# Long-Term Ambient Air-Stable Cubic $CsPbBr_3$ Perovskite Quantum Dots using Molecular Bromine

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### *S1. Materials and Physical Method*

***Chemicals:*** Caesium carbonate ($Cs_2CO_3$, 99.9%, Sigma-Aldrich), lead nitrate ($Pb(NO_3)_2$, (Sigma-Aldrich), lead acetate ($Pb(OAc)_2$ (Sigma-Aldrich), molecular Iodine ($I_2$, 99.5%) was purchased from Nice chemicals, molecular bromine ($Br_2$, ≥99%) was purchased from Sigma-Aldrich, oleic acid (OA, technical grade, Sigma-Aldrich), 1-octadecene (ODE, technical grade, Sigma-Aldrich), oleylamine (OAm, technical grade, Sigma-Aldrich), anhydrous toluene (99.8%, Sigma-Aldrich), and anhydrous hexane (95%, Sigma-Aldrich) were purchased. Degassed OA and OAm were prepared by heating the OA or OLA at 120 $^{o}$C under vacuum overnight and stored in a glovebox.

***UV-Vis spectrophotometer:*** The UV-Visible absorption spectra were collected using Perkin Elmer spectrophotometer (scan rate: 480 nm/s). The sample was dispersed in anhydrous hexane for measurements.

***Vis-NIR spectrofluorometer:*** The PL spectra of $CsPbI_3$ NCs were collected using HORIBA Scientific spectrophotometer (Model: PTI-QM 510). The NCs were dispersed in hexane and the solution was excited at 480 nm.

***UV-Vis spectrofluorometer:*** The PL spectra of $CsPbBr_3$ NCs were collected using Perkin Elmer (Model: LS 55). The NCs were dispersed in hexane and the solution was excited with a wavelength of 400 nm.

***X-ray Diffractometer (XRD):*** The purified NCs in hexane were drop-casted on a clean and dry the glass slide. The film on glass slide was run under the PANalytical X-Ray diffractometer using Cu Kα ($\lambda$= 1.54 Å) as the incident radiation (40 kV and 30 mA).

***X-ray Photoelectron Spectroscopy (XPS):*** XPS samples were fabricated in glovebox on carbon-coated silicon wafers to minimize charging. XPS spectra were obtained using Thermo-Scientific ESCALAB $Xi^+$ spectrometer with Al K$\alpha$ (1486.7 eV) X-ray source. For high-resolution spectra constant analyzer energy (CAE) of 50 eV was used and for survey spectra (CAE) of 100 eV.

***Transmission Electron Microscopy (TEM):*** TEM images were taken in JEOL-JEM-2100 Plus electron microscope. HRTEM images were obtained using a 200-kV electron source. Samples were prepared by drop-casting of nanocrystal solution in hexane on a carbon-coated copper grid, purchased from EMS, the grids were kept overnight in a vacuum desiccator. The average particle size was measured using 400 particles. The lattice plane was obtained from lattice fringes. Image J software was used for calculations.

***Nuclear Magnetic Resonance (NMR):*** $^1$H NMR and 2D (COSY) NMR were obtained in $CDCl_3$ using Bruker ASCEND$^{TM}$ 400.

***Fourier Transform Infrared Spectroscopy (FTIR):*** FT-IR spectra were obtained using Bruker ALPHA E, 200396.

### *S2. Synthesis and Purification*

***Preparation of Cs-oleate solution:*** 812.5 mg (2.5 mmol) of $Cs_2CO_3$ was dissolved in 20 mL ODE and 2.5 mL OA. The solution was degassed at room temperature for 15 min, followed by degassing at 120$^o$C under vacuum until the clear solution was obtained. The solution was kept in an inert atmosphere at 100$^o$C for further use (**solution A**).

***Synthesis of phase stable cubic CsPbBr₃ NCs***: 32.5 mg (0.1 mmol) of lead acetate, 0.2 mL OA, 0.5 mL of OAm and 4 mL of ODE were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 $^o$C for 15 min until the silky white solution was obtained. To this solution, 30.0 μL (0.6 mmol) of $Br_2$ solution taken in 0.1 mL ODE was added rapidly and then degassed under vacuum at 120 $^o$C for 15 minutes. Subsequently, the temperature was maintained at 200 $^o$C under inert ($N_2$) atmosphere. To this solution, 0.4 mL of Cs-oleate (**solution A**) was quickly injected. The reaction was quenched quickly after 10s by immersing the reaction flask in ice-bath.

***Emission tunability of $CsPbBr_3$ NCs:***

Lower wavelength emitting $CsPbBr_3$ NCs could be synthesised the same as above by simply increasing the $Br_2$ concentration and/or decreasing the reaction temperature. In general, increasing $Br_2$ concentration (0.2-1.2 mmol) decreases the emission wavelength at the same temperature (150

$^{o}$C) whereas the increasing the reaction temperature (75-200 $^{o}$C) decreases the emission wavelength at the same $Br_2$ concentration (0.6 mmol). The blue emitting $CsPbBr_3$ NCs ($\lambda_{max}$ 478 nm) can be synthesised under high $Br_2$ concentration 60 µL (1.2 mmol) and low temperature (75 $^{o}$C) conditions.

***Synthesis of $CsPbI_3$ NCs:*** 33.1 mg (0.1 mmol) of lead nitrate, 50.7 mg (0.2 mmol) of $I_2$, 0.2 mL OA, 0.5 mL of OAm and 4 mL of ODE were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 $^{o}$C for 30 min until the clear red solution was obtained. Subsequently, the temperature was maintained at 200 $^{o}$C under inert ($N_2$) atmosphere. To this solution, 0.4mL of Cs-oleate (**solution A**) was quickly injected that gives rise to a red precipitate. The reaction was quenched quickly after 10s by immersing the reaction flask in ice-bath.

***Emission tunability of $CsPbI_3$ NCs:***

Lower wavelength emitting $CsPbI_3$ NCs could be synthesised the same as above by simply increasing the $I_2$ concentration and/or decreasing the reaction temperature. In general, increasing $I_2$ concentration (0.1-0.2 mmol) decreases the emission wavelength at the same temperature (150 $^{o}$C) whereas the increasing the reaction temperature (75-200 $^{o}$C) decreases the emission wavelength at the same $I_2$ concentration (0.2 mmol).

***Purification:*** To 4 mL of the crude solution of $CsPbX_3$ NCs solution, 4 mL of dry/anhydrous toluene was added and the mixture was divided equally into two tubes and was centrifuged at 5000 rpm for 10 min. The solution was decanted, leaving behind the brownish-red ($CsPbI_3$) or yellowish-green ($CsPbBr_3$) precipitate in the tube. To this, 2 mL of anhydrous toluene was added and was centrifuged for 5 min. The NCs were then centrifuged for 3 min with 1 mL of anhydrous hexane and were finally re-dispersed in hexane for further characterization.

### *S3. Determination of Quantum yield (QY)*

Fluorescence quantum yield was determined by comparison of the integrated fluorescent intensity of QDs against the integrated standard (blanks were used as integrated standards– hexane (organic) milli-Q water (aqueous), using an integrating sphere. The sample (including blank) was excited at 480 nm for spectra to be produced in QY measurements. Alternatively, the relative quantum yield of an unknown sample was determined by comparing the emission and absorption of the sample with that of the NCs of known quantum yield (determined by an integrated sphere) using the equation:

$$QY_S = QY_R \times \frac{I_S \times A_R \times {n_S}^2}{I_R \times A_S \times {n_R}^2}$$

Where I is the integrated PL intensity, *n* is the refractive index, and A is the absorbance (at the excitation wavelength). Subscripts *R* and *S* stand for reference and sample respectively.

### *S4. Phase Stability Studies*

For stability of the films, purified NCs were deposited on a clean and dry glass substrate. The sample was stored in the air under ambient condition (25 $^{o}$C, a relative humidity of 50-60 %). The XRD spectra were recorded regularly till the samples exhibited an additional peak accompanied by a change in colour of the film.

For optical stability, the evolution of absorption and emission properties of the as-synthesised crude solution of the NCs were monitored regularly using UV-Vis absorption spectrophotometer and UV-Vis-NIR spectroflourometer.

### *S5. $^1$H NMR study of OA/OAm mixture*

0.5 mL of OAm, 0.5 mL OA and 0.5 mL of ODE were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 $^{o}$C for 30 min until the clear red solution was obtained. Aliquots were taken from the solution maintained at different temperatures (~75-200 $^{o}$C) under $N_2$ atmosphere and $^1$HMR was recorded in $CDCl_3$ using Bruker ASCEND$^{TM}$ 400.

### *S6. $^1$H NMR study of $Br_2$/OAm mixture*

30 µL (0.6 mmol) of $Br_2$, 0.5 mL of OAm and 0.5 mL of ODE were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 $^{o}$C for 30 min until the clear red solution was obtained. Aliquots were taken from the solution maintained at different temperatures (~75-200 $^{o}$C) under $N_2$ atmosphere and $^1$HMR was recorded in $CDCl_3$ using Bruker ASCEND$^{TM}$ 400.

### *S7. $^1$H NMR study of $I_2$/OAm mixture*

50.7 mg (0.2 mmol) of $I_2$, 0.5 mL of OAm and 0.5 mL of ODE were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 $^{o}$C for 30 min until the clear red solution was obtained. Aliquots were taken from the solution maintained at different temperatures (~75-200 $^{o}$C) under $N_2$ atmosphere and $^1$H NMR was recorded in $CDCl_3$ using Bruker ASCEND$^{TM}$ 400.

## *S8. Synthesis of Pristine $CsPbBr_3$ and $PbBr_2$ treated $CsPbBr_3$ following a literature method.*

**Preparation of Cs-oleate solution:** Cs-oleate solution was prepared by dissolving 0.163 g of $Cs_2CO_3$ in 8 mL of ODE with 0.5 mL of OA in a 50 mL 3-neck flask and degassed for 2 h at 110 ℃. After degassing, the solution was further heated to 150 ℃ under nitrogen flow.

**Synthesis of pristine-$CsPbX_3$ NCs.:** 0.138 g of $PbBr_2$ (0.376 mmol), 1 mL of degassed OA, 1 mL of degassed OAm, and 10 mL of ODE were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum degassed at 110 ℃ for 2 h. Subsequently, the temperature was maintained at 170 $^oC$ under inert ($N_2$) atmosphere. To this solution, 0.8 mL of Cs-oleate was quickly injected that gives rise to a fluorescent yellow-green precipitate. The reaction was quenched quickly after 5-10 s by immersing the reaction flask in ice-bath.

**Synthesis of $PbBr_2$-$CsPbBr_3$ NCs.** 0.138 g of $PbBr_2$ (0.376 mmol), 1 mL of degassed OA, 1 mL of degassed OAm, and 10 mL of ODE along with an extra 0.155 g PbBr2 (0.422 mmol) were mixed in 50 mL three-neck round-bottom flask and degassed under vacuum degassed at 110 ℃ for 2 h. Subsequently, the temperature was maintained at 170$^oC$ under inert ($N_2$) atmosphere. To this solution, 0.8 mL of Cs-oleate was quickly injected that gives rise to a fluorescent yellow-green precipitate. The reaction was quenched quickly after 5-10 s by immersing the reaction flask in ice-bath. were loaded in a 50 mL 3-neck flask.

**Purification:** The NCs were washed following the same procedure as that in our case (**Section S2**).

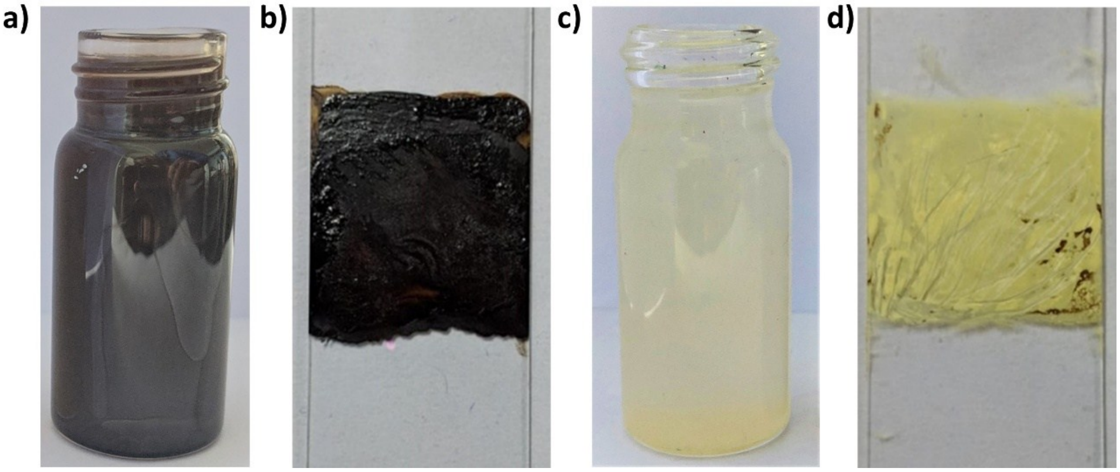

**Figure S1:** Photographs of typical cubic (a and b) and non-perovskite, orthorhombic phases (c and d) of $CsPbI_3$ NCs in solution and as film.

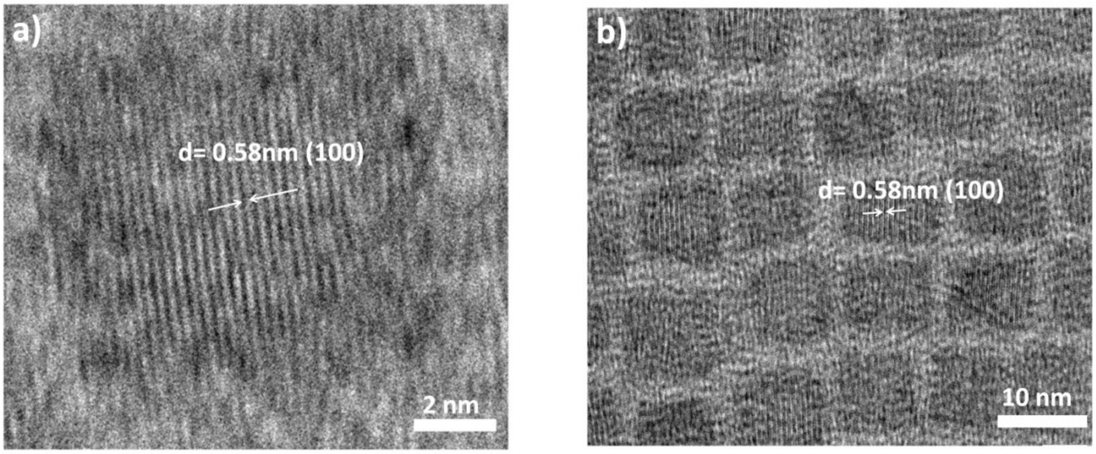

**Figure S2:** HRTEM images (a, b) of the $CsPbBr_3$ perovskite NCs at different magnifications showing lattice fringes with a d-spacing of 0.58 nm consistent with cubic phase of $CsPbBr_3$ (001) plane.

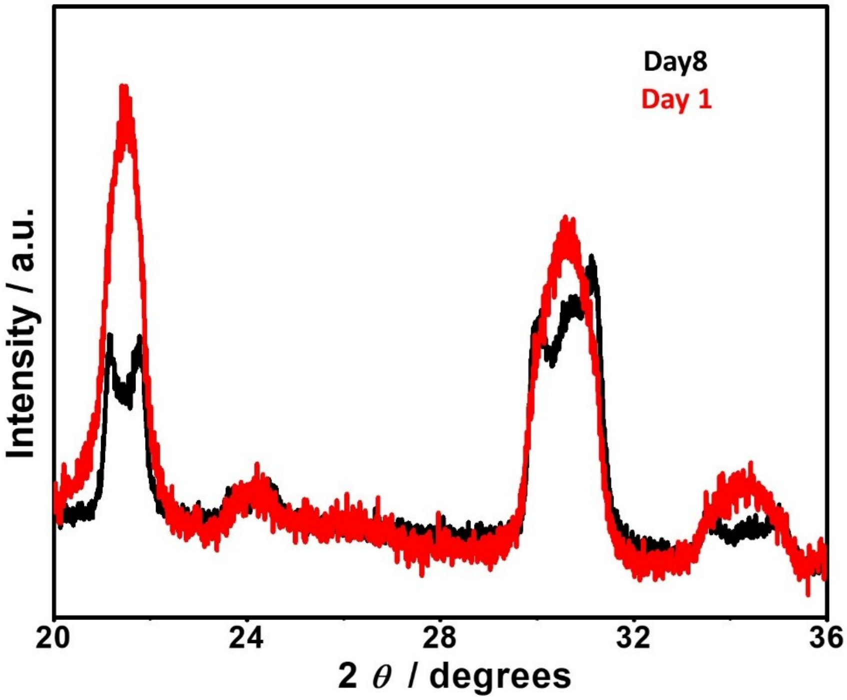

**Figure S3:** $PbBr_2$ treated cubic $CsPbBr_3$NCs undergoes transformation to orthorhombic phase after 6 days, accompanied by splitting of the (200) peak in XRD.[1]

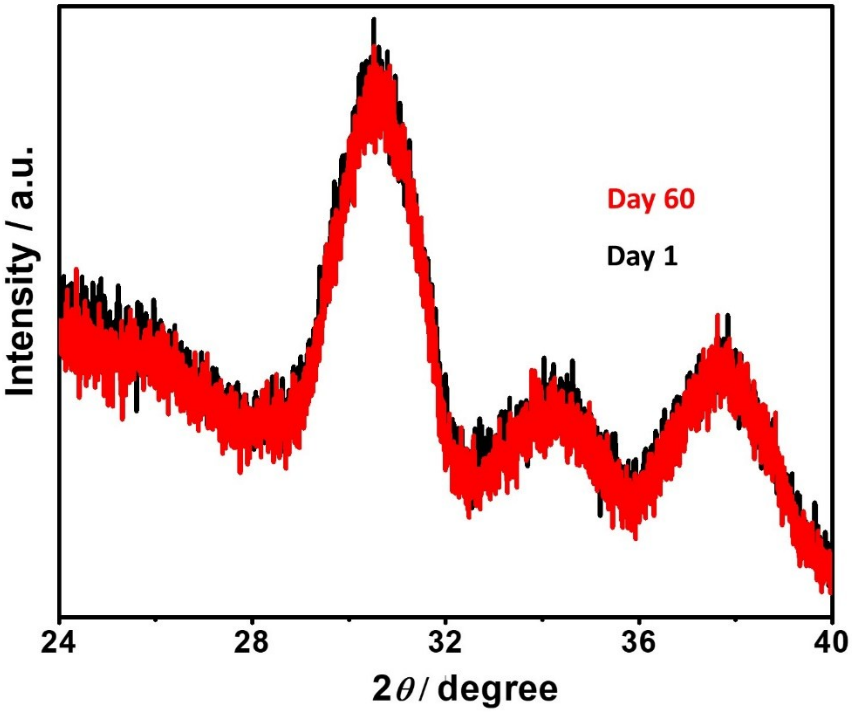

**Figure S4:** XRD spectra of $CsPbBr_3$ showing no sharpening or splitting of the peak at 30.5 ($2\Theta$ degrees) even after 60 days exposure to ambient conditions. The $CsPbBr_3$ NCs is cubic ($\alpha$) phase with diffraction peaks at 2θ = 15.2°, 21.5°, 26.3°, 30.7°, 37.6°, and 43.7° corresponding to (100), (110), (111), (200), (211), and (202) crystal planes (JCPDS 00-054-0752).

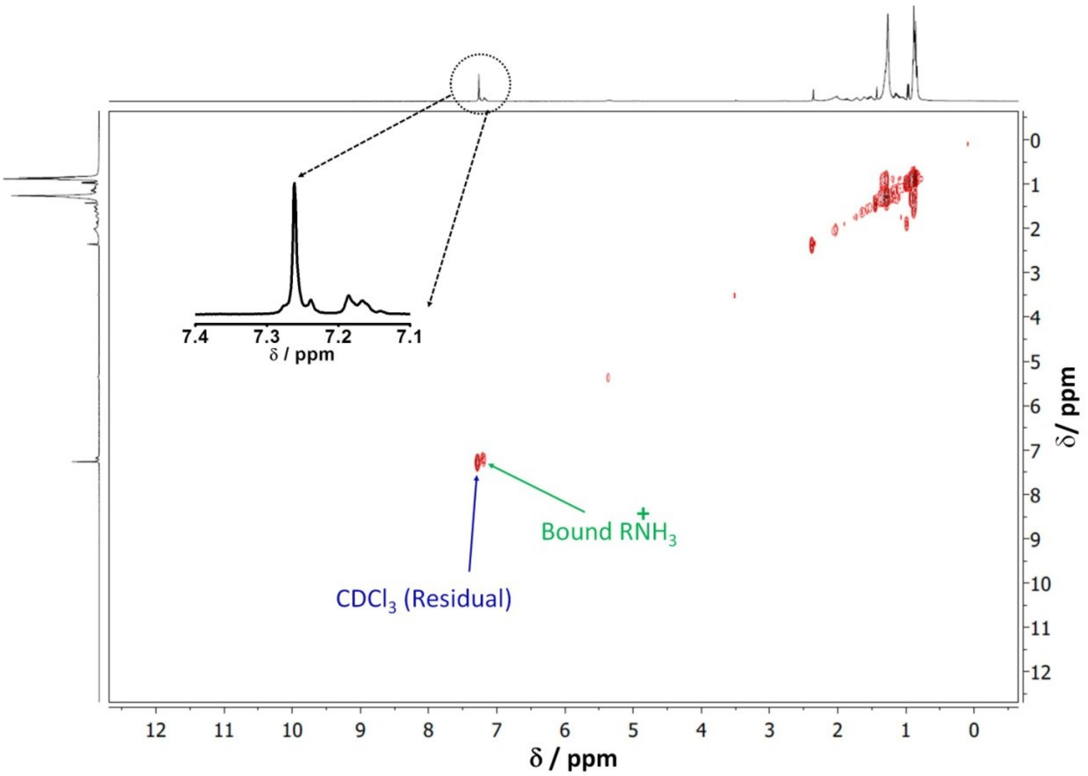

**Figure S5:** $^1$H-$^1$H COrrelated SpectroscopY (COSY) NMR spectra of purified cubic CsPbBr$_3$NCs showing oleylammonium ion signature (multiplet) at δ = 7.1-7.2 ppm (indicated by a red arrow), which does not correlate with any other resonance.

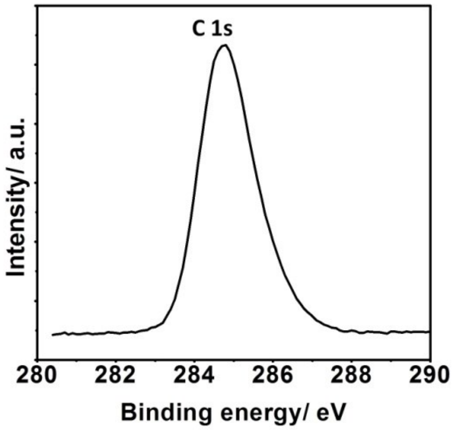

**Figure S6:** XPS spectrum of C 1s of cubic $CsPbBr_3$ NCs calibrated at 284.8 eV.

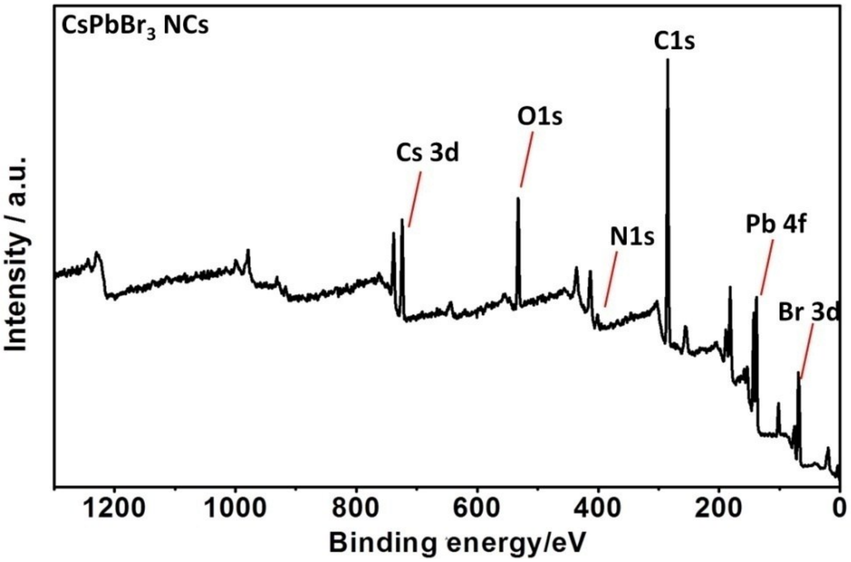

**Figure S7:** XPS (survey) spectra of cubic $CsPbBr_3$ perovskite NCs.

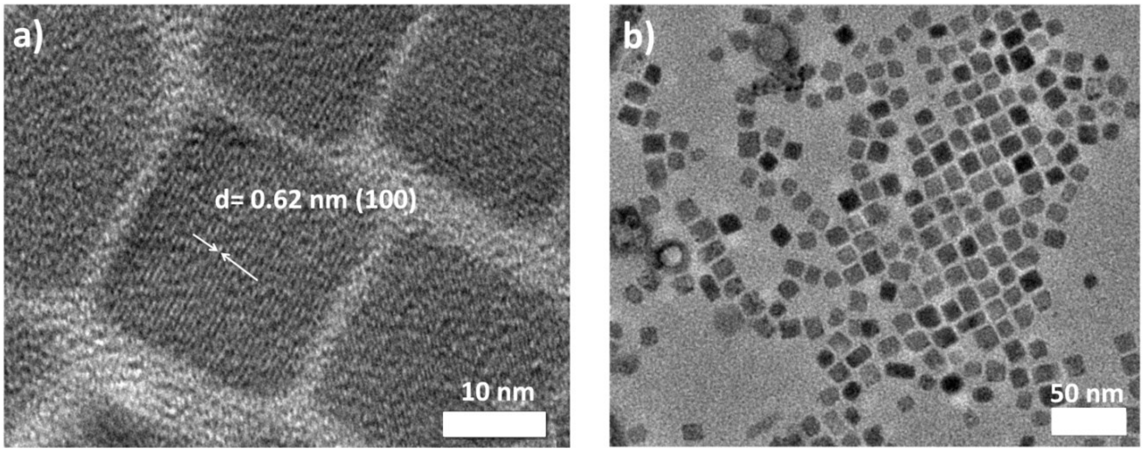

**Figure S8:** (a) High-resolution TEM image of the stable cubic $CsPbI_3$ NCs showing 100 lattice planes (d=0.62 nm), corresponding to the cubic $CsPbI_3$ phase. (b) The TEM image of the $CsPbI_3$ NCs at lower magnification. The calculated size of the NCs is 11.11±2.2 nm.

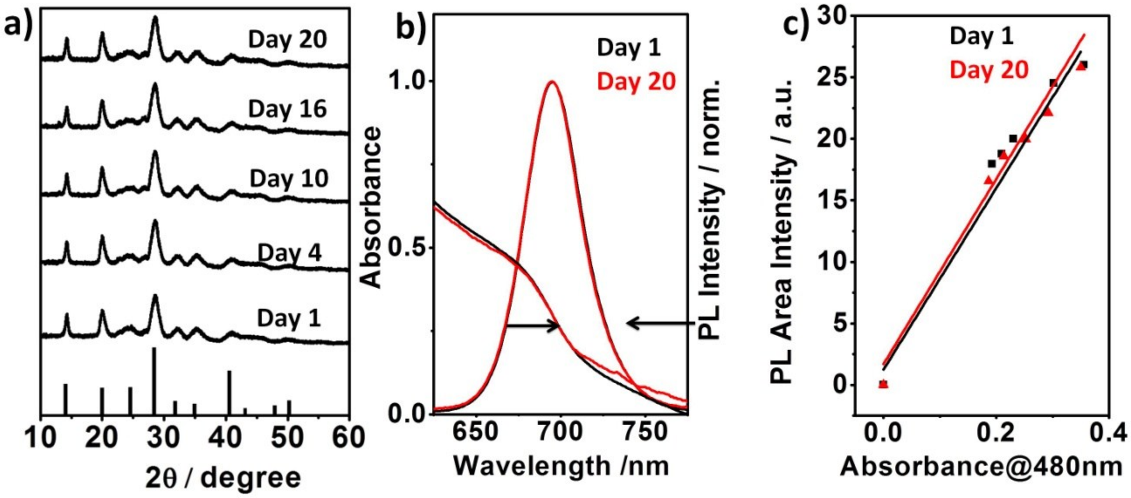

**Figure S9:** (a) XRD patterns showing film stability of $CsPbI_3$ NCs over the period of 20 days in the air under ambient condition (Relative humidity ~50-60%). The pattern of $\alpha$-$CsPbI_3$ (JCPDS 01-076-8588) is indicated as black bars for comparison. (b) UV-Vis absorption and normalized PL spectra of as-prepared $\alpha$-$CsPbI_3$ NCs and the same sample stored in ambient air for 20 days as the colloidal solution (hexane). (c) Integrated photoluminescence vs absorbance plot[2] for day 1 (black) and day 20 (red). Absorbance is measured at 480 nm. The Excitation wavelength is 480 nm.

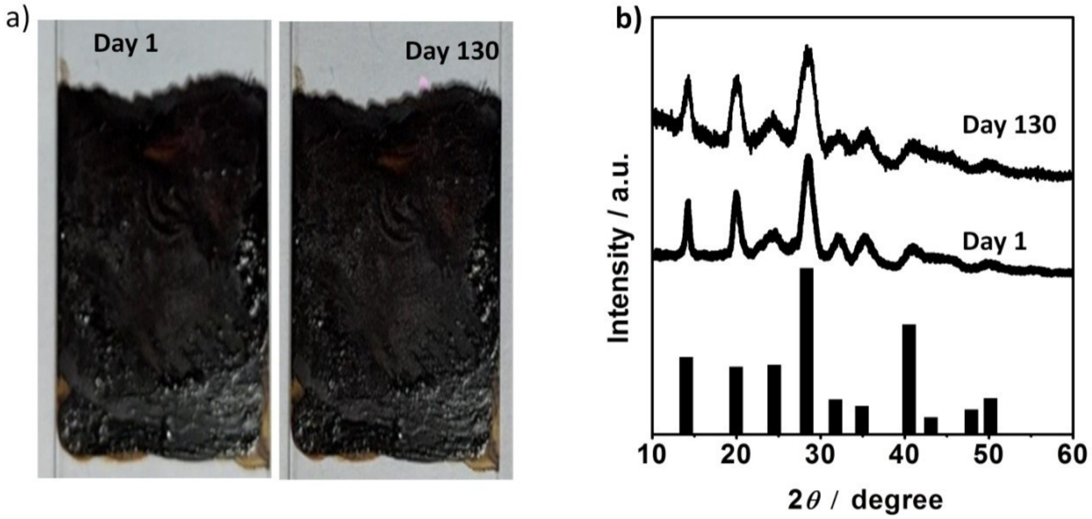

**Figure S10:** (a) Drop-cast film of the purified $CsPbI_3$ NCs on day 1 and after 130 days (stored in dry inert air at ambient temperature). Corresponding XRD spectra showing film stability of the $CsPbI_3$ NCs. The pattern of $\alpha$-$CsPbI_3$ (JCPDS 01-076-8588) is indicated as black bars for comparison.

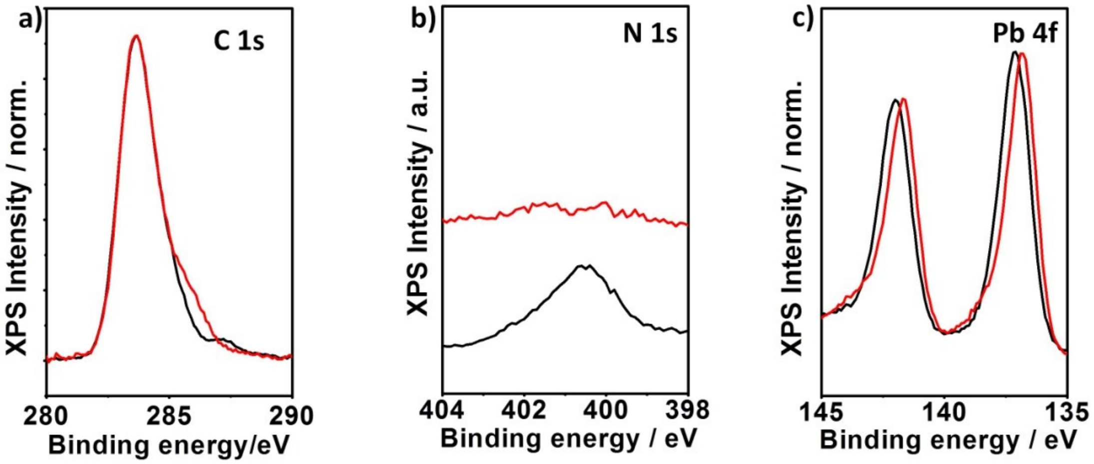

**Figure S11:** (a) C 1s XPS spectra of stable $\alpha$-CsPbI$_3$ NCs (black) and of $\delta$-CsPbI$_3$ NCs (red) calibrated at 284.8 eV; Corresponding (b) N 1s spectraand (c) Pb 4f XPS spectra.

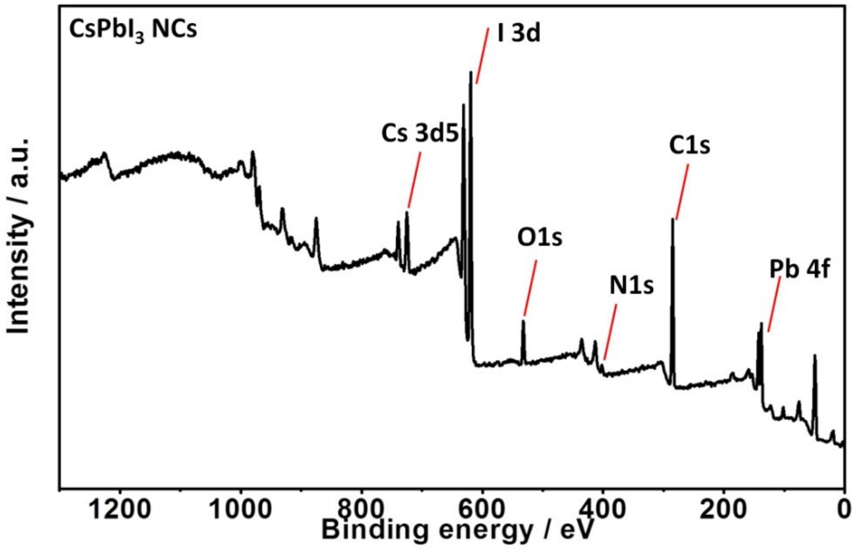

**Figure S12:** XPS (survey) spectra of cubic CsPbI$_3$ perovskite NCs.

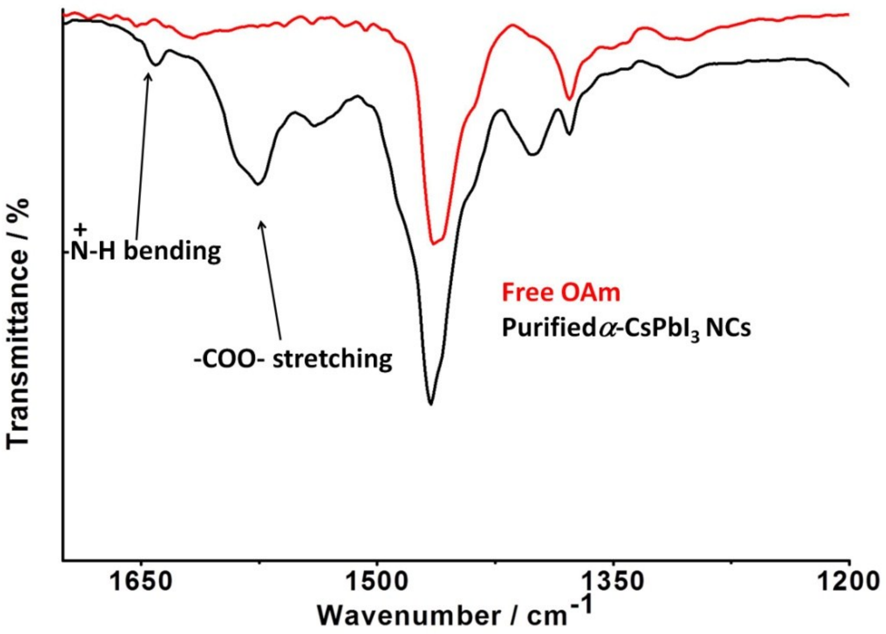

**Figure S13:** FTIR spectra of the stable cubic CsPbI$_3$ NCs showing $\bar{\nu}$ NH$_2^+$ symmetric bending/-COO- stretching at 1570 cm$^{-1}$ and prominent $\bar{\nu}$ NH$_2^+$ asymmetric bending at 1643 cm$^{-1}$ (black). The FTIR spectrum of the pure oleylamine (red) is given for comparison.

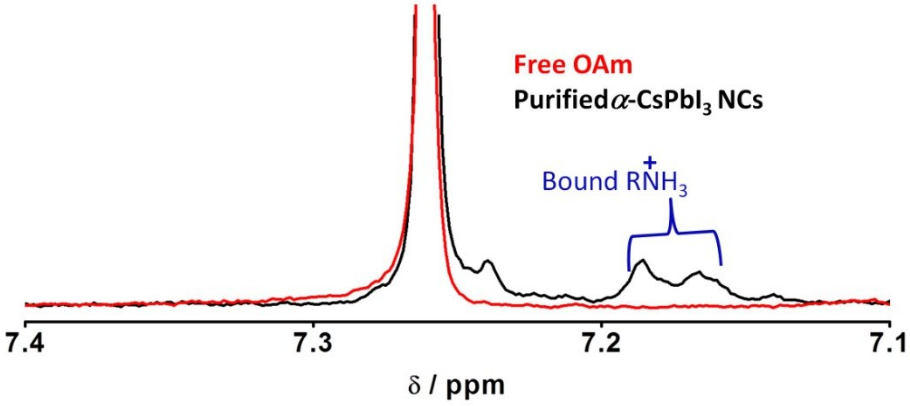

**Figure S14:** $^1$H NMR of purified $\alpha$-CsPbI$_3$ NCs in CDCl$_3$ (black)compared to free OAm (red)

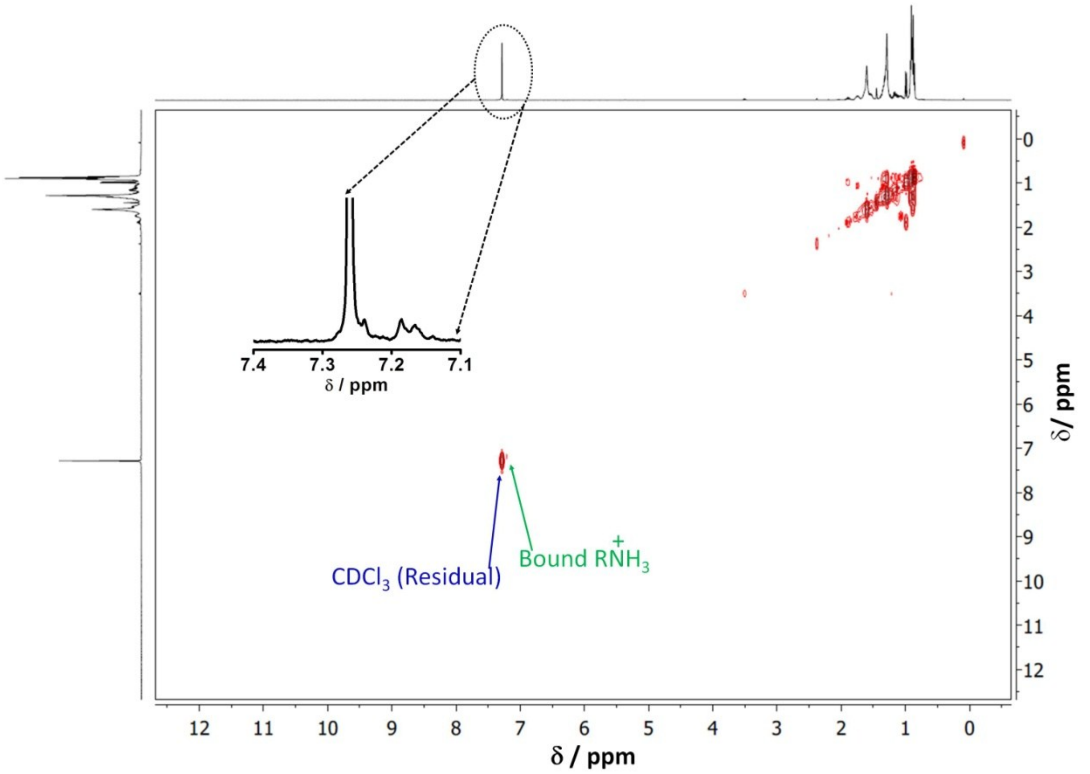

**Figure S15:** 2D (COSY) NMR spectra of cubic $CsPbI_3$ showing oleylammonium ion peak at δ = 7.1-7.2 ppm (indicated by an arrow), which does not correlate with any other resonance.[3] Inset shows the corresponding 1D $^1$H NMR in the same region.

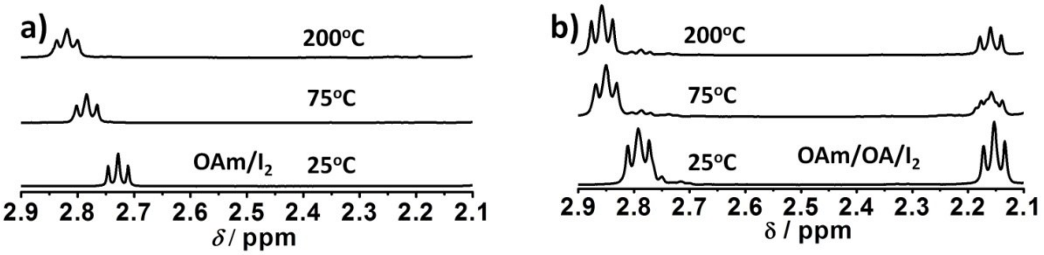

**Figure S16:** (a) (c) $^1$H NMR spectraof a mixture of OAm and $I_2$in $CDCl_3$showing the downfield shift of the $\alpha$–$CH_2$ (amine) resonance with the increase in temperatures (25-200

°C). (d) Resonance of $\alpha$–$CH_2$ (amine) protons exhibited by a mixture of OAm, OA and $I_2$ at different temperatures (25 °C to 200 °C).

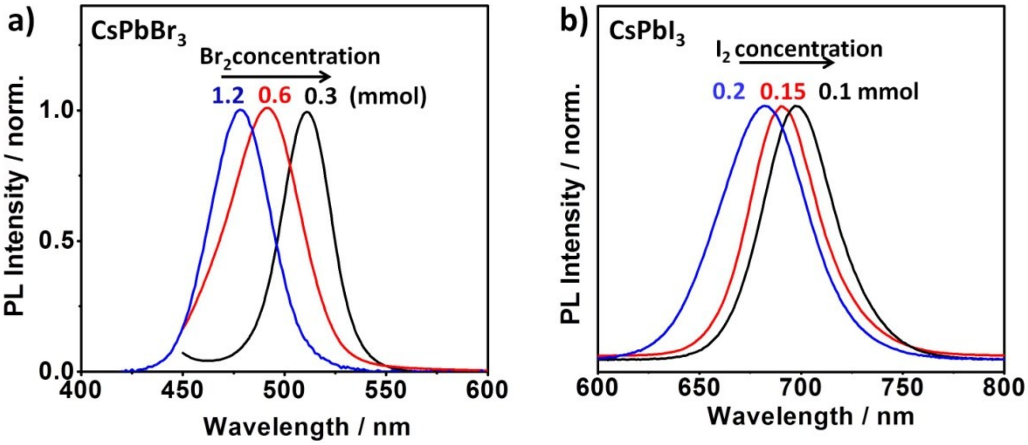

**Figure S17:** Emission spectra of (a) $CsPbBr_3$ and (b) $CsPbI_3$ NCs showing emission tunability by changing the concentration of $X_2$. All samples were synthesized at 150 °C except the blue emitting ($\lambda_{max}$ ~ 478 nm) $CsPbBr_3$ NCs ($Br_2$ concentration: 1.2 mmol) which was prepared at 75 °C. Excitation wavelength: 400 nm.

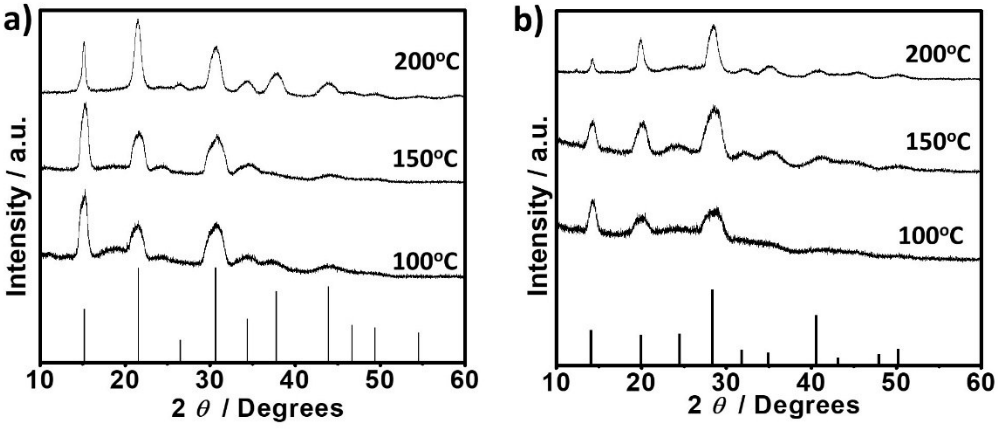

**Figure S18:** XRD spectra of (a) $CsPbBr_3$ and (b) $CsPbI_3$ NCs showing decrease in peak width (FWHM) when the reaction temperature is increased. The crystallite sizes have been calculated and tabulated below (Table S1). The precursor ratio of Cs:Pb:$Br_2$ = 1:1:6 and Cs:Pb:$Br_2$ = 1:1:1.5 is maintained for $CsPbBr_3$ NCs and $CsPbI_3$ NCs respectively

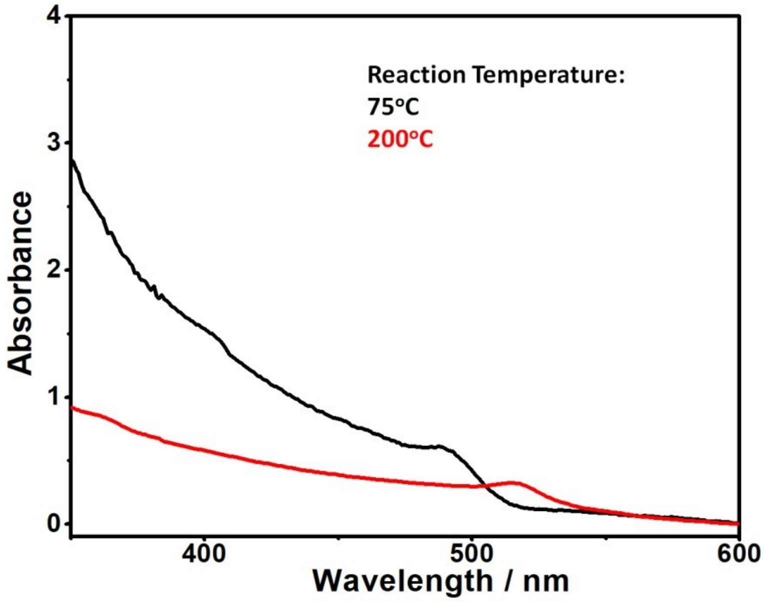

**Figure S19:** UV-Vis absorption spectra of aliquots taken from $CsPbBr_3$ NCs crude solution synthesized at two different temperatures showing differences in absorption maximum and absorbance. NCs were synthesized at Cs: Pb: $Br_2$ ratio of 1:1:6 in both the cases.

**Table S1:** Overview of size/emission tunability, stability and experimental details. Entries 1-3 are for $CsPbBr_3$ NCs and 4-7 are for $CsPbI_3$ NCs. Crystallite sizes are calculated using Scherrer equation. The mean size was calculated from (110) and (200) planes diffraction planes.

| **Sr. no.** | **Experimental details (Cs: Pb: $X_2$)** | **Temp. (°C)** | **XRD stability** | **Crystallite size (nm)** | **TEM size (nm)** | **$\lambda_{max}$ (nm)** |
|---|---|---|---|---|---|---|
| **1.** | **1:1:6** | **200** | **60 days** | **7.7±1.4** | **7.6±1.0** | **517** |
| **2.** | **1:1:6** | **150** | **20 days** | **6.2±0.4** | | **508** |
| **3.** | **1:1:6** | **100** | **2 day** | **4.6±0.8** | | **498** |
| **4.** | **1:1:2** | **200** | **20 days** | **7.8±0.9** | **11.11±2.2** | **696** |
| **5.** | **1:1:1.5** | **150** | **3 days** | **4.9±0.7** | | **684** |
| **6.** | **1:1:1.5** | **100** | **2 days** | **4.1±0.3** | | **650** |
| **7.** | **1:1:1.5** | **200** | **7 days** | **9.5±4.8** | | **698** |

## References:

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2 S. Tamang, G. Beaune, I. Texier and P. Reiss, *ACS Nano*, 2011, **5**, 9392–9402.

3 A. Dutta, S. K. Dutta, S. Das Adhikari and N. Pradhan, *Angew. Chem. Int. Ed.*, 2018, **57**, 9083–9087.