Supporting information

Exceptional structural phase transition near room temperature in an organic-inorganic hybrid ferroelectric

Ping Wang,‡ Yu-Qiao Tong,‡ Shi-Qing Yin, Qian-Jun Gu, Bo Huang* and Ai-Xin Zhu*

Faculty of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, China.

Materials and instrumentations. All chemicals were obtained from commercial sources and used without further purification. *In situ* powder X-Ray diffraction (PXRD) patterns (Cu-Kα, λ = 1.54056 Å) were collected on a Smartlab9 ϑ–2ϑ diffractometer. Thermogravimetric (TG) analysis was carried out on a TA Q50 system at a heating rate of 5 K/min under a N_2 atmosphere. Differential Scanning calorimeter (DSC) measurement was performed by cooling-heating the powder sample at a rate of 5 K/min on a TA DSC Q2000 instrument. Single-crystal X-ray data were performed on RAXIS IP diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The complex permittivity was measured using a Tonghui TH2838A LCR meter (applied electric field of 1.0 V) connected to a cryogenic environment controller for a single crystal sample at a rate of about 3 K/min at various frequencies (1, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, 200, 400, 600, 800, 10000 kHz). Second harmonic generation (SHG) was measured using a WITec alpha 300RS microscope with a 1064 nm laser. The pyroelectric current was measured with Keithley 6517B electrometer. The ferroelectric hysteresis loop was recorded on aixACCT/ TF-2000E under 1 kHz.

Synthesis. 2-Phenylethylammonium iodide ($C_6H_5C_2H_4NH_3I$) was first synthesized from ethanol solution containing stoichiometric quantities of 2-phenylethylamine and hydroiodic acid (57%). Menthol (30 mL), HgI_2 (1.83 g, 5 mmol) and 2-phenylethylammonium iodide (2.49 g, 10 mmol) was added into a beaker which was covered with tinfoil to avoid light and stirred for 20 min. The clear solution was located in a dark place for slow evaporation at room temperature. Light yellow crystals of $(C_6H_5CH_2CH_2NH_3)_2HgI_4$ (**1**) were obtained in a few days with about 81% yield based on Hg. Elemental analysis: calcd C: 20.17%, N: 2.94%, H: 2.54%; found C: 20.11%, N: 2.96%, H: 2.32%. The phase purity of **1** was further verified by powder X-ray diffraction pattern (PXRD), which matches well with the simulated one in terms of the single-crystal structure (Fig. S2).

Table S1. Summary of crystal data and structural refinements of **1** at 270 and 330 K.

Empirical formula	$(C_6H_5CH_2CH_2NH_3)_2[HgI_4]$	
Formula weight	952.56	
Phase type	LTP	HTP
T / K	270(2)	330(2)
Space group	$P2_1$	$P2_1/c$
a / Å	10.663(3)	10.8622(9)
b / Å	8.316(3)	8.4041(7)
c / Å	13.502(4)	27.147(2)
β / °	98.809(5)	98.605(3)
V / Å^3	1183.2(6)	2450.2(3)
Z	2	4
D_{calcd} / g cm^{-3}	2.674	2.582
μ / mm^{-1}	11.724	11.323
GOF	1.034	1.008
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0243, 0.0599	0.0416, 0.0830
R_1, wR_2 (all data)	0.0248, 0.0602	0.0820, 0.1017
Flack parameter	0.396(6)	–
Completeness	99.5%	99.4%

[a] $R_1 = F_o - F_c / F_o$, $wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$

Table S2. The geometry (Å, °) of hydrogen bonds for **1** at 270 and 330 K.

	D–H⋯A	D–H	H⋯A	D⋯A	∠D–H⋯A
270 K	N1–H1A–I2	0.890	2.937	3.625	135.39
	N2–H2A–I2[a]	0.890	3.229	3.679	113.76
	N2–H2C–I3[b]	0.890	2.730	3.616	173.72
	N2–H2B–I4	0.890	2.839	3.592	143.18
330 K	N1–H1B–I2	0.890	2.931	3.698	145.28
	N2–H2E–I2[c]	0.890	3.020	3.687	133.22
	N2–H2C–I3[d]	0.890	2.834	3.644	152.07
	N2–H2D–I4	0.890	2.874	3.669	149.52

Symmetry codes: [a] -x, y-1/2, -z+1; [b] -x, y+1/2, -z+1; [c] -x+2, -y+2, -z+1; [d] -x+2, -y+1, -z+1

Table S3. The selected bond lengths (Å) of **1** at 270 and 330 K.

270 K	Hg1–I1	2.810(1)	Hg1–I2	2.7686(8)
	Hg1–I3	2.7447(9)	Hg1–I4	2.761(1)
330 K	Hg1–I1/ Hg1–I1'	2.772(7)/2.839(7)	Hg1–I2	2.7637(7)
	Hg1–I3	2.7652(7)	Hg1–I4	2.7639(7)

Table S4. The selected bond angles (°) of **1** at 270 and 330 K.

270 K	∠I2–Hg1–I1	107.27(3)	∠I2–Hg1–I3	108.26(3)
	∠I3–Hg1–I1	112.51(2)	∠I2–Hg1–I4	107.41(2)
	∠I4–Hg1–I1	110.874(17)	∠I4–Hg1–I3	110.31(2)
330 K	∠I2–Hg1–I1/∠I2–Hg1–I1'	104.44(9)/113.5(1)	∠I2–Hg1–I3	108.07(2)
	∠I3–Hg1–I1/∠I3–Hg1–I1'	115.6(1)/106.6(1)	∠I2–Hg1–I4	108.74(2)
	∠I4–Hg1–I1/∠I4–Hg1–I1'	111.5(1)/111.4(1)	∠I4–Hg1–I3	108.27(2)
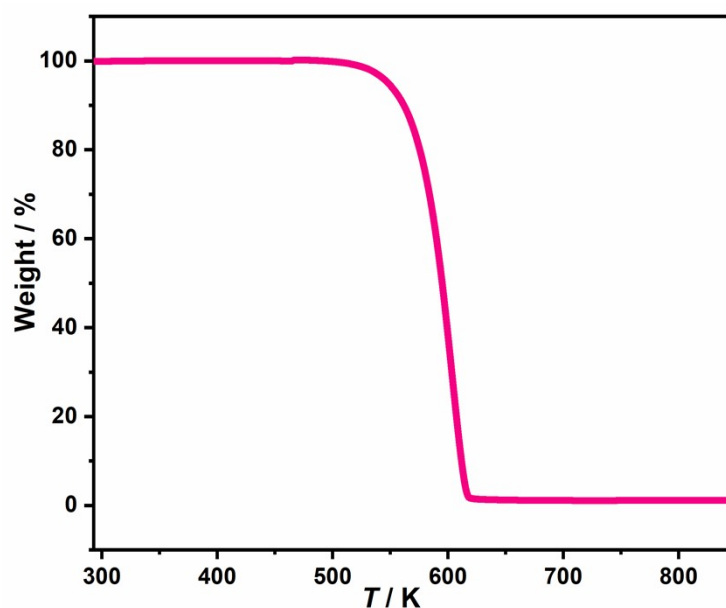
Fig. S1 Thermogravimetric (TG) curve measured at a rate of 5 K min^{-1} under N_2 atmosphere of **1**. It reveals that compound **1** was stable up to about 496 K.
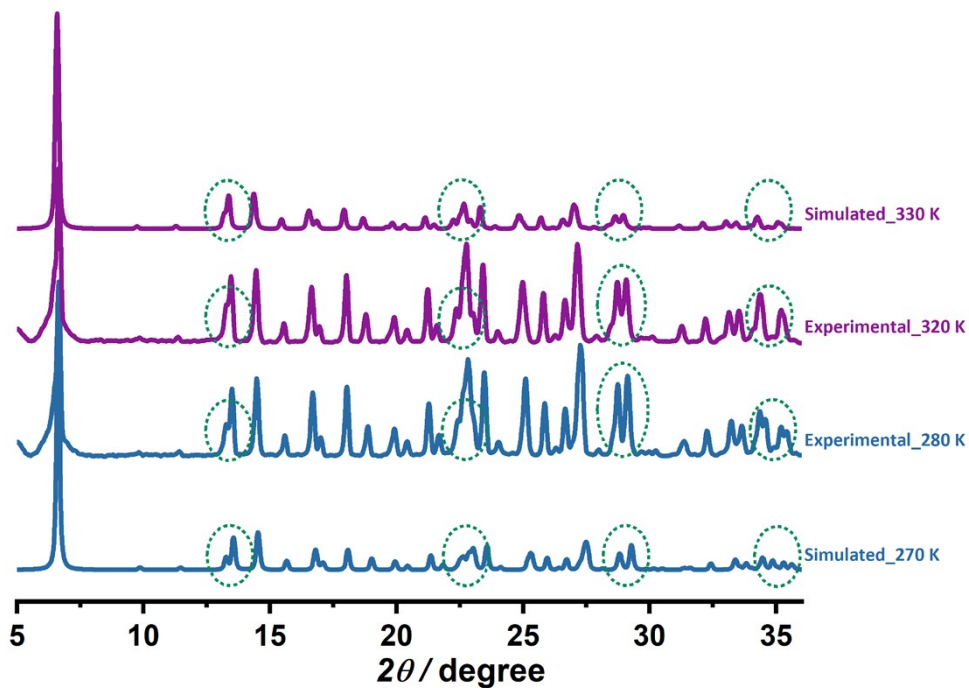
Fig. S2 The simulated (270 and 330 K) and *in situ* variable-temperature (280 and 320 K) powder XRD patterns of **1**.
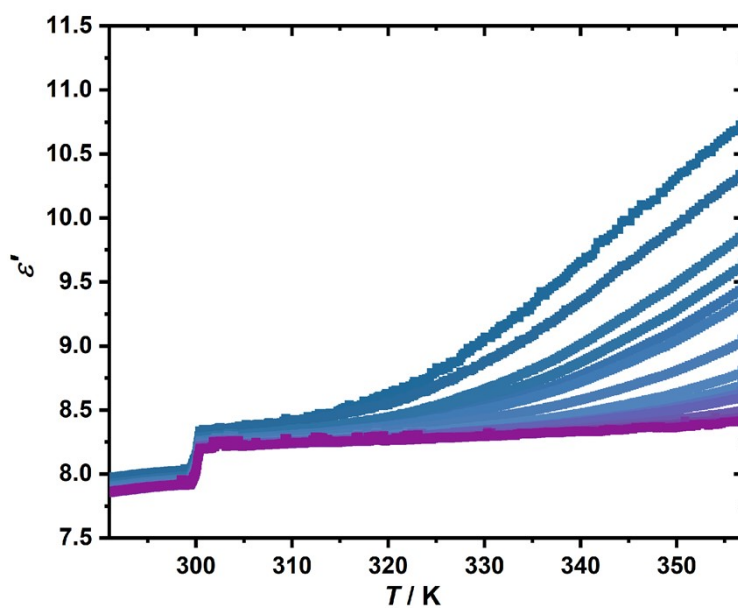

Fig. S3 Temperature dependence of dielectric constant (ε') of **1** at various frequencies from 1 kHz (cobalt blue) to 1000 kHz (rose red) in a cooling process.
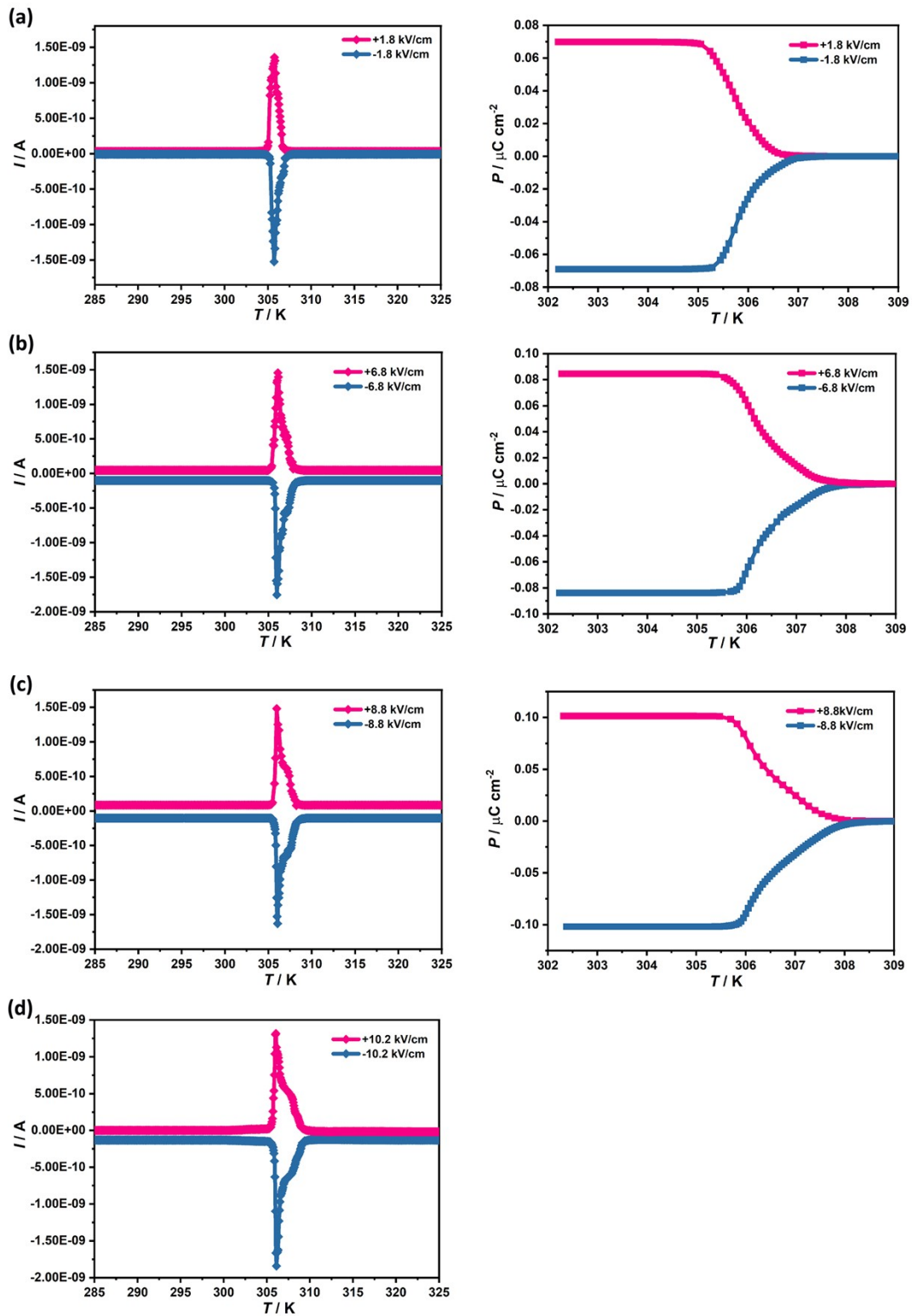
Fig. S4 The pyroelectric current was obtained from heating mode under zero electric filed in the vicinity of the ferroelectric phase transition. Before measuring the pyroelectric current, the sample was cooled down from 330 K to 270 K with an applied electric field of different conditions (±1.8 kV/cm (a), ±6.8 kV/cm (b), ±8.8 kV/cm (c), ±10.2 kV/cm (d), respectively), and short cut the sample for enough time to release the remaining charge. The spontaneous polarizations were calculated by integrating the pyroelectric current with respect to time.

Calculation of the Polarization of Crystalline (C$_6$H$_5$CH$_2$CH$_2$NH$_3$)$_2$[HgI$_4$] in LTP.

$P = \Sigma Ze\Delta r/V$

P: polarization

e: elementary charge

Z: formal charge of ions

Δr: displacement of ions

V: unit cell volume

In LTP, **1** crystallizes in a polar monoclinic space group of $P2_1$, with cell parameters of a = 10.663(3) Å, b = 8.316(3) Å, c = 13.502(4) Å, V = 1183.2(6) Å^3. The two protonated N atoms and Hg atom of a unit cell are located at N1 (0.6096, 0.4998, 0.3726), N2 (-0.0410, 0.4910, 0.6572), and Hg1 (0.23120, 0.51098, 0.45507). The centers of the positive and negative ions are located at (0.2843, 0.4954, 0.5149) and (0.23120, 0.51098, 0.45507).

Displacement of Hg atom along the b-axis: (0.51098-0.4954)/2 × 8.316 = 0.0648 Å.

P = 2 × 1.602 ×10^{-19} × 0.0648 × 10^{-10} × 2 / 1183.2 × 10^{-30} = 0.0035 C m^{-2} = 0.35 μC cm^{-2}