Efficient Quantum Dot Light-Emitting Diodes Based on Trioctylphosphine Oxide-Passivated Organometallic Halide Perovskites

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ABSTRACT: Metal halide perovskite quantum dots (QDs) have attracted significant research interest in the next-generation display and solid illumination fields due to their excellent optical properties of high photoluminescence quantum efficiency, high color purity, obvious quantum confinement effect, and large exciton binding energy. A large amount of surface defects and nonradiative recombination induced by these defects are considered as major problems to be resolved urgently for practical applications of perovskite QDs in high-efficiency light-emitting diodes (LEDs). Herein, we report an efficient passivation of green perovskite QD CH3NH3PbBr3 with trioctylphosphine oxide (TOPO). By simply adding the appropriate amount of TOPO into the nonpolar toluene solvent to synthesize CH3NH3PbBr3 QDs, the surface defects of these as-synthesized perovskite QDs are obviously reduced, along with an increased photoluminescence lifetime and suppressed nonradiative recombination. Further investigation indicates that electronegative oxygen from TOPO (Lewis base) bonds with uncoordinated Pb2+ ions and labile lead atoms in perovskite. With TOPO passivation, the green perovskite QD LEDs based on CH3NH3PbBr3 show significant performance improvement factors of 93.5, 161.1, and 168.9% for luminance, current efficiency, and external quantum efficiency, respectively, reaching values of 1635 cd m−2, 5.51 cd A−1, and 1.64% in the eventual optimized devices. Furthermore, the presence of TOPO dramatically improves stabilities of CH3NH3PbBr3 QDs and related devices. Our work provides a robust platform for the fabrication of low-defect-density perovskite QDs and efficient, stable perovskite QD LEDs.

INTRODUCTION

In recent years, perovskite materials have attracted significant research interest in photovoltaics due to their advantages of easy synthesis, low cost, high absorption coefficient, and long carrier diffusion distance.1–3 The power conversion efficiencies of perovskite solar cells have remarkably increased from 3.8 to 23.6% over the past few years.4–7 In addition to their high performance in photovoltaic fields, perovskites have also been intensively investigated as attractive semiconductor materials for other optoelectronic devices, such as light-emitting diodes (LEDs), photodetectors, and lasers.8–14 Especially, perovskite quantum dots (QDs) have shown tunable emission color from the ultraviolet to infrared wavelengths,15 a high photoluminescence quantum efficiency (PLQY) of over 90%,16 and high color purity with a narrow full width at half-maximum (FWHM) of about 20 nm.17 Moreover, compared with bulk materials, QDs have exhibited obvious quantum confinement effects and large exciton binding energies,18–20 and so they generally have a higher luminescence efficiency. Since the first hot-injection synthesis work of colloidal CH3NH3PbBr3 perovskite nanoparticles (NPs) reported by Schmidt et al.,5 several methods for synthesizing perovskite QDs have been developed, for example, the template-based growth method,22,23 the ligand-assisted reprecipitation technique,24,25 and the non-aqueous emulsion synthesis method,20 and perovskite QD-based LEDs have also become the focus of research work.27–29

In addition to a high luminescence efficiency, stability problem is another key factor that restrains further applications of perovskite QDs into LEDs. All-inorganic perovskite QDs, typical CsPbBr3 QDs, have shown the best thermal and...
chemical stability among all kinds of perovskite QDs. Notably, the hot-injection method is the best option for obtaining high-quality all-inorganic perovskite QDs, but it requires inert gas protection and high-temperature growth conditions, which conflict with low-cost consumption. Meanwhile, CsPbBr$_3$ QDs cannot fully match the pure green color (~520 nm) in the National Television System Committee chromaticity diagram because their photoluminescence (PL) peak wavelength is located within a range of <520 nm, even though the size of the CsPbBr$_3$ QD is slightly larger than the exciton Bohr diameter.

Compared with all-inorganic ones, CH$_3$NH$_3$PbBr$_3$ QDs undergo extremely fast degradation under moisture, oxygen, UV light, and high-temperature circumstances due to the inherent instability of organic CH$_3$NH$_3^+$ cations, but fortunately they have the advantages of pure green emission and easy one-step room-temperature (RT) synthesis by simply dropping their precursor solution containing PbBr$_2$, CH$_3$NH$_3$Br, oleic acid, $n$-octylamine, and N,N-dimethylformamide (DMF) into a nonpolar solvent toluene. Surface defect site passivation is usually considered as a useful approach to reduce surface defects and simultaneously enhance the stability of perovskite QDs. Several groups utilized Lewis bases and acids to reduce defect densities and improved performances of perovskite films and devices. Koscher and Yang et al. reported the surface treatment of perovskite QDs with inorganic salts, for example, thiocyanate, sodium nitrate, etc. Additionally, ligand-exchange methods were also used to enhance the PL performances of perovskites. Unfortunately, the above-reported methods have been rarely applied in organic–inorganic hybrid perovskite-based electroluminescent (EL) devices due to the limited conductivity of perovskite QDs after treatment. In addition, researchers have also used triethyl orthosilicate, tetramethyl orthosilicate, and (3-aminopropyl) triethoxysilane to synthesize silica-coated perovskite NPs, but the shell thickness has a notable influence on device performances due to the insulative characteristics of silica.

These NPs are usually used for down-conversion luminescence devices. TOPO, as a kind of alkylphosphine oxide, is a commonly coordinating material during the synthesis of II–VI and IV–VI quantum dot systems. In 2016, Ginger et al. post-treated CH$_3$NH$_3$PbI$_3$ with TOPO, realizing organic–inorganic hybrid perovskite films with PL lifetimes exceeding 8 μs. Sun et al. reported that TOPO treatment can dramatically improve the stability of CsPbX$_3$ NCs against ethanol treatment. Manna et al. used TOPO instead of aliphatic amines to synthesize bright, size-tunable CsPbBr$_3$ QDs with narrow size distributions and high yields. You et al. first reported efficient green perovskite LEDs based on a quasi-two-dimensional composition, and the PL lifetimes were significantly increased by coating TOPO onto the perovskite film surface, with which green LEDs reached a current efficiency (CE) of 62.4 cd A$^{-1}$ and an external quantum efficiency (EQE) of 14.36%. Despite significant improvements in the film quality and device performances, particularly for two-dimensional perovskites, TOPO has not been applied in organometallic halide perovskite QDs yet and its influence on the electrical properties of LEDs remains unclear. Herein, we deduce that TOPO as a passivation material is also suitable for organic–inorganic halide perovskite QDs yet and its influence on the electrical properties of LEDs remains unclear. In You’s work, it is noteworthy that the entire QD film cannot be completely passivated using the above-mentioned post-treatment technique since this technique is mainly aimed at the passivation of the film surface. To solve this problem, we add TOPO into toluene, a key nonpolar solvent, for forming perovskite QDs to sufficiently passivate the surface defects of these QDs. By optimizing the TOPO doping concentration, we fabricate highly efficient green perovskite QD LEDs with the maximum luminance, CE, and EQE values of 1635 cd m$^{-2}$, 5.51 cd A$^{-1}$, and 1.64%, showing improved factors of 93.5, 161.1, and 168.9% compared with those of control devices without any treatment. Meanwhile, CH$_3$NH$_3$PbBr$_3$ QDs and...
LEDs also show significantly improved stability after TOPO passivation.

**RESULTS AND DISCUSSION**

Figure 1a schematically illustrates the typical synthesis process of perovskite QDs. A mixture of CH$_3$NH$_3$Br, PbBr$_2$, oleic acid, and $n$-octylamine was dissolved into DMF to form a precursor solution, and then a fixed amount of the precursor solution was dropped into toluene mixed with TOPO under vigorous stirring at RT. With the addition of precursors, yellow-green colloidal solutions are formed (Figure 1b), and under the illumination of a 365 nm ultraviolet lamp, all QD samples show very bright green light emissions, which from left to right are denoted as Control, TOPO-50, TOPO-100, and TOPO-150, corresponding to TOPO addition amounts of 0, 50, 100, and 150 $\mu$L.

The high-resolution transmission electron microscopy (HRTEM) of the as-synthesized CH$_3$NH$_3$PbBr$_3$ QDs at various TOPO concentrations and their corresponding fast Fourier transform (FFT) patterns (Figure 2a−d) indicate the presence of monodisperse cubic-shaped QDs with high crystallinity. The HRTEM images show that the lattice spacing and the FFT patterns are well-defined spots that are in accordance with the crystallographic parameters for the CH$_3$NH$_3$PbBr$_3$. The TEM (left images in Figure 2a−d), HRTEM (upper right images in Figure 2a−d), and FFT (bottom right images in Figure 2a−d) show a QD size of $\sim$6±2 nm and an interplanar distance of 2.96 Å, which correspond to the (200) crystal face. The statistical data on QD diameters in Figure S1 demonstrate slightly smaller sizes for QDs with TOPO passivation compared with their Control counterparts. The QD size will increase first and then slightly decline with a continuous increase in the doping TOPO amount.

To clearly observe the passivation effect of TOPO and better elucidate its influence on the radiative recombination of QDs, we measured the PLQY of the CH$_3$NH$_3$PbBr$_3$ QD solution by using a fluorescence spectrometer equipped with an integrating sphere, with an excitation wavelength of 405 nm. The PLQY for the series of RT-synthesized CH$_3$NH$_3$PbBr$_3$ QDs with a variable concentration of TOPO increases from 44% for the control sample to 66% (TOPO-50), 67% (TOPO-100), and 69% (TOPO-150). We also characterized the time-resolved PL (TRPL) decay curves of these CH$_3$NH$_3$PbBr$_3$ film samples at the same excitation wavelength of 405 nm, with the corresponding measurement results presented in Figure 3a. The recombination lifetimes were extracted from the TRPL decay curves with the biexponential fitting function of $I(t) = A_f e^{-t/\tau_f} + A_s e^{-t/\tau_s}$. Here, $\tau_f$ and $\tau_s$ are the fast and slow decay lifetimes, respectively, and $A_f$ and $A_s$ are their respective decay amplitudes. The average lifetime ($\tau_{avg}$) is calculated with $\tau_{avg} = A_f \tau_f + A_s \tau_s$. Generally, fast decay represents trap-assisted recombination at the crystal surface and the long-lifetime component means radiative recombination inside the crystals. Figure 3a and Table 1 clearly indicate that the PL kinetics of the TOPO-passivated QDs is slower than that of the control without any modification. CH$_3$NH$_3$PbBr$_3$ QDs...
passivated with TOPO show relatively long PL lifetimes compared with their counterpart without TOPO, indicative of the suppression of nonradiative recombination via a reduction in electronic trap sites. Figure 3b shows the PL spectra of CH$_3$NH$_3$PbBr$_3$ QDs. As the concentration of TOPO increases, the PL peak position of the QDs shows a slight red shift of 3 nm (from 518 to 521 nm), whereas the FWHM of the PL spectra remains at $\sim$23 nm regardless of the TOPO concentration, and this result is consistent with previous reports. The slight red shift in the PL spectra is unrelated to compositional changes at the grain boundaries and variations in crystallinity. Moreover, the TOPO treatment does not trigger a microscopic restructuring of CH$_3$NH$_3$PbBr$_3$ QDs, as evidenced by X-ray diffraction (XRD) (Figure S2). The XRD patterns clearly display the CH$_3$NH$_3$PbBr$_3$ perovskite characteristic peaks at 14.9, 21.2, 30.1, and 35.2°, which correspond respectively to the (100), (110), (200), and (210) crystal planes of a cubic phase structure. Compared with the Control sample, the two small peaks of TOPO-150 located at 21.2 and 35.2° indicate that the introduction of TOPO increases the crystallinity of the QDs on both the (110) and the (210) crystal planes. However, the small peak at 14.4° of samples indicates that a small amount of PbBr$_2$ was present in the perovskite films, which was always located at the grain boundary. As the concentration of TOPO increases, the gradual disappearance of that small shoulder may be attributed to the action of TOPO on PbBr$_2$. Furthermore, the FWHM of the diffraction peak for these TOPO-treated samples remarkably becomes wider than that of the Control, meaning that the smaller QDs are obtained with the use of TOPO. However, with the continuous increase in TOPO concentration, the FWHM of these TOPO-treated samples becomes narrow, indicating that larger QDs are then obtained with more amount of TOPO used. On the whole, the size of the QDs passivated with TOPO is smaller than that of the Control counterpart, which is consistent with statistical results of HRTEM images (Figure S1).

The organic small molecule TOPO is a typical example of L-type ligands (Lewis bases), which is able to bind to electron-deficient (electrophilic) surface sites of perovskite QDs with undercoordinated metal ions and further generate a fine surface passivation effect. To confirm this point, Fourier transform infrared (FTIR) spectroscopy measurements on TOPO, PbBr$_2$, and TOPO-passivated PbBr$_2$ film were performed, with the corresponding result shown in Figure S2.

| Type  | $\tau_f$ (ns) | $A_f$ (%) | $\tau_s$ (ns) | $A_s$ (%) | $\chi^2$ | $\tau_{avg}$ (ns) |
|-------|--------------|-----------|---------------|-----------|---------|-------------------|
| Control | 1.47 | 36.84 | 6.36 | 63.16 | 1.171 | 4.56 |
| TOPO-50 | 1.89 | 34.37 | 8.55 | 65.63 | 1.158 | 6.26 |
| TOPO-100 | 1.89 | 28.28 | 9.80 | 71.72 | 1.128 | 7.56 |
| TOPO-150 | 1.29 | 32.23 | 6.37 | 67.77 | 1.151 | 4.73 |

*All of the samples were fitted with a biexponential function.*

Figure 3. (a) TRPL decay curves and (b) steady-state PL spectra of colloidal CH$_3$NH$_3$PbBr$_3$ QDs. Samples were synthesized at RT with a fixed amount of precursors and a varying amount of TOPO in toluene. (c) Fourier transform infrared (FTIR) spectra of TOPO, PbBr$_2$, and the TOPO-passivated PbBr$_2$ film.
No obvious peak occurs in the FTIR spectra of PbBr₂ in a wavenumber range of 900–1800 cm⁻¹ mainly due to the location of PbBr₂ characteristic peaks at 200 and 64 cm⁻¹. An observable absorption peak located at 1150 cm⁻¹ in the control TOPO film corresponds to the P=O bond stretching vibration, whereas this P = O bond absorption peak shifts to approximately 1100 cm⁻¹ in the film comprising TOPO:PbBr₂, indicative of the bond formation between PbBr₂ and TOPO. X-ray photoelectron spectroscopy (XPS) determinations were also performed to further investigate the surface properties of colloidal CH₃NH₃PbBr₃ QDs (Figure S3). Figure 4a–d shows the Pb 4f XPS spectra of the resulting QDs. The XPS spectra of Pb 4f for all samples have two symmetric peaks, which are respectively attributed to Pb 4f⁷/₂ and Pb 4f⁵/₂ levels. Both Pb 4f⁷/₂ and Pb 4f⁵/₂ peaks from TOPO-modified samples slightly shift toward lower binding energies compared with those of the control counterpart. In addition, both Pb 4f⁷/₂ and Pb 4f⁵/₂ can be further fitted with two peaks, where the high-energy peak comes from the contributions of Pb–Br bonding (136.1 and 141.0 eV) and the low-energy one originates from the metallic Pb (134.3 and 139.0 eV). With the increase in TOPO concentration, the metallic Pb peaks (134.3 and 139.0 eV) disappear and the Pb²⁺ peak intensities at 136.1 and 141.0 eV decrease, both of which indicate that the introduced TOPO will strip off the labile lead atoms and uncoordinated Pb²⁺, leaving perovskite QDs with fewer surface defects. The O 1s peaks shown in Figure S4 can be fitted into two peaks. The small band centered at 529.8 eV can be associated with the oleic acid bound on the QD surface, whereas the peak of the O 1s core level at a high binding energy can be originated from oxygen bound with lead atoms. Notably, the high-energy peak of all TOPO-modified samples is centered at 530.3 eV, slightly higher than those of the control counterpart at 530.0 eV, indicative of the bond formation between the electronegative oxygen and the uncoordinated Pb⁺/metallic Pb. The Br 3d peaks shown in Figure S5 can be divided into two peaks of 66.2 and 67.2 eV, corresponding to the inner and surface Br ions, respectively. Both peak intensities decline with the increasing TOPO amount, revealing the possible reaction of TOPO with PbBr₂. The N 1s spectrum of CH₃NH₃PbBr₃ QDs (see Figure S6) shows two peaks with binding energies of 398.0 and 399.5 eV, implying the existence of two chemical conditions of the N element. The peak with a binding energy of 398.0 eV can be assigned to the presence of n-octylamine in the CH₃NH₃PbBr₃ QDs, whereas the peak at 399.5 eV originates from methylamine.

This part verifies the TOPO’s influence on CH₃NH₃PbBr₃ QD stabilities by locating them within a RT ambient atmosphere. A group of QD solutions with different TOPO addition amounts were simultaneously measured for a comparison. According to the photographs shown in Figure S7, the fresh Control QDs without TOPO obviously aggregated into large particles 5 h later and then precipitated from the solution after 5 days of being present in ambient atmosphere at 20 ± 2 °C and 50 RH%, whereas the TOPO-passivated samples significantly prolonged lifetimes of CH₃NH₃PbBr₃ QD solutions. The greater the amount of TOPO we added, the longer the lifetime achieved. With the addition of 100 μL and 1 mL of TOPO, denoted as TOPO-100 and TOPO-1000, respectively, the aggregation time can be
delayed to 3 and >20 days, respectively. We summarized solution stabilities of perovskite QDs from recently published literature into Table S1. The statistics indicate that all-inorganic perovskite QDs universally have significantly longer lifetimes than their organic–inorganic counterparts, reaching more than 4 months. In contrast, most of the organic–inorganic perovskite QDs, even with the encapsulation of an inorganic salt matrix or oxide shell (NaNO₃, SiO₂, etc.), still show a relatively short life of under 1 month or several days. However, insulated layer encapsulation or shell layer protection prevents carrier transportation within films, thus restraining its further applications in the light-emission layer of LEDs. Our organic–inorganic perovskite QDs are comparable to or slightly better than the organic–inorganic ones with a potential applied into the EL layer. Based on the above analysis, the efficient passivation and stability improvement in CH₃NH₃PbBr₃ QDs indicate a potential application of our perovskite QDs in LEDs, particularly used as a good candidate for a highly efficient EL layer.

In some literature, excessive ligands or long-chain ligands protect QD surfaces with reduced defects and improved stability and realize a high PLQY with unity, but they also trigger poor carrier injection and transportation in the eventual assembled film, which will seriously damage the EL performances of devices. To verify the influence of TOPO employment on electrical transportation and EL properties, we prepare perovskite QD LEDs with device structures of glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 40 nm)/poly(9-vinylcarbazole) (PVK, 40 nm)/TOPO-passivated CH₃NH₃PbBr₃ or CH₃NH₃PbBr₃/1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi, 45 nm)/LiF (1 nm)/Al (Figure 5a) and then test the device performances. Here, ITO and Al are respectively used as the anode and cathode, PEDOT:PSS and PVK are respectively
used as the hole-injection and transport layers, TPBi and LiF act as the electron-transport and injection layers, respectively, and the CH$_3$NH$_3$PbBr$_3$ QDs with or without TOPO passivation are employed as the emitting layer. According to the amount of TOPO added, four different devices with 0, 50, 100, and 150 μL of TOPO are named as LED$_{\text{Control}}$, LED$_{\text{TOPO-50}}$, LED$_{\text{TOPO-100}}$ and LED$_{\text{TOPO-150}}$ respectively. All devices exhibit an emission area of 10 mm$^2$ and a major EL peak at 520 nm with a FWHM of ∼22 nm (Figure 5b), coincident with the peak of the PL spectra. However, unfortunately, an obvious shoulder at ∼440 nm occurs along with the CH$_3$NH$_3$PbBr$_3$ emission in most of the devices, which originates from the emission of the hole-transport layer PVK, as shown in the EL spectra of QD LEDs in Figure S8. It is worth noting that we clearly observe gradual declines of the 5.51 cd A$^1$ and maximum brightness, CE, and EQE values of 1635 cd m$^{-2}$ under a 6 V bias, indicating that the device displays bright and uniform emission under normal current density and working voltage (see Supporting Information Movie S1). The current density–voltage ($J$–$V$), luminance–voltage ($L$–$V$), CE–voltage (CE–$V$), and EQE–voltage (EQE–$V$) characteristics for all devices are plotted in Figure 5c–f, and the electrical output characteristics of the devices are summarized in Table 2. The performances of the perovskite QD LEDs are optimized by altering TOPO concentrations, and the optimized amount of TOPO added is 100 μL. The QD LED$_{\text{TOPO-100}}$ device exhibits a turn-on voltage ($V_{\text{on}}$) of 3.25 V and maximum brightness, CE, and EQE values of 1635 cd m$^{-2}$, 5.51 cd A$^{-1}$, and 1.64%, respectively, which are significantly better than those of other devices. It can be observed that the device’s current density gradually decreases with the increasing TOPO concentration, which is mainly due to the insulation property of TOPO. When an appropriate amount of TOPO is added, the performance of the perovskite QD film layer is improved owing to its effective passivation, which is beneficial to the highly efficient radiative recombination of carriers in the emitting region, with brightness significantly improved. Although the introduction of high-concentration TOPO can effectively passivate the surface defects of perovskites, its insulation property will in contrast reduce the charge injection into QDs and eventually affect the electrical injection and transport abilities of devices, leading to a significant decrease in both CE and EQE (Figure 5e,f).

Device stability is a necessary parameter to evaluate perovskite LEDs, and so we tested the half-lifetimes of 32 sets of LEDs with and without TOPO, with statistic results shown in Figure S9. Here, the half-lifetime ($T_{1/2}$) is defined as the degradation time corresponding to 50% of the initial luminance. It should be noted that all devices were measured in an ambient atmosphere at RT and 50 RH%. As a result, $T_{1/2}$ values for the TOPO-passivated and control devices are respectively about 7 min and 44 s, indicative of the beneficial effects of TOPO passivation on device stability. Table S2 lists some stability-related literature about perovskite QD devices published recently. From Table S2, we notice that the half-lifetimes for LEDs with all-inorganic perovskite QDs as the emission layers are universally longer than those with organic–inorganic ones, but notably our devices represent the best level among organic–inorganic perovskite QDs.

### CONCLUSIONS

In summary, to overcome surface defect-induced nonradiative recombination and enhance emission performances, we offer a simple and effective approach of employing TOPO to passivate CH$_3$NH$_3$PbBr$_3$ perovskite QDs. Prior to dropping the perovskite precursor into the nonpolar toluene solvent, we add different concentrations of TOPO into toluene and find that the electronegative oxygen from TOPO can passivate the labile lead atoms and uncoordinated Pb$^{2+}$ ions in CH$_3$NH$_3$PbBr$_3$ by forming coordinate bonding, leading to a reduced surface trap density and an increased radiative lifetime and PLQY in the resultant perovskite QDs. With the optimal TOPO amount to treat CH$_3$NH$_3$PbBr$_3$ QDs, we eventually obtain 93.5, 161.1, and 168.9% improvements in luminance, CE and EQE, reaching 1635 cd m$^{-2}$, 5.51 cd A$^{-1}$, and 1.64%, respectively. Moreover, TOPO passivation significantly improves CH$_3$NH$_3$PbBr$_3$ QD solution and device stability. This work provides a method for the fabrication of high-quality perovskite QD films and highly efficient, stable perovskite QD LEDs.

### EXPERIMENTAL SECTION

#### Materials.
All chemicals used in this work are commercially available and used without further purification. Aqueous dispersions of PEDOT:PSS (CLEVIOS P VP AI 4083) were obtained from Heraeus Materials Technology Co. Ltd. PbBr$_2$ (99.999%), CH$_3$NH$_3$Br, and PVK were purchased from Shanghai MaterWin New Materials Co. Ltd. TPBi was purchased from Nichem Fine Technology Co. Ltd. N-octylamine, oleic acid, chlorobenzene (CB), and DMF were purchased from Sigma-Aldrich.

#### Synthesis of Hybrid CH$_3$NH$_3$PbBr$_3$ QDs.
For the synthesis of CH$_3$NH$_3$PbBr$_3$ QDs, a mixture of 0.48 mmol CH$_3$NH$_3$Br and 0.4 mmol PbBr$_2$, was dissolved in 4 mL of DMF containing 30 μL of n-octylamine and 0.4 mL of oleic acid to form a precursor solution. Then, 250 μL of the precursor solution was dropped into 10 mL of toluene or TOPO–toluene mixed solution with vigorous stirring. A strong green PL emission was observed immediately upon mixing. To obtain the mixed TOPO–toluene solutions, 50 μL, 100 μL, and 150 μL of TOPO were respectively added into 10 mL of toluene.

#### Fabrication of LED Devices.
ITO glass substrates were washed with acetone, ethanol, and deionized water in sequence, followed by ultrasonic cleaning with deionized water.
water, acetone, and ethanol for 15 min, respectively. Then, the PEDOT:PSS layer was spin-coated onto the ITO-coated glasses at 3000 rpm for 45 s, followed by a drying process of 120 °C for 30 min. The solid PVK was dissolved in CB solution to prepare a 10 mg mL−1 PVK solution, and then the PVK solution was spin-coated onto the PEDOT:PSS layer at 3000 rpm for 45 s to form a PVK layer, followed by a drying process of 120 °C for 30 min. After that, these glasses were moved into a glovebox to spin-coat the CH3NH3PbBr3 QD layer via a five-step spin-coating with rotation speeds of 5000, 4000, 4000, 4000, and 4000 rpm in sequence, followed by a 30 min RT annealing. Finally, all samples were transferred into a vacuum chamber to evaporate TPBi (45 nm), LiF (1.2 nm), and Al electrode (100 nm) under a high vacuum of 1 × 10−3 Pa, forming the perovskite QD LEDs with the structure schematically shown in Figure 5a.

Characterizations. The shape and size of the perovskite QDs were measured with a transmission electron microscope (TEM) (Hitachi, HT7700) and a high-resolution TEM (HRTEM) (Talos, F200X). The crystal structures of CH3NH3PbBr3 thin films were characterized using a Bruker D8 ADVANCE X-ray diffraction equipment. The Fourier transform infrared (FTIR) spectra were measured on IRPrestige-21. The current density–voltage–luminance characteristics and EL spectra of the CH3NH3PbBr3 QD LEDs were measured with a Keithley 2400 sourcemeter and a coupled PR655 Spectra Scan spectrophotometer. All measurements were carried out at RT under ambient conditions. The UV–vis absorption spectra of perovskite films were obtained using a PerkinElmer Lambda 650 S spectrophotometer with an excitation wavelength of 350 nm. The PL spectra and the PL lifetimes of perovskite QDs with and without TOPO were measured with an excitation wavelength of 350 nm. The absolute PLQYs of all CH3NH3PbBr3 QD solution samples were characterized with a Quantaurus-QY absolute photoluminescence quantum yield spectrometer (C11347-11, Hamamatsu Photonics) equipped with an integrating sphere under an excitation wavelength of 405 nm. The wide spectra together with N, Br, O, and Pb spectra of perovskite QDs were measured with XPS (Kratos Axis Supra).

■ ASSOCIATED CONTENT

© Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00464.

QD diameters, XRD patterns, XPS survey scans, O 1s XPS spectra, Br 3d XPS spectra, N 1s XPS spectra, QD solution stabilities, EL spectra, and half-lifetimes of LEDs (PDF)

Bright and uniform emission under normal working voltage (MPG)

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