**Supporting Information**

**(C$_2$H$_5$NH$_3$)$_3$[InBr$_6$]: an indium(III) organic-inorganic hybrid phase transition compound exhibiting switchable dielectric response**

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**Methods:**

**Thermal measurements**

Differential scanning calorimetry (DSC) analysis was performed on a Netzsch 200F3 instrument from 230 K to 270 K with sweeping rates of 10 K/min under a nitrogen atmosphere.

**Single crystal X-ray diffraction**

The single crystal X-ray diffraction data for compound **1** at low temperature (110 K) and room temperature (293 K) were recorded by a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). The crystal structures of LTP and RTP were solved by the *OLEX2* software package. All non-H atoms were subjected to anisotropic refinement and all H atoms were introduced in calculated positions. The structure refinement parameters and crystallographic data of **1** at different temperatures are listed in Table 1. The selected bond angles and bonds lengths are given in Table S1. The crystal data of $(C_2H_5NH_3)_3[InBr_6]$ have been deposited in the Cambridge Crystallographic Database Centre as supplementary material, CCDC 2083460 (for **1** at 110 K) and 2083461 (for **1** at 293 K).

**Dielectric measurements**

The temperature dependence of real electric constant $\varepsilon$ ($\varepsilon = \varepsilon' - i\varepsilon''$), where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts, respectively, was carried out on a TH2828 Precision LCR meter at temperatures range from 210 to 270 K with sweeping rate of approximately 5 K/min at 10 kHz with an applied voltage of 1.0 V. In the dielectric experiments, the crystals of compound **1** were ground and pressed into dense slice. 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.

**Infrared measurements**

Fourier transform infrared (FT-IR) spectrum of compound **1** was obtained using a Bruker Vertex 70 spectrophotometer within the range of 4000–400 cm$^{-1}$.

**PXRD measurements**

The powder X-Ray diffraction (PXRD) pattern was obtained on Rigaku SmatrLab SE advance diffractometer with Cu–Kα radiation ($\lambda = 1.54056$ Å) in the range of $5° < 2\theta < 50°$.
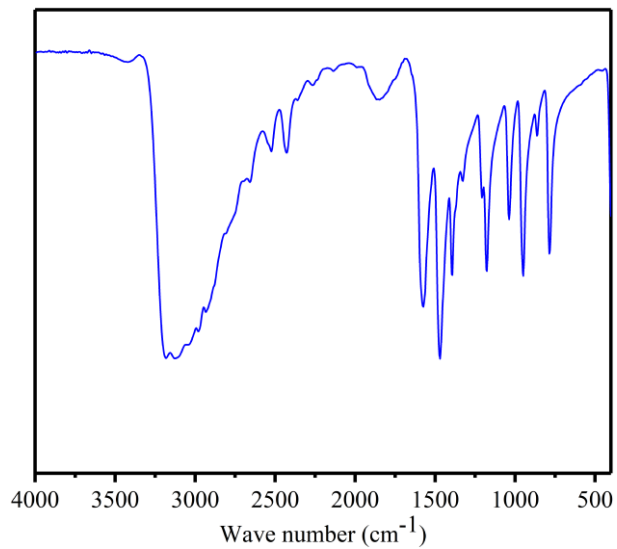
Figure S1. IR spectrum of compound **1.**
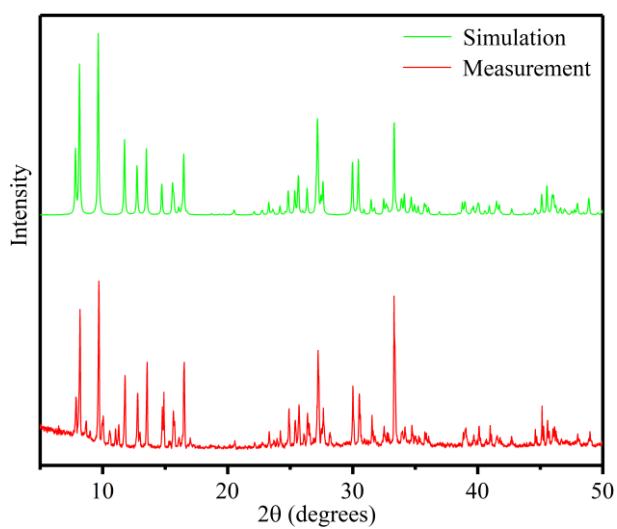


Figure S2. PXRD of compound **1**.

Table S1. Selected bond lengths (Å) and angles (°) for **1** at 110 K and 293 K.

110 K

| | | | |
|---|---|---|---|
| In1–Br1 | 2.673(4) | N1–C2 | 1.484(7) |
| In1–Br5 | 2.676(1) | N2–C4 | 1.476(7) |
| In1–Br2 | 2.709(3) | N3–C6 | 1.479(7) |
| In1–Br6 | 2.735(6) | C5–C6 | 1.520(8) |
| In1–Br4 | 2.643(1) | C2–C1 | 1.477(8) |
| In1–Br3 | 2.640(4) | N3–C4 | 1.480(9) |
| Br1–In1–Br5 | 90.397(2) | Br3–In1–Br1 | 92.127(2) |
| Br1–In1–Br2 | 89.117(2) | Br3–In1–Br5 | 92.060(2) |
| Br1–In1–Br6 | 85.981(2) | Br3–In1–Br2 | 90.377(2) |
| Br5–In1–Br6 | 88.305(2) | Br3–In1–Br4 | 92.195(2) |
| Br2–In1–Br6 | 89.246(2) | C1–C2–N1 | 111.5(5) |
| Br4–In1–Br5 | 91.055(2) | C5–C6–N3 | 110.1(4) |
| Br4–In1–Br2 | 89.247(2) | C3–C4–N2 | 111.2(6) |
| Br4–In1–Br6 | 89.687(2) | | |

293 K

| | | | |
|---|---|---|---|
| In1–Br1 | 2.655(5) | N3–C6 | 1.44(2) |
| In1–Br1A | 2.655(5) | C2–C3 | 1.500(2) |
| In1–Br3 | 2.707(8) | N1–C5 | 1.449(2) |
| In1–Br3A | 2.707(8) | C6–C1 | 1.499(2) |
| In1–Br4 | 2.713(8) | C6–C1A | 1.499(2) |
| In1–Br2 | 2.631(3) | C5–C4 | 1.499(2) |
| N2–C3 | 1.42(2) | | |
| Br1–In1–Br1A | 91.84(7) | Br2–In1–Br1A | 92.01(5) |
| Br1–In1–Br3A | 89.59(5) | Br2–In1–Br1 | 92.01(5) |
| Br1A–In1–Br3 | 89.60(5) | Br2–In1–Br3A | 91.23(5) |
| Br1A–In1–Br4 | 89.59(4) | Br2–In1–Br3 | 91.23(5) |
| Br1–In1–Br4 | 89.59(4) | N2–C3–C2 | 115.8(2) |
| Br3A–In1–Br3 | 88.79(7) | N3–C6–C1A | 123.0(2) |
| Br3A–In1–Br4 | 87.13(4) | N3–C6–C1 | 123.0(2) |
| Br3–In1–Br4 | 87.13(4) | N1–C5–C4 | 124.0(2) |

Symmetry transformations (293 K): a = 1+x, 1-y, +z.

Table S2 Hydrogen bonds for compound **1** at 110 K and 293 K

**110 K**

| D–H···A | d(D−H) | d(H···A) | d(D···A) | ∠(DHA) | A |
|---|---|---|---|---|---|
| N1–H1A···Br5 | 0.91 | 2.57 | 3.458(4) | 165 | [1/2-x, 3/2-y, 1-z] |
| N2–H2D···Br1 | 0.91 | 2.43 | 3.296(5) | 160 | [1-x, y, 3/2-z] |
| N2–H2E···Br2 | 0.91 | 2.58 | 3.311(5) | 137 | [1-x, y, 3/2-z] |
| N3–H3E···Br6 | 0.91 | 2.57 | 3.333(4) | 142 | [x, 1+y, z] |

**293 K**

| D–H···A | d(D−H) | d(H···A) | d(D···A) | ∠(DHA) | A |
|---|---|---|---|---|---|
| N1–H1F···Br1 | 0.89 | 2.77 | 3.634(2) | 164 | [x, 1-y, z] |
| N2–H2C···Br4 | 0.89 | 2.60 | 3.350(1) | 143 | [3/2-x, 1/2+y, 1-z] |
| N3–H3C···Br3 | 0.89 | 2.53 | 3.314(2) | 148 | [1-x, y, 1-z] |
| N3–H3D···Br3 | 0.89 | 2.50 | 3.314(2) | 152 | [1-x, 1-y, 1-z] |