Dibenzylammonium trichloroacetate: an above-room-temperature order–disorder switchable dielectric material†

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Solid-state phase transition materials with a controllable dielectric response are of great interest owing to their technological importance. In the present work, a new molecular electric-ordered compound, dibenzylammonium trichloroacetate (compound 1), showing switchable and tunable dielectric properties, has been successfully synthesized and grown as bulk crystals. It is found that 1 undergoes a reversible solid-to-solid phase transition at 329 K (Tc), which was confirmed by differential scanning calorimetry (DSC), dielectric measurements and variable-temperature powder X-ray diffraction. Structural analyses reveal that intermolecular N⋯O hydrogen bonds connect the functional groups together and form a chain-like supramolecular architecture along the a-axis. Further, variable-temperature single-crystal X-ray diffraction discloses the order–disorder feature of its structural change, which is mainly induced by the disordering of trichloroacetate anions upon gradual heating. Moreover, the dielectric constants of 1 display a step-like anomaly around Tc, suggesting that its dielectric responses could be switched or even tuned by external temperature. It is believed that this finding might provide a possible candidate with controllable dielectric performance for potential application.

Introduction

Switchable dielectric materials, due to their convertible dielectric behavior between high and low dielectric states, could find potential applications in data storage, data communication, signal processing, etc.¹ These materials can change their properties between different states by external stimuli, such as an electric field, extra light, temperature, etc.² Among them, solid-to-solid reversible phase transition, induced by a change in temperature, is a common principle for constructing switchable dielectric materials. The rational design and synthesis of such temperature-responsive materials exhibiting switchable dielectric properties is not only beneficial for the exploration of novel optoelectronic devices, but also for the studies of structure–property relationships.³ Although a few types of molecule-based phase-change materials (PCMs), such as perovskite-type metal–organic frameworks (MOFs),⁴ crown-ether-based rotator–stators,⁵ and co-crystals based on electronic⁶ or hydrogen transfer,⁷ have been found in recent years, potential materials which can be practically used have not been well developed. In this context, the search for high-temperature PCMs is still a great challenge for scientists,⁸ owing to the lack of knowledge regarding the control of the motions of dipole moments in the crystal lattice.

Generally, structural phase transition is triggered by diverse stimuli, including atomic displacements, hydrogen bond effects and molecular order–disorder transformations.⁹ Among them, introduction of disordered moieties into molecular crystals is one of the most effective strategies.¹⁰ Throughout many of the highest-profile areas of research within contemporary solid-state science, disorder plays a central role in driving phase transition. It has been reported that order–disorder structural changes could dominate phase transitions in metal–organic compounds, which present outstanding optical and electrical effects.¹¹ For instance, the inorganic K₃[Fe(CN)₆] cage combines with the organic imidazolium guest part to build a new architecture showing exceptional dielectric anomalies, triggered by the order–disorder transformation of the imidazolium ring.¹² Consequently, several kinds of disordered primitives have been utilized to construct new PCMs. In the past few decades, haloacetic acids have been taken as anionic moieties to fabricate phase...
transition compounds, in which the halogen atoms usually exhibit order–disorder changes with varying temperatures resulting in structural phase transition.\textsuperscript{13,14} As verified by the molecular co-crystal of betainium chlorodifluoroacetate, exceptional dielectric performances were induced by the order–disorder transformation of fluorine atoms in chlorodifluoroacetate.\textsuperscript{15}

However, most of those compounds suffer from low temperatures, which may restrict their potential application.\textsuperscript{16,17} Further exploration of new PCMs with a high-temperature phase transition point ($T_c$), especially above-room-temperature materials, is strongly desired. Recently, our group discovered a high-temperature switchable dielectric material, N-isopropylbenzylammonium dichloroacetate, which shows dielectric relaxation.\textsuperscript{18} Here, as a continuation of our work, a new hydrogen-bonded phase transition compound, dibenzylammonium trichloroacetate (1), is reported as a switchable dielectric material. In 1, dibenzylamine can be treated as a stator due to its conjugated benzene rings, while the trichloroacetate anion acts as a rotor to trigger an order–disorder phase transition. It is interesting that 1 undergoes an order–disorder phase transition at 329 K, and presents a tunable temperature-dependent dielectric response. Moreover, the $T_c$ of 1 is beyond but not far from room temperature, probably due to the more stable conjugated dibenzylamine, which will be greatly favourable to its potential application.

### Experimental section

All the starting materials used were of analytical reagent grade. Compound 1 was synthesized through reaction of dibenzylamine (1.97 g, 0.01 mol) and trichloroacetic acid (1.63 g, 0.01 mol) in absolute ethanol with stirring at room temperature. Bulk crystals were successfully grown from the aqueous solution containing dibenzylamine and trichloroacetic acid with an equal ratio. The beaker was covered with filter paper and subsequently kept for slow evaporation at room temperature. After several days, high-quality single crystals with the largest size of $6 \times 4 \times 3$ mm$^3$ were obtained, as shown in Fig. 1.

The phase purity of 1 at room temperature was verified by powder X-ray diffraction (PXRD) and compared with that determined from single-crystal structural analysis (ESI, Fig. S1). Besides, variable-temperature PXRD patterns were collected at 293 K, 343 K and 293 K (from HT cooling back to RT) on a D/MAX2500 Powder X-ray Diffractometer to confirm the reversible structural phase transition.

Differential scanning calorimetry (DSC) measurements were performed by heating and cooling the samples (5.987 mg) in the temperature range of 303–363 K on a NETZSCH DSC 200 F3 instrument. The measurements were carried out under nitrogen at atmospheric pressure in aluminum crucibles at heating/cooling rates of 2 K min$^{-1}$, 5 K min$^{-1}$ and 10 K min$^{-1}$, respectively (ESI, Fig. S2). For dielectric experiments, pressed powder pellets of 1, using silver painted electrodes, were prepared for measuring the dielectric constants. Its dielectric constants were measured by a TH2828A impedance analyzer over the frequency range from 100 KHz to 1 MHz with an applied electric field of 0.5 V.

Variable-temperature X-ray single-crystal diffraction data at high temperatures (HT, 320, 315, and 310 K) and low temperature (LT, 293 K) were collected on a Super Nova CCD diffractometer. All of the HT phases were measured with graphite monochromated Cu-Kα radiation ($\lambda = 1.54184$ Å), while the LT phase was measured with Mo-Kα radiation ($\lambda = 0.71073$ Å). Colorless crystals with approximate dimensions $0.45 \times 0.35 \times 0.25$ mm$^3$ were used in data collection. The CrystalClear software package (Rigaku) was used for data collection, cell refinement and data reduction. Crystal structures were solved by direct methods and refined by the full-matrix least squares method on $P^2$ data using the SHELXL-97 software package.\textsuperscript{19} All non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were generated geometrically. Crystallographic data and structural refinement of the high temperature phase (HTP) and low temperature phase (LTP) are listed in Table S1.‡ CCDC 1400882–1400885 contain the supplementary crystallographic data for this paper.

### Results and discussion

DSC measurement is a common method used to detect whether the compound displays a reversible phase transition triggered by temperature or not. Here, DSC measurements of 1 were performed in the temperature region of 303–363 K and the results are shown in Fig. 2. The heating and cooling curves present one pair of reversible peaks, an exothermic peak at 328 K and an endothermic peak at 329 K (Fig. 2a), which indicates that 1 undergoes a reversible phase transition. It is interesting that such a phase transition temperature is higher than room temperature, but far away from its decomposition point of $\sim$420 K (as shown in the TG/DTA curves, Fig. S3‡). This temperature interval will be greatly favourable to its potential application. Moreover, a relatively small thermal hysteresis of around $\Delta T \approx 1.5$ K was recorded between the heating and cooling modes (Fig. 2a), which would suggest that the phase transition of 1 possesses a second-order feature.\textsuperscript{20}
From the $C_p$–$T$ curves (Fig. 2b), the specific heat ($\Delta H$) is estimated to be equal to 2.22 g J g$^{-1}$, and the corresponding changes in entropy have been calculated on the basis of the equation $\Delta S = \Delta H/T_c$. Hence, the value of $\Delta S$ is estimated to be 2.315 J mol$^{-1}$ K$^{-1}$. According to the Boltzmann equation of $\Delta S = k \ln N$, where $k$ is the gas constant and $N$ is the ratio of numbers of respective geometrically distinguishable orientations, $N$ is equal to 1.32. This value suggests that 1 might undergo a complex phase transition, being different from a typical order–disorder transition ($N = 2$). Its order–disorder feature will be discussed in the forthcoming variable-temperature structural analysis.

To further investigate the structural phase transition, its crystal structures were determined at different temperatures. The CIF files together with the detailed structural information of 1 are provided in the ESI.$^\dagger$ At room temperature, compound 1 belongs to the point group $D_16h$ and the orthorhombic space group $Pnma$ with $a = 27.9771$ Å, $b = 17.8261$ Å, $c = 10.0751$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 5024.7(3)$ Å$^3$ and $Z = 8$. A protonated dibenzylamine cation ($\text{C}_{14}\text{H}_{16}\text{N}^+$) and an isolated trichloroacetate anion ($\text{Cl}_3\text{CCOO}^-$) compose the basic unit. No disordered atom is shown at room temperature (Fig. 3). Some strong N–H⋯O hydrogen bonds (2.815 Å) are revealed in the basic unit and the packing diagram of 1 along its $a$-axis (Fig. 3a).

These strong hydrogen bonds between N atoms of ($\text{C}_{14}\text{H}_{16}\text{N}^+$) and O atoms of ($\text{Cl}_3\text{CCOO}^-$) combine the anions and cations together. As a result, an infinite 1D chain configuration is constructed through H-bonding interactions (Fig. 3a). Further, highly-symmetric dimers are formed, as disclosed by the packing structure in Fig. 3b.

Fig. 4 displays the unit cell parameters as a function of temperature obtained from single-crystal X-ray diffraction analysis on heating from 290 to 350 K, in which the structural anomalies of 1 around $T_c$ (329 K) match well with the DSC measurement. The $b$ and $c$ axis lengths remain unchanged within the whole temperature range, while the $a$ axis length drops sharply to one-third as the phase changes from low temperature to high temperature. As a result, the cell volume is reduced to a third of the initial value at the same time. Although the $a$ axis length and volume exhibit
momentous changes, compound 1 still belongs to the orthorhombic system. Moreover, the change point at 329 K reveals reversible phase transition characteristics, which agrees fairly well with the thermal analysis.

When the HTP single crystal data of 1 were collected above 330 K, it was quite difficult to solve the disordered anion part, owing to the lower point and low I/σ of the high-angle range. Consequently, variable-temperature PXRD experiments were carried out to reveal the phase transition in 1 (Fig. 5). From the PXRD patterns, RT PXRD (red line) matched well with the simulated data result (black line). In comparison with the room temperature phase (red line), the diffraction peaks circled on the green line (343 K) indicate the changes in the main Bragg diffractions of the (022), (024) and (124) planes, revealing the existence of phase transition. These visible changes in diffraction patterns may be triggered by the re-orientational motions of the trichloroacetic acid moiety unit. Besides, the blue line in Fig. 5 confirms the reversibility of the phase transition in 1. All these diffraction transformations obviously reveal a distinct structural phase transition during the heating process.

To obtain a deeper understanding of the phase transition in 1, single crystal structures were collected at 310, 315 and 320 K (near but below \( T_c \)), respectively. The results give a gradual disorder condition of its asymmetric unit (Fig. 6). According to the geometric parameters, Cl atoms are split into two and the angles between splitting Cl atoms vary as the temperature changes. Bigger and bigger angle variation approves its severe thermodynamic motions and may finally give rise to phase transition. Besides, the thermal vibration parameters \( U_{\text{eq}} \) of the chlorine atoms in trichloroacetate anions increase obviously (Fig. 6c and Table S4†). The distorted chlorine atoms displayed in ORTEP are indicative of more disorder. We can certainly propose that the trichloroacetate part will be completely disordered above \( T_c \). It is conclusive that the above-mentioned phenomena reveal that the trichloroacetate anion turns from ordered to disordered as the temperature increases, finally resulting in structural phase transition above \( T_c \).

Furthermore, dielectric measurement is treated as an effective indicator of structural phase transition. Here, the pressed powder pellet of 1 was applied to the dielectric measurements between 310 K and 340 K. As shown in Fig. 7, in the temperature range of 310 to 329 K (below \( T_c \)), the dielectric constant \( (\varepsilon') \) remains stable with a quite small rise. Around \( T_c \), it shows an obvious step-like anomaly, which changes from 5.28 to 5.50 (at 1 MHz). Such a temperature-dependent dielectric behavior is fairly consistent with the characteristic of switchable dielectric materials, revealing that 1 might be a switchable dielectric compound. Moreover, the anomalies of variable-temperature dielectric responses in the vicinity of \( T_c \) are strong evidence for discriminating the structural phase transition, triggered by the order–disorder change in chlorine atoms of the trichloroacetate moieties in 1.22 It is clear that no obvious dielectric relaxation process was

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**Fig. 5** Variable-temperature PXRD patterns of 1 showing the structural phase transition in the temperature range 293–343 K.

**Fig. 6** a) The ordered structural unit of 1 at room temperature (293 K) and b) the disordered unit at high temperature (320 K). c) Changes in thermal ellipsoids for the trichloroacetate anions at different temperatures.

**Fig. 7** Temperature-dependent dielectric constants of 1 at different frequencies.
observed in the vicinity of $T_c$ at different frequencies, which might indicate relatively fast dipolar and molecular motions in the system during phase transitions.\textsuperscript{51} Taking into account the relatively small dielectric anomaly and the crystallographic data of 1 at various temperatures, it is clear that the phase transition of 1 is neither ferroelectric nor antiferroelectric.

**Conclusions**

In summary, we have successfully presented a new switchable molecular dielectric material, which undergoes a solid-state phase transition at around 329 K. The reversible second-order phenomenon has been investigated by DSC measurements, specific heat capacity determination, dielectric measurements, variable-temperature cell parameter analyses, etc. X-ray single-crystal diffraction reveals clearly that the ordered trichloroacetate anion undergoes a gradual change to the disordered state with temperature warming up to $T_c$. Variable temperature PXRD tests strongly confirm the structural phase transition. The slight ordering caused by the chlorine atoms based on single-crystal structural analyses makes 1 a promising material. These process findings will possibly provide a new avenue for designing switchable dielectric materials.

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**Notes and references**


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