Engineering green-to-blue emitting CsPbBr$_3$

quantum-dot films with efficient ligand passivation

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Contributions

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ABSTRACT: A series of challenging issues such as field-driven spectra drift for the CsPbCl₃Brₓ system and mixed phases in quasi-two-dimensional structures still exist when devising blue-emitting perovskites. In this paper, the CsPbBr₃ quantum-dot (QD) system is proposed to overcome the above challenges. However, to date the CsPbBr₃ QD films with tunable colors from green to blue still cannot be achieved yet using existing methods. Herein, a simple one-step spin-coating route incorporated with efficient ligand passivation is developed to realize this. The size restriction of CsPbBr₃ QDs is enabled by a diammonium ligand, propane-1,3-diammonium bromide (PDAB). A mixed ligand system of phenethylammonium bromide (PEAB) with PDAB is further explored to enhance their optical performance. The CsPbBr₃ QDs experience a second growth process upon controlled air exposure, which is utilized to realize their size control and emission wavelength tunability. The CsPbBr₃ QDs-based devices exhibit no spectra drift in electroluminescence under voltage bias.

TOC GRAPHICS
Solution-processed lead halide perovskite APbX₃ materials (A represents monovalent cations and X represents halide anions) have attracted much attention for their potential applications in solar cells, light-emitting diodes (LEDs), photodetectors, lasers, etc.¹⁻⁵ For luminescence related studies, for example, green-, red- and near-infrared- perovskite LEDs have gained much progress with high external quantum efficiency.⁶⁻¹⁰ However, the study of perovskites with emissions shifting from green to blue region (500 - 450 nm) has remained challenging due to their limited photo- and electrical- stability.¹¹⁻¹²

Generally, two approaches, namely compositional engineering and quantum-confinement engineering, have been employed to devise blue emitting perovskites, taking CsPbBr₃ as a typical example.¹³⁻¹⁴ In the compositional engineering approach, mixing Cl⁻ in CsPbBr₃ has been proven to be an efficient way to adjust its bandgap.¹⁵⁻¹⁸ However, the spectrum drift under voltage bias in this Cl-alloyed system has been an obstacle for their practical applications.¹³,¹⁹ The other strategy is to reduce the dimensionality of perovskites within the quantum-confinement regime. Thereinto, one popular way is to form quasi-two-dimensional (quasi-2D) structures, which can indeed result in blue-shifted photoluminescence (PL) spectral features.²⁰⁻²¹ However, for electroluminescence (EL) applications of the quasi-2D structures with mixed phases, the blue-emitted region may completely vanish due to charge transfer from low-dimensional 2D perovskites to high-dimensional 2D/3D perovskites. In most cases, the reported quasi-2D CsPbBr₃ system only results in green EL emissions.²²⁻²⁴

Another important class of luminescent perovskites are nanocrystal systems via colloidal synthesis. Perovskite nanocrystals exhibit a high PL quantum yield benefitted from space-confined exciton recombination and well-defined surface passivation.²⁵⁻²⁸ To date, however, almost all the reports based on colloidal CsPbBr₃ nanocrystals are devoted to green EL emissions.²⁹⁻³¹ Further
size decrease of CsPbBr$_3$ nanocrystals into the quantum confinement region may result in blue-emitting CsPbBr$_3$ QDs. CsPbBr$_3$ QDs with blue emissions have been produced via the colloidal synthesis method; however, the excess long-chain acid and amine ligands, inorganic salts such as ZnBr$_2$ or organic long-chain ammonium halide are needed in the synthesis and subsequent purification processes to sustain their size stably.$^{26,32-34}$ These excessive additives are not ideal for device fabrication due to their poor charge transport properties.$^{35-36}$ Furthermore, when depositing the CsPbBr$_3$ QDs solution onto a substrate, the film formation process from the colloidal solution may result in severe aggregation, which leads to size increase of CsPbBr$_3$ QDs. Accordingly, the blue emissions below 500 nm in EL have not been realized for colloidal CsPbBr$_3$ QD based films.$^{18,37}$

Considering all the disadvantages encountered in Cl-alloyed systems, quasi-2D systems, and colloidal CsPbBr$_3$ QD systems, it is imperative to perform fundamental studies as well as to search for alternative approaches to realize stable blue-shifted emissions of CsPbBr$_3$. We propose the CsPbBr$_3$ QDs composed film system to deal with the above challenges. Indeed, the concept of CsPbBr$_3$ QD films has been attracting much attention of researchers,$^{12,37}$ but unfortunately the CsPbBr$_3$ QD films still cannot be produced successfully with the existing methods to date. The efforts to produce CsPbBr$_3$ QD films should be made prior to exploring their properties and applications.

In this work, we developed a new methodology of preparing spin-coated blue CsPbBr$_3$ QD films based on the enhanced ligand passivation (Figure 1a). It’s known that the crystallization of 3D or quasi-2D perovskite thin films can be realized via simple spin-coating method from the precursor solution after annealing.$^7,13$ Following this route, the core question is how to restrict the growth of CsPbBr$_3$ domains during the spin-coating and annealing processes? Hints come from reports
showing that formation of quasi-2D CsPbBr\textsubscript{3} structures is induced by the passivation effect of organic ammonium ligands such as butylammonium bromide and phenethylammonium bromide (PEAB).\textsuperscript{20-21} The ammonium groups of these ligands directly coordinate with perovskite crystals, while the opposite organic end groups terminate the further growth of perovskite crystals. However, the hydrophobicity of these organic end groups in a polar precursor solution leads to oriented stacks so that the layered structures are formed. The hydrophobic interaction of the organic end groups can be minimized chemically by increasing their polarity. In view of this, we tried to adopt a short-chain diammounium salt as the ligand, namely propane-1,3-diammonium bromide (PDAB). We assume that the two primary ammonium groups of PDAB synergistically passivate the surface of CsPbBr\textsubscript{3} crystals. Also, this di-bromide ligand may provide a halide-rich environment, resulting in defect healing of halide vacancies. Inspired by these ideas, we successfully fabricated CsPbBr\textsubscript{3} QDs-based thin films with tunable PL and EL from green to blue colors. To further enhance their optical performance, a mixed ligand system of PDAB and PEAB was further developed. The PL and EL properties of CsPbBr\textsubscript{3} QD films were studied to explore their humidity-induced size control of CsPbBr\textsubscript{3} QDs and their spectra-stability under voltage bias.

The CsPbBr\textsubscript{3} thin films were deposited directly by spin-coating the precursor solution (prepared by mixing 1.1 mmol PbBr\textsubscript{2}, 1 mmol CsBr and certain molar amount of ligands in dimethyl sulfoxide solvent) onto poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) coated indium-doped tin oxide (ITO/PEDOT:PSS) substrates, followed by annealing (Figure 1a). The CsPbBr\textsubscript{3} QDs could be synthesized in situ and patterned with a form of thin film, which is named as CsPbBr\textsubscript{3} QD film below. Our procedure has the advantage of the simplicity for the preparation of CsPbBr\textsubscript{3} QD films when compared to the traditional colloidal synthesis route, which requires the separated steps of synthesis, purification, and thin film processing. Note that when exploring optoelectronic
device applications based on colloidal CsPbBr₃ QDs, the purification and film formation processes may result in destructive effects on their morphology and optoelectronic properties as reported.⁴⁶

Figure 1. PDAB ligands assisted formation of CsPbBr₃ QD films. (a) Schematic illustration of one step spin-coating route to prepare CsPbBr₃ QD films. The molecular structure of PDAB is provided on the right panel. (b) PL and (c) UV-vis spectra for CsPbBr₃ thin films processed with different molar amounts of PDAB. The PL curves in (b) are normalized by the maximal PL intensity of CsPbBr₃ thin film processed with 1.2 mmol of PEAB (dot-line). (d) Schematic illustration of the proposed passivation mechanism of PDAB on CsPbBr₃. The red dot-lines imply the interaction of negative bromide ions and positive ammonium groups of PDAB.
For the control experiment without any ligand, weak PL is detected with an emission of bulk CsPbBr$_3$ at 520 nm (Figure 1b), and the time-resolved PL measurement shows a fast decay lifetime for this Pb-excess film inferring a high density of defects (Figure S1). To restrict the growth of CsPbBr$_3$ crystal domains, initial attempts were conducted with the widely used ammonium ligands, typically PEAB. According to the reports and our own results (Figures 1b and S2), the PEAB ligands can enhance the PL intensity of CsPbBr$_3$ to some extent, but cannot blue-shift the PL wavelength below 500 nm without the occurrence of quasi-2D structures.

In contrast, the PDAB ligands gave impressive results in blue-shifting the PL wavelength. Once the PDAB ligands are added into the precursor solution, the PL peak of the produced CsPbBr$_3$ QD film is dramatically blue-shifted (Figure 1b). Moreover, the PL intensity of the CsPbBr$_3$ QD film is greatly enhanced, and the corresponding PL lifetime is prolonged (Figures 1b and S1). These results reveal that the surface defect density of the CsPbBr$_3$ QD film could be effectively reduced via the surface passivation strategy of PDAB ligands, thus the non-radiative recombination of CsPbBr$_3$ QDs could be inhibited. With 0.6 mmol of PDAB, the CsPbBr$_3$ QD film shows a maximal PL intensity. Relatively, we tried to evaluate the light-emitting intensities of our films by comparison with a control sample, namely the 1.2 mmol PEAB processed CsPbBr$_3$ thin film, considering that PEAB has been one of the most popular ligands to increase the PL quantum yield and to enhance the LEDs performance of CsPbBr$_3$ thin film. Note that the two cases of 0.6 mmol PDAB and 1.2 mmol PEAB have the same molar amounts of ammonium and bromide ions, but the former shows much more blue-shifted PL peak and enhanced PL intensity than the latter. Thus, PDAB ligands can provide efficient passivation for CsPbBr$_3$ and restrict the growth of CsPbBr$_3$ nanodomains within the quantum-confinement regime. Although the absolute PL quantum yield information of our films cannot be provided currently in this report, the above
results exactly demonstrate great potential of PDAB ligands to achieve bright blue-emitting CsPbBr$_3$ thin films, considering their comparison results with the films processed without any ligands or with PEAB ligands.

As the amount of PDAB ligands are increased from 0 mmol to 0.8 mmol, the PL wavelength undergoes a dramatic blue-shift from 521 nm to 483 nm, which is consistent with the blue-shifted UV-vis spectra (Figure 1c). In Figure 1c, it’s worthy of pointing out that the first exciton absorption peak of the CsPbBr$_3$ QD films cannot be clearly observed as more PDAB is introduced, and this phenomenon has been also reported in some other monodisperse and polydisperse colloidal CsPbBr$_3$ QDs solution systems$^{33, 40}$ or in quantum confined quasi-2D perovskite film systems with higher dimensionality.$^{11, 13-14}$ In addition, for the X-ray diffraction (XRD) data in Figure S4, the nanosized CsPbBr$_3$ crystal domains are further demonstrated by the decreased peak intensity and the broadened peak full-width at half-maximum (FWHM) gradually as more PDAB ligands are introduced into the system. On the other hand, no peaks ascribed to 2D perovskites could be observed in our films, as evidenced in the PL, UV-vis and XRD spectra (Figures 1b-c, S3 and S4).

The absorption in 400 – 500 nm in Figure 1c is contributed by CsPbBr$_3$. As the amount of PDAB is increased over 0.4 mmol, the absorbance in this region decreases. Correspondingly, a new absorption peak around 378 nm occurs, which is obviously observed for the 0.8 mmol and 1.0 mmol PDAB processed CsPbBr$_3$ thin films. In particular, for the 1.0 mmol PDAB processed thin film, the absorption above 400 nm completely vanishes, revealing that this thin film is composed of pure second-phase with an absorption around 378 nm. Note that, no PL could be detected for this second-phase composed thin film (Figures 1b and S3). Therefore, the sharp absorption peak around 378 nm does not contribute to the PL emission in blue color region as observed in Figure 1b, and the corresponding second-phase is classified as one kind of the unnecessary by-products.
The UV-vis absorption peak around 378 nm has been observed in reference. For example, when Subila et al. adopted some ammonium ligands to exfoliate out the fragments of ligand$^+\cdot$[PbBr$_3$]$^-$ complexes from CsPbBr$_3$ nanocrystals, the dominated UV-vis absorption around 320 nm occurred, accompanied by the phase transformation of CsPbBr$_3$ nanocrystals into crystalline CsPb$_2$Br$_5$ 2D nanosheets with a lower dimensionality.$^{41}$ Along with this, an absorption shoulder peak around 380 nm also occurred, and its phase was not affirmed in the mixture system. In other reports of CsPb$_2$Br$_5$ 2D nanosheets or single crystals with relatively simplified phase environment, no sharp absorption peak around 378 nm was observed.$^{42-44}$ Thus the sharp absorption peak around 378 nm in our system may not correspond to the CsPb$_2$Br$_5$ perovskite phase. More solid evidence is provided by XRD characterization for the 0.8 mmol and 1.0 mmol PDAB processed thin films. In Figure S4, no peaks corresponding to CsPb$_2$Br$_5$ occur. Particularly, for the 1.0 mmol PDAB processed thin film, even no any XRD peak is detected (Figure S4), which demonstrates that no long-range orderly crystal structure (e.g., CsPbBr$_3$, CsPb$_2$Br$_5$, Cs$_4$PbBr$_6$) dominates in this second-phase composed thin film. Thereby, the experimental evidences of UV-vis absorption (e.g., sharp absorption peak around 378 nm), PL (no PL emission) and XRD results (no obvious crystal structures) exclude the possibility that the second-phase corresponds to any known perovskite crystal phases, such as CsPb$_2$Br$_5$ and Cs$_4$PbBr$_6$.$^{42-46}$ In addition, the sharp absorption peak around 378 nm is much blue-shifted than that of monolayer A$_2$Cs$_{n+1}$Pb$_n$Br$_{3n+1}$ (n = 1) quantum-well around 405 nm in UV-vis spectrum.$^{14, 23}$ Overall, all the evidences point to that the second phase corresponds to nanosized molecular clusters (also called as nanoclusters, molecular clusters or magic size clusters),$^{47-50}$ namely Cs-Pb-Br-PDAB nanoclusters. The nanoclusters, which are similar to regular nanocrystals but smaller in size (usually < ~1.5 nm), are widely observed with sharp high-energy UV-vis absorption in classical colloidal QDs system.$^{47-50}$ Unfortunately, beyond
few methods such as UV-vis spectrum, synchrotron technology, etc.,\textsuperscript{51} most conventional laboratory methods are difficult to identify the nanoclusters experimentally. The exact composition of the nanoclusters is not further identified in this report; indeed, this second-phase is classified as one kind of the unnecessary by-products, which needs to be avoided. We would highlight more on how to inhibit their formation in our report, which is discussed below.

On the other hand, as mentioned above, the incorporation of PDAB ligands into the films would enhance their PL intensity through defect reduction. However, when an excessive amount of PDAB ligands (e.g., 0.8 mmol) were incorporated, the PL intensity decreased. Two main reasons are proposed to explain this observation. First, nonluminous by-products (i.e., nanoclusters) are formed instead of the desired CsPbBr\textsubscript{3} QDs when more PDAB ligands are introduced. Second, the particle size of CsPbBr\textsubscript{3} QDs decreases when more PDAB ligands are incorporated. When the ligand concentration was increased to 0.8 mmol, the PL spectrum showed further blue-shift, which is due to the quantum confinement effect when the particle size gets smaller. As the size of CsPbBr\textsubscript{3} QDs decreases, the surface to volume ratio increases, which can introduce more surface defects.\textsuperscript{13, 23} As a consequence, these defects reduce the PL intensity, which has also been observed in 2D perovskite structures\textsuperscript{13} and classical QD systems.\textsuperscript{52}
Figure 2. Control experiment using DMPDAB as ligands. (a) Schematic illustration showing that the primary and tertiary ammonium groups of one DMPDAB molecule are difficult to synergistically coordinate with CsPbBr$_3$. (b) PL spectrum of 0.6 mmol DMPDAB processed CsPbBr$_3$ thin films. Inset is a partial enlarged figure evidencing formation of quasi-2D structures. The enhanced passivation of PDAB is proposed to be induced by its quasi-bidentate coordination with CsPbBr$_3$, in which the two primary ammonium groups of PDAB synergistically occupy around the locations of two adjacent Cs$^+$ lattice sites of CsPbBr$_3$ (Figures 1d and S5). To verify this, a control experiment was performed using N,N-dimethyl-1,3-propanediamine dihydrobromide (DMPDAB) as ligands (Figure 2). DMPDAB consists of a primary ammonium group and a tertiary ammonium group (Figure 2a). The former is expected to interact with the perovskite structure easily similar to PDAB. However, considering the Goldschmidt tolerance factor,$^{53-54}$ the size of the tertiary ammonium group is too large to fit in the crystal structure to stabilize the PbBr$_6^{4-}$ octahedra as reported earlier.$^{55}$ Therefore, it is proposed that DMPDAB would not passivate the perovskite structure as effectively as PDAB, because PDAB has two primary ammonium groups participating in the coordination. In addition, the opposite “free” tertiary ammonium groups of DMPDAB may tend to stack via electrostatic interactions, hydrogen bonds or other kinds of polar interactions in the process of crystal formation. This proposal is supported by the formation of quasi-2D perovskites for the DMPDAB processed thin film (Figure S6). Furthermore, no obvious PL blue-shift is detected in this system (Figure 2b), which further suggests the importance of ligand engineering in the CsPbBr$_3$ QDs system. Thus, the synergistic coordination of two primary ammonium groups of PDAB contributes to its enhanced passivation with CsPbBr$_3$. Due to the fully utilized/coordinated functional ammonium groups of the PDAB
ligands, no stack structures namely 2D perovskites could be formed in the PDAB processed thin films.

**Figure 3.** Mix-ligand (PDAB and PEAB) assisted formation of CsPbBr$_3$ QD films. (a) Molecular structures of PDAB and PEAB. (b) PL and (c) UV-vis spectra of CsPbBr$_3$ QD films processed by mixed PDAB and PEAB ligands. The PL curves of 0.6:0- and 0.8:0- CsPbBr$_3$-QD-films are also integrated in (b). The PL curves in (b) are normalized by the maximal PL intensity of CsPbBr$_3$ thin films processed with 1.2 mmol of PEAB. (d) Schematic illustration of possible passivation pattern of PDAB and PEAB on CsPbBr$_3$.

PDAB is effective in forming CsPbBr$_3$ QDs with simultaneous PL blue-shift and intensity enhancement, but excessive PDAB induces the formation of nanoclusters and decreases the PL intensity (Figure 1b-c). To avoid that, we intended to weaken the strong passivation effect of PDAB by introducing another competitor with a single ammonium ligand, namely PEAB (Figure 3a). Control experiments were performed taking into account the same total molar amounts of ligands for PDAB only or the mixed ligands of PDAB and PEAB. For the 0.6 mmol of ligand
usage, the PL spectrum of the CsPbBr$_3$ thin film processed with 0.5 mmol PDAB and 0.1 mmol PEAB (marked as 0.5:0.1-CsPbBr$_3$-QD-film) shows almost no peak shift in comparison with that of the film processed with 0.6 mmol PDAB, while the intensity is enhanced (Figure 3b). In addition, the absorption around 378 nm is greatly inhibited (Figure 3c). The inhibition effect for nanocluster formation via mixed ligands of PDAB and PEAB is more obvious upon comparing the absorption around 378 nm for 0.5:0.3- and 0.8:0-CsPbBr$_3$-QD-film (Figures 1c and 3c), while there still exists slight clusters absorption for the 0.5:0.3-CsPbBr$_3$-QD-film around 378 nm. The PL wavelengths exhibit a result of 0.5:1 ≈ 0.6:0, 0.5:0.3 ≈ 0.8:0, indicating that the two systems with the same total molar amounts of ligands emerge with similar particle size, respectively. However, the PL relative intensities exhibit a result of 0.5:1 > 0.6:0, 0.5:0.3 > 0.8:0, respectively. Thus, better optical performance of CsPbBr$_3$ QD films is obtained via the mixed ligand system in comparison with the single PDAB ligand system. On the other hand, for both the single and mixed ligand systems, 0.8 mmol of total ligand usage (0.5:0.3 and 0.8:0) would lead to more blue-shifted emission wavelength, which corresponds to a smaller particle size, than 0.6 mmol of total ligand usage (0.5:0.1 and 0.6:0). The decrease of PL intensity with 0.8 mmol of total ligand usage may be also associated with the increased surface-volume ratio and defects or the formation of nonluminous by-product, as discussed above. Besides, no 2D perovskite structures are formed for the mixed ligands processed thin films (Figures 3b-c and S4). A possible passivation form for the mixed PDAB and PEAB ligand system is proposed in Figure 3d, which shows the co-existing coordination of positive single- and di- ammonium groups with the negative bromide ions.

It’s known that humidity affects the crystallization and stability of perovskites. Considering this, we further studied the humidity’s influence on our films (Figures 4, S7-9 and Table S1). One typical example for 0.5:0.1-CsPbBr$_3$-QD-film is provided in Figure 4. Once exposed in air, all the
PDAB-contained CsPbBr₃ thin films show a gradual PL red-shift, accompanied by a narrowing of peak FWHM, which is consistent with the red-shifted UV-vis absorption spectra (Figures 4a-b, S7-8). Considering the quantum confinement effect, the red-shift phenomenon reveals the size increase of CsPbBr₃ QDs, which is further demonstrated by transmission electron microscope (TEM) characterization (Figure 4c). The size of CsPbBr₃ QDs could be increased from 5.1 nm to 10.0 nm approximately before and after 30 min air exposure. Actually, the PL intensity would be greatly enhanced within a short time of air exposure. This observation is important to achieve a brighter emission from the CsPbBr₃ QD film. Moreover, the PL red-shift emerges with the character of continuous change (Figure S7), implying the size tunability of CsPbBr₃ QDs. Thus, the influence of humidity turns to be an effective method to realize the size control and color tunability of CsPbBr₃ QDs via simple control of exposure time in air, which is regarded as an aging treatment in ambient.

**Figure 4.** Second growth of CsPbBr₃ QDs in 0.5:0.1-CsPbBr₃-QD-film upon air exposure (34 ~ 37% relative humidity (RH)), characterized by (a) PL, (b) UV-vis, and (c) TEM respectively. The
Figure 5. Evolution of EL of the 0.5:0.1-CsPbBr$_3$-QD-films. (a) EL spectra recorded at various applied voltages (4 V – 9 V). The spectral changes at different aging times (0 s – 30 min) and the corresponding peak emission wavelengths are presented in different panels. The films were aged in ambient (34 ~ 37% RH and room temperature) for different times (0 s – 30 min) prior to thermal
evaporation. (b) Commission Internationale de l'Éclairage (CIE) values of the EL spectra of 0.5:0.1-CsPbBr$_3$-QD-films with various aging time in air. (c) Overall comparison of max EL curves and (d) the statistic information of peak position and maximal luminance (Lmax) as a function of aging time in air.

Indeed, the humidity plays an important role for the second-growth phenomenon. Control experiments were performed by storing the 0.5:0.1-CsPbBr$_3$-QD-film in a dry room of 16% relative humidity (RH) and in a N$_2$ glove box (Figure S9). After 24 h in the dry room, the PL of CsPbBr$_3$ thin film only red-shifts to 500 nm, while the storage in ambient for 24 h results in the emission at 520 nm, which is same as bulk CsPbBr$_3$. Thus, the red-shift phenomenon could be greatly inhibited by decreasing the humidity. This conclusion is further supported by the result of control sample after one-month storage in a N$_2$ glove box, which showed no red-shift phenomenon.

The ammonium group shows a polar character which favors adsorption of moisture in air. Upon air exposure, the polar ammonium ligands undergo a partial solvation at the surface, which induces a second crystal growth of the CsPbBr$_3$ QDs through the Ostwald ripening process. Accompanied by the size increase, the CsPbBr$_3$ QDs may also experience a so-called “self-healing” process of the perovskite lattice in ambient air as reported. For example, Snaith and coworkers have reported that the exposure to moisture could enhance the PL intensity of perovskite film due to partial solvation of the ammonium component and “self-healing” of the perovskite lattice. A recent study by Stranks and coworkers reveals that O$_2$/H$_2$O in atmosphere under light soaking may help remove the trap states at the perovskite surface, thus an enhanced PL intensity could be obtained within short-time exposure in air.

EL studies were performed taking the 0.5:0.1-CsPbBr$_3$-QD-films as an example. As discussed above, continuously tunable emissions for the thin films can be achieved via simple control of
exposure time in air. With this consideration, the thin films were firstly treated by aging in ambient (34 ~ 37% RH and room temperature) for 0 s - 30 min, respectively. The CsPbBr$_3$ QD films exhibit smooth surface roughness within the exposure period in ambient (Figure S10). Notably, no Pb$^0$ is observed for the thin films after aging treatment (Figure S11). In the subsequent step, electron injection layer 4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B$_3$PYMPM) and LiF/Al electrode were sequentially evaporated onto the CsPbBr$_3$ QD films in high vacuum (Figure S12). The EL properties were evaluated directly in air. The samples with various aging time exhibit continuously tunable emissions in EL spectra (Figure 5), from 479 nm (0 s) to 505 nm (30 min), respectively. Accompanied by the EL wavelength changes, the EL emission intensity is also enhanced with the luminance increasing from 165 Cd/m$^2$ (at 479 nm, 0 s) to 5058 Cd/m$^2$ (at 505 nm, 30 min) as shown in Figure 5b-c. For each sample with the exact aging time in air, the EL spectra do not show any shift under various voltage biases, which obviously differ from the results in mixed halide system as reported.$^{13, 19}$ On the other hand, this result also demonstrates that the evaporation process of organic electron transfer material and electrode onto CsPbBr$_3$ QD films can inhibit the direct influence of humidity upon the size change of CsPbBr$_3$ QDs.

In summary, for the first time, we successfully developed a new CsPbBr$_3$ QD film system via one-step spin-coating route that differs from the traditional colloidal synthesis route. The PDAB ligands were found to efficiently inhibit the crystal growth of CsPbBr$_3$ QDs. The mixed ligand system of PDAB and PEAB was further developed to enhance their emission properties. The CsPbBr$_3$ QDs showed a second growth process in air, which provided another feasible way to realize the size control of CsPbBr$_3$ QDs via simple control of aging time in air. As a result, continuously tunable emissions from green to blue colors were achieved in the PL and EL spectra. Importantly, the produced CsPbBr$_3$ QD films demonstrate no spectra-drift in EL upon voltage bias.
These results are expected to accelerate the exploration of blue-emitting applications of perovskites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:xxxxx.

Chemicals, film/device fabrication procedures, characterization method; additional discussion; PL, PL lifetime, XRD, UV-vis, AFM, X-ray photoelectron spectroscopy (XPS) and EL (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENT**

This work was supported by funding from the Energy Materials and Surface Sciences Unit of the Okinawa Institute of Science and Technology Graduate University, the OIST Proof of Concept (POC) Program, and the OIST R&D Cluster Research Program. We would like to thank OIST Mech. Eng. & Microfabrication Support Section for maintenance of cleanroom.

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