An organic–inorganic hybrid co-crystal complex as a high-performance solid-state nonlinear optical switch†

Tianliang Chen, Zhihua Sun,* Sangen Zhao, Chengmin Ji and Junhua Luo*

Solid-state nonlinear optical (NLO) switches have attracted great interest, while high performance solid-state nonlinear optical (NLO) switches still remain scarce. Herein, we firstly present a high-performance solid-state NLO switch based on an organic–inorganic hybrid co-crystal complex, [H₂dabcoCl₂][FeCl₃(H₂O)₃] (1, dabco = 1,4-diazabicyclo[2.2.2]octane). It is found that 1 exhibits a moderately large NLO response of ~0.31 pm V⁻¹, a superior switching contrast (~25) and a highly tunable repeatability, which may guarantee its potential device applications. In addition, microscopic crystal structural analyses reveal that its NLO switching is attributed to the order–disorder transformation of the dabco cation, cooperating with the reorientational displacement of the inorganic [FeCl₃(H₂O)₃] component. Owing to the broader designability of organic–inorganic hybrids, this work opens up an attractive approach for exploring new high-performance NLO switches.

Introduction

Controllable and switchable nonlinear optical (NLO) materials are those that can reversibly change NLO efficiencies to enable responses to external stimuli, such as temperature, light, pressure, electric and magnetic fields. In comparison with the switching of third-order NLO properties in solutions, solid-state NLO switches are more promising because their macroscopic NLO properties can be modulated at the bulk scale. However, the exploration of high-performance solid-state NLO switches remains a challenge. The first example of switching second-harmonic generation (SHG) properties in a bulk sample was demonstrated in poled azobenzene and spirogyra-containing polymers. Nevertheless, the thermal randomization of chromophores leads to an irreversible decay of the NLO properties and eventually to a centrosymmetric structure. After that, photochromic crystals and thin films of ruthenium complexes (based on redox switching) were used as classic examples to design solid-state NLO switches. However, their NLO contrasts reported have fallen to a low value of 1.3–10 and only a limited number of “on/off” cycles were obtained. A more appealing approach of switching NLO response of compounds is a reversible phase transition (PT) from the non-centrosymmetric (NCS) to the centrosymmetric (CS) order. Using this conceptually new scheme, a few solid-state NLO switches of simple organic salts and metal–organic frameworks have been reported. They usually exhibit a macroscopic NLO response between 0.05 and 0.3 pm V⁻¹, and high-performance NLO switches with relatively large optical nonlinearities are still very sparse. In this context, it is highly desirable to explore new and high-performance solid-state NLO switches.

Recently, as one of the most promising strategies, co-crystals have received a great deal of attention as a means of modifying the properties of compounds (NLO, ferroelectric and stability, etc.) by the synergistic effects of the individual components. Among them, the organic–inorganic hybrid co-crystal has been highlighted to have great potential due to the possibility of combining desirable organic and inorganic characteristics within a single molecular scale composite. However, it has never been reported to utilize this promising scheme to design high-performance NLO switches based on PT up to now. Lately, simple organic salts based on a flexible unit have been pioneered to be used to construct structural phase transition materials due to the rotations of the flexible molecule in the crystal lattices. From this point of view, 1,4-diazabicyclo[2.2.2]octane (dabco), a highly symmetric tertiary diamine with a globular shape, will undergo dynamic motions under external stimuli. Such a structural feature is favorable for the occurrence of a phase transition, as well as the generation of NLO effects. In addition, inorganic phase transition compounds are usually associated with atomic displacement. The well-known representative is BiTiO₃, in which the transition is triggered by the Ti⁴⁺ atom along the c-axis. When combining a flexible organic component with a simple neutral inorganic...
Crystal structures were determined by the direct methods and utilized for data collection, cell refinement and data reduction. The CrystalClear software package (Rigaku) was carried out on a SuperNova CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7 Å) at 100 K and 290 K, respectively. The CrystalClear software package (Rigaku) was used for data collection, cell refinement and data reduction. Crystal structures were determined by the direct methods and refined by the full-matrix method based on F2 using the SHELXL17 software package. Anisotropic thermal parameters were refined for the non-hydrogen atoms using all reflections. The positions of the hydrogen atoms were generated geometrically. The asymmetric units and the packing diagrams were drawn using DIAMOND (Brandenburg and Putz, 2005). Distances and angles between some atoms were calculated using DIAMOND, while other calculations were carried out using SHELXL17. Table S1 (ESI†) shows the crystal data and structure refinement of 1. CCDC 1058268 and 1058269.

Experimental section

Synthetic procedures

All the starting materials were of analytical reagent grade and were used without further purification. Firstly, the dihydrochloride salts of triethylenediamine (dabco-2HCl) were prepared by mixing a solution of concentrated hydrochloric acid and dabco with a 3:1 molar ratio in water; secondly, a filtered solution of iron(III) chloride (1 molar equiv.) was put in the above solution. Finally, the solution was filtered and kept for evaporation at room temperature. The purity of co-crystal 1 was confirmed by its X-ray powder diffraction (PXRD) pattern (Fig. S2, ESI†).

Single-crystal X-ray crystallography

Variable-temperature X-ray single crystal diffraction experiments were carried out on a SuperNova CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7 Å) at 100 K and 290 K, respectively. The CrystalClear software package (Rigaku) was utilized for data collection, cell refinement and data reduction. Crystal structures were determined by the direct methods and refined by the full-matrix method based on F2 using the SHELXL17 software package. Anisotropic thermal parameters were refined for the non-hydrogen atoms using all reflections. The positions of the hydrogen atoms were generated geometrically. The asymmetric units and the packing diagrams were drawn using DIAMOND (Brandenburg and Putz, 2005). Distances and angles between some atoms were calculated using DIAMOND, while other calculations were carried out using SHELXL17. Table S1 (ESI†) shows the crystal data and structure refinement of 1. CCDC 1058268 and 1058269.

DSC and specific heat measurements

Differential scanning calorimetry (DSC) at different scanning rates (10 K min⁻¹, 5 K min⁻¹ and 2 K min⁻¹) and specific heat (Cp) measurements were carried out on a NETZSCH DSC 200 F3 instrument in the temperature range from 240–290 K. The experiments were performed under nitrogen conditions in an Aluminium crucible.

SHG activities measurements

All of the NLO properties were measured using an Nd:YAG laser with an input pulse of 420 mV (pulsed at a wavelength of 1064 nm, a 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate). SHG-switching experiments were performed on crystals in the range of 240–290 K. Compound 1 with sizes in the range of 25–210 μm, sieved through a series of meshes, was utilized to perform phase-matching experiments at 160 K by the approximate model of Kurtz and Perry. The measured SHG effects were compared with those of KH2PO4 (κ(2) = 0.39 pm V⁻¹). The SHG switching contrast was defined as the ratio of the SHG signals below and above the phase transition point. In its CS state, the measured standard deviation of the noise level was used as the denominator.

Results and discussion

Compound 1 was prepared as orange bulk single crystals up to 6 × 6 × 3 mm³ by slow evaporation (Fig. S1, ESI†). DSC and Cp measurements (Fig. 1) indicate a structural phase transition of 1 at Tc = 279.9 K. The corresponding enthalpy change ΔS in the heating mode is estimated to be 0.663 J mol⁻¹ K⁻¹ from the Cp–T curve. Given that the Boltzmann equation of ΔS = R ln N in which R is the gas constant and N is the ratio of numbers of respective geometrically distinguishable orientations, N = 1.94 is obtained, showing a typical disorder-order feature of the phase transition. To further confirm the type of phase transition, DSC measurement of 1 at different cooling/heating rates was performed. As shown in Fig. S3 (ESI†), when the heating/cooling rates were reduced to 2 K min⁻¹, the thermal hysteresis is 0.9 K. Such a narrow thermal hysteresis indicates a characteristic of a second-order phase transition.

Variable-temperature single-crystal structures of 1 were performed at 293 K (high-temperature phase, HTP) and 100 K
(low-temperature phase, LTP), respectively. In the HTP, 1 crystallizes in the orthorhombic crystal system, Pnma (No. 62) and point group D_{2h}. The asymmetric unit of 1 contains one-half of organic dabcodihydrochloride (H2dabco·2Cl) species and one-half of inorganic [FeCl3(H2O)3] species (Fig. 2a). The iron(II) ion adopts a distorted octahedral geometry in which the apical atom is the Cl1 anion, and the four equatorial atoms are O1, O2, O3 atoms and a Cl2 anion, respectively. Due to the equatorial plane and the iron(II) atoms lying on a mirror plane, the inorganic [FeCl3(H2O)3] octahedron, which are connected to the inorganic layer by the hydrogen bonds O–H·⋅Cl3 (Fig. 3a), can be generated from the unique atoms by the equatorial plane parallel to the ac plane (Fig. 2a, 3b and Fig. S4, ESI†). In addition, the corresponding angle of the equatorial plane of the neighbouring two [FeCl3(H2O)3] octahedra is 0° (Fig. S5, ESI†). In the inorganic layer, the distances of the nearest neighbouring Fe ions along the c-axis and the a-axis are 7.035 Å and 6.933 Å, respectively (Fig. 3a). Furthermore, the adjacent inorganic layers are interlinked via the bifurcated hydrogen bonds N1–H1·⋅Cl provided by the dabco cations (Fig. 2a). The dabco cations coincide with the inversion center of the unit cell, in which the C atoms are distributed between two positions related to a refined site occupancy factor equal to 0.5.

In the LTP, 1 still belongs to the orthorhombic crystal system, but its symmetry is refined in the space group P212121 (No. 19) and point group D_{2}. The relationship between the two temperature cells is a_{293K} = b_{100K}, c_{293K} ≈ c_{100K}, c_{293K} ≈ b_{100K}. The asymmetric unit contains one organic H2dabco·2Cl species and one inorganic [FeCl3(H2O)3] species (Fig. 2b). The Fe(II) ion still adopts a distorted octahedral geometry, in which the bond lengths (Fe–Cl and Fe–O) and bond angles (Cl–Fe–O) exhibit just a little difference within 0.009 Å and 1.12°, compared to those in the HTP (Tables S2 and S3, ESI†). However, the Fe ions are delocalized from the mirror plane with a deviation value of 0.012 Å along the c-axis (Fig. 3d), leading to the disappearance of the mirror plane in the inorganic layer. At the same time, the angle of the equatorial plane of the neighboring [FeCl3(H2O)3] octahedron changes into 7.23° (Fig. 3d and Fig. S5, ESI†), indicating that there exists a remarkable reorientation in the [FeCl3(H2O)3] octahedron. In the inorganic layer, the corresponding distances of the nearest neighbouring Fe ions change to 6.934 Å and 7.588 Å (Fig. 3c), suggesting that there are evidently cooperative displacements between the Fe ions. Besides the pronounced change in the inorganic species, another dramatic difference occurs in the cationic part. That is, the disordered dabco cations become completely ordered and the carbon atoms can be determined in exclusive atomic positions when the temperature decreases to 100 K (Fig. 2b and 3d). Therefore, considering the ordering of the dabco cation and the reorientation of the octahedron [FeCl3(H2O)3] accompanied with the collective relative displacements of the Fe atoms in the LTP, it can be proposed that the order-disorder transition of the dabco cation cooperating with the reorientational displacement of the octahedron [FeCl3(H2O)3] may be the driving force of the structural phase transition in such a co-crystal complex.4e

From the viewpoint of symmetry breaking, the HTP crystallizes in the centrosymmetric point group mmm and the LTP in the chiral point group 222. Namely, a symmetry breaking phenomenon occurs during the transition process with the symmetric elements decreasing by half from eight (E, i, σ_hb, σ_v, C2, C2, C2, C2) to four (E, C2, σ_v, σ_v), which is in good agreement with the Landau phase transition theory (Fig. 4).11 Furthermore, the symmetry breaking from the CS phase to the NCS phase can be also confirmed by the following temperature-dependent SHG experiments.

An effective quadratic NLO switch is often associated with its SHG coefficients, switching contrasts and reversible switching cycles, etc. The absorption spectrum reveals that 1 has a wide transmission range from 500–1800 nm with an absorption edge of 425 nm, which might be caused by the absorption of
Fe$^{3+}$ ions. Such a result indicates that 1 is suitable for NLO application under an Nd:YAG laser ($\lambda = 1064$ nm). Here, these SHG-switching performances of 1 were investigated in detail. A study of the temperature dependence of the SHG signal is presented in Fig. 5a. Above $T_c$, the SHG signal is absolutely negligible, treated as its switch-off state. While the appearance of its SHG signal in the vicinity of the phase transition temperature reveals that 1 enters into its switch-on state, which is in good accordance with the structure change from the CS phase to the NCS phase. Additionally, it is clearly shown that the SHG signal is gradually amplified in intensity and approached almost saturation with the temperature decreasing from $T_c$ to 160 K, suggesting a second-order phase transition feature, which is in good agreement with the aforementioned thermal analyses.

In order to measure the relative value of the SHG efficiency of 1, powdered KDP was selected as a standard sample.

The SHG intensity at the saturation value is estimated to be $\sim$0.8 times as large as that of KDP (Fig. 5a); namely, the quadratic NLO coefficient of 1 is calculated to be 0.31 pm V$^{-1}$ (KDP, 0.39 pm V$^{-1}$). This value is larger than that for other solid-state NLO switches such as NH2-MIL-53(Al) ($\sim 0.05 \pm 0.02$ pm V$^{-1}$)$^{1b}$ bis(imidazolium hydrochlorolate)dihydrate 18-crown-6 ($\sim 0.08$ pm V$^{-1}$)$^{4c}$ and comparable with that of $\beta$-(H$_3$N(CH$_2$)$_2$-S(S(CH$_2$)$_2$NH$_3$)Bi$_5$ (about 0.3 pm V$^{-1}$).$^{4d}$ Such a moderately large SHG coefficient will lead to an obvious quadratic NLO switching activity between the SHG-ON and SHG-OFF states with the contrast to be approximately 25, which is higher than most of the reported solid-state NLO switches (1.3–20).$^{3c-h}$ It is believed that an improved contrast value of 1 would be obtained when the NLO switching experiment is performed along its phase-matchable direction.

Fig. 5b shows that 1 exhibits a high repeatability of SHG switching with at least 8 cycles, which is much superior to many photochromic polymer films and photochromic crystals.$^{3c}$ Importantly, after a long time switching experiment, the intensities of its SHG signal still maintain their initial level without any obvious fatigue. As we all know, the NLO intensity is commonly related to the arrangement of dipoles in the structure.$^{15}$ In poled polymers and redox-based switching LB films, the limited number of “ON/OFF” cycles is possibly ascribed to their irreversible changes in the initial chromophore alignment.$^{7}$ However, for 1, the SHG switching scheme is established on its thermally induced structural change, which guarantees the molecular dipole moments to be reversibly tuned in a collective manner and results in a highly reversible process.

Additionally, phase-matchable experiments of 1 were performed using the Kurtz and Perry method. As expected, the intensity of 1 increases with the particle size and approaches almost saturation with a particle size up to 200 μm (Fig. S6, ESI†) at 160 K, confirming the phase-matchable properties. All these findings indicate that 1 will possess potential applications in SHG-switching.

In an ionic crystal, the marked atomic displacements could induce large molecular dipole moments, which may be closely related to the macroscopic NLO response. Since the organic–inorganic hybrid co-crystal 1 is composed of one organic neutral component (H$_4$Dabco-2HCl) and one inorganic component ([FeCl$_{3}$(H$_{2}$O)$_{3}$]$_{n}$), its molecular dipole moments may be estimated from the synergistic effects of the molecular dipole moments of the individual components. In the “SHG-OFF” state, the C atoms and N atoms of the organic dabco cation are distributed between two positions related by the centre of symmetry. Meanwhile, the inorganic [FeCl$_{3}$(H$_{2}$O)$_{3}$] component is located on the mirror plane due to the symmetry requirement. Consequently, the molecular dipole moments of the organic H$_4$Dabco-2Cl component and the inorganic [FeCl$_{3}$(H$_{2}$O)$_{3}$] component are cancelled out, resulting in the vanishing SHG activity of 1 (as shown in Fig. 6a). However, in the “SHG-ON” state of the LTP, the organic dabco cations are frozen to be ordered and all atoms can be exclusively determined, in which all of the atoms are crystallographically inequivalent. At the same time, a concomitant remarkable reorientational displacement occurs in the inorganic [FeCl$_{3}$(H$_{2}$O)$_{3}$] component. Accordingly, the Cl anions,
the Fe(III) centre ion, and N atoms are displaced from their equilibrium positions and the molecular dipole moments will be generated in the two individual components (Fig. S7 and S8, ESI†). For the H₂dabco-2HCl species, N and Cl atoms were displaced from their equilibrium sites by a magnitude of $-0.0046 \times |\mathbf{b}|$ and $0.0096 \times |\mathbf{b}|$, respectively. Furthermore, we assume that the dipole centres are located at the average protonated N of the dabco cation and the average two uncoordinated Cl atoms. The molecular dipole moment of the organic species was calculated to be $0.716 \times 10^{-29} \text{C m}$; for the inorganic $[\text{FeCl}_3(\text{H}_2\text{O})_3]$ component, due to the more pronounced deviation of the Fe(III) centre ion and the Cl₂ ion from their equilibrium sites ($-0.0061 \times |\mathbf{b}|$ and $-0.1428 \times |\mathbf{b}|$, respectively), larger molecular dipole moments of the inorganic species are obtained (−$11.1 \times 10^{-29} \text{C m}$). Finally, a large molecular dipole moment of 1 was achieved ($-10.3 \times 10^{-29} \text{C m}$), resulting in a relatively large SHG signal (Fig. 6b). Hence, the SHG switching of 1 may be assigned to the ionic displacements, triggered by organic cationic orderings coupled with the reorientation displacements of the inorganic $[\text{FeCl}_3(\text{H}_2\text{O})_3]$ sheet.

Conclusions

In summary, a high-performance NLO switch based on an organic–inorganic hybrid co-crystal complex has been firstly reported. It exhibits an attractive NLO switching performance with a moderately large NLO response of $\sim 0.31 \text{ pm V}^{-1}$, a superior contrast of $\sim 25$ and a highly tunable repeatability, induced by the reversible solid-state phase transition. These results make 1 a promising material for a prospective NLO switch. Furthermore, the origin of NLO switching is induced by the coupling of the order–disorder transformation of the organic cation and the reorientational displacements of the inorganic $[\text{FeCl}_3(\text{H}_2\text{O})_3]$ component. Considering the structural diversity and tunability, inorganic–organic compounds afford abundant room for exploring new solid-state NLO switches. For instance, one can utilize $\pi$-conjugated charge-transfer dipoles to induce large molecular hyperpolarizability, as well as NLO effects. It is believed that such delicate chemical modifications will provide potential to construct new high-performance NLO switches.

Acknowledgements

This work was supported by NSFC (21525104, 21222102, 91422301, 21373220, 51402296, 21571178, 51502288, 51502290, 21171166 and 21301172), the NSF for Distinguished Young Scholars of Fujian Province (2014J06015), the NSF of Fujian Province (2014J01067, 2014J05068 and 2015J05040), and the Youth Innovation Promotion of CAS (2014262, 2015240, 2016274). Z.S. and S.Z. thanks the supports from “Chunmiao Projects” of Haixi Institute of Chinese Academy of Sciences (CMZX-2013-002 and CMZX-2015-003).

Notes and references


