Mechanochemistry enables optical-electrical multifunctional response and tunability in two-dimensional hybrid perovskites

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ABSTRACT Two-dimensional (2D) organic-inorganic hybrid perovskites (OIHPs) have attracted phenomenal attention because of their superior optoelectronic performances. The combination of their structural tunability and material stability offers an unprecedented opportunity to engineer materials with unique functionalities. However, developing a rapid and effective design method for introducing luminescence into dielectric switch and realizing controllable regulation has been an enormous challenge. Thus far, materials with tunable optoelectronic multichannel response have not been successfully implemented. In this study, we successfully developed a facile and effective mechanochemical method for realizing the integration and regulation of luminescence and dielectric switch in 2D perovskites, which is unprecedented for the design of dielectric switching materials. The mild external mechanical stimuli enabled the formation of Mn^{2+} ion-doped 2D hybrid perovskites $(\text{Cyclopropylammonium})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ with excellent dielectric switch and rapidly controllable luminescence of highly efficient blue light, white light, pink light, and orange light. This work will provide a new perspective on the rapid and effective design of multifunctional materials and can inspire the future development of low-cost and high-efficiency electronics.

Keywords: 2D hybrid perovskite, tunable optoelectronic response, mechanochemistry, multifunctional material

INTRODUCTION

As a new area of current research, two-dimensional (2D) organic-inorganic hybrid perovskites (OIHPs) have attracted phenomenal research interest because of their intriguing applications in high-efficiency solar cells, light-

emitting diodes, lasers, and photodetectors [1–6]. The structurally 2D perovskites are more stable in air and light than the 3D analogues, which endows the former with a greater application potential in optoelectronic devices [7–9]. In particular, the perovskite-based solid-state lighting materials are highly desired as attractive solutions to the disadvantages of traditional fluorescent lighting sources [10,11]. Compared with the 3D analogues, the 2D OIHPs with relaxed structural constraints open a richer platform for material design and property tuning, providing more possibilities for their functional diversity [12–15]. Nevertheless, the effective design and regulation of 2D OIHPs have been a huge challenge, owing to the complexity of multifunctional integration and accidental prediction of the properties for functional materials.

Responsive switching materials, designated as switchable dielectrics, whose physical properties can be reversibly switched between different relatively stable states under external stimuli, have been extensively investigated because of their widespread applications, such as in thermoelectric switch, data communication, thermal energy storage, and signal processing [16–22]. However, most reported switchable dielectrics still suffer from single functional response performance, cumbersome preparation processes, low operating temperature, and safety risks [23–28]. To solve these issues and break the boundaries in generating various desired multifunctionalities, exploring a facile effective preparation method to integrate and regulate luminescence and switching characteristics is undoubtedly a highly attractive scientific undertaking. Doping transition metals, especially divalent manganese, into halide perovskites has

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drawn significant research interest; it is thought to be an effective strategy to reduce toxicity and obtain new fascinating properties [29–32]. Up to now, the 4T_1 – 6A_1 transitions of Mn^{2+} with strong sensitized luminescence in 3D halide perovskites and nanocrystals, considering the energy transfer between the host and the dopant ions, have been extensively reported [33–35]. The combined strategy of doping with Mn^{2+} ions has been proposed as a useful means to improve the optical performance, whereas its valuable role in developing responsive switch has yet to be further explored [36–38]. In addition, the structural phase transition mechanisms of switchable dielectrics are mainly associated with the dynamic motion of organic cations in hybrid materials [39–42]. Given this, doping Mn^{2+} ions in low-dimensional semiconductor materials that contain suitable cations has the potential to enable multifunctionality in electric and optical channels.

Herein, we adopted a facile and effective mechanochemical method whereby Mn^{2+} ions are incorporated into 2D OIHPs to realize multifunctional response and the rapid regulation of responsive switching and luminescence. Considering the 2D purplish-blue-lighting perovskite $(CPA)_2PbBr_4$ (CPA = cyclopropylammonium) and the dielectric switching behavior triggered by the unique cationic motion in orange-lighting perovskite $(CPA)_2MnBr_4$, we used $(CPA)_2PbBr_4$ as the active semiconductor host of the Mn^{2+} dopant ions (Fig. 1). As expected, the Mn-doped perovskite series were rapidly synthesized only by mild mechanical stimulus and showed fascinating luminescence of blue light, white light, pink light, and orange light. More strikingly, the $(CPA)_2Pb_{1-x}Mn_xBr_4$ ($x = 0.3, 0.4, 0.5$) all exhibited excellent dielectric switch characteristics, achieving a dramatic enhancement of 99 K for the phase transition temperature (T_p), compared with $(CPA)_2MnBr_4$. To the best of our knowledge, such a facile mechanochemical approach for obtaining and designing multifunctional responsive switching materials is unprecedented. This

pioneering work, which integrates the merits of dielectric switching, symmetry breaking, doping, and luminescence into one molecular device unit by a simple mechanochemical method, will reveal new insights into smart optical/electrical-responsive multifunctional materials.

EXPERIMENTAL SECTION

Sample preparation

Single crystals of $(CPA)_2MnBr_4$ and $(CPA)_2PbBr_4$ were easily obtained by the slow evaporation of an HBr aqueous solution containing cyclopropylamine and the corresponding metal bromide at a 2:1 molar ratio. Furthermore, $(CPA)_2Pb_{1-x}Mn_xBr_4$ ($x = 0, 0.01, 0.015, 0.02, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5$) perovskite series were rapidly synthesized by mechanical grinding at room temperature (Fig. 1). The synthesis procedures of these materials are detailed in Supplementary information.

Material characterizations and theoretical calculations

The single-crystal X-ray diffraction (XRD), powder XRD (PXRD), differential scanning calorimetry (DSC) measurements, dielectric measurements, Hirshfeld surface calculations, photoluminescence measurements, and computational methods are comprehensively described in Supplementary information. CCDC 1991294–1991296 contains the supplementary crystallographic data for this paper. These data are freely accessible from The Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Single-crystal X-ray structure determinations were performed to study the structural details. The perovskites $(CPA)_2PbBr_4$ and $(CPA)_2MnBr_4$ were isostructural, adopting a layered 2D perovskite structure, in which the infinite and staggered layers of corner-sharing XBr_6 ($X = Pb, Mn$) octahedron were separated by CPA cation bi-

Figure 1 (a) Experimental illustration diagram for the synthesis of $(CPA)_2PbBr_4$ via mechanical grinding and solution processing method. (b) Experimental illustration of Mn^{2+} ions entering 2D layered perovskite $(CPA)_2PbBr_4$.

layers (Fig. S1). Each central metal atom is linked with six Br atoms to form a slightly twisted octahedron, and the protonated CPA cations are anchored to the halide ions of the octahedral structure through N–H...Br hydrogen bonds (Fig. 2). Differentially, at 293 K, the $(\text{CPA})_2\text{PbBr}_4$ crystallized in the monoclinic space group $P2_1/c$, while $(\text{CPA})_2\text{MnBr}_4$ located in the tetragonal space group $P4_2/ncm$ (Table S1). Moreover, the CPA cations in $(\text{CPA})_2\text{PbBr}_4$ are ordered in a static state, while those in $(\text{CPA})_2\text{MnBr}_4$ show a dynamically disordered state. Interestingly, $(\text{CPA})_2\text{MnBr}_4$ exhibits reversible structural phase transitions at 208.8 and 232.4 K. Moreover, $(\text{CPA})_2\text{MnBr}_4$ transforms into the orthorhombic space group $Pca2_1$ at 143 K and its structure is totally ordered.

The hydrogen bonds (N–H...Br) between the terminus of organic cations and the end of inorganic layers can affect the structural arrangement, which is the cause of the staggered conformation of the inorganic lattice in $(\text{CPA})_2\text{PbBr}_4$ and $(\text{CPA})_2\text{MnBr}_4$. As shown in Fig. 2a, b, the CPA cations of $(\text{CPA})_2\text{MnBr}_4$ are positioned in the center of the diagonal of the square, while those of $(\text{CPA})_2\text{PbBr}_4$ are very close to an obtuse angle position of the parallelogram. With the temperature decreased to 143 K, the hydrogen bonds in the ordered low-symmetrical $(\text{CPA})_2\text{MnBr}_4$ become stronger, causing a slight distortion of $[\text{MnBr}_6]$ octahedron layers, and the CPA cations slightly deviate from the center of the parallelo-

gram (Fig. 2c). The hydrogen bonds in $(\text{CPA})_2\text{PbBr}_4$ are stronger than those in $(\text{CPA})_2\text{MnBr}_4$ (Table S2), resulting in a more distorted lattice structure of the $[\text{PbBr}_6]$ octahedron layers (Fig. 2e, f). The bilayers of CPA cations are anchored to the space between the inorganic layers by some hydrogen bonds, which also results in long inter-layer halide–halide distances of 6.269 Å for $(\text{CPA})_2\text{PbBr}_4$, 6.261 Å for $(\text{CPA})_2\text{MnBr}_4$ at 293 K and 6.236 Å for $(\text{CPA})_2\text{MnBr}_4$ at 143 K, respectively. The distance between inorganic layers of $(\text{CPA})_2\text{PbBr}_4$ is so close to that of $(\text{CPA})_2\text{MnBr}_4$, making the mechanical grinding strategy to dope Mn feasible and easy to implement.

To further clarify the hydrogen bonding effect between cations and metal skeletons on structural characteristics and properties, both Hirshfeld surfaces and 2D-fingerprint plots of CPA cations in $(\text{CPA})_2\text{PbBr}_4$ at 293 K, $(\text{CPA})_2\text{MnBr}_4$ at 143 and 293 K are discussed (Fig. 3 and Fig. S2) [43,44]. The interactions between the CPA cation and surrounding molecules in $(\text{CPA})_2\text{PbBr}_4$ are stronger than those in $(\text{CPA})_2\text{MnBr}_4$, based on the Hirshfeld surfaces, in which red, white, and blue are used to distinguish the contacts shorter than, equal to, and longer than the van der Waals distances, respectively (Fig. 3). The close contacts from elements of $\text{H}_{\text{inside}}\text{--Br}_{\text{outside}}$ (the hydrogen bonding contacts between the N atoms of CPA cations and the end of inorganic layers) are highlighted in the 2D fingerprint plots. In 2D fingerprint plots, each

Figure 2 (a) Magnified views of the hydrogen bridging geometries of (a) $(\text{CPA})_2\text{PbBr}_4$ at 293 K, (b) $(\text{CPA})_2\text{MnBr}_4$ at 293 K and (c) $(\text{CPA})_2\text{MnBr}_4$ at 143 K, showing the octahedron of $[\text{PbBr}_6]$ in comparison with $[\text{MnBr}_6]$ and the position of CPA cations relative to the corner-sharing octahedrons. Structure fragments of (d) $(\text{CPA})_2\text{PbBr}_4$ at 293 K, (e) $(\text{CPA})_2\text{MnBr}_4$ at 293 K, and (f) $(\text{CPA})_2\text{MnBr}_4$ at 143 K, showing the hydrogen bonding network between the CPA cations and the corresponding inorganic skeleton in perovskites.

Figure 3 (a) Comparison for Hirshfeld surfaces of CPA cation in (a) $(\text{CPA})_2\text{PbBr}_4$ at 293 K, (b) $(\text{CPA})_2\text{MnBr}_4$ at 143 K and (c) $(\text{CPA})_2\text{MnBr}_4$ at 293 K. Close contacts are highlighted from elements of Hinside–Broutside in (d) $(\text{CPA})_2\text{PbBr}_4$ at 293 K, (e) $(\text{CPA})_2\text{MnBr}_4$ at 143 K and (f) $(\text{CPA})_2\text{MnBr}_4$ at 293 K.

point represents an individual pair (d_i , d_e), reflecting the distances to the nearest atom inside (d_i) and outside (d_e) of the Hirshfeld surface, and the frequency of occurrence for these points correspond to the color from blue (low), through green, to red (highest). Notably, not only is the minimum (d_i , d_e) of the N–Br contacts in $(\text{CPA})_2\text{PbBr}_4$ (0.84, 1.55) shorter than those in $(\text{CPA})_2\text{MnBr}_4$ (0.96, 1.70), but the surface area of the contacts in $(\text{CPA})_2\text{PbBr}_4$ (44.4%) is also larger than those in $(\text{CPA})_2\text{MnBr}_4$ (39.7%), confirming that the stronger hydrogen bonding is associated with the more distorted lattice structure of the $[\text{PbBr}_6]$ octahedron layers. Considering that the order-disorder transition of CPA cations plays a significant role in phase transition, this stronger hydrogen bonding contacts also limit the dynamic motion of CPA cations, which makes it difficult for $(\text{CPA})_2\text{PbBr}_4$ to undergo a phase transition under thermal stimulation.

The luminescence property of OIHPs is generally associated with the structure of the inorganic layers. For $(\text{CPA})_2\text{PbBr}_4$, the Pb–Br–Pb bond angle is 148.25° , much deviated from 180° (Table S3), indicating a serious structural distortion inside the inorganic skeleton. In contrast, the Mn–Br–Mn bond angles of $(\text{CPA})_2\text{MnBr}_4$ at 293 K are 161.08° and 180° , which are closer to the ideal octahedron, consistent with its high symmetry. Moreover, the dynamic changes in cations can also affect the inorganic skeleton. At 143 K, the Mn–Br–Mn bond angles are changed to 161.33° and 163.54° , indicating a very

slight distortion. From these structural results, the phase transition mechanism of $(\text{CPA})_2\text{MnBr}_4$ can be mainly attributed to the order-disorder transition of CPA cations.

Based on the information of crystal structures, the high distortion of the inorganic layer in $(\text{CPA})_2\text{PbBr}_4$ perovskite results in a band-edge purplish-blue-light emission, whereas the orange emission of $(\text{CPA})_2\text{MnBr}_4$ is attributed to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Mn^{2+} [35,45]. To control luminescence characteristics, we prepared a series of perovskites by mixing the $(\text{CPA})_2\text{PbBr}_4$ and $(\text{CPA})_2\text{MnBr}_4$ through a simple mechanochemical route. PXRD measurements were performed to confirm and study the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ perovskite series. Fig. 4a and Fig. S3 show the PXRD patterns of $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ with various Mn^{2+} concentrations. The Pawley refinements for all these PXRD patterns reveal a monoclinic unit cell with a point group $2/m$ (Figs S4 and S5) [46,47]. The structural refinement results show that the unit cell volumes tended to decrease with the increase in Mn^{2+} concentrations (Fig. 4b), indicating that the lattice positions of Pb^{2+} are gradually substituted by Mn^{2+} ions, because the ionic radius of Mn^{2+} is smaller than that of Pb^{2+} . There is no significant difference between the PXRD patterns of $(\text{CPA})_2\text{PbBr}_4$ to $(\text{CPA})_2\text{Pb}_{0.8}\text{Mn}_{0.2}\text{Br}_4$. Notably, as the Mn^{2+} concentration continues to increase, the PXRD pattern of $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$ begins to show noticeable differences. The phenomenon of $(\text{CPA})_2\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Br}_4$ and

Figure 4 (a) High-resolution PXRD patterns for the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0, 0.01, 0.015, 0.02, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5$) perovskite series. (b) Unit cell volumes with different Mn^{2+} doping concentrations.

$(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ are the same as that of $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$, except for a slight shift of diffraction peaks (Fig. 4a). From the comparison for the PXRD patterns of $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$, $(\text{CPA})_2\text{MnBr}_4$, and $(\text{CPA})_2\text{PbBr}_4$ (Fig. S6), after doping Mn^{2+} ions on $(\text{CPA})_2\text{PbBr}_4$, the PXRD pattern shows some changes; for example, some diffraction peaks emerge at 17.56° , 18.10° , 19.56° , 28.68° , 29.54° , 33.56° , and 46.10° , and some diffraction peaks show shifts and splits. The newly emerged diffraction peaks show weak intensity, making the PXRD patterns feature a slight change, which should be attributed to the fact that the entry of Mn did not cause large damage to the lattice; the lattice still maintain the 2D structure. The PXRD patterns of $(\text{CPA})_2\text{PbBr}_4$ and $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ (Fig. S7) exhibit a series of intense sharp ($a\ 0\ 0$) ($a = 1-6$) diffraction peaks, indicating the perfect periodicity of the stacking along the $\langle 1\ 0\ 0 \rangle$ direction as well as high crystallinity. In addition, the refinement results of the PXRD patterns can also prove the pure phase of the highly doped samples. The variation in the PXRD patterns reveals that the entry of Mn into the lattice caused the deformation of the inorganic skeleton, possibly affecting the state of the cation, which consequently results in the optical-electrical multifunctional response and tunability.

Considering the variation in PXRD patterns, we carried out DSC measurements to detect the phase transitions. As shown in Fig. 5a, two pairs of thermal anomaly peaks are observed for $(\text{CPA})_2\text{MnBr}_4$ upon heating/cooling runs, indicative of two reversible continuous structural phase transitions at ~ 209 and ~ 232 K. Remarkably, the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0.3, 0.4, 0.5$) all exhibit an obvious phase transition at ~ 331 K (Fig. 5b and Fig. S8), suggesting that the mechanical grinding strategy is indeed effective; that is, the incorporation of Mn^{2+} into $(\text{CPA})_2\text{PbBr}_4$ can successfully induce the phase transition and

improve the T_p . These sharp exothermic/endothermic peaks and wide thermal hysteresis reveal first-order phase transition. For convenience, the phase below T_p is regarded as the “low-temperature phase” (LTP), and the phase above T_p as the “high-temperature phase” (HTP). In 2D hybrid perovskite structures, the organic cations and inorganic components are connected by some weak interactions (e.g., hydrogen bonding) and affect each other; these weak interactions and mutual effect are related and crucial to perovskite properties. With the increase in Mn^{2+} ions, the lattice positions of Pb^{2+} are gradually replaced by Mn^{2+} ions, which causes changes in the inorganic components, and thereby affect the states of CPA cations. As mentioned above, at room temperature, the CPA cations in $(\text{CPA})_2\text{PbBr}_4$ show statically ordered state, while those in $(\text{CPA})_2\text{MnBr}_4$ are dynamically disordered. When the Mn^{2+} ion concentration reaches a certain value, the structural change of the perovskite is enough to cause a change in its properties, making the T_p sufficiently increase from 232 K in $(\text{CPA})_2\text{MnBr}_4$ to 331 K in $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0.3, 0.4, 0.5$). The structures and phase transition properties of $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0.3, 0.4, 0.5$) are similar; therefore, we here take $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ as an example to further discuss the phase transition information and its device applications. As shown in Fig. 5c, the PXRD patterns show obvious changes from LTP to HTP, where the diffraction peaks at 17.5° and 18.0° disappear, a new diffraction peak was observed at 11.9° , and some diffraction peaks in high-angle areas showed shifts and splits, meaning a structural phase transition occurred. In addition, the structure at 373 K is refined in a tetragonal unit cell with a point group $4/mmm$ (Fig. S9). The relationship of the cells at 273 and 373 K is $a_{\text{LTP}} \approx b_{\text{HTP}} - 0.5c_{\text{HTP}}$, $b_{\text{LTP}} \approx a_{\text{HTP}} - c_{\text{HTP}}$, $c_{\text{LTP}} \approx c_{\text{HTP}}$ (a , b and c are cell parameters of crystal). The PXRD pattern obtained at 293 K is consistent with the

Figure 5 DSC curves of (a) $(\text{CPA})_2\text{PbBr}_4$ and (b) $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$. (c) Variable-temperature PXRD patterns of $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$. (d) The ϵ' of $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ vs. temperature. (e) Schematic diagram of dielectric measurements on electrodes made of the sample, and logic diagram in optoelectronic smart-controlled device. (f) Simulated application of the studied optoelectronic dual response material as a smart sensor in a media alarm system.

one obtained upon cooling back to 293 K, demonstrating the reversibility of the phase transition.

Dielectric permittivity as a function of temperature generally shows noticeable anomalies near T_p . We performed temperature-dependent dielectric measurements on electrodes made of $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ to study the application of the dielectric switching device. The real part of dielectric permittivity (ϵ') for $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ undergoes a remarkable “step-like” anomaly at ~ 330 K upon heating (Fig. 5d), consistent with the DSC results. The ϵ' exhibits a corresponding anomaly at ~ 297 K in cooling mode, showing the excellent dielectric switching characteristics. The dielectric permittivity of $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ exhibits two distinct dielectric steady states and can undergo transition between high dielectric state (corresponding to HTP) and low dielectric state (corresponding to LTP), satisfying the operation of ON/OFF switching, which thus can be used as intelligent control devices driven by the thermal signal. As shown in Fig. 5e, the logic diagram displays the process of multichannel control in imaginary smart systems, combining photo-

luminescence and switchable properties. In a single device unit, multiple commands can be simultaneously executed on multiple physical channels to meet multiple application requirements, and the channels can control one another to achieve automatic operation. Notably, realizing a high temperature dielectric switch and high stability has always been a great challenge, while the $(\text{CPA})_2\text{MnBr}_4$ is easy to deliquescent that makes it difficult to use in dielectric devices. The strategy of incorporating Mn^{2+} into $(\text{CPA})_2\text{PbBr}_4$ to construct $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ greatly improves the stability of dielectric devices and achieves a dramatic enhancement of 99 K for T_p , which demonstrates the effectiveness of this strategy as a new way to design novel switchable materials, having great scientific significance for the further exploration of smart dielectric switches. For operational purposes of media alarm signals, under an external heat stimulus, the device would automatically identify or decode the optical/electrical signal and perform selective response from an “inactive” state to an “active” state at the critical point (T_p), and enable the full automation of the overall switching pro-

cess based on different physical conditions (Fig. 5f).

To study the mechanism for Mn incorporation into the Pb site, we investigated the impurity formation energy of Mn^{2+} ions in the host $(\text{CPA})_2\text{PbBr}_4$ using density functional theory (DFT) calculations. The impurity formation energy (E_f) of a particular substitutional dopant is given by the equation of $E_f = E(\text{doped}) - E(\text{pure}) + \mu_{\text{Pb}} - \mu_{\text{Mn}}$, where in this study $E(\text{doped})$ and $E(\text{pure})$ are the total energies of $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$ and $(\text{CPA})_2\text{PbBr}_4$, respectively, and μ_{Mn} and μ_{Pb} are the chemical potentials of substitutional Mn and Pb atoms, respectively. According to the calculation results (Table S4), the E_f of $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$ is -3.52 eV, indicating that the doped compound could be easily formed, which further verifies the successful incorporation of Mn^{2+} into $(\text{CPA})_2\text{PbBr}_4$; that is, the phase transition and luminescent features can

be rapidly changed by the simple grinding method at room temperature.

The luminescence properties of the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ perovskite series are readily tunable through the modulation of Mn^{2+} ion concentration by simple grinding. The pure $(\text{CPA})_2\text{PbBr}_4$ exhibits a narrow emission band peak at ~ 414 nm (Fig. 6a), while the $(\text{CPA})_2\text{MnBr}_4$ shows a broad emission band peak at ~ 598 nm upon 365 nm excitation (Fig. S10). When the Mn^{2+} ions are incorporated into the host $(\text{CPA})_2\text{PbBr}_4$, $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x > 0$) samples exhibit both a narrow emission and a broad emission band peak at ~ 414 and ~ 598 nm, respectively, as seen from the normalized emission spectra in Fig. 6a, b. Meanwhile, the ratio of narrow emission to broad emission decreases with increasing Mn^{2+} concentration because of the Pb^{2+} lattice

Figure 6 (a, b) The normalized emission spectra of $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ perovskite series with different Mn^{2+} concentrations upon 365 nm excitation. (c) CIE color coordinates of the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ perovskite series with $x = 0$ (●), 0.01 (▲), 0.015 (▼), 0.02 (◀), 0.05 (▶), 0.1 (★), 0.15 (■), 0.2 (◆), 0.3 (♣), 0.4 (♠), 0.5 (♥), 1 (✱) in a 1931 color space chromaticity diagram. (d) Schematic energy diagram of different luminescence processes in Mn^{2+} ion-doped $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$. (e) Blue light, white light, pink light and orange light from the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ perovskite series under ultraviolet (UV) light with excitation wavelength $\lambda_{\text{ex}} = 365$ nm.

positions being gradually replaced by Mn^{2+} ions, which also indicates that the effective fluorescence of Mn^{2+} can be induced by energy transfers in this system. To confirm the existence of multiple luminescence centers and clarify the photophysical process, decay curves of $(\text{CPA})_2\text{PbBr}_4$ and $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0.02, 0.3, 0.5$) samples were measured at different monitoring wavelengths (Fig. S11). From the decay curve monitored at 414 nm, the lifetime of band gap transition shows a continuous decrease from 7.93 to 3.43 ns with the increasing Mn^{2+} ion content, indicating energy transfer existed between the host and Mn^{2+} . Especially, the lifetime at a monitored wavelength of 598 nm tends to decrease with the increase in Mn^{2+} concentration, suggesting the gradual enhancement of the energy transfer efficiency. The purplish-blue and orange emissions of $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ series can be attributed to the coupling effects of band-edge emission and the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Mn^{2+} due to an efficient energy transfer in this system (Fig. 6d).

The corresponding Commission Internationale de L'Eclairage (CIE) color coordinates calculated from the emission spectra of samples are shown in the 1931 color space chromaticity diagram (Fig. 6c and Fig. S12). The pure $(\text{CPA})_2\text{PbBr}_4$ has CIE coordinates of (0.1877,

0.1528), corresponding to purplish-blue emission. Moreover, the intermediate compounds $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0.015, 0.02$) exhibit white emissions with CIE color coordinates of (0.3122, 0.2623) and (0.3447, 0.2784) (Table S5). The correlated color temperatures of these materials indicate that the former emits a cold white light while the latter emits a warmer light. In addition, with the increase in Mn^{2+} ions, the $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$ begins to enter into the pink light region until the $(\text{CPA})_2\text{Pb}_{0.5}\text{Mn}_{0.5}\text{Br}_4$ emits an orange light. Moreover, the photoluminescence quantum yields (PLQYs) of $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ ($x = 0, 0.02, 0.3, 0.5$) are measured as 12.2%, 23.9%, 35.1% and 62.9%, respectively (Fig. S13). It reaches a highly level in PLQY value, larger than that of most ever reported OIHPs as white-light-emitting materials [10,11]. As shown in Fig. 6e, by the regulation of the Mn^{2+} ion concentration at room temperature through the simple grinding method, luminescence of blue light, white light, pink light, and orange light from the $(\text{CPA})_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ perovskite series were easily realized.

To further investigate the optical properties and emission mechanisms, the electronic band structures and densities of states of $(\text{CPA})_2\text{PbBr}_4$ and $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$

Figure 7 Electronic band structures of (a) the host $(\text{CPA})_2\text{PbBr}_4$ and (b) the doped sample $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$. The total and partial densities of states of (c) $(\text{CPA})_2\text{PbBr}_4$ and (d) $(\text{CPA})_2\text{Pb}_{0.7}\text{Mn}_{0.3}\text{Br}_4$.

Br₄ were calculated by DFT [48–50]. As illustrated in Fig. 7, the calculated band gap of (CPA)₂PbBr₄ is 2.66 eV, while the band gap value of (CPA)₂Pb_{0.7}Mn_{0.3}Br₄ is lower, 2.37 eV. This result agrees well with the measurements, although slightly different from the experimental values (3.04 and 2.82 eV), due to the limitation of DFT methods (Fig. S14). The optical parameters of lead hybrid perovskites are mainly determined by the overlapping of s/p antibonding orbitals between the lead and halide ions, so this reduction in band gap implies that Mn²⁺ ions successfully entered the lattice to replace Pb²⁺ sites. The calculated partial densities of states (PDOS) projected onto the constituent elements in (CPA)₂PbBr₄ and (CPA)₂Pb_{0.7}Mn_{0.3}Br₄ are displayed in Fig. 7c, d. Both the top of valence bands and the bottom of conduction bands are only constituted by the orbitals of the inorganic part in (CPA)₂PbBr₄, indicating that the fluorescence emission from self-trapping excitons mainly occurred within [PbBr₆] octahedra. After the Mn²⁺ incorporation, it can be observed in (CPA)₂Pb_{0.7}Mn_{0.3}Br₄ that the Mn orbitals emerged at both the top of valence bands and the bottom of conduction bands, which demonstrates that photo-generated electrons could easily jump from the conduction band minimum to Mn together with energy transfer, and thereby causes the efficient luminescence of Mn²⁺ ions (Fig. 7d). In addition, the positions of the Pb and Br orbitals in the electronic structure are almost unchanged. This indicates that the Mn²⁺ ions introduced a new fluorescence emission wavelength without affecting the position of the intrinsic emission peak, resulting in the fascinating multiple light emissions.

CONCLUSIONS

In summary, to realize multifunctional integration and regulation of luminescence and responsive switching, we successfully adopted a facile and effective mechanochemical synthesis method whereby Mn²⁺ ions are incorporated into (CPA)₂PbBr₄. The unique crystal structure of the 2D hybrid perovskite allowed the Mn²⁺ ions to rapidly enter the crystal lattice only by room-temperature grinding to form Mn²⁺ ion-doped 2D hybrid perovskites (CPA)₂Pb_{1-x}Mn_xBr₄, showing the fascinating luminescence variations of blue-light, white-light, pink-light, and orange-light. The (CPA)₂Pb_{1-x}Mn_xBr₄ (x = 0.3, 0.4, 0.5) exhibit responsive dielectric switching characteristics at 331 K, achieving a dramatic enhancement of 99 K for T_p, compared with (CPA)₂MnBr₄. Systematic characterizations and analyses indicate that the structural phase transition mechanisms are mainly ascribe to the order-disorder transition of CPA cations, and the pho-

toluminescences corresponding to emissions at 414 and 598 nm are attributed to (CPA)₂Pb_{1-x}Mn_xBr₄ band-edge emission and the ⁴T₁–⁶A₁ transition of Mn²⁺ owing to an efficient energy transfer in the system. This work opens up new possibilities for the design and rapid preparation of multifunctional optoelectronic response materials *via* mechanochemical synthesis and would further benefit the development toward practical applications compatible with miniaturized multifunctional devices.

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

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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机械化学促成可调谐光-电多功能响应二维杂化钙钛矿材料

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摘要 二维有机-无机杂化钙钛矿因在光伏、光电子等领域的巨大应用潜力而备受关注. 此外, 该类材料具有突出的结构可调性和材料稳定性, 为功能性质的设计调控及器件应用提供了丰富的材料设计平台. 然而, 将多种物理通道的性质整合实现材料的多功能性仍具有挑战性, 而对其进行快速有效的调节更是难上加难. 迄今为止, 尚未成功实现可调谐的光电多通道响应材料. 本文成功开发了一种简便有效的机械力化学合成方法, 可实现二维杂化钙钛矿中的多功能光电集成和调控. 温和的外部机械刺激可快速形成锰掺杂的二维杂化钙钛矿(Cyclopropylammonium)₂Pb_{1-x}Mn_xBr₄, 并迅速调节其光学性质并诱导高温介电开关, 实现高效的蓝色、白色、粉红色和橙色荧光特性. 这项工作将为多功能光电响应材料的快速有效设计提供新的视角, 也将为低成本、高效率智能设备的进一步开发和应用提供新的机遇.