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Authors

Zhang, Heng
Leano, Remi J
Xie, Geng
[et al.](#)

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Low Frequency Vibrational Modes of Two-Dimensional Lead-Free Metal Halide Double Perovskites

Heng Zhang¹, Remi J. Leano², Geng Xie³, Celia Todd¹, Jieping Liu⁴, Timothy C. Johnstone¹, David Lederman⁵, Qi Pang⁴, Lingzi Sang³, David A. Strubbe^{6*}, Jin Z. Zhang^{1*}

¹ Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

² Department of Chemistry and Biochemistry, University of California, Merced, CA 95343, USA

³ Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

⁴ School of Chemistry and Chemical Engineering,

Guangxi University, Nanning, Guangxi 530004, China

⁵ Department of Physics and Materials Science & Engineering Program, University of California, Santa Cruz, CA 95064, USA University of California, Santa Cruz, CA 95064, USA

⁶ Department of Physics, University of California, Merced, CA 95343, USA

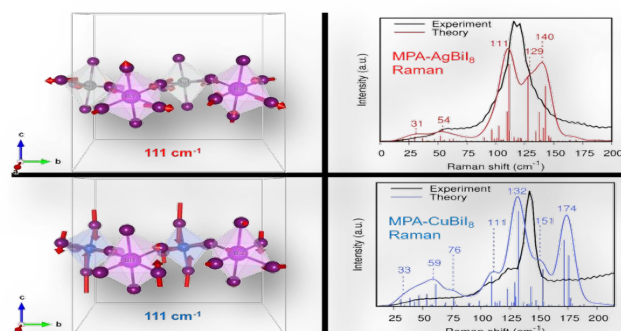
* Corresponding Author. Email: dstrubbe@ucmerced.edu; zhang@ucsc.edu

Abstract

2D layered double perovskites of (S-MPA)₄AgBiI₈ (MPA-AgBiI₈) and (S-MPA)₄CuBiI₈ (MPA-CuBiI₈) (S-MPA, S-β-methylphenethylammonium) were synthesized with a hydrothermal method. The crystal structure of MPA-AgBiI₈ was determined using single-crystal X-ray diffraction (scXRD). Powder XRD (pXRD) data suggest that the crystal structure of MPA-CuBiI₈ is more complex than that of MPA-AgBiI₈. UV-Vis electronic absorption spectra of these perovskites reveal a bandgap of 2.03 eV for both. Short exciton lifetime from time-resolved photoluminescence (TRPL) results and low PL intensity of the Cu-based perovskite suggest a high density of trap states within the bandgap. Low frequency Raman spectra of both materials show distinct peaks and a slightly higher frequency for the Cu-based perovskite than the Ag-based perovskite. Density functional theory (DFT) calculations were conducted to simulate the low frequency Raman spectra and help explain the different phonon modes, which are collective vibrations of metal halide bond bending and stretching within the Ag- and Cu-centered octahedra coupled with MPA libration and twisting within the inorganic layer. The DFT theory also quantified octahedral distortions in the two perovskites. This combined experimental and computational study provides new insights into the low frequency

vibrations of 2D perovskites.

TOC Graphic



INTRODUCTION

Metal halide (MH) perovskites attract increasing attention because of their exceptional optoelectronic properties, highly tunable composition, and facile synthesis.^{1–3} Now, perovskites of different dimensions (i.e., 3D, 2D, 1D, and 0D) have been synthesized^{4–8} and reported with defined structures and controlled properties. Intriguing properties, particularly a more substantial quantum confinement effect, were observed as dimensionality decreases.^{9,10}

However, 3D perovskites suffer from undesirable attributes such as environmental instability and Pb toxicity. 2D perovskites hold superior chemical stability, as well as tunable structures and properties.¹¹ Large organic cations such as methylphenethylammonium (MPA) are essential for constructing 2D perovskites. The MPA cation plays dual roles in the perovskite: the -NH₂ terminal forms N-H···halogen hydrogen bonds anchoring the inorganic framework, and the bulky aromatic backbone exerts a pronounced steric effect that induces octahedral distortion, thereby enabling structural control over material properties.¹² Also, chiral MPA is potentially useful for chiral metal halides for applications such as circularly polarized luminescence (CPL) and chirality-induced spin selectivity.^{13–15} In the 2D perovskites, the metal cations dominate in determining the structural and optical properties. To replace toxic Pb, Ag(I), Cu(I) and Sn(II) metal halide perovskites have been explored and found to have exceptional optical properties, with Cu-halide clusters exhibiting more disordered structures.^{16–18} Among the metals, Ag-Bi double halide perovskites remain highly promising due to their exceptional stability and optoelectronic properties, and their atomic and electronic structures have been well studied.^{11,19–21} Raman spectra were utilized as a simple way to interrogate structural changes because of the characteristic changes in the vibrational modes

when transitioning, for example, from 3D to 2D.^{19,20} In the low-frequency Raman region, the metal halide bond vibrations will be prominent and were studied for Ag-Bi-based perovskite structures. The Raman signals change after replacing Ag with Cu due to the varied Bi-I and Cu-I bond lengths,^{11,21,22} but assignment of these modes and the structural insight they could afford remain elusive.

There are many reports about the determination of the structures of low-dimensional perovskite materials by X-ray diffraction (XRD).^{22–26} In contrast, studies of their structures using Raman spectroscopy are less common, especially for 2D layered double perovskites, due to the difficulty in acquiring high-quality data in the low frequency region. Such low frequency phonon modes ($<200\text{ cm}^{-1}$) can reveal interaction between layers and provide atomic-level information about the role of hydrogen bonding or van der Waals forces in the crystal structure. For example, the THz Raman modes for layered structures, such as MoS_2 and WSe_2 , reflect shear or breathing modes between the layers.^{27–30} In the high frequency “fingerprint” region ($>200\text{ cm}^{-1}$), Raman spectra are used for chemical bond and functional group identification.^{31–33} Density functional theory (DFT) calculations can be used to predict Raman peaks and link them to specific vibrational modes.^{30,34} By combining experimental data with DFT simulations, the low frequency Raman spectra can reveal the large-scale spatial structure of the crystal, whereas the conventionally studied high-frequency Raman modes are sensitive primarily to the local structure.

Here, by using a hydrothermal method, MPA- CuBiI_8 and MPA- AgBiI_8 (MPA, methylphenethylammonium) perovskites were prepared. Single-crystal XRD demonstrates that the Ag-based perovskite exhibits a 2D layered structure, aligning with previously reported data.¹³ Simulated and experimental powder XRD, Raman, and IR data for the Cu-based perovskite indicate that its structure is more complex than that of the Ag-based perovskite, with evidence of multiple phases. Nevertheless, the UV-Vis and photoluminescence (PL) spectra show a similar electronic structure and the Tauc plot shows the same bandgap at 2.03 eV for both materials. From the time-resolved photoluminescence (TRPL) results, a shorter exciton lifetime is extracted in the Cu-based perovskite, which we ascribe to distortion-induced trap states in the structure. In addition, first-principles DFT calculations were performed to simulate the low frequency vibrational modes and structural distortion of the two 2D layered double perovskites.

RESULTS AND DISCUSSION

Figure 1 shows the morphology and shape of the MPA-AgBiI₈ and MPA-CuBiI₈ crystals. MPA-AgBiI₈ forms slabs around 100 μm in size with a roughly 20 μm distance between the cracks (Figure 1 (a,b)), which we attribute to weak van der Waals forces between the organic layers. MPA-CuBiI₈ forms small rods with a length of about 10 μm (Figure 1 (c,d)). From the images, the crystallinity of the Cu-based perovskite is not comparable to that of the Ag-based perovskite. We were unable to grow single-crystals of MPA-CuBiI₈ suitable for X-ray structure determination, however, scanning electron microscopy (SEM) confirms that microcrystals are present.

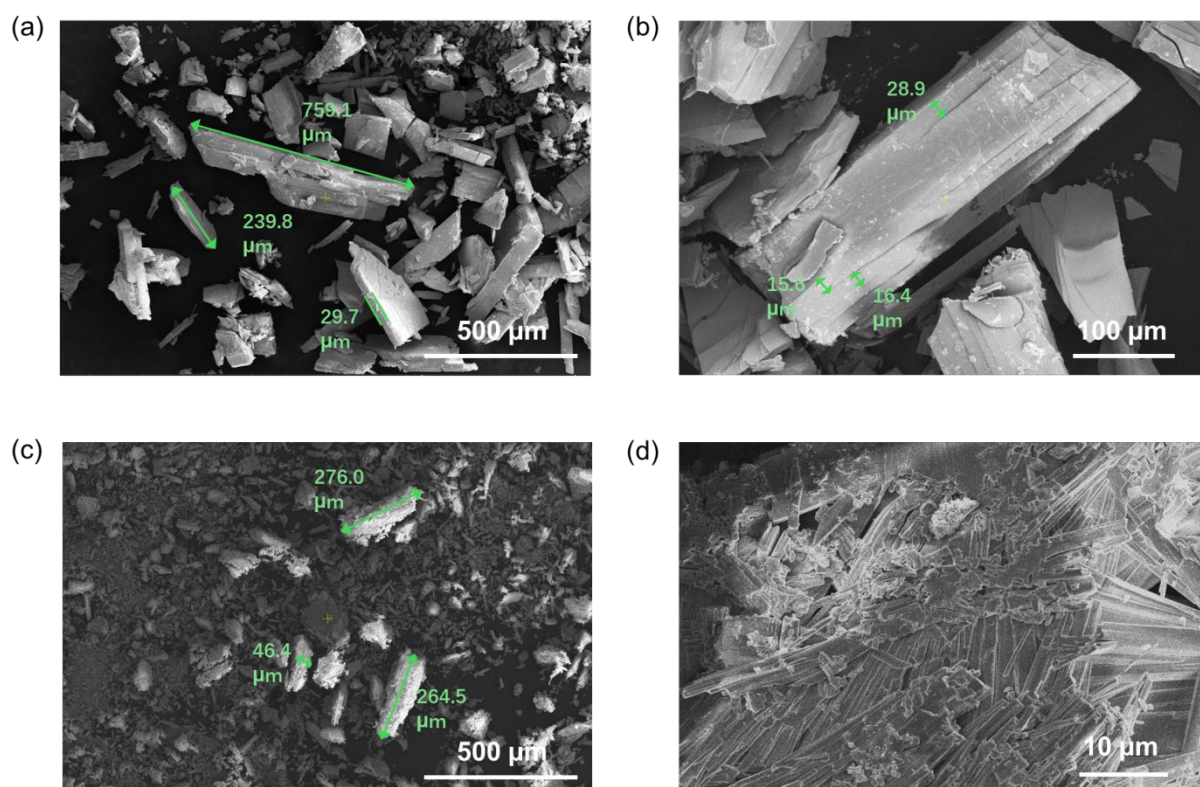


Figure 1 SEM images of the MPA-AgBiI₈ (a, b) and MPA-CuBiI₈ (c, d) crystals. The green labels show the size of individual crystals and the distance between the cracks along the cleavage direction.

Figure 2 shows the powder XRD pattern of MPA-AgBiI₈ and MPA-CuBiI₈ to confirm the 2D layered structure. In Figure 2 (a), the diffraction peaks for the Ag-based perovskite were observed at 10.6, 15.8, 20.5, 25.5, 27.6, 30.3, 32.6, 37.7, 41.1, and 47.0°. The 10.6, 15.8, 20.5, 27.6, 32.6, 37.7° diffraction peaks match with reported XRD data of MPA-AgBiI₈ films, indicating a 2D layered structure in our case.¹³ For the Cu-based double perovskite, in addition to the diffraction peaks observed for the Ag-based perovskite, there are new peaks at 12.1,

22.4, 29.4, 32.5, 38.0 and 44.4°. Closer examination of the experimental XRD peaks in Figure 2 (b) reveals different intensities in the same diffraction peaks between two perovskites. We were able to grow diffraction-quality single crystals of MPA-AgBiI₈ and solve and refine its crystal structure (*vide infra*). The Ag-I bonds that are parallel to the *c* axis are 2.665(3) and 2.683(3) Å long, and the equatorial Ag-I bond lengths range from 3.335(6) to 3.524(6) Å, indicating a distorted octahedra structure of [AgI₆]⁵⁻. In contrast, all the Bi-I bonds fall within a narrow range from 3.023(5) to 3.112(5) Å (see Figure S2). As Cu⁺ (0.77 Å) has a much smaller radius than Ag⁺ (1.15 Å) and Bi³⁺ (1.03 Å), more distorted [CuI₆]⁵⁻ octahedra are expected.³⁵ According to Jahn-Teller distortion theory, the octahedrally coordinated transition metals Cu⁺, Ag⁺ will split e_g orbitals to stabilize the double perovskites by elongating or shortening the metal halide bonds, leading to a crystal symmetry-breaking.³⁶ The XRD pattern of the Cu-based perovskite retains most of the characteristic peaks of the Ag-based counterpart but exhibits additional peaks, suggesting a similar but more complex composition, possibly due to multiple phases arising from oxidized Cu compounds or unreacted starting materials.

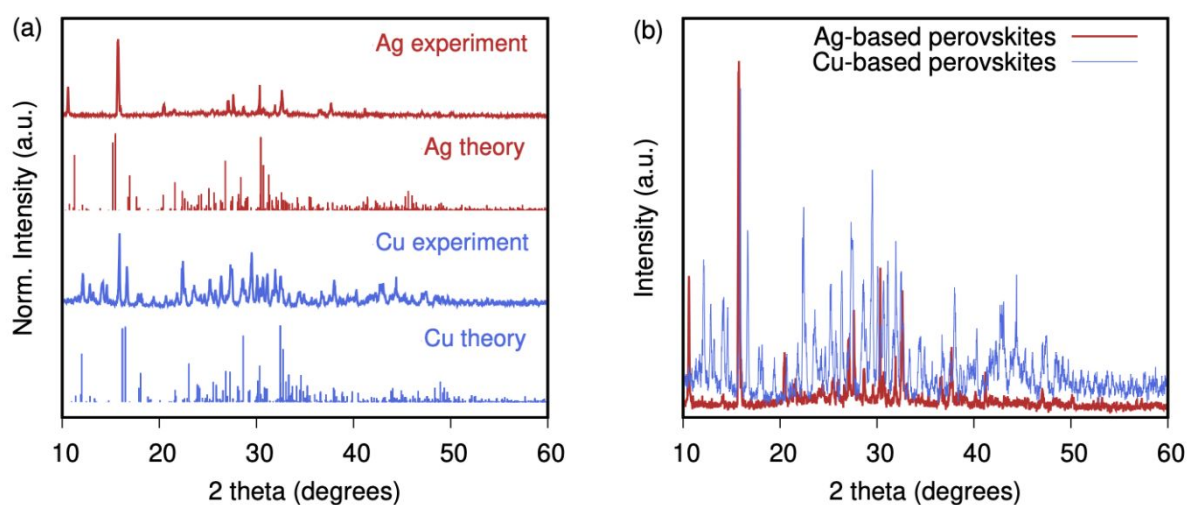


Figure 2 Powder XRD pattern of the MPA-AgBiI₈ and MPA-CuBiI₈. (a) The experimental and simulated XRD pattern comparison. (b) Overlaid plots of experimental XRD results of MPA-AgBiI₈ and MPA-CuBiI₈.

Figure 3 shows the UV-Vis electronic absorption spectra and Tauc plot of the MPA-AgBiI₈ and MPA-CuBiI₈. In Figure 3 (a), the absorption peaks reside at 330 and 550 nm for both materials, and the Cu-based perovskite has a slightly broader absorption spectrum shape, suggesting a more complex composition for Cu. From the Tauc plot in Figure 3 (b), the

bandgaps of both materials were determined to be 2.03 eV, indicating no change in the bandgap between Ag- and Cu-based perovskites.

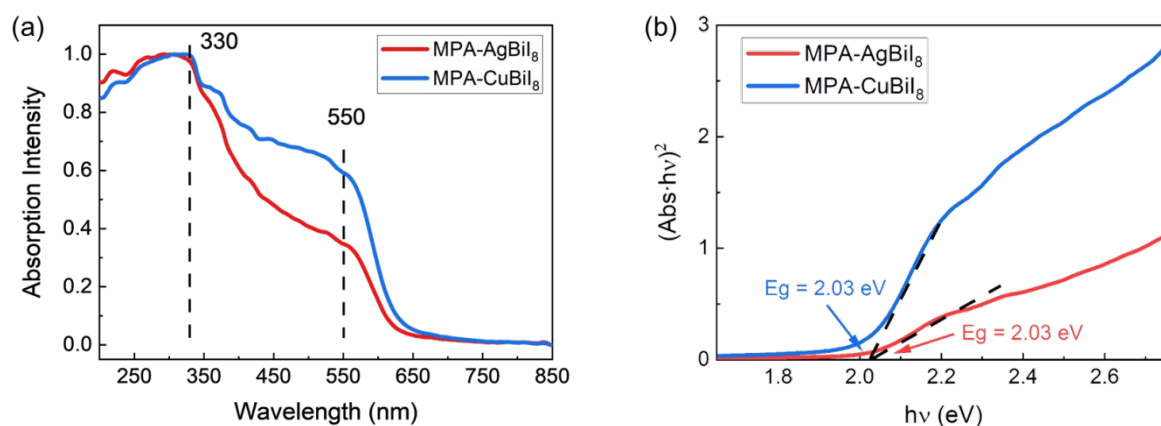


Figure 3 UV-Vis electronic absorption spectra (a) and Tauc plot (b) of MPA-AgBiI₈ and MPA-CuBiI₈.

Figure 4 shows the PL spectra and TRPL profiles of the two materials. In Figure 4 (a), a narrow emission peak is observed at 548 nm with a full width at half maximum (FWHM) of 50 nm for MPA-AgBiI₈. A 550 nm main emission peak was also observed for MPA-CuBiI₈, with another shoulder peak at 472 nm. The PL shape of the Cu-based perovskite is broader than that of the Ag-based perovskite, suggesting a more distorted structure.³⁷ The 472 nm peak is attributed to the transition associated with Cu. Meanwhile, the PL intensity (see Figure S1) of the Cu-based perovskite is one order of magnitude lower than that of the Ag-based perovskite, indicating more non-radiative recombination and a high density of trap states. The TRPL in Figure 4 (b) shows exciton lifetimes of the Ag and Cu-based perovskites and both materials exhibit long decay curves to 4000 ns. The TRPL curves are fitted with a bi-exponential function, and the average lifetime (τ_{avg}) was calculated based on the following equations:^{38–41}

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (1)$$

where A_1 and A_2 denote fast and slow component amplitudes, τ_1 and τ_2 denote fast and slow component time constants. The τ_{avg} resolves to be 348 ± 40 and 326 ± 40 ns for microcrystalline

MPA-AgBiI₈ and MPA-CuBiI₈, respectively, with the lifetime of the Cu-based perovskite being 22 ns shorter. After considering the margin of errors, no exciton lifetime difference is observed at ~550 nm between two crystalline materials, implying the same decay channels at ~550 nm, possibly due to domination by Bi metal energy levels. The slightly shorter exciton lifetime indicates more trap states in MPA-CuBiI₈, possibly involving oxidized Cu compounds.

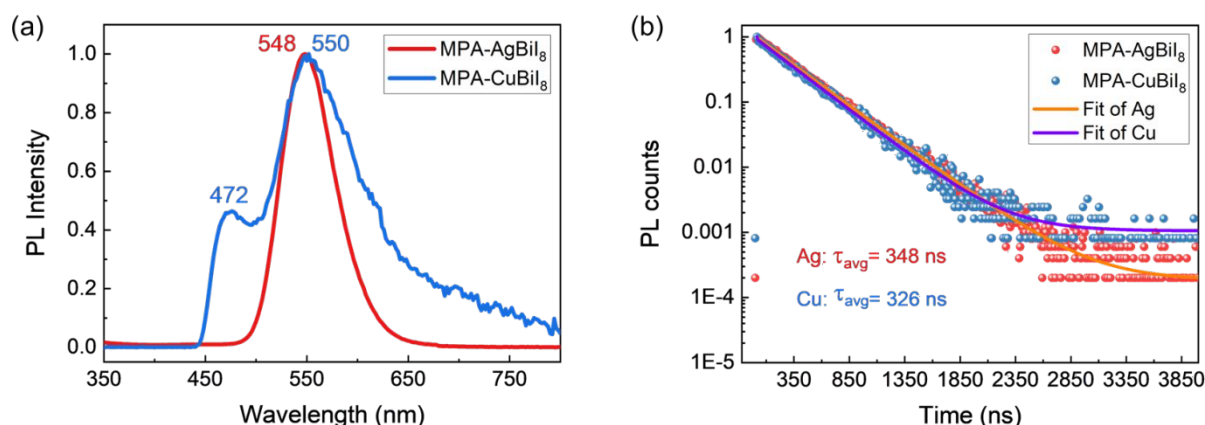
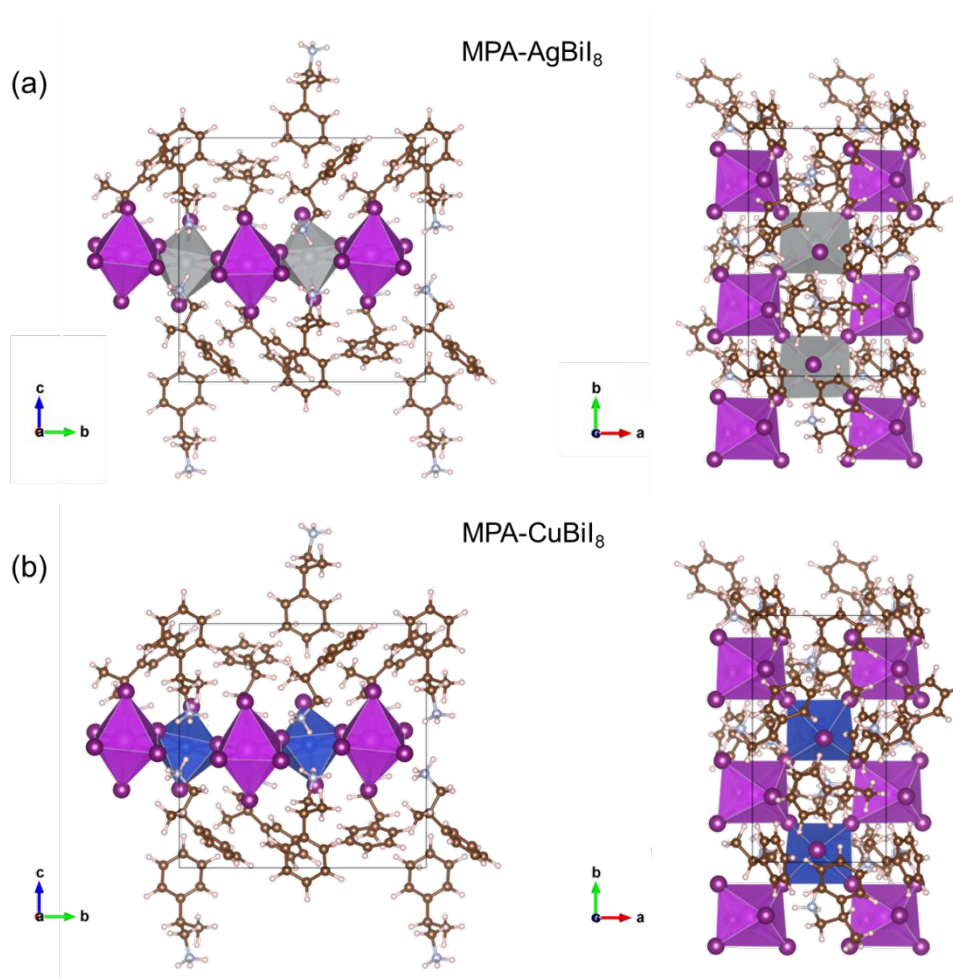


Figure 4 (a) PL spectra of MPA-AgBiI₈ and MPA-CuBiI₈, excited at 278 nm and 254 nm, respectively. (Excitation at 303 nm for the Ag-based perovskite shows the same PL peak at 548 nm.) (b) TRPL spectra of Ag- and Cu-based perovskites. Ag-based perovskite: excited at 278 nm and monitored at 548 nm. Cu-based perovskite: excited at 260 nm and monitored at 550 nm.

Figures 5 (a) and (b) show the DFT-optimized crystal structures of MPA-AgBiI₈ and MPA-CuBiI₈ along the in-plane (equatorial) and out-of-plane (axial) directions (detailed lattice parameters in Table S2). Both exhibit a 2D layered structure. The structures were optimized starting from the crystal structure of MPA-AgBiI₈.¹³ In Figures 5 (c) and (e), the hydrogen bond lengths are slightly longer in the Ag-based perovskite, with a range from 3.427 to 5.157 Å, than in Cu-based perovskite, which span from 3.232 to 4.775 Å, indicating a longer distance between the organic and inorganic layers. In Figures 5 (d) and (f), the Cu-I bonds are shown to be shorter than Ag-I bonds, and the metal halide bond lengths between Ag/Cu-I and Bi-I bonds are unmatched in the corner-connecting direction, along the equatorial plane. Specifically, the metal halide bonds in both octahedra are compressed with two axial bonds of 2.758 Å, four equatorial bonds ranging from 2.977 to 3.067 Å in the Ag-based perovskite and two axial bonds of ~2.568 Å, four equatorial bonds ranging from 2.689 to 2.783 Å in the Cu-based perovskite, indicating a Jahn-Teller distortion. The Jahn-Teller distortion allows empty metal d orbitals with low enough energy to mix with filled non-metal p orbitals, stabilizing a

distorted geometry.^{42,42,43} These Jahn-Teller distortions are present in the Cu and Ag-centered octahedra, but not in Bi-centered octahedra, due to Bi's fully occupied d-orbitals. These are evidenced by the relatively large distortion index (D) values obtained for Cu and Ag-centered octahedra compared to Bi (SI Table S7), with Bi octahedra having values near 1×10^{-2} in the theoretical structures and values of 2.97×10^{-2} in the Cu-centered octahedra and 4.26×10^{-2} in Ag-centered octahedra.



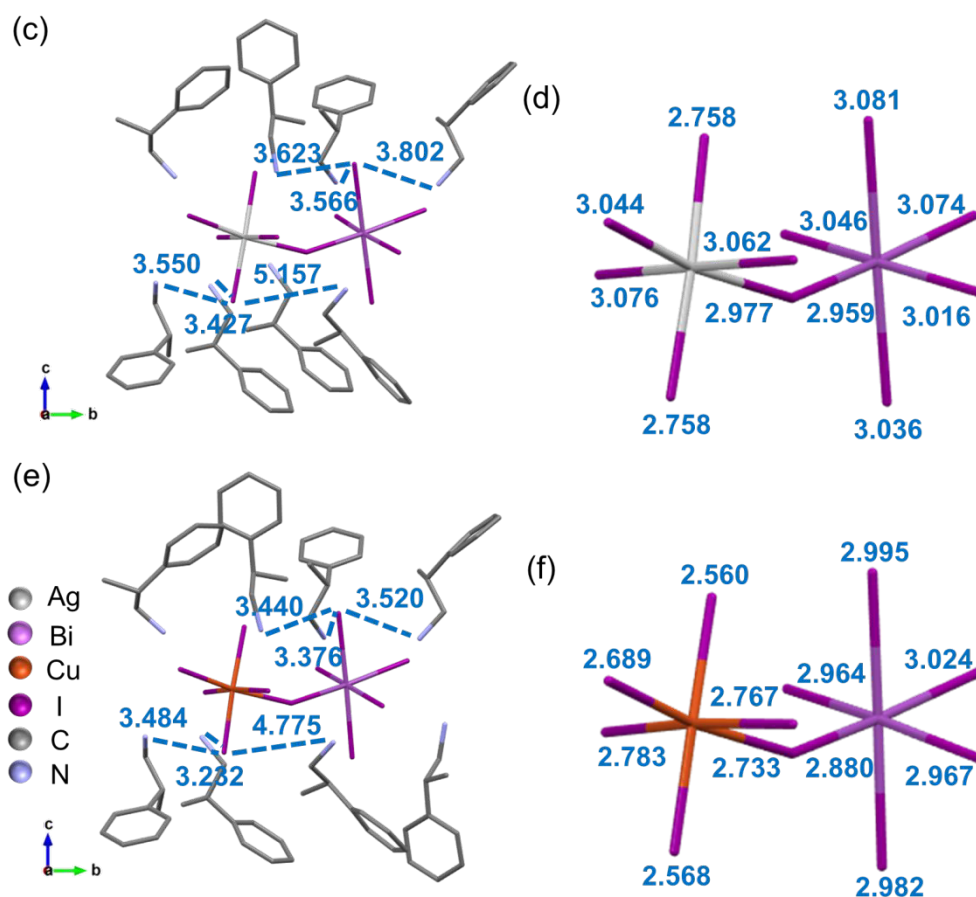


Figure 5 DFT-PBE-simulated crystal structure of the (a) MPA-AgBiI₈ and (b) MPA-CuBiI₈ viewed along the *a* and *c* axes. Ag, Bi, and Cu-centered octahedra are shown in silver, magenta, and blue colors. (c) The hydrogen bond lengths between N and I atoms between the organic and inorganic layers in MPA-AgBiI₈ and (d) Ag-I, Bi-I bond lengths inside the octahedra. (e) The hydrogen bond lengths between N and I atoms between the organic and inorganic layers in MPA-CuBiI₈ and (f) Cu-I and Bi-I bond lengths inside the octahedra. The hydrogen atoms are omitted for clarity in figures (c) and (e). All bond lengths are in Å.

Figure 6 shows the comparison between experimental and calculated Raman and IR spectra for crystalline MPA-AgBiI₈ and MPA-CuBiI₈. The experimental data were adjusted to remove temperature dependence to generate the reduced Raman spectra⁴⁴ (see treatment method in SI), and the theoretical data were treated with a 6 cm⁻¹ Gaussian broadening to match the experimental result. The original Raman spectra with temperature dependence are shown in Figure S3 for comparison. Figures 6 (a) and (b) show the comparison of experimental and

1
2
3 calculated Raman spectra in the low frequency range from 0-200 cm^{-1} . The broad low-energy
4 Raman bands from the experiment indicate strong molecular interactions within the
5 perovskites.⁴⁵ For both materials, the theoretical results match the experimental peaks except
6 that theory shows a separate peak at 140 cm^{-1} for the Ag-based perovskite and 174 cm^{-1} for the
7 Cu-based one. One reason for the mismatch between the experimental and theoretical Raman
8 spectra is that disorder from thermal or other causes is inevitably present in the structure, which
9 changes interactions between neighboring unit cells and leads to shifts and broadening of
10 vibrations, especially of low-frequency vibrations.⁴⁷ In contrast, the DFT calculations use an
11 idealized crystal structure without disorder. In the high-frequency region from 200-1800 cm^{-1}
12 in Figures (c) and (d), the theoretical peak positions match the experimental Raman data, but
13 this is not the case for the intensities. Comparison of the IR spectra in Figures (e) and (f) shows
14 good agreement for both the peak positions and intensities. Together with the comparison of
15 XRD patterns, these results suggest a correspondence between the DFT-simulated crystal
16 structures and the actual crystal structures.
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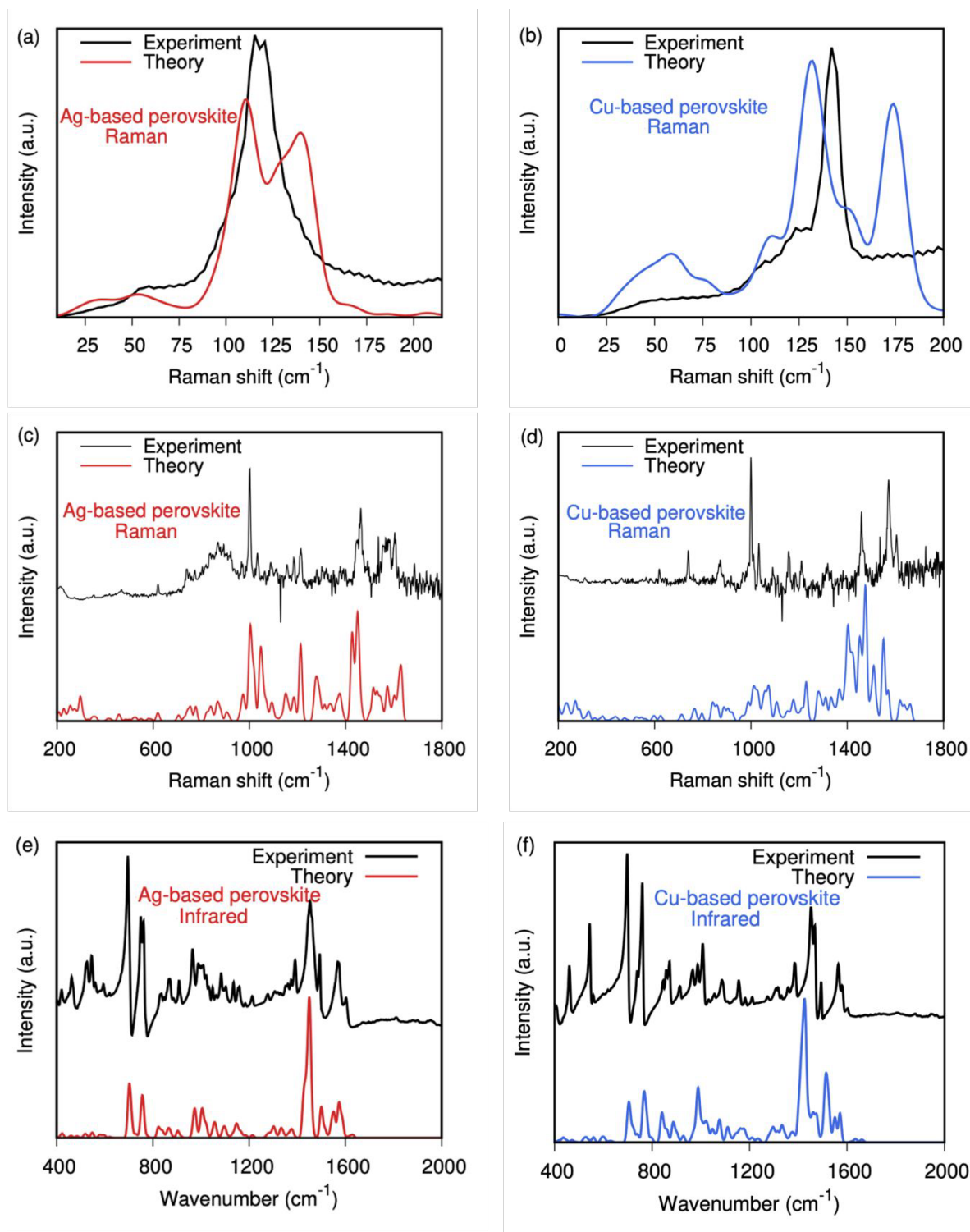


Figure 6 Low frequency (0-200 cm⁻¹) (a, b), high frequency (200-1800 cm⁻¹) (c, d) Raman and IR spectra (400-2000 cm⁻¹) (e, f) of MPA-AgBiI₈ and MPA-CuBiI₈.

To decipher the character of the low frequency vibrational modes, the DFT calculations were conducted and compared to the experimental results. Only the most significant contributions to each vibrational peak are shown here to match the experimentally measured

ones, though 636 modes in total are obtained from the calculation, with the subset in the range 0-200 cm^{-1} shown by vertical lines at the bottom of Figures 7. It should be noted that the motions repeat periodically in each unit cell of the lattice. Comparing the low frequency Raman spectra between Ag- and Cu-based perovskites, more and broader peaks are generated from the Cu-based perovskite based on the DFT computation. This could be due to the stronger hydrogen bond between the organic and inorganic layer, which broadens the vibrational peak and a more distorted lattice structure and lower symmetry, leading to more vibrational modes.^{43,46}

Figure 7 shows the assignment of experimentally measured vibrational modes from Raman spectra of MPA-AgBiI₈ and MPA-CuBiI₈ aided with simulated Raman spectra below 200 cm^{-1} . We provide here only the most dominant characteristics of each mode, and where a distortion or motion is mentioned without specifying whether it is in or out of plane, the distortion has components in both directions. In the Ag spectrum, the peak at 31 cm^{-1} is ascribed to both in-plane and out-of-plane bond angle distortions of octahedra, coupled with tilting of the Ag octahedra. The mode at 54 cm^{-1} is assigned to octahedra bond angle distortions and in-plane and out-of-plane motion of Bi and Ag centers. The mode at 111 cm^{-1} arises from in-plane bond length distortions and out-of-plane Bi bond length distortions. The mode at 129 cm^{-1} consists of in-plane bond length distortions on both octahedra, bond angle distortions of Bi-centered octahedra, out-of-plane Ag bond length distortions, and in-plane motion of Bi. The peak at 140 cm^{-1} consists of in-plane bond-length distortions on both octahedra, and motion of Bi centers.

In the Cu spectrum, at 33 cm^{-1} , the dominant motions are octahedra bond angle distortions coupled with in-plane motions of the octahedral centers. The peak at 59 cm^{-1} is characterized by angle distortions of both in-plane and out-of-plane octahedra bonds, with significant contributions from motion of Cu atoms. At 76 cm^{-1} , in-plane bond angle distortions on both Cu and Bi octahedra, bond angle distortions of out-of-plane Cu-I bonds, and tilting of Bi-centered octahedra are dominant. At 111 cm^{-1} , Cu centers move in plane, Cu octahedra exhibit in-plane bond angle distortions, and both Cu and Bi octahedra display bond length distortions. At 132 cm^{-1} , Cu atoms move in plane, Cu octahedra undergo bond angle distortion, both Bi and Cu octahedra have in-plane bond length distortions, and Bi octahedra have bond length distortions along out-of-plane Bi-I bonds. The 151 cm^{-1} mode includes in-plane bond length distortions on Bi and Cu octahedra, while Cu atoms move in plane. The peak at 174 cm^{-1} contains bond length distortions of octahedra, and significant NH₃ group rotation on MPA

molecules. In both the Ag-containing and Cu-containing materials, all peaks listed in this range exhibit libration and internal twisting of MPA molecules coupled to the vibration of the inorganic layers.

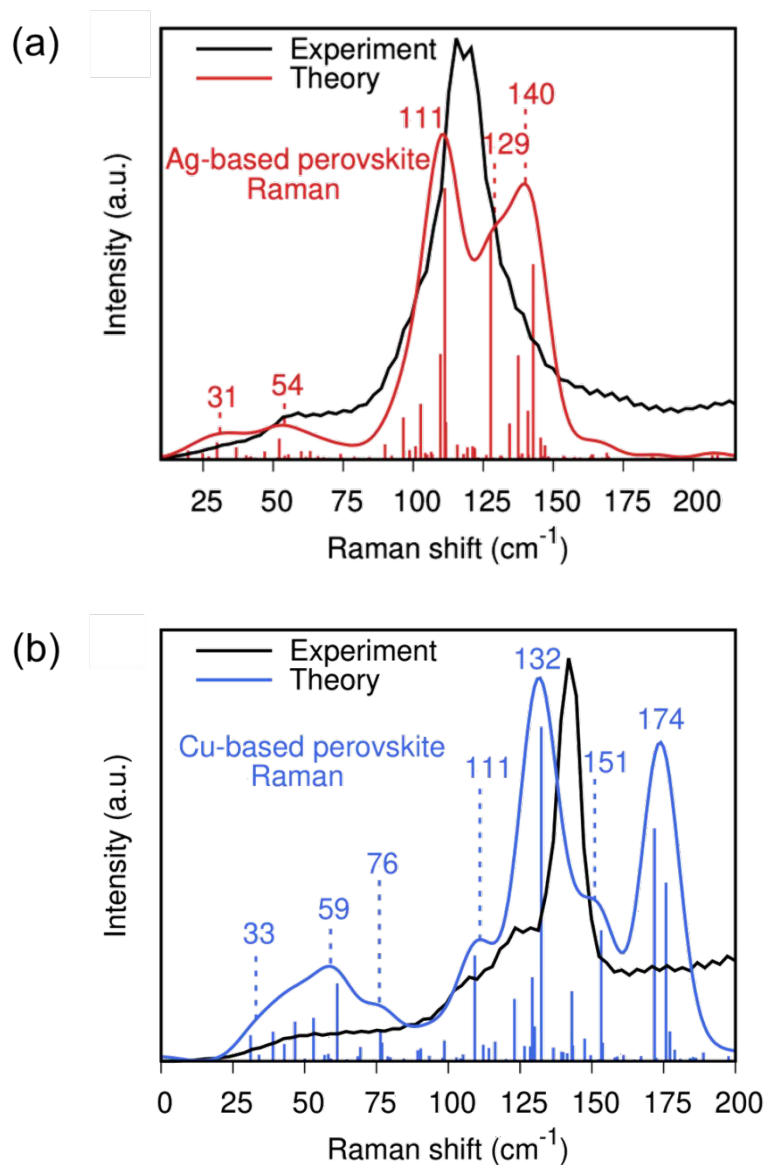


Figure 7 Reduced experimental and theoretical (with 6 cm⁻¹ Gaussian broadening) Raman spectra of (a) MPA-AgBiI₈ and (b) MPA-CuBiI₈. Solid vertical lines show all the individual mode positions and intensities in the DFT calculation within the 0-200 cm⁻¹ range.

Table 1 Summary of experimental and theoretical vibration modes in the low Raman frequency region (0-200 cm⁻¹) of MPA-AgBiI₈ and MPA-CuBiI₈.

MPA-AgBiI ₈ (cm ⁻¹)			MPA-CuBiI ₈ (cm ⁻¹)		
Experiment	Theory	Assignment	Experiment	Theory	Assignment
31	31	Ag-I-Bi bending	32	33	Cu-I-Bi bending
		Ag-I-Bi bending			Cu-I-Bi bending
53	54	I-Ag/Bi-I stretching	43	59-76	I-Cu-I bending
		MPA librating			Cu-I-Bi stretching
101-116	111	I-Ag/Bi-I stretching	107	111	Cu-I-Bi stretching
		MPA librating			Cu-I-Bi stretching
121	129	I-Ag/Bi-I stretching	123	132	Cu-I-Bi stretching
		MPA librating			Cu-I-Bi stretching
	140	I-Ag/Bi-I stretching	142	151	Cu-I-Bi stretching
		MPA librating			Cu-I-Bi stretching
				174	Cu-I-Bi stretching
					Cu-I-Bi stretching

Figure 8 presents the calculated partial vibrational density of states (VDOS) of MPA-AgBiI₈ and MPA-CuBiI₈ based on the DFT-optimized crystal structures. The VDOS figures describe the number of vibrational states in each unit frequency and the partial VDOS describes how individual elements contribute to the total vibrational states, which is shown over a 0-3300 cm⁻¹ frequency range. In Figure 8 (a), in the 0-500 cm⁻¹ region, the main contributions to vibration involve C and H, while contributions from Bi, Ag, and I are at their strongest compared to the rest of the spectrum. In the 500-1500 cm⁻¹ region, these contributions from Bi, Ag, and I are less present and are superseded by contributions from C, H and N atoms. In the vicinity of 3000 cm⁻¹, characteristic high frequency vibrations involving H atoms, for example, N-H or C-H stretching, are observed. After replacing Ag with lighter Cu (Figure 8 (c)), vibrations with higher frequency were observed.

In the enlarged low frequency regions in Figure 8 (b) and (d), there is a pronounced vibrational contribution from Bi element near 55 cm⁻¹ in the Ag-based perovskite, but that contribution peak shifts slightly to 60 cm⁻¹ and broadens in the Cu-based one. This demonstrates that Bi contributes significantly to low frequency modes, involving bond bending with Bi, and

makes a greater contribution when Cu metal is involved. Ag contributes around 70 cm^{-1} and a broader peak is observed from Cu atoms in the $60\text{--}140\text{ cm}^{-1}$ range, indicating that Cu contributes more pronouncedly in low-frequency vibrations than Ag. This is likely due to the smaller mass of Cu and greater bond strength.^{47,48} The I atom contributes to vibrations in the $80\text{--}150\text{ cm}^{-1}$ region for both materials, with slightly higher frequency for MPA-CuBiI₈. The observation that the I atoms contributed to higher frequencies in Cu than Ag highlights that I atoms couple strongly to metal (Bi, Ag, and Cu) atoms, and the shift reflects structural differences in bonding geometry and octahedral distortion, as shown in Table S7. C and N show broad contributions across the low frequency range in both perovskites. These mode peaks are broad and overlap with inorganic lattice motions, showing that the MPA twisting and rocking vibrations are coupled with the inorganic layer.

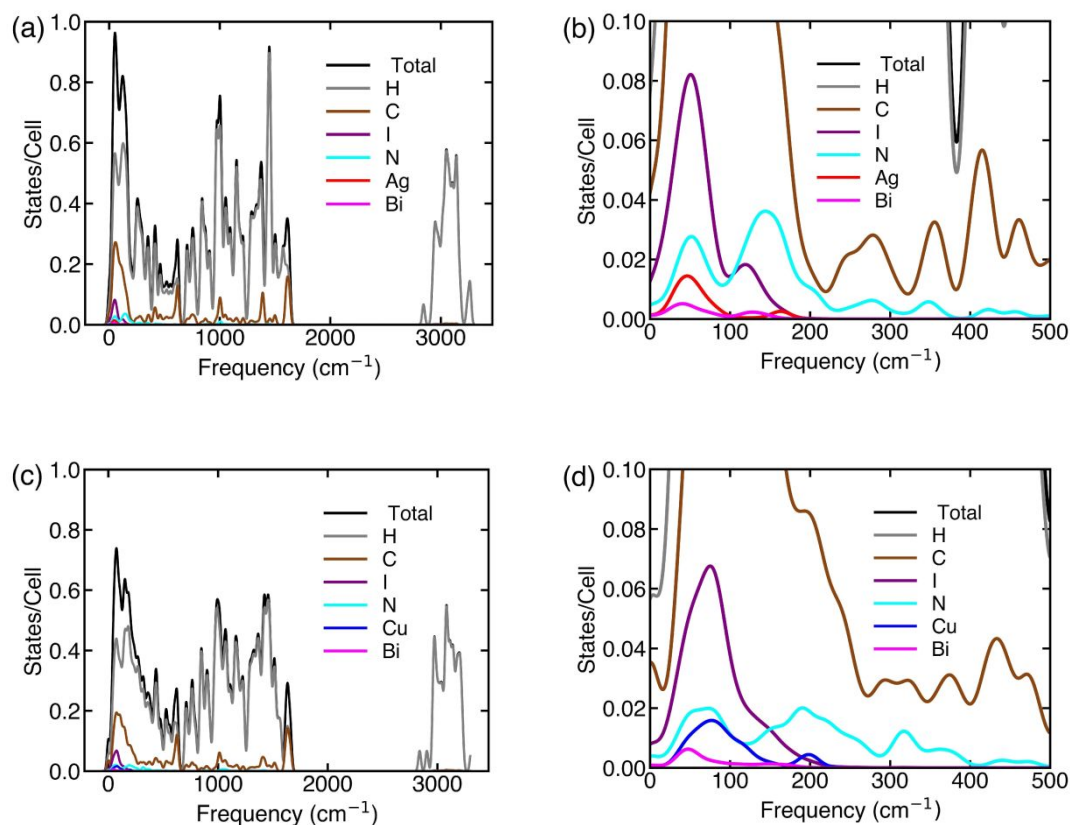


Figure 8 Calculated partial vibrational density of states (VDOS) of (a, b) MPA-AgBiI₈ and (c, d) MPA-CuBiI₈.

For MPA-AgBiI₈, the experimental Raman vibration modes reside at 31, 53, 101, 116,

and 121 cm⁻¹, while for MPA-CuBiI₈, the vibration modes are at 32, 43, 107, 123, and 142 cm⁻¹. According to Hooke's law,

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (2)$$

where k is the force constant, m is the reduced mass, f is the frequency.⁴⁹ After treating the atoms and bonds as harmonic oscillators, k is directly proportional to bond strength. Since the mass of Cu is smaller than the Ag and the force constant of a Cu-I bond (173 N/m) is higher than that of an Ag-I bond (145.8 N/m),^{47,48} the vibrational frequencies of Cu-based perovskite are expected to shift to higher positions as can be confirmed by experimental results with an increase from 101 to 107, 116 to 123 and 121 to 142 cm⁻¹, respectively.

Some researchers have combined experiments and DFT simulations to assign the peaks to the vibration modes in low frequency Raman. For example, Quarti *et al.* attributed the vibrational frequency at 62 cm⁻¹ to Pb-I bending, 94 cm⁻¹ to Pb-I stretching in inorganic layers and the libration of organic cations at 119 and 154 cm⁻¹ in the CH₃NH₃PbI₃ 3D structure.¹³ Other studies exploited single crystal XRD to help elucidate the structural distortion, such as A site libration and metal halide bond length and angle changes that account for the low frequency vibrational peaks in 2D perovskites.²⁶

In terms of the optical properties of double perovskites, previous reports revealed via partial density of states (PDOS) that they are mainly dominated by the inorganic layer.^{13,43} The valence band maximum (VBM) is largely contributed by I 5p states with a small contribution from Ag 4d and Bi 6s states and the conduction band minimum (CBM) is mainly contributed by the Bi 6p orbitals.^{43,50} From our bandstructure (Figure S7) and PDOS (Figure S8) calculations, we found that the band edges are mostly due to p-orbitals from I atoms, with small contributions from Ag d-orbitals and Cu d-orbitals in the VBM and Bi p-orbitals in the CBM. Our calculations give a bandgap of 1.6 eV for the Cu-based perovskite and 2.1 eV for the Ag-based perovskite, showing a substantial difference between the two, unlike the bandgaps determined from the Tauc plots. While it is unsurprising that our DFT results do not quantitatively match the experimental bandgap, it is unclear why there is such a discrepancy in the *difference* between the two structures' bandgaps. Possible reasons are given in SI.

In other work on 1D organic metal halide hybrids, specifically C₄N₂H₁₄PbBr₄, the VBM was dominated by p-orbitals of Br, while the CBM was dominated by p-orbitals of Pb.⁵¹ In a study of 2D lead bromide perovskites, VBM had strong Br p-orbital character followed by Pb s-orbitals, and the CBM had strong Pb p-orbital character.⁵² Our results match with the existing trend of the VBM being dominated by metal and the CBM having significant contributions

from halide (I, Cl, or Br) p-orbitals. In each case, the halide atom is a major contributor to the band edges, with the metal atoms affecting the size of the band gap, but not significantly changing the character or shape of the band edges. It is expected that the contribution from Ag and Cu would be less than the contribution from iodine in the density of states because there are more iodine atoms in the unit cell.

One application of a highly distorted structure is to induce a larger Rashba effect to modulate the spin lifetime, because the lattice distortion could break the inversion symmetry in the crystal, which arises from the organic cation rotation and unmatched metal halide bonds.^{53–55} The Rashba effect will split the electronic band into finer structures and affect the spin-related excited state lifetime.^{56–58} To this end, we have calculated octahedral distortion parameters, in particular, ΔD_{tilt} , which is an indicator of inversion symmetry breaking and has been tied to chiral light emission. We can compare the octahedral parameters, as a measure of distortion, for the experimental Ag structure and theoretical Ag and Cu structures. These parameters have been used as predictors of experimental properties such as broadband emission, band gaps, and exciton trapping. In particular, Smith *et. al.* found that broadband emission upon near-ultraviolet excitation becomes more intense with increasing out-of-plane angle distortion.⁵⁹ Additionally, larger values of ΔD_{tilt} indicate inversion symmetry-breaking,^{55,60} which enables chiral emission.^{52,61} Larger octahedra tilt angles also show wider bandgaps and greater exciton trapping.^{62,63} We find that DFT overestimates the level of angle distortion compared to experiment, as quantified by ΔD_{tilt} , in agreement with previous work.⁵²

As shown in Figure S6 and Table S7, the arrangement of Cu octahedra in MPA-CuBiI₈ is more distorted than the Ag octahedra in MPA-AgBiI₈ based on ΔD_{tilt} , and therefore MPA-CuBiI₈ has the greater inversion symmetry-breaking. In Tables S8 and S9, the bond length distortion of Bi octahedra is about the same in both theoretical Cu and Ag structures, but the bond angle variance of Bi octahedra is much higher in the Cu theoretical structure. Cu and Ag-centered octahedra have greater bond length distortion than Bi, due to Jahn-Teller effects. Ag has greater bond angle variance than Bi, but Bi has more than Cu. DFT underestimates the disparity between Ag/Cu and Bi octahedra within a structure. The level of distortion between Bi atoms in the theoretical Cu-based and Ag-based structures differs. The bond length distortion index D is nearly identical (1.07 in Cu vs 1.05 in Ag). However, the bond angle variance, σ^2 , is quite different (70.53°² in Cu and 38.63°² in Ag).

CONCLUSION

In conclusion, crystalline MPA-AgBiI₈ and MPA-CuBiI₈ were successfully synthesized using a hydrothermal method. Their structural, photophysical and Raman vibration modes have been studied. The structure of MPA-CuBiI₈ is more complex than that of MPA-AgBiI₈, as confirmed by XRD. This enhanced complexity may stem from oxidation. The optical studies show a similar electronic band structure and the same bandgap, and more trap states are inferred for the Cu-based perovskite from the TRPL measurements, implying structural distortion and strong electron-phonon coupling. The vibrational modes of the Cu-based perovskite are at higher frequencies than those of the Ag-based perovskite due to stronger metal halide bonds and smaller metal mass. Furthermore, the decreased exciton lifetime supports stronger electron-phonon coupling in the more distorted Cu-containing perovskite. The vibrational modes for both Ag- and Cu-based Pb-free double perovskites are fully investigated by first-principles DFT simulation and assigned to metal halide bond bending and stretching in the octahedra, coupled to vibrations of the organic layer of the 2D perovskites. At higher vibrational frequencies, stronger vibrational motion from the organic layers in the structure manifests for both perovskites. DFT also shows a slightly larger lattice distortion for the Cu-based perovskite compared to the Ag-based perovskite, as indicated by ΔD_{tilt} value. Induced centrosymmetry-breaking by lattice distortions may open a new avenue to achieve larger Rashba effects in double perovskites.

Supporting Information

Experimental details

DFT-relaxed CIFs, complete eigenvectors in Quantum ESPRESSO and molder formats

Crystallographic refinement parameters

Crystal structure data (CIF)

Vibrational mode images, descriptions

Band structure

Partial electronic density of states (PDOS)

Octahedral parameters

Accession Codes

Deposition Number 2456327 contains 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.

Competing interest

The authors declare no competing financial interest.

Author Information

Corresponding Author

Jin Z. Zhang – Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064, United States; orcid.org/0000-0003-3437-912X
Phone: +1-831-459-3776; Email: zhang@ucsc.edu

Authors

Heng Zhang – Department of Chemistry and Biochemistry, University of California Santa Cruz, California 95064, United States; orcid.org/0000-0001-8521-5403

Remi J. Leano – Department of Chemistry and Biochemistry, University of California, Merced, CA 95343, United States; orcid.org/0000-0003-4949-3419

Geng Xie - Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2; orcid.org/0000-0002-7099-4747

Celia Todd – Department of Chemistry and Biochemistry, University of California Santa Cruz, California 95064, United States.

Jieping Liu – School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, China.

Timothy C. Johnstone – Department of Chemistry and Biochemistry, University of California Santa Cruz, California 95064, United States.

David Lederman – Department of Physics and Materials Science & Engineering Program, University of California, Santa Cruz, California 95064, United States; <https://orcid.org/0000-0001-8423-5138>[orcid.org](https://orcid.org/0000-0001-8423-5138)

Qi Pang – Department of School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, China; [orcid.org](https://orcid.org/0000-0001-8423-5138)

Lingzi Sang – Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2; [orcid.org](https://orcid.org/0000-0001-8423-5138)

David A. Strubbe – Department of Physics, University of California, Merced, CA 95343, United States; orcid.org/0000-0003-2426-5532

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References

- (1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050–6051. <https://doi.org/10.1021/ja809598r>.
- (2) Suresh Kumar, N. and Chandra Babu Naidu, K. A Review on Perovskite Solar Cells (PSCs), Materials and Applications. *J. Materiomics.* **2021**, *7* (5), 940–956. <https://doi.org/10.1016/j.jmat.2021.04.002>.

- (3) Zhao, B.; Guo, B.; Xing, S.; Liu, Z.; Yuan, Y.; Ren, Z.; Tang, W.; Lian, Y.; Zhang, G.; Zou, C., et al. Highly Stable Perovskite Light-Emitting Diodes. *Matter* **2024**, 7 (3), 772–793. <https://doi.org/10.1016/j.matt.2023.11.022>.
- (4) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, 15 (6), 3692–3696. <https://doi.org/10.1021/nl5048779>.
- (5) Ding, N.; Wang, N.; Liu, S.; Wang, Y.; Zhou, D.; Xu, W.; Song, H. Research Progress on Doped Perovskite Materials. *Laser Optoelectron. Prog.* **2021**, 58 (15), 1516011. <https://doi.org/10.3788/LOP202158.1516011>.
- (6) Chen, Q.; Wu, J.; Ou, X.; Huang, B.; Almutlaq, J.; Zhumeckenov, A. A.; Guan, X.; Han, S.; Liang, L.; Yi, Z., et al. All-Inorganic Perovskite Nanocrystal Scintillators. *Nature* **2018**, 561 (7721), 88–93. <https://doi.org/10.1038/s41586-018-0451-1>.
- (7) Chen, X.; Zhou, H.; Wang, H. 2D/3D Halide Perovskites for Optoelectronic Devices. *Front. Chem.* **2021**, 9. <https://doi.org/10.3389/fchem.2021.715157>.
- (8) Lin, H.; Zhou, C.; Tian, Y.; Siegrist, T.; Ma, B. Low-Dimensional Organometal Halide Perovskites. *ACS Energy Lett.* **2018**, 3 (1), 54–62. <https://doi.org/10.1021/acsenergylett.7b00926>.
- (9) Zhou, C.; Lin, H.; Tian, Y.; Yuan, Z.; Clark, R.; Chen, B.; Burgt, L. J. van de; C. Wang, J.; Zhou, Y.; Hanson, K., et al. Luminescent Zero-Dimensional Organic Metal Halide Hybrids with near-Unity Quantum Efficiency. *Chem. Sci* **2018**, 9 (3), 586–593. <https://doi.org/10.1039/C7SC04539E>.
- (10) Lee, S.; Karkee, R.; Ben-Akacha, A.; Luong, D.; Winfred, J. S. R. V.; Lin, X.; Strubbe, D. A.; Ma, B. One-Dimensional Organic Metal Halide Nanoribbons with Dual Emission.

- Chem. Commun.* **2023**, 59 (25), 3711–3714. <https://doi.org/10.1039/D3CC00044C>.
- (11) Jana, M. K.; Janke, S. M.; Dirkes, D. J.; Dovletgeldi, S.; Liu, C.; Qin, X.; Gundogdu, K.; You, W.; Blum, V.; Mitzi, D. B. Direct-Bandgap 2D Silver–Bismuth Iodide Double Perovskite: The Structure-Directing Influence of an Oligothiophene Spacer Cation. *J. Am. Chem. Soc.* **2019**, 141 (19), 7955–7964. <https://doi.org/10.1021/jacs.9b02909>.
- (12) Chakraborty, N.; Ngo, T. A.; Dominguez Montero, A.; Liyanage, T.; McCandless, G. T.; Chan, J. Y.; Nguyen, T. D.; Whittaker-Brooks, L. Decoding Chirality Transfer Strengths and Structure–Property Relationships in Bismuth-Containing Chiral Hybrid Organic–Inorganic Semiconductors. *J. Am. Chem. Soc.* **2025**, 147 (32), 29431–29443. <https://doi.org/10.1021/jacs.5c09713>.
- (13) Li, D.; Liu, X.; Wu, W.; Peng, Y.; Zhao, S.; Li, L.; Hong, M.; Luo, J. Chiral Lead-Free Hybrid Perovskites for Self-Powered Circularly Polarized Light Detection. *Angew. Chem. Int. Ed.* **2021**, 60 (15), 8415–8418. <https://doi.org/10.1002/anie.202013947>.
- (14) Huizi-Rayó, U.; Gutierrez, J.; Seco, J. M.; Mujica, V.; Diez-Perez, I.; Ugalde, J. M.; Tercjak, A.; Cepeda, J.; San Sebastian, E. An Ideal Spin Filter: Long-Range, High-Spin Selectivity in Chiral Helicoidal 3-Dimensional Metal Organic Frameworks. *Nano Lett.* **2020**, 20 (12), 8476–8482. <https://doi.org/10.1021/acs.nanolett.0c02349>.
- (15) Naskar, S.; Mujica, V.; Herrmann, C. Chiral-Induced Spin Selectivity and Non-Equilibrium Spin Accumulation in Molecules and Interfaces: A First-Principles Study. *J. Phys. Chem. Lett.* **2023**, 14 (3), 694–701. <https://doi.org/10.1021/acs.jpcllett.2c03747>.
- (16) Zhou, Y.; Chen, J.; Bakr, O. M.; Mohammed, O. F. Metal Halide Perovskites for X-Ray Imaging Scintillators and Detectors. *ACS Energy Lett.* **2021**, 6 (2), 739–768. <https://doi.org/10.1021/acsenergylett.0c02430>.
- (17) Hu, Y.; Jin, J.; Han, K.; Xia, Z. Unveiling The Role of Cu⁺ Doping in Rb₂AgBr₃ Scintillators toward Enhanced Photoluminescence Quantum Efficiency and Light Yield.

- Adv. Opt. Mater.* **2024**, *12* (9), 2302063. <https://doi.org/10.1002/adom.202302063>.
- (18) Han, K.; Zhang, S.; Jin, J.; Sun, Y.; Wang, Y.; Xia, Z. Lattice Distortion Promoting Wavelength-Tunable Emissions in Cu(I)-Based Halides for Thermography and Anti-Counterfeiting. *Angew. Chem. Int. Ed.* **2025**, *64* (32), e202504406. <https://doi.org/10.1002/anie.202504406>.
- (19) Martín-García, B.; Spirito, D.; Lin, M.-L.; Leng, Y.-C.; Artyukhin, S.; Tan, P.-H.; Krahne, R. Low-Frequency Phonon Modes in Layered Silver-Bismuth Double Perovskites: Symmetry, Polarity, and Relation to Phase Transitions. *Adv. Opt. Mater.* **2022**, *10* (14), 2200240. <https://doi.org/10.1002/adom.202200240>.
- (20) Rury, A. S.; Sanni, A. M.; Konadu, D.; Danielson, T. Evidence of Defect-Induced Broadband Light Emission from 2D Ag–Bi Double Perovskites Grown at Liquid–Liquid Interfaces. *J. Chem. Phys.* **2023**, *158* (1), 011101. <https://doi.org/10.1063/5.0134568>.
- (21) Su, C.-Y.; Yao, Y.-F.; Zhang, Z.-X.; Wang, Y.; Chen, M.; Huang, P.-Z.; Zhang, Y.; Qiao, W.-C.; Fu, D.-W. The Construction of a Two-Dimensional Organic–Inorganic Hybrid Double Perovskite Ferroelastic with a High T_c and Narrow Band Gap. *Chem. Sci.* **2022**, *13* (17), 4794–4800. <https://doi.org/10.1039/D1SC07045B>.
- (22) Jaffe, A.; Lin, Y.; Beavers, C. M.; Voss, J.; Mao, W. L.; Karunadasa, H. I. High-Pressure Single-Crystal Structures of 3D Lead-Halide Hybrid Perovskites and Pressure Effects on Their Electronic and Optical Properties. *ACS Cent. Sci.* **2016**, *2* (4), 201–209. <https://doi.org/10.1021/acscentsci.6b00055>.
- (23) Mao, L.; Stoumpos, C. C.; Kanatzidis, M. G. Two-Dimensional Hybrid Halide Perovskites: Principles and Promises. *J. Am. Chem. Soc.* **2019**, *141* (3), 1171–1190. <https://doi.org/10.1021/jacs.8b10851>.
- (24) Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E., et al. One-Dimensional Organic Lead Halide

- Perovskites with Efficient Bluish White-Light Emission. *Nat. Commun.* **2017**, *8* (1), 14051. <https://doi.org/10.1038/ncomms14051>.
- (25) Sun, S.; Lu, M.; Gao, X.; Shi, Z.; Bai, X.; Yu, W. W.; Zhang, Y. 0D Perovskites: Unique Properties, Synthesis, and Their Applications. *Adv. Sci.* **2021**, *8* (24), 2102689. <https://doi.org/10.1002/advs.202102689>.
- (26) Gao, L.; Hu, P.; (Frank) Liu, S. Low-Dimensional Perovskite Modified 3D Structures for Higher-Performance Solar Cells. *J. Energy Chem.* **2023**, *81*, 389–403. <https://doi.org/10.1016/j.jechem.2023.01.061>.
- (27) Zhang, X.; Han, W. P.; Wu, J. B.; Milana, S.; Lu, Y.; Li, Q. Q.; Ferrari, A. C.; Tan, P. H. Raman Spectroscopy of Shear and Layer Breathing Modes in Multilayer MoS₂. *Phys. Rev. B* **2013**, *87* (11), 115413. <https://doi.org/10.1103/PhysRevB.87.115413>.
- (28) Scheuschner, N.; Gillen, R.; Staiger, M.; Maultzsch, J. Interlayer Resonant Raman Modes in Few-Layer MoS₂. *Phys. Rev. B* **2015**, *91* (23), 235409. <https://doi.org/10.1103/PhysRevB.91.235409>.
- (29) Zhao, Y.; Luo, X.; Li, H.; Zhang, J.; Araujo, P. T.; Gan, C. K.; Wu, J.; Zhang, H.; Quek, S. Y.; Dresselhaus, M. S., et al. Interlayer Breathing and Shear Modes in Few-Trilayer MoS₂ and WSe₂. *Nano Lett.* **2013**, *13* (3), 1007–1015. <https://doi.org/10.1021/nl304169w>.
- (30) Guerrero, E.; Karkee, R.; Strubbe, D. A. Phase Stability and Raman/IR Signatures of Ni-Doped MoS₂ from Density Functional Theory Studies. *J. Phys. Chem. C* **2021**, *125* (24), 13401–13412. <https://doi.org/10.1021/acs.jpcc.1c02974>.
- (31) Zhang, H.; Vickers, E. T.; Erickson, S.; Guarino-Hotz, M.; Barnett, J. L.; Ghosh, S.; Zhang, J. Z. Synthesis and Properties of Stable Amino Metal Halide Molecular Clusters in the Solid State. *J. Phys. Chem. Lett.* **2022**, *13* (45), 10543–10549. <https://doi.org/10.1021/acs.jpcclett.2c02977>.

- (32) Xue, X.; Liu, Z.; Eisenberg, S.; Ren, Q.; Lin, D.; Coester, E.; Zhang, H.; Zhang, J. Z.; Wang, X.; Li, Y. Regulated Interfacial Proton and Water Activity Enhances $\text{Mn}^{2+}/\text{MnO}_2$ Platform Voltage and Energy Efficiency. *ACS Energy Lett.* **2023**, 8 (11), 4658–4665. <https://doi.org/10.1021/acsenergylett.3c01354>.
- (33) Zhang, H.; Oduntan, A.; Zhuo, Z.; Chuang, S. S. C.; Guo, J.; Zhang, J. Z. New Insights into Nonthermal Plasma-Assisted Poly(Vinyl Alcohol) Depolymerization Catalyzed by TiO_2 . *J. Phys. Chem. C* **2025**, 129 (10), 4950–4963. <https://doi.org/10.1021/acs.jpcc.4c07876>.
- (34) Pérez-Osorio, M. A.; Lin, Q.; Phillips, R. T.; Milot, R. L.; Herz, L. M.; Johnston, M. B.; Giustino, F. Raman Spectrum of the Organic–Inorganic Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ from First Principles and High-Resolution Low-Temperature Raman Measurements. *J. Phys. Chem. C* **2018**, 122 (38), 21703–21717. <https://doi.org/10.1021/acs.jpcc.8b04669>.
- (35) Volonakis, G.; Filip, M. R.; Haghighirad, A. A.; Sakai, N.; Wenger, B.; Snaith, H. J.; Giustino, F. Lead-Free Halide Double Perovskites via Heterovalent Substitution of Noble Metals. *J. Phys. Chem. Lett.* **2016**, 7 (7), 1254–1259. <https://doi.org/10.1021/acs.jpcclett.6b00376>.
- (36) Ji, G. and Xiao, Z. Jahn–Teller Distortion-Stabilized Halide Double Perovskites with Unusual Rock-Salt-Type Ordering of Divalent B-Site Cations. *Chem. Mater.* **2022**, 34 (18), 8207–8212. <https://doi.org/10.1021/acs.chemmater.2c01496>.
- (37) Ma, Z.; Lv, P.; He, X.; Wang, F.; Li, Y.; Xiao, G.; Zou, B. Self-Trapped Excitons or Bi^{3+} Ions for Broad Emission in a Lead-Free Double Perovskite? Hearing What Pressure Says. *Nano Lett.* **2025**. <https://doi.org/10.1021/acs.nanolett.5c01709>.
- (38) Vickers, E. T.; Xu, K.; Dreskin, B. W.; Graham, T. A.; Li, X.; Zhang, J. Z. Ligand Dependent Growth and Optical Properties of Hybrid Organo-Metal Halide Perovskite Magic Sized Clusters. *J. Phys. Chem. C* **2019**, 123 (30), 18746–18752.

- <https://doi.org/10.1021/acs.jpcc.9b05521>.
- (39) Vickers, E. T.; Enlow, E. E.; Delmas, W. G.; DiBenedetto, A. C.; Chowdhury, A. H.; Bahrami, B.; Dreskin, B. W.; Graham, T. A.; Hernandez, I. N.; Carter, S. A.; Ghosh, S.; Qiao, Q.; Zhang, J. Z. Enhancing Charge Carrier Delocalization in Perovskite Quantum Dot Solids with Energetically Aligned Conjugated Capping Ligands. *ACS Energy Lett.* **2020**, *5* (3), 817–825. <https://doi.org/10.1021/acsenergylett.0c00093>.
- (40) Zhang, H.; Zeitz, D. C.; Zhang, J. Z. Ultrafast Study of Excited State Dynamics of Amino Metal Halide Molecular Clusters. *J. Phys. Chem. Lett.* **2023**, *14* (36), 8095–8099. <https://doi.org/10.1021/acs.jpcclett.3c01952>.
- (41) Cherrette, V. L.; Zeitz, D.; Khvichia, M.; Cooper, J. K.; Ping, Y.; Zhang, J. Z. Enhancing the Photoexcited Carrier Spin Relaxation Lifetime in CsPbBr₃ Perovskite Quantum Dots by ²⁰⁸Pb Isotope Enrichment. *J. Phys. Chem. Lett.* **2025**, *16* (13), 3336–3342. <https://doi.org/10.1021/acs.jpcclett.5c00123>.
- (42) Bhuvanesh, N. S. P. and Gopalakrishnan, J. Solid-State Chemistry of Early Transition-Metal Oxides Containing d⁰ and d¹ Cations. *J. Mater. Chem.* **1997**, *7* (12), 2297–2306. <https://doi.org/10.1039/a703996d>.
- (43) Connor, B. A.; Leppert, L.; Smith, M. D.; Neaton, J. B.; Karunadasa, H. I. Layered Halide Double Perovskites: Dimensional Reduction of Cs₂AgBiBr₆. *J. Am. Chem. Soc.* **2018**, *140* (15), 5235–5240. <https://doi.org/10.1021/jacs.8b01543>.
- (44) Brooker, M. H.; Nielsen, O. F.; Praestgaard, E. Assessment of Correction Procedures for Reduction of Raman Spectra. *J. Raman Spectrosc.* **1988**, *19* (2), 71–78. <https://doi.org/10.1002/jrs.1250190202>.
- (45) Tuschel, D. Raman Spectroscopy and Imaging of Low Energy Phonons. *Spectroscopy* **2015**, *30* (9), 18–31. <https://www.spectroscopyonline.com/view/raman-spectroscopy-and-imaging-low-energy-phonons>.
- (46) Zhang, J.; Wang, C.-Z.; Zhu, Z. Z.; Dobrovitski, V. V. Vibrational Modes and Lattice

- Distortion of a Nitrogen-Vacancy Center in Diamond from First-Principles Calculations. *Phys. Rev. B* **2011**, *84* (3), 035211. <https://doi.org/10.1103/PhysRevB.84.035211>.
- (47) Bowmaker, G. A.; Healy, P. C.; Kildea, J. D.; White, A. H. Far Infrared Spectroscopy of Complexes of Copper(I) Halides with Phosphine and Amine Ligands. *Spectrochim. Acta A Mol. Spectrosc.* **1988**, *44* (11), 1219–1223. [https://doi.org/10.1016/0584-8539\(88\)80096-5](https://doi.org/10.1016/0584-8539(88)80096-5).
- (48) Stephens, S. L.; Tew, D. P.; Walker, N. R.; Legon, A. C. $\text{H}_3\text{P}\cdots\text{AgI}$: Generation by Laser-Ablation and Characterization by Rotational Spectroscopy and Ab Initio Calculations. *Phys. Chem. Chem. Phys.* **2016**, *18* (28), 18971–18977. <https://doi.org/10.1039/c6cp03512d>.
- (49) Castner, E. W. Modern Spectroscopy, 4th Edition (J. Michael Hollas). *J. Chem. Educ.* **2005**, *82* (1), 43. <https://doi.org/10.1021/ed082p43.1>.
- (50) Brandt, R. E.; Stevanović, V.; Ginley, D. S.; Buonassisi, T. Identifying Defect-Tolerant Semiconductors with High Minority-Carrier Lifetimes: Beyond Hybrid Lead Halide Perovskites. *MRS Commun.* **2015**, *5* (2), 265–275. <https://doi.org/10.1557/mrc.2015.26>.
- (51) McClintock, L. M.; Yuan, L.; Song, Z.; Pettes, M. T.; Yarotski, D.; Karkee, R.; Strubbe, D. A.; Tan, L. Z.; Ben-Akacha, A.; Ma, B., et al. Surface Effects on Anisotropic Photoluminescence in One-Dimensional Organic Metal Halide Hybrids. *Small Struct.* **2023**, *4* (8), 2200378. <https://doi.org/10.1002/ssstr.202200378>.
- (52) Masud, M. M.; Viera, J.; Ben-Akacha, A.; Ma, B.; Strubbe, D. A. Computational and Experimental Investigation of Chiral and Achiral 2D Organic Lead Bromide Perovskites: Octahedral Distortions and Electronic and Optical Properties. arXiv September 8, 2025. <https://doi.org/10.48550/arXiv.2509.07152>.
- (53) Etienne, T.; Mosconi, E.; De Angelis, F. Dynamical Origin of the Rashba Effect in Organohalide Lead Perovskites: A Key to Suppressed Carrier Recombination in

- Perovskite Solar Cells? *J. Phys. Chem. Lett.* **2016**, 7 (9), 1638–1645.
<https://doi.org/10.1021/acs.jpcllett.6b00564>.
- (54) Park, I.-H.; Zhang, Q.; Kwon, K. C.; Zhu, Z.; Yu, W.; Leng, K.; Giovanni, D.; Choi, H. S.; Abdelwahab, I.; Xu, Q.-H., et al. Ferroelectricity and Rashba Effect in a Two-Dimensional Dion-Jacobson Hybrid Organic–Inorganic Perovskite. *J. Am. Chem. Soc.* **2019**, 141 (40), 15972–15976. <https://doi.org/10.1021/jacs.9b07776>.
- (55) Jana, M. K.; Song, R.; Xie, Y.; Zhao, R.; Serce, P. C.; Blum, V.; Mitzi, D. B. Structural Descriptor for Enhanced Spin-Splitting in 2D Hybrid Perovskites. *Nat. Commun.* **2021**, 12 (1), 4982. <https://doi.org/10.1038/s41467-021-25149-7>.
- (56) Kepenekian, M.; Robles, R.; Katan, C.; Saponi, D.; Pedesseau, L.; Even, J. Rashba and Dresselhaus Effects in Hybrid Organic–Inorganic Perovskites: From Basics to Devices. *ACS Nano* **2015**, 9 (12), 11557–11567. <https://doi.org/10.1021/acsnano.5b04409>.
- (57) Kepenekian, M. and Even, J. Rashba and Dresselhaus Couplings in Halide Perovskites: Accomplishments and Opportunities for Spintronics and Spin–Orbitronics. *J. Phys. Chem. Lett.* **2017**, 8 (14), 3362–3370. <https://doi.org/10.1021/acs.jpcllett.7b01015>.
- (58) Becker, M. A.; Vaxenburg, R.; Nedelcu, G.; Serce, P. C.; Shabaev, A.; Mehl, M. J.; Michopoulos, J. G.; Lambrakos, S. G.; Bernstein, N.; Lyons, J. L., et al. Bright Triplet Excitons in Caesium Lead Halide Perovskites. *Nature* **2018**, 553 (7687), 189–193. <https://doi.org/10.1038/nature25147>.
- (59) Smith, M. D.; Jaffe, A.; Dohner, E. R.; Lindenberg, A. M.; Karunadasa, H. I. Structural Origins of Broadband Emission from Layered Pb–Br Hybrid Perovskites. *Chem. Sci.* **2017**, 8 (6), 4497–4504. <https://doi.org/10.1039/C7SC01590A>.
- (60) Liu, S.; Kepenekian, M.; Bodnar, S.; Feldmann, S.; Heindl, M. W.; Fehn, N.; Zerhoch, J.; Shcherbakov, A.; Pöthig, A.; Li, Y., et al. Bright Circularly Polarized Photoluminescence in Chiral Layered Hybrid Lead-Halide Perovskites. *Sci. Adv.* **2023**,

- 9 (35), eadh5083. <https://doi.org/10.1126/sciadv.adh5083>.
- (61) Zhao, X.-H.; Li, N.-N.; Peng, J.; Xu, J.; Luo, P.; Dong, X.-Y.; Hu, X. Circularly Polarized Luminescence Enlargement from Crystals to Oriented Films of Enantiopure 2D Hybrid Perovskites. *Chem. Commun.* **2023**, 59 (45), 6881–6884. <https://doi.org/10.1039/D3CC01739G>.
- (62) Prasanna, R.; Gold-Parker, A.; Leijtens, T.; Conings, B.; Babayigit, A.; Boyen, H.-G.; Toney, M. F.; McGehee, M. D. Band Gap Tuning via Lattice Contraction and Octahedral Tilting in Perovskite Materials for Photovoltaics. *J. Am. Chem. Soc.* **2017**, 139 (32), 11117–11124. <https://doi.org/10.1021/jacs.7b04981>.
- (63) Shao, Y.; Gao, W.; Yan, H.; Li, R.; Abdelwahab, I.; Chi, X.; Rogée, L.; Zhuang, L.; Fu, W.; Lau, S. P. et al. Unlocking Surface Octahedral Tilt in Two-Dimensional Ruddlesden-Popper Perovskites. *Nat. Commun.* **2022**, 13 (1), 138. <https://doi.org/10.1038/s41467-021-27747-x>.

Supporting information

Low Frequency Vibrational Modes of Two-Dimensional Lead-Free Metal Halide Double Perovskites

Heng Zhang¹, Remi J. Leano², Geng Xie³, Celia Todd¹, Jieping Liu⁴, Timothy C. Johnstone¹, David Lederman⁵, Qi Pang⁴, Lingzi Sang³, David A. Strubbe^{6}, Jin Z. Zhang^{1*}*

¹ Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

² Department of Chemistry and Biochemistry, University of California, Merced, CA 95343, USA

³ Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

*⁴ School of Chemistry and Chemical Engineering,
Guangxi University, Nanning, Guangxi 530004, China*

⁵ Department of Physics and Materials Science & Engineering Program, University of California, Santa Cruz, CA 95064, USA University of California, Santa Cruz, CA 95064, USA

⁶ Department of Physics, University of California, Merced, CA 95343, USA

* Corresponding Author. Email: dstrubbe@ucmerced.edu; zhang@ucsc.edu

A. Experimental and Computational Methods

1. Materials

Ag₂O (99+%) was purchased from Acros, Cu₂O (97%) was purchased from Aldrich, and Bi₂O₃ (99.99%) was purchased from Thermo Scientific. (S)-(+)-b-methylphenethylamine (*S*-β-MPA) and hydroiodic acid (57 wt% in H₂O, 99.99%) were purchased from Sigma-Aldrich without any further purification.

2. Synthesis of MPA-AgBiI₈ and MPA-CuBiI₈

Ag₂O (0.232 g, 1.00 mmol) or Cu₂O (0.143 g, 1.00 mmol) and Bi₂O₃ (0.476 g, 1.00 mmol) were dissolved in 48% wt% aqueous HI solution (diluted to 48% from 57 wt%) (20 mL) under heating at 120 °C, and medium-speed stirring, resulting in a red solution. Subsequent addition of *S*-β-MPA (0.540 g, 4.00 mmol) to the hot solution led to the formation of a red precipitate, which subsequently redissolved with continued stirring, ending up with a red solution. The solution was then cooled to room temperature and concentrated by evaporation to yield red crystals of the product, followed by a rinse with ethyl acetate three times.

3. SEM Measurements

SEM images were acquired with Thermo Scientific Scios 2 DualBeam, equipped with an Oxford Instruments AZtecLive Ultim Max 100 EDS detector.

4. Spectroscopy Measurements

The electronic absorption spectra of the powder were measured with a UV2600 variable slit UV-Vis spectrophotometer based on reflection mode (converted to absorption via Kubelka-Munk function) from Shanghai Tianmei Scientific Instrument. The scanning speed was set at 600 nm/min, and the slit width was set at 5.0.

The photoluminescence (PL) spectra of the samples were acquired at room temperature using an Edinburgh Instruments FLS1000 fluorescence photometer with an Xe900 excitation source and a PMT1700 detector.

Time-resolved photoluminescence (TRPL) profiles of samples were determined at room temperature using the Edinburgh μF2 light source of the FLS1000 fluorescence photometer from Edinburgh Instruments.

5. Single Crystal X-ray Diffraction (scXRD)

A single crystal of (*S*-MPA)₄AgBiI₈ was selected under a microscope, loaded onto a MiTeGen polyimide sample loop using Type NVH Cargille immersion oil, and mounted onto a Rigaku XtaLAB Synergy-S single-crystal diffractometer. The crystal was cooled to 100 K under a stream of nitrogen. Diffraction of Cu Kα radiation from a PhotonJet-S microfocus

source was detected using a HyPix6000HE hybrid photon counting detector. Screening, indexing, data collection, and data processing were performed with CrysAlisPro. The structures were solved using SHELXT and refined using SHELXL following established strategies.¹⁻³ All non-H atoms were refined anisotropically. C-bound H atoms were placed at calculated positions and refined with a riding model and coupled isotropic displacement parameters ($1.2 \times U_{eq}$ for non-methyl C-H atoms and $1.5 \times U_{eq}$ for methyl groups). Crystal structure visualization was performed with Mercury.⁴

6. Powder X-ray Diffraction (pXRD)

Powder XRD patterns were collected on a Bruker D8 Discover Diffractometer using Cu K α radiation (40 kV and 40 mA) with degrees per step and time/step parameters of 0.02 degrees per step and 0.4 s/step, respectively, at 2θ angle from 10 to 60°. The simulated pXRD pattern is based on the MPA-AgBiI₈ scXRD data at 290 K from Li's work.⁵

7. Low Frequency Raman Spectroscopy (0 cm⁻¹ to 200 cm⁻¹)

Low frequency Raman spectra were acquired by an Olympus BX51 microscope equipped with an ONDAX THz-Raman spectroscopy probe. 976 nm excitation laser was generated at the source (THz-Raman) with a power of 500 mW, and the power onto the sample is about 150 mW after decaying. The built-in amplified spontaneous emission filter and notch filter enable measurements of Raman signals down to 5 cm⁻¹ and we can still attain data down to 0 cm⁻¹ with uncertainties. Signal was captured by using a 10X objective lens (Olympus, NA = 0.3, FN = 26.5). The Raman scattering signal was directed into spectrograph (Andor SR-303i-B, 300 l/m, Blaze 1000) through fiber optics (Diamond USA) and eventually detected by InGaAs CCD (Andor DU90A). Each spectrum was accumulated from 90 scans (1 s/scan).

8. High Frequency Raman Spectroscopy (200 cm⁻¹ to 1800 cm⁻¹)

High frequency Raman spectra were acquired using a Thermo Fisher DRX3 Raman microspectrometer. The laser excitation source was a diode laser ($\lambda_{ex} = 785$ nm). Spectra were recorded under the following conditions: stainless-steel substrate, 50 $\times$ objective, collect exposure time 30 s for five accumulations, laser power 30 mW (in focus), and aperture 50 μ m slit.

9. FTIR Spectroscopy

The FTIR spectra of the perovskites were collected using a PerkinElmer FTIR Spectrum Two series spectrometer with a universal ATR sampling accessory (UATR). This solid FTIR uses a high refractive index diamond to apply pressure on the solid samples and guide the beam up to a few microns to the samples. To make the IR signal intensities consistent, the pressure applied to all the samples was around 100.

10. DFT Calculation

We performed first-principles density-functional perturbation theory⁶ calculations as implemented in Quantum ESPRESSO⁷ on R -MPA-XBiI₈ (X=Ag, Cu) with the Perdew-Burke-Ernzerhof (PBE)⁸ exchange-correlation functional to predict and understand its vibrational modes (Raman and IR). PBE was used for both structural relaxation and for the calculation of Raman frequencies. Another exchange-correlation functional, Local Density Approximation (LDA), was used to calculate the Raman tensor as a separate calculation, as calculation of the Raman tensor is not yet implemented for PBE in Quantum ESPRESSO version 7.2, allowing us to obtain Raman intensities. The calculation of intensities as implemented in Quantum ESPRESSO is described in Lazzeri *et al.*⁹ We selected PBE as our exchange functional due to its closer agreement with the experimental lattice parameters compared to LDA and PBE with Grimme dispersion correction, version 2 (GD2)¹⁰ (Table S3). Norm-conserving scalar-relativistic pseudopotentials from ONCVSP (Optimized Norm-Conserving Vanderbilt Pseudopotential) code version 3.3.0 with standard accuracy were used as obtained from Pseudo Dojo.^{11,12} Relaxation fixed at the experimental lattice parameters resulted in imaginary phonon modes.

For the Ag-based perovskite, we ran a variable-cell relaxation calculation starting from the experimental XRD structure of $(R\text{-MPA})_4\text{AgBiI}_8$ from Ref.⁵ The R -version of the structure was used for simulation, and all the properties would be identical for R and S enantiomers.¹³ The unit cell has 212 atoms. The planewave cutoff energy is 56 Ry. Energy convergence thresholds are 10⁻⁸ Ry. Our variable-cell relaxation forces thresholds are set to 10⁻⁵ Ry/bohr. Our self-consistency convergence thresholds for the ground state are set to 10⁻¹⁸ Ry. The BFGS geometry optimization algorithm is used for structural relaxation, with the trust radius set to 10⁻⁵ bohr. The components of the stress tensor were converged to a magnitude of less than 1 kbar. We use only the Γ -point for k -point sampling, given the large unit cell. We use 10⁻¹⁶ for the phonon convergence threshold. These strict thresholds for both structural relaxation and calculation of phonons were required to accurately obtain the lowest frequency phonon modes – at less stringent thresholds, imaginary phonon modes were obtained. We combine PBE Raman frequencies with LDA Raman intensities and apply the acoustic sum rule. Our methods for MPA-CuBiI₈ are the same, starting again from the experimental Ag-based structure of Ref.⁵ but substituting Cu atoms for Ag before structural relaxation.

The DFT results are a temperature-independent reduced Raman spectrum. Temperature dependence has been removed from the experimental Raman spectra, to generate a reduced Raman spectrum, by multiplying the experimental intensity by the temperature factor¹⁴:

$$\omega \left(1 - e^{-\frac{\hbar\omega}{kT}} \right) \quad (\text{S1})$$

where ω is frequency in s⁻¹, $\hbar$ is the reduced Planck constant ($1.054571817 \times 10^{-34}$ J·s⁻¹), k is the Boltzmann constant (1.380649×10^{-23} J·K⁻¹), and T is the temperature in Kelvin (293 K).

B. Non-normalized PL spectra, fitting method and parameters for the TRPL

The PL spectra were acquired with excitation of 278 nm for the Ag-based perovskite and 254 nm for the Cu-based perovskite, and the Ag sample shows a 16-fold greater intensity as

compared to that of the Cu-based material at the PL peak position. The excitation wavelength in the bluer region is to show the difference in PL spectra for the two materials.

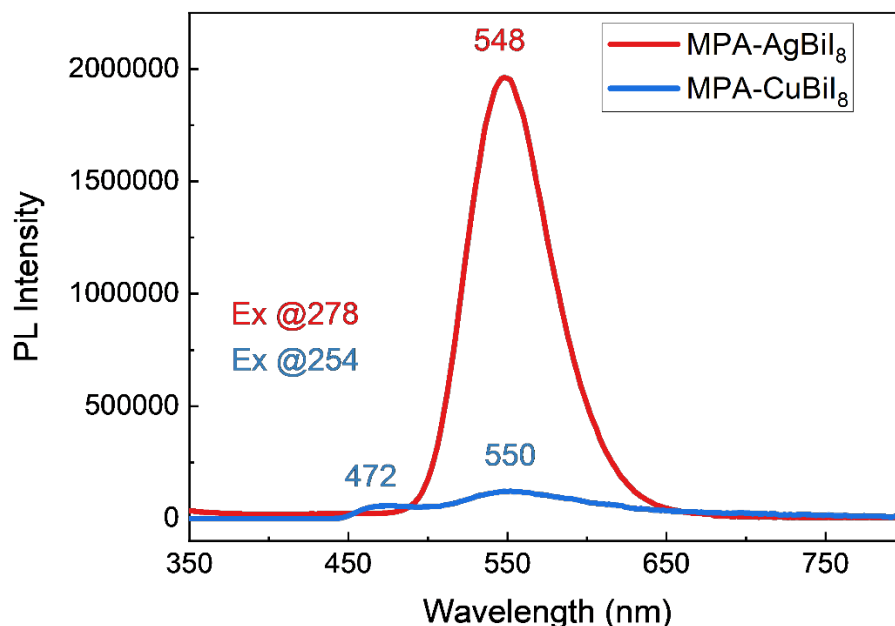


Figure S1 Non-normalized PL spectra of MPA-AgBiI₈ (red) and MPA-CuBiI₈ (blue).

The TRPL profiles were recorded using the time-correlated single-photon counting (TCSPC) technique. Ag-based perovskite was excited at 278 nm and monitored at 548 nm, and Cu-based perovskite was excited at 260 nm and monitored at 550 nm. The profiles are fit using the function: $y = y_0 + A_1 e^{(-x/\tau_1)} + A_2 e^{(-x/\tau_2)}$ (1)

where A_1 and A_2 denote fast and slow component amplitudes, τ_1 and τ_2 denote fast and slow component time constants. The detailed fitting parameters are summarized in Table S1.

Table S1 Summary of fitting parameters of the TRPL results.

Components	Ag @ 548 nm	Cu @ 550 nm
y_0	$1.9 \pm 0.4 \times 10^{-4}$	$1.1 \pm 0.5 \times 10^{-3}$
A_1	0.5 ± 0.1 (45%)	1.6 ± 0.2 (62%)
τ_1 (ns)	300 ± 40	5 ± 2
A_2	0.6 ± 0.1	1.0 ± 0.2

	(55%)	(38%)
τ_2 (ns)	378±40	334±40

C. Crystal structure of MPA-AgBiI₈

Figure S2 shows the structure of the MPA-AgBiI₈ double perovskite in which layers of the organic *S*-β-MPA cation alternate with inorganic [AgBiI₈]⁴⁻. The inorganic layer features vertex-sharing [AgI₆]⁵⁻ and [BiI₆]³⁻ octahedra. Three of the I atoms were each disordered across two closely spaced positions, as was the Ag atom. The bond metrics in Table S2 were calculated using the centroid for each pair of disordered atoms. The Bi–I distances range from 3.023(5) to 3.112(5) Å and the I–Bi–I angles closely approach those of an octahedron. The Ag–I distances exhibit a much greater distribution. As expected, the Ag(I) center adopts a linear geometry with two tightly bound I atoms, I21 and I22, at distances of 2.665(3) and 2.683(3) Å, respectively. The remaining four I atoms are vertices shared with the [BiI₆]³⁻ octahedra and the Ag–I distances are substantially longer, ranging from 3.335(6) to 3.524(6) Å. These four Ag–I interactions are paired with a short distance (3.335(6) or 3.388(4) Å) *trans* to a long distance (3.423(7) or 3.524(6) Å). The I–Ag–I angle with the tightly bound, non-bridging I atoms is nearly linear, but the remaining equatorial I atoms exhibit a greater range of angles, with one *cis* I–Ag–I angle even exceeding 105°. Although the Bi and Ag atoms are arrayed on a nearly centrosymmetric lattice, with the Ag atoms almost coincident with Bi–Bi centroids, the tilting of the octahedra (Figure S2) breaks the overall inversion symmetry between the layers.

Table S2 Selected bond lengths and angles for MPA-AgBiI₈.^a

Bond length (Å)		Bond angle (degrees)	
Bi1–I1	3.112(5)	I1–Bi1–I2	177.01(13)
Bi1–I2	3.025(6)	I3–Bi1–I4	176.99(10)
Bi1–I3	3.023(5)	I5–Bi1–I6	178.65(3)
Bi1–I4	3.1077(9)	I1–Bi1–I3	91.84(12)
Bi1–I5	3.0721(8)	I1–Bi1–I6	89.26(5)
Bi1–I6	3.0816(8)	I3–Bi1–I6	89.82(8)
Ag1–I21	2.665(3)	I21–Ag1–I22	177.95(16)
Ag1–I22	2.683(3)	I2–Ag1–I3	176.92(17)
Ag1–I2	3.423(7)	I1–Ag1–I4	178.07(13)
Ag1–I3	3.335(6)	I21–Ag1–I2	87.54(13)
Ag1–I4	3.388(4)	I21–Ag1–I4	91.39(11)
Ag1–I1	3.524(6)	I2–Ag1–I4	105.34(13)

^a Ag1, I1, I2, and I3 were each disordered across two positions. These bond metrics were calculated using the centroid of the two disordered atom positions.

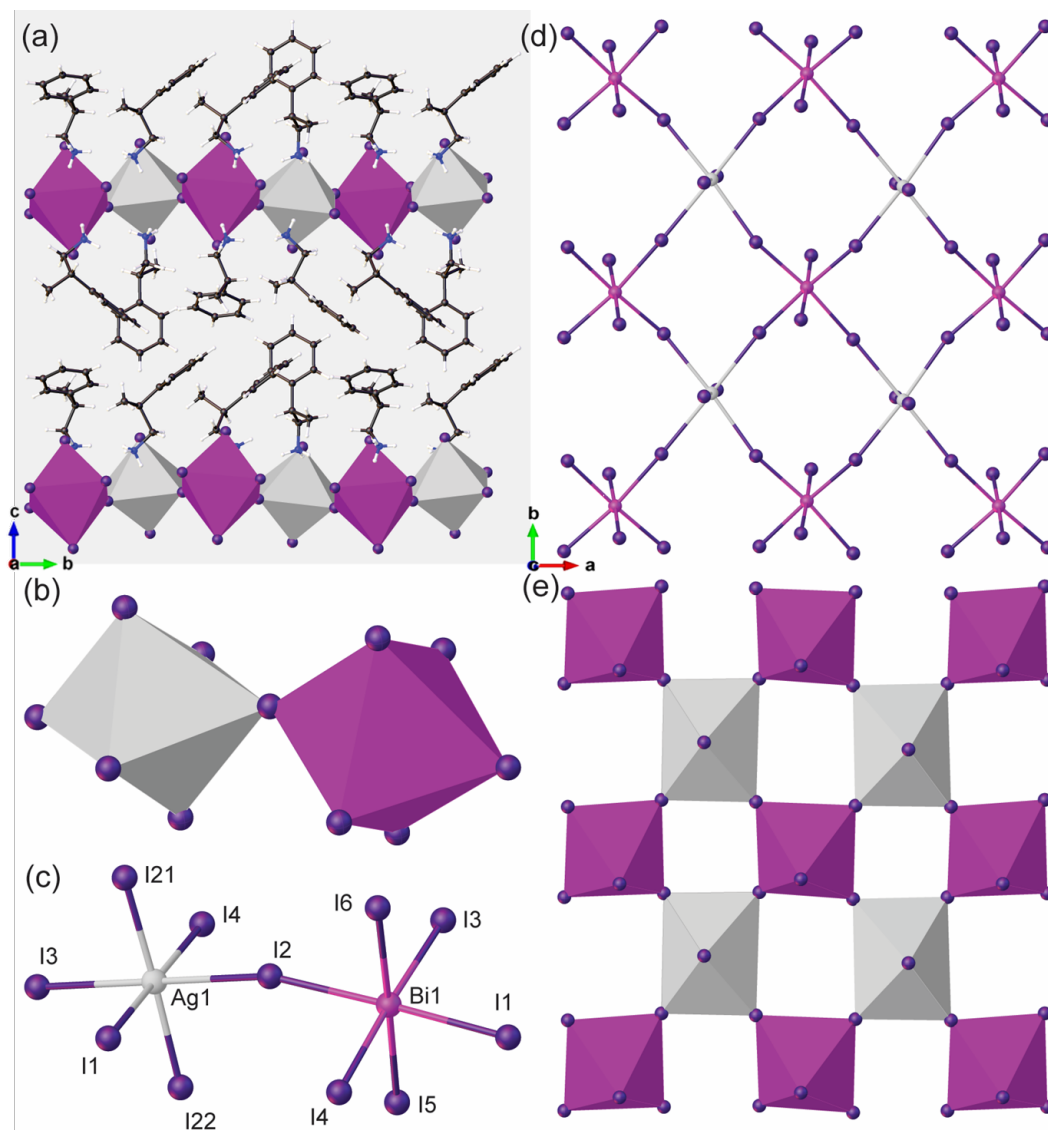


Figure S2 (a) View of the layered structure of MPA-AgBiI₈ along *a* with *S*-β-MPA cations as balls and sticks and Bi and Ag as polyhedra. (b) One vertex-bridged AgI₆/BiI₆ pair shown as polyhedra. (c) The same atoms and orientation as (b) but without polyhedra and atom labels corresponding to Table S2. (d) View of the inorganic layer along *c* with atoms shown as balls and sticks. (e) The same orientation as (d) but with Ag and Bi polyhedra. For all depictions, disordered Ag1, I1, I2, and I3 atoms are represented with a single sphere at the position of the centroid of the two disordered atoms. Color code: C black, N blue, H white, Ag grey, Bi magenta, I purple.

Table S3 The summary of the experimental and calculated lattice parameters of MPA-XBiI₈ (X=Ag or Cu) single crystal.^a

	a (Å)	b (Å)	c (Å)	β (°)	Unit-cell Volume (bohr ³)	Temp (K)
Exp. Ag structure from literature⁵	9.657	17.051	16.754	102.503	18173.7	290
Exp. Ag structure in this work	9.568	16.767	16.570	102.508	17232.1	104
Theory Ag structure (PBE)	8.728	15.891	16.047	101.651	14711.2	0
Theory Ag structure (LDA)	8.339	15.178	15.367	101.398	12866.4	0
Theory Ag structure (PBE+GD2)	8.566	15.423	15.408	101.701	13452.2	0
Theory Cu structure (PBE)	8.239	14.880	15.035	101.763	12178.0	0

^a The α and γ angles are both 90° in monoclinic crystal system.

D. Low Frequency Raman vibration modes of MPA-AgBiI₈ perovskite

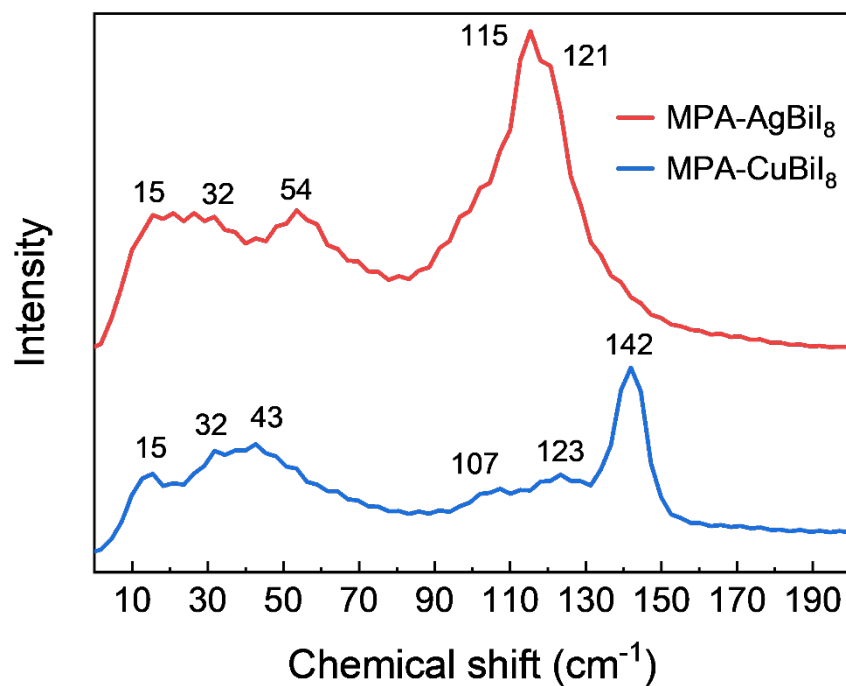
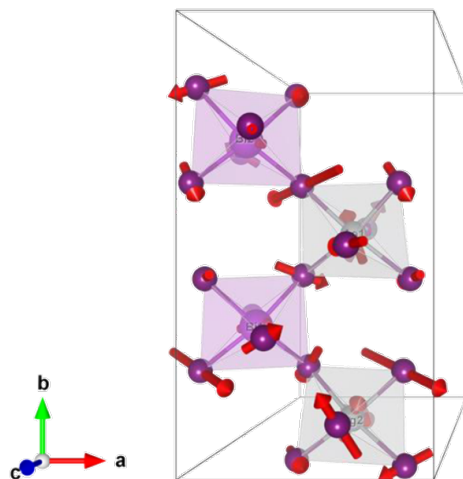
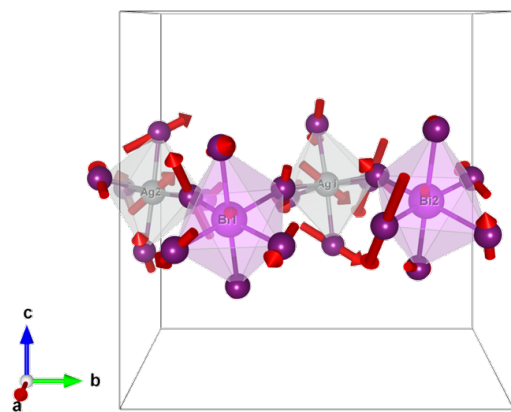
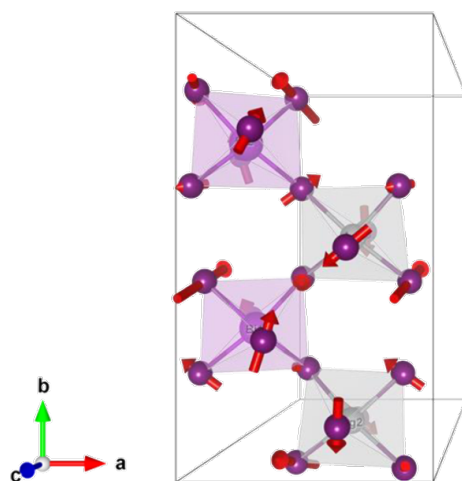
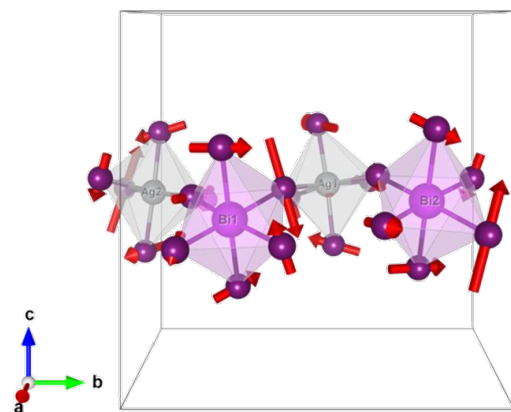


Figure S3 Experimental Raman spectrum in the low frequency region (0-200 cm⁻¹) with temperature dependence.

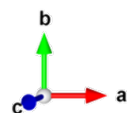
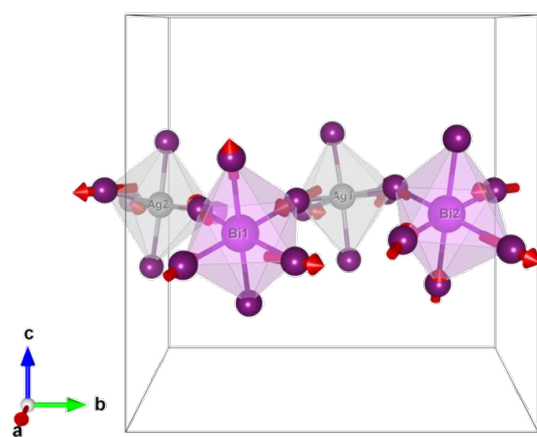
Density-functional perturbation theory calculations were applied to calculate and understand the vibrational modes of *S*-MPA-AgBiI₈ with the computational method described in Section A 10. The mode illustrations are in Figure S4, and the symmetry and description of different modes are summarized in Table S4.



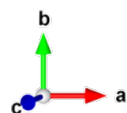
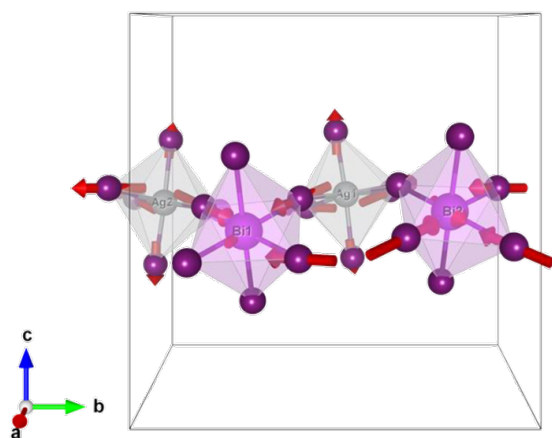
31 cm⁻¹



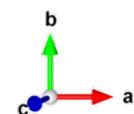
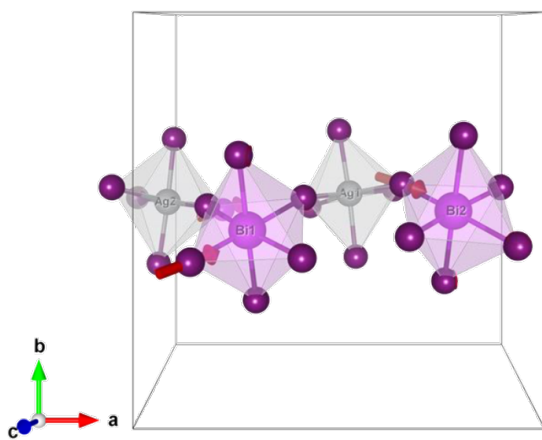
54 cm⁻¹



111 cm⁻¹



129 cm⁻¹



140 cm⁻¹

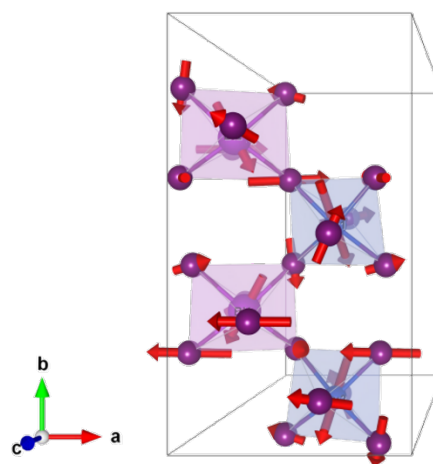
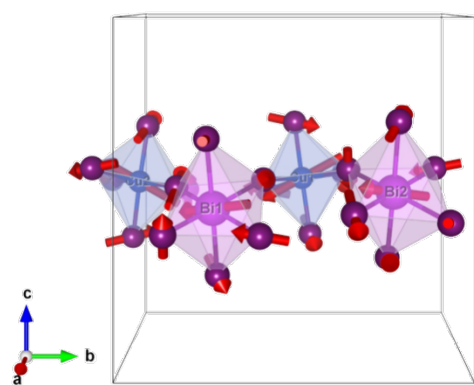
Figure S4 Low frequency vibration modes in the crystal structure as calculated for MPA-AgBiI₈ perovskite, shown from two different perspectives.

Table S4 Full description of the assignments of the vibration modes in the low Raman frequency region (0-200 cm⁻¹) of Ag-based 2D double perovskite. In all modes, molecules librate and have some degree of internal twisting. Where a distortion or motion is mentioned without specifying whether it is in or out of plane, the distortion has components in both directions. A and B are Mulliken symbols, irreducible representations for *P2*₁, where A is symmetric and B is antisymmetric.

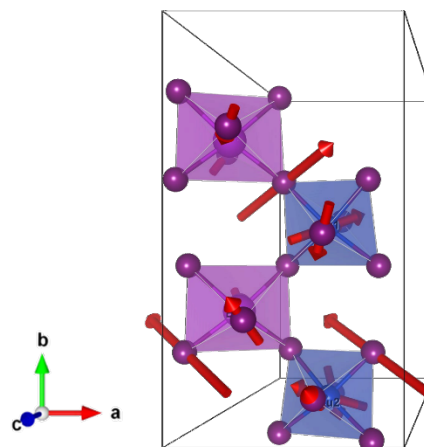
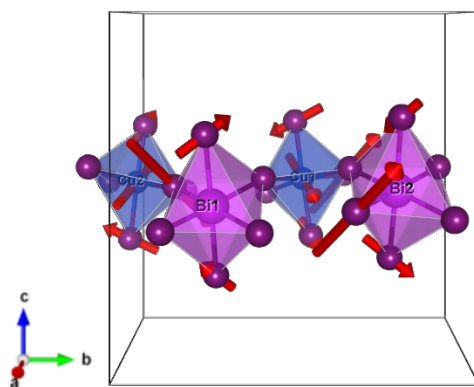
Frequency [cm ⁻¹]	Symmetry	Description	Mode #
31	A	In- and out-of-plane bond angle distortions of octahedra. Ag octahedra tilt.	9
54	A	Bond angle distortions. In-plane and out-of-plane motion of Bi and Ag centers.	31
111	B	In-plane bond length distortion on octahedra. Bond length distortion along out-of-plane I-Bi-I bonds.	77
129	A	In-plane bond length distortion on octahedra. Bond angle distortion on Bi-centered octahedra. Symmetric bond length distortion on out-of-plane I-Ag-I bonds. In-plane motion of Bi centers.	92
140	A	In-plane bond-length distortion of octahedra. Motion of Bi centers.	103

E. Low frequency Raman vibration modes for MPA-CuBiI₈ perovskite

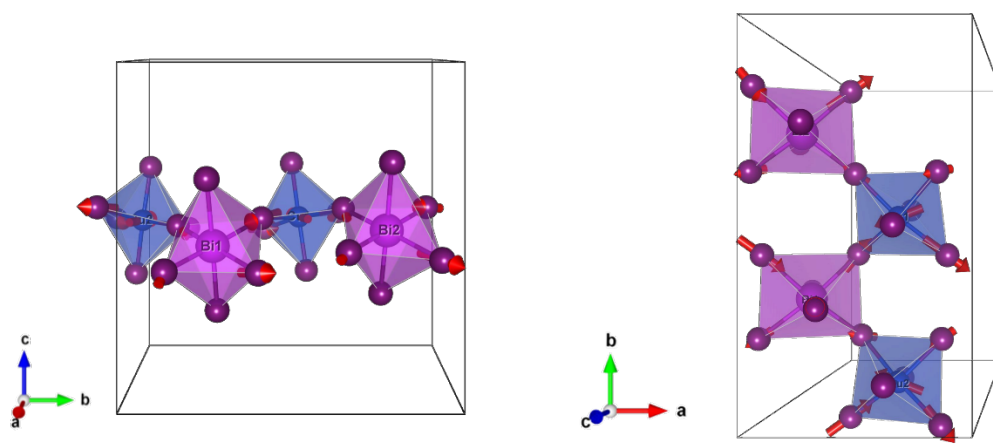
The simulation of the Raman vibration modes is based on DFT calculations. The mode illustrations are in Figure S5, and the symmetry and description of different modes are in Table S5.



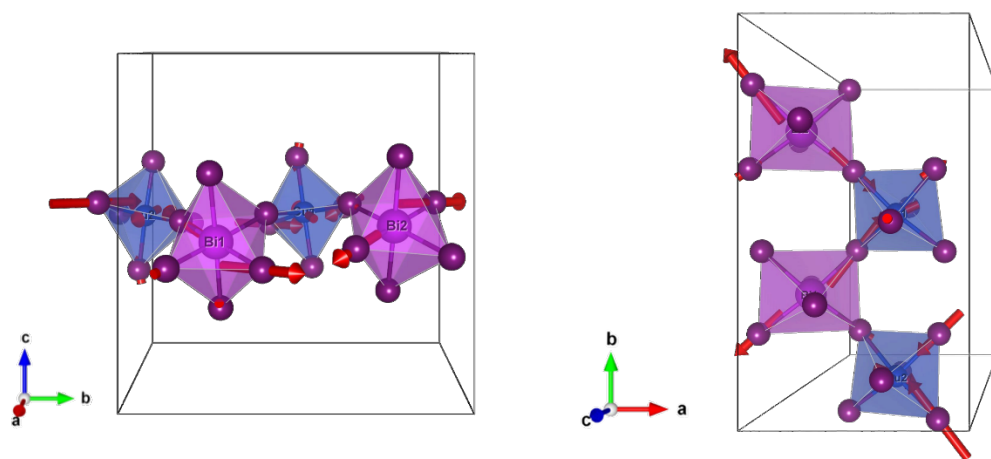
33 cm⁻¹



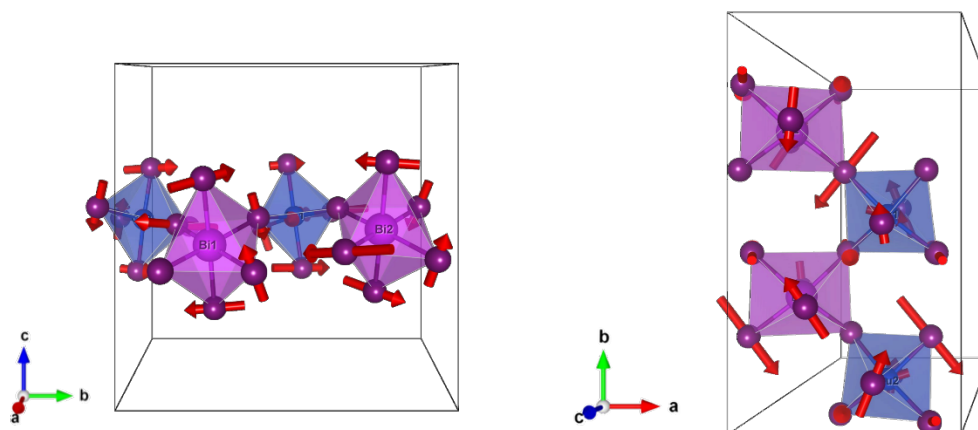
59 cm⁻¹



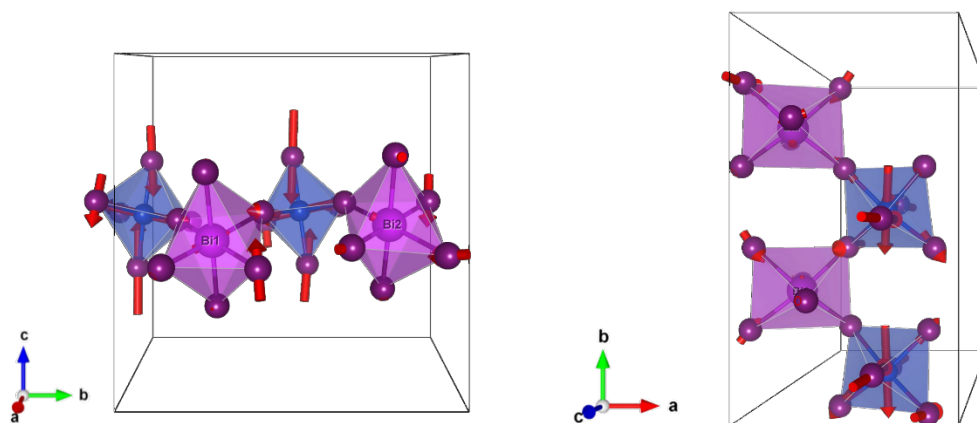
132 cm^{-1}



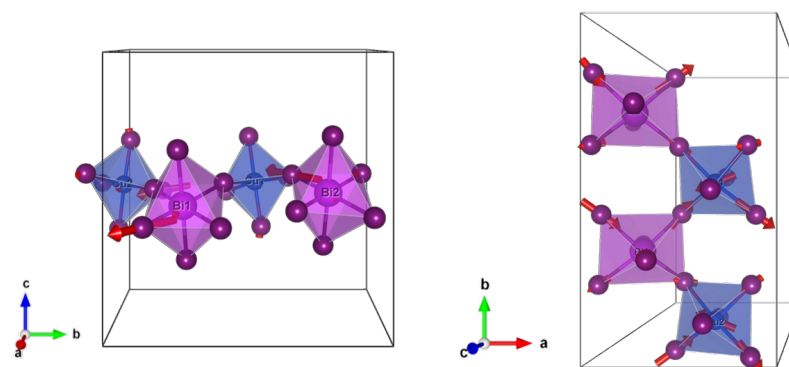
151 cm^{-1}



76 cm⁻¹



109 cm⁻¹



174 cm⁻¹

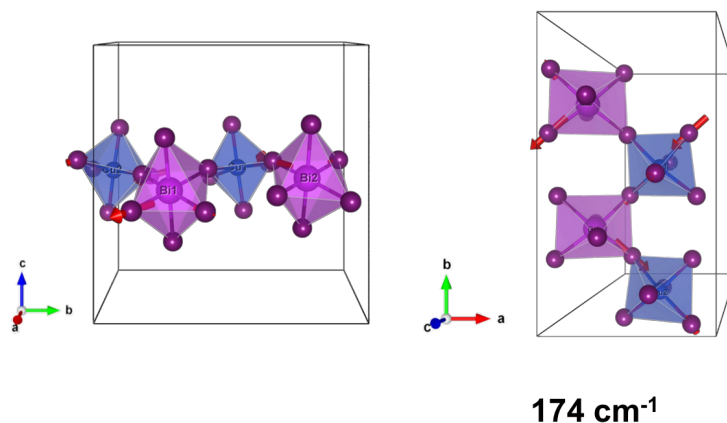


Figure S5 Low frequency vibration modes in the crystal structure as calculated for MPA-CuBiI₈ perovskite, shown from two different perspectives.

Table S5 Full description of the assignments of the vibration modes in the low Raman frequency region (0-200 cm⁻¹) of Cu-based 2D double perovskite. In all modes, molecules librate and have some degree of internal twisting. Where a distortion or motion is mentioned without specifying whether it is in or out of plane, the distortion has components in both directions. A and B are Mulliken symbols, irreducible representations for *P2*₁, where A is symmetric and B is antisymmetric.

Frequency [cm ⁻¹]	Symmetry	Description	Mode #
33	A	Octahedra bond angle distortion. In-plane motion of octahedral centers.	11
59	A	Angle distortion of in-plane and out-of-plane octahedra bonds. Motion of Cu.	21
76	A	In-plane bond angle distortion of in-plane bonds. Bond angle distortion of out-of-plane Cu octahedra bonds. Tilting of Bi octahedra.	33
111	A	Cu centers move in plane. In-plane Cu octahedra bond angle distortion. Octahedra bond length distortion.	54
132	B	Bond angle distortion on Cu octahedra. In-plane	67

		bond length distortion of both Bi and Cu octahedra. Bond length distortion of out-of-plane Bi octahedra bonds. Cu atoms move in plane.	
151	A	In-plane bond length distortion on Bi and Cu octahedra. Cu atoms move in plane.	80
174	A	Bond length distortion of octahedra. NH ₃ group rotation.	90, 92

Table S6 Crystal and refinement data for MPA-AgBiI₈ perovskite

Empirical formula	C ₃₆ H ₅₈ AgBiI ₈ N ₄ O
Formula Weight	1894.91
Temperature (K)	104(6)
Wavelength (Å)	1.54184
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> (Å)	9.56840(10)
<i>b</i> (Å)	16.7665(2)
<i>c</i> (Å)	16.5699(2)
<i>β</i> (°)	102.5080(10)
Volume (Å³)	2595.19(5)
<i>Z</i>	2
ρ_{calc} (Mg/m³)	2.425
Crystal size (mm³)	0.11 × 0.04 × 0.02
θ range (°)	5.464 to 134.154
Total reflections	31574
Unique reflections	9260
Parameters	510
Completeness	100.0
<i>R</i>_{int}	0.0436
<i>R</i>₁ (<i>I</i> > 2σ)	0.0285
<i>R</i>₁ (all data)	0.0309
<i>wR</i>₂ (<i>I</i> > 2σ)	0.0689
<i>wR</i>₂ (all data)	0.0700

F. Octahedral Parameters

There are four octahedra in each unit cell, but only two of the four octahedra are unique, by symmetry. We calculated octahedral parameters, including bond-length deviations (D), tilting (D_{tilt}), in- and out-of-plane tilting defined with respect to the (0 0 1) plane¹⁵ (D_{in} and D_{out}), and bond angle variance (σ^2) as defined in SI ref.¹³ Code from SI Ref.¹⁶ is used to calculate these octahedral distortion parameters. We have calculated ΔD_{tilt} as the difference between the largest and smallest D_{tilt} angles for a given structure. Each similarly labeled iodine atom in the three structures is in a similar molecular environment between the three structures due to the orientation of the organic molecules, even if bonded to different metal atoms (Ag or Cu).

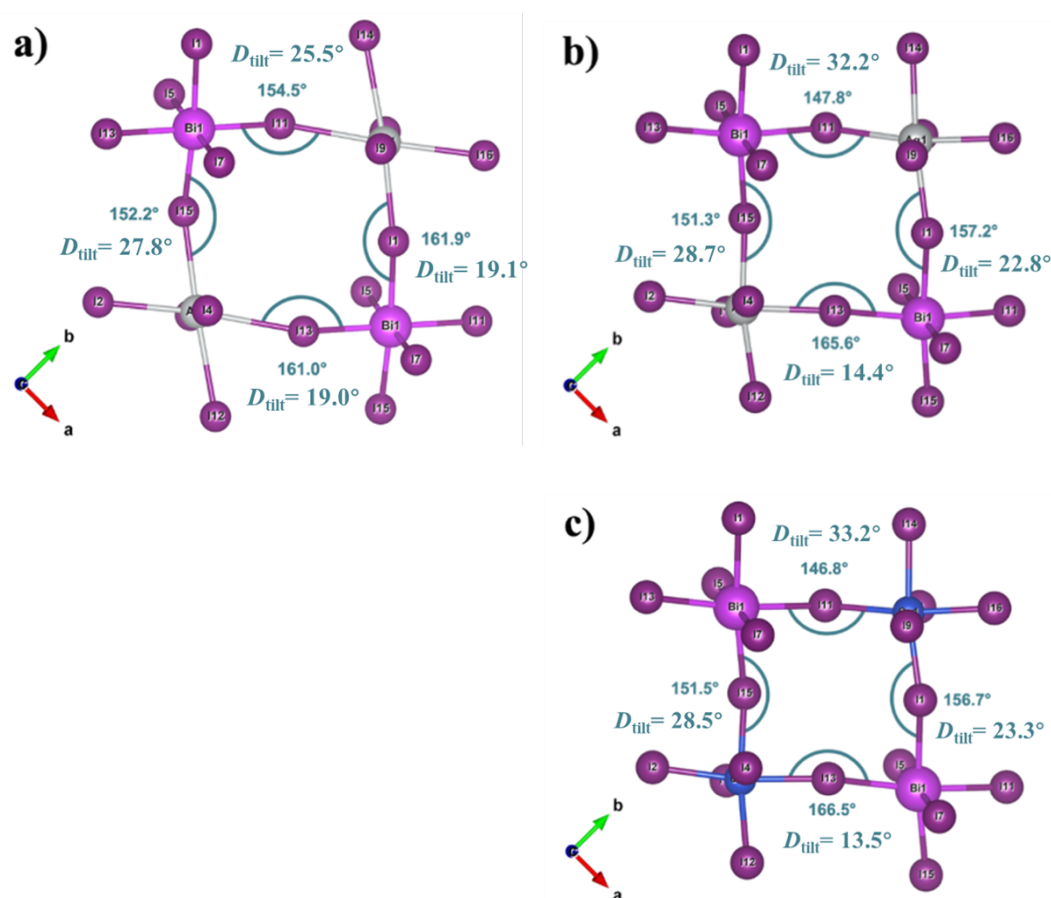


Figure S6 Octahedral tilt angles for (a) the experimental Ag-based perovskite structure, (b) the theoretical Ag-based perovskite structure, and (c) the theoretical Cu-based perovskite structure.

Table S7 Octahedral tilt angles and parameters for the Ag-based and Cu-based perovskites.

Each iodine has one equivalent site within the unit cell, by symmetry. I1 is equivalent to I2, I11 is equivalent to I12, I13 is equivalent to I14, and I15 is equivalent to I16. D is the distortion index (bond length). σ^2 (degrees²) is the bond angle variance.

Structure	Vertex	$D_{\text{tilt}} (^{\circ})$	$D_{\text{out}} (^{\circ})$	$D_{\text{in}} (^{\circ})$	$\Delta D_{\text{tilt}} (^{\circ})$	$D (\times 10^{-2})$ Bi	$D (\times 10^{-2})$ M=Ag,Cu	$\sigma^2 (^{\circ}^2)$ Bi	$\sigma^2 (^{\circ}^2)$ M=Ag,Cu
Exp. Ag ⁵	I1	19.05	17.50	4.83	9.7	0.56	11.70	2.39	106.82
	I11	25.50	23.52	10.10					
	I13	19.00	15.30	11.48					
	I15	27.80	26.07	10.15					
Theory Ag	I1	22.80	21.86	6.78	17.8	1.05	4.26	38.63	53.89
	I11	32.20	31.16	8.64					
	I13	14.40	13.58	4.76					
	I15	28.70	27.33	9.08					
Theory Cu	I1	23.30	22.54	5.89	19.7	1.07	2.97	70.53	44.66
	I11	33.20	33.16	1.10					
	I13	13.50	10.78	8.13					
	I15	28.50	26.06	11.85					

*Each similarly labeled iodine atom in the three structures is in a very similar molecular environment between the three structures due to the orientation of the organic molecules, even if bonded to different metal atoms (Ag or Cu).

Table S8 M-I bond lengths (M = Ag or Cu) to numbered iodine, as indicated in each column. I3 and I9 are out of plane, and the rest are in plane. All values are in Å.

Structure	I3	I9	I1	I11	I14	I16
Exp. Ag ⁵	2.669	2.663	3.368	3.603	3.681	3.418
Theory Ag	2.758	2.758	3.076	3.044	3.062	2.977
Theory Cu	2.560	2.568	2.783	2.689	2.767	2.733

Table S9 Bi-I bond lengths to numbered iodine, as indicated in each column. I5 and I7 are out of plane, and the rest are in plane. All values are in Å.

Structure	I5	I7	I1	I11	I13	I15
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Exp. Ag ⁵	3.090	3.076	3.091	3.051	3.078	3.039
Theory Ag	3.036	3.081	3.074	3.016	3.046	2.960
Theory Cu	2.982	2.995	3.024	2.967	2.964	2.880

G. Band structure

The band structure is calculated using plane-wave DFT with the PBE functional on the relaxed theoretical structures to show the band gap of the two systems. SeeK-path was used to obtain the k -path.^{17,18} The k -point path Γ , X, Y, Γ , G, Z, R₂, and Γ is used for the bandstructure calculation on the theoretical Ag- and Cu-based perovskite structures, with 30 points between each high-symmetry point. 340 bands are calculated in total, but we only depict those closest to the band edges in Figure S7. All inputs for the SCF are the same as used for relaxation, with the exception of a denser of $3 \times 3 \times 3$ k -points grid.

Both band gap transitions are direct at the Γ and Z points in the Brillouin zone. We have found that the top of the valence band is composed of I p-orbitals, with small contributions from Ag or Cu d-orbitals, and the bottom of the conduction band is composed of Bi p-orbitals and I p-orbitals. Our calculations show a band gap difference of about 0.5 eV, with the Cu-based perovskite having a theoretical bandgap of 1.6 eV, and the Ag-based perovskite having a bandgap of 2.1 eV. There are a variety of factors that can lead to discrepancy between theory and experiment, but it's not clear from our calculations why the experimental band gaps are similar. We confirmed via random-phase approximation optical absorption calculations in BerkeleyGW¹⁹ that the lowest transition in the Cu-based perovskite is dipole-allowed. Additionally, we did not include the spin-orbit coupling (SOC) effect in our calculations, which, while typically PBE is comparable to the true bandgap, could account for some discrepancy between our theoretical results and experiment. Spin-orbit coupling may be especially relevant due to the presence of heavy elements Bi and I in our structure.^{20,21} Compared to the experimentally obtained values of the bandgaps of 2.03 eV for both Ag and Cu structures, the theoretical value for the Cu-based perovskite is smaller, and the theoretical value of the Ag-based perovskite is higher. Previous work²² on the 1D organic metal halide hybrid C₈H₂₈N₅Pb₃Cl₁₁ resulted in a difference of 0.27 eV, a nearly 8% difference between DFT with PBE and experiment. Our results show a difference of 21% for the Cu-based perovskite, and a 3% difference for the Ag-based perovskite compared to experiment. It appears that in the Cu-based perovskite spin-orbit coupling or quasiparticle effects do not cancel closely and must be directly accounted for in calculations.

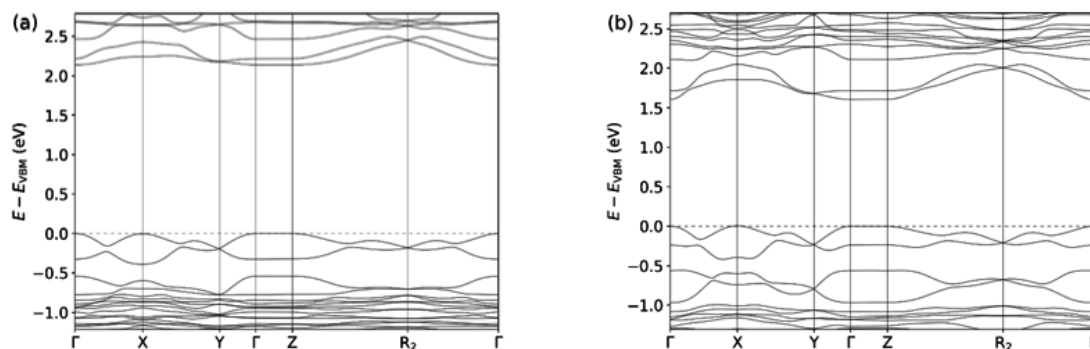


Figure S7 Band structure for (a) the Ag-based perovskite, and (b) the Cu-based perovskite. Energies are plotted with reference to the valence band maximum (VBM).

H. Partial electronic density of states (PDOS)

The partial electronic density of states was calculated using DFT with PBE to determine the atomic orbital character of the band edges. The same input parameters used for relaxation of the structure were used for the SCF and non-SCF calculations to obtain the DOS, except for a $4 \times 4 \times 4$ unshifted k-grid with Blöchl's tetrahedron method for Brillouin-zone integrations²³ being used for the non-SCF calculation.

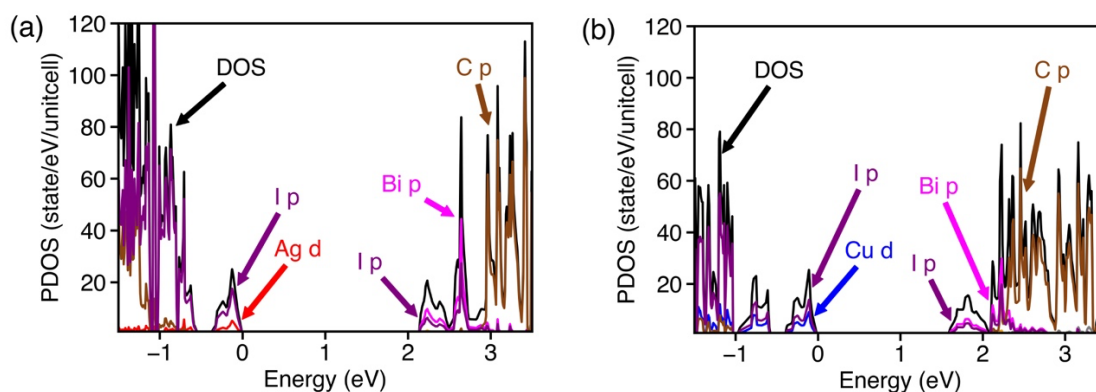


Figure S8 Partial electronic density of states for (a) Ag-based perovskite, and (b) Cu-based perovskite. Energies are plotted with reference to the valence band maximum (VBM).

References

- (1) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta. Cryst. A* **2015**, *71* (1), 3–8. <https://doi.org/10.1107/S2053273314026370>.
- (2) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta. Cryst. C* **2015**, *71* (1), 3–8. <https://doi.org/10.1107/S2053229614024218>.

- (3) Müller, P. Practical Suggestions for Better Crystal Structures. *Crystallogr. Rev.* **2009**, *15* (1), 57–83. <https://doi.org/10.1080/08893110802547240>.
- (4) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M., et al. Mercury 4.0: From Visualization to Analysis, Design and Prediction. *J. Appl. Cryst.* **2020**, *53* (1), 226–235. <https://doi.org/10.1107/S1600576719014092>.
- (5) Li, D.; Liu, X.; Wu, W.; Peng, Y.; Zhao, S.; Li, L.; Hong, M.; Luo, J. Chiral Lead-Free Hybrid Perovskites for Self-Powered Circularly Polarized Light Detection. *Angew. Chem. Int. Ed.* **2021**, *60* (15), 8415–8418. <https://doi.org/10.1002/anie.202013947>.
- (6) Baroni, S. Phonons and Related Crystal Properties from Density-Functional Perturbation Theory. *Rev. Mod. Phys.* **2001**, *73* (2), 515–562. <https://doi.org/10.1103/RevModPhys.73.515>.
- (7) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I., et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21* (39), 395502. <https://doi.org/10.1088/0953-8984/21/39/395502>.
- (8) Perdew, J. P. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (9) Lazzeri, M. and Mauri, F. First-Principles Calculation of Vibrational Raman Spectra in Large Systems: Signature of Small Rings in Crystalline SiO₂. *Phys. Rev. Lett.* **2003**, *90* (3), 036401. <https://doi.org/10.1103/PhysRevLett.90.036401>.
- (10) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27* (15), 1787–1799. <https://doi.org/10.1002/jcc.20495>.
- (11) Hamann, D. R. Optimized Norm-Conserving Vanderbilt Pseudopotentials. *Phys. Rev. B* **2013**, *88* (8). <https://doi.org/10.1103/PhysRevB.88.085117>.
- (12) van Setten, M. J.; Giantomassi, M.; Bousquet, E.; Verstraete, M. J.; Hamann, D. R.; Gonze, X.; Rignanese, G.-M. The PseudoDojo: Training and Grading a 85 Element Optimized Norm-Conserving Pseudopotential Table. *Comput. Phys. Commun.* **2018**, *226*, 39–54. <https://doi.org/10.1016/j.cpc.2018.01.012>.
- (13) Masud, M. M.; Viera, J.; Ben-Akacha, A.; Ma, B.; Strubbe, D. A. Computational and Experimental Investigation of Chiral and Achiral 2D Organic Lead Bromide Perovskites: Octahedral Distortions and Electronic and Optical Properties. arXiv September 8, 2025. <https://doi.org/10.48550/arXiv.2509.07152>.
- (14) Brooker, M. H.; Nielsen, O. F.; Praestgaard, E. Assessment of Correction Procedures for Reduction of Raman Spectra. *J. Raman Spectrosc.* **1988**, *19* (2), 71–78. <https://doi.org/10.1002/jrs.1250190202>.
- (15) Jana, M. K.; Song, R.; Xie, Y.; Zhao, R.; Sercel, P. C.; Blum, V.; Mitzi, D. B. Structural Descriptor for Enhanced Spin-Splitting in 2D Hybrid Perovskites. *Nat. Commun.* **2021**, *12* (1), 4982. <https://doi.org/10.1038/s41467-021-25149-7>.
- (16) Liu, S.; Kepenekian, M.; Bodnar, S.; Feldmann, S.; Heindl, M. W.; Fehn, N.; Zerhoch, J.; Shcherbakov, A.; Pöthig, A.; Li, Y., et al. Bright Circularly Polarized Photoluminescence in Chiral Layered Hybrid Lead-Halide Perovskites. *Sci. Adv.* **2023**, *9* (35), eadh5083. <https://doi.org/10.1126/sciadv.adh5083>.

- (17)Hinuma, Y.; Pizzi, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band Structure Diagram Paths Based on Crystallography. *Comput. Mater. Sci.* **2017**, *128*, 140–184. <https://doi.org/10.1016/j.commatsci.2016.10.015>.
- (18)Togo, A.; Shinohara, K.; Tanaka, I. Spglib: A Software Library for Crystal Symmetry Search. *Sci. Technol. Adv. Material, Meth.* **2024**, *4* (1), 2384822. <https://doi.org/10.1080/27660400.2024.2384822>.
- (19)Deslippe, J.; Samsonidze, G.; Strubbe, D. A.; Jain, M.; Cohen, M. L.; Louie, S. G. BerkeleyGW: A Massively Parallel Computer Package for the Calculation of the Quasiparticle and Optical Properties of Materials and Nanostructures. *Comput. Phys. Commun.* **2012**, *183* (6), 1269–1289. <https://doi.org/10.1016/j.cpc.2011.12.006>.
- (20)Azimul Haque, M.; C. Beard, M. Spin Effects in Metal Halide Perovskite Semiconductors. *Nanoscale* **2025**, *17*, 9895-9906. <https://doi.org/10.1039/D5NR00127G>.
- (21)Connor, B. A.; Leppert, L.; Smith, M. D.; Neaton, J. B.; Karunadasa, H. I. Layered Halide Double Perovskites: Dimensional Reduction of Cs₂AgBiBr₆. *J. Am. Chem. Soc.* **2018**, *140* (15), 5235–5240. <https://doi.org/10.1021/jacs.8b01543>.
- (22)Lee, S.; Karkee, R.; Ben-Akacha, A.; Luong, D.; Winfred, J. S. R. V.; Lin, X.; Strubbe, D. A.; Ma, B. One-Dimensional Organic Metal Halide Nanoribbons with Dual Emission. *Chem. Commun.* **2023**, *59* (25), 3711–3714. <https://doi.org/10.1039/D3CC00044C>.
- (23)Blöchl, P. E. Improved Tetrahedron Method for Brillouin-Zone Integrations. *Phys. Rev. B* **1994**, *49* (23), 16223–16233. <https://doi.org/10.1103/PhysRevB.49.16223>.