ESI

Precise design and preparation of two 3D organic−inorganic perovskite ferroelectrics (1,5-diazabicyclo[3.2.2]nonane)RbX3 (X = Br, I)

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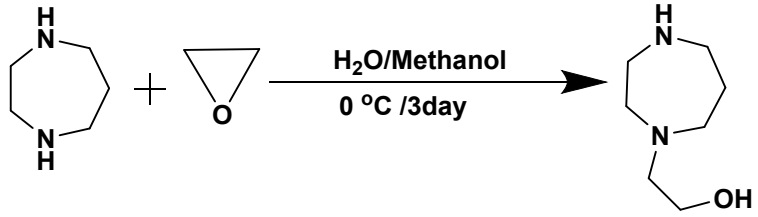
Experimental section

1,5-Diazabicyclo[3.2.2]nonane was prepared according to the reported literature with little modification (ESI). Other reagents and solvents were purchased from the reagent company and used as received. FT−IR spectra were recorded using KBr pellets in the range of 4000−400 cm^{-1} on an ALPHA spectrometer. PXRD analyses were performed using a D8 ADVANCE diffractometer (Cu Kα graphite, λ = 1.5406 Å) operating at 40 kV/15 mA with a Kβ foil filter. DSC measurement was carried out on NETZSCH DSC 214 Polyma at a heating/cooling rate of 10 $K \cdot min^{-1}$. Temperature-dependent dielectric constant measurements of powder samples were performed on a TH2828 analyzer in the frequency range of 0.5 kHz to 1 MHz. The Variable-temperature X-ray single-crystal diffraction data were collected on a Rigaku Saturn 924 diffractometer. The structures were solved by direct methods and refined using the SHELXLTL software package.

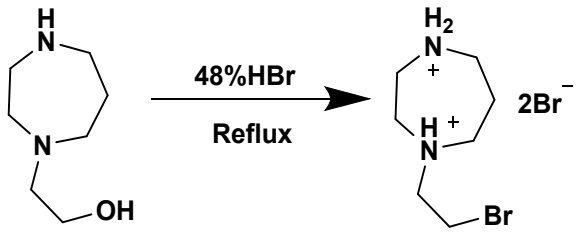
Synthesis of 1,5-diazabicyclo[3.2.2]nonane

(1) 1 -(2-Hydroxyethyl)-homopiperazine



A solution of homopiperazine (60 g, 0.60 mol) in 500 mL deionized water / methanol (1 : 1) was cooled to 0 °C. After 30 mL of ethylene oxide (26.6 g, 0.60 mol) was added, the reaction bottle was immediately sealed tightly, stored at 0 °C for 12 hours. The reaction was continued to stir at room temperature for 3 days, and the solvent was removed by rotary evaporation. Then the light yellow transparent oily product (2-hydroxyethyl) homopiperazine was obtained by vacuum distillation. Yield: 38.0 g, 44.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (t, J = 5.5 Hz, 2H), 2.92–2.74 (m, 4H), 2.70–2.57 (m, 6H), 1.78–1.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 59.30 (s), 58.60 (s), 58.13 (s), 54.36 (s), 49.01 (s), 47.44 (s), 30.52 (s).

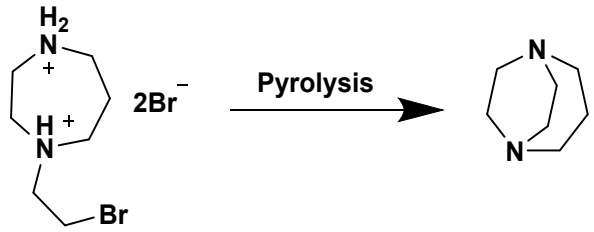
(2) 1 -(2-Bromoethyl)-homopiperazine dihydrobromide



To a solution of 500 mL of 48% hydrobromic acid, 1-(2-hydroxyethyl) homopiperazine (38 g, 0.26 mol), was added. The mixture was refluxed overnight for 12 h, and then the excess acid solution was removed by rotary evaporation. The

product was a dark red viscous oily liquid, which was then triturated with acetone for 6 h to give 1-(2-bromoethyl)-homopiperazine dihydrobromide as a white solid. Yield: 89.1 g, 91.5%. ^{1}H NMR (400 MHz, D_2O) δ 4.07–3.81 (m, 8H), 3.76 (s, 2H), 3.63–3.51 (m, 2H), 2.50–2.36 (m, 2H). ^{13}C NMR (101 MHz, D_2O) δ 57.86 (s), 54.14 (s), 50.30 (s), 45.13 (s), 40.92 (s), 24.01 (s), 20.68 (s).

(3) 1,5-Diazabicyclo[3.2.2]nonane

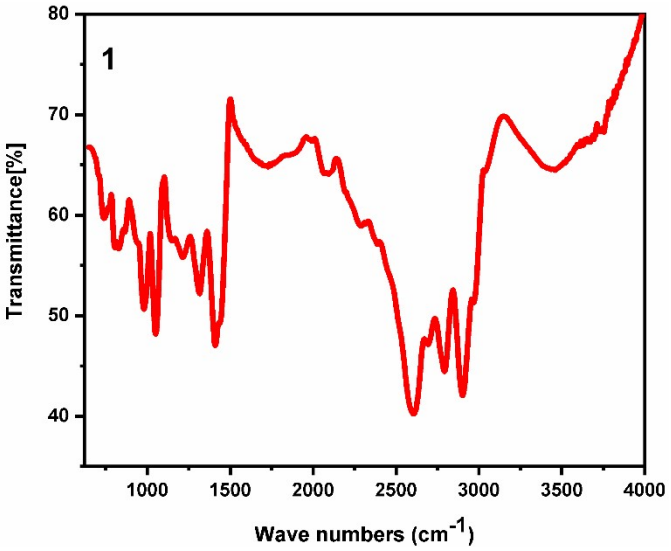


Pyrolysis of 1-(2-bromoethyl)-homopiperazine dihydrobromide (40 g, 0.11 mol) at 235-245 °C with mechanical stirring, after 90 min the melt became very hard and sticking to the side to keep the flask from stirring was effective, and the pyrolysis process continued for 3.5 hours as hydrogen bromide was still released. After the reaction was completed, the crude mixture was dissolved in a concentrated KOH aqueous solution for alkalization. After reaction for 3 h, the mixture was extracted with toluene, dried with anhydrous sodium carbonate, and then rotary evaporated to remove the solvent toluene to obtain a pale yellow needle-like solid product 1,5-diazabicyclo[3.2.2]nonane. Yield: 5.4931 g, 40.2%. ^{1}H NMR (400 MHz, D_2O) δ 3.01–2.93 (m, 4H), 2.92–2.82 (m, 4H), 2.80–2.70 (m, 4H), 1.89–1.81 (m, 2H). ^{13}C NMR (101 MHz, D2O) δ 55.07 (s), 46.06 (s), 25.54 (s).

Synthesis of [3.2.2-dabcn]$RbBr_3$ (1): To a HBr aqueous solution, 3.2.2-dabcn (0.38 g, 3 mmol) and RbBr (0.50 g, 3mmol) were added, and the mixture was stirred at 70

℃ for one hour. Evaporation of the aqueous solution under the heating gave block white crystals **1**. Yield: 1.12 g, 82% (based on RbBr). Anal. Calcd for $C_7H_{16}N_2RbBr_3$: C 18.54, H 3.56, N 6.18%. Found: C 18.27, H 3.44, N 6.37%. IR (KBr disc, cm^{-1}): 3457(w), 2902(vs), 2796(vs), 1723(m), 1413(s), 1050(s), 983(m), 815(m), 735(m).

Synthesis of [3.2.2-dabcn]RbI_3 (2): According to the similar procedures to synthesize compound **1**, led to the formation of compound **2** as block crystals. Yield: 1.52 g, 85% (based on RbI). Anal. Calcd for $C_7H_{16}N_2RbI_3$: C 14.14, H 2.71, N 4.71%. Found: C 14.54, H 2.39, N 4.61%. IR (KBr disc, cm^{-1}): 3436(w), 2912(vs), 2798(vs), 2596(vs), 1059(s), 988(m), 839(m), 750(m).



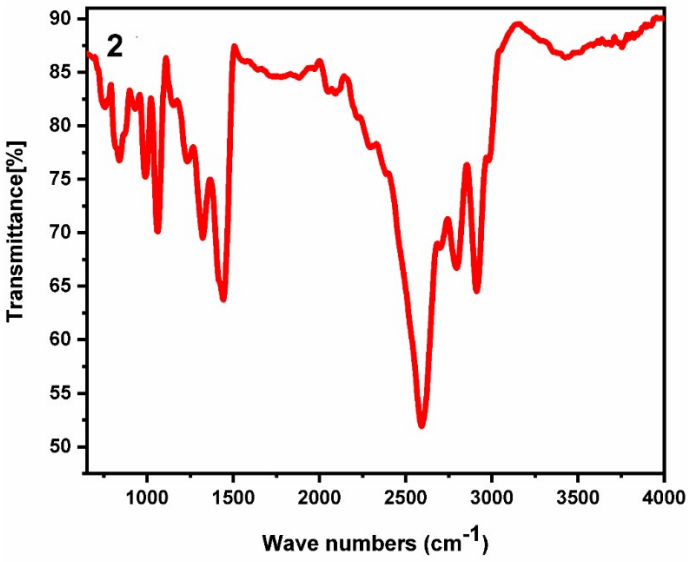


Figure S1. IR spectra of **1** and **2**.

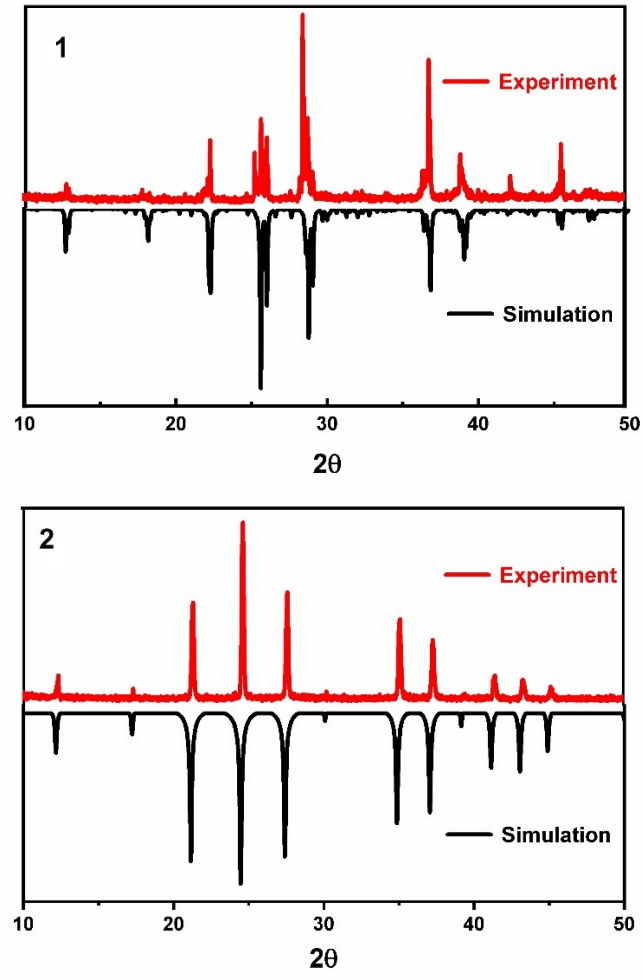


Figure S2. The powder X-ray diffraction patterns of compounds **1** and **2** with the simulated one in black and the experimental one in red.

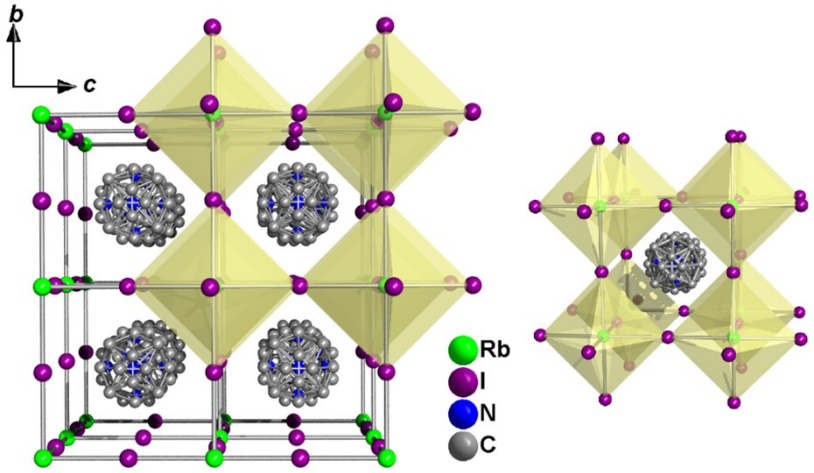


Figure S3. Crystal structures of [3.2.2-dabcn]RbI_3 (**2**) at 298 K.

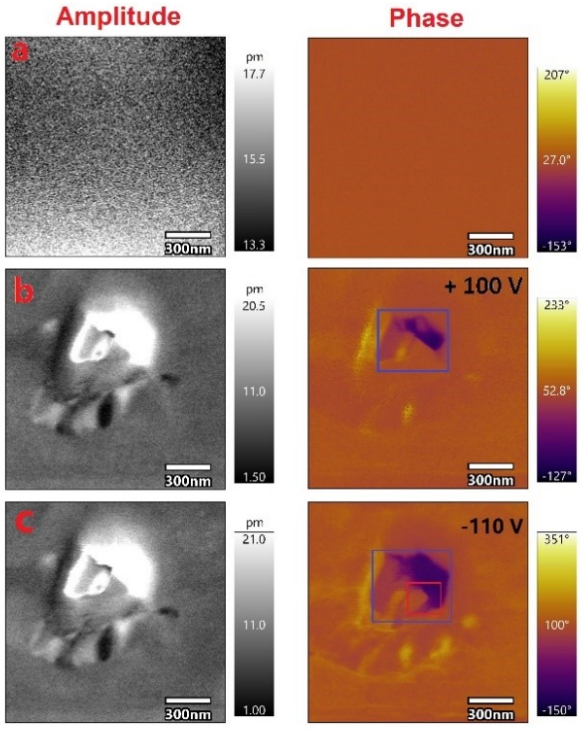


Figure S4. Domain manipulation. VPFM amplitude image (left), and VPFM phase image (right). (a) Images for the initial state of the as-grown crystallite. (b) Images for the state after the first switching operation in the region of the blue rectangle, produced by scanning with the tip bias of 100 V. (c) Images for the state after the succeeding back-switching operation in the region of the smaller red rectangle, produced by scanning with the tip bias of −110 V.

Table S1. Crystal data and structure refinement for compound **1** at LTP and HTP.

Compound	LTP (281 K)	HTP (358 K)
CCDC numbers	2171392	2171586
Formula	$C_7H_{16}N_2Br_3Rb$	$C_7H_{16}N_2Br_3Rb$
Formula Mass	453.39	453.39
Crystal system	Orthorhombic	Cubic
Space group	$Pmn2_1$	$Pm\bar{3}m$
a (Å)	48.9591(6)	6.94400(10)
b (Å)	6.84360(10)	6.94400(10)
c (Å)	9.86670(10)	6.94400(10)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å)^3	3305.90(7)	334.834(8)
Z	2	1
D_{calc} (g·cm^{-3})	2.277	2.325
F(000)	2140.0	213.8
θ_{max}	76.63	72.74
μ(Mo Ka,mm^{-1})	15.483	15.294
Total no. of reflns.	12219	360
No. of unique reflns.	7057 [$R_{(int)}$ = 0.0813]	95 [$R_{(int)}$ = 0.0587]
No. of variables	299	17

R_1, wR_2 (obsd data)	0.0611, 0.1595	0.0446, 0.1365
R_1, wR_2 (all data)	0.0628, 0.1617	0.0477, 0.1422
GOF, S	1.019	1.179
Max./min. peak (e. Å^{-3})	1.44, -1.44	0.91, -0.56
Flack parameter	0.08(6)	/

Table S2. Hydrogen bond lengths [Å] and bond angles [°] of compound **1**

D-H···A	D-H [Å]	H···A[Å]	D···A[Å]	D-H···A[°]
N1-H1···Br8^{3}	0.98	2.39	3.237	143.87
N2-H2···Br3^{1}	0. 98	2.27	3.214	162.09
N3-H3···Br4^{3}	0. 98	2. 29	3.254	167.13
N4-H4···Br2^{2}	0. 98	2. 33	3.254	157.51
N5-H5···Br5	0. 98	2. 29	2.236	161.90

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

Table S3. The bond length [Å] and bond angle [°] of compound **1** at 281 K

label	Lengths [Å]	label	Angles [°]
Rb1–Br1	3.4134(13)	Br1–Rb1–Br1^{1}	169.97(7)
Rb1–Br1^{1}	3.4565(13)	Br1–Rb1–Br2^{2}	99.02(4)
Rb1–Br2	3.496(2)	Br1^{1}–Rb1–Br2^{2}	86.24(4)
Rb1–Br2^{2}	3.490(2)	Br1^{1}–Rb1–Br2	91.64(4)
Rb1–Br3	3.4934(19)	Br1–Rb1–Br2	79.76(4)

label	Lengths [Å]	label	Angles [°]
Rb1–Br4	3.617(2)	Br1–Rb1–Br3	94.06(4)
Rb2–Br3^{3}	3.4917(19)	Br1^{1}–Rb1–Br3	80.74(4)
Rb2–Br4	3.540(2)	Br1–Rb1–Br4	91.53(4)
Rb2–Br5	3.4214(14)	Br1^{1}–Rb1–Br4	97.56(4)
Rb2–Br5^{1}	3.4881(14)	Br2^{2}–Rb1–Br2	91.28(3)
Rb2–Br6	3.432(2)	Br2^{2}–Rb1–Br3	166.91(4)
Rb2–Br8^{4}	3.522(2)	Br2–Rb1–Br4	169.30(4)
Rb3–Br6^{5}	3.470(2)	Br2^{2}–Rb1–Br4	83.92(5)
Rb3–Br6	3.470(2)	Br3–Rb1–Br2	90.42(5)
Rb3–Br7	3.502(2)	Br3–Rb1–Br4	96.43(4)
Rb3–Br7^{6}	3.454(2)	Br3^{3}–Rb2–Br4	83.33(4)
Rb3–Br8	3.5377(18)	Br3^{3}–Rb2–Br8^{4}	167.16(5)
Rb3–Br8^{5}	3.5377(18)	Br51–Rb2–Br3^{3}	83.12(4)
		Br5–Rb2–Br3^{3}	94.77(4)
		Br5–Rb2–Br4	93.82(4)
		Br5^{1}–Rb2–Br4	101.48(4)
		Br5–Rb2–Br5^{1}	164.17(7)
		Br5–Rb2–Br6	79.94(4)
		Br51–Rb2–Br8^{4}	91.08(4)
		Br5–Rb2–Br8^{4}	93.87(4)
		Br6–Rb2–Br3^{3}	90.96(5)

label	Lengths [Å]	label	Angles [°]
		Br6–Rb2–Br4	171.20(5)
		Br6–Rb2–Br5^{1}	84.40(4)
		Br6–Rb2–Br8^{4}	99.90(5)
		Br8^{4}–Rb2–Br4	86.63(5)
		Br6^{5}–Rb3–Br6	84.14(7)
		Br6^{5}–Rb3–Br7	101.64(5)
		Br6–Rb3–Br7	101.64(5)
		Br6^{5}–Rb3–Br8^{5}	82.52(4)
		Br6–Rb3–Br8	82.52(4)
		Br6–Rb3–Br8^{5}	166.16(6)
		Br6^{5}–Rb3–Br8	166.16(6)
		Br7^{6}–Rb3–Br6	93.64(5)
		Br7^{6}–Rb3–Br6^{5}	93.64(5)
		Br7^{6}–Rb3–Br7	159.32(11)
		Br7^{6}–Rb3–Br8^{5}	83.57(5)
		Br7–Rb3–Br8^{5}	84.69(4)
		Br7^{6}–Rb3–Br8	83.57(5)
		Br7–Rb3–Br8	84.69(4)
		Br8$_{5}$–Rb3–Br8	110.52(8)
		Rb1–Br1–Rb1$_{6}$	169.96(7)
		Rb1^{7}–Br2–Rb1	166.61(4)

label	Lengths [Å]	label	Angles [°]
		Rb2[4]–Br3–Rb1	166.83(4)
		Rb2–Br4–Rb1	161.49(6)
		Rb2–Br5–Rb2[6]	164.17(7)
		Rb2–Br6–Rb3	172.14(5)
		Rb3[1]–Br7–Rb3	159.32(11)
		Rb2[3]–Br8–Rb3	157.88(6)

[1] + *x*,1 + *y*, + *z*; [2]1/2 - *x*, - *y*, 1/2 + *z*; [3] + *x*, + *y*, 1 + *z*; [4]+ *x*, + *y*, -1 + *z*; [5]- *x*, + *y*, + *z*; [6] + *x*, -1 + *y*, + *z*; [7]1/2 - *x*, - *y*, -1/2 + *z*.

Table S4. The bond length [Å] and bond angle [°] of compound **1** at 358 K

label	Lengths [Å]	label	Angles [°]
Rb1–Br1[1]	3.47200(5)	Br1[1]–Rb1–Br1	90
Rb1–Br1[2]	3.47200(5)	Br1[2]–Rb1–Br1[3]	90
Rb1–Br1	3.47200(5)	Br1[2]–Rb1–Br1[4]	90
Rb1–Br1[3]	3.47200(5)	Br1[5]–Rb1–Br1[3]	90
Rb1–Br1[4]	3.47200(5)	Br1–Rb1–Br1[4]	90
Rb1–Br1[5]	3.47200(5)	Br1[5]–Rb1–Br1[4]	90
Rb1–Br1A[6]	3.4986(9)	Br1[1]–Rb1–Br1[2]	90
Rb1–Br1A[7]	3.4986(9)	Br1[1]–Rb1–Br1[5]	180
Rb1–Br1A[8]	3.4986(9)	Br1–Rb1–Br1[2]	180
Rb1–Br1A[9]	3.4986(9)	Br1[1]–Rb1–Br1[4]	90
Rb1–Br1A[4]	3.4986(9)	Br1[5]–Rb1–Br1[2]	90

label	Lengths [Å]	label	Angles [°]
Rb1–Br1A^{10}	3.4986(9)	Br1–Rb1–Br1^{5}	90
Br1A–Br1A^{10}	0.609(11)	Br1^{1}–Rb1–Br1^{3}	90
Br1A–Br1A^{11}	0.609(11)	Br1–Rb1–Br1^{3}	90
Br1A–Br1A^{8}	0.862(15)	Br1^{3}–Rb1–Br1^{4}	180
		Br1^{3}–Rb1–Br1A^{2}	90
		Br1^{5}–Rb1–Br1A^{6}	90
		Br1–Rb1–Br1A^{2}	172.92(12)
		Br1^{1}–Rb1–Br1A^{7}	97.08(12)
		Br1^{4}–Rb1–Br1A^{6}	97.08(12)
		Br1^{5}–Rb1–Br1A^{7}	82.92(12)
		Br1^{1}–Rb1–Br1A^{8}	82.92(12)
		Br1^{3}–Rb1–Br1A^{7}	90
		Br1^{2}–Rb1–Br1A^{6}	172.92(12)
		Br1^{1}–Rb1–Br1A^{9}	97.08(12)
		Br1–Rb1–Br1A^{9}	90
		Br1^{5}–Rb1–Br1A^{9}	82.92(12)
		Br1^{2}–Rb1–Br1A^{9}	90
		Br1^{4}–Rb1–Br1A^{9}	172.92(12)
		Br1–Rb1–Br1A^{6}	7.08(12)
		Br1^{1}–Rb1–Br1A^{10}	90
		Br1^{2}–Rb1–Br1A^{2}	7.08(12)

label	Lengths [Å]	label	Angles [°]
		Br1–Rb1–Br1A^{10}	172.92(12)
		Br1^{5}–Rb1–Br1A^{8}	97.08(12)
		Br1^{5}–Rb1–Br1A^{10}	90
		Br1^{1}–Rb1–Br1A^{2}	82.92(12)
		Br1^{2}–Rb1–Br1A^{10}	7.08(12)
		Br1^{4}–Rb1–Br1A^{2}	90
		Br1^{3}–Rb1–Br1A^{10}	97.08(12)
		Br1^{3}–Rb1–Br1A^{6}	82.92(12)
		Br1^{4}–Rb1–Br1A^{10}	82.92(12)
		Br1–Rb1–Br1A^{7}	7.08(12)
		Br1–Rb1–Br1A^{8}	90
		Br1^{5}–Rb1–Br1A^{2}	97.08(12)
		Br1^{2}–Rb1–Br1A^{8}	90
		Br1^{2}–Rb1–Br1A^{7}	172.92(12)
		Br1^{4}–Rb1–Br1A^{8}	7.08(12)
		Br1^{3}–Rb1–Br1A^{8}	172.92(12)
		Br1^{3}–Rb1–Br1A^{9}	7.08(12)
		Br1^{4}–Rb1–Br1A^{7}	90
		Br1^{1}–Rb1–Br1A^{6}	90
		Br1A^{6}–Rb1–Br1A^{9}	82.98(12)
		Br1A^{6}–Rb1–Br1A^{8}	97.02(12)

label	Lengths [Å]	label	Angles [°]
		$Br1A^{9}$–Rb1–$Br1A^{8}$	180.0(2)
		$Br1A^{10}$–Rb1–$Br1A^{9}$	97.02(12)
		$Br1A^{7}$–Rb1–$Br1A^{9}$	89.13(3)
		$Br1A^{7}$–Rb1–$Br1A^{8}$	90.87(3)
		$Br1A^{10}$–Rb1–$Br1A^{8}$	82.98(12)
		$Br1A^{2}$–Rb1–$Br1A^{9}$	90.87(3)
		$Br1A^{2}$–Rb1–$Br1A^{8}$	89.13(3)
		$Rb1^{11}$–Br1–Rb1	180
		$Rb1^{11}$–Br1A–Rb1	165.8(2)
		$Br1A^{12}$–Br1A–Rb1	85.00(9)
		$Br1A^{6}$–Br1A–Rb1	85.00(9)
		$Br1A^{7}$–Br1A–Rb1	82.92(12)

$^{1}1 + y, + z, + x$; $^{2} + x,1 + y,+ z$; $^{3} + z,+ x,+ y$; $^{4} + z, + x,1 + y$; $^{5} + y,+ z, + x$; $^{6} + z, + y, - x$; $^{7} - x, -1 - y, - z$; $^{8} + x, + z, - y$; $^{9} - x, - z, + y$; $^{10} - z, - y, + x$; $^{11} + x, -1 + y, + z$; $^{12} - z, -1 - y, + x$; $^{13} + x, + y, 1 - z$; $^{14} + z, -1 - y, + x$; $^{15} + x, - z, - y$; $^{16} + x, -1 + z, - y$; $^{17} + z, -1 + x, 1 + y$; ^{18} $1 + y, -1 + z, + x$; $^{19} + z, - x, - y$; ^{20} $1 + y, - z, + x$; ^{21} $1 - z, -1 - y, + x$.

Table S5. Crystal data and structure refinement for compound **2** at RTP.

Compound	RTP (298 K)
CCDC numbers	2171585
Formula	$C_7H_{16}N_2I_3Rb$
Formula Mass	593.76

Crystal system	Cubic
Space group	$Pm\bar{3}m$
a (Å)	7.4069(6)
b (Å)	7.4069(6)
c (Å)	7.4069(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å)^3	406.36(6)
Z	1
D_{calc} (g·cm^{-3})	2.392
F(000)	255.6
θ_{max}	27.24
μ(Mo Ka,mm^{-1})	8.716
Total no. of reflns.	2445
No. of unique reflns.	128 [R(int) = 0.0280]
No. of variables	16
R_1, wR_2 (obsd data)	0.0378, 0.0849
R_1, wR_2 (all data)	0.0430, 0.0868
GOF, S	1.471
Max./min. peak (e. Å^{-3})	0.38, -0.85

Table S6. The bond length [Å] and bond angle [°] of compound **2** at 298 K

label	Lengths [Å]	label	Angles [°]
Rb1–I1[1]	3.7034(3)	I1[1]–Rb1–I1	90
Rb1–I1[2]	3.7035(3)	I1[2]–Rb1–I1[3]	90
Rb1–I1[3]	3.7034(3)	I1[2]–Rb1–I1[4]	90
Rb1–I1	3.7034(3)	I1[1]–Rb1–I1[2]	90
Rb1–I1[4]	3.7034(3)	I1[1]–Rb1–I1[4]	180
Rb1–I1[5]	3.7034(3)	I1–Rb1–I1[2]	180
I1–Rb1[6]	3.7034(3)	I1–Rb1–I1[3]	90
		I1[1]–Rb1–I1[5]	90
		I1[5]–Rb1–I1[3]	180
		I1–Rb1–I1[5]	90
		I1–Rb1–I1[4]	90
		I1[2]–Rb1–I1[5]	90
		I1[3]–Rb1–I1[4]	90
		I1[1]–Rb1–I1[3]	90
		I1[5]–Rb1–I1[4]	90
		Rb1[6]–I1–Rb1	180

[1] + *y*, 1 + *z*, + *x*; [2] + *x*, + *y*, 1 + *z*; [3] 1+ *z*, + *x*, + *y*; [4] + *y*, + *z*, + *x*; [5] + *z*, + *x*, + *y*; [6] + *x*, + *y*, -1 + *z*; [7] + *x*, + *y*, - *z*; [8] - *x*, + *y*, - *z*; [9] - *x*, + *y*, + *z*; [10] + *z*, + *y*, - *x*; [11] - *z*, + *y*, - *x*; [12] - *x*, + *z*, + *y*; [13] - *y*, + *z*, - *x*; [14] + *x*, + *z*, - *y*; [15] + *y*, + *x*, + *z*; [16] - *y*, - *x*, + *z*; [17] - *z*, + *x*, + *y*; [18] - *x*, - *y*, + *z*