²¹ The $\text{Cu}_2(\text{CO}_2)_4$ clusters stitch the perovskite layers to the adjacent ones through a series of covalent bonds,²² leading to the pseudo 3D crystal structure of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ (Fig. 2b). Despite the clear differences in the interlayer space, the PbBr_4^{2-} perovskite layers in this compound are identical to that of the other 2D layered perovskites based on the octahedral PbBr_6 building block.

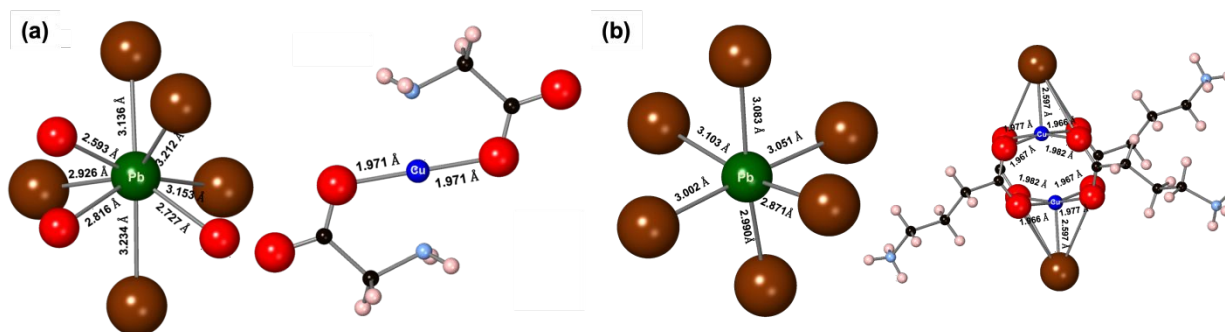


Fig. 3 Coordination environments of metals in (a) $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and (b) $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. Copper, lead, bromine, oxygen, nitrogen, carbon, and hydrogen are represented by blue, green, brown, red, cyan, black, and peach spheres, respectively.

To the best of our knowledge, $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ has a brand-new structure type. In fact, the structure of this compound differs from that of layered halide perovskites and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ both within the inorganic layer and in the “organic interlayer”. The depictions of the coordination environments of lead and copper are shown in Fig. 3. The inorganic lead bromide layer is made of edge-sharing dodecahedral PbBr_5O_3 building blocks in which each lead is coordinated with bromine and oxygen atoms (Fig. 3a). Moreover, the intercalated Cu^{2+} ions in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ form linear complex with the anionic form of glycine, oxygen atoms of which connect to the PbBr_5O_3 units of the lead bromide layers. Thus, there are no direct Cu-Br contacts in the structure of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, instead Cu(II) connects the nearest-neighbor lead bromide layers through the amino acid ligand linkers into a pseudo-3D structure. Important to note, the lead bromide portion of the structure, Pb_2Br_4 , is charge neutral and the Cu coordination cluster, $\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2$ is also charge neutral in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$. These notable differences in the coordination environments of metal cations also result in the marked difference in the distance between adjacent inorganic layers. The interlayer distances (as measured by the distance between Pb atoms in the adjacent layers) for compounds $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are 8.548 Å and 13.311 Å, respectively (Fig. S7, ESI). These values are much shorter than that of 2D lead bromides such as $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$, for which the interlayer distance is determined to be 17.562 Å due to thick organic bilayer in between the perovskite sheets (Fig. S8, ESI). The presence of densely packed inorganic layers may have important implications for the observed physical properties of these compounds such as improved air stability through structural rigidity in the Cu(II) intercalated compounds (owing to their pseudo-3D structural packing) and a greater 3D character of their electronic structures.

To probe if the origin of structural differences between $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ was due to their differing solution chemistries, UV-vis spectroscopy, Electrospray Ionization Mass Spectrometry (ESI-MS) and Small-Angle X-ray scattering (SAXS) measurements were performed on the respective precursor solutions. The results demonstrate the presence of complexes of Cu(II) with both bromide and amino acids as ligands, suggesting that the differences are likely arising during the crystallization stage (see Supplementary Information for more details, Fig. S9-S10 and Tables S6-S8).

To compare the structures and properties of the intercalated compounds with that of the non-intercalated 2D lead halide perovskites, we synthesized the crystals of a known layered perovskite, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$, using a literature reported synthesis procedure (Fig. S11, ESI).¹⁹ $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are found to be stable in ambient air for months (Fig. S12, ESI), whereas $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ shows significant loss of crystallinity in the same time period (Fig. S13, ESI). The enhanced stability of the Cu(II) intercalated compounds is attributed to the network of covalent bonds formed by the incorporated metal ions with the carboxylate groups of amino acids. Furthermore, the pseudo-3D crystal structures of the intercalated compounds with densely packed inorganic layers are likely contributing factors for their improved air stability.

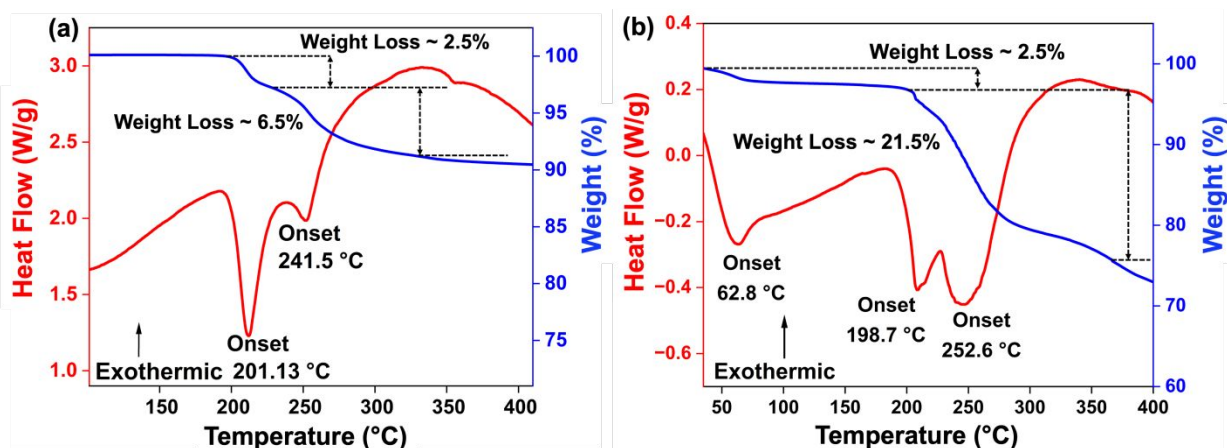


Fig. 4 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) curves for (a) $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and (b) $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$.

To assess the thermal stabilities of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed. The TGA results suggest that $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ undergo multi-step decomposition pathways at elevated temperatures (Fig. 4). The observed weight losses are likely due to the decomposition of the organic structural component, which is typical for hybrid metal halides.^{23, 24} On comparing these results with that of the known halide perovskite $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$, it was observed that $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are less thermally stable. Specifically, $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ demonstrates a significant mass loss beyond 200 °C, while $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ shows a weight reduction of 2.5% even below 100 °C. This finding is in contrast with the results reported in a recent article¹⁰ focused on $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, which claims that the material exhibits no substantial weight loss up to 200 °C. However, our repeated TGA/DSC measurements on different samples of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ reproduced the weight loss observed below 100 °C. A possible explanation for the discrepancy is the fact that the literature reported TGA data¹⁰ does not show the low temperature region below 50 °C where we observe the first weight loss step for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. Notwithstanding this, both the prior and current work shows that $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ decompose above 200 °C with significant weight losses. In comparison, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ shows an approximate weight loss of 48% after reaching 300 °C; this

is attributed to the loss of the organic structural component (Fig. S14a, ESI). In the compounds $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, the individual weight reductions are attributed to the loss of two units of glycine molecule from $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and the removal of 4-aminobutyric acid from $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, respectively.

DSC curves were recorded from room temperature to 400 °C and two endothermic peaks were observed for both compounds $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. In addition, a significantly broad endothermic feature beyond 240 °C was also observed for these intercalated metal halides. The endothermic peaks at 201 °C and 198.7 °C for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, respectively, correspond to their melting transitions as the solid samples melt on the melting point checking apparatus at this temperature. The marked differences between thermal properties of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ and $\text{Cu}(\text{II})$ containing lead bromides can be related to the changes in structure and composition. The second endothermic peak in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ can be directly related to the thermal decomposition of glycine according the reported literature which reveals that the organic component shows an endothermic peak around 240 °C accompanied by a weight reduction²⁵. Similarly, the second endothermic peak in $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ is attributed to the thermal degradation of 4-aminobutyric acid.

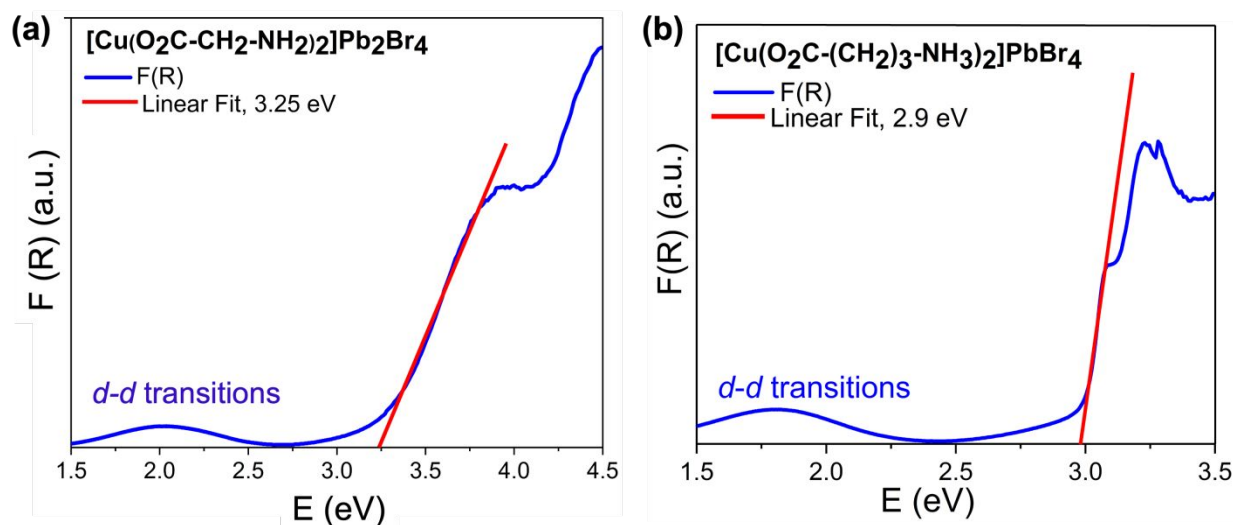


Fig. 5 Diffuse reflectance data plotted as the Kubelka–Munk function, denoted as $F(R)$, for compounds (a) $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and (b) $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$.

To understand optical properties of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, diffuse reflectance measurements were carried out on their polycrystalline powder samples (Fig. 5). The pseudo absorbance spectra of the compounds are similar, both exhibiting sharp onsets of optical absorptions above 2.9 eV and broad absorption bands in the visible region, which are responsible for the observed blue color of their crystals. The low energy absorption bands originate from the $d-d$ transitions of Cu^{2+} ,²⁶ and the high energy onset of absorption is due to the matrix (ligand to metal) optical transitions. The band gaps of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are determined to be 3.25 eV and 2.9 eV, respectively, based on the matrix absorption. Note here that a recent report¹⁰ assigns an

unusually low bandgap of 0.96 eV for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$ based on the onset of the $d-d$ absorption band. Such low band gap conflicts with the blue color of the crystals (the prior report shows a thicker and darker crystal) and the high semiconductor resistivity measured for this material.¹⁰ Another interesting aspect of this finding, the band gap of the perovskite derivative $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$ reported in this work is very close to that of the 2D layered perovskite $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$, which has a band gap of 2.94 eV (Fig. S14b, ESI). In contrast, the new compound $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ has a wider band gap of 3.25 eV attributed to a stark difference in the structure of this material (including the presence of oxygen in the coordination environment of Pb) as compared to that of 2D halide perovskites.

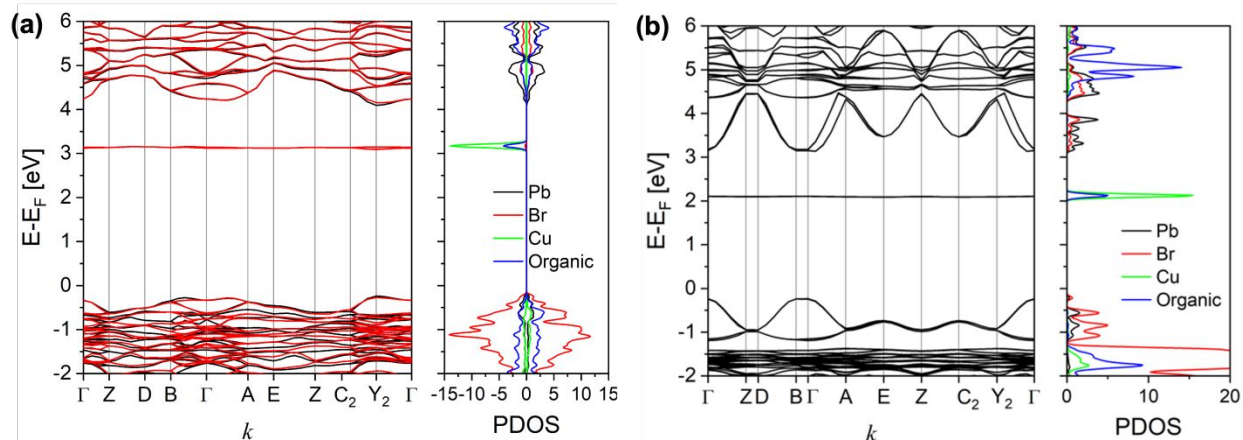


Fig. 6 Band structures and projected density of states (PDOS) plots for (a) $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and (b) $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$. In the band structure for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, black and red lines are for spin up and down, respectively. In the PDOS for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, positive and negative values denote spin up and down, respectively.

To gain insight into the electronic structures of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$, as compared to the experimental measurements, we report on DFT calculations. Optimization of the crystal structures using the PBE functional demonstrated that the FM (ferromagnetic) and AFM (antiferromagnetic) configurations for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ are lower in energy than the nonmagnetic (NM) structure by -0.4342 and -0.4346 eV/cell, respectively, indicating a very small difference of 4×10^{-4} eV per unit cell. The two neighboring Cu atoms in a unit cell may not have a favored relative spin orientation in this case, and could be considered consistent, in part, with the paramagnetic state observed experimentally, in addition to other factors, as mentioned in the next section. For $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$, the AFM configuration is lower in energy than the FM state by 0.2726 eV/cell, and is the energetically favored ground state, where four $\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3$ moieties are linked by two Cu atoms, with antiparallel spins and a separation of about 2.6 Å, unlike $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, where the distance is 6.9 Å. Calculated magnetic moments, which primarily originate from Cu atoms, were determined for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ as 0.70 $\mu\text{B}/\text{Cu}$ and 1.93 per unit cell (0.97 $\mu\text{B}/\text{f.u.}$) (with 2 Cu per unit cell). Similarly, values of 0.72 $\mu\text{B}/\text{Cu}$ and 1.97/unit cell were computed for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$ (0.99 $\mu\text{B}/\text{f.u.}$).

Fig. 6 presents a summary of the band structures and projected density of states (PDOS) obtained through DFT calculations using the HSE06 exchange-correlation functional. The calculated band gap for

$[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ is slightly higher at 3.37 eV than the experimentally determined optical gap of 3.25 eV. Conversely, the calculated band gap for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$ is lower at 2.34 eV compared to the experimental optical gap of 2.9 eV (Fig. 5b). We note that the calculated band gap for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$ of 0.42 eV in Ref.¹⁰ is unclear because the authors do not report on the level theory employed, while we have used here the hybrid range-separated functional HSE, which addresses, in part, the issue of band gap underestimation. Our theoretical results indicate a consistent trend of a larger optical gap for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ compared to $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$ and in relatively good agreement with experiment considering the idealized model system with no defects that was employed in the calculations. The calculated band structures and projected density of states (PDOS) depicted in Figure 6a and b illustrate distinct band dispersions between spin up and spin down states in the case of ferromagnetic $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, whereas they coincide for antiferromagnetic $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$. Interestingly, the bottom conduction band is a flat band for both $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ (spin down) and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$. The PDOS indicate that this band originates mainly from Cu with contributions from the organic component (O and N for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and O for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$). This observation is in accordance with the decomposed magnetic moment on each atom. The PDOS reveal that in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, the valence bands near the Fermi level are predominantly from Br, while the conduction bands near the flat bottom conduction band are primarily from Pb. On the other hand, in $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3\text{NH}_3)_2]\text{PbBr}_4$, there is mixture of Br and Pb contributions to both the valence bands near the Fermi level, and the conduction bands near the flat bottom conduction band.

A previous study reported $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ to be a promising material for sensitive X-ray detector applications.¹⁰ Therefore, in addition to optical and thermal studies, we investigated potential of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ for X-ray radiation detection applications. Fig. 7a shows a comparison of the photon attenuation capability of commercial X-ray detector material cadmium telluride (CdTe), $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, and single element semiconductor silicon (Si) for soft low-energy X-rays and high-energy gamma-ray. As expected, due to similar chemical compositions, $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ have comparable photon attenuation ability for low-energy soft X-rays. Fig. 7b shows the current-voltage (I-V) measurement along the *a*-axis and *bc*-plane, respectively, for compound $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$. Along the *a*-axis (perpendicular to the layer propagation direction), the resistivity measured is $1.44 \times 10^{10} \Omega \cdot \text{cm}$, which is lower than the resistivity for *bc*-plane ($2.17 \times 10^{10} \Omega \cdot \text{cm}$). The results indicate that for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, the *a*-axis is more conductive compared to the *bc*-plane. This unexpected finding suggests that 3D structural connectivity in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ also results in a substantial 3D character of the electronic structure of this material. In addition, unlike the typical layered halide perovskites, the inorganic layers containing the dodecahedral PbBr_5O_3 building blocks are a lot more insulating in the case of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$. In comparison, the resistivity is estimated to be $\sim 10^{12} \Omega \cdot \text{cm}$ for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ (measured along the *c*-axis). Our result for this material is in a good agreement with the reported resistivity value for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ single crystals ($8.85 \times 10^{11} \Omega \cdot \text{cm}$).¹⁰ Note that this interlayer resistivity value is significantly higher than that of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$.

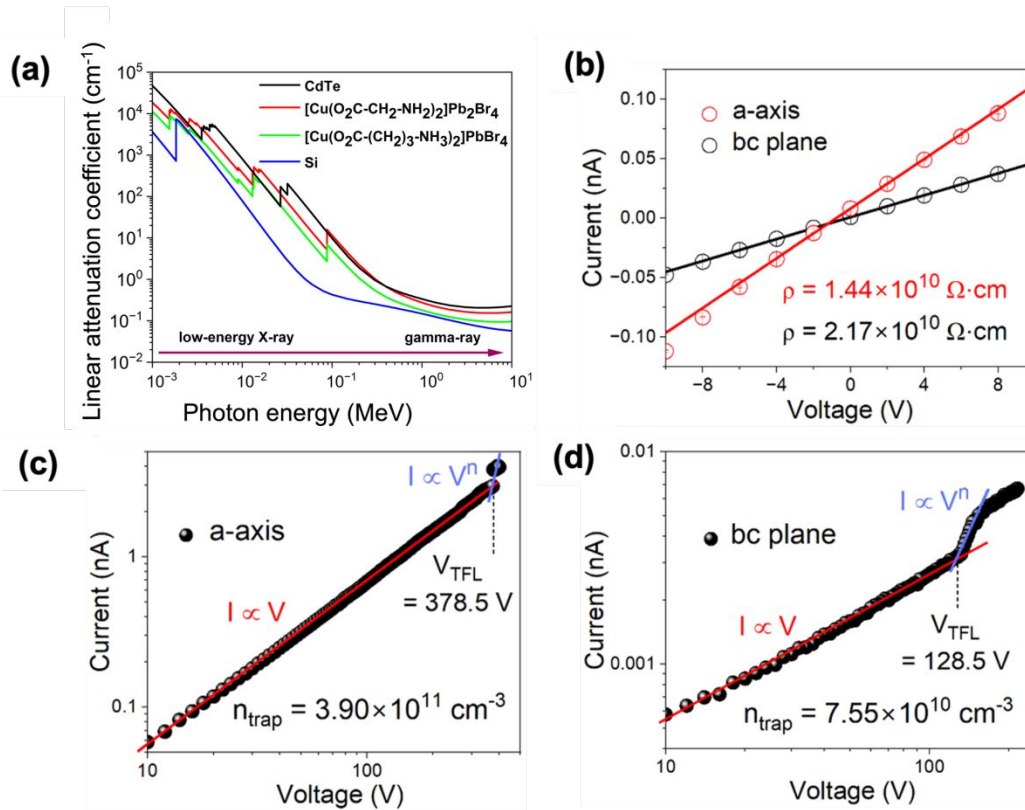


Fig. 7 (a) Comparison plot for the photon attenuation capability of CdTe, for [Cu(O₂C-CH₂-NH₂)₂]Pb₂Br₄, [Cu(O₂C-(CH₂)₃-NH₃)₂]PbBr₄, and Si for soft low-energy X-rays and high-energy gamma-ray. (b) Current-Voltage measurement results for [Cu(O₂C-CH₂-NH₂)₂]Pb₂Br₄ along the *a*-axis and *bc*-plane. (c) and (d) Space-charge-limited-current measurements for [Cu(O₂C-CH₂-NH₂)₂]Pb₂Br₄ along the *a*-axis and *bc*-plane.

To understand the defect trap levels related to the charge transport properties in [Cu(O₂C-CH₂-NH₂)₂]Pb₂Br₄, we performed the space-charge-limited-current (SCLC) measurements shown in Fig. 7c and d. In the SCLC curve, there are two identified current transition regimes, Ohmic (where current is linearly proportional to voltage, $I \propto V$) and trap-filled-limited (TFL, where $I \propto V^n$ and n is larger than 2). The density of trap states (n_{trap}) in [Cu(O₂C-CH₂-NH₂)₂]Pb₂Br₄ can be estimated using the formula below,²⁷

$$n_{\text{trap}} = \frac{2\epsilon\epsilon_0}{eL^2} V_{\text{TFL}}$$

where ϵ is the dielectric constant ($=9.33$), ϵ_0 is the vacuum permittivity, V_{TFL} is the onset voltage of the TFL regime, e is the electronic charge, and L is the crystal thickness. The n_{trap} estimated along the *a*-axis is $3.90 \times 10^{11} \text{ cm}^{-3}$, which is an order of magnitude higher than that for the *bc*-plane ($7.55 \times 10^{10} \text{ cm}^{-3}$). This may be attributed to the presence of Cu²⁺ ions in between the lead bromide layers. Note that the obtained n_{trap} values here are comparatively higher than that for [Cu(O₂C-(CH₂)₃-NH₃)₂]PbBr₄ ($7.2 \times 10^9 \text{ cm}^{-3}$).¹⁰

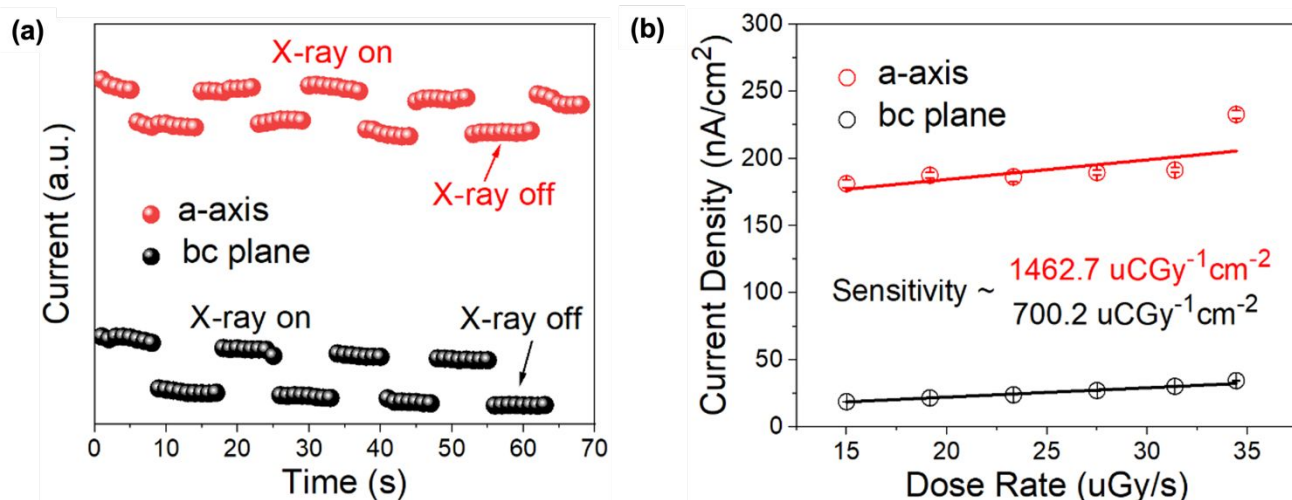


Fig. 8 (a) X-ray 'on' and 'off' measurement along the *a*-axis and *bc*-plane. (b) X-ray detection sensitivity plot along the *a*-axis and *bc*-plane for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$.

To further demonstrate the potential of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ for X-ray detection, we fabricated a prototype X-ray detector using the obtained single crystals. The fabricated detector was then exposed to soft 8 keV X-rays. Fig. 8a shows the X-ray 'on' and 'off' measurement along the *a*-axis and *bc*-plane for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$. According to Fig. 8a, the signal-to-noise (SNR) ratio (where $\text{SNR} = I_{\text{on}} - I_{\text{off}} / I_{\text{off}}$) for *a*-axis and *bc*-plane is determined to be 0.27 and 0.78, respectively. Measured along the *a*-axis, the X-ray induced current rise time τ_{rise} and decay time τ_{decay} (determined using 10% to 90% of the current amplitude) are ~ 1.32 s and ~ 1.22 s, accordingly. For *bc*-plane, the τ_{rise} and τ_{decay} are ~ 1.3 s and ~ 1.55 s. Compared to other well-known metal halides (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$),²⁸ the obtained rise and decay times for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ are on the inferior side, indicating a need for further improvement strategies. For X-ray detection applications, detector sensitivity is another important figure-of-merit. Here, we determined the sensitivity for $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ to be $1462.7 \mu\text{CGy}^{-1}\text{cm}^{-2}$ (at electric field $E = 50$ V/mm) and $700.2 \mu\text{CGy}^{-1}\text{cm}^{-2}$ (at $E = 33.3$ V/mm), respectively, along the *a*-axis and *bc*-plane (see Fig. 8b). Along the *a*-axis, the detection sensitivity is twofold of the sensitivity value obtained for the *bc*-plane. The fabricated $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ -based detector shows a lower detection sensitivity value compared to $21097 \mu\text{CGy}^{-1}\text{cm}^{-2}$ at 175 V/mm for the reported $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ compound.¹¹ However, noticeably, the detector sensitivity determined here for intercalated system is much better than a few other reported 2D metal halides (e.g., $242 \mu\text{CGy}^{-1}\text{cm}^{-2}$ at $E = 0.31$ V/um for BDAPbI_4 ($\text{BDA} = \text{NH}_3\text{C}_4\text{H}_8\text{NH}_3$), $222.03 \mu\text{CGy}^{-1}\text{cm}^{-2}$ at $E = 24$ V/mm for $\text{Rb}_4\text{Ag}_2\text{BiBr}_9$).^{29, 30}

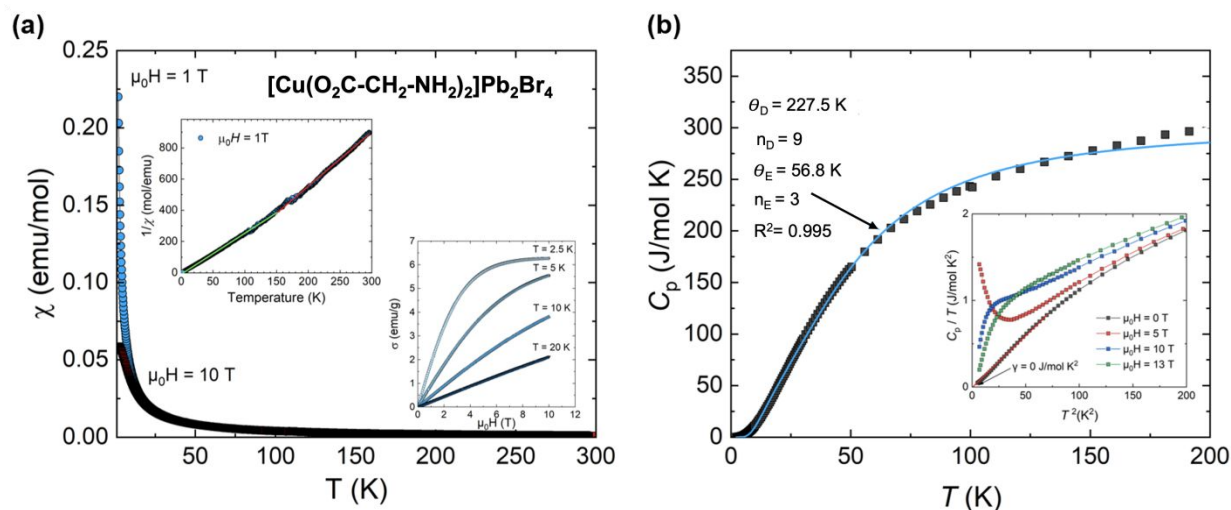


Fig. 9 (a) Temperature dependence of magnetic susceptibility $\chi(T)$ of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ (b) Temperature dependence of the specific heat $C_p(T)$ of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ measured from 2K to 200K.

The magnetic properties of hybrid organic-inorganic metal halides are diverse, showing a shift from paramagnetic to ferromagnetic/antiferromagnetic states. By altering their structure and composition, these hybrids can have highly variable magnetic characteristics. Consequently, the structural and compositional variations of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are also reflected in their magnetic properties. Fig. 9a demonstrates the temperature dependence of magnetic susceptibility of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ measured in magnetic fields $\mu_0H = 1\text{ T}$ and 10 T . The inverse susceptibility ($1/\chi$) plot shows that data obtained in $\mu_0H = 1\text{ T}$ can be described by Curie–Weiss law irrespective of the slight change of slope around 150 K (inset of Fig. 9a). The fitting of the data regions with two different slopes gives similar values of magnetic moment and Curie's constant i.e., $C = 0.38\text{ emu mol}^{-1}\text{ K}$, and $\mu_{\text{eff}} = 1.74\text{ }\mu_{\text{B}}/\text{f.u.}$ for the region of 2–150 K (green) and $C = 0.29\text{ emu mol}^{-1}\text{ K}$ and $\mu_{\text{eff}} = 1.51\text{ }\mu_{\text{B}}/\text{f.u.}$ for the region of 150–300 K (red). The magnetization isotherms measured at 2.5, 5, 10 and 20 K indicate that field dependence changes from linear (at 20 K) to saturation tendency ($\approx 1\text{ }\mu_{\text{B}}/\text{f.u.}$ at 2.5 K and $\mu_0H = 10\text{ T}$) which roughly follows the Brillouin function (inset of Fig. 9a). Considering the structural and chemical features of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, its magnetism can originate from several sources. The most likely source of the magnetic moment in this compound is the Cu^{2+} ion, which has the electronic configuration $[\text{Ar}]3\text{d}^9$. The ideal effective moment of the spin only system with one unpaired electron $S = \frac{1}{2}$ equals to $1.73\text{ }\mu_{\text{B}}$. This value is very close to the ones that were obtained from the fit using the Curie–Weiss law (especially in the 2–150 K region). However, the contribution of Pb to magnetism cannot be ruled out. Considering that $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ showcases previously unexplored 2D structure, edge-sharing dodecahedra coordination of Pb^{2+} with bromine and oxygen atoms can contribute to magnetism via possible defects. Diamagnetic Pb^{2+} ions may generate Pb^+ or Pb^{3+} paramagnetic ions by trapping an electron or a hole, respectively. Previously, the dynamic formation of paramagnetic Pb^{3+} species was observed in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. Electron Paramagnetic Resonance (EPR) and DFT calculations suggest that the formation of Pb–O defects could be responsible for this observation³¹. Moreover, theoretical studies of MAPbI_3 suggest that iodine and lead vacancies are the primary sources of magnetism in its cubic and orthorhombic

structure³². Additionally, the influence of zwitterionic form of glycine on the Cu^{2+} ion as well as the change of Cu surrounding it due to cooling can be explained as the effect of structural rearrangement of the compound in the same manner as the reorganization of the CH_3NH_3^+ ion in methylammonium lead halides,³³ and structural changes in $(\text{CH}_3\text{NH}_3)_2[\text{Fe}^{\text{II}}\text{Cl}_4]$ ³⁴ has generated observable changes in magnetic properties of these metal halides.

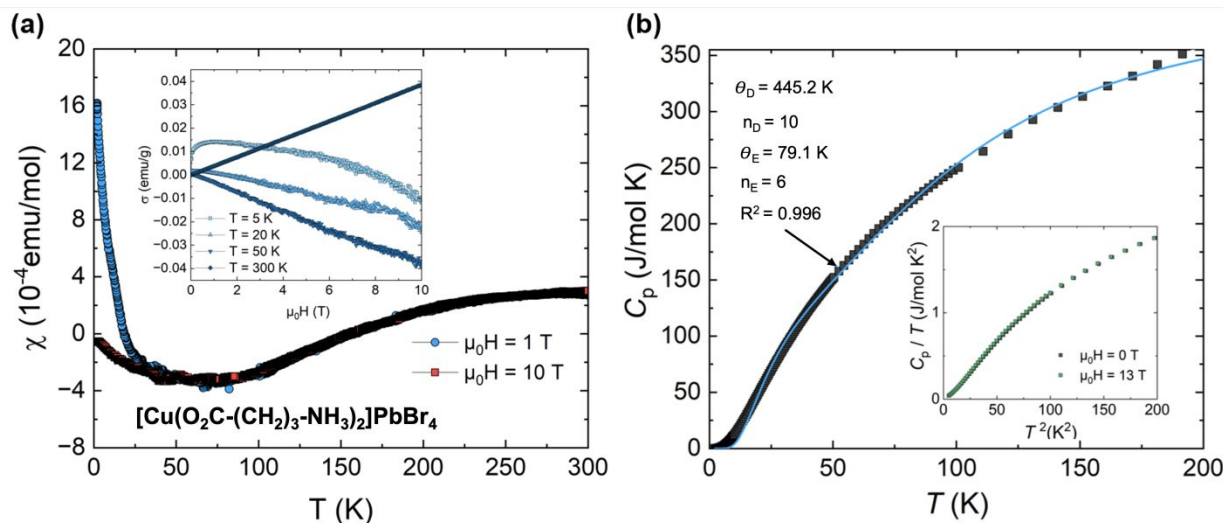


Fig. 10 (a) Temperature dependence of magnetic susceptibility $\chi(T)$ of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. (b) Temperature dependence of the specific heat $C_p(T)$ of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ measured from 2 K to 200 K (inset highlights the fact that low-T part of $C_p(T)$ measured in magnetic fields μ_0H equal to 0 and 13 T).

Hybrid organic-inorganic metal halides can exhibit various phase transitions even at room temperature. To analyze the thermal properties of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$, specific heat $C_p(T)$ is measured from 2 K down to 200 K. The $C_p(T)$ curve does not show any sign of a possible phase transition (Fig. 9b). The behavior of specific heat over a broad temperature range can be approximated using a combination of Debye and Einstein models with the following parameters: $\theta_D=227.5$ K, $n_D \approx 9$, $\theta_E=56.8$ K, $n_E \approx 3$ (where n is the number of corresponding vibrational modes³⁵, θ_D is Debye temperature, θ_E is Einstein temperature, n_D is number of Debye modes, n_E is number of Einstein vibration modes and $R^2=0.995$ (goodness of fit)) (Fig. 10a). Low-temperature data obtained in a zero magnetic field are well described by $\frac{C_p}{T} = \gamma + \beta T^2$, which yields the Sommerfeld coefficient $\gamma = 0$ J/mol K², in agreement with the insulating ground state of this system (inset of Fig. 9b). At low temperatures, specific heat exhibits noticeable field dependence. It is visible that the application of the magnetic field $\mu_0H = 5$ T moves some entropy to measurable temperatures. The anomaly observed in the low-T part of the $C_p(T)/T$ versus T^2 representation of specific heat can be related to the splitting of the energy level of the ground state of the magnetic ion.

$[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ exhibits completely different magnetic properties than $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ due to the difference in coordination of Cu and Pb atoms. In $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, the

Cu^{2+} ions are integrated as $\text{Cu}_2(\text{CO}_2)_4$ paddle wheel clusters between the layers of lead bromide octahedra. It exhibits complex temperature- and field-dependent behavior of magnetization. Magnetic susceptibility of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ measured in magnetic fields $\mu_0H = 1\text{ T}$ and 10 T is shown in Fig. 10a, from which it is visible that it is few orders of magnitude lower than that of $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$. From room temperature down to 150 K its value is positive, but in the temperature range of $18\text{--}150\text{ K}$, susceptibility is negative. This is suggestive of a significant diamagnetic contribution from the PbBr_4^{2-} perovskite layers or from the organic ligands associated with the copper centers. At lower temperatures (below 18 K), the material exhibits a considerable increase in magnetic susceptibility.

The magnetization isotherms shown in the inset of Fig. 10a present the field dependence of magnetization measured in temperatures of 2.5 , 5 , 10 and 20 K which confirm the tendencies: 1) at 300 K $\sigma(\mu_0H)$ is linear and positive; 2) measurements indicate diamagnetic responses at intermediate temperatures of 20 K and 50 K , with a linear decrease in magnetization; 3) at 2.5 K magnetization is complex (it increases and saturates at $\mu_0H=1\text{ T}$, higher fields decrease the values down to negative ones). The analysis of the magnetization studies clearly demonstrates that the magnetic properties of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ are characterized by the interplay between diamagnetic contributions, likely from the lead bromide layers and organic ligands, and weak paramagnetic or antiferromagnetic interactions originating from the $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel clusters (weak antiferromagnetic interaction were typically observed in different copper(II) polymers with different paddle-wheel clusters)^{36, 37}. The presence of antiferromagnetic interactions is also consistent with our above-described computational results. The specific structural distortions within the $\text{Cu}_2(\text{CO}_2)_4$ clusters or the overall 2D framework could fine-tune the magnetic interactions and can result into the complex temperature and field dependence.

Temperature dependence of specific heat $C_p(T)$ measured from 2 K down to 200 K shows no sign of structural phase transition for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ (see Fig. 10b). The behavior of specific heat over the broad temperature range can be also described using combination of Debye and Einstein models with following parameters $\theta_D = 445.2\text{ K}$, $n_D \approx 10$, $\theta_E = 79.1\text{ K}$, $n_E \approx 6$ (where n – number of corresponding vibrational modes; $R^2 = 0.996$) (Fig. 10b). Low-temperature data measured in zero magnetic field and $\mu_0H=13\text{ T}$ are not different (inset of Figure 10b). At low temperatures specific heat doesn't exhibit any noticeable field dependence. At low temperature $\frac{C_p(T)}{T}$ versus T^2 measured in zero magnetic field is not linear due to the additional contribution to heat capacity due to low energy excitations, most probably related to low energy Einstein-like modes. Low temperature part of $\frac{C_p(T)}{T}$ versus T^2 indicates that data cannot be described simply by $\frac{C_p}{T} = \gamma + \beta T^2$ that highlights the contribution of electrons and Debye phonon modulation. Investigation of the magnetic properties and heat capacity of the compound do not reveal all the reasons for the complex behavior; however, it is worth to mention that similar magnetic dependences were observed in optoelectronic double perovskite $\text{Cs}_2\text{AgBiBr}_6$ alloyed by Fe^{3+} . The observed phenomena were tentatively attributed to a weak ferromagnetic or antiferromagnetic response from localized regions containing phase separated magnetic clusters³⁸. For a comprehensive analysis of the magnetic interactions and ordering in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$, further studies can be insightful. These include variable-temperature and field EPR spectroscopy to investigate the local magnetic environments and investigation of the structure at different temperatures.

4. Conclusions

In conclusion, this work summarizes the crystal growth, optical, thermal, electronic, and magnetic property characterization results for a new hybrid halide $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and a previously reported 2D layered organic-inorganic halide $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$. Zwitterionic amino acids like glycine and 4-aminobutyric acid were used for the Cu^{2+} intercalation, producing a different outcome in each case: $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ have differing structures both in the inorganic layers and organic interlayers. The resultant $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ adopts a $\langle 100 \rangle$ -oriented 2D layered perovskite structure,²² whereas $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ contains layers formed by edge-sharing dodecahedral PbBr_5O_3 building blocks. As a result of the oxygen incorporation into inorganic layers, $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ has a larger bandgap of 3.25 eV as compared to 2.9 eV bandgap determined for $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ based on diffuse reflectance data.

$[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ and $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ show enhanced resistance towards air and moisture, making them candidates for semiconductor detector applications. $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ single crystals (SCs) exhibit a semiconductor resistivity of $1.44 \times 10^{10} \Omega \cdot \text{cm}$ (measured along the a -axis) and $2.17 \times 10^{10} \Omega \cdot \text{cm}$ (along the bc -plane), respectively. The more insulating nature of the inorganic layer formed by the dodecahedral PbBr_5O_3 building blocks in $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ explains the small difference between conductivity values along and perpendicular to the layers. The fabricated X-ray detector based on $[\text{Cu}(\text{O}_2\text{C}-\text{CH}_2-\text{NH}_2)_2]\text{Pb}_2\text{Br}_4$ SCs shows a detector sensitivity of $1462.7 \mu\text{CGy}^{-1}\text{cm}^{-2}$, indicating its potential application for ionizing radiation detection. Importantly, the findings reported in this work suggest that the further expansions of the exciting family of hybrid organic-inorganic metal halides containing transition metal intercalants are possible, and such expansions may yield new chemistries, unique structures and physical properties leading to potential practical applications.

Author contributions

Kanika Parashar: methodology, investigation, formal analysis, visualization, software, validation, writing-original draft, writing-review & editing. **Zheng Zhang:** methodology, investigation, formal analysis, data curation, writing-original draft, writing-review & editing. **Volodymyr Buturlim:** investigation, formal analysis, data curation, software, resources, writing-original draft, writing-review & editing. **Jie Jiang:** software, formal analysis, resources, writing-original draft. **Alexander Roseborough:** investigation, formal analysis, software, resources, writing-original draft. **May Nyman:** investigation, formal analysis, software, resources, data curation, supervision, writing-review & editing. **Krzysztof Gofryk:** investigation, conceptualization, data curation, software, resources, writing-original draft, writing-review & editing. **Ruth Pachter:** software, formal analysis, resources, writing-original draft. **Bayram Saporov:** conceptualization, resources, writing-original draft, writing-review & editing, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work received funding support from the U.S. Department of Energy under award no. DE-SC0021158. We thank Douglas R. Powell at the Department of Chemistry and Biochemistry, University of Oklahoma, for his assistance in conducting SCXRD measurements. X-ray response tests were performed at the Biomolecular Structure Core (BSC)-Norman facility. The BSC-Norman is supported in part by Institutional Development Award (IDeA) from the National Institute of General Medical Sciences of the National Institutes of Health (award P20GM103640 and award P30GM145423), the National Science Foundation (award 0922269), and the University of Oklahoma Department of Chemistry and Biochemistry. We thank Dr. Leonard Thomas for his kind help with the X-ray response tests. Work at INL was supported from Idaho National Laboratory's Laboratory Directed Research and Development (LDRD) program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

References

1. R. Wang, T. Huang, J. Xue, J. Tong, K. Zhu and Y. Yang, *Nat. Photonics*, 2021, **15**, 411-425.
2. K.-G. Lim, T.-H. Han and T.-W. Lee, *Energy & Environ. Sci.*, 2021, **14**, 2009-2035.
3. Z. Zhang and B. Saparov, *Appl. Phys. Lett.*, 2021, **119**.
4. C. Zhou, H. Lin, S. Lee, M. Chaaban and B. Ma, *Mater. Res. Lett.*, 2018, **6**, 552-569.
5. C. Huo, B. Cai, Z. Yuan, B. Ma and H. Zeng, *Small Methods*, 2017, **1**, 1600018.
6. M. Braun, W. Tuffentsammer, H. Wachtel and H. Wolf, *Chem. Phys. Lett.*, 1999, **303**, 157-164.
7. K. Tanaka, T. Takahashi, T. Kondo, T. Umebayashi, K. Asai and K. Ema, *Phys Rev B*, 2005, **71**, 045312.
8. N. Mercier and A. Riou, *Chemical comm*, 2004, 844-845.
9. M. L. Aubrey, A. Saldivar Valdes, M. R. Filip, B. A. Connor, K. P. Lindquist, J. B. Neaton and H. I. Karunadasa, *Nature*, 2021, **597**, 355-359.
10. K. Guo, W. Li, Y. He, X. Feng, J. Song, W. Pan, W. Qu, B. Yang and H. Wei, *Angew Chem.*, 2023, **135**, e202303445.
11. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.
12. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
13. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
14. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**.
15. H. Beck, C. Gehrman and D. A. Egger, *APL Mater.*, 2019, **7**.
16. L. Zhang and W. Liang, *J. Phys. Chem. Lett.*, 2017, **8**, 1517-1523.
17. J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207-8215.
18. X. Zuo, G. Cui, K. M. Merz Jr, L. Zhang, F. D. Lewis and D. M. Tiede, *Proceedings of the National Academy of Sciences*, 2006, **103**, 3534-3539.
19. R. Guo, Z. Zhu, A. Boulesbaa, F. Hao, A. Puzetzy, K. Xiao, J. Bao, Y. Yao and W. Li, *Small Methods*, 2017, **1**, 1700245.
20. L. Dou, A. B. Wong, Y. Yu, M. Lai, N. Kornienko, S. W. Eaton, A. Fu, C. G. Bischak, J. Ma and T. Ding, *Science*, 2015, **349**, 1518-1521.
21. R. J. Doedens, *Prog. Inorg. Chem*, 1976, **21**, 209-231.
22. B. Saparov and D. B. Mitzi, *Chem. Rev.*, 2016, **116**, 4558-4596.
23. D. Banerjee, D. A. Popy, B. C. Leininger, T. D. Creason, V. N. Mapara, M. Furis, M. F. Borunda and B. Saparov, *ACS Appl. Mater. Interfaces.*, 2023.
24. T. Pinky, D. A. Popy, Z. Zhang, J. Jiang, R. Pachter and B. Saparov, *Inorg. Chem.*, 2024.
25. I. M. Weiss, C. Muth, R. Drumm and H. O. Kirchner, *BMC Biophys.*, 2018, **11**, 1-15.
26. Y. Liu, J. Liang, Z. Deng, S. Guo, X. Ji, C. Chen, P. Canepa, X. Lü and L. Mao, *Angewandte Chemie*, 2023, e202314977.
27. R. H. Bube, *J. Appl. Phys.*, 1962, **33**, 1733-1737.
28. Y. Song, L. Wang, Y. Shi, W. Bi, J. Chen, M. Hao, A. Wang, X. Yang, Y. Sun and F. Yu, *Light Sci. Appl.*, 2023, **12**, 85.
29. Y. Shen, Y. Liu, H. Ye, Y. Zheng, Q. Wei, Y. Xia, Y. Chen, K. Zhao, W. Huang and S. Liu, *Angew. Chem., Int. Ed.*, 2020, **59**, 14896-14902.
30. Z. Zhang, Y.-Z. Ma, L. Thomas, K. Gofryk and B. Saparov, *Cryst. Growth Des.*, 2021, **22**, 1066-1072.
31. S. Colella, M. Todaro, S. Masi, A. Listorti, D. Altamura, R. Caliandro, C. Giannini, E. Carignani, M. Geppi and D. Meggiolaro, *ACS Energy Lett.*, 2018, **3**, 1840-1847.
32. B. Bandyopadhyay, H. Luitel, S. Sil, J. Dhar, M. Chakrabarti, P. Nath, P. P. Ray and D. Sanyal, *Phys. Rev. B*, 2020, **101**, 094417.
33. L. Meng, M. M. Zhao, Y. Y. Xu, C. X. Peng, Y. Yang, T. T. Xing, P. Ren and F. Yen, *Scr. Mater.*, 2023, **226**, 115229.

34. J. Han, S. Nishihara, K. Inoue and M. Kurmoo, *Inorg. Chem.*, 2014, **53**, 2068-2075.
35. M. Falkowski, P. Doležal, A. Andreev, E. Duverger-Nédellec and L. Havela, *Phys. Rev. B*, 2019, **100**, 064103.
36. P. Wang, L. Luo, J. Fan, G.-C. Lv, Y. Song and W.-Y. Sun, *Microporous Mesoporous Mater.*, 2013, **175**, 116-124.
37. M. Mikuriya, R. Indrawati, R. Hashido, S. Matsubara, C. Nakamura, D. Yoshioka, K. Yokota, M. Fukuzaki and M. Handa, *Magnetochemistry*, 2018, **4**, 22.
38. W. Ning, J. Bao, Y. Puttisong, F. Moro, L. Kobera, S. Shimono, L. Wang, F. Ji, M. Cuartero and S. Kawaguchi, *Sci. Adv.*, 2020, **6**, eabb5381.