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COMMUNICATION

A host-guest inclusion compound for reversible switching of quadratic nonlinear optical properties

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Chengmin Ji, Zhihua Sun, Shuquan Zhang, Sangen Zhao, Tianliang Chen, Yuanyuan Tang, Junhua Luo*

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A host-guest inclusion compound [(DPA)(18-crown-6)]ClO₄ (DPA = Dipropylamine) undergoes a reversible phase transition at 214 K, which enables it to switch the NLO response between SHG-ON and SHG-OFF states associated with the order-disorder transition of the guest DPA cations and a slight tilting of the host 18-crown-6 molecules.

Recent years have witnessed a growing interest in the research of controllable nonlinear optical switch materials (NLO switch) due to the potential for practical applications in electronics and optics.¹ Reversible switching of quadratic nonlinear optical activity (i.e., second harmonic generation, SHG) between SHG-ON and SHG-OFF states with an appropriate external stimuli such as light, heat, pH, electricity, will no doubt broaden the application of the NLO materials in the fields of photo-switching, biosensors, data storage, etc.² To date, in most cases, much of the attention for the NLO switch has been focused on chemical modification (e.g. redox process, protonation, or ion capture trapping) in liquid phase.³ NLO switch materials in the solid state that are able to alternate, however, are much more scarce.

Generally, a necessary requirement for a quadratic NLO switch material is that it should be non-centrosymmetric (NCS) phase at SHG-ON state and centrosymmetric (CS) phase at SHG-OFF state. Therefore, it is always a critical issue about how to achieve the reversible transition of the NLO optical activity between SHG-ON and SHG-OFF states with changing crystallographic symmetry. To our best knowledge, host-guest inclusion compounds represent a very promising class of molecule functional materials which have been widely studied for the fascinating properties induced by the delicate host-guest interaction.⁴ Particularly, host-guest aggregation, in which a reversible phase transition was driven by the external stimuli, enabling it to change the crystallographic symmetry, recently, has been employed in modulating the magnetic and electronic order.⁵ However, there are much less attention on the solid molecule NLO switch materials in host-guest inclusion compounds with reversible phase transition. 18-crown-6 (18-crown-6 = 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane) molecule is a good candidate for host-guest compounds

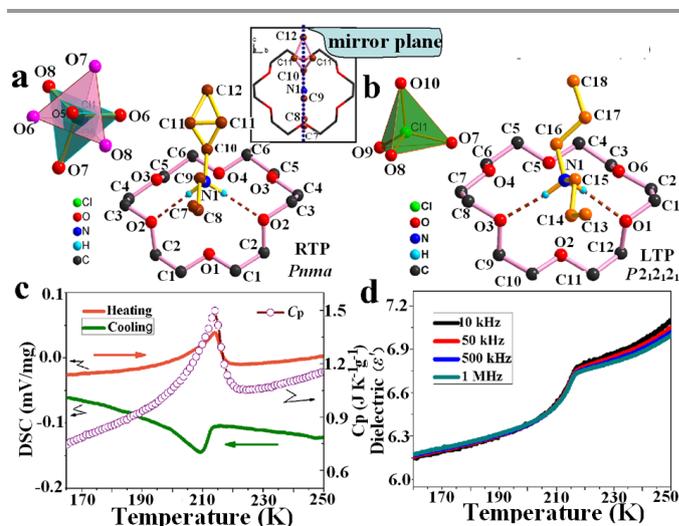


Figure 1. Structural unit of **1** in (a) room-temperature phase (293 K, RTP) and (b) low-temperature phase (100 K, LTP). (c) Temperature dependence of DSC and heat capacity (C_p) curves obtained on heating/cooling process. (d) Temperature dependence of dielectric constant at different frequencies.

assembly, where the 18-crown-6 part acts as a host and the six O atoms afford lone-pair electrons to be capable of anchoring a suitable guest molecule or ion in its cavity.⁵⁻⁶ Moreover, the guest molecules can frequently undergo rotation/twisting motions or local distortion behaviours, affording an opportunity to arouse a rearrangement of the molecule dipole associated with crystallographic symmetry change and the NLO activity switch, which will pave a new way to design the novel host-guest molecule NLO switch materials.^{6(a)}

Here, a host-guest supramolecular inclusion [(DPA)(18-crown-6)]ClO₄ (**1**, DPA = Dipropylamine), as a novel host-guest molecule NLO switch material, has been successfully assembled by the 18-crown-6 host molecule and DPA guest cation via strong N–H \cdots O hydrogen-bond interactions (Fig. 1), in which the DPA cation undergoes an order-disorder transition,

resulting in a CS-NCS structural phase transition and NLO switch property. The reversible structural phase transition with a significant NLO activity switching behaviour has been confirmed by the thermal analyses, variable-temperature (VT) dielectric experiments, VT crystal structure measurements and VT-SHG measurements.

Thermal analyses including differential scanning calorimetry (DSC) and specific heat capacity (C_p) were first carried out on the polycrystalline samples of **1** in order to probe the phase transition. DSC measurement shows a pair of peaks around 214 K on cooling and heating process [Fig. 1(c)]. The reversible endothermic and exothermic peaks with little thermal hysteresis reveal the reversible second-order phase transition. Moreover, the broad specific heat capacity peak at 214 K, suggesting the continuous characteristics, further confirms the features of a typical second order phase transition.^{6(a)} An entropy change ΔS is estimated with a value of $4.69 \text{ J K}^{-1} \text{ mol}^{-1}$. Given that $\Delta S = R \ln N$, it is found that $N = 1.76$, indicating the uncomplicated disordered-ordered phase transition originating from freezing of the thermal motion within the host-guest inclusion compound, which accords with XRD structure analyses mentioned below. Temperature-dependent dielectric constant measurements of **1** reveal relatively obvious dielectric anomalies at about 214 K upon the heating process, basically being consistent with that of thermal analyses [Fig. 1(d)]. The dielectric constant remains about 6.2 below the T_c and displays a pronounced step-like increase up to about 6.8 around T_c , further strongly suggesting the reversible phase transition.⁷

The crystal structures of **1** at 293 K (RTP) and 100 K (LTP) both crystallize in orthorhombic crystal system while crystal symmetry transforms from a centrosymmetric space group of $Pnma$ in the RTP to a non-centrosymmetric one of $P2_12_12_1$ in the LTP as shown in Fig. 1. In the RTP, the crystal structure consists of host 18-crown-6 molecules and guest DPA cations with ClO_4^- as counterpart anions. The DPA cation is situated in the cavity of the well-ordered 18-crown-6 via strong $\text{O-H} \cdots \text{N}$ (2.916 Å) hydrogen bond interactions between oxygen atoms of the crown ether and nitrogen atoms of the $(-\text{NH}_2)^+$ group in DPA. The counteranion ClO_4^- is disordered over two discrete orientations and the Cl atom is located on the inversion center. As shown in Fig. S2, the DPA cations and 18-crown-6 molecules were arranged alternately along the a/c -axis direction from packing views. Although the $(-\text{NH}_2)^+$ group almost fixes in the center cavity of the 18-crown-6 ether by the hydrogen bond interactions, the cation above the phase transition temperature is disordered with C11 existing in two equilibrium occupations, which leads to a related dynamic behaviour and creates a crystallographic m mirror plane, while N1, C7, C8, C9, C10 and C12 were located on the common m mirror plane. Therefore, the whole cation, in the RTP, looks like a pendulum or swings from side to side along b -axis as shown in inset of Fig. 1(a). The 18-crown-6 molecule is also located on the special position with mirror symmetry. Due to the steric hindrance between the skeleton of the 18-crown-6 molecule and the DPA cation, the 18-crown-6 molecule adopts a boat-shaped configuration that is different from the usual symmetrical disk-shaped structure.⁸

The crystal structure of **1** at 100 K was measured in order to investigate the phase transition related to the CS-NCS symmetry transformation. Although the lattice parameters at 100 K are almost the same as those at 293 K (Table S1), the mirror symmetry in the (010) plane is lost and a non-centrosymmetric space group $P2_12_12_1$ is adopted for the low-temperature structure [Fig. 1(b)]. The thermal vibration

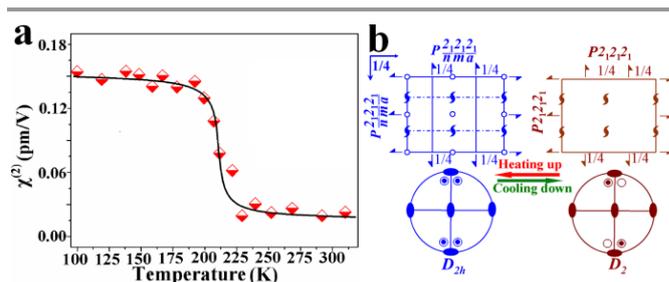


Figure 2. (a) The temperature-dependence of the SHG effect measured in the powdered state of **1** clearly showing that below T_c , the SHG effect is active, while above T_c , the SHG effect is zero. (b) Symmetry breaking change diagram from point group D_{2h} to D_2 with a loss of four symmetric elements.

parameters of all atoms at 100 K are obviously smaller than those found at 293 K (Table S3 and S4), which means the motions of all molecules are almost frozen. As expected, the disordered DPA moiety turns from disorder to order with the temperature decreasing and all atoms can be exclusively determined. In addition, the geometry configuration of the DPA clearly changes with obvious distortion of the carbon chain due to the inherent flexibility of the chain-type configuration. As shown in Fig. S3, in LTP, the ordered DPA cation deviates from its previously ideal symmetric positions with a distinct twisting along b -axis direction, supported by the change of torsion angles for C–C–C–N. Whilst it is clearly seen that the counteranion ClO_4^- in the molecule becomes totally ordered in LTP from the serious disordered state in RTP.

Variable-temperature second harmonic generation (VT-SHG) measurements were performed by applying the Kurtz and Perry model to polycrystalline sample of **1** ($\lambda = 1064 \text{ nm}$, Nd:YAG pulsed laser).⁹ Results of Fig. 2(a) present the VT-SHG digital signals of **1** converted from the photoeffects. Above 214 K, SHG signal is completely obliterated, with the effective second-order nonlinear optic susceptibility $\chi^{(2)}$ basically being of zero and remaining stable and monotonous in accord with the CS structure in RTP. However, with the temperature decrease, the SHG effect gradually becomes active, exhibiting a nonzero $\chi^{(2)}$ in the vicinity of the phase transition temperature (T_c), which suggests that the crystal of **1** becomes NCS in LTP. Upon further cooling to exceed T_c , a step-like jump of SHG signal was observed, reaching a saturation value approximately 0.3 times that of KH_2PO_4 (KDP); namely, the quadratic NLO coefficients of **1** are estimated to be 0.15 pm V^{-1} (KDP, 0.39 pm V^{-1}).¹⁰ Unambiguously, the VT-SHG results revealed the controllable switching ability on quadratic NLO activity between SHG-ON and SHG-OFF states, associated with CS-NCS crystalline symmetry transformation triggered by the reversible structural phase transition as shown in X-ray diffraction analyses, DSC and VT dielectric constant measurements. To our best knowledge, [(DPA)(18-crown-6)] ClO_4 is the first example of molecule NLO switch material with host-guest architecture through flexible aliphatic amine cations and 18-crown-6 molecule and this finding clearly points out a new avenue to assemble the NLO switch material. In order to further understand the relationship between NLO switching ability and the crystalline symmetry transformation, the symmetry breaking phenomenon with the reversible phase transition between HTP and LTP were analyzed. As shown in Fig. 2(b), the eight symmetric elements (E, C_2 , C_2' , C_2'' , i , σ_h , σ_v , σ_v') in HTP are halved into four (E, C_2 , σ_v , σ_v') in LTP in the phase transition. The loss of the inversion symmetry from the

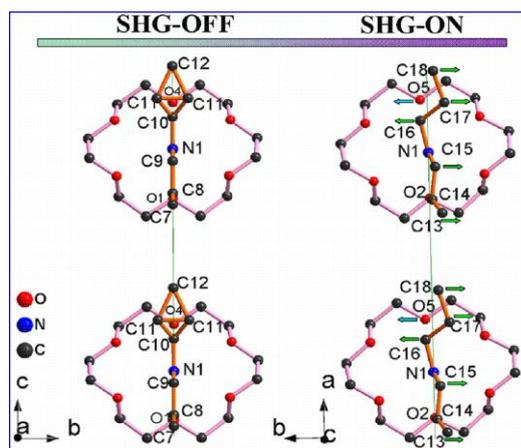


Figure 3. Schematic diagram of the SHG switching process in **1**. Atomic disordering result in the loss of NLO activity in the RTP, while the outline arrows illustrate the atomic displacement of DPA cations and a slight tilt of 18-crown-6 molecules in the “SHG-ON” state.

view of symmetry breaking, which is initially ascribed to the ordering of the partial component in the molecule, results in a NCS phase accompanied with a significant NLO response generation in LTP.

While, the simple salt without the 18-crown-6, (DPA)ClO₄ (compound **2**), displays rather different phase transitions from **1**. As shown in Fig. S4, **2**, shows two successive reversible phase transitions at 151 and 249 K. However, all of the crystal structures of **2** in the three phases crystallize in the centrosymmetric point group of *D*_{2h} without any dynamic disorder for DPA, and there is not a NLO response generation in this sequential phase transition.

It is believed that the quadratic nonlinear optical effect should be associated with the local distortion of the building unit in the crystal structure,¹¹ which is closely related to atomic relative displacements. Therefore, there is a necessary to investigate the origin of the NLO switching activity from the viewpoint of atomic displacements for **1**. Assuming the dipole centers are located on the mirror plane paralleled to *ac* plane. As shown in Fig. 3, in the RTP, the centrosymmetric requirement is satisfied by the orientational disordering of the DPA cation through the mirror plane and the displacement vector of the carbon atoms achieves a general balance, resulting in a vanished SHG activity. However, in the “SHG-ON” state of LTP, the molecules become more ordered and DPA chain show a clearly distorted geometry configuration with the C atoms of DPA deviating from their equilibrium or symmetric sites along *b*-axis with the deviation values of $\Delta d_{(C13)} = 0.5526$, $\Delta d_{(C14)} = 0.1251$, $\Delta d_{(C15)} = 0.2805$, $\Delta d_{(C16)} = 0.3129$, $\Delta d_{(C17)} = 0.7353$ and $\Delta d_{(C18)} = 0.2886$ Å, respectively. A nonzero deviation vector sum along *b*-axis is achieved, which breaks the symmetrical balance and creates a NCS organization in **1**, unambiguously resulting in the SHG switching signals. For the 18-crown-6 molecule, in addition, it is noteworthy that there is a slight tilt resulting in O5 (corresponding to O4 in RTP) deviating from the symmetric plane by the magnitude of $\Delta d_{(O5)} = 0.3283$ Å, which synergistically facilitates the generation of molecule dipole moments and simultaneously contribute to the SHG response as well as DPA cations.

In summary, we have presented a novel NLO switch material, [(DPA)(18-crown-6)]ClO₄, with a host-guest architecture through guest flexible aliphatic amine cations and host 18-

crown-6 molecules. A significant switching capacity of SHG response has been demonstrated, which is associated with the reversible NCS-CS solid-state phase transition at 214 K in **1**. SHG switching signals result from the generation of nonzero molecule dipole moment induced by the order-disorder transition and distortion behaviour of the DPA cations. In addition, a slight tilt of the host 18-crown-6 molecule was synergistically in support of the NLO switching activity. It is believed that, all these findings point out a new avenue to explore and design novel molecule NLO switch materials by constructing host-guest phase transition inclusion compounds.

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Notes and references

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) 0591483730955. Tel: (+86) 0591483730955.

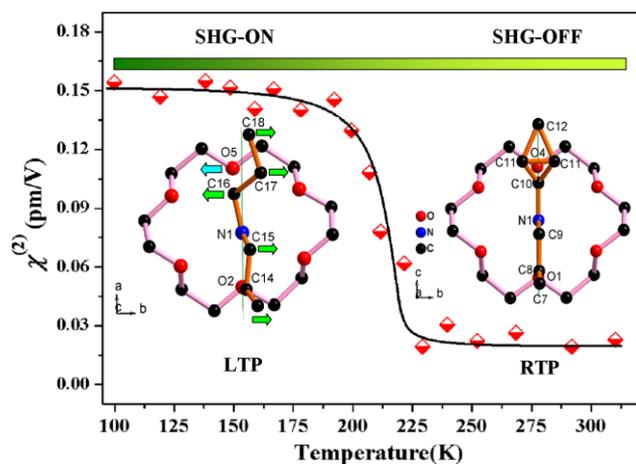
† Electronic Supplementary Information (ESI) available: The experimental details and characterizations. CCDC 1028137-1028141. For ESI and crystallographic date in CIF or other electronic format see DOI: 10.1039/c000000x/

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Table of Contents

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