Fine tuning of optical band gap in mixed halide aziridinium lead perovskites

Olesia I. Kucheriv,[a] Dmytro A. Haleliuk,[a] Sergiu Shova,[b] Il'ya A. Gural'skiy*[a]

[a.] *Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska St. 64, 01601 Kyiv, Ukraine. E-mail: illia.guralskyi@univ.kiev.ua*
[b.] *Department of Inorganic Polymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Aleea Gr. Ghica Voda, 700487 Iasi, Romania*

Table S1. Goldschmidt's tolerance factors for **(AzrH)PbBr$_x$I$_{3-x}$** mixed halide perovskites.

x_{Br}	t
0.04	0.939
0.09	0.939
0.85	0.943
1.96	0.950
2.01	0.950
2.08	0.951
2.79	0.955

Values of effective atomic radii used for the calculations:

Ion	Radius (Å)
Pb^{2+}	1.19
Br^-	1.96
I^-	2.2
$AzrH^+$	2.30

r_{Xeff} was calculated from r(Br^-), r(I^-) and content of the corresponding halides in **(AzrH)PbBr$_x$I$_{3-x}$** products:

x_{Br}	x_I	Radius (Å)
0.04	2.96	2.20
0.09	2.91	2.19
0.85	2.15	2.13
1.96	1.04	2.04
2.01	0.99	2.04
2.08	0.92	2.03
2.79	0.21	1.98

Crystallographic tables

Table S2.1 Crystal data and structure refinement for **(AzrH)PbBr$_{0.04}$I$_{2.96}$**

Empirical formula	$Br_{0.04}C_2I_{2.96}NPb$
Formula weight	624.04
Temperature/K	250
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.35060(10)
Volume/Å^3	256.120(12)
Z	1
ρ_{calc}g/cm^3	4.046
μ/mm^{-1}	25.466
Crystal size/mm^3	0.8 × 0.5 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.416 to 61.71
Reflections collected	287
Independent reflections	287 [R_{sigma} = 0.0090]
Data/restraints/parameters	287/2/9
Goodness-of-fit on F^2	1.132
R_1 [I>=2σ (I)]	0.0300
wR_2 [all data]	0.0861

Table S2.2 Bond Lengths for **(AzrH)PbBr$_{0.04}$I$_{2.96}$**

	Length/Å
Pb1–Br1	3.17530(5)
Pb1–I1	3.17530(5)
C1–N1^1	1.43(3)
C1–C1^2	1.45(3)

$^1+z, +x, +y$; $^2-x, -y, -z$;

Table S2.3 Bond Angles for **(AzrH)PbBr$_{0.04}$I$_{2.96}$**

	Angle/°
Br1^1–Pb1–Br1	90.0
Br1–Pb1–Br1^2	180.0
I1–Pb1–Br1^3	90.0
I1–Pb1–Br1^2	180.0
Pb1^5–Br1–Pb1	180.0
Pb1^5–I1–Pb1	180.0
C1^7–N1–C1^4	61(2)
N1^8–C1–C1^6	59.6(11)

$^1+y, +z, 1+x$; $^2 1+x, +y, +z$; $^3+z, 1+x, +y$; $^4+y, +z, +x$; $^5-1+x, +y, +z$; $^6-x, -y, -z$; $^7-y, -z, -x$; $^8+z, -x, -y$

Table S3.1 Crystal data and structure refinement for **(AzrH)PbBr$_{0.09}$I$_{2.91}$**

Empirical formula	$Br_{0.09}C_2I_{2.91}NPb$
Formula weight	621.69
Temperature/K	250
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.33861(18)
Volume/Å^3	254.67(2)
Z	1
ρ_{calc}g/cm^3	4.054
μ/mm^{-1}	25.655
Crystal size/mm^3	0.12 × 0.08 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.428 to 59.358
Reflections collected	1083
Independent reflections	104 [R_{int} = 0.0195, R_{sigma} = 0.0101]
Data/restraints/parameters	104/2/9
Goodness-of-fit on F^2	1.250
R_1 [I>=2σ (I)]	0.0140,
wR_2 [all data]	0.0428

Table S3.2 Bond Lengths for **(AzrH)PbBr$_{0.09}$I$_{2.91}$**

	Length/Å
Pb1–I1	3.16931(9)
Pb1–Br1	3.16931(9)
C1–C1^1	1.45(2)
C1–N1^2	1.42(2)

$^1 -1-x, 1-y, -1-z$; $^2 +x, -z, -1+y$.

Table S3.3 Bond Angles for **(AzrH)PbBr$_{0.09}$I$_{2.91}$**

	Angle/°
I1^1–Pb1–I1	90.0
I1^1–Pb1–I1^4	180.0
Br1–Pb1–I1^3	90.0
Br1–Pb1–I1^2	180.0
Pb1^5–I1–Pb1	180.0
N1^9–C1–C1^8	59.3(7)
C1^6–N1–C1^7	61.3(14)
Pb1^5–Br1–Pb1	180.0

$^1 +x, -z, +y$; $^2 +x, -1+y, +z$; $^3 -y, +x, +z$; $^4 +x, -z, -1+y$; $^5 +x, 1+y, +z$; $^6 -1-x, 1+z, -y$; $^7 -y, -z, +x$; $^8 -1-x, 1-y, -1-z$; $^9 -1-z, 1-y, +x$.

Table S4.1 Crystal data and structure refinement for **(AzrH)PbBr$_{0.85}$I$_{2.15}$**

Empirical formula	$Br_{0.85}C_2I_{2.15}NPb$
Formula weight	585.98
Temperature/K	293
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.2570(2)
Volume/Å^3	244.96(2)
Z	1
ρ_{calc}g/cm^3	3.972
μ/mm^{-1}	90.091
Crystal size/mm^3	0.1 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	14.154 to 142.308
Reflections collected	195
Independent reflections	195 [R_{sigma} = 0.0187]
Data/restraints/parameters	195/2/9
Goodness-of-fit on F^2	1.185
R_1 [I>=2σ (I)]	0.0663
wR_2 [all data]	0.1852

Table S4.2 Bond Lengths for **(AzrH)PbBr$_{0.85}$I$_{2.15}$**

	Length/Å
Pb1–I1	3.12850(10)
Pb1–Br1	3.12850(10)
C1^1– N1^3	1.44(3)
C1^1– C1^2	1.45(4)

$^1 + z, -x, -y$; $^2 + z, +x, +y$; $^3 + y, +z, +x$.

Table S4.3 Bond Angles for **(AzrH)PbBr$_{0.85}$I$_{2.15}$**

	Angle/°
Br1^1–Pb1–Br1	90.0
Br1–Pb1–Br1^2	180.0
I1–Pb1–Br1^3	90.0
I1–Pb1–Br1^2	180.0
Pb1^4–Br1–Pb1	180.0
Pb1^4–I1–Pb1	180.0
C1^3–N1–C1^5	60(2)

$^1 + y, 1 + z, +x$; $^2 + x, +y, 1 + z$; $^3 + y, +z, +x$; $^4 + x, +y, -1 + z$; $^5 - y, +z, -x$;

Table S5.1 Crystal data and structure refinement for **(AzrH)PbBr$_{1.96}$I$_{1.04}$**

Empirical formula	$Br_{1.96}C_2I_{1.04}NPb$
Formula weight	533.82
Temperature/K	230
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.10960(10)
Volume/Å^3	228.054(11)
Z	1
ρ_{calc}g/cm^3	3.887
μ/mm^{-1}	72.969
Crystal size/mm^3	0.08 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	14.498 to 141.558
Reflections collected	570
Independent reflections	69 [R_{int} = 0.0174, R_{sigma} = 0.0079]
Data/restraints/parameters	69/2/9
Goodness-of-fit on F^2	1.227
R_1 [I>=2σ (I)]	0.0171
wR_2 [all data]	0.0578

Table S5.2 Bond Lengths for **(AzrH)PbBr$_{1.96}$I$_{1.04}$**

	Length/Å
Pb1–I1	3.05480(5)
Pb1–Br1	3.05480(5)
C1^1– N1	1.43(2)
C1^1– C1^2	1.45(2)

$^1 + x, 1 - z, 1 + y$; $^2 + x, -1 + z, 1 - y$.

Table S5.3 Bond Angles for **(AzrH)PbBr$_{1.96}$I$_{1.04}$**

	Angle/°
Br1^1–Pb1–Br1	90.0
Br1^1–Pb1–Br1^3	180.0
I1–Pb1–Br1^2	90.0
Pb1^4–Br1–Pb1	180.0
Pb1^4–I1–Pb1	180.0
C1^{10}–N1–C1^5	61.1(14)

$^1 1 + y, + z, + x$; $^2 + z, + x, + y$; $^3 + y, + z, + x$; $^4 + x, -1 + y, + z$; $^5 - y, 1 - z, 1 - x$; $^6 + y, -1 + z, 1 + x$.

Table S6.1 Crystal data and structure refinement for **(AzrH)PbBr$_{2.01}$I$_{0.99}$**

Empirical formula	$Br_{2.01}C_2I_{0.99}NPb$
Formula weight	531.47
Temperature/K	293
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.0891(2)
Volume/Å^3	225.77(2)
Z	1
ρ_{calc}g/cm^3	3.909
μ/mm^{-1}	30.871
Crystal size/mm^3	0.14 × 0.1 × 0.04
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.692 to 57.996
Reflections collected	232
Independent reflections	232 [R_{sigma} = 0.0411]
Data/restraints/parameters	232/1/9
Goodness-of-fit on F^2	1.001
R_1 [I>=2σ (I)]	0.0353
wR_2 [all data]	0.0847

Table S6.2 Bond Lengths for **(AzrH)PbBr$_{2.01}$I$_{0.99}$**

	Length/Å
Pb1–I1	3.04455(10)
Pb1–Br1	3.04455(10)
C1– N1	1.42(3)
C1– C1^1	1.45(14)

$^1 - x, - y, - z$.

Table S6.3 Bond Angles for **(AzrH)PbBr$_{2.01}$I$_{0.99}$**

	Angle/°
Br1^1–Pb1–Br1	90.0
Br1^1–Pb1–Br1^2	180.0
I1–Pb1–Br1^2	90.0
I1–Pb1–Br1^3	180.0
Pb1^4–Br1–Pb1	180.0
Pb1^4–I1–Pb1	180.0
C1–N1–C1^9	62(7)
N1–C1–C1^9	59(3)

$^1 + y, 1 + z, + x$; $^2 + y, + z, + x$; $^3 + x, + y, 1 + z$; $^4 + x, + y, - 1 + z$; $^5 - x, - y, - z$.

Table S7.1 Crystal data and structure refinement for **(AzrH)PbBr$_{2.08}$I$_{0.92}$**

Empirical formula	$Br_{2.08}C_2I_{0.92}NPb$
Formula weight	528.18
Temperature/K	250
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.0775(3)
Volume/Å^3	224.48(3)
Z	1
ρ_{calc}g/cm^3	3.907
μ/mm^{-1}	31.118
Crystal size/mm^3	0.1 × 0.08 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.704 to 58.578
Reflections collected	379
Independent reflections	83 [R_{int} = 0.0243, R_{sigma} = 0.0160]
Data/restraints/parameters	83/3/10
Goodness-of-fit on F^2	1.116
R_1 [I>=2σ (I)]	0.0176
wR_2 [all data]	0.0423

Table S7.2 Bond Lengths for **(AzrH)PbBr$_{2.08}$I$_{0.92}$**

	Length/Å
Pb1–I1	3.03875(15)
Pb1–Br1	3.03875(15)
C1^1– N1	1.433(15)
C1^1– C1^2	1.466(15)

$^1 - z, + y, + x$; $^2 - y, + z, - x$.

Table S7.3 Bond Angles for **(AzrH)PbBr$_{2.08}$I$_{0.92}$**

	Angle/°
Br1–Pb1–Br1^2	90.0
Br1–Pb1–Br1^1	180.0
I1–Pb1–Br1^1	180.0
Pb1^3–Br1–Pb1	180.0
Pb1^3–I1–Pb1	180.0
C11^1–N1–C1^4	61.1(15)

$^1 + x, 1 + y, + z$; $^2 + y, + z, + x$; $^3 + x, - 1 + y, + z$; $^4 - y, + z, - x$.

Table S8.1 Crystal data and structure refinement for **(AzrH)PbBr$_{2.79}$I$_{0.21}$**

Empirical formula	$Br_{2.8}C_2I_{0.2}NPb$
Formula weight	494.35
Temperature/K	293
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	5.9968(3)
Volume/Å^3	215.65(3)
Z	1
ρ_{calc}g/cm^3	3.806
μ/mm^{-1}	58.117
Crystal size/mm^3	0.14 × 0.08 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	14.772 to 141.708
Reflections collected	169
Independent reflections	65 [R_{int} = 0.0386, R_{sigma} = 0.0259]
Data/restraints/parameters	65/2/8
Goodness-of-fit on F^2	1.174
R_1 [I>=2σ (I)]	0.0437
wR_2 [all data]	0.0437

Table S8.2 Bond Lengths for **(AzrH)PbBr$_{2.79}$I$_{0.21}$**

	Length/Å
Pb1–I1	2.99840(15)
Pb1–Br1	2.99840(15)
C1^1– N1	1.45(2)
C1^1– C1^2	1.45(2)

$^1 - y, + x, + z$; $^2 + y, - x, + z$.

Table S8.3 Bond Angles for **(AzrH)PbBr$_{2.79}$I$_{0.21}$**

	Angle/°
Br1^1–Pb1–Br1	90.0
Br1–Pb1–Br1^4	180.0
I1–Pb1–Br1^2	90.0
I1–Pb1–Br1^4	180.0
Pb1^5–Br1–Pb1	180.0
C1^6–N1–C1^3	60.1(14)

^{1} + y, + z, 1 + x; ^{2} + y, + z, + x; ^{3} + z, + x, + y; ^{4} 1 + x, + y, + z; ^{5} – 1 + x, + y, +z; ^{6} – z, – x, – y.