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A reversible phase transition and dielectric anomaly in a spherical molecule [(3,2,1-dabco)<sub>2</sub>PbBr<sub>6</sub>]

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#### Abstract

Organic-inorganic hybrid materials were attracted most interests due to their potential applications in phase transition and photoelectric fields. Within this context, a spherical molecule 1, 5-diazabicyclo[3,2,1]octane (3,2,1-dabco) was used to react with PbBr<sub>2</sub> in concentrated HBr acid and led to a discrete organic inorganic hybrid compound [(3,2,1-dabco)<sub>2</sub>PbBr<sub>6</sub>] (1). Thermodynamic DSC analyses and dielectric measurement of 1 showed an apparently reversible phase transition at about 427 K. The variable temperature X-ray single crystal diffraction demonstrated compound 1 underwent an order-disorder transition from orthorhombic to cubic systems at room and high temperatures.

**Keywords**: phase transition, dielectric anomaly, organic-inorganic hybrid, spherical molecule, crystal structure

#### Introduction

Phase transition materials can absorb or release a large amount of latent heat, and it will become the

best green environmental protection carrier for energy saving and environmental protection[1-5]. On the basis of composition, phase transition materials can be divided into inorganic and organic phase transition materials, in which inorganic materials can provide good optoelectronic properties and high thermal stability[6, 7], organic materials have an advantage on mechanical tunability and structural multiplicity[8, 9]. In order to integrate the comprehensive functions of organic and inorganic phase transition materials into one molecule, the organic-inorganic hybrid materials are attracted more attentions because they are kinds of excellent composite materials with superior optical, electrical, thermal, magnetic, and mechanical properties[10-16].

As it to know, the most common general formula of an organic-inorganic compound is ABX<sub>3</sub>, where A is an organic molecule, B is a metal, and X is a halogen[17-19]. The metal B and halogen X form octahedra [BX<sub>6</sub>] through coordination, thus 3D to 1D inorganic moieties are constructed by sharing edges or corners of octahedra[20-22]. The organic molecule A as the role of templating agents locate in cavities surrounded by  $BX_6$  octahedra or between the inorganic layers, have considerable freedom of motion, so they tend to exhibit kinetic turbulence at relatively high temperatures and become ordered as temperatures decrease, thus leading to structure reversible phase transition. This order-disorder phase transitions have been found in a substantial number of organic-inorganic hybrid materials[23-27].

According to the numbers of inorganic dimension, the organic-inorganic hybrid compounds can be divided into 3D, 2D 1D and 0D four categories[28-31]. As to 3D type, the number is scare, and the famous 3D organic inorganic hybrid perovskite structure is methylammonium lead iodide (MAPbI<sub>3</sub>), which possesses an appropriate bandgap energy and large absorption coefficient, and its photoelectric conversion efficiency (PCE) has raised from 3.9% to 23% in just few years[32]. On the other hand,

the 2D layered and 1D chain organic-inorganic hybrid compound structures are intensively reported and their processability and the adjustable structures have potential application in phase transition materials[33-37]. However, organic-inorganic hybrid materials with lower dimensions are rare and need to be further discovered and studied.

In recent years, with our in-depth research on organic-inorganic hybrid materials, a new discrete hybrid compound  $[(3,2,1-dabco)_2PbBr_6]$  with reversible phase transition was prepared by reacting a spherical molecule 1,5-diazabicyclo[3,2,1]octane (3,2,1-dabco) with PbBr<sub>2</sub> in concentrated HBr aqueous solution. Herein, we report the synthesis, characterization and phase transition of compound 1.

#### **Results and discussion**

### Preparation and phase transition

1,5-diazabicyclo[3,2,1]octane (3,2,1-dabco) was a isomer of 1,4-diazabicyclo[2,2,2]octane (2,2,2dabco), both are spherical molecules. Reaction of [3,2,1-dabco] with PbBr<sub>2</sub> gave a high phase transition temperature compound [(3,2,1-dabco)<sub>2</sub>PbBr<sub>6</sub>] (1) with relatively high yield. Compound 1 can be kept stability in air for a month. The differential scanning calorimetry (DSC) curve of 1 was shown in Figure 1. During the heating and cooling runs, compound 1 exhibited an endothermic peak at 427 K, an exothermic peak at 414 K, indicating compound 1 experienced a reversible phase transition. Notably, the observed thermal hysteresis 13 K in the heating and cooling processes represented a first-order phase transition[38,39]. The corresponding entropy changes ( $\Delta S$ ) was calculated to be approximately 12.5 J mol<sup>-1</sup>K<sup>-1</sup> for the phase transition at T<sub>c</sub> according to the records of DSC curve. Based on the Boltzmann equation,  $\Delta S = RlnN$ , (where R is the gas constant and N is the ratio of the numbers of respective geometrically distinguishable orientations), the N is calculated

to be 4.5, which suggests an ordered-disordered phase transition of the spherical [3,2,1-debaco] component in **1**. Such high transition temperatures have also been found in other organic-inorganic hybrid compound phase transition materials[40, 41].



Figure 1 The DSC curve of 1 in heating / cooling runs.

As we all know, the phase transition will be accompanied by abnormal physical properties near the phase transition point of the structure[42, 43]. The dielectric constant of **1** was measured as a function of temperature at 1 MHz frequency. As shown in Figure 2, the real part  $\varepsilon'$  and imaginary part  $\varepsilon''$  ( $\varepsilon = \varepsilon' - i\varepsilon''$ , where  $\varepsilon''$  is imaginary part of  $\varepsilon$ ) of dielectric constants of compacted pellets of polycrystalline sample **1** both show a step-like change during heating and cooling with the anomalous peak at T<sub>c</sub> = 427 K. The maximum peak in real part is more than 2 times larger than that of the peak valley. It is more effective to prove that this phase transition was corresponded to the order and disorder of [3,2,1-dabco]<sup>2+</sup> cations, which is consistent with the DSC analysis.



Figure 2. (a) Real part and (b) imaginary part of dielectric constants of 1 at 1MHz frequency in a heating / cooling run.

### Variable temperature X-ray single structure

In order to accurately analyze the origin of high phase transition, variable-temperature single X-ray diffraction analysis of **1** was performed at 298 K and 403 K respectively. The phase above T<sub>c</sub> was defined as high temperature phase (HTP) and the phase below T<sub>c</sub> as the low temperature phase (LTP). At LTP, compound **1** crystallized in the orthorhombic system, adopted centrosymmetric *Pnnm* space group (point group *mmm*) with a = 9.4410(5) Å, b = 13.3307(7) Å, c = 9.3549(4) Å, and V = 1177.36(10) Å<sup>3</sup>. The asymmetric unit contains half of the [3,2,1-dabco]<sup>2+</sup> cation and one-fourth of [PbBr<sub>6</sub>]<sup>4-</sup> anion as shown in Figure 3. The [3,2,1-dabco]<sup>2+</sup> cations are located on the 2-fold rotational axis parallel to the crystallographic *b*-axis, and the [PbBr<sub>6</sub>]<sup>4-</sup> anions are situated on the mirror plane perpendicular to the *b*-axis and a 2-fold rotational axis passes through the axis of octahedron [PbBr<sub>6</sub>]. As shown in Table 1s, in the discrete [PbBr<sub>6</sub>]<sup>4-</sup> anion, the octahedral geometry is slightly distorted with the Pb–Br bond lengths varying from 3.0141(12) Å to 3.0157(8) Å, and the bond angles in the *cis* position are at the ranges of 83.37(3)- 96.63(3)°, in the *trans* position are 180°, which are compared to the analogue[44]. Interestingly, the protonated spherical [3,2,1-dabco]<sup>2+</sup> cation exhibits ordered state, and

connected with the discrete  $[PbBr_6]^{4-}$  anion through N–H···Br hydrogen bonds. The protonated H atoms are linked to the two terminal Br atoms to give an infinite linear organic-inorganic hybrid chain along *c* direction.



Figure 3 The structure of compound 1 at LTP.

At HTP, compound **1** crystallized in the cubic system,  $Fm\overline{3}m$  space group with a = b = c = 13.4704(5)Å, V = 2444.2(3) Å<sup>3</sup>. In the structure, the [PbBr<sub>6</sub>]<sup>4–</sup> octahedron exhibited regular configuration with six Pb–Br bond lengths at 3.012(2) Å and the bond angles Br-Pb-Br in *cis* and trans positions were at 90° and 180° to satisfy the high symmetry sites. The central Pb<sup>2+</sup> ion was located on the crystallographic mirror plane, the terminal I ions are on the fourfold axis. On the contrary, the [3,2,1dabco]<sup>2+</sup> cation was located on the special high symmetry site of m3m point group, consequently required a total disorder. Because of the inconsistency between crystallographic symmetry and molecular symmetry, the [3,2,1-dabco]<sup>2+</sup> cation was modeled with a spherical structure discarding its chemical sense, Figure 4. This suggests that the cation with dynamic disorder is nearly freely rotating at the HTP, which was also observed in those with spherical geometries, such as [3-oxoquinuclidinium]ClO<sub>4</sub>[45] and [MeHdabco]RbI<sub>3</sub>[46]. Thus, the order-disorder transition of organic cation induces the phase transitions in compound **1**.



Figure 4. The structure of compound 1 at HTP

## Experimental

Synthesis: 1,5-diazabicyclo[3.2.1]octane was synthesized according to the reported literature by reactions of homopiperazine with formaldehyde aqueous solution in toluene/H<sub>2</sub>O systems at 130 °C for six hours[47]. The obtained 1,5-diazabicyclo[3.2.1]octane (0.112 g, 1 mmol) was reacted with PbBr<sub>2</sub> (0.3610 g, 1.0 mmol) in 47% hydrobromic acid solution (10.0 mL) on the heating of 60 °C for half hour, leading to the formation of white block crystals **1**, which were isolated by filtration and dried under vacuum. Yield: 0.52 g, 65%. Anal. Calcd for  $C_{12}H_{28}N_4PbBr_6$ : C 15.75, H 3.08, N 6.12%. Found: C 15.49, H 3.13, N 5.93%.

**Measurements.** The methods of DSC, dielectric experiments were described in detail previously. Intensity data of structure **1** were collected at 298 K and 400 K on a Rigaku synergy diffractometer using Mo K $\alpha$  ( $\lambda = 0.71075$  Å) radiation. The structures were solved by the direct methods and refined by full-matrix least-squares refinement base on  $F^2$  with the SHELXL program[48]. Selected crystallographic data and structure refinement are listed in Table 2s.

## Conclusion

In summary, a new discrete organic-inorganic hybrid compound  $[(3.2.1-dabco)_2PbBr_6]$  (1) exhibited a reversible first-order phase transition which was proved by DSC and dielectric constant. The variable temperature single crystal structure analysis revealed the origin of the reversible phase transition was attributed to order and disorder of spherical geometry of  $[3.2.1-dabco]^{2+}$  cation at LTP and HTP.

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## Author contributions

Zhenhong Wei designed research;

Xiuli You and Xingcong Wang performed research and solved the crystal structure.

## Declaration of Interest Statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript entitled.

Zhenhong Wei (on the behalf of all the authors)

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## Graphic abstract

A discrete organic-inorganic hybrid compound  $[(3.2.1-dabco)_2PbBr_6]$  exhibited a reversible phase transition which was originated from the order to disorder of spherical  $[3.2.1-dabco]^{2+}$  cation at RTP and HTP.



Highlights

1. A spherical molecule 1, 5-diazabicyclo[3,2,1]octane was chose to react with PbBr<sub>2</sub> to give an organic-inorganic compound.

2. The obtained hybrid compound showed a reversible phase transition.

3. The variable temperature X-ray single crystal diffraction revealed the phase transition was derived from the order and disorder of spherical molecule at room temperature and high temperature.