Manuscript version: Author’s Accepted Manuscript
The version presented in WRAP is the author’s accepted manuscript and may differ from the published version or Version of Record.

Persistent WRAP URL:
http://wrap.warwick.ac.uk/160740

How to cite:
Please refer to published version for the most recent bibliographic citation information. If a published version is known of, the repository item page linked to above, will contain details on accessing it.

Copyright and reuse:
The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher’s statement:
Please refer to the repository item page, publisher’s statement section, for further information.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk.
The Effect of Organic Cation Dynamics on the Optical Properties in (PEA)$_2$(MA)[Pb$_2$I$_7$] Perovskite Dimorphs

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Journal of Materials Chemistry C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>TC-ART-09-2021-004181</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>03-Sep-2021</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Yulia, Lekina; Nanyang Technological University, Division of Physics and Applied Physics, School of Physical and Mathematical Sciences; Dintakurti, Sai; Nanyang Technological University, Interdisciplinary Graduate School; University of Warwick, Physics; Febriansyah, Benny; Nanyang Technological University, Energy Research Institute @ Nanyang Technological University; Bradley, David; University of Warwick; Yan, Jiaxu; Nanjing Tech University (NanjingTech), Institute of Advanced Materials; Shi, Xiangyan; Nanyang Technological University, Division of Physics and Applied Physics, School of Physical and Mathematical Sciences; England, Jason; Nanyang Technological University, School of Physical and Mathematical Sciences; White, T.; ntu; Hanna, John; University of Warwick, Department of Physics; Shen, Zexiang; Nanyang Technological University, School of Physical and Mathematical Sciences</td>
</tr>
</tbody>
</table>

SCHOLARONE™ Manuscripts
The Effect of Organic Cation Dynamics on the Optical Properties in (PEA)$_2$(MA)[Pb$_2$I$_7$] Perovskite Dimorphs

Yulia Lekina, a,b Sai S.H. Dintakurti, c,d Benny Fębriansyah, e D.J. Bradley, f Jiaxu Yan, g Xiangyan Shi, b Jason England, h Tim White, i John V. Hanna, i,a,g Ze Xiang Shen i,a,b

Two-dimensional (2D) phenylethyl ammonium (PEA)-methyl ammonium (MA)- lead iodide ([(PEA)$_2$(MA)[Pb$_2$I$_7$])] hybrid perovskites exist as temperature-dependent dimorphs exhibiting an ill-defined phase transition occurring over 150 - 200 K range. Raman scattering, photoluminescence, optical absorbance and solid state MAS NMR spectroscopic methods are employed to investigate the structural complexity, disorder and structure/function of this system. The Raman and $^1$H MAS NMR data indicate that the lower bounds of the phase transition at ~150 K is characterised by attenuated rotational modes and slower motional dynamics throughout the disordered MA$^+$ organic sublattice, inducing a strengthening of the MA$^--$I hydrogen bonds and a 5 meV increase in the excitonic and photoluminescence energies. It is evident that different recombination mechanisms are dominant for the room temperature and low temperature phases reflecting the importance of MA$^+$ dynamics in the optical properties of the material. Single crystal X-ray studies are unable to position the organic cations within the PbI$_2$ framework; however, $^1$H/$^1$C MAS NMR measurements describe elements of local structural disorder based on conformational isomerism within the PEA$^+$ sublattice. Concomitant I$^-$ and Pb$^{2+}$ migration and [Pb$_2$I$_7$]$^-$ framework defects create stacking disorder, dislocations and dispersed octahedral tilting leading to additional disorder and distributed MA$^+$ and PEA$^+$ cation dynamics.

Introduction

Hybrid organic-inorganic halide perovskites have attracted intense attention due to their high performance and low cost for light harvesting applications. 1-3 These materials can also be deployed as light emitting diodes (LEDs), 1,4,5 X-ray and photo detectors, 6,7 spintronics 8 and lasing applications. 9 The solar cell performance of AMX$_3$ perovskites (A is an organic cation, usually MA = CH$_3$NH$_3^+$, M = Pb, Sn, X = I, Br, Cl or a mixture of them) has evolved much faster than other photovoltaic materials, 1,10 with a power conversion efficiency (PCE) of more than 25% being achieved. 11-13 However, poor moisture stability and degradation of the photoluminescence characteristics remain as significant obstacles to the fabrication of low-cost and long lifetime devices from 3D hybrid perovskite systems 14-18. In comparison, 2D perovskites have demonstrated improved stability and flexible chemical engineering possibilities for solar light-harvesting and LED applications 6,14-18. These materials have been found to be excellent candidates for light emitting diode (LED) applications due to tenability, high quantum efficiencies, and broadband emission 6,14-19.

The crystal structures of 2D perovskites are derived from the cubic perovskite aristotype by slicing on the (100) planes and intercalating organic cations to yield a layered structure with corner-sharing MX$_6$ octahedral blocks occupying the basal plane (Fig. 1). This yields the general formula $R(A)_{n-1}M_nX_{3n+1}$, where $R$ is the long organic cation-spacer, $A$ is a small organic (or inorganic) cation such as methylammonium (MA$^+$), and $n$ indicates the number of octahedral layers within each inorganic block. 20 Introducing hydrophobic organic layers simultaneously provides protection from moisture and creates intrinsic quantum wells that widens the band gap and promotes strong excitonic properties due to quantum confinement. 21-24

In general, the typical architecture of 2D hybrid perovskite systems relies on the electronic structure being directly controlled by the inorganic sublattice, while the organic cations provide more subtle steric influences. 20,22,25 Previous work has reported that the top of the valence band is influenced by the Pb 6$s$ and I 5$p$ orbitals, while conversely the bottom of the conduction band by Pb 6$p$ and I 5$s$ orbitals. 25 In particular, the Pb-I bond length within the PbI$_6$ octahedron and Pb-I-Pb bridging angle between PbI$_6$ octahedra correlate closely with the electronic structure and optical properties. 22,26,27 Consequently, temperature driven polymorphism leads to abrupt changes in optical and electronic properties, and device

![Fig. 1 Generalized scheme of the crystal structure types comprising 2D perovskite systems.](image-url)
performance, in these materials. For example, the 2D perovskite \((\text{PEA})_2[\text{PbI}_4]\) \((n = 1, \text{PEA} = \text{phenylethylyl ammonium})\) system is structurally stable over a 10 - 340 K temperature range; however, in contrast the 3D perovskite system \(\text{MAPbI}_3\) \((n = \infty)\) undergoes two phase transitions over similar temperature ranges. Furthermore, hydrogen bonding between the methylammonium cations was shown to be extremely important in 3D perovskites as this significantly increases the overall stability, and provides possibilities for tuning of the electronic states.

The 2D \((n = 2)\) perovskite system \((\text{PEA})_2[\text{MA}][\text{PbI}_2]\) is intermediate to \(\text{MAPbI}_3\) and \((\text{PEA})_2[\text{PbI}_4]\), and it possesses MA\(^+\) and PEA\(^+\) cations which are both capable of forming hydrogen bonds. Substantial ambiguity and uncertainty surrounds the complete ambient and low temperature single crystal structure determinations of the \((\text{PEA})_2[\text{MA}][\text{PbI}_2]\) system as the light elements are essentially invisible to the XRD technique. It is postulated that structural disorder throughout the organic substituents is responsible for the disorder, although this is yet to be established conclusively. This uncertainty precludes an understanding of the low temperature photophysical properties, and consequently the influence of hydrogen bonding in this process has not been thoroughly investigated. Raman spectroscopy has been demonstrated to be a very sensitive probe for studying hydrogen atom vibrational modes in hybrid perovskite systems, with recent studies characterizing the vibrational interactions between the MA\(^+\) cation and halogen atoms in 3D perovskites.

This study describes a low temperature Raman spectroscopic investigation of the N-H bond vibrations, particularly those related to the formation of N-H-I hydrogen bonds in \((\text{PEA})_2[\text{MA}][\text{PbI}_2]\), to provide complementary information to single crystal X-ray diffraction where lighter elements evade detection. The absorption, emission and Raman vibrational modes of \((\text{PEA})_2[\text{MA}][\text{PbI}_2]\) over the 80 - 293 K temperature range have been analyzed, with a correlation of the MA\(^+\) cation vibrations and excitonic features revealing a broad phase transition occurring over a wide temperature of range between 150 - 200 K. This study also utilizes solid state \(^{1}H\) and \(^{13}C\) MAS NMR to investigate and constrain the structural disorder that influences the organic PEA\(^+\) and MA\(^+\) cations, and shows that the broad phase transition could be attributed to gradual thermal rearrangement of the stacking disorder of the PEA\(^+\) cations within the 2D interplanar channels, which also concomitantly disrupts the hydrogen bonding network.

**Experimental**

**Synthesis**
The synthesis procedure described previously by Stoumpos et. al. was used to obtain crystalline \((\text{PEA})_2[\text{MA}][\text{PbI}_2]\), however, the method was modified to include an excess of methyl ammonium iodide. Inorganic lead iodide (99.999%, trace metals basis, perovskite grade), phenyl ethyl amine (99%), 57% w/w non-stabilized aqueous HI solution, and 50% aqueous H\(_2\)PO\(_4\) were obtained from Sigma Aldrich, while methyl ammonium iodide was purchased from Dyesol. These reagents were used without purification unless otherwise stated in the associated procedure.

Phenyl ethyl ammonium iodide was prepared by slowly mixing the amine with a stoichiometric amount of hydroiodic acid in ethanol at 0 °C for 1 hour, after which the solvents were removed by rotary vacuum evaporation at 50 °C. Where necessary, excess ethanol was added to form an azeotropic mixture with water to remove the latter completely. The solid product was washed with diethyl ether to remove the remaining iodosides. Finally, the ammonium salt was dried under vacuum at 50 °C overnight (1.76g; 83% yield). \(^{1}H\) NMR (400 MHz, DMSO-d6): \(\delta\) 7.78 (bs, 3 H, NH\(_3\)), 7.32-7.20 (m, 5 H, ArH), 3.06-3.03 (m, 2 H, CH\(_2\)), 2.88-2.84 (m, 2 H, CH\(_2\)). \(^{13}C\)\(^{(1}H)\) NMR (100 MHz, DMSO-d6): \(\delta\) 137.1, 128.6, 128.6, 126.7, 40.0, 32.8.

Then \((\text{PEA})_2[\text{MA}][\text{PbI}_2]\) \((n = 2)\) was prepared. A two-necked round bottom flask was used to combine PbI\(_2\) powder (230 mg, 0.5 mmol), methyl ammonium (53 mg, 0.33 mmol) and phenyl ethyl ammonium iodide salts (125 mg, 0.5 mmol) with magnetic stirring. Methyl ammonium iodide was added with 30% excess. Subsequently, 57% w/w aqueous HI solution (2.0 mL mL) and 50% aqueous H\(_2\)PO\(_4\) (0.20 mL) were added sequentially in a dropwise manner. The suspension was brought to reflux under flowing N\(_2\) with continuous stirring (30 - 60 mins) to yield a clear, bright yellow solution. Stirring was discontinued and the solution cooled slowly to room temperature while red rectangular plates precipitate. The crystals were finally isolated by vacuum filtration, washed with copious amounts of diethyl ether, and thoroughly dried under vacuum for several hours.

**Solid State \(^{13}C\) and \(^{1}H\) MAS NMR:**
All solid-state MAS NMR measurements were acquired at 18.8 T using a Bruker Avance III-800 spectrometer operating at \(^{1}H\) and \(^{13}C\) Larmor frequencies of 800.16 and 201.19 MHz, respectively. These measurements were undertaken using a Bruker 0.7 mm triple channel H/C/N ultrafast MAS probe which enabled a MAS frequency of 110 kHz throughout this study. The \(^{1}H\) MAS NMR data were acquired using single pulse methods which utilised a \(\pi/2\) pulse length of 1.0 \(\mu\)s (calibrated using adamantane) and a recycle delay of 30 s. In contrast, the \(^{1}H\)-\(^{13}C\) cross-polarisation (CP)MAS NMR data were measured using an initial \(^{1}H\) \(\pi/2\) pulse time of 1.0 \(\mu\)s, a Hartmann-Hahn contact period (in the form of a CP ramp) of 2 ms, in conjunction with \(^{1}H\) de-coupling fields of >100 kHz during data acquisition. Both \(^{1}H\) and \(^{13}C\) chemical shifts were both referenced against TMS as the primary IUPAC reference (\(\delta_{\text{iso}} = 0.00\) ppm) via a secondary solid adamantane reference (\(\delta_{\text{iso}} = 1.99\) ppm for \(^{1}H\); \(\delta_{\text{iso}} = 37.7\) ppm for \(^{13}C\)). The \(^{1}H\) MAS NMR data were accurately simulated using the DMFit NMR software package to quantitatively estimate the relative proportions of the individual PEA\(^+\) and MA\(^+\) cations present.
Two-dimensional heteronuclear \(^1\text{H}-^{13}\text{C}\) correlation data was achieved through the use of the inversely detected hCH HETCOR experiment utilising forward \(^{13}\text{C}-^{1}\text{H}\) CP, evolution of the \(^{13}\text{C}\) magnetisation under fast MAS and high \(^{1}\text{H}\) decoupling conditions, and then reverse \(^{13}\text{C}-^{1}\text{H}\) CP for detection of the \(^{1}\text{H}\) magnetisation. The preparatory \(^{1}\text{H}\) and \(^{13}\text{C}\) \(\pi/2\) pulse lengths prior to the forward and reverse CP processes were both \(1\ \mu\text{s}\) in duration, while the forward and reverse CP ramps (contact periods) were both \(2\ \text{ms}\). The 2D homonuclear \(^{1}\text{H}-^{1}\text{H}\) NOESY data were acquired using mixing times of \(100\) and \(300\ \text{ms}\), a recycle delay of \(5\ \text{s}\), with each experiment acquiring \(160\) slices in the indirect \(F_1\) dimension. The 2D homonuclear \(^{1}\text{H}-^{1}\text{H}\) single quantum-double quantum BABA recoupling experiment was performed using a single rotor synchronised recoupling loop of \(9.1\ \mu\text{s}\), a double quantum evolution period of \(15\ \mu\text{s}\), with \(1280\) slices comprising the indirect \(F_1\) dimension. All data were processed using the Bruker TopSpin (v 4.0.8) NMR data processing package. The \(^{1}\text{H}\) \(T_1\) relaxation times were measured using a saturation-recovery experiment. An initial pulse train of \(100\ \pi/2\) pulses with a separation delay of \(50\ \text{ms}\) was used to achieve complete saturation prior to single pulse acquisition. The resulting data were deconvoluted and integrated using Dmfit simulation program.\(^{39}\) The resulting integrated intensity data from each \(^{1}\text{H}\) resonance was fitted with a single exponential function using OriginPro (2019) software to obtain the \(^{1}\text{H}\) \(T_1\) (spin-lattice) relaxation times.

**Optical Characterization**

A WITec Alpha 300RAS confocal Raman microscope was used to record Raman, photoluminescence (PL) and optical absorption spectra. The \(633\ \text{nm}\) (red) line from an \(8\ \text{mW}\) He–Ne gas laser coupled to an Acton spectrometer with a diffraction grating of \(1800\) grooves/mm (\(1.3\ \text{cm}^{-1}\) resolution) and a thermoelectrically cooled Andor CCD detector was chosen to avoid photoluminescence. The backscattered Raman signal passed through two \(633\ \text{nm}\) BraggGrate Notch Filters (BNF) for effective laser line rejection. The blue line of a linearly polarized CW solid laser (457 nm) was chosen for PL measurements with the excitation power maintained below \(0.8\ \mu\text{W}\) to avoid detector photo-degradation and saturation. A halogen lamp (15 V, 150 W, 3100 K) served as the white light source for the absorption measurements. A long working distance \(20\times\) microscope objective (spot size of \(\sim 2\ \mu\text{m}\)) was used for the low temperature experiments. All data were measured between \(293\ \text{K}\) and \(78\ \text{K}\) using a nitrogen gas flow cryostat.

**Powder and Single Crystal X-ray Diffraction**

Laboratory powder X-ray diffraction data were measured using a Shimadzu XRD-600004 diffractometer in \(\theta-2\theta\) scan mode with a measurement rate of \(1\ \text{degree/min}\). Cu-K\(\alpha\) (1.5406 \(\AA\)) X-ray line was chosen as a source while using scintillation NaI detector. Single crystal X-ray diffraction data were collected on a Bruker X8 CCD diffractometer using a graphite-monochromated Mo-K\(\alpha\) source (\(\lambda = 0.71073\ \text{Å}\)) equipped with a CCD detector at room temperature. A full sphere collection was undertaken ranging from \(2.325^{\circ}\) to \(29.000^{\circ}\). A total of \(9178\) reflections were observed of which \(7388\) had an intensity above the threshold limit of \(I > 2\sqrt{\sigma(I)}\); these reflexions were used to fit the structural model in the \(P1\) triclinic space group. Data reduction and absorption corrections were performed with SAINT and SADABS respectively. The motif of the inorganic sublattice was determined by direct methods and refined by full-matrix least-squares procedures on \(F^2\) using the Bruker SHELXL-2018 package. The location of the organic MA\(^+\) and PEA\(^+\) moieties could not be determined.

**DFT Computation**

First principle calculations, including atomic structure optimization, band structure and phonon frequencies simulation, were based on the Density Functional Theory (DFT). The Vienna \textit{Ab initio} Simulation Package (VASP) code was used, employing the previously reported crystal structure\(^{35}\) as the initial parameters. The exchange correlation potential was described using the Perdew, Burke and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).\(^{40}\) The Brillouin zone was sampled by a \(3\times3\times1\) \(k\)-point mesh using Monkhorst-Pack (MP) method. The energy convergence for the relaxation was chosen to be less than \(10^{-5}\) eV/Å. The newly developed vdW density functional (vdW-DF2) was deployed to account for nonlocal van der Waals interactions\(^{41}\).

**Results and Discussion**

**Structural Characterization**
The formation of the 2D \((n = 2)\) \((\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]\) phase was confirmed by powder XRD analysis of the horizontally oriented platelets shown in Fig. S1. These data exhibit reflections that are consistent with results previously reported by Peng et al.\(^{12}\) An additional single crystal X-ray structure determination was conducted in order to obtain the accurate atomic coordinates. A partial structural solution with only the Pb and I atoms being located resulted in an unusually high \(R_i\) value of 0.13 and Goof of 2.44. The refined lattice parameters, positional coordinates and equivalent isotropic displacement parameters are reported in Fig. S2 and Table S1. The organic atoms could not be located due to disorder in the organic sublattice. The highest \(q\) peak with an intensity of 13 electrons occurs at a distance of 1.69 \(\text{Å}\) from Pb1 site. Splitting the Pb1 site reduces the site occupancy factor by \(\sim 5\%\). Similarly, I5 has a \(q\) peak at a distance of 1.65 \(\text{Å}\) having an intensity corresponding to \(\sim 4\%\). The distance of 1.7 \(\text{Å}\) is lesser than the Pb-I bond distance of \(>3.1\) \(\text{Å}\), excluding the possibility of a presence of another atom so close to Pb1 site.

Detection of positional disorder at Pb and I sites with a distance of 1.7 \(\text{Å}\) in the same direction strongly suggests the presence of stacking dislocations at the 4 - 5\% level. Stacking dislocations within the inorganic sublattice are attributed to the positional and conformational disorder in the organic sublattice accommodating the \(
\text{MA}^+\) and \(
\text{PEA}^-\) cations. The I and Pb Ueq values in Table S1 range from 0.053 - 0.063 \(\text{Å}^2\) and 0.0336 - 0.0334 \(\text{Å}^2\), respectively, indicating that the halogen atoms are comparatively more disordered. From Fig. S2, positions I8 and I9 protruding perpendicularly out of the PbI\(_6\) plane exhibit the highest displacements, suggesting that this positional irregularity in the I species defining the interplanar channels is directly associated with the disorder perturbing the organic sublattice.

A characterisation of the disorder within the organic sublattice can be achieved using high resolution solid state \(^1\text{H}\) and \(^{13}\text{C}\) MAS NMR which is very sensitive to the short-range chemical environment defining each atomic species. Fig. 2 shows the \(^1\text{H}\) ultra-fast MAS NMR data \((\upsilon_i = 110 \text{ kHz})\) from the \((\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]\) system presented with the spectral simulation and deconvolution, and the assigned \(^1\text{H}\) chemical shifts representing the aromatic, amine and aliphatic moieties are summarized in Table 1. These data were acquired under fully relaxed conditions thus allowing a quantitative estimate of the \(\text{H}\) speciation. As observed from the \(^1\text{H}\) shift assignments in Table 1, a quantitative simulation of the \(^1\text{H}\) MAS NMR spectrum in Fig. 2 can be preserved only when a distribution of chemical shifts is introduced for the methylene positions 5 and 6. These assignments were corroborated by the 2D heteronuclear and homonuclear MAS NMR data exhibited in Fig. 3. The 2D \(^1\text{H},^{13}\text{C}\) hCH HETCOR data displayed in Fig. 3(a) shows the basic heteronuclear correlations expected for the aromatic, amine and aliphatic species comprising the \(
\text{PEA}^-\) and \(
\text{MA}^+\) cations. However, an expansion of the \(^1\text{H}\) and \(^{13}\text{C}\) aliphatic special regions (see Fig. 3(b)) indicates that the broader \(^1\text{H}\) correlations are associated with both the \(\alpha\text{-CH}_2\) (H position 5) and \(\delta\text{-CH}_2\) (H position 6) clearly span two well-defined \(\text{H}\) chemical environments. As represented in Fig. 2 and 3(b), it can be deduced that positional disorder characterizing the ethylamine side chain distributes the \(\text{H}\) intensity from the \(\alpha\text{-CH}_2\) moiety between H positions 5 and 5'; similarly, the \(^1\text{H}\) intensity from the \(\delta\text{-CH}_2\) moiety is distributed between the H positions 6 and 6'. From the \(^1\text{H}\) chemical shift assignments presented in Table 1, it is inferred that this rationalisation results in a \(
\text{PEA}^-\):\(\text{MA}^+\) cation ratio of \(\sim 2:1\) which is consistent with the nominal \((\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]\) compositional stoichiometry.

The \(^1\text{H}\) ultra-fast MAS NMR data of Fig. 2(a) and S3(a) also indicates the presence of structural \(\text{H}_2\text{O}\) evidenced by the broad upfield resonances at \(\delta \sim 1.4\) ppm. As observed in Fig. 3(a) and (b), the hCH HETCOR data establishes an absence of

### Table 1: Assignments and integrated intensities of the \(^1\text{H}\) MAS NMR data acquired using a MAS frequency of 110 kHz (see Figure 2), presented with the \(^1\text{H}\) \(T_2\) data measured using saturation-recovery technique, and the \(T_2\) data estimated from the FWHM of the assigned \(^1\text{H}\) resonances.

<table>
<thead>
<tr>
<th>Label</th>
<th>Assignment</th>
<th>(^1\text{H}) Chemical Shift (ppm)</th>
<th>Number of Protons</th>
<th>Integrated Intensity ((%))</th>
<th>Theoretical Intensity (%)</th>
<th>(^1\text{H}) (T_1) (s)</th>
<th>FWHM (Hz)</th>
<th>(^1\text{H}) (T_2) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PEA(^+) aromatic</td>
<td>7.7</td>
<td>4</td>
<td>11.9</td>
<td>13.3</td>
<td>2.5±0.3</td>
<td>424±10(^\pm)0.7</td>
<td></td>
</tr>
</tbody>
</table>

This journal is © The Royal Society of Chemistry 20xx
| 2 | PEA⁺ aromatic   | 7.4 | 6     | 20.6 | 20  | 2.6±0.3 | 829±10/~0.4 |
| 3 | PEA⁺ NH₃⁺      | 6.6 | 6     | 20.2 | 20  | 2.4±0.3 | 428±10/~0.7 |
| 4 | MA⁺ NH₃⁺       | 6.3 | 3     | 11.2 | 10  | 2.8±0.3 | 352±10/~0.9 |
| 5,5' | PEA⁺ α-CH₂   | 4.2, 3.6 | 4     | 8.5, 4.4 | 8.4, 4.9⁺ | 2.6±0.4 | 556±10/~0.6 |
| 6,6' | PEA⁺ β-CH₂   | 3.6, 3.1 | 4     | 4.7, 7.6 | 4.9, 8.4⁺ | 2.6±0.4 | 572±10/~0.6 |
| 7 | MA⁺ CH₃      | 3.1 | 3     | 10.9 | 10  | 3.1±0.4 | 329±10/~1.0 |
| 8 | H₂O          | 1.4 | -     | -     | -   | -         | -         |

a) Estimates from the integrated intensities; b) Estimates from the FWHM of each resonance using the equation FWHM=1/(πT²).

Fig. 3 Solid state 2D MAS NMR studies undertaken (ν₀ = 800.16 MHz, νᵢ = 110 kHz) including, (a) the 2D heteronuclear ¹H-¹³C hCH HETCOR data, (b) an expansion of the aliphatic region of the 2D hCH HETCOR data highlighting the positional disorder in the ethylammonium substituent of the PEA⁺ cation, (c) the 2D homonuclear ¹H-¹H DQ/SQ BABA data highlighting through-bond associations, and (d) - (f) the 2D homonuclear ¹H-¹H NOESY data acquired with mixing times of 10, 100 and 300 ms, respectively, disclosing the through-space associations.

connectivity to any aliphatic or aromatic carbon species. Furthermore, the highly shielded (upfield) shift suggests that these H₂O position(s) that are distant from the PEA⁺ or MA⁺ amine cations, thus avoiding H-bonding arrangements that would introduce a deshielded (downfield) ¹H chemical shift. Previous studies have demonstrated that 2D perovskites exhibit a propensity for H₂O absorption.¹,⁸ While the highly shielded ¹H shift shown in Fig. S2(a) and S3(a) suggests that these H₂O molecules reside in the inter-planar spacing between the aromatic rings of the PEA⁺ cations, other positions such as those near the [Pb₂I₇]^{3⁻} framework or within the cubo-octahedral cage accommodating the MA⁺ cation may also be possible.

The positional disorder exhibited by the PEA⁺ cation emanates from different structural conformers associated with the positioning of the ethylamine side-chain, as shown by the 1D ¹H MAS NMR and 2D ¹H-¹³C hCH HETCOR data (see Fig. 2(a), and 3(a) and (b), respectively). These conformers differ markedly in
the proximity of the amine functionality with respect to the aromatic ring. PEA+ conformer 1 positions the amine functionality at a maximum distance away from the aromatic ring, while PEA+ conformer 2 suggests that the aliphatic side-chain and amine moiety wrap back towards the aromatic ring introducing much closer contact. Direct evidence for this conformational isomerism is provided by both the 2D homonuclear $^1$H-$^1$H double quantum/single quantum (DQ/SQ) BAck-tO-BAck (BABA) and 2D homonuclear $^1$H-$^1$H NOESY experiments.43,44

The former experiment provides short-range information that relies on the selection of DQ dipolar coherence. As depicted in Fig. 3(c), the 2D $^1$H-$^1$H BABA data show correlations (highlighted in red) that emphasize the expected short range correlations that are fundamental to the structure of the PEA+ and MA+ cations; however, this data also reveals evidence for the occurrence of conformer 2 with a short range aromatic-CH$_3$+($\text{PEA}$) correlation between the $^1$H shifts at $\delta$ 7.6 ppm and $\delta$ 6.6 ppm.

In contrast, the 2D homonuclear $^1$H-$^1$H NOESY data of Fig. 3(d)-(f) are sensitive to longer range dipolar through-space interactions between nuclear spins. The spatial sensitivity limits of the NOESY technique are ~2 - 3 times that of the BABA experiment with the NOESY experiment able to detect correlated dipolar interactions out to ~6 Å,45,46 thus making it a powerful complement to the BABA approach. Due to its elongated arrangement of the pendant ethylamine sidechain into the free volume towards the 2D perovskite surface bisecting the Pb$_6$ octahedra, the PEA-NH$_3^+$ moiety of conformer 1 is unlikely to experience a significant homonuclear $^1$H-$^1$H dipolar interaction with the phenyl group anchoring the molecule. Although not measured in the 2D $^1$H-$^1$H NOESY data utilizing a short 10 ms mixing time (see Fig. 3(f)), experiments employing longer mixing times of 100 and 300 ms detect weak–moderately strong intermolecular off-diagonal correlations between the PEA-NH$_3^+$ moiety ($\delta$ 6.6 ppm) of conformer 1 and the CH$_3$+ group of MA+ ($\delta$ 3.1 ppm) in the next-nearest-neighbor cuboctahedral cavity (see the data in Fig. 3(e) and (f), respectively). Such a spatial relationship must be confined to be within the ~6 Å detection limit of this experiment. This scenario differs markedly from the evidence supporting the local structure of PEA conformer 2 where intense intramolecular off-diagonal correlations are exhibited in the 2D $^1$H-$^1$H NOESY data of 3s 2(d)-(f) relating the chemical shifts of the aromatic protons ($\delta$ 7.6 ppm) with the PEA-NH$_3^+$ moiety ($\delta$ 6.6 ppm) for mixing times as short as 10 ms. These observations emphasizes the strong homonuclear $^1$H-$^1$H dipolar interaction between these proton species, and corroborates the 2D $^1$H-$^1$H BABA data above (see Fig. 3(c)). These findings contrast with those from low field (2.35 T)/broadline $^1$H $T_1$ relaxation measurements and mid-field ($^9$H T)/$T_1$ relaxation measurements on the more ordered (PEA)$_2$[Pbl$_4$] system which highlight no detectable disorder in the NH$_3^+$ position of the PEA+ cation.47,48

The structural disorder based solely around discrete PEA+ conformers outlined above is only a simplistic representation of the total disorder (and disruption to the H-bonding network) characterizing the PEA+ cations in the organic sublattice. As illustrated in Fig. S3(a) and (b), realistic descriptions must accommodate more complex arrangements such as in-plane and out-of-plane conformers, head-head and head-tail stacking, and orientational stacking faults that are underpinned by the basic PEA+ cation conformers proposed above. The breadth of this phase transition suggests that it is comprised of thermal re-ordering processes within a highly disordered network comprised of distributions of these structural realizations within the PEA+ cation network. This is supported by the $^1$H $T_2$ values provided in Table 1 which are 3 - 4 orders of magnitude shorter than the corresponding $T_1$ values, thus suggesting that the correlation times of reorientation are slow. As shown in Fig. S4(b) for a dominant dipolar relaxation mechanism, the divergent $T_1$ and $T_2$ values are characteristic of correlation times that are on the slow motion side of the extreme narrowing limit in a regime normally associated with polymers and macromolecules. The disordered PEA+ cations in the 2D channels form a highly occluded network lacking cooperative modes of fast motion. Furthermore, the broad 1D $^1$H MAS NMR resonances of Fig. 2(a) and 2D $^1$H-$^1$H MAS NMR contours observed within Fig. 3(c)-(d) are influenced by widespread chemical shift dispersion. It is important to note that, although these measurements are performed under ultra-fast MAS conditions ($\nu$ = 110 kHz), this dispersion is unable to be averaged (and resonances further narrowed) by these ultra-fast MAS frequencies. The extent of the disorder represented in the $^1$H MAS NMR data, coupled with the very broad second-order phase transition characteristics identified in the DSC data, are consistent with the XRD results which are limited to the location of the inorganic framework positions only.

Optical Properties

An exfoliated (PEA)$_2$[MA][Pbl$_4$] sample exhibits strong excitonic photoluminescence and absorbance at room temperature due to intrinsic crystallographic quantum confinement (see Fig. 4(a)).49,50 The optical images are presented as supplementary information in Fig. S5. The photoluminescence (PL) data in Fig.s S6(a)-(c) were simulated using asymmetric pseudo-Voigt peaks which accounted for both homogeneous and inhomogeneous broadening,51 while Fig. S6(d)-(f) shows that the evolution of the excitonic absorption edge was monitored by applying a linear fit to the lower energy slope of the optical absorbance (OA) spectra.

As observed in Fig.4 and S7, the PL and the OA exhibit no abrupt intensity or frequency changes during cooling above 200 K apart from the gradual narrowing of the full-width-at-half-maximum (FWHM) which is ascribed to phonon population depletion. The excitonic absorption energy is almost unchanged during cooling from the gradual narrowing of the full-width-at-half-maximum (FWHM) which is ascribed to phonon population depletion. The excitonic absorption energy is almost unchanged during cooling from room temperature before a distinct blueshift of ~5 meV below 200 K , and it shows continuous redshift below 150 K (see Fig. 4(b) and S7(a)). An earlier study of (PEA)$_2$[MA][Pbl$_4$] reported a small continuous red shift in absorption between 10
- 293 K with absorption peak asymmetry providing inconclusive evidence of a phase transition.\textsuperscript{37,52} The integrated PL intensity exhibited in Fig. 4(d) generally increases during cooling with a discontinuity at \textasciitilde200 K appearing concomitantly with the excitonic anomaly. A similar evolution of the optical properties was observed under decreasing and increasing temperature regimes (see Fig. 4 and S7, respectively). The combined data provided by the differential scanning calorimetry (DSC) results of Fig. 4c and the optical spectroscopy provides corroborating evidence of a very broad and diffuse second-order phase transition phenomenon extending over the 150 - 200 K range.

Photoluminescence decreases with heating due to thermal quenching,\textsuperscript{18,53} whereby the integrated PL intensity conforms to:\textsuperscript{29,54}

\[ \text{I} = \frac{\text{I}_0}{1 + \alpha e^{-\frac{E_0}{kT}}} \quad (1) \]

where \( \text{I}_0 \) is PL intensity at 0 K, \( E_0 \) is the activation energy and \( \alpha \) is a ratio of radiative and non-radiative lifetimes at 0 K. The fitting of the logarithmic integrated PL intensity vs inverse temperature is shown in Fig. 4(d). The activation energy of 250(40) meV measured from the room temperature phase was much larger than the value of 125(10) meV elucidated from the low temperature polymorph. This latter energy value is significantly smaller than reported exciton binding energy value of 170 meV.\textsuperscript{52} These results, together with the significant reduction in PL intensity at 200 K, suggests that the transformation into the low temperature phase introduces non-radiative pathways through the formation of longer-lived defect structures via reduced I\textsuperscript{–} and Pb\textsuperscript{2+} migration throughout the framework.\textsuperscript{29,43} Both Pb\textsuperscript{2+} and (in particular) I\textsuperscript{–} defects can be associated with stacking faults influencing some elements of the PEA\textsuperscript{+} cation disorder in the 2D channels, and also introduces distributions within the shape, size and tilting of the cuboctahedral cavity thus affecting the MA\textsuperscript{+} dynamics. These assertions corroborate the findings of the \textsuperscript{1}H MAS NMR study and shape the structure/function relationship of the material. At lower extremes of the phase transition (~150 K), reduced ionic migration at throughout the inorganic [Pb\textsubscript{2}I\textsubscript{7}\textsuperscript{3–}] framework is directly associated with attenuated rotational modes and slower motional dynamics throughout the disordered organic sublattice.
PL intensity is proportional to excitation intensity with a power law coefficient \( k \), \( I(PL) \sim P^k \), where the coefficient \( k = 1 \) describes free exciton recombination, \( k = 1.5 \) describes trapped exciton recombination, and \( k = 2 \) relates to bimolecular free carrier recombination.\(^{55,56}\) Therefore, defect-related recombination pathways can be examined using excitation intensity dependent experiments. Fig. 4(e) shows the log-log graphs of integrated PL intensity of \((\text{PEA})_2(\text{MA})[\text{PbI}_7]\) with excitation power having slopes of 1.5 at room temperature, consistent with non-radiative defects, and 1 at low temperature, suggesting an absence of defects. However, it is noted that defects may not be activated at 80 K.

**Methylammonium Dynamics**

![Raman data](image)

Fig. 5 Raman data from the \((\text{PEA})_2(\text{MA})[\text{PbI}_7]\) system showing, (a) the high wavenumber spectra measured over the temperature range of 78 - 293 K, and (b) a schematic depiction of the assignments of the MA\(^+\) vibrational modes. In (a) the MA\(^+\) modes are highlighted and the red points indicate the onset of the broad phase transition phenomenon. (c) Raman data from the \((\text{PEA})_2(\text{MA})[\text{PbI}_7]\) system showing ultra-low wavenumber spectra measured over the temperature range of 78 - 293 K.

To further investigate the structural evolution of the \((\text{PEA})_2(\text{MA})[\text{PbI}_7]\) system, a temperature dependent Raman spectroscopic study was undertaken. These results are shown in Fig. 5 and 6. The larger wavenumber bands can be attributed to molecular vibrations of the PEA\(^+\) and MA\(^+\) cations, while the smaller wavenumbers emanate from the inorganic sublattice as reported for the MAPbBr\(_3\) and MAPbI\(_3\) systems.\(^{10,31}\) This interpretation was supported by direct comparison with the Raman data from the \((\text{PEA})_2[\text{PbI}_4]\) and \((\text{PEA})_2(\text{MA})[\text{PbI}_7]\) systems (see Fig. 5a and S8) that allows the unambiguous assignment of MA\(^+\) bands (910 (\(\rho\) MA), 970 (\(\nu\) C-N), 1247 (\(\rho\) MA),1478 cm\(^{-1}\) (\(\delta\) NH\(_3^+\))) with the remainder contributed by the PEA\(^+\) cation. The vibrational modes are illustrated in Fig. 5(b). Over the 78 - 293 K temperature range neither the PEA\(^+\) nor \(\nu\) C-N MA\(^+\) bands split or change intensity, in contrast to the NH\(_3^+\) vibrations. The relative intensity of the 910 cm\(^{-1}\) (\(\rho\) MA\(^+\)) band increases continuously below ~200 K, while the intensity of the bands at 1247 cm\(^{-1}\) (\(\rho\) MA\(^+\)) and 1478 cm\(^{-1}\) (\(\delta\) NH\(_3^+\)) increase below ~200 K (see Fig. 5). It is important to note that the C-N bond stretching frequency and intensity do not undergo any changes with temperature, confirming that only one end (rather than both ends) of the MA\(^+\) cation is involved in the phase transition. Thus, spectral changes involving the NH\(_3^+\) bending or rocking vibrations demonstrate that the phase transition is strongly associated with the NH\(_3^+\) moiety and its participation within the hydrogen bonding network.

As shown in Fig. 5(c), further evidence of a low temperature dimorph of \((\text{PEA})_2(\text{MA})[\text{PbI}_7]\) is observed by low wavenumber Raman spectroscopy. It is notable that distinct bands below <150 cm\(^{-1}\) persist even at room temperature as the PEA\(^+\) cations are relatively static and do not participate in large amplitude vibrations. This observation is consistent with the \(^1\)H MAS NMR study that is characterized by broad resonance linewidths and short \(T_2\)s from slower motional correlation times and occluded structural disorder. Furthermore, this feature is in sharp
contrast to that observed in 3D perovskites which only exhibit broad Raman bands due to dynamic MA⁺ and FA⁺ disorder,10,31,57 emphasizing that the presence of the PEA⁺ cations induces a more rigid inorganic sublattice with distinct low wavenumber Raman bands. The bands below ~30 cm⁻¹ are attributed to PbI₂ tilting modes, those below 80 cm⁻¹ are assigned to 1-Pb-I bending modes, the peaks between 80-150 cm⁻¹ and 150 cm⁻¹ are assigned to Pb-I stretches, while those bands <50 cm⁻¹ cannot be assigned unique Raman modes. Nevertheless, temperature dependent features are evident in Fig. 5(c). For instance, the feature at ~30 cm⁻¹ is distinct only after cooling, while the mode at 100 cm⁻¹, assigned to Pb-I stretching in the PbI₂ octahedron, develops a splitting. This phenomenon is caused by octahedral distortion resulting in the improved peak resolution due to theformation of a more ordered and rigid structure; this assertion is supported by increased hydrogen bonding at low temperatures.58 These temperature dependent features in the variable temperature Raman data of Fig. 5(c) infer a discontinuous evolution of crystal structure at around 200 K that is consistent with the other evidence of the ill-defined phase transition.

The ¹H MAS NMR data presented in Table 1 corroborates the Raman findings reported above. As shown in Fig. S9, the octahedral tilting induces a reduction in the 1-Pb-I angle (labelled α) to ~155°; this represents a substantial distortion from 179° measured from the MAPbI₃ structure at room temperature.59 This octahedral tilt distorts the bond lengths, bond angles and shape of the cuboctahedral cavities accommodating the MA⁺ cations. The volume of the cavity, containing MA⁺ cations, decreases from ~80Å³ in tetragonal phase of the 3D MAPbI₃ to ~50Å³ in (PEA)₂(MA)(PbI₃) (Fig. S10). In this case the degrees of freedom available for the MA⁺ cation motion become restricted, thus resulting in altered MA⁺ dynamics in comparison to MAPbI₃. The MA⁺ cation dynamics in MAPbI₃ at room temperature has been shown to undergo ultrafast reorientation using quasi elastic neutron scattering, GHz spectroscopy, ¹H NMR and electron diffraction, with the summarized results of Table 1 and Fig. 6 describing significantly shorter values falling within a narrow range of ~2.4 - 3.1 s.

The optical and Raman spectroscopic results consistently demonstrate a broad phase change commencing at 200 K which is attributed to MA⁺ dynamics and its hydrogen bonding state. In particular, the Raman study provides unambiguous evidence that part of the evolution of the organic sublattice with temperature involves the vibrations of the NH₃⁺ constituent of the MA⁺ cation. These spectral changes are manifested from MA⁺ ordering through hydrogen bonding that promotes harmonic vibrations and a more rigid structure, thus yielding more intense and narrower bands as demonstrated from previous studies for 3D perovskites MAPbX₃ (X = Br, I).10,31,43,67 Verthelye, the ¹H MAS NMR study indicates that the timescale of MA⁺ motion in (PEA)₂(MA)(PbI₃) is much slower than that in MAPbI₃ by approximately four orders of magnitude; as outlined above, this is governed by distortion of the cuboctahedral cavities. In contrast, the PEA⁺ component of the organic sublattice also contributes to the broad phase change behavior through different thermally driven mechanisms of reorientation. It represents a connected organic network of highly occluded and disordered cations that also participates in
slow molecular reorientation and is also underpinned by the $^1$H MAS NMR data. The contrasting influences dominating the different parts of the organic sublattice suggest that the observed broad phase transition of Fig. 4(b) is highly inhomogeneous, and the overall thermal response probably represents a superposition of discrete thermal rearrangement processes pertaining to the MA$^+$ and PEA$^+$ cations.

Previous single crystal X-ray diffraction measurements on the (PEA)$_2$[MA][Pb$_2$I$_7$] system and those undertaken within this study, have been unable to elucidate a structural determination of the complete system. While longer-range periodic elements defining the inorganic [Pb$_2$I$_7$]$^{2-}$ framework can be determined, the short-range structural detail yielding the exact coordinates of the MA$^+$ or PEA$^+$ cations is hindered by the structural disorder within the organic sublattice, as demonstrated by the solid state NMR technique. This precludes a measure of the hydrogen-bonding lengths influencing the MA$^+$ cations and further corroboration of the effects observed in the Raman data. A full DFT computational analysis of the statistical distributions of structural realisations generated to simulate the disorder within the organic sublattice is being undertaken to support the spectroscopic and thermal response observations reported for the first time.

Conclusions

In this work, the significant structural disorder characterizing the MA$^+$ and PEA$^+$ cations constituting the organic sublattice within the 2D (n = 2) (PEA)$_2$[MA][Pb$_2$I$_7$] system as reported by the $^1$H and $^{13}$C MAS NMR technique has been presented with photophysical and Raman spectroscopic studies characterizing this material. The structural disorder described in this work represents the first rationalization of disorder for 2D hybrid perovskites, and it corroborates the partial structural solution (inorganic framework only) obtained by single crystal X-ray diffraction and the very broad phase transition as exhibited by the DSC data. The phase transition observed to occur over a 200 - 150 K temperature range is probably an inhomogeneous process involving the rearrangement of both the MA$^+$ and PEA$^+$ cations in discrete thermally driven processes. While the $^1$H MAS NMR data demonstrates that the MA$^+$ dynamics in 2D (PEA)$_2$[MA][Pb$_2$I$_7$] is slow in comparison to its 3D MAPbI$_3$ counterpart (by approximately four orders of magnitude), the Raman study shows that the MA$^+$ hydrogen bonding network is strengthened over this temperature range. The importance of MA$^+$ dynamics over this temperature range on the changing photophysical and optical properties was also emphasized for this 2D perovskite system. In addition, the $^1$H MAS NMR data determines that the PEA$^+$ cations are also in a slow motional regime, and the structural disorder comprised of conformational isomers and stacking and orientational dislocations produce a highly occluded network down the 2D channels that also structurally readjusts over this temperature range. Furthermore, the ability for these 2D channel structures to absorb water was observed, thus potentially augmenting the disorder phenomenon throughout the PEA$^+$ cation network.

Author Contributions

We strongly encourage authors to include author contributions and recommend using CRediT for standardised contribution descriptions. Please refer to our general author guidelines for more information about authorship.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge Ministry of Education of Singapore for the funding of this research through the following grants, AcRF Tier 1 (Reference No: RG195/17 and RG156/19); AcRF Tier 3 (MOE2016-T3-1-006 (S)). JVH and ZXS also acknowledges the Centre of High Field NMR Spectroscopy and Imaging, and the Facility for Analysis, Characterization, Testing and Simulation (FACTS) at NTU, Singapore, for access to their solid state NMR, electron microscopy and X-ray diffraction facilities.

Notes and references

Optical properties of the quasi-2D perovskite are related to the significant structural disorder involving both the MA$^+$ and PEA$^+$ cations.
Supplementary Information

The Effect of Organic Cation Dynamics on the Optical Properties in \((\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]\) Perovskite Dimorphs

Yulia Lekina,\textsuperscript{a,b} Sai S.H. Dintakurti,\textsuperscript{c,d} Benny Febriansyah,\textsuperscript{*} D.J. Bradley,\textsuperscript{d} Jiaxu Yan,\textsuperscript{4} Xiangyan Shi,\textsuperscript{b} Jason England,\textsuperscript{e} Tim White,\textsuperscript{8} John V. Hanna,\textsuperscript{*d,g} Ze Xiang Shen\textsuperscript{*a,b}

Figure S1. Powder XRD data of the horizontally oriented PEA\textsubscript{2}MAPb\textsubscript{2}I\textsubscript{7} platelets.

\textsuperscript{a} Centre for Disruptive Photonic Technologies, Nanyang Technological University, 637371, Singapore.
\textsuperscript{b} Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore.
\textsuperscript{c} Interdisciplinary Graduate School (IGS), Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
\textsuperscript{d} Department of Physics, University of Warwick, Gibbet Hill Rd., Coventry CV4 7AL, UK
\textsuperscript{e} Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore.
\textsuperscript{f} Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (Nanjing Tech), Nanjing 211816, China.
\textsuperscript{g} School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
Figure S2. Structure \((\text{PEA})_2(\text{MA})\text{[Pb}_2\text{I}_7]\) obtained by single crystal X-Ray analysis and unit cell parameters. Only coordinates of inorganic atoms were determined.

Table S1. Refined positions and equivalent isotropic atomic displacement parameters obtained from best fit single crystal structural model.

<table>
<thead>
<tr>
<th>Atom site</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq} (\text{Å}^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB1</td>
<td>0.29527(9)</td>
<td>0.77484(9)</td>
<td>0.14482(4)</td>
<td>0.0336(3)</td>
</tr>
<tr>
<td>PB2</td>
<td>0.79762(9)</td>
<td>0.27700(9)</td>
<td>0.14486(4)</td>
<td>0.0334(3)</td>
</tr>
<tr>
<td>I3</td>
<td>0.4915(2)</td>
<td>0.0771(2)</td>
<td>0.14074(9)</td>
<td>0.0526(5)</td>
</tr>
<tr>
<td>I4</td>
<td>-0.0076(2)</td>
<td>0.9730(2)</td>
<td>0.14142(9)</td>
<td>0.0549(5)</td>
</tr>
<tr>
<td>I5</td>
<td>0.0991(2)</td>
<td>0.4709(2)</td>
<td>0.14172(10)</td>
<td>0.0616(5)</td>
</tr>
<tr>
<td>I6</td>
<td>0.5973(2)</td>
<td>0.5774(2)</td>
<td>0.14138(9)</td>
<td>0.0551(5)</td>
</tr>
<tr>
<td>I7</td>
<td>0.2496(2)</td>
<td>0.7522(2)</td>
<td>0.00021(7)</td>
<td>0.0566(5)</td>
</tr>
<tr>
<td>I8</td>
<td>0.3507(3)</td>
<td>0.8041(3)</td>
<td>0.28379(9)</td>
<td>0.0626(5)</td>
</tr>
<tr>
<td>I9</td>
<td>0.8403(3)</td>
<td>0.2885(3)</td>
<td>0.28374(9)</td>
<td>0.0622(5)</td>
</tr>
</tbody>
</table>
Figure S3. Schematic representations of the structural disorder in the organic sublattice as incurred (a) by the PEA$^+$ cations in the 2D interlayer channels, and (b) by the MA$^+$ cations in the octahedral cavities.
Figure S4. Additional $^1$H MAS NMR characterisation of the (PEA)$_2$(MA)[Pb$_2$I$_7$] system showing, (a) spectral evidence for H$_2$O absorption (H$_2$O resonance marked with an asterisk, $\nu_0 = 800.16$ MHz, $\nu_r = 35$ kHz) commensurate with increasing times of atmospheric exposure, and (b) mapping of the motional regime of the PEA$^+$ and MA$^+$ cations according the relationship between the $^1$H $T_1$ and $T_2$ relaxation times.
Figure S5. Optical images of the exfoliated crystal a) in transmission light, b) in reflected light.

Figure S6. Fitting of PL spectra of (PEA)$_2$(MA)[Pb$_2$I$_7$] using one Pseudo-Voight component.
Figure S7. Temperature dependent (heating from 80K to 300 K) PL response under 457 nm excitation showing, (a) PL peak position vs temperature, (b) dependence of integrated PL intensity (logarithmic scale) vs 1/T and the fit of these data using \( I = \frac{I_0}{1 + \exp\left(-\frac{E_a}{kT}\right)} \), (c) excitation intensity dependence of integrated PL intensity (bilogarithmic scale) vs laser power (green points correspond to RT measurements, brown points represent the main component, blue points represent an additional component at low temperature), (d) integrated PL intensity vs 1/T under 457 nm excitation (cooling from 300 to 80K) where a fit of the whole range is presented, (e) full-width-half-maximum (FWHM) of the PL data from the (PEA)$_2$(MA)[Pb$_2$I$_7$] systems as a function of temperature.
Figure S8. Raman data from (PEA)$_2$[Pbl$_4$] ($n = 1$) hybrid perovskite system at 80 K (bottom), and the (PEA)$_2$(MA)[Pb$_2$I$_7$] ($n = 2$) system at room temperature and at 80 K. The (PEA)$_2$[Pbl$_4$] spectrum is shown for comparison as the framework charge is balanced by PEA$^+$ cations only. This provides clear evidence that the highlighted peaks appearing in the (PEA)$_2$(MA)[Pb$_2$I$_7$] ($n = 2$) spectrum yet absent from the (PEA)$_2$[Pbl$_4$] ($n = 1$) spectrum correspond to MA$^+$ modes. From these data, only the peaks assigned to MA$^+$ cation vibrations exhibit a strong temperature dependence.

Figure S9. Representations of the inorganic sublattices in 3D (P4mm) and 2D (P1) perovskites.
Figure S10. The MA$^+$ cavities is a) MAPbI$_3$ in the tetragonal phase at room temperature (volume = 78.5 Å$^3$), b) in (PEA)$_2$(MA)[Pb$_2$I$_7$] at room temperature (volume = 59.1 Å$^3$). The voids are calculated by means of Mercury software with the following parameters: Probe Radius = 1.8 (MA$^+$ ionic radius), Grid Spacing = 0.7.