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Authors

Mao, Lingling
Guo, Peijun
Kepenekian, Mikael
[et al.](#)

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Organic Cation Alloying on Intralayer A and Interlayer A' sites in 2D Hybrid Dion-Jacobson Lead Bromide Perovskites (A')(A)Pb₂Br₇

Lingling Mao^{1,2}, Peijun Guo³, Mikael Kepenekian⁴, Ioannis Spanopoulos¹, Yihui He¹, Claudine Katan⁴, Jacky Even⁵, Richard D. Schaller^{1,3}, Ram Seshadri², Constantinos C. Stoumpos^{1*}, and Mercouri G. Kanatzidis^{1*}

¹Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

² Materials Department and Materials Research Laboratory, Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

³Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Lemont, Illinois 60439, United States

⁴Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, Rennes F-35000, France

⁵Univ Rennes, INSA Rennes, CNRS, Institut FOTON – UMR 6082, Rennes F-35000, France

Supporting Information Placeholder

ABSTRACT: Hybrid layered halide perovskites have achieved impressive performance in optoelectronics. New structural types in the two-dimensional (2D) halide system such as the Dion-Jacobson phases have attracted wide research attention due to the short interlayer distance and unique layer orientation that facilitate better charge-transport and higher stability in optoelectronic devices. Here, we report the first solid solution series incorporating both A and A' cations in the 2D Jacobson-Dion family, with the general formula (A')(A)Pb₂Br₇ ((A' = 3-(aminomethyl)piperidinium (3AMP) and 4-(aminomethyl)piperidinium) (4AMP); A= methylammonium (MA) and formamidinium (FA)). Mixing the spacing A' cations and perovskite A cations generates the new (3AMP)_a(4AMP)_{1-a}(FA)_b(MA)_{1-b}Pb₂Br₇ perovskites. The crystallographically refined crystal structures using single-crystal X-ray diffraction data reveal that the distortion of the inorganic framework is heavily influenced by the degree of A' and A alloying. A rising fraction of 4AMP in the structure, decreases the Pb-Br-Pb angles, making the framework more distorted. On the contrary, higher FA fractions increase the Pb-Br-Pb angles. This structural evolution fine tunes the optical properties where the larger the Pb-Br-Pb angle, the narrower the band gap. The photoluminescence emission energy mirrors this trend. Raman spectroscopy reveals a highly dynamical lattice similar to MAPbBr₃ and consistent with the local distortion environment of the [Pb₂Br₇] framework. Density Functional Theory (DFT) calculations of the electronic structures reveal the same trend as the experimental results where (3AMP)(FA)Pb₂Br₇ has the smallest band gap while (4AMP)(MA)Pb₂Br₇ has the largest band gap. The structural effects from solely the organic cations in the 2D system highlight the importance of understanding the high sensitivity of the optoelectronic properties on the structural tuning in this broad class of materials.

INTRODUCTION

Hybrid organic-inorganic halide perovskite materials have established themselves as one of the leading semiconducting materials because of their superior performances in optoelectronics.¹⁻⁴ The ease of thin-film preparation and favorable properties of the hybrid perovskites such as long carrier diffusion length, long carrier lifetime, high carrier mobility and optimal absorption properties

are helping to elevate the performance even better, currently up to 25.2% power conversion efficiency (PCE).⁵ Substituting the iodide with bromide increases the band gap of the hybrid perovskite materials, making them more suitable for tandem solar cells^{6,7} and green LEDs.⁸⁻¹² Breakthroughs with perovskite-based materials have also been reported recently in light emitting diodes (LEDs), where the highest external quantum efficiency (EQE) has reached 20%.¹³ A recent strategy for fabricating high performance photovoltaic devices is to mix

various of A-site cations (Cs^+ , FA^+ , MA^+) that boosts the performance compared to the pristine samples.^{7,14-16} This performance boost is achieved mainly from an increased charge-carrier mobility,¹⁷ which generally connects with the fine crystal structure details of the perovskite. Other chemical strategies that aid device performance involve composition tuning with halide-mixing and incorporating additives in the thin-films.¹⁸⁻²⁰ In most cases, despite the PCE improvement, structural details and insights were not provided, mainly because of complications from the dynamical disorder in the 3D systems.²¹⁻²³

The 2D hybrid perovskites expand the range of properties and possibilities because of their highly diverse chemistry,²⁴⁻³⁰ excellent photo-physical properties^{31,32}, and intriguing physical phenomena such as electron/exciton-phonon coupling³³ and Rashba splitting³⁴ for spintronics.³⁵⁻³⁷ The reduction in dimensionality from 3D to 2D lends additional flexibility to the crystal lattice and as a result, the tolerance factor limitation that occurs in the 3D perovskite can be somewhat relaxed in 2D perovskite.^{38,39} Typical examples are the 2D perovskites which based on the tolerance-“forbidden” cations ethylammonium (EA)^{28,40}, isopropylammonium (IPA)⁴¹ and a series of larger A-site cations.⁴² An added important benefit of the 2D perovskites is that large organic spacer cations with appropriate functional groups can be inserted between the 2D layers.⁴³⁻⁴⁵ The organic spacer cations engage in various supramolecular interactions such as fluoroaryl-aryl interactions and hydrogen bonding,^{46,47} and can exhibit chemical reactivity such as halogen insertion⁴⁸ and Diels-Alder cycloaddition.⁴⁹ Aside from the diversity of the organic part, the inorganic lattice can adopt different layer orientation (100-oriented,^{50,51} 110-oriented^{45,52,53} and 111-oriented^{54,55} with respect to the ideal cubic perovskite), and layer thickness ($n=1-7$).⁵⁶⁻⁵⁹ Layered double perovskites with alternating 1+ and 3+ metal cations are also reported.⁶⁰⁻⁶³ Moreover, 2D layered perovskites further divide the into two main subcategories, the Ruddlesden–Popper (RP) phases (with 1+ cations)⁶⁴ and the Dion–Jacobson (DJ) phases (with 2+ cations),⁶⁵ according to the charge of the organic cation and stacking modes of the layers. Several cases of multilayered hybrid lead bromide perovskites have been recently reported, including $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{CsPb}_2\text{Br}_7$,⁶⁶ $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{NH}_2\text{CHNH}_2)\text{Pb}_2\text{Br}_7$,⁶⁷ $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$ ⁶⁸ and $[\text{CH}_3(\text{CH}_2)_3\text{NH}_3]_2(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{Br}_7$,⁶⁹

Herein, we present organic cation mixing in the new family 2D DJ $(\text{A}')(\text{A})\text{Pb}_2\text{Br}_7$ perovskites aiming to reveal the links between the fine-tuning of the structural features and optoelectronic properties. Through controlled mixing of both A-site cation (MA, FA), which we refer to as the “perovskitizer” cations (meaning they template/occupy only the perovskite cuboctahedral cage), and A'-cation (the large organic spacer), we demonstrate that the degree of distortion of the perovskite in each individual layer can be controlled. We take advantage of the similar size and functionality of the 3AMP and 4AMP cations,

to build double solid-solutions composed of both mixed A' and A cations. By combining A' (3AMP/4AMP) and A (MA/ FA), we synthesized nine different compounds based on the $(\text{A}')(\text{A})\text{Pb}_2\text{Br}_7$ ($\text{A}' = 3\text{AMP}$ or 4AMP , $\text{A} = \text{FA}$ or MA) formula. They exhibit distinctive perovskite distortion modes ranging from out-of-phase tilting to in-phase tilting along with the undistorted structural prototype (Figure 1). The powder X-ray diffraction (PXRD) data shows pure phase for each solid solution and small Bragg peak shifts due to the change of the unit cell volume. We determined the inorganic distortion (i.e. the Pb-Br-Pb angles) in the crystal structure using single-crystal X-ray diffraction for selected compositions of the $(3\text{AMP})_a(4\text{AMP})_{1-a}(\text{FA})_b(\text{MA})_{1-b}\text{Pb}_2\text{Br}_7$ (a and $b = 1, 0.5$ or 0) system. We find a dependence of the Pb-Br-Pb angles on both a and b variables, with the angle becoming smaller (i.e. larger distortion) with decreasing value of a and b . The optical band gap obeys the general “rule” of the halide perovskites which states that the larger the Pb-Br-Pb angle, the smaller the band gap, which is also seen in the emission energy of the photoluminescence (PL).⁷⁰ The compositional mapping employed in this work provides an excellent tool for understanding how subtle changes at the organic cation sites drive the structural evolution within the inorganic layer of a given 2D hybrid halide perovskite, thus acting as synthetic knobs to control the semiconducting properties of the materials.

RESULTS AND DISCUSSION

Table 1. Crystal data and structure refinement for (3AMP)_a(4AMP)_{1-a}(FA)_b(MA)_{1-b}Pb₂Br₇ (a and b = 1, 0.5 or 0).

Compound	(3AMP)(FA)Pb ₂ Br ₇	(3AMP)(MA)Pb ₂ Br ₇	(4AMP)(FA)Pb ₂ Br ₇	(4AMP)(MA)Pb ₂ Br ₇
Chemical formula	(C ₆ N ₂ H ₁₆) [HC(NH ₂) ₂] Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) (CH ₃ NH ₃)Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) [HC(NH ₂) ₂] Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) (CH ₃ NH ₃)Pb ₂ Br ₇
Space group	<i>Cm</i>	<i>Pc</i>	<i>Pc</i>	<i>Cc</i>
Unit cell dimensions	a = 8.4615(17) Å, b = 8.4650(17) Å, c = 16.004(3) Å, β = 89.99(3)°	a = 15.952(3) Å, b = 8.4134(17) Å, c = 8.4135(17) Å, β = 90.07(3)°	a = 16.138(3) Å, b = 11.909(2) Å, c = 11.905 (7) Å, β = 90.00(3)°	a = 33.433(7) Å, b = 8.3738(17) Å, c = a8.3760(17) Å, β = 104.45(3)°
Vol (Å ³), Z	1146.3(4), 2	1129.2(4), 2	2288.0(8), 4	2270.8(8), 4
ρ (g/cm ³)	3.288	3.300	3.295	3.282
Indepd. refl.	3034 [R _{int} = 0.0308]	5582 [R _{int} = 0.1475]	11594 [R _{int} = 0.1533]	3739 [R _{int} = 0.1023]
Data / restr. / param.	3034 / 30 / 75	5582 / 30 / 119	11594 / 55 / 236	3739 / 80 / 117
R indices [I > 2σ(I)]	R _{obs} = 0.0460, wR _{obs} = 0.1138	R _{obs} = 0.0897, wR _{obs} = 0.2695	R _{obs} = 0.0633, wR _{obs} = 0.1319	R _{obs} = 0.0795, wR _{obs} = 0.1826

Table 2. Crystal data and structure refinement for (3AMP)_a(4AMP)_{1-a}(FA)_b(MA)_{1-b}Pb₂Br₇ (a and b = 1, 0.5 or 0)

Compound	(3AMP) _{0.5} (4AMP) _{0.5} (FA) _{0.5} (MA) _{0.5} Pb ₂ Br ₇	(4AMP)(FA) _{0.5} (MA) _{0.5} Pb ₂ Br ₇	(3AMP)(FA) _{0.5} (MA) _{0.5} Pb ₂ Br ₇	(3AMP) _{0.5} (4AMP) _{0.5} (FA)Pb ₂ Br ₇	(3AMP) _{0.5} (4AMP) _{0.5} (MA)Pb ₂ Br ₇
Chemical formula	(C ₆ N ₂ H ₁₆) [HC(NH ₂) ₂] 2]0.5(CH ₃ NH ₃) _{0.5} Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) [HC(NH ₂) ₂] 2]0.5(CH ₃ NH ₃) _{0.5} Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) [HC(NH ₂) ₂] 2]0.5(CH ₃ NH ₃) _{0.5} Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) [HC(NH ₂) ₂] Pb ₂ Br ₇	(C ₆ N ₂ H ₁₆) (CH ₃ NH ₃)Pb ₂ Br ₇
Space group	<i>Pc</i>	<i>Pc</i>	<i>C2</i>	<i>Pc</i>	<i>Cc</i>
Unit cell dimensions	a = 16.0142(12) Å, b = 8.4185(7) Å, c = 8.4164(6) Å, β = 90.024(3)°	a = 16.193(2) Å, b = 8.3678(11) Å, c = 8.3469(10) Å, β = 89.921(6)°	a = 8.4121(8) Å, b = 8.4176(9) Å, c = 15.9228(19) Å, β = 89.983(4)°	a = 16.0382(13) Å, b = 8.4484(7) Å, c = 8.4494(6) Å, β = 89.9940(15)°	a = 33.2368(17) Å, b = 8.3841(5) Å, c = 8.3801(4) Å, β = 104.599(2)°
Vol (Å ³), Z	1134.66(15), 2	1131.0(3), 2	1127.5(2), 2	1144.87(16), 2	2259.8(2), 4
ρ (g/cm ³)	3.372	3.295	3.346	3.293	3.2977
Indepd. refl.	5492 [R _{int} = 0.0537]	5029 [R _{int} = 0.0436]	2707 [R _{int} = 0.0365]	5599 [R _{int} = 0.0510]	5412 [R _{int} = 0.0542]
Data / restr. / param.	5492 / 27 / 119	5029 / 27 / 118	2707 / 20 / 65	5599 / 29 / 119	5412 / 28 / 118
R indices [I > 2σ(I)]	R _{obs} = 0.0448, wR _{obs} = 0.1400	R _{obs} = 0.0576, wR _{obs} = 0.1690	R _{obs} = 0.0443, wR _{obs} = 0.1365	R _{obs} = 0.0505, wR _{obs} = 0.1528	R _{obs} = 0.0461, wR _{obs} = 0.1348

Synthesis. The synthesis procedure for the two-layered (A')(A)Pb₂Br₇ (A' = 3AMP or 4AMP, A = FA or MA) series of compounds was as previously reported for the iodides,⁶⁵ changing only the solvent from hydroiodic acid to hydrobromic acid (see Methods). To synthesize the solid-solutions using mixed

cations, the experimental ratios of the A' and A cation was controlled stoichiometrically, e.g. for $(3\text{AMP})_{0.5}(4\text{AMP})_{0.5}(\text{FA})_{0.5}(\text{MA})_{0.5}\text{Pb}_2\text{Br}_7$, the experimental ratio of 3AMP:4AMP:FA:MA was 1:1:1:1. The resulting compositions of the hybrid compounds are listed in Table S10, which are based on the ^1H NMR results.⁷¹ Although the initial input of each component is the same for $(3\text{AMP})_{0.5}(4\text{AMP})_{0.5}(\text{FA})_{0.5}(\text{MA})_{0.5}\text{Pb}_2\text{Br}_7$, the outcome is slightly different as more 4AMP and MA were incorporated in the compound, which was a general trend seen in the series. The as-synthesized compounds grow as yellow crystals with a thin, rectangular plate-like morphology (Figure 1 and S1). Using powder X-ray diffraction (PXRD), we were able to confirm the compositional purity of the compounds, with all of them exhibiting the characteristic diffraction pattern of the bi-layered perovskite (Figure 2a), in excellent agreement with the calculated ones. Because $(3\text{AMP})(\text{MA})\text{Pb}_2\text{Br}_7$ decomposes relatively quickly, we could perform only single-crystal XRD analysis. The PXRD patterns of the compounds have the trademark characteristics of a solid-solution with no new peaks emerging showing only a slight peak shift. Considering the 15° and 30° peaks in 3FA and 4FA, they obviously exist in every compound since they correspond to the (110) and (220) diffraction planes. The difference in intensity is due to preferred orientation (See Figure S1). Typically, 2D perovskite plate crystals exhibit strong preferred orientation along the [100] direction of the plates, exhibiting mainly the (200), (400), (600)... (*h*00) reflections in the PXRD pattern as seen in Figure 2a.

Crystal structure. To evaluate the effect of the addition of A' and A cations, we group the patterns in three triads (Figure 2b-2d). The first triad, groups the $(3\text{AMP})_a(4\text{AMP})_{1-a}(\text{FA})\text{Pb}_2\text{Br}_7$ series, where the (10 0 0) peak shifts to lower diffraction angle with increasing amount of 4AMP. This trend matches with the long axis expansion (perpendicular to the layers) determined by single-crystal X-ray diffraction, which the long axes for 3FA, 34FA and 4FA ($3\text{FA} = (3\text{AMP})(\text{MA})\text{Pb}_2\text{Br}_7$, $34\text{FA} = (3\text{AMP})_{0.5}(4\text{AMP})_{0.5}(\text{FA})\text{Pb}_2\text{Br}_7$, $4\text{FA} = (4\text{AMP})(\text{FA})\text{Pb}_2\text{Br}_7$) having values of 16.004(3) Å, 16.0382(13) Å, 16.138(3) Å, respectively. Similarly, in the $(3\text{AMP})_a(4\text{AMP})_{1-a}(\text{FA})_{0.5}(\text{MA})_{0.5}\text{Pb}_2\text{Br}_7$ series, the peak shifts to lower angles, correspond to the long axis expansion in the 3FAMA (15.923(2) Å) < 34FAMA (16.0142(12) Å) < 4FAMA (16.193(2) Å) order. Finally, for the $(3\text{AMP})_{0.5}(4\text{AMP})_{0.5}(\text{FA})_b(\text{MA})_{1-b}\text{Pb}_2\text{Br}_7$ series, the change of the shift becomes much less severe, as the change in the unit cell is much smaller, with the long axis expansion following the 34MA < 34FAMA < 34MA order having values of 16.0382(13), 16.0142 (12) and 16.082 (transformed),⁷² respectively. The pronounced lattice expansion reveals the accentuated role of the organic spacer (3AMP vs 4AMP) over the impact of the perovskitizer (FA vs MA), with the large organic spacer causing a much larger change in the unit cell. The nature of the spacer cations influences the interlayer separation by anchoring deeper or shallower in the “pockets” of the inorganic

framework surfaces. On the contrary, the perovskitizer sits within the relatively tight inorganic cage, which can only deform within shorter bounds and therefore the effect is less prominent.

Table 3. Detailed Pb-Br-Pb (deg) angles solved from the crystal structures and band gap of the nine compounds with the formula (A')(A)Pb₂Br₇ (A' = 3AMP or 4AMP, A = FA or MA).

Compound	Abbreviation	Averaged horizontal Pb-Br-Pb angle	Averaged axial Pb-Br-Pb angle	Average Pb-Br-Pb angle	E _g (eV)	PL (eV)
(4AMP)(MA)Pb ₂ Br ₇	4MA	159.9	174.6	164.8	2.82	NA
(4AMP)(FA) _{0.5} (MA) _{0.5} Pb ₂ Br ₇	4FAMA	160.2	179.8	166.8	2.81	2.48
(4AMP)(FA)Pb ₂ Br ₇	4FA	163.9	179.3	169.0	2.78	2.34
(3AMP) _{0.5} (4AMP) _{0.5} (MA)Pb ₂ Br ₇	34MA	163.2	179.6	168.7	2.73	2.42
(3AMP) _{0.5} (4AMP) _{0.5} (FA) _{0.5} (MA) _{0.5} Pb ₂ Br ₇	34FAMA	167.7	179.8	171.7	2.73	2.34
(3AMP) _{0.5} (4AMP) _{0.5} (FA)Pb ₂ Br ₇	34FA	169.3	177.7	172.1	2.73	2.39
(3AMP)(MA)Pb ₂ Br ₇	3MA	178.2	173.5	176.6	NA	NA
(3AMP)(FA) _{0.5} (MA) _{0.5} Pb ₂ Br ₇	3FAMA	176.8	177.6	177.1	2.66	2.31
(3AMP)(FA)Pb ₂ Br ₇	3FA	176.5	175.4	176.1	2.69	2.30

To take a closer look at the role of the organic spacers and perovskitizer in the lattice, we determined the crystal structures of the nine new compounds (Figure 3). Because of the asymmetry of the organic cations, all structures were refined in non-centrosymmetric monoclinic space groups (*Cm*, *Pc* or *Cc*), as justified previously.⁶⁵ The refinement details are provided in Table 1 and 2. According to their structural distortion, the inorganic [Pb₂Br₇] framework can be divided into three different modes that originate from the parent compounds 3M A, 3FA, 4MA and 4FA. The three compounds (3MA, 3FAMA and 3FA) in the left column belong to the least distorted mode (mode α). 34MA and 4MA (top row middle and right) are heavily distorted and together belong to the same mode (mode β) that has the perovskite octahedra connecting out-of-phase along the long axis, so that Br anions do not overlap with each other in parallel projection view. The remaining four compounds (34FAMA, 4FAMA, 34FA and 4FA) share another structural mode (mode γ), that has the octahedra tilting in-phase resulting in an eclipsed overlap of the Br anions in parallel projection view.

Compared to the common single-layered perovskite structure where the Pb-X-Pb angles distort parallel to the layer (horizontal tilt), in thicker 2D perovskites the Pb-X-Pb angles perpendicular to the layer (axial tilt) also become relevant. These independent values are illustrated in Figure 3 and are tabulated in order of increasing distortion in Table 3. Bases on this analysis, we were able to quantify the imposed distortion induced by the organic cations to the inorganic lattice. The two clear-cut trends observed relate to the content of 4AMP, for which the Pb-Br-Pb angle decreases as

4AMP incorporation increases. On the antipode, the addition of FA is also very clear. Irrespective of whether the system contains 3AMP or 4AMP, the averaged Pb-Br-Pb angle increases with increasing amounts of FA.

Optical absorption. The variation of templating cation within the system and the accumulated structural distortions affect the band gap much more than changing the perovskitizer. This is clearly demonstrated in the optical absorption of the (3AMP)_a(4AMP)_{1-a}(FA)Pb₂Br₇ and (3AMP)_a(4AMP)_{1-a}(FA)_{0.5}(MA)_{0.5}Pb₂Br₇ series. When changing the composition of 3AMP vs. 4AMP with a fixed perovskitizer (Figure 4a, b), the band gap changes significantly, up to 0.15 eV between 3FAMA and 4FAMA. On the other hand, in the (4AMP)(FA)_b(MA)_{1-b}Pb₂Br₇ system, in which the perovskitizer ratio MA/FA varies, the band gap changes only marginally (0.04 eV) from 2.82 eV to 2.78 eV. In terms of the ability in affecting the band gap energy, the spacing cations (3AMP and 4AMP) have stronger effect (~0.15 eV) than the perovskitizers (MA and FA, ~0.04eV) in the current bilayer system as demonstrated above.

The band gap of these materials follows a general trend that, the larger the Pb-Br-Pb angle (less distorted), the smaller the band gap, Figure 4d.⁷³ Increasing Pb-Br-Pb angle results in a higher degree of overlapping Pb s and Br p orbitals, which leads to strengthening of both bonding and antibonding interactions that broadens the band width and raises the energy level of the valence band maximum (VBM), see discussion below.⁷⁴

Raman and PL spectroscopy. The room temperature low frequency Raman spectra of this

mmol) of PbBr_2 was dissolved in 5 mL of HBr (vial A). 312 mg (3 mmol) of formamidinium acetate was added into the previous solution after all PbBr_2 was dissolved. In a separate vial (vial B), 1 mL HBr was added into 57 mg (0.5 mmol) of 3-(aminomethyl)piperidine. Under heating and stirring to boil, vial B was poured into vial A and the reaction continued for another 5-10 min until the solution became clear. Plate-like yellow crystals precipitated during slow cooling to room temperature. Yield 372 mg (21.8%) based on total Pb content). This procedure applies to the rest of the compounds, except the amount of the cations changes to the ratio shown in Table S11. Only a small amount of single crystals of $(3\text{AMP})(\text{MA})\text{Pb}_2\text{Br}_7$ could be obtained because of the tendency of the material to decompose.

Single Crystal X-ray Diffraction. Full sphere data were collected after screening for a few frames using either a STOE IPDS 2 or IPDS 2T diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) (50 kV/40 mA) under N_2 at 293K ($(3\text{AMP})(\text{MA})\text{Pb}_2\text{Br}_7$, $(3\text{AMP})(\text{FA})\text{Pb}_2\text{Br}_7$, $(4\text{AMP})(\text{MA})\text{Pb}_2\text{Br}_7$ and $(4\text{AMP})(\text{FA})\text{Pb}_2\text{Br}_7$). The collected data was integrated and applied with numerical absorption corrections using the STOE X-AREA programs. The rest of the compounds were collected using a Bruker Molly instrument with Mo $K\alpha$ μS microfocus source ($\lambda = 0.71073 \text{ \AA}$) with MX Optics at 293K. The collected data was integrated and applied with numerical absorption corrections using the APEX3 software. Crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the OLEX2 program package.⁷⁷ Note that for the solid solution structures with mixed 3AMP/4AMP or MA/FA, the A' cation was refined as 4AMP and A cation as MA. The actual ratio was given in Table S11 measured by NMR. In the case of $(3\text{AMP})(\text{FA})_{0.5}(\text{MA})_{0.5}\text{Pb}_2\text{Br}_7$, the cation is disordered and cannot be fully resolved.

Steady-state Photoluminescence. Steady-state PL spectra were collected using HORIBA LabRAM HR Evolution Confocal RAMAN microscope. 473 nm laser (25mW, 0.1% power) was used to excite all samples at 10 \times or 50 \times magnification (2 μm beam size).

Computational details. First-principles calculations are based on density functional theory (DFT) as implemented in the SIESTA package.^{1,2} Experimental structures are used for the inorganic skeleton, well characterized by X-ray diffraction. By contrast, the atomic positions of organic cations have been optimized using the non-local van der Waals density functional of Dion *et al.* corrected by Cooper (C09).^{3,4}

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Spin-orbit coupling is taken into account through the on-site approximation as proposed by Fernández-Seivane *et al.*⁵ To prevent conflicts between the on-site treatment and the non-locality of C09, single points calculations are conducted with the revPBE functional on which C09 is based.⁶ Core electrons are described with Troullier-Martins pseudopotentials.⁷ The valence wavefunctions are developed over double- ζ polarized basis set of finite-range numerical pseudoatomic orbitals.⁸ In all cases, an energy cutoff of 150 Ry for real-space mesh size has been used.

ASSOCIATED CONTENT

Supporting Information

Additional crystallographic details (CIF), time-resolved PL, ^1H NMR spectra and photo-response of selected compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*m-kanatzidis@northwestern.edu

*cstoumpos@materials.uoc.gr

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TOC graphic

Hybrid Dion-Jacobson Lead Bromide Phases

