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Molecular design of high-temperature organic dielectric switches[†]

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A design strategy of reducing the molecular symmetry was used to obtain a series of picrate-based high-temperature phase transition compounds. Their dielectric switching behaviours accompanied by phase transitions can be attributed to the order-disorder transitions of the cations and the displacements of both cations and anions.

Switchable dielectrics, undergoing transitions between different dielectric states, have captured great interest owing to their potential applications in data communications, sensing, signal processing, and rewritable optical data storage, etc.¹⁻³ Essentially, the switching of the dielectric constant at the phase transition temperature $(T_{\rm tr})$ is caused by the motional changes of polar moieties, such as order-disorder transformations and orientational motions.⁴⁻⁷ Until now, it is the inorganic materials that mainly dominate the dielectrics market, although most inorganic materials are of high-cost, require high-temperature processing and are environmentally unfriendly. As a matter of fact, organic materials possess the advantages of light weight, metal free nature, mechanical flexibility, structural diversity, low cost and easy processing, and could be potential alternatives or supplements to inorganic dielectric materials.8 These properties allow organics to hold a great potential for materials science and technology applications. Nevertheless, organic switchable dielectric materials are rarely reported so far. Due to the lack of knowledge about control over the dipole motions, it is still nontrivial to find several obviously different dielectric states in a dielectric material. Experimentally, flexible moieties, whose motional states are susceptible to temperature, have been introduced to materials to bring about structural phase transitions and switchable dielectric properties, such as [Hdabco]⁺ (dabco is 1,4diazabicyclo[2.2.2]octane) and $[(CH_3)_4N]^+$ cations, or $[ClO_4]^-$ and picrate anions (picrate is trinitrophenolate).9,10 Research studies

on picrate-based phase transition materials are scarce, but have made significant progress recently. For example, Sun *et al.* reported a bi-step structural phase transition compound, *N*-methylcyclohexylamine picrate, which exhibits remarkable switchable quadratic NLO properties around 240 K.¹¹ More recently, *N*-methylmorpholinium picrate was also discovered to possess the fastest room-temperature switching of polarization (263 kHz) among organic ferroelectrics.¹² Unfortunately, the relatively low T_{tr} of both compounds may be unfavourable for their practical device applications, which is still a common hindrance to the development of molecular dielectrics.

Phosphonium ions possess similar structures to ammonium ions, but are rarely used to construct molecular phase transition materials. Compared with the N atom, the heavier P atom may make the potential energy barrier of cation motion higher, so replacing the ammonium with a phosphonium cation might be a good way to improve T_{tr} .^{13,14} Therefore, the $[(CH_3)_4P]^+$ cation, as an analogue of the $[(CH_3)_4N]^+$ cation, was chosen initially to obtain tetramethylphosphonium picrate (1). It does exhibit a phase transition, while its $T_{\rm tr}$ is just at room temperature. In order to further increase the potential energy barrier of molecular motion and then tune the $T_{\rm tr}$, we proposed to replace a methyl group of $[(CH_3)_4P]^+$ with a longer side-chain to disturb its spherical symmetry. Herein, we successfully synthesize four high- T_{tr} picrate-based organic salts: propyl-trimethyl-phosphonium picrate (2), methoxymethyl-trimethyl-phosphonium picrate (3), allyl-trimethyl-phosphonium picrate (4) and (2-hydroxy-ethyl)trimethyl-phosphonium picrate (5) (Scheme 1). They display structural phase transitions and switchable dielectric behaviours at 367 K, 393 K, 352 K and 347 K, respectively. After modifying the phosphonium cations, their $T_{\rm tr}$ all get greatly improved, being much higher than those of the reported picrate salts and 1. Such a molecular design strategy of reducing the molecular symmetry of the cations opens a new pathway to explore high-temperature organic dielectric switches. Besides, the switchable quadratic NLO properties observed in 5 near $T_{\rm tr}$ suggests its potential application as a dual-switching material.

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Scheme 1 Chemical structures of the (a) propyl-trimethyl-phosphonium, (b) methoxymethyl-trimethyl-phosphonium, (c) allyl-trimethyl-phosphonium, (d) (2-hydroxy-ethyl)-trimethyl-phosphonium cations in **2–5**, respectively.

Yellow crystals of 1-5 were obtained by the evaporation of a mixed acetonitrile aqueous solution containing an equimolar amount of picric acid and the respective phosphonium halide at room temperature. Infrared spectra and powder X-ray diffraction (PXRD) measurements confirm the phase purities of 1-5 (Fig. S1, S2 and S8, ESI⁺). Differential scanning calorimetry (DSC) measurements were performed to detect the phase transitions. As shown in Fig. 1 and Fig. S1 (ESI⁺), pairs of endothermic/exothermic peaks were observed at 305/293 K (T_{tr1}), 367/348 K (T_{tr2}), 393/370 K (T_{tr3}), 352/325 K (T_{tr4}) and 347/298 K (T_{tr5}) upon heating/cooling process for 1-5, respectively, indicating the reversible phase transitions. It is clear that 2–5 all exhibit higher $T_{\rm tr}$ than 1, indicating that the design strategy works. Despite the similar shape and size of the cations in 2–5, the different $T_{\rm tr}$ values suggest that the variation of the side-chain could make a distinct difference in the thermal properties. The corresponding thermal hystereses of 2-5 are observed at 19, 23, 27 and 49 K, respectively, indicating the first order characteristic of these transitions.¹⁵ The large enthalpy changes (ΔH) and entropy changes (ΔS) are shown in Table S1 (ESI⁺), implying severe structural transformations during the phase transition. For convenience, the phases below and above $T_{\rm tr}$ are designated as α phase and β phase, respectively.

To reveal what differences the side-chain will make in the crystal structures, single-crystal X-ray diffraction analyses were performed on 2–5 at room temperature (α phase). In the α phase, both 2 and 3 crystallize in the monoclinic space group $P2_1/c$ (point group 2/*m*). The –CH₂OCH₃ group in 3 is a little shorter than the –CH₂CH₂CH₂ group in 2 (for bond lengths and



Fig. 1 DSC curves of 2 (a), 3 (b), 4 (c) and 5 (d).

angles see Table S4, ESI[†]), while the two have similar flexibility, resulting in the isostructure. When the methyl group of the $[(CH_3)_4P]^+$ cation is replaced with an allyl, 4 crystallizes in the orthorhombic space group *Pcab* (point group *mmm*). The -CH₂CH=CH₂ group is more rigid and shorter than the -CH₂OCH₃ and -CH₂CH₂CH₃ groups, and consequently, 4 shows a higher crystallographic symmetry compared to 2 and 3. As for 5, its second harmonic generation (SHG) activity at room temperature (*vide infra*) helps to define it in the noncentrosymmetric space group *P*1 (point group 1). It is the one with the lowest symmetry among the four compounds.

The asymmetric units of 2-4 all contain one phosphonium cation and one picrate anion, while 5 contains two inequivalent phosphonium cations and two picrate anions (Fig. S3, ESI⁺). For the picrate anion of 2, the oxygen atoms of the para-NO₂ group are located on the benzene ring plane, while those of the ortho-NO₂ groups deviate away from the benzene ring plane, especially the O6 and O7 atoms. Similar conformations of picrate anions were also found in 3-5 and other picrate salts.^{11,16} The picrate anions of 2, 3 and 5 arrange into planar layers alternately stacking in an ABAB... sequence, while those of 4 arrange into a set of zig-zag sheets perpendicular to the a-axis (Fig. 2 and Fig. S4-S6, ESI†). This indicates that the rigidity of the side-chain has a significant effect on the molecular geometries. For 2, the adjacent picrate anions from the A and B layers adopt antiparallel orientations, among which the obvious $\pi - \pi$ stacking interactions (Cg-Cg: $d_1 = 3.5977$ Å and d_2 = 3.5025 Å, C_g is the centroid of the benzene ring) were found, forming one-dimensional infinite anion chains extending along the *a*-axis. These chains are surrounded and connected by the propyl-trimethyl-phosphonium cations via weak C-H···O hydrogen bond interactions. The π - π stacking interactions also exist in 3-5, and the corresponding distances are depicted in Fig. S5, S6 (ESI[†]) and Fig. 2. Different from 2–4, the π - π stacking interactions in 5 are intermittent and exist only between each pairs of the neighbouring A and B layers (C_g - C_g = 3.4887 Å). The introduction of 2-hydroxy-ethyl groups gives rise to O-H···O hydrogen bonds between the O atoms of the (2-hydroxy-ethyl)trimethyl-phosphonium cations and the O1 atoms of the picrate anions in 5 (d_{O-O} = 2.760 Å), forming hydrogen-bonding dimers. Sometimes, the formation of a strong hydrogen bond between molecules with well-matched proton affinities might be a useful strategy for designing molecular functional dielectrics.^{17,18} To sum up, the variation of the side-chain results in quite a different structure.

Although the structures of 2–5 in the α phases are clarified well, their structures in the β phases are hard to determine due to their weak diffraction at high temperature. The structure of 5 in the β phase was roughly refined at 353 K to depict the structural changes, which could help understand the origins of the phase transitions in this series of compounds. At 353 K (5 β phase), 5 transforms to a centrosymmetric orthorhombic space group *Cmcm* (point group *mmm*), and the thermal ellipsoids of all atoms are much bigger than those of the 5 α phase, demonstrating the severe molecular motions at high temperature (Fig. S3, ESI†). The relationship of the unit cell axes is $a^{5\alpha}$ (10.232(2)) $\approx a^{5\beta}$



Fig. 2 (a) Packing view of the 2α phase along the *a*-axis and π - π stacking interactions. (b) Planar picrate anions layers in the 2α phase. (c) The zig-zag anion sheets in the 4α phase. (d) Packing view of the crystal structure of 5α , showing the layered structure. The cell edges of the 5α and 5β phases are drawn in black and pink, respectively. For the cations, only P atoms are drawn for clarity. (e) π - π stacking interactions along the *c*-axis in the 5α and 5β phases. For each compound, the anions are drawn in two colours to show the neighbouring sheets A and B, respectively, and the cation adopts the same colour as that of its nearest anion sheet. All hydrogens are omitted for clarity.

 $(11.5686), b^{5\alpha}(9.883(2)) \approx a^{5\beta/2} + b^{5\beta/2}(11.5684), c^{5\alpha}(8.5961(17)) \approx$ $c^{5\beta}$ (7.0578), and the unit cell angles of 102.92(3)°, 99.20(3)° and $68.34(3)^{\circ}$ in the 5 α phase correspond to those of 90.000° , 90.000° and 60.000° in the 5 β phase, respectively. The significant change of the unit cell is due to the tilting of the picrate anions and the shifts of the cations as shown in Fig. S7 (ESI⁺). The most obvious structural changes take place in the stacking pattern of the picrate anions, which are neatly lined up along the *c*-axis after the phase transition. Consequently, the intermittent π - π stacking interactions become successive in the 5 β phase (C_g-C_g = 3.5294 Å), leading to the shrinkage in cell parameter c (Fig. 2e). Similar changes of the molecular stacking patterns occur in 7,7,8,8tetracyanoquinodimethane-p-bis(8-hydroxyquinolinato)copper(II) accompanied by dimensional changes under mechanical stimulation.¹⁹ The rearrangement of the anions in 5 should be aroused by the highly disordered motions of the (2-hydroxyethyl)-trimethyl-phosphonium cations at high temperature, which are the main driving force for the phase transition. Due to the difficulties in obtaining the complete crystal structures of the β phases, variable-temperature PXRD measurements were performed on 2-5 to further verify the phase transitions (Fig. S8, ESI[†]). Upon increasing the temperatures above the phase transition points, some diffraction peaks vanish and new peaks emerge in the β phases compared with the data obtained at 293 K. And the significant decreases in the numbers of peaks in the measured PXRD patterns was found, demonstrating the higher symmetries of the crystal structures at high temperature.²⁰ These changes confirm the occurrence of the phase transitions, agreeing well with the DSC and structural analyses. The possible cell parameters and space groups of the 2β , 3β and 4β phases suggested by the indexing of the PXRD patterns and Pawley refinement are listed in Table S3 (ESI[†]).

Generally, the presence of the pseudo center of symmetry always makes the crystal symmetry difficult to be accurately determined. Thus, the SHG effect that cannot exist in the 11 centrosymmetric point groups is an effective supplementary method to detect inversion symmetry breaking.²¹ At room temperature, 2-4 are not SHG-active, while 5 shows SHG signals approximately 0.4 times that of potassium dihydrogen phosphate (KDP), manifesting its non-centrosymmetric crystal structure in the 5α phase.²² Variable-temperature SHG measurements were performed on 5 within 250-388 K. As shown in Fig. 3, upon heating, the SHG signals maintain a relatively stable value until about 340 K (SHG-ON state), then a step-like collapse appears and the SHG signals are negligible above 352 K (SHG-OFF state). Moreover, the SHG signals obtained upon cooling show a reversible change and almost recover to their previous value below 300 K. The reversible thermal-induced 'on-off' SHG switching makes 5 to be a promising candidate as a solid-state SHG switch. The whole SHG curve upon a heating and cooling cycle exhibits a SHG bistability with a large hysteresis window of ~ 50 K.

Considering that the dielectric constant ε ($\varepsilon = \varepsilon' - i\varepsilon''$, where ε' is the real part and ε'' is the imaginary part) is sensitive to structural changes, 2–5 are expected to exhibit interesting dielectric responses with the phase transitions. As illustrated in Fig. 4, the values of ε' for 2–5 are around 5.0 at 1 MHz and change little below T_{tr} , corresponding to the α phases and the low dielectric states. Then, they all display a fast increase near 364 K for 2, 393 K for 3, 352 K for 4 and 345 K for 5 upon heating, which is in good agreement with the DSC results mentioned above. The ε' quickly reaches a high value and increases slowly with the increase of the temperature in the β phases (high-dielectric states), corresponding to a step-like dielectric switching behaviour.^{5,23} For 2, the value of ε' increases from



Fig. 3 Temperature dependence of the SHG effects of 5 (inset: oscilloscope traces of SHG signals for 5 and KDP).



Fig. 4 Temperature dependence of the real part of the dielectric constant of 2 (a), 3 (b), 4 (c) and 5 (d).

6.2 at 358 K to 18.2 at 367 K, that is, it undergoes a 2.9-fold increase after the phase transition. For 3–5, the changes of ε' near $T_{\rm tr}$ are 4.2, 3.2 and 2.8 times, respectively. Such large changes are closely associated with the severe structural changes during the phase transitions. The temperature-dependent ε' and dielectric loss ($\tan \delta = \varepsilon''/\varepsilon'$) of 2–5 at 100 and 1000 kHz are depicted in Fig. S9 (ESI†). It can be seen that the phase transition temperatures almost show no change under different frequencies, *i.e.*, no relaxation in the measured frequency range, manifesting the fast motions of dipoles.²⁴ Additionally, the ε' -switching of 5 exhibits a high repeatability with at least six cycles (Fig. S10, ESI†). And the different electrode (Ag or C) and electrode area have little effect on the dielectric switching of 5 (Fig. S11, ESI†).

In conclusion, by reducing the molecular symmetry of the tetramethylphosphonium cations, four high- T_{tr} organic dielectric switches are successfully obtained. The high T_{tr} will facilitate the practical utilization of these materials. The structural phase transitions and switchable dielectric behaviours of this series of compounds are supposed to rely on the order–disorder transitions of the cations and the concomitant displacement of both cations and anions. Meanwhile, (2-hydroxy-ethyl)-trimethyl-phosphonium picrate exhibits switchable SHG behaviour. This work provides a new way to design high-temperature phase transition materials by the symmetry reduction of spherical moieties, and will promote the exploration and construction of switchable materials.

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Conflicts of interest

There are no conflicts to declare.

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