

The More the Merrier: Optimizing Monomer Concentration for Supersaturation Controlled Synthesis of Stable Ultra-Small CsPbBr₃ Nanocrystals for Blue Emission

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Supporting Information

Experimental Section:

Chemicals: Cesium carbonate (Cs₂CO₃, 99.9%, Sigma-Aldrich), lead (II) bromide (PbBr₂, 99.999%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), oleylamine (OLA, technical grade 70%, Sigma-Aldrich), 1-octadecene (ODE, technical grade 90%, Sigma-Aldrich), methyl acetate (MeOAc, anhydrous, 99.8%, Sigma-Aldrich), Hexane (anhydrous, 95%, Sigma-Aldrich), Octane (anhydrous, > 99%, Sigma Aldrich), deuterated chloroform (CDCl₃, 99.8 atom % D, Sigma-Aldrich), 9,10-Diphenylanthracene (97%, Sigma-Aldrich).

Synthesis of CsPbBr₃ nanocrystals (NCs):

(a) Drying of OA, OLA, and ODE: OA, OLA, and ODE are dried by taking 50 mL each in a separate round bottom flask and then degassed under vacuum for 2 hours at 110 °C. It is then purged with N₂ for 15 minutes. This process is repeated 2 more times. Finally, the dried OA, OLA, and ODE are stored in the glass vial under an inert atmosphere.

(b) Cesium oleate (Cs-oleate) preparation: 500 mg of Cs_2CO_3 along with 50 mL of ODE and 2.0 mL of dried OA are taken together in a round bottom flask. The mixture is then degassed at 120 °C for 1 hour under vacuum. It is then placed in the flow of Nitrogen (N_2) for 15 min. The above process of degassing and N_2 flow is repeated 3 times. Finally, the temperature of the mixture is raised to 150 °C till the complete dissolution of Cs_2CO_3 . The Cs-oleate solution is then brought down to room temperature and stored in an inert atmosphere (sealed glass vial and purged with N_2).

(c) Synthesis of green-emitting conventional CsPbBr_3 NCs,¹ 1S_{CPB} : In a three-necked round bottom flask, 5 mL ODE and 69 mg (0.188 mmol) of PbBr_2 are added and the mixture is kept under vacuum at 120 °C for 30 min followed by N_2 purging. This alternate vacuum and N_2 purging cycle are repeated three times to ensure the effective removal of moisture and oxygen. Dried OA and OLA (0.5 mL each) are added to the mixture at 120 °C under N_2 flow. After the solubilization of PbBr_2 , the reaction temperature is increased to 170 °C, and 0.8 mL of Cs-oleate (pre-heated at 80 °C) is injected into the mixture. The reaction is stopped after 5 seconds using an ice bath. Similarly, blue emitting CsPbBr_3 NCs (1S_{CPB} @80 °C) are synthesized by keeping all the parameters the same except the injection temperature of Cs-oleate is set at 80 °C.

(d) Relative supersaturation controlled synthesis of CsPbBr_3 NCs: For the relative supersaturation controlled synthesis of CsPbBr_3 NCs, the concentration of the precursors is increased by 3 times (3S_{CPB}), 6 times (6S_{CPB}), 9 times (9S_{CPB}) and 12 times (12S_{CPB}) while keeping the reaction volume same. Similarly, the concentration of precursors is halved for 0.5S_{CPB} . Briefly, for 3S_{CPB} , 207 mg of PbBr_2 and 1.5 mL each of OA and OLA along with 3 mL of ODE is taken and 2.4 mL of Cs-oleate is injected at 170 °C. For 6S_{CPB} , 414 mg of PbBr_2 and 3 mL each of OA and OLA are taken and 4.8 mL of Cs-oleate is injected at 170 °C. For 9S_{CPB} , 621 mg of PbBr_2 and 3 mL each of OA and OLA are taken and 7.2 mL of Cs-oleate is injected at 170 °C. For 12S_{CPB} , 828 mg of PbBr_2 and 3 mL each of OA and OLA are taken and 9.6 mL of Cs-oleate is injected at 170 °C. For 0.5S_{CPB} , 34.5 mg of PbBr_2 and 0.25 mL each of OA and OLA along with 5.5 mL of ODE is taken and 0.4 mL of Cs-oleate is injected at 170 °C.

Purification of CsPbBr_3 NCs: After quenching the reaction, the crude dispersion is diluted with an additional 10 mL of ODE. It is left for 24 hours to precipitate out unreactive precursors. The crude dispersion is then centrifuged at 4000 rpm and the supernatant is collected. Methyl acetate

as an anti-solvent is added to the supernatant (roughly 4:1 V/V, till turbidity appears) and centrifuged at 9500 rpm for 10 min. The precipitate is collected and dispersed in 1 mL of hexane and again precipitated by methyl acetate. Finally, the NCs are dispersed in toluene and stored in a glove box for further characterization.

Photoluminescence Quantum Yield Measurement: Photoluminescence (PL) quantum yield (QY) of NCs in colloidal dispersion has been calculated relative to 9,10-Diphenylanthracene as reference dye ($\phi_f = 0.95$ in ethanol).² The NCs are dispersed in toluene and dilute solutions are used for recording absorbance and PL spectra. In the case of PL, the NCs and dye are excited at 330 nm while keeping all the other parameters constant. To calculate the PLQY the following equation has been used.

$$QY_s = QY_{ref} \cdot \frac{F_s}{F_{ref}} \cdot \frac{A_{ref}(\lambda_{exc})}{A_s(\lambda_{exc})} \cdot \frac{n_s^2}{n_{ref}^2}$$

where,

QY_s = Unknown PL quantum yield of sample

QY_{ref} = Known PL quantum yield of reference (Here, for DPA it is 0.95 in ethanol,)

F_s = Integrated PL intensity of sample (Area under the PL Curve of the sample at fixed excitation wavelength).

F_{ref} = Integrated PL intensity of reference (Area under the PL curve of the reference at fixed excitation wavelength).

$A_{ref}(\lambda_{exc})$ = Absorbance value of the reference (λ in its absorbance spectrum at that fixed PL excitation wavelength).

$A_s(\lambda_{exc})$ = Absorbance value of the sample in its absorption spectrum at that fixed PL excitation wavelength.

n_s = Refractive index of the solvent (toluene) in which the sample is dispersed.

n_{ref} = Refractive Index of the solvent (ethanol) in which reference is dispersed.

Stability of NCs under UV irradiation and ambient light: To check the stability of the blue emitting NCs (10S_{CPB} @170 °C and 1S_{CPB} @80 °C), dilute dispersions of NCs are taken in quartz cuvettes and sealed inside the glove box with parafilm. It is then irradiated with UV light (365 nm, 50 W), and the absorbance and PL is recorded after regular intervals of time.

Characterization: UV-visible absorption and PL experiments are recorded by dispersing NCs in toluene as a solvent. UV-visible absorption spectra are recorded using a Cary 5000 UV–vis–NIR spectrophotometer. PL spectra are measured using Horiba QuantaMaster 8075-21 equipped with double-excitation and single-emission monochromators. The samples are excited at 360 nm (5 nm bandwidth) using a Xe arc lamp. The spectrum is corrected for wavelength-dependent detector response. X-ray diffraction (XRD) patterns are collected using a Bruker AXS D8 Discover GADDS microdiffractometer equipped with a Cu-K α source. Transmission electron microscopy (TEM) images are recorded using an FEI Titan Themis field emission transmission electron microscope at 200 kV. The samples for TEM are prepared by putting a drop of dilute colloidal solution of NCs on the carbon-coated copper grids. Energy dispersive X-ray spectroscopy (EDAX) technique is used for determining the elemental composition of the NCs using a MERLIN Carl Zeiss Field Emission Scanning Electron Microscope. ^1H (500 MHz) nuclear magnetic resonance (NMR) spectra are recorded on a Bruker Avance spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS), with the solvent resonance (CDCl_3 , $\delta = 7.26$ ppm) as the internal reference. Thermogravimetric Analysis (TGA) is performed using a TA instrument TGA550. Samples are heated in ultrapure nitrogen from 23 °C to 110°C at 10°C min $^{-1}$ followed by a 10-minute isothermal hold and a second ramp to 600 °C at 10 °C min $^{-1}$.

Supporting Figures and Tables:

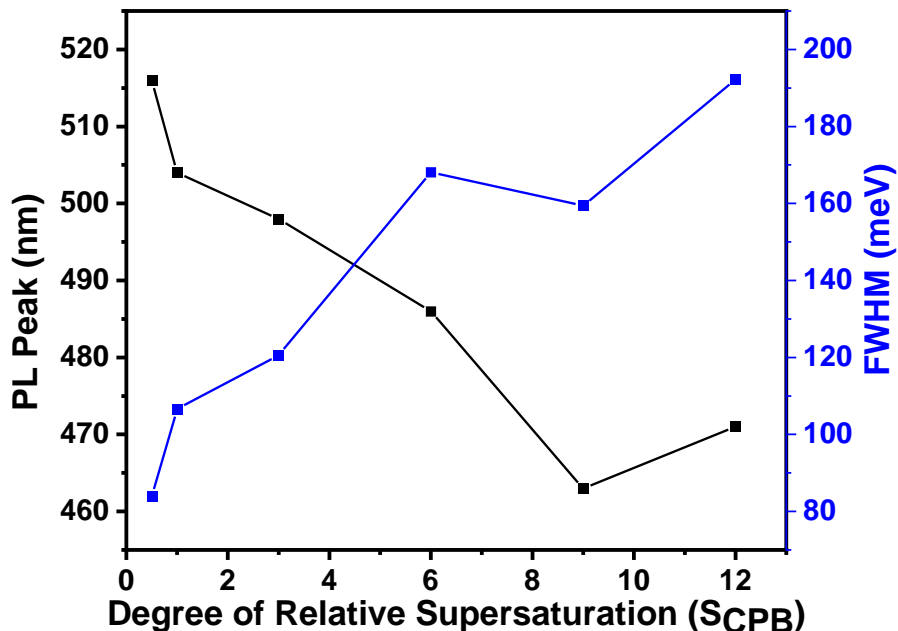


Figure X1: Variation of PL peak and the corresponding full width at half maxima (FWHM) of CsPbBr₃ NCs synthesized at different relative supersaturation conditions. The synthesis is done at the temperature of 170 °C. The line serves as a guide to the eye.

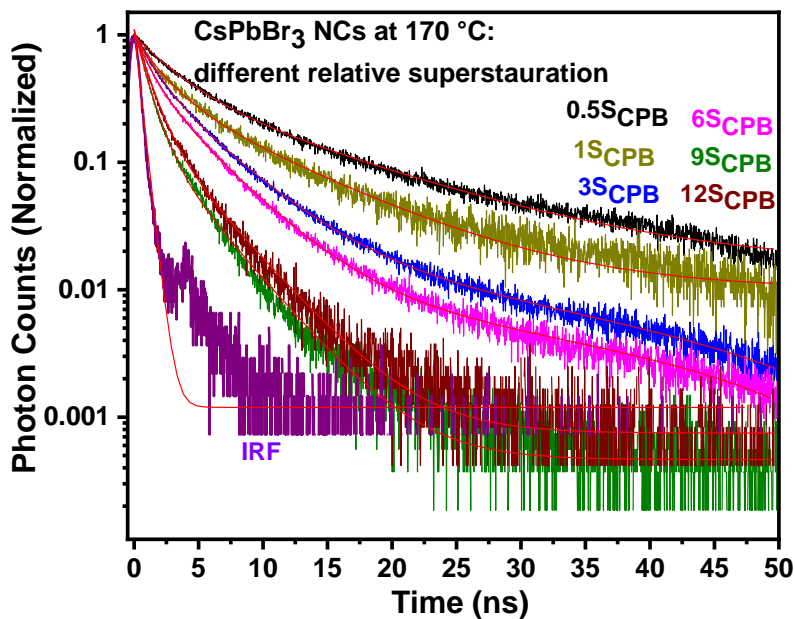


Figure X2: PL decay of CsPbBr₃ NCs synthesized at different relative supersaturation conditions at their peak PL wavelength. The decay becomes faster as the relative supersaturation increases (smaller size) suggesting better overlap of electron and hole wavefunction. Decay curves are fitted with a bi-exponential decay function while IRF is fitted with a mono-exponential decay function. Fitting parameters are given in Table X1.

Sample	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{avg} (ns)
0.5S _{CPB}	0.61	2.97	0.39	11.82	9.32
S _{CPB}	0.63	2.04	0.37	8.64	6.75
3S _{CPB}	0.51	1.43	0.49	4.57	3.80
6S _{CPB}	0.54	1.21	0.46	4.15	3.40
9S _{CPB}	0.85	0.99	0.15	3.67	2.04
12S _{CPB}	0.80	1.09	0.20	3.84	2.37
IRF	1	0.46			

Table X1: PL decay lifetime of CsPbBr₃ NCs obtained from Figure X2 at their emission peak wavelength. $\tau_{avg} \text{ (ns)} = (\sum A_i \tau_i^2 / \sum A_i \tau_i)$.

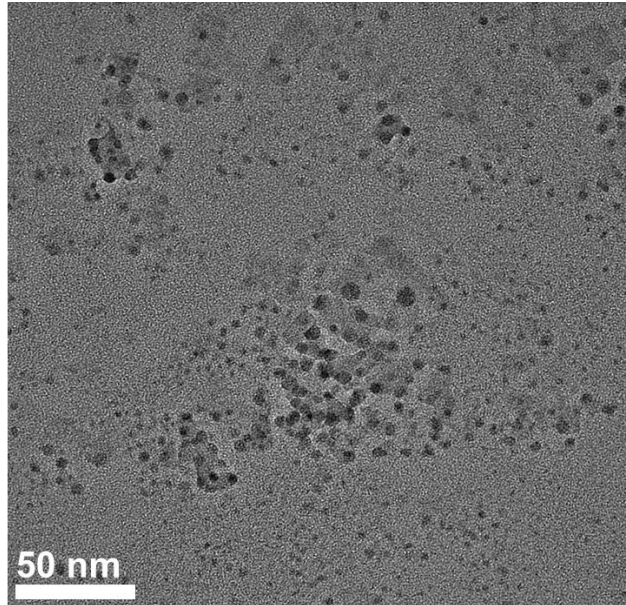


Figure X3: Representative TEM image of CsPbBr₃ NCs synthesized at relative supersaturation condition of 6S_{CPB}.

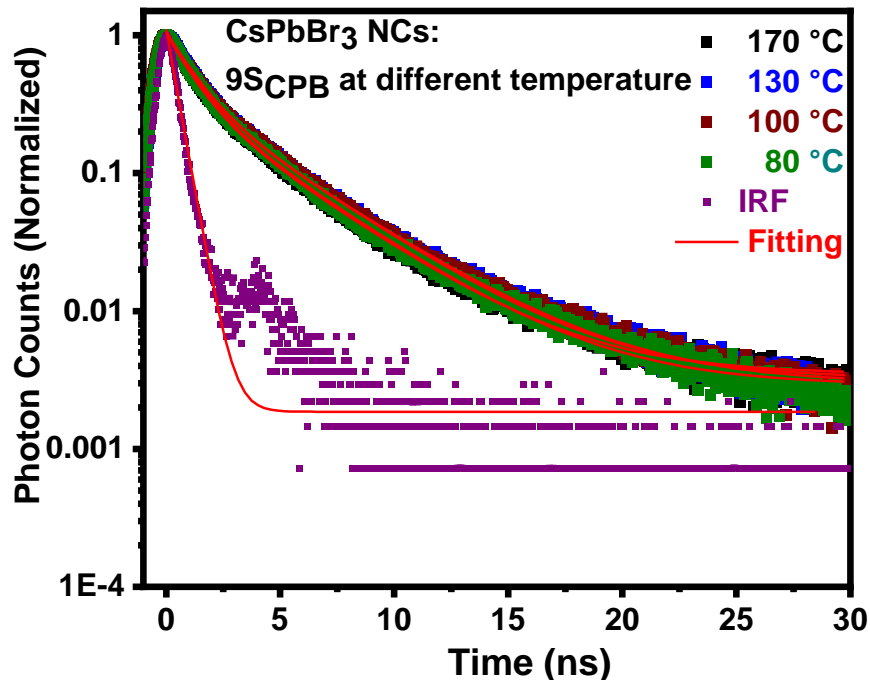


Figure X4: PL decay of CsPbBr₃ NCs synthesized at 9S_{CPB} relative supersaturation but at different temperatures at their PL peak wavelength. Decay curves are fitted with a bi-exponential decay function while IRF is fitted with a mono-exponential decay function. Fitting parameters are given in Table X2.

Sample	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{avg} (ns)
170 °C	0.65	1.08	0.35	3.80	2.87
130 °C	0.66	1.99	0.34	4.10	3.07
100 °C	0.60	1.12	0.40	3.91	3.07
80 °C	0.64	1.10	0.36	3.86	2.93
IRF	1	0.46			

Table X2: PL Decay lifetime of CsPbBr₃ NCs obtained from Figure X4 at their emission peak wavelength. $\tau_{avg} \text{ (ns)} = (\sum A_i \tau_i^2 / \sum A_i \tau_i)$.

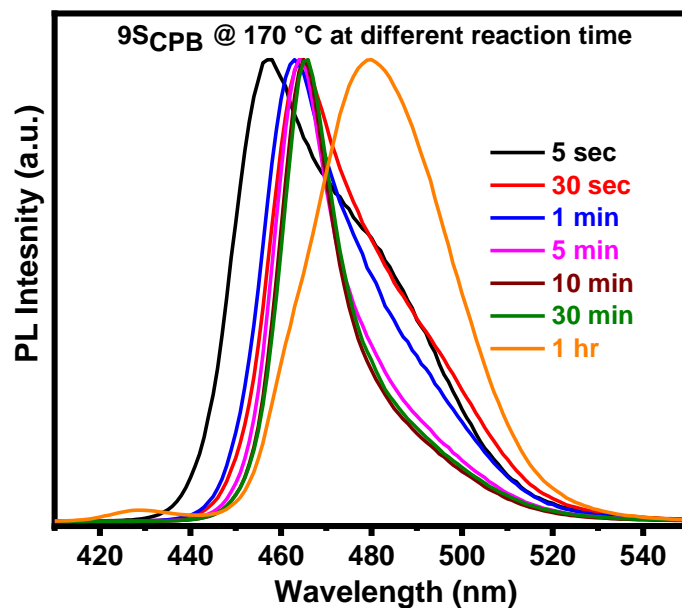


Figure X5: Growth of $9S_{CPB}$ $CsPbBr_3$ NCs with time. The reaction time of 10 minutes is optimized for further samples. (Note: sec = seconds, min = minutes, hr =hours)

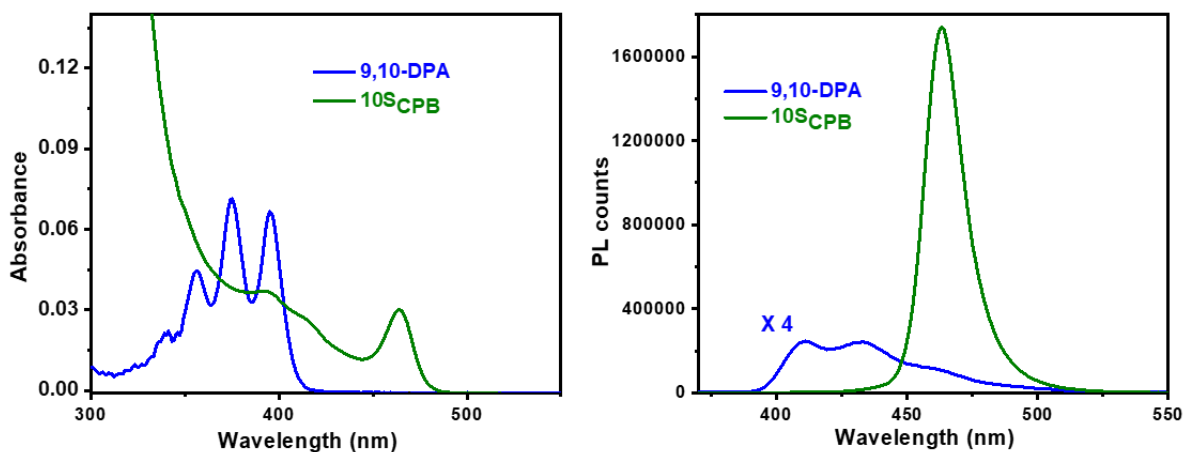


Figure X6: (a) Absorbance and (b) PL spectra of $10S_{CPB}$ $CsPbBr_3$ NCs along with the reference sample 9,10-diphenylanthracene (9,10-DPA) employed in measuring PL quantum yield of the $CsPbBr_3$ NCs.

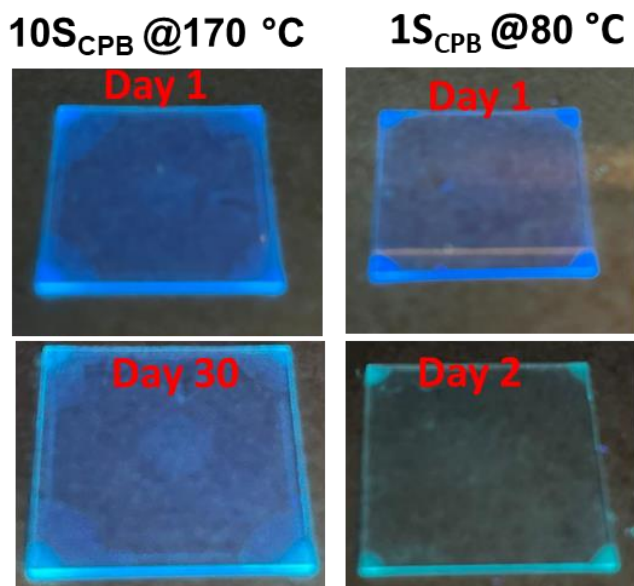


Figure X7: Photograph of CsPbBr₃ NCs thin films on glass under UV light to show the stability under ambient conditions. The blue emitting CsPbBr₃ NCs, 1S_{CPB} @80 °C synthesized at a lower temperature loses its blue emission within 1 day and the film shows green emission. However, the blue emitting CsPbBr₃ NCs, 10S_{CPB} @170 °C synthesized at higher temperature at higher relative supersaturation have their blue emission maintained even after 30 days.

Sample	Cs	Pb	Br	Cs : Pb
10S _{CPB} @170 °C	12.7 ± 0.2	21.0 ± 0.2	66.3 ± 0.3	0.6
1S _{CPB} @80 °C	20.1 ± 0.2	17.3 ± 0.3	62.6 ± 0.2	1.2

Table X3: Chemical composition (shown as Atomic%) obtained from EDAX for blue emitting CsPbBr₃ NCs, 10S_{CPB} @170 °C and 1S_{CPB} @80 °C. Smaller NCs synthesized at higher temperature at higher relative supersaturation (10S_{CPB} @170 °C) are more deficient in Cs while smaller NCs synthesized at lower temperature are deficient in Pb. This shows the different surface compositions of smaller NCs synthesized at different temperatures and at different relative supersaturation.

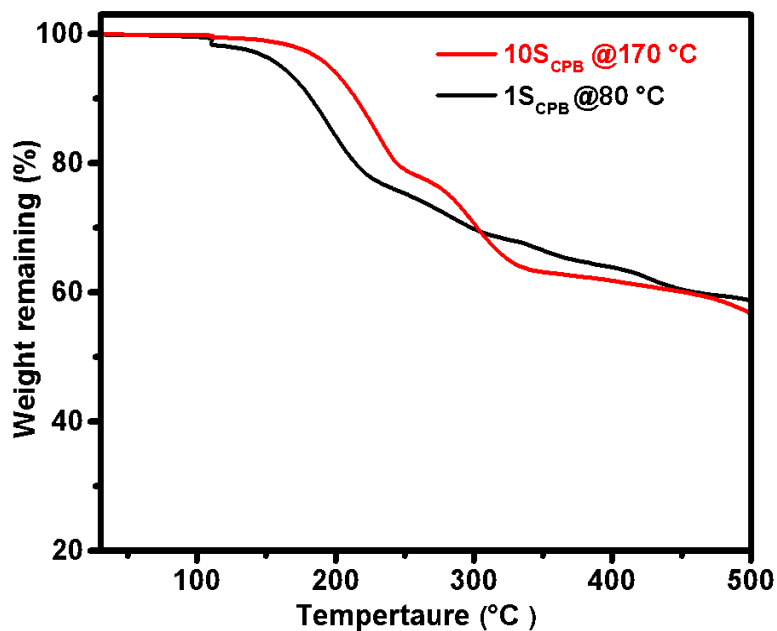


Figure X8: TGA of 10S_{CPB} @170 °C and 1S_{CPB} @80 °C. Both the samples show similar weight loss suggesting similar ligand density at the NCs surface.

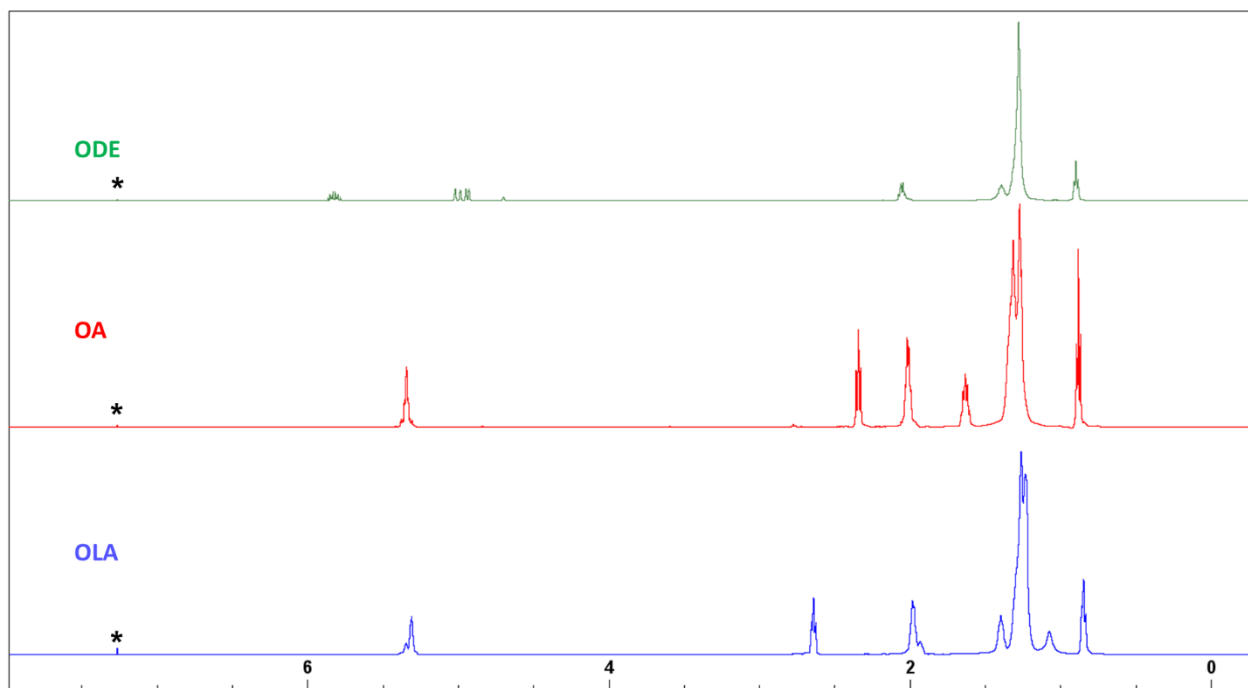


Figure X9: ¹H NMR spectra of OLA, OA, and ODE. The resonance peak for solvent CDCl₃ is marked with *.

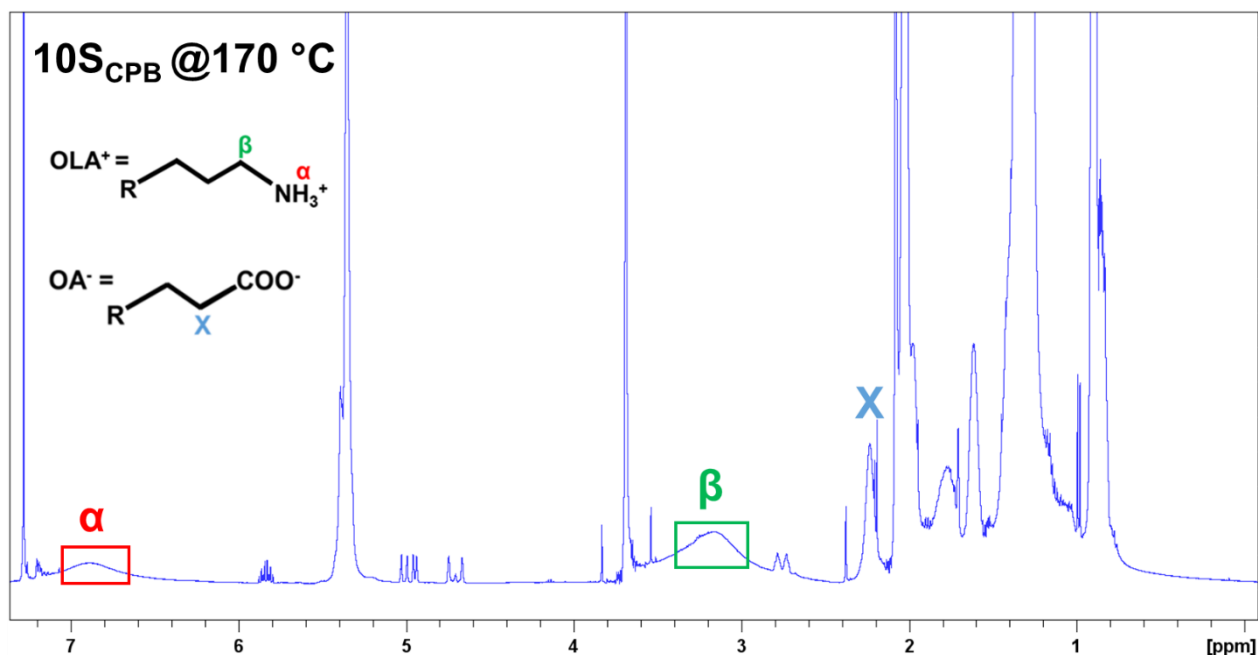


Figure X10: ¹H NMR spectrum of 10S_{CPB} @170 °C. The given NMR plot has the signature of oleylammonium binding (OLA⁺) which we hypothesize is due to the substitution of surface Cs⁺ ions from the CsPbBr₃ NCs surface.³

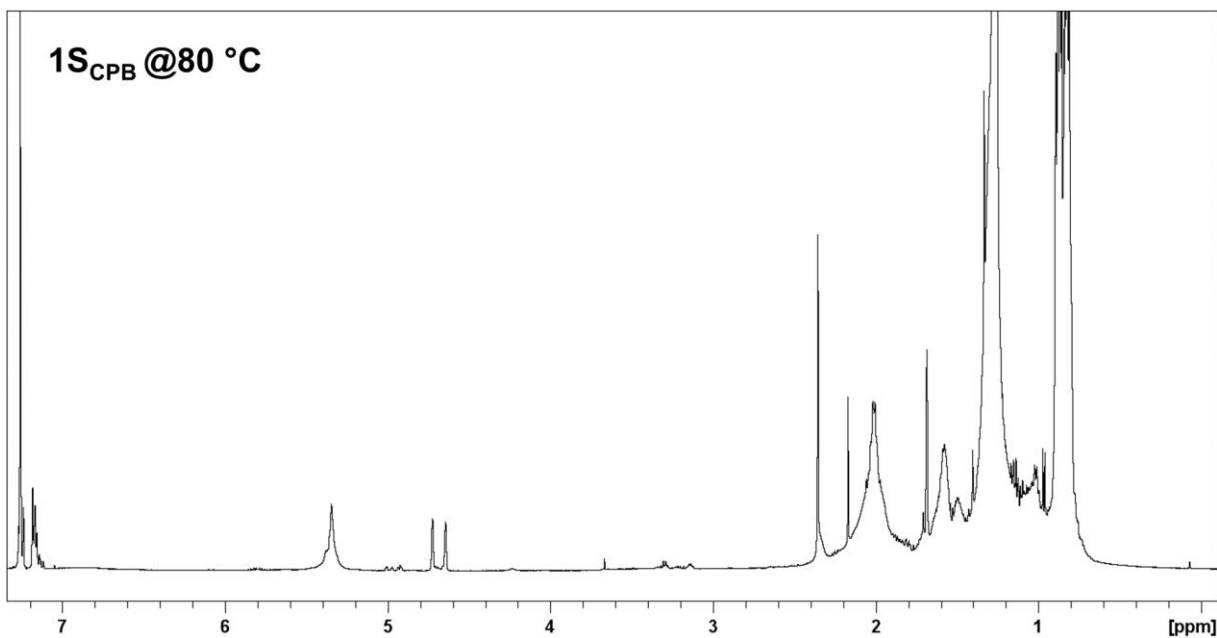


Figure X11: ¹H NMR spectrum of 1S_{CPB} @80 °C. Here, the signature of OLA⁺ binding is absent, suggesting that the surface composition and ligands here are different compared to the case of 10S_{CPB} @170 °C.

References:

- (1) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692–3696.
- (2) Morris, J. V.; Mahaney, M. A.; Huber, J. R. Fluorescence Quantum Yield Determinations. 9,10-Diphenylanthracene as a Reference Standard in Different Solvents. *J. Phys. Chem.* **1976**, *80*, 969–974.
- (3) Ravi, V. K.; Santra, P. K.; Joshi, N.; Chugh, J.; Singh, S. K.; Rensmo, H.; Ghosh, P.; Nag, A. Origin of the Substitution Mechanism for the Binding of Organic Ligands on the Surface of CsPbBr_3 Perovskite Nanocubes. *J. Phys. Chem. Lett.* **2017**, *8*, 4988–4994.