

Supporting Information

Bromopropane as Novel Bromine Precursors for the Completely Amine Free Colloidal Synthesis of Stable and Highly Luminescent Green-Emitting Cesium Lead Bromide (CsPbBr₃) Perovskite Nanocrystals

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Experimental section:

Materials:

Cesium carbonate (Cs₂CO₃, 99.9%), lead acetate (Pb(OAc)₂, 98%), oleic acid (OA, 90%), and oleylamine (OAm, 90%) were purchased from Alfa Aesar. Bromopropane (99%), n-triethylphosphine (TOP, 90%), and 1-octadecene (ODE, 90%) were purchased from Sigma Aldrich. All the above-mentioned chemicals were used without any further purification.

We have synthesised in open air atmospheric condition for all these CsPbBr₃ PNCs using the 800 rpm with magnetic stirrer.

Synthesis of Cesium-oleate solution:

In typical synthesis of Cesium-oleate solution, Cs₂CO₃ (0.2 g, 0.046mmol), ODE (7.5 mL) and OA (0.88 mL, 5mmol) were taken in 25 mL round bottomed flask and dried at 120 °C for 1 hour with continuous stirring until Cs₂CO₃ was completely dissolved and form the clear solution of Cs-oleate. It was again preheated at 100 °C before use because the Cs-oleate precipitates at room temperature.

Synthesis of completely amine-free (Bromopropane) CsPbBr₃ PNCs:

For synthesis of completely amine free Bromopropane CsPbBr₃ PNCs taken from our previously reported work with some modifications.¹ In two necked round bottomed flask, Pb(OAc)₂ (61.15 mg, 0.188 mmol), ODE (2mL) and OA (0.25 mL, 0.79 mmol) were taken and kept for continuous stirring with up to 100 °C and then TOP (0.5 mL, 1.12 mmol) and Bromopropane (68.3 μL, 0.752 mmol) were added after dissolving the Pb(OAc)₂. To get the clear solution the temperature was raised to 150-160 °C, at this temperature the preheated Cesium oleate (0.4 mL, 0.125M) was shiftily injected into the reaction mixture, after 30 Sec the reaction was quenched using ice water bath; CsPbBr₃ PNCs were formed with bright green colour. We have varied the various concentrations of Bromopropane (μL, mmol), TOP (mL, mmol), Cesium oleate (μL, mmol) and lead acetate (mg, mmol) were shown in the below tables. As synthesised crude CsPbBr₃ PNCs were purified by centrifuging at 6000 rpm for 8 minutes and precipitate was dispersed in hexane and supernatant was discarded. These CsPbBr₃ PNCs were further used for various characterizations and other studies as mentioned.

Synthesis of conventional Amine method:

Amine-CsPbBr₃ PNCs were adopted from the previously reported method.² In short, where PbBr₂ was taken along with OAm and OA in ODE at temperature 140 °C, Cesium oleate was injected, to get the CsPbBr₃ PNCs.

Characterizations and its sample preparations:**UV-VIS absorption and Photoluminescence PL measurements:**

The UV- Visible absorption spectra recorded using the UV-Vis spectrophotometer UV-2600i Shimadzu. Photoluminescence spectra were measured using the FluoroLog-3 (Horiba Jobin Yvon) using the excitation wavelength of $\lambda_{\text{ex}} = 350$ nm for all the samples. All synthesised CsPbBr₃ PNCs were diluted using the Hexane and recorded using the quartz cuvettes with path length of 1 cm.

Photoluminescence PL Quantum Yields PLQY:

Photoluminescence quantum yields were measured using the cumarine 153 dye molecule as reference in ethanol with QY=0.546. For the PLQY measurement we have matched the solutions of C-153 dye in ethanol and PNCs in hexane with an Optical density of 0.17 at wavelength $\lambda = 420$ nm. The identical instrumental settings were used to measure the areas under the fluorescence spectra curves.

Time resolved PL measurements:

Time resolved photoluminescence measurements were measured by time correlated single photon counting by TCSPC instrument (Horiba Jobin Yvon IBH) with a output, $\lambda_{\text{ex}} = 372$ nm using laser diode as excitation source. Instrument was measured by recording the excitation profile by placing a scatterer solution (ludox in water) in place of the sample which act as scatter in the sample chamber. The fluorescence decay curve profiles were analysed by nonlinear least-squares iteration procedure using IBH DAS6 (version 2.2) decay analysis software.

Fourier Transform Infrared Spectroscopy (FTIR) measurement:

CsPbBr₃ PNCs dispersed in hexane with few microliters was used to measured ATR-FTIR attenuated total reflection- Fourier transform infrared spectroscopy spectra by using Bruker Alpha II spectrometer with broadband MCT detector.

Powder X-ray diffraction (P-XRD) measurement:

The PXRD analysis were performed using Empyrean PANalytical X-Ray Diffractometer using Cu-K α X-radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA power. The specimens were prepared by dropping the concentrated PNCs solution onto a well cleaned glass substrate with 2x2 cm. XRD data analysis was conducted using the High score 4.1 software from PANalytical.

Transmission Electron Microscopy (TEM):

The samples were prepared by dropping optimum solution of CsPbBr₃ PNCs in hexane onto carbon coated copper Cu grids. Low resolution transmission electron microscopy measurements were measured using the JEOL JEM-2100 with operating at an acceleration voltage of 100 kV with 0.23 nm point resolution.

Photostability test measurements:

Photostability test were conducted using the UV chamber with continuous irradiation using a UV light with wavelength of 365 nm with the power density of 8 W/cm². The total experiment was conducted in open air atmospheric room conditions at ~25 °C with 55 % -65 % humidity.

Fabrication of down-converted LEDs:

Down converted LEDs were fabricated by coating these as synthesized PNCs on the commercially available LEDs with wavelength of $\lambda = 400$ nm and taken electroluminescence from initial 0-96 hours at open air atmospheric room conditions with temperature at ~ 25 °C with humidity of 55 % 65 %.

Lifetime components of CsPbBr₃ samples with different precursor concentration ratios Cs:Pb:Br are mentioned in the below tables. Bi-exponential fits of the TCSPC data with the equation:

$$f(t) = A_1 e^{-\frac{t}{\tau_1}} - A_2 e^{-\frac{t}{\tau_2}}$$

τ_{avg} is the intensity-averaged lifetime from a Bi-exponential fit using equation: $\frac{\sum (\alpha_i \tau_i)}{\sum \alpha_i}$.

Table-T1: Variation of different molar ratio of bromopropane Cs:Pb:Br=1:6:6/12/24/36 with TOP-1.12 mmol.

Sample	α_1	τ_1 (ns)	α_2	τ_2 (ns)	τ_{avg} (ns)	CHISQ
0.188 mmol	0.76	4.92	0.24	28.62	10.60	1.15
0.376 mmol	0.52	10.13	0.48	55.99	32.14	0.97
0.752 mmol	0.5	9.26	0.5	52.99	31.12	1.01
1.128 mmol	0.68	4.70	0.32	51.15	19.56	1.13

Table-T2: Variation of TOP concentrations are 0.56, 1.12, 2.24 and 3.36 mmol with Cs:Pb:Br=1:6:24

Sample	α_1	τ_1 (ns)	α_2	τ_2 (ns)	τ_{avg} (ns)	CHISQ
0.56 mmol	0.57	8.18	0.43	53.41	27.62	1.08
1.12 mmol	0.52	10.13	0.48	55.99	32.14	0.97
2.24 mmol	0.5	9.26	0.5	52.99	31.12	1.01

3.36 mmol	0.58	5.08	0.42	52.65	25.05	1.11
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Table-T3: Variation concentrations of Cs precursor (Cs-oleate) Cs: Pb: Br =0.5/1/2:6:24 with TOP-1.12 mmol.

Sample	α_1	τ_1 (ns)	α_2	τ_2 (ns)	τ_{avg} (ns)	CHISQ
0.016 mmol	0.53	9.08	0.47	50.31	28.45	1.12
0.032 mmol	0.52	10.13	0.48	55.99	32.14	0.97
0.064 mmol	0.37	6.89	0.63	79.48	52.62	1.03

Table-T4: Variation concentrations of Pb precursor (Pb(OAc)₂) Cs: Pb: Br=1:3/6/12:24 with TOP-1.12 mmol.

Sample	α_1	τ_1 (ns)	α_2	τ_2 (ns)	τ_{avg} (ns)	CHISQ
0.094 mmol	0.65	8.02	0.35	46.71	21.56	1.04
0.188 mmol	0.52	10.13	0.48	55.99	32.14	0.97
0.376 mmol	0.46	9.36	0.54	74.58	44.57	1.03

Table-T5: PLQY (%) values of variation of different molar ratio of bromopropane Cs:Pb:Br=1:6:6/12/24/36 with TOP-1.12 mmol from the initial and after 120 days.

Sample	PLQY (%) Day-1	PLQY (%) Day-120
0.188 mmol	18.23	-
0.376 mmol	61.49	33.14
0.752 mmol	78.56	64.82

1.128 mmol	49.72	-
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Table-T6: PLQY (%) values of variation of TOP concentrations are 0.56, 1.12, 2.24 and 3.36 mmol with Cs:Pb:Br=1:6:24 from the initial and after 120 days.

Sample	PLQY (%) Day-1	PLQY (%) Day-120
0.56 mmol	35.13	-
1.12 mmol	78.56	64.82
2.24 mmol	69.21	47.54
3.36 mmol	11.09	-

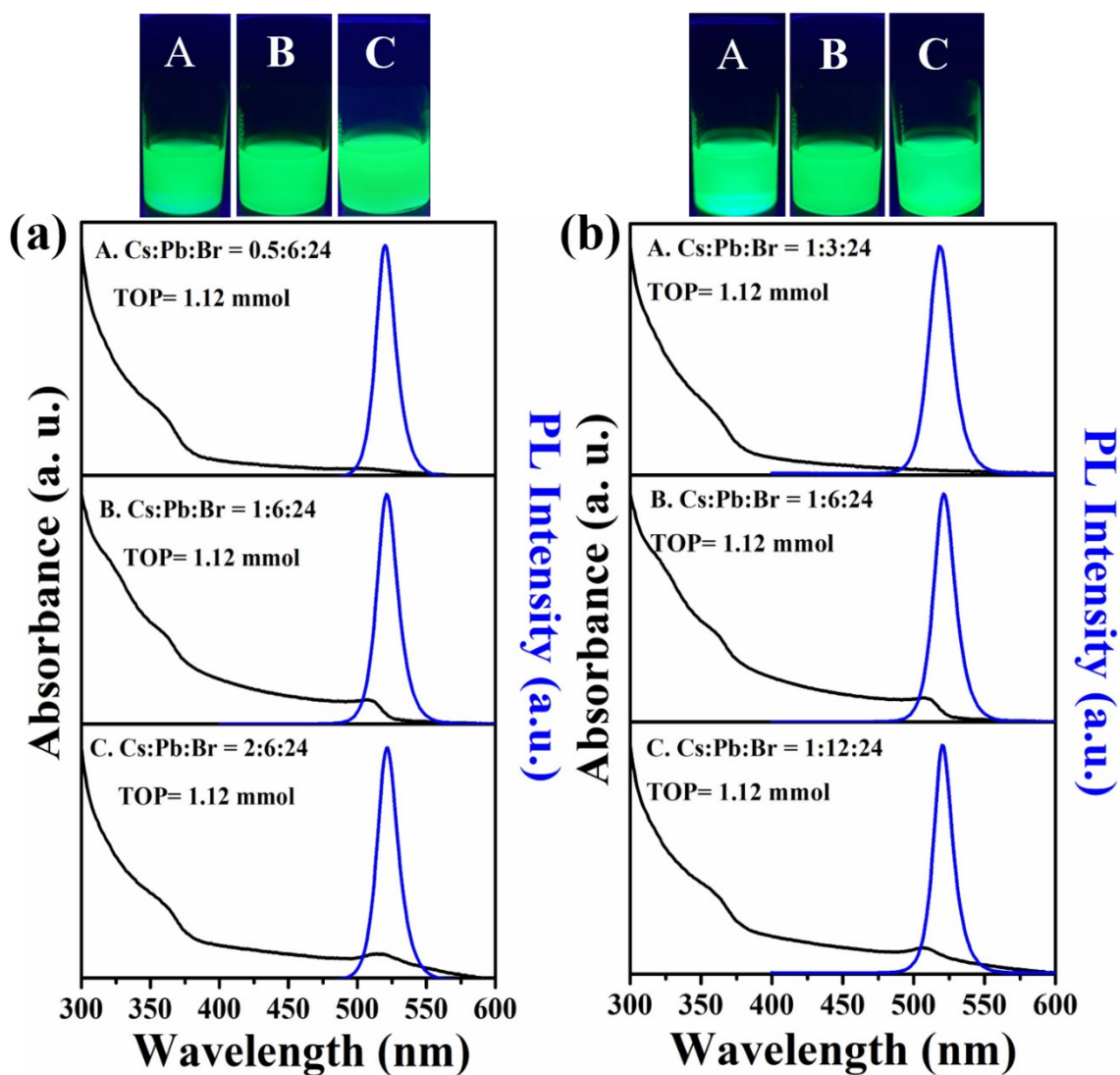


Figure-S1: Absorbance (black line) and Emission (blue line) spectrum of CsPbBr₃ PNCs (a) various concentrations of Cs precursor (Cs-oleate) Cs: Pb: Br =0.5/1/2:6:24 with TOP-1.12 mmol. (b) various concentrations of Pb precursor (Pb(OAc)₂) Cs: Pb: Br=1:3/6/12:24 with TOP-1.12 mmol. The digital images of colloidal solutions of as-synthesized CsPbBr₃ PNCs taken in the vials under UV light irradiation with excitation wavelength at 365 nm.

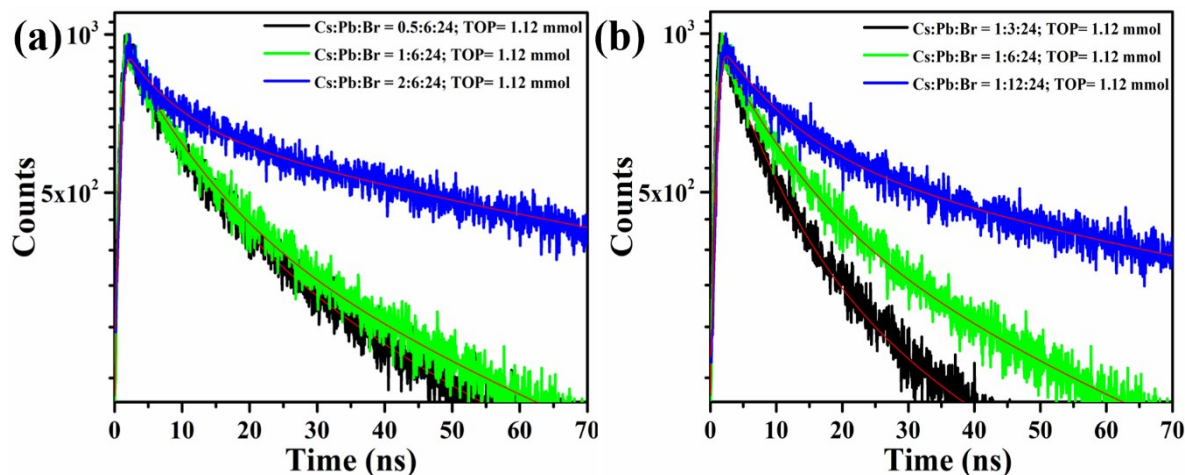


Figure-S2: Photoluminescence decay curves of as-synthesized CsPbBr₃ PNCs (a) with different molar ratio of Cs precursor (Cs-oleate) Cs: Pb: Br =0.5/1/2:6:24 with TOP-1.12 mmol. (b) with variation of Pb precursor (Pb(OAc)₂) Cs: Pb: Br=1:3/6/12:24 with TOP-1.12 mmol.

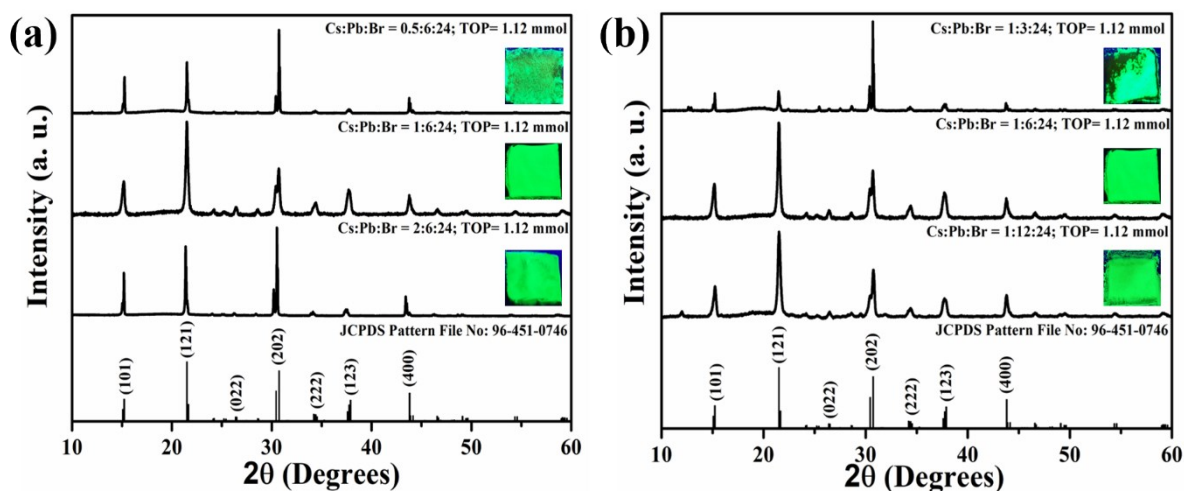


Figure-S3: XRD patterns of CsPbBr₃ PNCs with different optimizations (a) variation of Cs precursor (Cs-oleate) Cs: Pb: Br =0.5/1/2:6:24 with TOP-1.12 mmol. (b) variation of Pb precursor (Pb(OAc)₂) Cs: Pb: Br=1:3/6/12:24 with TOP-1.12 mmol. Inset digital photographs were taken under UV light with of their corresponding films of CsPbBr₃ PNCs.

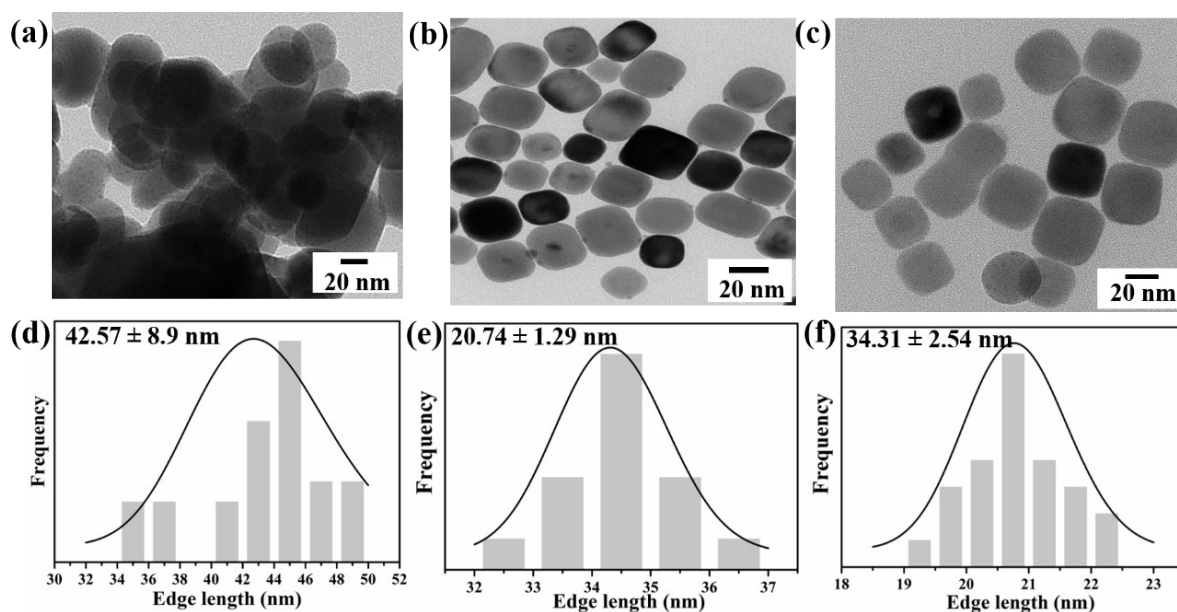
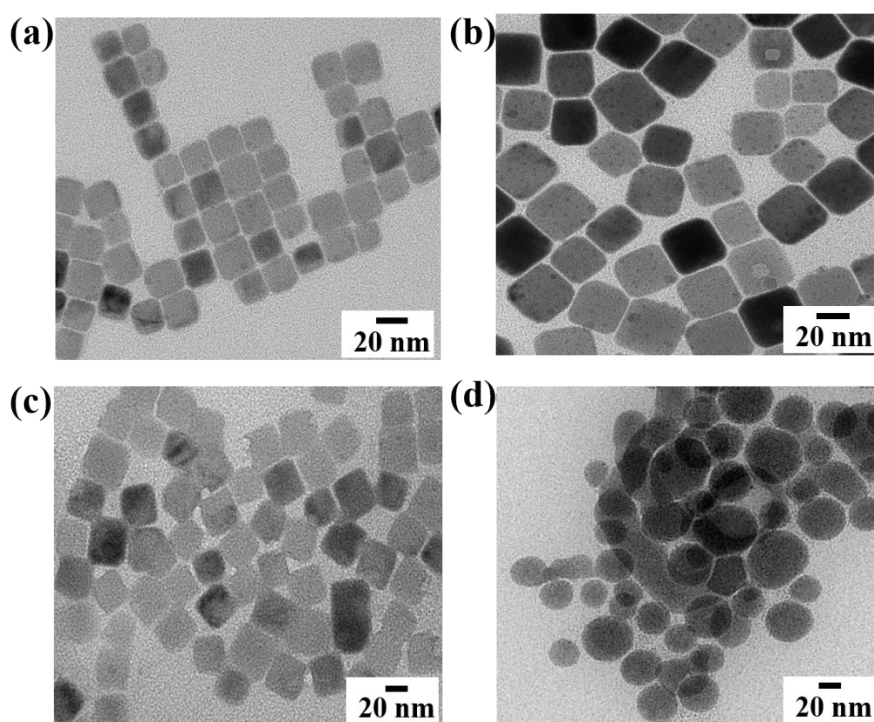


Figure-S4: TEM images of CsPbBr₃ NCs with TOP concentration of 1.12 mmol (a) Cs:Pb:Br=1:6:6 (b) Cs:Pb:Br=1:6:12 and (c) Cs:Pb:Br=1:6:36 with scale bar of 20 nm and (d-f) respective Size histogram analysis considering more than 100 nanocrystals of as-synthesized



CsPbBr₃ perovskite NCs.

Figure-S5: TEM images of CsPbBr₃ NCs with Cs:Pb:Br=1:6:24 and TOP concentrations of a) 0.56, b) 1.12, c) 2.24, and d) 3.6 mmol with scale bar of 20nm.

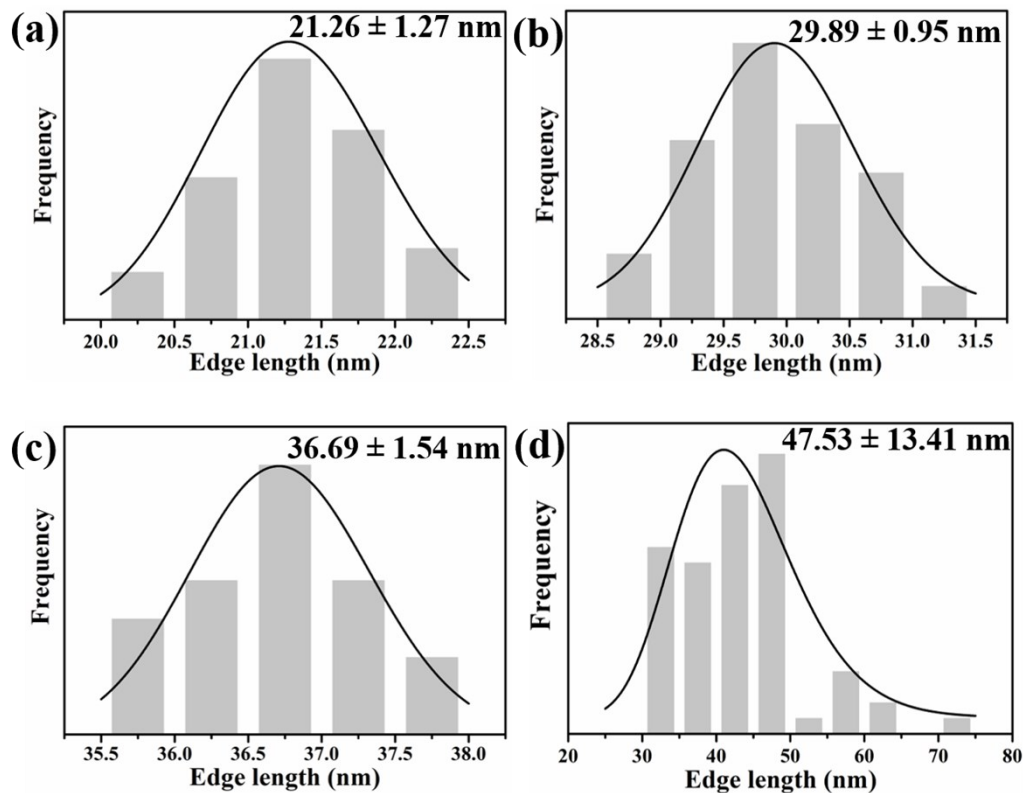


Figure-S6: Size histogram analysis considering more than 100 nanocrystals of as-synthesized CsPbBr₃ perovskite NCs with Cs:Pb:Br=1:6:24 and TOP concentrations of a) 0.56, b) 1.12, c) 2.24, and d) 3.6 mmol.

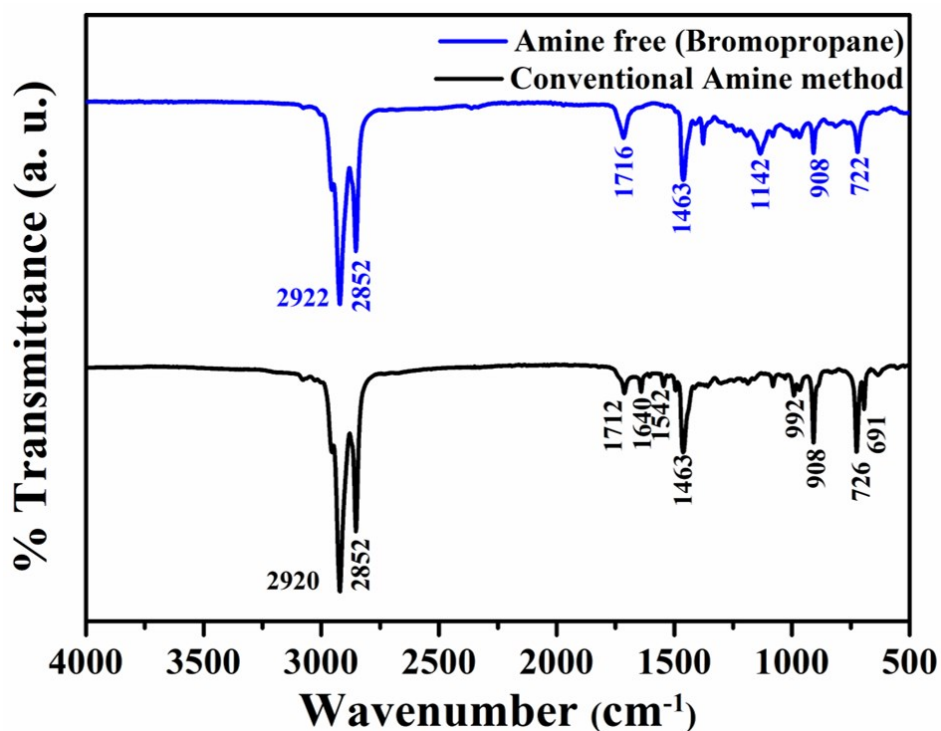


Figure-S7: FTIR Spectra of CsPbBr₃ PNCs synthesised by the completely amine free-Bromopropane (blue line) and conventional amine method (black line).

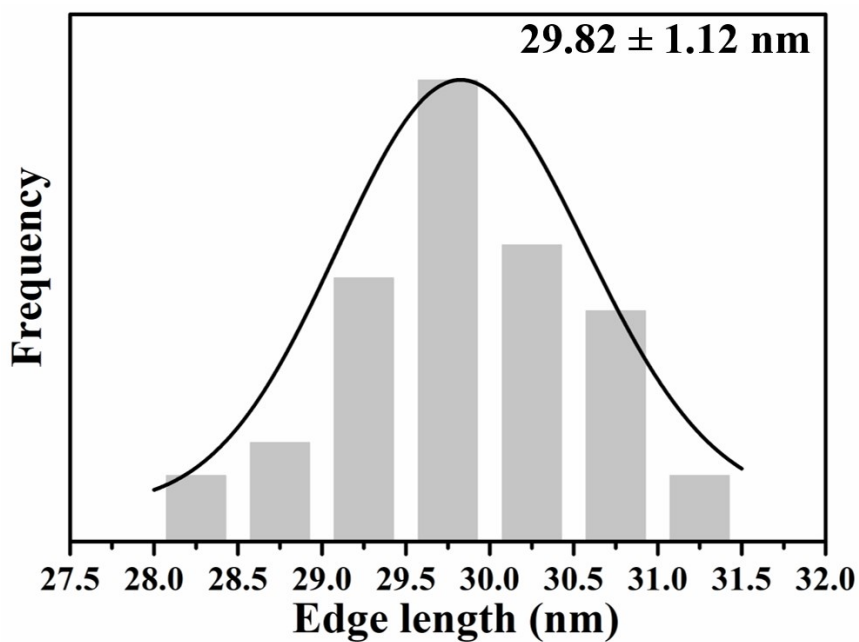


Figure-S8: Size histogram analysis considering more than 100 nanocrystals of as-synthesized CsPbBr₃ perovskite NCs of Cs:Pb:Br=1:6:24 with TOP-1.12 mmol after aging 120 days.

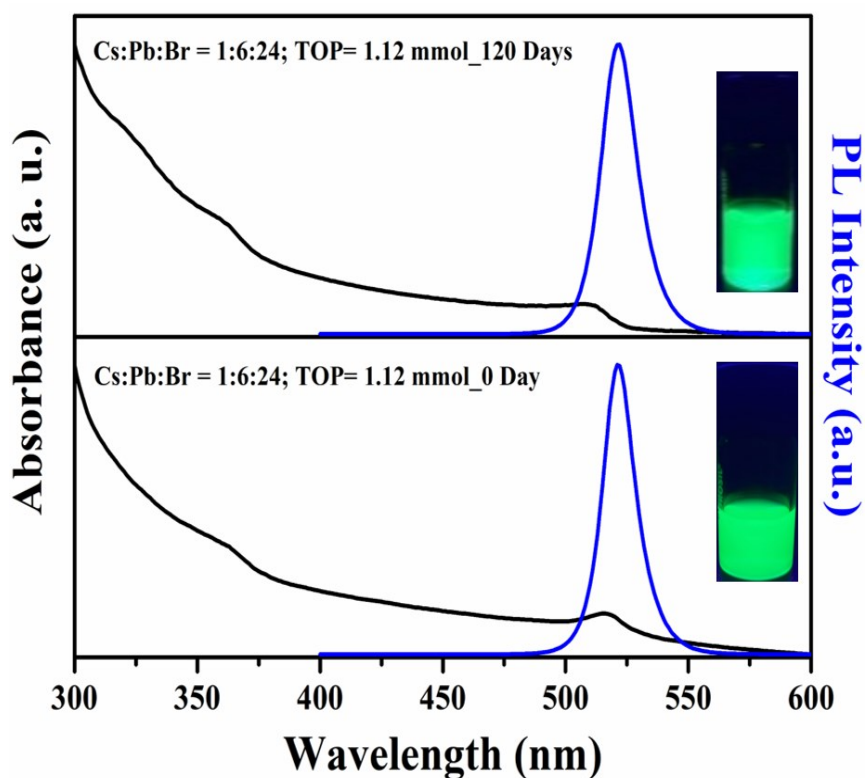


Figure-S9: Absorbance (black line) and PL emission (blue) spectra of amine-free method CsPbBr₃ PNCs colloidal solutions after synthesis (lower) and after ageing 120 days under ambient condition (upper) with inset digital images taken under UV light.

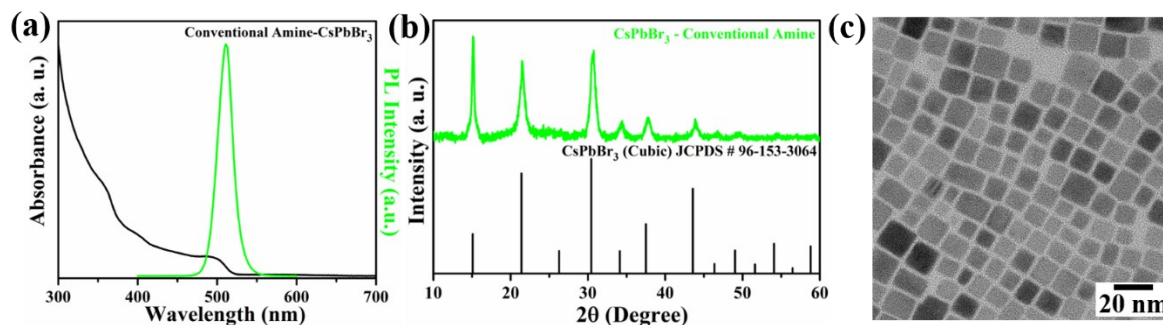


Figure-S10: Synthesized Conventional Amine-CsPbBr₃ PNCs dispersed in hexane (a) Absorbance (black line) and Emission (green line) spectra (b) XRD pattern and (c) TEM image with scalebar of 20 nm.

References:

- (1) Akhil, S.; Dutt, V. G. V.; Mishra, N. Completely Amine-Free Open-Atmospheric Synthesis of High-Quality Cesium Lead Bromide (CsPbBr₃) Perovskite Nanocrystals. *Chemistry – A European Journal* **2020**, *26* (71), 17195–17202. <https://doi.org/10.1002/chem.202003891>.
- (2) Dutt, V. G. V.; Akhil, S.; Mishra, N. Fast, Tunable and Reversible Anion-Exchange in CsPbBr₃ Perovskite Nanocrystals with Hydrohalic Acids. *CrystEngComm* **2020**, *22* (30), 5022–5030. <https://doi.org/10.1039/D0CE00722F>.