

## Supporting Information

### Lead-free organic-inorganic hybrid semiconductors and NLO switches tuned by dimensional design

*Hong-Yi Shen, Lei He, Ping-Ping Shi and Qiong Ye\**

(Ordered Matter Science Research Center, Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics, Southeast University, Nanjing, 211189, P.R. China)

#### Powder X-ray Diffraction

powder X-ray diffraction (PXRD) measurements on a PANalytical X'Pert PRO X-ray diffractometer were performed at room temperature. Diffraction patterns were recorded in the  $2\theta$  range  $5\text{--}50^\circ$  with a step size of  $0.02^\circ$ . Some medium sized (average  $2.5*0.5*0.7$  mm for **1** and  $3.3*2.3*0.8$  mm for **2**) and good quality crystals are ground into powder for PXRD testing. As shown in Fig. S1, PXRD patterns obtained at 298 K coincide well with the simulated patterns based on the crystal structures at room temperature, indicating the phase purity of the as-grown crystals of the two compounds.

#### Thermal Measurements

DSC measurement was performed by the Netzsch Model DSC 200 F3 instrument through the heating and cooling process. Some crystalline

samples of compounds **1** (16.4 mg), **2** (15.3 mg) were placed in aluminum crucible under a nitrogen atmosphere and were measured at a rate of 20 K/min over the temperature range of 150 K-403 K.

### **Single-Crystal X-ray Crystallography**

The crystal structures of **1** crystal at 143 K, 236 K and **2** crystal at 323 K were obtained by Mo K $\alpha$  radiation at the Bruker APEX II CCD detector. *Bruker SAINT* was used to perform data reduction and multi-scan absorption correction.

The structure of **1** crystal at 293 K was collected on a XtaLAB Synergy R, HyPix diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at different temperatures. *CrysAlisPro* 1.171.40.39a (Rigaku OD, 2019) was used to perform data reduction and multi-scan absorption correction.

The structure of **2** crystal at 173 K was obtained on a PHOTON 2 CMOS detector with Mo K $\alpha$  radiation. *Bruker SAINT* was used to perform data reduction and multi-scan absorption correction.

Crystal structures were solved with direct method, and then refined by the *SHELXLTL* software package (*SHELX-14*) using full-matrix least-squares refinements on  $F^2$ . Crystal data and refinement of **1** and **2** at different phases were given in Table S1. In addition, the size of the crystal **1** used to measure XRD is 0.04\*0.02\*0.02 mm, while **2** is 0.06\*0.06\*0.04 mm. Those crystals used to measure variable-temperature X-ray diffraction are

large enough and of good quality. CCDC 2056728, 2056730, 2056731, 2056732 and 2056733 contain the supplementary crystallographic data for this paper.

### **Second harmonic generation (SHG) measurement.**

Variable-temperature SHG experiments of **1** and **2** were performed on powder samples using the fundamental laser beam with a low divergence (pulsed Nd: YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate). The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a  $\text{KH}_2\text{PO}_4$  reference. The crystals used to measure SHG are medium in size (average  $2.7 \times 0.6 \times 0.6$  mm for **1** and  $3.8 \times 2.7 \times 0.9$  mm for **2**) and transparent without cracks.

### **Piezoelectric coefficients measurement.**

The piezoelectric coefficients of the samples were determined by a quasi-static  $d_{33}$  meter (Institute of Acoustics, Chinese Academy of sciences, model ZJ-4AN). The size and  $d_{33}$  of crystals **2** used to measure piezoelectric properties are listed in Table.S6 and those crystals are large enough and of good quality.

### **Dielectric Constant Measurements**

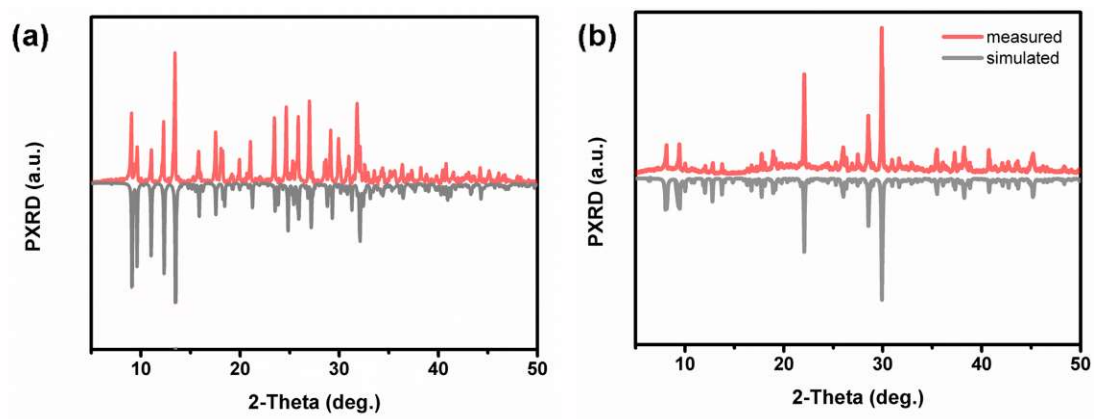
The temperature-dependent dielectric measurements were taken on a Tonghui TH2828A instrument, using pressed-powder tablets and observing any abnormal phenomenon between 113 K and 443 K within the frequency range of 500 Hz to 1 MHz. The pressed-powder pellets made by the samples of **1** and **2** were deposited with carbon conducting glue to act as the electrodes for dielectric measurements.

### **Ultraviolet–visible (UV–vis) absorption spectrum**

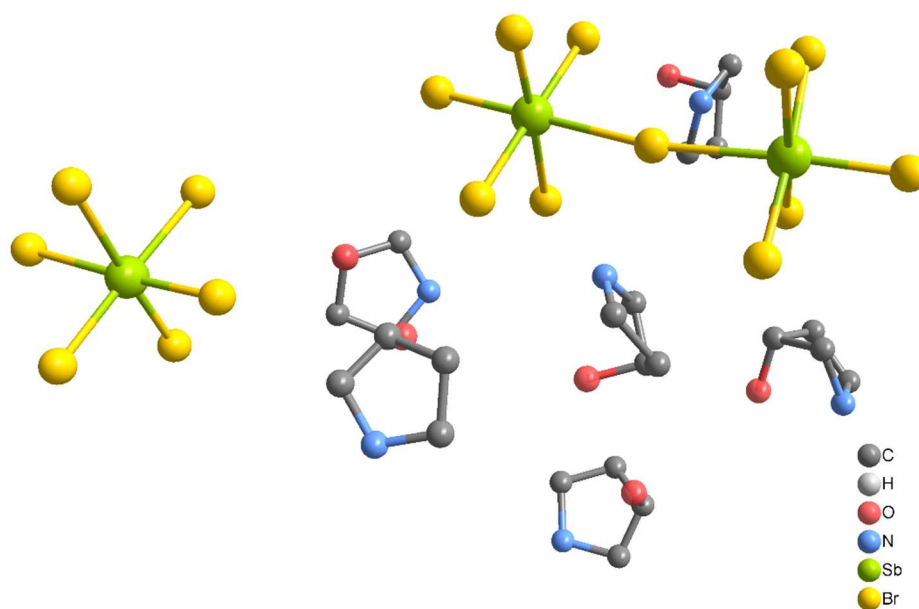
The plots of UV/Vis spectrum were measured on Shimadzu (Tokyo, Japan) UV-2600 spectrophotometer with powder samples of some single crystals at room temperature. BaSO<sub>4</sub> was used as the reference and powder of crystal **1** and **2** were prepared for the measurements

### **Thermogravimetric (TG)**

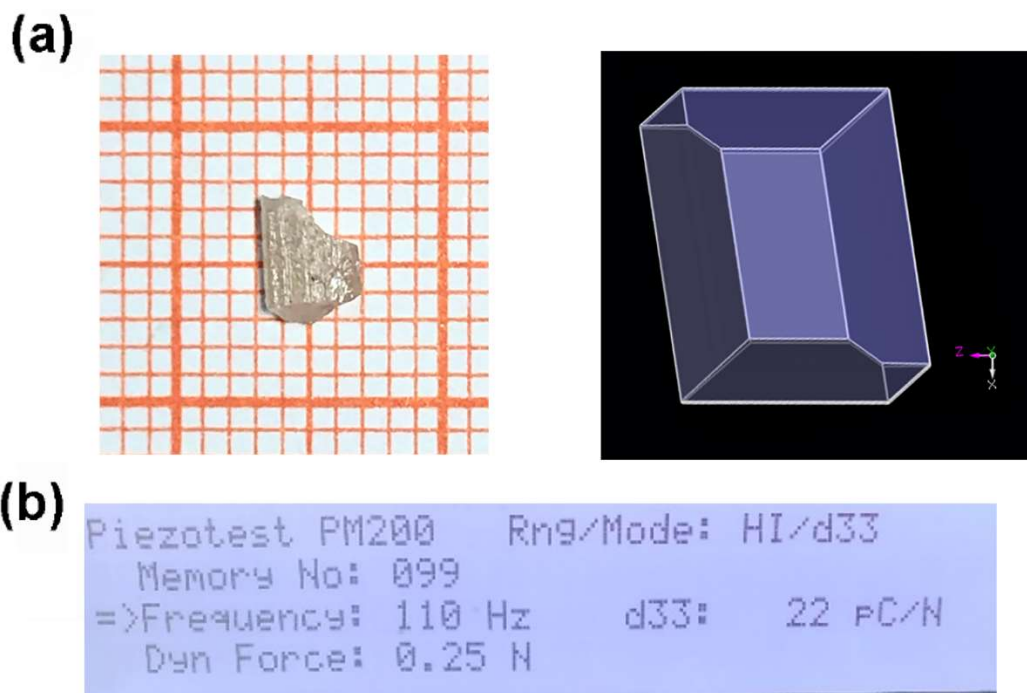
TG analyses were performed on a TAQ50 system with a heating rate of 10 K min<sup>-1</sup> in the air. Measurements were made at 300 K ~ 1050 K and the results showed that powder of crystal **1** and **2** began to decompose at 490 K and 422 K, respectively.



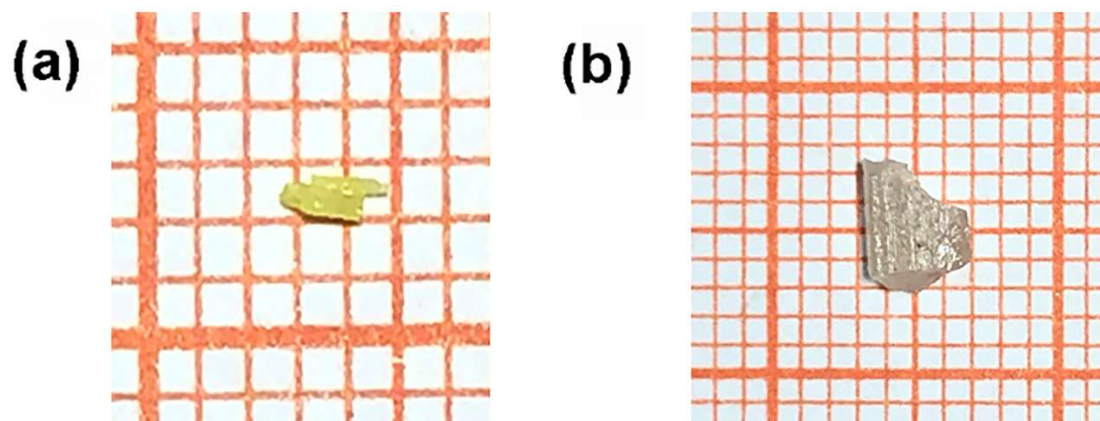
**Fig. S1** The experimental and simulated Powder X-ray diffraction (PXRD) patterns of **1** and **2** at room temperature, respectively.



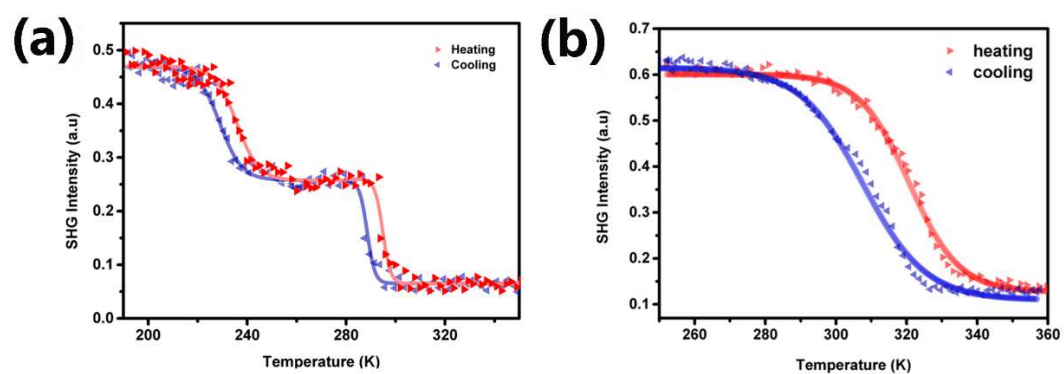
**Fig. S2** The asymmetry unit of **1** at 236 K. All hydrogen atoms are omitted for clarity.



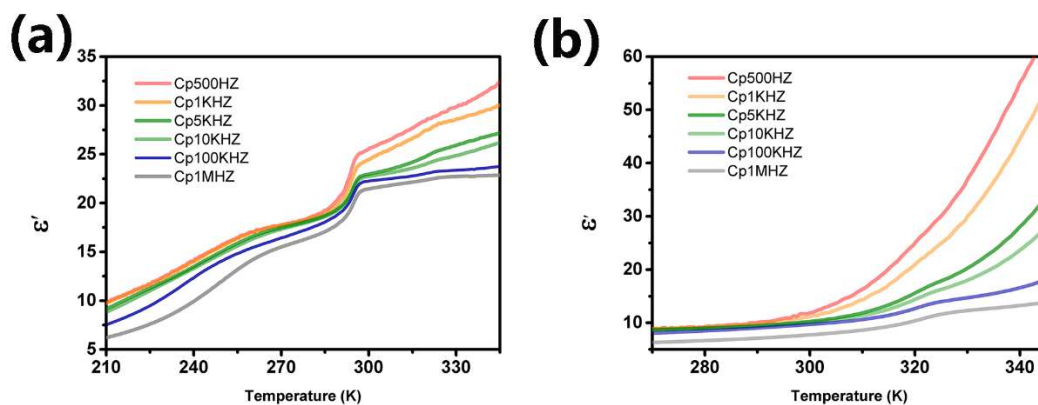
**Fig. S3** Piezoelectricity of **2**. (a) A picture of a large crystal and the simulative single crystal pattern of **2**. The largest natural face is (010)-face. (b) Recording the piezoelectric constant of a plate of **2** perpendicular to the largest natural face. The average size of the crystal **2** used to measure  $d_{33}$  is 4.12\*3.98\*2.75 mm.



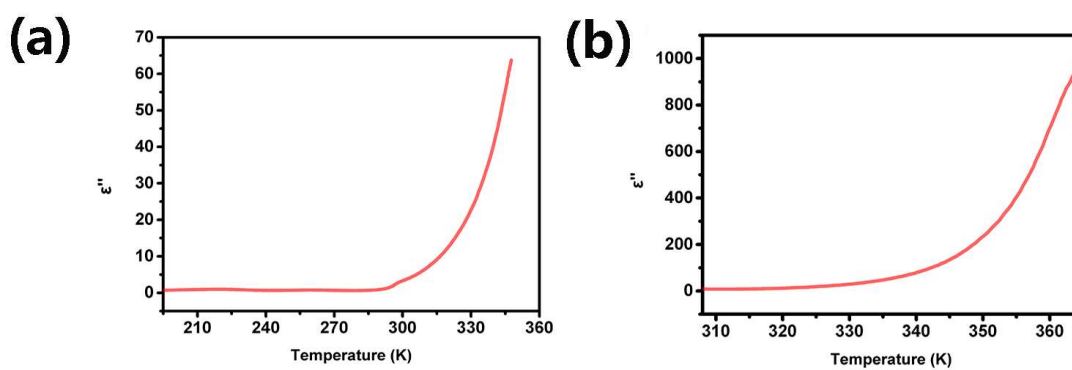
**Fig. S4** Obtained crystal photos of **1** and **2**.



**Fig. S5** The complete cycles of the SHG switching properties of **1** and **2**.

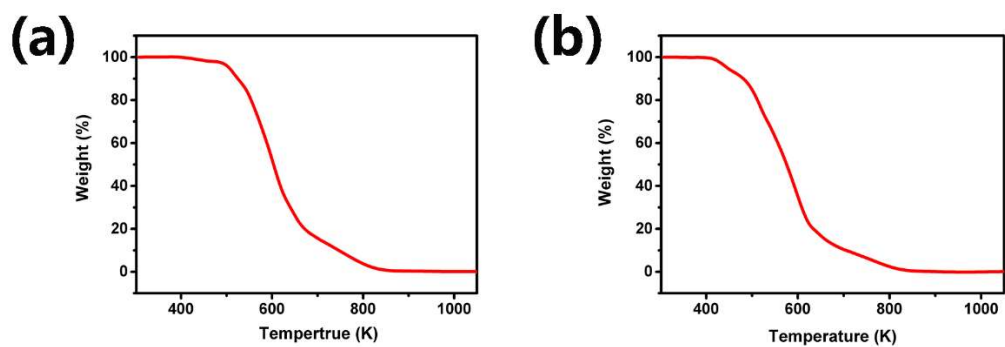


**Fig.S6** The real part ( $\epsilon'$ ) of pressed-powder pellet for **1** (a) and **2** (b) at 500 Hz, 1 kHz, 5 kHz, 10 kHz, 100 kHz and 1 MHz in cooling mode.

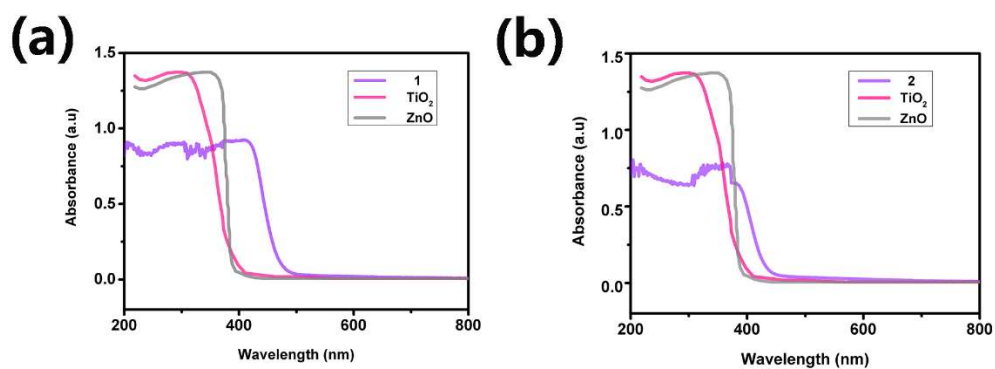


**Fig. S7** Imaginary parts of the dielectric constants of compounds **1**(a) and **2**(b) measured at 1 MHz frequency in cooling mode.

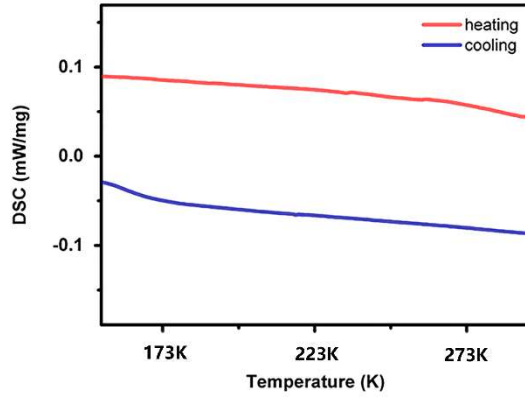




**Fig.S8** TG curves for **1** (a) and **2** (b).



**Fig. S9** Comparisons of UV spectra of **1** and **2** compounds with direct band gap ZnO and indirect band gap TiO<sub>2</sub>.



**Fig. S10** DSC traces for **2** below room temperature, indicating that there is no phase transition at low temperature.

Given space group  $P_{21}$  (belong to the point group 2) of **2** in the room temperature, the piezoelectric constant matrix  $[d]$  can be written as:

$$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & d_{26} \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix} \quad (\text{s1})$$

And the matrix  $[d]$  of converse piezoelectric can be derived as:

$$\begin{pmatrix} 0 & d_{21} & 0 \\ 0 & d_{22} & 0 \\ 0 & d_{23} & 0 \\ d_{14} & 0 & d_{34} \\ 0 & d_{25} & 0 \\ d_{16} & d_{26} & d_{36} \end{pmatrix} \quad (\text{s2})$$

Compound **1** also has piezoelectric properties because it belongs to the 222 point group. While, the crystal exhibits a fine needle-like morphology and no instrument can test other piezoelectric coefficients, resulting the piezoelectric properties of **1** are not characterized.

**Table S1.** Crystal data and Refinement of **1** and **2** collected at different phases.

	(C <sub>4</sub> H <sub>10</sub> NO) <sub>2</sub> SbBr <sub>5</sub> ( <b>1</b> )			(C <sub>4</sub> H <sub>10</sub> NO) <sub>5</sub> Sb <sub>4</sub> Br <sub>17</sub> ( <b>2</b> )	
Temp (K)	143	236	293	173	323
Cryst syst	orthorhombic			monoclinic	
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>			<i>P</i> 2 <sub>1</sub>	
Mr	2092.56			2285.99	
a (Å)	8.8393(19)	8.9134(18)	8.8663(8)	13.8913(4)	14.064(4)
b (Å)	18.357(4)	18.389(3)	18.7062(16)	17.7216(5)	17.655(5)
c (Å)	33.984(8)	34.305(6)	11.4394(10)	22.1687(6)	11.292(3)
$\beta$ (deg)	90	90	90	98.078(1)	81.036(5)
V(Å <sup>3</sup> )	5521(2)	5622.9(18)	1897.3(3)	5403.0(3)	2769.6(13)
Z	4			4	2
GOF	1.062	1.066	1.023	1.039	1.038
R <sub>1</sub> /wR <sub>2</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.0677/0.1953	0.0470/0.1508	0.0702/0.2558	0.0473/0.0801	0.0577/0.1791

**Table S2.** Selected bond angles [°] for **2** at different temperatures.

<b>173k</b>	<b>Angles (°)</b>	<b>323k</b>	<b>Angles (°)</b>
Br <sub>20</sub> -Sb <sub>5</sub> -Br <sub>18</sub>	89.25(6)	Br <sub>19</sub> -Sb <sub>5</sub> -Br <sub>18</sub>	85.56(3)
Br <sub>19</sub> -Sb <sub>5</sub> -Br <sub>18</sub>	86.77(6)	Br <sub>19</sub> -Sb <sub>5</sub> -Br <sub>20</sub>	91.31(3)
Br <sub>19</sub> -Sb <sub>6</sub> -Br <sub>17</sub>	93.36(6)	Br <sub>18</sub> -Sb <sub>5</sub> -Br <sub>20</sub>	89.49(3)
Br <sub>19</sub> -Sb <sub>6</sub> -Br <sub>20</sub>	86.83(5)	Br <sub>17</sub> -Sb <sub>6</sub> -Br <sub>20</sub>	85.48(3)
Br <sub>17</sub> -Sb <sub>6</sub> -Br <sub>20</sub>	86.62(6)	Br <sub>17</sub> -Sb <sub>6</sub> -Br <sub>19</sub>	86.48(2)
Br <sub>17</sub> -Sb <sub>7</sub> -Br <sub>18</sub>	85.17(6)	Br <sub>20</sub> -Sb <sub>6</sub> -Br <sub>19</sub>	88.71(2)
Br <sub>17</sub> -Sb <sub>7</sub> -Br <sub>20</sub>	89.31(6)	Br <sub>17</sub> -Sb <sub>7</sub> -Br <sub>18</sub>	85.66(2)
Br <sub>18</sub> -Sb <sub>7</sub> -Br <sub>20</sub>	85.85(6)	Br <sub>17</sub> -Sb <sub>7</sub> -Br <sub>20</sub>	84.61(3)
Br <sub>18</sub> -Sb <sub>8</sub> -Br <sub>19</sub>	85.70(6)	Br <sub>18</sub> -Sb <sub>7</sub> -Br <sub>20</sub>	88.19(2)
Br <sub>18</sub> -Sb <sub>8</sub> -Br <sub>17</sub>	82.24(6)	Br <sub>17</sub> -Sb <sub>8</sub> -Br <sub>18</sub>	89.66(3)
Br <sub>19</sub> -Sb <sub>8</sub> -Br <sub>17</sub>	88.02(6)	Br <sub>17</sub> -Sb <sub>8</sub> -Br <sub>19</sub>	90.69(3)
Sb <sub>4</sub> -Br <sub>1</sub> -Sb <sub>3</sub>	92.40(5)	Br <sub>18</sub> -Sb <sub>8</sub> -Br <sub>19</sub>	86.81(3)
Sb <sub>7</sub> -Br <sub>17</sub> -Sb <sub>6</sub>	93.75(6)	Sb <sub>8</sub> -Br <sub>17</sub> -Sb <sub>6</sub>	92.96(3)
Sb <sub>7</sub> -Br <sub>17</sub> -Sb <sub>8</sub>	94.88(6)	Sb <sub>7</sub> -Br <sub>17</sub> -Sb <sub>8</sub>	92.76(3)
Sb <sub>6</sub> -Br <sub>17</sub> -Sb <sub>8</sub>	86.39(6)	Sb <sub>6</sub> -Br <sub>17</sub> -Sb <sub>7</sub>	96.20(3)
Sb <sub>8</sub> -Br <sub>18</sub> -Sb <sub>5</sub>	94.60(6)	Sb <sub>8</sub> -Br <sub>18</sub> -Sb <sub>5</sub>	93.60(3)
Sb <sub>8</sub> -Br <sub>18</sub> -Sb <sub>7</sub>	97.70(6)	Sb <sub>8</sub> -Br <sub>18</sub> -Sb <sub>7</sub>	91.49(3)
Sb <sub>5</sub> -Br <sub>18</sub> -Sb <sub>7</sub>	91.99(6)	Sb <sub>5</sub> -Br <sub>18</sub> -Sb <sub>7</sub>	91.73(3)
Sb <sub>6</sub> -Br <sub>19</sub> -Sb <sub>5</sub>	93.59(7)	Sb <sub>8</sub> -Br <sub>19</sub> -Sb <sub>5</sub>	93.76(3)
Sb <sub>6</sub> -Br <sub>19</sub> -Sb <sub>8</sub>	91.24(6)	Sb <sub>8</sub> -Br <sub>19</sub> -Sb <sub>6</sub>	89.53(2)

Sb <sub>5</sub> -Br <sub>19</sub> -Sb <sub>8</sub>	92.69(6)	Sb <sub>5</sub> -Br <sub>19</sub> -Sb <sub>6</sub>	90.06(2)
Sb <sub>5</sub> -Br <sub>20</sub> -Sb <sub>7</sub>	92.47(6)	Sb <sub>5</sub> -Br <sub>20</sub> -Sb <sub>6</sub>	89.65(3)
Sb <sub>5</sub> -Br <sub>20</sub> -Sb <sub>6</sub>	90.66(6)	Sb <sub>5</sub> -Br <sub>20</sub> -Sb <sub>7</sub>	90.31(3)
Sb <sub>7</sub> -Br <sub>20</sub> -Sb <sub>6</sub>	90.32(6)	Sb <sub>6</sub> -Br <sub>20</sub> -Sb <sub>7</sub>	93.72(3)
Sb <sub>4</sub> -Br <sub>1</sub> -Sb <sub>2</sub>	89.59(6)		
Sb <sub>3</sub> -Br <sub>1</sub> -Sb <sub>2</sub>	88.04(6)		
Sb <sub>1</sub> -Br <sub>2</sub> -Sb <sub>3</sub>	91.05(6)		
Sb <sub>1</sub> -Br <sub>2</sub> -Sb <sub>4</sub>	92.21(6)		
Sb <sub>3</sub> -Br <sub>2</sub> -Sb <sub>4</sub>	95.75(5)		
Sb <sub>2</sub> -Br <sub>3</sub> -Sb <sub>1</sub>	94.20(7)		
Sb <sub>2</sub> -Br <sub>3</sub> -Sb <sub>4</sub>	90.78(6)		
Sb <sub>1</sub> -Br <sub>3</sub> -Sb <sub>4</sub>	88.56(6)		
Sb <sub>3</sub> -Br <sub>4</sub> -Sb <sub>1</sub>	89.81(6)		
Sb <sub>3</sub> -Br <sub>4</sub> -Sb <sub>2</sub>	91.71(6)		
Sb <sub>1</sub> -Br <sub>4</sub> -Sb <sub>2</sub>	92.68(6)		

**Table S3** Selected Sb-Br bonds for **2** at 173 K and 323 K.

Sb-Br bonds (Å)	173 K	323 K
Sb <sub>5</sub> -Br <sub>18</sub>	3.153(2)	3.184(1)
Sb <sub>5</sub> -Br <sub>19</sub>	3.120(2)	3.151(1)
Sb <sub>5</sub> -Br <sub>20</sub>	3.099(2)	3.215(9)
Sb <sub>6</sub> -Br <sub>17</sub>	3.223(2)	3.171(1)
Sb <sub>6</sub> -Br <sub>19</sub>	3.079(2)	3.276(1)
Sb <sub>6</sub> -Br <sub>20</sub>	3.253(2)	3.263(1)
Sb <sub>7</sub> -Br <sub>17</sub>	3.082(2)	3.199(1)
Sb <sub>7</sub> -Br <sub>18</sub>	3.211(3)	3.213(1)
Sb <sub>7</sub> -Br <sub>20</sub>	3.238(3)	3.261(1)
Sb <sub>8</sub> -Br <sub>17</sub>	3.367(2)	3.065(9)
Sb <sub>8</sub> -Br <sub>18</sub>	3.102(2)	3.118(1)
Sb <sub>8</sub> -Br <sub>19</sub>	3.233(3)	3.144(1)

**Table S4.** Hydrogen bonds for **2** at 173 K.

D—H···Acceptor	D—H	H···A	D···A	D—H···A
N <sub>1A</sub> -H <sub>1AD</sub> ···Br <sub>33</sub> <sup>#1</sup>	0.911	2.399	3.281	163.11
N <sub>1B</sub> -H <sub>1BD</sub> ···Br <sub>33</sub> <sup>#2</sup>	0.917	2.319	3.235	178.55
N <sub>1F_c</sub> -H <sub>1FD_c</sub> ···Br <sub>33</sub>	0.911	2.439	3.283	154.13
N <sub>1U_d</sub> -H <sub>1UD_d</sub> ···Br <sub>33</sub>	0.910	2.450	3.317	159.41
N <sub>1T_h</sub> -H <sub>1TD_h</sub> ···Br <sub>44_h</sub>	0.906	2.774	3.545	143.66

Symmetry transformations used to generate equivalent atoms: [#1] = x, y-1, z-1; [#2] = -x+1, y-1/2, -z+2

**Table S5.** Hydrogen bonds for **2** at 323 K.

D—H···Acceptor	D—H	H···A	D···A	D—H···A
N <sub>1</sub> -H <sub>1B</sub> ···Br <sub>33</sub> <sup>#1</sup>	0.890	2.684	3.569	172.57
N <sub>3</sub> -H <sub>3B</sub> ···Br <sub>33</sub>	0.890	2.184	3.073	176.56
N <sub>4</sub> -H <sub>4B</sub> ···Br <sub>33</sub>	0.890	3.113	3.675	123.09
N <sub>5</sub> -H <sub>5B</sub> ···Br <sub>33</sub> <sup>#2</sup>	0.890	2.721	3.466	141.97

Symmetry transformations used to generate equivalent atoms: [#1] = -x+1, y+1/2, -z+1, -z+1; [#2] = -x+1, y+1/2, -z+1

**Table S6** The sizes of crystals **2** for measuring piezoelectric properties.

(The average size of the crystal **2** used to measure  $d_{33}$  is 4.12\*4.05\*2.77 mm)

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i> <sub>33</sub>
Sample 1	4.13	4.02	2.85	22
Sample 2	4.22	3.94	2.83	22
Sample 3	4.09	4.08	3.12	22
Sample 4	3.89	3.78	2.25	19
Sample 5	4.28	4.43	2.78	26