

Electronic Supporting Information for

Ultra-Small α -CsPbI₃ Perovskite Quantum Dots with Stable, Bright and Pure Red Emission for Rec. 2020 Display Backlight

*Chuying Wang^a, Wen Meng^a, Yacong Li^a, Guangyong Xu^a, Min Peng^a, Shuming Nie^b and Zhengtao Deng^{*a}*

- a. College of Engineering and Applied Sciences, State Key Laboratory of Analytical Chemistry for Life Science, National Laboratory of Micro-structures, Nanjing University, Nanjing, Jiangsu, 210023, P. R. China.*
- b. Departments of Bioengineering, Chemistry, Electrical and Computer Engineering, and Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA*

EXPERIMENTAL SECTION

Materials. Cesium carbonate (Cs_2CO_3 , 99.9%, Aladdin), Oleic acid (OA, 85%, Aladdin, AR), Oleylamine (OAm, 80-90%, Aladdin), Lead iodide (PbI_2 , 99.9%, Aladdin), Lead bromide (PbBr_2 , 99.9%, Aladdin), Zinc Iodide (ZnI_2 , 98%, Macklin), Manganese acetate tetrahydrate ($\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$, 99.0%, Aladdin), 1-Iodopyrrolidine-2,5-dione (NIS, 98%, Bidepharmatech), Lauryl methacrylate (LMA, 85%, supplied by Thunway New Materials Technology Co., Ltd., Nanjing, China), 1-Octadecene (ODE, 90%, Aladdin), Hexane (AR, Sinopharm Chemical Reagent Co. Ltd), 2-Ethylhexanoic acid (EHA, 99.0%, Macklin), Toluene (99.9%, Sinopharm Chemical Reagent Co. Ltd), Methyl acetate ($\geq 99.0\%$, Macklin), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aladdin), polyester polyurethane acrylates oligomer (45 wt %, supplied by Thunway New Materials Technology Co., Ltd., Nanjing, China), and isobornyl acrylate (IBOA, $>85\%$, Nippon Shokubai Co., Ltd, Japan). All chemicals were used as received without any further purification.

Synthesis of CsPbI₃ QDs in ODE. 8 mL oleic acid, 8 mL oleylamine, 1 mL EHA, 16 mL ODE, 640 mg PbI_2 , 640 mg ZnI_2 , 640 mg $\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ and 608 mg NIS were loaded into a 100 mL three-necked round-bottom flask and degassed. The solution was heated up to dissolve the precursors and kept at 110 °C for 15 min under vacuum. The temperature was then elevated to 120 °C and 1.5 mL of Cs-OA precursor prepared followed the previous protocol^[32] was swiftly injected under vigorous stirring. After 5 minutes, the crude mixture was cooled down and centrifuged at 10000 rpm for 20 minutes for QD-polymer composite films.

Synthesis of CsPbI₃ QDs in LMA. 8 mL oleic acid, 8 mL oleylamine, 1 mL EHA, certain amount of LMA (6 mL~16 mL), 640 mg PbI_2 , 640 mg ZnI_2 , certain amount of $\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ (corresponding to the feed ratio in manuscript) and 608 mg NIS were loaded into a 100 mL three-necked round-bottom flask and degassed. The solution was heated up to dissolve the precursors and kept at 110 °C for 15 min under vacuum. The temperature was then elevated to 120 °C and 1.5 mL of as-prepared Cs-OA precursor was swiftly injected under vigorous stirring. After 5 minutes, the crude mixture was cooled down. For purification, the supernatant was mixed with methyl acetate at the volume ratio of 1:4 and centrifuged at 10000 rpm for

20 minutes for QD-polymer composite films. This synthesis could be scaled up to 10 times in a 1000 mL three-necked round-bottom flask to obtain 250 mL product.

Synthesis of CsPbBr₂ QDs. 10 mL oleic acid, 10 mL oleylamine, 15 mL ODE, 1.1 g PbI₂ and 580 mg PbBr₂ were loaded into a 100 mL three-necked round-bottom flask and degassed. The solution was heated up to dissolve the precursors and kept at 110 °C for 15 min under vacuum. The temperature was then elevated to 120 °C and 1.5 mL of as-prepared Cs-OA precursor was swiftly injected under vigorous stirring. After keeping for 5 minutes, the crude mixture was cooled down and centrifuged at 10000 rpm for 20 minutes for QD-polymer composite films.

Scale-up Synthesis of CsPbI₃ QDs in LMA. 80 mL oleic acid, 80 mL oleylamine, 10 mL EHA, 80 mL LMA, 6.40 g PbI₂, 6.40 g ZnI₂, 5.87g MnC₄H₆O₄•4H₂O and 6.08 g NIS were loaded into a 1L three-necked round-bottom flask and degassed. The solution was heated up to dissolve the precursors and kept at 110 °C for 30 min under vacuum. The temperature was then elevated to 120 °C and 15 mL of as-prepared Cs-OA precursor was swiftly injected under vigorous stirring. After 5 minutes, the crude mixture was cooled down by ice-water bath.

Fabrication of the CsPbI₃ QD-Polymer Composite Films. 1 g LMA solution containing QDs and 10 g adhesive containing a certain amount of polyester polyurethane acrylate oligomer, monomer (IBOA), and initiator (DMPA) were first stirred and mixed fully, then coated onto a transparent PET (Polyethylene Terephthalate) substrate using a doctor blade technique as shown in our previous report.^[21] finally a bright red emission polymer film with a thickness of $150 \pm 5 \mu\text{m}$ was obtained by UV light polymerization for 5 minutes. The control films were processed using a similar process.

Characterization Details. Ultraviolet and visible (UV-vis) absorption spectra were measured by Shimadzu UV-3600 plus spectrophotometer at room temperature. PL spectra were measured by Horiba PTI QuantaMaster 400. Transmission electron microscopy (TEM) images were measured by JEOL JEM-2800 and

FEI Tecnai G2 F20 electron microscope operating at 200 kV. X-ray diffraction (XRD) measurements were measured through Rigaku Ultima III X-ray diffractometer equipped with Cu K α radiation ($\lambda=1.541841\text{\AA}$). The fluorescence decay processes were recorded with time-correlated single-photon counting (TCSPC) technique on a system provided by a SOL confotec MR200 micro-PL-Lifetime and Raman system equipped with a 450 nm laser and a time-correlated single-photon counting system at room temperature. The absolute fluorescence quantum yields were measured using a Horiba PTI QuantaMaster 400 steady-state fluorescence system with an integrated sphere. Three independent experiments on three independent areas of the films are done for better evaluation.

Table S1. Compositional analysis of samples with different conditions characterized by XPS.

Amount of LMA	8 mL	16 mL	16 mL
Feed ratio of Mn/Pb	1.6	1.7	1.7
Cs	0.13	0.11	0.31
Pb	0.10	0.10	0.11
Mn	0.09	0.08	/
I	0.68	0.71	0.54
Mn/Pb	0.90	0.85	/

Time-resolved PL decay curves of CsPbI₃ NCs-polymer composites film were fitted by a triexponential function (see eqs 1):

$$A(t) = A_0 + A_1 \exp -(t - t_0)/\tau_1 + A_2 \exp -(t - t_0)/\tau_2 + A_3 \exp -(t - t_0)/\tau_3$$

(eqs 1);

The average lifetimes were calculated using

$$\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$$

(eqs 2).

Table S2. The PL lifetimes (τ_{avg}) CsPbI₃ QDs with different feed ratio of Mn/Pb.

Feed ratio of Mn/Pb	1.5	1.6	1.7
A ₁	18063.69	13642.10	6632.00
τ_1 (ns)	8.91	9.20	7.17
A ₂	233.16	2045.50	4126.52
τ_2 (ns)	25.65	15.30	12.35
A ₃	10880.76	/	1291.13
τ_3 (ns)	2.69	/	2.39
τ_{avg}	8.49	10.45	9.63

(a)



(b)



Fig. S1 Photo images of CsPbI₃ QDs synthesized in (a) ODE and (b) LMA at the same reaction condition.

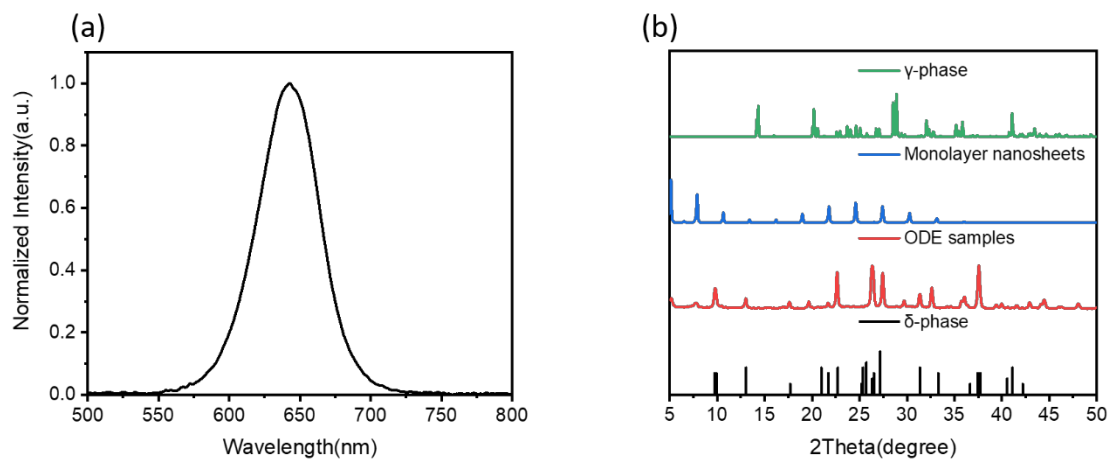


Fig. S2 (a) PL spectrum of CsPbI₃ QDs obtained by ODE. (b) XRD pattern of precipitate of ODE solution after stored for 2 days.

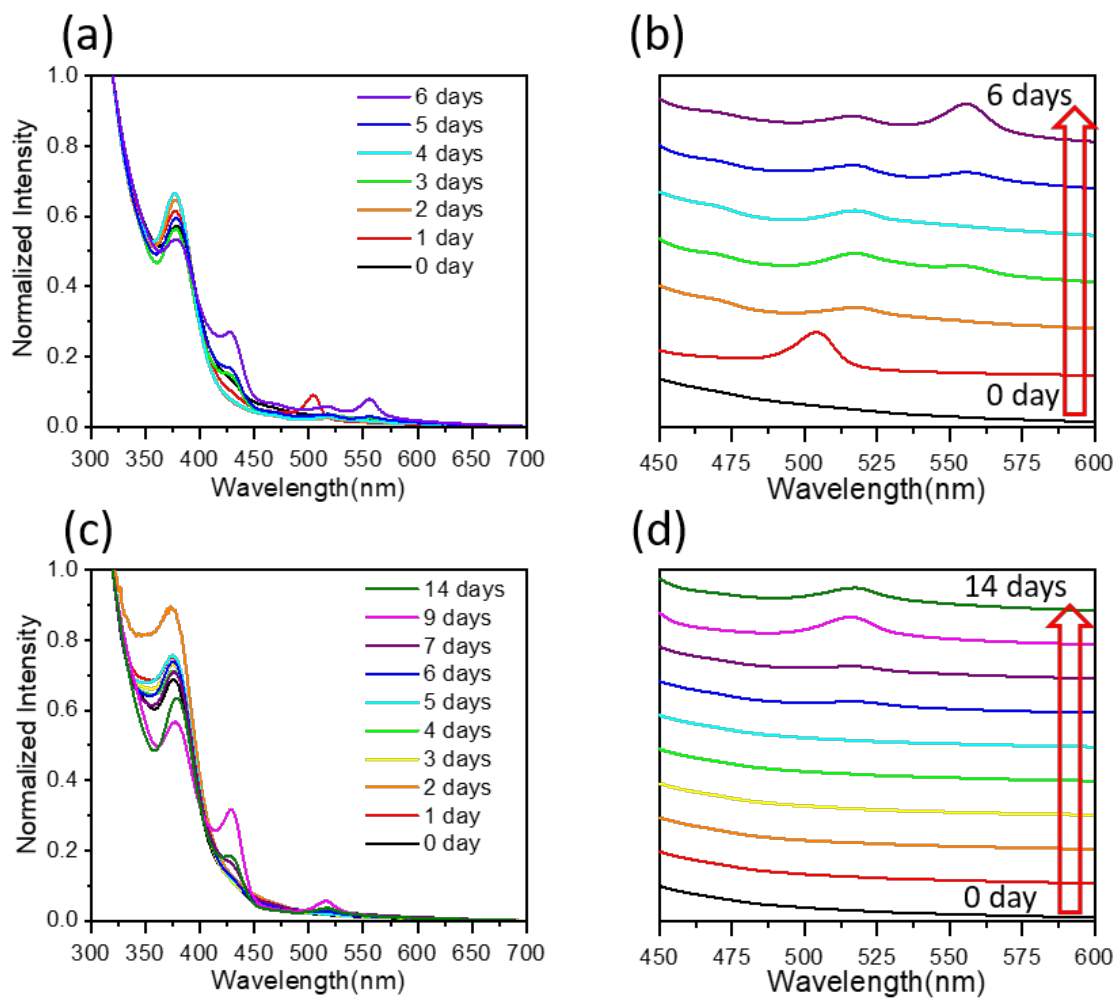


Fig. S3 Comparisons between CsPbI₃ QDs in ODE and LMA. Absorption spectra of CsPbI₃ QDs stored in pristine solution of (a)(b) ODE and (c)(d) LMA for different days without further purification.

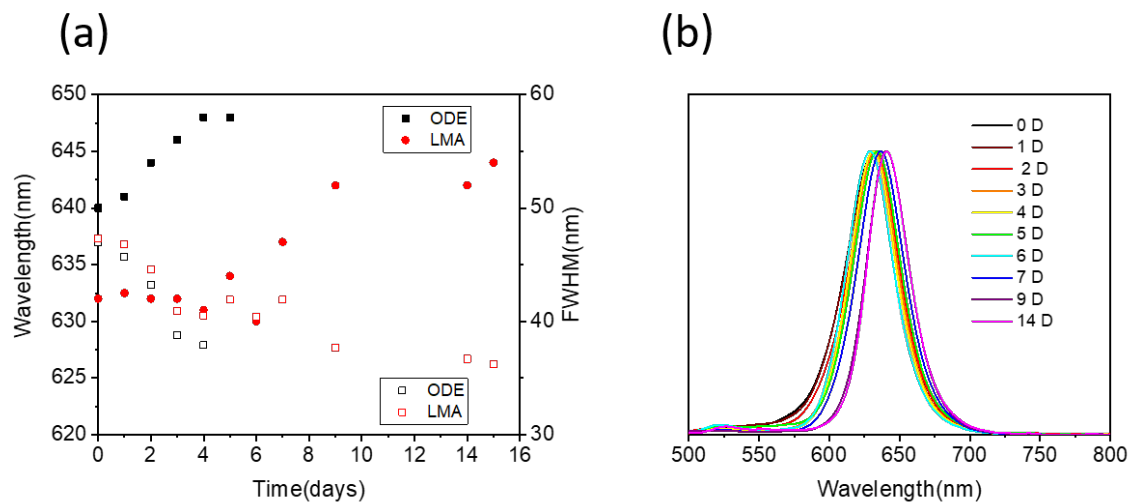


Fig. S4 (a) Comparisons between CsPbI₃ QDs in ODE and LMA and (b) PL spectra of pristine CsPbI₃ QDs in LMA with different preservation time.

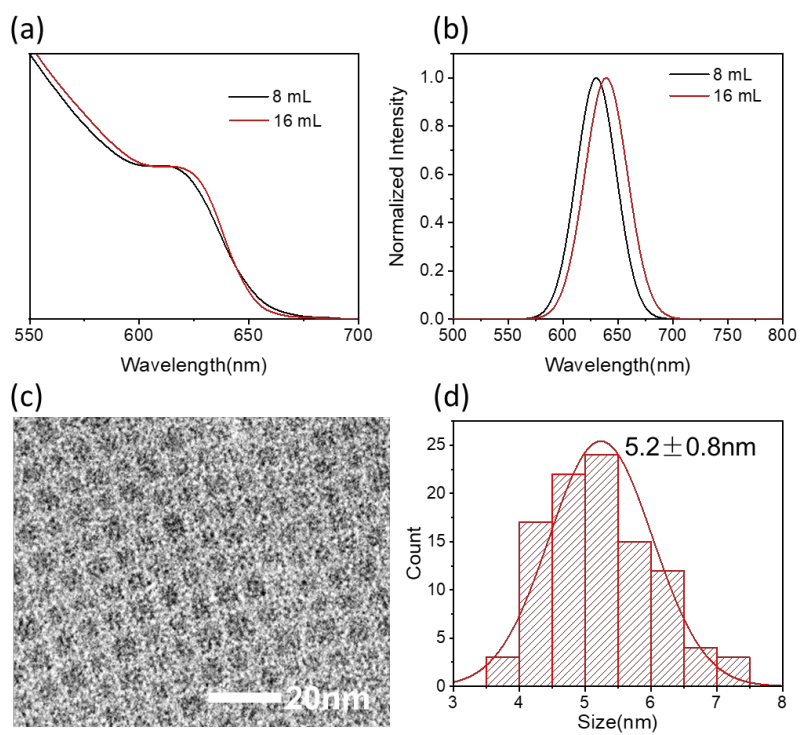


Fig. S5 (a) Absorption and (b) PL emission spectra of CsPbI₃ QD solution diluted in toluene. (c) TEM image and (d) size distribution of QDs synthesized through condition of 16 mL LMA.

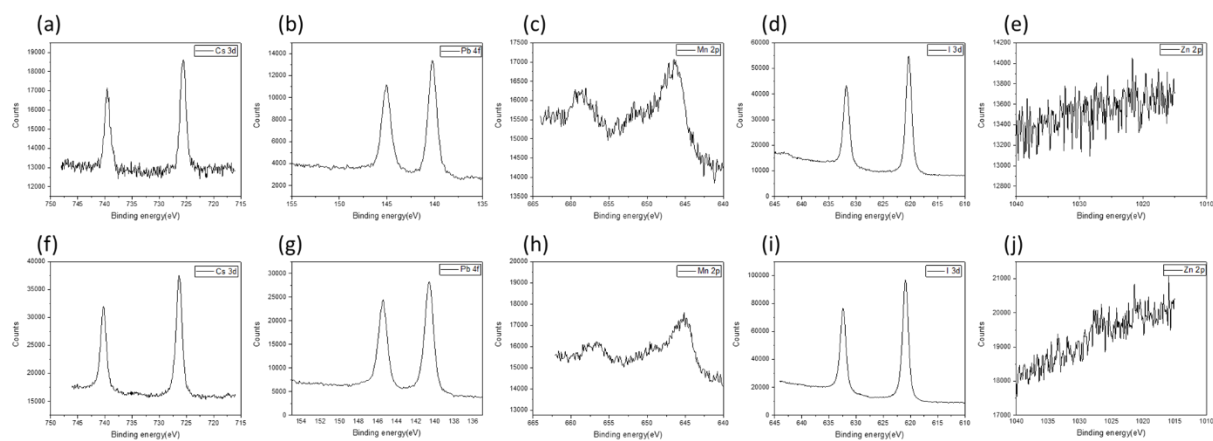


Fig. S6 XPS spectra of (a) Cs 3d, (b) Pb 4f, (c) Mn 2p, (d) I 3d, (e) Zn 2p for CsPbI₃ QDs through 16 mL LMA and (f) Cs 3d, (g) Pb 4f, (h) Mn 2p, (i) I 3d, (j) Zn 2p for CsPbI₃ QDs through 8 mL LMA.

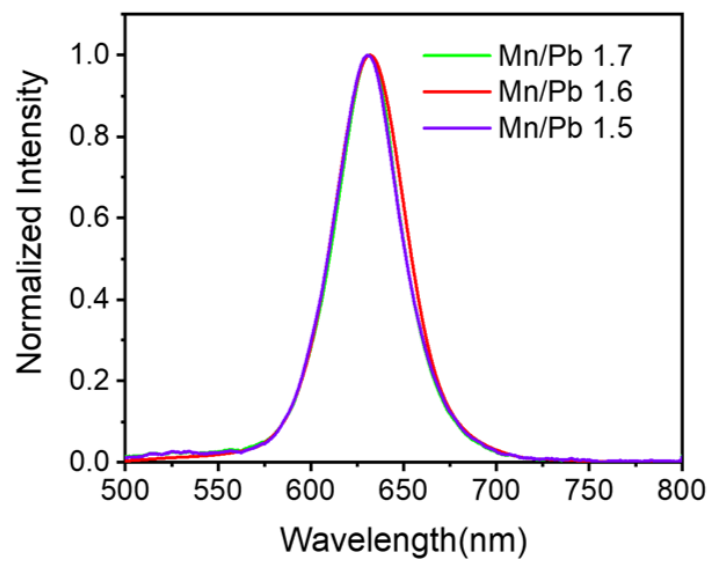


Fig. S7 (a) PL emission spectra of dilute pristine colloidal QD solution with condition of Mn/Pb=1.5, 1.6 and 1.7.

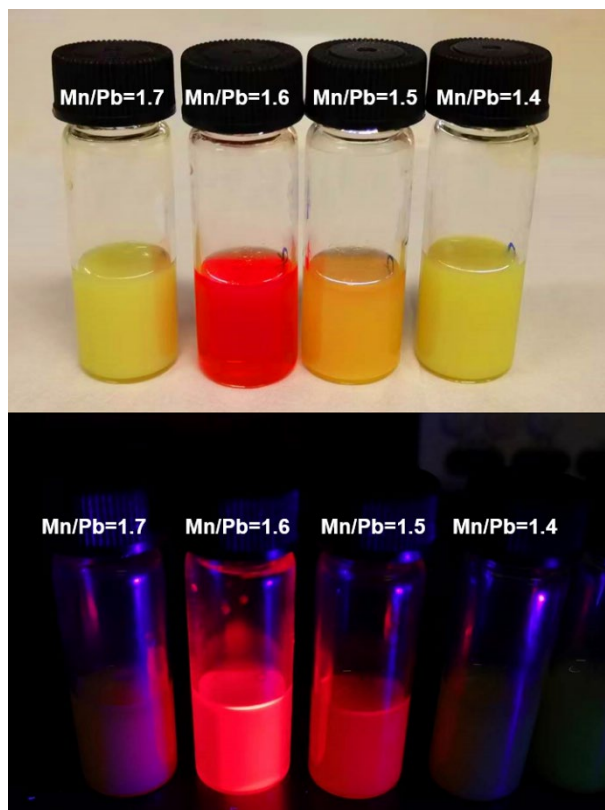


Fig. S8 Photo images of CsPbI₃ QDs synthesized with different feed ratio of Mn/Pb after purified by methyl acetate for twice under room light and irradiation at 400 nm.

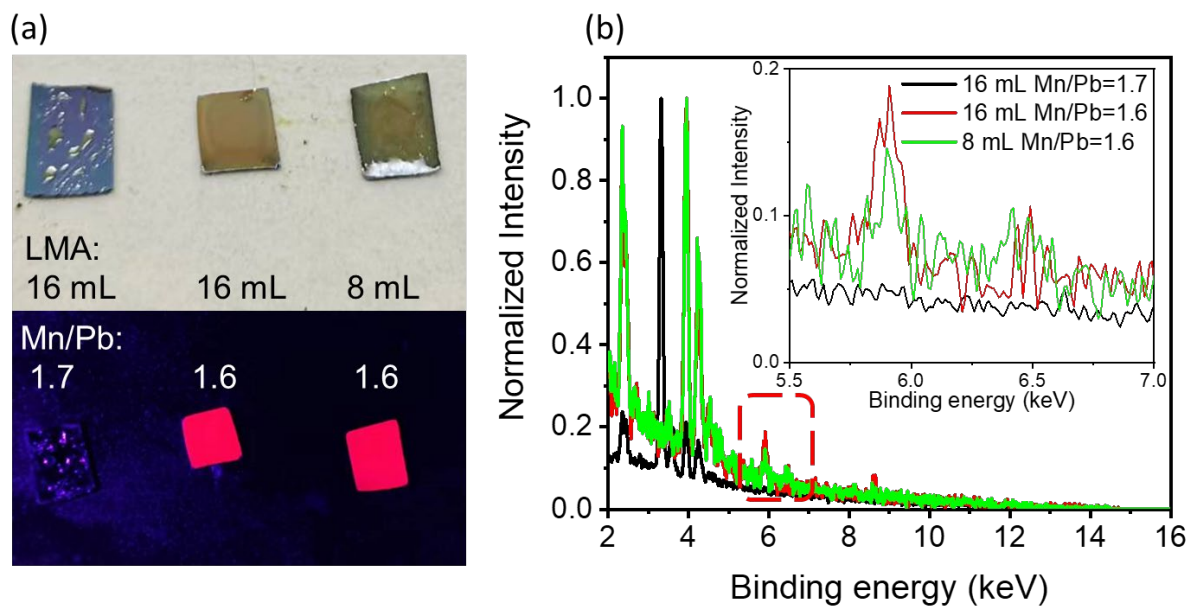


Fig. S9 (a) Photographs under room light and 400 nm irradiation and (b) EDS spectra of CsPbI₃ QDs with different reaction conditions after purified by methyl acetate. The inset is enlarged part of Mn.

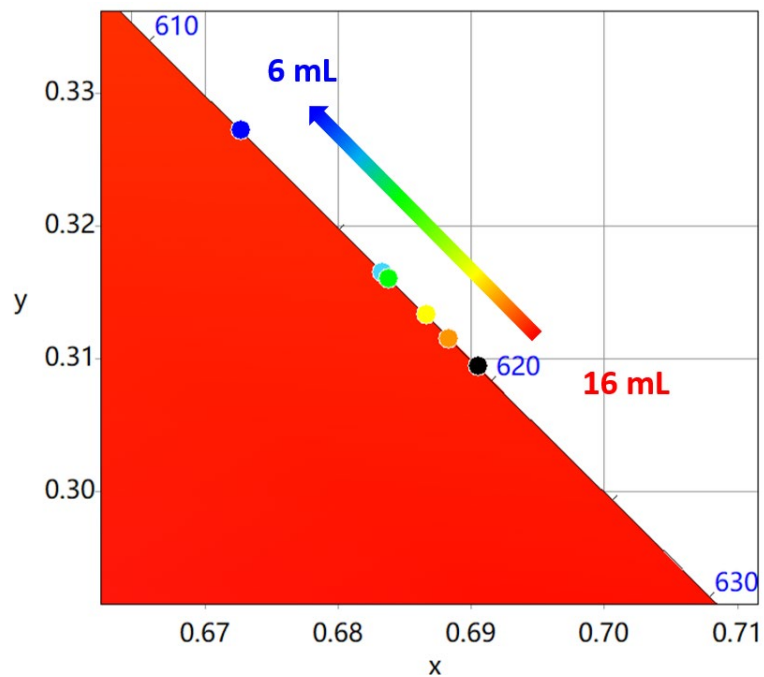


Fig. S10 Color gamut of the of red CsPbI₃ QD composite films from different amount of LMA in CIE diagram.

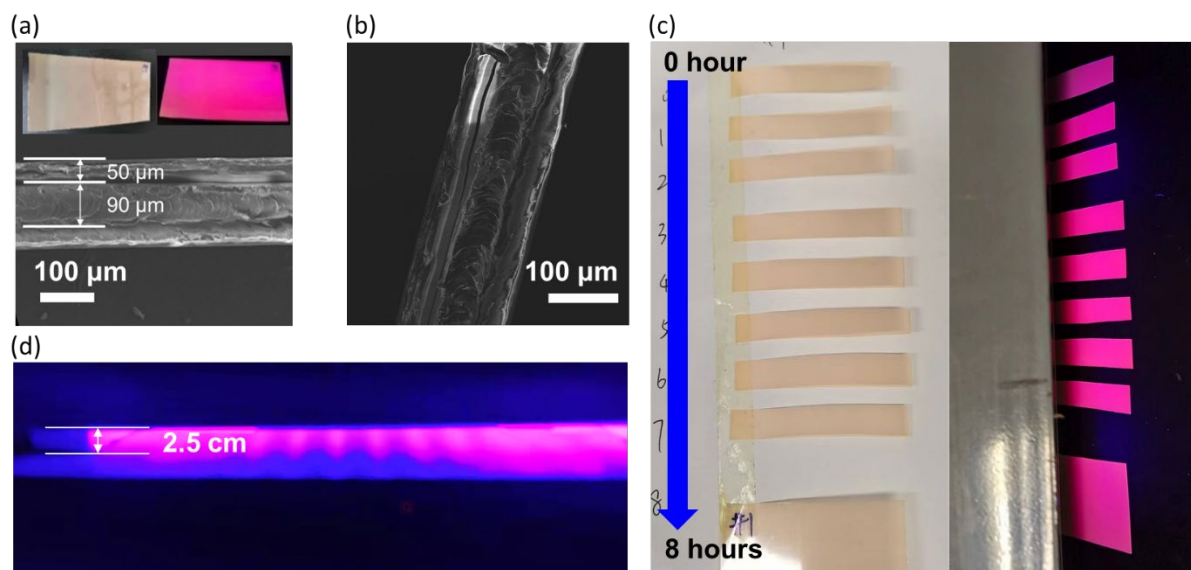


Fig. S11 SEM characterization displaying the cross section of CsPbI₃ QD composite film (a) before and (b) after continuous irradiation for 8 hours. The insets are photographs of the corresponding films under room light and UV illumination at 365 nm. (c) Photograph of CsPbI₃ QD composite films with different aging time under room light and 365 nm irradiation. (d) Photograph of aging test under home-made 450 nm LED lamp with irradiance of 1750mW/cm² in a dark room with a distance of 2.5 cm.

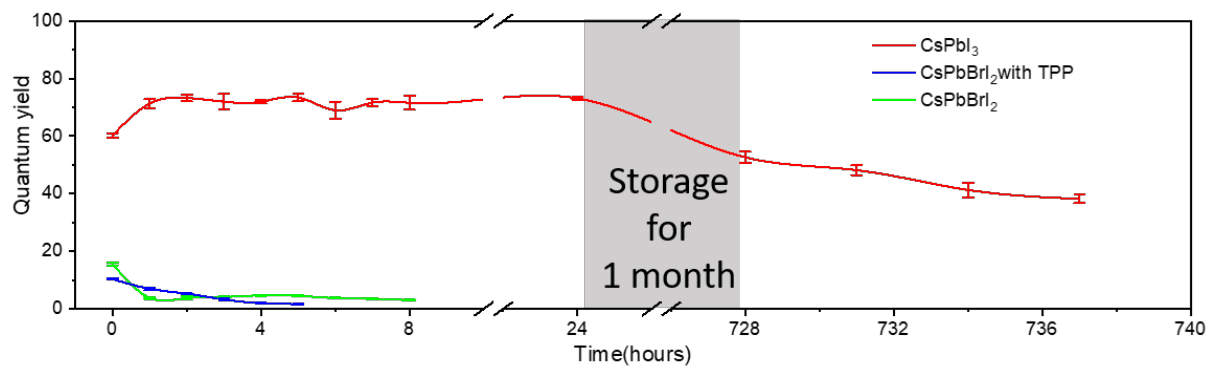


Fig. S12 Photostability curves of perovskite composite films under illumination evaluated through statistics of absolute PLQY.

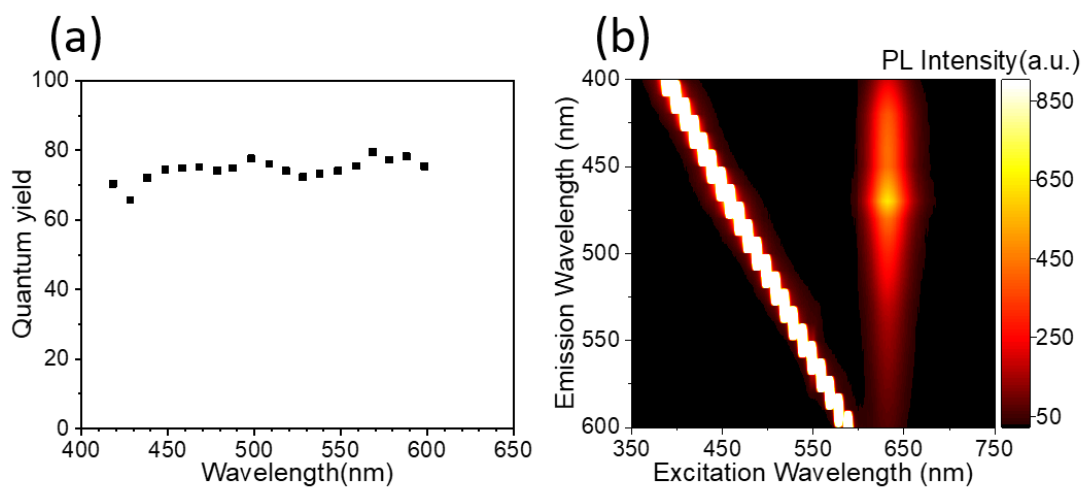


Fig. S13 (a) PLQY under various excitation wavelength and (b) three-dimensional excitation-emission matrix (EEM) fluorescence spectrum of CsPbI₃ QD film after continuous irradiation for 8 hours.

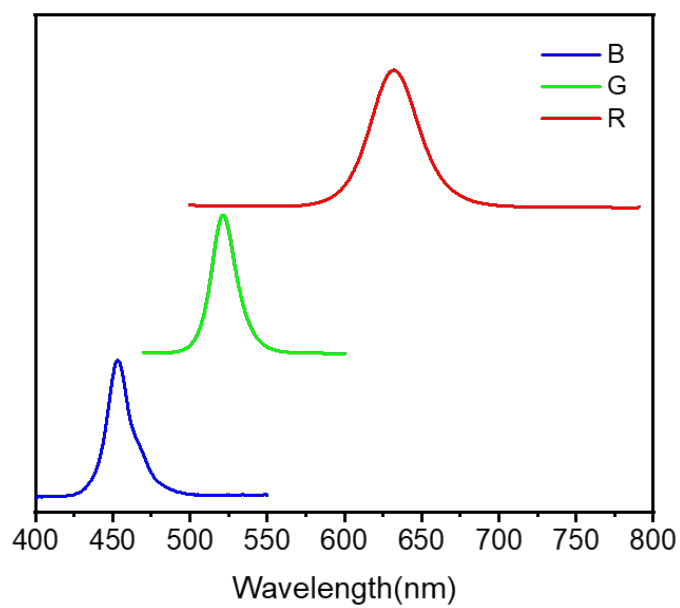


Fig. S14 PL emission spectra of blue chip, CsPbBr₃ nanocrystal composite film and CsPbI₃ QDs composite film of the LED backlight.

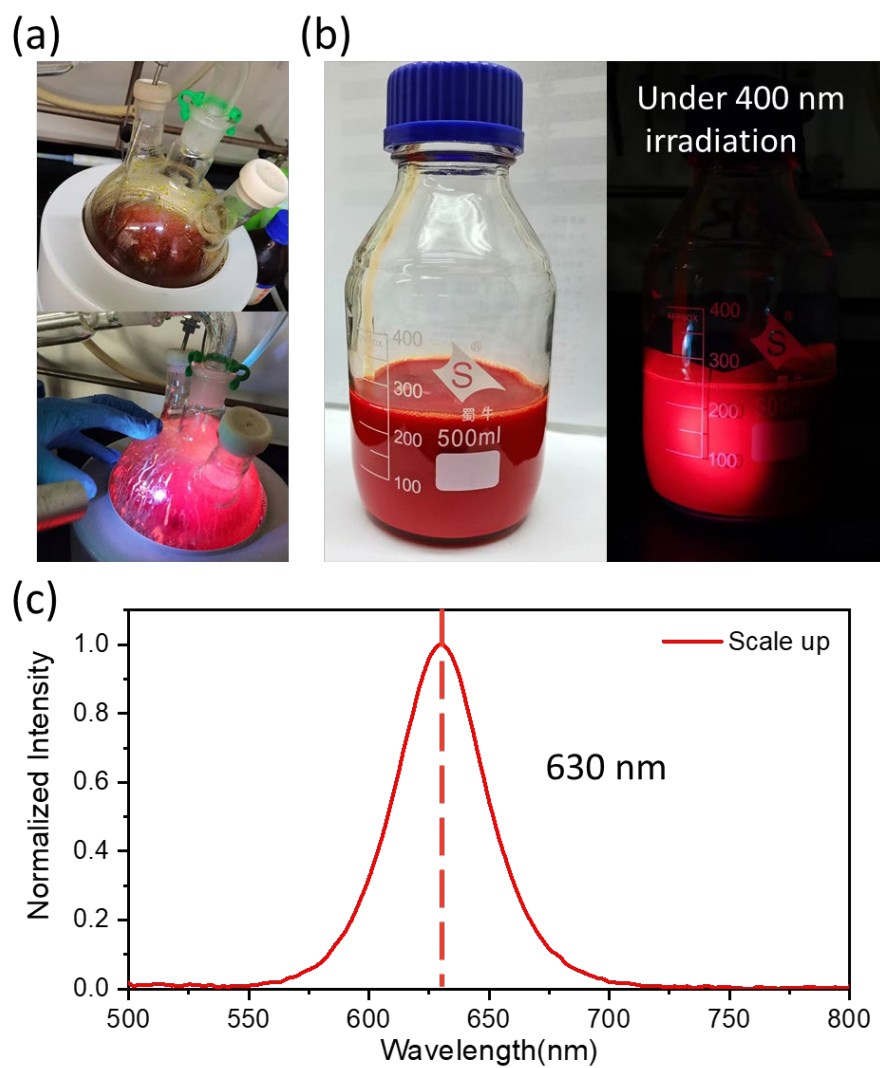


Fig. S15 Photograph of (a) reaction in 1L round bottom flask and (b) collected QD solution. (c) PL emission spectra of dilute pristine CsPbI₃ QDs through scale up method.