

Electron Delocalization in CsPbI₃ Quantum Dots Enables Efficient Light-Emitting Diodes with Improved Efficiency Roll-Off

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Perovskite quantum dot (QD) charging is prone to occur during light-emitting diode (LED) operation due to the electron accumulation inside the QD emitters, which is caused by the unbalanced charge injection and carrier transportation. Here in order to address this issue, an electron attractor of phenethylammonium (PEA⁺) is introduced to the surface of perovskite QDs. The PEA⁺ conjugated ligands can reversibly store and release electrons driven by the electron local density of states redistribution, which enhances the delocalization of electrons in QDs, and thus suppresses QD charging at high carrier concentrations, as evidenced by the excitation energy dependent photoluminescence. Besides, PEA⁺ down-shifts the Fermi level of perovskite QDs, consequently increases the hole concentration, leading to greatly improved hole conduction. Halogen-rich synthesis environment also reduces the number of halogen vacancies, consequently narrows the distribution of electronic states at the band edges, leading to slightly improved electron conduction. Taking advantage of the enhanced electron delocalization and improved charge transportation, the CsPbI₃ QDs LEDs show the maximum external quantum efficiency (EQE) of 15.6% with a low efficiency roll-off, and the maximum luminance of 1634 cd m⁻².

due to their high photoluminescence quantum yield (PLQY), narrow full width at half maximum (FWHM), and wide color gamut ($\approx 140\%$).^[1] Among perovskite QDs, the inorganic perovskite CsPbX₃ (X = Cl, Br, I) QDs present great potential due to their high thermal stability.^[2] The colloidal CsPbX₃ QDs with high PLQY over 90% were firstly reported in 2015,^[3] and their electroluminescence (EL) properties were reported following close in the same year.^[4] To date, the external quantum efficiency (EQE) of CsPbX₃ QD LEDs has increased rapidly, which is benefited from the development in both material chemistry and device physics.^[5]

It is well-known that the EQE of a LED is positively proportional to the emitter PLQY, carrier injection efficiency, and device light outcoupling efficiency.^[6] Reducing the crystal size to increase the exciton binding energy thus promoting the probability of radiative recombination is an efficient way to obtain high-performing

emitters, which is the merit of employing perovskite QDs as emitters in LEDs. Efforts have been paid to improve the perovskite QD PLQYs, such as surface engineering, component engineering, and crystal structure engineering.^[7] For instance, Choy and co-workers achieved stable and bright CsPbI₃ QDs through the incorporation of PMA (poly(maleicanhydride-alt-1-octadecene)) during the synthesis of QDs.^[8a] Xie and co-workers reported CsPbI₃ QDs with a near-unity PLQY, which is realized by carefully tuning the Sr²⁺-doping process using a hot injection method.^[8b] We have also established some facile methods in achieving CsPbX₃ QDs with ultralow trap densities, such as acid etching-driven ligand exchange, self-assembly, Cu²⁺ doping, and aminoethanethiol passivation,^[9] which provide easy ways toward perovskite QDs with near-unity PLQY. However, despite the above progress, only a few reports on CsPbI₃ QD LEDs have shown EQE values over 15%. Because the unbalanced charge carrier transportation process within the QD film degrades the performance of the LEDs.^[10] Usually, the mobility of electrons is faster than that of the holes, resulting in the unbalanced carrier transport of QDs film. Since the Fermi level of the CsPbI₃ QDs is close to the bottom of the conduction band (CB), which represents the *n*-type behavior

1. Introduction

Colloidal perovskite quantum dots (QDs) are promising light emitters for the next-generation light-emitting diodes (LEDs)

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and a high electron concentration, thus accelerating the injection and transport speed of electrons, which boosts unbalanced charge injection at high current density, thus damaging the LED performance. Therefore, the electric properties of CsPbI₃ QDs need to be optimized to increase the hole mobilities and enhance electron delocalization for achieving a more balanced carrier concentration during the LED operation.

In this work, we introduce phenethylammonium iodide (PEAI) to the synthesis of CsPbI₃ QDs to address the issues above. The PEA⁺ conjugated ligands serve as electrons attractors, which improves the electron delocalization in QDs, and thus suppresses QD charging at high carrier concentrations. Meanwhile, the short PEA⁺ partially replaces the long-chain protonated oleylamine (OAm⁺) at the QD surfaces to increase the charge conduction of the QD film. Moreover, the Fermi level of QDs moves toward the valence band (VB), and thus facilitates the hole transport from the hole transport layer to QD film for alleviating the unbalanced charge injection. The I⁻ ions from PEAI enable a halogen-rich synthesis, which reduces the density of surface halide vacancies, thereby promoting radiative recombination and improving electron mobilities. Consequently, the LEDs based on PEA⁺ modified CsPbI₃ QDs show the maximum external quantum efficiency (EQE) of 15.6% and brightness of 1634 cd m⁻², with a high EQE of 10.3% maintained at a high current density of 82.8 mA cm⁻².

2. Results and Discussion

The energy band structure of the CsPbI₃ QDs leads to an easier electron injection/transportation than that of the hole, thus resulting in carrier imbalance in the emitting layer, especially at high current density/brightness (Figure 1a). Therefore, the CsPbI₃ QDs suffer from severe charging due to the electron accumulation inside the QD emitters. At this time, the electron is easy to recombine with the hole to transfer the extra

energy to the second electron instead of emitting light (auger recombination), which damages the QD optical properties and the corresponding LED performance. Reducing the local electron density in the QD emitting layer (QD) can be an efficient strategy to improve radiative emission. Benzene ring of PEA⁺ can attract electrons via the conjugate structure.^[11] We, therefore, aim at modifying the CsPbI₃ QDs surface by PEA⁺ ligands with a benzene ring structure, which can work as an effective electron attractor. As shown in Figure 1b, for the QDs modified by PEA⁺ ligands, we believe that part of electrons can be reversibly stored and released from PEA⁺ ligands, which enhances the delocalization of electrons in QDs, thus reducing the local density of electrons. Attributed to the effect of PEA⁺ ligands on electron delocalization, electron concentration will better match that of the hole during LED operation (Figure 1c), thus improving the device performance. To obtain PEA⁺ ligands modified CsPbI₃ QDs, we developed co-precursor synthesis. As shown in Figure 1d, the CsPbI₃ QDs were synthesized by a hot-injection method with minor modifications, and the PEAI was added into the lead precursor solution to obtain PEAI-CsPbI₃ QDs. Figure S1, Supporting Information shows the photographs of the dilute solution of the as-prepared CsPbI₃ QDs and PEAI-CsPbI₃ QDs under ultraviolet (UV) irradiation, demonstrating the brighter red emission of PEAI-CsPbI₃ QDs than that of the control sample. Transmission electron microscopy (TEM) was used to investigate the morphologies of QDs (Figure S2, Supporting Information). Both the CsPbI₃ QDs and PEAI-CsPbI₃ QDs possess a cubic morphology. As the addition amount of PEAI (the feed ratios of PEAI to PbI₂ are 0, 0.25, 0.5, and 0.75, respectively) in lead precursor increases, the size of the QDs decreases gradually. As shown in Figure S3, Supporting Information, the average diameter of the QDs presents 15.8 ± 1.8, 12.1 ± 1.6, 11.0 ± 1.6, and 9.3 ± 1.7 nm for the feed ratios of 0, 0.25, 0.5, and 0.75, respectively. This is attributed to the additional I⁻ ions from PEAI that suppress the growth of the CsPbI₃ QDs in view of the previous reports.^[12] According

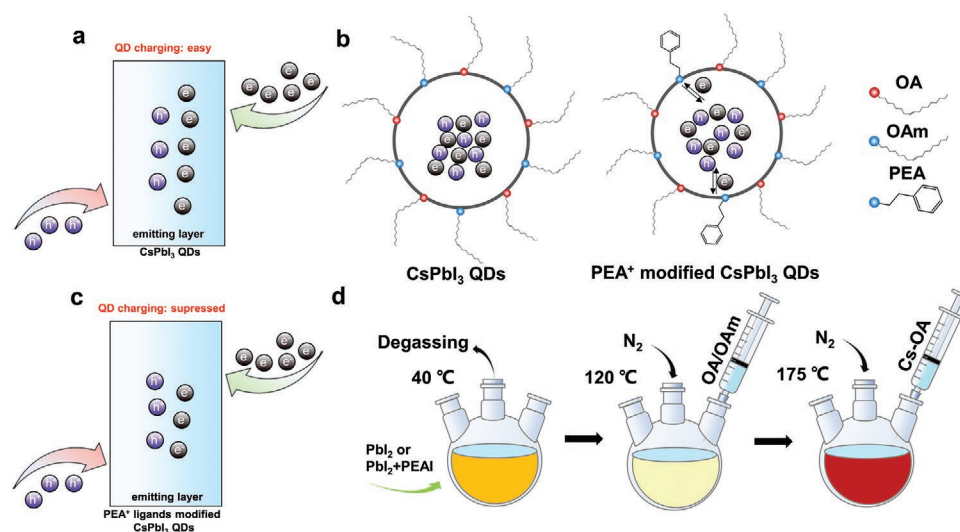


Figure 1. a) Schematic diagram of the carrier concentration of the CsPbI₃ QDs emitting layer. b) Schematic diagram of the effects of PEA⁺ ligands on carrier behavior in the QDs. c) Schematic diagram of the carrier concentration of the PEA⁺ ligands modified CsPbI₃ QDs emitting layer. d) The synthesis process of the QDs.

to the high-resolution TEM (HRTEM) images, all samples show highly crystalline and the same interplanar spacing of 0.63 nm corresponding to the (100) plane of the cubic structural α -phase, proving that the PEA^+ cations cannot serve as A-site doping ions to replace Cs^+ ions. We also performed X-ray diffraction (XRD) characterization of different QDs. As shown in Figure S4, Supporting Information, all the QDs show the same diffraction peaks at 14.2, 20.2, 24.6, 28.7, 32.1, 35.3, 41.1, and 43.3°, which are assigned to (100), (110), (111), (200), (210), (211), (220), and (300) planes of the cubic CsPbI_3 , respectively. This demonstrates that the synthesis with the assistance of PEAi has no influence on the crystal structure of the QDs. However, as the addition amounts of PEAi increase, the peak intensity ratio of (100) and (110) planes decrease gradually, which indicates that the change of synthesis environment affects the crystallization orientation of the QDs.

The UV-vis (UV) absorption and photoluminescence (PL) spectra of the QDs solutions are shown in Figure S5, Supporting Information. The absorption peak, PL peak, and PLQY as functions of the addition amount of PEAi are summarized in Figure 2a. The absorption peak shows a blue shift from 674 to 665 nm as the addition amounts increase. Simultaneously, the PL peak also moves from 686 to 679 nm. The blue shift of the first excitonic absorption and PL peaks is due to the quantum confinement effect, which agrees well with the decreased sizes observed in the TEM results, stemming from the halogen-rich environment of the synthesis.^[13] The PLQY of the QDs first increases and then drops as the addition amounts increase. When the ratio of PEAi to PbI_2 is 0.5, the PLQY reaches the highest value of 90.5%. A high PLQY suggests a high probability of radiative recombination in the QDs. To further demonstrate the behavior of the carriers in the QDs, the dynamics of photoexcited carriers of the QDs have been studied by the time-resolved PL (TRPL) decay measurements. The TRPL curves of the different QDs are exhibited in Figure 2b. A double-exponential function fitted the decay traces, and the fitting results are listed in Table S1. The average lifetimes of the QDs are 175, 44.7, 28.4, and 48.8 ns for the additional amount of 0 to 0.25, 0.5, and 0.75, respectively. Generally, the PL lifetime of QDs is determined by defect density and quantum confinement effect. For the former, the defect can capture the carriers to form non-radiative recombination centers to reduce PL lifetime. For the latter, when the particle size of QDs is less than or equal to the exciton Bohr radius, there is a strong quantum confinement effect in the QDs, and carriers tend to be recombined, thus leading to a shorter PL lifetime. All PEAi- CsPbI_3 QDs (PEAi = 0.25, 0.5, and 0.75) show a longer PL lifetime with a lower non-radiative decay rate (K_{nr}) than that of CsPbI_3 QDs, indicating a reduction of defects in PEAi- CsPbI_3 QDs, which can be attributed to the halogen-rich synthesis. Meanwhile, the PL lifetime of the 0.5-QDs with a strong quantum confinement effect is shorter than that of the 0.25-QDs because of the smaller particle size (11.0 nm for the 0.5-QDs and 12.1 nm for the 0.25-QDs). The particle size of the 0.75-QDs further reduces to 9.3 nm, indicating stronger quantum confinement. However, the PL lifetime of the 0.75-QDs (48.8 ns) is the longest among all the kinds of PEAi- CsPbI_3 QDs. Such an abnormal variation in PL lifetime can be attributed to the excess PEA^+ ligands on the QDs surface, which can serve as an electron attractor due to

the structure of the aromatic rings, leading to the over-delocalization of electrons in the QDs, thus reducing the recombination probability of excitons and further delaying the PL lifetime. PEA^+ ligands with aromatic rings are known as efficient electron acceptors,^[11] which can easily attract electrons. When the density of PEA^+ ligands is appropriate, carriers can normally recombine without affecting the optical property of the QDs. However, for the QDs with excess PEA^+ ligands on the surface, severe delocalization of electrons reduces the radiative recombination. Among all kinds of PEAi- CsPbI_3 QDs, the 0.5-QDs possess appropriate PEA^+ ligands density with a strong quantum confinement effect. In addition, their defects are also efficiently passivated. Therefore, 0.5-QDs show the lowest fraction of the fast decay component (35.1%) related to the non-radiative recombination and the highest PLQY of 90.5% (Figure 2a).

We also evaluated the optical performance of the QD films. The 0.5-QD film shows a relatively higher PLQY (65.3%) than that of the pristine CsPbI_3 QD film (41.2%) (Table S2, Supporting Information). Furthermore, the 0.5-QD film exhibit an average PL lifetime of 18.1 ns, which is longer than that of the pristine CsPbI_3 QD film (10.9 ns) (Figure S6, Table S2, Supporting Information), indicating the passivation of the surface defects in the 0.5-QD film (in the following, the “PEAi- CsPbI_3 QDs” refers to the QDs synthesized with the feed ratio of PEAi to PbI_2 is 0.5). The positive role of PEA^+ ligands on the local electron concentration of QDs has been further demonstrated by the excitation energy dependent PL intensity evolution (Figure S7a, Supporting Information). The charge carrier density is correlated with the excitation voltage. To qualitatively analyze the relationship between charge carrier density and excitation voltage, we tested the excitation energy dependent photoluminescence characterization based on the empty cuvette to obtain the relationship between the intensity of the xenon lamp and the excitation voltage (Figure S7b, Supporting Information). The charge carrier density can be believed proportional to the intensity of the xenon lamp. According to the fitting results, the relationship between the intensity of the xenon lamp (P) and excitation voltage (U) can be expressed by $P = k_1 \exp(U/77.6)$, where k_1 is a constant. Therefore, the charge carrier density (N) can be expressed by $N = k_2 \exp(U/77.6)$, where k_2 is a constant. As the excitation voltage increases from 300 V to 600 V, the PL intensity of the PEAi- CsPbI_3 QDs increases 129 times, which is higher than that of the CsPbI_3 QDs (114 times). The increase of voltage indicates the increase of charge carrier density. So, the high PL intensity for the PEAi- CsPbI_3 QDs demonstrates the more radiative recombination, attributing to the decrease of local electron concentration of QDs, which is beneficial to suppress the Auger recombination of LEDs under high current density.^[14]

The differences of Urbach band tail between the two QD samples further demonstrate the trap states decreasing. As shown in Figure S8a, Supporting Information, the slope of the Urbach band tail of PEAi- CsPbI_3 QDs film is higher than that of CsPbI_3 QDs films, indicating a more homogeneously distributed energy state in PEAi- CsPbI_3 QDs. Besides, the PEAi- CsPbI_3 QDs films show narrower FWHM (35 nm) than that of CsPbI_3 QDs films (39 nm), suggesting the narrower distribution of electronic states at the band edges in the PEAi- CsPbI_3 QDs (Figure S8b). Additionally, the PEAi- CsPbI_3 QDs show

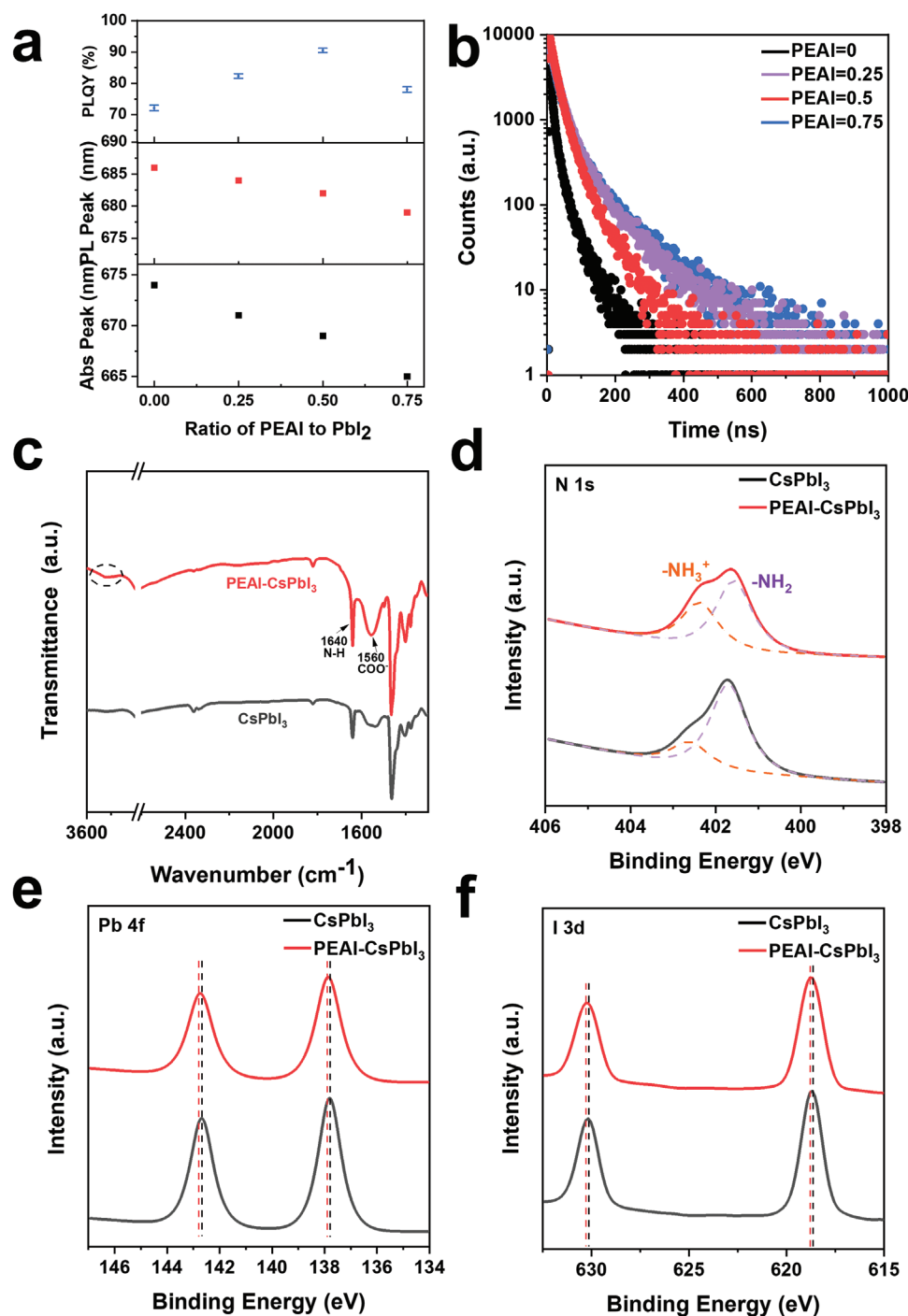


Figure 2. a) The absorption peak, PL peak position, and PLQYs of QDs with different addition amounts of PEAI. b) The PL decay time curves of the QDs with different addition amounts of PEAI. c) FTIR spectra, d–f) N 1s, Pb 4f and I 3d high-resolution XPS spectra of the pristine CsPbI₃ QDs and PEAI-CsPbI₃ QDs (feed ratio of PEAI = 0.5).

greatly improved environmental stability and phase stability than that of the CsPbI₃ QDs (Figure S9, Supporting Information). After being stored in the ambient environment for 7 days, the PEAI-CsPbI₃ QDs kept more than 90% of the initial PL intensity without changing their color, while the pristine CsPbI₃ QDs transferred from dark-red to yellow, along with a sharply declines (to 22%) of PL intensity. The mechanism

was revealed by the XRD characterization (Figure S9c–d, Supporting Information), showing that the PEAI-CsPbI₃ QDs maintained their cubic structure while the CsPbI₃ QDs transformed to the orthorhombic phase after 7 days in the air. It is known that phase transformation and decomposition start from the defects; the totally different in material stability further demonstrate that PEAI has decreased the QDs surface

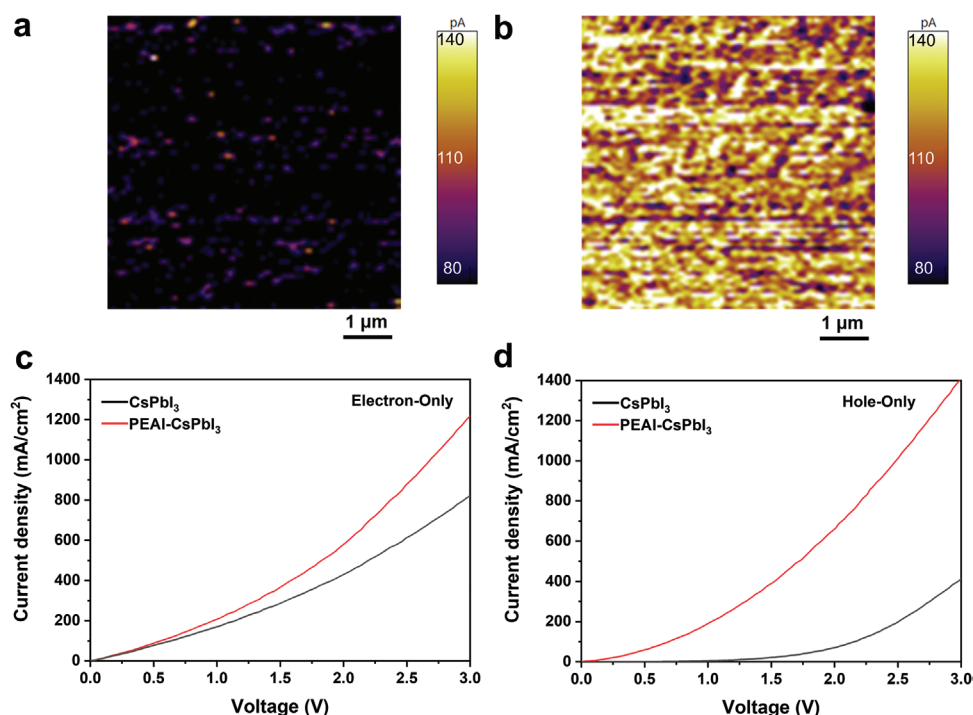


Figure 3. CAFM images of a) CsPbI_3 QDs and b) PEAI- CsPbI_3 QDs films. J - V curves of c) “electron-only” devices and d) “hole-only” devices based on CsPbI_3 QDs and PEAI- CsPbI_3 QDs.

defect density, and can retain on the QDs surface surviving the ambient environment.

To better understand how PEA⁺ interacts with the CsPbI_3 QDs, the Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were conducted. The absorption of PEA⁺ ligands to QDs surface was first confirmed by FTIR (Figure 2c). For the PEAI- CsPbI_3 QDs, the broad peak at around 3450 cm^{-1} can be observed, ascribed to PEA⁺ ligands.^[15] Moreover, both the CsPbI_3 QDs and PEAI- CsPbI_3 QDs show peaks at 1640 cm^{-1} and 1550 cm^{-1} , which are attributed to the N–H bending vibration of the amine functional groups and oleate anions ($-\text{COO}^-$) stretching, respectively. However, the peak intensity ratio of N–H bending vibration and $-\text{COO}^-$ stretching vibration decreases after introducing PEA⁺, indicating the different surfaces of the CsPbI_3 QDs and PEAI- CsPbI_3 QDs. N1s high-resolution XPS spectrum was used to further investigate the types of amine ligands on QDs surface. Figure 2d shows a dominant peak at the binding energy of 401.7 eV corresponding to non-protonated amine ($-\text{NH}_2$) and a weak peak at the binding energy of 402.6 eV corresponding to protonated amine ($-\text{NH}_3^+$) for the CsPbI_3 QDs. For the PEAI- CsPbI_3 QDs, the N1s peak intensity at 402.4 eV is higher than that of the CsPbI_3 QDs, indicating a more dominant existence of the protonated amine. The FTIR and N1s high-resolution XPS spectra demonstrate the successful absorption of PEA⁺ ligands to QDs surface. The Pb 4f and I 3d high-resolution XPS spectra were used to investigate the coordination of Pb^{2+} , showing that both the Pb 4f and I 3d peaks of the PEAI- CsPbI_3 QDs shift towards the higher binding energies, proving more proportionate coordination between Pb^{2+} and I^- than that of control samples,^[16] which is consistent with the XPS quantitative

analysis. The obtained atomic ratio of Cs:Pb:I are 1:0.96:2.80 and 1:1.01:3.05 for the CsPbI_3 QDs and the PEAI- CsPbI_3 QDs, respectively (Table S3, Supporting Information). The increased iodine element content further demonstrates that the reduced QDs surface defects belong to the iodine vacancy defects.^[8b]

The introduction of PEA⁺ also has positive influences on the electrical properties of QD films. The conductive atomic force microscope (C-AFM) was used to investigate the film’s electrical conductivity by mapping the local electrical current. As shown in Figure 3a,b a conductivity channel of 135 pA distributed across the PEAI- CsPbI_3 QD film is observed, which is nearly two times higher than that of the pristine CsPbI_3 QD film (72 pA). Besides the reduced trap density, the partial replacement of the long-chain ligands by PEA⁺ also plays an important role in improving the electrical conductivity. The enhanced charge transport was further confirmed by fabricating electron-only (ITO/PEI/QDs/TPBi/LiF/Al) and hole-only (ITO/Poly-TPD/QDs/MoO_x/Al) devices. As shown in Figure 3c,d, both electron- and hole-only devices based on the PEAI- CsPbI_3 QDs show higher current density than that of the control devices, confirming the positive effect of PEA⁺ ligands on improving the electrical conductivity of QDs film. It should be noted that the increased ratio of the hole current density is greater than that of the electron current density. Moreover, for the devices based on the pristine CsPbI_3 QDs, the electron current density is significantly higher than the hole current density. As a contrast, for the devices based on the PEAI- CsPbI_3 QDs, the electron current density is close to the hole current density. Therefore, with the help of PEA⁺ ligands, the increased mobility of the hole transport is higher than that of the electron transport, which is helpful for forming the balanced charge injection and

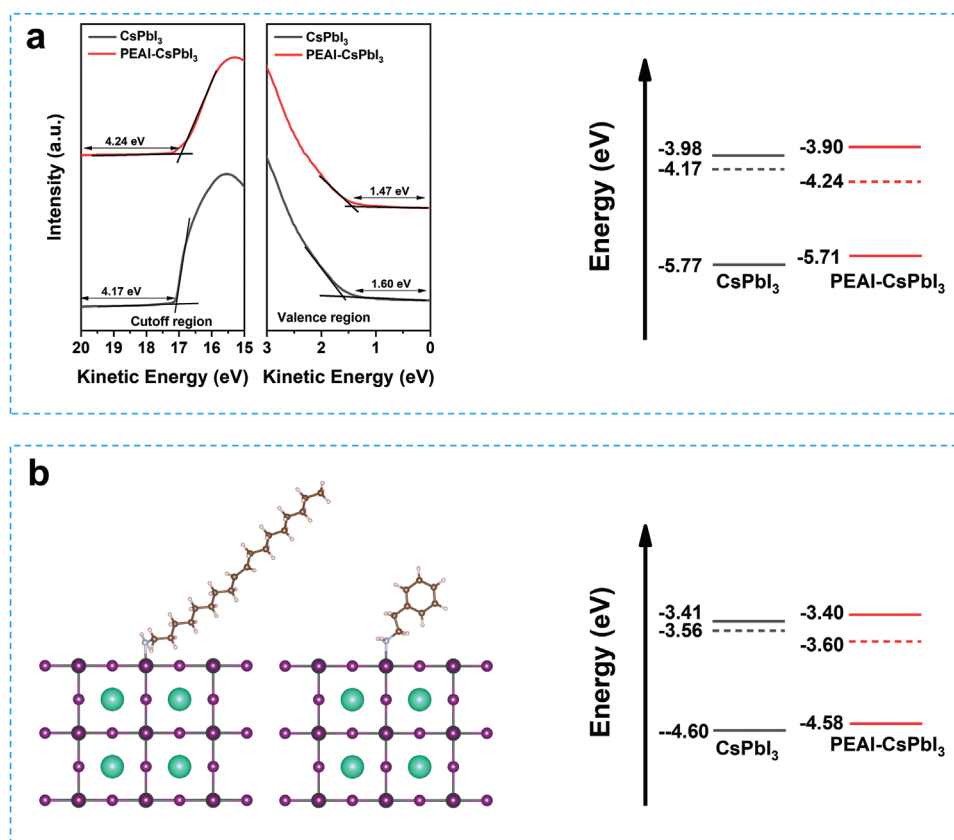


Figure 4. a) UPS spectra of the pristine CsPbI₃ and PEAI-CsPbI₃ QD films, the left panel of each shows the secondary electron cut-off region and the right panel shows the magnified spectra near Fermi edge, with the energy level diagram based on UPS results. b) DFT calculated energy band structure of OAM (left) and PEA (right) ligands on the CsPbI₃ surfaces, with the energy level diagram.

transport within the LEDs, thus improving the performance of the devices.^[17]

Balanced charge injection is as important as balanced charge transportation. For perovskite QD LEDs, the hole injection is typically more difficult than the electron injection, which always leads to unbalanced charge injection and causes serious efficiency roll-off.^[18] Thus, the influence of PEAI on the energy levels of CsPbI₃ QDs are investigated using ultraviolet photoemission spectroscopy (UPS) characterization and theoretical calculation.

We first carried out UPS characterization to study how PEAI changes the QDs energy band structures (Figure 4a). For the CsPbI₃ QDs, the Fermi level and conduction band minimum (CBM) are determined as -4.17 and -3.98 eV, respectively, identifying a heavily doped n-type behavior. For the PEAI-CsPbI₃ QDs, the Fermi level (-4.24 eV) shifts away from the CBM (-3.90 eV), identifying a nearly ambipolar behavior. PEAI also induced a 0.06 eV upshift of the valence band maximum (VBM) along with the switching from n-type behavior to nearly ambipolar. They together will promote the hole injection, thus a suppressed efficiency roll-off. The theoretical calculation results have shown a similar trend (Figure 4b). Detailed methods for the density functional theory (DFT) calculation are given in the supporting information.

As shown in Figure 5a, CsPbI₃ QD LEDs using a simple device structure of ITO/poly-TPD/QDs/TPBi/LiF/Al are

fabricated as a medium to evaluate the influence of the change of carrier behavior. As shown in the schematic flat-band energy diagram of LEDs, the hole injection barrier decreased from 0.37 to 0.31 eV with the help of PEAI (Figure 5b). Both the pristine and the PEAI-CsPbI₃ QD film are smooth and compact, with low surface roughness (≈ 4.8 nm and 4.1 nm for film samples without and with PEAI, respectively) as given by the AFM images (Figure S10, Supporting Information), which is beneficial for constructing LEDs. The normalized device electroluminescence (EL) and PL spectra match well with each other (Figure S11, Supporting Information), indicating that the PEAI-CsPbI₃ QDs are primary emitters during device operation^[8a] and further demonstrate that balanced carrier transport and charge injection have been achieved. The current density–voltage–luminance (J – V – L) curves are shown in Figure 5c. The LEDs based on the PEAI-CsPbI₃ QDs exhibit lower turn-on voltage compared to those based on the pristine CsPbI₃ QDs, stemming from the highly efficient and balanced charge injection. The PEAI-CsPbI₃ QD LEDs show the maximum luminance of 1634 cd m⁻² and a peak EQE of 15.6% (Figure 5d), which are much higher than those of the control device (179 cd m⁻² and 3.3%). Such significantly enhanced performances are attributed to the improved emitter PLQY and promoted carrier transportation/injection. Meanwhile, PEAI-CsPbI₃ QD LEDs maintain a high efficiency as the current density increases (EQE of 10.3% at 82.8 mA cm⁻²), showing a suppressed efficiency

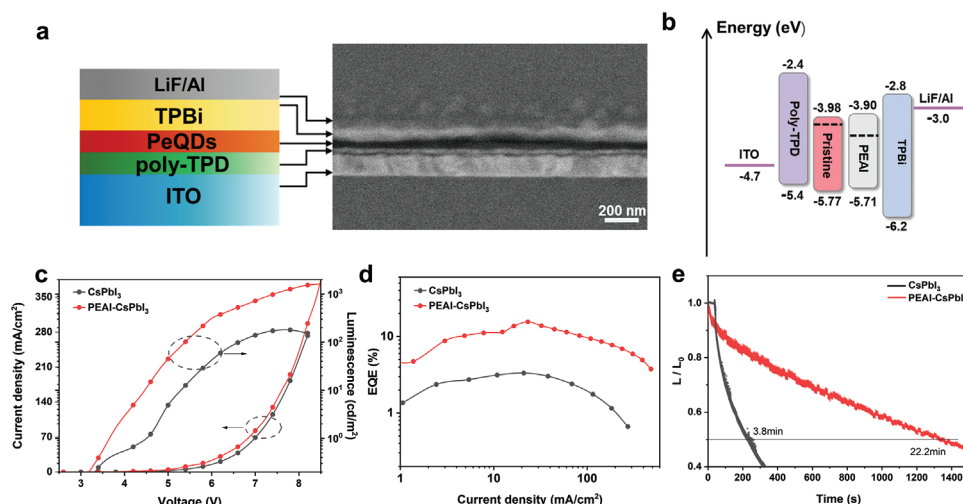


Figure 5. a) Schematic device architecture and the corresponding cross-sectional SEM image of the LEDs. b) Schematic flat-band energy diagram of LEDs. c) J - V - L curves, d) EQE- J curves, e) operational stability of the LEDs based on the pristine CsPbI₃ QDs and PEAI-CsPbI₃ QDs.

roll-off compared to the pristine CsPbI₃ QD LEDs, indicating that the PEA⁺ ligands, which serve as the electron attractor, have successfully suppressed the occurrence of QD charging. Figure S12, Supporting Information shows the statistical data of the EQE of the LEDs based on the PEAI-CsPbI₃ QDs, indicating the average EQE of 11.2%. Moreover, the PEAI-CsPbI₃ QD LEDs show better operational stability (T_{50} = 22.2 min) than that of the pristine CsPbI₃ QD LED (T_{50} = 3.8 min) (Figure 5e).

3. Conclusion

We have improved the EL property of CsPbI₃ QDs by simply precursor engineering with PEAI. The improved LED performances benefit from the decreased trap density and the switching in semiconductor properties. On one hand, PEAI can help the perovskite QDs to realize a proportionate coordination, leading to decreased iodine vacancy defects, and thus improved PLQY, stability, and charge transportation. On the other hand, PEA⁺ ligands as efficient electron acceptors switch the QDs from heavily n-doped behavior to nearly ambipolar, which decreases the hole-injection barrier. As a result, both the carrier transportation and charge injection balance are realized, leading to a high EQE of 15.6%, indicating one of the state-of-the-art CsPbI₃ QD based LEDs. Besides, PEA⁺ ligands serve as electron attractors, which can reversibly attract and release electrons driven by the redistribution of electron density, leading to a proper electron delocalization and suppressing the occurrence of QD charging, and thus an improved LED efficiency roll-off. Our work demonstrated a convenient synthesis strategy to improve both the optical and electrical properties of CsPbI₃ QDs for LED applications.

4. Experimental Section

Materials: Cesium carbonate (Cs₂CO₃, alfa, 99.9%), lead (II) iodide (PbI₂; 99.9%, Youxuan), phenethylammonium iodide (PEAI, 99.5%),

p-OLED), oleylamine (OAm; 90%, Aladdin), 1-octadecene (ODE; technical grade, 90%, Alfa), octane (96%, MACKLIN), ethyl acetate (EtOAc; anhydrous, 99.5%, Aladdin), hexane (analytical reagent, 97%, Aladdin), and oleic acid (OA; analytical reagent, 90%, Sigma Aldrich). All the chemicals were used without any purification.

Preparation of Cesium Oleate: Cs₂CO₃ (0.203 g), OA (1.2 mL), and ODE (10 mL) were added into a 100 mL three-necked flask and dried for 1 h at 120 °C. The mixture was then heated to 120 °C under N₂ circumstances to totally dissolve the Cs₂CO₃ powders. The Cs-oleate solution was preheated to 100 °C before using in QDs synthesis.

Synthesis of CsPbI₃ QDs and PEAI-CsPbI₃ QDs: PbI₂ (0.173 g) and ODE (10 mL) were loaded into a 100 mL three-necked flask and dried under vacuum at 40 °C for 0.5 h and then dried under vacuum at 120 °C for 1 h. Then, OA (1 mL) and OAm (1 mL) were injected at 120 °C under N₂ flow. The temperature was increased to 175–180 °C and Cs-oleate (0.8 mL) was swiftly injected. After five seconds, the reaction mixture was immediately cooled down to room temperature by immersing in a cold-water bath. For the synthesis of PEAI-CsPbI₃ QDs, additional PEAI was introduced in the lead precursor. All other steps were the same as CsPbI₃ QDs.

Purification of QDs: As-prepared QDs were transferred to the 100 mL centrifuge tube, and then centrifuged with high speed at 7500 rpm for 10 min. The isolated precipitate in the tube was redispersed in 4 mL toluene. EtOAc (4 mL) was added into the centrifuge tube to isolate QDs, which was centrifuged at 7500 rpm for 5 min. Finally, the supernatant was poured and the precipitate was dispersed in 5 mL of hexane. The QD solution was centrifuged at 4000 rpm for 5 min, the supernatant was collected, the hexane was dried, and QDs were redispersed in octane (30 mg mL⁻¹) for further device fabrication.

Device Fabrication: The indium tin oxide (ITO) coated glass substrates were sequentially cleaned with detergent, deionized water, acetone, and ethanol by ultrasonic spin cleaning. The cleaned substrates were dried with N₂ flow and then treated by UV-ozone for 15 min. After the UV-ozone treatment, the hole transporting layer of poly-TPD (4 mg mL⁻¹ in chlorobenzene) was spin-coated at 3000 rpm for 40 s in a N₂ filled glove box, followed by thermal annealing at 120 °C for 30 min. QDs were sequentially spin-coated twice onto the poly-TPD layer (4000 rpm for 40 s) to fully cover the underneath layer. Subsequently, TPBi (35 nm), LiF (1 nm), and Al (120 nm) were deposited by thermal evaporation under a high vacuum ($\approx 1 \times 10^{-5}$ Pa). The active area of the PeLED was 4.25 mm², defined by the intersection of ITO and Al strips.

Characterization: PL spectra of QDs were obtained by a Gangdong F-280 fluorescence spectrometer. Time-resolved PL decay spectra of QDs were obtained by a Horiba Fluorolog spectrometer. PLQYs were obtained

by an integrating sphere (Edinburgh, FLS920). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL JEM-2010 microscope operated at 200 kV. The XRD spectra of QDs were obtained by a MXP21VAHF X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). XPS spectra of QDs were tested by a PHI 5000 Versa Probe III spectrometer using a monochromatic Al K α radiation source (1486.6 eV). FTIR spectra of QDs were obtained by a Varian 3100 FTIR spectrometer. cAFM (Bruker Dimension ICON) measurement was conducted with the structure of ITO/poly-TPD/QDs in the air at the applied bias of 5 V. A Keithley 2635 sourcemeter and a fiber optic integration sphere (Ocean Optics FOIS-1) coupled to a spectrometer (Ocean Optics QE 65000) were used for the current density–voltage–luminance measurements. The LEDs were characterized in the N₂ filled glove box without encapsulation at room temperature. The measurement system was calibrated by a standard tungsten halogen light source (Ocean Optics HL-3P-INT-CAL). The cross-section view of PeLEDs was obtained by a FIB/SEM double beam system (FEI, Helios NanoLab 600i).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

efficiency, electron delocalization, light-emitting diodes, perovskite quantum dots

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