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# Multifunctional molecular ferroelectric with high Curie temperature and electrical−thermal double switch coexistence: $(C_8H_{14}NO)[FeCl_4]$

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## Experimental Sections

**Synthesis.** All chemicals were purchased from Aladdin's Reagent and not further purified. 2 mmol 1-methyl-3-quininocyclone and 2mmol $FeCl_3$ were added to an aqueous solution (15 mL) containing hydrochloric acid (40 wt%, 2mL). After stirring and dissolving at room temperature, it was slowly evaporated under 323 K conditions to obtain light yellow transparent crystals. Moreover, the crystal will not be oxidized after being placed in the air for a long time, nor will it absorb moisture. The phase purity of the crystal was confirmed by infrared spectroscopy (Fig. S1) and PXRD pattern obtained at 293 K matches well with the simulated results from the single crystal structure, revealing high crystallinity and phase purity (Fig. S3). Elemental analysis, calculated value (%) of **1**: C, 24.03; N,4.671; H, 5.379. Found: C, 24.25; N, 4.589; H, 5.365.

**Differential Scanning Calorimetry (DSC).** DSC measurements were performed on a Perkin-Elmer Diamond DSC Instrument. The compound **1** (8.3 mg) using powder samples were placed in aluminum crucibles, which were measured in a temperature range of 298 K-373 K under a nitrogen atmosphere at a heating/cooling rate of 10 K/min.

**Thermogravimetric Analysis (TGA).** TGA measurements of compound **1** (1.4mg) 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 293 K-1073 K.

**X-Ray Single-Crystal Crystallography**. The single-crystal X-ray diffraction studies were performed with a

Bruker Smart Apex II single-crystal diffractometer operating with a graphite-mono-chromated Mo-sealed tube source (Ka radiation, λ= 0.71073 Å). The crystal structure of **1** were determined at 300 K. The structures were solved and the models were refined using the SHELXS and SHELXL programs. The data collection and structure refinement of these crystals are summarized in Table S1. The crystallographic information on the crystal structures of **1** determined at 300 K had been deposited in CIF format in the Cambridge Crystallographic Database Centre, CCDC: 2243166.

**Powder X-Ray Diffraction (PXRD).** The powder X-ray diffraction (PXRD) pattern was performed on the Rigaku D/MAX 2000 PC X-ray diffractometer with Cu radiation ($K_{\alpha1}$= 1.54060 Å, $K_{\alpha2}$ = 1.54443 Å). The data is collected in the temperature range of 298-359 K during the heating process, and $2\vartheta$ is in the range of 5-50°.

**Dielectric Constant Measurements.** For dielectric tests, the pressed powder pellets (0.3 mm thick and 4 $mm^2$ 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 constant tests were carried out using the sample on a TH2828A instrument between 293 K-360 K over the frequency range of 500 Hz to 1 MHz, with an applied electric field of 1 V, controlling heating/cooling rate of 10 K/min.

**Second Harmonic Generation (SHG) Measurements.** The SHG responses experiments, 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) was used.

**Ferroelectric Measurement.** The ferroelectric properties of solid-state samples were measured from a single crystal sample in the form of a pellet using a standard RT 6000 ferroelectric tester (Radiant Technologies, Albuquerque, USA) at different temperatures while the sample was immersed in insulating oil, and the electric hysteresis loop was observed by Virtual Ground Mode (the measurement uses alternating current and the frequency is 10-60 Hz).

**Piezoelectric Response Force Microscopy (PFM) Measurements.** The blue film specially used for mechanical stripping is used to prepare the samples required for PFM test. Cover the blue film on the crystal surface. After compaction for 1 h, tear the blue film off the crystal. A film like chip of compound **1** will be attached to the blue film, and then attach the side of the blue film not attached to the crystal to the ITO conductive glass with silver glue. The test instrument is Asylum Research Atomic Force Microscope (MFP-3D) produced by Oxford Instruments, and the test probe is a silicon conductive probe coated with Pt/Ir.

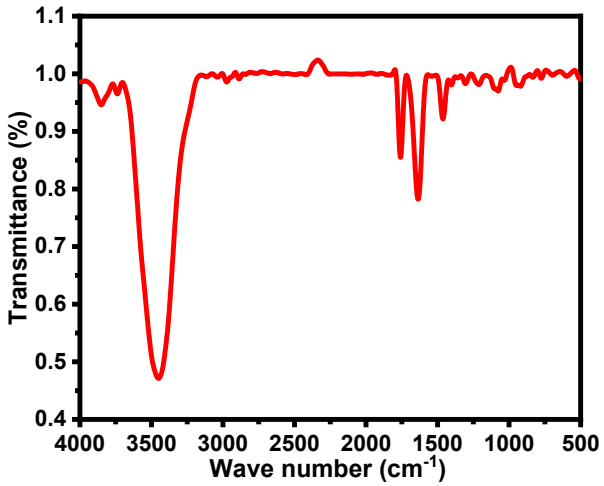


**Fig. S1** Infrared spectrum of compound **1**.

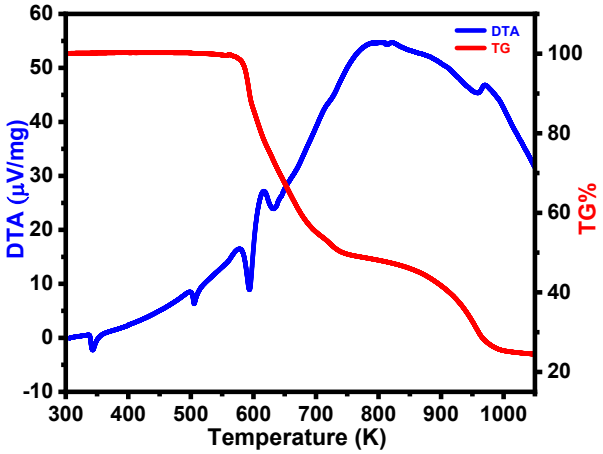


**Fig. S2** TG-DTA curves for **1.**

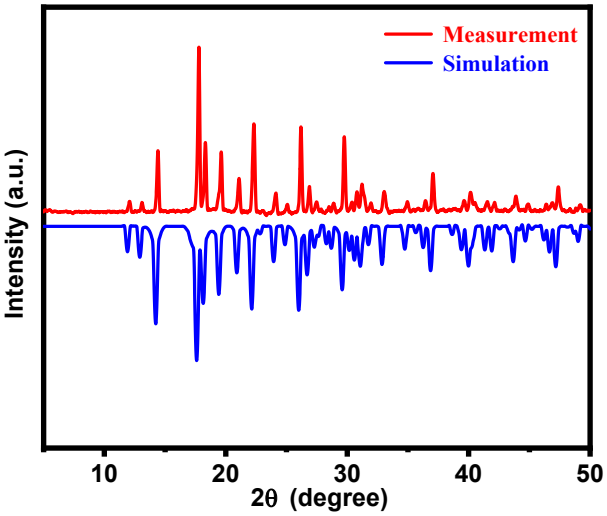


**Fig. S3** The powder XRD of **1** with the simulated one in blue and the measurement in red.

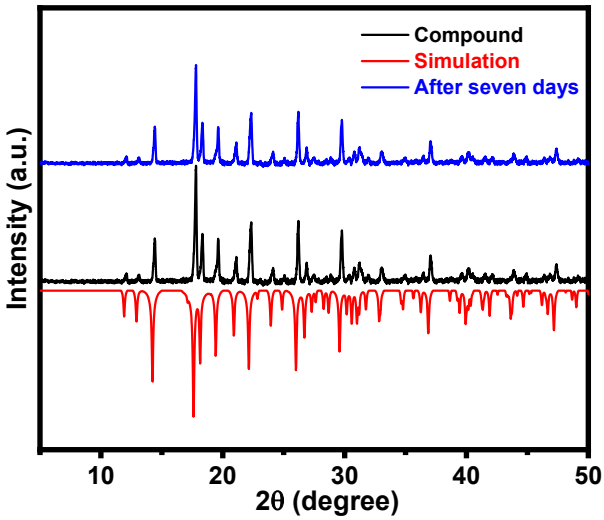


**Fig. S4** Experimental powder diffraction patterns(red), XRD patterns measure for the freshly-prepared samples(black) of compound **1** and those after seven days storage open in air(blue).

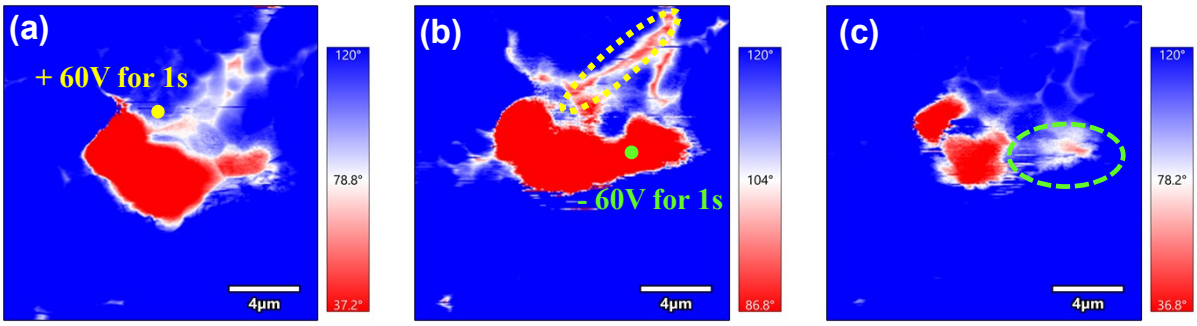


**Fig. S5** Pristine PFM mapping for a region of 4 μm × 4 μm (a). Vertical PFM phase image after applying DC bias voltage +60 V at yellow point.(b). Vertical PFM phase image after applying DC bias voltage -60 V at green point (c).

**Table S1.** Crystal data and structure refinement for **1**

| **Compound** | **1** |
|---|---|
| Empirical formula | $C_8H_{14}Cl_4FeNO$ |
| Formula weight | 337.85 |
| Temperature/K | 301.32(10) |
| Crystal system | orthorhombic |
| Space group | $Cmc2_1$ |
| *a*/Å | 9.1323(5) |
| *b*/Å | 10.3481(6) |
| *c*/Å | 14.8559(8) |
| *α*/° | 90 |
| *β*/° | 90 |
| *γ*/° | 90 |
| Volume/Å$^3$ | 1403.91(14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.598 |
| μ/mm$^{-1}$ | 1.811 |
| F (000) | 684.0 |
| Crystal size/mm$^3$ | 0.2 × 0.15 × 0.1 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.484 to 61.714 |
| Index ranges | -11 ≤ h ≤ 12, -12 ≤ k ≤ 13, -19 ≤ l ≤ 16 |
| Reflections collected | 4576 |
| Independent reflections | 1715 [$R_{int}$ = 0.0195, $R_{sigma}$ = 0.0222] |
| Data/restraints/parameters | 1715/1/106 |
| Goodness-of-fit on $F^2$ | 1.104 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0294, $wR_2$ = 0.0814 |
| Final R indexes [all data] | $R_1$ = 0.0335, $wR_2$ = 0.0843 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.30/-0.20 |
| Flack parameter | 0.013(15) |

**Table S2.** Selected bond lengths (Å) for Compound **1**

| Compound | **1** | |
|---|---|---|
| Bond Lengths[Å] | Fe1-Cl1 | 2.1953(10) |
| | Fe1-Cl1[1] | 2.1954(10) |
| | Fe1-Cl1 | 2.1746(18) |
| | Fe1-Cl1 | 2.1812(18) |
| | N1-C1 | 1.506(8) |
| | N1-C8 | 1.487(7) |
| | N1-C6 | 1.56(3) |

[1]3-X, +Y, +Z

**Table S3.** Selected bond angles (°) for **1**

| Compound | **1** | |
|---|---|---|
| Bond angles (°) | Cl1-Fe1-Cl1 | 107.68(7) |
| | Cl3-Fe1-Cl1[1] | 108.68(5) |
| | Cl3-Fe1-Cl1 | 108.68(5) |
| | Cl3-Fe1-Cl2 | 113.20(10) |
| | Cl2-Fe1-Cl1 | 109.23(6) |
| | Cl2-Fe1-Cl1[1] | 109.23(6) |
| | C1-N1-C6 | 106.2(10) |
| | C8-N1-C1 | 109.6(5) |
| | C8-N1-C6 | 105.7(11) |
| | C2-N1-C1 | 114.5(12) |
| | C2-N1-C8 | 111.4(13) |
| | C2-N1-C6 | 108.9(8) |

[1]3-X, +Y, +Z

## Calculation of Δ*S* and N of 1

**In the heating cycle mode**

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

$$= \frac{38.36\, J \cdot g^{-1} \times 337.90 g \cdot mol^{-1}}{341.8K}$$

$$= 37.92\, J \cdot mol^{-1} \cdot K^{-1}$$

$$N_H = \exp\left(\frac{\Delta S_H}{R}\right) = \exp \frac{37.92\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}} = 95.68$$

**In the cooling cycle mode**

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

$$= \frac{36.32 J \cdot g^{-1} \times 337.90 g \cdot mol^{-1}}{328.2K}$$

$$= 37.39\, J \cdot mol^{-1} \cdot K^{-1}$$

$$N_C = \exp\left(\frac{\Delta S_C}{R}\right) = \exp \frac{37.39\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}} = 89.75$$