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Engineering Green-to-Blue Emitting CsPbBr₃ Quantum-Dot Films with Efficient Ligand Passivation

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1 Engineering green-to-blue emitting CsPbBr₃
2 quantum-dot films with efficient ligand passivation

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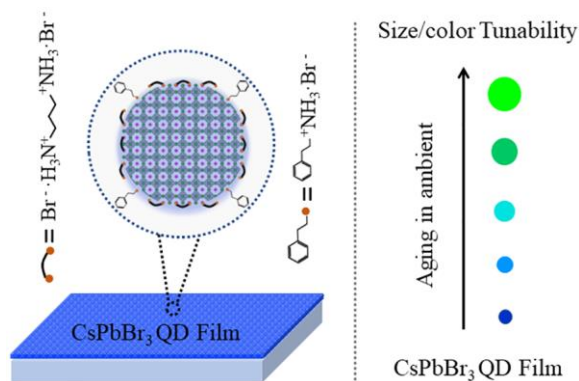
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8 **Contributions**

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

22 TOC GRAPHICS



23

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

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

43 Another important class of luminescent perovskites are nanocrystal systems via colloidal
44 synthesis. Perovskite nanocrystals exhibit a high PL quantum yield benefitted from space-confined
45 exciton recombination and well-defined surface passivation.²⁵⁻²⁸ To date, however, almost all the
46 reports based on colloidal CsPbBr₃ nanocrystals are devoted to green EL emissions.²⁹⁻³¹ Further

47 size decrease of CsPbBr₃ nanocrystals into the quantum confinement region may result in blue-
48 emitting CsPbBr₃ QDs. CsPbBr₃ QDs with blue emissions have been produced via the colloidal
49 synthesis method; however, the excess long-chain acid and amine ligands, inorganic salts such as
50 ZnBr₂ or organic long-chain ammonium halide are needed in the synthesis and subsequent
51 purification processes to sustain their size stably.^{26, 32-34} These excessive additives are not ideal for
52 device fabrication due to their poor charge transport properties.³⁵⁻³⁶ Furthermore, when depositing
53 the CsPbBr₃ QDs solution onto a substrate, the film formation process from the colloidal solution
54 may result in severe aggregation, which leads to size increase of CsPbBr₃ QDs. Accordingly, the
55 blue emissions below 500 nm in EL have not been realized for colloidal CsPbBr₃ QD based
56 films.^{18, 37}

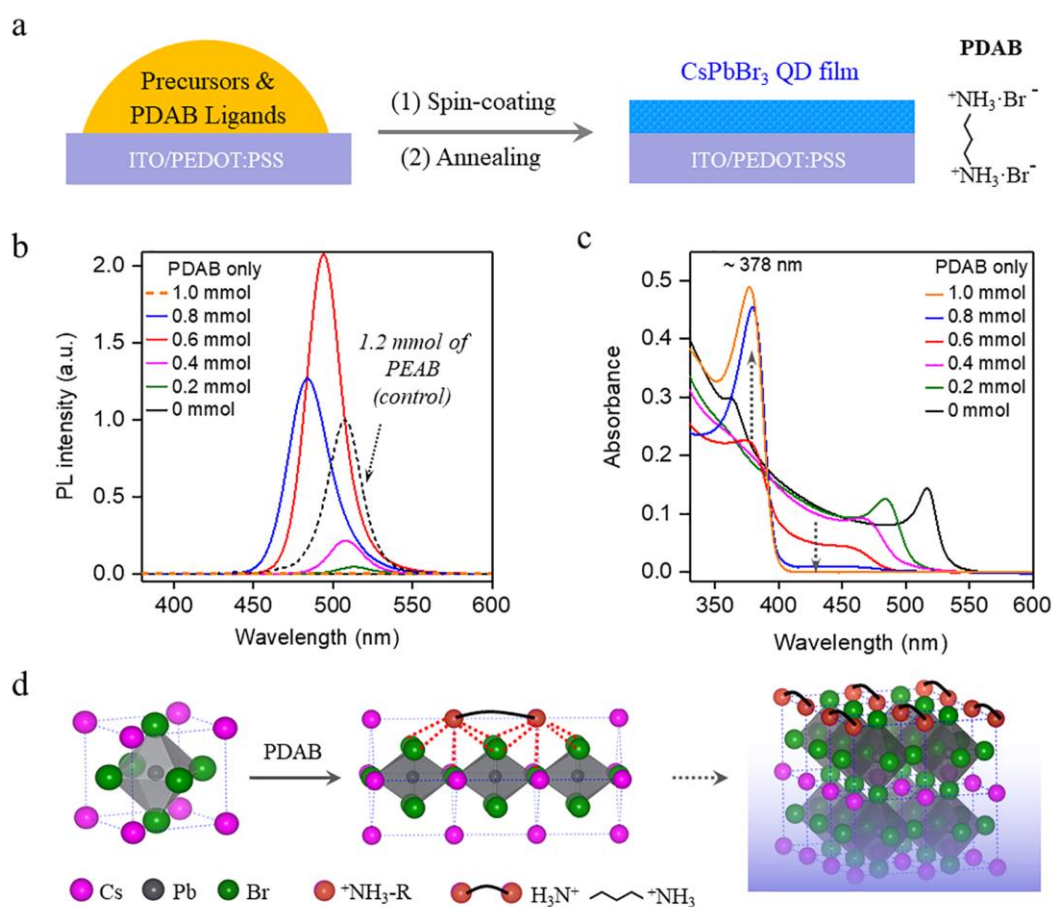
57 Considering all the disadvantages encountered in Cl-alloyed systems, quasi-2D systems, and
58 colloidal CsPbBr₃ QD systems, it is imperative to perform fundamental studies as well as to search
59 for alternative approaches to realize stable blue-shifted emissions of CsPbBr₃. We propose the
60 CsPbBr₃ QDs composed film system to deal with the above challenges. Indeed, the concept of
61 CsPbBr₃ QD films has been attracting much attention of researchers,^{12, 37} but unfortunately the
62 CsPbBr₃ QD films still cannot be produced successfully with the existing methods to date. The
63 efforts to produce CsPbBr₃ QD films should be made prior to exploring their properties and
64 applications.

65 In this work, we developed a new methodology of preparing spin-coated blue CsPbBr₃ QD films
66 based on the enhanced ligand passivation (Figure 1a). It's known that the crystallization of 3D or
67 quasi-2D perovskite thin films can be realized via simple spin-coating method from the precursor
68 solution after annealing.^{7, 13} Following this route, the core question is how to restrict the growth of
69 CsPbBr₃ domains during the spin-coating and annealing processes? Hints come from reports

70 showing that formation of quasi-2D CsPbBr₃ structures is induced by the passivation effect of
71 organic ammonium ligands such as butylammonium bromide and phenethylammonium bromide
72 (PEAB).²⁰⁻²¹ The ammonium groups of these ligands directly coordinate with perovskite crystals,
73 while the opposite organic end groups terminate the further growth of perovskite crystals.
74 However, the hydrophobicity of these organic end groups in a polar precursor solution leads to
75 oriented stacks so that the layered structures are formed. The hydrophobic interaction of the
76 organic end groups can be minimized chemically by increasing their polarity. In view of this, we
77 tried to adopt a short-chain diammonium salt as the ligand, namely propane-1,3-diammonium
78 bromide (PDAB). We assume that the two primary ammonium groups of PDAB synergistically
79 passivate the surface of CsPbBr₃ crystals. Also, this di-bromide ligand may provide a halide-rich
80 environment, resulting in defect healing of halide vacancies. Inspired by these ideas, we
81 successfully fabricated CsPbBr₃ QDs-based thin films with tunable PL and EL from green to blue
82 colors. To further enhance their optical performance, a mixed ligand system of PDAB and PEAB
83 was further developed. The PL and EL properties of CsPbBr₃ QD films were studied to explore
84 their humidity-induced size control of CsPbBr₃ QDs and their spectra-stability under voltage bias.

85 The CsPbBr₃ thin films were deposited directly by spin-coating the precursor solution (prepared
86 by mixing 1.1 mmol PbBr₂, 1 mmol CsBr and certain molar amount of ligands in dimethyl
87 sulfoxide solvent) onto poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) coated indium-
88 doped tin oxide (ITO/PEDOT:PSS) substrates, followed by annealing (Figure 1a). The CsPbBr₃
89 QDs could be synthesized in situ and patterned with a form of thin film, which is named as CsPbBr₃
90 QD film below. Our procedure has the advantage of the simplicity for the preparation of CsPbBr₃
91 QD films when compared to the traditional colloidal synthesis route, which requires the separated
92 steps of synthesis, purification, and thin film processing. Note that when exploring optoelectronic

93 device applications based on colloidal CsPbBr₃ QDs, the purification and film formation processes
 94 may result in destructive effects on their morphology and optoelectronic properties as reported.³⁶⁻
 95 37



96
 97 **Figure 1.** PDAB ligands assisted formation of CsPbBr₃ QD films. (a) Schematic illustration of
 98 one step spin-coating route to prepare CsPbBr₃ QD films. The molecular structure of PDAB is
 99 provided on the right panel. (b) PL and (c) UV-vis spectra for CsPbBr₃ thin films processed with
 100 different molar amounts of PDAB. The PL curves in (b) are normalized by the maximal PL
 101 intensity of CsPbBr₃ thin film processed with 1.2 mmol of PEAB (dot-line). (d) Schematic
 102 illustration of the proposed passivation mechanism of PDAB on CsPbBr₃. The red dot-lines imply
 103 the interaction of negative bromide ions and positive ammonium groups of PDAB.

104 For the control experiment without any ligand, weak PL is detected with an emission of bulk
105 CsPbBr₃ at 520 nm (Figure 1b), and the time-resolved PL measurement shows a fast decay lifetime
106 for this Pb-excess film inferring a high density of defects (Figure S1).^{9, 38} To restrict the growth of
107 CsPbBr₃ crystal domains, initial attempts were conducted with the widely used ammonium
108 ligands, typically PEAB. According to the reports^{14, 22} and our own results (Figures 1b and S2),
109 the PEAB ligands can enhance the PL intensity of CsPbBr₃ to some extent, but cannot blue-shift
110 the PL wavelength below 500 nm without the occurrence of quasi-2D structures.

111 In contrast, the PDAB ligands gave impressive results in blue-shifting the PL wavelength. Once
112 the PDAB ligands are added into the precursor solution, the PL peak of the produced CsPbBr₃ QD
113 film is dramatically blue-shifted (Figure 1b). Moreover, the PL intensity of the CsPbBr₃ QD film
114 is greatly enhanced, and the corresponding PL lifetime is prolonged (Figures 1b and S1). These
115 results reveal that the surface defect density of the CsPbBr₃ QD film could be effectively reduced
116 via the surface passivation strategy of PDAB ligands, thus the non-radiative recombination of
117 CsPbBr₃ QDs could be inhibited.^{13, 39} With 0.6 mmol of PDAB, the CsPbBr₃ QD film shows a
118 maximal PL intensity. Relatively, we tried to evaluate the light-emitting intensities of our films by
119 comparison with a control sample, namely the 1.2 mmol PEAB processed CsPbBr₃ thin film,
120 considering that PEAB has been one of the most popular ligands to increase the PL quantum yield
121 and to enhance the LEDs performance of CsPbBr₃ thin film.^{13, 22} Note that the two cases of 0.6
122 mmol PDAB and 1.2 mmol PEAB have the same molar amounts of ammonium and bromide ions,
123 but the former shows much more blue-shifted PL peak and enhanced PL intensity than the latter.
124 Thus, PDAB ligands can provide efficient passivation for CsPbBr₃ and restrict the growth of
125 CsPbBr₃ nanodomains within the quantum-confinement regime. Although the absolute PL
126 quantum yield information of our films cannot be provided currently in this report, the above

127 results exactly demonstrate great potential of PDAB ligands to achieve bright blue-emitting
128 CsPbBr₃ thin films, considering their comparison results with the films processed without any
129 ligands or with PEAB ligands.

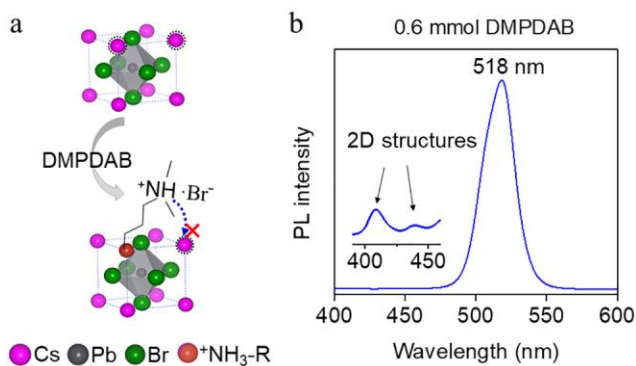
130 As the amount of PDAB ligands are increased from 0 mmol to 0.8 mmol, the PL wavelength
131 undergoes a dramatic blue-shift from 521 nm to 483 nm, which is consistent with the blue-shifted
132 UV-vis spectra (Figure 1c). In Figure 1c, it's worthy of pointing out that the first exciton absorption
133 peak of the CsPbBr₃ QD films cannot be clearly observed as more PDAB is introduced, and this
134 phenomenon has been also reported in some other monodisperse and polydisperse colloidal
135 CsPbBr₃ QDs solution systems^{33, 40} or in quantum confined quasi-2D perovskite film systems with
136 higher dimensionality.^{11, 13-14} In addition, for the X-ray diffraction (XRD) data in Figure S4, the
137 nanosized CsPbBr₃ crystal domains are further demonstrated by the decreased peak intensity and
138 the broadened peak full-width at half-maximum (FWHM) gradually as more PDAB ligands are
139 introduced into the system. On the other hand, no peaks ascribed to 2D perovskites could be
140 observed in our films, as evidenced in the PL, UV-vis and XRD spectra (Figures 1b-c, S3 and S4).

141 The absorption in 400 – 500 nm in Figure 1c is contributed by CsPbBr₃. As the amount of PDAB
142 is increased over 0.4 mmol, the absorbance in this region decreases. Correspondingly, a new
143 absorption peak around 378 nm occurs, which is obviously observed for the 0.8 mmol and 1.0
144 mmol PDAB processed CsPbBr₃ thin films. In particular, for the 1.0 mmol PDAB processed thin
145 film, the absorption above 400 nm completely vanishes, revealing that this thin film is composed
146 of pure second-phase with an absorption around 378 nm. Note that, no PL could be detected for
147 this second-phase composed thin film (Figures 1b and S3). Therefore, the sharp absorption peak
148 around 378 nm does not contribute to the PL emission in blue color region as observed in Figure
149 1b, and the corresponding second-phase is classified as one kind of the unnecessary by-products.

150 The UV-vis absorption peak around 378 nm has been observed in reference. For example, when
151 Subila et al. adopted some ammonium ligands to exfoliate out the fragments of $\text{ligand}^+ - [\text{PbBr}_3^-]$
152 complexes from CsPbBr_3 nanocrystals, the dominated UV-vis absorption around 320 nm occurred,
153 accompanied by the phase transformation of CsPbBr_3 nanocrystals into crystalline CsPb_2Br_5 2D
154 nanosheets with a lower dimensionality.⁴¹ Along with this, an absorption shoulder peak around
155 380 nm also occurred, and its phase was not affirmed in the mixture system. In other reports of
156 CsPb_2Br_5 2D nanosheets or single crystals with relatively simplified phase environment, no sharp
157 absorption peak around 378 nm was observed.⁴²⁻⁴⁴ Thus the sharp absorption peak around 378 nm
158 in our system may not correspond to the CsPb_2Br_5 perovskite phase. More solid evidence is
159 provided by XRD characterization for the 0.8 mmol and 1.0 mmol PDAB processed thin films. In
160 Figure S4, no peaks corresponding to CsPb_2Br_5 occur. Particularly, for the 1.0 mmol PDAB
161 processed thin film, even no any XRD peak is detected (Figure S4), which demonstrates that no
162 long-range orderly crystal structure (e.g., CsPbBr_3 , CsPb_2Br_5 , Cs_4PbBr_6) dominates in this second-
163 phase composed thin film. Thereby, the experimental evidences of UV-vis absorption (e.g., sharp
164 absorption peak around 378 nm), PL (no PL emission) and XRD results (no obvious crystal
165 structures) exclude the possibility that the second-phase corresponds to any known perovskite
166 crystal phases, such as CsPb_2Br_5 and Cs_4PbBr_6 .⁴²⁻⁴⁶ In addition, the sharp absorption peak around
167 378 nm is much blue-shifted than that of monolayer $\text{A}_2\text{Cs}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ ($n = 1$) quantum-well around
168 405 nm in UV-vis spectrum.^{14, 23} Overall, all the evidences point to that the second phase
169 corresponds to nanosized molecular clusters (also called as nanoclusters, molecular clusters or
170 magic size clusters),⁴⁷⁻⁵⁰ namely Cs-Pb-Br-PDAB nanoclusters. The nanoclusters, which are
171 similar to regular nanocrystals but smaller in size (usually $< \sim 1.5$ nm), are widely observed with
172 sharp high-energy UV-vis absorption in classical colloidal QDs system.⁴⁷⁻⁵⁰ Unfortunately, beyond

173 few methods such as UV-vis spectrum, synchrotron technology, etc.,⁵¹ most conventional
174 laboratory methods are difficult to identify the nanoclusters experimentally. The exact composition
175 of the nanoclusters is not further identified in this report; indeed, this second-phase is classified as
176 one kind of the unnecessary by-products, which needs to be avoided. We would highlight more on
177 how to inhibit their formation in our report, which is discussed below.

178 On the other hand, as mentioned above, the incorporation of PDAB ligands into the films would
179 enhance their PL intensity through defect reduction. However, when an excessive amount of
180 PDAB ligands (e.g., 0.8 mmol) were incorporated, the PL intensity decreased. Two main reasons
181 are proposed to explain this observation. First, nonluminous by-products (i.e., nanoclusters) are
182 formed instead of the desired CsPbBr₃ QDs when more PDAB ligands are introduced. Second, the
183 particle size of CsPbBr₃ QDs decreases when more PDAB ligands are incorporated. When the
184 ligand concentration was increased to 0.8 mmol, the PL spectrum showed further blue-shift, which
185 is due to the quantum confinement effect when the particle size gets smaller. As the size of CsPbBr₃
186 QDs decreases, the surface to volume ratio increases, which can introduce more surface defects.¹³
187 ²³ As a consequence, these defects reduce the PL intensity, which has also been observed in 2D
188 perovskite structures¹³ and classical QD systems.⁵²

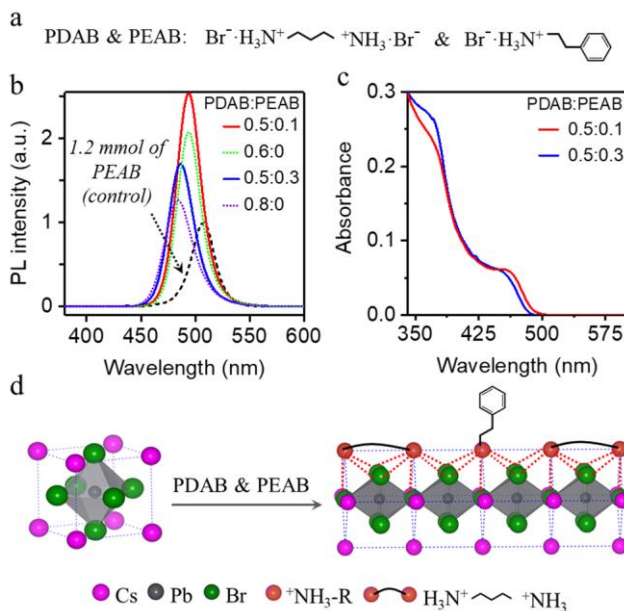


189

190 **Figure 2.** Control experiment using DMPDAB as ligands. (a) Schematic illustration showing that
191 the primary and tertiary ammonium groups of one DMPDAB molecule are difficult to
192 synergistically coordinate with CsPbBr₃. (b) PL spectrum of 0.6 mmol DMPDAB processed
193 CsPbBr₃ thin films. Inset is a partial enlarged figure evidencing formation of quasi-2D structures.

194 The enhanced passivation of PDAB is proposed to be induced by its quasi-bidentate coordination
195 with CsPbBr₃, in which the two primary ammonium groups of PDAB synergistically occupy
196 around the locations of two adjacent Cs⁺ lattice sites of CsPbBr₃ (Figures 1d and S5). To verify
197 this, a control experiment was performed using N,N-dimethyl-1,3-propanediamine
198 dihydrobromide (DMPDAB) as ligands (Figure 2). DMPDAB consists of a primary ammonium
199 group and a tertiary ammonium group (Figure 2a). The former is expected to interact with the
200 perovskite structure easily similar to PDAB. However, considering the Goldschmidt tolerance
201 factor,⁵³⁻⁵⁴ the size of the tertiary ammonium group is too large to fit in the crystal structure to
202 stabilize the PbBr₆⁴⁻ octahedra as reported earlier.⁵⁵ Therefore, it is proposed that DMPDAB would
203 not passivate the perovskite structure as effectively as PDAB, because PDAB has two primary
204 ammonium groups participating in the coordination. In addition, the opposite “free” tertiary
205 ammonium groups of DMPDAB may tend to stack via electrostatic interactions, hydrogen bonds
206 or other kinds of polar interactions in the process of crystal formation. This proposal is supported
207 by the formation of quasi-2D perovskites for the DMPDAB processed thin film (Figure S6).
208 Furthermore, no obvious PL blue-shift is detected in this system (Figure 2b), which further
209 suggests the importance of ligand engineering in the CsPbBr₃ QDs system. Thus, the synergistic
210 coordination of two primary ammonium groups of PDAB contributes to its enhanced passivation
211 with CsPbBr₃. Due to the fully utilized/coordinated functional ammonium groups of the PDAB

212 ligands, no stack structures namely 2D perovskites could be formed in the PDAB processed thin
 213 films.



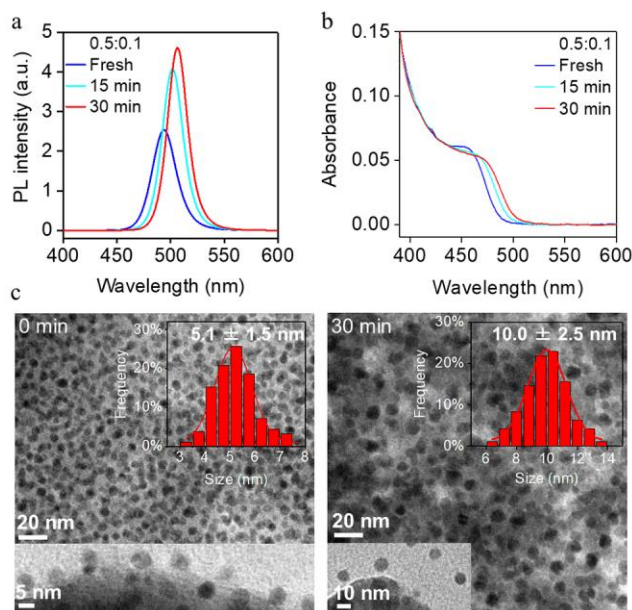
214
 215 **Figure 3.** Mix-ligand (PDAB and PEAB) assisted formation of CsPbBr₃ QD films. (a) Molecular
 216 structures of PDAB and PEAB. (b) PL and (c) UV-vis spectra of CsPbBr₃ QD films processed by
 217 mixed PDAB and PEAB ligands. The PL curves of 0.6:0- and 0.8:0- CsPbBr₃-QD-films are also
 218 integrated in (b). The PL curves in (b) are normalized by the maximal PL intensity of CsPbBr₃ thin
 219 films processed with 1.2 mmol of PEAB. (d) Schematic illustration of possible passivation pattern
 220 of PDAB and PEAB on CsPbBr₃.

221 PDAB is effective in forming CsPbBr₃ QDs with simultaneous PL blue-shift and intensity
 222 enhancement, but excessive PDAB induces the formation of nanoclusters and decreases the PL
 223 intensity (Figure 1b-c). To avoid that, we intended to weaken the strong passivation effect of
 224 PDAB by introducing another competitor with a single ammonium ligand, namely PEAB (Figure
 225 3a). Control experiments were performed taking into account the same total molar amounts of
 226 ligands for PDAB only or the mixed ligands of PDAB and PEAB. For the 0.6 mmol of ligand

227 usage, the PL spectrum of the CsPbBr₃ thin film processed with 0.5 mmol PDAB and 0.1 mmol
228 PEAB (marked as 0.5:0.1-CsPbBr₃-QD-film) shows almost no peak shift in comparison with that
229 of the film processed with 0.6 mmol PDAB, while the intensity is enhanced (Figure 3b). In
230 addition, the absorption around 378 nm is greatly inhibited (Figure 3c). The inhibition effect for
231 nanocluster formation via mixed ligands of PDAB and PEAB is more obvious upon comparing
232 the absorption around 378 nm for 0.5:0.3- and 0.8:0-CsPbBr₃-QD-film (Figures 1c and 3c), while
233 there still exists slight clusters absorption for the 0.5:0.3-CsPbBr₃-QD-film around 378 nm. The
234 PL wavelengths exhibit a result of 0.5:1 \approx 0.6:0, 0.5:0.3 \approx 0.8:0, indicating that the two systems
235 with the same total molar amounts of ligands emerge with similar particle size, respectively.
236 However, the PL relative intensities exhibit a result of 0.5:1 > 0.6:0, 0.5:0.3 > 0.8:0, respectively.
237 Thus, better optical performance of CsPbBr₃ QD films is obtained via the mixed ligand system in
238 comparison with the single PDAB ligand system. On the other hand, for both the single and mixed
239 ligand systems, 0.8 mmol of total ligand usage (0.5:0.3 and 0.8:0) would lead to more blue-shifted
240 emission wavelength, which corresponds to a smaller particle size, than 0.6 mmol of total ligand
241 usage (0.5:0.1 and 0.6:0). The decrease of PL intensity with 0.8 mmol of total ligand usage may
242 be also associated with the increased surface-volume ratio and defects or the formation of
243 nonluminous by-product, as discussed above. Besides, no 2D perovskite structures are formed for
244 the mixed ligands processed thin films (Figures 3b-c and S4). A possible passivation form for the
245 mixed PDAB and PEAB ligand system is proposed in Figure 3d, which shows the co-existing
246 coordination of positive single- and di- ammonium groups with the negative bromide ions.

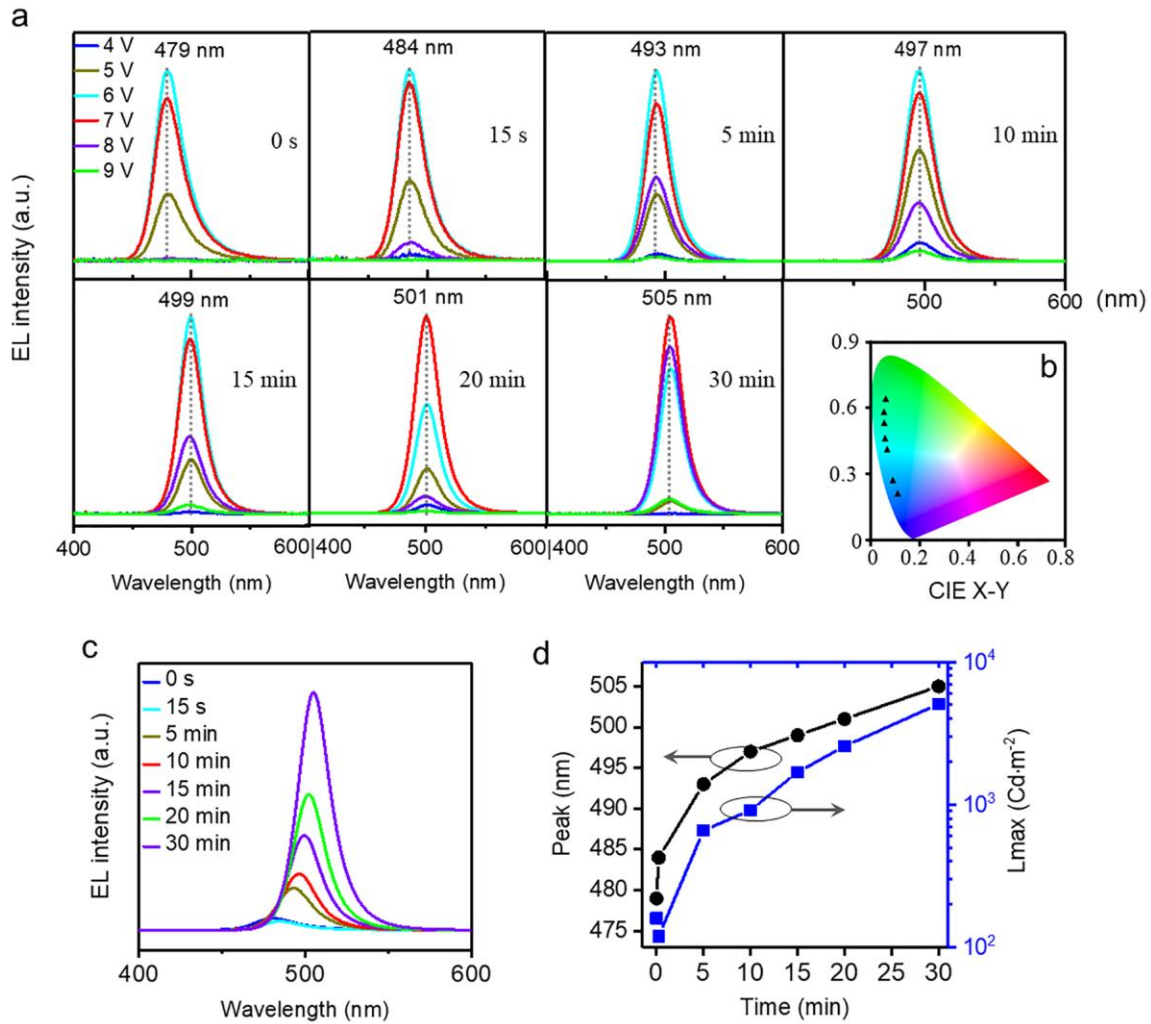
247 It's known that humidity affects the crystallization and stability of perovskites.⁵⁶⁻⁵⁷ Considering
248 this, we further studied the humidity's influence on our films (Figures 4, S7-9 and Table S1). One
249 typical example for 0.5:0.1-CsPbBr₃-QD-film is provided in Figure 4. Once exposed in air, all the

250 PDAB-contained CsPbBr₃ thin films show a gradual PL red-shift, accompanied by a narrowing of
 251 peak FWHM, which is consistent with the red-shifted UV-vis absorption spectra (Figures 4a-b,
 252 S7-8). Considering the quantum confinement effect, the red-shift phenomenon reveals the size
 253 increase of CsPbBr₃ QDs, which is further demonstrated by transmission electron microscope
 254 (TEM) characterization (Figure 4c). The size of CsPbBr₃ QDs could be increased from 5.1 nm to
 255 10.0 nm approximately before and after 30 min air exposure. Actually, the PL intensity would be
 256 greatly enhanced within a short time of air exposure. This observation is important to achieve a
 257 brighter emission from the CsPbBr₃ QD film. Moreover, the PL red-shift emerges with the
 258 character of continuous change (Figure S7), implying the size tunability of CsPbBr₃ QDs. Thus,
 259 the influence of humidity turns to be an effective method to realize the size control and color
 260 tunability of CsPbBr₃ QDs via simple control of exposure time in air, which is regarded as an aging
 261 treatment in ambient.



262
 263 **Figure 4.** Second growth of CsPbBr₃ QDs in 0.5:0.1-CsPbBr₃-QD-film upon air exposure (34 ~
 264 37% relative humidity (RH)), characterized by (a) PL, (b) UV-vis, and (c) TEM respectively. The

265 PL curves in (a) are normalized by the maximal PL intensity of the 1.2 mmol PEAB processed
 266 CsPbBr₃ thin film. The “fresh” sample corresponds to the measurement immediately after exposed
 267 in air. The histograms of size distribution in (c) are based on the statistic information of ~ 200
 268 particles (0 min) and 100 particles (30 min), respectively.



269

270 **Figure 5.** Evolution of EL of the 0.5:0.1-CsPbBr₃-QD-films. (a) EL spectra recorded at various
 271 applied voltages (4 V – 9 V). The spectral changes at different aging times (0 s – 30 min) and the
 272 corresponding peak emission wavelengths are presented in different panels. The films were aged
 273 in ambient (34 ~ 37% RH and room temperature) for different times (0 s – 30 min) prior to thermal

274 evaporation. (b) Commission Internationale de l'Éclairage (CIE) values of the EL spectra of
275 0.5:0.1-CsPbBr₃-QD-films with various aging time in air. (c) Overall comparison of max EL
276 curves and (d) the statistic information of peak position and maximal luminance (L_{max}) as a
277 function of aging time in air.

278 Indeed, the humidity plays an important role for the second-growth phenomenon. Control
279 experiments were performed by storing the 0.5:0.1-CsPbBr₃-QD-film in a dry room of 16%
280 relative humidity (RH) and in a N₂ glove box (Figure S9). After 24 h in the dry room, the PL of
281 CsPbBr₃ thin film only red-shifts to 500 nm, while the storage in ambient for 24 h results in the
282 emission at 520 nm, which is same as bulk CsPbBr₃. Thus, the red-shift phenomenon could be
283 greatly inhibited by decreasing the humidity. This conclusion is further supported by the result of
284 control sample after one-month storage in a N₂ glove box, which showed no red-shift phenomenon.
285 The ammonium group shows a polar character which favors adsorption of moisture in air. Upon
286 air exposure, the polar ammonium ligands undergo a partial solvation at the surface,⁵⁸ which
287 induces a second crystal growth of the CsPbBr₃ QDs through the Ostwald ripening process.
288 Accompanied by the size increase, the CsPbBr₃ QDs may also experience a so-called “self-
289 healing” process of the perovskite lattice in ambient air as reported.⁵⁸ For example, Snaith and
290 coworkers have reported that the exposure to moisture could enhance the PL intensity of perovskite
291 film due to partial solvation of the ammonium component and “self-healing” of the perovskite
292 lattice.⁵⁸ A recent study by Stranks and coworkers reveals that O₂/H₂O in atmosphere under light
293 soaking may help remove the trap states at the perovskite surface,⁵⁹ thus an enhanced PL intensity
294 could be obtained within short-time exposure in air.

295 EL studies were performed taking the 0.5:0.1-CsPbBr₃-QD-films as an example. As discussed
296 above, continuously tunable emissions for the thin films can be achieved via simple control of

297 exposure time in air. With this consideration, the thin films were firstly treated by aging in ambient
298 (34 ~ 37% RH and room temperature) for 0 s - 30 min, respectively. The CsPbBr₃ QD films exhibit
299 smooth surface roughness within the exposure period in ambient (Figure S10). Notably, no Pb⁰ is
300 observed for the thin films after aging treatment (Figure S11). In the subsequent step, electron
301 injection layer 4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B₃PYMPM) and LiF/Al
302 electrode were sequentially evaporated onto the CsPbBr₃ QD films in high vacuum (Figure S12).
303 The EL properties were evaluated directly in air. The samples with various aging time exhibit
304 continuously tunable emissions in EL spectra (Figure 5), from 479 nm (0 s) to 505 nm (30 min),
305 respectively. Accompanied by the EL wavelength changes, the EL emission intensity is also
306 enhanced with the luminance increasing from 165 Cd/m² (at 479 nm, 0 s) to 5058 Cd/m² (at 505
307 nm, 30 min) as shown in Figure 5b-c. For each sample with the exact aging time in air, the EL
308 spectra do not show any shift under various voltage biases, which obviously differ from the results
309 in mixed halide system as reported.^{13, 19} On the other hand, this result also demonstrates that the
310 evaporation process of organic electron transfer material and electrode onto CsPbBr₃ QD films can
311 inhibit the direct influence of humidity upon the size change of CsPbBr₃ QDs.

312 In summary, for the first time, we successfully developed a new CsPbBr₃ QD film system via one-
313 step spin-coating route that differs from the traditional colloidal synthesis route. The PDAB
314 ligands were found to efficiently inhibit the crystal growth of CsPbBr₃ QDs. The mixed ligand
315 system of PDAB and PEAB was further developed to enhance their emission properties. The
316 CsPbBr₃ QDs showed a second growth process in air, which provided another feasible way to
317 realize the size control of CsPbBr₃ QDs via simple control of aging time in air. As a result,
318 continuously tunable emissions from green to blue colors were achieved in the PL and EL spectra.
319 Importantly, the produced CsPbBr₃ QD films demonstrate no spectra-drift in EL upon voltage bias.

320 These results are expected to accelerate the exploration of blue-emitting applications of
321 perovskites.

322 ASSOCIATED CONTENT

323 **Supporting Information**

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

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

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339 M. J. and Z. H. contributed equally to this work.

340 **Notes**

341 The authors declare no competing financial interest.

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