Dibutylammonium Hydrogen Oxalate: An Above-Room-Temperature Order–Disorder Phase Transition Molecular Material

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ABSTRACT: An above-room-temperature new phase transition molecular material, dibutylammonium hydrogen oxalate (1), has been synthesized, which undergoes a reversible phase transition at 321.6 K. Differential scanning calorimetry (DSC) measurements confirm its reversible phase transition with a large heat hysteresis of ~10 K. The dielectric constants of 1 exhibit an obvious step-like anomaly, showing the high and low dielectric constant states at high and room-temperature phases, respectively, which reveal that 1 might be considered a potential switchable dielectric material. Variable-temperature single crystal X-ray diffraction analyses disclose that the origin of this phase transition is greatly attributed to the coupling of the order–disorder change and reorientation of the dibutylammonium cation; that is, the frozen ordering of ethyl group in butyl moiety triggered by the decreasing temperature forces the reorientation of cation, thus resulting in the structural phase transition.

INTRODUCTION

Reversible solid-to-solid structural phase transition materials (PTMs) have long drawn wide interest due to their applications in data communication, thermal energy storage, and mechanical energy transfer.1−7 Particularly, some properties of PTMs materials could be switched between at least two states, which have been used in switches, memory devices, and sensors.8,9 For example, their dielectric responses will be switched between different states under the external stimulus. For the molecular entities, reorientational order–disorder motion of the moieties is considered one of the most efficient strategies for constructing smart PTMs, and intensive efforts have been made by researchers for exploring a large number of such materials.10−30 For instance, reorientation of dimethylammonium (DMA) cation was recently noticed to induce the striking dielectric responses in metal–organic frameworks,26 coupled with the ferroelectric or antiferroelectric ordering in the temperature range of 160−185 K.27 Below the phase transition temperatures, they are the multifaceted materials with the coexistence of ferroelectricity, antiferroelectricity, and weak ferromagnetic order.

Similarly, many other PTMs have also been successfully assembled; however, the low phase transition temperature (Tc) restricts their potential device applications.27−29 In contrast to low temperature, the most popular range of Tc is 290−365 K30,31 which covers around the ambient temperature, possessing tremendously extensive applications including pyroelectric sensor, solar, medical, textile, electronic, and energy-saving applications.32−39 For example, various salts of glycine molecule with inorganic counterions were discovered to exhibit promising ferroelectricity and pyroelectricity at ambient temperature.36,39 A distinct representative pyroelectric material of triglycine sulfate (TGS), having ferroelectric Tc around 323 K, is considered a significant parameter for applications in pyroelectric detectors because of its large pyroelectric coefficient.39 These above-room-temperature compounds make the researcher curious to discover substances which offer great response in potential applications near or above room temperature. Recently, the work pertinent to the discussion was done by Xiong et al., where the combination of disordered cation and magnetic transition metal ion results in the formation of a magneto-dielectric molecule-based functional material (i.e., triethylmethylammonium tetrabromoferrate) with the above-room-temperature phase transition point.40 Significant spontaneous polarization and high Tc make this above-mentioned compound a promising candidate for the design of molecule-based ferroelectrics, and promote new electronic utilization of organic ferroelectrics. Therefore, these findings inspire us to investigate new above-room-temperature PTMs, utilizing the various organic moieties. As a flexible structural primitive, dibutylamine molecule is sensitive to the temperature change, which might be advantageous for

Supporting Information

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assembling smart PTMs with the order−disorder structural transitions.

Here, we report an above-room-temperature smart PTM, dibutylammonium hydrogen oxalate (1), which undergoes a reversible phase transition at \( T_\text{c} = 321.6 \) K and demonstrates dielectric anomaly. As expected, crystal structural studies show that the phase transition of 1 mainly originates from the order−disorder transformation of the terminal ethyl moiety of the dibutylammonium cation. Furthermore, the reorientation of cation relative to the anionic plane also occurs, in combination with the ordering of ethyl group, which induces the structural phase transition and symmetry breaking in 1. To the best of our knowledge, 1 is a new concrete example with the above-room-temperature phase transition, triggered by the reorientational order−disorder transition in dibutylammonium. This order−disorder and the apparent motion of the dibutylammonium cation in 1 are switched by temperature, which leads to the dielectric changes between low and high state. It is believed that this finding might provide the potential pathway to design the new above-room-temperature PTMs with properties through such organic moieties.

**Experimental Section**

**Synthesis.** All reagents and solvents were obtained commercially and used without further purification. Compound 1 was synthesized by evaporating the aqueous solution, containing dibutylamine base and oxalic acid monohydrate, in stoichiometric amount of 1:1 molar ratio. The reaction mixture was stirred and heated for 5 min to dissolve the components thoroughly. As the solution became cool, tiny colorless crystalline product was obtained. Subsequently, the resulting solution was filtered, and the filtrate was left undisturbed. Several days later, prism-like single crystals of 1 were obtained. The deuterated sample of 1 was synthesized and recrystallized from D2O solvent three times.

In the IR spectra of 1 (Figure S1, Supporting Information), the peaks at approximately 1714 and 1643 cm\(^{-1}\) are assigned to stretching vibration absorption of the carbonyl group (C==O) in the carboxyl and carboxylate groups, respectively. These absorptions reveal the existence of oxalic acid in 1, and only one carboxyl group is deprotonated, leading to the reaction of 1:1 stoichiometric ratio. The phase purity of 1 was confirmed by powder XRD (PXRD) patterns, which match very well with the results simulated from the single-crystal structure, as depicted in Figure S2.

**Thermal Measurements.** Differential scanning calorimetry (DSC) measurement was recorded on NETZSCH DSC 200 F3 instrument at heating and cooling rate of 5 K/min in the temperature range from 285 to 350 K. These measurements were accomplished under nitrogen atmosphere in aluminum crucibles. Specific heat (\( C_p \)) experiments were performed using a comparison method, of which sapphire standard was used as the reference. We first run the baseline on the desired temperature range and then sapphire disks for calibration were used as the standard prior to the measurement. Then the sample was measured and compared with the sapphire recorded formerly.

**Dielectric Measurements.** For dielectric experiments, well-ground powder samples connected by silver-conducting paste on electrodes were used for measuring the complex dielectric permittivities (\( \varepsilon = \varepsilon’ − i\varepsilon'' \)). The dielectric constants were measured using a TH2828A impedance analyzer at different frequencies of 1 MHz, 100 kHz, 10 kHz, and 5 kHz with the measuring AC voltage fixed at 1 V.

**Single-Crystal Structure Determination.** Variable-temperature X-ray single-crystal diffraction data of 1 were collected using Super Nova CCID diffractometer with graphite monochromated Mo K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å) at low (175 K) and high (330 K) temperatures, respectively. Crystal structures were solved by the direct methods and refined by the full-matrix least-squares method based on \( F^2 \) using the SHELXLTL software package. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically, located at the cation and the hydrogen atoms in carboxyl groups as determined from the Fourier electron density map. Due to the disorder characteristic of the terminal ethyl moiety, we split the carbon atoms C1 and C2 into two sites C1A, C1B and C2A, C2B, with occupancy of 0.60, 0.40 and 0.60, 0.40, respectively. Some atoms also show slight disorder; we try to solve the disorder, but the disorder was too small to split. Crystallographic data and details of data collection and refinement are listed in Table S1. CCDC 1046677−1046678 for 1 contains the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Results and Discussion**

**Thermal Properties of 1.** DSC measurement is an effective and useful method to confirm the existence of a reversible phase transition triggered by external temperature stimulus. Here, compound 1 was subjected to the preliminary DSC measurement (Figure 1a), which shows a couple of exothermic (311.4 K) and endothermic (321.6 K) peaks, revealing a reversible phase transition with a large thermal hysteresis of \( \sim 10.2 \) K. Such a large thermal hysteresis is also supported by the estimation from the differential scanning rates (Figure S3), which is the characteristic of a first-order phase transition for 1. In addition to DSC, the \( C_p − T \) curve further confirms the presence of phase transition in 1 (Figure 1b). The line shown at the bottom of Figure 1b denotes the measurement obtained from sapphire standard, which is used as the reference. The
curve of $C_p$ in the heating mode gives a sharp peak at 321.6 K, which is consistent with the DSC result. The enthalpy ($\Delta H$) associated with the endothermic peak (in $C_p$) was calculated as $8.887 \text{ J/g}$ and the corresponding total entropy change ($\Delta S$) was estimated to be $6.020 \text{ J/mol-K}$ by using the equation $\Delta S = \Delta H/T_c$. Moreover, the pronounced thermal anomaly was also observed in differential thermal analysis curve at $T_c$ as depicted in Figure S4. This curve matches quite well with the results obtained from the DSC and $C_p$ measurements.

**Variable-Temperature Powder X-ray Diffraction of 1.** Variable-temperature powder X-ray diffractions (VT-PXRD) offer the most powerful information on phase transition materials. In order to assist the exploration of phase transition in 1, finely ground powder was checked in VT-PXRD at different temperatures of 298, 308, 333, and 343 K, respectively (Figure 2). The experimental patterns obtained at low and high temperature in the VT-PXRD match well with the simulated data obtained from single crystal X-ray diffraction. However, drastic changes were found between the data obtained at low-temperature phase (LTP) and high-temperature phase (HTP), strongly confirming the occurrence of phase transition in 1. For instance, during the warming process, the Bragg diffractions of (101), (101), (022), (031), and (104) planes of LTP exhibit obvious shifts at HTP, respectively. Moreover, it is noteworthy that the profile patterns recorded at low temperature, before the phase transition point and on cooling back to 298 K from high temperature, appear to be the same. Such an observation reveals the reversible phase transition of 1, which is consistent with the thermal measurements of DSC and $C_p$ providing a solid proof of the existence of reversible phase transition in 1.

**Crystal Structural Analysis of 1.** X-ray diffraction analyses of 1 were performed at 175 K (the low-temperature phase, LTP) and 330 K (high-temperature phase, HTP), respectively. Distinct differences of structural parameters are observed between the HTP and LTP, which further confirm the existence of phase transition. In the HTP, 1 crystallized in the monoclinic crystal system with space group $P2_1/c$, and cell parameters are $a = 17.868(2)$, $b = 5.5508(3)$, $c = 14.4018(10)$ Å, $\beta = 112.102(11)^\circ$, $Z = 4$, $V = 1323.5(2)$ Å$^3$, as shown in Table S1. In the LTP, 1 transforms into the triclinic crystal system with a centrosymmetric space group $P1$ and the cell parameters are $a = 5.5144(3)$, $b = 9.4520(5)$, $c = 13.4040(5)$ Å, $\alpha = 74.36(4)^\circ$, $\beta = 84.747(4)^\circ$, $\gamma = 81.205(4)^\circ$, $Z = 2$, $V = 663.55(6)$ Å$^3$. These remarkable differences between HTP and LTP structures can also be perceived from the variation in the cell parameters. For 1, the anomalies of unit cell parameters during phase transition are measured as a function of temperature from 280 to 335 K. As shown in Figure 3, all the cell parameters of 1 are stable in LTP until the phase transition point at 321.6 K, where these values exhibit sharp changes and then become stable again at HTP. Its unit volume is doubled at $T_c$. The temperature-dependent lattice constants of $a$-axis demonstrate a considerable 3-fold increment while $b$- and $c$-axes exhibit a computable change. The abrupt changes in the cell parameters in the vicinity of $T_c$ ascertain the confirmation of phase transition which corresponds well to the DSC and $C_p$ measurements.

From the symmetry breaking point of view, the structure of 1 changes from a high centrosymmetric space group of $P2_1/c$ at HTP (point group of $C_{2h}$) to a low centrosymmetric space group of $P1$ at LTP (point group $C_i$). The symmetry breaking phenomenon occurs during the transition, showing an Aizu notation of $2/mP1$. Symmetric elements decrease by half from four ($E_i$, $i$, $C_2$, $\sigma_h$) at HTP to two ($E$ and $i$) at LTP, in strict accordance with Landau phase transition theory. As shown in Figure S5, the change of its spatial symmetry operations indicates that the symmetric elements (2 and $m$) disappear in 1 in LTP, which might be aroused by slight reorientations of molecules. According to the Curie symmetry principle, the space group of $P1$ is a subgroup of the one of $C2/i$, of which the maximal nonisomorphic subgroups include $C_{2h}$, $C_{2}$, and $P1$.

At HTP, the asymmetric unit contains one protonated dibutylammonium cation and one monodeprotonated oxalate anion, while the LTP asymmetric unit is composed of one dibutylammonium cation and two halves of oxalate anions (see Figure 4). Packing structures of 1 in both states are stabilized by the extensive O···H···O and N···H···O hydrogen bonding networks (Figure 5). As shown, a one-dimensional array of hydrogen bonding (O···H···O) is constructed involving the oxygen atoms of carboxylate and carboxylic acid moiety of the adjacent oxalate anions. Arrays of these interactions between the anionic moieties are aligned parallel to each other, extending in the direction of the $b$-axis. Moreover, dibutylammonium cations sandwiched between the neighboring oxalate anions chains form a butterfly-like skeleton via N···H···O hydrogen bonds with carbonyl oxygen atoms of the monodeprotonated anion. Thus, a strip-like motif is created by hydrogen-bond interactions along the $c$-axis, which imposes a great impact on the packing structures. The hydrogen-bonding skeleton formation by the anion-anion and anion-cation intermolecular interactions constitutes the two-dimensional

![Figure 2. Variable-temperature powder XRD patterns of 1.](image)
In the HTP crystal structure of 1, it is noteworthy that butyl groups of dibutylammonium cation are highly disordered, where the terminal carbon atoms present two atomic occupations of C1A/C2A and C1B/C2B, respectively. The splitting makes the high-temperature structure of 1 more acceptable. Such apparent disordered characteristics at HTP can also be deduced from the thermal ellipsoids of C1 and C2 atoms, which are relatively larger than those of other neighboring atoms. In reality, this is not the actual state but an average result of the atomic disordering, as shown in Figure S6. With the temperature decreasing from 330 to 175 K, it is interestingly found that the disordered terminal carbon atoms are frozen and its low-temperature structure becomes totally ordered, which does not possess sufficient thermal energy to switch between sites, as demonstrated in Figure 4b. This obvious order–disorder change would possibly result from the large freedom and flexibility of the cationic moieties, particularly the terminal ethyl parts of the butyl chain. However, the hydrogen-bonding interaction between the nitrogen atoms and oxalate anion makes the internal carbon atoms incapable of undergoing such severe order–disorder behavior. The deuterated sample of 1 shows no difference in DSC measurements with 1. Therefore, the role of hydrogen bonding in the phase transition would be excluded (Figure S7). In other word, such an observation reveals that order–disorder transformation of butyl part of the cation moiety is the driving force for the phase transition in 1.

Besides the order–disorder transformation, another striking feature of the structural change is the remarkable reorientation of the cation, which could be deduced from the angle between the normal line of the anionic plane and the C8–N1 line of the cation. For comparison, the angles between the cationic line and the line dropping vertically through the anionic plane are calculated, as depicted in Figure 6. Since the adjacent oxygen atoms of two alternate oxalate anions are nearly parallel, showing no obvious changes at both LTP and HTP, the plane consisting of carboxyl oxygen atoms is thus assigned as a reference plane. Furthermore, since another ordered butyl moiety is almost the same in the two phases, it is reasonable to appoint C8–N1 as a reference line. From Figure 6, it can be seen that the C8–N1 line inclines slightly with the angle of 5.70° between the vertical line passing through the plane of the anion and the line of the cation in LTP, while it becomes more...
tilted with the angle of 17.03° in HTP, induced by the dragging behavior of disordered terminal carbon atoms. Such distinct reorientation of 1 is not only demonstrated by the inclined position change of cation, but also confirmed by the alteration of bond length in the hydrogen bonds between anion and cation. In fact, the inclination of cation has a great impact on the hydrogen-bonding interactions of 1 (Figure 5), where the N atom plays an important role. Generally speaking, the acceptor/donor length of hydrogen bonds would cause variation with changing temperature, due to thermal expansion or contraction. In contrast, however, the length of N1–H2⋯O3 is shortened from 2.883 (LTP) Å to 2.858 (HTP) Å. The coexistence of elongation and shortening of acceptor/donor distances might be reminiscent of reorientation of cationic moieties. The above-mentioned analyses support the fact that the reorientational order–disorder motions of the terminal ethyl moiety between two phases are responsible for phase transition of 1.

From the above studies, it can be deduced that the phase transition of 1 is mainly induced by order–disorder change of the dibutylammonium cations together with the reorientation motion. In detail, single-crystal structural analyses reveal that one of the butyl groups in the cation is disordered at HTP. With decreasing temperature, it becomes more ordered below the Tc. Meanwhile, reorientational transformation of the dibutylammonium cation is also contributing to the structural phase transition of 1; that is, the cationic moiety reorients from its tilting position, affording a change of 11.3° for the included angle between the normal line of anionic plane and the cationic counterpart. Hence, the phase transition of 1 would be ascribed to the coupling of order–disorder change and reorientation of the dibutylammonium cation. To the best of our knowledge, this observation is unprecedented and differs from other PTMs containing the dibutylammonium cation, in which hydrogen bonds play an important role for the structural phase transition.21

**Dielectric Studies of 1.** Temperature-dependent dielectric constant measurement is of great importance and is a significant indicator of phase transition in a compound, which reveals the degree of electric polarizability of the material. For molecular crystals, dielectric transition between the low- and high-dielectric states could be established by the disorder or reorientation transformation.47 The structural analyses of 1 have disclosed the order–disorder mechanism of its phase transition. To further confirm this feature, we measured its temperature-dependent dielectric permittivities (ε = ε′ − iε″), where ε′ is the real part and ε″ is the imaginary part) on powder pressed pellets; Figure 7 displays its dielectric permittivities at different frequencies from 300 to 344 K. The obvious step-like dielectric anomaly was clearly recorded at 311.4 K in cooling mode, which corresponds well to thermal analyses, temperature-dependent dielectric measurement, and single-crystal structural analyses. The origin of phase transition of 1 is mainly attributed to the coupling of order–disorder change and reorientation of the dibutylammonium cation. In detail, the frozen ordering of ethyl groups caused by cooling down forces the reorientation of cations relative to the anionic plane, and thus results in the phase transition. We believe that this new finding might offer a new route to design potential phase transition materials.

**CONCLUSIONS**

In the present work, we present an above-room-temperature switchable dielectric material, which displays a reversible phase transition at 321.6 K, being confirmed by thermal analyses, temperature-dependent dielectric measurement, and single-crystal structural analyses. The origin of phase transition of 1 is mainly attributed to the coupling of order–disorder change and reorientation of the dibutylammonium cation. In detail, the frozen ordering of ethyl groups caused by cooling down forces the reorientation of cations relative to the anionic plane, and thus results in the phase transition. We believe that this new finding might offer a new route to design potential phase transition materials.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00758.

IR spectrum, PXRD patterns, DSC curves at different scanning rates, DTA, packing diagram showing hydrogen-bond geometries, thermal ellipsoids maps of cation, deuterated sample DSC and tables of compound 1 (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)
Crystal Growth & Design

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The authors declare competing financial interests.

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