Novel Bromide Quaternary Ammonium Ligand for Synthesizing High Fluorescence Efficiency CsPbBr₃ Perovskite Quantum Dots and Their Fabrication of White Light-Emitting Diodes with Wide Color Gamut

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Abstract: We proposed a novel bromine quaternary ammonium ligand to synthesize high quantum yield (QY) CsPbBr₃ quantum dots (QDs). The QY of CsPbBr₃ QDs synthesized by this ligand reached 95% and the full width at half maximum (FWHM) was as narrow as 17nm. The peak wavelength of the prepared CsPbBr₃ QDs was 530nm. And these QDs emitted high purity green light under ultraviolet light. The color coordinate of white LED (WLED) prepared with the CsPbBr₃ QDs was (0.29, 0.31), which was very close to pure white light. The color gamut of the WLED covered 130% of the national television system committee (NTSC) color standard and 96% of the ITU-R Recommendation BT.2020 (Rec.2020) color standard.

1. Introduction
Halide perovskite quantum dots (HPQDs) are a kind of novel semi-conduct optoelectronic material with high QY and narrow FWHM, and theirs emission wavelengths can be tuned in the range of the visible spectrum.¹,² Theirs excellent properties and extensive applications in the area of LED lighting and display have aroused the researchers’ attention widely. Considering that synthesizing high quality QDs is the basis of fabricating relevant devices, there are two main methods for the synthesis of HPQDs. Kovalanko et al.³ developed Hot Injection (HI) method firstly and synthesized a series of HPQDs with different and tunable emitting color. Zeng et al.⁴ proposed Supersaturated Recrystallization (SR) method to synthesize HPQDs at room temperature. Either HI method or SR method should use oleic acid (OA) and oleyamine (OLA) as the ligand to restrict the aging process of the QDs nucleation and control their size and morphology.

In this experiment, we used a newly synthetic bromine quaternary ammonium--allyl octadecyl dimethyl ammonium bromide (AODMAB) as the ligand and successfully synthesized green CsPbBr₃ QDs (AODMAB-CsPbBr₃ QDs) with high brightness and high luminescent purity. Fig. 1 shows the structure of this new ligand.
Figure 1. Structure of the AODMAB ligand

AODMAB is a kind of organic cations surfactant, Br⁻ is a part of the synthesis of CsPbBr₃ QDs and plays a role in passivating the Pb²⁺ on the surface of CsPbBr₃ QDs. Long chain cation is attached to the surface of QDs through the static electricity and restrict the nucleation process of the QDs and control their size and morphology. It can also keep the dispersity of CsPbBr₃ QDs in nonpolar solvents.

2. Experimental Section

Raw materials: Dimethyl octadecylamine (DOA) (Aladdin, 90%), Bromopropene (Aladdin, 98%), Acetone, PbBr₂ (Aladdin, 99.999%), CsBr (Aladdin, 99.999%), Dimethyl sulfoxide (Aladdin, super dry), Acetonitrile (Aladdin, 99.8%, super dry), Toluene.

2.1 Synthesis of AODMAB

The chemical equation of synthesizing AODMAB is as follows:

\[
+ \quad \text{N}^{+} \quad \text{Br}^{-}
\]

The solution of Bromopropene (0.05mol) in acetone (20ml) was slowly dropped into the solution of DOA (0.05mol) in acetone (30ml) at 40°C and the reaction was maintained for 30 minutes. The obtained AODMAB was white precipitate. It was dried for 24 hours at 25°C under vacuum after washing by acetone for 3 times.

2.2 Synthesis of CsPbBr₃ QDs

The mixture of PbBr₂ (0.5mmol), CsBr (0.15mmol) and AODMAB (0.35mmol) was dissolved in DMF, and then slowly dropped into toluene (100ml) with vigorous stirring. Faint yellow precipitate emitted green light under 365nm ultraviolet light was obtained. Acetonitrile (5ml) was added into the raw liquor and centrifuged at 10000rpm for 10 minutes. The precipitate was dispersed in toluene (100ml) and centrifuged at 4000rpm for 10 minutes. The supernatant was the CsPbBr₃ QDs dispersion liquid as prepared by AODMAB ligand.

2.3 Fabrication of the WLED

AODMAB-CsPbBr₃ QDs dispersion was evacuated under vacuum to remove solvent. The obtained QDs powder was fully mixed with ultraviolet adhesive specific for LED encapsulation, then degassed by ultrasonic for 5 minutes to get green light QDs gel. Besides, CdSe/ZnS QDs were fully mixed with that ultraviolet adhesive and degassed by ultrasonic for 5 minutes to get red light QDs gel. The red gel and green gel were dropped in sequence on the blue light LED which were cured under 365nm ultraviolet light.
2.4 Analysis and Characterization

Mass spectrometer was used to analyze whether the prospective compounds were formed or not in the synthetic reaction. Emission spectra and QY of the dispersion were collected by using HAMAMATSU C11347-11 Quantaurus-QY absolute quantum yield measurement system and the excitation wavelength is 365 nm. Absorption spectra was collected by PERSEE TU-1910 UV-Vis spectrophotometer. RIGAKU Ultima IV X-ray diffraction analyzer was used to analyze crystalline phase of QDs. Crystalline morphology was analyzed by using JEOL JEM-3200FS field emission scanning transmission electron microscope. YUANFANG AT-5000 Photochromic electric test system was used to record the emission spectra of the WLED and analyze its color coordinate and color gamut.

3. Results and discussion

3.1 Synthesis of AODMAB ligand and characterization

Fig. 2 shows the mass spectra of the synthetic AODMAB ligand. We could get the strongest peak in 338.38m/z which was consistent with the mass-to-charge ratio of the cations in AODMAB which confirmed the formation of ionic compound AODMAB in the reaction between bromopropene and DOA.

![Figure 2. Mass spectra of AODMAB ligand](image1.png)

3.2 Optical property and crystalline morphology of CsPbBr₃ QDs

![Figure 3. Emission and absorption spectra of AODMAB-CsPbBr₃ QDs](image2.png)

![Figure 4. XRD pattern of AODMAB-CsPbBr₃ QDs](image3.png)
Fig. 3 shows the emission and absorption spectra of the AODMAB-CsPbBr$_3$ QDs. Their QY reached 95% and FWHM was as narrow as 17nm. The peak wavelength of these QDs was 530nm. The first absorption peak located at 515nm from absorption spectra and the Stokes shift was only 15nm which meant that the PL emission mainly resulted from the exciton recombination.

The structure of AODMAB-CsPbBr$_3$ QDs was cubic (Fig. 4), which was confirmed by the TEM image (Fig. 5). The grain size was approximately 12nm. HR-TEM image revealed that crystal was in good condition, atoms placed in order and the interplanar spacing was 0.31nm which was corresponded to (111) crystal plane of cubic phase.

Figure 5. TEM image of AODMAB-CsPbBr$_3$ QDs, the inset shows HR-TEM image of QDs

3.3 Luminescence properties of the WLED
The structure, picture and luminescence spectra of as prepared WLED were showed in Fig. 6a, b and c. The color coordinate of the WLED was (0.29, 0.31), and the color gamut of the WLED covered 130% of the NTSC color standard and 96% of the ITU-R Rec.2020 color standard.

Figure 6. A) Schematic of the structure of the WLED fabricated by AODMAB-CsPbBr$_3$ QDs, B) picture of the lightened WLED, C) luminescence spectra of the WLED and D) CIE color coordinates of the WLED prototype, NTSC, and Rec.2020 standard.
4. Conclusion

In summary, we synthesized a novel bromine quaternary ammonium ligand successfully for CsPbBr$_3$ QDs. The QY of CsPbBr$_3$ QDs synthesized by this ligand reached 95% and FWHM was as narrow as 17nm. The peak wavelength of the as prepared CsPbBr$_3$ QDs was 530nm, and they emitted high purity green light under ultraviolet light. These synthetic CsPbBr$_3$ QDs with favorable morphology were cubic nanocrystals and their size were approximately 12nm. WLED prepared with the CsPbBr$_3$ QDs emitted bright white light. The color coordinate of the WLED was (0.29, 0.31), which was very close to pure white light. The color gamut of the WLED covered 130% of the NTSC color standard and 96% of the ITU-R Rec.2020 color standard. Our works provide a new method for researchers to synthesize high quality CsPbBr$_3$ QDs for wide color gamut WLED.

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