Supporting Information for

Incorporating Large A-Cations into Lead Iodide Perovskite Cages: 
Relaxed Goldschmidt Tolerance Factor and Impact on Exciton- 
Phonon Interaction

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I. Material and Methods

Synthesis and Single-Crystal Growth of Various Samples.

All chemicals and regents were purchased from Sigma-Aldrich and used as received, except for \( n \)-hexylammonium iodide (HAI) and AI (A = methylammonium (MA), formamidinium (FA), ethylammonium (EA), guanidinium (GA), acetamidinium (AA)) which were purchased from Dysol.

Safety Statement. Exposure to lead halides can cause acute and chronic lead poisoning. A respirator is recommended while handling powders of lead halides. For lead halides solvated in DMF, PPE compatible with DMF (i.e. butyl rubber gloves) should be used.

Antisolvent growth of non-perovskites of APbI\(_3\) and 2D RP perovskites of (HA)\(_2\)(A)Pb\(_2\)I\(_7\). The various non-perovskite compounds of APbI\(_3\) were synthesized by adding chloroform into a solution of APbI\(_3\), which was made by dissolving stoichiometric PbI\(_2\) and the respective AI in dimethylformamide (DMF). The precipitated yellow powders were collected by centrifugation at 10 k rpm for 1 min and then dried at 60 °C in an oven. The various 2D RP perovskites of (HA)\(_2\)(A)Pb\(_2\)I\(_7\) were synthesized by adding chloroform into a solution of APbI\(_3\) with additional excessive HAI in dimethylformamide (DMF). Experimental parameters, such as the concentration and added volume of each component, are summarized in Table S1. The precipitated red powders were collected by centrifugation at 10 k rpm for 1 min, and then washed with chloroform several times before dried at 60 °C in an oven. The suspended solutions of various (HA)\(_2\)(A)Pb\(_2\)I\(_7\) were prepared by adding 10 μL of APbI\(_3\) solution with HAI into ~2 mL chloroform. Experimental parameters, such as the concentration and volume of each chemical, for obtaining precursor solutions are summarized in Table S2.
**Table S1.** Experimental parameters for the synthesis of various \((\text{HA})_2(\text{A})\text{Pb}_2\text{I}_7\).

|                | Conc (APbI\textsubscript{3}) | Vol (APbI\textsubscript{3}) | Vol (HAI) | Vol (CHCl\textsubscript{3}) |
|----------------|------------------------------|------------------------------|-----------|-----------------------------|
| \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 40 μL     | 0.6 mL                      |
| \((\text{HA})_2(\text{FA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 30 μL     | 0.3 mL                      |
| \((\text{HA})_2(\text{DMA})\text{Pb}_2\text{I}_7\) | 0.67 M                       | 10 μL                        | 40 μL     | 0.4 mL \textsuperscript{a} + 0.15 mL |
| \((\text{HA})_2(\text{EA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 10 μL     | 0.3 mL                      |
| \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) | 1.0 M                        | 10 μL                        | 30 μL     | 0.6 mL                      |
| \((\text{HA})_2(\text{AA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 22.5 μL   | 0.3 mL \textsuperscript{a} + 0.2 mL |

Note, the concentration of HAI solution in DMF is 2 M. \textsuperscript{a} The initial precipitate after adding the first portion of chloroform was isolated and discarded, as it also contains non-perovskite phase.

**Table S2.** Experimental parameters for preparing suspended solutions of various \((\text{HA})_2(\text{A})\text{Pb}_2\text{I}_7\).

|                | Conc (APbI\textsubscript{3}) | Vol (APbI\textsubscript{3}) | Vol (HAI) | Vol (CHCl\textsubscript{3}) |
|----------------|------------------------------|------------------------------|-----------|-----------------------------|
| \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 40 μL     | 0.4 mL                      |
| \((\text{HA})_2(\text{FA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 30 μL     | 0.3 mL                      |
| \((\text{HA})_2(\text{DMA})\text{Pb}_2\text{I}_7\) | 0.67 M                       | 10 μL                        | 40 μL     | 0.2 mL                      |
| \((\text{HA})_2(\text{EA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 10 μL     | 0.3 mL                      |
| \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) | 1.0 M                        | 10 μL                        | 30 μL     | 0.6 mL                      |
| \((\text{HA})_2(\text{AA})\text{Pb}_2\text{I}_7\) | 0.5 M                        | 10 μL                        | 22.5 μL   | 0.3 mL                      |

Note, after centrifugation, 10 μL of top clean solution was added into ~2 mL chloroform to obtain suspended solutions of \((\text{HA})_2(\text{A})\text{Pb}_2\text{I}_7\) for absorption measurement.

*Growth of \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) and \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) single crystals.* To grow \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) single crystals, powders of PbI\textsubscript{2} (922 mg, 2.00 mmol) and GAI (187 mg, 1.00 mmol) were
dissolved in 2.0 mL of HI solution (57 wt % in H₂O) and 0.2 mL of H₃PO₂ in a vial. In a separate vial, n-hexylamine (700 μL, 5.33 mmol) was slowly added into 6 mL of HI solution and 0.2 mL of H₃PO₂ to form an HAI solution. The HAI solution (0.6 mL) was then added into the solution of PbI₂ and GAI. The solution was heated to 150 °C on a hot plate to completely dissolve all the solids. The mother liquour was then transferred into another vial in an oven and held at a constant temperature of 70 °C. Flake-like red-colored single crystals of (HA)₂(GA)Pb₂I₇ were produced within a few hours. To grow (HA)₂(MA)Pb₂I₇ single crystals, powders of PbI₂ (922 mg, 2.00 mmol) and MAI (159 mg, 1.00 mmol) were dissolved in 2.0 mL of HI solution (57 wt % in H₂O) and 0.2 mL of H₃PO₂ in a vial. HAI solution (1.0 mL) was then added into the solution of PbI₂ and MAI. The solution was heated to 150 °C on a hot plate to completely dissolve all the solids. The mother liquor was allowed to sit undisturbed at room temperature for several hours to yield flake-like red-colored single crystals.

Single-Crystal X-ray Structure Determination

*Single Crystal Diffraction Data Collection of (HA)₂(GA)Pb₂I₇ and (HA)₂(MA)Pb₂I₇.* Red crystals with approximate dimensions of 0.12 × 0.04 × 0.04 mm³ [(HA)₂(GA)Pb₂I₇] and 0.003 × 0.03 × 0.04 mm³ [(HA)₂(MA)Pb₂I₇] were selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. Note that compounds are referred to in the order of (HA)₂GAPb₂I₇, (HA)₂MAPb₂I₇ for the rest of the description. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of (6.00; 4.96 cm)¹. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about
ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of (4599; 9941) strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of (0.80; 0.77 Å). A total of (40129; 61721) data were harvested by collecting (6; 10) sets of frames with (0.4°; 0.5°) scans in ω and φ with exposure times of (20; 11) sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.

Single Crystal Diffraction Data Collection of (GA)PbI₃. A colorless crystal with approximate dimensions 0.046 × 0.046 × 1.00 mm³ was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm¹. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about ω with the exposure time of 1 second per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX3 program suite. The final cell constants were calculated from a set of 9885 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.66 Å. A total of 31655 data were harvested by collecting 10 sets of frames with 0.3/0.5° scans in ω and φ with exposure times of 1/6 sec per frame. These highly redundant datasets were
corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements\(^2\). A structural figure with probability ellipsoids of GAPbI\(_3\) is shown in Figure S6.

Structure Solution and Refinement of (HA)\(_2\)(GA)Pb\(_2\)I\(_7\): The systematic absences in the diffraction data were consistent for the space groups P1 and P1. The \(E\)-statistics strongly suggested the centrosymmetric space group P1 that yielded chemically reasonable and computationally stable results of refinement\(^3\). A successful solution by the direct methods provided most non-hydrogen atoms from the \(E\)-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. In the N5 hexan-1-aminium, the carbon atoms are equally disordered over two positions. The disordered components were refined with restraints and constraints. The crystal selected for the single-crystal X-ray diffraction experiment proved to be a two-component non-merohedral twin with a 30.15(12) % second component contribution. The twin domains are related by a 179.9° rotation about direct axis [010]. The final least-squares refinement of 298 parameters against 28779 data resulted in residuals \(R\) (based on \(F^2\) for \(I\geq2\sigma\)) and \(wR\) (based on \(F^2\) for all data) of 0.0315 and 0.0928, respectively. Evaluation of the CIF using the CheckCIF routine at CheckCIF Website (https://checkcif.iucr.org/) yielded one B alert. The missing reflection 101 was affected by the beam stop. However, its presence does not noticeably affect the refinement. A structural figure with probability ellipsoids of (HA)\(_2\)(GA)Pb\(_2\)I\(_7\) is shown in Figure S7.
**Structure Solution and Refinement of (HA)$_2$(MA)Pb$_2$I$_7$:** The systematic absences in the diffraction data were consistent for the space groups $C2/c$ and $Cc$. The $E$-statistics strongly suggested the centrosymmetric space group $C2/c$ that yielded chemically reasonable and computationally stable results of refinement$^{3,4,5,6,7,8}$. A successful solution by the direct methods provided most non-hydrogen atoms from the $E$-map. The remaining non-hydrogen atoms, unless specified otherwise, were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms, unless otherwise noted, were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The asymmetric unit contains $\frac{1}{2}$ of Pb$_2$I$_7^{3-}$, one hexylammonium, and $\frac{1}{2}$ methyl ammonium. Atom I3 of this Pb$_2$I$_7^{3-}$ dimer resides on a crystallographic two-fold axis. The methylammonium is disordered over two positions near a crystallographic two-fold axis and thus there are four positions shared by this cation. The relative occupancies of these four positions are 30.2(6), 19.8(6), 30.2(6), and 19.8(6), but only two of these are symmetry-independent. The methylammoniums were refined with distant restraints and anisotropic displacement parameter constraints. It is not possible to decisively distinguish between the nitrogen and carbon atoms in the methylammonium. The final least-squares refinement of 125 parameters against 3931 data resulted in residuals $R$ (based on $F^2$ for $I\geq 2\sigma$) and $wR$ (based on $F^2$ for all data) of 0.0211 and 0.0509, respectively. The final difference Fourier map contained several residual electron density peaks (ca. 2.36 e/Å$^3$). These peaks were located in the vicinity of the heaviest atoms and were considered noise. A structural figure with probability ellipsoids of (HA)$_2$(MA)Pb$_2$I$_7$ is shown in Figure S8.
Structure Solution and Refinement of (GA)\textsubscript{PbI\textsubscript{3}}: The systematic absences in the diffraction data were uniquely consistent for the space group \(P2_1/n\) that yielded chemically reasonable and computationally stable results of refinement \(^3,4,5,6,7,8\). A successful solution by the direct methods provided most non-hydrogen atoms from the \(E\)-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 73 parameters against 2393 data resulted in residuals \(R\) (based on \(F^2\) for \(I \geq 2\sigma\)) and \(wR\) (based on \(F^2\) for all data) of 0.0233 and 0.0523, respectively. The final difference Fourier map was featureless.

Crystal structure data of \((HA)\textsubscript{2}(GA)\textsubscript{PbI\textsubscript{7}}\) and \((HA)\textsubscript{2}(MA)\textsubscript{PbI\textsubscript{7}}\), and \(GAPbI_3\) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under reference numbers 1888368, 1886888, and 1886889, respectively. These data can be obtained free of charge from the website (https://www.ccdc.cam.ac.uk/structures/).

Other Structural and Spectroscopic Characterizations.

The PXRD patterns were collected on as-prepared samples on glass substrates using a Bruker D8 Advance Powder X-ray Diffractometer with Cu K\(\alpha\) radiation. The optical images of the single crystals were obtained on an Olympus BX51M optical microscope.

Absorption and PL measurements. Bulk powder UV–vis absorption data were obtained with a Cary-5000 UV–vis–NIR spectrophotometer equipped with an integrating sphere attachment.
(Agilent) in reflectance mode. The UV–vis absorption data of suspended solutions were collected using a JASCO V-550 spectrometer.

The steady-state photoluminescence of \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) and \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) single crystals were collected with an Aramis Confocal Raman Microscope using a 442 nm laser source. The temperature dependent PL spectra of \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) and \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) single crystals were measured with a 488 nm CW laser at different temperature from 10 K to 290 K in a Microscope Cryostat System (Link Physics C01-001-122). Time-resolved PL decay kinetics of \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) and \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) single crystals were collected using a streak camera (Hamamatsu C10910) with a confocal microscope (WITec, alpha-300), and with an excitation light of Ti:Sapphire laser pulses at 400 nm (repetition rate of 80 MHz, pulse width of 80 fs). The 400 nm excitation light was generated by the second harmonic of an 800 nm laser from a mode-locked oscillator (Tsunami 3941-X1BB, Spectra-Physics) after a BBO crystal. The laser beam was focused onto the sample surface by an objective lens (50×, Zeiss, 0.75 NA) with a spot diameter of 3 µm, and the PL emission was collected by the same objective lens. The laser power was calibrated with a power meter (PM100D from THORLABS).

Raman measurements. The Raman spectra of \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) and \((\text{GA})_2\text{PbI}_4\) single crystals (shown in Figure S3) were collected with an Aramis Confocal Raman Microscope using a 633 nm laser source. The low-frequency Raman spectra of \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) and \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) single crystals were collected on a home-built microscopic Raman setup with a 1064 nm YAG laser. A volume Bragg grating (VBG) beamsplitter filter (BPF, OptiGrate, Inc.) was used to purify the incident laser wavelength and guided the laser towards the sample in a cryostat (Oxford Instruments Microstat HiRes2) under vacuum of \(10^{-6}\) to \(10^{-5}\) Torr. A 40× objective with a numerical aperture of 0.6 (S Plan Fluor, Nikon) was applied to focus the beam and collect the
scattered light. Three ultra-narrow band BVG notch filters attenuated the Rayleigh line each with O. D. > 3.0, then the light containing large enough portion of Raman signal was sent into a 4-f spectrometer with 600 grooves/mm diffraction grating through a special filter (resolution of 0.8 cm\(^{-1}\)). The signal was read out by an InGaAs CCD camera (Pylon IR 1024, Princeton Instruments) with liquid nitrogen cooling. Each spectrum was acquired after the sample was stabilized at the target temperature for 10 min.

II. Supporting Figures, Tables, and Equations

*Equations used to calculate Quadratic Elongation (\(\langle \lambda \rangle \)) and Bond angle variance (\(\sigma^2\)).*\(^9\)

Equation S1: Quadratic Elongation (\(\langle \lambda \rangle \))

\[
\langle \lambda \rangle = \frac{1}{6} \sum_{i=1}^{6} \left( \frac{d_i}{d_o} \right)^2
\]

Where \(d_i\) is the Pb-I bond length, \(d_o\) is the Pb-I bond length from an ideal octahedron of the same volume, \(\langle \lambda \rangle\) is dimensionless.

Equations S2: Bond angle variance (\(\sigma^2\))

\[
\sigma^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2
\]

Where \(\alpha_i\) is the I-Pb-I bond angles of the octahedra.
Figure S1. (a) PXRD patterns of non-perovskites of APbI₃ with various A cations prepared by antisolvent growth, together with the standard PXRD patterns of GAPbI₃ (non-perovskite phase), hexagonal FAPbI₃ (non-perovskite phase), and tetragonal MAPbI₃ (perovskite phase). Insets are photographs of various APbI₃ powders on glass slides. The crystal packing diagrams of (b) GAPbI₃ with edge-shared connection (crystallographic data in Table S6), (c) hexagonal FAPbI₃ with face-shared connection,¹⁰ and (d) tetragonal MAPbI₃ perovskite¹⁰ with corner-shared connection.
Figure S2. PXRD patterns of the (BA)$_2$(A)Pb$_2$I$_7$ with the various A cations prepared by antisolvent growth of APbI$_3$ with excessive $n$-butylammonium iodide (BAI), in comparison with the standard PXRD of (BA)$_2$(MA)Pb$_2$I$_7$ and (BA)$_2$(MA)$_2$Pb$_3$I$_{10}$.$^{11}$ The results show that the Goldschmidt tolerance factor relaxation is general in 2D RP structures with different LA cations. The PXRD pattern for the case of EA and BA cations is very different from those of other A-site cations, which suggests this product is not a (pure) $n = 2$ perovskite structure. Instead, the pattern seems to be more similar to that of (BA)$_2$(MA)$_2$Pb$_3$I$_{10}$, and the diffraction peaks just slightly shift to lower angle. The color of the powder appears to be the darkest (suggesting the smallest bandgap). These suggest the possible formation of higher-$n$ (i.e. $n > 2$) structures for the EA cation.
Figure S3. (a) Raman spectra of (HA)$_2$(GA)Pb$_2$I$_7$ and (GA)$_2$PbI$_4$ single crystals, showing the different vibrational behaviors of GA cations in the cage and gallery. (b) The crystal structure of (GA)$_2$PbI$_4$ with GA cation in the gallery.$^{12}$ (c) The crystal structure of (HA)$_2$(GA)Pb$_2$I$_7$ with GA cation in the perovskite cage.
**Figure S4.** 2D pseudo-color plots of the TRPL spectra of (HA)$_2$(GA)Pb$_2$I$_7$ and (HA)$_2$(MA)Pb$_2$I$_7$ single crystals.
**Figure S5.** Temperature-dependent low-frequency Raman spectra of $(\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7$ and $(\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7$ single crystals from 77 K to 300 K. Representative curves at 3 temperatures are highlighted in Figure 4a,b in the main text.

**Figure S6.** A molecular drawing of the asymmetric unit of GAPbI$_3$ shown with 50% probability ellipsoids.
**Figure S7.** A molecular drawing of the asymmetric unit of $(HA)_2(GA)Pb_2I_7$ shown with 50% probability ellipsoids. Only one disorder component at N5 is shown.

**Figure S8.** A molecular drawing of the asymmetric unit of $(HA)_2(MA)Pb_2I_7$ shown with 50% probability ellipsoids except for the methylammonium. All H atoms are omitted.
**Figure S9.** Evolution of PL spectra of (a) \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) and (b) \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) single crystals collected under constant laser illumination \(\lambda_{\text{ex}} = 532 \text{ nm}, 9 \text{ mW/cm}^2\) in ambient conditions. (c) Plot of PL intensity (at \(\lambda_{\text{max}}\)) vs. time, demonstrating that \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) is slightly more stable under illumination (34% initial intensity (GA) vs. 13% initial intensity (MA)).

**Table S3.** Complete crystal data and structure refinement details of \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) and \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\).

| Compound name                  | \((\text{HA})_2(\text{MA})\text{Pb}_2\text{I}_7\) | \((\text{HA})_2(\text{GA})\text{Pb}_2\text{I}_7\) |
|-------------------------------|---------------------------------|---------------------------------|
| Empirical formula             | \((\text{C}_6\text{H}_{13}\text{NH}_3)\text{C}_2\text{H}_3\text{NH}_3)\text{Pb}_2\text{I}_7\) | \((\text{C}_6\text{H}_{13}\text{NH}_3)\text{C}_2\text{[NH}_2\text{]_3}\text{Pb}_2\text{I}_7\) |
| Formula weight                | 665.04                          | 1567.16                         |
| Crystal system                | monoclinic                      | triclinic                       |
| Space group                   | \(\text{C}2/c\)                 | \(\text{P}-\text{I}\)          |
| \(a/\text{Å}; \alpha/^{\circ}\) | 45.146(16); 90                  | 8.8195(14); 79.965(13)          |
| \(b/\text{Å}; \beta/^{\circ}\) | 8.814(3); 100.030(5)            | 9.0300(15); 87.341(9)           |
| \(c/\text{Å}; \gamma/^{\circ}\) | 8.695(3); 90                    | 21.699(4); 89.986(10)           |
| Volume/\(\text{Å}^3\)        | 3407(2) \(\text{Å}^3\)         | 1699.8(5)                       |
| \(Z\)                         | 4                               | 2                               |
| Property                                      | Value 1       | Value 2       |
|----------------------------------------------|---------------|---------------|
| Temperature (K)                              | 99.99         | 99.92         |
| $\rho_{\text{calc}}$, g/cm$^3$               | 3.000         | 3.062         |
| Absorption Coefficient $\mu$/mm$^{-1}$       | 16.217        | 16.259        |
| F(000)                                       | 2688          | 1372          |
| $2\Theta$ range for data collection/°        | 3.664 to 55.148 | 1.908 to 53.004 |
| Index ranges                                 | -58 $\leq$ h $\leq$ 58, | -11 $\leq$ h $\leq$ 11, |
|                                             | -11 $\leq$ k $\leq$ 11, | -11 $\leq$ k $\leq$ 10, |
|                                             | -11 $\leq$ l $\leq$ 11 | -27 $\leq$ l $\leq$ 27 |
| Reflections collected                        | 61721         | 28779         |
| Independent reflections                      | 3931 [R$_{int}$ = 0.0456, R$_{\text{sigma}}$ = 0.0170] | 28779 [R$_{int}$ = 0.0390, R$_{\text{sigma}}$ = 0.0463] |
| Data/restraints/parameters                   | 3931/2/125    | 28779/105/298 |
| Goodness-of-fit on $F^2$                     | 1.061         | 1.047         |
| Final R indexes [I$\geq$2$\sigma$(I)]      | R$_1$ = 0.0211, wR$_2$ = 0.0497 | R$_1$ = 0.0315, wR$_2$ = 0.0886 |
| Final R indexes [all data]                  | R$_1$ = 0.0241, wR$_2$ = 0.0509 | R$_1$ = 0.0335, wR$_2$ = 0.0928 |
| Largest diff. peak/hole / e Å$^{-3}$         | 2.36/-1.32    | 2.40/-1.74    |
Table S4. Comparison of the perovskite cage volume of \((HA)_{2}(GA)PbI_7\) with all previously reported 2D RP lead iodide perovskites with \(n = 2\).

| Structure                  | Temp. (K) | Cage volume \((\text{Å}^3)\) | Pb-I-Pb angle (a,b) \(^\circ\) | Pb-I-Pb angle (c) \(^\circ\) | Pb-plane to Pb-plane (cage) | (a,b axis)(Å) | (c-axis) (Å) |
|----------------------------|-----------|-------------------------------|---------------------------------|-------------------------------|-----------------------------|---------------|--------------|
| \((HA)_{2}(GA)PbI_7\) (this work) | 100       | 264.44                        | 162.62, 161.42                  | 178.87                        | 6.29, 6.31                  | 6.66          |              |
| \((HA)_{2}(MA)PbI_7\) (this work) | 100       | 250.25                        | 155.73                          | 179.23                        | 6.62, 6.20                  | 6.52          |              |
| \((HO_2C(CH_2)_3NH_3)_2(MA)Pb_2I_7\) \(^{13}\) | 293       | 256.94                        | 160.22, 159.75                  | 179.94                        | 6.41, 6.33                  | 6.49          |              |
| \((CH_3C_6H_4CH_2NH_3)_2(MA)Pb_2I_7\) \(^{14}\) | 295       | 252.36                        | 155.39, 158.86                  | 178.28                        | 6.22                        | 6.52          |              |
| \((C_3H_7NH_3)_2(MA)Pb_2I_7\) \(^{15}\) | 300       | 257.35                        | 164.31                          | 164.05                        | 6.30, 6.29                  | 6.48          |              |
| \((CH_3(CH_2)_3NH_3)_2(MA)Pb_2I_7\) \(^{11}\) | 293       | 256.82                        | 164.2, 173.1                    | 165.64                        | 6.30, 6.29                  | 6.48          |              |
| \((C_4H_3SCH_2NH_3)_2MAPb_2I_7\) \(^{16}\) | 293       | 252.96                        | 154.50, 157.97                  | 178.37                        | 6.24, 6.53                  | 6.21          |              |

Table S5. Comparison of the average PL lifetimes of \((HA)_{2}(GA)PbI_7\) and \((HA)_{2}(MA)PbI_7\).

| GA # | \(A_1\tau_1 + A_2\tau_2(ps)\) | MA # | \(A_1\tau_1 + A_2\tau_2(ps)\) |
|------|---------------------------------|------|---------------------------------|
| 1    | 41                              | 1    | 124                             |
| 2    | 57                              | 2    | 119                             |
| 3    | 58                              | 3    | 111                             |
| 4    | 52                              | 4    | 109                             |
| 5    | 49                              | 5    | 109                             |
| 6    | 62                              | 6    | 111                             |
| 7    | 60                              | 7    | 104                             |
| Average | 54 ± 7            |      | 114 ± 6                        |
**Table S6. Complete crystal data and structure refinement details of (GA)PbI$_3$.**

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Compound name                 | (GA)PbI$_3$                                |
| Empirical formula             | [C(NH$_2$)$_3$]PbI$_3$                      |
| Formula weight                | 647.98                                     |
| Crystal system                | monoclinic                                 |
| Space group                   | P2$_1$/n                                   |
| a/Å; α/°                      | 4.5694(12); 90                             |
| b/Å; β/°                      | 11.748(3); 94.147(14)                      |
| c/Å; γ/°                      | 19.504(4); 90                              |
| Volume/Å$^3$                  | 1044.2(4)                                  |
| Z                             | 4                                          |
| Temperature (K)               | 100.0                                      |
| $\rho_{\text{calc}}$, g/cm$^3$| 4.122                                      |
| Absorption Coefficient $\mu$/mm$^{-1}$| 24.961                                    |
| F(000)                        | 1096.0                                     |
| 2θ range for data collection/°| 4.05 to 55                                 |
| Index ranges                  | -5 ≤ h ≤ 5, -15 ≤ k ≤ 15, -25 ≤ l ≤ 25    |
| Reflections collected         | 31655                                      |
| Independent reflections       | 2393 [R$_{\text{int}}$ = 0.0357, R$_{\text{sigma}}$ = 0.0141] |
| Data/restraints/parameters    | 2393/0/73                                  |
| Goodness-of-fit on $F^2$      | 1.389                                      |
| Final R indexes [I≥2σ (I)]   | R$_1$ = 0.0233, wR$_2$ = 0.0523            |
| Final R indexes [all data]   | R$_1$ = 0.0234, wR$_2$ = 0.0523            |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.31/-1.04     |

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