

Supplementary information for

Manipulation of structure and optoelectronic properties through bromine inclusion in a layered lead bromide perovskite

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Table S 1: Refinement Details of Phase 2 and Phase3 of [H₃N(CH₂)₆NH₃]PbBr₄

Sample	[H ₃ N(CH ₂) ₆ NH ₃]PbBr ₄ Phase 2	[H ₃ N(CH ₂) ₆ NH ₃]PbBr ₄ Phase 3
CCDC Code	2203749	2203750
Formula	Pb ₃ Br ₁₂ C ₁₈ N ₆ H ₅₄	Pb ₄ Br ₁₆ C ₂₄ N ₈ H ₇₂
Formula Weight	645.05	645.05
Crystal Description	Colourless Prism	Colourless Prism
Crystal Size (mm ³)	0.05 x 0.05 x 0.05	0.08 x 0.05 x 0.03
Temperature (K)	93	298
Crystal System	Monoclinic	Monoclinic
Space group	<i>P2</i> ₁	<i>P2</i> ₁
<i>a</i> (Å)	16.601(11)	16.382(7)
<i>b</i> (Å)	8.049(4)	8.055(3)
<i>c</i> (Å)	17.329(11)	24.680(10)
β (deg)	97.702(12)	107.187(11)
<i>V</i> (Å ³)	2294.6(2)	3111.3(2)
<i>Z</i>	2	2
ρ_{calc} (g/cm ³)	2.801	2.754
μ (mm ⁻¹)	21.446	21.090
<i>F</i> (000)	1740	2320
Reflections collected	27314	21917
Independent reflections (<i>R</i> _{int})	8316 (0.0508)	9721 (0.0656)
Parameters, Restraints	221 22	478 2354
Goodness-of-fit on <i>F</i> ²	1.023	0.799
<i>R</i> ₁	0.0689	0.1127
<i>R</i> ₁ [<i>l</i> >2 σ (<i>l</i>)]	0.0398	0.0520
<i>wR</i> ₂	0.0821	0.1438
<i>wR</i> ₂ [<i>l</i> > σ (<i>l</i>)]	0.0729	0.1210
Largest diff. peak and hole (e/Å ³)	2.132 and -2.255 e.Å ⁻³	1.944 and -2.624 e.Å ⁻³

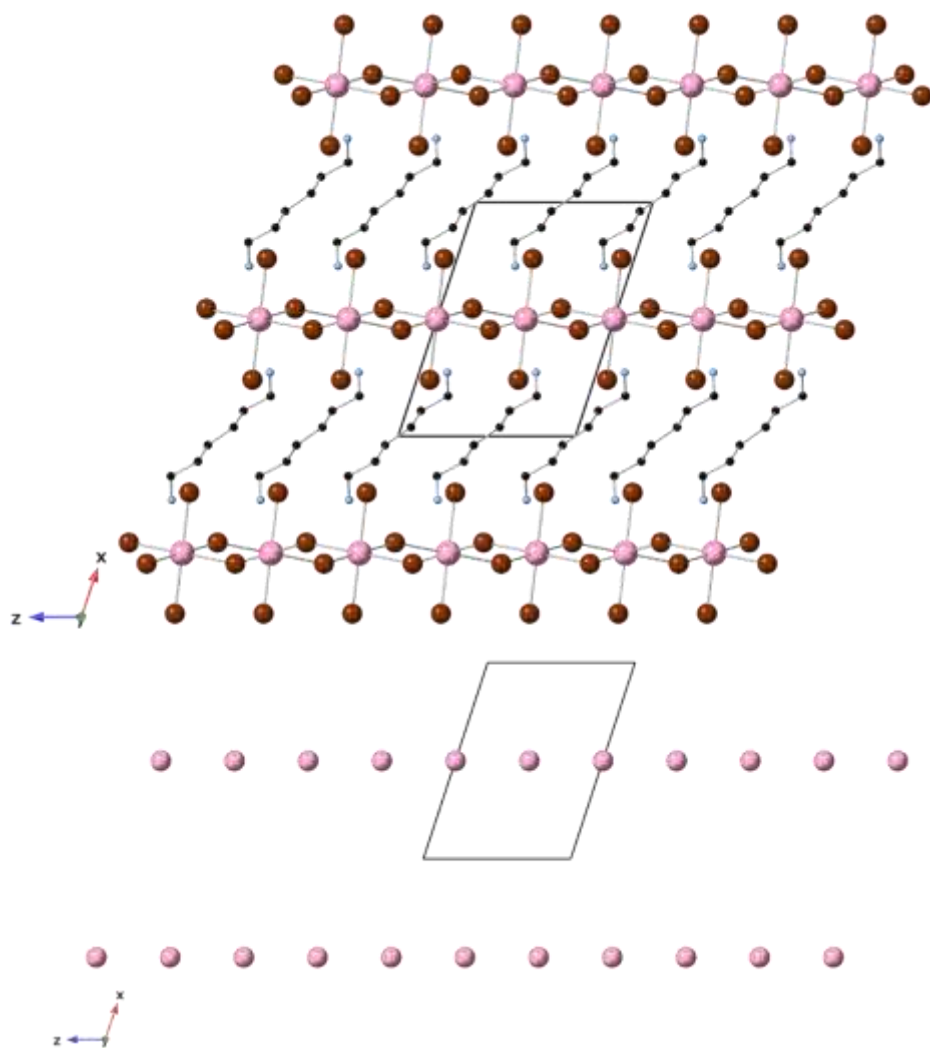


Figure S 1: Phase 1 of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$. The bottom image shows a representation of the Pb atoms only for comparison with Phases 2 and 3. Note the strictly 'flat' Pb layers.

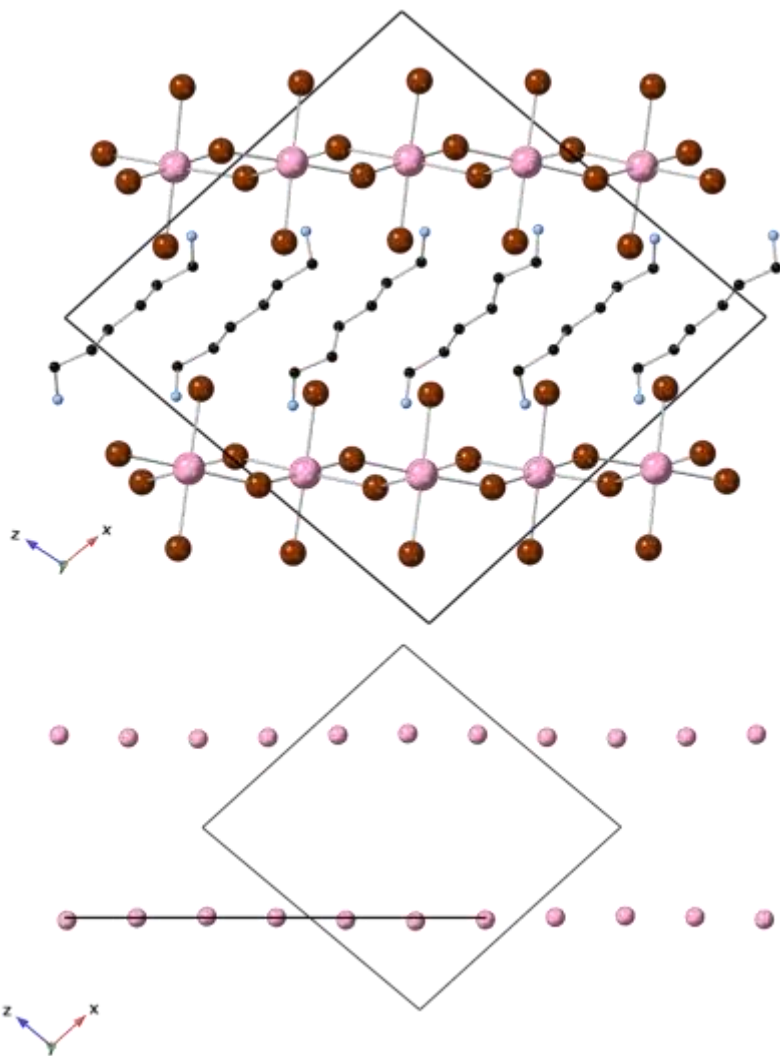


Figure S 2: Phase 2 of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$. Note the very slight undulation of the Pb layers, with a wavelength of six Pb centres.

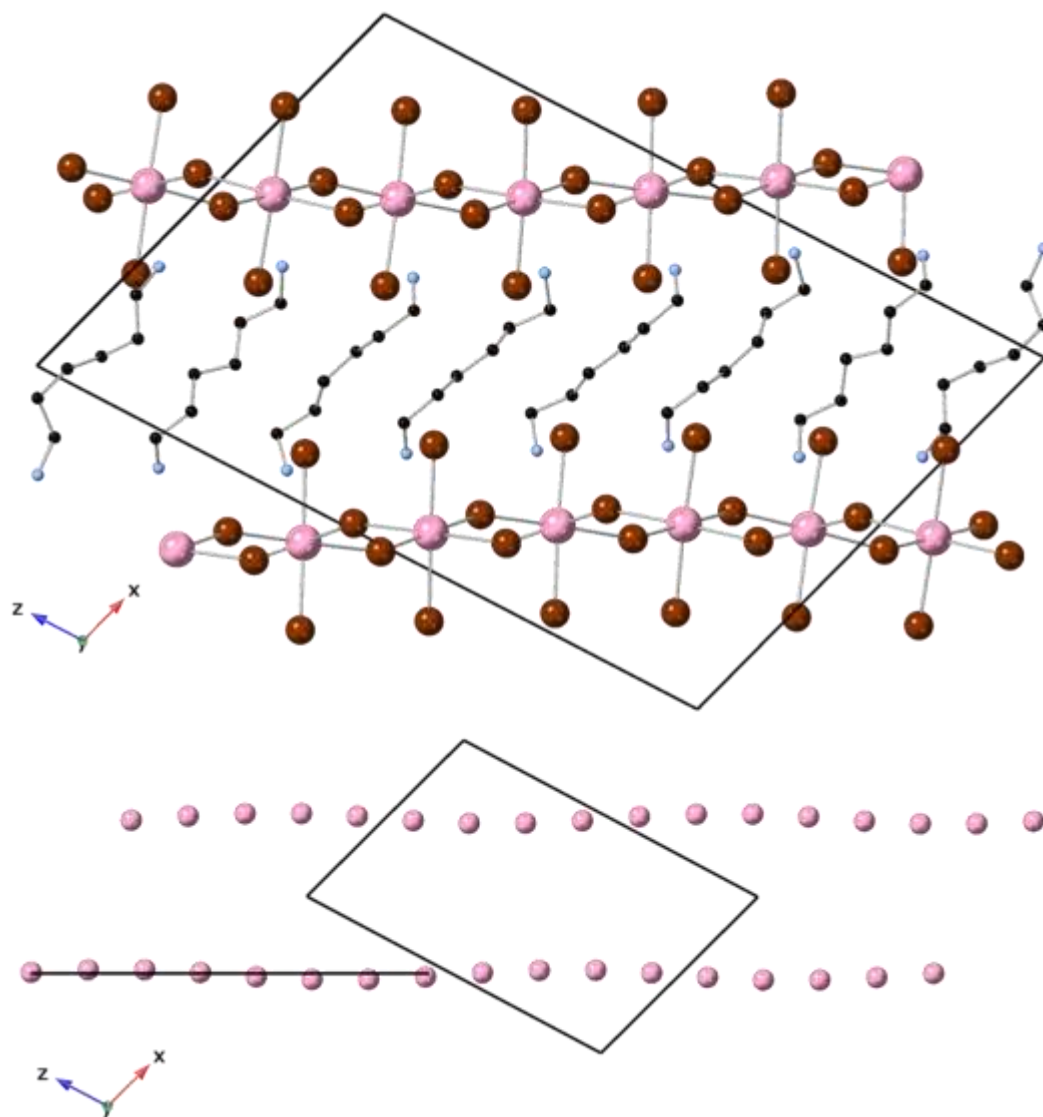


Figure S 3: Phase 3 of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$. Note the more significant undulation of the Pb layers, with a wavelength of eight Pb centres, and also the more significant variations in positioning of the amine moieties.

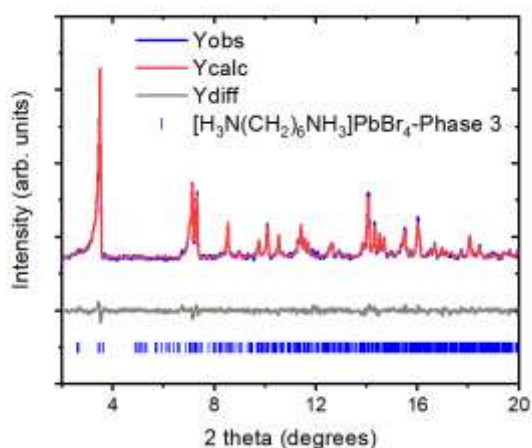


Figure S 4: Rietveld fit of laboratory PXRD data, collected at room temperature using MoK α_1 radiation, before VT-PXRD experiment, which was carried out on [H₃N(CH₂)₆NH₃]PbBr₄. Structural model for [H₃N(CH₂)₆NH₃]PbBr₄ Phase 3 was used in the refinement. Unit cell parameters are as follows: $a = 16.3940(17)$ Å, $b = 8.0510(8)$ Å, $c = 24.691(2)$ Å, $\beta = 107.159(7)^\circ$.

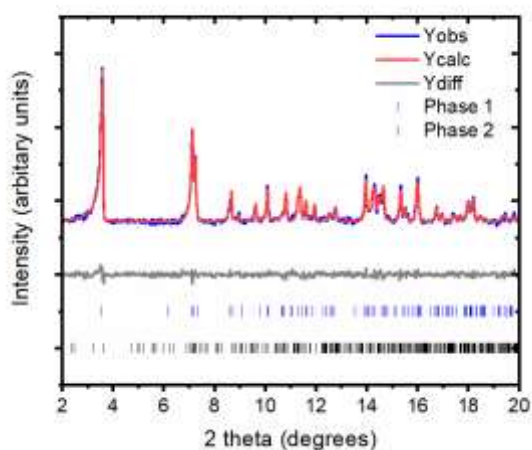


Figure S 5: Rietveld fit of laboratory PXRD data, collected at -50°C using MoK α_1 radiation, during VT-PXRD experiment, which was carried out on [H₃N(CH₂)₆NH₃]PbBr₄. Structural model for [H₃N(CH₂)₆NH₃]PbBr₄ Phase 1 and Phase 2 was used in the refinement. Unit cell parameters for Phase 1 are $a = 11.879(5)$ Å, $b = 8.047(4)$ Å, $c = 8.351(4)$ Å and $\beta = 105.85(5)^\circ$ whilst the unit cell parameters for Phase 2 are $a = 16.537(2)$ Å, $b = 8.0494(8)$ Å, $c = 17.4063(18)$ Å and $\beta = 96.715(7)^\circ$.

The SEM image of [H₃N(CH₂)₆NH₃]PbBr₄ is shown in Figure S 6, which shows that [H₃N(CH₂)₆NH₃]PbBr₄ has adopted a predominantly square prismatic morphology, with dimensions of around 300-400 μm and a thickness of approximately 50 μm . EDS found the Pb: Br ratio to be 20.71 (0.10): 79.29 (0.36), giving a Pb: Br ratio of 1: 3.83, which is within experimental error of the expected 1:4 Pb:Br ratio in the de-intercalated sample.

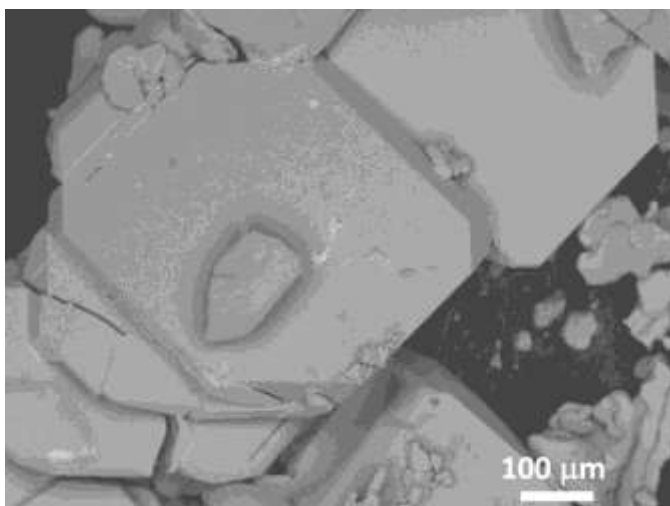


Figure S 6: SEM image of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$

The SEM image of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4 \cdot \text{Br}_2$ is shown in Figure S7. Like $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$, the morphology adopted is square prismatic, with dimensions of around 600-800 μm .

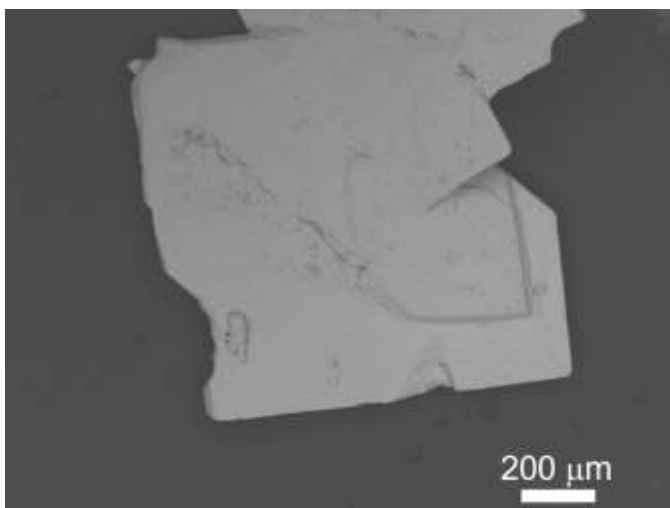


Figure S 7: SEM image of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4 \cdot \text{Br}_2$

Table S 1: Pb-Br bond lengths and octahedral distortions for [H₃N(CH₂)₆NH₃]PbBr₄ and [H₃N(CH₂)₆NH₃]PbBr₄.Br₂

	[H ₃ N(CH ₂) ₆ NH ₃]PbBr ₄ .Br ₂ LT	[H ₃ N(CH ₂) ₆ NH ₃]PbBr ₄ .Br ₂ RT
	Pb1	Pb1
Pb-Br (Å)	2.9623(8)	2.9665(8)
	2.9623(8)	2.9666(8)
	2.9640(7)	2.9771(8)
	2.9640(7)	2.9771(8)
	2.9672(8)	2.9790(8)
	2.9672(8)	2.9790(8)
Br-Pb-Br range (deg)	87.247(9) - 92.753(9)	87.332(10) - 92.667(10)
Pb-Br-Pb (deg)	180.0	180.0
	180.0	180.0
	180.0	180.0
Δd (×10 ⁻⁶)	0.47	3.39
σ ²	3.43	3.35

	[H ₃ N(CH ₂) ₆ NH ₃]PbBr ₄ Phase 2			[H ₃ N(CH ₂) ₆ NH ₃]PbBr ₄ Phase 3			
	Pb1	Pb2	Pb3	Pb1	Pb2	Pb3	Pb4
Pb-Br (Å)	2.9868(9)	2.9783(10)	2.9937(12)	2.9724(13)	2.9717(14)	2.9957(19)	2.9694(17)
	2.9939(9)	2.9851(10)	3.0073(11)	2.9856(15)	2.9883(15)	3.0048(16)	3.0050(16)
	3.0300(9)	3.0358(10)	3.0324(11)	2.9969(14)	2.9920(17)	3.0063(16)	3.0058(16)
	3.0362(9)	3.0386(10)	3.0352(11)	2.9988(14)	2.9953(15)	3.0091(18)	3.0081(16)
	3.0461(9)	3.0438(10)	3.0357(10)	3.0242(14)	3.0199(14)	3.0118(18)	3.0117(17)
	3.0469(9)	3.0469(10)	3.0510(10)	3.0258(15)	3.0300(14)	3.0126(18)	3.0248(17)
Br-Pb-Br range (deg)	85.63(2)	86.30(3)	86.16(3)	87.18(4)	87.07(4)	86.64(5)	86.76(4)
	-	-	-	-	-	-	-
	94.43(2)	94.48(3)	94.31(3)	93.73(4)	93.62(4)	93.54(5)	93.38(5)
Pb-Br-Pb (deg)	178.60(3)	179.01(3)	179.09(4)	177.03(5)	177.06(5)	179.48(6)	178.85(6)
	178.48(2)	179.20(3)	179.00(3)	178.21(4)	178.36(4)	178.15(6)	178.94(4)
	178.07(2)	178.96(3)	178.82(3)	178.16(4)	177.77(4)	178.26(5)	178.59(5)
Δd (×10 ⁻⁶)	63.50	88.20	40.70	41.30	42.90	3.53	31.60
σ ²	8.69	9.47	7.44	5.00	5.08	4.82	4.03

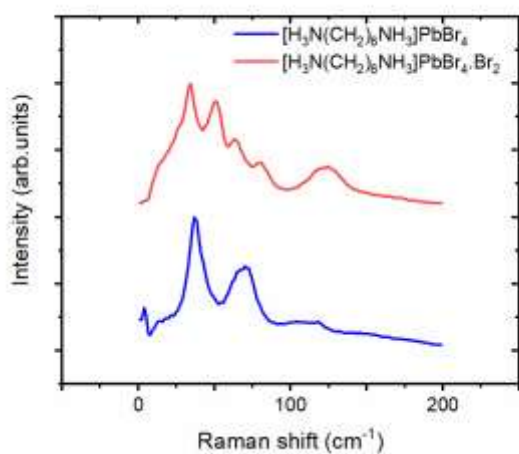


Figure S 8: Raman spectra of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$ and $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4 \cdot \text{Br}_2$

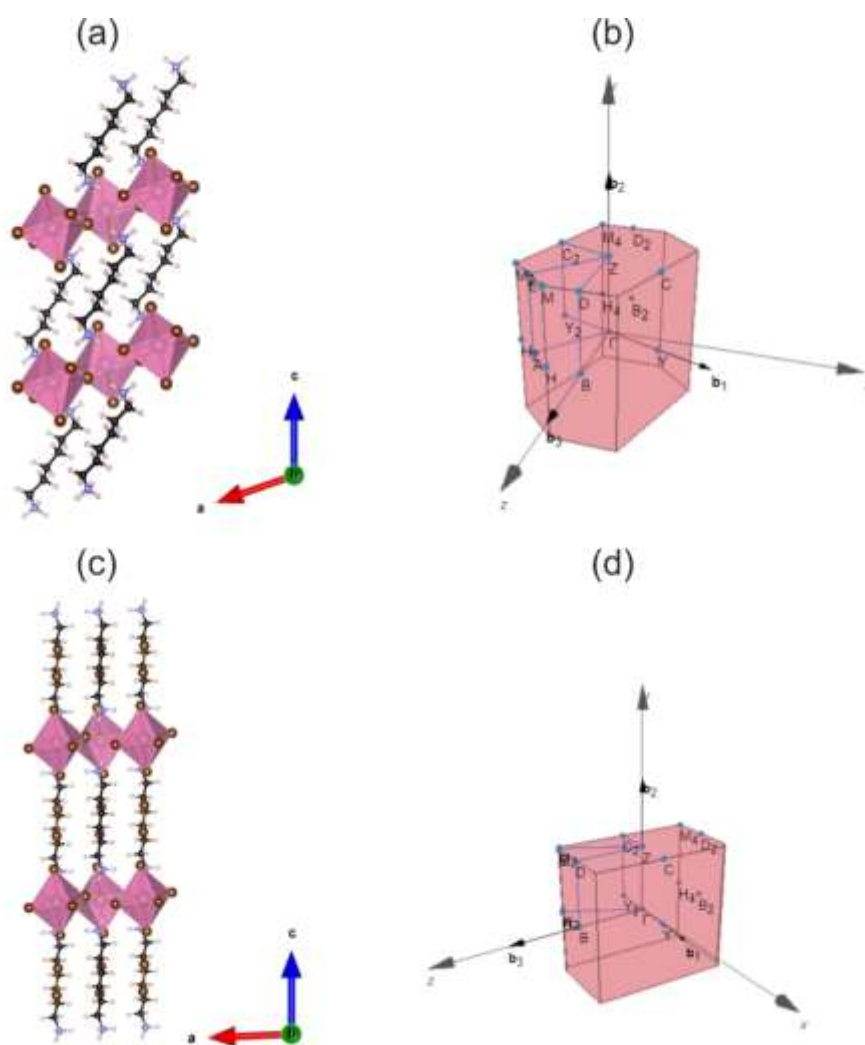


Figure S 9: Computational crystal structure model and Brillouin zone with high symmetry points of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$ (a, b) and $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4 \cdot \text{Br}_2$ (c, d)

Stability studies

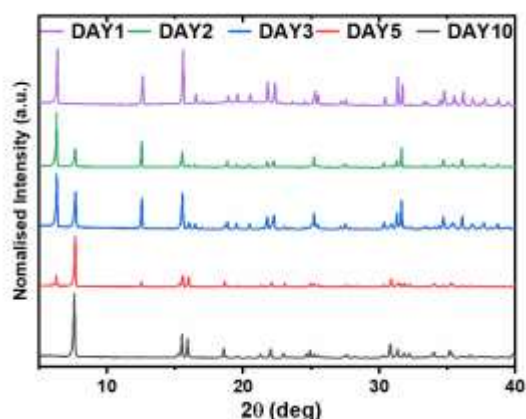


Figure S 10: PXRD patterns of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$ collected at room temperature over ten days.

In order to probe the stability of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$, powder X-ray diffraction patterns were collected at room temperature over the course of 10 days (see Figure S10). On day 1, PXRD show that the sample consisted of phase pure $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$, with no evidence of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$. On day 2, extra peaks appeared in the diffraction pattern which could be indexed to the deintercalated $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$ Phase 3, but this phase was the minor phase. The phase fraction of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$ continued to increase even further and on day 10 showed no evidence of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$ at all. The unit cell parameters of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$ and $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$ do not change significantly over time and we have not seen any evidence of ordered phases with bromine and bromine vacancies. In terms of stability, this is better than $(\text{BA})_2\text{PbI}_4\cdot\text{I}_2$ which full reverted to $(\text{BA})_2\text{PbI}_4$ 24hrs after intercalation.¹

In order to probe the influence of temperature on the long term stability of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$, samples of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$ were stored in the refrigerator at 5 °C for 21 days. The sample was taken out of the refrigerator in order to collect PXRD data at room temperature. The PXRD data collected on day 1 and after 21 days in the refrigerator is shown in Figure S11. No peaks corresponding to the parent $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4$ material or any other impurities were observed. Therefore, the PXRD studies have shown that the $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4\cdot\text{Br}_2$ is stable when kept in the refrigerator for at least 21 days.

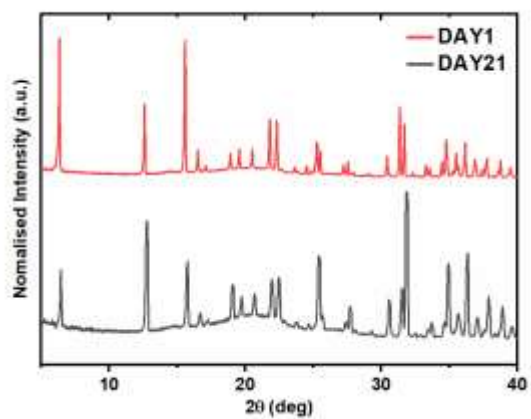


Figure S 11: Powder X-ray diffraction pattern of $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbBr}_4 \cdot \text{Br}_2$ after storing for 1 day and 21 days in the refrigerator at approximately 3 to 5 °C

1. T. Sheikh, V. Nawale, N. Pathoor, C. Phadnis, A. Chowdhury and A. Nag, *Angew. Chem. Int. Edit.*, 2020, **59**, 11653-11659.