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### Introduction

Ferroelastic materials, known for their ability to alter internal structures under external stress, exhibit shape memory effects and superelasticity—properties pivotal for the advancement of innovative multifunctional materials and devices.<sup>1–5</sup> Currently, ferroelastic materials across various dimensionalities are of active interest,<sup>6–10</sup> especially the ferroelasticity of three-dimensional (3D) lead–iodine hybrid perovskites, which has been experimentally verified to contribute to its superior photoelectric conversion efficiency.<sup>11,12</sup> Compared to their 3D counterparts, low-dimensional hybrid perovskites offer several advantages, including greater structural flexibility and stability.<sup>13–19</sup> Moreover, the reduction of dimensionality in perovskites could also integrate various functional metals to couple ferroelasticity with other intriguing physical features such as magnetic<sup>20,21</sup> and luminescence properties,<sup>22</sup> *etc.* for

# High phase transition temperature and photoluminescence properties in low-dimensional molecular perovskite ferroelastic crystals<sup>†</sup>

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Ferroelastic materials, as a relative of ferroelectric and ferromagnetic materials, have attracted great attention in developing materials with multifunctions and smart devices for many high-end realms. In this work, we synthesized two new one-dimensional ABX<sub>3</sub> type molecular perovskite crystals, *N*,*N*-dimethylpropargylaminium CdCl<sub>3</sub> (DMPACdCl<sub>3</sub>) and *N*,*N*-dimethylpropargylaminium MnCl<sub>3</sub> (DMPAMnCl<sub>3</sub>). DMPACdCl<sub>3</sub> undergoes a reversible *mmmF2/m* type ferroelastic phase transition at 358 K, accompanied by an order-disorder transition of DMPA cations. The ferroelasticity of DMPACdCl<sub>3</sub> has been verified by the evolution of observable ferroelastic domains. When the B-site metal is substituted by Mn<sup>2+</sup>, the DMPAMnCl<sub>3</sub> crystal exhibits structural phase transition behavior similar to that of DMPACdCl<sub>3</sub> but occurs at a higher phase transition temperature (*T*<sub>tr</sub> = 396 K) with a significant enhancement of 38 K. Besides, DMPAMnCl<sub>3</sub> emits strong red luminescence at room temperature, with a photoluminescence quantum yield (PLQY) of 20.1%. This work highlights the regulation of phase transition temperature and photoluminescence in one-dimensional molecular perovskites by B-site metal substitution and offers significant inspiration for developing multiple function coupling materials for promising optoelectronics and smart devices.

multi-purpose functional materials.<sup>23–26</sup> Ferroelastic materials with high phase transition temperatures are essential for practical applications due to their ability to maintain unique physical properties over a wider temperature range, especially concerning the stability and reliability in the actual applications of devices.<sup>27–29</sup> However, most of the phase transition temperatures of molecular ferroelastics are generally not high and even below room temperature.<sup>30–32</sup> Therefore, developing ferroelastic materials featuring high phase transition temperature, coupled with the exploration of strategies for structural modification aimed at further fine-tuning their properties, is of great significance and high desirability.<sup>33–38</sup>

The structural multiplicity of low-dimensional hybrid perovskites is attributed to their remarkable capacity to incorporate a wide array of components.<sup>39,40</sup> This inherent characteristic, in essence, paves the way for rational design and meticulous performance optimization *via* a plethora of structural modification strategies.<sup>41–44</sup> In recent times, an array of highly effective chemical design approaches has been extensively utilized for the directed design of molecular ferroelectrics.<sup>45–48</sup> Intriguingly, these strategies can be readily extrapolated to the design of other ferroic materials,<sup>49</sup> molecular ferroelastic materials not excluded.<sup>50</sup> For example, H/F substitution on organic cations induces an evident increase ( $\Delta T$ = 10 K) of phase transition temperature in a 1D hybrid [(CH<sub>3</sub>)<sub>3</sub>-PCH<sub>2</sub>F][Cd(SCN)<sub>3</sub>] perovskite ferroelastic material.<sup>51</sup> The

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introduction of fluorine atoms increases the potential barrier for molecular motion without altering the crystal structure, thereby raising the phase transition temperature. Moreover, the strategic introduction of hydrogen bonds represents another potent approach capable of substantially adopting ferroelastic materials with higher phase transition temperatures. For example, the specific intermolecular hydrogen bonds formed between cationic molecules in a 1D hybrid perovskite [N.Ndimethylethanolammonium]PbBr3 plays a pivotal role in enhancing the barrier to molecular motion under thermal stimuli, thereby influencing the phase transition at elevated temperatures.<sup>52</sup> The phase transition temperature of materials can be effectively modulated by means of doping or substituting inorganic anions within the skeletal structure, such as (IAA)<sub>2</sub>- $PbX_4$  (IAA = isoamylammonium cation and X = Cl, Br, and I)<sup>53</sup> and (DMTP)PbX<sub>3</sub> (X = Br and I).<sup>54</sup> It is noteworthy that the preponderance of reported effective regulation strategies predominantly relies upon the modification of organic components or the substitution of inorganic anions in lowdimensional molecular perovskites. However, investigations into the substitution of transition metals for augmenting the phase transition temperature coupled with other intriguing features in ferroelastic materials remain conspicuously scarce.<sup>55</sup>

Herein, we synthesized a 1D organic–inorganic hybrid perovskite crystal DMPACdCl<sub>3</sub> with high phase transition temperature at 358 K. Variable temperature structural analysis reveals a significant order–disorder transition of organic DMPA cations accompanied by an evident *mmm*F2/*m* symmetry change in the DMPACdCl<sub>3</sub> crystal around this temperature point. Under a microscope with polarized light, ferroelastic domain evolution has been clearly captured, indicating the ferroelasticity of DMPACdCl<sub>3</sub> with ferroelastic domain switching.

We further attempted to replace the metal ions at the B-site with  $Mn^{2+}$  and thus obtained the isostructural DMPAMnCl<sub>3</sub>, which features a higher phase transition temperature at 396 K with a significant enhancement of 38 K. The main reason for the increase in the phase transition temperature can be ascribed to the introduction of  $Mn^{2+}$  with a smaller ionic radius leading to a significant contraction of the crystal lattice, thereby constricting the free movement space of the cations. Moreover, DMPAMnCl<sub>3</sub> simultaneously exhibits a distinct emission of red light with a PLQY of 20.1%. This work offers a design approach for regulating the phase transition temperature and coupling the luminescence properties through the substitution of metal sites and paves the way for the development of desired materials with tailored functions for potential practical applications.

#### Results and discussion

#### Thermal properties

Differential scanning calorimetry (DSC) analysis was employed to ascertain the phase transition behaviors of [DMPA]CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub>. Fig. 1a reveals that [DMPA] CdCl<sub>3</sub> exhibits a pair of thermal anomalies at 358 K and 351





K in a heating and cooling run respectively, indicating the occurrence of high-temperature phase transition at around 358 K. For convenience, we designate the phase above 358 K as the high-temperature phase (HTP) and the phase below 351 K as the room-temperature phase (RTP). This nomenclature is similarly applied to [DMPA]MnCl<sub>3</sub>. It demonstrates distinct endothermic and exothermic peaks at 396 K and 386 K, respectively (Fig. 1b). The phase transition temperature of [DMPA]MnCl<sub>3</sub> is approximately 38 K higher than that of [DMPA]CdCl<sub>3</sub>, indicating a significant thermal shift in the phase transition when Cd<sup>2+</sup> was substituted with  $Mn^{2+}$ . The spiked peak anomalies around the  $T_{tr}$ accompanied by thermal hysteresis of 7 and 10 K for [DMPA] CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub> respectively denote that the phase transitions are of a typical first-order nature.56,57 Based on the DSC thermal analysis, the calculated  $\Delta S$  are 8.5598 J mol<sup>-1</sup> K <sup>-1</sup> for [DMPA]CdCl<sub>3</sub> and 3.8135 J mol<sup>-1</sup> K <sup>-1</sup> for [DMPA]MnCl<sub>3</sub>. According to the Boltzmann equation,  $\Delta S = R$  $\ln(N)$ , where R represents the ideal gas constant, and N represents the possible configuration of the substance, the N values for both [DMPA]CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub> are determined to be approximately 2, indicating an orderdisorder transition in the process of phase transition. TGA results show that [DMPA]CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub> are stable up to 449 K and 473 K, respectively (Fig. S1, ESI<sup>+</sup>).

#### Crystal structure analysis

To confirm the structural phase transition behaviors, variable-temperature single-crystal X-ray diffraction was employed to ascertain crystal structures and to elucidate the phase transition mechanism. At room temperature, both [DMPA]CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub> crystallize in the monoclinic crystallographic system with the space group  $P2_1/n$  (point group 2/m). The unit cell parameters of [DMPA]CdCl<sub>3</sub> are a = 6.6640(9) Å, b = 17.112(2) Å, c = 18.366(3) Å,  $\beta = 97.266^{\circ}$ , and V = 2077.6(5) Å<sup>3</sup> (Table S1, ESI†). As shown in Fig. 2a, the asymmetric unit of [DMPA]CdCl<sub>3</sub> consists of two independent organic DMPA cations and one inorganic [CdCl<sub>3</sub><sup>-</sup> motif. They are interconnected *via* N-H···Cl hydrogen bonds with bond lengths of 2.41 and 2.51 Å (Table S2, ESI†). The Cd–Cl bonds



**Fig. 2** Crystal structure of DMPACdCl<sub>3</sub> at 300 K (RTP) (a) and 403 K (HTP) (b); packing views of the structure along the *a*-axis of DMPACdCl<sub>3</sub> at 300 K (RTP) (c) and along the *b*-axis of DMPAMnCl<sub>3</sub> at 403 K (HTP) (d). The pink dotted line represents the hydrogen bond.

and Cl-Cd-Cl bond angles in the range of 2.6144-2.7136 Å and 83.66-99.81° (Table S3, ESI<sup>+</sup>) lead to a slight distortion of [CdCl<sub>6</sub>] octahedra, which extend infinitely along the *a*-axis to form chain-like 1D perovskite stacking (Fig. 2c). Upon heating to 403 K (HTP), [DMPA]CdCl<sub>3</sub> adopts the centrosymmetric orthorhombic space group Pnma (point group *mmm*), with cell parameters of a = 17.6713(11) Å, b =6.7314(3) Å, c = 18.1716(10) Å, and V = 2161.6(2) Å<sup>3</sup>. The relationship between the unit cell parameters of the roomtemperature phase (RTP) and HTP is that *a*RTP  $\approx$  *b*HTP,  $bRTP \approx aHTP$ , and  $cRTP \approx cHTP$ . The component of the asymmetric unit of [DMPA]CdCl<sub>3</sub> and its perovskite packing (Fig. 2b and d) in HTP are the same as those in RTP (Table S4, ESI<sup>†</sup>), but the DMPA cations exhibit a disordered state symmetrically distributed on either side of the mirror plane perpendicular to the b-axis (Fig. S3a, ESI<sup>†</sup>), indicating that [DMPA]CdCl<sub>3</sub> undergoes an order-disorder structural phase transition from HTP to RTP, in which the six symmetrical elements (E,  $C_2$ ,  $2C'_2$ , i,  $\sigma_h$ ,  $2\sigma_v$ ) in HTP are reduced to four symmetrical elements  $(E, C_2, i, \sigma_h)$  in RTP. According to the principle of Aizu notation, the phase transition of [DMPA] CdCl<sub>3</sub> accompanied by significant symmetry change from the point group 2/m to mmm can be classified as a possible ferroelastic species of mmmF2/m (Fig. S4, ESI<sup>†</sup>), which is one of the 94 types of paraelastic-ferroelastic phase transitions.<sup>58</sup> [DMPA]MnCl<sub>3</sub> at 300 K (RTP) exhibits similar unit cell parameters and molecular structure analogous to [DMPA] CdCl<sub>3</sub>, as depicted in Fig. S5a and Tables S5 and S6 (ESI<sup>+</sup>). Notably, the a- and b-axes lengths of [DMPA]MnCl<sub>3</sub> are marginally contracted to 6.37 Å and 16.94 Å compared to those of 6.66 Å and 17.11 Å in [DMPA]CdCl<sub>3</sub> (Fig. 3). The Mn-Cl bond lengths in [DMPA]MnCl<sub>3</sub> exhibit shorter distances ranging from 2.5112 Å to 2.5935 Å than the Cd-Cl bonds in [DMPA]CdCl<sub>3</sub> (Table S7, ESI<sup>†</sup>). The reduced unit cell of [DMPA]MnCl<sub>3</sub> implies a more compact atomic space, which in turn limits the ability of components to move freely, which may increase the energy barrier for a higher phase transition temperature in [DMPA]MnCl<sub>3</sub>. In HTP (428 K), [DMPA]MnCl<sub>3</sub> crystallizes in the orthorhombic space group Pnma and the



Fig. 3 Comparison of the crystal structures in the unit cells of DMPACdCl<sub>3</sub> and DMPAMnCl<sub>3</sub>. Perspective view of DMPACdCl<sub>3</sub> plotted at 298 K (a) and DMPAMnCl<sub>3</sub> at 298 K (b).

DMPA cations also exhibit a disordered state occupying the mirror relation symmetry position (Fig. S3b, ESI<sup>+</sup>).

Besides, the distortions of the octahedral complexes have been calculated according to the following equation,

$$\Delta d = \frac{1}{6} \sum \left[ \left| \frac{d_{\rm n} - \overline{d}}{\overline{d}} \right| \right]$$

 $\Delta d$  is equal to the distortion of the octahedron,  $d_n$  stands for different metal–Cl bond lengths and  $\tilde{d}$  denotes the average metal–Cl bond lengths. The calculated  $\Delta d$  values for [DMPA] CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub> in RTP are 8.543 × 10<sup>-3</sup> and 7.565 × 10<sup>-3</sup> respectively. While in HTP,  $\Delta d$  values are 6.687 × 10<sup>-3</sup> for [DMPA]CdCl<sub>3</sub> and 3.159 × 10<sup>-2</sup> for [DMPA]MnCl<sub>3</sub>. Obviously, the distortion of [MnCl<sub>6</sub>]<sup>-</sup> octahedra in HTP becomes larger than that of [CdCl<sub>6</sub>]<sup>-</sup> ones, with an order of magnitude change. Combined with the crystal structure analysis, the *a*and *c*-axes of [DMPA]MnCl<sub>3</sub> in HTP are significantly smaller than those of [DMPA]CdCl<sub>3</sub>. To ensure that the DMPA cations remain disordered within the smaller space formed by the inorganic chains, the distortion of [MnCl<sub>6</sub>]<sup>-</sup> octahedra must inevitably increase. This change is a crucial structural adjustment during the phase transition process.

Variable temperature X-ray powder diffraction (PXRD) measurements were performed to further support the occurrence of structural phase transition. As depicted in Fig. S6 (ESI<sup>†</sup>), within the temperature interval of 293-353 K, the PXRD patterns for [DMPA]CdCl<sub>3</sub> remain almost invariant. As the temperature rose reaching 383 K, significant vanishing in the diffraction peaks at 8.1°, 10.4°, 12°, 16.2°, and 18.4° was observed, suggesting a structural transition from a lower to a higher symmetry phase. Similarly, for DMPAMnCl<sub>3</sub>, the PXRD patterns exhibit distinct differences at various temperatures. Particularly above 418 K, the diffraction peak intensities at 11.0°, 18.4°, 19.4°, and 23.1° are significantly reduced, while the diffraction peak intensities at 10.28 and 16.0 are slightly increased. These observations from PXRD patterns are in concordance with the thermal behavior detected by DSC and structural analysis.



Fig. 4 Real part ( $\epsilon'$ ) of the complex dielectric constant of [DMPA] CdCl<sub>3</sub> (a) and [DMPA]MnCl<sub>3</sub> (b) at a frequency of 1 MHz.

#### Dielectric and ferroelastic properties

The temperature-dependent real part ( $\varepsilon'$ ) of the complex dielectric permittivity was also obtained to indicate the structural phase transition. As illustrated in Fig. 4, the  $\varepsilon'$  of [DMPA]CdCl<sub>3</sub> at a frequency of 1 MHz exhibits a pair of reversible step-like anomalies near 358 K and 351 K upon heating and cooling respectively. For  $[DMPA]MnCl_3$ ,  $\varepsilon'$  shows a rapid increase at around 400 K and reaches the maximal value with a jump change. Then, the  $\varepsilon'$  exhibits a slow decrease and a small peak anomaly occurred at around 386 K in the cooling run. The evident dielectric responses to the temperature robustly support the presence of structural phase transitions in [DMPA]CdCl<sub>3</sub> and [DMPA]MnCl<sub>3</sub> To confirm the ferroelastic behavior, the evolution of ferroelastic domains was documented under a microscope with polarized light. As shown in Fig. 5a, the film of [DMPA]CdCl<sub>3</sub> at 300 K displays distinct alternating stripe regions as the ferroelastic domains, which have no relation to the morphology (Fig. 5c). Upon heating to 410 K, these stripe regions vanished abruptly (Fig. 5b). Upon



**Fig. 5** Ferroelastic domain evolution during the heating and cooling processes (a, b and d) and its corresponding morphology image (c).

subsequent cooling back to 300 K, the stripe shape domains remerged, as shown in Fig. 5d. The disappearance and reappearance of these stripe domains throughout the thermal cycles are indicative of the paraelastic–ferroelastic phase transition and the ferroelasticity of [DMPA]CdCl<sub>3</sub>. Regrettably, ferroelastic domains of [DMPA]MnCl<sub>3</sub> are hard to observe and record because the crystalline thin film is highly hygroscopic. Based on the determined crystal lattice parameters, the spontaneous strain of [DMPA]CdCl<sub>3</sub> was calculated. The spontaneous strain tensors  $X_s$  in the monoclinic phase for two orientation states  $S_1$  and  $S_2$  are given as

$$X_{s}(S_{1}) = \begin{bmatrix} 0 & 0 & e_{13} \\ 0 & 0 & 0 \\ e_{31} & 0 & 0 \end{bmatrix}$$
$$X_{s}(S_{2}) = \begin{bmatrix} 0 & 0 & -e_{13} \\ 0 & 0 & 0 \\ -e_{31} & 0 & 0 \end{bmatrix}$$

As the symmetric second-rank one,  $e_{13}$  is equal to  $e_{31}$ . According to the unit cell parameter  $\beta_{mon} = 97.266^{\circ}$  of the monoclinic phase of [DMPA]CdCl<sub>3</sub>,  $e_{13} = e_{31} = (\beta_{mon} - \pi/2)/2 = 0.0634$  rad can be obtained.

$$X_{s}^{2} = \sum_{i=1}^{3} \sum_{j=1}^{3} X_{sij}^{2}$$

Therefore, the spontaneous strain in the monoclinic phase should be calculated as  $X_s(Cd) = \sqrt{2}e_{13} = 0.089$ .

#### Photoluminescence properties

DMPAMnCl<sub>3</sub> featuring manganese ions at the octahedral coordination center tends to demonstrate luminescence properties. The white crystal of DMPAMnCl<sub>3</sub> can show strong red luminescence at about 650 nm under ultraviolet excitation. As shown in Fig. 6a, the excitation and emission spectra of DMPAMnCl<sub>3</sub> at 298 K show three prominent excitation peaks at 375 nm, 450 nm, and 540 nm, along with a strong emission peak around 650 nm, which is attributed to the  ${}^{6}A_{eg} \rightarrow {}^{4}T_{2g}$  (D),  ${}^{6}A_{eg} \rightarrow {}^{4}T_{2g}$  (G),  ${}^{6}A_{eg} \rightarrow {}^{4}T_{11g}$  (G), respectively.<sup>59</sup> The photoluminescence (PL) emission wavelength remains unchanged across different excitation wavelengths from 515 nm to 570 nm, indicating that this transition is independent of the excitation light's wavelength. As long as the electronic transition of the manganese ion is excited, the PL emission wavelength will remain constant, as depicted in Fig. 6b. At room temperature, the PLQY of DMPAMnCl<sub>3</sub> is 20.1% (Fig. S7, ESI<sup>†</sup>). To investigate the potential impact of the phase transition on the optical properties of DMPAMnCl<sub>3</sub>, variable-temperature photoluminescence (VT-PL) measurements were conducted. The results revealed a progressive decrease in the PL intensity of DMPAMnCl<sub>3</sub> with increasing temperature, accompanied by a



Fig. 6 Excitation and emission spectra of DMPAMnCl<sub>3</sub> at 300 K (a); VT-PL spectra of DMPAMnCl<sub>3</sub> (b); the integrated PL intensity as a function of the temperature of DMPAMnCl<sub>3</sub> during the heating process (c); the variation of peak centers with temperature in VT-PL spectra of DMPAMnCl<sub>3</sub> (d).

corresponding reduction in fluorescence lifetime, as illustrated in Fig. S8 (ESI<sup>†</sup>). At about 400 K, there is an inflection point in the lifetime, which corresponds to the phase transition temperature, further indicating that the luminescence has a good response to the phase transition. Fig. 6c presents the temperature-dependent PL intensity curve of DMPAMnCl<sub>3</sub> during heating, with a notable inflection point in the quenching rate near the phase transition temperature. Below the transition point, the quenching rate is approximately  $3.7 \times 10^6$  counts per kelvin. Above that, the PL intensity exhibits a significantly accelerated quenching rate, quantified at  $1.3 \times 10^7$  counts per kelvin, which is over an order of magnitude higher. Furthermore, the temperature dependence curves of the peak center (Fig. 6d) and the full width at half maximum (Fig. S9, ESI<sup>†</sup>) in the VT-PL spectrum of DMPAMnCl<sub>3</sub> show an obvious inflection point near the phase transition temperature, that is, the rate is significantly different before and after  $T_{\rm tr}$ . The markedly different PL responses of DMPAMnCl<sub>3</sub> at room temperature and high temperature suggest a coupling between the phase transition and PL.

## Conclusions

In conclusion, we present two new isostructural 1D organicinorganic hybrid ABX<sub>3</sub> type molecular perovskite crystals DMPACdCl<sub>3</sub> and DMPAMnCl<sub>3</sub>. Both hybrid perovskites undergo a reversible solid–solid structural phase transition at high temperatures with significant *mmm*F2/*m* symmetry change around the phase transition temperature. Besides, the obvious evolution of ferroelastic domains with temperature strongly proves the ferroelasticity of DMPACdCl<sub>3</sub>. Therefore, DMPACdCl<sub>3</sub> undergoes a high-temperature ferroelastic phase transition at 358 K. DMPAMnCl<sub>3</sub> as the homolog of DMPACdCl<sub>3</sub> exhibits a higher structural phase transition temperature at 396 K. Such significant enhancement of 38 K has been clearly explained by variable temperature single crystal analysis, which denotes that a contracted space for the lower degree of free motion of organic cations in DMPAMnCl<sub>3</sub> contributes to the enhanced phase transition temperature. Moreover, DMPAMnCl<sub>3</sub> exhibits red light emission with a PLQY of 20.1%. At the same time, the photoluminescence intensity shows a significant response to the structural phase transition. This work reveals the potential of low-dimensional perovskite materials for the development of multifunctional materials with coupled properties.

### Experimental

#### Materials and synthesis

*N*,*N*-Dimethylpropargylamine, CdCl<sub>2</sub>·2.5H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, and concentrated hydrochloric acid (36 wt%) were of analytical grade and used without further purification. Firstly, a large scale of pure DMPACl solid was synthesized by dissolving *N*,*N*-dimethylpropargylamine in a hydrochloric acid ethanol solution. White needle-like crystals of DMPACdCl<sub>3</sub> were obtained by slow evaporation of DMPACl and CdCl<sub>2</sub>·2.5H<sub>2</sub>O in aqueous solution for one week. Red needle-like crystals of DMPACl and MnCl<sub>3</sub>·4H<sub>2</sub>O in a mixed solvent of acetonitrile/methanol (3:1) at 60 °C for two weeks. PXRD patterns confirm the purity of DMPACdCl<sub>3</sub> and DMPAMnCl<sub>3</sub> (Fig. S2, ESI<sup>†</sup>).

Methods. Powder X-ray diffraction (PXRD) data were performed using a Rigaku D/MAX 2000 PC diffractometer with Cu K $\alpha$  radiation over a  $2\theta$  range of 10° to 45°, at a step size of 0.02° and a scanning speed of 10° per minute. The simulated powder patterns were computed using the Mercury software package, based on crystallographic data derived from singlecrystal X-ray diffraction. Single-crystal X-ray diffraction data were acquired on a Rigaku Saturn 924 diffractometer utilizing Mo-Ka radiation ( $\lambda$  = 0.71073 Å). The Rigaku CrystalClear software version 1.3.5 facilitated data collection, cell refinement, and reduction. Crystal structures were determined by direct methods and refined using the full-matrix least-squares method on  $F^2$ , employing the SHELXLTL software package. A summary of the crystallographic data and structure refinement is presented in Tables S1-S8.† Differential Scanning Calorimetry (DSC) measurements were conducted using a NETZSCH DSC 200F3 instrument. These measurements were executed under a nitrogen atmosphere at atmospheric pressure within aluminum crucibles, with heating and cooling rates set at 20 K min<sup>-1</sup>. TGA was carried out on a PerkinElmer TGA 8000 instrument by heating a polycrystalline sample (5 mg) from 300 K to 800 K with a rate of 30 K min<sup>-1</sup> under a nitrogen atmosphere. Dielectric measurements were conducted using a TH2828A impedance analyzer to determine the complex dielectric permittivities. The silver conductive paste was applied to the plate surfaces of the samples to serve as top and bottom electrodes. For the preparation of the thin film, the precursor solution for DMPACdCl3 was prepared by dissolving 10 mg of crystals in 100 µL of water. Next, 20 µL of this solution was applied to a pristine indium-doped tin oxide (ITO) glass substrate, allowed to evaporate at room temperature for 2 hours, and then annealed at 410 K for 5 minutes to complete

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the fabrication process. The surface morphology and ferroelastic domains of the film were examined using an Olympus BX53-P polarizing microscope. Photoluminescence spectroscopy was employed to measure the emission and excitation spectra of powder samples using a Fluorolog-QM spectrophotometer (Horiba), with a xenon lamp serving as the excitation source. Time-resolved spectra were captured using the same setup but with a flash xenon lamp for excitation. The photoluminescence quantum yield was determined with an sphere temperature integrating accessory. Variable photoluminescence spectra were acquired on the spectrofluorometer, which was equipped with a liquid nitrogen cryostat (V-100, Physike).

## Data availability

All data generated and analyzed in this study are included in the article and its ESI.<sup>†</sup>

## Author contributions

J.-M. Z. and Z.-K. X. synthesized the samples and carried out the general characterizations. Y. Q. performed the photoluminescent measurements. P.-F. Li carried out the observation of ferroelastic domains. Z.-X. W. conceived the study and wrote the manuscript with input from other authors.

## Conflicts of interest

There are no conflicts to declare.

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