Exceptional Three-Level Switching Behaviors of Quadratic Nonlinear Optical Properties in a Tristable Molecule-Based Dielectric

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ABSTRACT: Significant progress on a new brilliant scheme for the solid phase transition has opened up new possibilities of highly efficiently switching the quadratic nonlinear optical (NLO) properties. However, the NLO switching capacities of previously reported solid-state materials were restrictively modulated between the conventional bistable states. Exploring NLO tristability is strongly required for multistep operations in multilevel memory elements and optoelectronic devices. Here, we first report a tristable molecule-based dielectric, dipropylammonium trichloroacetate (DPA-TCA), which shows an exceptional three-level switching of quadratic NLO effects (i.e., NLO-off, low-NLO, and high-NLO states). This unprecedented three-level switching of the NLO effect originates from the stepwise ordering of the dynamic molecular components in DPA-TCA, associated with the tristability of dielectric phase transitions at 142 and 228 K. It is believed that this finding will shed light on the further design of new multilevel NLO switching materials and promote their prospective device applications.

INTRODUCTION

Nonlinear optical (NLO) switch material, as an exciting new branch of NLO material science, allows us to convert the intrinsic NLO effects under the influence of external stimuli, such as heat, laser radiation, pressure, electric and magnetic fields, etc. These materials are of great interest because of their potentials in controllable intelligent devices.1–7 Although great progress has been achieved, the switchable NLO activities of previously reported solid-state NLO switches were restrictively modulated only between bistable states, such as “NLO-on” and “NLO-off” states (or high-NLO and low-NLO states), which severely limits their practical application in multistep operations for multilevel memory elements and optoelectronic devices.8–12 For instance, the three-level conversion among distinguishable spin states in tristable spin-crossover systems has long been established as an applicable way to assemble multilevel magnetic switches.13–15 As a counterpart, however, there is still a rare report of three-level NLO switches. In this circumstance, it is highly desirable to develop new conceptually tristable materials that allow us to switch the quadratic NLO effects at three levels.

In the past few decades, much of the attention in exploring NLO switches has been focused on the conventional strategies of chemical modification (e.g., redox process, protonation, or ion capture trapping) and thermochromic/photochromic responses.18–24 Recently, the solid-state phase transition represents a new brilliant scheme that relies on the structural transformation for the development of new NLO switching candidates.25–31 It has proven that solid-state phase transitions with a change in the crystallographic symmetry from the centrosymmetric (CS) phase to the noncentrosymmetric (NCS) phase can generate drastic variations in NLO effects, which has significantly enhanced the development of high-performance quadratic NLO switches.32–35 Since Mercier et al. first reported the organic–inorganic hybrid NLO switch, [(H3N(CH2)2SS-(CH2)3NH3)PbI5]·H2O, great progress in NLO switch materials has been achieved on the basis of this principle in metal–organic hybrids and multicomponent ionic salts.36 In particular, a plastic molecular NLO switch shows a record high “on/off” contrast of ≲150 by extending the principle of structural transformation to a plastic material system.37 However, to the best of our knowledge, all NLO switches mentioned above can allow conversion of NLO activities between only common bistable states, and studies of stimulus-responsive NLO tristability are in their infancy. Zhang et al. recently discussed a two-step NLO switch within a variable confined space based on the sequential solid-state phase transitions.38 Unfortunately, it shows an “off–on–off” NLO switching capacity, with the NLO active state merely existing in a narrow intermediate temperature range between 198 and 240 K. Therefore, further exploration of new phase transition materials is quite necessary to achieve three-level switching of quadratic NLO properties accompanied by the step-by-step enhancement of NLO effects.

Here, we have reported a tristable molecule-based dielectric, dipropylammonium trichloroacetate (DPA-TCA), which...
undergoes tristable dielectric phase transitions at 142 and 228 K. Emphatically, it shows an exceptional three-level switching of quadratic NLO effects, changing from an “NLO-off state” to low-NLO and high-NLO states. Stepwise ordering of the flexible components dominates such a unique NLO switching behavior, as well as the tristable dielectric states in DPA-TCA. To the best of our knowledge, this is the first tristable molecular dielectric with unprecedented three-level NLO switching, which opens up a new strategy for designing the stimulus-responsive multistable materials.

Experimental Section

All the chemical reagents were purchased as high-purity (AR grade) compounds and used without any further purification. Colorless block single crystals of DPA-TCA were obtained by slow evaporation of an aqueous solution containing equimolar dipropylimine (DPA) and trichloroacetic acid (TCA) at room temperature. Powder X-ray diffraction (PXRD) patterns were recorded by an X-ray diffractometer (Rigaku Corp., SCXmini). The diffraction patterns were collected in the 2θ range of 5°–50° with a step size of 0.02°. The experimental PXRD patterns obtained at room temperature match well with the calculated data based on the single-crystal structure, which solidly confirm the purity of the as-grown crystals of DPA-TCA.

Variable-temperature X-ray single-crystal diffraction experiments were performed on a SuperNova diffractometer with Cu Kα radiation (λ = 1.5406 Å). Crystal structures were determined by direct methods and refined by the full-matrix method based on F2 using the SHELXS-97 software package. All non-hydrogen atom positions were located using difference Fourier methods as implemented in SHELXL-97. All of the non-hydrogen atoms were refined anisotropically. These crystal data, structural refinements, and selected geometrical parameters can be found in Tables S1–S7.

Thermal properties were measured by a differential thermal analyzer (Netzsch DSC 200 F3) under a nitrogen atmosphere in aluminum crucibles with a heating/cooling rate of 10 K/min. For dielectric measurements, the samples of DPA-TCA were made with single crystals cut into the form of a thin plate perpendicular to the crystal axis. Silver conduction paste deposited on the plate surfaces was used as the electrodes. Dielectric experiments were performed with a TongHhui TH2828 Precision LCR Meter at different frequencies in the temperature range of 115–325 K with a heating/cooling rate of ±10 K/min. The UV–vis optical transmission spectra of the samples of DPA-TCA were recorded on a Lambda-950 UV/vis/NIR spectrophotometer, which show that DPA-TCA presents good transparency from 350 to 800 nm.

SHG switching experiments with DPA-TCA were performed on the powder samples (particle size range of 72–100 μm), using the fundamental laser beam with a low divergence (pulsed Nd:YAG laser at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, and 10 Hz repetition rate). The instrument is model FLS 920 from Edinburgh Instruments; the temperature range is 100–300 K (DE 202), while the laser is a model Vibrant 355 II laser from OPOTEK.

Results and Discussion

Differential scanning calorimetry (DSC) was first performed to probe the tristable structural phase transitions of DPA-TCA. It clearly shows two sets of thermal anomalies, indicating two sequential phase transitions at 228 and 142 K (Figure 1a). The phase above T1 is designated the high-temperature phase (HTP), the phase between T1 and T2 as the intermediate-temperature phase (ITP), and the phase below T2 as the low-temperature phase (LTP). The broad peaks of the observed thermal anomalies and the slight temperature hysteresis at T2 reveal that two transitions are both of typical second-order phase transition with continuous characteristics.39–41 Entropy changes (ΔS) are estimated to be 4.58 and 5.71 J K⁻¹ mol⁻¹ accompanying the transition around T1 and T2, respectively. Given that ΔS = R ln N, it is found that N(T1) = 1.73 and N(T2) = 1.91, revealing the disorder–order feature of phase transitions at T1 and T2.42–44 This originates from stepwise ordering of thermal motions, which coincides well with the structural analyses mentioned below.

It is known that crystal structure transformation should be associated with the molecular dipole motions, which are closely related to the tunable dielectric permittivity.45–48 The temperature dependence of the real part (ε”) of the complex relative dielectric permittivity of DPA-TCA was measured on a single-crystal sample. The results reveal two relatively obvious dielectric anomalies at T1 and T2 upon cooling and heating, being consistent with the DSC results, which is reminiscent of the tristable dielectric states in DPA-TCA (Figure 1b and Figure S2). Below T3, the dielectric constants remain stable and display a small change from 4.4 to 4.6 around the phase transition point, whereas a sharp dielectric anomaly is observed at T1 with a pronounced steplike increase to ~5.7. Above T3, it then remains almost constant until room temperature is reached. There is no distinct dielectric relaxation process in the vicinity of T1 and T2 at different frequencies (Figure S3), indicating a relatively fast dipolar motion associated with these two structural transformations.49

Quadratic NLO switching performances were studied by using the method of Kurtz and Perry to examine the polycrystalline sample of DPA-TCA (λ = 1064 nm; Nd:YAG pulsed laser).50 As shown in the inset of Figure 2, it is notable that there is not any NLO signal at 532 nm above T1. Via in situ measurement of NLO effects upon cooling, the NLO signals gradually become active with NLO intensity peaks emerging at 532 nm. With a further decrease in temperature, NLO intensities increase significantly. As shown in Figure 2, from the integral results of NLO signals, it is clearly shown that NLO effects are completely oblitative above T1, with the effective second-order NLO susceptibility χ² basically being zero.
corresponding to the NLO-off state. Upon DPA-TCA was further cooled from HTP to ITP, a steplike jump of the NLO signals emerge at T2 and reach a new level with the temperature decreasing far below T2. Compared with common bistable NLO switches that rely on the CS–NCS phase transition,25–37 DPA-TCA shows a three-level “off–low–high” NLO switching behavior with step-by-step enhancements of NLO effects from T1 to T2. To the best of our knowledge, DPA-TCA is the first example of a tristable dielectric material with a significant three-level NLO switching, which shows great potential in multilevel optoelectronic devices. To understand the origin of the tristable NLO switching capacities, variable-temperature crystal structures of DPA-TCA were determined at 100 K (LTP), 150 K (ITP), and 240 K (HTP) (Table S1).51 As shown in Figure 3, the crystal structures of DPA-TCA, composed of protonated DPA cations and TCA counterions, crystallize in the orthorhombic crystal system. However, its crystal symmetry transforms from a CS space group of Pnma in HTP to a NCS one of P212121 in ITP and LTP. At 240 K, two diverse geometry configurations of DPA cations and TCA anions were observed in the unit cell (abbreviated as DPA1 and DPA2 and as TCA1 and TCA2, respectively). It is interesting to note that the DPA1 and DPA2 cations and the TCA1 anion are highly disordered with N2, C8, and C11 of DPA1 and C5 of DPA2 apparently existing in two possible equilibrium occupations. Meanwhile, all the Cl atoms in TCA1 also exhibit dynamical disorder, which exhibits seven possible equilibrium occupations. The related dynamic characteristics of DPA1, DPA2, and TCA1 create a crystallographic mirror plane parallel to [010]. The mirror symmetry is satisfied by the orientational disorder of DPA1 and DPA2 cations and TCA1 anions. In addition, the TCA2 anion shows a relatively ordered state, in which C13, C14, and Cl2 are located on the special position with mm2m symmetry. This centrosymmetric construction was adopted in HTP for DPA-TCA with mutually canceled dipole moments, corresponding to the NLO-off state in HTP.

The crystal structure of DPA-TCA at 150 K was measured to investigate the phase transition related to the CS–NCS symmetry transformation. Although the structure of DPA-TCA in ITP remains in the orthorhombic crystal system and the lattice parameters are almost the same as those in HTP (Figure S1), the loss of the mirror symmetry in the (010) plane results in the structural phase transition from CS space group Pnma to chiral space group P212121. This transformation significantly enhances the NLO activity at T1. The thermal vibration parameters of all atoms in ITP are obviously smaller than those found in HTP (Tables S2 and S3), which suggests a deceleration of the molecular thermal motions. The disordered DPA1 and DPA2 moieties turn from disorder to ordered states, and all atoms of DPA cations can be exclusively determined in ITP. It can be seen that the geometry configuration of DPA cations clearly changes with obvious distortion of the carbon chain because of the inherent flexibility of the chain-type configuration. As shown in Figure 4a, DPA1 adopts a usual zigzag geometry configuration with normal C–C(N) bond distances (1.455–1.546 Å) and C–C(N)–C bond angles (108.1–114.3°). The DPA2 cation chain is not a regular zigzag geometry with a torsion angle of 18° (N1–C4–C5–C6) in ITP, which is different from the N2–C10–C11–C12 torsion angle for DPA1 (Table S6). In addition, it is worth mentioning that all cationic atoms lie in approximate plane (1) for DPA1 and plane (2) for DPA2 in ITP (Figure 4a).

With respect to the crystal structure at 100 K in LTP, all the DPA cations and TCA anions are frozen to be totally ordered, and the Cl atoms of TCA are definitely distinguishable. As shown in Figure 4b, it is notable that the geometry configurations of DPA1 and DPA2 cations are different from those in ITP, the C atoms of DPA deviating from their common plane of ITP with the following deviation values: Δd(C1) = 0.5526, Δd(C2) = 0.1251, Δd(C5) = 0.2805, and Δd(C12) = 0.3129 Å. The clear twisting of DPA chains significantly increases the molecular dipole moments, which favors the enhancement of NLO activities and triggers the second-step NLO effects modulated from the low-NLO state in ITP to the high-NLO state in LTP.

We notice that the role of the hydrogen-bonding interactions should not be underemphasized. As shown in Figure 5, in HTP,

![Figure 2](image-url)

**Figure 2.** Variable-temperature second-order NLO coefficients of DPA-TCA, revealing the three-level NLO switching response. The inset shows the relative intensity of NLO signals as a function of wavelength at various temperatures.

![Figure 3](image-url)

**Figure 3.** Variable-temperature crystal structures of DPA-TCA in (a) HTP, (b) ITP, and (c) LTP.

![Figure 4](image-url)

**Figure 4.** Molecular geometry configuration of DPA1 and DPA2 at (a) 150 and (b) 100 K.
the stable and enhanced NLO activity in LTP. The stepwise ordering of dielectric phase transitions, that is, two-step phase transitions levels. Such an exceptional NLO switching closely involves its dynamic components in DPA-TCA, accompanied by the hydrogen bond dimers becoming much stronger, with N−H···O hydrogen-bonding dimer interactions of 2.796 and 2.816 Å between the cation and anion tangles the stable and enhanced NLO activity in LTP.

**CONCLUSION**

In summary, a new tristable molecule-based dielectric has been reported as the NLO switch candidate, which exhibits the unprecedented switching of quadratic NLO effects at three levels. Such an exceptional NLO switching closely involves its dielectric phase transitions, that is, two-step phase transitions from the CS phase to the NCS state. The stepwise ordering of the dynamic components in DPA-TCA, accompanied by the distortion of flexible chain alkylamine, dominates the tristability of its dielectric responses and NLO properties. This finding paves a new pathway for the further design of multilevel molecular NLO switching materials and encourages their future application to switch bulk optoelectronic properties in multistable states.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00524.

**REFERENCES**


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(51) Crystal data for DPA-TCA. In LTP (100 K): C₈H₁₆Cl₃NO₂, Mᵣ = 264.57, orthorhombic, P₂₁₂₁₂₁, a = 8.6082(10) Å, b = 16.5540(3) Å, c = 17.9068(3) Å, V = 2551.72(7) Å³, Z = 8, Dᵣ = 1.377 mg/Å³, R₁ [I > 2σ(I)] = 0.0449, wR₂ (all data) = 0.1180, S = 1.04. In ITP (150 K): C₈H₁₆Cl₃NO₂, Mᵣ = 264.57, orthorhombic, P₂₁₂₁₂₁, a = 8.5305(10) Å, b = 17.1390(3) Å, c = 17.9709(3) Å, V = 2627.42(7) Å³, Z = 8, Dᵣ = 1.338 mg/Å³, R₁ [I > 2σ(I)] = 0.0659, wR₂ (all data) = 0.1825, S = 1.066. In HTP (240 K): C₈H₁₆Cl₃NO₂, Mᵣ = 264.57, orthorhombic, Pnma, a = 17.925(7) Å, b = 8.584(2) Å, c = 17.704(6) Å, V = 2724.50(15) Å³, Z = 8, Dᵣ = 1.226 mg/Å³, R₁ [I > 2σ(I)] = 0.1037, wR₂ (all data) = 0.3676, S = 1.081.