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Single-phase alkylammonium cesium lead iodide quasi-2D perovskites for color-tunable and spectrum-stable red LEDs†

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While red is one of the primary colors for display applications, the investigation of visible red emitting perovskites, particularly 2D perovskites, is relatively limited. In this work, we demonstrate a single-phase Ruddlesden–Popper quasi-2D $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CsPb}_2\text{I}_7$ perovskite for red color LEDs. Through increasing the annealing temperature of $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CsPb}_2\text{I}_7$ perovskite thin films, we have successfully achieved tunable emission wavelengths from 654 to 691 nm. Equally important, for all the quasi-2D perovskite LEDs, once the annealing temperature is fixed, the emission spectrum is independent of bias voltages, which is very important for their use in lighting and displays. With the analysis of the crystallinity, morphology, and thermodynamic stability of the quasi-2D perovskite, we find that the obtained $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CsPb}_2\text{I}_7$ perovskite is a single-phase quasi-2D perovskite with only $n = 2$ phase. Besides, we found that the red shifting of emission wavelength is caused by the increase of perovskite crystal size while increasing the annealing temperature. Our results also show that the temperature-induced color tunability can be applied to a series of quasi-2D perovskites with different alkylammonium cations. Importantly, we find that short alkylammonium spacers offer better electrical properties for efficient current transport and high performance in LED applications. This work contributes to controlling the optoelectronic properties of quasi-2D perovskites via controlling their crystal growth as well as paves the way to realize practical lighting and display applications of perovskite LEDs.

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1. Introduction

Organic–inorganic lead halide perovskites emerge as one of the most promising luminescent sources because of their high quantum efficiency^{1,2} and high color purity.^{3–5} They have also been demonstrated as efficient emissive materials in light-emitting-diodes (LEDs)^{6–10} and lasers.^{11–13} For the practical application of perovskite-based LEDs (PeLEDs) in the display field, all the red, green, and blue light electroluminescence (EL) is needed. With these three primary colors, one can obtain numerous colors through suitable mixing. However, near-infrared (750–800 nm)^{14–20} and green (500–550 nm)^{21–27} PeLEDs are extensively investigated while visible red

PeLEDs are relatively less studied. One of the reasons lies in the difficulty of fabricating phase-stable perovskites with band gaps (E_g) between 1.97 eV (~ 630 nm) and 1.77 eV (~ 700 nm).

Mixed halide perovskites, such as $\text{CH}_3\text{NH}_3\text{PbBr}_x\text{I}_{3-x}$ ^{21,28,29} and $\text{CsPbBr}_x\text{I}_{3-x}$,³⁰ have been designed to achieve red emission by controlling the proportion of bromide and iodide. However, EL shifting or splitting has been observed in these mixed halide PeLEDs, which is attributed to halide migration induced by an electrical field under continuous operation.^{30,31} The halide migration leads to the formation of I-rich and Br-rich perovskite regions, resulting in perovskite phase separation. Hence, the obtained EL is quite different from the original designed red colors. Instead of using mixed halide perovskites, cubic phase cesium lead triiodide (CsPbI_3) can be used to achieve red EL for its suitable band gap (1.73 eV).³² However, cubic phase CsPbI_3 is unstable at room temperature and tends to become a non-emissive orthorhombic phase ($E_g = 2.82$ eV). To avoid phase transformation, Joseph M. Luther *et al.* synthesized CsPbI_3 quantum dots and demonstrated their red EL (~ 690 nm).³³ Besides, anion exchanged $\text{CsPb}(\text{Br/I})_3$ quantum dots with external quantum efficiency (EQE) over 20% also showed red EL at 645 nm and 653 nm

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with different additives. However, the operation lifetime of highly efficient devices is a concern with a fast decrease in emission intensity within only a few minutes.³⁴ It should be noted that the perovskite quantum dots are stabilized with large amounts of ligands which will easily influence the current injection in PeLED devices. Removing excess ligand usually brings about reduced phase stability to the cubic phase CsPbI₃. Alternatively, Wei Huang *et al.* fabricated cesium-based two-dimensional (2D) NCPI₇ PeLEDs and obtained red EL (689 nm) with improved device stability.³⁵ It should be noted that the EL was predominantly the emission from the mixed lowest band-gap region with emission energy close to that of three-dimensional (3D) cubic phase CsPbI₃, and the designed multiple 2D phases did not contribute to the emission but worked as barriers that form multiple quantum well structures in the NCPI₇ film. This NCPI₇ can be categorized into a quasi-2D Ruddlesden–Popper type perovskite which has a general formula of B₂A_{n−1}M_nX_{3n+1}, where B is a long-chain organic cation such as benzyl ammonium (BA) or phenylethyl ammonium (PEA); A is methylammonium (MA), formamidinium (FA), or Cs; M is a divalent metal like Pb or Sn; X is a halogen F, Cl, Br, I, *etc.* The variable *n* indicates the number of metal cation layer(s) between the two organic insulating layers (cation B).³⁶ When *n* = ∞, the Ruddlesden–Popper perovskite becomes a 3D perovskite, and becomes a pure 2D perovskite when *n* = 1. By increasing *n*, one may tune the optical properties of the quasi-2D perovskites with reduced bandgaps.³⁷ High-*n* members of quasi-2D Ruddlesden–Popper perovskites are typically used for solar cells,^{38,39} and mixed-*n* members of quasi-2D Ruddlesden–Popper perovskites are reported in PeLEDs.^{6,8,35} However, both the exciton-bonding energy and quantum confinement effect decrease with the increasing of the *n* value, which is a detriment to the application of quasi-2D perovskites in PeLEDs,^{6,8,40} and the co-existence of multiple phases in the 2D perovskite will deteriorate the emission color purity under electrical biases.⁴¹ Recent breakthroughs introduced innovative strategies to obtain pure phase 2D perovskites with *n* > 2 for efficient photovoltaic and bright LEDs, which enabled fine controlling of *n* numbers for potential 2D perovskite applications.^{42,43}

Here, we demonstrate a new low-*n* member and pure phase Ruddlesden–Popper perovskite, (C₃H₇NH₃)₂CsPb₂I₇ (PA₂CsPb₂I₇), for achieving color-tunable and spectrum-stable red EL. From the results of X-ray Diffraction (XRD) and grazing-incidence wide-angle X-ray scattering (GIWAXS), we confirmed that the obtained PA₂CsPb₂I₇ thin films are single-phase quasi-2D perovskites with only an *n* = 2 (orthorhombic, *a* = 6.210 Å, *b* = 6.210 Å, *c* = 41.840 Å) phase. We also find a unique feature that the EL peak of PA₂CsPb₂I₇ PeLEDs is tunable from 654 nm to 691 nm through controlling the annealing temperature of PA₂CsPb₂I₇ thin films. Different from the color tunability originating from varying the number of metal cation layers (*i.e.* change in *n* values), the tunable emission color from our PA₂CsPb₂I₇ is attributed to the quantum confinement adjustment by tuning the size of 2D PA₂CsPb₂I₇ nanoplates controlled by their formation tempera-

ture. This temperature induced EL tunability is further demonstrated in other quasi-2D perovskites with different alkylammonium spacers. Another important feature is that all the quasi-2D PeLEDs are spectrally stable against the bias voltages, which is very useful for their use in real applications. The obtained red EL with high color purity is important for use as one of the three primary colors for display and lighting applications of PeLEDs. Our work contributes to controlling the optoelectronic properties of pure phase quasi-2D Ruddlesden–Popper perovskites *via* controlling their crystal growth.

2. Results and discussion

2.1. Tunable red PA₂CsPb₂I₇ PeLEDs

According to the empirical Goldschmidt's tolerance factor, the *n*-propylammonium (C₃H₇NH₃, PA) cation is too large to fit into the corner of the [PbI₆]^{4−} octahedron,⁴⁴ leading to the natural formation of quasi-2D perovskites. Here, PA₂CsPb₂I₇ is designed to form a quasi-2D Ruddlesden–Popper perovskite with *n* = 2 by stoichiometry constraints, as illustrated in Fig. 1(a). It is synthesized *via* the stoichiometric reaction of *n*-propylammonium iodide (PAI), cesium iodide (CsI), and lead iodide (PbI₂) with a molar ratio of 2:1:2 (detailed in the Experimental section).

To investigate the optoelectronic application of PA₂CsPb₂I₇ thin films, we have fabricated PA₂CsPb₂I₇ PeLEDs and investigated their performances. Interestingly, we observed that the EL spectrum of PA₂CsPb₂I₇ PeLEDs depends on the annealing temperature of PA₂CsPb₂I₇ thin films, as shown in Fig. 1(b). Specifically, by increasing the annealing temperature from 60 °C to 80 °C, 100 °C, and 120 °C, the EL peak of PA₂CsPb₂I₇ PeLEDs gradually redshifted from 655 nm (CIE_{xy}: 0.708, 0.289) to 658 nm (CIE_{xy}: 0.703, 0.287), 668 nm (CIE_{xy}: 0.685, 0.285), and then 691 nm (CIE_{xy}: 0.711, 0.277), respectively. To the best of our knowledge, this temperature induced EL tunability has never been reported in any quasi-2D Ruddlesden–Popper PeLED with a single phase.

The peak EQE of each PeLED fabricated under different temperatures is 0.63%, 1.84%, 1.38%, and 0.97% for PA₂CsPb₂I₇ thin films annealed at 60 °C, 80 °C, 100 °C, and 120 °C, respectively. And the maximum luminance for each PeLED is 96 cd m^{−2} (655 nm), 106 cd m^{−2} (658 nm), 189 cd m^{−2} (668 nm) and 104 cd m^{−2} (691 nm), respectively. In the CIE diagram shown in Fig. 1(d), all the red PeLEDs fully meet the requirement for HDTV displays (Rec. 709), and are capable of being used in UHD TV displays (Rec. 2020). Another important feature is that under different applied voltages, no clear EL shifting or splitting is observed for the PA₂CsPb₂I₇ PeLEDs fabricated under certain annealing temperature. In other words, the PA₂CsPb₂I₇ PeLEDs are spectrally stable once fabricated, which is an important requirement in real applications. The EL spectra of the typical case of the PA₂CsPb₂I₇ PeLED prepared at 100 °C are shown in Fig. 1(f) and a picture of its corresponding working device is shown in Fig. S1.† The EL spectra of PA₂CsPb₂I₇ PeLEDs prepared at other temperatures

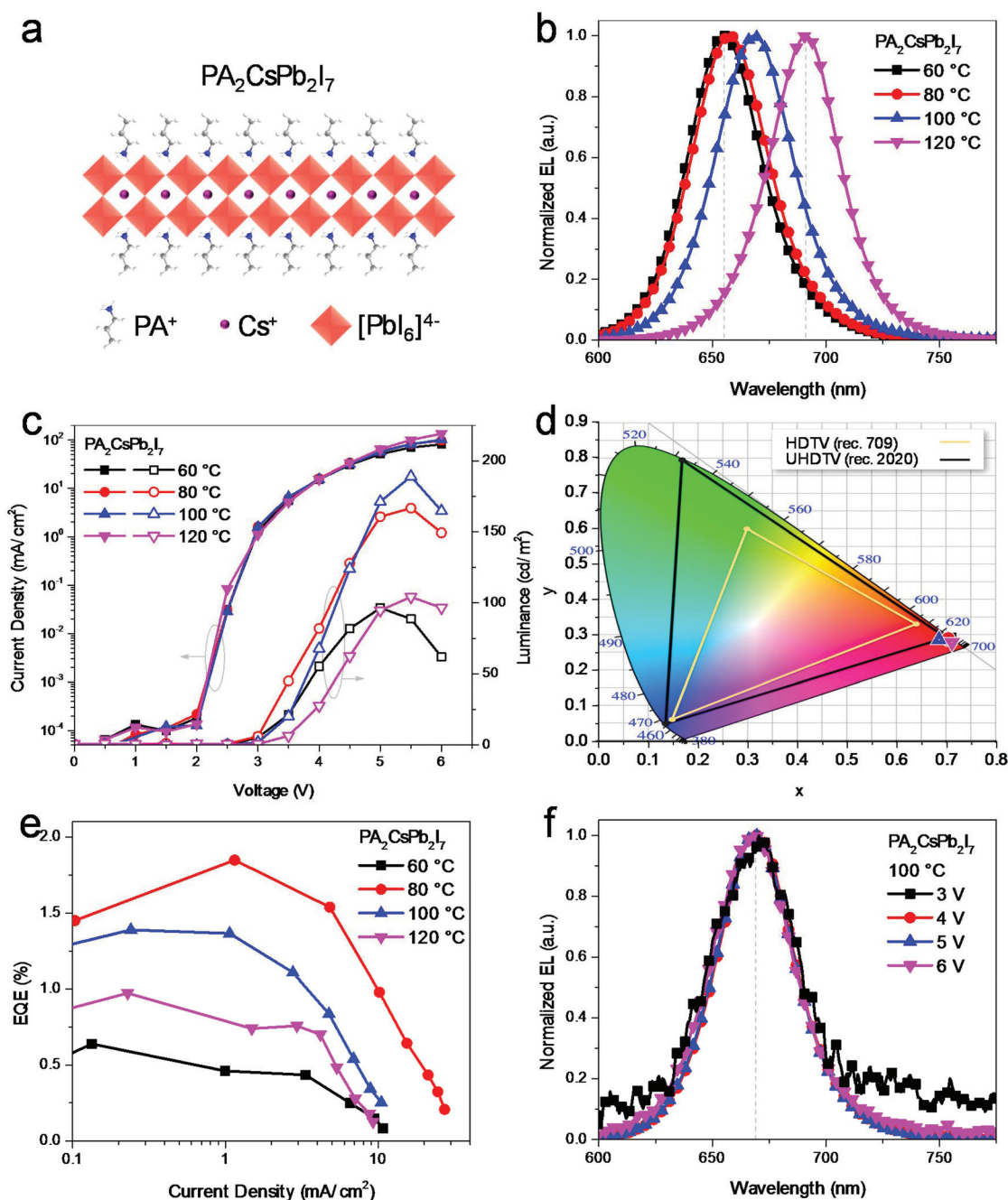


Fig. 1 (a) Crystal structure of designed $\text{PA}_2\text{CsPb}_2\text{I}_7$, (b) normalized EL spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ annealed at different temperatures, (c) current density–voltage and luminance–voltage curves, (d) CIE diagram, (e) EQE–voltage curves and (f) EL spectra under various applied voltages for 100 °C annealed $\text{PA}_2\text{CsPb}_2\text{I}_7$ device.

are shown in Fig. S2.† Along with the stable spectra under various biases, we also traced the spectrum with long-time operation of the $\text{PA}_2\text{CsPb}_2\text{I}_7$ (120 °C) PeLED under a fixed current density of 10 mA cm^{-2} . As shown in Fig. S3,† the elapsed time for the EL intensity decay to 50% of its initial EL intensity ($3.72 \text{ W sr}^{-1} \text{ m}^{-2}$) is about 11 hours, which is comparable to that of the recent reported stable 2D PeLEDs.^{41,43} Importantly, the spectra of the $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLED were also stable against the measurement time, with no wavelength

shifting nor splitting during the stability measurement (Fig. S3(b)†). These stable EL emission spectra against applied biases and operation times favor the practical application of the red PeLEDs.

2.2. Characterization of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films

To figure out the underlying mechanism of color tunability, we have investigated the optical properties, crystal structure, and morphology of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films annealed at different

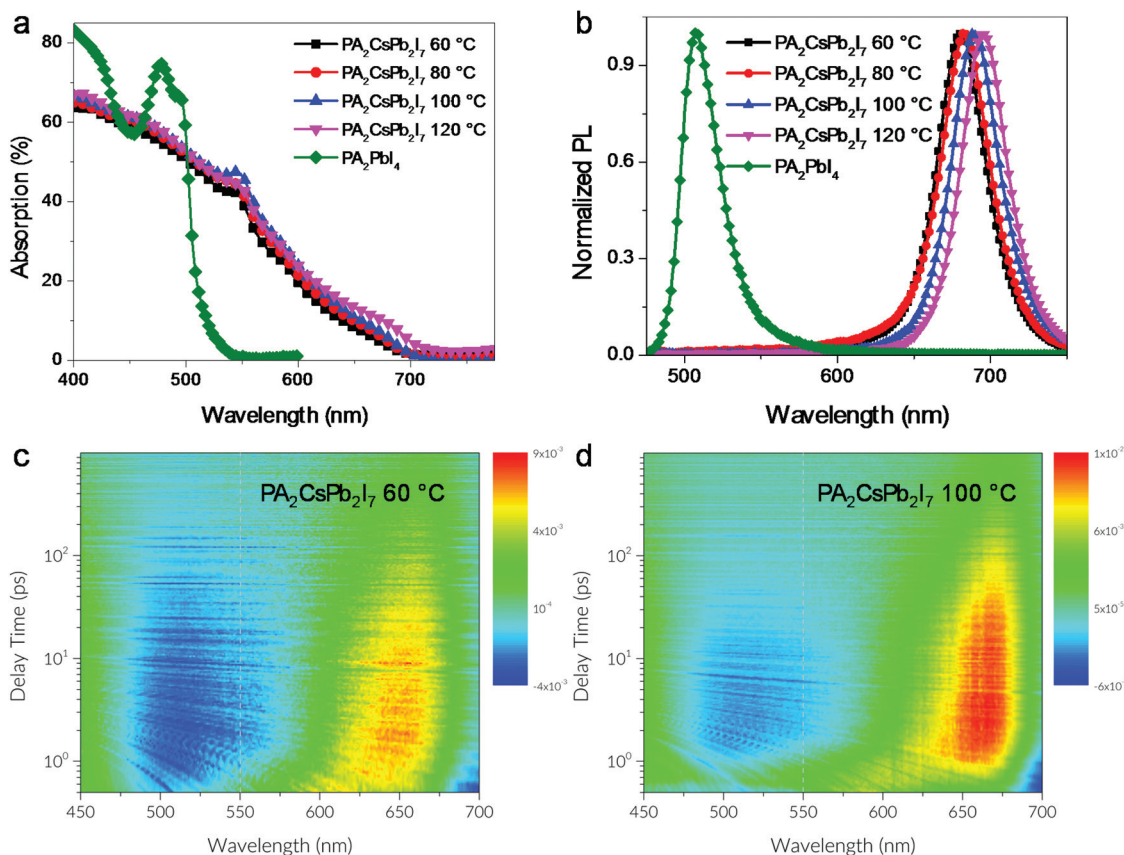


Fig. 2 (a) Absorption spectra and (b) normalized PL spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films (60 °C, 80 °C, 100 °C, and 120 °C) and PA_2PbI_4 thin films. And transient absorption spectrograms of (c) 60 °C and (d) 100 °C annealed $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films.

temperatures. Fig. 2(a) and (b) show the absorption and photoluminescence (PL) spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films annealed at 60 °C, 80 °C, 100 °C, and 120 °C. Pure 2D $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbI}_4$ (PA_2PbI_4) thin films are also included for comparison. The absorption and PL spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films are distinguished from that of pure 2D PA_2PbI_4 thin films. Particularly, $\text{PA}_2\text{CsPb}_2\text{I}_7$ and PA_2PbI_4 show respective absorption peaks at around 550 nm and 498 nm. These two peaks are in accordance with the reported excitonic absorption peaks in Ruddlesden–Popper perovskites with $n = 2$ and $n = 1$, respectively.^{6,45} In addition, in the log scale PL spectra shown in Fig. S4,[†] no extra emission peaks can be found in the PL spectrum of all the $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films. These results indicate that all the $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films are composed of single phase 2D perovskites with $n = 2$, while phase impurity caused by the existence of the $n = 1$ phase could not be observed from either absorption or PL spectra. To further check the phase purity, pump–probe transient absorption (TA) measurements were conducted on $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films that were annealed at 60 and 100 °C, respectively. All TA measurements were performed at room temperature with a low pump fluence of $\sim 0.3 \mu\text{J cm}^{-2}$ so that only the single exciton dynamics are considered. In the TA spectrograms shown in Fig. 2(c) and (d) and Fig. S5,[†] only one negative signal region that results from ground state bleaching (GSB) can be observed

from both samples. Also, the edge of the GSB signal is about 550 nm, which aligns well with the excitonic peak in the steady state absorption spectra which confirms that the $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films are formed by pure phase 2D layers ($n = 2$) rather than multiple phases. Besides, we observed that the absorption onset and PL peak in $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films are gradually red shifted with increasing annealing temperature. This PL red-shifting trend is also reflected in the red-shifted EL tendency in $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLEDs, which explained that the tunable EL peak of $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLEDs is attributed to the intrinsic optical properties of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films under various annealing temperatures. It should be noted that the emission color tunability is mainly ascribed to the selected annealing temperature. The change of annealing time does not affect the emission peak but affects the 2D $\text{PA}_2\text{CsPb}_2\text{I}_7$ nanoplate formation. As shown in Fig. S6,[†] the PL peak wavelength of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films annealed at 100 °C with annealing time varied from 5 to 20 minutes has negligible variations. But a narrower PL spectrum was found in the 10 minute annealed sample, which could contribute to better $\text{PA}_2\text{CsPb}_2\text{I}_7$ crystallinity under such conditions.

In order to understand the crystallinity properties of $\text{PA}_2\text{CsPb}_2\text{I}_7$ formed at different annealing temperatures, we have studied GIWAXS and XRD of the $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films, as shown in Fig. 3 and 4(a), respectively. The XRD and GIWAXS

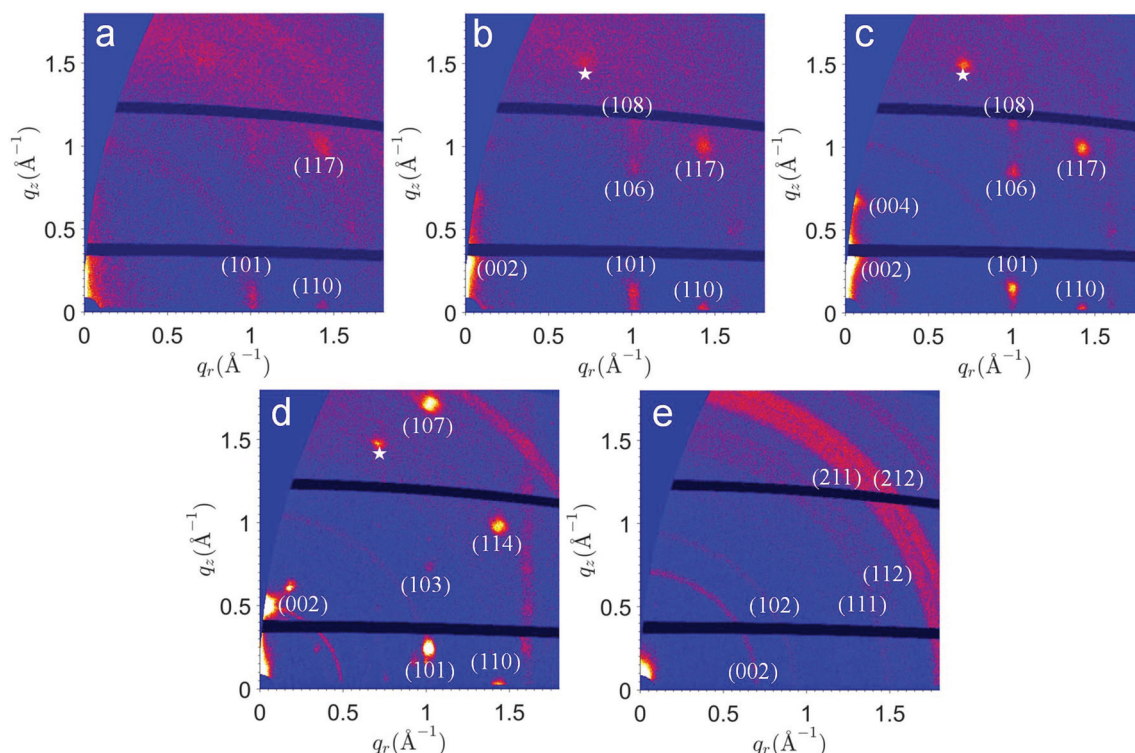


Fig. 3 Grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films (60 °C (a), 80 °C (b), 100 °C (c)), PA_2PbI_4 thin films (d), and CsPbI_3 thin films (e) on the ITO substrate. The GIWAXS pattern of 120 °C annealed $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film can be found in our recent report.⁴⁶ The unindexed peak at $q = 1.66 \text{ \AA}^{-1}$ (labeled with an asterisk) should be attributed to the impurity from the PAI raw material as this peak exists in $\text{PA}_2\text{CsPb}_2\text{I}_7$ and PA_2PbI_4 but not CsPbI_3 .

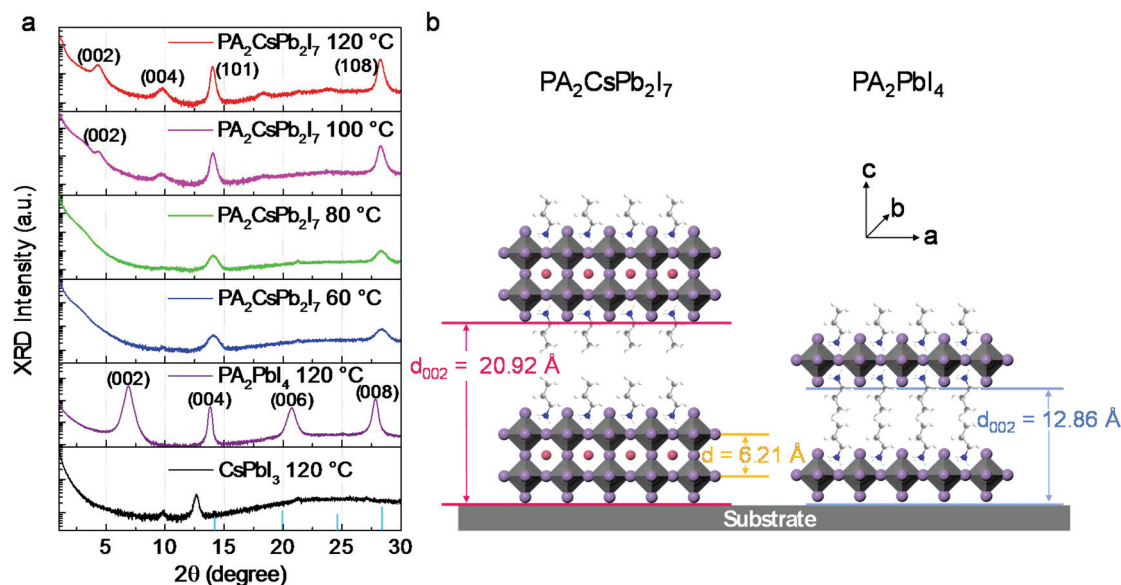


Fig. 4 (a) X-ray diffraction (XRD) pattern of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films (annealed at 60 °C, 80 °C, 100 °C, 120 °C), CsPbI_3 , and PA_2PbI_4 thin films (annealed at 120 °C) on the ITO substrate. The cyan lines at the bottom indicate cubic CsPbI_3 pattern from ICSD 181288; (b) schematic image of quasi-2D $\text{PA}_2\text{CsPb}_2\text{I}_7$ and 2D PA_2PbI_4 grown on the substrate.

patterns of PA_2PbI_4 and CsPbI_3 thin films that are annealed at 120 °C are also included for comparison, and the GIWAXS pattern for the 120 °C annealed $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film can be

found in our recent report in ref. 46. The clear discrete Bragg spots in GIWAXS patterns in Fig. 3(a)–(d) conclusively indicate that the $\text{PA}_2\text{CsPb}_2\text{I}_7$ and PA_2PbI_4 thin films are formed in 2D

structures. The discrete spots are caused by the highly oriented growth of 2D perovskites on the substrate.^{45,47} Otherwise, we should only observe some Debye–Scherrer rings like those in Fig. 3(e), because of the random growth nature of 3D CsPbI₃ on the substrate. Based on these discrete Bragg spots in GIWAXS and XRD patterns in Fig. 4(a), we determined the lattice parameters of PA₂CsPb₂I₇ (orthorhombic, $a = 6.210$ Å, $b = 6.210$ Å, $c = 41.840$ Å) and PA₂PbI₄ (orthorhombic, $a = 6.214$ Å, $b = 6.037$ Å, $c = 25.712$ Å). The large c parameter (41.840 Å) for PA₂CsPb₂I₇ indicates the two-layer structure ($n = 2$)⁴⁸ which is in accordance with the conclusion from the absorption spectrum in Fig. 2(a).

Furthermore, it is found that the discrete Bragg spots in the PA₂CsPb₂I₇ thin films become prominent when the annealing temperature increases. The results reflect the better crystallinity of PA₂CsPb₂I₇ obtained from high-temperature annealing, which is consistent with the XRD results of PA₂CsPb₂I₇ thin films in Fig. 4(a). For instance, the full width at half maximum (FWHM) of the XRD peak at 28.2° reduces from 0.693° at 60 °C to 0.660° at 80 °C, 0.463° at 100 °C, and 0.410° at 120 °C. The reduced FWHM indicates a larger crystal size of PA₂CsPb₂I₇ at high temperatures, which can cause the red-shifted emission properties.^{49,50} From Fig. 4(a), we can only observe two wide diffraction peaks at 14.1° and 28.2° in PA₂CsPb₂I₇ thin films annealed at 60 °C and 80 °C. While increasing the annealing temperature to 100 °C and 120 °C, new Bragg reflections at low angles of 4.3° and 9.8° form indicating that the unit cells are enlarged.⁵¹ The orientation of the Bragg peak (002) in the reciprocal space indicates that the [PbI₆]^{4−} slabs in PA₂CsPb₂I₇ are aligned parallel to the substrate, which is different from the reported pure phase (BA)₂(MA)₃Pb₄I₁₃ in which 2D slabs favor a vertical alignment.⁴³ By the way, no peak is found at around 19.9° or 24.5° in the XRD of each PA₂CsPb₂I₇ thin film, which allows us to exclude the existence of cubic phase 3D CsPbI₃ in the obtained PA₂CsPb₂I₇ thin films.⁵² On the other hand, if CsPbI₃ exists in the PA₂CsPb₂I₇

thin films, there should also exist residual PA₂PbI₄ or PbI₂ in the PA₂CsPb₂I₇ thin films since the precursor is composed of PAI:CsI:PbI₂ = 2:1:2 (molar ratio). However, no XRD peaks of PA₂PbI₄ or PbI₂ can be found in the PA₂CsPb₂I₇ thin films, which confirm that the red emission solely came from the single $n = 2$ phase quasi-2D PA₂CsPb₂I₇ perovskite. This is different from the reported NCPI₇ PeLEDs where the red emission was attributed to the highest- n phase emission and multiple low n phases act as energy barriers that form quantum well structures.³⁵

To understand the thermodynamic stability of single phase PA₂CsPb₂I₇, first-principles total energy calculations have been performed for PA₂Cs _{$n-1$} Pb _{n} I _{$3n+1$} , $n = 1-6$, as shown in Fig. 5(a). The formation enthalpies of PA₂Cs _{$n-1$} Pb _{n} I _{$3n+1$} (ΔH_n), with respect to PA₂Cs _{$n-2$} Pb _{$n-1$} I _{$3n-2$} and CsPbI₃, are shown in Fig. 5(b). ΔH_n is defined as $E_n - (E_{n-1} + E_{\text{bulk}})$, where E_n , E_{n-1} , and E_{bulk} are total energies of PA₂Cs _{$n-1$} Pb _{n} I _{$3n+1$} , PA₂Cs _{$n-2$} Pb _{$n-1$} I _{$3n-2$} and bulk CsPbI₃. Negative/positive values of ΔE_n mean that the system of PA₂Cs _{$n-1$} Pb _{n} I _{$3n+1$} is stable/unstable, *i.e.* thermodynamically unfavorable/favorable to decompose into PA₂Cs _{$n-2$} Pb _{$n-1$} I _{$3n-2$} and CsPbI₃. It is interesting to find that only the $n = 2$ phase is stable, which is consistent with the experimental observations of the single-phase PA₂CsPb₂I₇ perovskite. In addition, as the absorption spectra shown in Fig. S7(a),† the excitonic absorption peaks of PA₂Cs₂Pb₃I₁₀ ($n = 3$) and PA₂Cs₃Pb₄I₁₃ ($n = 4$) can only be observed in thin films that are annealed at a high temperature of 120 °C. The results suggest that the formation energy of stable high- n members is higher than that of the $n = 2$ phase. Also, the PL spectra of these high- n phase perovskites exhibited noticeable PA₂PbI₄ emission with a broad shoulder peak that arises from CsPbI₃ and mixed low- n phases, clearly indicating that $n > 2$ phases are unstable and tend to decompose into CsPbI₃ and PA₂Cs _{$n-2$} Pb _{$n-1$} I _{$3n-2$} phases. The results can be understood from surface calculations by Yang *et al.*,⁵³ which shows that the AX-terminated APbX₃ surface is much more

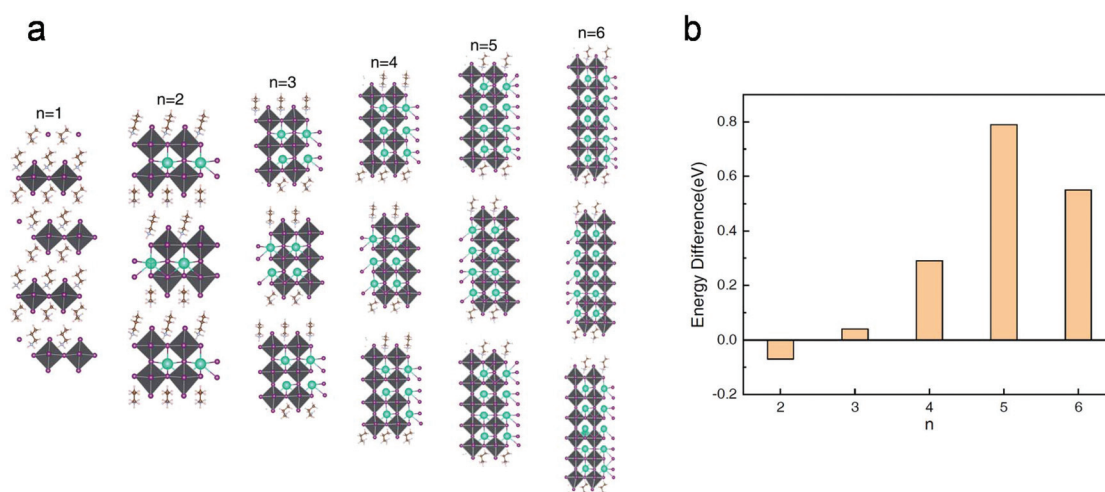


Fig. 5 (a) The crystal structures of layered 2D perovskites PA₂Cs _{$n-2$} Pb _{$n-1$} I _{$3n-2$} with $n = 1-6$; (b) the formation enthalpies of PA₂Cs _{$n-2$} Pb _{$n-1$} I _{$3n-2$} with $n = 2-6$.

stable than the PbX_2 -terminated surface due to fewer surface dangling bonds. The surface energy of the AX-terminated APbX_3 surface can be zero or even negative. Notably, the calculations by Yang are based on a bare surface. If the surfaces were passivated by organic molecules such as the case in $\text{PA}_2\text{Cs}_{n-1}\text{Pb}_n\text{I}_{3n+1}$, they could be further stabilized. In this sense, the stability of single-phase $\text{PA}_2\text{CsPb}_2\text{I}_7$ can be explained by its large surface ratio, in comparison to the structures of $n > 2$ phases.

The morphology evolution of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films annealed at different temperatures has also been investigated. In the scanning electron microscopy (SEM) images shown in Fig. 6, the grain size gradually enlarges when the annealing temperature of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films increases. Notably, obvious large nanoplates are observed in $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films formed under the annealing temperature of 120 °C, as shown in Fig. 6(d). Indeed, the histograms of grain size distribution shown in Fig. S8† show that the average grain size is 14.2 nm, 24.0 nm, 29.1 nm, and 65.5 nm for $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films annealed at 60 °C, 80 °C, 100 °C, and 120 °C, respectively. This increased grain size agrees well with the enhanced scattering peak intensity in GIWAXS and reduced FWHM in XRD. It should be noted that intermediate quantum confinement has been reported in cubic CsPbI_3 with crystal size between 6 nm and 16 nm.⁵² The quantum confinement leads

to the increased valence band maximum of $\text{PA}_2\text{CsPb}_2\text{I}_7$ at lower annealing temperatures as the ultraviolet photoelectron spectroscopy result shown in Fig. S9.† Thus, we rationally attribute the red-shifted EL in $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLEDs to the quantum confinement of size-tunable 2D $\text{PA}_2\text{CsPb}_2\text{I}_7$ nanoplates controlled by the annealing temperature. Low temperature leads to the formation of $\text{PA}_2\text{CsPb}_2\text{I}_7$ small crystals with a large band gap because of the strong quantum confinement effect. Different from 3D perovskites, such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, which grow in all directions on the substrate, the long alkylammonium PA confines the growth of the $\text{PA}_2\text{CsPb}_2\text{I}_7$ crystal along the plane of the substrate while the PA extends perpendicular to the substrate (Fig. 4(b)). After gaining energy from the increased annealing temperature, $\text{PA}_2\text{CsPb}_2\text{I}_7$ small crystals grow into bigger sizes. The growth of the $\text{PA}_2\text{CsPb}_2\text{I}_7$ crystal on the substrate contributes to a strong scattering peak at $q_z = 0.33 \text{ \AA}^{-1}$ ((002) plane of $\text{PA}_2\text{CsPb}_2\text{I}_7$) in GIWAXS, as shown in Fig. 3. As a result, the quantum confinement effect disappears, and the quasi-2D $\text{PA}_2\text{CsPb}_2\text{I}_7$ perovskite with large crystal size shows its bulk properties. Consequently, the crystal size enlarges with the increment of annealing temperature. The increased crystal size contributes to weaker quantum confinement and reduced bandgaps that induced the redshift of PL and EL of the quasi-2D $\text{PA}_2\text{CsPb}_2\text{I}_7$ perovskite.

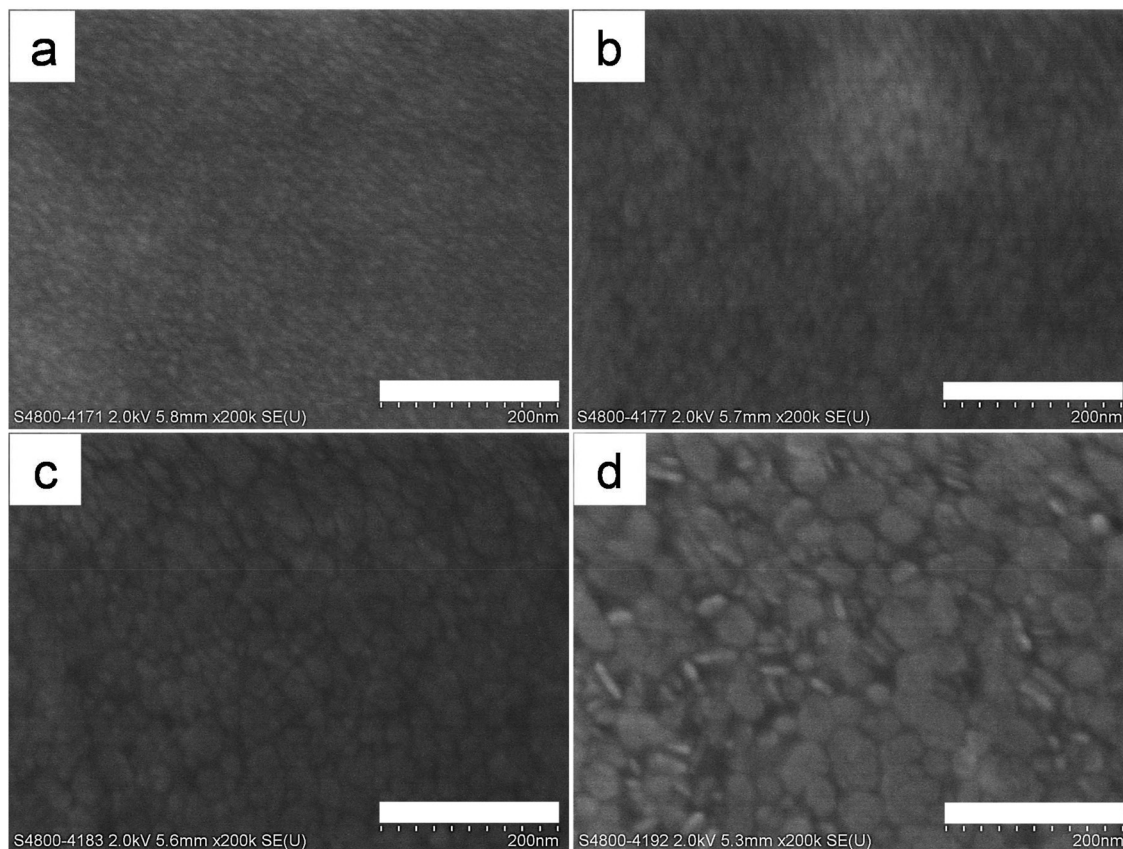


Fig. 6 Scanning electron microscopy (SEM) images of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films annealed at 60 °C (a), 80 °C (b), 100 °C (c), and 120 °C (d). The scale bar is 200 nm.

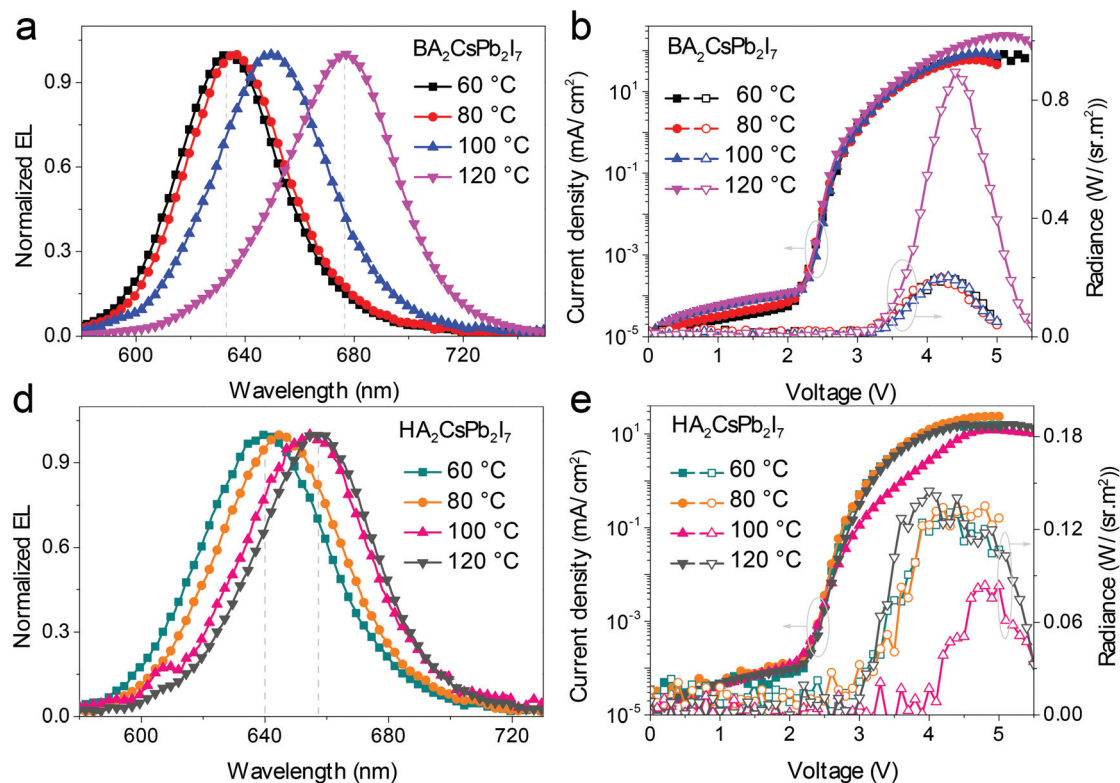


Fig. 7 Normalized EL spectrum and current density/radiance–voltage curves of BA₂CsPb₂I₇ PeLEDs (a and b) and HA₂CsPb₂I₇ PeLEDs (d and e) with annealing temperatures at 60 °C, 80 °C, 100 °C and 120 °C, respectively.

2.3. Tunable red-color B₂CsPb₂I₇ PeLEDs

We further systematically studied the emission properties of quasi-2D B₂CsPb₂I₇ PeLEDs with different alkylammonium cations (B), from C₃H₇NH₃ (*i.e.*, PA) to C₄H₉NH₃ (BA), and then C₆H₁₃NH₃ (HA), with gradually increased length of carbon chain. Their performances are given in Fig. 7. Interestingly, like the PA₂CsPb₂I₇ PeLEDs, the BA₂CsPb₂I₇ and HA₂CsPb₂I₇ PeLEDs also show tunable EL spectra at different annealing temperatures (Fig. S10–S12†). Specifically, the EL peak of BA₂CsPb₂I₇ PeLEDs shifts from 633 nm to 677 nm when the annealing temperature increases from 60 °C to 120 °C. Similarly, HA₂CsPb₂I₇ PeLEDs show tunable red emission from 640 nm to 657 nm when the annealing temperature increases from 60 °C to 120 °C. Their EL tunability should also be attributed to the quantum confinement of 2D perovskites with different crystal sizes formed at different annealing temperatures. Consequently, all the 2D perovskites with different carbon chains in alkylammonium share a similar red trend of wavelength tunability.

Differently, we find that the emission intensity and current density of HA₂CsPb₂I₇ PeLEDs are much lower than those of BA₂CsPb₂I₇ or PA₂CsPb₂I₇ PeLEDs. This can be understood in terms of the crystal structure and crystal growth direction of the quasi-2D perovskite on the substrate. PA₂CsPb₂I₇, BA₂CsPb₂I₇, and HA₂CsPb₂I₇ form quasi-2D perovskites with two-layer [Pb_nI_{3n+1}]_(1+n)[−] that stacks in a direction parallel to the substrate. Extended planes of [Pb_nI_{3n+1}]_(1+n)[−] slabs are par-

allel to the substrate with the remaining layers stacked over them and separated by the insulative long alkylammonium (PA, BA, and HA), as illustrated in Fig. 4(b). Longer alkylammonium, such as HA, leads to larger layer spacing.⁵⁴ As a result, the electrical transportation across the 2D structure is restricted and the performance of the PeLED decreases. PeLED with even longer alkylammonium, such as C₈H₁₇NH₃ (OA), has a limited current injection and very weak EL. As shown in Fig. S12,† the current density of OA₂CsPb₂I₇ PeLED is limited at a very low level even at high applied voltages. Consequently, in the series of quasi-2D perovskites, shorter alkylammonium contributes to better electrical properties and thus higher performance of PeLEDs.

3. Conclusions

Single-phase quasi-2D PA₂CsPb₂I₇ thin films are demonstrated for the first time. With this quasi-2D perovskite, we achieved tunable red emission in PA₂CsPb₂I₇ PeLEDs by changing the annealing temperature in PA₂CsPb₂I₇ thin film formation. The crystallinity, morphology and thermodynamic stability of the perovskite have been studied in detail for confirming the single-phase quasi-2D PA₂CsPb₂I₇ perovskite and the crystal size change leads to a tunable EL spectrum. The EL tunability is attributed to the quantum confinement effect in PA₂CsPb₂I₇ nanocrystals with different crystal sizes. Meanwhile, the emis-

sion color is stable against the bias voltages once the annealing temperature of the $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film is settled, and the PeLED device showed stable spectra under continuous operations, which is very useful for PeLED applications. Our results also show that the temperature induced EL tunability even applies to other perovskites with different alkylammonium cations, such as $\text{BA}_2\text{CsPb}_2\text{I}_7$ and $\text{HA}_2\text{CsPb}_2\text{I}_7$. We have also observed that shorter alkylammonium in the quasi-2D perovskite (*i.e.*, $\text{PA}_2\text{CsPb}_2\text{I}_7$) is more beneficial for achieving efficient current injection and high performance of PeLEDs. This work contributes to controlling the optoelectronic properties of pure phase quasi-2D perovskites *via* controlling their crystal growth as well as paves the way to realize practical lighting and display application of PeLEDs.

4. Experimental

4.1. Perovskite precursor synthesis

The $\text{PA}_2\text{CsPb}_2\text{I}_7$ precursor was synthesized through dissolving 37.4 mg (0.2 mmol) *n*-propylammonium iodide (PAI, Dyesol), 26 mg (0.1 mmol) cesium iodide (CsI, 99.999%, Aladdin), and 92.2 mg (0.2 mmol) lead iodide (PbI_2 , TCI, 99.99%) in 1 ml dimethylformamide (DMF, 99.8%, extra dry, Acros). The PA_2PbI_4 precursor was prepared through dissolving 74.8 mg (0.4 mmol) PAI and 92.2 mg PbI_2 in 1 ml DMF. The CsPbI_3 precursor was fabricated through dissolving 52 mg (0.2 mmol) CsI and 92.2 mg PbI_2 in 1 ml DMF. The $\text{BA}_2\text{CsPb}_2\text{I}_7$ precursor was synthesized through dissolving 40.8 mg (0.2 mmol) *n*-butylammonium iodide (BAI, Dyesol), 26 mg CsI, and 92.2 mg PbI_2 in 1 ml DMF. The $\text{HA}_2\text{CsPb}_2\text{I}_7$ precursor was prepared through dissolving 45.8 mg (0.2 mmol) *n*-hexylammonium iodide (HA, Dyesol), 26 mg CsI, and 92.2 mg PbI_2 in 1 ml DMF. The $\text{OA}_2\text{CsPb}_2\text{I}_7$ precursor was prepared through dissolving 51.4 mg *n*-octylammonium iodide (OA, Dyesol), 26 mg CsI, and 92.2 mg PbI_2 in 1 ml DMF.

4.2. PeLED fabrication

The structure of PeLEDs is ITO (150 nm)/PEDOT:PSS (50 nm)/ $\text{PA}_2\text{CsPb}_2\text{I}_7$ ($\text{BA}_2\text{CsPb}_2\text{I}_7$ or $\text{HA}_2\text{CsPb}_2\text{I}_7$, 70–80 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al (120 nm). The PEDOT:PSS thin film was fabricated *via* spin coating its precursor (Heraeus Clevios 4083) at 4000 rpm and annealing at 150 °C for 10 min. Perovskite $\text{PA}_2\text{CsPb}_2\text{I}_7$ ($\text{BA}_2\text{CsPb}_2\text{I}_7$ or $\text{HA}_2\text{CsPb}_2\text{I}_7$) thin films were deposited *via* spin coating their precursors on PEDOT:PSS at 6000 rpm and annealing at 60 °C, 80 °C, 100 °C, and 120 °C for 10 min. 30 nm 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, Nichem), 0.5 nm LiF, and 120 nm Al were evaporated with a rate of 0.5 Å s⁻¹, 0.05 Å s⁻¹, and 1 Å s⁻¹, respectively under vacuum less than 5 × 10⁻⁶ torr. The active area of the PeLED is 4.25 mm².

4.3. Characterization

The absorption spectrum of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films was obtained using a home-built system with a xenon lamp as the light source and an integrated sphere associated with the

charge-coupled device (CCD, Ocean Optics QE Pro) as the detector. The PL spectrum of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and PA_2PbI_4 thin films was recorded with a 375 nm pulse laser (repetition of 5 MHz) and a photomultiplier (PMA-C 192 M) detector. The XRD of $\text{PA}_2\text{CsPb}_2\text{I}_7$, PA_2PbI_4 , and CsPbI_3 thin films were measured using a Rigaku Smartlab. The X-ray source was copper (Cu) and its wavelength was 1.54 Å. The grazing-incidence wide-angle X-ray scattering (GIWAXS) of perovskites was measured with an in-house device Xeuss2.0 manufactured by Xenocs. The X-ray source was Cu and its wavelength was 1.54 Å. The incidence angle was 0.2°. The SEM images of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin films were obtained with a Hitachi S-4800 FEG. The $\text{PA}_2\text{CsPb}_2\text{I}_7$, $\text{BA}_2\text{CsPb}_2\text{I}_7$, and $\text{HA}_2\text{CsPb}_2\text{I}_7$ PeLEDs were measured in the glove box with a Keithley 2635 SourceMeter and recorded with an integrated sphere associated with CCD QE6500 (Ocean Optics). The integrating sphere was calibrated with a Newport standard lamp.

Conflicts of interest

There are no conflicts to declare.

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