

Supporting information

Shape-Controlled Synthesis of CsPbBr₃ Nanorods with Bright Pure Blue Emission and High Stability

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1. Experimental details.

Materials and Chemicals:

Cesium carbonate (Cs_2CO_3 , 99.9%, Aladdin), lead bromide (PbBr_2 , 99%, Aladdin), oleic acid (OA, analytically pure (AR), Aladdin), oleylamine (OAm, 80-90%, Aldrich), octadecene (ODE, >90%, Macklin), ethylacetate (EAC, 99%, Macklin), isopropanol (IPA, $\geq 99.5\%$, Macklin), n-Hexane (AR, Macklin), deionized water, methyl acetate (MAC, 98%, Aladdin), butyl acetate (BAC, AR, Aladdin) acetone (99.5%, KESHI), Protein Content Assay Kit (Macklin), PEDOT: PSS solutions (A14083 CLEVIOS), PTAA (Xi'an Polymer Light Technology Corp), Chlorobenzene (MCB AR, Aldrich), PO-T2T (Xi'an Yuri solar co., Ltd), lithium fluoride (LiF , Luminescence Technology Corp.), All reagents were used as received without further purification.

Preparation of Cs-Oleate:

Cs_2CO_3 (0.4 g) was loaded into a 50 mL three-necked flask along with ODE (18 mL) and OA (2 mL), dried for 1 h at 120 °C, Heat to 150 °C under N_2 and hold for 30 minutes until Cs_2CO_3 fully reacts with OA. Free cooling at room temperature. Because Cs-oleate precipitates out from ODE at room temperature, it must be preheated to injection temperature before the following injection process.

Synthesis and Purification of CsPbBr_3 NRs:

Add 0.207g PbBr_2 and 15mL ODE to a 50ml three necked flask. Vacuum the mixed solution at room temperature. Then introduced N_2 into the flask to remove H_2O and O_2 , repeating the process three times. Vacuum dried at 120 °C for 30 minutes. Then, OA (0.9 mL) and OAm (2.1 mL) were injected into a three necked flask at 120 °C under N_2 flow. After completed dissolution of PbBr_2 in ODE, the temperature was lowered to the predetermined temperatures (60, 70 and 80 °C), and a cesium oleate ODE solution

(1.2 mL) was quickly injected. After 10 seconds, the reaction mixture was cooled by an ice water bath. The injection speed of Cs-OA precursor was accelerated using 0.61 mm diameter syringe needles, which was helpful for obtaining uniform and tiny nucleus. Added different components of anti-solvents (EAC, MAC, BAC, IPA, IPA, and a mixture of EAC) to the crude solution to make the volume ratio of the crude solution to the anti-solvent 1:1, and then centrifuge at 10000 rpm for 5 minutes to purify the sample. After centrifugation, the precipitate was dispersed into an anti-solvent with the same composition as the first step for centrifugation, and centrifuged at 8000 rpm for 3 minutes. The final CsPbBr₃ NRs were dispersed in 2 mL of hexane for further use.

Bicinchoninic acid (BCA) assay:

Reagent A and reagent B in Protein Content Assay Kit were mixed in a ratio of 50:1 as working solution, and preheat in a 60 °C water bath for more than 30 minutes. First, took the EP tube and add 20 µL in sequence standard and 1000 µL preheated working solution, mixed well and placed in a 60 °C water bath for insulation for 30 minutes. Cool with running tap water for 10 minutes, measure at 562 nm, and recorded the absorbance value. Took the EP tube and added 20 µL in sequence test solution and 1000 µL preheated working solution, mixed well and placed in a 60 °C water bath for insulation for 30 minutes. Cooled with running tap water for 10 minutes, measured at 562 nm, and recorded the absorbance value.

Added a mixture of EAC and IPA of the same volume but in different proportions to a solution of OA: OAM=3:7, and centrifuged for five minutes at a speed of 10000 rpm/min.

Under alkaline conditions, peptide bonds can reduce Cu²⁺ to Cu⁺; Two molecules of BCA combine with Cu⁺ to form a purple clathrate with a strong absorption peak at 562 nm. According to formula S1, the concentration of amide can be calculated as

shown in Table S3.

$$\begin{aligned} C_{pr(\text{mg/ml})} &= C_{\text{standard}} \times (A_{\text{sample}} - A_{\text{blank}}) \div (A_{\text{standard}} - A_{\text{blank}}) \\ &= 0.05 \times (A_{\text{sample}} - A_{\text{blank}}) \div (A_{\text{standard}} - A_{\text{blank}}) \end{aligned} \quad (\text{S1})$$

2. LED Fabrication and Performance Test:

Indium tin oxide (ITO) patterned glass was ultrasonically cleaned with deionized water, isopropanol and acetone for three times. Afterwards, the substrate was dried under N₂ and treated by UV-ozone for 15 min. Under environmental conditions, PEDOT:PSS was spin-coated on the surface of ITO substrate at 4000 rpm for 50 s, and then heated at 140 °C for 20 minutes. PTAA was dissolved in chlorobenzene to make a solution of 6 mg mL⁻¹. The solution was spin-coated on the PEDOT:PSS layer at 2000 rpm for 60 s and annealed at 120 °C for 20 min under N₂. Then CsPbBr₃ NRs in n-Hexane were spin-coated onto the PTAA layer at 1000 rpm for 60s and baked at 60 °C for 5 min. finally, under a high vacuum (~2×10⁻⁴ Pa), PO-T2T (40 nm) and LiF/Al electrodes (1 nm/100 nm) were deposited by thermal evaporation system with shadow mask. The active area of as-prepared device was 4 mm². In order to obtain the current-voltage characteristics, the working efficiency of as-prepared LED device was explored on Keithley 2400 Source Meter. The luminescence characteristics of the device (luminous flux of the silicon photodiode and the electroluminescence (EL) spectrum of the device) were obtained by using PR-670 spectroscopic sweep luminance meter and a Marine optical Jaz spectrometer, respectively. Assuming that the emission of LED presents Lambert mode, EQE used to characterize LED can be calculated according to L-J-V and EL measurements. External quantum efficiency (η_{EQE}) is the ratio of the number of photons emitted from the LEDs to the number of charge carriers injected into the device, which can be expressed as:

$$\eta_{EQE} = \frac{q}{hcf} \times \frac{\int \lambda S(\lambda) d\lambda}{\int S(\lambda) R(\lambda) d\lambda} \times \frac{I_{det}}{J_D A} \quad (1)$$

where q is the electric charge, h is Planck's constant, c is the speed of light, f is the geometry factor (representing the fraction of emitted photons reaching the detector), I_{det} is the photocurrent, A is the device area, and J_D is the injection current density to LEDs. η_{EQE} can also be calculated from the luminous power efficiency, which is:

$$\eta_{EQE} = \frac{qV}{hc} \times \frac{\int \lambda S(\lambda) d\lambda}{\int G(\lambda) S(\lambda) d\lambda} \times \eta_{PE} \quad (2)$$

Power efficiency (η_{PE}) is defined as the ratio of the output luminous flux to the input power of LEDs can be expressed as:

$$\eta_{PE} = \frac{L}{J_D} \times \frac{\pi}{V} \quad (3)$$

where V is the applied voltage to LEDs, L is luminance.

3. Characterizations:

Transmission electron microscope (TEM) was measured using Thermofisher talosF200X G2 with an accelerating voltage of 120 kV to describe morphologies and crystal structure. High resolution electron microscope (HRTEM) with mapping mode of energy dispersive X-ray spectroscopy (EDS) was characterized with a Transmission electron microscopy (SUPER X). X-ray diffractometers (D/Max 2500 PC and D8 ADVANCE) were used to obtain diffraction patterns. In optical characterization, spectrometer (UV-8000, METASH) was used to record the UV-vis spectra of NCs dispersed in n-hexane using transmission mode. Spectrofluorometer equipped with a time-correlated single-photon counting system (Fluorolog-3, HORIBA) was used to collect photoluminescence (PL) and carrier lifetime. To evaluate thermal stability, the

PL spectra of CsPbBr₃ nanorods (Linkam, THMS 600) aged at different temperatures were recorded using a variable temperature fluorescence spectrometer (Ocean Optics, USB2000+).

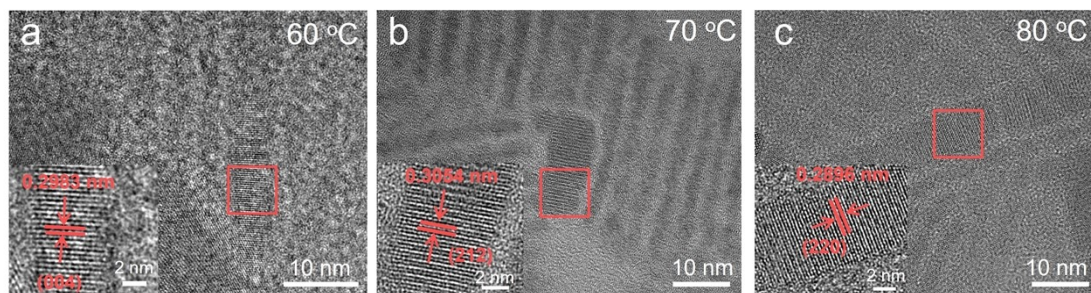


Figure S1. HRTEM image of CsPbBr₃ NRs.

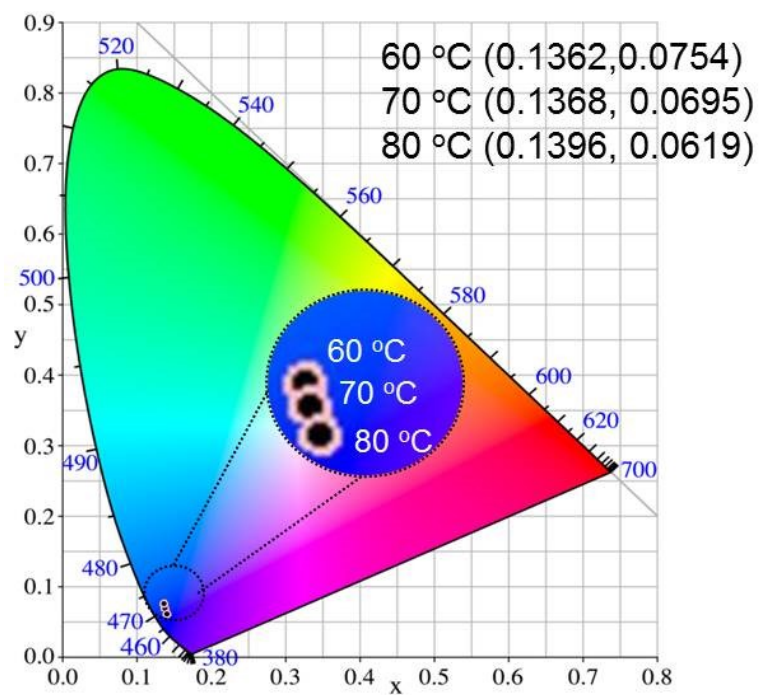


Figure S2. CIE coordinate of the synthesized CsPbBr₃ NRs.

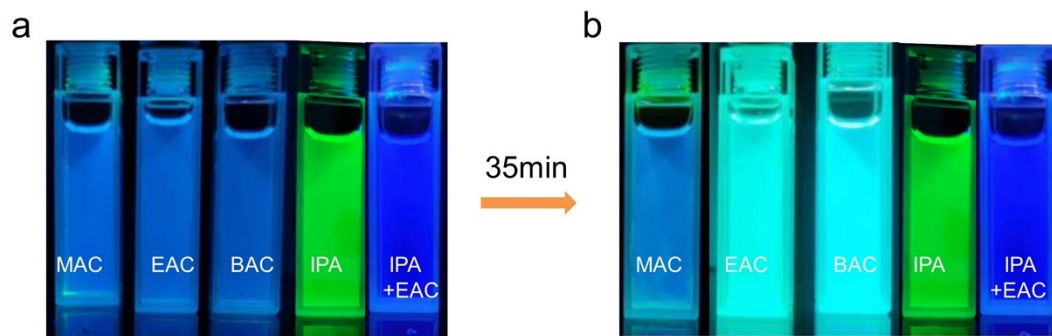


Figure S3. Photos of emission of CsPbBr₃ NRs (under 365 nm UV light) synthesized at 80 °C purified with MAC, EAC, BAC, IPA, IPA, and EAC solutions (a) initial and (b) after 35 min.

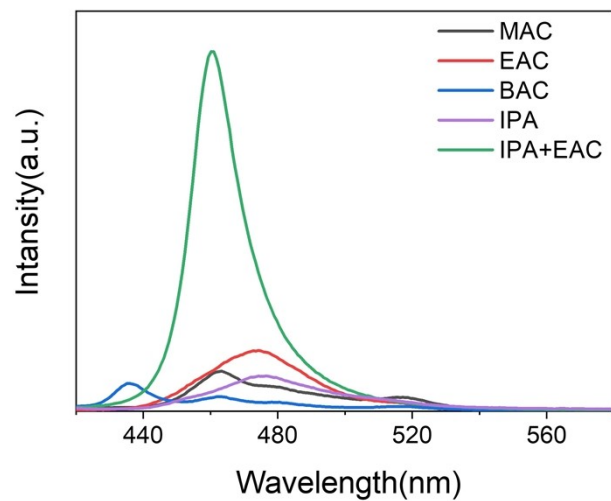


Figure S4. PL spectra of CsPbBr₃ NRs purified with different anti-solvent.

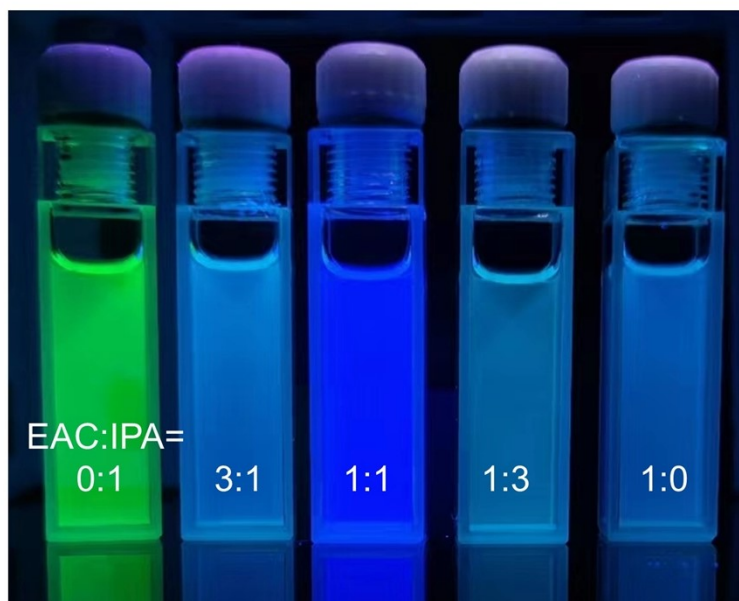


Figure S5. Effect of EAC and IPA ratio on PL spectra of CsPbBr₃ NRs under 365 nm irradiation.

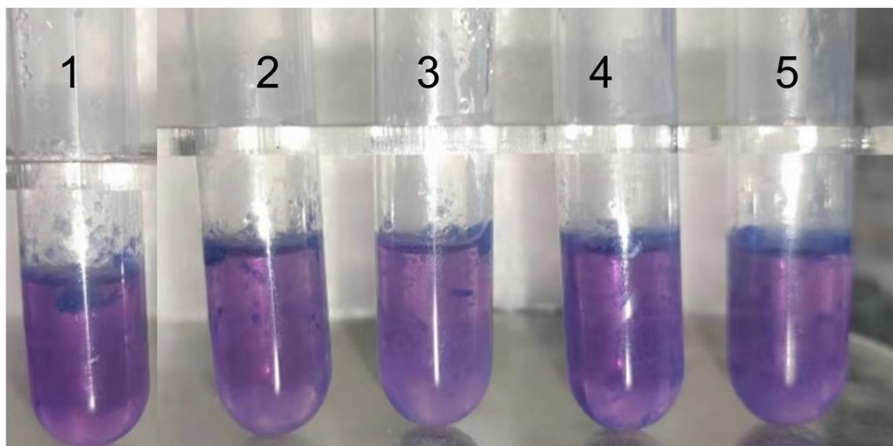


Figure S6. Two molecules of BCA combine with Cu^+ to generate a purple clathrate.

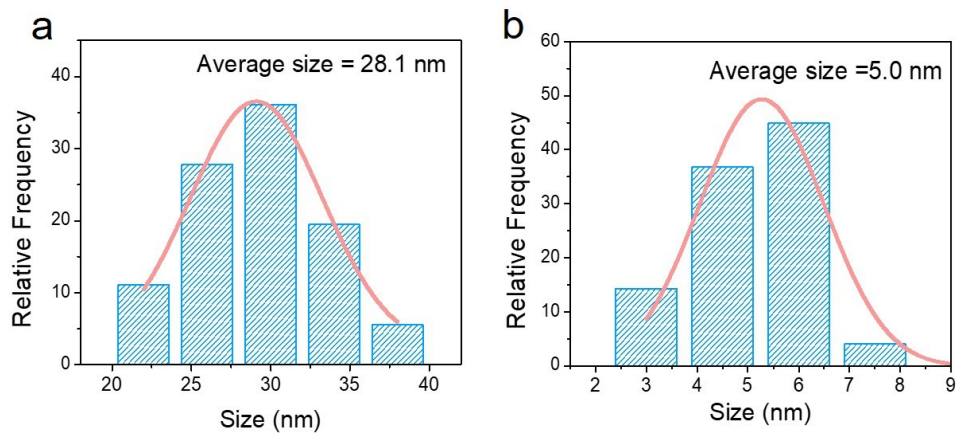


Figure S7. Size statistics of CsPbBr₃ NCs washed with pure EAC and EAC/IPA mixed solvents after added water.

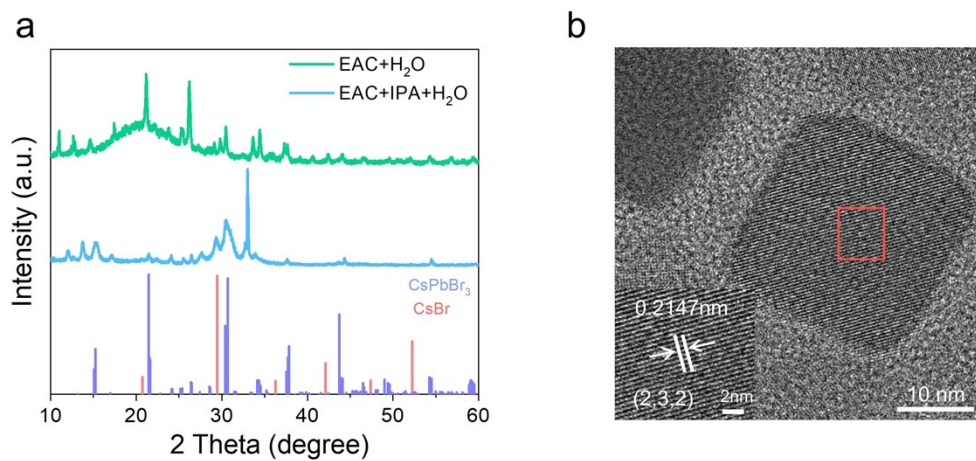


Figure S8. (a) XRD patterns of NRs purified with EAC and a mixture of EAC and IPA after the action of trace amounts of water. (b) HRTEM of NRs phase transformed into NCs under the action of water.

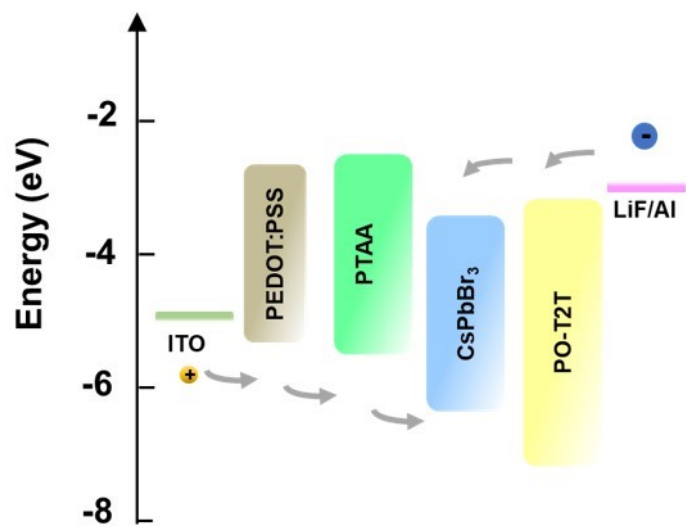


Figure S9. Energy-level diagram of the LED device structure.

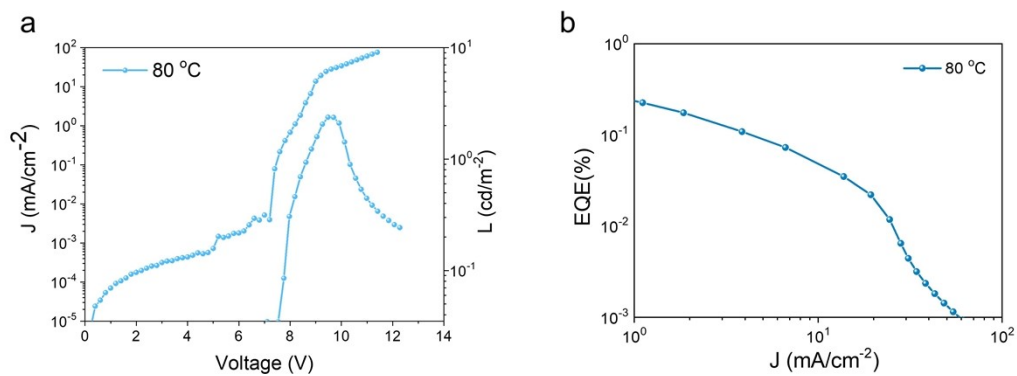


Figure S10. (a) Current density and luminance versus driving voltage curves for the LED based on 80 °C-CsPbBr₃ NRs films. (b) EQEs of perovskite LEDs based on CsPbBr₃ NRs film at different current densities.

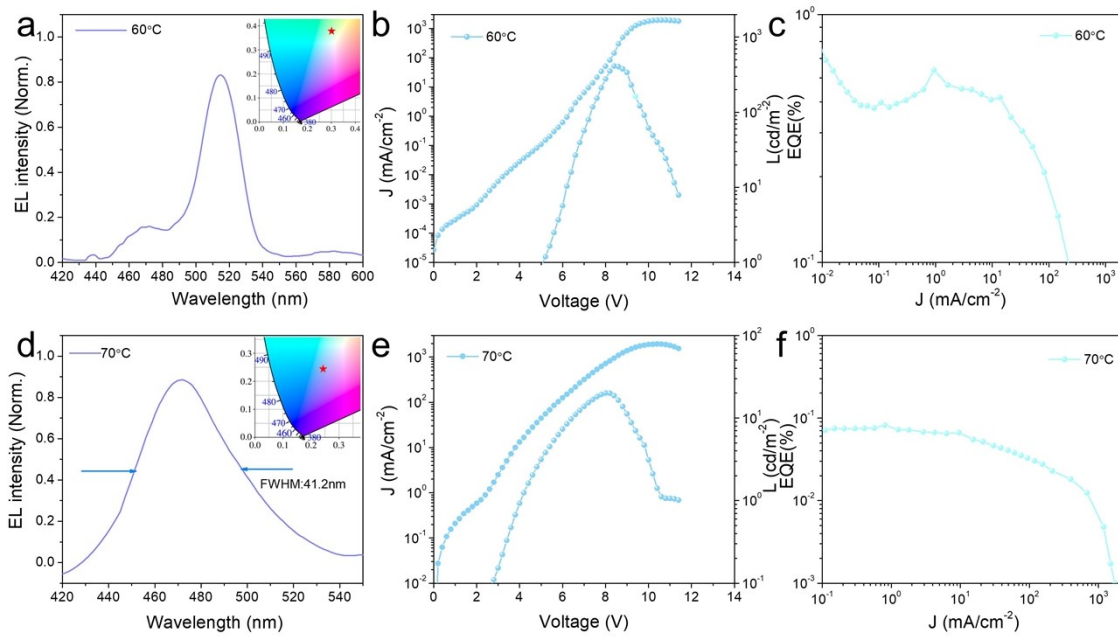


Figure S11. EL spectra, current density and luminance versus driving voltage curves, EQEs of the perovskite LED based on the 60、70 °C-CsPbBr₃ NRs films.

Table S1. Detailed information on PL lifetimes.

sample	τ_1	τ_2	τ_{ave}
60 °C	4.98ns	20.63ns	6.19ns
70 °C	5.14ns	36.52ns	9.91ns
80 °C	5.17ns	29.78ns	6.91ns

Table S2. Comparison of stability of blue light perovskite nanomaterials.

Material compositions	Wavelength (nm)	FWHM (nm)	PLQY (%)	Stability in air	Ref.
CsPbBr ₃ NCs	460	12	98	60 days	1
CsPbBr ₃ NCs	480	21	91	45 days	2
CsPbBr ₃ @Hal	460-489	25	~32	60 days	3
CsPbBr ₃ (Ni ²⁺) NPLs	~454	14.1	78	30 days	4
CsPbBr ₃ NPLs	460	20	80	8 days	5
CsPb(Br/Cl) ₃ (Cu ²⁺)	453	23	80	30 days	6
CsPbBr ₃ (C ₆ H ₁₅ O ₃ P) NPLs	450	15	40	1 month	7
CsPbBr ₃ (Sb ³⁺) NCs	461	14	73.8	20 days	8
CsPbBr ₃ NPLs polysalt-[Pb _x Br _y] _{2x-y}	460	16	80	10 days	9
CsPbBr ₃ (Lu ³⁺) NPLs	430	—	25.3	25 days (85%)	10
CsPbCl ₃ (Cu ²⁺) NCs	430-460	14	92–98	6 days (10%)	11
CsPbCl ₃ (Y ³⁺) NCs	404	—	60	14 days (100%)	12

CsPbCl ₃ (Cd) NCs	413	9	85	10 days (86%)	¹³
CsPbCl ₃ (Mg ²⁺) NCs	403	—	7	30 days (>90%)	¹⁴
CsPbCl ₃ (Fe ³⁺) NCs	410	18	4.32	30 days	¹⁵
CsPbBr ₃ NRs	462	15.8	62.6	120 days	This work

Table S3. Calculated the amount of oleyl oleamide by BCA method.

Number	1	2	3	4	5
OA:OAM	3:7				
EAC:IPA	1:1	1:0	0:1	2:1	1:2
Absorption	0.892105	0.747963	0.603259	0.710312	0.688115
Concentration (mg/mL)	0.034236	0.018803	0.003309	0.014771	0.012395

References:

- 1 J.J. Cao, C. Yan, C.Luo, W. Li, X. K. Zeng, Z. Xu, X. H. Fu, Q. Wang, X. Chu, H. C. Huang, X. Y. Zhao, J. Lu, W. Q. Yang, Cryogenic-Temperature Thermodynamically Suppressed and Strongly Confined CsPbBr₃ Quantum Dots for Deeply Blue Light-Emitting Diodes. *Adv. Optical Mater.*, 2021, 2100300.
- 2 C. H. Bi, S. X. Wang, S. V. Kershaw, K. B. Zheng, T. Pullerits, S. Gaponenko, J. J. Tian, A. L. Rogach, Spontaneous Self-Assembly of Cesium Lead Halide Perovskite Nanoplatelets into Cuboid Crystals with High Intensity Blue Emission, *Adv.Sci.*2019., 6, 1900462.
- 3 Y. Zhao, Z. Y. He , F. Y. Ren , W. Xia, X. J. Liang , L. L. Zhai, W. D. Xiang, One-step preparation of blue-emitting CsPbBr₃ quantum dots loaded on natural mineral halloysite nanotube, *Appl Clay Sci.*, 2021, 106110.
- 4 S. J. Su, J. Q. Tao, C. Sun, D Xu, H Zhang ,T Wei, Z. H. Zhang, Z. Y. Wang, C. Fan, W. G. Bi, Nickel-bromide passivation strategy enabled highly efficient blue-emitting CsPbBr₃ nanoplates for monochrome LED application, *Opt Mater.*, 138. 2023. 113611.
- 5 H. R. Wang, F. H. Ye, J. Y. Sun, Z. J. Wang, C. Zhang, J. Y. Qian, X. Y. Zhang, W. C. H. Choy, X. W. Sun, K. Wang, W. W. Zhao, Efficient CsPbBr₃ Nanoplatelet-Based Blue Light-Emitting Diodes Enabled by Engineered Surface Ligands, *ACS Energy Letters* ., 2022, 3, 1137–1145.
- 6 C. H. Bi, S. X. Wang, Q. Li, S. V. Kershaw, J. J. Tian, A. L. Rogach, Thermally Stable Copper(II)-Doped Cesium Lead Halide Perovskite Quantum Dots with Strong Blue Emission, *J. Phys. Chem. Lett.*, 2019, 10, 943–952. *ACS Energy Lett.*, 2022, 7, 1137–1145.
- 7 J. Shamsi, D. Kubicki, M. Anaya, Y. Liu, K. Ji, K. Frohna, C. Grey, R. Friend and S. Stranks, Stable

Hexylphosphonate-Capped Blue-Emitting Quantum-Confined CsPbBr₃ Nanoplatelets, *Acs Energy Lett.*, 2020, 1900-1907.

8 X. T. Zhang, H. Wang, Y. Hu, Y. X. Pei, S. X. Wang, Z. F. Shi, V. L. Colvin, S. N. Wang, Y. Zhang, W. W. Yu, Strong Blue Emission from Sb³⁺-Doped Super Small CsPbBr₃ Nanocrystals, *J. Phys. Chem. Lett.*, 2019, 10, 8, 1750–1756

9 S. S. Wang, W. T. Wang, S. Donmez, Y. Xin, H. Mattoussi, Engineering Highly Fluorescent and Colloidally Stable Blue-Emitting CsPbBr₃ Nanoplatelets Using Polysalt/PbBr₂ Ligands, *Chem. Mater.*, 2022, 34, 4924–4936.

10 Q. X. Cao, A. Ilyas, S. Zhang, Z. J. Ju, F. L. Sun, T. Y. Liu, Y. Yang, Y. H. Lu, X. F. Liu, R. R. Den, Lanthanide-doping enables kinetically controlled growth of deep-blue two-monolayer halide perovskite nanoplatelets. *Nanoscale.*, 2021, 13, 11552–11560.

11 A. De, S. Das, N. Mondal, A Samanta, Highly Luminescent Violet- and Blue-Emitting Stable Perovskite Nanocrystals, *ACS Materials Lett.*, 2019, 1, 116–122.

12 G. H. Ahmed, J. K. El-Demellawi, J. Yin, J. Pan, D. B. Velusamy, M. N. Hedhili, Erkki Alarousu, O. M. Bakr, H. N. Alshareef, O. F. Mohammed, Giant Photoluminescence Enhancement in CsPbCl₃ Perovskite Nanocrystals by Simultaneous Dual-Surface Passivation, *ACS Energy Lett.* 2018, 3, 2301–2307.

13 C. Xie, Y. B. Zhao, W. B. Shi, P. Yang, Postsynthetic Surface-Treatment of CsPbX₃ (X = Cl, Br, or I) Nanocrystals via CdX₂ Precursor Solution toward High Photoluminescence Quantum Yield, *Langmuir* 2021., 37, 3, 1183–1193.

14 S. Das, A. De, A. Samanta, Ambient Condition Mg²⁺ Doping Producing Highly Luminescent Green- and Violet-Emitting Perovskite Nanocrystals with Reduced Toxicity and Enhanced Stability, *J. Phys.*

Chem. Lett., 2020, 11, 1178–1188.

15 P. J. S. Rana, T. Swetha, H. Mandal, A. Saeki, P. R. Bangal, S. P. Singh, Energy Transfer Dynamics of Highly Stable Fe³⁺ Doped CsPbCl₃ Perovskite Nanocrystals with Dual-Color Emission. J. Phys.

Chem. C., 2019, 123, 17026–17034.