

Supporting information

A near-room-temperature organic-inorganic hybrid ferroelectric: [C₆H₅CH₂CH₂NH₃]₂[CdI₄]

Bo Huang,^a Lin-Ying Sun,^a Sha-Sha Wang,^a Jian-Yu Zhang,^a Cheng-Min Ji,^b Jun-Hua Luo,^b Wei-Xiong Zhang,^{a,*} Xiao-Ming Chen^a

^a MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China.

^b Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

Materials and instrumentations. All chemicals were obtained from commercial sources and used without further purification. Powder X-Ray diffraction (PXRD) patterns (Cu-K α , λ = 1.54056 Å) were collected on a D8 DA VANCE θ -2 θ diffractometer. Thermogravimetric analyses (TGA) were carried out on a TA Q50 system at a heating rate of 5 K/min under a N₂ atmosphere. Differential Scanning calorimeter (DSC) measurements were performed by heating/cooling 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-K α radiation (λ = 0.71073 Å). The complex permittivity was measured using a Tonghui TH2828A LCR meter in a Mercury iTC cryogenic environment controller of Oxford Instrument for a single crystal sample at a rate of 2 K/min. The SHG effect was measured using a FLS 920, Edinburgh Instruments. The pyroelectric current was measured with Keithley 6517B electrometer. The ferroelectric hysteresis loop was recorded on a Radiant Precision Premier II.

Synthesis. 2-Phenylethylammonium iodide (C₆H₅C₂H₄NH₃I) was first synthesized from ethanol solution containing stoichiometric quantities of 2-phenylethylamine and hydroiodic acid (57%). Menthol (30 mL), CdI₂ (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. Colorless crystals of (C₆H₅C₂H₄NH₃)₂CdI₄ (**1**) were obtained in a few days with about 90% yield based on Cd.

Table S1. Summary of crystallographic data and structural refinements for **1** at 220 and 320 K.

Empirical formula	$C_{16}H_{24}N_2CdI_4$	
Formula weight	864.37	
T / K	220 (2)	320(2)
Phase	LTP	HTP
Space group	$P2_1$	$P2_1/m$
$a / \text{\AA}$	10.764(1)	10.873(2)
$b / \text{\AA}$	8.4013(8)	8.454(1)
$c / \text{\AA}$	13.579(1)	13.619(2)
β / degree	98.698(3)	98.521(4)
$V / \text{\AA}^3$	1213.8(2)	1238.0(3)
Z	2	2
μ / mm^{-1}	5.988	5.870
GOF	1.058	1.221
$R_1, wR_2 [I > 2\sigma(I)]^a$	0.0415, 0.1022	0.0704, 0.1979
R_1, wR_2 (all data)	0.0453, 0.1076	0.0820, 0.2099
Flack parameter	0.52(7)	-

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

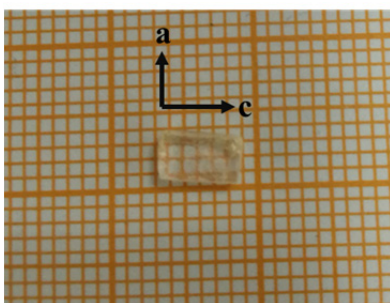


Figure S1. The crystal of **1** was grinded to the cuboid with fine grit sandpaper.

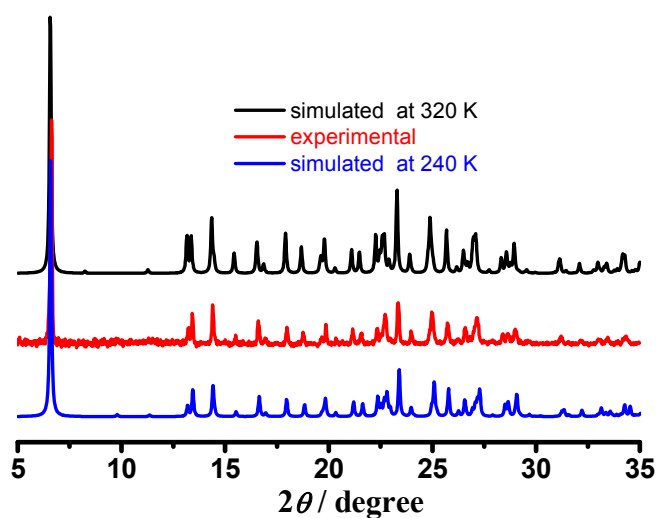


Figure S2. The simulated (240 K and 320 K) and experimental powder XRD patterns of **1**.

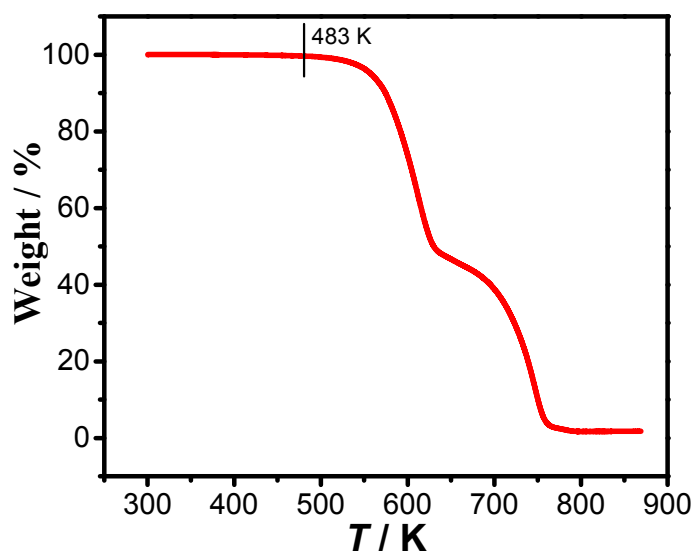


Figure S3. TGA curve measured at a rate of 5K/min under N_2 atmosphere shows that **1** can be stable up to about 483 K.

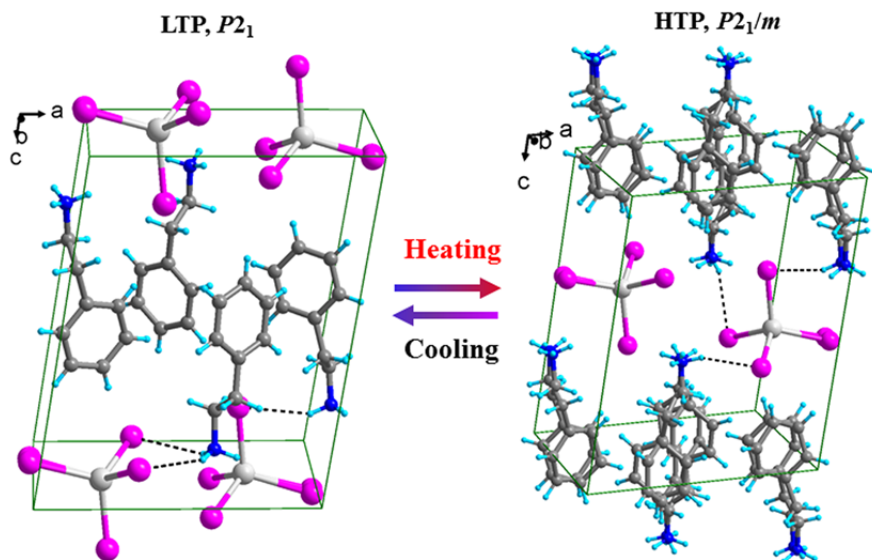


Figure S4. Crystal structures of **1** at LTP and HTP. Cd, I, N, C and H atoms are shaded in light gray, pink, blue, gray and sky blue, respectively. Hydrogen bonds are represented by dashed lines.

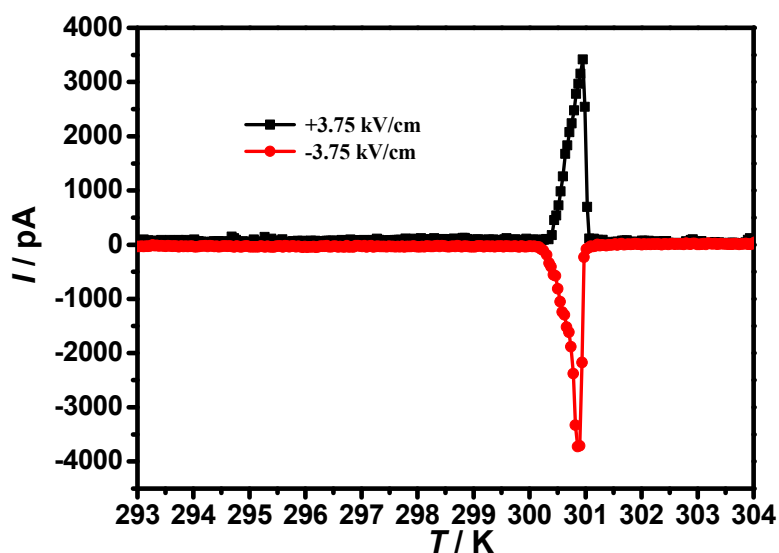


Figure S5. The pyroelectric current was obtained from heating mode under zero electric field in the vicinity of the ferroelectric phase transition. Before measuring the pyroelectric current, the sample was cooled down from 320 K to 270 K with an applied electric field of about ± 3.75 kV/cm and short cut the sample for enough time to release the remaining charge.