

Electronic Supplementary Materials (ESI)

Ferroelectric properties, narrow band gap and ultra-large reversible entropy change in a novel nonlinear ionic chromium (VI) compound

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Experimental section

Synthesis

All chemicals and reagents were purchased directly from the chemical reagent company and used directly without further purification. The synthesis of compound **1** is mainly carried out in two steps: the first step is the synthesis of precursor: measured 50 mL of triethylamine and poured into a round-necked flask, then measured 100 mL of dichloromethane as the solvent and the reactant to pour into the flask, heated and stirred in a water bath at a constant temperature of 70 °C for 72 hours, filtered and left the clear liquid to volatilize into a white solid, and finally dried it to become the precursor chloromethyl-triethylammonium chloride; in the second step, weighed the precursor (0.186 g, 1 mmol) and dissolved it in 15 mL of deionized water, then weighed chromium trioxide (0.099 g, 1 mmol) and poured into the solution, stirred for 45 min, filtered to obtain an orange-yellow solution, and finally volatilized at room temperature for about 2 weeks to obtain an orange-yellow block crystals (yield 36 %). The purity of compound **1** was well confirmed by the infrared spectrum (IR) (**Fig. S1**) and powder X-ray diffraction (PXRD) pattern (**Fig. S2**). Elemental analysis calcd. for compound **1**: C: 29.385 %, N: 4.896 %, H: 5.988 %; Found: C: 29.32 %, N: 4.96 %, H: 5.94 %. IR (KBr, cm⁻¹) analysis for compound **1**: 3740 (w), 3410 (w), 2987 (w), 2360 (w), 1639 (w), 1469 (m), 1153 (m), 943 (s), 803 (m), 426 (m).

Differential Scanning Calorimetry (DSC)

DSC tests were performed on a Perkin-Elmer Diamond DSC Instrument. The compound **1** (7.2 mg) using powder samples were placed in aluminum crucibles, and were tested in a temperature range of 315 K-370 K under a nitrogen atmosphere at a heating/cooling rate of 10 K/min.

Thermogravimetric Analysis (TGA)

TGA measurements of compound **1** (2 mg) were carried out on a TA-Instrument STD2960 system at a heating rate of 10 K/min under a nitrogen atmosphere in the temperature range of 310 K-1050 K. During the heating process, the peak of the DTA pattern at 340.5 K was an endothermic peak, while the exothermic decomposition peak was around 443 K. The arrow marked in the figure is the direction of heat release.

X-Ray Single-Crystal Crystallography

The X-ray single crystal diffraction data of compound **1** was collected on a Rigaku Oxford Diffraction with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at the room temperature. The data was corrected for L_p and absorption effects. The structure was solved by direct methods and refined by the full-matrix methods based on F^2 by using the SHELXLTL software package. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated geometrically and refined by using a "riding" model with $U_{iso} = 1.2 U_{eq}$ (C). The occupancy rate of the disordered part was refined with free variables. The crystallographic data and structural refinement details of compound **1** are shown in **Table S1**. The CCDC (Cambridge Crystallographic Data Centre) of compound **1** is No.: 2091371.

Powder X-Ray Diffraction (PXRD) and Elemental Analysis

Variable-Temperature PXRD measurements of compound **1** on a PANalytical X' Pert PRO X-ray diffractometer were carried out in the temperature range of 300 K-370 K and the diffraction patterns were collected in the range of $2\theta = 5^\circ$ - 50° with a step size of 0.02° . Elemental analysis (C, H, N) of compound **1** was performed by elemental vario EL cube organic element analyzer, Germany.

Dielectric Constant Measurements

For dielectric experiments, the pressed powder pellets (0.2 mm thick and 3 mm^2 in area) of compound **1** were sandwiched between two parallel copper electrodes with silver-conducting glue to be used for dielectric measurements. The temperature-dependent dielectric constants tests were carried out using the sample on a TH2828A instrument between 303 K-355 K over the frequency range of 500 Hz to 1 MHz, with an applied electric field of 1 V, controlling heating and cooling rate of 10 K/min.

Second Harmonic Generation (SHG) Measurements

The SHG signal tests of powder samples of compound **1**, using an unexpanded laser beam with low divergence (pulsed Nd: YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) were carried out on the Ins1210058, INSTEC Instruments at the room temperature.

Solid-State Circular Dichroism (CD) Spectra

The CD spectra for compound **1** were recorded on a Jasco-1500 CD spectropolarimeter at the room temperature in the wavelength range 200 nm-700 nm. The CD spectra were obtained on the resulting complexes as crystals (ca. 0.4 mg) in 100 mg of oven-dried KBr made into disks of 0.3 mm thickness.

Ultraviolet-Visible (UV-vis) Spectrometry

The UV-vis absorption spectrum was obtained at room temperature in the wavelength range of 200 nm-700 nm by using a Shimadzu (Tokyo, Japan) UV-2550 spectrophotometer by measuring the powder of compound **1**. Determining the band gap with the variation of Tauc equation:¹

$$[h\nu \cdot F(R_\infty)]^{1/n} = A(h\nu - E_g)$$

where h is the Planck's constant, ν represents the frequency of vibration, A is the proportional constant, E_g is the band gap and $F(R_\infty)$ is Kubelka-Munk equation: $F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$.²

Ferroelectric Property

The ferroelectric property of single crystal samples of compound **1** were measured by using a standard RT 6000 ferroelectric tester (Radiant Technologies, Albuquerque, USA) at different temperatures after the samples were immersed in insulating oil and dried at the room temperature. And the polarization-electric hysteresis loops were observed by virtual ground mode (the measurement used alternating current and the frequency was 10-60 Hz).

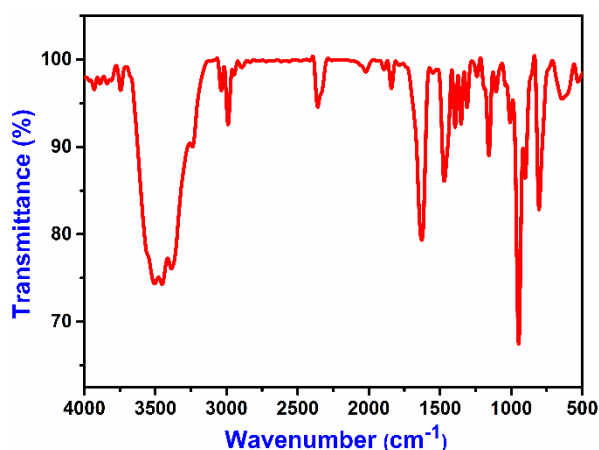


Fig. S1 Infrared (IR) spectra of solid compound **1** at room temperature.

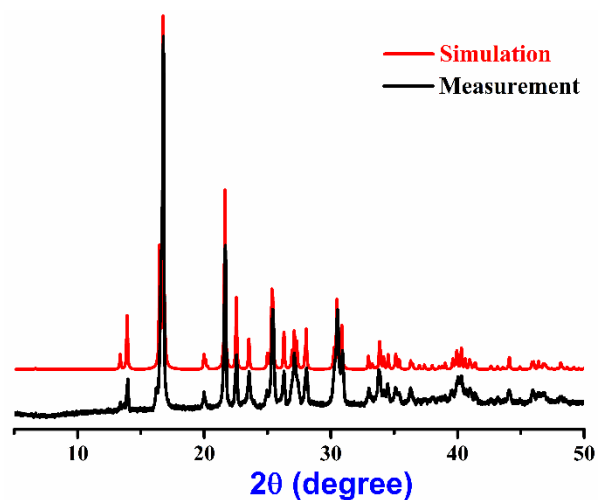


Fig. S2 PXRD (powder x-ray diffraction) measurement comparison with single crystal simulation of compound **1** at room temperature.

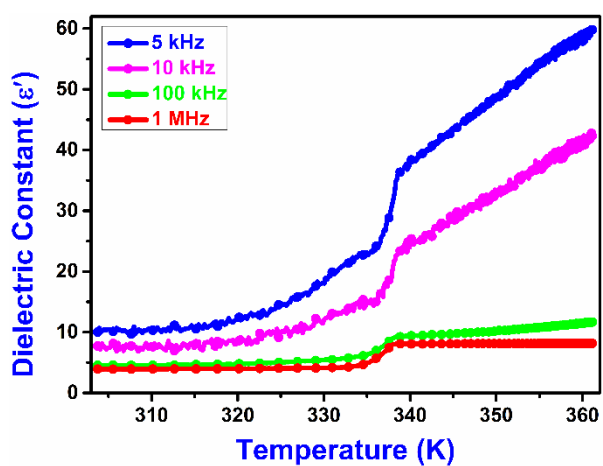


Fig. S3 Temperature dependence of the real parts (ϵ') of the dielectric constants for compound **1** at selected frequencies (5 kHz, 10 kHz, 100 kHz and 1 MHz).

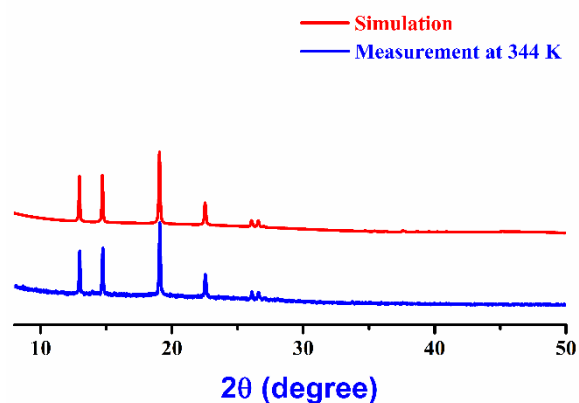


Fig. S4 Le Bail refinement of PXRD data of compound **1** at 344 K, revealing a unit cell of $a = 7.89479 \text{ \AA}$, $b = 7.89479 \text{ \AA}$, $c = 12.7266 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 120^\circ$.

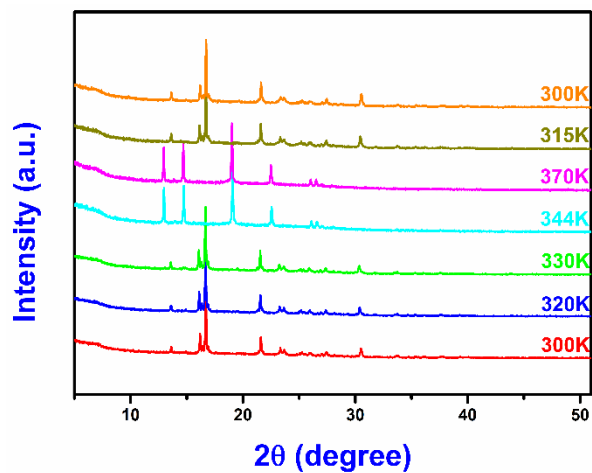


Fig. S5 Variable-Temperature PXRD for compound **1** in the temperature range of 300 K-370 K.

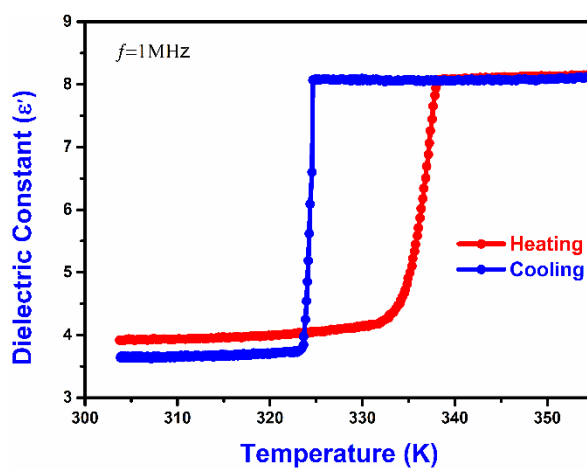


Fig. S6 The temperature-dependence of dielectric constant at 1MHz during heating and cooling runs for compound **1**.

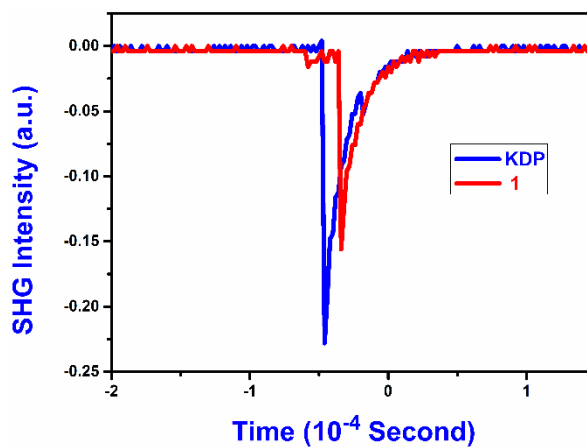


Fig. S7 The comparison of KDP, SHG response of compound **1** under the same condition.

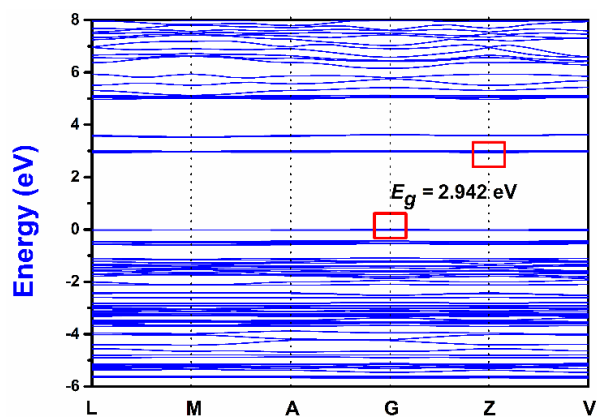


Fig. S8 The calculation diagram band structures of compound **1**.

Table S1. The crystallographic data and structure refinements for compound **1** at the room temperature.

[(CH ₃ CH ₂) ₃ N(CH ₂ Cl)] [CrO ₃ Cl]			
298 K			
Formula weight	286.11	Z	4
Crystal system	monoclinic	Density (g/cm ³)	1.539
Space group	C2	m (mm ⁻¹)	1.342
<i>a</i> (Å)	11.8344(6)	F (000)	592.0
<i>b</i> (Å)	7.8851(3)	Data/restraints/parameters	2527/3/173
<i>c</i> (Å)	14.4218(12)	GOF	1.097
α (°)	90	$R_1, wR_2 [I \geq 2\sigma(I)]$	$R_1 = 0.0346$ $wR_2 = 0.1007$
β (°)	113.414(5)	R_1, wR_2 (all data)	$R_1 = 0.0369$ $wR_2 = 0.1026$
γ (°)	90	$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ ⁻³)	0.31/-0.49
<i>V</i> (Å ³)	1234.96(14)		

Calculation of ΔS and N

In the heating cycle mode

$$\Delta S_1 = R \ln N_1$$

$$\Delta S_1 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T_c}$$

$$= \frac{75.65 \text{ g}^{-1} \text{ J} \times 286.11 \text{ mol}^{-1} \text{ g}}{340.9 \text{ K}}$$

$$= 63.49 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$N_1 = \exp\left(\frac{\Delta S_1}{R}\right) = \exp\left(\frac{63.49 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}\right)$$

$$= 2072$$

In the cooling cycle mode

$$\Delta S_2 = R \ln N_2$$

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T_c}$$

$$= \frac{71.48 \text{ g}^{-1} \text{ J} \times 286.11 \text{ mol}^{-1} \text{ g}}{322.15 \text{ K}}$$

$$= 63.48 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$N_2 = \exp\left(\frac{\Delta S_2}{R}\right) = \exp\left(\frac{63.48 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}\right)$$

$$= 2070$$

Notes and references

- 1 J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721-729.
- 2 W. J. Wei, C. Li, L. S. Li, Y. Z. Tang, X. X. Jiang and Z. S. Lin, *J. Mater. Chem. C*, 2019, **7**, 11964-11971.