

# Boosting the photoluminescence of 2D organic–inorganic perovskite films by mixing with polymers

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#### Abstract

Herein, Poly(4-Vinylpyridine) (PVP) and Poly(ethylene oxide) (PEO) mixed  $(PEA)_2PbI_4$  films are fabricated by spin-coating method. The optical and SEM images exhibit improved morphology with more uniform and homogeneous surfaces after mixing PVP and PEO polymers, which increases with the concentrations of the polymers. XRD and FTIR measurements show that the crystal structure and functional group of the  $(PEA)_2PbI_4$  film don't change after introducing the polymer. The optical bandgap of the polymer-mixed  $(PEA)_2PbI_4$  films gradually increased with increasing the concentrations of PVP and PEO polymers. Moreover, the two-photon-pumped photoluminescence (TPL) has been boosted by 3.5 and 3.8 folds by mixing with 25% PVP and 25% PEO, respectively. Time-resolved PL measurements indicate that the PL lifetimes of the polymer-mixed  $(PEA)_2PbI_4$  films have been increased, proving that the increased TPL emission is due to the improved crystalline quality and decreased trap states. This work provides an effective strategy to improve the crystalline quality and photoemission of the 2D perovskite films, which shows great promise for manufacturing high-performance optoelectronic devices based on 2D perovskites.

Keywords 2D Perovskites · Polymer · Photoluminescence boosting · Optoelectronic devices

# **1** Introduction

Recently, 3D hybrid organic–inorganic perovskites (HOIPs) have presented a great outlook for application in light-emitting devices, photodetectors, and solar cells [1–5]. However, the instability of 3D perovskites in an ambient environment still hinders the practical applications [6, 7]. Instead, 2D HOIPs are derived from 3D HOIPs to solve this issue due to their outstanding humidity resistance [8]. 2D HOIPs possess

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a general chemical formula  $(RNH_3)_2(CH_3NH_3)_{n-1}M_nX_{3n+1}$ , where R is a long-chain organic group, M represents a metal cation, X indicates a halide anion, and n refers to the number of octahedrons layers among the organic spacers [9–11]. The shrinking of 3D HOIPs to 2D fetches individual properties, such as stronger quantum confinement, a greater tenability, and a higher exciton binding energy owing to the multiplequantum-well structure [12–15]. Accordingly, 2D HOIPs have opened new avenues for optoelectronic applications [16–19].

Although 2D perovskite has several excellent advantages, these materials still suffer from severe trap states [20, 21]. This issue remains a challenge for obtaining highperformance optoelectronic devices based on 2D perovskites. Accordingly, a lot of works have been suggested for enhancing photoemission by improving the surface morphology and crystalline grains. For example, Song et al. [22] improved the surface morphology of 2D perovskite using UV-light illumination during growth, which helps decrease trap-assisted recombination and improves the PL emission. Yang et al. used small-molecule trioctylphosphine oxide for coating the surface of quasi-2D perovskite film, reducing the non-radiative recombination and increasing the green emission [23]. Besides, polymer's addition is also effective for improving the stability and photoemission of the perovskites. As the polymer can tune the surface morphology and grain size, reducing the trap state and enhancing the radiative recombination [24, 25]. Chang et al. improved the PCE by 25% after adding 1, wt.% of PEG into perovskite, improving the surface morphology and controlling in size and gathering of crystals [26]. Further, Yavari et al. displayed that inserting a fluffy interlayer of PVP polymer among the perovskite and the hole transport layer (HTL) decreased the non-radiative recombination, increasing the photoemission [27]. Despite polymer mixing was widely studied in 3D perovskites, the effect of polymer mixing on optical properties of 2D HOIPs still needs further investigation.

In this work, we propose to boost the photoluminescence of 2D HOIP films by mixing them with polymers. We fabricate Poly(4-Vinylpyridine) (PVP) and Poly(ethylene oxide) (PEO) mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films by spin-coating method. The polymer-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films exhibit more uniform and homogeneous surfaces compared with the pristine films, indicating an improved morphology by polymer mixture. We investigate the two-photon-pumped photoluminescence (TPL) of the fabricated (PEA)<sub>2</sub>PbI<sub>4</sub> films, which can be attributed to the exciton recombination. Moreover, we observe an enhancement of the (TPL) polymer-mixed  $(PEA)_2PbI_4$  films, by 3.5 and 3.8 folds, respectively, with 25% PVP and 25% PEO. The time-resolved PL measurement indicates that the PL lifetime of the polymer-mixed  $(PEA)_2PbI_4$  films has been increased, indicating that the increased TPL emission is due to the improved crystalline quality and decreased trap states.

## 2 Experimental part

## 2.1 Materials

All powders and solvents are applied as received without further refinement. Phenylethylamine iodide (PEAI, MW 249) was purchased from Dyesol and Lead iodide (PbI<sub>2</sub>, MW 461) from Alfa Aesar. Poly(4 Vinylpyridine) (PVP, MW 58 000), Polyethylene Oxide (PEO, MW 100 000). N, N-dimethylformamide (DMF) (anhydrous, 99.8%) were obtained from Sigma-Aldrich. Toluene (99.8%) was bought from Sigma-Aldrich.

## 2.2 Preparation of (PEA)<sub>2</sub>Pbl<sub>4</sub> films

The 2D (PEA)<sub>2</sub>PbI<sub>4</sub> films were synthesized by spin-coating method, as illustrated in Fig. 1a [28]. Firstly, the glass substrates were cleaned by consecutive ultrasonic, thereby in detergent, acetone, deionized water, and ethanol. After that, the substrates were dried at 60 °C for 10 min. And then,

the powders of PbI<sub>2</sub> (461 mg, 1 mol) and PEAI (498.4 mg, 2 mol) were mingled and resolved in 1.0 mL of DMF at 80 °C via a magnetic stirrer for one hour; 25 µL of the solution was dropped onto the clear substrate for two-step spin coating (1000 rpm, 10 s in the first step, and 3000 rpm, 30 s in the second step). The second step was used to spread the perovskite solution over all the substrate and make the film more homogeneous. In addition, 15  $\mu$ L of toluene was dropped during the second spinning agenda onto the substrate after 10 s from the onset of the spinning process to make the film more homogeneity. Lastly, the films were annealed at 80 °C for 10 min on a hotplate. To prepare the (PEA)<sub>2</sub>PbI<sub>4</sub> films mixed with polymers, Poly(4-Vinylpyridine) (PVP) and Poly(ethylene oxide) (PEO) powders were, respectively, dissolved in DMF to form the polymer solutions (18 mg/mL). Subsequently, PVP and PEO solutions with different concentrations (5%, 15%, and 25%) were, respectively, added to the (PEA)<sub>2</sub>PbI<sub>4</sub> solution and then mixed via magnetic stirrer for one hour. The  $(PEA)_2PbI_4$ films mixed with polymers were also prepared by the same spin-coating procedures.

#### 2.3 Physical characterization

The surface morphology of the pristine and the mixed  $(PEA)_2PbI_4$  films was studied using scanning electron microscopy SEM (SEM, Nova NanoSEM 450) with an optical microscope (IX73, Olympus). The structural properties of the films were demonstrated by using XRD (XRD, Empyrean. UV–Vis spectrometer has been carried out in the range from 400 to 800 nm to determine the absorption spectra of the samples. Steady-state two-photon absorption induced photoluminescence (TPL) measurements were performed through utilizing a Ti: sapphire oscillator (Vitara, Coherent, 800 nm, ~ 30 fs, 80 MHz) for excitation. The TPL signal was directed to a spectrometer (Andor 193i) for spectral measurement or a TCSPC system (PicoHarp 300, PicoQuant) for lifetime measurement.

# **3** Results and discussion

Figure 1b and c show the optical microscope images of the as-prepared and polymer-mixed  $(PEA)_2PbI_4$  films. It can be observed that the  $(PEA)_2PbI_4$  films have been formed with great grain sizes and inhomogeneous surfaces. In contrast, the films become with a regular form and uniform surfaces after incorporating PVP and PEO polymers inside the 2D perovskite films. Figure 2a and b show the SEM image of the pristine and polymer-mixed  $(PEA)_2PbI_4$  films with different concentrations of PVP and PEO, respectively. It is observed that the pristine (PEA)\_2PbI\_4 film manifests large grains with average sizes between 4 and 12 µm, where some



**Fig. 1** a Schematic diagram for the spin coating of  $(PEA)_2PbI_4$  films. b Optical microscope images of the pristine  $(PEA)_2PbI_4$  film and the 5%-, 15%-, 25%-PVP mixed  $(PEA)_2PbI_4$  films. c Optical microscope

images of the pristine  $(PEA)_2PbI_4$  film and the 5%-, 15%-, 25%- PEO mixed  $(PEA)_2PbI_4$  films

grains are linked with their neighbors to form larger-sized islands. Moreover, the surface of the pristine film is inhomogeneous and contains several bores and cracks. However, the morphology of the mixed films with different concentrations of PVP and PEO appears more uniform, without pinholes and cracks. Obviously, the amount of grain boundary is decreased after adding PVP and PEO polymer, which is a benefit for reducing the defect density and improving the surface morphology [29, 30]. This effect agrees well with many previously reported studies to find better quality perovskite films, which facilitates the improvement of optoelectronic performance [30, 31]. Additionally, one can observe that increasing the concentrations of PVP and PEO polymers leads to a great improvement in the surface morphology of the perovskite film.

Figure 2c and d display the XRD pattern of the pristine and polymer-mixed  $(PEA)_2PbI_4$  films, respectively. The pristine  $(PEA)_2PbI_4$  film show strong peaks located at  $2\theta = 10.67^\circ$ ,  $16.11^\circ$ ,  $21.6^\circ$ ,  $26.6^\circ$ ,  $32.7^\circ$ , and  $38.4^\circ$ , respectively, which correspond to the (00 *l*) of the 2D layered structure, which agrees well with the reported results [32–34]. In particular, the XRD patterns of the (PEA)\_2PbI\_4 films remain unvaried after mixing with different concentrations of PVP and PEO, which indicate that mixing of polymer does not change the crystal structures of the 2D perovskites. In addition, the stronger and sharper peaks of the XRD patterns for the polymer-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films imply an improvement of the crystalline and molecular ordering of the intermediate phase induced by the long-chain polymer. For further confirmation, the average crystallite size (D) is calculated of the pristine and mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films for the main peak (00<u>10</u>) using the following relation (listed in Table 1) [35]:

$$D = \frac{0.9\lambda}{\beta \text{COS}\theta}$$

It is found that the crystal size of the pristine film was increased after introducing PVP and PEO polymers. The increase in crystal size is able to form a regular film with lower grain boundaries and pinholes on the surface and leads to high optoelectronic performance. Additionally, the dislocation density ( $\delta$ ) is also an important parameter to reveal the degree of crystallinity, which is deduced from the following relation [36]: Fig. 2 a SEM images of the pristine (PEA)<sub>2</sub>PbI<sub>4</sub> film and the 5%-, 15%-, 25%-PVP mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films. **b** SEM images of the pristine (PEA)<sub>2</sub>PbI<sub>4</sub> film and the 5%-, 15%-, 25%-PEO mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films. **c** XRD patterns of the pristine (PEA)<sub>2</sub>PbI<sub>4</sub> film and the 5%-, 15%-, 25%-PVP mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films. **d** XRD patterns of the pristine (PEA)<sub>2</sub>PbI<sub>4</sub> film and the 5%-, 15%-, 25%-PEO mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films



Table 1 The quantitative induced changes in the microstructural parameters of the  $(PEA)_2PbI_4$  films after introducing different concentrations of PVP and PEO polymers

	(PEA) <sub>2</sub> PbI <sub>4</sub>	+5% PVP	+15% PVP	+25% PVP	+5% PEO	+15% PEO	+25% PEO
Crystal size [nm]	64.53	68.03	69.29	70.31	68.42	69.47	70.49
dislocation density [10 <sup>-4</sup> lines/m <sup>2</sup> ]	2.41	2.16	2.08	2.02	2.14	2.07	2.01

$$\delta = \frac{1}{D^2}$$

We found that the average dislocation density of the pristine film was  $1.44 \times 10^{-5}$ , and, respectively, decreased to  $1.154 \times 10^{-5}$  and  $1.164 \times 10^{-5}$  lines/m<sup>2</sup> of the (PEA)<sub>2</sub>PbI<sub>4</sub>/25%PVP and (PEA)<sub>2</sub>PbI<sub>4</sub>/25%PEO (listed in Table 1). These results confirm enhancing the crystallinity after introducing PVP and PEO polymers, which decreases the defect state and hence the trap states. And this is an important aspect of photoluminescence improvement.

FTIR analysis was performed to describe the chemical interactions between the  $(PEA)_2PbI_4$  and polymers. Figure 3a and b show the FTIR of the non-mixed and mixed films with different concentrations of PVP and PEO, respectively. It is observed that the pristine film has absorption

peaks at ~2847.64, 2912.68, and 3018.34 cm<sup>-1</sup>, corresponding to the stretching or bending vibrations of  $-CH_3$  and  $-CH_2$  [37]. Further, the absorption bands which are located at about 3061.59 and 3160 cm<sup>-1</sup> are referred to as N–H stretching vibrations [38]. Additionally, the FTIR spectra of the mixed films with different concentrations of PVP and PEO polymers are well similar to the spectrum of the pristine perovskite film. Nevertheless, the peaks are shifted to a lower wavenumber, and the intensity is decreased after introducing both polymers to the original film. This could be attributed to the interaction between the polymers and the perovskite molecules.

Figure 4a shows the absorption spectra of the pristine and PVP-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films. All films manifest a narrow absorption peak at 518 nm, which agrees with the excitonic absorption of  $(PEA)_2PbI_4$  [39]. Further, the figure also



shows that introduction of polymers into the perovskite layer leads to a slight decrease in the light absorption, which may be attributed to increasing the crystal size of the polymermixed films. In addition, the optical bandgap ( $E_g$ ) of the pristine and polymer-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> film is extracted using Tauc's equation [40, 41]:

$$\alpha h\nu = B (h\nu - E_g)^n$$

where  $\alpha$  refers to the absorption coefficient, the factor n is 1/2 for a direct allowed transition, and B represents the absorption edge parameter. Figure 4b is utilized for determining the perovskite bandgap as a function of the PVP concentrations. It was found that the optical bandgap of the (PEA)<sub>2</sub>PbI<sub>4</sub> film is 2.334 eV, which gradually increased with

increasing the concentrations of PVP polymers. Thus, the bandgap is enhanced to 2.348 of the  $(PEA)_2PbI_4/25\%$  PVP. This change may be due to increasing the crystallinity and shifting of the Pb<sup>2+</sup> 4f core-level peak, which dominates the bandgap [42]. Similar results were obtained for the PEO-mixed (PEA)\_2PbI\_4 films, as shown in Fig. 4c and d, in which the bandgap of the (PEA)\_2PbI\_4/25\% PEO increased to 2.343 eV.

To investigate the photoemission properties, the PL images of the pristine and polymer-mixed  $(PEA)_2PbI_4$  films are measured for comparison. Figure 5a and b show the PL images of the pristine and mixed  $(PEA)_2PbI_4$  films with different concentrations of PVP and PEO, respectively. The figures manifest that  $(PEA)_2PbI_4$  film holds strong fluorescence due to the high exciton binding energy, which leads to rapidly radiative recombination



**Fig. 5 a** PL images, and **b** the TPL spectra of the pristine and PVPmixed (PEA)<sub>2</sub>PbI<sub>4</sub> films. **c** Linear absorption and TPL spectra of the (PEA)<sub>2</sub>PbI<sub>4</sub>, (PEA)<sub>2</sub>PbI<sub>4</sub>/5%- PVP, and (PEA)<sub>2</sub>PbI<sub>4</sub>/5%- PEO, films.

and enhanced PL [43]. Moreover, the green PL emission gradually increases with increasing the concentrations of PVP and PEO polymers. Figure 5c presents the normalized absorption and TPL spectra of the pristine (PEA)<sub>2</sub>PbI<sub>4</sub>, (PEA)<sub>2</sub>PbI<sub>4</sub>/5% PVP, (PEA)<sub>2</sub>PbI<sub>4</sub>/5% PEO, respectively. It is observed that these spectra are well overlapped, and the absorption onset is complemented by almost identical with PL spectra, which demonstrates that the E<sub>o</sub> was maintained. For quantitative characterization, the TPL spectra of the pristine and mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films with different concentrations of PVP were measured, as shown in Fig. 5d. The TPL spectra display a homogenous PL peak located at ~ 535 nm, which is consistent with the reported results [44, 45]. More importantly, the photoemission intensity of the PVP-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films increases gradually with the concentration of PVP, which has been increased by 3.5 folds after incorporating by 25%-concentration PVP. Figure 5e also shows that mixed with PEO is also beneficial for increasing the PL emission of the  $(PEA)_2PbI_4$  films, and the TPL intensity of the  $(PEA)_2PbI_4$ film has been increased by 3.8 folds. As analyzed above, the pyridine part (side chain) in PVP polymer can passivate lead ions which are caused by misalignment surface defects and can fill the iodine on the surface of the perovskite film vacancy trap. Therefore, it leads to reducing the trap state and enhancing the radiative recombination and PL [42, 46]. Besides, the PEO polymer chemically interacts with lead ions on the perovskite surface, which leads to passivating the undercoordinated defect states. As a result, the trap state is decreased, thus boosting the radiative recombination and PL emission [47].

**d** PL images, and **e** the TPL spectra of the pristine and PEO-mixed  $(PEA)_2PbI_4$  films

We also measured the power-dependent TPL intensities for the  $(PEA)_2PbI_4$  films to reveal the photoemission nature. Figure 6a-c show the power-dependent TPL spectra for the pristine, PVP-mixed, and PEO-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films, respectively. Correspondingly, Fig. 6d-f show plots of the TPL intensity as a function of the excitation power. In the large-area (PEA)<sub>2</sub>PbI<sub>4</sub> crystals, the surface traps will lead to a bimolecular recombination process, which results in a super-quadratic power dependence of the TPL on the excitation power [48, 49]. However, in this work, we can observe that for all the  $(PEA)_2PbI_4$  films, the power-dependent TPL intensities are quadratic-dependent on the excitation power, which can well prove that the TPL emission is originated from the exciton recombination in the pristine and polymer-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films [45, 48]. Therefore, we can conclude that the TPL enhancement in the polymer-mixed  $(PEA)_2PbI_4$  films do not originate from the bimolecular recombination process but due to the improved crystalline quality and decreased traps.

In order to demonstrate the mechanism for the TPL enhancement, the PL lifetimes of the pristine and polymer-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films were measured. Figure 7a and b display the time-resolved PL decay traces for the pristine, PVP-mixed, and PEO-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films, respectively. As reported, the radiative recombination of 2D perovskites can be constructed from the intrinsic exciton recombination and the trap-states recombination [50]. A bi-exponential decay function is used to fit the PL decay curves [22].



**Fig.6** Power-dependent TPL spectra for (**a**) pristine  $(PEA)_2PbI_4$  film, **b** 25%-PVP mixed  $(PEA)_2PbI_4$  films, and (**c**) 25%-PEO mixed  $(PEA)_2PbI_4$  films. Plots of the TPL intensity as a function of the

excitation power for (d) pristine  $(PEA)_2PbI_4$  film, e 25%-PVP mixed  $(PEA)_2PbI_4$  films, and f 25%-PEO mixed  $(PEA)_2PbI_4$  films



$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right)$$

where  $A_1$  and  $A_2$  represent the decay amplitude, the fast part  $\tau_1$  refers to the surface trapping, and the slow part  $\tau_2$  represents the radiative recombination [51]. The fitted itemized results of the (PEA)<sub>2</sub>PbI<sub>4</sub> films are summarized in Table 2. From the fitted data, the mean recombination lifetimes ( $\tau_{ave}$ ) is calculated by the following equation [52, 53]:

$$\tau_{\text{ave}} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$

It can be obtained that the PL lifetime of the pristine film has a fast decay component  $\tau_1 = 0.573$  ns, and a slow decay component  $\tau_2 = 3.34$  ns ( $\tau_{ave} = 1.71$  ns). Correspondingly, the

Table 2Fitted PL decay lifetimes of  $(PEA)_2PbI_4$  films fabricated withdifferent concentrations of PVP and PEO polymers

	A <sub>1</sub>	$\tau_1$ (ns)	A <sub>2</sub>	$\tau_2$ (ns)	$\tau_{\rm avg}  ({\rm ns})$
(PEA) <sub>2</sub> PbI <sub>4</sub>	1897.5	0.573	233.11	3.340	1.78
(PEA) <sub>2</sub> PbI <sub>4</sub> /05%PVP	1914.8	0.588	571.6	3.564	2.53
(PEA) <sub>2</sub> PbI <sub>4</sub> /15%PVP	2210.8	0.601	1448.8	3.640	3.07
(PEA) <sub>2</sub> PbI <sub>4</sub> /25%PVP	1795.7	0.583	764.8	3.825	2.96
(PEA) <sub>2</sub> PbI <sub>4</sub> /05%PEO	2151.3	0.588	793.9	3.509	2.59
(PEA) <sub>2</sub> PbI <sub>4</sub> /15%PEO	2272.8	0.583	636.1	3.660	2.56
(PEA) <sub>2</sub> PbI <sub>4</sub> /25%PEO	1840.2	0.608	930.1	3.828	3.08

fast and slow decay components increase after incorporating the various proportions of PVP and PEO polymers, reaching the values of  $\tau_1 = 0.583$  ns,  $\tau_2 = 3.825$  ns ( $\tau_{avg} = 3.63$  ns) for PVP-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films, and  $\tau_1 = 0.583$  ns,  $\tau_2 = 3.66$  ns ( $\tau_{avg} = 3.16$  ns) for PEO-mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films, respectively. The average PL lifetimes of the (PEA)<sub>2</sub>PbI<sub>4</sub> films increase after introducing the PVP and PEO. These results indicate that the non-radiative recombination is reduced in the polymer-mixed perovskite films, which demonstrate the mechanism proposed above [54, 55].

## 4 Conclusion

In conclusion, PVP and PEO mixed (PEA)<sub>2</sub>PbI<sub>4</sub> films have been fabricated by the spin-coating method. The polymermixed (PEA)<sub>2</sub>PbI<sub>4</sub> films exhibit improved morphology with more uniform and homogeneous surfaces, which increases with the concentrations of the polymers. XRD and FTIR analyses confirm that the crystal structure and functional group of the pure film don't vary after mixing PVP and PEO polymers. The optical bandgap of the  $(PEA)_2PbI_4$  film was 2.334 eV, which increased to 2.348 eV and 2.343 eV of the (PEA)<sub>2</sub>PbI<sub>4</sub>/25% PVP and (PEA)<sub>2</sub>PbI<sub>4</sub>/25% PEO, respectively. Moreover, the TPL emission of the (PEA)<sub>2</sub>PbI<sub>4</sub> films is demonstrated to originate from the exciton recombination, which has been boosted by 3.5 and 3.8 folds by mixing with 25% PVP and 25% PEO, respectively. Time-resolved PL measurements indicate that the PL lifetimes of the polymermixed (PEA)<sub>2</sub>PbI<sub>4</sub> films have been increased, demonstrating that the increased TPL emission is due to the improved crystalline quality and decreased trap states. This work provides an effective strategy to improve the crystalline quality and photoemission of the 2D perovskite films, which shows great promise for manufacturing high-performance optoelectronic devices based on 2D perovskites.

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