High-Performance CsPbX$_3$ Perovskite Quantum-Dot Light-Emitting Devices via Solid-State Ligand Exchange

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Supporting Information

ABSTRACT: Recently, all-inorganic perovskite quantum dots (PeQDs), CsPbX$_3$ have become attractive because of their excellent optoelectronic properties and superior air/moisture stabilities compared with conventional organic–inorganic hybrid perovskites, and the application of CsPbX$_3$ PeQDs to light-emitting devices (LEDs) has also become competitive. To enable the use of CsPbX$_3$ PeQDs for thin-film-type perovskite quantum-dot LEDs (PeQLEDs), a paradox associated with the ligand property and surface passivation must be overcome during thin-film fabrication. A decline in the photoemission performance was observed at relatively low amounts of surface-passivating ligands, while the quality of the thin film deteriorated in the presence of excessive ligands. To address this conflict, in this study, the performance of PeQLEDs based on CsPbX$_3$ fabricated by a novel method involving solid-state ligand exchange (SLE) with aromatic acid/amine was investigated. Using this strategy, most of the excess ligands were removed while preserving the surface passivation of CsPbX$_3$ in the thin film. We discovered that an optimal aromatic acid/amine ligand ratio is required for CsPbX$_3$-based PeQLEDs to retain the solubility of the PeQDs and simultaneously accomplish the SLE process without affecting the properties of the PeQD. Moreover, an improvement in the overall photoemission efficiency of the resulting PeQLED device was confirmed under red, green, and blue conditions. In addition, a luminance of 1889 cd/m$^2$ and a current efficiency of 6.28 cd/A was achieved for the PeQLED.

KEYWORDS: cesium–lead halide, perovskite, quantum dot, solid-state ligand exchange, light-emitting device

The optoelectronic properties of perovskite-based semiconductors have been intensively studied. In particular, there has been significant effort toward their application in the field of solar cells, with a recently reported high efficiency of 21.2%.† This is due to the inherently advantageous properties of perovskite materials, for instance, long diffusion length, high absorption coefficient, and low ratio of the deep trap site due to the weak exciton binding strength.‡,3 In addition, focus has also been on down-conversion devices,§ lasing,‖ and electroluminescence (EL) devices§ because of the facile band-gap control, narrow full-width at half-maximum (fwhm) of the photoluminescence (PL) peaks, and high PL quantum yield. Among the various perovskite materials, two organometallic halides, which are organic–inorganic hybrid perovskites composed of methylammonium lead halide (MAPbX$_3$) and formamidinium lead halide (FA$\text{PbX}_3$), have been actively studied because of their excellent optoelectronic properties. However, organic–inorganic hybrid perovskites are vulnerable to moisture-mediated degradation because of the hydroscopic properties of methylammonium and formamidinium. In order to render the perovskite materials more versatile, it is necessary to improve their lifetimes. In this respect, many studies have been devoted to replacing the organic part of the perovskite with an inorganic atom like cesium.6,9*

In the case of perovskite solar cells, a film-type bulk perovskite has been mainly used for the preparation of high-efficiency devices. The bulk-type perovskite is required to have a structure that is optimized for separation of the electron–hole pairs by maximizing the exciton diffusion length.2,3 However, as a candidate for a light-emitting device (LED), photoemission must be optimized, such that the exciton diffusion length is reduced to maximize the radiative recombination of the electron–hole pair.10–12 For effective confinement of the electron–hole pairs, it is necessary to reduce the domain size of the perovskite. To achieve this, diverse studies are being actively conducted using perovskite nanoparticles12,13 and nanoplatelets11,14 as photoemission materials. The implementation of CsPbX$_3$ perovskite quantum dots (PeQDs) for a LED was initiated by Song and colleagues.13 With increasing appeal of the material, extensive studies are directed toward achieving efficient PeQD LEDs (PeQLEDs).
with bright and narrow EL, high external quantum efficiency (EQE), and relatively improved long-term stability through optimized PeQD thin films, which is critical for optimizing their function.\textsuperscript{13,15−17} Because the surface-capping ligands of quantum dots (QDs) critically influence their optical properties, there has been significant attention on the surface passivation of CsPbX\textsubscript{3}. De Roo et al. reported that the number of surface-defect sites increased as the ratio of the surface-passivating ligands decreased, leading to a decline in the photoemission.\textsuperscript{18} Another study reported a luminance of 2335 cd/m\textsuperscript{2} and an EQE of 0.19\% for the green emission by cross-linking the PeQD layers via atomic layer deposition.\textsuperscript{16} A luminance of 330 cd/m\textsuperscript{2} at 9.0 V and an EQE of 3.0\% at 4.5 V were reported under the same conditions by adding excessive ligands to minimize the rate of diffusion of the ligands from the surface of CsPbX\textsubscript{3} PeQDs.\textsuperscript{17} These results demonstrate that the surface ligand binding state directly affects the photoemission characteristics of CsPbX\textsubscript{3} PeQDs used as the core component of PeQLED.

Pristine QDs synthesized in organic solvents are typically protected by long-chain aliphatic molecules like oleic acid (OA) and oleylamine (OAm). These hydrocarbon chains are electronically insulating and act as potential barriers in QD-based optoelectronic devices. To resolve this, short-chain ligand-exchange methods are used for the development of conventional QD solar cells, toward reducing the resistance of the photoactive layer.\textsuperscript{19−21} However, employing this method to PeQDs is quite challenging because the original capping ligands on the PeQDs are relatively labile and the stability of PeQDs is very low during the ligand-exchange reaction, which results in the poor photoemission properties of PeQDs. To preserve the photoemission property of the purified PeQDs, some excess ligands are required to improve the adsorption rate of the surface ligands. However, these excess ligands enhance the insulating properties of the PeQD films fabricated with ligand-rich PeQD dispersions.

Conventional solid-state ligand-exchange (SLE) methods involve dropping a solution of the short-chain ligands in an antisolvent for QDs onto the surface of a QD film.\textsuperscript{22} However, it is difficult to apply the traditional SLE method for CsPbX\textsubscript{3} PeQD layers because they are prone to decomposition when they are in direct contact with hydrophilic antisolvents such as alcohols.

To resolve these issues, we introduce the concept of SLE with ligand-assisted solubility adjustment (LASA) for optimization of the PeQD layer. LASA involves solubility control of the ligands and the resulting ligand-exchanged PeQDs using the appropriate solvents during the ligand-exchange process. LASA provides two advantages for optoelectronic applications, particularly PeQLEDs. First, because of the solubility control between the ligand and solvent, PL quenching of the PeQDs was well-suppressed owing to the prevention of loss of surface-bound ligands. Second, from the optimized combinations of the ligand and solvent, PL quenching of the PeQDs was well-suppressed owing to the prevention of loss of surface-bound ligands. Second, from the optimized combinations of the ligand and solvent, PL quenching of the PeQDs was well-suppressed owing to the prevention of loss of surface-bound ligands. Moreover, it was also possible to suppress the generation of surface defects on the CsPbX\textsubscript{3} PeQD layer and thereby further enhance the photoemission. Thus, the fabrication of CsPbX\textsubscript{3} PeQLED based on PeQDs with short ligands, with dramatic improve-

![Figure 1. Schematic illustration of the SLE concept based on short aromatic ligands: (a and b) LASA; (c) SLE. Alkyl chain ligands are soluble in octane or benzene; however, aromatic ligands are insoluble in octane but soluble in benzene.](image-url)
ment in the luminance and current efficiency compared to those without the SLE process, could be successfully demonstrated.

In this work, we investigate the effect of the ligand type and length on the optical properties of CsPbX₃ PeQDs and fabricate thin films of these QDs with improved photoemission properties and lower surface-defect densities of the PeQDs. In addition, the high quality of the thin-film morphology achieved as a result of this SLE process led to impressive device performances in red-, green-, and blue-emitting PeQLEDs. The CsPbX₃ PeQDs used in this work were synthesized via a hot-injection method, as described previously. Figure 1 provides a schematic illustration of the ligand-exchange process used to fabricate optimized thin films of PeQDs. We hypothesized that PeQDs passivated with short rigid ligands might be more optically stable because of the dense overcoating of the QDs and could also advantageously influence the PeQLED performance by decreasing the potential barrier of the PeQD film after the ligand-exchange process, compared to that of the as-synthesized PeQDs with long hydrocarbon tails. For this, ligand-exchange experiments were carried out using ligands with different chain lengths, and it turned out that the solubility of the treated PeQDs in hydrophobic solvents could be dramatically modified depending on the ligand length. This was adjusted by tuning the ratio of the employed ligands and the polarity of the solvents, which is essential to fabricating a nanocrystal film with high surface coverage, resulting in the superior performance of the PeQLEDs.

Figure 2. Characterization of the shape and surface of the PeQDs. TEM image of the PeQDs subjected to SLE: (a) pristine PeQDs; PeQDs after SLE treatment with (b) 2.5% and (c) 10% of the short-chain ligand in an exchange solution. FT-IR spectra of the ligand-exchanged QDs for defined surface states: (d) overall peak shape and shift and (e) 1300–1800 cm⁻¹ range demonstrating the emergence of the peak at 1395 cm⁻¹ after ligand exchange.

Parts a and b of Figure 1 illustrate the concept of the LASA process employed to prevent dissociation of the ligand from the surface of PeQDs, as well as to tune the colloidal solubility via ligand exchange with short-chain ligands. LASA is a pretreatment step of the overall SLE process used for improving the optoelectronic properties of PeQD films via optimization of the surface defects, based on the solubility of the PeQDs. As shown in Figure 1a, long-chain hydrocarbon ligands, such as OA and OAm, inherently attached to the surface of as-synthesized CsPbX₃ PeQDs are quite labile and detach from the QD surface during the washing process, generating surface defects on the QDs, which leads to undesirable deterioration of the PL. We found that, in the ligand-exchange experiment with short-chain ligands including aromatic acid/amine, the solubility of the ligand treated PeQDs in hydrophobic solvents gradually decreased with an increase in the ratio of the short-chain ligands on the surface of the QDs. This indicated that the PeQDs with short-chain ligands became less sterically hindered than those with the original long-chain ligands, resulting in the precipitation of PeQDs when all of the long-alkyl-chain ligands were exchanged with the short-chain ones. It is worth emphasizing that octane was adopted as a key solvent because aromatic acid/amine has a low solubility in octane, whereas the solubility of long-alkyl-chain ligands in it is quite high. This implies that it is difficult for short-chain ligands to diffuse out into the solvent during the ligand-exchange process and that the surface defects formed by the ligand dissociation can be
minimized, thereby conserving the high photoemission property (Figure 1a,b). In addition, benzene is essential to dissolving aromatic short-chain ligands such as benzoic acid or 4-phenylbutylamine in our experiments in spite of its relative toxicity. Alternative solvents that are appropriate for our system also include aromatic functional groups like xylene or toluene. Through LASA, the optimized ratio of the long-chain-to-short-chain ligands (long-chain ligand:short-chain ligand = 95:5 mole ratio in a 30 mg/mL PeQD solution) to maintain the dispersibility of the resulting PeQDs was determined. At this point, we conceived that the controllable precipitation of PeQDs by adding a certain amount of short-chain ligand could be utilized to fabricate high-quality PeQD thin films with short-chain ligands to achieve the SLE process without polar solvents. As shown in Figure 1c, after optimization of the precipitation condition of PeQDs with the designated ratio of long-chain-to-short-chain ligands, as-synthesized PeQDs with long-chain hydrocarbon ligands were spin-coated on the substrate, and the solution containing short-chain ligands was deposited on the PeQD thin film, accomplishing the antisolvent-free SLE method without decomposition of the PeQDs. Figure S1 demonstrates the solubility tuning for PeQDs by varying the concentration of the introduced short-chain ligands, successfully resulting in the fabrication of a robust PeQD thin film in nonpolar solvents.

CsPbX3 PeQDs (X = I, Br, and Cl) were synthesized as described elsewhere, and the color of PeQDs successfully could be tuned by varying the type of halide anion, with the result being that CsPbI3, CsPbBr3, and CsPbClBr2 PeQDs provided red, green, and blue emission, respectively. Crystal structure characterization was carried out using X-ray diffraction (XRD) to determine the halide-ion composition (see Figure S2a). The particle sizes of the CsPbX3 PeQDs were determined by transmission electron microscopy (TEM), with the result being that the size of the PeQD was around 8–10 nm regardless of the type of halide anion, as shown in Figure S3. It is worth noting that some fused PeQDs were observed, depending on the ligand-exchange ratio during the SLE process. It was possible to confirm that the particles were not aggregated before the SLE process (Figure 2a). However, when SLE proceeded by spin coating the solution with a 2.5% short-chain ligand, it was possible to confirm the tendency of the particles to connect with each other (Figure 2b). A severely aggregated PeQD film was observed when SLE was conducted with more than 5% short chain containing solution (Figure 2c). The XRD patterns in Figure S2b show that the peak intensity corresponding to the (200), (210), (211), and (220) planes tends to increase slightly after exchange with short-chain ligands, indicating that the crystal domain size could be increased. This observation is further supported by the fact that the particle-to-particle connection leads to bonding between the lattices, as observed in the TEM image, which shows an
effect similar to an increase in the particle size. These results indicate that a PeQD solid is formed by fusion of the lattice between individual PeQDs constituting the film, when SLE is performed. To observe the more detailed morphology of the PeQD film, atomic force microscopy and scanning electron microscopy were used, as shown in Figure S4, demonstrating that the PeQD film was deposited with many aggregated nanoparticles, but uniform morphology of PeQDs with full surface coverage was prepared in the long range after SLE treatment. For a comparison of the PeQD thin films in a large area between before and after SLE treatment, fluorescence microscopy was utilized, as shown in Figure S5, demonstrating that SLE treatment provided a more uniform thin film with fewer pinholes.

Parts d and e of Figure 2 show the Fourier transform infrared spectroscopy (FT-IR) spectra of CsPbX_{3} PeQDs exchanged with ligands of different chain lengths. Figure 2d shows the −CH\(_{3}\) and −CH\(_{2}\) symmetric and asymmetric stretching vibrations in the range of 2840−2950 cm\(^{-1}\) and the −CH\(_{2}\) bending vibration at 1466 cm\(^{-1}\). Figure 2e shows two asymmetric vibrations and one symmetric stretching vibration of the carboxylic group in the range of 1540 and 1408 cm\(^{-1}\). These vibration peaks originate from the carboxylate group of OA and OAm. When the SLE method was performed using benzoic acid and 4-phenylbutylamine, the ratio of the peak intensities in the range of 2840−2950 cm\(^{-1}\), which are the vibration peaks of the aliphatic group, tend to decrease with an increase in the ratio of the short-chain ligand.

Moreover, Figure 2e shows the 1395 cm\(^{-1}\) peak corresponding to the C\(-\)C vibration after the introduction of the aromatic ligand. The results confirm that the peaks become stronger as the ratio of the short-chain ligand increases. The decrease in the aliphatic C\(-\)H vibration peak and the appearance of the C\(-\)C vibration peak along with an increase in the ratio of the C\(-\)C vibration peak for a sample subjected to ligand exchange with short-chain ligands reveal a decrease in the proportion of OA and OAm, which contain the carboxylate and amine groups, and an increase in the proportion of aromatic ligands occurring simultaneously.

To investigate the changes due to short-chain ligand exchange, Figure 3 shows the changes in the optical property according to the ligand exchange ratio. Figure 3a shows the absorbance and PL of red-, green-, and blue-emitting CsPbX\(_{3}\) PeQDs (red, CsPbI\(_{3}\), green, CsPbBr\(_{3}\), blue, CsPbBr\(_{3}\)Cl). The results confirm that the PL peak maximum of the red emission is 670 nm, that of the green emission is 510 nm, and that of the blue emission is 478 nm, and the fwhm of the red emission is 30 nm, that of the green emission is 23 nm, and that of the blue emission is 18 nm. Figure 3b shows comparative results according to the type of short-chain ligands before and after vacuum treatment in a vacuum chamber. This experiment was conducted to confirm that the surface-passivating ligands can withstand the vacuum condition of the thermal evaporation step during the device fabrication step because the boiling points of the short-chain ligands are lower than those of conventional long-chain ligands. The experiment was conducted with short-alkyl-chain ligands for a direct comparison with OA and OAm used in the past. The short-alkyl-chain ligands have low boiling points, and the binding strength of the perovskite with these ligands are weak, as described above. Owing to these properties, the short-alkyl-chain ligands could not withstand the vacuum chamber condition, as shown in Figure 3b. As shown, the PL intensity is directly dependent on the number of carbon atoms, which is related to their boiling points. These results confirm that the surface-passivating ligands of PeQDs evaporated when the chain length of the ligand (and the corresponding boiling point) was below a threshold level; the surface defects increased and the photo-emission efficiency decreased. Thus, the alkyl-chain-based short-chain ligands presented limitations in terms of reducing the chain length, for optimization of the PL intensities, under vacuum evaporation conditions used for the fabrication of optoelectronic devices, especially PeQLEDs.

To solve this issue, we searched for a short acid/amine ligand that has a higher boiling point and a shorter chain length compared to those of alkyl chain ligands and introduced aromatic acid/amine ligands that satisfy these properties. The PL intensity of surface-modified PeQDs was compared according to the number of carbon atoms to identify the differences in the PL properties after vacuum treatment. Figure 3b shows that aniline, an aromatic ligand with six carbon atoms, exhibited a PL intensity drop of 20% compared to that before vacuum treatment, whereas hexylamine, an alkyl ligand with six carbon atoms, showed a PL intensity drop of 70%, which confirms that the PL intensity drop is lower with aniline. Furthermore, the carbon number that yielded an unchanged PL intensity after vacuum treatment was found to be 12 in the aromatic ligand, compared to 18 in the alkyl chain ligand. According to the molecular structure shown in Figure 3b, the chain length of the aromatic ligand is shorter than that of the alkyl ligand. The results of these studies are shown in Figures S6−S8. These results showed that, for a ligand to be used in PeQLED fabrication by SLE, using an aromatic acid/amine as ligands is more suitable than using an alkyl chain acid/amine. Figure 3c shows the changes in the relative PL intensity according to the ratio of the short-chain ligand. A series of aromatic acid/amine ligands were used in this study, and the ligand content was adjusted on a micromolar scale. Controlling the ligand quantity led to an increase in the PL intensity by 201% for the red emission, 208% for the green emission, and 230% for the blue emission compared to those without the ligand passivation condition. Although aggregation of PeQDs with 10% of short-chain ligands occurred, the PL intensity showed the maximum value because the surface defects of PeQDs were passivated by enough ligands, as shown in Figure 3c. The IR spectrum also clearly confirmed that the ratio of short-chain ligands on PeQDs was increased, as shown in Figure 2d. However, the results indicated a tendency toward reduction in the PL intensity induced by the decomposition of PeQDs above a threshold level of the ligand content, and in the case of the red emission, the PeQDs lost the PL properties due to decomposition. We found that the short-chain ligands over the 10% ligand content induced decomposition of the PeQDs because of too much acidic environment. As shown in Figure 3d, a time-correlated single-photon-counting (TCSPC) analysis was conducted to obtain information on surface-defect-level control by the short-chain ligand exchange. The aim of this analysis was to investigate the variation in the exciton lifetime according to the passivation ratio of the short-chain-to-long-chain ligands within the range from 0% to 5% of short-chain ligands, which provided colloidal stability. Figure 3d shows the results from TCSPC analysis, confirming that the exciton lifetime tends to increase from 5.7 to 6.3 ns as the ratio of the passivating ligand increases. An increase in the exciton lifetime implies that the proportion of exciton quenching that constitutes nonradiative recombination is reduced, and the
decrease in the quenching rate with increasing passivation ratio implies that short-chain ligand passivation effectively suppresses the surface-defect level. Because of increased surface-passivating ligands, the decay curves changed from multi-exponential to single-exponential (Figure 3d). These PL decay curvature transitions indicate that the surface-defect sites of the PeQDs were suppressed via surface passivation of PeQDs after the aromatic ligand treatment.

As shown in Figure 3, the study could reveal the aromatic short-chain ligand system that effectively suppresses the surface-defect level even after being subjected to vacuum treatment. The current results can predict that the SLE can be used (1) to increase the surface passivation of PeQDs, (2) to decrease the surface ligand length of PeQDs constituting the active layer, and (3) to enhance the overall optoelectronic property of the active layer by the formation of PeQD solids via particle–particle connection.

Figure 4 illustrates the concept of PeQLED with SLE. On the basis of the optical characterization results shown in Figure 3, the study was further aimed to demonstrate the possibility of optimizing the photoemission property of PeQLED through surface passivation by the SLE with LASA when the EL device condition is applied in comparison to the conventional long-chain ligand condition. For the device structure in this study, ITO/PEDOT:PSS/PeQDs/TPBi/LiF/Al, which is a regular QLED structure, was used, as illustrated in Figure 4a. Using this device structure, the results confirmed that the EL spectrum, such as the PL peak with the red, green, and blue emissions, can be implemented, as shown in Figure 4b, because the electron injection ratio is similar to the hole injection ratio, and thus the carrier recombination zone without the luminescence from the carrier injection layer can be confined to the active layer. As shown in Figure 4d, the results confirm that PeQLED implementation with various colors ranging from red to blue is possible. By adjustment of the surface-passivating ligands of the PeQDs constituting the active layer in this PeQLED structure (Figure 4c), this study is further aimed at confirming whether the enhanced photoemission property achieved by the short-chain ligand passivation shown in Figure 3 as well as the changes in the device performance owing to the improved electronic property due to PeQD coupling shown in Figure 2 could be valid in various band-gap conditions by halide ratio control.

Figure 5 shows the current/voltage/luminance (IVL) results of PeQLEDs under the green condition after being subjected to SLE. To observe the correlation between the short-chain ratio and device performance during the SLE process, we characterized the device performance with an increase of the short-chain ligands in the exchange solution. As the ligand concentration in the SLE solution was increased, the ratio of the short-chain ligand passivation increased. Figure 5a shows the corresponding luminance/voltage characteristics; the luminance increases as the short-chain ligand content increases. Under the condition without SLE, the luminance increases from 821 to 1889 cd/m² after SLE, implying that the luminance increases by 230% after SLE. The results are similar to the PL characterization results shown in Figure 3c. These results suggest that surface-defect-level control (photoemission property control) of the active layer directly influences the photoemission property of PeQLED. Figure 5c shows the current/voltage characteristics, confirming that the current density tends to decrease as the SLE treatment progresses. The
decrease in the current with an increase in the short-chain passivation ratio is due to the decrease in the current leakage according to the increase in the packing density of PeQDs with increasing particle–particle connection, as shown in Figure 2. In addition, PeQD films with short-chain ligands after SLE treatment provided a dense and uniform thin film with fewer pinholes, as shown in Figure S5. From a reduction of the pinhole ratio at the PeQD film, the current leakage was well suppressed. Figure 5d shows that an increase in the current efficiency is due to an increase in the luminance and a decrease in the current leakage, which are induced by SLE. Figure 5d confirms that there is an improvement in the current efficiency from 0.82 corresponding to a device without SLE to 6.28 cd/A after SLE. The current efficiency is enhanced by 765% after SLE. In addition to the current green emission shown in Figure 5, the red emission shown in Figure S9 confirms that the luminance increases by 333% from 65 to 217 cd/m² after SLE and the current efficiency increases by 100% (from 0.42 to 0.84 cd/A). Furthermore, Figure S10 confirms that, for the blue emission, the luminance increases by 472% from 7.62 to 36 cd/m² after SLE and the current efficiency increases by 244% from 0.045 to 0.11 cd/A. These results are obtained because of the improvement in the photoemission property of PeQDs by short-chain passivation through SLE as well as the improvement in the electronic property due to the coupling of lattices through increased particle–particle connection. The improvement in the optoelectronic properties is applicable to all halides, not limited to a specific halide. Using these properties, optimization of the active layer of a color-tunable PeQLED can be easily and effectively performed, as shown in Table 1. In addition, in order to demonstrate the effect of the short-chain ligand exchange, we utilized the hole-only-device (HOD) characterization, as shown in Figure S11 and Table S1. From the HOD characterization, we could find the carrier mobility increasing via short-chain ligand exchange. HOD using the PeQDs with short-chain ligands resulted in a reduction in the internal resistance of the PeQD films. To eliminate the effect of residual ligands, we tried to wash out the residual ligands, and HOD results demonstrate that the electrical device performance was directly related to the effect of the chain lengths of the surface binding ligands not the residual excess ligands.

**Table 1. Summary of the PeQLED Device Performances for Devices with Red-, Green-, and Blue-Emitting CsPbX₃ PeQD Films Subjected to SLE**

<table>
<thead>
<tr>
<th>PeQD</th>
<th>color</th>
<th>EL peak (nm)</th>
<th>current efficiency (cd/A)</th>
<th>L_max (cd/m²)</th>
<th>power efficiency (lm/W)</th>
<th>EQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbI₃ red</td>
<td>660</td>
<td>0.84</td>
<td>217</td>
<td>0.68</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>CsPbBr₃ green</td>
<td>510</td>
<td>6.28</td>
<td>1889</td>
<td>5.67</td>
<td>2.09</td>
<td></td>
</tr>
<tr>
<td>CsPbBrCl₂ blue</td>
<td>484</td>
<td>0.11</td>
<td>36</td>
<td>0.056</td>
<td>0.044</td>
<td></td>
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*Measurement conditions: ambient air conditions and without encapsulation. Cell area: 4.75 mm².*
In conclusion, optimization of the properties of the PeQD layer via ligand exchange, which was introduced to improve the surface and electrical properties of CsPbX\textsubscript{3} PeQDs, was achieved. LASA was utilized under a colloidal state in an appropriate solvent to prevent ligands from diffusing out of the QD surface via solubility control, and the PeQD films were subjected to SLE to minimize the surface defects and insulating properties. PL and TCSPC measurements were performed to examine the surface passivation properties of the CsPbX\textsubscript{3} layer after being subjected to SLE. The results, i.e., enhanced photoemission properties, confirmed the reduction in the surface-defect sites due to the improvement in the surface passivation properties. Finally, CsPbX\textsubscript{3} PeQD subjected to SLE was used as a photoemission layer of PeQLED to confirm the effect of surface passivation. The PeQLED showed enhanced photoemission property under the red, green, and blue emission conditions, thereby demonstrating the favorable impact of SLE based on LASA.

## EXPERIMENTAL METHODS

**Synthesis of CsPbX\textsubscript{3} PeQDs.** Unless otherwise noted, all syntheses were performed under a purified argon atmosphere in a M. Braun glovebox or via standard Schlenk-line techniques. A stock solution of the cesium-surfactant complex was prepared by reacting cesium carbonate (5 mmol), oleic acid (OA; 16 mmol), and stearic acid (8 mmol) in 1-octadecene (ODE, 8 mL) under vacuum with vigorous mixing and heating to 120 °C. The lead halide precursor solution was prepared by dissolving a lead halide source (0.188 mmol; PbI\textsubscript{2} for red-emitting PeQDs, PbBr\textsubscript{2} for green-emitting PeQDs, and PbI\textsubscript{2}:PbCl\textsubscript{2} = 2:1 for blue-emitting PeQDs) in ODE (5 mL) under vacuum, increasing the temperature to 120 °C, OA (0.5 mL) were added, and the resulting solution was heated to a constant temperature (150 °C for red-emitting PeQDs, 160 °C for green-emitting PeQDs, and 165 °C for blue-emitting PeQDs). Then the stock solution (0.2 mL) containing cesium was quickly injected into the batch solution, and 3 s later, the reaction mixture was rapidly quenched to room temperature using an ice bath, thereby preventing further reaction. For purification of the CsPbX\textsubscript{3} PeQDs, a precipitation/redispersion method was employed. The crude solution was precipitated by centrifugation, and the flocculated CsPbX\textsubscript{3} PeQDs were redispersed in benzene.

**LASA Treatment of CsPbX\textsubscript{3} PeQDs.** In a typical synthesis, a ligand stock solution was prepared by mixing 0.29 mmol of 4-phenylbutylamine and 0.82 mmol of benzoic acid in benzene. This stock solution was added to 0.15 mL of a PeQD solution. After incubation, 1 mL of acetonitrile was added to precipitate the QDs, and the resulting precipitates were washed with acetonitrile. The final product was redispersed in 1 mL of benzene.

**SLE of CsPbX\textsubscript{3} PeQDs.** The exchange solution containing the short-chain ligand was prepared by mixing the acid (0.4 mmol) and the amine (0.25 μmol) in octane and benzene cosolvents (octane/benzene = 9:1; the net volume was 1 mL). The excess ratio of acid-to-amine ligands was required to avoid precipitation of the aromatic acid and aromatic amine ligands in cosolvents. In a typical experiment, more than a 10-fold excess of acid-to-amine ligand provided the clear and well-dissolved solution conditions. For SLE, various ligand solutions with different chain lengths and boiling points, including alkyamines (hexylamine, octylamine, and hexadecylamine) and aromatic amines (aniline, phenethylamine, and 4-phenylbutylamine), were prepared in optimized cosolvent conditions. Ligand solutions in the SLE step were prepared by dissolving a ligand stock solution above with proper amount of octane and benzene cosolvents of the 9:1 ratio. To investigate the effect of different short-chain ligands during SLE, we compared aniline, phenethylamine, and 4-phenylbutylamine ligands. The resulting solutions of the short-chain ligands were spin-coated onto the PeQD films at 2000 rpm, under an inert atmosphere in the glovebox. The residual ligands on the PeQD films subjected to SLE were removed by rinsing with benzene at 2000 rpm using a spin coater.

**Characterization of the CsPbX\textsubscript{3} PeQDs.** The morphology, crystal structure, and composition of the CsPbX\textsubscript{3} PeQDs were determined by high-resolution TEM (JEOL JEM-2100F), XRD (Rigaku D/MAXZ 2500 V/PC; Cu Kα radiation source and λ = 0.15418 nm), and FT-IR (PerkinElmer Elan DRC-II). The optical properties of the CsPbX\textsubscript{3} PeQDs were evaluated by UV–vis spectroscopy (Agilent), room-temperature solution PL spectroscopy (Agilent), and TCSPC (Pico-quant) techniques.

TCSPC experiments: The PL decays of the CsPbX\textsubscript{3} PeQDs were investigated using TCSPC measurements. A pulsed diode laser head (LDH-P-C-375, PicoQuant) coupled with a laser diode driver (PDL 800-B, PicoQuant) was used as the excitation source. The excitation wavelength was λ = 400 nm and the repetition rate was 10 MHz. A TCSPC module (PicoQuant FluoTime 300) was used for the ultrafast measurement of the PL decay. The total instrument response function (IRF) for the PL decay was less than 140 ps, and the temporal resolution was less than 10 ps. Deconvolution of the actual fluorescence decay and IRF was performed using a curve-fitting software (FlouFit; PicoQuant) to determine the time constant associated with each of the observed exponential decays.

**Device Fabrication and Characterization.** The fabricated PeQLEDs had the following structure: ITO/PEDOT:PSS (40 nm)/PeQDs (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). The hole injection layer with the thickness of 40 nm was prepared by spin-coating a PEDOT:PSS solution (A14083, Clevios) onto the ITO-coated glass substrate at 4000 rpm and then annealed at 150 °C for 30 min. For the preparation of light-emitting PeQD films, the CsPbX\textsubscript{3} PeQD solution (30 mg/mL in a cosolvent containing octane and benzene; octane/benzene = 9:1) was spin-coated onto the PEDOT:PSS layer at 3000 rpm for 30 s. A 40-nm-thick TPBI was thermally deposited at a deposition rate of ~1–1.5 Å/s as the electron injection layer. Finally, 1-nm thick LiF and 100-nm-thick Al layers were sequentially thermally evaporated on top of the TPBI layer to serve as the cathode. The current/voltage/fluorescence characteristics of the PeQLED were measured using a Keithley 2400 source measurement unit and a luminance meter (Minolta CS-100A). The EL spectra were recorded using a fiber-optic spectrometer (K-MAC SV 2100).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.7b00212.

**XRD and TEM characterization of CsPbX\textsubscript{3} PeQDs, UV–vis absorption and PL spectrum of CsPbX\textsubscript{3} PeQDs with long alkyl chains or aromatic short ligands before and after vacuum treatments, and light-emitting characteristics of PeQLEDs with red-emitting CsPbI\textsubscript{3} PeQDs and blue-emitting CsPbCl\textsubscript{2} Br\textsubscript{2} PeQDs (PDF)**

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. J.P. and C.-L.L. designed the project. Y.-H.S. conducted most of this work and wrote the paper. T.K.
contributed the PeQD synthesis and data analysis. J.W.C. contributed the LED fabrication and device data analysis.

**Notes**
The authors declare no competing financial interest.

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