

Short communication

Switchable dielectric phase transition in tris(1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octane) tetra(tetrafluoroborate) dichloride

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ABSTRACT

Tris(1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octane) tetra(tetrafluoroborate) dichloride, $[\text{C}_7\text{H}_{15}\text{ClN}_2^+]_3 \cdot [\text{BF}_4^-]_4 \cdot 2\text{Cl}^-$, was synthesized and separated as colorless rodlike crystals. Differential scanning calorimetry detected that this compound underwent a reversible phase transition at ca. 242.9 K with a hysteresis of 3.7 K width. Single crystal X-ray diffraction data suggested that a room-temperature phase with a space group of $Pnma$ ($a = 20.0644(12)$ Å, $b = 7.3121(4)$ Å, $c = 25.6369(15)$ Å, $V = 3761.3(4)$ Å³ and $Z = 4$) was transitioned to a low temperature one with a space group of $P2_1/c$ ($a = 7.184(3)$ Å, $b = 25.579(10)$ Å, $c = 20.074(8)$ Å, $\beta = 91.348(6)^\circ$, $V = 3688(3)$ Å³ and $Z = 4$), and symmetry breaking occurred with an Aizu notation of $mmmF2/m$. The order–disorder transition of BF_4^- anions and the ordering of twisting motions of dabco rings may drive the phase transition.

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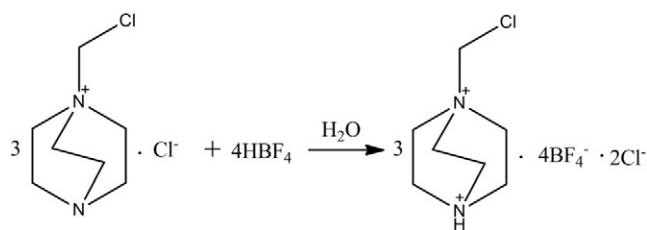
Owing to potential applications in signal processing, data storage, switchable dielectric devices, sensing, etc., substantial attention has recently been focused on phase transition materials including ferroelectrics. Phase transition occurring in the solid state is accompanied by changes of structure, situation or motion of molecules or ions, thermal capacity and electric physical properties, which encourages attention from the viewpoints of memory applications, environment-monitoring, and novel physical properties of phase transition materials [1]. Preparing new temperature-triggered molecular-based phase transition materials is crucial, not only for theoretically studying the relationship of structure–property, but also for exploring novel physical properties [2]. In order to design molecular-ionic crystals with phase transitions, one of the most efficient strategies is to introduce moieties that can reorient with the change of temperature [3]. Upon a temperature decrease, reorientations of such moieties may lead to symmetry breaking, probably inducing phase transitions. In close-packed molecular ionic crystal structures, moieties with smaller volume and higher intra-molecular symmetry are eligible for reorientation due to a lower energy barrier. Due to ‘frozen’ ordering or molecular rotation in the crystal lattice, 1,4-diazabicyclo[2.2.2]octane (dabco), which is a highly symmetric tertiary diamine with a globular shape, allows the design of molecular-based phase transition materials, as verified recently [4]. Because of moderate sizes and highly symmetric shapes, well-known

ball-like anions such as BF_4^- , are stable and prone to position changes with varying temperature and weakness interactions in crystals. The interaction of the cations with monovalent tetrahedral counteranions (e.g. ClO_4^- and BF_4^-) is expected to generate phase transition materials [5]. However, 1-(chloromethyl)-1,4-diazabicyclo-[2.2.2] octan-1-ium chloride, as a potential bridging ligand, has rarely been studied regarding the coordination chemistry. Taking all these into consideration, as a continuation of our systematic studies of phase transitions [6], we reported herein a new compound tris(1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octane)-tetra(tetrafluoroborate) dichloride (**1**), with reversible structural phase transition properties, which was characterized by variable-temperature single crystal X-ray diffraction, differential scanning calorimetry (DSC) and unit-cell-temperature dependence parameters.

Compound **1** was readily obtained as colorless rodlike crystals by treating tetrafluoroboric acid and 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride in aqueous solution as shown in Scheme 1 [7]. The structure of **1** was identified by elemental analysis, IR, thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) (Support information) (caution! Although no problems have been encountered herein, tetrafluoroboric acid is strongly corrosive and stimulating and should be handled with care and only in small quantities).

DSC is one of the thermodynamic methods that detect the dependence of reversible phase transition on temperature. When a compound undergoes structural phase transition accompanied by thermal entropy change, heat anomalies can be observed during heating and cooling. When the compound is subjected to disorder–order transition of ions

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Scheme 1. Synthesis of compound 1.

or protons, reversible heat anomalies can be detected in DSC upon heating and cooling. Heating the crystalline sample of **1** shows a main endothermic peak at 246.6 K and a main exothermic peak on cooling at 242.9 K (Fig. 1), which is in good agreement with that found in variable-temperature X-ray single crystal diffraction. This phase transition is accompanied by the release of heat and the thermodynamic quantities (internal energy, enthalpy, volume etc.) are discontinuous; this is known as a first order phase transition.

It is well-known that phase transition is accompanied by anomaly of physical properties near the structural phase transition point, such as the dielectric constant [8]. Herein, the dielectric property of **1** was further investigated, and plots of the dielectric constant (ϵ') versus temperature at different frequencies are displayed in Fig. 2. As expected, **1** displays a clear dielectric anomaly at around 249.3 K upon heating, being consistent with the DSC result and mutations of cell parameters at approximately 246.6 K. Furthermore, these figures show the following features: (i) **1** has an invariant ϵ' (about 1.7) in the low-temperature regime below 153.2 K; (ii) the dielectric constant rapidly increases when the temperature rises to above 198.4 K, and no maximum peak appears in the plots of ϵ' versus T below 249.3 K; (iii) increases in the dielectric constant with temperature depend strongly on the frequency of the AC electric field, which is obvious when the frequency is below 5 KHz. In addition, continuously increasing the frequency from $5 \times 10^3 \rightarrow 10^4 \rightarrow 10^5 \rightarrow 10^6$ Hz gradually decreases the dielectric constant as 57.2, 39.4, 9.9, and 4.3 respectively. Compound **1** was, as suggested by these features, a potential tunable dielectric material.

The phase transition of **1** was further confirmed by determining variable-temperature crystal structures at 298 K and 120 K, respectively (Fig. 3a–b) [9]. The crystal structure of **1** at room temperature (298 K) is orthorhombic, with the centrosymmetric space group $Pnma$ and the point group D_{2h} . When the temperature decreases to 120 K, **1** becomes a monoclinic crystal system, with the centrosymmetric space group $P2_1/c$ and the point group C_{2h} . Upon cooling, symmetry breaking occurs with an Aizu notation of $mmmF2/m$ [10]. The crystal structures of **1** at 298 K and 120 K were compared as follows.

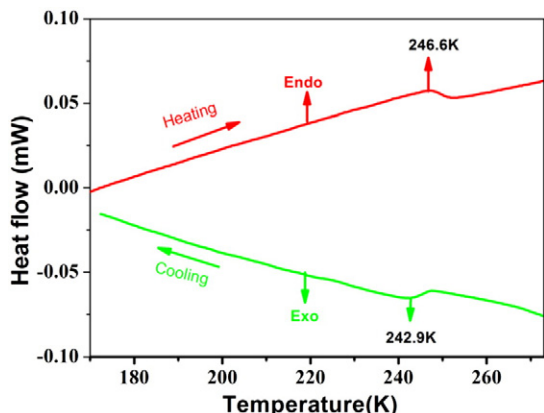


Fig. 1. DSC curves of **1** obtained in a heating-cooling mode.

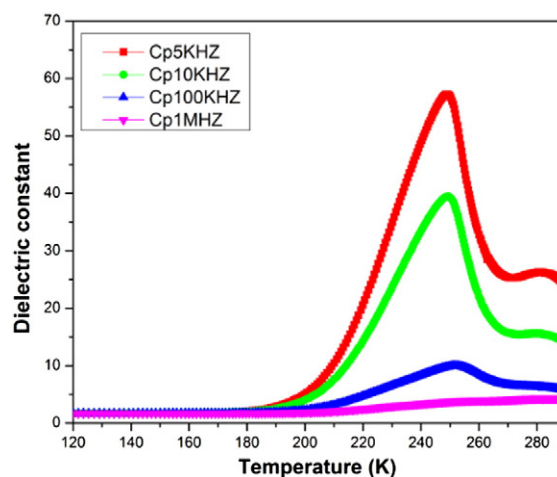


Fig. 2. Temperature-dependent dielectric constants of **1** at different frequencies.

At room temperature (298 K), the crystals are in the orthorhombic space group $Pnma$ (No. 62), with $a = 20.0644(12)$ Å, $b = 7.3121(4)$ Å, $c = 25.6369(15)$ Å, $V = 3761.3(4)$ Å³ and $Z = 4$. When cooled (120 K), the crystals are monoclinic, space group $P2_1/c$ (No. 14), with $a = 7.184(3)$ Å, $b = 25.579(10)$ Å, $c = 20.074(8)$ Å, $\beta = 91.348(6)^\circ$, $V = 3688(3)$ Å³ and $Z = 4$. The crystals do not differ obviously at the two temperatures. Molecular (ion pair) volume decreases from $3761.3(4)$ Å³ in the orthorhombic cell to $3688(3)$ Å³ in the monoclinic cell.

In the crystal structure of the room-temperature phase (RTP) (298 K) (Fig. 3a), an asymmetric unit consists of three 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]-octane-1,4-dium cations, four isolated BF_4^- anions and two free Cl^- anions in different geometries. One BF_4^- anion is seriously disordered with F atoms over two positions. The other three BF_4^- anions in the asymmetric unit adopt an ideal tetrahedral geometry respectively, with the B–F distances from 1.320(2) to 1.466(14) Å and the F–B–F angles from 100.8(7) to 143.4(11) $^\circ$ (Table S3), being in good agreement with those observed in similar compounds [11]. As shown in Fig. 3a, there are two kinds of hydrogen bonds, one being made up of free Cl^- anions with N atoms from the dabco rings, such as $N5-H5 \cdots Cl5$ and $N1-H1 \cdots Cl4^{#4}$ (bond lengths of $N-H \cdots Cl$ are 3.014(6) Å and 2.985(5) Å, and bond angles are 169 $^\circ$ and 170 $^\circ$, respectively) and the other comprised by an F atom with an N atom, such as $N3-H3 \cdots F12$ and $N3-H3 \cdots F12^{#3}$ (bond lengths of $N-H \cdots F$ are both 2.915(6) Å, and bond angles are both 146 $^\circ$).

In the crystal structure of the low-temperature phase (LTP) (120 K) (Fig. 3b), an asymmetric unit consists of three 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]-octane-1,4-dium cations, four isolated BF_4^- anions and two Cl^- anions. However, both Cl atoms are disordered, with each atom over two positions. At 120 K, BF_4^- anions become ordered by being frozen, and the four anions adopt an ideal tetrahedral geometry, with the B–F distances from 1.339(9) to 1.422(7) Å and the F–B–F angles from 107.8(5) to 111.1(5) $^\circ$ (Table S4), which are comparable with those found in RTP. Moreover, there are also two kinds of hydrogen bonds, i.e. $N3-H3WA \cdots Cl4$, $N3-H3WA \cdots Cl4A$, $N1-H1WA \cdots Cl5$, $N1-H1WA \cdots Cl5A$, $N5-H5WA \cdots F9$ and $N5-H5WA \cdots F12$. The bond lengths of $N-H \cdots Cl$ range from 3.005(5) to 3.207(5) Å and the bond angles range from 142 $^\circ$ to 169 $^\circ$. In addition, the bond lengths of $N-H \cdots F$ are 3.075(6) Å and 2.828(6) Å, and the bond angles are 136 $^\circ$ and 157 $^\circ$, which are all different from those found in RTP. Hydrogen bond lengths and bond angles of **1** at 298 K and 120 K are shown in Table S2.

Meanwhile, conformations of the dabco rings showed significant differences between RTP (298 K) and LTP (120 K). The N–C–C–N torsion angles are 0.00(2)–1.40(6) $^\circ$ at 298 K. Moreover, N–C–C–N in the two dabco rings exhibits large twisting conformations with the torsion

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