Hydrogen-Bonded Switchable Dielectric Material Showing the Bistability of Second-Order Nonlinear Optical Properties

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Supporting Information

ABSTRACT: Physical properties of phase transition materials are directly linked to the transformation of structural moieties. Here, we report a new hydrogen-bonded binary crystal of cyclohexylaminium chlorodiﬂuoroacetate (1), consisting of two distinct types of the anion—cationic structural moieties, which shows an order—disorder phase transition around 153 K (phase transition point, \( T_c \)). Thermal analyses, dielectric, and second-order nonlinear optical (NLO) measurements solidly conﬁrm the symmetry transformation from the point group \( mmm \) to \( mm \). It is noteworthy that 1 exhibits a coexistence of switchable dielectric behaviors and bistable NLO effects. In detail, it is NLO-active below \( T_c \), while its quadratic NLO effects completely disappear above \( T_c \). Such a change reveals the bistable feature of its quadratic NLO properties. Further, variable-temperature structure analyses reveal that the emergence of NLO effects below \( T_c \) is ascribed to partial ordering of anions and small-angle reorientation of cations. This mechanism is different from that of the precedent NLO-switching materials, which affords a potential avenue to design new electric-ordered molecular compounds as multifunctional materials.

1. INTRODUCTION

Stimuli-responsive materials are those that are able to change physical and/or chemical properties under external stimuli such as temperature, pressure, light radiation, electric and magnetic fields, etc.1 The bulk switchable performance between different states can be used in sensors, switches, memory devices, and so forth.2 This has been well illustrated by switchable dielectric materials, of which the dielectric constants can be reversibly switched between low-dielectric and high-dielectric states. Such a transformation is often established through the reorientations or molecular motions of polar components during structural changes. For instance, the ordered solid-state molecules usually exhibit smaller dielectric constants than that in the disordered state, owing to the freezing of molecular motional freedom.3 Meanwhile, it is noteworthy that the structural dynamics directly involves collective quadratic nonlinear optical (NLO) properties. As one class of the most important photoelectric devices, the NLO switches demonstrate similar bistable behaviors analogous to switchable dielectric materials.3 A recent advance discloses that both dielectric constants and NLO properties can be switched in a reversible manner through structural phase transitions.3c Nevertheless, it still remains challenging to design switchable dielectric materials with bistable NLO effects, since the macroscopic arrangement of NLO-active moieties should be controlled into a non-centrosymmetric (NCS) manner.4

Using the conceptual scheme of structural phase transitions, organic salts and inorganic−organic hybrids have been recently found to show prominent bistable NLO properties.5 Particularly, crystals that undergo structural changes from a centrosymmetric (CS) phase to the NCS state display outstanding physical properties in the vicinity of phase transition point (\( T_c \)). For instance, the hydrogen-bonded binary compounds of [Hdabc]\( ^+ \) [A]\(^– \) (dabc = 1, 4-
diazabicyclo[2.2.2]octane; A = ClO₄, BF₄, and ReO₄) show obvious NLO-switching activities due to the synergistic effects of the individual components. In addition to dynamic multiple states of the monoprotonated Hdabc⁺ cation, the ordering of anionic components also makes an important contribution to their NLO bistability. Owing to the appearance of strong anionic components also makes an important contribution to obvious NLO-switching activities due to the synergistic effects of the monoprotonated Hdabc⁺ cation, the ordering of anionic moieties and small-angle reorientations of cationic parts contribute to its dielectric properties of such candidates exhibit peak-like anomalies, instead of the low/high switchable electric polarization, dielectric properties of such candidates, deposited with silver conducting glue, were performed using a Tonghui TH2828A analyzer in the temperature range of 120–250 K (Figure S5). Temperature dependence of the real part (∊′) of the complex dielectric constant (∊ = ∊′ – i∊″ where ∊′ is the imaginary part) was recorded with the frequency range of 100 kHz to 1 MHz. The UV/vis diffuse reflection spectrum of 1 was collected in Shimadzu UV−2600 spectrometer in the range of 800–200 nm at room temperature, and the absorption edge near the UV side of 1 is measured to be ∼260 nm (Figure S6). Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer (Figure S7). Measurements of variable-temperature NLO properties were carried out on FLS 920, Edinburgh Instruments, in the temperature range of 100–250 K, using an expanded laser beam with low divergence (pulsed by Nd:YAG laser at a wavelength of 1064 nm). The laser is Vibrant 355 II, OPOTEK. The potassium dihydrogen phosphate (KDP) is used as the reference standard.

2. EXPERIMENTAL SECTION

Compound 1 was synthesized by the reaction of cyclohexylamine and chlorodifluoroacetic acid with a molar ratio of 1:1 at room temperature. Transparent block crystals were obtained by the temperature-cooling method from the aqueous solutions with the cooling rate of 0.5 °/day (Figure 1). Powder X-ray diffraction (PXRD) analyses of 1 was measured on a Rigaku Ultima-IV X-ray diffractometer. The diffraction patterns were collected in the 2θ range of 5−45° with a step size of 0.02°, which match fairly well with the calculated results based on its room-temperature structure. This result confirms the bulk purity of the grown crystals (Figure S1).

DSC and ∊‴ measurements were performed using a NETZSCH DSC 200 F3 instrument in the temperature range between 100 and 250 K. The crystalline samples were placed in the aluminum crucibles with different heating and cooling rates under the nitrogen atmosphere. Dielectric measurements of powder and crystal samples, deposited with silver conducting glue, were performed using a Tonghui TH2828A analyzer in the temperature range of 120–250 K (Figure S5). Temperature dependence of the real part (∊′) of the complex dielectric constant (∊ = ∊′ − i∊″ where ∊′ is the imaginary part) was recorded with the frequency range of 100 kHz to 1 MHz. The UV/vis diffuse reflection spectrum of 1 was collected in Shimadzu UV−2600 spectrometer in the range of 800–200 nm at room temperature, and the absorption edge near the UV side of 1 is measured to be ∼260 nm (Figure S6). Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer (Figure S7). Measurements of variable-temperature NLO properties were carried out on FLS 920, Edinburgh Instruments, in the temperature range of 100–250 K, using an expanded laser beam with low divergence (pulsed by Nd:YAG laser at a wavelength of 1064 nm). The laser is Vibrant 355 II, OPOTEK. The potassium dihydrogen phosphate (KDP) is used as the reference standard.

Single-crystal X-ray diffractions were performed on a SuperNova diffractometer with Cu-Kα radiation (λ = 1.54184 Å). Crystals with approximate dimensions of 0.29 × 0.36 × 0.52 mm³ were used for data collections at different temperatures. The crystal data were processed by the Crystalclear software package (Rigaku, 2005). The variable-temperature crystal structures were solved by the direct method and refined by the full-matrix least-squares refinements on F² using the SHELXLTL software package. Non-hydrogen atoms were refined anisotropically based on all the reflections with I > 2σ(I), and hydrogen atoms were generated by geometrical considerations. Crystallographic data and structure refinements of 1 are listed in Tables S1 and S2.

3. RESULTS AND DISCUSSION

3.1. Thermal Properties. Differential scanning calorimeter (DSC) and specific heat (∊‴) measurements are effective to detect thermally induced solid-state phase transitions, especially for crystals involving the dynamically disordered molecules. When the compound undergoes a structural phase transition accompanied by thermal entropy change, a heat anomaly can be observed during heating and cooling process. Here, the structural phase transition of 1 is preliminarily determined by thermal measurements, including DSC and ∊‴ analyses. As shown in Figure 2a, the DSC curves in the heating and cooling
runs clearly reveal a couple of reversible peaks. The respective temperature peaks are calculated to be ∼151/153 K (the phase transition point, $T_c$) upon cooling and heating modes. The peak-like thermal anomaly of DSC trace suggests the discontinuous characteristics for the structural phase transition in 1. Besides, with the heating/cooling rates reducing to 2 K/min, a thermal hysteresis of ∼1.8 K was still observed (Figure S2), which discloses the first-order feature of its phase transition. This result corresponds well to the thermal peak of its $C_p-T$ trace, as shown in Figure 2b. Moreover, the relevant enthalpy change ($\Delta S$) in the heating mode is calculated to be $\sim 3.37 \text{ J mol}^{-1} \text{K}^{-1}$ from the $C_p-T$ curve. According to the Boltzmann equation of $\Delta S = R \ln N$, where $R$ is the gas constant and $N$ denotes the ratio of numbers of respective geometrically distinguishable orientations for the disordered system, the $N$ value is estimated as $\sim 1.5$, which suggests a more complex phase transition than a typical order–disorder transition undergoing the two-site reorientations.

3.2. Crystal Structure Analyses. To further confirm the structural phase transition of 1, we have determined its variable-temperature structures. For convenience, its single-crystal structure above $T_c$ is labeled as high-temperature phase (HTP), and the phase below $T_c$ is denoted as low-temperature phase (LTP). Variable-temperature X-ray single-crystal diffraction reveals that 1 crystallizes in the orthorhombic crystal system at HTP, with a CS space group of $Pcmn$ and point group $D_{2h}$. At 170 K, the cell parameters are determined as $a = 10.912$, $b = 17.184$, $c = 17.738$ Å, $Z = 12$, and $V = 3326.29$ Å$^3$ (Table S1). Figure 3 shows that the asymmetric unit of 1 contains two types of structural moieties, which display different crystallographic orientations. Apparently, one set consists of the protonated cyclohexylaminium cation and the disordered chlorodifluoroacetic anion (labeled as Type-B, Figure 3a), while the other only contains a half of anion–cation moieties with a highly symmetric molecular configuration (labeled as Type-A). On the basis of crystallographic symmetry, all the components including type-A and type-B moieties exhibit the CS configurations with respect to the mirror planes (Figure S3). Particularly, the Type-B chlorodifluoroacetate anions in 1 are highly disordered; that is, both the F and Cl atoms of the chlorodifluoromethyl groups locate at two possible equilibrium positions. These atoms reside over two sets of different atomic sites as $C_{1i}$, $Cl_{1i}$, $F_{1i}$, $F_{2i}$ and $C_{1Bi}$, $Cl_{1Bi}$, $F_{1Bi}$, $F_{2Bi}$ respectively. This similar disordering has been observed in several other molecular compounds, such as 4-diazabicyclo[2.2.2]octane trifluoroacetate and tri-$n$-butylammonium trifluoroacetate, which affords the driving force to their order–disorder phase transitions. Moreover, it is interesting that the intramolecular N–H···O H-bonds between N atoms of cyclohexylaminium cations and O atoms of anionic moieties construct the H-bonded dimmers (Figure 3b). As far as we are aware, the H-bonded binary compounds have been reported to show strong ferroelectric polarization induced by order–disorder structural changes, such as disopropylammonium chloride and disopropylammonium bromide salts. Hence, it is expected that 1 might also exhibit promising electric polarization, which is indispensable for the generation of quadratic NLO activities in the crystalline samples.

At 100 K, crystal structure of 1 still belongs to the orthorhombic crystal system but crystallizes in a NCS space group of $Pca2_1$ with the polar point group $C_{2i}$. During the cooling process, its crystallographic symmetry transforms from the point group $mmm$ to $mm2$ that is, the eight symmetric elements ($E$, $C_2$, $C_2'$, $C_2''$, $i$, $\sigma_v$, $\sigma_d$, and $\sigma_d'$) in the HTP are halved into four elements ($E$, $C_2$, $\sigma_d$, and $\sigma_d'$) in the LTP (Figure 4). Figure 4 shows the symmetry elements of 1 in the LTP within one unit cell and in the HTP within two unit cells, respectively. The doubling of the $a$-axis after phase transition leads to that the sequential symmetry operation of reflection and then translation along the $a$-axis become that of glide. Accordingly, the location of the $a$-glide is at that of the mirror-

![Figure 3](image-url)  
Figure 3. (a) Asymmetry unit of 1 with atomic numbering scheme at HTP. There are two types of cation–anion structural moieties with the distinct crystallographic configurations, which are named as type-A and type-B, respectively. (b) Hydrogen-bonding interactions between the nitrogen and oxygen atoms in 1 at HTP.

![Figure 4](image-url)  
Figure 4. Symmetry transformation of 1 during its phase transition.
in the HTP. Therefore, the disappearance of two 2-fold screw axes and the inversion center leads to the NCS space group of \( Pca_2_1 \) at LTP.

Upon cooling down below \( T_c \), the splitting of diffraction peaks is reminiscent of the possible lowering of crystallographic symmetry. On data reduction, the space group of \( Pcmn \) was initially assumed with the \( R_{int} \) value of 0.09. However, the lower value (\( R_{int} = 0.0697 \)) was obtained for the solution in the space group of \( Pca_2_1 \) (Table S1, Supporting Information). The cell parameters become \( a = 21.5734, b = 17.1630, c = 17.7854 \), \( Z = 24 \), and \( V = 6585.3 \) Å\(^3\). From the structural viewpoint, the asymmetric unit of \( 1 \) contains six cyclohexylaminium cations and stoichiometric chlorodifluoroacetate anions at LTP. As shown in Figure 5a, the orientational conformations of organic cations closely resemble those in the high-temperature structure. The most explicit change is that the disordering of chlorodifluoroacetate anions has been greatly reduced; that is, two-thirds of the anionic moieties become ordered. However, it is unexpected that other two anions remain still disordered (in Figure 5a). For instance, both the F and Cl atoms of the chlorodifluoromethyl group in one disordered anion locate at two possible equilibrium positions. These atoms reside over two sets of different atomic sites as Cl\(_3\)/Cl\(_{FB}\), F\(_3\)/F\(_{FB}\) and F\(_3\)/F\(_{FB}\), respectively. Meanwhile, the C\(_9\) of another one is split to C\(_9\) and C\(_{9B}\). The partial ordering of chlorodifluoroacetate anions differs from the typical order–disorder transition, coinciding well with DSC result. From the packing view, due to the disorder of its structural moieties, the dipolar moments are canceled to display CS packing at HTP (Figure 3b). In contrast, the disordering of anionic groups has been greatly inhibited at LTP, and the cationic dipoles exhibit the reorientational arrangement. Hence, molecular dipoles could not cancel each other and finally result in electric polarization of \( 1 \).

Above-mentioned studies reveal that \( 1 \) crystallizes in the space group \( Pca_2_1 \) at LTP, which is expected to show electric polarization or ferroelectricity.\(^{12} \) However, to define a ferroelectric, some sufficient conditions or requirements should also be satisfied in this system, such as ferroelectric hysteresis loop, electric domain and dielectric anomaly, etc. Among them, the spontaneous polarization (\( P \)) and electric field (\( E \)) hysteresis loops usually behave as the direct evidence for ferroelectric crystals. Here, we also tried to measure the \( P–E \) hysteresis loops on crystal samples using the Sawyer–Tower circuit. Unfortunately, it fails to switch the electric polarization even under large electric field of \( \sim 50 \) kV/cm. Actually, it is known that switching of polarization becomes almost impossible for some polar materials, because their coercive electric field is so large that crystals would be destroyed when being switched.\(^{16} \) At present, it is quite difficult to measure the ferroelectric \( P–E \) hysteresis loops for crystals of \( 1 \) with an acceptable degree of accuracy. A further study on the domain motions is needed for accurate determination of ferroelectricity of \( 1 \) in future.
To further study the origin of phase transition in 1, we performed a comparison of its structures at HTP and LTP. It is clear that partial ordering of chlorodifluoroacetate anions dominates its phase transition. However, the role of cationic moieties should not be underemphasized, although the cationic moieties look the same during the phase transition. First, it assembles the components into a binary hydrogen-bonded architecture through intermolecular N–H···O hydrogen bonds, as shown in Figure 5b. These H-bonding interactions might exert delicate constraints on the thermally induced atomic vibrations of anionic moieties. Such cooperative intermolecular interactions are indispensable for the occurrence of polarization in crystalline samples, which is an essential result of the long-range coupling interactions. Further, the cationic parts display a small-angle reorientation during the phase transition. Take the ammonium groups as example: they deviate away from the initial equilibrium positions and lead to the disappearance of mirror plane (as shown in Figure 5b). Hence, it is supposed that its phase transition of 1 is induced by the partial ordering of anions, along with the small-angle reorientation of cations.

3.3. Dielectric Properties. Bulk physical properties generally show abrupt changes in the vicinity of \( T_c \) and variation magnitude relates to the characteristics of structural changes.\(^{14}\) Here, temperature dependence of the real part \( (\varepsilon') \) of the complex dielectric permittivities of 1 was measured on crystal samples at different frequencies, and the (010) crystal surface was determined according to the simulated morphology (in Figure S4). As shown in Figure 6a, the \( \varepsilon' \) values of 1 remain almost stable below \( T_c \), well corresponding to its low-dielectric state. Upon heating, its dielectric constants exhibit the step-like changes around \( T_c \) and the values increase up to \( \sim 7.5 \) in the high-dielectric state. Such a reversible transformation between the low-dielectric and high-dielectric states, resembling that of improper ferroelectric materials of \((\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3\) and \(\text{Gd}_2(\text{MoO}_4)_3\),\(^{15}\) discloses that 1 should be a switchable dielectric material. Besides, a relatively narrow thermal hysteresis of \( \sim 2 \) K is observed in the heating and cooling runs, which corresponds well to the DSC results (Figure 6b). As mentioned above, the order–disorder structural changes of 1 dominates its phase transition from a CS state to the NCS one. In this regard, these dielectric behaviors coincide fairly well with the partial ordering of dynamic motions in 1 during its phase transition.

3.4. Bistable NLO Properties. The low-temperature structure of 1 belongs to the NCS space group \( \text{Pca}2_1 \). Hence, it is expected to display the second harmonic generation (SHG) effects at LTP. First, we measured the UV/vis diffuse reflection spectrum of 1 in the range of 800–200 nm, and the result indicates that the absorption edge of 1 is \( \sim 260 \) nm (Figure S6). The optical absorption is quite low at \( 532 \) nm, which suggests that 1 should be suitable for NLO application using a Nd:YAG laser (\( \lambda = 1064 \) nm). As shown in Figure 7a, the temperature-dependent SHG signals confirm the structure change of 1. In detail, there is not any SHG signal above 153 K, which corresponds fairly well to its CS structure of \( \text{Pcmn} \). With the temperature decreasing below \( T_c \), 1 becomes NLO-active and exhibits nonzero SHG signals. This step-like change of SHG signals suggests that 1 becomes NCS in LTP, being consistent with the structure analysis (space group changes from \( \text{Pcmn} \) to \( \text{Pca}2_1 \)). When temperature decreases far away from \( T_c \), the SHG intensities become saturated and were estimated to be \( \sim 0.3 \) times as large as that of KDP (at 120 K, Figure 7b). Hence, the quadratic NLO coefficients \( \chi^{(2)} \) of 1 is calculated to be \( \sim 0.12 \) pm V\(^{-1}\) (\( \chi^{(2)} \text{KDP} = 0.39 \) pm V\(^{-1}\)) at LTP.\(^{16}\) This value is comparable with some reported NLO switching materials, such as (cystaminium)\( \text{BiI}_5 \),\(^{5a}\) (pyrrolidinium)\( \text{CdCl}_3 \),\(^{16c}\) and bis(imidazolium hydrochlorate) dihydrate 18-crown-6.\(^{6c}\) Actually, this change of SHG effects clearly discloses the feature of 1 as a potential NLO-switching material. In detail, the complete vanishing of SHG signals at HTP corresponds to the low-NLO state, while the emergence of SHG effects at LTP satisfies the essential requirement for NLO switches (treated as the high-NLO state). The NLO switching contrast of between high-NLO state and low-NLO state is calculated as \( \sim 12 \), which is comparable with some crystalline materials,\(^{17}\) such as anil crystals, thin films of ruthenium complexes and metal–organic frameworks, etc.\(^{18}\) Such a result suggests that 1 may be a potential NLO-switching molecular material.

4. CONCLUSIONS

In summary, the present work has successfully reported a solid-state molecular material, which undergoes an order–disorder phase transition at \( \sim 153 \) K. It is noteworthy that it exhibits switchable dielectric responses and controllable NLO effects, that is, the coexistence of dielectric- and NLO-switching behaviors. Structural analyses disclose that partial ordering of anionic moieties and small-angle reorientation of cations predominate the phase transition. This coexistence mechanism...
for the emergence of second-order NLO effects is distinct from the preceding NLO-switching compounds. It is believed that, in the search for new multifunctional materials, this finding affords a potential pathway to construct new electric-ordered molecular materials.

## Associated Content

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00240.

Figure S1. Experimental and calculated powder X-ray diffraction patterns of I; Figure S2. DSC traces measured with the different heating/cooling rates; Figure S3. Packing diagram of 1 viewed along the a HTP-axis; Figure S4. Crystal morphology of I simulated from the single-crystal structure; Figure S5. Temperature dependence of dielectric constants of I measured on powder sample; Figure S6. UV-Vis diffuse reflection spectrum of I with the absorption edge at 260 nm; Figure S7. TG curves of I; Table S1. Crystal data and structure refinement for I; Table S2. N–H···O Hydrogen bonds of 1 at HTTP (PDF)

### Accession Codes

CCDC 1498369 and 1498384 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Notes**

The authors declare no competing financial interest.

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### References


5. (a) Department of Science and Technology (DST), the Major Research Project of National Natural Science Foundation of China (51422301, 21373220, 51402296, and 51502290), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000) and the Youth Innovation Promotion of CAS (2014262). Z.S. thanks the State Key Laboratory of Luminescence and Applications (SKLA-2016-09).