

Alkyl modification to optimize the ferroelastic properties in molecular crystals

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Experimental Measurement Methods

Single-crystal X-ray diffraction.

Single crystal X-ray diffraction data for (DMP)PbBr₃ (DMP=*N,N*-dimethyl-3-pyrroline) (compound **1**) and (EMP)PbBr₃ (EMP=*N*-ethyl-*N*-methyl-3-pyrroline) (compound **2**) were obtained using a Rigaku Saturn 724 diffractometer using Mo-K α Radiation ($\lambda = 0.71073 \text{ \AA}$). The refinement of the structure factor was achieved by the method of least squares on SHELXT and OLEX2 software packages.

Differential Scanning Calorimetry (DSC).

DSC measurement was performed on powder sample of two compounds by a NETZSCH-214 instrument. The sample was placed in aluminum crucible under nitrogen at atmospheric pressure. The experiment was conducted under nitrogen and atmospheric pressure, with heating and cooling rates of $20 \text{ K} \cdot \text{min}^{-1}$.

Dielectric Measurements.

The temperature-dependent dielectric permittivity ϵ ($\epsilon = \epsilon' - \epsilon''$, where ϵ' is the real part, and ϵ'' is the imaginary part) of these four compounds was performed through a Tonghui TH2828A Precision LCR meter with an AC voltage of 1 V. The powder is pressed into thin sheets, and the copper wire and sample are made into electrodes using silver glue. then, measure the dielectric constant of the sample at different temperatures and frequencies using the TH2828A instrument.

Thin-Film Preparation

The precursor solution of two compounds were prepared respectively by dissolving 20 mg of the as-grown crystals in 0.5 mL of HBr aqueous solution (40% in water). Then, 20 μL of precursor solution was dropped and spread on a clean indium-doped tin oxide (ITO) glass substrate ($1 \times 1 \text{ cm}$). The thin film of two compounds obtained after annealing at 328 K for 30 min.

Powder X-ray diffraction.

Powder X-ray diffraction (PXRD) measurements were performed at room temperature on a Rigaku D/MAX 2000 PC X-ray diffractometer. The diffraction pattern was recorded at 2θ between

5-50° within the range, the step size is 0.02°.

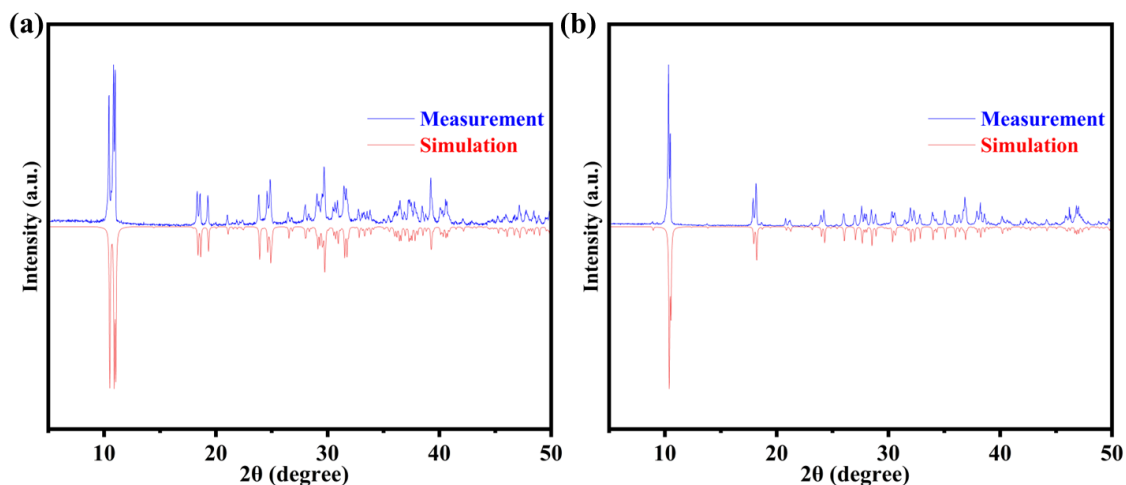


Fig. S1 The measured and simulated PXRD patterns of compound 1 (a) and compound 2 (b).

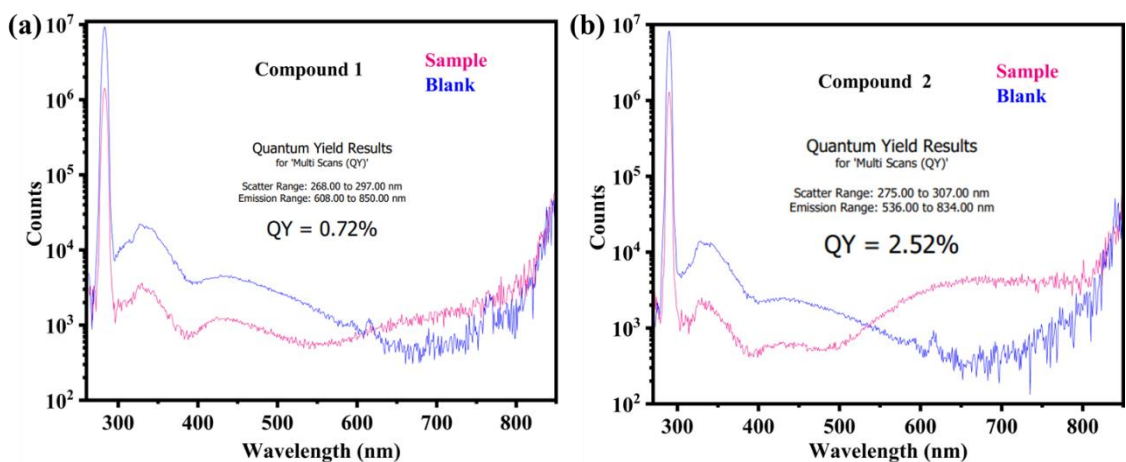


Fig. S2 The photoluminescence quantum efficiency of two compounds at room temperature.

The calculation formula of spontaneous strain (Lagrangian linear strain tensor):

$$e_{11} = \frac{a_1 \sin \beta_1 \sin \gamma_1}{a_0 \sin \beta_0 \sin \gamma_0} - 1$$

$$e_{22} = \frac{b_1 \sin \alpha_1}{b_0 \sin \alpha_0} - 1$$

$$e_{33} = \frac{c_1}{c_0} - 1$$

$$e_{12} = e_{21} = \frac{1}{2} \left[\frac{b_1 \sin \alpha_1 \cos \gamma_0}{b_0 \sin \alpha_0 \sin \gamma_0} - \frac{a_1 \sin \beta_1 \cos \gamma_1}{a_0 \sin \beta_0 \sin \gamma_0} \right]$$

$$e_{13} = e_{31} = \frac{1}{2} \left[\frac{a_1 \cos \beta_1}{a_0 \sin \beta_0 \sin \gamma_0} + \frac{\cos \gamma_0}{\sin \gamma_0} \times \left(\frac{b_1 \cos \alpha_1}{b_0 \sin \alpha_0} - \frac{c_1 \cos \alpha_0}{c_0 \sin \alpha_0} \right) - \frac{c_1 \cos \beta_0}{c_0 \sin \beta_0 \sin \gamma_0} \right]$$

$$e_{23} = e_{32} = \frac{1}{2} \left[\frac{b_1 \cos \alpha_1}{b_0 \sin \alpha_0} - \frac{c_1 \cos \alpha_0}{c_0 \sin \alpha_0} \right]$$

$a_1, b_1, c_1, \alpha_1, \beta_1, \gamma_1$ are the crystal data in the ferroelastic phase, $a_0, b_0, c_0, \alpha_0, \beta_0, \gamma_0$ are the crystal data in the paraelastic phase.

For compound 1:

$$e_{11}=0.137, e_{12}=e_{21}=0.25, e_{13}=e_{31}=-0.01, e_{22}=0.211, e_{33}=-0.51, e_{23}=e_{32}=0$$

$$\beta_{ss} = \sqrt{0.137^2 + 2 \times 0.25^2 + 2 \times (-0.01)^2 + 0.211^2 + (-0.51)^2 + 0} = \sqrt{0.44859}=0.6698$$

For compound 2:

$$e_{11}=-0.116, e_{12}=e_{21}=0.255, e_{13}=e_{31}=0.0359, e_{22}=0.418, e_{33}=0.0016, e_{23}=e_{32}=0$$

$$\beta_{ss} = \sqrt{(-0.116)^2 + 2 \times 0.255^2 + 2 \times 0.0359^2 + 0.418^2 + 0.0016^2 + 0} = \sqrt{32081}=0.5656$$

The variation of bond lengths and bond angles of the inorganic frameworks of two compounds:

$$\Delta d = \frac{1}{6} \sum_{i=1}^6 [(d_i - d_0) / d_0]^2$$

$$\beta^2 = \frac{1}{11} \sum_{i=1}^{12} (\beta_i - 90^\circ)^2$$

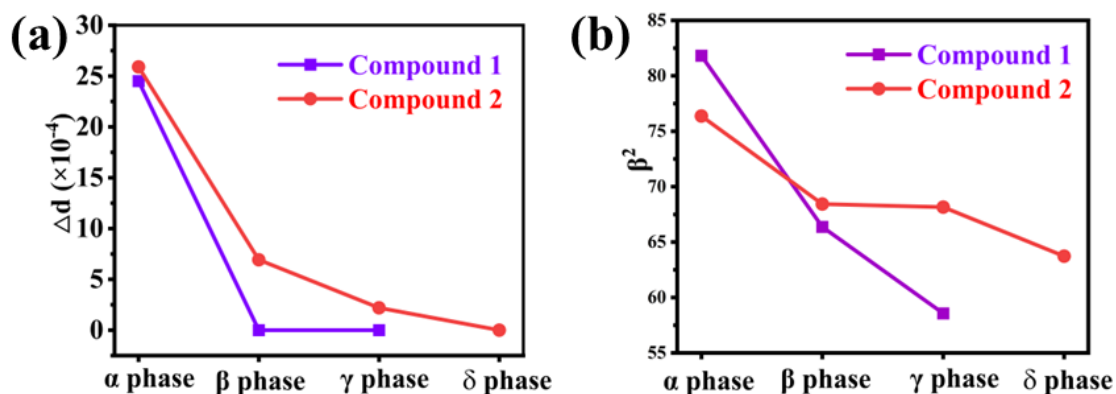


Fig. S3 Bond length distortion (a) and bond angle variance (b) of two compounds calculated based on the crystal structures.

" d_0 " represents the average length of the Pb–Br bond, " d_i " refers to the distance of each Pb–Br bond, and " β_i " denotes the angle of each Br–Pb–Br bond. For compound 1 in the α_1 phase, $\Delta d = 0.00245$ and $\beta_2 = 81.8041$, in the β_1 phase, $\Delta d = 0$ and $\beta_2 = 66.3709$, in the γ_1 phase, $\Delta d = 0$ and $\beta_2 = 58.5654$. While for compound 2, in the α_2 phase $\Delta d = 0.00259$ and $\beta_2 = 76.3666$, in the β_2 phase, $\Delta d = 0.00069$ and $\beta_2 = 68.4318$, in the γ_2 phase, $\Delta d = 0.00022$ and $\beta_2 = 68.1482$ in the δ_2 phase, $\Delta d = 0$ and $\beta_2 = 63.7259$. It is not difficult to find that the inorganic framework changes of two compounds are both large from α to β phase and weak in the subsequent phase transitions.

Table S1. Crystal data and structure refinement for compound 1 at 273 K, 300 K, 303 K, 333 K.

Compound 1	(DMP)PbBr ₃			
Temperature	273 K	300 K	303 K	333 K
Empirical formula	C ₆ H ₁₂ Br ₃ NPb	C ₆ H ₁₂ Br ₃ NPb	C ₆ Br ₃ NPb	C ₆ Br ₃ NPb
Formula weight	545.09	545.09	532.99	532.99
Crystal system	Monoclinic	Monoclinic	Hexagonal	Hexagonal
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P6₃/mmc</i>	<i>P6₃/mmc</i>

$a/\text{\AA}$	9.657(4)	9.6477(10)	9.503	9.613
$b/\text{\AA}$	7.966(3)	7.9361(7)	9.503	9.613
$c/\text{\AA}$	16.008(7)	16.0202(19)	7.812	7.840
$\alpha/^\circ$	90	90	90	90
$\beta/^\circ$	92.539(9)	92.416(9)	90	90
$\gamma/^\circ$	90	90	120	120
$V/\text{\AA}^3$	1230.3(9)	1225.5(2)	611.0	627.4
Z	4	4	2	2
GOF	1.070	1.086	1.042	1.002
F(000)	968	968	460	460
R1 [$ I \geq 2\sigma(I)$]	0.0892	0.0748	0.1735	0.0423
wR2 [$ I \geq 2\sigma(I)$]	0.1991	0.1932	0.3366	0.1103

Table S2. Crystal data and structure refinement for compound **2** at 273 K, 300 K, 373 K, 423 K.

Compound 2	(EMP)PbBr ₃			
Temperature	273 K	300 K	373 K	423 K
Empirical formula	C ₇ H ₁₄ Br ₃ NPb	C ₇ H ₁₄ Br ₃ NPb	C ₇ Br ₃ NPb	C ₇ Br ₃ NPb
Formula weight	559.11	545.09	545.00	545.00
Crystal system	Monoclinic	Monoclinic	Monoclinic	Hexagonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 6 ₃ / <i>m</i> <i>m</i> <i>c</i>
$a/\text{\AA}$	9.761(2)	9.6477(10)	9.897(12)	10.073
$b/\text{\AA}$	7.9767(14)	7.9361(7)	17.309(19)	10.073
$c/\text{\AA}$	16.706(4)	16.0202(19)	7.897(8)	7.910
$\alpha/^\circ$	90	90	90	90
$\beta/^\circ$	92.053(6)	92.416(9)	94.10(2)	90
$\gamma/^\circ$	90	90	90	120
$V/\text{\AA}^3$	1299.9(5)	1225.5(2)	1349(3)	695.0
Z	4	4	4	2
GOF	1.032	1.086	0.986	0.952
F(000)	1000	968	944	472
R1 [$ I \geq 2\sigma(I)$]	0.0388	0.0395	0.0715	0.0457
wR2 [$ I \geq 2\sigma(I)$]	0.1165	0.0631	0.1789	0.1164

Table S3. The bond lengths (Å) and angles (°) of compound **1** at 273 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br3	2.872(3)	Br3–Pb1–Br1 ^{#1}	83.64(9)
Pb1–Br1	2.965(3)	Br3–Pb1–Br1	92.57(9)
Pb1–Br1 ^{#1}	3.119(3)	Br3–Pb1–Br2	92.48(10)
Pb1–Br2	2.938(3)	Br3–Pb1–Br2 ^{#1}	83.10(9)
Pb1–Br2 ^{#1}	3.177(3)	Br1–Pb1–Br1 ^{#1}	175.15(8)
		Br1 ^{#1} –Pb1–Br2 ^{#1}	81.31(8)
		Br1–Pb1–Br2 ^{#1}	95.25(9)
		Br2–Pb1–Br1	88.03(9)
		Br2–Pb1–Br1 ^{#1}	95.15(9)

Br2–Pb1–Br2 ^{#1}	174.59(8)
Pb1–Br3–Pb1 ^{#1}	79.79(8)
Pb1–Br1–Pb1 ^{#2}	81.76(8)
Pb1–Br2–Pb1 ^{#2}	81.20(8)

Symmetry codes: #1 0.5-X, -0.5+Y, 0.5-Z; #2 0.5-X, 0.5+Y, 0.5-Z;

Table S4. The bond lengths (Å) and angles (°) of compound **1** at 300 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br1	2.8648(17)	Br1–Pb1–Br1 ^{#1}	168.78(5)
Pb1–Br1 ^{#1}	3.3028(17)	Br1–Pb1–Br3	92.48(5)
Pb1–Br3 ^{#2}	3.0982(19)	Br1–Pb1–Br3 ^{#2}	84.10(5)
Pb1–Br3	2.9659(18)	Br1–Pb1–Br2 ^{#2}	83.04(5)
Pb1–Br2	2.9264(19)	Br1–Pb1–Br2	92.61(5)
Pb1–Br2 ^{#2}	3.1698(19)	Br3–Pb1–Br1 ^{#1}	79.05(5)
		Br3 ^{#2} –Pb1–Br1 ^{#1}	104.70(5)
		Br3–Pb1–Br3 ^{#2}	175.58(5)
		Br3–Pb1–Br2 ^{#2}	95.58(5)
		Br3 ^{#2} –Pb1–Br2 ^{#2}	81.25(5)
		Br2–Pb1–Br1 ^{#1}	79.81(5)
		Br2 ^{#2} –Pb1–Br1 ^{#1}	104.93(5)
		Br2–Pb1–Br3 ^{#2}	95.24(6)
		Br2–Pb1–Br3	87.69(6)
		Br2–Pb1–Br2 ^{#2}	174.66(5)
		Pb1–Br3–Pb1 ^{#1}	81.72(4)

Symmetry codes: #1 -0.5-X, 0.5+Y, 1.5-Z; #2 -0.5-X, -0.5+Y, 1.5-Z;

Table S5. The bond lengths (Å) and angles (°) of compound **1** at 303 K(cooling)

Bond lengths [Å]		Bond angles [°]	
Pb1–Br1	3.000(8)	Br1–Pb1–Br1 ^{#1}	180.0
Pb1–Br1 ^{#1}	3.000(8)	Br1 ^{#2} –Pb1–Br1 ^{#3}	97.8(2)
Pb1–Br1 ^{#2}	3.000(8)	Br1 ^{#2} –Pb1–Br1 ^{#4}	82.2(2)
Pb1–Br1 ^{#3}	3.000(8)	Br1–Pb1–Br1 ^{#2}	82.2(2)
Pb1–Br1 ^{#4}	3.000(8)	Br1–Pb1–Br1 ^{#4}	82.2(2)
Pb1–Br1 ^{#5}	3.000(8)	Br1 ^{#1} –Pb1–Br1 ^{#2}	97.8(2)
		Br1 ^{#1} –Pb1–Br1 ^{#3}	82.2(2)
		Br1–Pb1–Br1 ^{#5}	97.8(2)
		Br1 ^{#5} –Pb1–Br1 ^{#3}	82.2(2)
		Br1 ^{#1} –Pb1–Br1 ^{#5}	82.2(2)
		Br1 ^{#1} –Pb1–Br1 ^{#4}	97.8(2)
		Br1 ^{#2} –Pb1–Br1 ^{#5}	180.0
		Br1 ^{#5} –Pb1–Br1 ^{#4}	97.8(2)
		Br1–Pb1–Br1 ^{#3}	97.8(2)
		Br1 ^{#3} –Pb1–Br1 ^{#4}	180.0
		Pb1–Br1–Pb1 ^{#6}	81.2(3)

Symmetry codes: #1: -4-X, -2-Y, -Z; #2: -X+Y, -X, 0.5-Z; #3: -4+Y, -X+Y, -Z; #4: -Y, +X-Y, +Z; #5: +X-Y, +X, -0.5+Z; #6: +X-Y, +X, 0.5+Z; #7: 1-Y, +X-Y, +Z; #8: 1-X+Y, 1-X, +Z; #9: +X, +Y, 0.5-Z; #10: 1-Y, +X-Y, 0.5-Z; #11: 1-X+Y, 1-X, 0.5-Z; #12: +X, +X-Y, 0.5-Z; #13: 1-Y, 1-X, 0.5-Z; #14: 1-X+Y, +Y, +Z;

Table S6. The bond lengths (Å) and angles (°) of compound **1** at 333 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br1 ^{#1}	3.030(2)	Br1 ^{#1} –Pb1–Br1 ^{#2}	180.0
Pb1–Br1 ^{#2}	3.030(2)	Br1–Pb1–Br1 ^{#3}	97.32(6)
Pb1–Br1 ^{#3}	3.030(2)	Br1 ^{#4} –Pb1–Br1 ^{#5}	97.32(6)
Pb1–Br1 ^{#4}	3.030(2)	Br1 ^{#1} –Pb1–Br1	82.68(6)
Pb1–Br1	3.030(2)	Br1 ^{#1} –Pb1–Br1 ^{#5}	82.68(6)
Pb1–Br1 ^{#5}	3.030(2)	Br1 ^{#2} –Pb1–Br1	97.32(6)
		Br1 ^{#2} –Pb1–Br1 ^{#3}	82.68(6)
		Br1 ^{#1} –Pb1–Br1 ^{#4}	97.32(6)
		Br1 ^{#4} –Pb1–Br1 ^{#3}	82.68(6)
		Br1 ^{#2} –Pb1–Br1 ^{#4}	82.68(6)
		Br1 ^{#2} –Pb1–Br1 ^{#5}	97.32(6)
		Br1–Pb1–Br1 ^{#4}	180.0
		Br1 ^{#3} –Pb1–Br1 ^{#5}	180.0
		Br1 ^{#1} –Pb1–Br1 ^{#3}	97.32(6)
		Br1–Pb1–Br1 ^{#5}	82.68(6)
		Pb1–Br1–Pb1 ^{#6}	80.60(8)

Symmetry codes: #1: -X+Y, -X, 1.5-Z; #2: +X-Y, +X, 0.5+Z; #3: +Y, -X+Y, 2-Z; #4: -X, -Y, 2-Z; #5: -Y, +X-Y, +Z; #6: +X-Y, +X, -0.5+Z; #7: -Y, -1+X-Y, +Z; #8: 1-X+Y, -X, +Z; #9: +X, +Y, 1.5-Z; #10: 1-X+Y, -X, 1.5-Z;

Table S7. The bond lengths (Å) and angles (°) of compound **2** at 273 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br3	2.9014(12)	Br3–Pb1–Br3 ^{#1}	173.99(4)
Pb1–Br3 ^{#1}	3.2062(13)	Br3–Pb1–Br1	92.86(4)
Pb1–Br1 ^{#2}	3.1390(13)	Br3–Pb1–Br1 ^{#2}	84.20(4)
Pb1–Br1	2.9593(13)	Br1–Pb1–Br3 ^{#1}	82.11(4)
Pb1–Br2	2.8828(12)	Br1 ^{#2} –Pb1–Br3 ^{#1}	101.03(3)
		Br1–Pb1–Br1 ^{#2}	175.19(4)
		Br2–Pb1–Br3	93.30(4)
		Br2–Pb1–Br3 ^{#1}	83.13(4)
		Br2–Pb1–Br1 ^{#2}	97.66(4)
		Br2–Pb1–Br1	86.30(4)
		Pb1–Br3–Pb1 ^{#2}	81.38(3)
		Pb1–Br1–Pb1 ^{#1}	81.64(3)

Symmetry codes: #1: 0.5-X, -0.5+Y, 1.5-Z; #2: 0.5-X, 0.5+Y, 1.5-Z;

Table S8. The bond lengths (Å) and angles (°) of compound **2** at 300 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br1	2.9165(7)	Br1–Pb1–Br1 ^{#1}	171.83(2)

Pb1–Br1 ^{#1}	3.1803(7)	Br1–Pb1–Br2 ^{#2}	82.91(2)
Pb1–Br2 ^{#2}	3.0637(7)	Br1–Pb1–Br2	92.58(2)
Pb1–Br2	3.0239(7)	Br1–Pb1–Br3	96.03(2)
Pb1–Br3	3.0045(7)	Br1–Pb1–Br3 ^{#2}	85.45(2)
Pb1–Br3 ^{#2}	3.0803(7)	Br2–Pb1–Br1 ^{#1}	79.304(18)
		Br2 ^{#2} –Pb1–Br1 ^{#1}	98.966(19)
		Br2–Pb1–Br2 ^{#2}	97.82(2)
		Br2–Pb1–Br3 ^{#2}	177.992(19)
		Br2 ^{#2} –Pb1–Br3 ^{#2}	81.594(19)
		Br3 ^{#2} –Pb1–Br1 ^{#1}	102.677(19)
		Br3–Pb1–Br1 ^{#1}	82.264(19)
		Br3–Pb1–Br2	83.51(2)
		Br3–Pb1–Br2 ^{#2}	178.327(18)
		Br3–Pb1–Br3 ^{#2}	97.05(2)
		Pb1–Br1–Pb1 ^{#2}	80.631(17)
		Pb1–Br2–Pb1 ^{#1}	80.900(17)
		Pb1–Br3–Pb1 ^{#1}	80.938(17)

Symmetry codes: #1: +X, -0.5-Y, -0.5+Z; #2: +X, -0.5-Y, 0.5+Z;

Table S9. The bond lengths (Å) and angles (°) of compound **2** at 373 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br3	2.956(4)	Br3–Pb1–Br3 ^{#1}	176.34(9)
Pb1–Br3 ^{#1}	3.110(4)	Br3–Pb1–Br1	96.37(11)
Pb1–Br1	3.025(4)	Br3–Pb1–Br1 ^{#2}	82.66(10)
Pb1–Br1 ^{#2}	3.041(4)	Br3–Pb1–Br2 ^{#2}	83.80(11)
Pb1–Br2	3.033(4)	Br3–Pb1–Br2	96.77(11)
Pb1–Br2 ^{#2}	3.025(3)	Br1–Pb1–Br3 ^{#1}	80.42(10)
		Br1 ^{#2} –Pb1–Br3 ^{#1}	99.43(10)
		Br1–Pb1–Br1 ^{#2}	97.00(13)
		Br1–Pb1–Br2	82.62(12)
		Br2–Pb1–Br3 ^{#1}	81.11(10)
		Br2 ^{#2} –Pb1–Br3 ^{#1}	99.43(10)
		Br2 ^{#2} –Pb1–Br1	179.45(9)
		Br2 ^{#2} –Pb1–Br1 ^{#2}	82.49(12)
		Br2–Pb1–Br1 ^{#2}	179.29(9)
		Br2 ^{#2} –Pb1–Br2	97.89(13)
		Pb1–Br3–Pb1 ^{#2}	81.17(11)
		Pb1–Br1–Pb1 ^{#1}	81.23(10)
		Pb1 ^{#1} –Br2–Pb1	81.35(10)

Symmetry codes: #1: +X, 0.5-Y, -0.5+Z; #2: +X, 0.5-Y, 0.5+Z;

Table S10. The bond lengths (Å) and angles (°) of compound **2** at 423 K

Bond lengths [Å]		Bond angles [°]	
Pb1–Br1 ^{#1}	3.044(3)	Br1 ^{#1} –Pb1–Br1 ^{#2}	82.35(7)

Pb1–Br1 ^{#2}	3.044(3)	Br1 ^{#3} –Pb1–Br1 ^{#4}	97.65(7)
Pb1–Br1 ^{#3}	3.044(3)	Br1 ^{#3} –Pb1–Br1	82.35(7)
Pb1–Br1 ^{#4}	3.044(3)	Br1 ^{#1} –Pb1–Br1 ^{#3}	97.65(7)
Pb1–Br1 ^{#5}	3.044(3)	Br1 ^{#1} –Pb1–Br1	180.0
Pb1–Br1	3.044(3)	Br1 ^{#2} –Pb1–Br1 ^{#3}	180.0
		Br1 ^{#2} –Pb1–Br1 ^{#4}	82.35(7)
		Br1 ^{#1} –Pb1–Br1 ^{#5}	97.65(7)
		Br1 ^{#5} –Pb1–Br1 ^{#4}	180.0
		Br1 ^{#2} –Pb1–Br1 ^{#5}	97.65(7)
		Br1 ^{#2} –Pb1–Br1	97.65(7)
		Br1 ^{#3} –Pb1–Br1 ^{#5}	82.35(7)
		Br1 ^{#5} –Pb1–Br1	82.35(7)
		Br1 ^{#1} –Pb1–Br1 ^{#4}	82.35(7)
		Br1 ^{#4} –Pb1–Br1	97.65(7)
		Pb1–Br1–Pb1 ^{#6}	81.04(9)

Symmetry codes: #1: 2-X, 2-Y, 1-Z; #2: 1+X-Y, +X, 1-Z; #3: 1-X+Y, 2-X, +Z; #4: +Y, 1-X+Y, 1-Z; #5: 2-Y, 1+X-Y, +Z; #6: 2-X, 2-Y, -0.5+Z; #7: +X, +Y, 0.5-Z; #8: 2-X+Y, 2-X, 0.5-Z; #9: 2-X+Y, 2-X, +Z; #10: 2-Y, +X-Y, 0.5-Z; #11: 2-Y, +X-Y, +Z;