Electronic Supplementary Material (ESI) for Dalton Transactions.

A lead bromide organic-inorganic hybrid perovskite material showing reversible dual phase transition and robust SHG switching

Keke Han, Zhenhong Wei*, Xing Ye, Bo Li, Pan Wang, Hu Cai*

School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, 330031, P. R. China

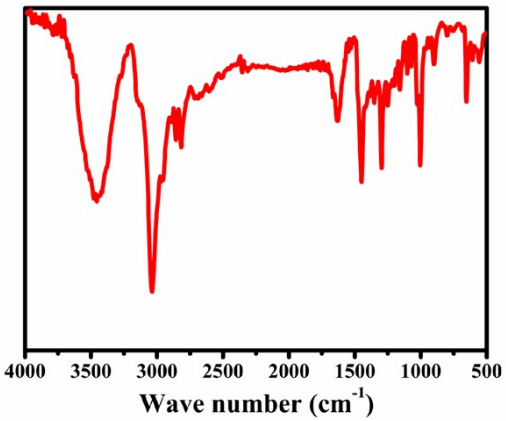

Fig. S1 Infrared (IR) spectra of solid **1** in KBr pellet recorded at room temperature.

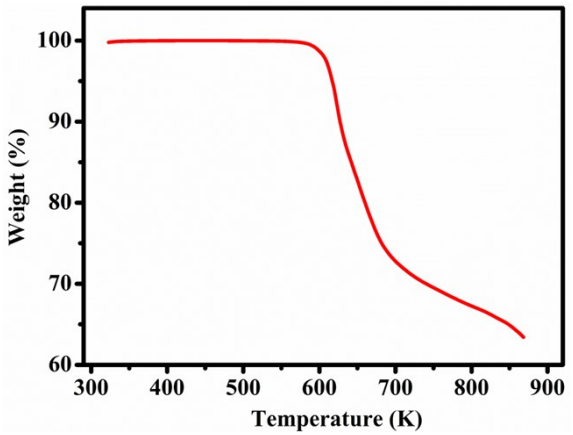

Fig. S2. TGA curves of compound **1** at heating rate of 40 °C /min, under nitrogen atmosphere.

Methodology

Powder X-ray diffraction

The variable-temperature powder X-ray diffraction (PXRD) measurements were performed on a Rigaku D/MAX 2000 PC X-ray diff-ractometer. PXRD patterns were recorded in the 2θ range of 0°–50° with a step size of 0.02°.

Thermal measurements

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer Diamond DSC instrument by heating and cooling the polycrystalline samples over the temperature range 300−480 K with the rate of 20 K/min at atmospheric pressure in aluminum crucibles

Dielectric Measurements

The temperature-dependent dielectric constant was measured on the Tonghui TH2828A instrument using silver-coated pressed powder pellets as electrodes, under the conditions of an applied electric field of 1V, a temperature range of 300K to 450K, at frequencies of 500 Hz to 1 MHz.

SHG measurements.

SHG switching experiments were performed on powder samples using an Nd:YAG laser (1064 nm, Vibrant 355 II, OPOTEK) with an input pulse of 350 mV on a FLS 920 (Edinburgh Instruments) at a scan rate of 10 K min^{-1}. The numerical value of the nonlinear optical coefficient of SHG was determined by comparison with the reference value of potassium dihydrogen phosphate (KDP).

Tab. S1. Selected bond lengths (Å) and angles (°) of **1** at 293 K, 398 K and 443 K.

293 K		398 K		443 K	
Pb1 - Br3^{1}	3.225 (8)	Pb1 - Br2^{1}	3.025(2)	Pb1 - Br1^{1}	3.010(9)
Pb1 - Br3	2.926 (7)	Pb1 - Br2	3.025(2)	Pb1 - Br1^{2}	3.010(9)
Pb1 - Br2^{2}	3.232 (8)	Pb1 - Br1	3.032(2)	Pb1 - Br1^{3}	3.010(9)
Pb1 - Br2	2.860 (8)	Pb1 - Br1^{1}	3.032(2)	Pb1 - Br1^{4}	3.010(9)
Pb1 - Br1	2.955 (8)	Pb1 - Br3^{2}	3.0378(19)	Pb1 - Br1	3.010(9)
Pb1 - Br1^{1}	3.096 (8)	Pb1 - Br3	3.0378(19)	Pb1 - Br1^{5}	3.010(9)
Br3 - Pb1 - Br3^{1}	170.7 (2)	Pb2 - Br4^{3}	3.022(2)	Br1^{1} - Pb1 - Br1^{2}	180.0
Br3 - Pb1 - Br2^{2}	81.48(2)	Pb2 - Br4	3.022(2)	Br1^{2} - Pb1 - Br1	98.4(2)
Br3^{1} - Pb1 - Br2^{2}	106.0(19)	Pb2 - Br5	3.028(2)	Br1^{1} - Pb1 - Br1^{3}	98.4(2)
Br3 - Pb1 - Br1	85.75(2)	Pb2 - Br5^{3}	3.028(2)	Br1- Pb1 - Br1^{3}	98.4(2)
Br3 - Pb1 - Br1^{1}	94.88(2)	Pb2 - Br6^{3}	3.0448(19)	Br1^{4} - Pb1 - Br1	180.0
Br2 - Pb1 - Br3	90.54(2)	Pb2 - Br6	3.0448(19)	Br1 - Pb1 - Br1^{5}	81.6(2)
Br2 - Pb1 - Br3^{1}	82.60(2)	Br1 - Pb1^{4}	3.032(2)	Br1^{1} - Pb1 - Br1^{5}	81.6(2)
Br2 - Pb1 - Br2^{2}	169.5(3)	Br2 - Pb1^{4}	3.025(2)	Br1^{1} - Pb1 - Br1^{4}	98.4(2)
Br2 - Pb1 - Br1	90.03(2)	Br3 - Pb1^{5}	3.0378(19)	Br1^{4} - Pb1 - Br1^{5}	98.4(2)
Br2 - Pb1 - Br1^{1}	86.72(2)	Br4 – Pb2^{6}	3.022(2)	Br1^{2} - Pb1 - Br1^{5}	98.4(2)
Br1 - Pb1 - Br3^{1}	100.4(2)	Br5 - Pb2^{6}	3.028(2)	Br1^{3} - Pb1 - Br1^{5}	180.0
Br1^{1} - Pb1 - Br3^{1}	78.51(19)	Br6 - Pb2^{7}	3.0448(19)	Br1^{2} - Pb1 - Br1^{4}	81.6(2)
Br1 - Pb1 - Br2^{2}	82.70(2)	Br2^{1} - Pb1 - Br2	179.69(16)	Br1^{2} - Pb1 - Br1^{3}	81.6(2)
Br1^{1} - Pb1 - Br2^{2}	100.6(2)	Br2^{1} - Pb1 - Br1	99.34(9)	Br1^{4} - Pb1 - Br1^{3}	81.6(2)
Br1 - Pb1 - Br1^{1}	176.6(2)	Br2 - Pb1 - Br1	80.45(9)	Br1^{1} - Pb1 - Br1	81.6(2)
Pb1 - Br3 - Pb1^{2}	79.39(16)	Br2^{1} - Pb1 - Br1^{1}	80.45(9)	Pb1^{6} - Br1 - Pb1	82.1(3)
Pb1 - Br2 - Pb1^{1}	80.22(16)	Br2 - Pb1 - Br1^{1}	99.34(9)		
Pb1 - Br1 - Pb1^{2}	81.10(17)	Br1 - Pb1 - Br1^{1}	96.16(13)		
		Br2^{1} - Pb1 - Br3^{2}	97.11(7)		
		Br2 - Pb1 - Br3^{2}	83.09(7)		
		Br1 - Pb1 - Br3^{2}	81.59(8)		
		Br1^{1} - Pb1 - Br3^{2}	176.41(11)		

Br2[1] - Pb1 - Br3	83.09(7)
Br2 - Pb1 - Br3	97.11(7)
Br1 - Pb1 - Br3	176.40(11)
Br1[1] - Pb1 - Br3	81.59(8)
Br3[2] - Pb1 - Br3	100.80(9)
Br4[3] – Pb2 - Br4	180.00(7)
Br4[3] - Pb2 - Br5	96.53(8)
Br4 - Pb2 - Br5	83.47(8)
Br4[3] - Pb2 - Br5[3]	83.47(8)
Br4 - Pb2 - Br5[3]	96.53(8)
Br5 - Pb2 - Br5[3]	180.0
Br4[3] - Pb2 - Br6[3]	99.25(8)
Br4 - Pb2 – Br6[3]	80.75(8)
Br5 - Pb2 – Br6[3]	80.88(7)
Br5[3] - Pb2 – Br6[3]	99.12(7)
Br4[3] - Pb2 – Br6	80.75(8)
Br4 - Pb2 – Br6	99.25(8)
Br5 - Pb2 - Br6	99.12(7)
Br5[3] - Pb2 - Br6	80.88(7)
Br6[3] - Pb2 - Br6	180.00(13)
Pb1 - Br1 - Pb1[4]	81.85(7)
Pb1 - Br2 - Pb1[4]	82.09(7)
Pb1 - Br3 - Pb1[5]	81.67(6)
Pb2[6] - Br4 - Pb2	82.19(7)
Pb2 - Br5 - Pb2[6]	81.99(7)
Pb2[7] - Br6 - Pb2	81.44(6)

Tab. S2 Hydrogen bond lengths [Å] and angles [°] of **1** at 293 K.

D-H…A	D-H [Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N-H…Br	0.910	2.442	163.93	3.326