Aziridinium Cation Templating 3D Lead Halide Hybrid Perovskites

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ELECTRONIC SUPPLEMENTARY INFORMATION

SYNTHESIS AND CRYSTALLIZATION

Note: these perovskites are unstable in acidic media and should be processed very quickly. Important: aziridine is a highly reactive and volatile compound; it should be operated with precautions under ventilation hood only.

Synthesis of (AzrH)PbI₃ bulk

Lead iodide (231 mg, 0.5 mmol, 1 eq.) was dissolved in conc. hydroiodic acid (c.a. 57 %, 1 ml) and diluted with acetonitrile (2 ml). Aziridine (129 mg, 3 mmol, 6 eq.) was dissolved in acetonitrile (0.5 ml) and added to the first solution under vigorous stirring. A black precipitate was formed immediately. It was filtered off and dried in air. Yield is 35 %.

Synthesis of (AzrH)PbBr₃ bulk

Lead bromide (184 mg, 0.5 mmol, 1 eq.) was dissolved in conc. hydrobromic acid (c.a. 48 %, 2 ml) and diluted with water (4 ml). Aziridine (129 mg, 3 mmol, 6 eq.) was dissolved in water (1 ml) and added to the first solution. An orange precipitate was formed immediately. It was filtered off and dried in air. Yield is 96 %.

Synthesis of (AzrH)PbCl₃ bulk

Lead chloride (139 mg, 0.5 mmol, 1 eq.) was mixed with conc. hydrochloric acid (c.a. 38 %, 4 ml) and heated to 50 °C until PbCl₂ is dissolved completely. Aziridine (129 mg, 3 mmol, 6 eq.) was dissolved in water (1 ml) and added to the first solution. A white precipitate was formed within 10 min. It was filtered off and dried in air. Yield is 23 %.

Crystallization of (AzrH)PbI₃ bulk

Lead iodide (23,1 mg, 0.05 mmol, 1 eq.) was dissolved in conc. hydroiodic acid (c.a. 57 %, 0.2 ml) and put in a 1 ml vial. This small vial was placed in a larger one (5 ml) containing aziridine (43 mg, 1 mmol, 20 eq.) in acetonitrile (1 ml). After vapor diffusion of aziridine small black crystals were formed on the top of the first solution. They were separated from solution after 1 h.

Crystallization of (AzrH)PbBr3 bulk

Lead bromide (184 mg, 0.5 mmol, 1 eq.) was dissolved in conc. hydrobromic acid (c.a. 48 %, 2 ml) and diluted with water (4 ml). Aziridine (129 mg, 3 mmol, 6 eq.) was dissolved in water (1 ml) and added to the first solution. An orange precipitate was formed immediately. The mixture was heated to 60 °C and cooled to room temperature. Orange crystals were formed on the tube walls within 10 min.

Crystallization of (AzrH)PbCl3 bulk

The precipitate obtained upon the synthesis of (AzrH)PbCl3 bulk contains small colorless crystals suitable for an X-ray diffraction experiment.

PHYSICAL CHARACHTERIZATION

X-ray Diffraction. Single-crystal X-ray diffraction data were collected on Oxford-Diffraction XCALIBUR Eos CCD diffractometer with graphite-monochromated Mo-Kα radiation at 293 K. The unit cell determination and data integration were carried out using the CrysAlisPro package from Oxford Diffraction. Multi-scan correction for absorption was applied. The structures were solved with ShelXT program using intrinsic phasing method and refined by full-matrix least-squares method on F² with ShelXL.^{1,2} Olex2 was used as an interface to the ShelX programs.³ Lead and halogen atoms were refined anisotropically. Aziridinium cation is higly disordered and its C and N atoms were refined isotropically. Detailed crystallographic data are provided in crystallographic tables **S3-S7**. Specific details of each refinement are given in the crystallographic information files (CIF-files deposition numbers 2153152-2153154). PXRD patterns were recorded on Benchtop Rigaku Miniflex 600 and Shimadzu XRD 6000 diffractometers.

Spectroscopy. UV-Vis spectra were recorded on Varian Cary 50 UV-Vis Spectrophotometer in transmission mode using powders of perovskites grinded over a quarts substrate. IR spectra were recorded on Perkin Elmer spectrometer BX II in ATR mode.



Figure S1. Experimental and calculated PXRD patterns of (AzrH)PbCl₃.



Figure S2. Experimental and calculated PXRD patterns of (AzrH)PbBr3.



Figure S3. Experimental and calculated PXRD patterns of $(AzrH)PbI_3$. Minor peaks at 21-23 ° and 29-30 ° can be from $(ICH_2CH_2NH_3)_2PbI_4$ impurities, but the peaks are too small for a definite identification of this phase.



Figure S4. PXRD patterns of initial and stored for 1.5 months (AzrH)PbCl₃.



Figure S5. PXRD patterns of initial and stored for 1.5 months (AzrH)PbBr₃.



Figure S6. PXRD patterns of initial and stored for 1.5 months (AzrH)PbI₃. The last PXRD pattern is of lower quality because of a smaller quantity of the perovskite used for the measurement.



Figure S7. IR spectra (ATR) of (AzrH)PbHal₃ perovskites (Hal = Cl, Br, I).



Figure S8. Thermogravimetric curves for (AzrH)PbHal₃ perovskites (Hal = Cl – red, Br – blue, I – green). Temperature range is 30 - 700 °C, heating rate is 10 °C/min.

Table S1. Cell parameters (a, Å) of aziridinium lead halide perovskites in comparison with methylammonium and formamidinium compounds.

	Azr	MA	FA
Cl	5.7610	5.68^{4}	5.7379 ⁵
Br	5.9739	5.92^{4}	5.96976 ⁶
Ι	6.3640	6.27^{4}	6.3532^{7}

Table S2. Optical bandgaps (eV) of aziridinium lead halide perovskites in comparison with methylammonium and formamidinium compounds.

	Azr	MA	FA
Cl	2.99	2.97^{8}	3.00^{9}
Br	2.27	2.31^{10}	2.27^{10}
Ι	1.52	1.59^{10}	1.52^{10}

CRYSTALLOGRAPHIC TABLES

Identification code	(AzrH)PbCl ₃	(AzrH)PbBr ₃	(AzrH)PbI ₃
Empirical formula	C ₂ Cl ₃ NPb	Br ₃ C ₂ NPb	C ₂ I ₃ NPb
Formula weight	351.57	484.95	625.92
Temperature/K	293.00	293.00	293(2)
Crystal system	cubic	cubic	cubic
Space group	Pm-3m	Pm-3m	Pm-3m
a/Å	5.7610(2)	5.9739(3)	6.3640(4)
b/Å	5.7610(2)	5.9739(3)	6.3640(4)
c/Å	5.7610(2)	5.9739(3)	6.3640(4)
$\alpha/^{\circ}$	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å ³	191.20(2)	213.19(3)	257.75(5)
Z	1	1	1
$\rho_{calc}g/cm^3$	3.053	3.777	4.033
µ/mm ⁻¹	23.000	33.745	25.270
F(000)	152.0	206.0	260.0
Crystal size/mm ³	$0.14 \times 0.11 \times 0.1$	$0.15 \times 0.13 \times 0.12$	$0.01 \times 0.01 \times 0.01$
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo K α (λ = 0.71073)
20 range for data collection/°	7.074 to 57.602	6.82 to 58.276	6.402 to 57.416
Index ranges	$-7 \le h \le 2, -4 \le k \le 7, -4 \le l \le 4$	$-2 \le h \le 6, -4 \le k \le 7, -8$ $\le 1 \le 4$	$-8 \le h \le 4, -5 \le k \le 5, -3 \le 1 \le 8$
Reflections collected	215	264	298
Independent	71 [$R_{int} = 0.0309$,	$80 [R_{int} = 0.0498,$	92 [$R_{int} = 0.0371$,
reflections	$R_{sigma} = 0.0335$]	R _{sigma} = 0.0492]	$R_{sigma} = 0.0423$]
Data/restraints/para meters	71/0/7	80/0/7	92/0/6
Goodness-of-fit on F ²	1.170	1.197	1.066
Final R indexes	$R_1 = 0.0199, wR_2 =$	$R_1 = 0.0338, wR_2 =$	$R_1 = 0.0318, wR_2 =$
[I>=2σ (I)]	0.0431	0.0693	0.0470
Final R indexes [all	$R_1 = 0.0199, wR_2 =$	$R_1 = 0.0338, wR_2 =$	$R_1 = 0.0344, wR_2 =$
data]	0.0431	0.0694	0.0476
Largest diff. peak/hole / e Å ⁻³	0.83/-1.49	0.82/-0.84	1.14/-0.70

Table S3. Crystal data and structure refinement.

Atom	x	у	z	U(eq)		
(AzrH)PbCl	(AzrH)PbCl ₃					
Pb1	5000	5000	5000	23.0(5)		
Cl1	5000	0	5000	66.2(17)		
C1	0	8970(60)	8970(60)	120(30)		
N1	0	8970(60)	8970(60)	120(30)		
(AzrH)PbB1	(AzrH)PbBr ₃					
Pb1	0	0	0	21.1(9)		
Br1	0	0	5000	62.5(11)		
C1	5980(60)	5980(60)	5000	70(30)		
N1	5980(60)	5980(60)	5000	70(30)		
(AzrH)PbI ₃						
Pb1	10000	10000	10000	27.5(4)		
I1	10000	5000	10000	74.2(7)		
C1	14100(30)	5000	14100(30)	70(20)		
N1	14100(30)	5000	14100(30)	70(20)		

Table S4 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Table S5 Anisotropic Displacement Parameters ($Å^2 \times 10^3$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U11	U_{22}	U 33	U23	U13	U12
(AzrH)PbCl ₃						
Pb1	23.0(5)	23.0(5)	23.0(5)	0	0	0
C11	85(3)	28(2)	85(3)	0	0	0
(AzrH)PbBr ₃						
Pb1	21.1(9)	21.1(9)	21.1(9)	0	0	0
Br1	83.7(17)	83.7(17)	20.1(14)	0	0	0
(AzrH)PbI3						
Pb1	27.5(4)	27.5(4)	27.5(4)	0	0	0
I1	100.2(11)	22.2(9)	100.2(11)	0	0	0

 Table S6 Bond Lengths.

	(AzrH)PbCl ₃	(AzrH)PbBr ₃	(AzrH)PbI ₃
Pb–Hal (Å)	2.8805(1)	2.9870(2)	3.1820(2)
C1C1/N1 (Å)	1.45(4)	1.43(3)	1.40(2)

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