

Supporting Information

Ca²⁺-Doping for Stable Pure Red CsPbI₃ Quantum Dots Light-Emitting Diodes

Wei Shen^a, ‡ *Hao Cui*^a, ‡ *Yanxing He*^a, *Zhan Su*^a, *Suyun Liu*^a, *Wei Zhao*^a, *Kun Cao*^a,
Junmin Xia^a, *Gang Cheng*^b, *Lihui Liu*^{a*}, and *Shufen Chen*^{a*}

^a State Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210023, P. R. China.

^b State Key Laboratory of Synthetic Chemistry, HKU-CAS Joint Laboratory on New Materials, and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong (P. R. China).

Email: iamlhliu@njupt.edu.cn; iamsfchen@njupt.edu.cn.

W. S. and H. C. contributed equally to this work.

Experimental Section

Materials: Cesium carbonate (Cs_2CO_3 , 99.99%), lead iodide (PbI_2 , 99.99%), ammonium iodide (NH_4I , 99%), Calcium acetate ($\text{Ca}(\text{Ac})_2$, 99.99%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OLA, 80-90%), dodecylbenzenesulfonic Acid (DBSA, 90%), methyl acetate (MeOAc, 99%), isopropyl alcohol (IPA, 99%), hexane (99%), and octane (99%) were purchased from Aladdin. Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulphonate) (PEDOT:PSS, CLEVIOS P VP AI 4083) was purchased from Heraeus Materials Technology Co. Ltd. 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-Hbenzimidazole) (TPBi) was purchased from Nichem Fine Technology Co. Ltd. Patterned indium-tin oxide (ITO) glasses were purchased from Hua Yu United Technology Co. Ltd. All chemicals and materials were directly used without further purification.

Synthesis of Cs-OA: 0.5 g Cs_2CO_3 , 2.5 mL OA and 50 mL ODE were mixed into a 100 mL three-neck flask and dried under vacuum at 120 °C for 1 h. Then the mixture was heated to 150 °C under N_2 until the Cs_2CO_3 powders were completely dissolved to form a transparent solution. The solution was cooled down to room temperature in an ice-water bath and preheated to 120 °C before use.

Synthesis of Ca^{2+} -Doped CsPbI_3 QDs: CsPbI_3 QDs were synthesized by following method. 0.5 g PbI_2 , 25 mL ODE and a certain amount of $\text{Ca}(\text{Ac})_2$ ($\text{Ca}^{2+}/\text{Pb}^{2+}$ are 0%, 10%, 20%, and 30%, respectively) were mixed into a 100 mL three-neck flask. The mixture was degassed and dried in vacuum for 1 h at 120 °C. Then 2.5 mL OLA mixed with 0.25 g DBSA and 2.5 mL OA were injected into the reaction flask, respectively. The mixed solution became clear and was degassed in vacuum for 30 min at 120 °C. Finally, the temperature was increased to 160 °C and 4.0 mL Cs-OA was swiftly injected. After 5 s, the reaction flask was immediately transferred to an ice-water bath to stop the reaction.

Purification of Ca^{2+} -Doped CsPbI_3 QDs: 0.1 g NH_4I was dissolved in 1 mL IPA to make NH_4I solution. The as-prepared QDs crude solution was centrifuged at 8000 rpm for 3 min to remove the large particles. After mixing QDs solution with MeOAc by a volume ratio of 1:3, 20 μL of NH_4I solution was added. The mixture was

centrifuged at 10000 rpm for 5 min at room temperature (RT) to obtain precipitate. The precipitate was redispersed into hexane mixing with MeOAc by a volume ratio of 1:2. Then 20 μ L of NH_4I solution was added again, and the mixture was centrifuged at 10000 rpm for 5 min at RT. After removing the precipitate, the supernatant was centrifuged at 10000 rpm for 5 min at $-15\text{ }^\circ\text{C}$ to obtain precipitate (DLAB, D1524R, temperature range -20 - $40\text{ }^\circ\text{C}$), which was redispersed into octane to obtain NH_4I treated QDs. Finally, NH_4I treated QD solution was centrifuged at 10000 rpm for 5 min at RT to discard the precipitate, and the supernatant was preserved for characterization and device fabrication

Fabrication of LED Devices: ITO glass substrates were cleaned by ultrasonic cleaning for 15 min in acetone, ethanol, and deionized water, separately, and dried with N_2 flow. The clean ITO substrates were exposed in UV-ozone environment for 15 min. Then, PEDOT:PSS solution was spincoated onto the ITO substrates at 3000 rpm for 30 s and annealed at $120\text{ }^\circ\text{C}$ for 15 min in air. Ca^{2+} -Doped CsPbI_3 QDs were spin-coated onto the PEDOT:PSS layer at 1500 rpm for 30 s. This process was repeated four times. Finally, 40 nm TPBi layer, 1 nm LiF layer, and 100 nm Al electrode were deposited in sequence by a thermal evaporation system under a high vacuum ($\approx 2 \times 10^{-4}$ Pa). The active area of each device was 10 mm^2 , as defined by the overlapping area of the ITO and Al electrodes.

Characterization: The chemical compositions were measured by a PerkinElmer NexION 2000 inductively coupled plasma mass spectrometry (ICP-MS). The ultraviolet-visible (UV-Vis) absorption spectra were measured by a PerkinElmer Lambda 35S instrument in transmission mode. Photoluminescence (PL) spectra were collected by a RF6000 spectrofluorometer with an excitation wavelength of 500 nm. The PL lifetimes were measured by a FLS920 fluorescence spectrometer with a pulse laser at 375 nm, and the detection wavelengths were the peak positions for each samples. Photoluminescence fluorescence quantum yield (PLQY), which is defined as the ratio of emitted photons to absorbed ones, was determined by a FLS920 fluorescence spectrometer equipped with an integrating sphere. The morphology, size and composition of QDs were confirmed by transmission electron microscope (TEM)

(Hitachi, HT7700), high-resolution TEM (HRTEM) (Talos, F200X), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS). The cross-sectional morphologies and scanning electron microscope (SEM) images were captured by a field-emission SEM (Hitachi S-4800). X-ray diffraction (XRD) data were collected by a Bruker D8 Advance X-ray powder diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The electroluminescent (EL) spectra and luminance (L) current density (J) - voltage (V) characteristics were collected by using a Keithley 2400 source and a PR-655 spectra scan spectrophotometer (Photo Research). The characterization for LED devices was measured at room temperature in air.

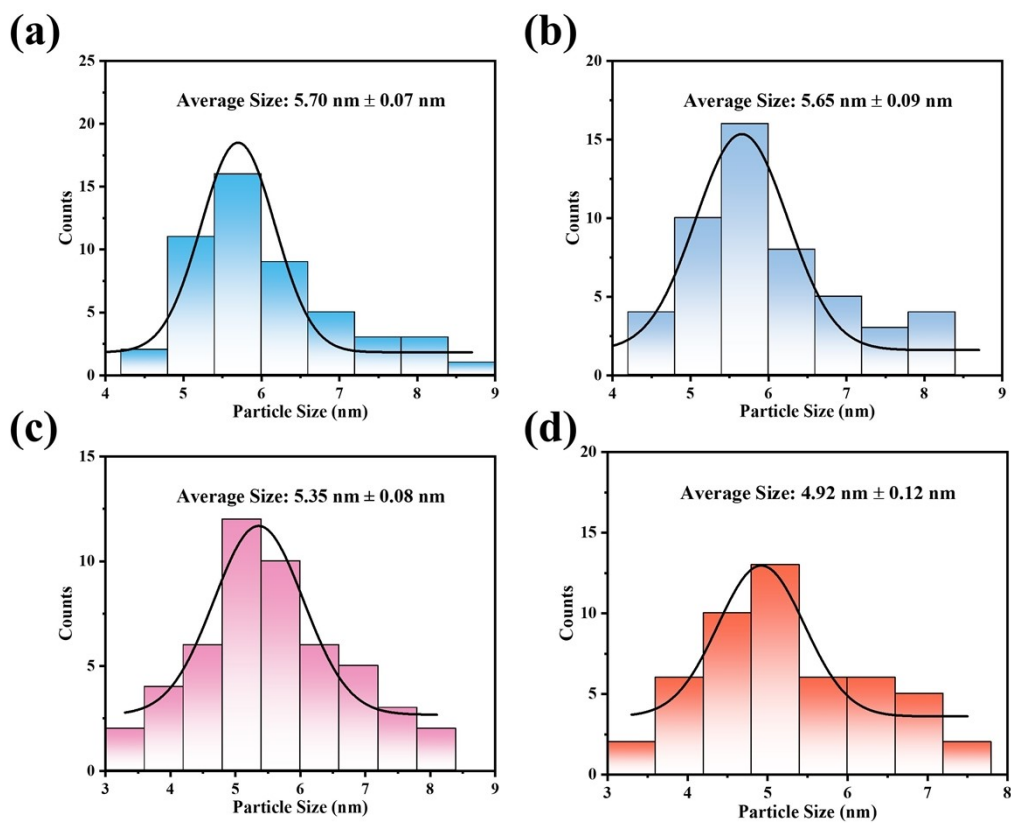


Figure S1. The particle size statistical histograms of CsPbI₃ QDs with various of Ca²⁺/Pb²⁺ ratios: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

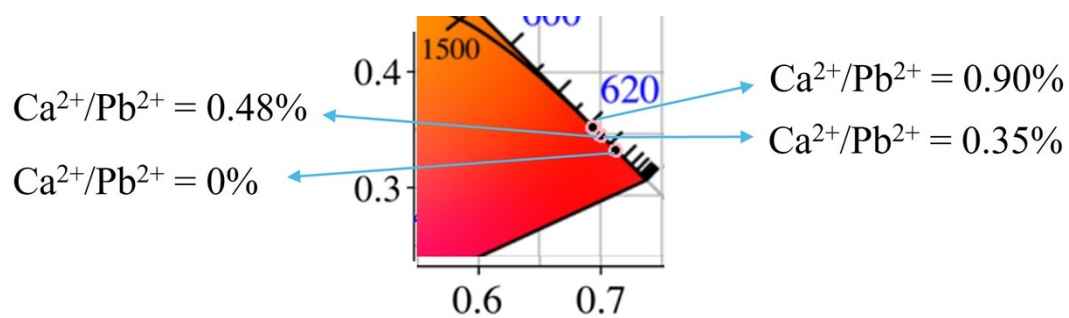


Figure S2. CIE coordinate evolutions for CsPbI₃ QDs solutions with various of Ca²⁺/Pb²⁺ ratios.

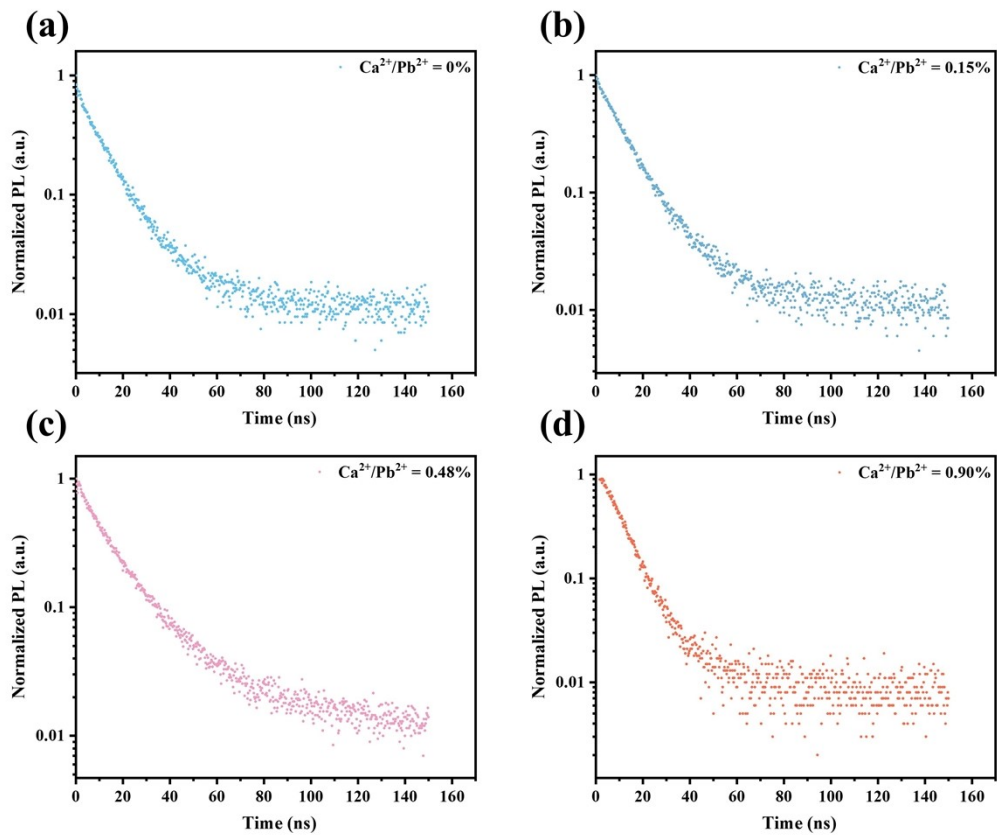


Figure S3. Time-dependent fluorescence decay curves of CsPbI₃ QDs solution with various Ca²⁺/Pb²⁺ ratios (a) Ca²⁺/Pb²⁺ = 0%, (b) Ca²⁺/Pb²⁺ = 0.15%, Ca²⁺/Pb²⁺ = 0.48%, and Ca²⁺/Pb²⁺ = 0.90%.

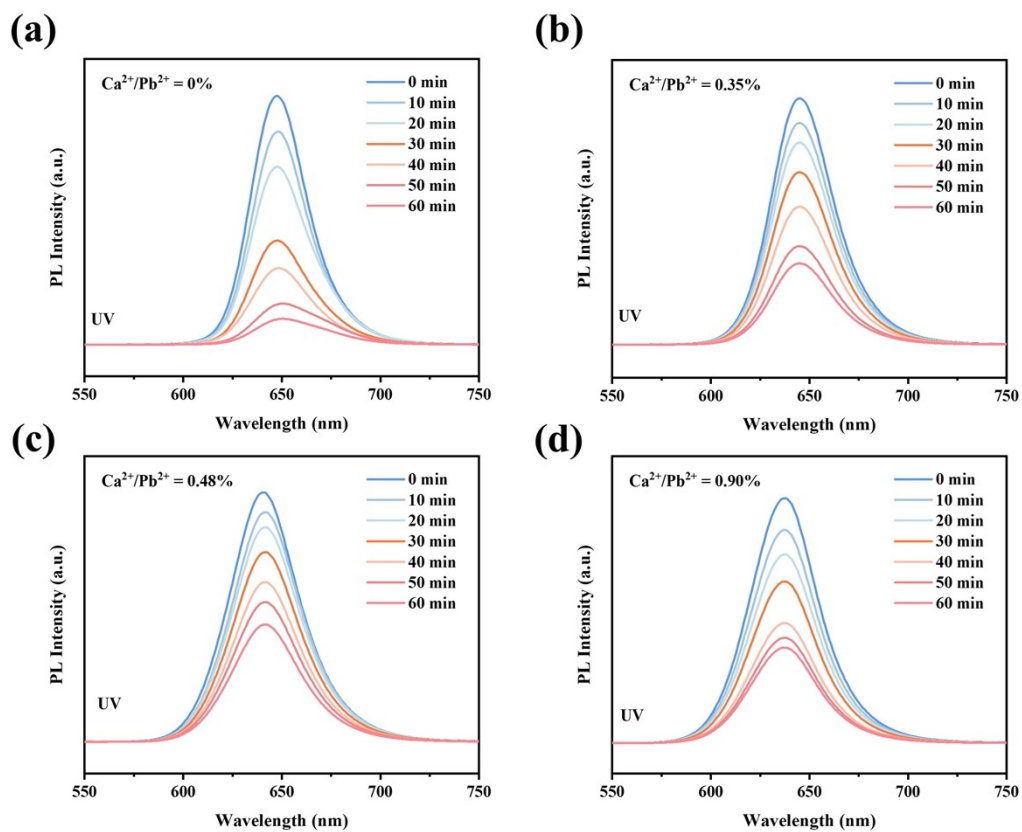


Figure S4. Time-dependent PL spectra of CsPbI₃ QDs solutions under continuous UV irradiation with various of Ca²⁺/Pb²⁺ ratios: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

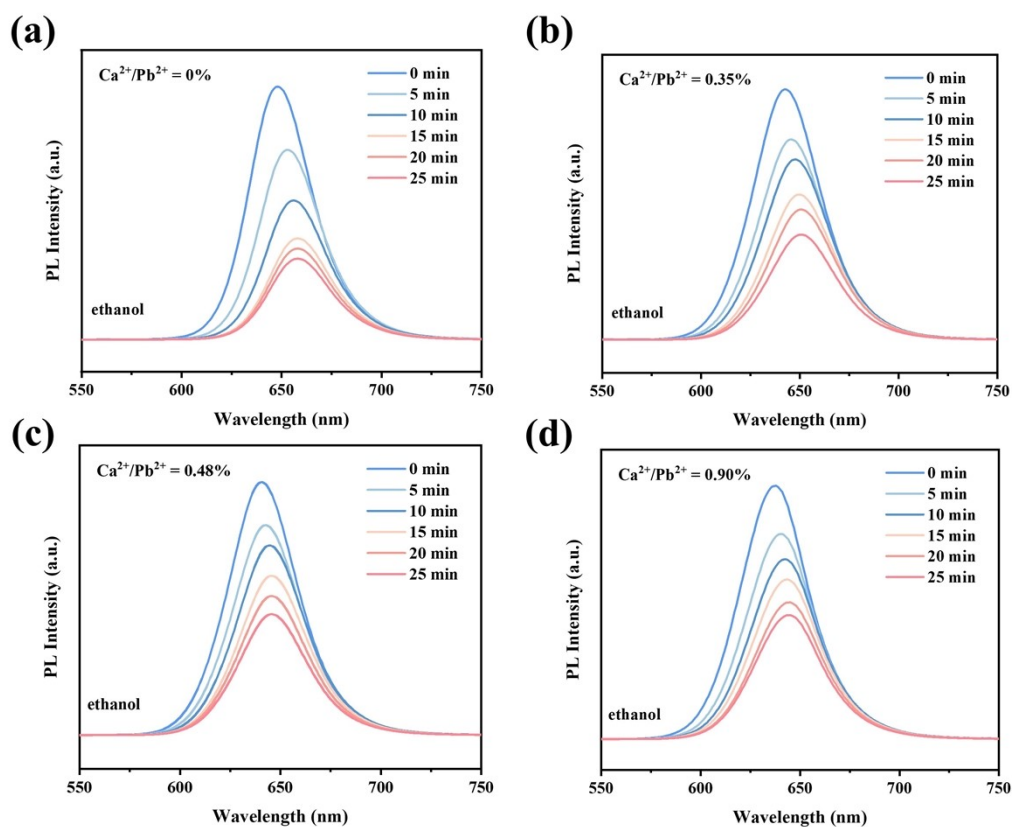


Figure S5. Time-dependent PL spectra of CsPbI₃ QDs solutions after adding ethanol with various of Ca²⁺/Pb²⁺ ratios: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

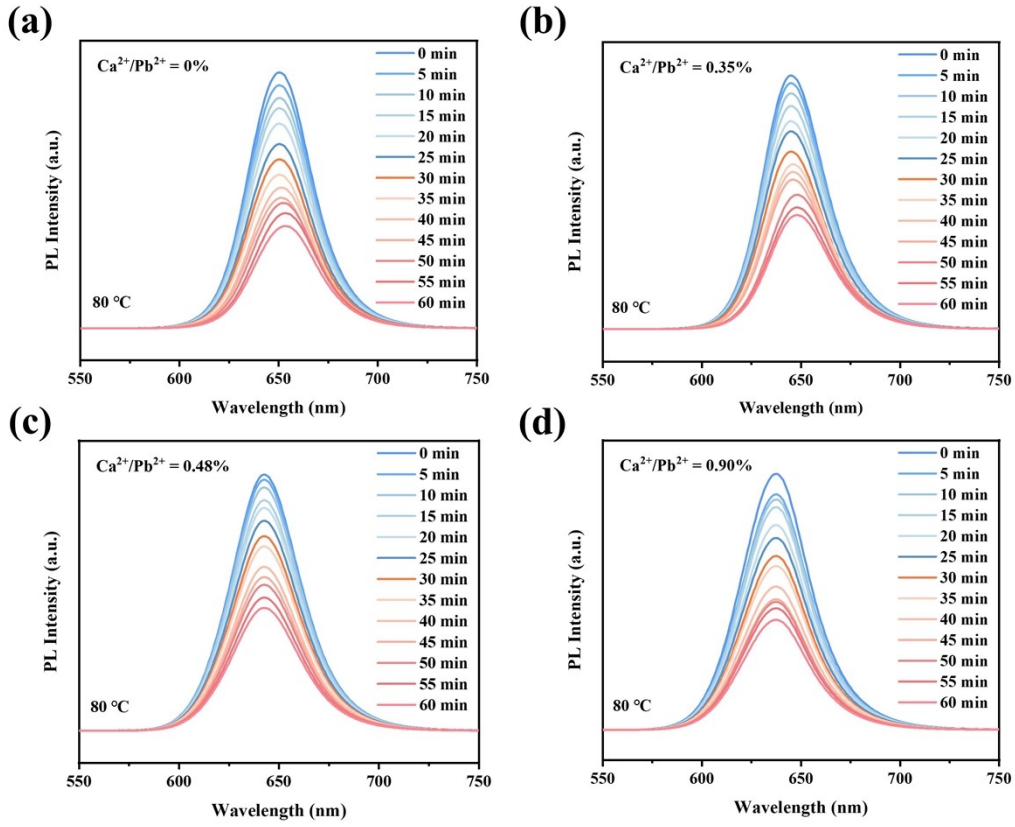


Figure S6. Time-dependent PL spectra of CsPbI₃ QDs solutions on a hot plate at 80 °C: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

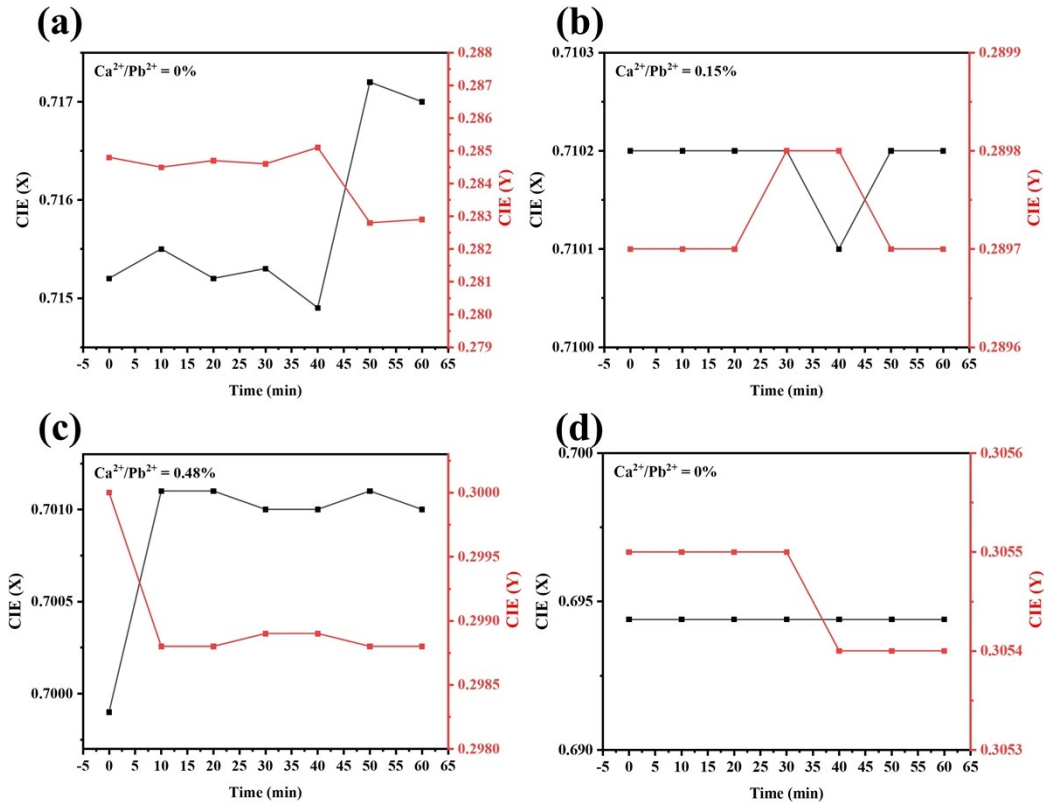


Figure S7. Evolving X and Y Coordinates in CIE of CsPbI₃ QDs solutions under continuous UV irradiation with various of Ca²⁺/Pb²⁺ ratios: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

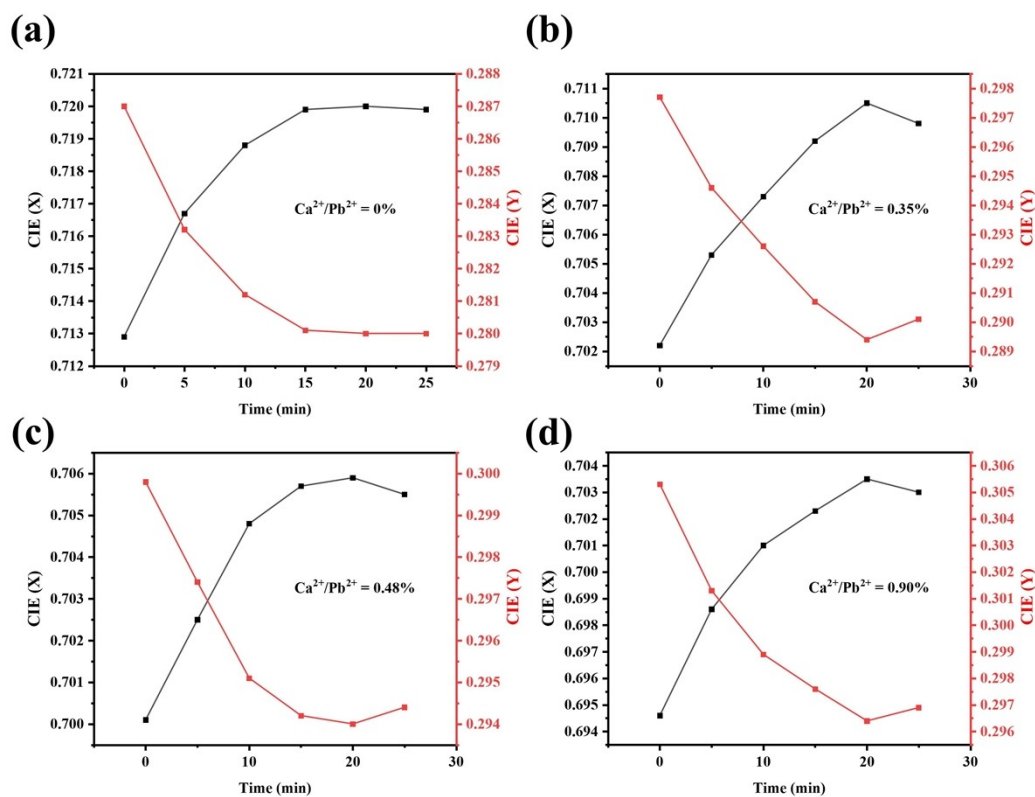


Figure S8. Evolving X and Y Coordinates in CIE of CsPbI₃ QDs solutions after adding ethanol with various of Ca²⁺/Pb²⁺ ratios: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

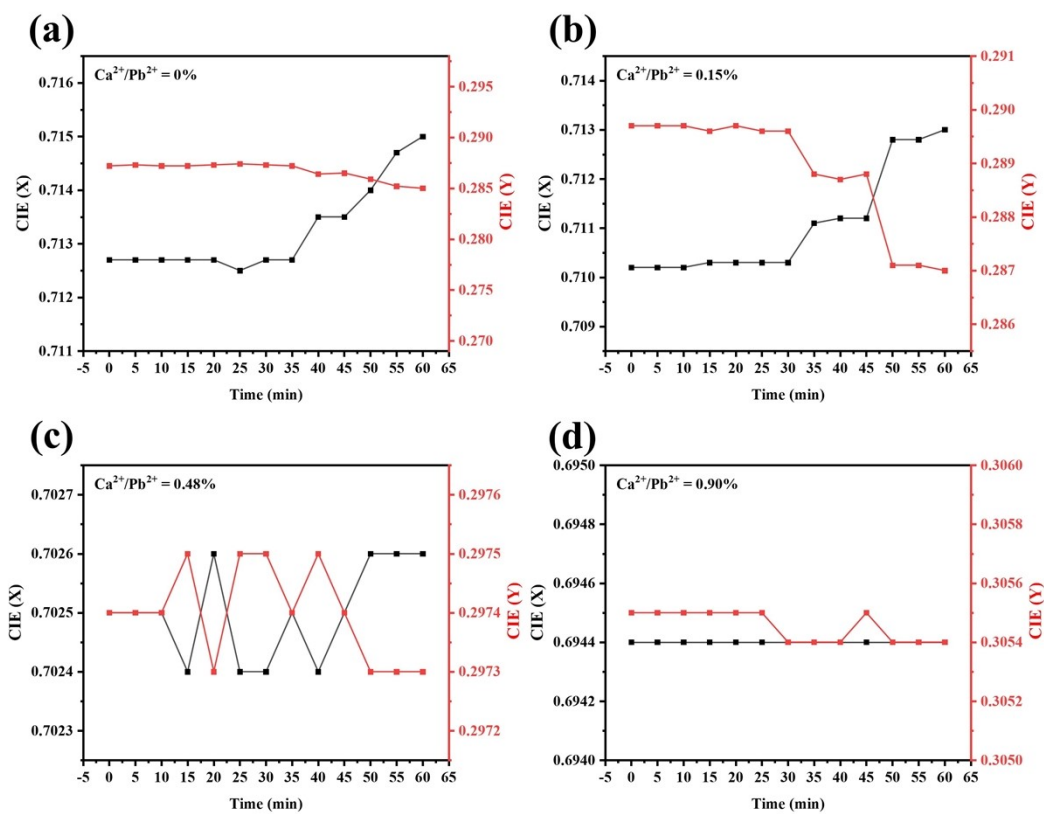


Figure S9. Evolving X and Y Coordinates in CIE of CsPbI_3 QDs solutions on a hot plate at $80\text{ }^\circ\text{C}$: (a) 0%, (b) 0.35%, (c) 0.48%, (d) 0.90%.

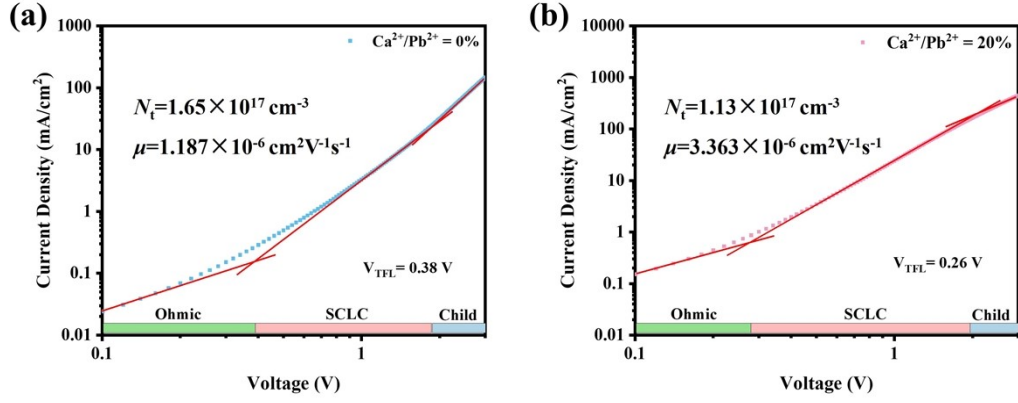


Figure S10. J - V curves of hole-only devices: (a) $\text{Ca}^{2+}/\text{Pb}^{2+} = 0\%$, (b) $\text{Ca}^{2+}/\text{Pb}^{2+} = 0.48\%$.

The defect density (N_t) is calculated according to the following equation:

$$N_t = \frac{2\varepsilon_0\varepsilon_r V_{TFL}}{qd^2}$$
 where ε_0 and ε_r are the vacuum dielectric constant and the relative dielectric constant, respectively; V_{TFL} is the trap filled limit voltage; L is the thickness of the NC film; and q is the elementary electronic charge. The hole migration rates (μ) were estimated by fitting the space-charge-limited-current region with Child's law:

$$J = \frac{9\varepsilon\varepsilon_0\mu V^2}{8L^3}$$
 , where ε_0 is the vacuum permittivity; ε is the average relative dielectric constant of CsPbI_3 ; L is the thickness of the perovskite film; and J , μ , and V are the measured current density, carrier migration rates, and applied voltage, respectively.

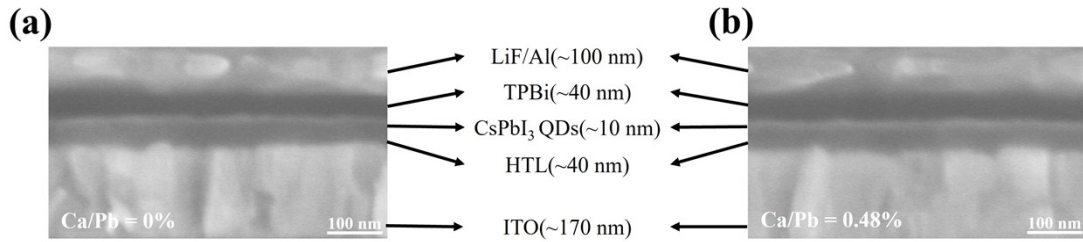


Figure S11. The cross-section SEM images of LEDs: (a) $\text{Ca}^{2+}/\text{Pb}^{2+} = 0\%$, (b) $\text{Ca}^{2+}/\text{Pb}^{2+} = 0.48\%$.

Table S1. The data of ICP-MS testing

Ca/Pb feed ratio	Ca concentrated 100 times (ppb)	Pb (ppb)	Ca/Pb real ratio
0.1 : 1	6.73	99.612	0.0035 : 1
0.2 : 1	5.24	56.388	0.0048 : 1
0.3 : 1	9.62	55.133	0.0090 : 1

Table S2. PL lifetimes of CsPbI₃ QDs solution with various of Ca²⁺/Pb²⁺ ratios.

Ca ²⁺ /Pb ²⁺ (%)	0	0.35	0.48	0.90
τ_1 (ns)	7.68	11.92	12.93	11.32
τ_2 (ns)	13.28	14.72	16.36	14.28
A1	74	70	60	66
A2	26	30	40	34
τ_{avg} (ns)	9.81	12.88	14.49	12.48

Table S3. Radiative decay rate (k_r) and non-radiative decay rate (k_{nr}) of CsPbI₃ QDs solution with various of Ca²⁺/Pb²⁺ ratios.

Ca ²⁺ /Pb ²⁺ (%)	0	0.35	0.48	0.90
τ_{ave} (ns)	9.81	12.88	14.49	12.48
PLQY(%)	81	84	86	74

τ_r (ns)	12.11	15.33	16.85	16.86
k_r ($\times 10^{-2} \text{ ns}^{-1}$)	8.26	6.52	5.93	5.93
τ_{nr} (ns)	51.63	80.50	103.50	48.00
k_{nr} ($\times 10^{-2} \text{ ns}^{-1}$)	1.93	1.24	0.97	2.08
k_r/k_{nr}	4.28	5.26	6.11	2.85

Radiative recombination lifetime, $\tau_r = \tau_{avg} / \text{PLQY}$;

Non-radiative recombination lifetime, $\tau_{nr} = \tau_{avg} / (1 - \text{PLQY})$;

Radiative decay rate constant, $k_r = 1/\tau_r$;

Non-radiative decay rate constant, $k_{nr} = 1/\tau_{nr}$.