Molecular Engineering towards Efficient White-Light-Emitting Perovskite

Mingming Zhang

Qingdao University of Science & Technology

Lili Zhao

Nanjing University

Qian Zhang

Qingdao University of Science & Technology

Najma Yaqoob

Forschungszentrum Jülich

Zhengmao Yin

College of Materials Science and Engineering, Qingdao University of Science and Technology / State Key Laboratory of Crystal Materials, Shandong University

Payam Kaghazchi

Freie University <https://orcid.org/0000-0002-1541-7760>

Weigao Xu

Nanjing University <https://orcid.org/0000-0002-3014-756X>

Lei Wang

Qingdao University of Science and Technology <https://orcid.org/0000-0001-7275-4846>

Jun Xing (✉ xingjun@qust.edu.cn)

Qingdao University of Science & Technology <https://orcid.org/0000-0003-4499-4062>

Article

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Abstract

Low-dimensional organic-inorganic hybrid perovskites have demonstrated excellent performance as efficient white-light emitters. The broadband emission with large Stokes shift originates from self-trapped excitons (STEs). Since the mechanism of STEs formation in perovskites is still not clear, preparation of new low-dimensional white perovskites relies mostly on screening lots of intercalated organic molecules rather than a rational design. Here, we report an atom-substituting strategy to trigger STEs formation in layered perovskites. We applied halogen substituting hydrogen of C-H bond in intercalated organic molecules. The halogen-substituents with high electronegativity will withdraw electrons from the tail - NH_3^+ in the molecule. This results in a large positive charge accumulation on $-\text{NH}_3^+$, and thus a stronger attractive Coulomb force in ionic bond $\text{NH}_3^+-\text{PbBr}_3^-$. This plays an important role in transformation of free excitons (FEs) into STEs. Our designed white perovskites reached a high photoluminescence quantum yield of 32%, high color rendering index of near 90 and excellent Commission International de l'Eclairage coordinates close to the standard white-light (0.33, 0.33). This work provides atomic insights into the STEs formation in low-dimensional perovskites and will benefit tailoring white perovskites with boosting performance.

Introduction

Artificial lighting consumes about one-fifth of global electricity. The traditional method to produce white light is mixing multiple color emitters, which suffers from several problems, such as unstability in emission color due to different degradation rates of emitters and efficiency loss due to the overlapping absorption. Thus, developing a single-phase material with an efficient broadband white-light (BWL) emission and comparable stable colors as well as good color rendition is ideal for lighting application. In recent years, metal halide perovskites have emerged as a class of material with low-temperature solution processing, tunable band structure and efficient photoluminescence, which offer an intriguing potential application for low-cost light-emitting devices.¹⁻⁵ In 2014, Karunadasa et al. observed a BWL emission from a two-dimensional (2D) lead-halide perovskite.⁶ Subsequently, a variety of low-dimensional perovskites were demonstrated to be BWL emissive.⁷⁻¹¹ The large Stokes shift and broad photoluminescence (PL) of low-dimensional perovskites originate from self-trapped excitons (STEs), which form through strong coupling of excited excitons with surrounding deformable lattice.¹² Because of unclear mechanism of STEs formation, most of the reported low-dimensional white perovskites have been so far discovered by screening a series of intercalating organic molecules; it is still a big challenge to design new white perovskite materials with boosting BWL emission on atomic level.

STEs is a common phenomenon in metal halides, since their ionic and polar crystal structures possess relative strong electron-phonon interaction.¹³ Photoinduced excitons in low-dimensional perovskites have large binding energies of several hundreds of meV (Frenkel exciton), in which an electron-hole pair sharing a common bond. Due to the electroneutrality feature of Frenkel excitons, STEs are dominated by

short-range electron-phonon interactions.¹⁴ Thus, the chemical bonds confining the excitons should play an important role in the formation of STEs in perovskites.

Herein, we report an atomic-level tailoring strategy to enhance the Coulomb force of ionic bonds in 2D perovskites. The strengthened bonds trigger excitons self-trapping at room temperature, resulting in an efficient BWL emission from 400 to 800 nm. Our proposed white perovskites offer high PLQY of 32% and high color-rendering index (CRI) of about 90 as well as excellent Commission International de l'Eclairage (CIE) coordinates close to the standard white-light (0.33, 0.33). This work not only develops a series of perovskites with BWL emission, but more importantly discovers the effect of their chemical bonds on the STEs formation, and thus offers a rational approach to design new white perovskite emitters.

Results And Discussion

2D lead-bromide perovskite crystals were synthesized according to the previous reported anti-solvent diffusion method.^{15,16} A vial containing PbBr_2 , $\text{R-NH}_3\text{Br}$ and DMF/DMSO solution was put in a bigger sealed vial container with anti-solvent. Perovskites crystalized gradually as anti-solvent diffuses into perovskite precursor and the crystals were then taken out after several days (see Methods for details).

Phenylmethylammonium lead bromide $((\text{PMA})_2\text{PbBr}_4)$ is a typical violet emissive perovskite without STEs phenomenon at room temperature.¹⁷ To investigate the influence of chemical bonds on the formation of STEs, halogen atoms were introduced as substituents in phenyl to tailor the chemical property of PMA cations. We performed first-principles density-functional-theory (DFT) to simulate $(\text{PMA})_2\text{PbBr}_4$ and a series of its corresponding halogen-substituted (F, Cl and Br) perovskite samples. We take Cl-substituted perovskite $(\text{CIPMA})_2\text{PbBr}_4$ as the model. Figure 1a shows the atomic structure of $(\text{PMA})_2\text{PbBr}_4$, $(2\text{-CIPMA})_2\text{PbBr}_4$ (ortho-substitution), $(3\text{-CIPMA})_2\text{PbBr}_4$ (meta-substitution) and $(4\text{-CIPMA})_2\text{PbBr}_4$ (para-substitution). As expected, $(\text{PMA})_2\text{PbBr}_4$ shows a corrugated 2D perovskite structure with PbBr_6 octahedrons connecting with corners, which crystalizes in the polar space group $\text{Cmc}2_1$.¹⁷ The interlayer spacing is 1.656 nm (Table S1). When Cl replaces ortho-hydrogen, the crystal lattice slightly expands in-plane-orientation due to the longer bond length of C-Cl (1.77 Å) compared to C-H (1.08 Å). Meanwhile, the interlayer spacing is compressed to 1.600 nm. However, in $(3\text{-CIPMA})_2\text{PbBr}_4$ and $(4\text{-CIPMA})_2\text{PbBr}_4$ perovskites, crystal lattices in-plane-orientation nearly remain unchanged, but the interlayers are pushed aside (Table S1). Powder XRD testing also verified these results. In Figure 1b, the well-defined diffraction peaks are corresponding to the $(00h)$ reflections series of $(\text{PMA})_2\text{PbBr}_4$ and $(\text{CIPMA})_2\text{PbBr}_4$. All the diffraction peaks of $(2\text{-CIPMA})_2\text{PbBr}_4$ shift to larger degrees in comparison to $(\text{PMA})_2\text{PbBr}_4$, indicating a decreased interlayer distance. On the contrary, the diffraction peaks of $(3\text{-CIPMA})_2\text{PbBr}_4$ and $(4\text{-CIPMA})_2\text{PbBr}_4$ shift to smaller degrees. According to Bragg's diffraction equation ($2d \times \sin\theta = n\lambda$), interlayer distances of $(\text{PMA})_2\text{PbBr}_4$, $(2\text{-CIPMA})_2\text{PbBr}_4$, $(3\text{-CIPMA})_2\text{PbBr}_4$ and $(4\text{-CIPMA})_2\text{PbBr}_4$ were measured to be 1.669, 1.628, 1.744 and 1.750 nm, respectively, which are in fair agreement with above DFT simulation results (Table S1). As shown in Figure 1b, the crystal lattices of (2-

FPMA)₂PbBr₄ and (3-FPMA)₂PbBr₄ remain almost the same as those of (PMA)₂PbBr₄, which is attributed to the smaller bond length of C-F (1.41 Å) compared to C-Cl (1.77 Å). The interlayer spacing of (4-FPMA)₂PbBr₄ increased to 1.710 nm, which is smaller than that of (4-CIPMA)₂PbBr₄. Therefore, it follows that perovskites (BrPMA)₂PbBr₄ with a larger bond length of C-Br (1.91 Å) induces larger expansion of crystal lattice (Figure 1b). However, the impact of halogen-substitution on distortion of the inorganic sheet is likely to be minimal. As shown in Figure S1, out-of-plane Pb-Br-Pb angles in the perovskites (PMA)₂PbBr₄ and (CIPMA)₂PbBr₄ are all 180 degrees, without any distortion as reported before in white perovskite.¹⁸ Meanwhile, the corresponding in-plane Pb-Br-Pb angles were measured to be around 140 degrees with small variations.

Despite the structural similarities between pristine and halogen-substituted (PMA)₂PbBr₄, their optical properties are distinct. At room temperature, (PMA)₂PbBr₄ displays only a narrow violet emission located at 410 nm (Figure 2a). However, the PL spectra of (2-F/Cl/BrPMA)₂PbBr₄ show broadband emissions from 400 to 800 nm, which are composed of a narrow free-excitons (FEs) peak and a much broad STEs peak (Figure 2a-c). The CIE chromaticity coordinates of the overall spectra of (2-FPMA)₂PbBr₄, (2-CIPMA)₂PbBr₄ and (2-BrPMA)₂PbBr₄ were determined to be (0.342, 0.361), (0.300, 0.330) and (0.312, 0.338), which give correlated color temperatures (CCT) of 5139 K, 7215 K, 6478K, respectively (Figure 2d). These locations are very close to the standard white light (0.33, 0.33). They display CRI values of 89, 86 and 88, respectively, which are higher than that of most commercial white light-emitting diodes (CRI of about 80). The PLQYs of (2-F/Cl/BrPMA)₂PbBr₄ crystals were measured to be 5%, 32% and 15%, respectively. The performance is much better than that of most low-dimensional white perovskites reported (Table S2). It should be noted that these FEs emissions of (2-F/Cl/BrPMA)₂PbBr₄ exhibit an asymmetric band spectra, including one main PL peak and two shoulder peaks. The location of the high-energy shoulder is corresponding to the absorption band edge. According to previous studies, this high energy shoulder peak may arise from the reabsorption of high energy region of the FEs emission spectrum in thick perovskite.¹⁶ The low-energy shoulder is similar to that reported in low-dimensional perovskites, which might derive from a vibrational replica of the intrinsic band.^{10,18} The STEs origin of the BWL emission was experimentally confirmed by implementing power dependent PL measurement, which shows a linear dependence from 0.024 to 23.5 W cm⁻² (Figure 3a). Otherwise, PL from permanent defects usually shows a sublinear dependence on the excited power with a saturation of limited defect sites under high excitation intensity.^{2,7,8} We also observed a similar broad spectrum from (2-CIPMA)₂PbBr₄ powders synthesized by fast reprecipitation method (See Methods for details, Figure S2), which further confirms that the broadband emission does not originate from the defects in crystals. Compared to (2-F/Cl/BrPMA)₂PbBr₄ perovskites, the PL intensity ratios $I_{\text{STEs}}/I_{\text{FEs}}$ of (3-F/Cl/BrPMA)₂PbBr₄ decrease significantly. Para-substituted perovskites (4-F/Cl/BrPMA)₂PbBr₄ show negligible STEs emissions, almost the same as pristine (PMA)₂PbBr₄. This phenomenon could also be observed in the digital image of the samples (2-CIPMA)₂PbBr₄, (3-CIPMA)₂PbBr₄, (4-CIPMA)₂PbBr₄ under UV light (Figure 2e), as well as the image of (F/BrPMA)₂PbBr₄ perovskites crystals (Figure S3).

Figure 4b shows the temperature dependent PL spectra of (2-CIPMA)₂PbBr₄. The PL intensities of STEs and FEs both increase when temperature decreases from 298 K to 77 K. The $I_{\text{STEs}}/I_{\text{FEs}}$ increases from 2.9 at 298 K to 100 at 77 K (Figure 4c), which is determined by a strong electron-phonon interaction induced transformation between FEs and STEs and PL quenching. At high temperature, it is more probable that FEs relax into STEs, however, the PL quenching is dominated due to the strong electron-phonon interaction. At low temperatures, the reverse applies. During the cooling process, a reduced electron-phonon interaction would narrow the full width at half maximum (FWHM) of both FEs and STEs emission (Figure 4c). Figure 4d illustrates the PL lifetime of (2-CIPMA)₂PbBr₄ and (3-CIPMA)₂PbBr₄. The PL decay curves can be well fitted with a bi-exponential decay model. The PL lifetime is considered as a combination of a slow-decay component (radiative recombination) and a fast-decay component (nonradiative process) that give a long lifetime τ_1 and a short lifetime τ_2 , respectively (Table S3). According to previous report, the emission ratio $I_{\text{STEs}}/I_{\text{FEs}}$ at a given temperature is related to $\Delta G_{\text{self-trap}}$ (self-trapping depth = $E_{\text{STEs}} - E_{\text{FEs}}$) and the radiative emission rates from the STE and FEs states ($k_{r,\text{STEs}}$ and $k_{r,\text{FEs}}$).¹⁸

$$\ln\left(\frac{I_{\text{STEs}}}{I_{\text{FEs}}}\right) \propto \ln\left(\frac{k_{r,\text{STEs}}}{k_{r,\text{FEs}}}\right) - \frac{\Delta G_{\text{self-trap}}}{K_b T}$$

Due to the similar radiative PL lifetime and much lower energy of STEs state than that of FEs state, the $I_{\text{STEs}}/I_{\text{FEs}}$ is dominated by the $\Delta G_{\text{self-trap}}$ (See Table S3 for detailed discussion).

In low-dimensional perovskites, excitons are confined in the inorganic sheets. Two kinds of bonds, namely $\text{Pb}^{2+}\text{-Br}^-$ and $\text{NH}_3^+\text{-PbBr}_3^-$, might affect the formation of STEs. According to aforementioned crystal structural analysis, the structure of inorganic sheet containing PbBr_6 octahedrons remains almost unchanged after the halogen-substitution, suggesting $\text{Pb}^{2+}\text{-Br}^-$ bonds were not interfered and may not be the critical factor. Due to high electronegativity of halogen atoms, they would withdraw electrons from the phenyl group and the branched chain $\text{-CH}_2\text{NH}_3^+$, induces more positive charge accumulating on -NH_3^+ . As shown in Table 1, we obtained the charge quantities of eight -NH_3^+ in the unit cell using DFT calculations. The average charges of -NH_3^+ in (PMA)₂PbBr₄, (2-CIPMA)₂PbBr₄, (3-CIPMA)₂PbBr₄ and (4-CIPMA)₂PbBr₄ were calculated to be 0.272, 0.297, 0.279 and 0.285, respectively. We assume that the centers of the positive charges of -NH_3^+ cations and the negative charges of PbBr_3^- anions are located on the N atoms and Pb atoms, respectively. The average Coulomb force was calculated to be 0.83 nN for (2-CIPMA)₂PbBr₄ (Table S4), which is smaller than that of (PMA)₂PbBr₄ (0.73 nN). (3-CIPMA)₂PbBr₄ and (4-CIPMA)₂PbBr₄ have similar Coulomb force, 0.77 and 0.78 nN. Overall, the value of the Coulomb force is proportional to the $I_{\text{STEs}}/I_{\text{FEs}}$ ratio of perovskites. Therefore, it can be speculated that the strengthened ionic bonds would trigger the STEs formation in perovskites.

To further verify the effect of halogen substituents (electron-drawing group) on the formation of STEs, a typical electron-donating group ($-\text{CH}_3$) ortho-substituted molecule 2- CH_3PMA was used to synthesize the perovskite $(2\text{-CH}_3\text{PMA})_2\text{PbBr}_4$. The bond length of C-CH_3 is close to that of C-Cl . As expected, the XRD diffraction peaks of $(2\text{-CH}_3\text{PMA})_2\text{PbBr}_4$ also shift to larger degrees in comparison to $(\text{PMA})_2\text{PbBr}_4$ (Figure S4). However, we did not observe obvious broadband emission from STEs (Figure S4). Moreover, we fabricated the phenylethylammonium lead bromide $((\text{PEA})_2\text{PbBr}_4)$ and corresponding halogen-substituted $(\text{FPEA})_2\text{PbBr}_4$ and $(\text{ClPEA})_2\text{PbBr}_4$ perovskites. The broad emissions are also observed in $(2\text{-FPEA})_2\text{PbBr}_4$ and $(2\text{-ClPEA})_2\text{PbBr}_4$ (Figure S5), but their PL intensity ratios $I_{\text{STEs}}/I_{\text{FEs}}$ are smaller than that of $(2\text{-FPMA})_2\text{PbBr}_4$ and $(2\text{-ClPMA})_2\text{PbBr}_4$. The PEA molecule has a longer branched chain ($-\text{CH}_2\text{CH}_2\text{NH}_3^+$) than PMA. Thus, the effect of electron-withdrawing from $-\text{NH}_3^+$ to halogen substituents is weaker than that in PMA. As a result, the Coulomb force increase in halogen-substituted $(\text{PEA})_2\text{PbBr}_4$ is lower than that in halogen-substituted $(\text{PMA})_2\text{PbBr}_4$.

In summary, we designed and synthesized novel halogen-substituted perovskite $(\text{F/Cl/BrPMA})_2\text{PbBr}_4$ crystals by wet chemical methods. These perovskites display BWL emission with high PLQY, good CRI and excellent CIE coordinates close to standard white light (0.33, 0.33), indicating promising application for solid-state lighting. Combining DFT calculation and experimental analysis, we discovered that the halogen substituents withdraw electrons from $-\text{NH}_3^+$, leading to an increase in the Coulomb force in $\text{NH}_3^+-\text{PbBr}_3^-$ bonds and enhancement of broadband emission from STEs. Thus, we believe that chemical bonds confining the excitons are of high importance for STEs formation, and new white perovskites can be designed and produced according to this approach.

Methods

Materials and chemicals. Lead bromide (PbBr_2) was purchased from Alfa Aesar. All alkylamine, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), chloroform were purchased from Aladdin. All chemicals were used as received.

Synthesis of alkylamine bromide. Alkylamine bromide was prepared by adding alkylamine solution into hydrobromic acid (HBr , 48 wt% in water) with molar ratio 1.2 : 1 at room temperature. The reaction mixture was stirred for 1 hour. The solvent was removed via rotary evaporation at 50 °C. The raw product was washed with ethanol/diethyl ether for three times and dried at 60 °C in a vacuum oven for 12 h.

Synthesis of perovskite crystals. 0.5 mmol $\text{R-NH}_3\text{Br}$ and 0.25 mmol PbBr_2 were dissolved in a mixed solvent of 0.25 mL DMF and 0.25 mL DMSO. In previous report, DMF/DMSO mixed solution is favorable for high-quality perovskite crystal growth.¹⁶ Above perovskite precursor solution was put into a 5 mL vial without cap, which was put in a 30 mL vial with 10 mL anti-solvent chloroform. The larger vial was sealed and kept in an oven at 40 °C. Perovskite crystals grow gradually with anti-solvent diffusing into perovskite precursor solution. After few days, the final products were taken out and washed with anti-solvent for two times.

Synthesis of perovskite powders by fast reprecipitation method. 0.5 mmol 2-CIPMABr and 0.25 mmol PbBr₂ were dissolved in a mixed solvent of 0.25 mL DMF and 0.25 mL DMSO. The precursor solution was drop into a vial containing 10 mL chloroform. The precipitation product was washed by chloroform for two times, and then dried at ambient atmosphere.

Perovskite crystals characterizations. Powder XRD measurements were performed using a Bruker D8 Advance diffractometer. The UV-vis absorption was measured by using Shimadzu UV3600. Steady-state PL and temperature dependent PL spectra were measured by using Horiba HR Evolution spectrometer and a 365 nm LED lamp was used as the excitation source. A bandpass filter was applied to narrow the FWHM of the LED light to 10 nm. The power dependent PL intensity was recorded by using a femtosecond-pulse laser (NPI Laser, Rainbow 780, 80 MHz) with 390 nm output after passing through a double frequency crystal.. Before measurements, we ground the crystals to avoid any angle dependence of incident/emissive light or heterogeneity between the connecting crystals. PLQY measurements were carried out by coupling an integrating sphere to fluorescent spectrometer (QEPro, Oceanoptics) with optical fibers. A 365 nm LED lamp was used as excitation source. Absolute irradiance was calibrated by a standard light source (HL-3plus, Oceanoptics). The accuracy of this system was verified by measuring Rhodamine 6G/ethanol solution (0.1 μmol/L), and the PLQY was measured to be 97 ± 2%, which is consistent with previous reports.^{19,20} For lifetime measurements, single-photon counting was conducted with a PicoHarp 300 module (PicoQuant), excitation with the abovementioned 780 nm fs-pulsed laser. Two band-pass filters (405 nm and 618 nm) are used to separated decay dynamics for FEs and STEs, respectively.

DFT calculations. Spin-polarized DFT calculations were performed using the projector augmented wave (PAW)²¹ potential method implemented in the Vienna *Ab Initio* Simulation Package (VASP) code.²² Generalized gradient approximation (GGA) within the scheme of Perdew–Burke–Ernzerhof (PBE) was chosen as the exchange-correlation functional.²³ We also considered the D3 dispersion correction method of Grimme et al.²⁴ A Gamma-centered *k*-point mesh of 1 × 2 × 2 and an energy cut off of 500 eV were applied. Electronic and force convergence criteria of 10⁻⁴ eV and 10⁻³ eV Å⁻¹, respectively, were considered. Atomic structures were visualized with the VESTA program.²⁵

Declarations

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Author contributions

J.X. conceived the idea and designed the experiments. M.Z. prepared the samples and performed the XRD, UV-vis absorption measurements. L.Z. and W.X. performed the optical measurements and analyzed the data. M.Z. analyzed the results assisted by Q.Z, L.W and W.X.. Z.Y assisted to measured the PLQY. Q.Z., N.Y. and P.K. did the first-principle calculations. J.X., W.X., M.Z. and S.W. wrote the manuscript. All authors read and commented on the manuscript

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com. Correspondence and requests for materials should be addressed to J.X..

Competing interests

The authors declare no competing financial or non-financial interests.

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Table

Table 1. Charge quantities of -NH_3^+ in perovskites $(\text{PMA})_2\text{PbBr}_4$ and $(\text{CIPMA})_2\text{PbBr}_4$.

	PMA	2-CIPMA	3-CIPMA	4-CIPMA
NH ₃ (1)	0.272	0.296	0.278	0.297
NH ₃ (2)	0.272	0.300	0.278	0.272
NH ₃ (3)	0.272	0.301	0.282	0.297
NH ₃ (4)	0.272	0.297	0.279	0.281
NH ₃ (5)	0.272	0.301	0.277	0.286
NH ₃ (6)	0.272	0.291	0.280	0.272
NH ₃ (7)	0.272	0.299	0.283	0.283
NH ₃ (8)	0.272	0.292	0.275	0.297
Average	0.272	0.297	0.279	0.285

Note: NH₃ (1-8) are eight -NH₃⁺ in a unit cell.

Figures

Figure 1

Structure of pristine and halogen-substituted perovskites. (a) Atomic structure of (PMA)₂PbBr₄ (upper left), (2-CIPMA)₂PbBr₄ (upper right), (3-CIPMA)₂PbBr₄ (lower left) and (4-CIPMA)₂PbBr₄ (lower right). (b) XRD patterns of perovskites (PMA)₂PbBr₄, (FPMA)₂PbBr₄, (CIPMA)₂PbBr₄ and (BrPMA)₂PbBr₄.

Figure 2

Optical properties of pristine and halogen-substituted perovskites. (a-c) Absorption (dashed lines) and PL spectra (solid lines) of (FPMA)2PbBr4, (CIPMA)2PbBr4 and (BrPMA)2PbBr4. (d) CIE chromaticity coordinates of (PMA)2PbBr4 (black dot), (2-FPMA)2PbBr4 (yellow dot), (2-CIPMA)2PbBr4 (red dot) and (2-BrPMA)2PbBr4 (pink dot). (e) Digital images of (PMA)2PbBr4, (2-CIPMA)2PbBr4, (3-CIPMA)2PbBr4 and (4-CIPMA)2PbBr4 crystals under ambient light (upper) and UV light (lower).

Figure 3

Photophysical properties of perovskite. (a) Emission intensity versus excitation power for (2-CIPMA)2PbBr4. The linear fit result has high R2 value of 0.998. (b) Temperature-dependent PL spectra of (2-CIPMA)2PbBr4. Inset is the zoom-in picture from 395 to 420 nm. (c) Temperature-dependent FWHM and ratio I_{STEs}/I_{FEs} of (2-CIPMA)2PbBr4 from 298 to 77 K. (d) PL decay profiles from FEs and STEs of (2-CIPMA)2PbBr4 and (3-CIPMA)2PbBr4.

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