Full-temperature covered switching material with triple optic-dielectric states in a lead-free hybrid perovskite

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ABSTRACT Optic-electric responsive materials have attracted much attention for their applications in temperature-sensing, actuators, and memory switches. However, it is a challenge to integrate various functions to form multi-functional responsive materials. As molecule-based hybrid materials usually consist of organic and inorganic components, the introduction of multiple functions can be achieved through structural construction. Thus far, even though full-temperature cover is required for device applications, full-temperature covered multi-switchable hybrid materials have rarely been successfully synthesized. Herein, the dynamic $[(\text{CH}_3)_3\text{NOH}]^+$ cation and luminous center Mn(II) were introduced to form a hybrid material $[(\text{CH}_3)_3\text{NOH}][\text{MnCl}_3]$, showing multiple temperature-responsive behaviors. Upon temperature change, it exhibits multi-state dielectric switching response and intensity or peak shift response of luminous in full-temperature range (low, room, and high temperatures). These responsive behaviors are triggered by the motion or reorientation of $[(\text{CH}_3)_3\text{NOH}]^+$ cations and inorganic framework. Overall, the switchable photoelectric material has potential applications in multiple encrypted storage and sensor devices.

Keywords: responsive material, multiple dielectric states, crystal, perovskite

INTRODUCTION

Making appropriate changes to adapt to the surrounding environment is essential for all living creatures to sustain life or biological activities. Similar to organisms, some materials can imitate this “behavior” for adapting to ex-

ternal stimuli such as temperature, light radiation, pressure, electric and magnetic fields, namely stimuli-responsive materials (SRMs) [1–5]. Usually, by structural change, these materials possess the feature of changing their physical and/or chemical properties under external stimuli, which has aroused considerable attention for sensors, actuators, memory devices, switches, surface engineering, and other intelligent material industries [6–9]. Thermal SRMs (TSRMs), one group of SRMs, can alter their electric, luminescence, surface, and magnetic properties by thermal stimulation [10–14]. In the past years, extensively studied polymers and inorganic materials have undergone great development [12,15,16]. Nevertheless, the difficulty of regulating their structures has hindered their development, especially in the multi-functional material field. Molecular-based hybrid materials, the rising star among this group, have become the focus of TSRMs because of their excellent structural compositions [11,17–19]. Self-assembly of organic and inorganic components is an effective method for synthesis of these hybrid materials. Furthermore, some phase-transition hybrid materials exhibit reversible switchable chemical or physical properties under the external stimuli, which have taken a dominant position in basic research and technical application [20–23].

As is known, for the prospect of inducing bright fluorescence in hybrid halide perovskites, Mn-based hybrid compounds have aroused much attention [24–27]. Recently, Zhang *et al.* [28,29] revealed two Mn-based ABX_3 -type perovskites that exhibited ferroelectricity and luminescence properties. Moreover, Bhaskaran *et al.* [30]

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also studied the optical transmittance and dielectricity of a Mn-based compound systematically. Especially, a two dimensional (2D) Pb–Mn heterometallic halide hybrid, $(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{Pb}_4\text{MnCl}_{14}$, showed excellent luminescence properties [31]. However, they could not respond to electricity and luminescence simultaneously under temperature stimulation, or achieve multi-segment temperature responses [20,32]. Therefore, searching for materials with multiple switchable physical properties and multiple temperature states in the full temperature range remains a challenge.

As a luminous activator, the emission of Mn(II) complexes originates from the ${}^4\text{T}_{1\text{g}}(\text{G}) \rightarrow {}^6\text{A}_{1\text{g}}(\text{S})$ transition of Mn^{2+} ions, which facilitates the preparation of fluorescent hybrid materials. For example, the green luminescence of the tetrahedral manganese halides is produced by d electron transition configuration from $(\text{e}_{\text{g}})^2(\text{t}_{2\text{g}})^3$ to $(\text{e}_{\text{g}})^1(\text{t}_{2\text{g}})^4$ and the pink luminescence of the octahedral manganese halides is produced by d electron transition configuration from $(\text{t}_{2\text{g}})^3(\text{e}_{\text{g}})^2$ to $(\text{t}_{2\text{g}})^4(\text{e}_{\text{g}})^1$. Therefore, using the self-assembly of a proper organic cation with the manganese halide skeleton is a feasible strategy to design TSRMs with multiple responses and multiple temperature states. Inspired by our previous work on $[(\text{CH}_3)_3\text{NOH}]\text{[CdCl}_3]$ [33] and considering the interaction of $(\text{CH}_3)_3\text{NOH}^+$ cations with the inorganic framework, a novel 1D organic-inorganic hybrid perovskite $[(\text{CH}_3)_3\text{NOH}][\text{MnCl}_3]$ (**1**) was prepared. The differential scanning calorimetry (DSC) measurement shows that **1** has three reversible structural phase transitions at around 198.4/183.2, 268/248.2, and 312.3/301.5 K, respectively. Accompanying with multi-state dielectric switching responses in the full temperature range, it also presents interesting fluorescence response by the thermal stimulus. More strikingly, its luminescence response includes the decrease of intensity and blue shift of peak under temperature stimulation. Furthermore, the switching mechanism can be ascribed to the movement of organic cations and the distortion of the inorganic framework or the intensity of their atomic movements. In general, this work successfully achieves triple optic-dielectric state responses under thermal stimulation.

EXPERIMENTAL SECTION

Synthetic procedures

The crystals of $[(\text{CH}_3)_3\text{NOH}]\text{MnCl}_3$ were prepared by slow evaporation of the mixed solution containing trimethylamine *N*-oxide dihydrate, hydrochloric acid, and manganese chloride in equal molar ratios. Crystal-

lographic data and structure refinement details showed homogeneous and uniform morphology.

Characterizations

Single-crystal X-ray diffraction (XRD) data were acquired by using a Rigaku Oxford diffractometer equipped with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and successive Fourier synthesis and then refined by the full-matrix least-squares method based on F_2 utilizing the SHELXLTL software package. All non-hydrogen atoms were refined anisotropically and added geometrically. Moreover, the molecular units and the packing views were drawn using DIAMOND (Brandenburg and Putz, 2005). DSC was measured on a PerkinElmer Diamond DSC instrument in the temperature range of 165–330 K with a heating or cooling rate of 20 K min^{-1} under a nitrogen atmosphere. Complex dielectric constants were measured with a Tonghui TH2828A instrument in the range of 165–330 K. Moreover, ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy measurements were performed by using a Shimadzu (Tokyo, Japan) UV-2600 spectrophotometer with an ISR-2600Plus integrating sphere operating from 200 to 1000 nm at room temperature. BaSO_4 was used as the 100% reflectance reference.

RESULTS AND DISCUSSION

Compound **1** was prepared in a mixed solution including acetonitrile and methanol, as orange-red rod-like crystals. In the single-crystal XRD study of **1** at 300 K (room temperature), it crystallized in an orthogonal space group *Pbcm*, with $a = 9.2187 \text{ \AA}$, $b = 15.1758 \text{ \AA}$, and $c = 6.4710 \text{ \AA}$. Linear $[\text{MnCl}_3]_n^-$ chains of the face-sharing MnCl_6 octahedra constructed the framework of the crystal lattice, and the organic cations $[(\text{CH}_3)_3\text{NOH}]^+$ (named as TMNO) were embedded into the free space between the chains. The structural features formed the typical perovskite structure— ABX_3 , similar to BaNiO_3 . Moreover, it could remain stable until 560 K, which was verified by thermogravimetric analysis (TGA) (Fig. S1). The functional groups of organic cation TMNO and the purity of the material were proved by the infrared spectrum and powder XRD (PXRD) spectrum respectively (Figs S2 and S3).

As a direct physical method to reveal the solid-to-solid (STS) phase transitions, the structural phase transitions of compound **1** were verified by DSC firstly (Fig. 1a). During the heating and cooling cycles in the temperature range of 165–330 K, we noted that the material exhibited three pairs of *exo*- and *endo*-thermal peaks at around

Figure 1 (a) Thermal characterization (DSC plots) of the structural phase transitions in **1**. The simulated single crystal shape of **1** for: 208 K (b); 300 K (c); and 323 K (d).

198.4/183.2 (T_{1a}), 268/248.2 (T_{1b}), and 312.3/301.5 K (T_{1c}), respectively. The average entropy changes ΔS of phase transitions corresponding to compound **1** were calculated as 5.66, 8.94, and 1.10 J mol⁻¹ K⁻¹, respectively. Conveniently, we divided the whole process into four parts according to the phase transition temperature, as Phases I–IV. Further exploring the microscopic mechanism of the STS phase transitions, we obtained the structures of **1** at different phase states by using single-crystal XRD. These four phases are represented by structures at 323, 300, 208, and 153 K, respectively. However, we only obtained crystal structures and simulated crystals at 208, 300, and 323 K. As Fig. 1b–d show, the changes of their crystal planes indicate the phase transitions. As for 153 K (Phase IV), due to poor crystal

data collection, we could not obtain the specific crystal structure and its simulated crystal. Fortunately, we obtained the cell parameters at different temperatures. The angle value of β changed distinctly from 90° for Phase III to 93° for Phase IV (Fig. 2a). Moreover, variable-temperature PXRD measurements were performed to prove their phase transitions. As depicted in Fig. 2b, the PXRD patterns recorded at 148 and 168 K match quite well; however, as the temperature increased, the diffraction at $2\theta = 16.17^\circ$, 22.07° , and 26.52° appeared as clear peaks, and the diffraction peak at $2\theta = 37.63^\circ$ gradually disappeared from Phase IV to Phase III. Based on the above analysis, the evident variations of the PXRD patterns at around T_{1a} verified the occurrence of the structural phase transition.

Other phases were compared with the specific crystal data (Table S1), packing structures (Figs 3 and 4), and molecular structures (Fig. 5) to discuss their differences and similarities. At 208 K of Phase III, it crystallized in space group *Pmcn*, which also belongs to the orthorhombic crystal system with $a = 9.6079$ Å, $b = 14.2701$ Å, and $c = 6.4163$ Å. As shown in Fig. 3a, linear $[\text{MnCl}_3]_n^-$ chains (along the c axis) of face-sharing MnCl_6 octahedra construct the framework of the crystal lattice, of which the Mn atoms and one-third of the Cl atoms lie in the mirror plane, while the other Cl atoms do not. This mirror also passes through the oxygen atoms of TMNO cations, as shown in the sky blue area of Fig. 3a. When the temperature rises to 300 K of Phase II, all the Mn–Cl bond lengths and Cl–Mn–Cl bond angles are changed within the normal ranges (Table S2). It is worth noting that the dynamics of their organic cations change from relatively stationary motions to tumbling motions, causing the phase transition. As shown in Fig. 3b, all Cl atoms are in the mirror plane, while Cd atoms are not. The tumbling motions of TMNO cations are symmetrical in

Figure 2 (a) Changing of cell parameters a , b , c , and β value at different temperatures. (b) PXRD patterns of $[(\text{CH}_3)_3\text{NOH}][\text{MnCl}_3]$ at different temperatures.

Figure 3 Packing views of **1** in: (a) Phase III (208 K); and (b) Phase II (300 K). The sky blue plane represents the mirror plane. The H atoms of the cations were omitted for clarity.

the mirror plane, and all C atoms lie in the mirror plane too. These differences can be attributed to the change of symmetry elements. In general, the overall unit cell frameworks at 208 and 300 K have almost no differences (Fig. 3). The main reason for the phase transition (Phase III to Phase II) is the movement of organic cations (Fig. 5a, b).

To reveal the mechanism of phase transition above room temperature, we compared the crystal structures at 300 and 323 K. Compound **1** of Phase I at 323 K belongs to the hexagonal centrosymmetric space group $P6_3/mmc$. The spatial symmetry operations change from eight

Figure 4 (a) The crystal cell of **1** in Phase II (outlined in blue solid lines) and its unit cell in Phase I (outlined in black solid lines). (b) Schematic diagram of the lattice of **1** from Phase II to Phase I.

elements (E , C_2 , C_2' , C_2'' , i , σ_h , σ_v , and σ_v') in Phase II to the twenty-four symmetry elements (E , $2C_6$, $2C_3$, C_2 , $3C_2'$, $3C_2''$, i , $2S_6$, $2S_3$, σ_h , $3\sigma_v$, and $3\sigma_v'$) in Phase I (Fig. S4). Each Mn atom, lying in the $3m$ symmetry site, is octahedrally coordinated with six bridging Cl atoms with Mn–Cl bond length changing to 2.538 (2) Å and the Cl–Mn–Cl bond angles ranging from 83.93(6)–96.07(6)° to 180.00(4)° (Table S2). During the heating process, 1D chains remains running along the c axis, but the structural parameters change tremendously [a , b , c (Å): 9.6079 (19), 14.2701(3), and 6.4163(14) vs. 8.9670(7), 8.9670(7), and 6.4506(5); V (Å³): 945.5(3) vs. 449.18(9)]. The unit cells of these two phases are shown in Fig. 4. Thermal vibrations of the atoms become more intense at a high temperature (Phase I), especially for N, C, and O atoms (Fig. 5b, c).

Based on the above analysis, to understand the changes

Figure 5 Crystal structures of **1** with thermal ellipsoids drawn at 30% probability for the inorganic part and 10% for the organic part, with hydrogen atoms omitted for clarity: (a) 208 K for Phase III; (b) 300 K for Phase II; and (3) 323 K for Phase I. Comparison between the Hirshfeld d_{norm} surfaces of different phases (d). On Hirshfeld surfaces, the red, white, and blue regions represent molecular contacts shorter than, equal to, and longer than the van der Waals distance, respectively.

in the interaction between TMNO cations and $[\text{MnCl}_3]_n^-$ chains, Hirshfeld surface analysis was performed. As shown in Fig. 5d, the red spots on their Hirshfeld surfaces become larger from phases III to I, indicating that the interaction between TMNO cations and $[\text{MnCl}_3]_n^-$ chains gradually increases. It is probably caused by the more intense movement of TMNO cations in a limited space, corresponding to crystal structure analysis.

Generally, the solid phase transitions can bring dielectric anomalies. Here, we measured the temperature-dependent dielectric constant of **1**. Fig. 6a, b show the temperature-dependent real part (ϵ') of the permittivity in the ranges of 165–280 K and 280–330 K, respectively.

Three distinct dielectric anomalies were scattered among the range, consistent with the DSC results. Upon heating, at 1000 kHz, the value of the real part ϵ' started at about 4 at 165 K and then increased slowly with the temperature increasing in the Phase IV state. At 201 K (around T_{1a}), the value of ϵ' presented the anomalies. Above T_{1a} , compound **1** is in the Phase III state and the ϵ' values increase more slowly than in Phase IV with the temperature increasing. At around 261 K (T_{1b}), the real part (ϵ') of **1** remained at approximately 5.5, afterward, an inverted peak appeared. The dielectric anomalies were Z-shaped, corresponding to the second phase transition (Phase III to Phase II). As the temperature continued to

Figure 6 (a) Temperature-dependent real part dielectric constant of **1** at 1000 kHz upon heating and cooling below room temperature. (b) Temperature-dependent real part dielectric constant of **1** at 1000 kHz upon heating and cooling above room temperature. (c) Temperature-dependent real part dielectric constant of **1** cooling below room temperature. (d) Temperature-dependent real part dielectric constant of **1** cooling above room temperature. (e) Schematic diagram of dielectric measurements for powder-pressed pellets. (f) Logic diagram in temperature-controlled device.

rise above room temperature, the real part (ϵ') was still rising (from Phase II to Phase I), accompanied by the third dielectric anomaly in the vicinity of 312 K, which supports the existence of the phase transition. As for the cooling process, similar dielectric anomalies appeared, confirming the reversibility of the phase transitions. In addition, we display the temperature-dependent dielectric of selected frequencies 10–1000 kHz. As shown in Fig. 6c, d, the dielectric anomalies at different frequencies of **1** keep similar behaviors. Overall, these results confirm that **1** can be regarded as a temperature-responsive dielectric material. The details of the dielectric measurement mechanism schematic are illustrated in Fig. 6e. The logic diagram in Fig. 6f shows the temperature-control process in the imaginary system. When the temperature was above T_{1b} , it entered the cooling system; above T_{1c} , the cooler was on, while below it was off. On the contrary, when the temperature was below T_{1b} , it entered the heating system; above T_{1a} , the heater was off, while below it was on. This could also give feedback to the temperature system.

Besides the switching dielectric response under the thermal stimulus, **1** also shows intriguing luminescence properties. As shown in Fig. 7a and b, the crystals (put into quartz cuvettes and formed into the shape of “TSRM”) were orange-red and somewhat transparent under ambient light. When illuminated with a UV lamp, they showed a strong red light (Fig. 7c, d). Fig. 7e presents the three strong absorption peaks that were observed for the absorption spectrum of **1**. The first one is in the UV band at around 375 nm, and the other two are in the visible region centered at around 445 and 535 nm respectively. Then, upon excitation at around 375, 450, and 540 nm, the emission spectra of compound **1** exhibited broad emission at around 640 nm (the full width at half maximum (FWHM) is approximately 86 nm) (Fig. 7f). The red fluorescence at around 640 nm is produced by octahedrally coordinated manganese, which is attributable to the $(t_{2g})^3(e_g)^2 \rightarrow (t_{2g})^4(e_g)^1$ electronic transition [34]. By using the strong fluorescence emission wavelength (640 nm), the photoluminescence excitation (PLE) spectrum was recorded, as shown in Fig. 7e. Obviously, the PLE spectra and UV-vis absorption spectra had similar peak positions.

Further exploring the thermo-responsiveness of their luminescent properties, we studied the fluorescence properties of the material (powder samples) at different temperatures. As shown in Fig. 8a, upon increasing the temperature from 153 to 323 K, the emission intensity of **1** significantly decreases. According to the numerical

Figure 7 Photoluminescence properties of compound **1**. The orange-red crystal of compound **1** was put into two quartz cuvettes under natural light (a) and emitted strong red light under UV light in the darkroom (b). The shape of “TSRM” formed by crystal samples of **1** under natural light (c) and UV light (d). (e) UV-vis absorption spectra and PLE spectrum. (f) Emission spectra at various excitation wavelengths.

calculation of the highest emission peak, the emission intensity dropped by 25% over this temperature range. This phenomenon can be attributed to intense molecular motions as the temperature increasing, improving the rate of on-radiative transition. Besides, the emission maximum gradually shifted from 660 to 635 nm in the temperature range. Especially, from 238 to 265 K, the peak shape and position of the emission maximum changed relatively significantly (Fig. 8b).

CONCLUSIONS

By rational design and chemical synthesis, we obtained a new thermal stimuli-responsive material, $[(CH_3)_3NOH][MnCl_3]$, with switchable dielectric and luminescence responses. In the low, room, and high temperatures, three dielectric anomaly signals are distributed. It also shows noticeable stimulating responses about the intensity and peak position of fluorescence. More strikingly, the decrease rate in fluorescence intensity is fastest from Phase III to Phase II and the blue shift rate of fluorescence maximum absorption peak is also the fastest within the entire temperature range. Through the crystal structure analysis at different temperatures, these responses can be ascribed to the motions or reorientations of $[(CH_3)_3NOH]^+$ cations and the weak distortion of the inorganic framework. The lead-free hybrid perovskite with triple optic-dielectric states has great significance for

Figure 8 (a) Temperature-responsive emission properties of crystal 1 between 153 and 323 K. (b) The blue line represents the peak value changes of luminescent intensity from crystal 1 in the heating process and the red line represents the peak wavelength position changes of luminescent from crystal 1 in the heating process.

developing full-temperature covered switching material. Therefore, the method, introducing the self-assembly of organic and inorganic components, provides ideas for designing multi-responsive thermal stimulating materials.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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全温度覆盖的三重介电及荧光响应无铅杂化钙钛矿开关材料

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摘要 光电响应材料在温度传感、执行器、存储和功能开关领域的应用引起了广泛关注。然而将各种功能整合形成多功能响应材料仍具有挑战性。分子基杂化材料通常是有机和无机成分的杂化混合物。因此，可以通过结构构建将多个功能复合在一个材料中。虽然器件应用需要全温度覆盖，迄今为止却很少能成功地合成全温度覆盖的多开关响应杂化材料。在本文中，动态[(CH₃)₃NOH]⁺阳离子和发光中心Mn(II)形成杂化材料[(CH₃)₃NOH][MnCl₃]，该材料在温度刺激下显示出多重响应行为。温度变化时，[(CH₃)₃NOH][MnCl₃]在全温度范围(低温、室温和高温)下表现出多重介电态及发光强度或峰值变化的开关响应。这些响应行为是由[(CH₃)₃NOH]⁺阳离子和无机骨架的运动或重新取向而触发的。总之，这种光电开关材料在多重加密存储和传感设备中具有潜在的应用。