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**Structural diversity in layered hybrid perovskites, A_2PbBr_4
or $AA'PbBr_4$, templated by small disc-shaped amines**

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4 **Structural diversity in layered hybrid perovskites, A_2PbBr_4 or $AA'PbBr_4$,**
5 **templated by small disc-shaped amines**
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24 **Abstract**
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27 We present three new hybrid layered lead(II) bromide perovskites of generic composition
28 A_2PbBr_4 or $AA'PbBr_4$, which exhibit three distinct structure types. $[TzH]_2PbBr_4$, ($[TzH^+]$
29 = 1,2,4-triazolium), adopts a (001)-oriented layer structure, $[AaH]_2PbBr_4$, ($[AaH^+]$ =
30 acetamidinium), adopts a (110)-oriented type, whereas $[ImH][TzH]PbBr_4$, ($[ImH^+]$ =
31 imidazolium), adopts a rare (110)-oriented structure with enhanced corrugation (*i.e.* ‘3 ×
32 3’ type). The crystal structures of each are discussed in terms of the differing nature of
33 the templating molecular species. Photoluminescent spectra for each are reported and the
34 behaviours discussed in relation to the different structure of each composition.
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41 **Introduction**
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44 The promising photophysical properties and enormous chemical and structural diversity shown
45 by lead(II) halide perovskites (LHPs) has led to a considerable amount of exploratory synthetic
46 work in this field.^{1,2} Amongst these, lower dimensional layered perovskites can be imagined as
47 structural derivatives of the ABX_3 composition aristotype cubic perovskite structure, formed
48 by slicing along specific crystallographic directions, and inserting additional moieties between
49 these layers. Thus, the (001)-oriented perovskites can be regarded as derived from ‘slicing’
50 along the (001) planes of the parent perovskite structure as shown in Figure 1a, resulting in
51 ‘*trans*’ ligands of the octahedral framework being terminal. The (001)-oriented layered
52 perovskites are evidently particularly tolerant not only to inorganic but also organic *inter-layer*
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components, producing a great diversity of compositional and structural variants. A related series of layered structure types, the (110)-oriented layered perovskites, can be regarded as derived from the parent ABX_3 perovskite by slicing along (110) planes, resulting in ‘*cis*’ ligands of the octahedral framework being terminal. Depending on the degree of ‘corrugation’ which occurs within the layers, these structures can be described as 2×2 , 3×3 *etc.*, as shown in Figure 1b.³

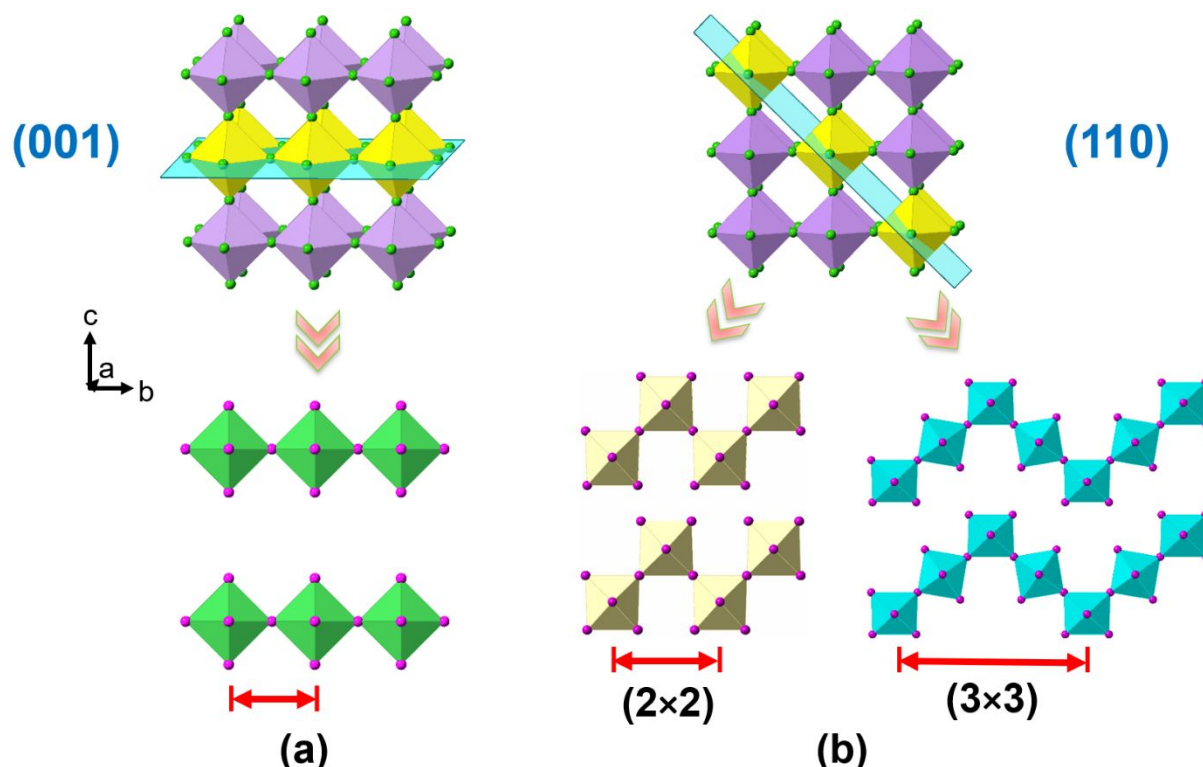


Figure 1. Schematic dimensional reduction of parent cubic perovskite to (a) (001)-oriented and (b) (110)-oriented layered perovskites.

A further degree of variability, common to each of these generic families, is that it is feasible to incorporate either one or two distinct cations in the *inter*-layer region, leading to generic compositions ABX_4 or $AA'BX_4$ (in the case of a single octahedral layer). Manipulations at the A and A' sites can obviously lead to consequent modifications to the arrangement of the perovskite-like layers themselves, thus helping to tailor the resultant physical properties. In the case of the (001)-oriented layers and in the field of purely inorganic perovskites, the two generic families are the well-known Dion-Jacobson (DJ)⁴ and Ruddlesden-Popper (RP)⁵ series, having stoichiometries ABX_4 and $AA'BX_4$, respectively for examples with single octahedral layers. The corresponding inorganic-only (110)-oriented phases are much less common.⁶ Indeed, the same can be said of the corresponding LHPs, where there are now countless examples of the (001)-type,² but still only a handful of the various (110)-types.^{2,7-9} In the case

of LHPs, the ABX_4 variant must contain a single divalent organo-cation, whereas the $AA'BX_4$ analogue will contain two (same or distinct) monovalent organic cations.⁷

In our previous work,⁷ we reported two examples of the latter series, *i.e.* the 2×2 (110)-oriented structure type. We specifically chose two similarly sized, 'disc-shaped' mono-protonated amines, in order to explore structure-directing effects, based on both size and H-bonding preferences, to produce $[ImH][GuH]PbBr_4$ ("IGPbBr₄") and $[TzH][GuH]PbBr_4$ ("TGPbBr₄"); $[ImH^+] =$ imidazolium, $[TzH^+] =$ 1,2,4-triazolium, $[GuH^+] =$ guanidinium). In the present work, we present another three new $AA'BX_4$ type LHPs: $[TzH]_2PbBr_4$ ("T₂PbBr₄"), $[AaH]_2PbBr_4$ ("A₂PbBr₄"; $[AaH^+] =$ acetamidinium), and $[ImH][TzH]PbBr_4$ ("ITPbBr₄"). Interestingly, they adopt three different structure types, *viz.* (001) for T₂PbBr₄, 2×2 (110) for A₂PbBr₄, and 3×3 (110) for ITPbBr₄. The crystal structures are discussed in detail in order to inform future considerations of the 'designability' of these various structure types.

Experimental Section

Synthesis

1,2,4-triazole (C₂H₃N₃, 99%), acetamide hydrochloride, (C₂H₆N₂·HCl, 97%), imidazole (C₃H₄N₂, 99%), lead (II) bromide (PbBr₂, ≥98%) and hydrobromic acid (HBr, 48%, w/w aqueous solution), were purchased from Alfa Aesar. Diethyl ether ((C₂H₅)₂O, 99.5%) was purchased from Sigma Aldrich. All chemicals were directly used without further purification.

The title compounds, T₂PbBr₄, A₂PbBr₄ and ITPbBr₄ were crystallized by a slow evaporation method.

T₂PbBr₄ (C₄H₈N₆PbBr₄), 1,2,4-triazole (276 mg, 4 mmol) and PbBr₂ (734 mg, 2 mmol) were dissolved in conc. HBr (3 mL) with moderate heating. By cooling for a few hours, bright yellow, plate-shaped crystals were obtained. These crystals were filtered and washed with diethyl ether (yield 48% based on PbBr₂). Elemental analysis: (Anal. Calc. (%) for T₂PbBr₄: C, 7.20; H, 1.21; N, 12.60. Found: C, 7.37; H, 1.15; N, 12.53).

A₂PbBr₄ (C₄H₁₄N₄PbBr₄), Acetamide hydrochloride (1890 mg, 20 mmol) and PbBr₂ (734 mg, 2 mmol) were dissolved in conc. HBr (6 mL) with moderate heating. By cooling for a few hours, colorless, plate-shaped crystals were obtained. These crystals were filtered and washed with diethyl ether (yield 41% based on PbBr₂). Elemental analysis: (Anal. Calc. (%) for A₂PbBr₄: C, 7.45; H, 2.19; N, 8.69. Found: C, 7.53; H, 2.11; N, 8.73).

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3 **ITPbBr₄ (C₅H₉N₅PbBr₄)**, imidazole (136 mg, 2 mmol), 1,2,4-triazole (138 mg, 2 mmol) and
4 PbBr₂ (734 mg, 2 mmol) were dissolved in conc. HBr (4 mL) with moderate heating. By
5 cooling for a few hours, pale yellow, needle-shaped crystals were obtained. These crystals were
6 filtered and washed with diethyl ether (yield 40% based on PbBr₂). Elemental analysis: (Anal.
7 Calc. (%) for ITPbBr₄: C, 9.02; H, 1.36; N, 10.52. Found: C, 8.94; H, 1.22; N, 10.54).
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14 **Characterization**

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17 Single crystal X-ray diffraction data were collected at 173 K and 298 K on a Rigaku SCX Mini
18 diffractometer using Mo-K_α radiation. Data were collected using CrystalClear (Rigaku)
19 software.¹⁰ Structures were solved by direct methods using SHELXT,¹¹ and full-matrix least-
20 squares refinements on F² were carried out using SHELXL-2018/3¹¹ incorporated in the
21 WinGX program.¹² Absorption corrections were performed empirically from equivalent
22 reflections on the basis of multi-scans by using CrystalClear.¹⁰ Non-H atoms were refined
23 anisotropically and hydrogen atoms were treated as riding atoms. Powder X-ray diffraction data
24 were collected on a PANalytical EMPYREAN diffractometer using Cu K_{α1} (λ = 1.5406 Å)
25 radiation in the range of 3 to 70° to confirm the purity of each sample. Ambient temperature
26 solid UV-Vis absorbance spectra of powder T₂PbBr₄, A₂PbBr₄ and ITPbBr₄ were collected on
27 a JASCO-V550 ultraviolet–visible spectrophotometer with the wavelength range at 200 nm to
28 900 nm. Temperature dependent steady-state PL measurements were carried out on powdered
29 pellet samples of T₂PbBr₄, ITPbBr₄ and A₂PbBr₄ using a home-built setup, that is described in
30 more detail elsewhere.¹³ In brief, the pellets were placed in a continuous flow cryostat (Oxford
31 Instruments, Optistat CF) connected to a temperature controller (Oxford Instruments ITC503S)
32 and the sample was excited with a pulsed 337 nm nitrogen laser (LTB MNL 100). The PL-
33 signal was detected by a spectrograph (Andor Shamrock SR3030i) coupled to a CCD-camera
34 (Andor iDus420a-OE). For PLQY measurements, we used the method described by de Mello
35 *et al.*¹⁴ The samples were excited using a 375 nm diode laser by PicoQuant and the spectra
36 were recorded with a CCD-camera (Andor DU420A-OE).
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54 **Results and Discussion**

57 **Crystal Structures**

The single crystal X-ray structures suggest no phase transitions in the regime $173 < T < 298$ K, so the crystallographic details will be discussed based on the structures at 298 K. Details of the structures at 173 K are provided in ESI. Crystallographic parameters for all three structures at 298 K are given in Table 1.

Table 1. Crystal and Structure Refinement Data at 298 K

	T₂PbBr₄	A₂PbBr₄	ITPbBr₄
Formula	C ₄ H ₈ N ₆ PbBr ₄	C ₄ H ₁₄ N ₄ PbBr ₄	C ₅ H ₉ N ₅ PbBr ₄
Formula weight	666.99	645.02	666.00
Colour/Habit	Yellow/Block	Colorless/Block	Colorless/Prism
Crystal size (mm³)	0.23 × 0.17 × 0.09	0.22 × 0.18 × 0.13	0.21 × 0.12 × 0.11
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>P2₁/c</i>	<i>Pbcm</i>
<i>a</i> (Å)	11.9243(9)	12.6949(9)	6.0154(5)
<i>b</i> (Å)	11.9327(9)	9.2998(7)	25.873(2)
<i>c</i> (Å)	19.3394(15)	12.2739(7)	18.9242(17)
α (°)	90	90	90
β (°)	95.212(6)	90.996(6)	90
γ (°)	90	90	90
<i>V</i> (Å³)	2740.4(4)	1448.84(18)	2945.3(4)
<i>Z</i>	8	4	8
ρ_{calc} (g/cm³)	3.233	2.957	3.004
μ (mm⁻¹)	23.958	22.648	22.289
F(000)	2368	1152	2368
Reflns collected	11310	14371	23202
Independent reflns	2394	3294	2664
Goodness of Fit	[R(int) = 0.0545]	[R(int) = 0.0478]	[R(int) = 0.0834]
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	R ₁ = 0.0245 wR ₂ = 0.0538	R ₁ = 0.0233 wR ₂ = 0.0459	R ₁ = 0.0259 wR ₂ = 0.0537
Largest diff. peak/hole (e Å⁻³)	1.504/-1.513	0.956/-1.224	1.028/-1.656

T₂PbBr₄

T₂PbBr₄ crystallises in a (001)-oriented structure type (Figure 2). Whilst octahedral tilting occurs within each [PbBr₄]_∞ layer, adjacent octahedral layers occur in an almost ‘eclipsed’ conformation relative to each other, which resembles the DJ rather than the RP family, despite the A₂BX₄ stoichiometry. We note that there is currently controversy regarding the naming of families of layered hybrid perovskites in relation to structural and compositional features¹⁵

though in terms of describing and comparing structural distortions within the inorganic layers in these materials, such comparisons can be helpful. Although the original naming of the RP and DJ phases referred to compositional differences, $A_2'A_{n-1}B_nO_{3n+1}$ and $A'A_{n-1}B_nO_{3n+1}$, respectively, a more useful distinction in the context of LHPs regards the nature and degree of ‘staggering’ of adjacent perovskite-like octahedral layers. Here, we choose to describe the present structure as related to the DJ family, despite the compositional resemblance to the RP family, as the octahedral layers are almost eclipsed.

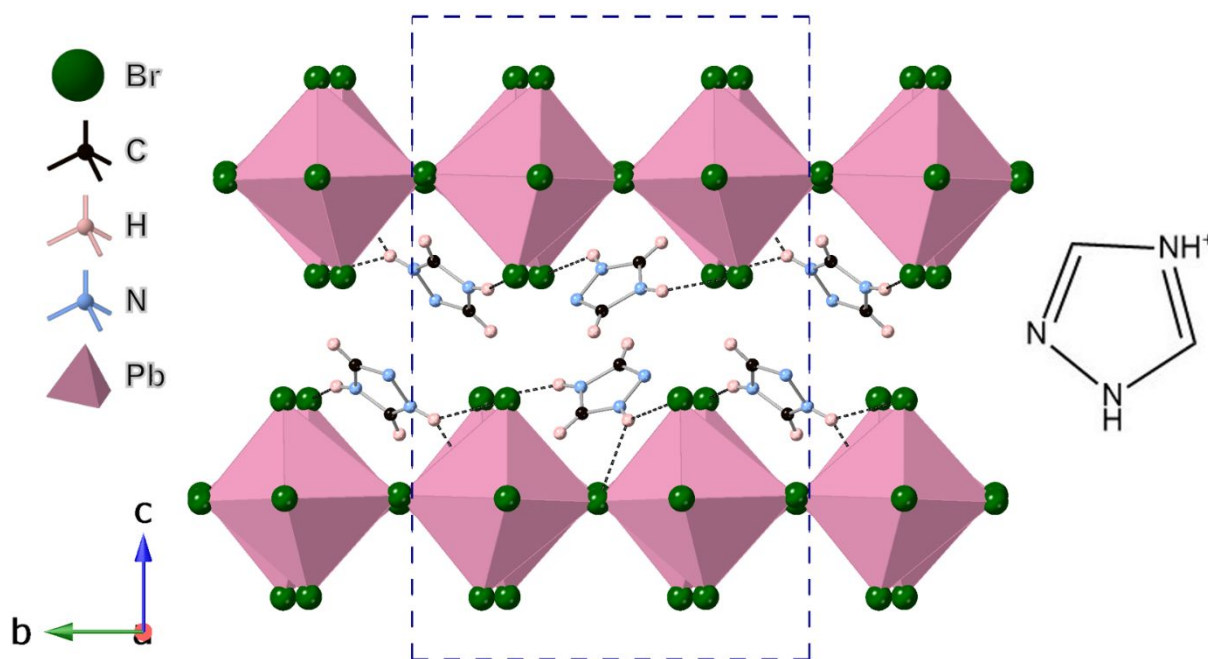


Figure 2. Crystal structure of T_2PbBr_4 .

The unit cell of T_2PbBr_4 has a $2a_p \times 2a_p \times 2c_p$ supercell relative to the parent DJ structure ($TlAlF_4$), which is caused by a combination of octahedral tilting/distortion together with ordering of $[TzH^+]$ cations over two distinct sites and the cooperative minor staggering of adjacent octahedral layers. Figure 2 shows the packing arrangement, together with the H-bonding of the $[TzH^+]$ moieties to the inorganic layers. The driving force for this expanded supercell may be broken down into the effects of octahedral tilting together with the effects of the arrangement of the organic species. In the notation used by Li *et al.*¹⁶ the tilt system of T_2PbBr_4 is an unusual one: a^-b^0c , signifying rotation of octahedra around the c -axis and out-of-phase tilting of adjacent octahedra along *only one* of the in-plane axes. These tilt modes acting alone would lead to a supercell $2a_p \times 2a_p \times c_p$ in space group $C2/m$, with perfectly eclipsed octahedral layers: it can be seen that the additional c -axis doubling is due to the slight staggering of the adjacent layers, in an antiferrodistortive style along the b -axis, presumably

caused by accommodation of the *inter*-layer species. Tremblay *et al.*¹⁷ have discussed the nature and variable extent of staggering of octahedral layers (*i.e.* the transition from ‘DJ-like’ to ‘RP-like’), which serves as a useful parameter for comparison of structures of this type. We can find no previous example of a similar $2a_p \times 2a_p \times 2c_p$ supercell for a LHP of APbX₄, A₂PbX₄ or AA’PbX₄ composition. The near-eclipsing of adjacent [PbBr₄]_∞ layers leads to noticeably short *inter*-layer Br---Br non-bonded contacts of 4.096(1) Å. We can also find no previous examples of such a short *inter*-layer contacts in a single-layer LHP, although Ke *et al.*¹⁸ suggest I---I distances of around 4.2 Å in some iodide members of this family.

The different distortion modes, *i.e.* the distinct octahedral tilting schemes and the presence or absence of staggering of adjacent layers, which occur in T₂PbBr₄ and related materials, are most easily identified using the on-line software ISODISTORT,¹⁹ which uses a normal mode analysis: further details for T₂PbBr₄ are given in ESI. A similar analysis of all previously reported APbX₄ or A₂PbX₄ LHPs may be enlightening for the understanding of structure-directing effects of other amines, but this is beyond the scope of the present work.

Selected geometrical parameters and octahedral distortion parameters are given in Table 2. It can be seen that the two nitrogen atoms in the 1-position of the triazolium participate in two H-bonds each to Br; in contrast the two in the 4-position only donate a single H-bond to Br. There are no H-bonds between triazolium moieties (Table S2).

Table 2. Selected geometrical and octahedral distortion parameters at 298 K.

	T ₂ PbBr ₄	A ₂ PbBr ₄	ITPbBr ₄	
	Pb1	Pb1	Pb1	Pb2
Pb-Br (Å)	2.9841(6)	2.8901(5)	3.0023(7)	2.9082(6)
	2.9924(3)	2.9141(5)	3.0024(7)	2.9082(6)
	3.0041(8)	2.9297(5)	3.0024(9)	3.0027(9)
	3.0055(7)	3.1395(5)	3.0130(9)	3.0127(9)
	3.0157(3)	3.2112(5)	3.0152(6)	3.1597(6)
	3.0282(7)	3.3221(5)	3.0152(6)	3.1598(6)
Pb-Br-Pb (°)	162.92(4)	162.35(2)	171.41(2)	
	165.82(3)	166.45(2)	179.53(4)	
	169.54(4)		180	
Br-Pb-Br range (°)	81.921(15)-	80.551(16)-	85.616(13)-	85.233(11)-
	97.984(15)	99.560(16)	94.384(13)	94.767(11)

$\Delta d (\times 10^{-4})$	0.23	29.16	0.04	11.70
σ^2	33.56	26.12	7.01	26.58

A_2PbBr_4

A_2PbBr_4 crystallises in a “corrugated 2×2 layer” (110)-oriented structure type (Figure 3). The unit cell and space group, $P2_1/c$, are consistent with a slight distortion of the framework (*i.e.* octahedral tilts and distortions) of the type seen in the first reported all-inorganic example of this structure type, $NdBaInO_4$.²⁰ The aristotype phase of the $AA'BX_4$ (110)-type (*i.e.* no octahedral tilting) has space group $Cmcm$, typified by $NdBaScO_4$.⁶ This higher symmetry structure has not yet been seen amongst the known LHPs. The specific type of distortion (*i.e.* unit cell metrics and space group) seen here for A_2PbBr_4 has previously been observed in [(aminoethyl)isothioureia] $PbBr_4$ ²¹ but this is the first example of a LHP with this structure type of the formula $AA'BX_4$.

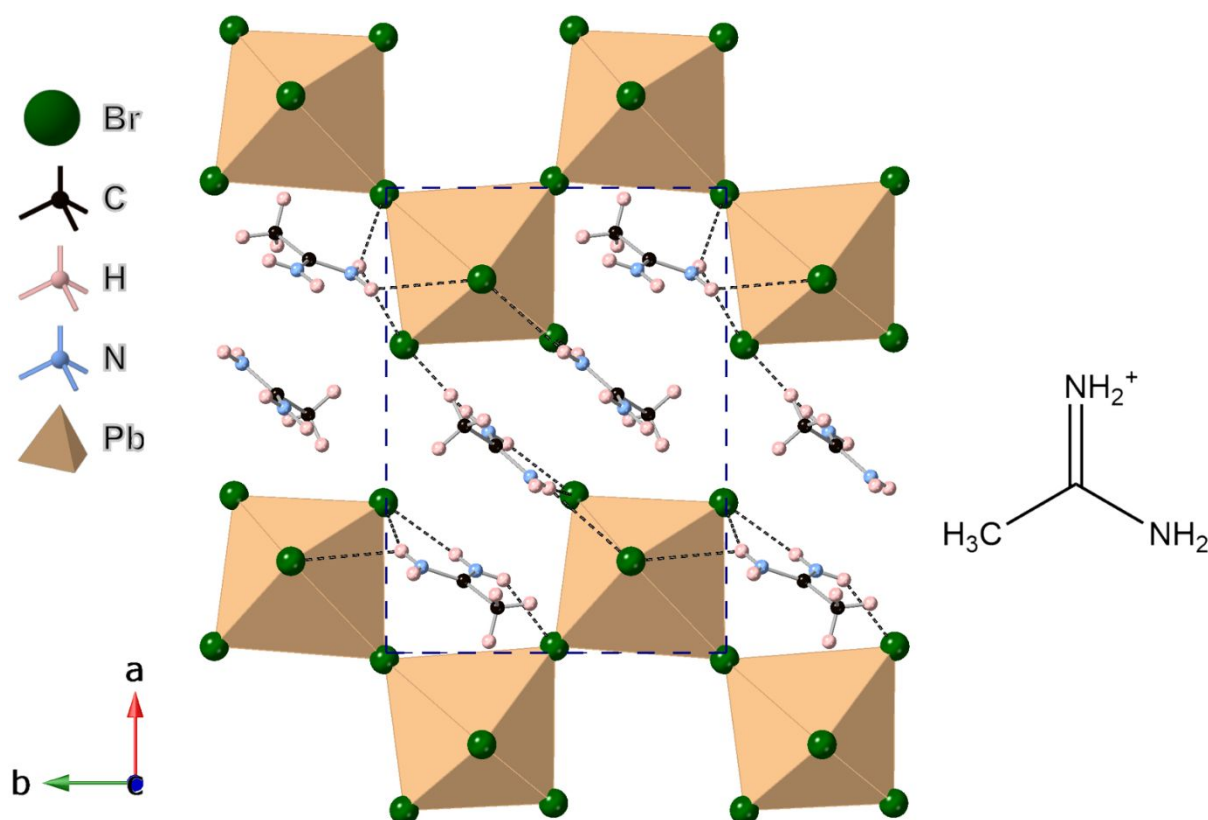


Figure 3. Crystal structure of A_2PbBr_4 .

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3 As is the case in T_2PbBr_4 there is only one crystallographically unique Pb site, but two distinct
4 $[AaH^+]$ sites. The *intra*-layer acetamidinium forms H-bonds only to the nearby $[PbBr_4]_{\infty}$ layer,
5 whereas the *inter*-layer $[AaH^+]$ forms H-bonds to adjacent inorganic layers *via* N1 and N2.
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7 Amongst the relatively small number of reported 2×2 (110)-oriented layered hybrid
8 perovskites, we have found only six that have a stoichiometry $AA'BX_4$ rather than ABX_4 .^{7,8,22,23}
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10 Four of these contain guanidinium $[GuH^+]$: $[GuH]_2PbI_4$, $[GuH]_2SnI_4$, $[ImH][GuH]PbBr_4$ and
11 $[TzH][GuH]PbBr_4$. The latter two examples are interesting as they show that $[GuH^+]$ is capable
12 of occupying either the *intra*-layer or *inter*-layer site, depending on competition between
13 $[GuH^+]$ and the second organic moiety. The occupation of both sites simultaneously by $[GuH^+]$
14 has recently been reported in a related 3×1 (110)-oriented perovskite, $[GuH]_{1.5}[4Me-$
15 $ImH]_{0.5}SnI_4$.²⁴ In $[TzH][GuH]PbBr_4$, it is perhaps surprising that $[TzH^+]$ occupies the *intra*-
16 layer site. This was discussed by Guo *et al.*⁷: the ionic sizes of $[GuH^+]$ and $[TzH^+]$ are
17 approximately the same, and it was reasoned that *inter*-molecular $[GuH^+]\cdots[TzH^+]$ hydrogen
18 bonds may play a significant role in stabilising the cation ordering in that case. Since $[AaH^+]$
19 is anticipated to be approximately the same size as $[GuH^+]$, it may be no surprise that A_2PbBr_4
20 adopts the (110)-oriented structure rather than any (001)-oriented option. The H-bonding
21 options are, of course, more restricted for $[AaH^+]$ versus $[GuH^+]$, nevertheless Figure 3 and
22 Table S4 show that there is *inter*-layer H-bonding present here *via* the *inter*-layer $[AaH^+]$.
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35 Selected geometrical parameters for A_2PbBr_4 are given in Table 2. Although there are currently
36 only a small number of (110)-oriented LHPs, these display quite a diversity of specific
37 structural distortions (*i.e.* unit cell metrics and space groups derived from the aristotype phase).
38 We therefore offer no universal trends regarding the nature of these distortions versus
39 compositional features, in terms of *inter*-layer interactions and other longer-range structural
40 features. Moreover, there appears little systematic behaviour regarding the local structural
41 features within this family, such as the level of individual PbX_6 octahedral distortions and *inter*-
42 octahedral angles. Amongst the known (110)-oriented structure layered hybrid perovskites of
43 $AA'BX_4$ stoichiometry, A_2PbBr_4 is seen to exhibit the largest octahedral distortions and
44 amongst the largest *inter*-octahedral distortions (*i.e.* B-X-B bond angles, Table 3). This is seen,
45 for example, in comparing to the two previous A_2BX_4 compositions, $[GuH]_2PbI_4$ and
46 $[GuH]_2SnI_4$, in their monoclinic polymorphs, which exist close to room temperature: these
47 compounds show the largest *inter*-octahedral distortions of this family. Surprisingly, and for
48 reasons we cannot explain, perhaps the closest compositional analogue to A_2PbBr_4 ,
49 $[GuH]_2PbBr_4$ does not adopt a (110)-oriented structure, instead preferring an unusual chain-
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like structure.²⁵ The series of [3APr]PbX₄ structures,²⁶ for X = Cl, Br, I, are also compared in Table 3. This also suggests little direct correlation of distortion parameters versus the nature of X, based on the existing small dataset.

Table 3. Octahedral and *inter*-octahedral distortions of known (110)-oriented layered hybrid perovskites.

	$\Delta d (\times 10^{-4})$	σ^2	B-X-B ($^\circ$)
A₂PbBr₄	29.16	26.12	162.35(2) 166.45(2)
[ImH][GuH]PbBr₄ ⁷	8.91	7.71	178.10(7) 180
[TzH][GuH]PbBr₄ ⁷	7.59	22.06	171.51(3) 180
[FA][HEA]PbBr₄ ⁸	5.70	11.59	173.13(6)
	13.66	14.46	177.96(4)
[GuH]₂PbI₄ ²²	7.78	12.65	154.27(2) 157.35(2)
	11.16	8.41	158.42(2) 176.06(2)
[GuH]₂SnI₄ ²²	20.06	6.78	157.08(2) 159.63(2)
	23.47	6.14	161.48(2) 177.10(2)
[IFA][MA]SnI₄ ²³	2.02	7.77	173.30(10) 180
[3APr]PbCl₄ ²⁶	12.32	34.50	169.70 170.50
[3APr]PbBr₄ ²⁶	9.81	21.07	171.31 173.24
[3APr]PbI₄ ²⁶	11.92	22.04	169.58 178.18

ITPbBr₄

ITPbBr₄ adopts an unusual variant of the (110)-oriented structure, which has also been described as a “corrugated 3 × 3 layer” structure. This structure type contains rows of alternating *cis*- and *trans*-shared octahedra linked into (110) sheets (Figure 4). There are only four previously reported examples of this structure type: [α -DMEN]PbBr₄ ([DMEN]²⁺ = 2-(dimethylamino)ethylammonium),³ [ImEA]PbI₄ ([ImEA]²⁺ = imidazoliumethylammonium)²⁷ and [4NPEA]PbX₄ (X = Br or I; 4NPEA = 4-nitrophenylethylammonium).²⁸ ITPbBr₄ is

therefore the first example of a bromide of this structure type incorporating two distinct molecular species. The two distinct types of PbX_6 octahedra (*i.e.* *cis*- and *trans*- ligands being terminal, respectively) in each case show very different degrees of distortion, with the *trans* site being much more regular (Table 2).

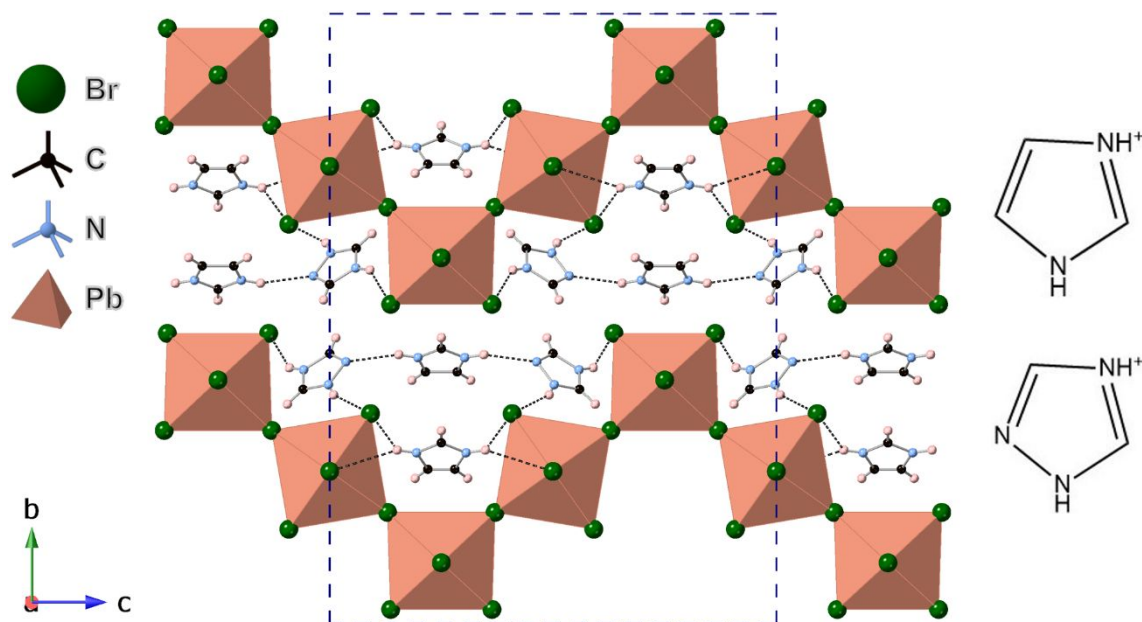


Figure 4. Crystal structure of ITPbBr_4 .

The unit cell metrics of this type of structure, in its simplest form, are characterised by two axial lengths determined by the geometry of the linked PbX_6 octahedra and one dictated by the packing of the adjacent layers, and the nature of the *inter*-layer moieties. Thus, an axial length of around 19 Å along the corrugation direction of the $[\text{PbX}_4]_\infty$ sheet (*c*-axis in ITPbBr_4 , Fig 4) arises from the lateral edge-to-edge width of four linked octahedra. A length of about 6 Å derives from the Pb-Br-Pb distance between two vertex-linked octahedra perpendicular to this (*a*-axis in ITPbBr_4), and a variable *inter*-layer distance is dictated by the nature and packing of the organic moieties ($b \sim 26$ Å in ITPbBr_4). By comparing the metrics of the known examples of this structure type (Table S9), it can be seen that ITPbBr_4 has one the ‘simplest’ variants of this basic unit cell, exhibiting the simple 6 Å metric perpendicular to the corrugation direction, whereas each of the other examples has a doubled axis, due to octahedral tilting. Interestingly, only one example ($[\text{ImEA}]\text{PbI}_4$) has a structure where the *inter*-layer unit cell axis represents the distance between adjacent $[\text{PbX}_4]_\infty$ sheets: each of the others has a doubled axis here, apparently due to alternating orientations of the *inter*-layer moieties.

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3 There are no direct *inter*-layer links *via* H-bonding in ITPbBr₄, although there are [ImH⁺]
4 [TzH⁺] H-bonds between the moieties that are both interacting with the same [PbBr₄]_∞ sheet.
5 Since our previous study⁷ suggested that [ImH⁺] and [TzH⁺] are approximately the same size,
6 it seems that these H-bonding preferences may play a subtle role in dictating the observed
7 cation ordering (*i.e.* ordering of [ImH⁺] into the *intra*-layer sites in this structure) although this
8 suggestion can only be speculative. Indeed, the features that favour the adoption of the 3 × 3
9 layer structure itself, rather than some of the possible competing polymorphs, are not clear
10 from the limited amount of data available at this stage. It is likely that the energy landscapes
11 discriminating different polymorphs in some of these systems are rather ‘flat’, for example
12 [DMEN]PbBr₄ crystallises in two distinct polymorphs, the thermodynamically stable α-phase,
13 having the 3 × 3 layer structure and the β-phase, the kinetic product, having a (001) layer
14 structure.³

Photophysical Properties

UV-Vis

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19 All three absorption spectra (Figure 5) revealed features similar to previously reported 2D
20 layered LHPs, *viz.*, two separated absorption peaks.^{7,29–31} That is, T₂PbBr₄ has two absorption
21 peaks at 3.05 eV (407 nm) and 2.85 eV (435 nm), ITPbBr₄ has peaks at 3.27 eV (379 nm) and
22 3.02 eV (411 nm) and A₂PbBr₄ has peaks at 3.56 eV (348 nm) and 3.29 eV (377 nm).
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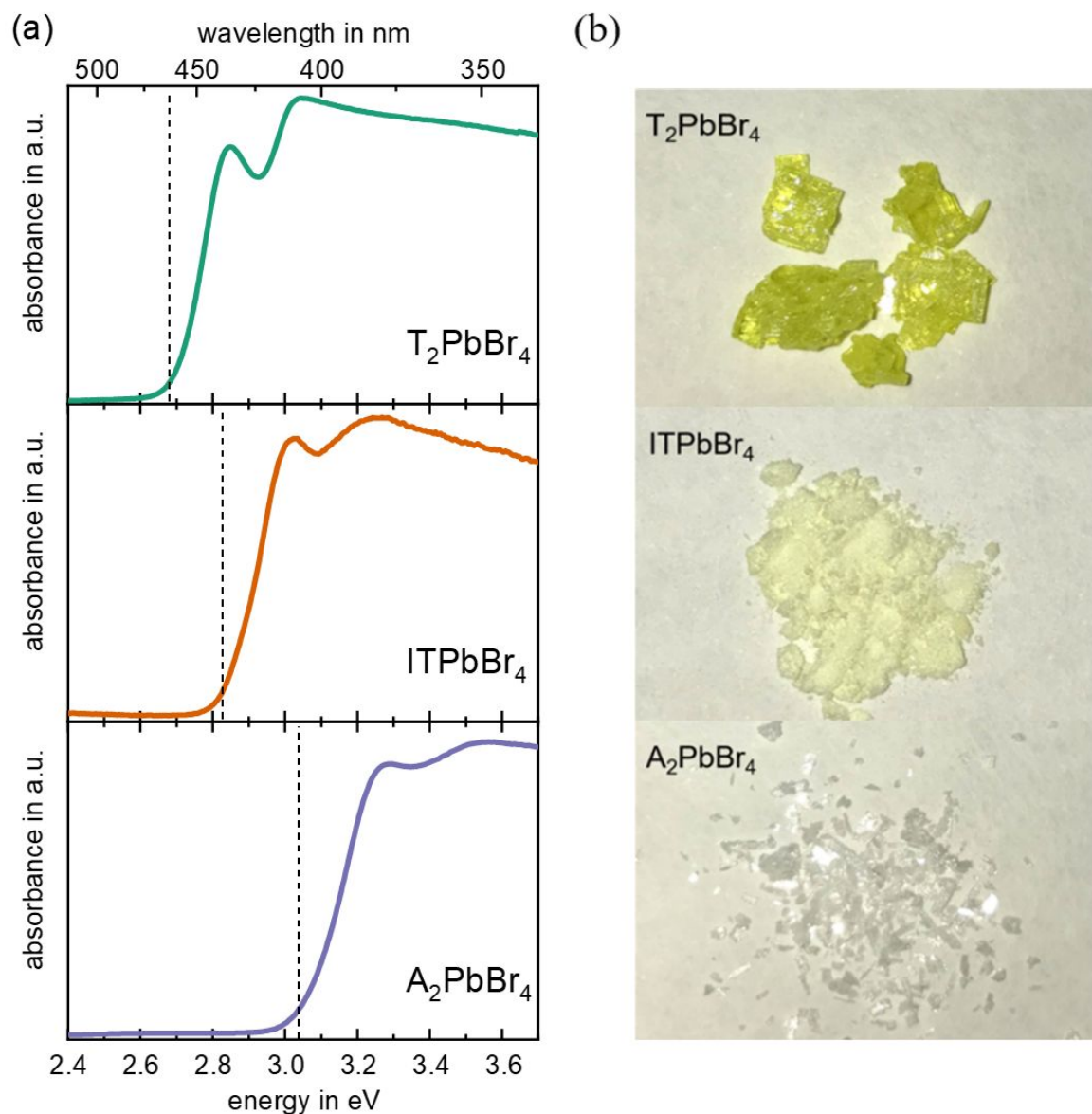


Figure 5. (a) UV-Vis absorption spectra of T_2PbBr_4 , $ITPbBr_4$ and A_2PbBr_4 and at room temperature; the dashed lines indicate the energy of the absorption onset and (b) crystals of T_2PbBr_4 , $ITPbBr_4$ and A_2PbBr_4 .

From these spectra, it also becomes clear that the energetic spacing between the two peaks increases from 0.20 eV and 0.25 eV to 0.27 eV for T_2PbBr_4 and $ITPbBr_4$ to A_2PbBr_4 respectively. The peaks at lower energies can be attributed to exciton absorption in each system,^{32,33} which precludes extracting the fundamental band gap with the help of a Tauc plot.³⁴ We thus estimate the optical gap from the absorption onset (dashed lines in Figure 5a), which increases from 2.68 eV (463 nm) and 2.82 eV (440 nm), to 3.03 eV (409 nm) when going from T_2PbBr_4 and $ITPbBr_4$ to A_2PbBr_4 , respectively. Both the increasing optical gap together with

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3 the increasing energetic spacing between the two absorption peaks are in agreement with the
4 idea of a greater electronic confinement,^{35,36} with the spread of the electron wavefunction being
5 inhibited where the connectivity between neighboring octahedra change between *cis*- and
6 *trans*- conformation ($\text{ITPbBr}_4 < \text{A}_2\text{PbBr}_4$).³⁷ While the increase in optical gap essentially stems
7 from the “particle in a box” solution to the Schrödinger equation,³⁸ the increased spacing
8 between the absorption peaks reflects an increased exciton binding energy with greater
9 confinement. Correspondingly, the colors of the three materials change from bright yellow
10 (T_2PbBr_4) to pale yellow (ITPbBr_4) and then to white (A_2PbBr_4) (Figure 5b).
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19 *PL spectra*

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22 Figure 6 shows the normalized PL spectra of all three compounds when they are excited
23 at 3.67 eV (337 nm). The emission spectrum of T_2PbBr_4 shows two distinct sharp peaks at 2.68
24 eV (463 nm) and 2.85 eV (435 nm). The emission spectrum of A_2PbBr_4 shows a different
25 behavior with a broad peak at ~ 1.97 eV (628 nm), corresponding to a large energetic spacing
26 between the PL peak and the absorption peak at 3.29 eV (377 nm). Furthermore, the full width
27 at half-maximum (FWHM) of the broad PL peak is ~ 0.72 eV (240 nm). In contrast, two PL
28 peaks are observed in the case of ITPbBr_4 . The dominating broad signal at 1.92 eV (647 nm)
29 has essentially the same shape as the PL of A_2PbBr_4 , and the PL peak at 2.75 eV (451 nm) is
30 in the energetic range similar to the emission of T_2PbBr_4 . We measured the photoluminescence
31 quantum efficiency PLQY at room temperature and found it to be below 1% for all three
32 samples. While these values are low compared to the highest reported PLQYs of low
33 dimensional lead bromide perovskites,^{29,39} several works also report comparably low PLQYs.
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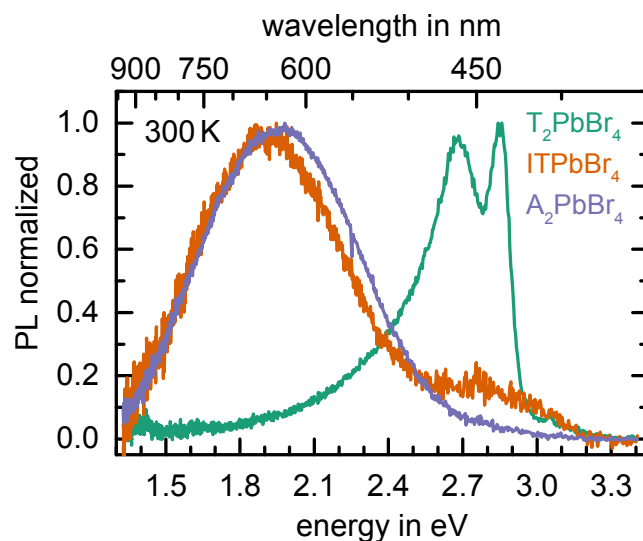


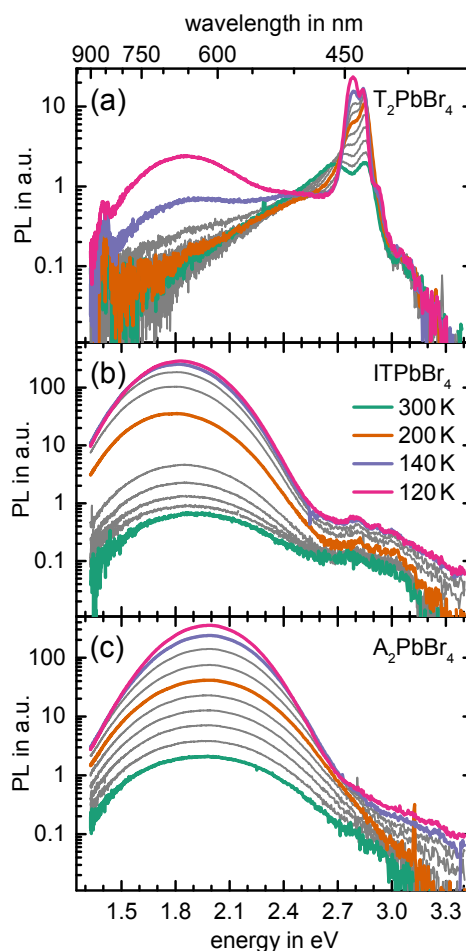
Figure 6. Normalized PL spectra (excited at 337 nm) for T_2PbBr_4 , $ITPbBr_4$ and A_2PbBr_4 at room temperature.

To better understand the origin of the different emitting states, temperature-dependent steady-state PL measurements were performed from 300 K to 120 K (20 K intervals) for all three compounds.

Figure 7 shows the temperature-dependent PL spectra for each perovskite system. For all materials, the overall PL intensity increases upon cooling to 120 K. For T_2PbBr_4 , the peak at 2.68 eV (463 nm) at 300 K gradually shifts to higher energies upon cooling to 200 K (Figure 7a). From 200 K onwards, it retains its position and raises in intensity, becoming the dominant PL feature at 120 K. Further, an additional low energy emission band (~ 1.87 eV, 663 nm) appears at temperatures below 160 K.

As mentioned above, $ITPbBr_4$ shows two emissive features, where the peak at higher energies (2.80 eV, 443 nm) exhibits a low relative intensity compared to the PL feature at lower energies at room temperature (Figure 7b). Upon cooling, the ratio between the PL peaks at high and low energy decreases. The emission band at lower energy (1.89 eV, 656 nm) remains the dominant PL feature in the entire investigated temperature range, where its FWHM narrows from 0.72 eV (258 nm) at 300 K to 0.46 eV (173 nm) at 120 K. Additionally, we observe that the high energy band becomes more structured at low temperatures, exhibiting several distinct PL features at similar peak positions compared to the high energy PL features of T_2PbBr_4 . PL of A_2PbBr_4 predominantly exhibits the low energy emission at ~ 1.97 eV in the investigated temperature range between 300 K and 120 K (Figure 7c). Upon cooling, the FWHM of the PL

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3 peak continuously reduces from 0.72 eV (240 nm) at RT to 0.48 eV (154 nm) at 120 K, while
4 its energetic position remains constant. Below 200 K, a weak PL at energies > 2.8 eV (443 nm)
5 appears. Compared to the PL band at ~ 1.97 eV, its intensity is lower by more than three orders
6 of magnitude.
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44 **Figure 7.** Temperature-dependent (300-120 K) steady-state PL spectra of (a) T_2PbBr_4 , (b)
45 $ITPbBr_4$ and (c) A_2PbBr_4 .

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50 The results of the PL measurements suggest two different emitting species since the high
51 energy signal in T_2PbBr_4 is rather narrow and structured, whereas the emission at lower
52 energies is broad and significantly separated in energy from corresponding absorption onsets.
53 The PL peak at 2.85 eV (435 nm) is nearly resonant with the exciton absorption shown in
54 Figure 5, so that we associate this high energy PL band with exciton recombination.^{42,43}
55 Broad emission features at low photon energies are often observed in 2D-perovskite systems,^{44–}
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60 ⁴⁷ and it was suggested that they stem from recombination via intrinsic (electron-phonon

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3 coupling) or extrinsic (electron-lattice defect) self-trapped excitons (STE).^{40,48} This may also
4 be a possible interpretation for the observed emission at lower energies of the materials
5 investigated in our case. In contrast, we deem the occurrence of the low energy features due to
6 a possible structural phase transition at low temperatures to be rather unlikely. In such a case,
7 we would expect a decrease of the PL signals associated to the high temperature phase, the
8 abrupt appearance of low temperature phase PL features, also with a similar spectral width
9 compared to the high temperature phase PL features.⁴⁹ Typically this all would happen within
10 a relatively small temperature range.⁵⁰

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12 The ratio between the high and low energy bands is temperature dependent, *i.e.* reflecting some
13 thermally activated detrapping process.^{40,51} Nevertheless, overall, we observe a stronger
14 dominance of the low energy band along the series from T_2PbBr_4 over $ITPbBr_4$ to A_2PbBr_4 .
15 This is in line with reports from literature showing that broad PL at low energies can be
16 facilitated by an increase of distortions and corrugation.^{44,45} Considering that the energy
17 differences between high and low energy bands are fairly similar for all three systems, the
18 lower intensity of the broad peak is likely to reflect a lower density of STE states in T_2PbBr_4
19 than in $ITPbBr_4$ and A_2PbBr_4 . In the literature, a change in the PL intensity between high and
20 low energy PL bands was associated with a change in the energy difference between the
21 absorption onset and the energy of the STE emission.^{26,52} It was suggested that a smaller energy
22 difference is favourable for STE detrapping leading to an increased PL intensity of the high
23 energy band. This at first sight is in line with our results, however such a thermal detrapping
24 process appears questionable to us, as the observed energy difference between low and high
25 energy PL bands is large (~ 0.7 eV) compared to thermal energy. Furthermore a recent study
26 shows that the low energy PL band originates from in-gap states, rather than being due to
27 STEs,⁵³ which emphasizes the general need for more detailed future studies.

28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 **Conclusions**

49 We have prepared three new examples of hybrid lead bromide layered perovskites of different
50 structural variations templated using small disc-shaped amines. The cationic ordering
51 behaviour of each composition have been discussed in terms of ionic size effects and hydrogen-
52 bonding environments. In T_2PbBr_4 we introduce a previously unreported ‘DJ-like’ (001)-
53 oriented structure type with a $2a_p \times 2a_p \times 2c_p$ supercell arising from octahedral tilting and the
54 arrangement of the $[TzH^+]$ moieties. The two (110)-oriented perovskites reported, A_2PbBr_4 and
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ITPbBr₄, represent two new examples of this rare structure-type featuring corrugation patterns of 2 × 2 and 3 × 3, respectively. The octahedral distortions present in A₂PbBr₄ are the largest reported for any material of the 2 × 2 type, however we are unable to identify any systematic behaviour amongst known (110)-oriented structures to explain this. ITPbBr₄ is the first example of a bromide 3 × 3 type structure incorporating two distinct molecular species and represents the ‘simplest’ variant of the basic unit cell among known materials of this structure type. All three materials exhibit peaks consistent with exciton absorption in UV-vis spectroscopy. Photoluminescence data indicate a distinct change in behaviour with increasing structural corrugation. In T₂PbBr₄, there is a narrow and structured emission observed at higher energies attributed to exciton recombination, as well as a broad emission at lower energies corresponding to recombination *via* extrinsic or intrinsic STE. With the increasing structural distortions and corrugation in ITPbBr₄ and A₂PbBr₄, the broad emission feature dominates. The diverse structures and photoluminescent behaviour exhibited in these materials obtained from similar disc-shaped amines highlights the need for greater exploration and study of hybrid layered perovskites towards potential functionalities.

Supporting Information

Crystallographic data at 173 K, hydrogen bonding details, octahedral distortion parameters, brief review of (110)-oriented layered perovskite unit cell details, ISODISTORT mode amplitudes for T₂PbBr₄.

The research data pertaining to this paper are available at <https://doi.org/10.17630/54781f80-3c71-48a2-aed7-45381cab7683>

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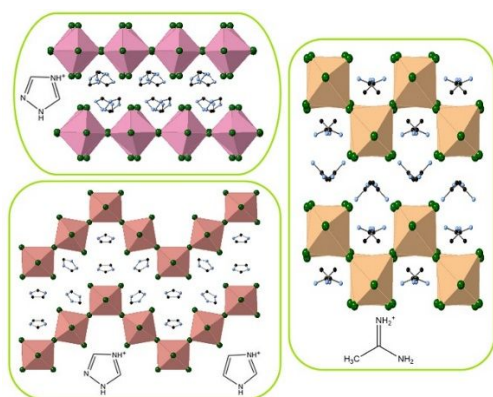
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Combinations of two disc-shaped small amines template a diversity of layered lead halide perovskites