



# Deuteration triggered downward shift of dielectric phase transition temperature in a hydrogen-bonded molecular crystal

Bei-Dou Liang, Tong Jin, Le-Ping Miao, Chao-Yang Chai, Chang-Chun Fan, Xiang-Bin Han\*, Wen Zhang\*

Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics and School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China

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## ABSTRACT

Deuteration of hydrogen-bonded phase transition crystals can increase the transition temperatures due to the isotope effect. But rare examples show the opposite trend that originates from the structural changes of the hydrogen bond, known as the geometric H/D isotope effect. Herein, we report an organic crystal, diethylammonium hydrogen 1,4-terephthalate, exhibits a reversible structural phase transition and dielectric switching. Structural study shows the cations reside in channels formed by one-dimensional hydrogen-bonded anionic chains and undergo an order-disorder transition at around 206 K. The deuterated counterpart shows an elongation of the O...O hydrogen bond by about 0.005 Å. This geometric isotope effect releases the internal pressure of the anionic host on the cation guests and results in a downward shift of the phase transition temperature by 10 K.

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Phase transition compounds are valuable materials due to phase transition associated with desired properties and functionalities [1,2]. For example, ferroelectricity [3–7] is an emergent property in the ferroelectric phase when the crystals undergo specific symmetry-breaking phase transitions. Another attractive property is the dielectric transition [2,8–11] or switching as a reflection of local polarization changes during structural phase transitions. In molecular materials, orientational polarization of dynamic polar components, including rotations and vibrations, majorly contributes to the dielectric transition, leading to a switchable dielectric constant between low and high dielectric states [12–15]. The responsive dielectric constant cannot only provide an approach to probe the local dynamics of the materials but also constitute a new type of switching properties.

Substitution, doping, and mixing are usually employed to modify the phase transition-related properties, such as introducing ferroicity and regulating the transition temperature. Deuteration is another tool to tune properties [16–19] with the advantages of minimizing changes of structures and electroproperty. In hydrogen-bonded crystals, deuteration can significantly impact the phase transition temperature [20,21]. For example, the ferroelectric  $\text{KH}_2\text{PO}_4$  exhibits a 107 K increase of the transition temperature

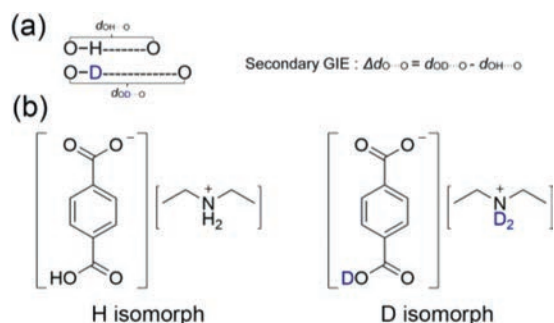
upon deuteration because the phase transition of  $\text{KH}_2\text{PO}_4$  is caused by the order-disorder transition of protons [22–25]. Particularly interesting is that the hydrogen bond can undergo structural changes after H/D exchange, known as geometric isotopic effect (GIE) [26], to achieve the aims of tuning the properties of compounds [27,28]. There are two kinds of GIE: primary GIE and secondary GIE (also called Ubbelohde effect), which refers to distance variations of the O–H and OH...O after deuteration, respectively [26,29]. A specific definition of secondary GIE is illustrated in Scheme 1a.

Herein, we report a pair of colorless (Fig. S1 in Supporting information) organic salt crystals diethylammonium hydrogen 1,4-terephthalate (**1-H**) [30] and its deuterated counterpart **1-D** (Scheme 1b). For **1-H**, the crystal undergoes a structural phase transition at 205 K due to the order-disorder state transition of the cations in the hydrogen-bonded anionic network. A typical dielectric switch occurs between the low-temperature phase (LTP) and high-temperature phase (HTP), accompanying the phase transition. Deuterated counterpart **1-D** shows an observable secondary geometric H/D isotope effect with an elongation of the O...O distance by about 0.005 Å to result in a downward shift of 10 K of the transition point.

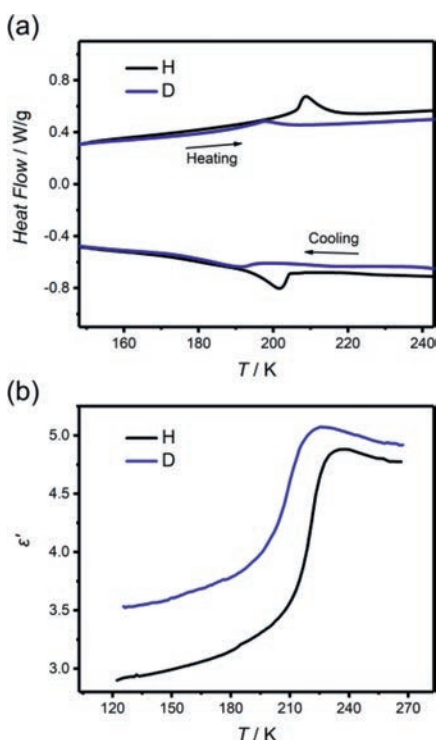
**1-H** was synthesized from a mixture of equimolar diethylammonium cation (DEA) and hydrogen 1,4-terephthalate monoanion (TPA). The detailed experimental procedure can be found in Supporting information. TGA measurements of **1-H** and **1-D** show the decomposition begins at about 400 K (Fig. S2 in Supporting infor-

\* Corresponding authors.

E-mail addresses: [hanxiangbin@seu.edu.cn](mailto:hanxiangbin@seu.edu.cn) (X.-B. Han), [zhangwen@seu.edu.cn](mailto:zhangwen@seu.edu.cn) (W. Zhang).



**Scheme 1.** (a) H/D GIE on the donor-acceptor distance of the O–H...O H-bond and (b) structural formula of **1-H** and **1-D**.



**Fig. 1.** (a) DSC and (b) dielectric constant curves of **1-H** and **1-D**.

mation). Differential scanning calorimetry (DSC) measurement indicates it undergoes a structural phase transition (Fig. 1a). A pair of thermal peaks appear at 202/209 K with a thermal hysteresis of 7 K. Enthalpy change obtained from the DSC curve and corresponding calculated entropy change  $\Delta S$  is 910 J/mol and  $3.1 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. Using Boltzmann equation  $\Delta S = R \ln N$ , where  $R$  and  $N$  are the gas constant and the proportion of the numbers of distinguishable geometrical orientations allowed in the HTP and LTP, the  $N$  is 1.6. This value is a rough description to indicate the average degree of motional freedom in the phase transition process. At the same time, the thermal peaks of **1-D** appeared 10 K lower compared with **1-H**.

Temperature-dependent dielectric constant measurement was performed on powdered crystalline samples of **1-H** and **1-D** with high purity (Fig. S3 in Supporting information) in the temperature range 120–270 K (Fig. 1b and Fig. S2). The real part of the dielectric constant  $\epsilon'$  of **1-H** shows a step-like change at about 210 K, which corresponds well to the phase transition point shown in the DSC curves. At 1 MHz, the  $\epsilon'$  value is about 2.7 in the LTP and 5.0 in the HTP. The nearly doubled change, though not large, corresponds to a dielectric switching. Variable-frequency measurement

**Table 1**

Donor–acceptor distance  $d_{\text{O}\cdots\text{O}}$  (Å) of the OH/D...O hydrogen bond. The standard uncertainty is calculated using the addition formula for error propagation.

$T$	$d_{\text{O}\cdots\text{H}\cdots\text{O}}$	$d_{\text{O}\cdots\text{D}\cdots\text{O}}$	$\Delta d_{\text{O}\cdots\text{O}}$
153 K	2.449(1)	2.455(1)	+0.006(1)
293 K	2.454(2)	2.458(2)	+0.004(3)

reveals no dispersion behavior at 1 kHz, 100 kHz and 1 MHz, indicating a quicker response of the polar components to the external electric field (Fig. S4 in Supporting information). As to **1-D**, the dielectric transition point also shows a 10 K downward shift compared to **1-H**, consistent with the DSC results.

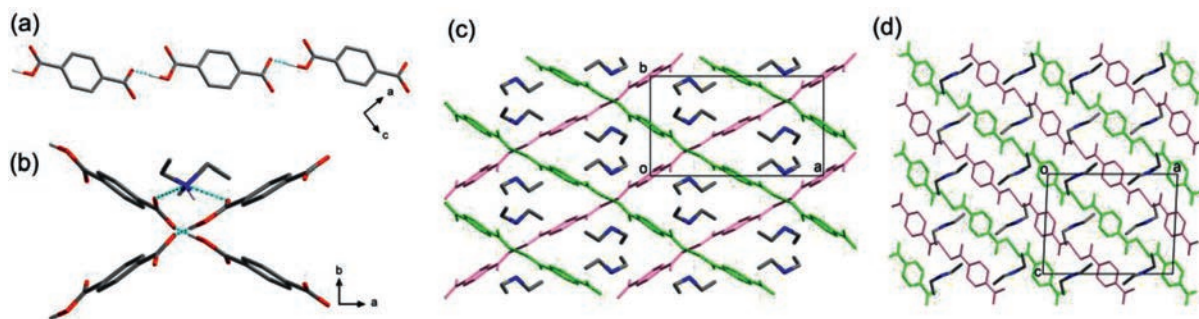
Variable-temperature single-crystal structure analysis was performed to understand the phase and dielectric transition of **1-H**. In the LTP at 153 K, **1-H** crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 14.056 \text{ Å}$ ,  $b = 8.1278 \text{ Å}$ ,  $c = 10.9132 \text{ Å}$ , and  $\beta = 93.073^\circ$  (Table S1 in Supporting information). In the TPA monoanion, the carboxyl (COOH) and carboxylate (COO<sup>-</sup>) groups slightly twist from the benzene ring plane about  $9.75^\circ$ . The TPA anions form a linear chain linked by the O–H...O hydrogen bond between the carboxyl and carboxylate groups (Fig. 2a). The O...O distance is 2.449 Å, identified as a short hydrogen bond [31]. The linear H-bonded chains run in two different directions, i.e.,  $[110]$  and  $[1\bar{1}0]$ , and thus form a stacking structure with parallelogram-like channels along the  $c$  axis (Figs. 2c and d). The DEA cations locate at the channels, anchored by two N–H...O hydrogen bonds with the anionic host (Figs. 2b and c). The N...O bond lengths are 2.794 and 2.909 Å, strikingly longer than the O...O distances, revealing weaker intermolecular interactions between the host and guest.

In the HTP at 293 K, **1-H** adopts a new space group  $C2/c$  with  $a = 17.2789 \text{ Å}$ ,  $b = 8.3218 \text{ Å}$ ,  $c = 11.0269 \text{ Å}$ , and  $\beta = 125.604^\circ$  (Table S1 in Supporting information). The DEA cations undergo a state change from the ordered state in the LTP to a two-site disordered state in the HTP. The two ethyl groups of the cation seem to swing in two sites (Fig. 3 and Fig. S5 in Supporting information).

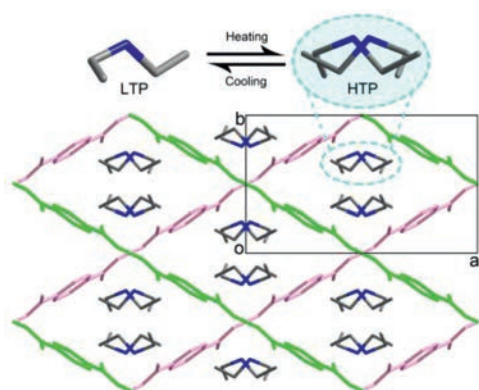
Cell parameters of **1-H** show that with the increase of the temperature, the  $b$  and  $c$  axis increase gradually and jump suddenly in the temperature point around 200 K while  $a$  axis shortens (Fig. S6 in Supporting information). The  $\beta$  remains nearly constant below the temperature point and then gradually decreases. All the inflection points and jumping points denote the phase transition, consistent with the DSC and dielectric constant measurements.

Due to the short O–H...O hydrogen bonds presented in **1-H** in quantity, we expected deuteration could modify the phase transition-related properties. Upon deuteration, the transition temperature of **1-D** shifts downward about 10 K. This downward shift is counterintuitive to the general isotope effect in H-bonded phase transition compounds such as  $\text{KH}_2\text{PO}_4$  and others [3,32] in which the proton itself undergoes the order-disorder transitions. However, in **1-H**, the proton in the H bonds only plays a role in forming the molecular packing, not for the order-disorder state change. Therefore, the deuteration does not directly affect the transition temperature but the packing structure, whose changes exert variable internal pressure on the cations to result in a change of the transition temperature. The crystal structure of **1-D** was examined to clarify the mechanism of the downward shift on the transition temperature. In addition, we compared the O...O distance before and after deuteration, i.e., the secondary GIE.

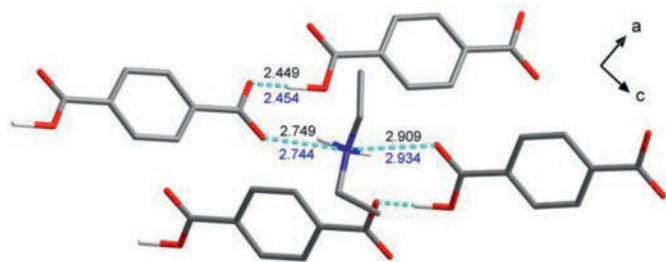
The distance of O...O becomes longer after deuteration (Fig. 4 and Table 1). For example, the O...O distance is lengthened by 0.006 Å at 153 K. Consequently, such a slight elongation causes a 10 K downward shift of the transition temperature because the elongation expands the rhombic host network to allow the cations



**Fig. 2.** Crystal structure of **1-H** in the LTP at 153 K: (a) The anionic O–H...O H-bonded chain formed by TPA monoanions. (b) Intermolecular interactions among the chains and cations. (c, d) Packing structures viewed along the c and b axis, respectively. Hydrogen atoms are omitted in need of clarity.



**Fig. 3.** Crystal structure of **1-H** in the HTP at 293 K, showing a disordered state of the DEA cations. Hydrogen atoms are omitted in need of clarity.



**Fig. 4.** Length of O/N...O for H-isomorph (black) and D-isomorph (blue) at 153 K. Hydrogen atoms are omitted in need of clarity.

move more easily. A similar phenomenon has been seen in strain-triggered phase transition materials (imidazolium)(TPA) [27] and (FA) (TFTPA) [28]. In (imidazolium)(TPA), a downward shift of the dielectric phase transition of about 35 K is shown due to the geometric isotope effect. Despite N–H...O hydrogen bonds were changed after deuteration, such weak hydrogen bonds contribute less to alter properties compared with strong O–H...O hydrogen bonds (Fig. 4 and Table S2 in Supporting information).

In summary, we report a hydrogen-bonded organic salt experiencing a structural phase transition associated with a dielectric switching between low and high dielectric states. The transition mechanism is ascribed to the order-disorder state change of the cations. Deuteration study shows a noticeable decrease of the transition temperature owing to positive GIE of the O–H...O upon deuteration, which reduces the internal pressure on the cations by expanding the host environment to result in a downward shift

of the phase transition temperature. This work provides an example of phase transition-related properties regulated by deuteration, which enriches the geometric H/D isotope effect study.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2021.08.032.

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