

Supporting Information

Branched Capping Ligands Improve the Stability of Cesium Lead Halide (CsPbBr₃) Perovskite Quantum Dots

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Abstract: Design principles of branched capping ligands named n-Propyltrimethoxysilane-Dimethyloctadecylammonium bromine (PDB) are developed to improve the stability of CsPbBr₃ perovskite quantum dots (QDs) for light-emitting application. As the PDB ligands polymerized on the surface of CsPbBr₃ QDs, it avoided the highly dynamic ligand absorption-desorption process, Ostwald Ripening and phase transition of CsPbBr₃ QDs with traditional oleic acid (OA) /oleylamine (OLA) ligands. Therefore, CsPbBr₃ QDs with PDB ligands exhibited much better stability for air, ethanol, high temperature and UV irradiation than OA/OLA-CsPbBr₃ QDs. As the light-induced ligand peeling and nanocrystal fusion was inhibited, the phosphor-converted LED with PDB-CsPbBr₃ QDs kept 82% of the initial photoluminescence (PL) intensity after 436 h of illumination, which is a 27-fold improvement over the LED with OA/OLA-CsPbBr₃ QDs. This is the best reported device stability of phosphor-converted LED based on CsPbBr₃ QDs to date.

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Experimental Procedures

1.0 Materials

Lead bromine (PbBr₂, 99.999%, Aladdin), cesium bromine (CsBr, 99.999%, Aladdin), N,N-Dimethylformamide (DMF, 99.8%, anhydrous, Aladdin), ethylene glycol (EG, anhydrous, 99.8%, Sigma Aldrich), toluene (AR, Lingfeng), oleic acid (OA, Aladdin), oleylamine (OLA, 90%, Aladdin), (3-Bromopropyl)trimethoxysilane (BPTEOS, 98%, J&K), N,N-Dimethyl-n-octadecylamine (DMOLA, 90%, J&K), polymethyl methacrylate (PMMA, AR, Aladdin), All the agents were used as received without any further treatment.

2.0 Methods

2.1 Synthesis of PDB Ligand: (3-Bromopropyl)-trimethoxysilane (187 μ L, 243.2 mg) and N, N-Dimethyl-n-octadecylamine (363 μ L, 298 mg) were added to DMF (450 μ L) in the Ar filled glove box. The solution was stirred in a sealed PTFE tube and heated at 40°C for 20 h. The resulted solution was the PDB/DMF solution with concentration of 1 mmol/ mL. The H-NMR Spectrum of BPTEOS, DMOLA and PDB are shown in Fig. S1 A. Compare to BPTEOS and DMOLA, the H nucleus resonance absorption peaks of PDB generally left shift, representing a decrease of the electron density around H atoms caused by reaction. The MS spectrum further confirmed that a quaternization reaction does occur, and PDB is indeed the chemical structure described in scheme1 and Fig. S1 A.

2.2 Synthesis of PDB-CsPbBr₃ QDs: PbBr₂ (1 mmol, 367.0 mg) and CsBr (1 mmol, 202.8 mg) were dissolved in a certain amount of DMF and EG respectively, preparing solutions of PbBr₂/DMF and CsBr/EG with concentration of 1 mmol/ mL. Then specified amount of PbBr₂/DMF, CsBr/EG and PDB/DMF solution was mixed and added to DMF to form 1 mL precursor solution (to find out the best additive amount of PDB, we modulated the molar ratio of PDB:Cs from 3:7 to 7:3, and kept the ratio of Pb: Br constant at 1:3, for instance, to prepare the sample with PDB:Cs equal to 5:5, 50 μ L PDB/DMF, 50 μ L CsBr/EG, and 100 μ L PbBr₂/DMF were mixed and added to 800 μ L DMF to form 1 mL precursor solution). Then the precursor solution was added dropwise to 20 mL vigorously stirring toluene. The solution turned green immediately under 365 nm UV light, indicating the formation of CsPbBr₃ QDs. All the manipulations above were conducted in an Ar filled glove box. And then the crude liquid was stirred in air for 30 min, followed by a centrifugation at 10000 rpm for 10 min. The precipitation was discarded, and the supernatant was the prepared PDB-CsPbBr₃ QDs dispersion.

2.3 Synthesis of OA/OLA-CsPbBr₃ QDs: The synthesis of OA/OLA-CsPbBr₃ QDs dispersion was optimized from the method previously reported by Xiaoming Li et al.^[1] Specifically, PbBr₂ (0.4 mmol, 146.8 mg) and CsBr (0.4 mmol, 85.1 mg) were added to 10 mL DMF, 1 mL OA and 0.5 mL OLA were added to prepare a precursor solution. Then 1 mL precursor solution was injected into 10 mL vigorously stirring toluene to form CsPbBr₃ QDs. After purification, the OA/OLA-CsPbBr₃ QDs dispersion was obtained for our contrast experiment.

3.0 Instrumentation and Sample Preparation:

3.1 UV-Vis Absorption, Photoluminescence (PL) Spectra, Photoluminescence Quantum Yield (PL QY), Time Resolved Photoluminescence Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR): The UV-Vis absorption spectra were recorded on a PERSEE TU-1910 UV-Vis spectrophotometer. PL spectrums and Values of PL QY were obtained by HAMAMATSU C11347-11 Quantaurus-QY absolute quantum yield measurement system, and the excitation wavelength was 365 nm. Time resolved photoluminescence spectroscopy was conducted on EDINBURGHFS5 Time-Correlated Single Photon Counting (TCSPC) system. The detective wavelengths for PDB-CsPbBr₃ QDs and OA/OLA-CsPbBr₃ QDs were 516 and 509 nm respectively, which were the peak wavelengths of the respective CsPbBr₃ QDs dispersion. For UV-Vis absorption and PL measurement, the sample were dispersed in toluene and taken in a cuvette. FTIR was conducted on Perkin Elmer Frontier FT-IR Spectrometer (Spectrum 10, spectral from 400cm⁻¹ to 4000cm⁻¹ with resolution of 4 cm⁻¹), where the samples were mixed with KBr powders and pressed to thin slices.

3.2 Transmission Electron Microscopy (TEM), High Resolution TEM (HRTEM), and Energy Dispersive X-Ray (EDX): TEM, HRTEM, and EDX images were recorded in JEOL JEM-3200FS field emission scanning transmission electron microscope, using 300 kV electron source. Specimens were prepared by dropping a drop of condensed dispersed solution of QDs in toluene on a carbon coated copper grid.

3.3 Powder X - ray Diffraction Measurement (XRD): XRD patterns were gained on RIGAKU Ultima IV X-ray diffraction analyzer, using Cu K α ($\lambda = 1.54 \text{ \AA}$) as the incident radiation, The samples were scanned from 5° < 2 θ < 70° at an increment of 5°/min.

3.4 Stability Test Conditions: For air stability test, the unsealed PDB-CsPbBr₃ QDs and OA/OLA-CsPbBr₃ QDs dispersion were stored in ultra-clean laboratory and PL QY was measured every 24 h. The ambient temperature was kept at 22 °C, and the humidity

was 60%. For thermostability test, the PDB-CsPbBr₃ QDs and OA/OLA-CsPbBr₃ QDs dispersion was dropped onto two 10×10 mm quartz plates separately and vacuum dried to form thin films. Then the two quartz plates were heated at 90 °C on a plate heater in Ar filled glove box and taken out for PL QY measurement every 5 min. For photostability test, two cuvettes filled with PDB-CsPbBr₃ QDs and OA/OLA-CsPbBr₃ QDs dispersion were put into a 365 nm UV lamp box with energy density of 170 mV/cm² and taken out for PL QY measurement at regular intervals. For resistance to ethanol test, equal volume of ethanol was added to the cuvettes filled with PDB-CsPbBr₃ QDs and OA/OLA-CsPbBr₃ QDs dispersion, measuring the value of PLQY at regular intervals.

3.5 Samples Preparation of White LED, Green LED, and PDB-CsPbBr₃/PMMA film: For white and green LED, PDB-CsPbBr₃ QDs core-shell CdSe/ZnS QDs were separately dispersed in UV cured adhesive. The mixture in the UV cured adhesive was dropped on the bounded blue GaN LED chips and then the samples were cured by UV light. The PDB-CsPbBr₃/PMMA film was obtained using 1.2 g PMMA dissolved in 20 mL toluene to form PMMA/toluene solution. The as prepared PDB-CsPbBr₃ QDs of 20 mL condensed to 4 mL and mixed with PMMA/toluene solution uniformly. Then the mixture pour into a 100×150×8 mm rectangular groove mold and stored in fuming cupboard to evaporate the toluene.

3.6 Stability Test Conditions of LED and Photo Stability of PMMA Film: LEDs measured on ATA500 LED Photoelectric Analysis and Test System with Temperature Automatic Controlled operating at a bias of 5 mA. For the photo stability of PMMA film test, the PDB-CsPbBr₃/PMMA film and OA/OLA-CsPbBr₃ /PMMA film were put into a 365 nm UV lamp box with energy density of 170mV/cm² and taken out for PLQY measurement at regular intervals.

4.0 Optimization Process:

4.1 Optimization of PDB⁺: Cs⁺ ratio: For optical performance and stability evaluation, we adjusted the ratio of PDB⁺: Cs⁺ in precursor from 3:7 to 7:3, keeping the ratio of Pb⁺: Br⁻ constant at 1:3 (Fig. S2). The PLQY was up to 80% when the ratio of PDB⁺: Cs⁺ was 6:4 (Fig. S2 C). After unsealed storage in ambient environment (Temperature (T) is 22 °C, relative humidity (RH) is 60%) for 120 h, the best sample with the ratio of PDB⁺: Cs⁺ was 5:5 could maintain 96% of initial PL QY (Fig. S2 D). Although there was no obvious regularity between stoichiometry and PLQY and stability, we could conclude from Fig. S2 D ~ F that the highest PLQY with the best stability was generated when the ratio of PDB⁺: Cs⁺ was 5:5.

Supporting Figures

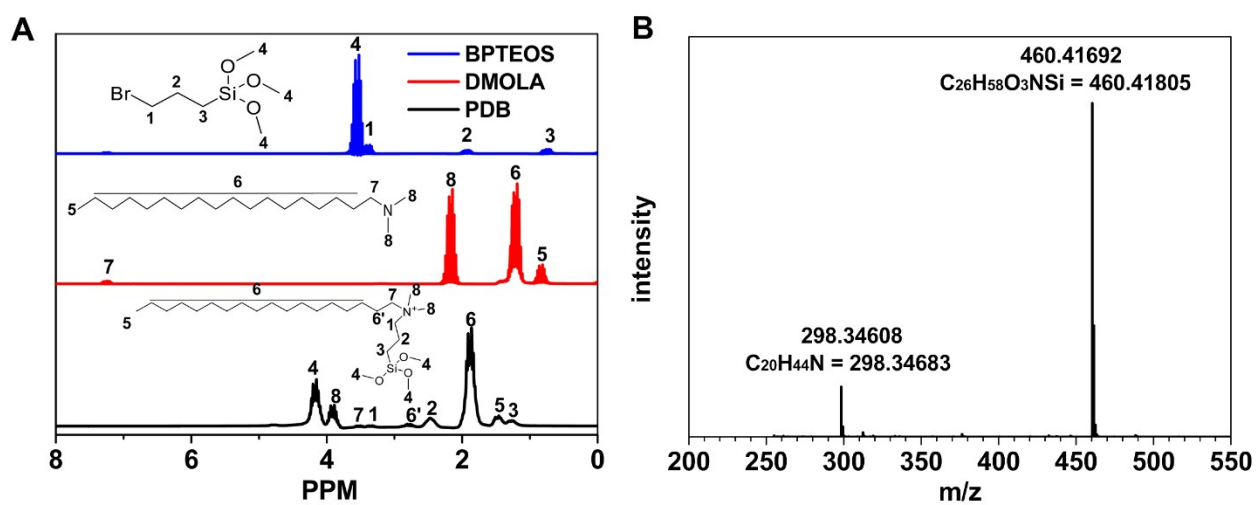


Fig. S1 (A) 1H -NMR spectrum and (B) Mass spectrum of PDB ligand

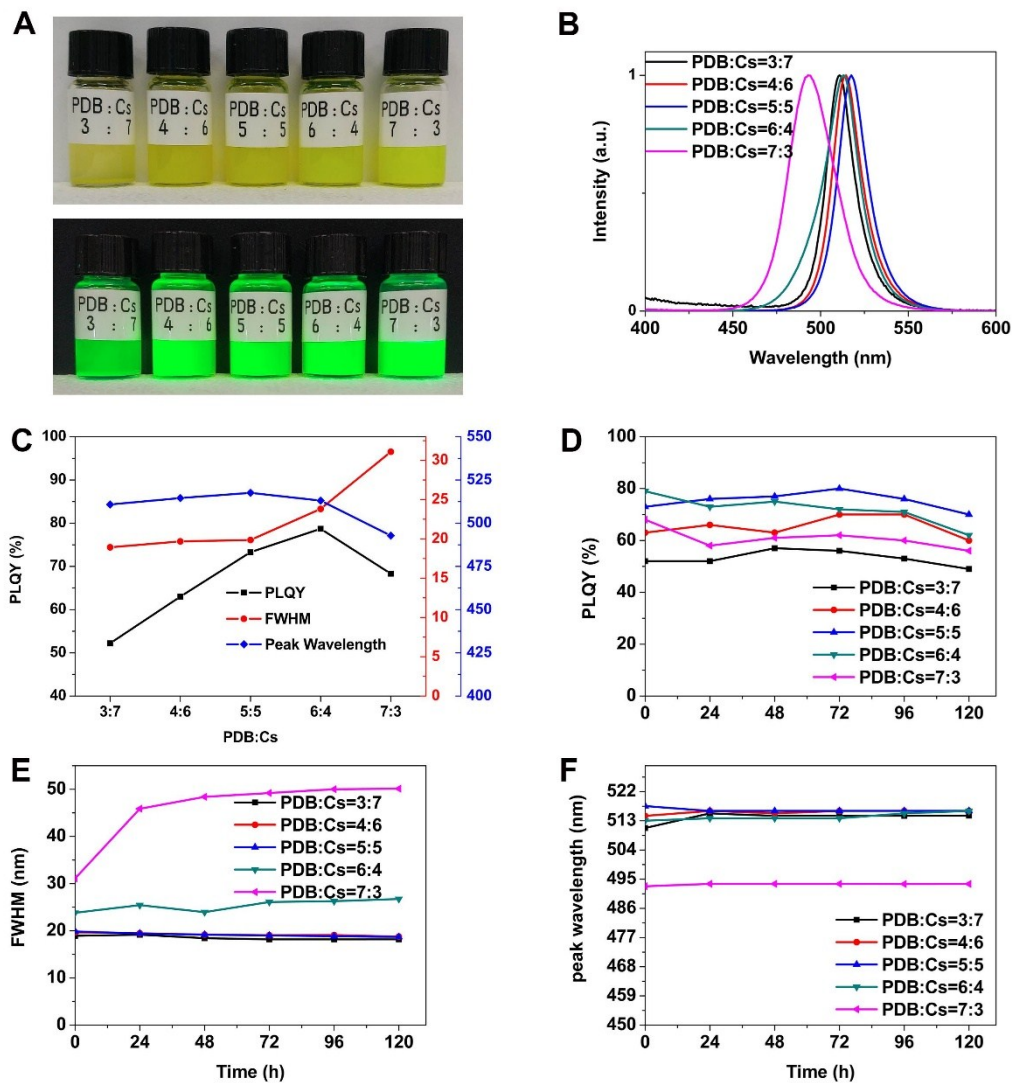


Fig. S2 (A) Real images of PDB-CsPbBr₃ QDs dispersion under the visible light (above) and UV light (below); (B) PL spectra and (C) PLQY, FWHM and peak wavelength of PDB-CsPbBr₃ QDs with PDB: Cs varying from 7:3 to 3:7, (D) PLQY, (E) FWHM and (F) peak wavelength of PDB-CsPbBr₃ QDs dispersions during storage of 120 h.

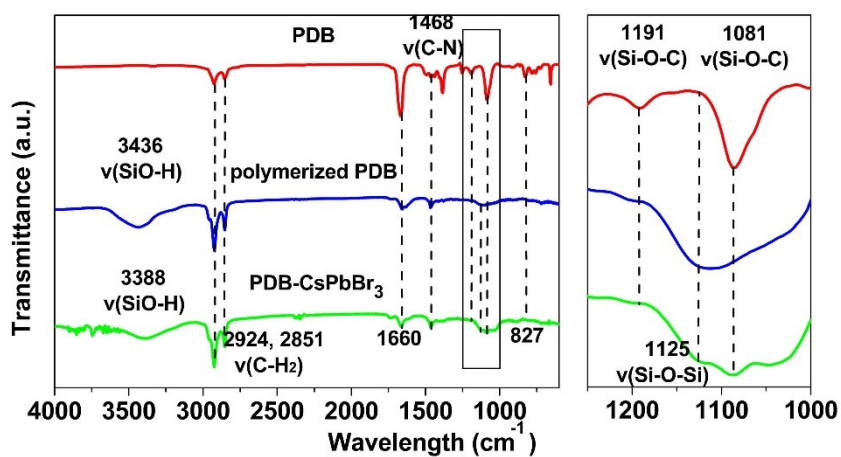


Fig. S3 FTIR spectrum of PDB, polymerized PDB and PDB-CsPbBr₃

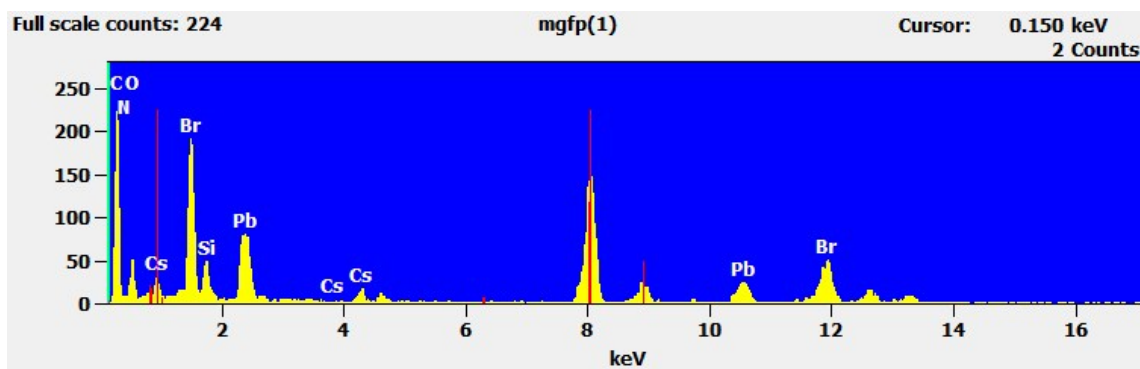


Fig. S4 EDX spectrum of PDB-CsPbBr₃ QDs.

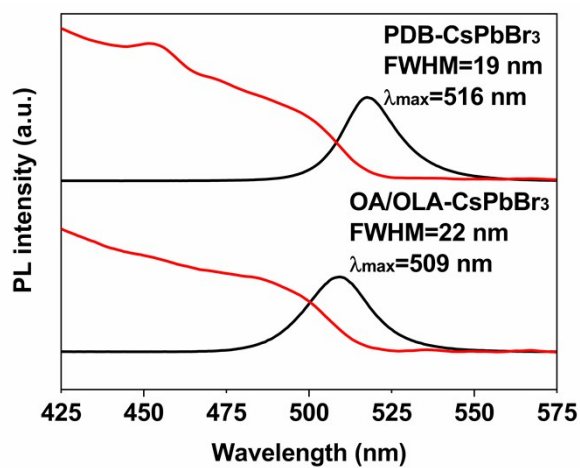


Fig. S5 PL and absorption spectra of PDB-CsPbBr₃ QDs with PDB: Cs=5:5 and OA/OLA-CsPbBr₃ QDs.

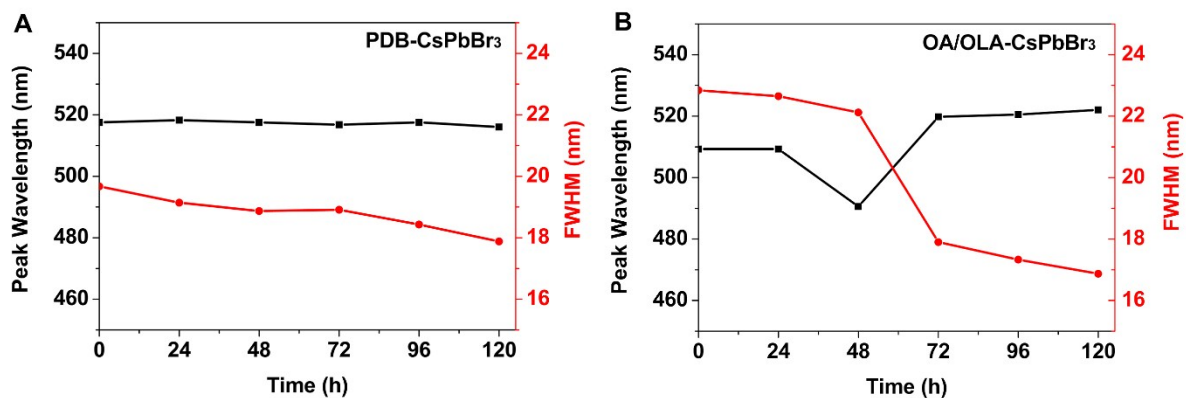


Fig. S6 Peak wavelengths and full width at the half maximum (FWHM) versus time of (A) PDB-CsPbBr₃ QDs and (B) OA/OLA-CsPbBr₃ QDs during 120 h storage.

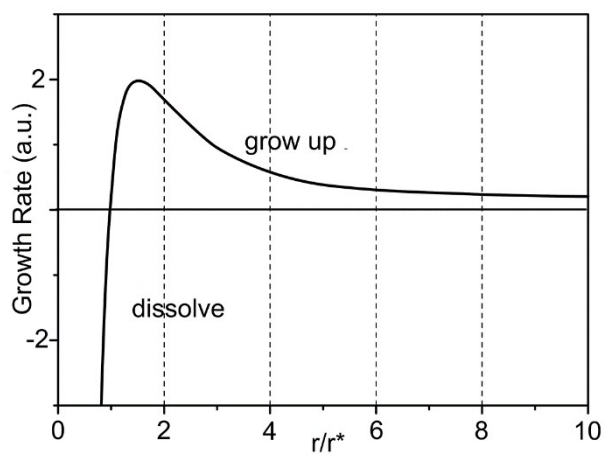


Fig. S7. The size dependent growth rate of QDs. r^* – critical radius.

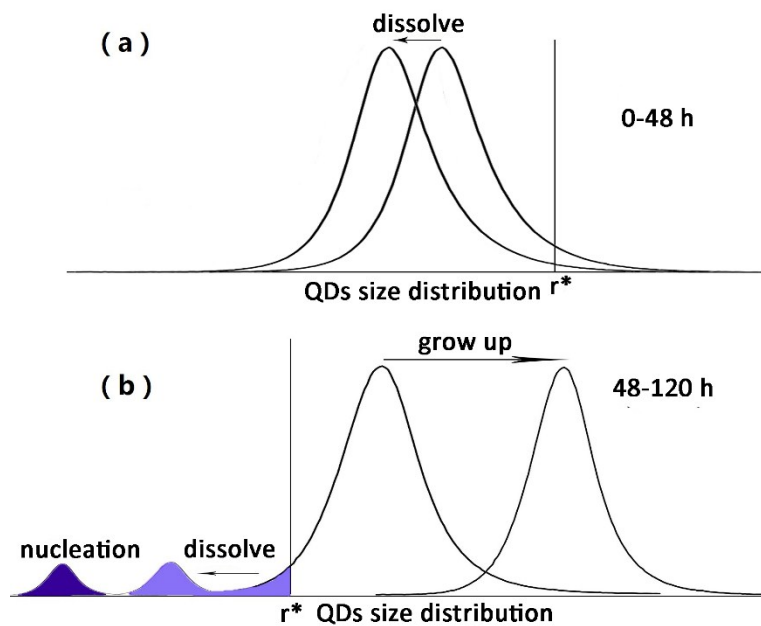


Fig. S8. Schematic CsPbBr₃-OA/OLA QDs size distribution changes with storage time

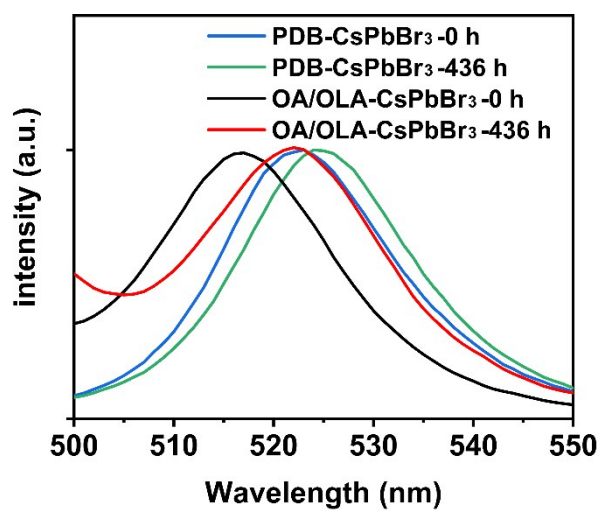


Fig. S9 Green PL spectrum of PDB-CsPbBr₃ LED and OA/OLA-CsPbBr₃ LED before and after lighting for 436 h.

Supporting Tables

Table S1. Lattice parameters of cubic CsPbBr₃, monoclinic CsPbBr₃ and tetragonal CsPb₂Br₅

phase	A[Å]	B[Å]	C[Å]	α [°]	β [°]	γ [°]	Volume[Å ³]	PDF card
Cubic CsPbBr ₃	5.83	5.83	5.83	90	90	90	198.2	PDF#54-0752
monoclinic CsPbBr ₃	5.827	5.827	5.891	90	90	89.65	200.0	PDF#18-0364
tetragonal CsPb ₂ Br ₅	8.483	8.483	15.25	90	90	90	1097.4	PDF#25-0211

Table S2. Lifetimes of PDB-CsPbBr₃ and OA/OLA-CsPbBr₃ QDs before and after 120 h storage

	τ_{average} [ns]	τ_1 [ns]	f_1	τ_2 [ns]	f_2	τ_{average} [ns]
CsPbBr ₃ -PDB	11.5	2.5	35%	16.3	65%	11.5
CsPbBr ₃ -PDB-120h	22.7	4.1	28%	30.1	72%	22.7
CsPbBr ₃ -OA/OLA	42.3	4.2	23%	54.0	77%	42.3
CsPbBr ₃ -OA/OLA-120h	27.1	3.0	26%	35.4	74%	27.1

Table S3. Summary of the PL properties and device lifetimes of CsPbBr₃ QDs performance in PL-LEDs

Composite	PLQY	Test condition	Test time	Remaining QY/intensity	Reported time	ref
CsPbBr ₃ -PDB	80%	on blue LED, 5mA	436h	82%		our work
CsPbBr ₃ /Cs ₄ PbBr ₆ /SiO ₂	40%	on blue LED, 5mA	400h	50%	2019	[2]
CsPbX ₃ -PLA	33–90%	on blue LED	50h	80%	2018	[3]
	50% (blue)					
CsPbX ₃ -CaF ₂	82% (green)	On blue LED 20mA	8h	90%	2018	[4]
	66% (red)					
CsPbBr ₃ /SiO ₂ -Al ₂ O ₃	90%	455 nm LED, 5 mA	96h	90%	2017	[5]
CsPbX ₃ -CB	—	on blue LED	30h	93%	2017	[6]
CsPbBr ₃ -TDPA	68%	on blue LED	15 h	60%	2017	[7]
CsPbX ₃ /SiO ₂	85% (green)	WLED	227h	50%	2016	[8]
	88% (red)					

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