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-1050 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 Kα radiation (λ = 0.71073 Å) at the room temperature. The data was corrected for Lp and absorption effects. The structure was solved by direct methods and refined by the full-matrix methods based on Fl by using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated geometrically and refined by using a “riding” model with Uiso = 1.2 Ueq(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 2θ = 5°-50° with a step size of 0.02°. Elemental analysis (C, H, N) of compound 1 was performed by elementar vario EL cube organic element analyzer, Germany.

**Dielectric Constant Measurements**

For dielectric experiments, the pressed powder pellets (0.2 mm thick and 3 mm² 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:

\[
(\text{hv} - \text{E}_g)\frac{1}{n} = A(\text{hv} - \text{E}_g)
\]

where \(h\) is the Planck’s constant, \(v\) represents the frequency of vibration, \(A\) is the proportional constant, \(E_g\) is the band gap and \(F(R_\infty)\) is Kubelka-Munk equation:

\[
F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty}
\]

**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 ($\varepsilon'$) of the dielectric constants for compound 1 at selected frequencies (5 kHz, 10 kHz, 100 kHz and 1 MHz).

Fig. S4 Lebail refinement of PXRD data of compound 1 at 344 K, revealing a unit cell of $a = 7.89479$ Å, $b = 7.89479$ Å, $c = 12.7266$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$ 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.

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<th>[(CH₃CH₂)₃N(CH₂Cl)][CrO₃Cl]</th>
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<tr>
<td></td>
<td>298 K</td>
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<tr>
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<td>β (°)</td>
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<tr>
<td>wR$_1$</td>
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<tr>
<td>$\triangle\rho_{max}$/$\triangle\rho_{min}$ (eÅ⁻³)</td>
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Calculation of $\Delta S$ and $N$

In the heating cycle mode

\[ \Delta S_1 = R \ln N_1 \]

\[ \Delta S_1 = \int \frac{T_1 q}{T_2} dT \approx \frac{\Delta H}{T_c} \]

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

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

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

\[ = 2072 \]

In the cooling cycle mode

\[ \Delta S_2 = R \ln N_2 \]

\[ \Delta S_1 = \int \frac{T_1 q}{T_2} dT \approx \frac{\Delta H}{T_c} \]

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

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

\[ N_2 = \exp \left( \frac{\Delta S_1}{R} \right) = \exp \left( \frac{63.48 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \right) \]

\[ = 2070 \]

Notes and references