

# Supporting Information

## Borate [C<sub>6</sub>N<sub>2</sub>H<sub>15</sub>]<sub>2</sub>[B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>] Ferroelectric crystal : Synthesis,

### Property and Film Fabrication

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### Experimental Section

#### Synthesis of 1

0.633g H<sub>3</sub>BO<sub>3</sub> and 0.243g C<sub>6</sub>H<sub>14</sub>N<sub>2</sub> were added to a 50ml beaker, and then 10ml water and 10ml ethanol were added to the beaker. At room temperature, the reactants and the solvent were stirred for 30 min under a constant temperature magnetic stirrer, and then placed at room temperature to allow natural evaporation and crystallization. After 30 days, massive crystals of **1** were obtained in the beaker. After replacing the water by 10ml heavy water, the proton-exchanged product can be obtained.

#### Materials and characterization

C<sub>6</sub>H<sub>14</sub>N<sub>2</sub> (Damao chemical, AR), H<sub>2</sub>O (self made), ethanol (Damao chemical, 99.7%), D<sub>2</sub>O (Sinopharm, AR), and H<sub>3</sub>BO<sub>3</sub> (Damao chemical, 99.5%). All chemicals are commercially available and do not require further purification.

Infrared spectra in the 400-4000 cm<sup>-1</sup> range was obtained by pressing samples on KBr pellets on a Nicolet 380 spectrometer. Using Cu K $\alpha$  radiation, powder X-ray diffraction (PXRD) data at an angle of 2 $\theta$  = 5-50° was recorded on the ULTIMA III powder diffractometer. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurement was taken on a JEM-2100F instrument at 200 kV. The scanning electron microscope (SEM) was acquired on Hitachi S-3400 N scanning electron microscope. Thermogravimetric analysis data were tested on the Perkin Elmer TGA/DSC 7 thermo gravimetric analyzer. Using N<sub>2</sub> as carrier gas, the flow rate was set at 40 mL/min, and the temperature range was generally 20-1000 °C and the heating rate was 10 °C/min. The instrument used in the atomic force microscope was Bruker Dimension FastScan, America. The working mode for the imaging of ferroelectric domains of ferroelectric thin films was piezoelectric response mode (PFM). All scanning was carried out in normal atmospheric environment and room temperature. The piezoelectric power microscope adopted a silicon probe coated with gold on the surface. The AC voltage amplitude

between the tip and the sample was 5 V, the frequency was 1 kHz, Force Ref. was -1.0, and the scanning period was 2 s. Ferroelectric properties of ferroelectric thin films were measured at 25 – 400 °C using Radiant Premier 2 (Radiant, USA). The hysteresis loop test rate range is 0.03 Hz ~ 100 KHz, and the temperature range is -180 ~ 200 °C. The sample size of ferroelectric thin film is 10 mm in diameter and less than 1 mm in thickness. The sample was tested for dielectric constant on Novocontrol (Germany) piezoelectric tester. The laser Raman spectroscopy of the samples were tested on a Renishaw inVia spectrometer from Renishaw, UK.

### Determination of crystal structure

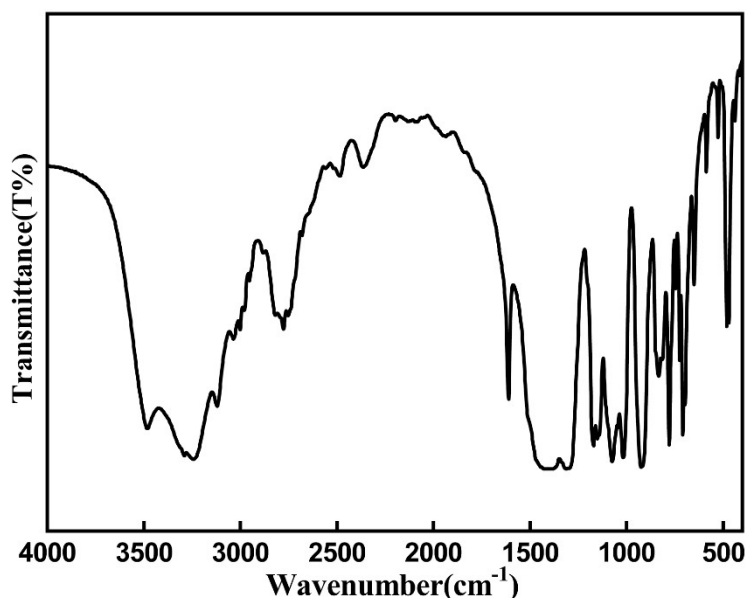
Using graphite monochromatic Mo  $\text{ka}$  ( $k=0.71073 \text{ \AA}$ ) radiation, the diffraction data was measured on the Bruker SMART APEX CCD diffractometer, and all absorption corrections were performed through the *Multiscan* program. The direct method is used to solve the structure, and the *Olex2* and *OlexSys* programs are used to refine the least-squares fitting of the full matrix of  $F^2$ . All H atoms were geometrically fixed at calculated distances and allowed to ride on the non-H parent atoms. All non-H atoms were refined anisotropically. Crystallographic data and the structure determination for **1** and **2** are summarized in **Table S1**. The crystallographic data (excluding structure factors) for the structure of **1** in this paper has been deposited in the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. A copy of the data can be obtained free of charge by quoting the depositary number CCDC - 2168887.

**Table S1** Crystal data and structure refinement for **1**.

Empirical formula	$\text{C}_6\text{H}_{19}\text{B}_5\text{N}_2\text{O}_{10}$	$\text{C}_6\text{H}_{19}\text{B}_5\text{N}_2\text{O}_{10}$
Formula weight	333.27	333.27
Temperature/K	298	150
Crystal system	Monoclinic	Monoclinic
Space group	Cc	Cc
$a/\text{\AA}$	9.786(4)	9.783(3)
$b/\text{\AA}$	20.930(20)	20.827(6)
$c/\text{\AA}$	14.577(6)	14.491(4)
$\beta/^\circ$	94.406(5)	94.955(5)
$V/\text{\AA}^3$	2977 (2)	2941.6(14)
$Z$	4	4
$D/g \text{ cm}^{-3}$	1.321	1.337
$\mu/\text{mm}^{-1}$	0.105	0.106
Reflection collected	9025	11589
Independent reflections	4404	6142
Parameters refined	415	415
Index ranges	$-12 \leq h \leq 11, -25 \leq k \leq 25, -17 \leq l \leq 12$	$-12 \leq h \leq 12, -26 \leq k \leq 26, -18 \leq l \leq 18$
Goodness-of-fit on $F^2$	1.019	0.939
Final $R_1, wR_2 [I > 2\sigma(I)]$	0.0379-0.1159	0.0497-0.1309
Final $R_1, wR_2 [\text{all data}]$	0.0399-0.1198	0.0567-0.1369

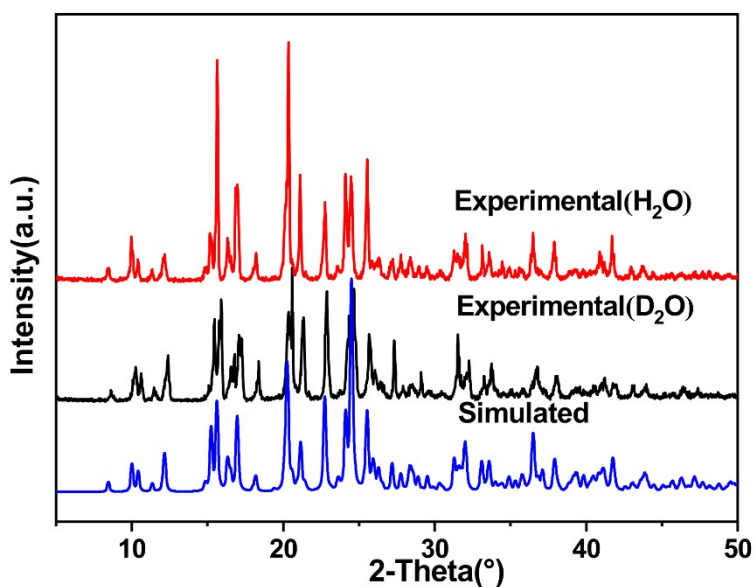
**Table S2.** Details of the H-Bs bond in **1** at 298 K and 150 K.

Temperature/K	D	H	A	d(H-A)/Å	d(D-A)/Å	D-H-A)/°
298	O1	H1A	O18	1.9795	2.8006	178.77
<b>150</b>	<b>O1</b>	<b>H1A</b>	<b>O18</b>	<b>1.9561</b>	<b>2.7751</b>	<b>178.95</b>
298	O2	H2A	O20	1.9173	2.7337	174.45
<b>150</b>	<b>O2</b>	<b>H2A</b>	<b>O20</b>	<b>1.9053</b>	<b>2.7228</b>	<b>175.14</b>
298	O3	H3A	O17	1.8998	2.7135	171.24
<b>150</b>	<b>O3</b>	<b>H3A</b>	<b>O17</b>	<b>1.8735</b>	<b>2.6864</b>	<b>171.02</b>
298	O11	H11A	O8	1.9472	2.7643	174.03
<b>150</b>	<b>O11</b>	<b>H11A</b>	<b>O8</b>	<b>1.9357</b>	<b>2.7514</b>	<b>173.52</b>
298	O13	H13A	O7	1.9502	2.7680	177.49
<b>150</b>	<b>O13</b>	<b>H13A</b>	<b>O7</b>	<b>1.9349</b>	<b>2.7547</b>	<b>179.10</b>
298	O14	H14A	O6	1.9074	2.7248	174.56
<b>150</b>	<b>O14</b>	<b>H14A</b>	<b>O6</b>	<b>1.8921</b>	<b>2.7100</b>	<b>174.76</b>



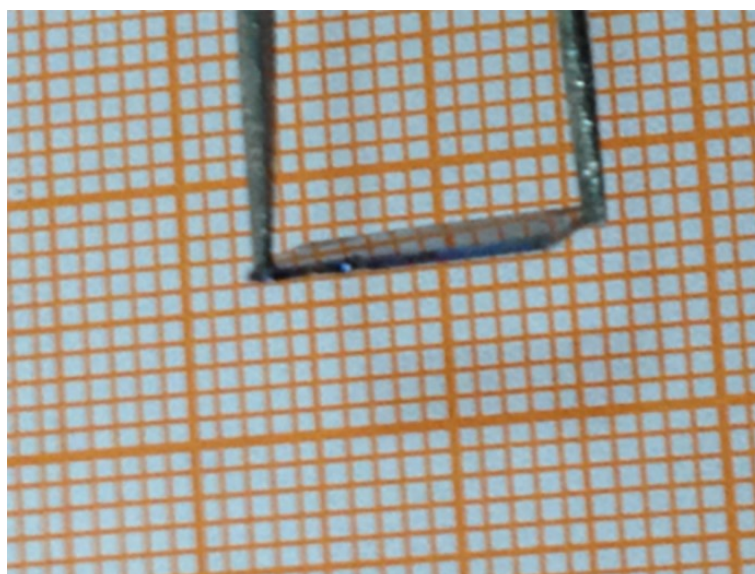
**Fig. S1** IR spectra of  $[\text{C}_6\text{N}_2\text{H}_{15}] \cdot [\text{B}_5\text{O}_6(\text{OH})_4]$ .

The FTIR spectrum of **1** is shown in **Fig. S1**. The bands at 3489, 3302 and 3239  $\text{cm}^{-1}$  are stretching modes of the N-H and O-H groups. The band at 1609  $\text{cm}^{-1}$  might be due to the bending mode of N-H. The band at 1399 and 1318  $\text{cm}^{-1}$  are assigned as the asymmetric stretching modes of B-O in  $\text{BO}_3$  triangles. The band at 1074  $\text{cm}^{-1}$  and 914  $\text{cm}^{-1}$  might be the asymmetric stretching modes of B-O in  $\text{BO}_4$  tetrahedra. The characteristic absorption band of pentaborate anion is at 478  $\text{cm}^{-1}$ .



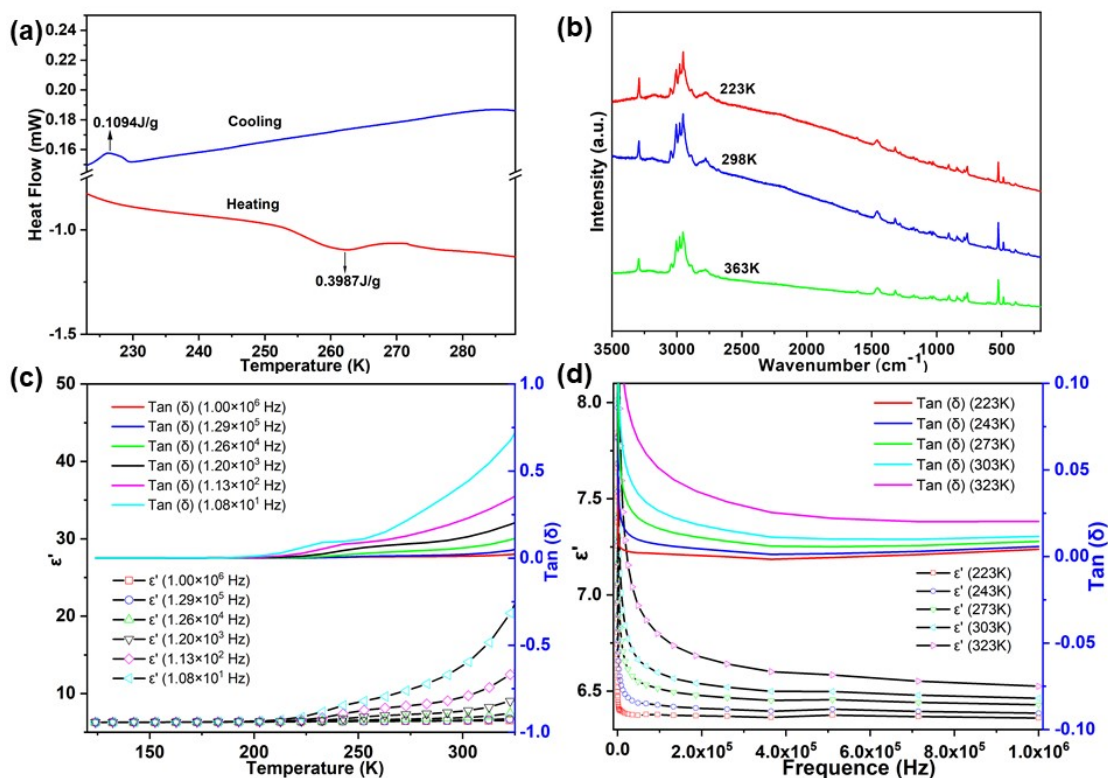
**Fig. S2** Experimental and simulated power XRD patterns of compound.

**Fig. S2** is an PXRD diagram of compound and the compound when water is replaced by heavy water. The actual peak of the compound basically coincides with the theoretical simulated diffraction peak, indicating that the compound is a pure phase, and the hydrogen in the compound is not the source water, which is consistent with the infrared spectrum.



**Fig. S3** The bulk crystal of **1**

As shown in **Fig. S3**, the dielectric hysteresis loop was measured using a bulk crystal of **1**.



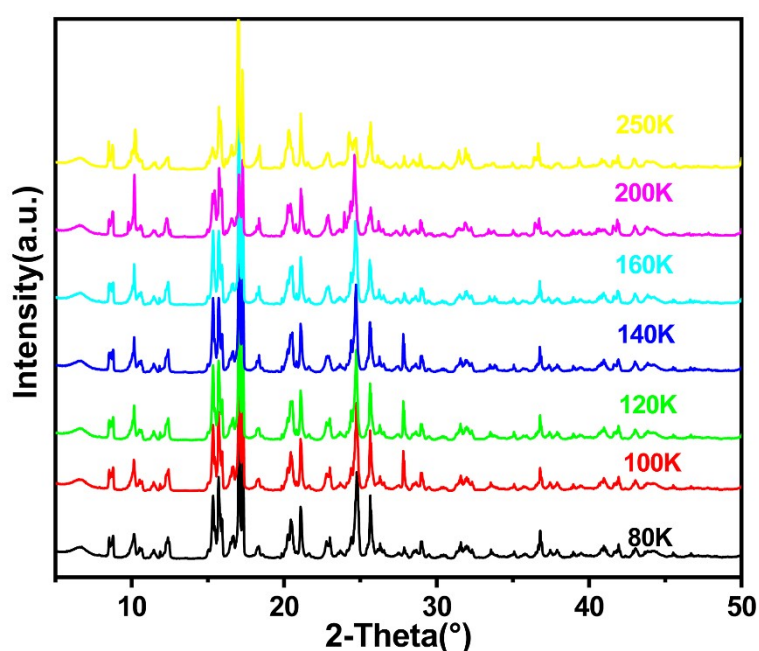
**Fig. S4** (a) DSC curves of **1**. (b) Laser Raman spectrum of **1** at different temperatures. (c) Temperature dependence of the dielectric constant and dielectric loss at different frequencies of **1**. (d) Frequency dependence of dielectric constant and dielectric loss of **1** at different temperatures.

The crystal was subjected to differential scanning calorimetry (DSC), which is a common method

for detecting the phase transition under external thermal stimulation. The differential scanning calorimetry (DSC) measurements of **1** show a very weak heat anomaly at 260 K of heating curve and 220 K of cooling curve, respectively, but there is no reversible phase transition, in which entropy changes for cooling or heating is 0.1094 or 0.3987 J/g, notably, which is too less than that observed in other molecular-based ferroelectrics (**Fig. S4a**).<sup>1-2</sup>

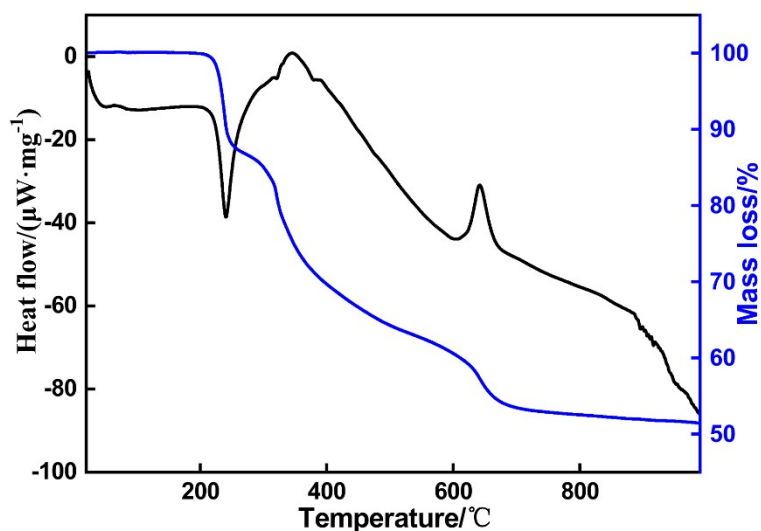
Laser Raman spectroscopy was further applied to study the crystal structure of **1**, sample of **1** was measured at 223 K, 298K and 363K. As shown in **Fig. S4b**, the spectrum of **1** obviously exhibits a peak at 528  $\text{cm}^{-1}$  resulting from the pentaborate polyanions and features at 3005 and 2874  $\text{cm}^{-1}$ , which are assigned to the organic cations. The bands at 1036 and 895  $\text{cm}^{-1}$  are probably attributed to the vibration of the  $\text{BO}_4$ . These peaks are remained kept as temperature decreasing, supplying additional proof to support the that no ferroelectric-paraelectric phase transition was observed during heating or cooling process.

The relationship between the dielectric constant and dielectric loss of the tablet of **1** measured at different frequencies is shown in **Fig. S4c**. The dielectric constant and dielectric loss of **1** increase with increasing temperature, there is no peak below 323K, and no phase transition occurs. For all we know, **1** is the first example of ferroelectric borate in which no phase transition was observed from 150K to 323K, such property is similar to that found in an inorganic ferroelectric  $\text{LiH}_3(\text{SeO}_3)_2$ . And **Fig. S4d** shows the variation law of dielectric constant and dielectric loss at different temperatures of **1**. It can be seen that this compound also does not show a peak below 323 K. TG-DSC analysis of **1** is carried out in air atmosphere with a heating rate of 10  $^\circ\text{C}/\text{min}$ . Moreover, single crystal X-ray diffraction at 150K and 298K (**Table S1**), as well as temperature dependent PXRD of **1** were tested at 80-250K and the measurements excluded the possibility of phase transition (**Fig S5**).



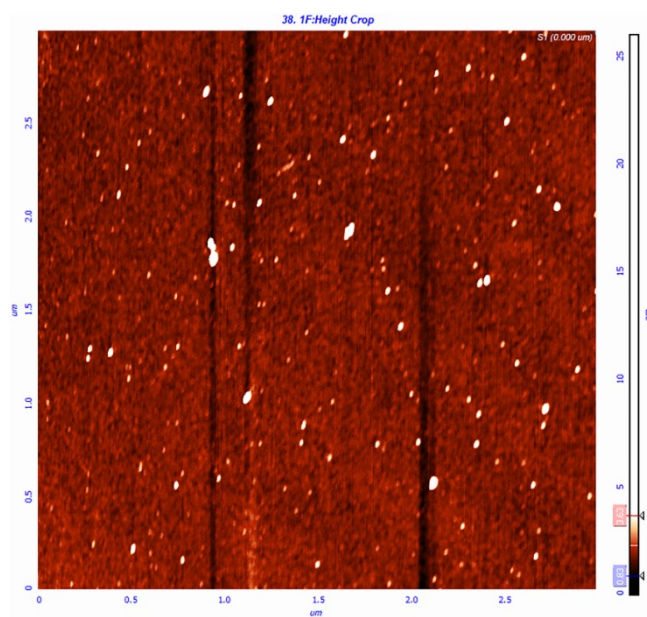
**Fig. S5** Power XRD patterns of **1** at 80-250K.

**Fig. S5** is the PXR diagram of the compound at 80-250K. The compound showed consistent diffraction peaks at different temperatures, indicating that the compound did not undergo phase change at low temperatures.

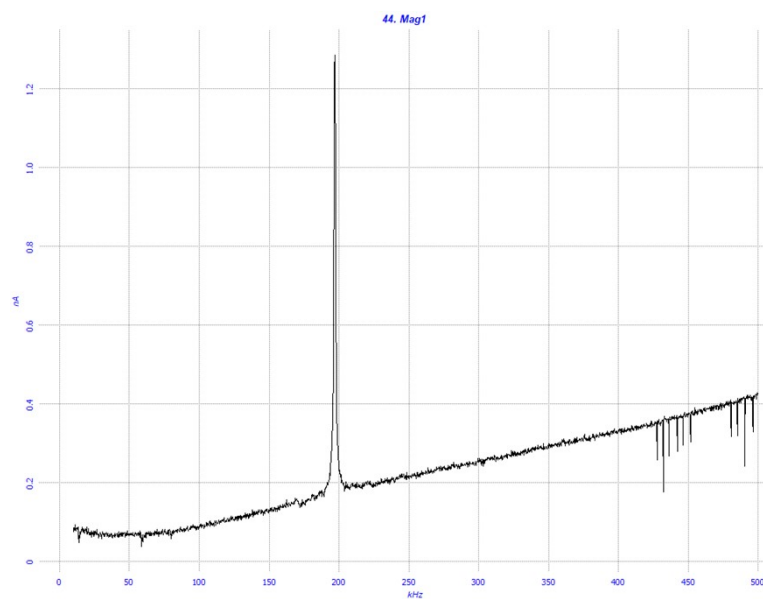


**Fig. S6** TG-DSC curve of **1**.

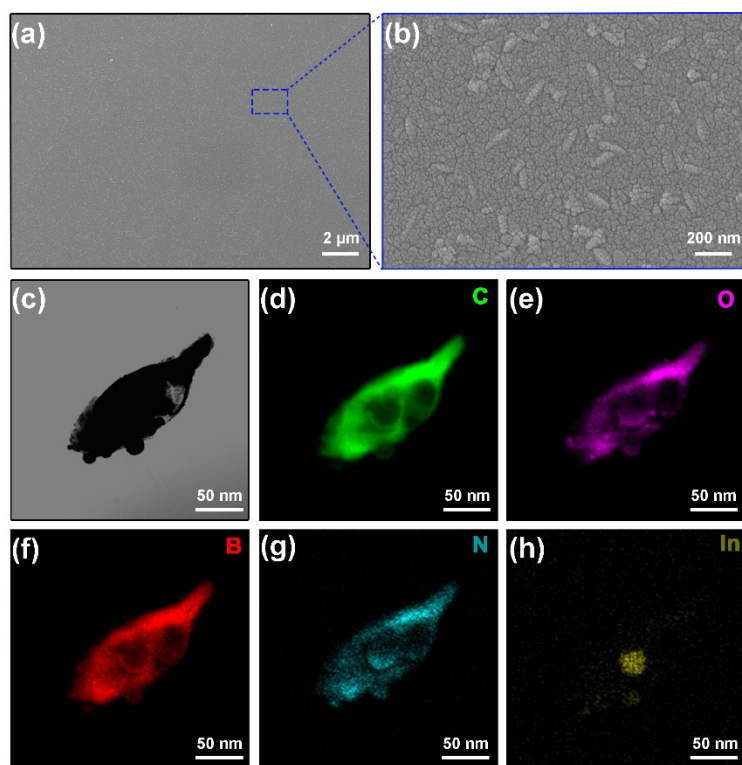
TG-DSC analysis of **1** was carried out in air atmosphere from 20 °C to 1000 °C with a heating rate of 10 °C /min. As shown in the **Fig. S6**, the temperature below 200 °C, **1** remained stable. When the temperature is between 200°C and 813°C, **1** had an obvious weight loss process. At 200°C, the compound lost weight by endothermic heat, and at 645°C, the compound lost weight by exotherm. During the whole process, the weight loss of the compound was lost in the form of water and organic matter, and the weight loss rate was about 47.6%. (Theoretical value was 45.3%)



**Fig. S7** The AFM image of the ferroelectric thin film **2**.

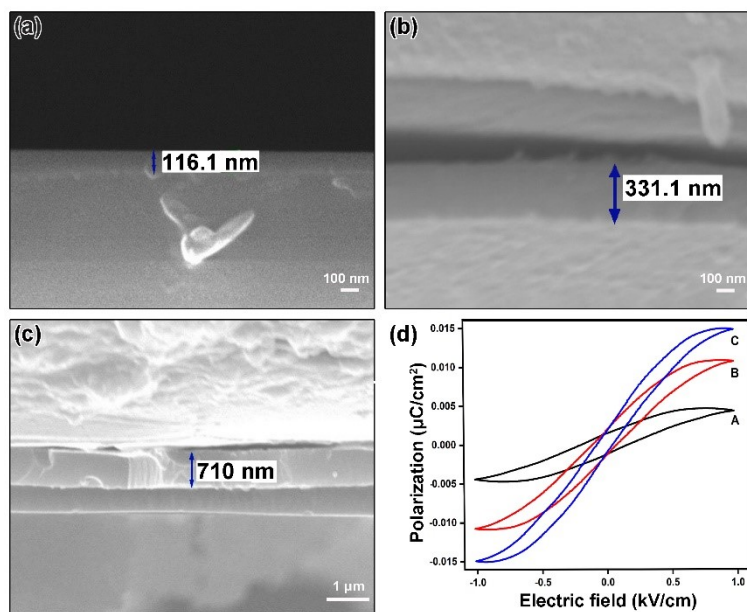


**Fig. S8** The contact resonance of film 2.



**Fig. S9** (a,b) The SEM image of film 3. (c) HAADF-STEM image of film 3 and EDX element mapping images of (d) C, (e) O, (f) B, (g) N, and (h) In.





**Fig. S10** (a,b,c) Thickness scan of film **3** spin-coated once, three times, and five times. (d) Room temperature ferroelectric hysteresis loops of film **3-A**, **3-B**, **3-C** at 50 Hz.

### Notes and references

- [1] R. Pepinsky, K. Vedam, *Phys. Rev.*, 1959, **114**, 1217.
- [2] T. Zhang, L. Z. Chen, M. Gou, Y. H. Li, R. G. Xiong, *Cryst. Growth Des.*, 2010, **10**, 1025-1027.