# Supporting Information

## Synthesis and Characterization of a New Organic-inorganic Hybrid Ferroelectric: $(C_4H_{10}N)_6[InBr_6][InBr_4]_3\cdot H_2O$

*Wen-Bo Xin, Guan-Cheng Xu*, Min Li*

1. Methods.
2. IR Characterization.
3. TG Characterization.
4. PXRD Characterization.
5. DSC Characterization.
6. Selected bond lengths (Å) and bond angles (°) for compound **1**.

## 1. Methods

**DSC, TG, XRD:** DSC measurements were conducted by a Netzsch 200F3 instrument under nitrogen atmosphere, upon cooling and heating the samples of 4.23 mg in the temperature range in 200-270 K with a 10 K/min scanning rate in aluminum crucibles. Thermogravimetric (TG) measurement was carried out by a Netzsch STA 449F3 thermogravimetric instrument at a heating rate of 10 K/min in an air atmosphere. The powder X-Ray diffraction (PXRD) pattern was obtained on Rigaku SmatrLab SE advance diffractometer with Cu-K$\alpha$ radiation ($\lambda$ = 1.54056 Å) in the range of 5° < 2$\theta$ < 50°.

**Elemental analysis, IR:** Elemental analyzed with the Elementar Vario EL cube analyzer. The FT-IR spectrum was obtained using a Bruker Vertex 70 spectrophotometer within the range of 4000-400 $cm^{-1}$. The sample was diluted with spectroscopic KBr and pressed into a slice.

**Dielectric, Ferroelectric Measurements:** The complex electric permittivity $\varepsilon$ was measured on a TH2828 Precision LCR meter with the frequencies of 10 kHz, 100 kHz, and 1 MHz, an applied voltage of 1.0 V, and a temperature sweeping rate of approximately 2 K/min. Crystals of the compound were ground and pressed into dense pellets at around 14 MPa. The capacitor was made by painting two faces of the tablet piece with silver conducting paste and using gold wires as the electrodes. After being dried by silica gel for two days, the capacitor was detected under a microscope with a Phenix CCD eye and the corresponding software. The crystals of ferroelectric hysteresis loops were performed by the Sawyer-Tower circuit method. The samples were made with single-crystals cut into the form of thin plate perpendicular to the crystal *c*-axis. Silver conductive paste deposited on the plate surfaces was used as the electrodes. The thickness (0.33 mm) and area (3.17 $mm^2$) of the crystals were accurately measured using the optical microscope. The frequency and amplitude of the applied voltage were 50 Hz and 250 V, respectively. The P-E hysteresis loops were recorded on a Precision LC, Premier II (Radiant Technologies, Inc.).

**Crystallography:** The variable-temperature single-crystal X-ray diffraction data for compound **1** at room temperature (300 K) and low temperature (150 K) were demonstrated by a Agilent SuperNova Dual Atlasdiffractometer equipped with a graphite-monochromated Cu-K*a* radiation ($\lambda$ = 0.71073 Å). The crystal structures of RTP and LTP were solved by *OLEX2* soft package direct methods. The structure was refined by *SHELXL*-97 software package according to the full-matrix method of $F^2$. The anisotropy of all non-hydrogen atoms was refined by the total reflections method of $I > 2s$ ($I$), the position of all hydrogen atoms in the graph was further refined by differential fourier.

## 2. IR Characterization.

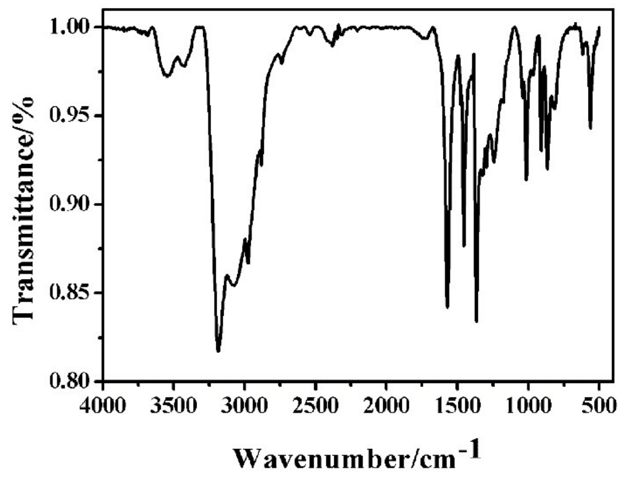


Figure S1. IR spectrum of compound **1.**

## 3. TG Characterization

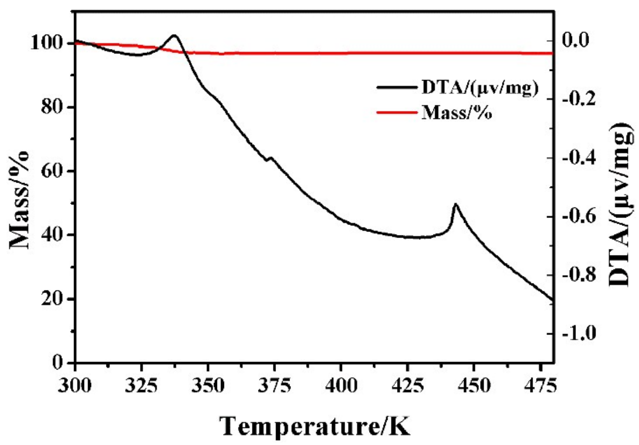


Fig. S2 The TG curves of compound **1** with a heating rate of 10 K/min.

## 4. PXRD Characterization

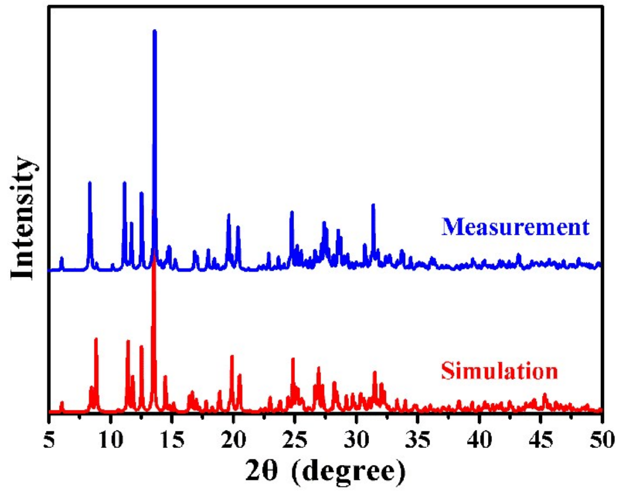


Fig. S3 PXRD pattern of compound **1**.

## 5. DSC Characterization.

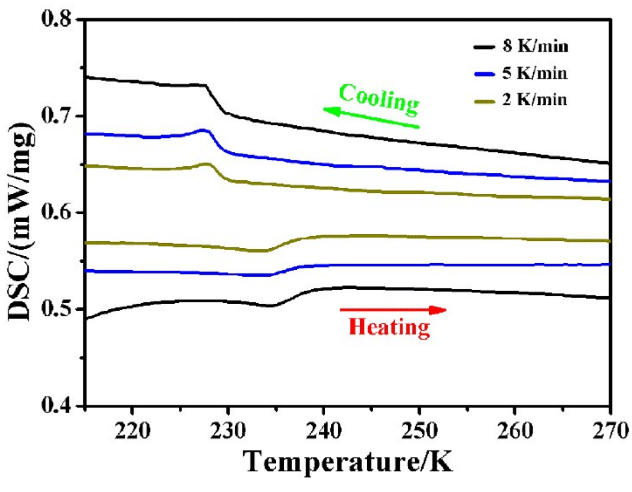


Fig. S4 DSC curves of compound **1** obtained in a heating-cooling mode at 8 K/min, 5 K/min, 2 K/min, respectively.

## 6. Table. S1 Selected bond lengths (Å) and bond angles (°) for compound 1 at 300 K and 150 K.

| **300 K** | | | |
|---|---|---|---|
| In2-Br6 | 2.409(10) | Br5A-In2-Br6[a] | 100.2(3) |
| In2-Br7 | 2.430(11) | Br5A-In2-Br7[a] | 100.4(3) |
| In2-Br8 | 2.354(7) | Br5A-In2-Br8[a] | 103.1(3) |
| In2-Br5[a] | 2.778(6) | Br6A-In2-Br7[a] | 112.4(4) |
| In2-Br6[a] | 2.409(10) | Br6A-In2-Br8[a] | 119.6(4) |
| In2-Br7[a] | 2.430(11) | Br7A-In2-Br8[a] | 116.9(4) |
| In2-Br8[a] | 2.354(7) | Br5-In2-Br6 | 100.2(3) |
| In2-Br5 | 2.778(6) | Br5-In2-Br7 | 100.4(3) |
| In3-Br10 | 2.664(2) | Br5-In2-Br8 | 103.1(3) |
| In3-Br11 | 2.647(2) | Br5-In2-Br5[a] | 177.3(3) |
| In3-Br9[b] | 2.685(2) | C1-C2 | 1.48(5) |
| In3-Br10[b] | 2.664(2) | C2-C3 | 1.47(5) |
| In3-Br11[b] | 2.647(2) | C3-C4 | 1.46(5) |
| In3-Br9 | 2.685(2) | C5-C6 | 1.37(4) |
| In1-Br1 | 2.472(3) | C6-C7 | 1.48(5) |
| In1-Br4 | 2.481(3) | C7-C8 | 1.47(4) |
| In1-Br3 | 2.474(4) | C9-C10 | 1.49(6) |
| In1-Br2 | 2.505(3) | C10-C11 | 1.50(6) |
| N1-C1 | 1.43(5) | C11-C12 | 1.48(5) |
| N1-C4 | 1.42(5) | Br9-In3-Br11 | 179.10(7) |
| N2-C5 | 1.45(4) | Br9-In3-Br9[b] | 90.18(7) |
| N2-C8 | 1.41(3) | Br9-In3-Br10 | 89.65(7) |
| N3-C9 | 1.43(4) | Br9B-In3-Br11 | 88.99(6) |
| N3-C12 | 1.45(4) | Br10B-In3-Br11 | 91.11(7) |
| Br5-In2-Br6a | 81.2(3) | Br11-In3-Br11[b] | 91.85(8) |
| Br5-In2-Br7a | 81.2(3) | Br9B-In3-Br10[b] | 89.65(7) |
| Br5-In2-Br8a | 74.2(3) | Br9B-In3-Br11[b] | 179.10(7) |
| Br6-In2-Br7 | 112.4(4) | Br10B-In3-Br11[b] | 90.66(7) |
| Br6-In2-Br8 | 119.6(4) | Br9-In3-Br11[b] | 88.99(6) |
| Br5A-In2-Br6 | 81.2(3) | Br10-In3-Br11 | 90.66(7) |
| Br6-In2-Br6[a] | 121.9(4) | Br9B-In3-Br10 | 88.56(7) |
| Br6-In2-Br7[a] | 20.1(3) | Br10-In3-Br10[b] | 177.46(9) |
| Br6-In2-Br8[a] | 116.4(4) | Br10-In3-Br11[b] | 91.11(7) |
| Br7-In2-Br8 | 116.9(4) | Br9-In3-Br10[b] | 88.56(7) |
| Br5A-In2-Br7 | 81.2(3) | Br3-In1-Br4 | 108.25(12) |
| Br6A-In2-Br7 | 20.1(4) | Br1-In1-Br2 | 109.79(12) |
| Br7-In2-Br7[a] | 109.8(4) | Br1-In1-Br3 | 108.65(13) |
| Br7-In2-Br8[a] | 131.1(4) | Br1-In1-Br4 | 114.13(11) |
| Br5A-In2-Br8 | 74.2(3) | Br2-In1-Br3 | 107.39(13) |

| | | | |
|---|---|---|---|
| Br6A-In2-Br8 | 116.4(4) | Br2-In1-Br4 | 108.42(11) |
| Br7A-In2-Br8 | 131.1(4) | C1-N1-C4 | 98(3) |
| Br8-In2-Br8[a] | 30.2(3) | C5-N2-C8 | 110.4(19) |
| **150K** | | | |
| In4-Br17 | 2.666(4) | Br14-In4-Br18 | 82.76(12) |
| In4-Br18 | 2.686(4) | Br15-In4-Br16 | 90.69(14) |
| In4-Br13 | 2.608(4) | Br14-In4-Br17 | 100.41(13) |
| In4-Br14 | 2.711(4) | Br1-In1-Br2 | 99.71(18) |
| In4-Br15 | 2.634(4) | Br1-In1-Br3 | 110.82(17) |
| In4-Br16 | 2.762(4) | Br2-In1-Br4 | 110.48(16) |
| In1-Br2 | 2.476(4) | Br3-In1-Br4 | 106.47(14) |
| In1-Br3 | 2.578(4) | Br1-In1-Br4 | 110.36(16) |
| In1-Br1 | 2.435(5) | Br2-In1-Br3 | 118.86(15) |
| In1-Br4 | 2.544(4) | Br5-In2-Br8 | 112.68(19) |
| In2-Br5 | 2.618(5) | Br5-In2-Br6 | 108.8(2) |
| In2-Br6 | 2.470(5) | Br5-In2-Br7 | 111.71(18) |
| In2-Br8 | 2.412(5) | Br7-In2-Br8 | 103.57(16) |
| In2-Br7 | 2.490(5) | Br6-In2-Br7 | 110.8(2) |
| In3-Br9 | 2.430(5) | Br6-In2-Br8 | 109.23(19) |
| In3-Br10 | 2.606(5) | Br9-In3-Br11 | 112.05(16) |
| In3-Br11 | 2.498(4) | N4-C16 | 1.45(5) |
| In3-Br12 | 2.463(6) | N4-C13 | 1.40(7) |
| N1-C1 | 1.38(6) | N5-C17 | 1.52(6) |
| N1-C4 | 1.51(8) | N5-C20 | 1.43(6) |
| N2-C8 | 1.44(5) | C1-C2 | 1.49(7) |
| N2-C5 | 1.44(5) | C2-C3 | 1.56(8) |
| N3-C9 | 1.43(5) | C3-C4 | 1.55(8) |
| N3-C12 | 1.47(5) | N6-C24 | 1.44(6) |
| Br15-In4-Br17 | 87.88(12) | N6-C21 | 1.43(6) |
| Br15-In4-Br18 | 91.05(13) | C5-C6 | 1.40(10) |
| Br16-In4-Br17 | 84.80(13) | Br10-In3-Br12 | 111.47(18) |
| Br16-In4-Br18 | 92.03(13) | Br9-In3-Br12 | 100.27(19) |
| Br17-In4-Br18 | 176.64(15) | Br10-In3-Br11 | 107.91(17) |
| Br14-In4-Br15 | 89.53(13) | Br9-In3-Br10 | 114.50(16) |
| Br14-In4-Br16 | 174.79(14) | Br11-In3-Br12 | 110.55(17) |
| Br13-In4-Br14 | 92.82(12) | C1-N1-C4 | 113(4) |
| Br13-In4-Br15 | 177.52(15) | C5-N2-C8 | 111(4) |
| Br13-In4-Br16 | 86.90(13) | C9-N3-C12 | 116(3) |
| Br13-In4-Br17 | 92.47(12) | C13-N4-C16 | 111(3) |
| Br13-In4-Br18 | 88.47(12) | | |

Symmetry codes:

a= 1-x, y, 1/2-z; b= 1-x, y, 3/2-z