Abstract: All inorganic CsPbBr$_3$ perovskite quantum dots (QDs) are potential emitters for electroluminescent displays. We have developed a facile hot-injection method to partially replace the toxic Pb$^{2+}$ with highly stable Sn$^{4+}$. Meanwhile, the absolute photoluminescence quantum yield of CsPb$_{1−x}$Sn$_x$Br$_3$ increased from 45 % to 83 % with Sn$^{IV}$ substitution. The transient absorption (TA) exciton dynamics in undoped CsPbBr$_3$ and CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs at various excitation fluences were determined by femtosecond transient absorption, time-resolved photoluminescence, and single-dot spectroscopy, providing clear evidence for the suppression of trion generation by Sn doping. These highly luminescent CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs emit at 517 nm. A device based on these QDs exhibited a luminance of 12,500 cd/m$^2$, a current efficiency of 11.63 cd/A, an external quantum efficiency of 4.13 %, a power efficiency of 6.76 lmW$^{-1}$, and a low turn-on voltage of 3.6 V, which are the best values among reported tin-based perovskite quantum-dot LEDs.

Inorganic CsPbBr$_3$ perovskite quantum dots (QDs) have attracted significant attention because of their high photoluminescence (PL), tunable and narrow emission wavelengths, and facile synthesis.$^{[1]}$ Given these advantages, perovskite QDs can be used in solar cells,$^{[2]}$ lasing,$^{[3]}$ light emitting diodes (LEDs),$^{[4]}$ and bioimaging.$^{[5]}$ At present, the most suitable substitute elements are Sn$^{II}$,$^{[6]}$ Sn$^{IV}$,$^{[7]}$ Bi$^{III}$,$^{[8]}$ and Mn$^{II}$.$^{[9]}$

CsSn$_X$ (X = Cl, Br, I) perovskite QDs have been fabricated by Jellicoe and co-workers by using the hot-injection method.$^{[10]}$ However, Sn$^{IV}$-based CsSn$_X$ QDs are unstable and need to be stored under an inert atmosphere. In this case, the Sn$^{II}$ ions are easily oxidized to Sn$^{IV}$, which results in low PL. To overcome this oxidation problem, Wang and co-workers replaced the divalent lead cation (Pb$^{II}$) with tetravalent tin (Sn$^{IV}$) and thus developed stable Cs$_2$Sn$_x$ perovskite QDs with a cubic structure.$^{[7]}$

Generally, Sn$^{II}$ is more stable towards oxidation than Sn$^{IV}$.$^{[10]}$ However, the PL quantum yield (PLOY) of Sn$^{IV}$-based perovskite QDs is only 0.48 %, which is too low for practical applications. Zhai and co-workers$^{[11]}$ proposed perovskite QDs with mixed-metal cations by synthesizing CsPb$_{1−x}$Sn$_x$Br$_3$ QDs with Sn$^{III}$ substitution at low temperature (110°C). However, the complete replacement of Pb$^{II}$ with Sn$^{III}$ or Sn$^{IV}$ seemed difficult owing to the lower ion conductivity of Sn. Low ionic conductivity in perovskite QDs causes surface defects and makes the material unstable.$^{[12]}$ This issue was expected to be solved by partially replacing the Pb$^{II}$ ions with the more conductive Sn$^{III}$ ions. The lead ions are necessary for retaining the perovskite framework. For mixed-metal-cation perovskite QDs, the optical properties are another important issue. Sn-based perovskite semiconductors have been widely applied in solar cells.$^{[13]}$ However, reports on Sn-based LEDs are scarce.$^{[14,15]}$ In QDs, nonradiative Auger recombination of biexcitons and trions (charged excitons) usually reduces the PL quantum efficiency.$^{[16]}$ The Auger lifetimes are much shorter than the single exciton lifetime. In Auger recombination processes, the exciton energy is nonradiatively transferred to an adjacent charge carrier instead of being converted into a single photon. The limited survival time of multiexcitons in QDs makes it difficult to achieve high power efficiencies in photonic devices. By using a combination of different optical techniques, we can easily understand the PL properties and above exciton decay dynamics.$^{[17,18]}$ Recently, Kanemitsu and co-workers$^{[19]}$ clarified the efficient formation of trions in perovskite QDs and the role of trions in the luminescence of CsPbBr$_3$ perovskite QDs by transient absorption (TA), time-resolved photoluminescence (TRPL), and single-dot PL spectroscopy. A thorough understanding of the behavior of single excitons, trions, biexcitons, and multiple excitons is important for the application of QDs in LEDs.

Herein, we describe the hot-injection synthesis of CsPb$_{1−x}$Sn$_x$Br$_3$ perovskite QDs with Sn$^{IV}$ substitution. Unexpectedly, the CsPb$_{1−x}$Sn$_x$Br$_3$ QDs with partial Sn$^{IV}$ replacement exhibited significantly improved PL. With an increase in the relative amount of Sn, the PLOY of the CsPb$_{1−x}$Sn$_x$Br$_3$ QDs decreased owing to the increasing impurity of the...
Cs$_2$SnBr$_6$ phase. The best substitution ratio is $x = 0.33$. The PL enhancement in CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs results from reduced trion formation. Consequently, LEDs based on these highly luminescent CsPb$_{1-x}$Sn$_x$Br$_3$ QDs display the highest current efficiencies (CEs) and external quantum efficiencies (EQEs) ever reported for such systems.

The partially tin-substituted perovskite QDs were prepared in a colloidal solution. After long reaction times, the maximum Sn$^{IV}$ ion substitution ratio was reached. After purification, the products were stored for spin-coating to produce QD emitting layers. The valence state of the Sn ions was determined by X-ray absorption near-edge spectroscopy (XANES). Pb L$_3$-edge XANES spectra of CsPb$_{1-x}$Sn$_x$Br$_3$ QDs with different amounts of Sn$^{IV}$ are shown in Figure 1a. The X-ray pre- and post-edge absorptions of the analyzed samples were normalized to 0 and 1, respectively. The absorption edge energy was the same for all analyzed samples and fits the Pb$^{II}$ ion standard curve. Sn K-edge XANES spectra of CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ and CsPb$_{0.50}$Sn$_{0.50}$Br$_3$ QDs are shown in Figure 1b. The absorption edge energy of the analyzed samples was again the same and fits the Sn$^{IV}$ ion standard curve. These results are due to the facile oxidation of the Sn$^{II}$ ions during the high-temperature synthesis. According to the inert-pair effect, the most stable valence state of Sn is Sn$^{IV}$. To improve the stability and structural integrity of the mixed-cation perovskite structure, Sn$^{IV}$ ions are the most suitable.

The XRD patterns of CsPb$_{1-x}$Sn$_x$Br$_3$ QDs with different amounts of Sn$^{IV}$ are shown in Figure 1c. All QDs exhibited purely cubic crystalline structures, except for CsPb$_{0.33}$Sn$_{0.67}$Br$_3$ with a high $x$ value. The XRD pattern of CsPb$_{0.33}$Sn$_{0.67}$Br$_3$ features many impurity peaks, which are manifestations of the presence of another phase in the sample (Cs$_2$SnBr$_6$). At a high Sn$^{IV}$ ratio, the byproduct Cs$_2$SnBr$_6$ reduces the stability and destroys the framework of the Pb-based perovskite QDs. Consequently, the CsPb$_{0.33}$Sn$_{0.67}$Br$_3$ samples are unstable and exhibit low quantum efficiencies.

Transmission electron microscopy (TEM) images of the CsPb$_{1-x}$Sn$_x$Br$_3$ QDs are shown in Figure 1d–g. The TEM image shows the cubic structure of the CsPb$_{1-x}$Sn$_x$Br$_3$ QDs. However, the CsPb$_{0.33}$Sn$_{0.67}$Br$_3$ QDs exhibit various shapes, which are caused by the Cs$_2$SnBr$_6$ byproduct. Selected electron diffraction (SAED) patterns of CsPb$_{1-x}$Sn$_x$Br$_3$ QDs are shown in the Supporting Information, Figure S3a.

The intensities of the PL spectra of CsPb$_{1-x}$Sn$_x$Br$_3$ QDs with different relative amounts of Sn are shown in Figure 2a. When the relative amount of Sn is greater than 33%, the PL intensity starts to decrease. The absorption and PL emission spectra are shown in Figure 2b. As observed from the absorption spectra, all QDs exhibited the same first excitation peak, which means that their band gaps are almost the same. This is due to the fact that the band gap is defined by the Pb 6s-Br 4p hybridized orbitals and the Pb 6p orbitals in the perovskite QDs.[20] This result is also supported by the absence of a blue shift in the emission wavelength with a change in the value of $x$ in the PL spectra. The Sn$^{IV}$ ions do not affect the band gap of the perovskite QDs but can facilitate exciton recombination via a radiative pathway.

![Figure 1](image_url)
excitation wavelength of 460 nm was used to measure the absolute quantum yield. The absolute PLOY remarkably increased from 45% to 83% upon doping of CsPbBr$_3$ with 33% Sn$^{III}$. To further confirm the enhancement of the PLOY, we measured PL intensities under different laser excitation fluences. The PLOYs of CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ and CsPbBr$_3$ QDs under different laser excitation fluences are shown in Figure 2c.

Here, the relative PLOY was obtained from the ratio of the PL intensities normalized by the optical density at the excitation wavelength. Under weak photoexcitation, the relative PLOY of the Sn-doped sample is approximately 1.8, which is consistent with the ratio of the absolute PLOYs. For higher excitation powers, the relative PLOY decreased to about 1.2. This decrease implies the efficient formation of multiple excitons, such as biexcitons, for both CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ and CsPbBr$_3$ samples under strong photoexcitation. Under these conditions, nonradiative Auger recombination of bieexcitons reduces the quantum yield in both samples. In contrast, under weak photoexcitation, the formation of bieexcitons is strongly decreased, and the recombination of excitons and trions determines the PLOY of both samples. In perovskite QDs, nonradiative Auger recombination of trions reduces the PLOY of the QDs$^{[19]}$. We tried to confirm the existence of trions by TA, TRPL, and single-dot PL spectroscopy. The experimental setups used for TA and single-dot PL spectroscopy are shown in Figures S1 and S2. In the TRPL measurements on CsPbBr$_3$ and CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs, an excitation wavelength of 430 nm was used, and the time resolution of the TRPL measurements was approximately 40 ps. Time-resolved PL spectra of CsPbBr$_3$ and CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs under 570 µm$^{-2}$ are shown in Figure S4a,c. The PL peak energies of the CsPbBr$_3$ and CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs are nearly 2.4 eV, confirming the absence of a blue shift for the Sn$^{III}$-substituted CsPbBr$_3$ QDs. The dependence of the PL decay time of the CsPbBr$_3$ and CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs on the excitation fluence is highlighted in Figure S4b,d. At high excitation densities, fast decay is observed owing to the nonradiative recombination of trions and bieexcitons. The slow decay gives the lifetime of the single excitons, which were determined to be 6.5 and 7.0 ns for CsPbBr$_3$ and CsPb$_{0.67}$Sn$_{0.33}$Br$_3$, respectively. Sn$^{III}$ substitution slightly reduces the density of nonradiative recombination centers because the PL efficiency and PL lifetime usually reflect the sample quality.

However, a large enhancement of the PL intensity cannot be explained by a lower number of nonradiative recombination centers of QDs alone. Therefore, we need to consider the nonradiative recombination of trions and bieexcitons in the QDs. To clarify the reason for the enhanced PLOY and reveal the individual properties of QDs, we performed femtosecond TA (Figure S5) and single-dot (Figure 3) measurements. As shown in Figure S4, a fast channel (within 1 ns) clearly appears for higher excitation powers. This fast decay channel results from the recombination of trions and bieexcitons$^{[18,19]}$. We clarified that the lifetimes of the bieexcitons and trions are a few tens of picoseconds and a few hundreds of picoseconds, respectively. The bieexciton lifetime is shorter than the trion lifetime$^{[19,21]}$. For two samples used in this work, the TA decay curves can also be described by triple exponential functions. In this case, bieexcitons (50 ps lifetime) are not efficiently generated, and the 300 ps lifetime was attributed to trions. To compare the trion formation probabilities for both QDs, the long-time normalized decay curves under weak excitation are shown in Figure S5c and Figure S6a. This direct comparison clearly shows that the trion generation is suppressed in CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs, as opposed to CsPbBr$_3$ QDs (Figure S6b). The TA dynamics in undoped CsPbBr$_3$ and CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs were determined at various excitation fluences. The amplitude of the decay component that is due to trion recombination (A$_3$) is lower in the CsPb$_{0.67}$Sn$_{0.33}$Br$_3$ QDs than in the CsPbBr$_3$ QDs, providing clear evidence for the suppression of trion generation.

We also confirmed the reduced trion formation by single-dot spectroscopy. The dominant part of the QDs (Fig-
ure 3a,c shows clear antibunching for 17 QDs in 24 CsPbBr$_3$ dots and 13 dots in 16 CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs. This high-contrast antibunching can be explained by the radiative recombination of single excitons. The central peak at zero delay time in the $g^{(2)}$ spectrum is caused by biexciton–exciton cascade emission. In contrast, we observed some QDs with low-contrast antibunching (Figure 3b,d). In this case, the side peaks from the single exciton emission significantly decrease because of the formation of trions. Trion formation signifies the creation of three charged particles (two electrons and one hole or one electron and two holes) in a single QD. The formation of trions promotes nonradiative Auger recombination and thereby reduces the single exciton emission intensity. The contrast in Figure 3b is very low compared to that in Figure 3d. In addition, the occurrence ratio is 7 dots in 24 CsPbBr$_3$ QDs and 3 dots in 16 CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs. The decrease in the occurrence ratio and the high contrast of the $g^{(2)}$ spectrum for the CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs imply that trion formation is suppressed. By suppressing the formation of trions, the PLQY of QDs can be significantly improved.

We also investigated whether this quantum yield enhancement results from an increase in the absorption cross-section of the QDs. The absorption cross-sections of CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs and CsPbBr$_3$ QDs were determined by TA spectroscopy (Figure S7). Both QDs show almost the same cross-section of $1.8 \times 10^{-14}$ cm$^2$. This result clearly confirmed that the enhancement of the PLOY is unrelated to a change in the absorption cross-section but results from increased radiative recombination of single excitons. We conclude that the reduction of trion formation mainly enhances the PL in CsPb$_{0.5}$Sn$_{0.5}$Br$_3$. The real amount of Sn$^{IV}$ ions was determined by inductively coupled plasma emission spectroscopy (ICP-AES). The analyzed formula of different amounts of Sn$^{IV}$ ions are shown in Table S1. The results of these spectroscopic investigations are summarized in Table S1.

The exceptional optoelectronic properties of the CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs encouraged us to further explore their application in LEDs. In general, the efficiency of QLEDs can be improved by 1) improving the charge balance by using hole injection materials with high hole mobility and appropriate energy levels or by 2) suppressing nonradiative quenching. In our developed devices, TFB was chosen as the hole injection material because of its higher hole mobility (1 cm$^2$V$^{-1}$s$^{-1}$) compared with Poly-TPD (1 cm$^2$V$^{-1}$s$^{-1}$) and PVK (1 cm$^2$V$^{-1}$s$^{-1}$). If the formation of trions can be suppressed, then the efficiency of the devices can be improved. Given that the CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs exhibit a high PLQY as a result of suppressed trion formation, LEDs based on CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs should perform well. After purification, CsPb$_{0.5}$Sn$_{0.5}$Br$_3$-based QLEDs consisting of ITO/PEDOT:PSS/TFB/QDs/TPBi/LiF/Al were fabricated. The energy level alignment of the device is shown in Figure S8b. The thickness of each layer was optimized and measured by cross-sectional TEM (Figure S8a). The thickness of the PQD films was about 10 nm.

Current density/luminance/voltage ($J/V/L$) curves of the devices are shown in Figure 4a. At a certain voltage, devices with CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs exhibit a remarkably large current density and small turn-on voltage, indicating that upon Sn$^{IV}$ substitution, the injection of charge carriers is easier. Therefore, the luminescence of devices with CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs is significantly better than that of CsPbBr$_3$-based devices, especially at high driving voltages. For example, the best device, based on CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QDs, exhibited a low turn-on voltage of 3.6 V and a maximum lumiance of 12,500 cd m$^{-2}$, which are the highest values ever reported for Sn-based QLEDs. The maximum EQE, PE, and CE values are 4.13%, 6.76 lm W$^{-1}$, and 11.63 cd A$^{-1}$, respectively (Figure 4b–d). A current density/voltage ($J/V$) curve is shown in Figure S9, and the performance of the CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ perovskite QLEDs is summarized in Table S2. Figure 4e shows the EL spectrum and a photograph of the optimized CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QLEDs operated at 12 V. The EL spectrum exhibits a central emission wavelength of 517 nm, and the CIE coordinates of the CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ QLEDs are (0.10,0.76), as shown in Figure 4f, which are almost located at the edge of the CIE chart, indicating the high color purity of this Sn-based device. This Sn-based QLED is thus particularly suitable for wide-color-gamut display applications. The performance of the Sn-based perovskite QLEDs is summarized in Table S3.

In summary, we have described the hot-injection synthesis of CsPb$_{0.5}$Sn$_{0.5}$Br$_3$ perovskite QDs with Sn$^{IV}$ substitution. Sn$^{IV}$ doping effectively suppresses the formation of trions, as revealed by single-dot, TRPL, and TA spectroscopy. The best LED device displayed a lumiance of 12,500 cd m$^{-2}$, a CE of 11.63 cd A$^{-1}$, an EQE of 4.13%, a PE of 6.76 lm W$^{-1}$, and a low

![Figure 4](https://www.angewandte.org)
turn-on voltage of 3.6 V, which are the best values reported for Sn-based perovskite QLEDs thus far.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: light-emitting diodes · perovskite phases · quantum dots · tin · trions

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