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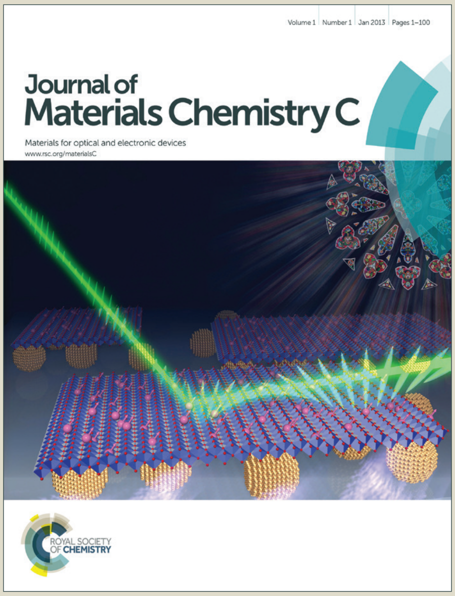

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Order-Disorder Phase Transition Coupled with Torsion in Tri-*n*-Butylammonium Trichloroacetate (TBAT)

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Muhammad Adnan Asghar,[ab] Chengmin Ji,[a] Yuelan Zhou,[a] Zhihua Sun,[a] Tariq Khan,[ab] Shuquan Zhang,[a] Sangen Zhao[a] and Junhua Luo[a,]*

A novel molecular phase transition compound, tri-n-butylammonium trichloroacetate (**TBAT**), has been successfully synthesized with a reversible phase transition at 196 K. Its phase transition behaviour was confirmed by specific heat capacity and differential scanning calorimetry (DSC) measurements with a 2 K thermal hysteresis, indicating that the phase transition is a first-order one. Dielectric measurements further reveal the reversible nature of phase transition, which exhibits distinctive step-like anomalies between low and high dielectric states. What's more, temperature dependent single-crystal X-ray diffraction analyses of **TBAT** disclose that the order-disorder transformation of the flexible tri-n-butylammonium cations and the haloscetic acids anion together with the torsion in cations stimulate the structural phase transition. All these results open a new way to design and assemble novel phase transition materials.

Introduction

During the past few decades, temperature induced solid-to-solid reversible phase transition materials have been captured renowned interest owing to their prospective applications in switchable dielectric, sensing, ferroelectric, optoelectronic, signal processing, data storage devices, etc [1,2]. Rationally design and constructing novel phase transition materials are not only imperative for searching technologically practical materials but also valuable for the exploring novel physical properties as well as for understanding the relationships between structure and properties [3]. One of the important structural design strategies for constructing potential phase transition compounds is the assembly of molecular systems with thermally activated molecular motions [2-8]. Generally, in the most cases, the phase transitions are triggered by only one type of motions in the compounds, which could be order-disorder transformation, rotation or orient.tational motion solely. For instance, Fu *et al*. discovered high temperature molecular ferroelectric material $[(CH_3)_2CH]_2NH_2$•Br with large spontaneous polarizations and large dielectric constants and the ferroelectric phase transition originates in the order-disorder transformations of diisopropylammonium cation [9]. In addition, order-disorder dynamical change of the polar dimethylammonium cation in $[(CH_3)_2NH_2]_2$•$[KCo(CN)_6]$ enables it to exhibit a switchable and tunable dielectric constant between the high and low dielectric state [10]. Besides of cations, some haloscetic acids anions could also play a vital role in triggering phase transitions. For example, Ji *et al.* reported N-Isopropylbenzylammonium dichloroacetate as an above room temperature switchable dielectric material induced by order-disorder transformation of chlorine atoms in dicholoroacetate [11]. However, a single order-disorder transformation in a molecule is not frequently sufficient to drive a structural phase transition under the external stimuli. For example, order-disordered transition behaviours of tripod-like triethylammonium cations between low temperature phase and high temperature phase in triethylammonium chloride and triethylammonium bromide do not trigger a structural phase transition associated with the change of the physical and chemical properties [12]. It is probably since that the small driving force from a single order-disorder transformation in a molecule is insufficient to cross the high potential barriers for a desired thermally activated phase transition [13]. Therefore introducing any other types of molecular motions, like twisting or torsion together with the order-disorder transformation may lead to a synergic effect to produce the reversible phase transition materials.

Long chain-type organic amine cation with alkyl chain is one of the promising constructional units for assembly of the phase transition compounds due to the inherent architectural flexibility with diversified molecule configurations. Therefore, we propose to combine branched and more flexible tri-n-butylammonium cation with renowned haloscetic acids in one molecular system. The branched tripod-like structure of TBA cation has three flexibile *n*-butyl chains, which could offer more opportunities to induce torsion with different molecule configurations as compared to triethyl amine with the short ethyl chains. To confirm this claim, we have studied some newly fabricated molecular compounds to see whether such a combination of these moieties yield the fruitful results. As expected, the combination of highly flexible cation with halosectic acids provides good room for the fabrication of reversible phase transition materials. To the best of our knowledge, herein, we present first time, a new temperature induced molecular phase transition material based on highly flexible tri-n-butylammonium cation and trichloroacetate anion. To investigate its phase transition mechanism, variable temperature single-crystal analyses, differential scanning calorimetry and dielectric measurements have been performed. The order-disorder behaviour of both ions together with the torsions of the cations has been found to collectively induce the phase transition in **TBAT**.

Experimental

All chemical reagents were used without further purification. **TBAT** was obtained through reaction of tri-n-butyl amine with trichloroacetic acid in 1:1 molar ratio with stirring at ambient conditions. Colourless needle like crystals of **TBAT** were obtained by slow evaporation from the CH_3OH solution after several days. The purity of the as-grown crystals was confirmed by powder X-ray diffraction patterns, which match well with the simulated one based on the room-temperature structure of **TBAT** (Fig. S1).

Super Nova CCD diffractometer was used to collect the variable-temperature X-ray single-crystal diffraction data at low temperature (100 K) and high temperature (220 K) with the graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å). The CrystalClear software package (Rigaku) was used for data collection, data reduction and cell refinement, while crystal structures were solved by the direct methods and refined by the full-matrix method based on F^2 using the *SHELXLTL* software package [14]. All non-hydrogen atoms were refined anisotropically, while the positions of hydrogen atoms in the tri-n-butylammonium (TBA) cations were generated geometrically. Data collection details, crystallographic data and refinement for **TBAT** at 220 and 100 K are given in Table S1.

Differential scanning calorimetry experiments were performed by heating and cooling the sample (8.94 mg) in the temperature range of 180-220 K on a NETZSCH DSC 200 F3 under nitrogen atmosphere in aluminum crucibles with the heating/cooling rate of 2 K/min.

In the dielectric experiments, the powder pressed pellets of TBAT with silver pasted as the electrodes were used for measuring the complex dielectric permittivities, $\varepsilon = \varepsilon' - i\varepsilon''$, with a TH2828A impedance analyzer at the respective frequencies of 1 MHz and 500 KHz with the measuring AC voltage fixed at 1 V.

Results and discussions

DSC and C_p measurements were carried out on the polycrystalline samples of **TBAT** to detect the reversible phase transition stimulated by temperature. The DSC curves show an exothermic peak at 196.0 K and an endothermic peak at 194.0 K, which demonstrate the reversible phase transition of **TBAT** (Fig. 1). The thermal hysteresis under different heating and cooling rates suggests its first-order phase transition features (Fig. S3). An entropy change (ΔS) based on the C_p measurement accompanying with the phase transition is calculated with a value of 3.33 $J \cdot mol^{-1} \cdot K^{-1}$. From the Boltzmann equation $\Delta S = R\ln N$, where R is the gas constant and N is the ratio of the numbers of respective geometrically distinguishable orientations, N is obtained as 1.49, suggesting a perspicuous order–disorder feature [15].

To further confirm the phase transition in **TBAT**, variable-temperature single-crystal X-ray structure determinations were performed at 220 K (high-temperature phase, HTP) and 100 K (low-temperature phase, LTP), respectively. The structure of **TBAT** at both phases reveals that the unit cell belongs to triclinic with a space group of $P\bar{1}$, and cell parameters at LTP are a = 9.633 Å, b = 10.713 Å, c = 18.828 Å, α = 98.74°, β = 100.48°, γ = 100.21°, V = 1846.15 $Å^3$ and Z = 4. While, **TBAT** cell parameters at HTP, deviate at c = 19.733 Å, β = 101.66°, γ =98.35° and V =1915.04 $Å^3$. The other cell parameters at HTP change a little at a = 9.6704 Å, b = 10.5407 Å and α = 98.77°.

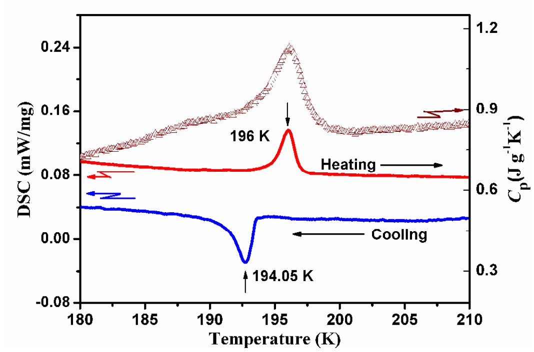

Fig. 1 The Cp and DSC curves of **TBAT.**

The phase transitions can be ascertained by the unit cell parameters as a function of temperature from 100 K to 250 K (Fig.2).

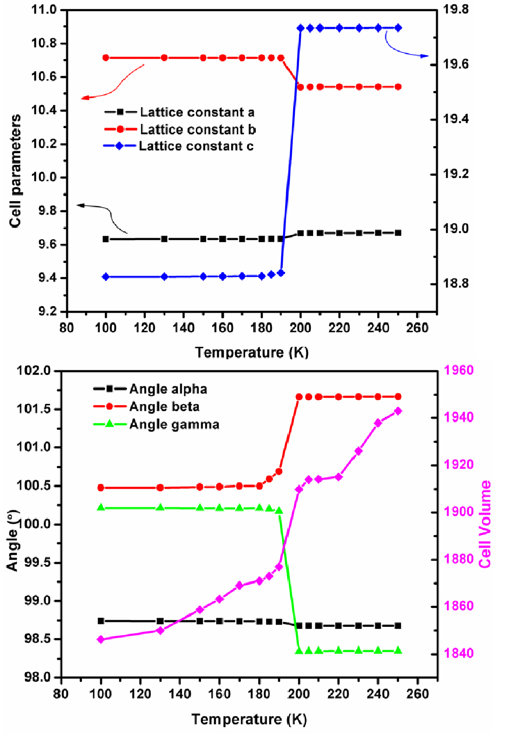

Fig. 2 Temperature dependence of cell parameters in the range from 100 to 250 K in **TBAT**.

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while other cell parameters, *c* axis, β angle, γ angle and volume, change at about 196 K, confirming the phase transition, which matches well with other results.

The asymmetric unit of **TBAT** is composed of two protonated TBA cations and two tricholoroacetate anions at both phases, as shown in Fig. 3 (a) and (b). Some strong H-bonds can be found between the O atoms in the tricholoroacetate anions and the N atoms in the TBA cations, resulting in the formation of distinct H-bonded dimers as shown in Fig. 3(c) and (d). In addition, N–H···O bond distances at HTP with ranges of 2.7-2.74 Å are slightly longer than those at LTP (2.67-2.71 Å). The packing structures of **TBAT** in both phases recognize by order-disorder transformation of ions and intermolecular hydrogen-bonding in discrete units. In HTP, there are two types of dimmers which can be distinguished by the disordering behavior of chlorine atoms in one of the anion. The ordered and disordered anion based dimmers found in their respective rows as independent units and alternate with each other along c-axis designated as HT1 and HT2, respectively (Fig. S4). In LTP, disordered atoms of ions frozen and consequently yield two different geometric configurations, interchange with each other along c-axis as shown in Fig. S3.

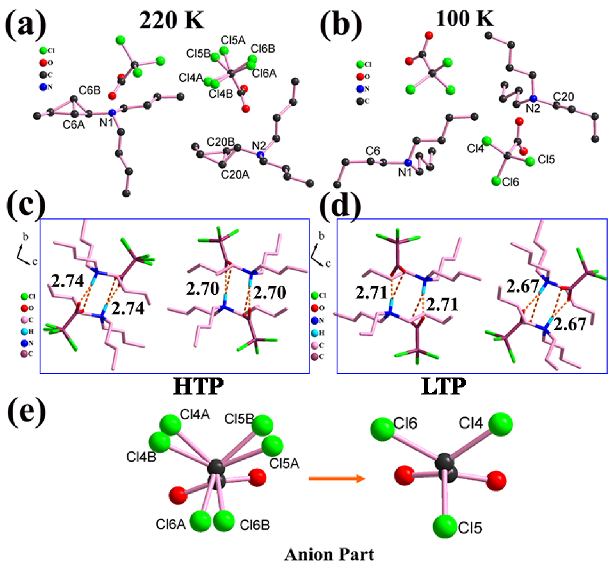

Fig. 3 Asymmetric unit of **TBAT** at (a) LTP and (b) HTP. Hydrogen bonding details at (c) HTP and (d) LTP and order-disorder transformations of anion (e) during the phase transition.

Each TBA cation consists of three flexible n-butyl parts connected through central protonated nitrogen atom. For the anion part, the bond distances and bond angles in the tricholoroacetate anions are similar with other previously reported tricholoroacetate compounds [16]. In the HTP, all cations and one anion were in disordered state while another anion maintains its order state. Viewed from the ellips_oid diagrams at HTP, the observed thermal ellipsoidal values of some atoms in the anion and cations are larger than those of the neighboring atoms. This demonstrates they are not in their appropriate state but the average outcome of the atomic disordering of atoms. For example, C6 and C20 from flexible parts of TBA cation acquire higher thermal ellipsoidal states, which will be more suitable when both carbon atoms splitted to two occupied disordered sites as C6A, C6B and C20A, C20B with the occupancies of 0.74, 0.26, 0.67 and 0.33, respectively (Fig. S5). While, the other two n-butyl parts of the cations are in normal ordered state. In addition, the thermal vibrations of Cl4, Cl5 and Cl6 in one anion is comparatively bigger than those of other atoms, thus, crystal structure is more appropriate when all these chlorine atoms splitted to two occupied sites Cl4A, Cl4B, Cl5A, Cl5B, Cl6A and Cl6B with the occupancies of 0.66, 0.34, 0.74, 0.26, 0.61 and 0.39, respectively. The detail of *Ueq* values of TBAT is given in the Table S3.

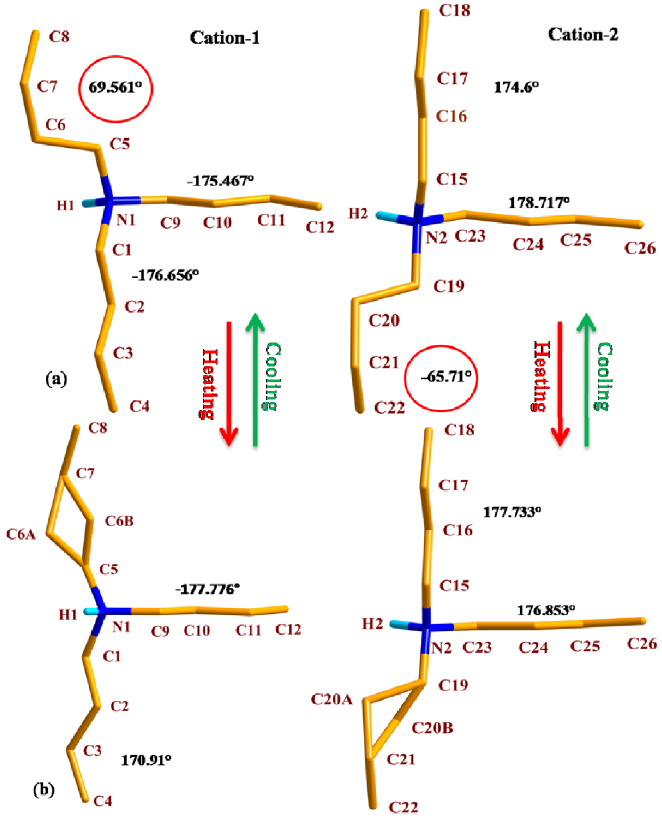

Fig. 4 The torsional change in n-butyl parts at (a) LTP and (b) HTP.

With the temperature decreasing from 220 K to 100 K, both of the disordered carbon atoms of cations and chlorine atoms of anion are frozen, subsequent into its highly ordered LTP (Fig. 3e). Such fascinating order-disorder transformations of both ions also have been found to result in the deviations of relative atomic positions. We examined the torsion angles of butyl parts of cations. As shown in Fig 4, butyl parts (C1-C2-C3-C4 and C9-C10-C11-C12) of cation-1 and (C15-C16-C17-C18, C23-C24-C25-C26) of cation-2 between RTP and TLP have a little changes in torsion angle values and the configurations of structure are almost coplanar. It is interesting to note that below phase transition point highly reorientations in disordered butyl parts (C5-C6-C7-C8 and C13-C14-C15-C16) of the two cations were observed with the torsion angle values recorded as 69.56° and -65.71°, respectively. It is believed that order-disorder transformations of both ions and the changes of torsions among

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flexible butyl parts collectively found as the driving force for this first-order phase transition.

The temperature dependent dielectric response usually shows an obvious anomaly at phase transition point, which is well-known as a valuable indicator for the structural phase transition. The powder pressed pellets of **TBAT** were subjected in dielectric measurements with the temperature dependence of the real part (ε') of the dielectric constants at 100 KHz and 1 MHz. As expected, distinct step like anomaly appear at about 197 K, confirming the presence of phase transition, well consistent with DSC and the temperature dependence of cell parameter results (Fig. 5). Furthermore, heating and cooling of **TBAT** yield hysteresis of permitivities at 500 KHz and 1 MHz as shown in Fig. S6. Comparative dielectric relaxation around phase transition point at different frequencies shows no obvious response, exhibiting that the dipolar motion is very fast during the phase transition [17]. The dielectric constants upon cooling and heating cycle as a function of temperature show anomaly with thermal hysteresis, enlightening the character of the reversible phase transition, reliable well with the DSC results.

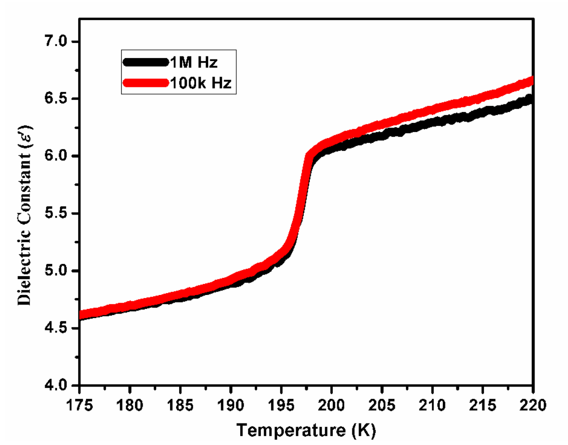

Fig. 5 Temperature dependent dielectric constant of **TBAT** at 1 MHz and 100 KHz.

Conclusions

In conclusion, we have discovered a new phase transition material $[(C_4H_9)_3NH]\cdot CCl_3CO_2$ (**TBAT**), which exhibits a reversible first-order phase transition at about 196 K confirmed by the combined differential scanning calorimetry, specific heat capacity, dielectric measurements and variable-temperature single-crystal structural analyses. The origin of the phase transition is ascribed to the combined synergetic effect of the order-disorder transformations of both ions and torsion of the flexible n-butyl moieties. Thus, we believe that the present findings would present a new avenue for the design of potential phase transition materials.

Acknowledgements

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Notes and references

[a] *Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian , 350002, P. R. China. E-mail: jhluo@fjirsm.ac.cn. Fax: (+86) 0591-83730955. Tel: (+86) 0591-83730955.*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China.*

Electronic Supplementary Information (ESI) available: [CIF files, PXRD patterns, TG/DTA curves, crystal data, thermal ellipsoidal view and the dielectric constant measured by cooling and heating cycles, CCDC reference numbers 1054128 and 1054129 for TBAT at 100 and 220 K]. See DOI: 10.1039/b000000x/

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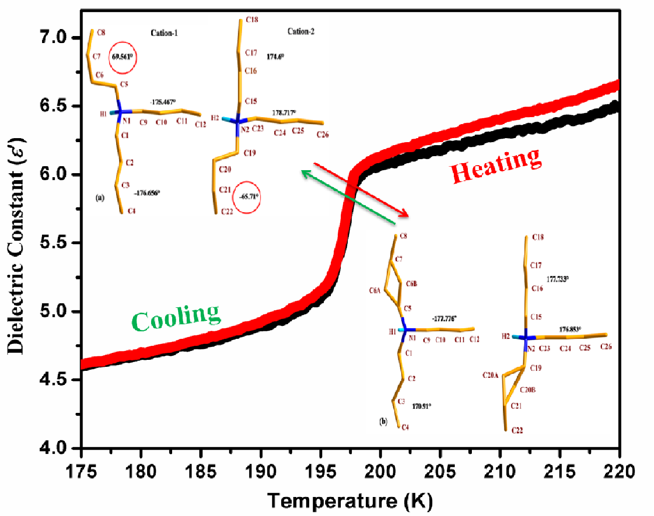
Order-Disorder Phase Transition Coupled with Torsion in Tri-*n*-butylammonium Trichloroacetate (TBAT)

Muhammad Adnan Asghar,[ab] **Chengmin Ji,**[a] **Yuelan Zhou,**[a] **Zhihua Sun,**[a] **Tariq Khan,**[ab] **Shuquan Zhang,**[a] **Sangen Zhao**[a] **and Junhua Luo**[a,*]



Tri-*n*-butylammonium Trichloroacetate (**TBAT**), a novel hybrid material, undergoes reversible phase transition around 196 K, triggered by torsion of cations and order-disorder transformations of both cations and anion.

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