Inorganic–organic hybrid switchable dielectric materials with the coexistence of magnetic anomalies induced by reversible high-temperature phase transition†

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An inorganic–organic hybrid compound that features a zero-dimensional inorganic structural framework, N-methylpiperidinium tetrabromoferrate(III) (compound 1, [C6H14N][FeBr4]), has been reported as a new switchable dielectric material with the coexistence of weak magnetic anomalies. It is noteworthy that 1 demonstrates remarkable dielectric responses, which can be tuned between two distinct dielectric states and reversibly switched by phase transition at ~340 K (Tc). Its high-dielectric constants are at least 4 times as large as that of the low-dielectric state. Structural analysis reveals that 1 belongs to the monoclinic crystal system with the space group P21/c at room temperature, but transforms into an orthorhombic system with the space group Cmcm above Tc. The disordering of organic cations affords a driving force for high-temperature phase transition in 1 along with its switchable dielectric activities. Besides, weak magnetic anomalies were also found in 1 at the vicinity of its Tc, which should be reminiscent of another possible physical channel to the phase transition. This finding suggests that 1 might be a potential multifunctional material with the coexistence of switchable dielectric bistability and magnetic responses, which opens up new possibilities to develop molecular functional materials.

Introduction

Physical properties of stimuli-responsive materials are highly sensitive to external stimuli such as temperature, light, press, electric and magnetic fields, etc. 1 In particular, the switching of bulk properties between at least two distinct states through multiple physical channels has potential applications as sensors, signal processing and memory devices. 2 Among them, switchable dielectric compounds, of which the dielectric constants can be converted between the low and high states, have taken an emerging position in the field of stimuli-responsive materials. 3 The dielectric constant of silicon nitride (~7) is usually used as a boundary between the high-dielectric and low-dielectric materials. Hence, the switching of dielectric constant in this vicinity will be of particular interest. 4 Because the dielectric constant or the electric permittivity \( \varepsilon' (\varepsilon = \varepsilon' - j\varepsilon'') \), where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts, respectively depends on the degree of electric polarizability, the dipolar motions such as molecular rotations play a significant role in the switching of the dielectric effect. 5 From the microscopic viewpoint of structure, the switchable dielectric constants can be achieved through the reorientation of polar components between static (frozen) and dynamic (motional) states. 6 However, it still remains difficult to chemically assemble both static and dynamic components together into crystals, because complicated interactions might exert resistance on the free motions of dynamic parts. 7

Among various stimuli, temperature behaves as the most frequently used and easily controlled trigger. 8 In this context, thermally-induced phase transition compounds have shown great potential as promising switchable dielectrics, and their physical responses display abrupt changes in the vicinity of phase transition. 9 For instance, the hybrid multiferroic material of triethylmethylammonium tetrabromoferrate(III), which undergoes paraelectric-to-ferroelectric phase transition, was found to show switchable dielectric responses with the coexistence of magnetic anomalies. 10 Furthermore, introducing the polar or flexible structural moieties into functional blocks probably leads to switchable dielectric activities, as well as other functional responses. Wang et al. has reported a series of well-designed...
perovskite-type compounds \([\text{[(CH}_3\text{)}_n\text{NH}_4\text{…n}][\text{Mn(N}_3\text{)}_3]] (n = 1–4)\) which combine dielectric phase transition and magnetic ordering properties. These materials showing electric and magnetic ordering are of great significance because of their potential applications in dynamic random access memories, data storage media, telecommunication systems, and electromagnetic sensors.

Encouraged by such results, we reported here an inorganic–organic hybrid compound, \(N\)-methylpiperidinium tetrachloroferrate(III) (compound 1, \([\text{C}_6\text{H}_{14}\text{N}[\text{FeBr}_4]]\), which features a zero-dimensional (0-D) inorganic structural framework. It is interesting that 1 shows remarkable dielectric responses that can be switched by phase transition at \(\sim 340\ K (T_c)\). Variable-temperature structural analyses reveal that 1 belongs to the monoclinic crystal system with the space group \(P2_1\text{/c}\) at room temperature, which transforms into the orthorhombic system with the space group \(Cmcm\) above \(T_c\). The order-disordering of organic cations makes a dominant contribution to its switchable dielectric activities. In addition, weak magnetic anomalies were also found in the vicinity of its \(T_c\) being reminiscent of a possible physical channel to phase transition. These findings suggest that 1 might be a potential multifunctional material with the coexistence of switchable dielectric bistability and magnetic response. The coexistence of multiple channels opens up new possibilities to develop multifunctional materials, which can simultaneously exploit more than one function for device applications.

**Experimental section**

**Synthesis**

All starting materials are of analytical grade and were directly used as purchased. 1 was synthesized by the reaction of \(N\)-methylpiperidinium and iron trichloride in the molar ratio of 1:1 with excessive hydrobromic acid at room temperature. Reddish brown crystals were easily obtained by slow evaporation of the aqueous solution. Elemental analyses for C, H contents were carried out on a VARIO EL cube elemental analyzer. Caiced: C, 15.15%; H, 2.967%. Found: C, 15.32%; H, 3.00%.

**Powder X-ray diffraction**

The phase purity of 1 was confirmed at room temperature using a powder X-ray diffractometer equipped with Cu-K\(\alpha\) radiation (\(\lambda = 1.54056\ \text{Å}\)) in the 2\(\theta\) range of 5–40\(^\circ\) with a step size of 0.02\(^\circ\). PXRD patterns obtained at 295 K match well with the calculated data based on the crystal structure, which confirm the purity of as-grown crystal of 1, as depicted in Fig. S1 (ESI†). Variable-temperature PXRD data for 1 were measured on a Mini Flex II Powder X-Ray Diffractometer at 303, 330, 340 and 355 K, respectively. Diffraction patterns were collected in the 2\(\theta\) range of 5°–50° with a step size of 0.02°.

**IR spectroscopy**

A Thermo-Nicolet Nexus 670 spectrometer has been used to record the attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of the powder sample of 1 in the range of 700–400 cm\(^{-1}\) at room temperature. The result is shown in Fig. S3 (ESI†).

**Single-crystal X-ray diffraction**

Single-crystal X-ray diffraction was performed on a Super Nova diffractometer with Cu-K\(\alpha\) radiation (\(\lambda = 1.54178\ \text{Å}\)). Crystals with approximate dimensions of 0.42 x 0.36 x 0.20 mm\(^3\) were used for data collection at different temperatures. Crystalline data were processed using the Crystalclear software package (Rigaku, 2005), and its variable-temperature crystal structures were solved using direct methods and refined using full-matrix least-squares refinements on \(F^2\) using the SHELXTL software package. Non-hydrogen atoms were refined anisotropically based on all the reflections with \(I > 2\sigma(I)\), and the hydrogen atoms were generated by geometrical considerations. Crystallographic data and detailed structural refinements of 1 are listed in Table S1 (ESI†).

**Thermal measurements**

Differential scanning calorimetry (DSC) and specific heat (\(C_p\)) analyses were performed using a NETZSCH DSC 200 F3 instrument in the temperature range between 295 and 358 K. The crystalline samples were placed in aluminum crucibles with the heating and cooling rates of 5 K min\(^{-1}\) under a nitrogen atmosphere. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Netzsch STA 449C unit in the temperature range of 300–1350 K with a heating rate of 10 K min\(^{-1}\).

**Dielectric measurements**

The pressed-powder pellets deposited with silver conducting glue were used for the dielectric measurements with the heating/cooling rates of about 10 K min\(^{-1}\). For 1, the temperature dependencies of dielectric constants were measured on a Tonghui TH2828 analyzer in the temperature range of 310–360 K. Temperature dependence of the real part (\(\varepsilon'\)) of the complex dielectric constant (\(\varepsilon = \varepsilon' - i\varepsilon''\), where \(\varepsilon''\) is the imaginary part) was recorded with a frequency range of 10 kHz to 100 kHz.

**Magnetic characterization**

The magnetic properties of compound 1 were measured on a Quantum Design SQUID (MPMSXL-7) magnetometer. Temperature and magnetic-field dependences of magnetization were measured in the temperature range of 2–360 K and in external magnetic field up to 40 kOe, using finely ground crystalline powders.

**Results and discussion**

**Thermal properties**

It is well-known that thermally-induced phase transitions are sensitive to DSC and \(C_p\) measurements. Herein, the DSC and \(C_p\) curves in Fig. 1 show that compound 1 undergoes a reversible phase transition around \(T_c \approx 340\ K\) (upon heating). The sharp peak-like anomalies and large thermal hysteresis of \(\sim 4\ K\) are indicative of a first-order phase transition. In addition, the...
entropy changes (ΔS) for the phase transition is estimated to be \(\approx 5.44 \text{ J mol}^{-1} \text{ K}^{-1}\). According to the Boltzmann equation, \(\Delta S = R \ln N\), where \(R\) is the gas constant and \(N\) represents the ratio of possible configurations; here \(N\) is approximately calculated as \(\approx 1.92\). The large value of \(N\) suggests that 1 undergoes a typical order–disorder phase transition and adopts two possible disordered positions \((N = 2)\). For convenience, we labeled the phase below \(T_c\) as the low-temperature phase (LTP) and the phase above \(T_c\) as the high-temperature phase (HTP). Interestingly, the prominent thermal anomaly at \(T_c\) is also noticed in the DTA curve, as shown in Fig. S2 (ESI†). The phase-transition temperature matches fairly well with the results obtained from DSC and \(C_p\) measurements. Moreover, the TG-DTA curve indicates that the melting point of 1 is approximately 424 K and no remarkable weight loss was recorded before 580 K, demonstrating that 1 will not decompose over the temperature ranging from 300 to 580 K.

Crystal structure discussion

X-ray diffraction analyses of 1 were performed at 100 K (the low-temperature phase, LTP) and 345 K (the high-temperature phase, HTP), respectively. Distinct differences of crystal structures have been observed between its LTP and HTP, which solidly confirm the existence of phase transition. At the LTP, 1 crystallizes in the monoclinic space group, \(P2_1/c\) (the point group \(2/m\)), with cell parameters of \(a = 6.5974(1)\), \(b = 13.7702(3)\), \(c = 14.6244(2) \text{ Å}\), \(\beta = 92.590(2)^\circ\), \(Z = 4\), and \(V = 1320.49(04) \text{ Å}^3\). As given in Fig. 2, at the LTP, the asymmetric unit of 1 consists of one protonated \(N\)-methylpiperidinium cation and one tetrabromoferrate(III) anion. Both the cationic and anionic moieties are fully ordered in the low-temperature structure. It is interesting that the geometry of the anionic framework in 1 can be described as a tetrahedron, which shows a slightly distorted coordination. This configurational distortion of the FeBr\(_4\) moiety has been deduced from bond lengths. As shown in Tables S2 and S3 (ESI†), in the case of the LTP, the Fe–Br bond lengths and Br–Fe–Br bond angles vary in the ranges of 2.2432–2.5020 Å and 105.86–113.59°, respectively. In contrast, in the HTP, the Fe–Br bond lengths become 2.3096–2.3333 Å, accompanied by the Br–Fe–Br bond angles of 106.74–112.16°. In particular, there are four different lengths of Fe–Br bonds in the anionic moiety at the LTP, while the anionic tetrahedron consists of two unequal Fe–Br bonds and two equal bonds at the HTP. Similarly, compared with six different Br–Fe–Br bond angles at the LTP, there are only three unequal Br–Fe–Br bond angles in the HTP. All these changes illustrate that the tetrabromoferrate(III) anion adopts a highly-symmetric configuration with the temperature decreasing from the LTP to the HTP; in other words, the crystallographic symmetry has been broken in 1 during the phase transition upon cooling. Hence, the change in bond lengths and bond angles might behave as another evidence for the occurrence of phase transition of 1.

At the HTP, 1 transforms into the orthorhombic system with the space group \(Cmcm\) (point group \(mmm\)). The cell parameters change as \(a = 9.9932(4)\), \(b = 9.5392(4)\), \(c = 14.8097(5) \text{ Å}\), \(Z = 4\), and \(V = 1411.77(9) \text{ Å}^3\). These remarkable differences between LTP and HTP structures can also be comprehended from the obvious variations of its crystallographic data. Such changes in cell parameters confirm the occurrence of phase transition in 1, which is in good agreement with DSC and \(C_p\) measurements. As given in Fig. 3a, the asymmetric unit at the HTP is composed of a one-half protonated \(N\)-methylpiperidinium cation and a one-half tetrabromoferrate(III) anion. In the highly-disordered structure of 1 at the HTP, the tetrabromoferrate framework still remains ordered, while the protonated \(N\)-methylpiperidinium cation becomes highly-disordered. As shown in Fig. 3b, the \(N\)-methylpiperidinium cation is sternly disordered with all the atoms adopting two equivalent disordered positions. This coincides fairly well with the conclusion deduced from the DSC results \((N = 2)\). In comparison of variable-temperature structures of 1, the most striking structural feature at the HTP is that the organic \(N\)-methylpiperidinium cation becomes highly-symmetric as the crystallographic point group changes from 2/m to \(mmm\).
As a result, the molecular structure of 1 adopts the structure with the higher symmetry at the HTP.

Moreover, the change in hydrogen-bonding interactions at different temperatures also behaves as the direct evidence to the symmetry-breaking phase transition in 1. Pertaining to the structures at both the LTP and the HTP, the crystal packing of 1 is characterized by N–H⋯Br hydrogen bonds (as shown in Fig. 4 and 5). Strong hydrogen bonds connect N-methylpiperidinium cations and tetrabromoferrate anions together, leading to the formation of H-bonded dimers. As temperature increases from the LTP to the HTP, the hydrogen bonds become much weaker with the “acceptor-hydrogen” distances changing from 3.475/3.596 Å to 3.842 Å (Tables S4 and S5, ESI†). In particular, the high-temperature N1–H⋯Br1 hydrogen bond features a highly-symmetric configuration compared with that of N1–H⋯Br1 and N1–H⋯Br3 at the LTP (Fig. 4b and 5b). This variation indicates that the crystallographic symmetry of 1 is enhanced above $T_c$, which behaves as a secondary indicator to its phase transition.

To further confirm the occurrence of reversible phase transition in 1, well-ground powder was used to check VT-PXRD patterns at 303, 330, 345, 355 K and back to 303 K, respectively. As illustrated in Fig. 6, the experimental VT-PXRD patterns obtained at room temperature and high temperatures match well with the corresponding simulated results (the bottom line and the top line) obtained from single crystal structures. In the temperature range of 303–330 K, the PXRD patterns remain unchanged. However, with the temperature increasing above $T_c$ (i.e. 345 and 355 K), obvious changes have been observed in comparison with the RTP. For instance, upon heating higher than $T_c$, the diffraction peaks at 25.88° and 26.18° display opposite movements towards low-angle and high-angle diffraction areas, respectively. In particular, the diffraction peaks at 14.20°, 26.86° and 28.66°, corresponding to the Bragg diffraction peaks of (012), (132) and (141) planes of the RTP, fully disappear at the HTP. This result strongly confirms the existence of phase transition in 1, and a sharp decrease of the number of diffraction peaks suggests a transition from low symmetry (2/m) to high symmetry (mmm). In addition, it is noteworthy that the PXRD patterns recorded at 303 K (the light-blue line) match well with the results obtained upon cooling back to 303 K (the green line). This observation also confirms the thermal reversibility of phase transition in 1, which is well consistent with DSC and $C_p$ measurements.

From the above-mentioned structural analyses and VT-PXRD chart, it is clear that 1 undergoes a phase transition within the range of 330–345 K. Here, we further record the lattice parameter values of 1 in the temperature range from 300 to 365 K. As depicted in Fig. 7, upon heating the bond lengths of $a$- and $b$-axes almost remain unchanged until 340 K. Subsequently, all these parameters display obvious changes while the temperature approaches 340 K. In detail, the value of the $b$-axis bond length shortens from 13.70 Å to 9.54 Å; in contrast, the $a$-axis bond length elongates from 6.60 Å to 9.99 Å. As a result, the...
cell volume changes from 1320 Å³ to 1411 Å³. These changes in the vicinity of \( T_c \) correspond well to the above-mentioned structural discussion, that is, the crystallographic symmetry transformation from \( P\bar{2}_1/c \) to \( Cmcm \). All these illustrations afford the convincing evidence that \( 1 \) undergoes a temperature-triggered phase transition at approximately 340 K.

During phase transition of \( 1 \), its crystallographic symmetry changes from the high-temperature space group \( Cmcm \) (the point group \( D_{2h} \)) to a low-temperature space group \( P\bar{2}_1/c \) (the point group \( P_{21} \)). As a result, its symmetric elements change from \((E, C_2, 2C_2', i, σh, 2σv)\) to \((E, i, C_2, σh)\), as shown in Fig. 8. This symmetry transformation suggests that structural moieties in \( 1 \) possess a higher crystallographic symmetry at the HTP, which coincides fairly well with the conformational changes in anionic and cationic moieties (Fig. 2 and 3). However, this symmetry transformation does not belong to one of the 88 species of ferroelectric type, disclosing that \( 1 \) could not be a ferroelectric material at room temperature.\(^{17}\)

**Dielectric properties**

Bulk physical properties generally display abrupt changes in the vicinity of \( T_c \) and the variable magnitudes are closely related to the characteristics of phase transition. Taking ferroelectric phase transition as an example, the temperature-dependent dielectric constants usually show noticeable anomalies, with peak values varying from tens to even \( ∼ 10^6 \).\(^{18}\) In contrast, the most significant feature for switchable dielectric materials is that dielectric constants can be converted between the low and high states. This is an effective indicator of the switchable dielectric material. Here, temperature dependence of the dielectric constants of \( 1 \) was measured in the heating/cooling runs to detect dielectric responses accompanied by phase transition. Fig. 9 displays the real part \( (\varepsilon') \) of the complex dielectric permittivities measured on the powder pressed pellets of \( 1 \) at different frequencies within the range of 320–350 K. The dielectric anomalies were recorded at 338 K in the cooling mode, which is in agreement with DSC and \( C_p \) results. Above \( T_c \), the dielectric constants remain almost stable until 337 K upon cooling. However, an obvious step-like anomaly was observed approaching \( T_c \), and the permittivity exhibits a slope with an obvious decrease. In detail, the values of \( \varepsilon' \) displays the changes from 25 to 6 \((f = 10 \text{ kHz})\) during the phase transition, where the change was sharp in the vicinity of \( T_c \). In general, we use the \( \varepsilon' \) value of silicon nitride \((∼ 7)\) as a boundary between high and low dielectric constant materials. During this process, the dielectric constant at the HTP is approximately 4 times that at the LTP, corresponding to its high- and low-dielectric states, respectively. Such a temperature dependence of dielectric constants resembles other inorganic–organic hybrids, such as \([(\text{CH}_3)_2\text{NH}_2][\text{KCo(CN)}_6]\] (the value of \( \varepsilon' \) changes from 19 at the HTP to 4 at the LTP).\(^{19}\) In addition, the imaginary part \( (\varepsilon'') \) also displays a significant change near \( T_c \), which also confirms the emergence of phase transition at 336 K in \( 1 \) (the inset in Fig. 9). More importantly, the dielectric responses of \( 1 \) could be tuned in two dielectric states and switched by the stepwise phase transition as well as the large changes between the corresponding high and low dielectric states. This result suggests that \( 1 \) should be an excellent candidate as a molecular switchable dielectric material.

**Magnetic properties**

Because the crystal structure contains the paramagnetic inorganic anion of \([\text{FeBr}_4]^-\) and the flexible organic \( \text{N-methylpiperidinium} \) cation, \( 1 \) is expected to display potential magnetic properties except for thermal and dielectric responses. Here, the temperature-dependent magnetic susceptibilities were measured under an applied direct-current field of 1000 Oe to investigate its magnetic properties in the temperature range of 2–360 K. As shown in Fig. 10, upon heating, it is noteworthy that \( χ_m \) first increased to a maximum value of 0.010 at 15 K and then decreased to 0.0013 at 360 K. The anomaly at low temperature usually suggests antiferromagnetic behaviour.\(^{20}\) Furthermore, the magnetic susceptibility was fitted by the Curie–Weiss law with \( \chi_0 = \frac{(T - \theta)}{C} \) in the temperature range of 15–360 K as depicted in Fig. S4 (ESI†). The calculated Curie constant \( C \) and Weiss constant \( \theta \) are 4.67 cm³ K mol⁻¹ and ∼22.68 K, respectively. Besides, isothermal magnetization was also measured at different temperatures. The magnetization increases linearly with increasing magnetic field and reaches 0.6305 Nζ at 2 K, 0.4591 Nζ at 50 K, 0.1028 Nζ at 295 K and 0.0873 Nζ at 350 K (at 40 kOe, Fig. S5, ESI†).

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**Fig. 8** Symmetry transformation of the space group in \( 1 \) from a LTP \((P\bar{2}_1/c)\) to a HTP \((Cmcm)\).

**Fig. 9** Temperature dependence of the real part \((\varepsilon')\) of the complex dielectric permittivities in \( 1 \) measured under different frequencies. Inset: The corresponding imaginary part \((\varepsilon'')\).

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The negative value and linear field-dependent magnetization at 2 K further confirm the existence of antiferromagnetic interactions between the adjacent Fe$^{3+}$ ions.21

At room temperature, the $\chi_m T$ values are measured to be approximately $\sim 4.3$ cm$^3$ K mol$^{-1}$, which coincide well with the calculated value of 4.38 cm$^3$ K mol$^{-1}$ (for a spin-only high-spin Fe$^{3+}$ ion, $S = 2.5$, $g = 2$). However, below 50 K, the $\chi_m T$ value decreases rapidly until it reaches 0.138 cm$^3$ K mol$^{-1}$ at 2 K. In order to further confirm the exact value of $\chi_m T$, temperature-dependent magnetizations of 1 were performed adopting two samples under different applied direct-current fields (1000/2000 Oe), respectively. As shown in Fig. S6 (ESI†), both results accord well with the theoretical value. That is, the experimental value of $\chi_m T$ remains unchanged at various magnetic fields. This temperature dependence of $\chi_m T$ results also resembles other inorganic–organic hybrid compounds, such as tetramethylphosphonium tetrachloroferrate(III) and tetramethylphosphonium tetrabromoferrate(III).22 It is interesting that weak magnetic anomalies were observed in the vicinity of $T_G$; that is, temperature-dependent $\chi_m T$ of 1 exhibits weak magnetic anomalies at approximately 340 K upon heating (the inset in Fig. 10). This agrees well with DSC results and suggests that such magnetic behaviors are closely involved with structural phase transition. In this context, the origin of these switchable but relatively small magnetic anomalies may influence the magnetic properties and contribute to their weaker magnetic interaction.23 As there is no direct interaction between the magnetic centers, the change in the surrounding environment induces merely weak magnetic responses, which still need further investigations.

Conclusions

In summary, we have reported a new inorganic–organic hybrid, [C$_6$H$_{14}$N][FeBr$_4$], which displays diverse temperature-responsive physical channels of dielectric and magnetic responses. In detail, its dielectric constants can be switched and tuned between two distinct states in the vicinity of the phase transition point. This behavior discloses its potential as a switchable dielectric material. Structural analyses reveal that order-disordering of organic cations dominates its switchable dielectric activities. Furthermore, weak magnetic anomalies are also triggered by structural changes of 1, which is reminiscent of another possible physical channel to its phase transition. As far as we are aware, this finding reveals that 1 might be a potential multifunctional material, which opens up new possibilities to develop molecular functional materials.

Acknowledgements

This work was supported by NSFC (21622108, 21525104, 91422301, 21373220, 51402296 and 51502290), the Youth Innovation Promotion of CAS (2014262) and the State Key Laboratory of Luminescence and Applications (SKLA-2016-09).

Notes and references
