
Supplementary information

**Directed assembly of layered perovskite
heterostructures as single crystals**

In the format provided by the
authors and unedited

Supplementary Information

Directed assembly of layered perovskite heterostructures as single crystals

Michael L. Aubrey,^{1,7} Abraham Saldivar Valdes,^{1,7} Marina R. Filip,^{3,4,5} Bridget A. Connor,¹ Kurt P. Lindquist,¹ Jeffrey B. Neaton,^{4,5,6} and Hemamala I. Karunadasa*,^{1,2}

¹Department of Chemistry, Stanford University, Stanford, California 94305, United States

²Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

³Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom

⁴Department of Physics, University of California Berkeley, Berkeley, California 94720, United States

⁵Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

⁶Kavli Energy NanoSciences Institute at Berkeley, Berkeley, California 94720, United States

⁷These authors contributed equally: Michael L. Aubrey and Abraham Saldivar Valdes

*email: hemamala@stanford.edu

Table of Contents

Powder X-ray Diffraction Data	3
Unit Cells Determined from Powder X-ray Diffraction.....	7
Crystallographic Data Tables	8
Supplementary UV- <i>vis</i> absorption spectra	11
Photoluminescence spectroscopy	15

Powder X-ray Diffraction

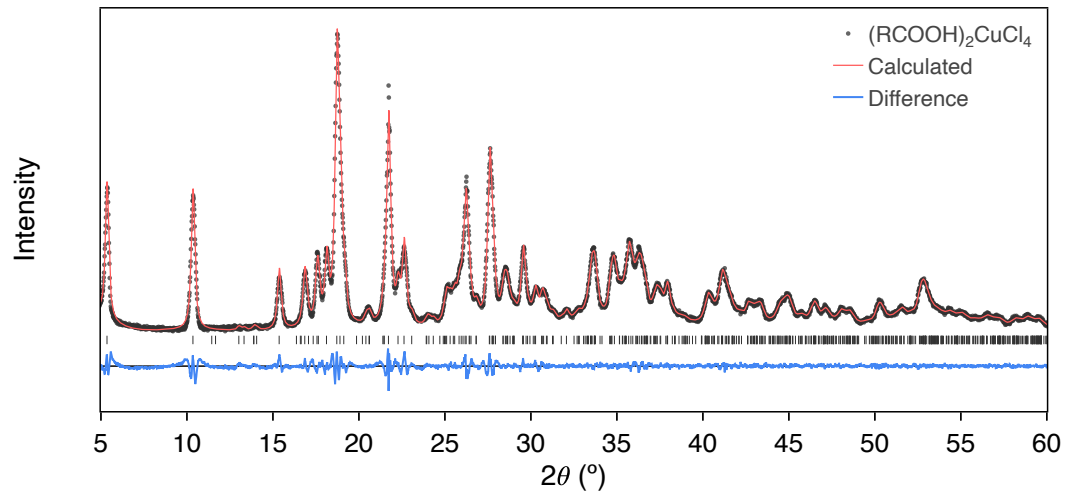


Figure S1| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $(\text{RCOOH})_2\text{CuCl}_4$. Reflection positions are shown as black tick marks. Radiation source is Cu-K α .

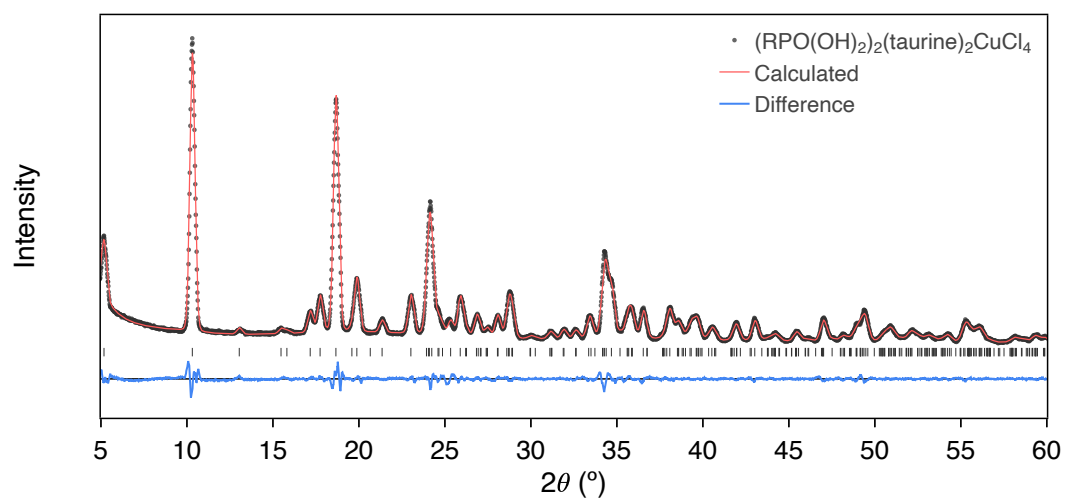


Figure S2| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $(\text{RPO}(\text{OH})_2)_2\text{CuCl}_4$. Reflection positions are shown as black tick marks. Radiation source is Cu-K α .

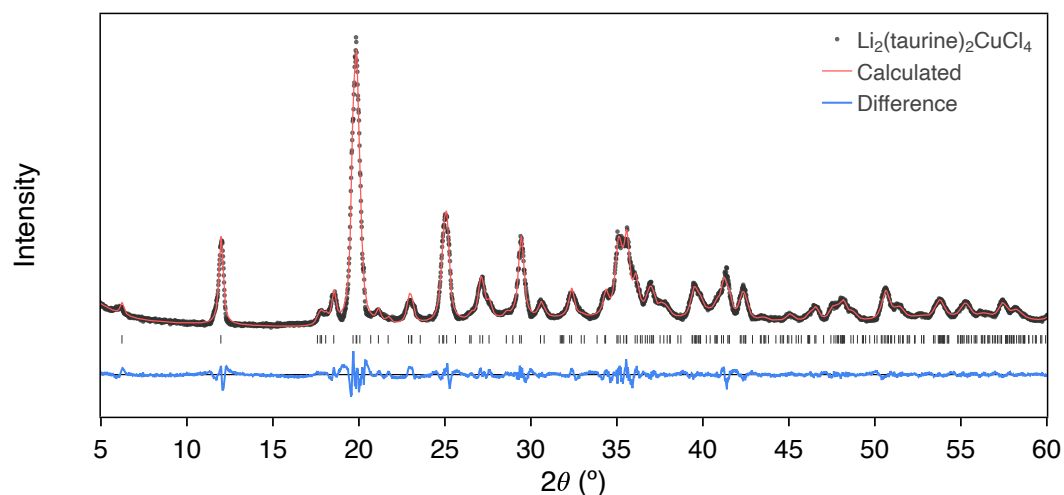


Figure S3| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $\text{Li}_2(\text{aurine})_2\text{CuCl}_4$. Reflection positions are shown as black tick marks. Radiation source is Cu-K α .

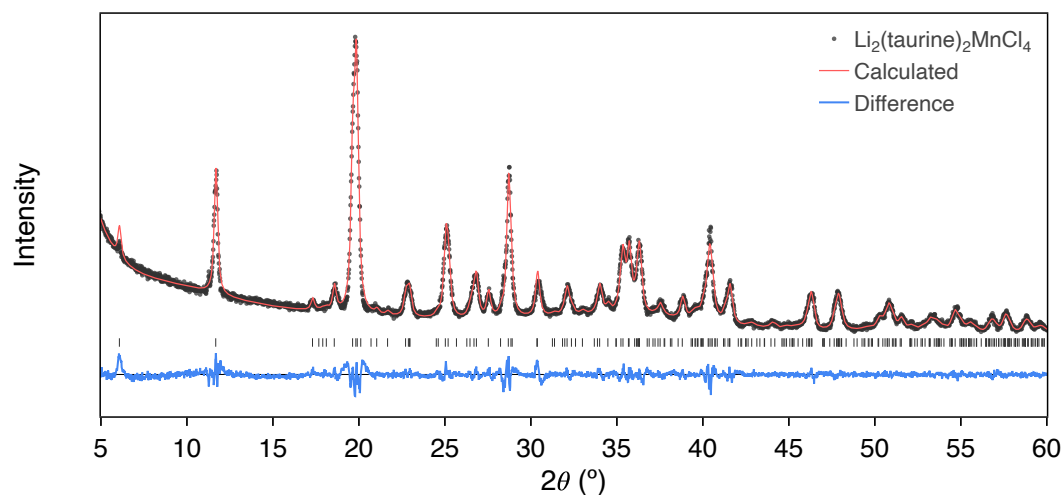


Figure S4| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $\text{Li}_2(\text{aurine})_2\text{MnCl}_4$. Reflection positions are shown as black tick marks. Radiation source is Cu-K α .

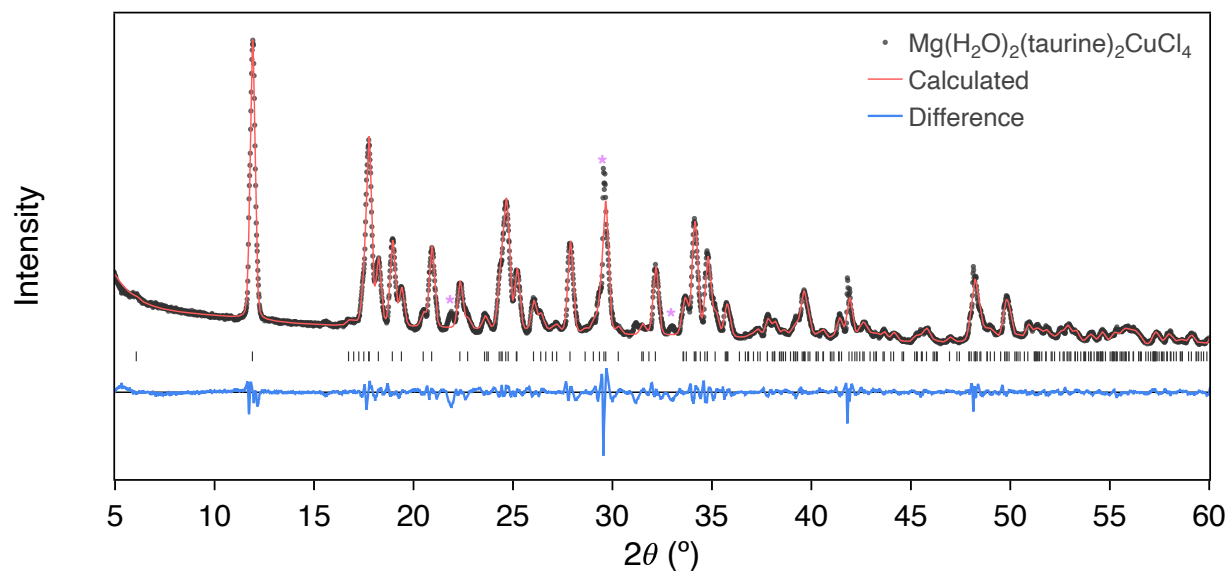


Figure S5| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $(\text{Mg}(\text{H}_2\text{O})_2)(\text{taurine})_2\text{CuCl}_4$. The starred peaks are consistent with a MgCl_2 impurity. Reflection positions are shown as black tick marks. Radiation source is $\text{Cu-K}\alpha$.

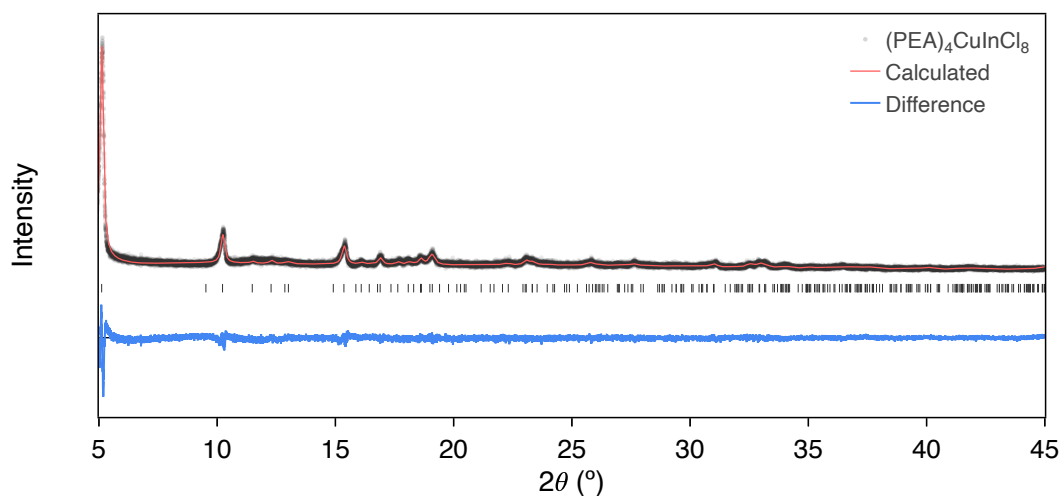


Figure S6| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $(\text{PEA})_4\text{CuInCl}_8$. Reflection positions are shown as black tick marks. Radiation source is $\text{Cu-K}\alpha$.

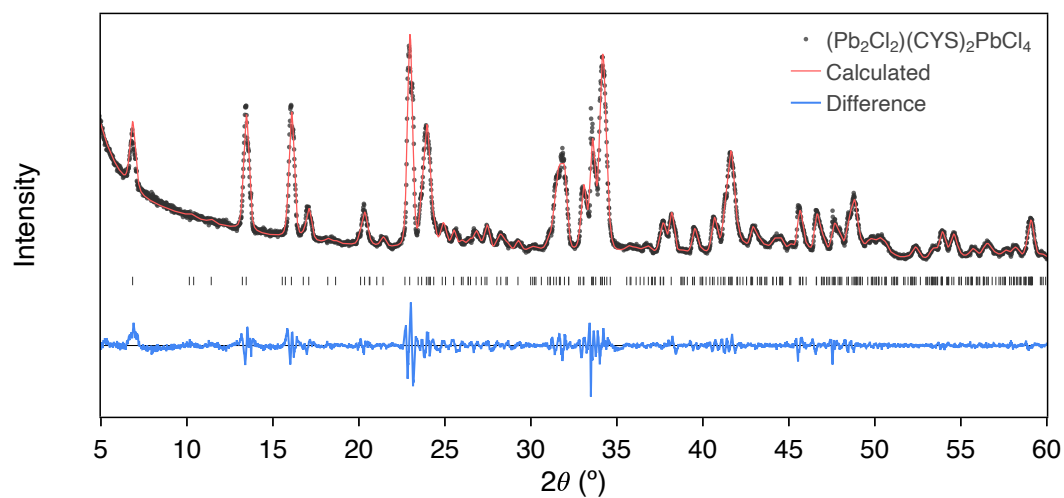


Figure S7| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $(\text{Pb}_2\text{Cl}_2)(\text{CYS})_2\text{PbCl}_4$. Reflection positions are shown as black tick marks. Radiation source is Cu-K α .

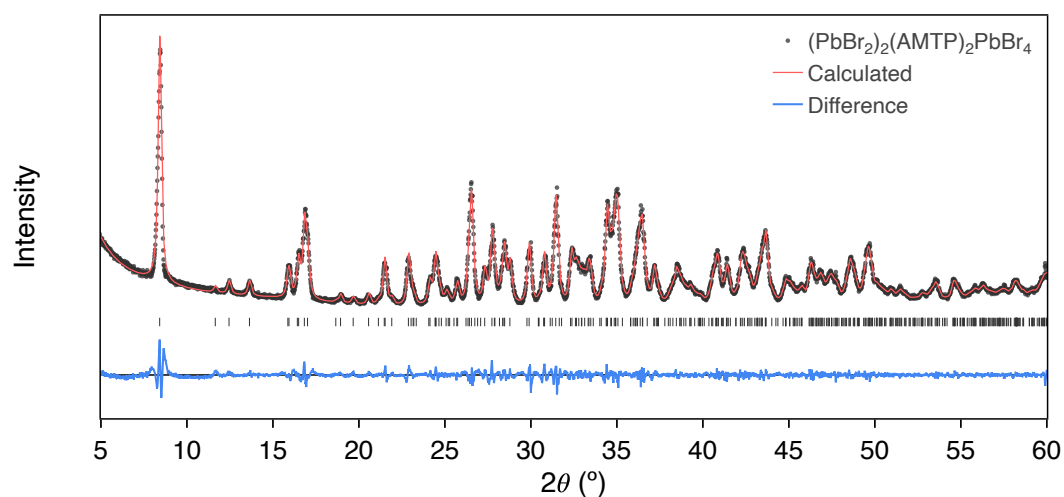


Figure S8| Whole diffraction pattern profile fitting using the LeBail method for the powder X-ray diffraction pattern of the compound $(\text{PbBr}_2)_2(\text{AMTP})_2\text{PbBr}_4$. Reflection positions are shown as black tick marks. Radiation source is Cu-K α .

Table S1. Crystallographic Data

	(RCOOH) ₂ CuCl ₄ ^a	(RPO(OH) ₂) ₂ CuCl ₄ ^b	(H ₃ O) ₂ (taurine) ₂ CuCl ₄	Li ₂ (taurine) ₂ CuCl ₄	(Mg(H ₂ O) ₂)(taurine) ₂ CuCl ₄
Formula	C ₁₆ H ₂₀ N ₂ O ₄ CuCl ₄	C ₆ H ₂₂ N ₂ O ₆ P ₂ CuCl ₄	Cu ₄ H ₂₀ N ₂ O ₈ Cl ₄ S ₂	CuLi ₂ C ₄ H ₁₄ N ₂ O ₆ Cl ₄ S ₂	CuMgC ₄ H ₁₈ N ₂ O ₈ Cl ₄ S ₂
Temperature (K)	296(2)	296(2)	100(2)	296(2)	100(2)
Crystal System	Triclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space Group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.9839(10), 8.1112(11), 17.998(3)	7.332, 7.3324(3), 34.6237(15)	15.2973(7), 7.8013(3), 7.2777(3)	10.391(2), 30.899(6), 5.1071(9)	5.2002(3), 30.226(2), 5.3197
α , β , γ (°)	100.450(5), 90.610(5), 92.308(5)	90/90/90	90, 103.742(2), 90	90, 90, 90	90, 92.661(2), 90
<i>V</i> (Å ³)	1001.6(2)	1861.41(11)	843.65(6)	1639.8(5)	835.24(10)
<i>Z</i>	2	8	2	4	2
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073	Synchrotron, 0.72880	Mo K α , 0.71073	Mo K α , 0.71073
2 θ Range for Data Collection (°)	5.112 to 50.484	4.71 to 50.48	5.62 to 68.36	5.28 to 59.82	5.40 to 56.77
Completeness to 2 θ	99.9% (2 θ = 50.484°)	99.9% (2 θ = 52.722°)	100.0% (2 θ = 56.548°)	100.0% (2 θ = 57.39°)	99.4% (2 θ = 56.878°)
Data / Restraints / Parameters	5137/0/257	1892/2/106	2092 / 6 / 112	2145 / 0 / 113	2116 / 0 / 128
Goodness of Fit on <i>F</i> ²	1.059	1.130	1.079	1.075	1.051
<i>R</i> ₁ ^c , <i>wR</i> ₂ ^d (<i>I</i> > 2 σ (<i>I</i>))	0.0336, 0.0796	0.0186, 0.0486	0.0170, 0.0448	0.0269, 0.0648	0.0228, 0.0529
<i>R</i> ₁ ^c , <i>wR</i> ₂ ^d (all data)	0.0526, 0.0866	0.0198, 0.0499	0.0171, 0.0449	0.0373, 0.0688	0.0285, 0.549
Largest Diff. Peak and Hole (e Å ⁻³)	0.759 and -0.296	0.506 and -0.250	0.431 and -0.296	0.467 and -0.343	0.452 and -0.425

^aRCOOH⁺ = 4-(ammoniomethyl)-benzoic acid. ^bRPO(OH)₂⁺ = 3-(ammoniopropyl)-phosphonic acid. ^c*R*₁ = $\sum||F_o| - |F_c|| / \sum|F_o|$. ^d*wR*₂ = $\{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

Table S2. Crystallographic Data

	(PEA) ₂ CuInCl ₈ ^a	(Cu ₂ Cl ₂) ₂ (HIS) ₄ CuInCl ₈ ^b	(Pb ₂ Cl ₂)(CYS) ₂ PbCl ₄ ^c	(PbBr ₂) ₂ (AMTP) ₂ PbBr ₄ ^d	Li ₂ (taurine) ₂ MnCl ₄
Formula	C ₃₂ H ₄₈ N ₄ Cl ₈ CuIn	C ₂₀ H ₄₄ N ₁₂ Cl ₁₆ Cu ₅ In	C _{3.72} H _{7.44} Cl _{6.07} N _{1.86} Pb ₃ S _{1.93}	C ₁₂ H ₂₈ Br ₈ N ₂ O ₂ Pb ₃	Li ₂ MnC ₄ H ₁₄ N ₂ O ₆ S ₂ Cl ₄
Temperature (K)	296(2)	296.15	296(2)	100(2)	296(2)
Crystal System	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>Ima</i> 2	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.3546(10), 11.0531(6), 10.8545(6)	7.6445(3), 15.1306(6), 20.2075(8)	53.510(5), 8.8064(7), 7.4849(6)	22.1203(7), 8.3159(3), 7.8356(2)	10.2356(7), 31.469(2), 5.0585(3)
α , β , γ (°)	90, 95.419(2), 90	98.7690(10), 95.3670(10), 90.0130(10)	90, 90, 90	90, 99.313(2), 90	90, 90, 90
<i>V</i> (Å ³)	2072.8(2)	2299.62(16)	3527.1(5)	1422.36(8)	1629.38(18)
<i>Z</i>	2	2	8	4	4
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073	Mo K α , 0.71073	Synchrotron, 0.7749	Mo K α , 0.71073
2 θ Range for Data Collection (°)	4.37 to 50.48	5.36 to 51.22	5.16 to 59.14	6.11 to 69.43	5.18 to 56.56
Completeness to 2 θ	99.8% (2 θ = 50.83°)	99.9% (2 θ = 51.378°)	99.5% (2 θ = 59.44°)	99.8% (2 θ = 62.23°)	99.9% (2 θ = 50.48°)
Data / Restraints / Parameters	3815/0/190	8751 / 0/ 494	5043 / 1 / 180	3536 / 75 / 125	2057/0/101
Goodness of Fit on <i>F</i> ²	1.034	1.023	1.040	1.018	1.101
<i>R</i> ₁ ^e , <i>wR</i> ₂ ^f (<i>I</i> > 2 σ (<i>I</i>))	0.0325, 0.0669	0.0419, 0.0862	0.0319, 0.0837	0.0324, 0.0480	0.0261, 0.0592
<i>R</i> ₁ ^e , <i>wR</i> ₂ ^f (all data)	0.0514, 0.0762	0.0842, 0.1029	0.0427, 0.0885	0.0532, 0.0519	0.0342, 0.0638
Largest Diff. Peak and Hole (e Å ⁻³)	0.463 and −0.366	1.537 and −0.778	2.382 and −1.725	0.431 and −0.296	0.79 and −0.36

^aPEA⁺ = 2-phenethylammonium, ^bHIS²⁺ = histammonium. ^cCYS = cysteammonium. ^dAMTP⁺ = 4-(aminomethyl)-tetrahydropyran. ^e*R*₁ = $\sum||F_o| - |F_c||/\sum|F_o|$. ^f*wR*₂ = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S3 | Unit cells determined from Le Bail refinement of powder X-ray diffraction data.

	(RCOOH) ₂ CuCl ₄	(RPO(OH) ₂) ₂ CuCl ₄	Li ₂ (taurine) ₂ CuCl ₄	Li ₂ (taurine) ₂ MnCl ₄
Space group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	6.9952(4)	7.4117(6)	10.354(4)	10.3036(8)
<i>b</i> (Å)	8.1189(12)	7.3951(5)	30.7756(12)	31.581(2)
<i>c</i> (Å)	17.999(5)	34.4470(17)	5.105(2)	5.0801(4)
α (°)	100.395(12)	90	90	90
β (°)	90.573(5)	90	90	90
γ (°)	92.277(3)	90	90	90
<i>V</i> (Å ³)	1004.53(15)	1888.18(19)	1627(2)	1656.3(3)
<i>wR</i>	2.9%	3.4%	4.6%	4.4%

Table S4 | Unit cells determined from Le Bail refinement of powder X-ray diffraction data.

	(Mg(H ₂ O) ₂)(taurine) ₂ CuCl ₄	(PEA) ₄ CuInCl ₈	(Pb ₂ Cl ₂)(CYS) ₂ PbCl ₄	(PbBr ₂) ₂ (AMTP) ₂ PbBr ₄
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Ima</i> 2	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	5.211(2)	17.373(6)	53.447(2)	22.238(6)
<i>b</i> (Å)	30.322(19)	11.016(2)	8.8058(4)	8.3915(15)
<i>c</i> (Å)	5.373(3)	10.831(4)	7.4850(3)	7.8942(16)
α (°)	90	90	90	90
β (°)	92.110(9)	94.98(4)	90	98.944(6)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	848.3(13)	2064.9(9)	3522.8(3)	14.552(8)
<i>wR</i>	5.46%	16.25%	6.98%	5.24 %

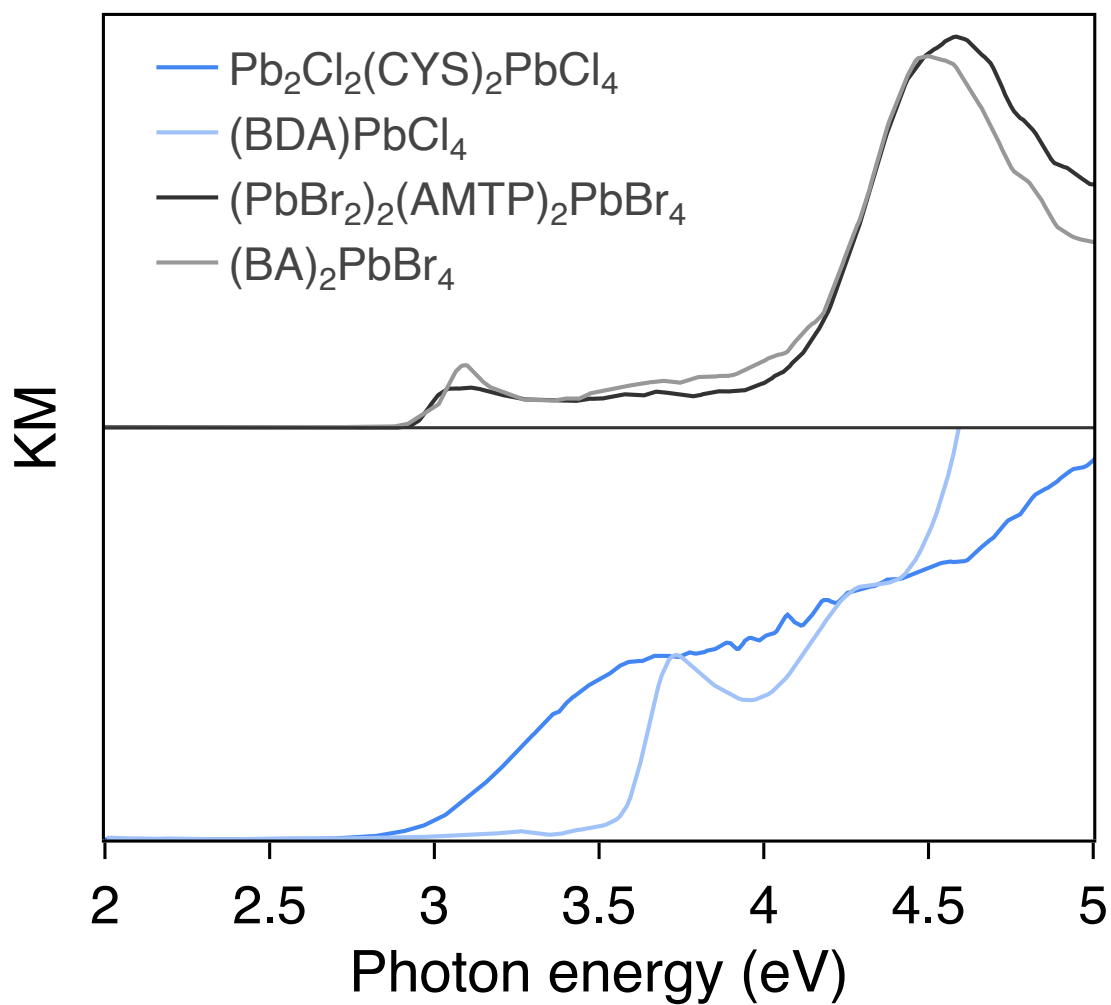


Figure S9| Room-temperature UV-vis diffuse reflectance spectra for the heterostructures $(\text{PbBr}_2)_2(\text{AMTP})_2\text{PbBr}_4$ and $(\text{Pb}_2\text{Cl}_2)(\text{CYS})_2\text{PbCl}_4$ compared to those for the layered perovskites $(\text{BA})_2\text{PbBr}_4$ (BA^+ = butylammonium) and $(\text{BDA})\text{PbCl}_4$ (BDA^{2+} = 1,4-butanediammonium). All samples are powders. Reflectance spectra were converted to pseudo-absorbance spectra using the Kubelka-Munk (KM) equation.

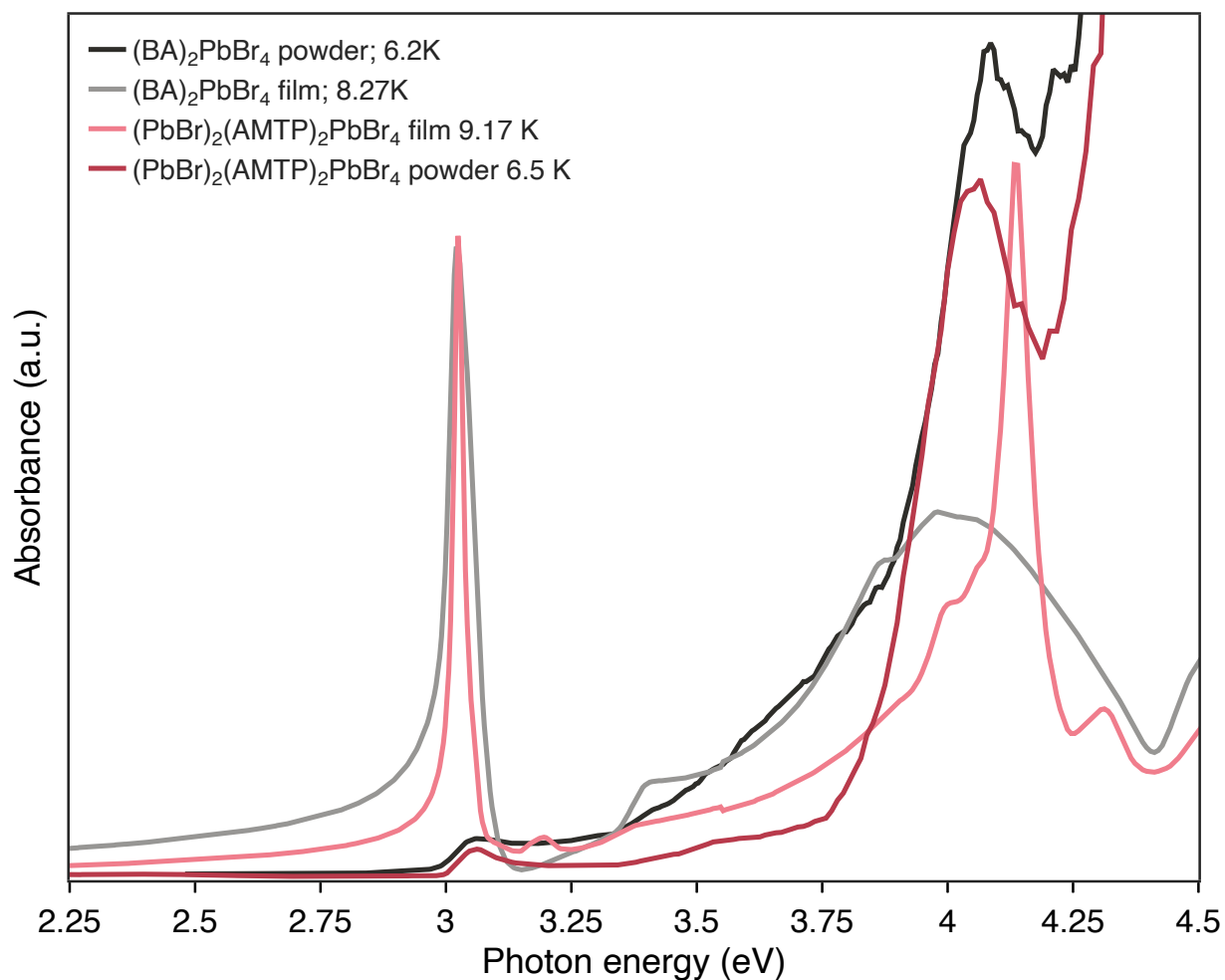


Figure S10 | Comparisons between the low-temperature diffuse reflectance spectra (collected on powders; plotted as Kubelka-Munk transformed pseudo-absorbance) and transmittance measurements (collected on thin films) for the heterostructure $(\text{PbBr}_2)_2(\text{AMTP})_2\text{PbBr}_4$ and the layered perovskite $(\text{BA})_2\text{PbBr}_4$ (BA^+ = butylammonium).

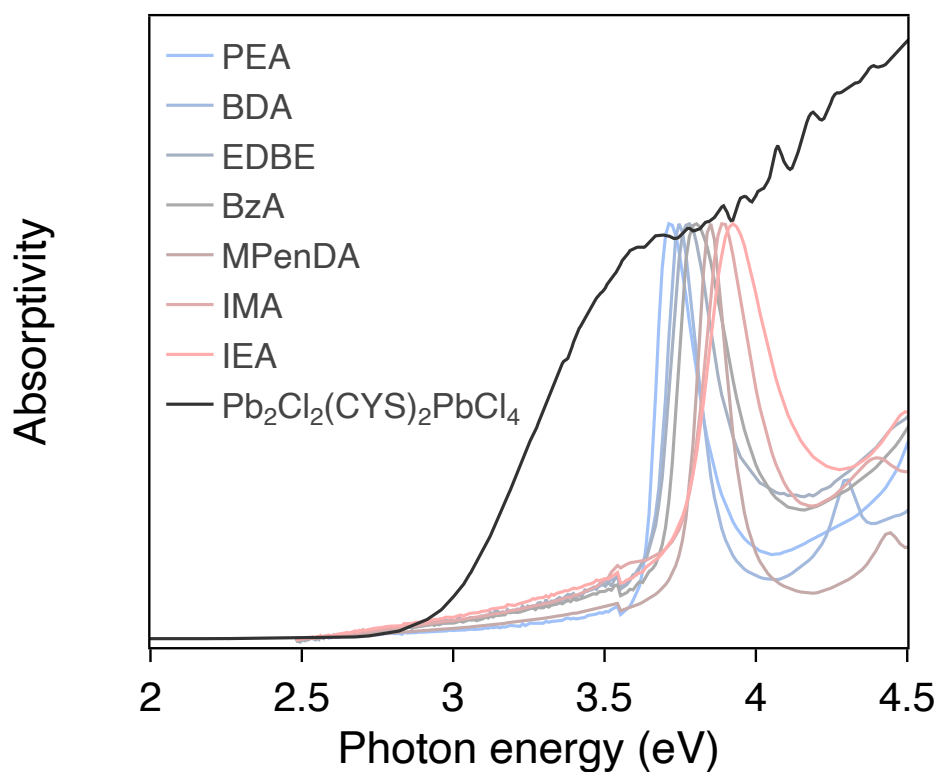


Figure S11 | Comparison of the room-temperature diffuse reflectance spectrum of $(\text{Pb}_2\text{Cl}_2)(\text{CYS})_2\text{PbCl}_4$ powder (plotted as Kubelka-Munk transformed pseudo-absorbance) and several (001) layered lead chloride perovskite films with different ‘A-site’ cations: BzA^+ = Benzylammonium, PEA^+ = 2-phenethylammonium, MPenDA^+ = 2-methyl-1,5-pentanediammonium, BDA^{2+} = 1,4-butanediammonium, EDBE^{2+} = 2,2’-(ethylenedioxy)bis(ethylammonium), and IMA^+ = (1H-imidazol-2-yl)methan ammonium, IEA^+ = 2-(1H-imidazol-2-yl)ethan-1-ammonium. Likely due to the 3D connectivity of the Pb–Cl framework in $(\text{Pb}_2\text{Cl}_2)(\text{CYS})_2\text{PbCl}_4$, it does not as readily crystallize as films.

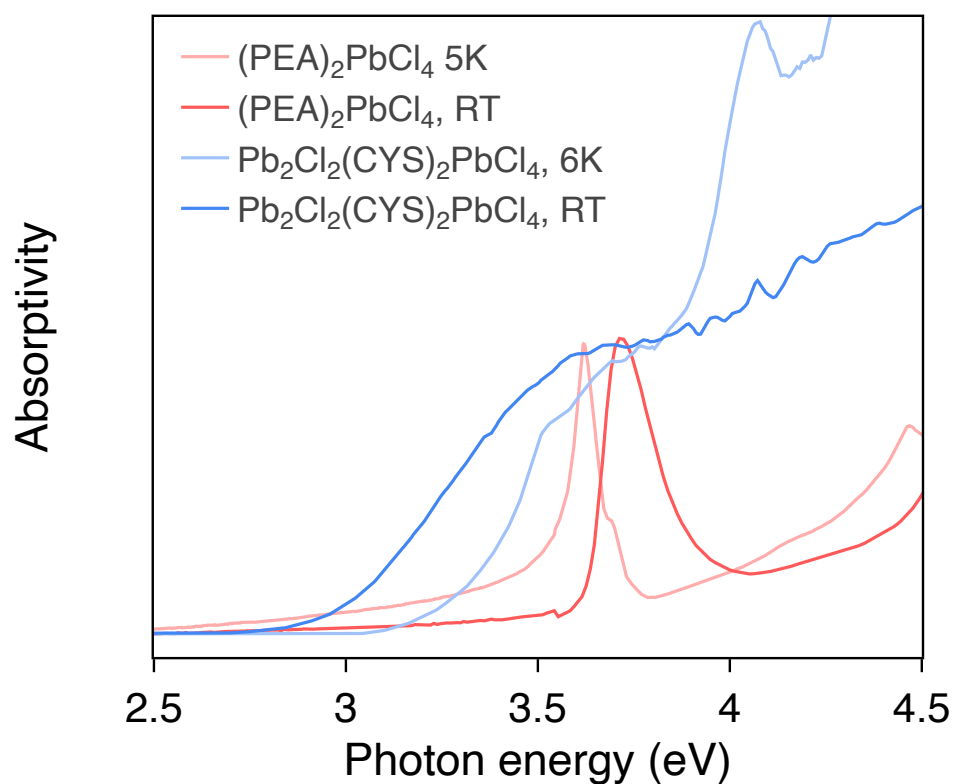


Figure S12 Comparison of the UV-*vis* absorption spectra for $(\text{Pb}_2\text{Cl}_2)(\text{CYS})_2\text{PbCl}_4$ powder (plotted as Kubelka-Munk transformed pseudo-absorbance) and $(\text{PEA})_2\text{PbCl}_4$ ($\text{PEA}^+ = 2\text{-phenethylammonium}$) thin films at room temperature and near liquid helium temperatures (5–6 K). The perovskite $(\text{PEA})_2\text{PbCl}_4$ has one of the lowest known exciton absorption energies for a (001) lead chloride perovskite (see **Figure S11**).

Photoluminescence spectroscopy

Low-temperature static photoluminescence spectra were acquired using a Horiba Jobin-Yvon Nanolog fluorimeter equipped with a 450-W xenon lamp and R928S detector. Samples were cooled using liquid nitrogen with a Janis ST-100H cryostat, with samples placed directly on the cold finger covered with AT205 Matt Black Foil Advanced Gaffa® Tape. Powder samples were prepared by first grinding crystals in a mortar and pestle or ball-milled using a Fritsch Pulverisette 7 planetary ball mill, followed by suspension in toluene with a solution of poly(methyl methacrylate) (average $M_w \approx 120,000$ by GPC) in toluene. This slurry was then allowed to dry at room temperature.

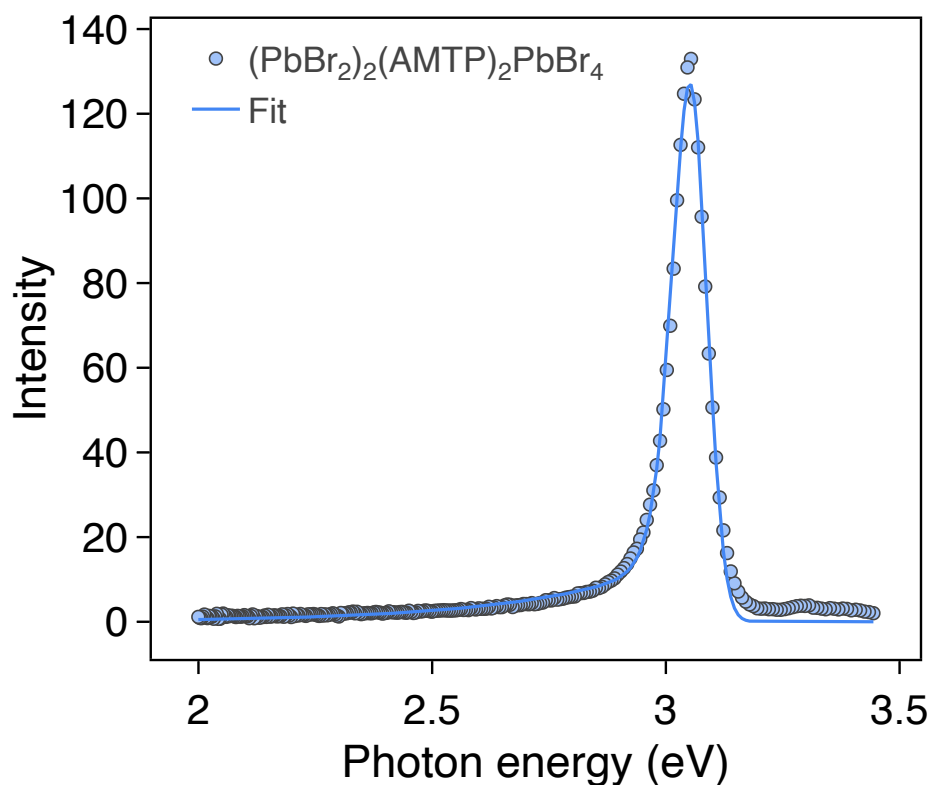


Figure S13 Photoluminescence spectrum for the heterostructure $(\text{PbBr}_2)_2(\text{AMTP})_2\text{PbBr}_4$ at room temperature. The spectrum was fit using an exponentially modified gaussian with two decay rates.

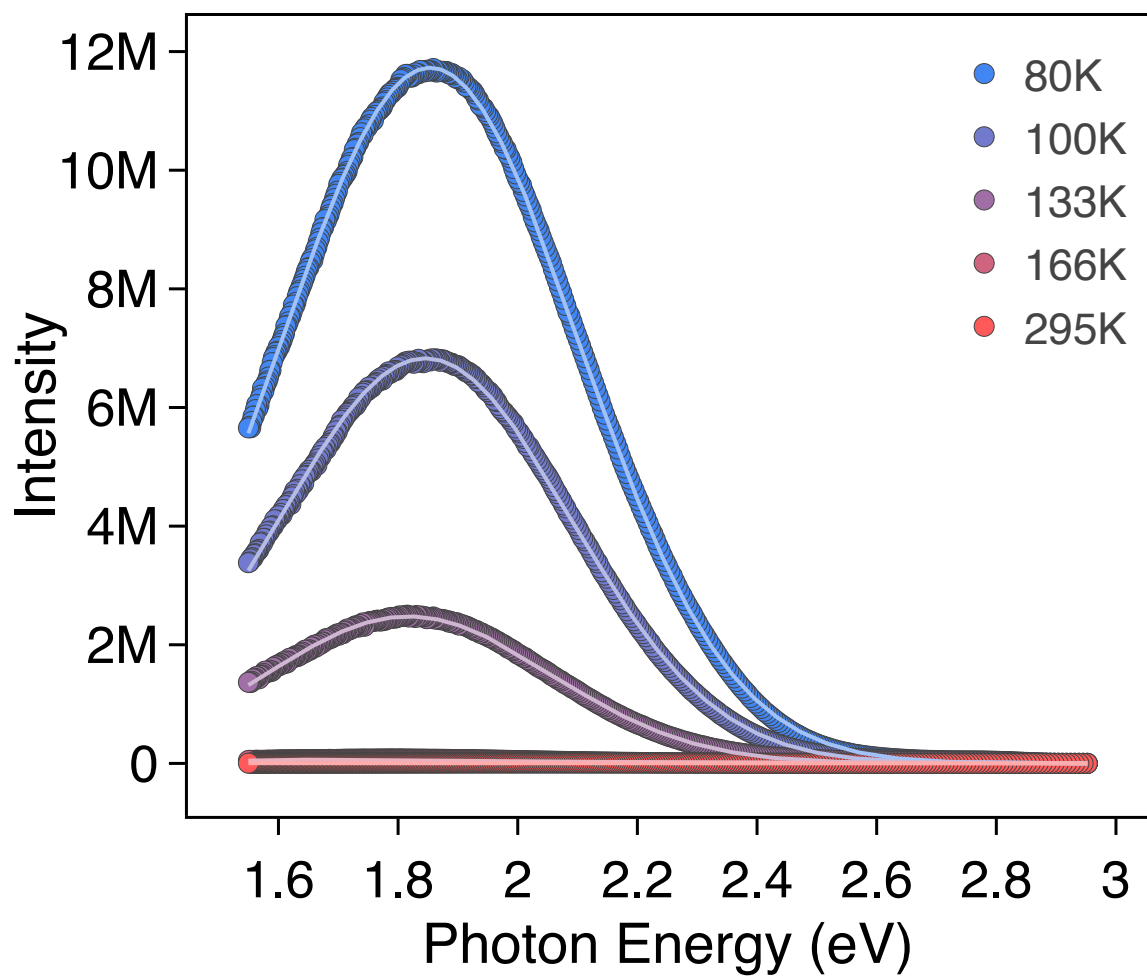


Figure S14 | Photoluminescence spectra for the heterostructure $(\text{Pb}_2\text{Cl}_2)(\text{CYS})_2\text{PbCl}_4$. The spectra were fit (lines) using a gaussian function.

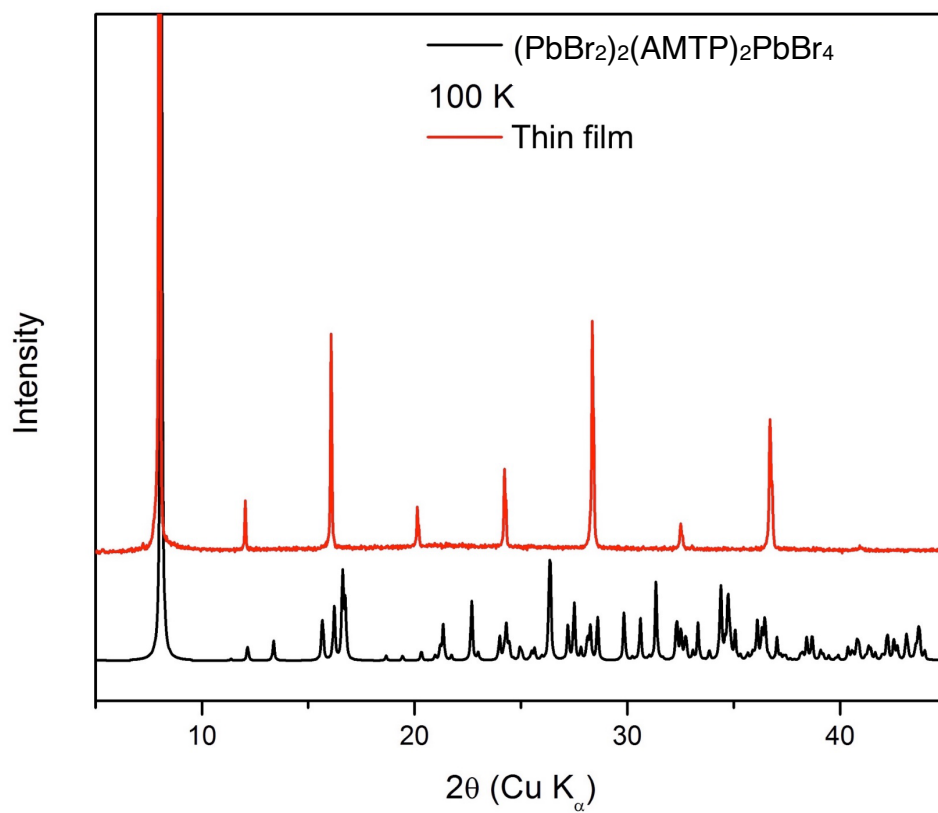


Figure S15 Room temperature powder X-ray diffraction pattern of a $(\text{PbBr}_2)_2(\text{AMTP})_2\text{PbBr}_4$ oriented film on quartz compared to the simulated powder pattern of the structure. Radiation source is $\text{Cu-K}\alpha$.