

Experimental and theoretical demonstration of ferroelectric anisotropy in a one-dimensional copper(II)-based coordination polymer†

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The anisotropy of polarization in a 1D copper(II)-based coordination polymer was investigated experimentally and theoretically for the first time, revealing that the origin of the ferroelectricity and its anisotropic nature are closely related to the coordination geometry of the metal ion and the packing mode of the coordination polymer.

Ferroelectric materials are characterized by spontaneous electric polarization. When subject to an appropriate external electric field, this spontaneous polarization can be switched. Because of such unique properties, ferroelectrics have found broad applications in microelectronics (*e.g.* tunable capacitors), computing (non-volatile memory devices) and transducers,¹ while more extensive applications are being envisioned. Development of new ferroelectric materials and realization of novel applications depend critically on our understanding of the structure–property relationship at the molecular level. So far the research on ferroelectric materials is focused on inorganic salts and organic polymers.² Recently, ferroelectricity in supramolecular assemblies of organic molecules and in metal–organic frameworks have been reported.^{3,4} Because the characterization of the ferroelectric properties of these materials was mainly carried out on polycrystalline pellets or powders,³ the question of how the local chemical environment induces the macroscopic ferroelectricity remains unclear, which hinders the rational design of ferroelectric materials. Here we report the synthesis, structural determination, and characterization of anisotropic ferroelectricity of single crystals of a coordination polymer formed by copper–(*o*-phthalate) with terminal imidazole.

Single crystals of $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2]_n$ (**1**) of a few millimeters dimensions were obtained by the hydrothermal reaction of copper acetate, imidazole and *o*-phthalic acid.† X-Ray structural analysis reveals that **1** crystallizes in the non-centrosymmetric and polar space group *Pna*2₁ (no. 33). The metal coordination environments are shown in Fig. 1.

Two similar yet distinct Cu(II) centers are identified in the asymmetric unit, each featuring the coordination of two imidazole and two *o*-phthalate. Each of the neutral imidazole provides one of its two N atoms, while each *o*-phthalate offers two carboxylate O atoms for coordination. Thus, the Cu(II) ion formally is situated in an octahedral coordination sphere. However, two of the Cu–O distances, 1.943 and 1.993 Å, are significantly shorter than the other two (2.727 and 3.081 Å).

Therefore, the *o*-phthalate is effectively monodentate and the coordination of Cu(II) can be described as a severely elongated octahedron, which typically arises from the Jahn–Teller effect of Cu(II). Each crystallographically independent copper(II) center coordinated by two imidazoles, and adjacent two crystallographically independent copper(II) centers bridged by *o*-phthalate in chelating mode, generate a 1D chain structure similar to those of $(\text{C}_{28}\text{H}_{24}\text{Cu}_2\text{N}_8\text{O}_8)_n \cdot 3n\text{H}_2\text{O}$, $(\text{C}_{16}\text{H}_{16}\text{CoN}_4\text{O}_4)_n$ and $(\text{C}_{32}\text{H}_{32}\text{N}_8\text{O}_8\text{Zn}_2)_n$.⁵ The 1D chains are zipped to each other *via* hydrogen-bonding interaction between the imidazole as a proton donor and the carboxylate group as proton acceptor $\text{N}(2) \cdots \text{O}(3) = 2.718(6)$ Å, $\text{N}(2) \cdots \text{O}(3) = 1.87$ Å, $\angle \text{N}(2) \cdots \text{H} \cdots \text{O}(3) = 167.4^\circ$, $\text{N}(4) \cdots \text{O}(5) = 2.872(5)$ Å, $\text{N}(4) \cdots \text{O}(5) = 2.04$ Å, $\angle \text{N}(2) \cdots \text{H} \cdots \text{O}(5) = 161.4^\circ$) to give a 2D structure that is further extended into a 3D supramolecular architecture through van der Waals interactions.

Since **1** crystallizes in the non-centrosymmetric space group *Pna*2₁, one of the ten polar point groups necessary for ferroelectricity to occur, the dielectrical hysteresis loops along different crystal axes of the single crystals were measured. Fig. 2 shows the polarization vs. electric field (*P*–*E*) curves of **1** at various ac electric fields of triangular waveform applied along the three main crystallographic axes. The hysteretic *P*–*E* loops were clearly displayed along the polar *c*-axis, indicating the presence of ferroelectricity. A saturation polarization (*P*_{sa}) of *ca.* 0.48 μC cm^{−2} and a remanent polarization (*P*_r) of *ca.* 0.17 μC cm^{−2} are obtained with a coercive field (*E*_c) of *ca.* 2.0 kV cm^{−1}. The *P*_{sa} value for **1** is significantly higher than that of 0.25 μC cm^{−2} reported for the typical ferroelectric compound NaKC₄H₄O₆·4H₂O and comparable to that of

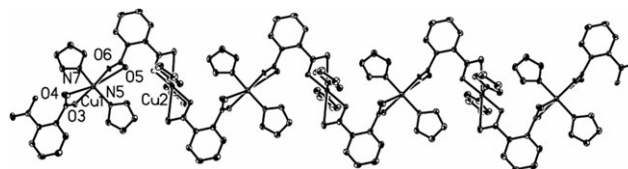


Fig. 1 The 1D chain structure in **1**.

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† Electronic supplementary information (ESI) available: Spontaneous polarization of **1** along the *c* axis calculated using different DFT methods. Crystallographic CIF file CCDC 704347 for **1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820500k

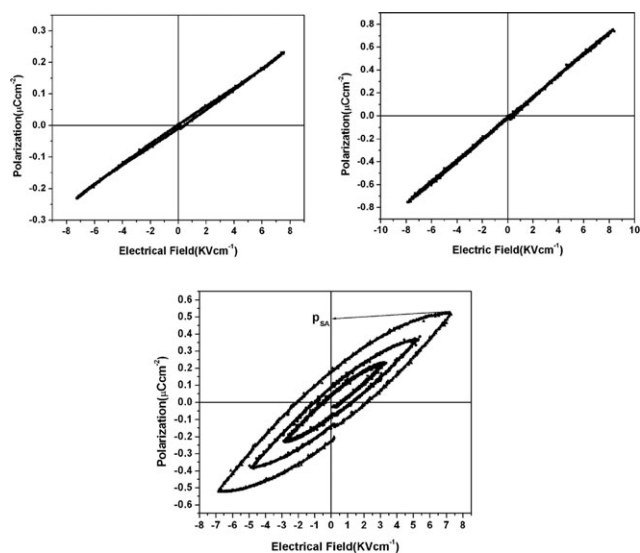


Fig. 2 The polarization vs. electric field (P - E) curves of **1** at various ac electric fields applied along a (top, left), b (top, right) and c (bottom) axes.

$0.50 \mu\text{C cm}^{-2}$ for $\text{C}_{13}\text{H}_{14}\text{ClN}_5\text{O}_2\text{Cd}$.⁴ Interestingly, while **1** exhibits clearly typical ferroelectric feature along the c axis, no P - E hysteresis loops are displayed along the a and b axes, indicating strong anisotropy in the ferroelectricity, which is consistent with the characteristics of the polar point group $mm2$.

The spontaneous polarization of **1** was also calculated theoretically based on the structural model. Given that the unit cell contains a n glide plane along a and b axes, and a 2_1 screw along the c axis, the local dipoles along a and b axes are cancelled out by symmetry,⁶ and the total macroscopic polarization lies parallel to the c axis, which constitutes the unique polar axis. Thus, the total polarization of **1** along the c axis in a unit cell ($Z = 4$) is calculated on the basis of density functional theory (DFT)⁷ using the GAUSSIAN 03 package.⁸ The spontaneous polarization of **1** along the c axis calculated using different DFT methods⁹ ranges from 1.138 to $1.270 \mu\text{C cm}^{-2}$ (ESI,† Table S1).

The above analyses confirm the structural origin of the spontaneous polarization and the observed anisotropy. However, the total polarization calculated on the basis of structural data is larger than that of $0.48 \mu\text{C cm}^{-2}$ measured. The possible reason for such a discrepancy is that the P - E loops do not saturate, *i.e.* the polarization switching was not complete. Such situation mainly originates from the following reasons: (1) the leakage of charges arising from the conduction of the crystal; (2) the Curie temperature is much higher than room temperature, thus requiring a higher field to fully switch the polarization.

Consistently, when a higher electric field was applied along the c axis, the leakage of charges was observed (Fig. 3). To find the Curie temperature (T_C), the variations of the real part of dielectric permittivity (ϵ' , *i.e.* dielectric constant) and the dissipation factor (*i.e.* loss tangent, $\tan\delta$) were measured as a function of temperature at various frequencies. As shown in Fig. 4, the dielectric constant remains relatively flat with values

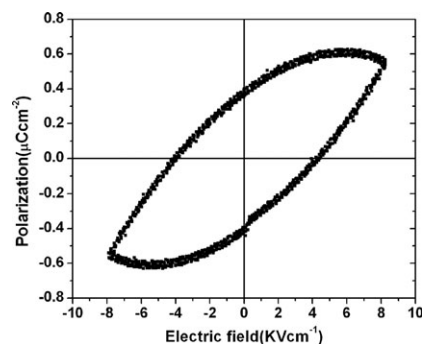


Fig. 3 The polarization vs. electric field (P - E) curves of **1** along the c axis at higher electric field.

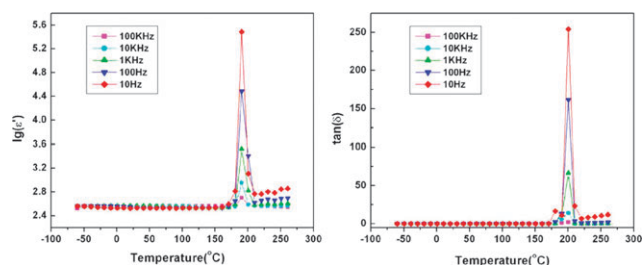


Fig. 4 The real part of dielectric permittivity (left) and the dielectric dissipation factor (right) for **1** measured as a functions of temperature at various frequencies (note that the values at the T_d temperature and above arise from the decomposed material).

between 300 and 350, and the loss tangent is almost temperature independent and low (<0.02) in the temperature range from -60 to 180 °C. Above 180 °C, both ϵ' and $\tan\delta$ at all measuring frequencies increase very sharply, and then reach the peak values at 195 °C. The temperature dependence of the dielectric properties clearly indicates that no solid-solid structural phase transition takes place in crystal **1** up to the decomposition point T_d , which is consistent with the thermal analysis of **1** (Fig. 5). It is therefore reasonable to deduce that the ferroelectric Curie temperature T_C would be higher than T_d . In other words, the ferroelectric state must be very stable at room temperature, which makes it difficult to switch the polarization fully. This could account for the observation that the polarization P_{sa} measured is smaller than the calculated value.

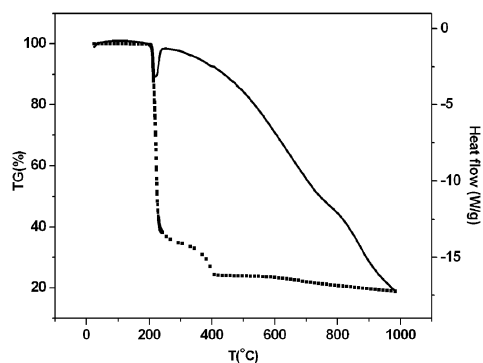


Fig. 5 Thermal analysis for **1** (dotted line represents TG curve, solid line is heat flow).

In summary, we have demonstrated a large anisotropy of polarization in a 1D copper(II)-based coordination polymer which crystallizes in the non-centrosymmetric polar space group $Pna2_1$. Ferroelectric coercivity was present only along the polar c axis of the crystals. Theoretical investigation reveals that the polar anisotropy and ferroelectricity are closely related to the coordination geometry of the metal ion and the packing mode of the coordination polymer. Thus, the present work would be useful for our rational design of ferroelectric coordination polymers.

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Notes and references

‡ *Preparation of 1*: *o*-Phthalic acid (0.166 g, 1.0 mmol), imidazole (0.140 g, 2.0 mmol) and cupric acetate (0.200 g, 1.0 mmol) were added into the mixture of 4 mL distilled water and 12 mL ethanol, while stirring at room temperature. When the pH value of the mixture was adjusted to about 6.2 with ammonia solution (~12%, v/v), the cloudy solution was put into a 25 mL Teflon-lined Parr and heated to 100 °C for 1000 min, and then cooled to room temperature at a rate of 2 °C h⁻¹. Dark-blue block crystals of **1** were obtained in 65% yield (based on cupric acetate). IR (KBr): 3154(s), 3076(m), 2871(m), 2851(m), 1472(w), 2964(w), 1602(s), 1091(s), 1457(s), 1546(s), 1485(m), 1447(m), 1076(s), 963(w), 864(w), 831(m), 768(m), 745(m), 713(w), 704(w), 655(m), 625(w), 466(w) cm⁻¹; Anal. Calc. for **1**: C 46.22, H 3.32, N 15.40. Found: C 45.20, H 3.14, N 14.81%.

§ *Crystal data for 1* (Cu(C₈H₄O₄)(C₃H₄N₂)₂): orthorhombic, space group $Pna2_1$, Flack parameter = 0.051(2), $T = 298(2)$ K, $a = 16.578(3)$, $b = 15.421(3)$, $c = 11.988(2)$ Å, $V = 3064.9(10)$ Å³, $Z = 4$, $D_c = 1.577$ g cm⁻³, $M = 727.63$, $\mu(\text{Mo-K}\alpha) = 1.450$ mm⁻¹, number of reflections measured/number of independent reflections = 23055/5997, $R_{\text{int}} = 0.0514$, $R_1(\text{obs.}) = 0.0454$, wR_2 (all data) = 0.1113.

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