

Shape Pure, Nearly Monodisperse CsPbBr_3 Nanocubes Prepared using Secondary Aliphatic Amines

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1. Details of a typical synthesis of shape pure, nearly monodisperse ~8.5 nm CsPbBr₃ nanocubes using didodecylamine (DiDDAm)

1st step, Degassing: 76 mg of lead (II) acetate trihydrate, 16 mg of cesium carbonate and 10 ml of octadecene (measured with a 5 ml mechanical pipette) were combined in air in a 25 ml 3-neck flask (one of the side necks is used as a glass finger for a thermocouple, and is filled with 0.5 ml of octadecene as a heat transfer medium). The flask with the mixture was equipped with a magnetic stirrer, and the open side neck was capped with a silicone septum and connected to a Schlenk line via a condenser that was inserted into the central neck. It was then placed into the heating mantle on top of a stirring plate. The vacuum was applied first at room temperature for ~5 minutes as a pre-degassing step. Within a few minutes, the contents of the flask were heated to 115 °C under stirring and were kept at that temperature, under vacuum, for approximately one 1 hr. The vacuum was ~50-70 mbar, as was measured with a digital vacuum gauge.

2nd step, Ligands: In the glovebox, 1 ml of anhydrous toluene was added to 443 mg of DiDDAm in a 4 ml glass vial, which was then placed on a preheated hot plate (set at 150 °C) until all the DiDDAm dissolved (m.p.= 45-47 °C). Next, 1.5 ml of the degassed oleic acid was added to the DiDDAm solution using a 5 ml mechanical pipette. The resulting mixture of ligands was shaken by hand, yielding a clear and colorless solution. The ligand solution was transferred into a 5 ml disposable syringe equipped with a 21G needle, which was then removed from the glovebox.

After the metal salts had degassed (1st step above), the flask with metal salts in ODE was switched from being under vacuum to being under nitrogen flow, and the ligand mixture in toluene was injected. After adding the ligands, the reaction mixture was kept at 115 °C under stirring until all of the metal salts dissolved (~15-20 minutes), yielding a clear, colorless solution without any visible solids inside. Next, the temperature controller was set to 80 °C (the injection temperature), and the reaction mixture was allowed to cool and stabilize at 80 °C.

3rd step, Injection of benzoyl bromide: In the glovebox, 50 uL of benzoyl bromide (measured with a 100 uL mechanical pipette) was mixed with 500 uL of degassed ODE (measured with a 1000 uL mechanical pipette) in a 4 ml glass vial; the mixture was shaken by hand and filled into a 3 ml disposable syringe equipped with a 21G needle. The benzoyl bromide solution was taken outside the glovebox, and injected into the mixture of metal salts and ligands at 80 °C under stirring. Upon the injection of the benzoyl bromide precursor, the reaction mixture immediately turned from being clear and colorless to being clear and yellow (which is characteristic of CsPbBr₃ NCs). After the injection, ~15 seconds were counted with a timer, and the reaction was quenched by replacing the heating mantle with a water bath (at ~20 °C). The reaction was left to cool until it reached ~40 °C, after which the water bath was removed. During both injection and cooling, the reaction was kept under a nitrogen atmosphere.

4th step, Isolation of nanocubes: Once the reaction had cooled down to near room temperature, the flask was opened in air and the contents were transferred into a 40 ml vial. 3 ml of anhydrous toluene was then added to the vial, followed by anhydrous ethyl acetate until the mixture turned turbid. Note that the total volume of ethyl acetate needed for nanocrystal precipitation depends on the size of the nanocubes. For the injection temperature and growth time described here (80 °C and ~15 seconds, respectively), it took ~20-30 ml of ethyl acetate to initiate nanocrystal agglomeration (mixture turns turbid). When agglomeration started, the mixture was centrifuged at 5000 rpm for 10 minutes, yielding yellow precipitate on the walls of the vial and a yellow supernatant. The supernatant was discarded and the precipitate was dispersed in a few ml of toluene for characterization and further experiments (such as self-assembly).

2. Amine-free synthesis of CsPbBr₃ NCs

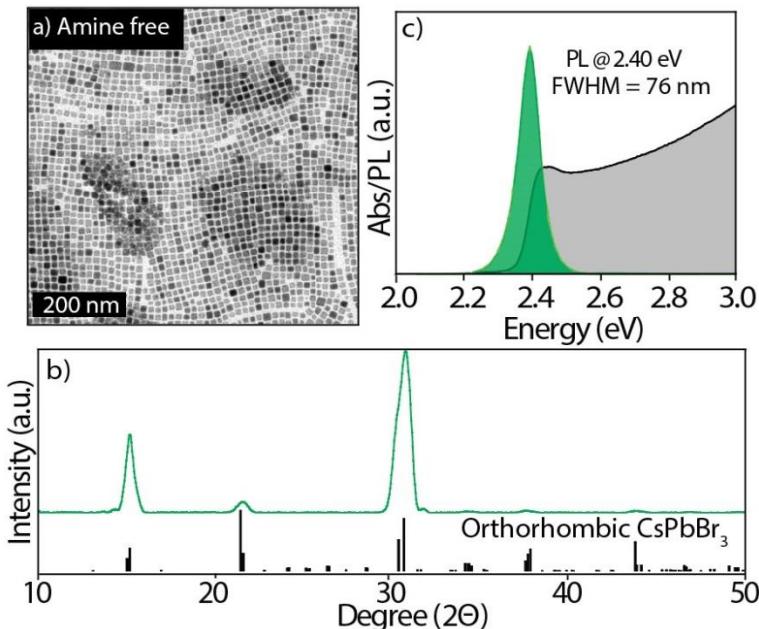


Figure S1. Amine free synthesis of CsPbBr₃ NCs; a) TEM image b) XRD pattern and c) UV-Vis absorption and PL spectra. Bulk pattern for CsPbBr₃ in b) has Reference code 96-451-0746. Syntheses was carried out as follows: the amount of each precursor used was 0.2mmol of PbAc₂·3H₂O, 0.05mmol of Cs₂CO₃, 4.75mmol of OA; the reaction temperature was 80 °C; 50 µl of benzoyl bromide was diluted in 0.5ml of octadecene; the reaction time was 15 seconds.

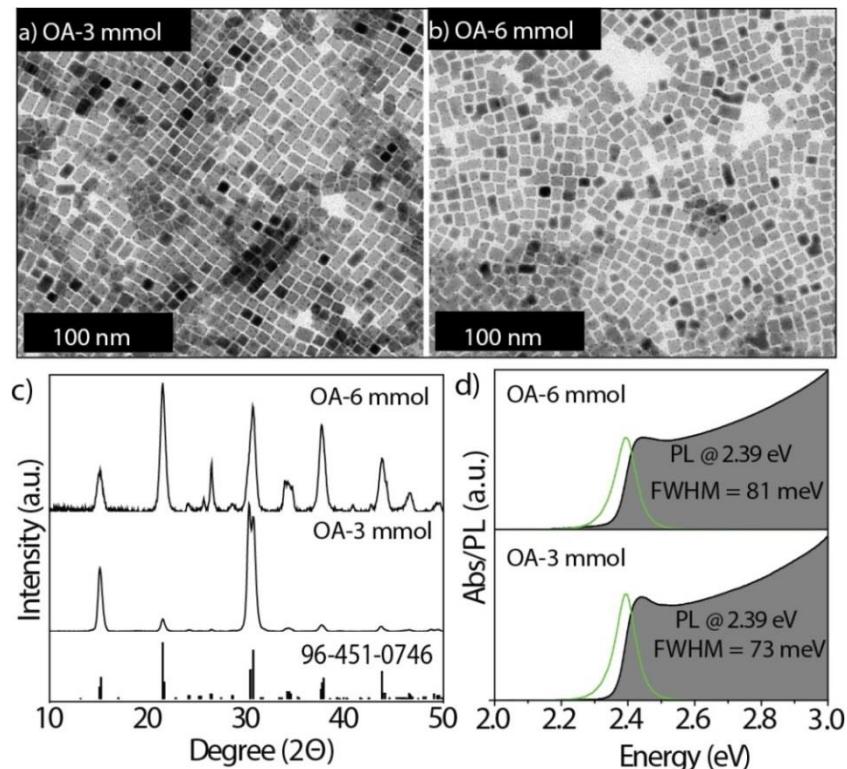


Figure S2. a-b) TEM images, c) XRD patterns, d) absorption and PL spectra of CsPbBr₃ NCs synthesized without any amine. The syntheses were carried out as follows: the amount of each precursor used was 0.2mmol of PbAc₂·3H₂O, 0.05mmol of Cs₂CO₃, two different amounts of OA were used (3 mmol and 6 mmol, respectively); the reaction temperature was 80 °C; 50 µl of benzoyl bromide was diluted in 0.5ml of octadecene; the reaction time was 15 seconds.

3. Photophysical properties of CsPbBr₃ nanocubes synthesized by using various secondary amines.

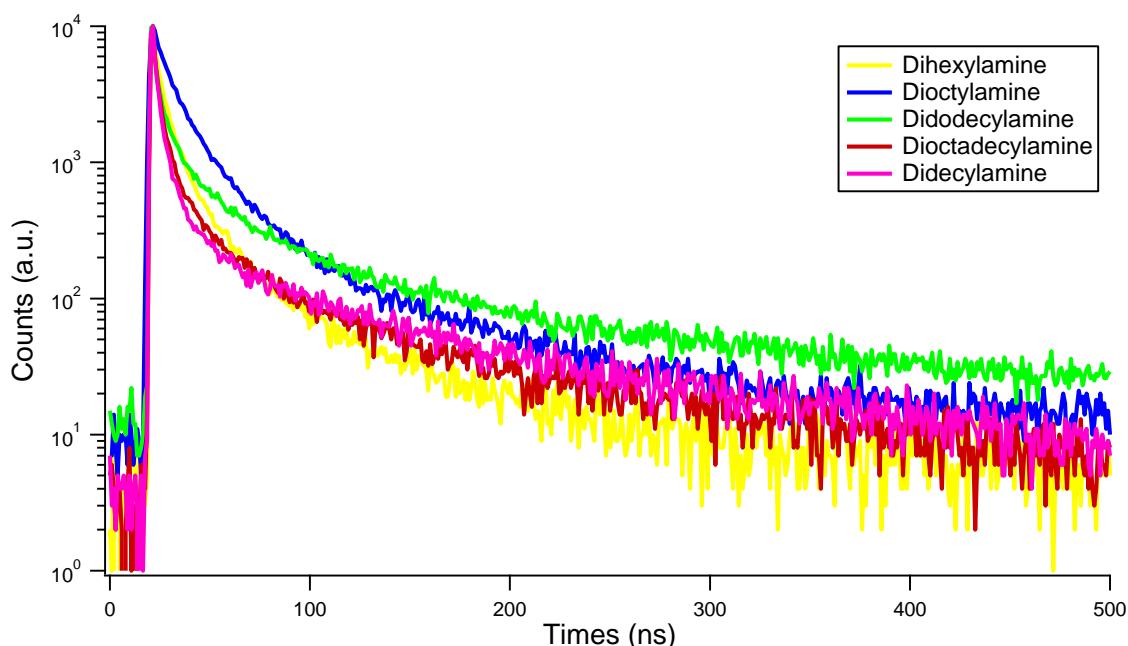


Figure S3. Decay lifetimes of CsPbBr₃ nanocubes prepared using various secondary amines.

Sample Name	PL max (nm)	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	A ₃	τ ₃ (ns)	τ _{AVG} (ns)	QY (%)
Dioctadecylamine	502	9220.28	3.77475	602.585	33.0702	57.0491	175.272	6.55	63
Didodecylamine	509	8829.71	3.11997	1501.01	22.8472	239.645	146.727	9.18	80
Didecylamine	513	11408.5	3.44428	363.521	38.1308	85.3936	167.707	5.69	57
Dioctylamine	515	8149.19	3.32575	4140.72	10	265.491	51.6817	6.55	69
Dihexylamine	516	8805.44	5.2776	1039.79	26.375	37.2879	166.154	8.10	48

Table S1. The summary of the PL, PLQY and life time measurements of CsPbBr₃ nanocubes prepared using secondary amines with various chain lengths.

4. Synthesis of 5.1 nm CsPbBr₃ nanocubes by using dioctadecylamine (DODAm) at 50 °C

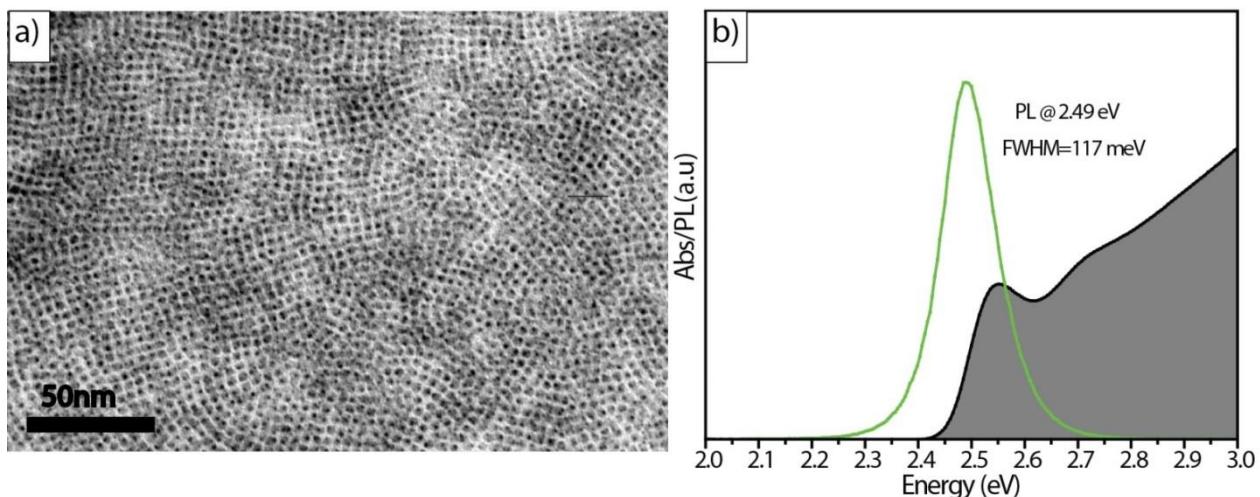


Figure S4. CsPbBr₃ nanocubes synthesized using DODAm. The synthesis was carried out using 0.2 mmol PbAc₂·3H₂O, 0.05 mmol Cs₂CO₃, 4.75 mmol of oleic acid, and 1.25 mmol of dioctadecylamine (DODAm) at an injection temperature of 50 °C. a) TEM image of CsPbBr₃ nanocubes and b) absorbance and PL spectra.

5. Controlling the size of CsPbBr_3 nanocubes by adjusting the reaction temperature

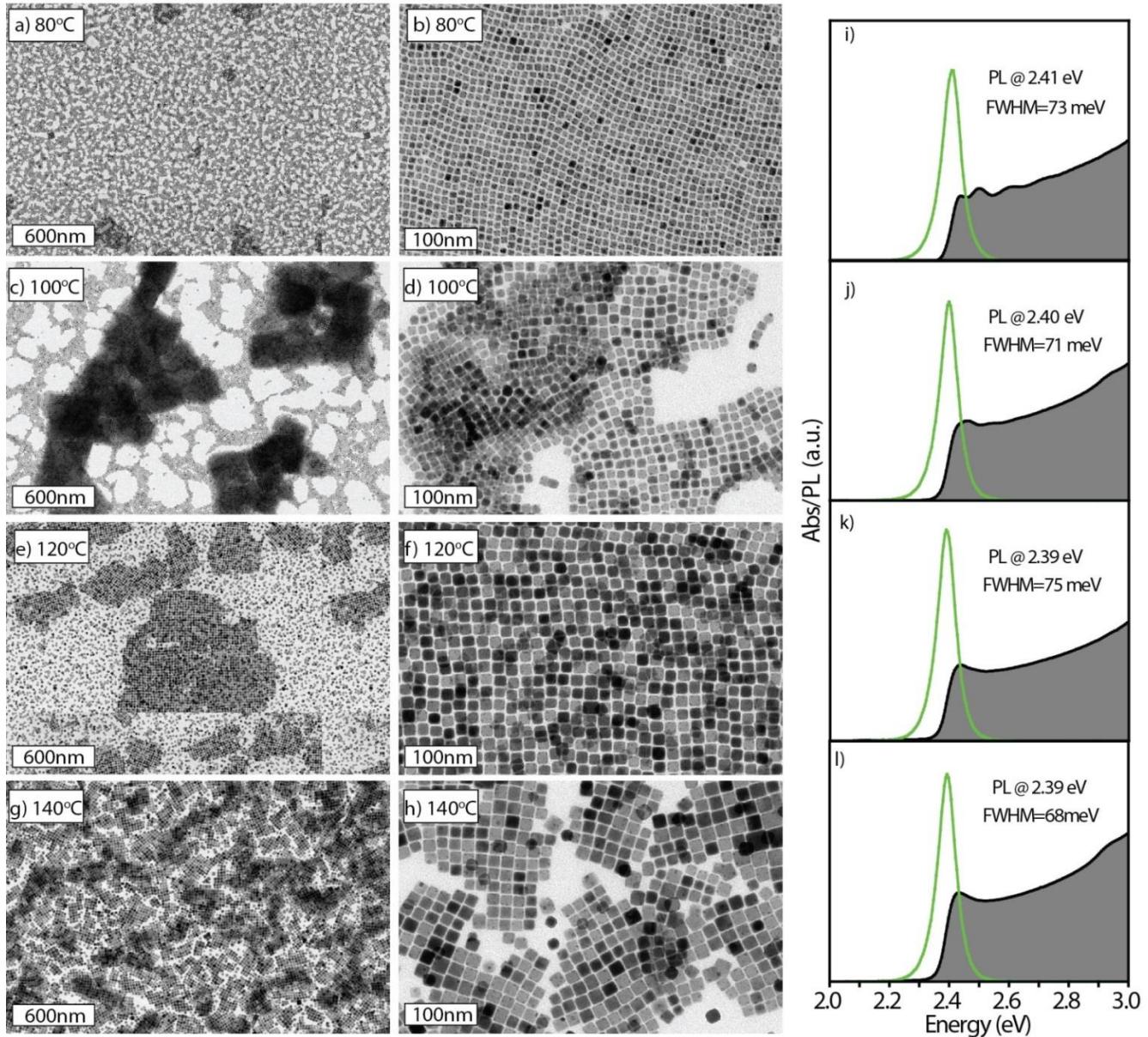


Figure S5. Representative TEM images (a-h), optical absorption and PL spectra (i-l) of CsPbBr_3 NCs synthesized by using 1.25 mmol of DDAm and 4.75 mmol of oleic acid at various injection temperatures. Reaction temperatures are indicated in panels (a-h). For each sample, two representative TEM images, at two different magnifications, are reported. Each row of panels refers to the same sample. For example, for the NCs synthesized at 80°C, panels (a-b) are representative TEM images at two different magnification, while the corresponding optical data are reported in panel i).

6. Effect of the oleic acid concentration on the formation of CsPbBr_3 nanocubes

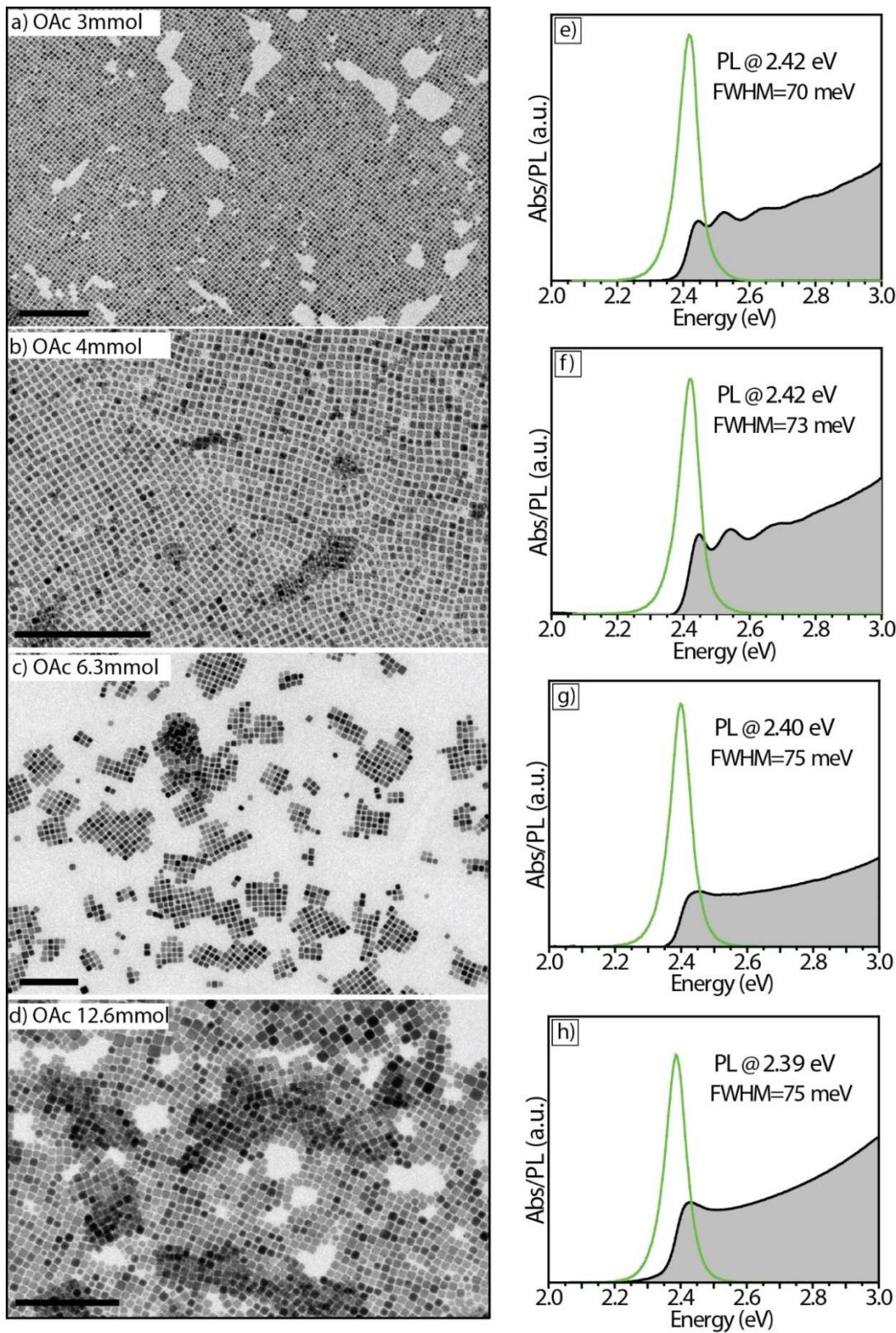


Figure S6. Representative TEM images (a-d), optical absorption and PL spectra (e-h) of CsPbBr_3 NCs synthesized using 1.25 mmol of DDDAm and various concentrations of oleic acid, at an injection temperature of 80 °C. Each row of panels refers to the same NC sample. For example, for the NCs synthesized at 3 mmol OAc, panel (a) is a representative TEM image, while the corresponding optical data are reported in panel e).

7. Control syntheses of CsPbBr_3 NCs in the presence of primary vs. secondary aliphatic amines of the same chain length under similar reaction conditions

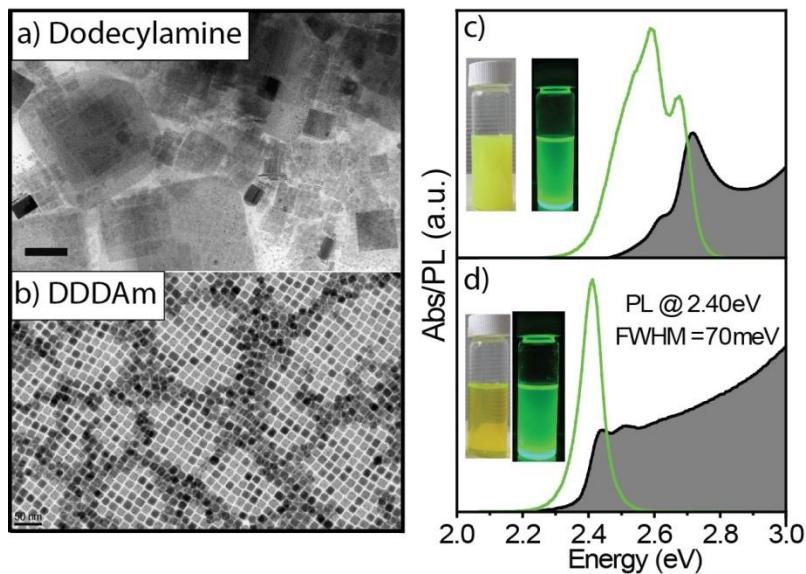


Figure S7. The syntheses were carried out using 0.2 mmol of $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$, 0.05 mmol Cs_2CO_3 , 4.75 mmol oleic acid, and 1.25 mmol of corresponding primary or secondary amines at an injection temperature of 100 °C. TEM images, absorption and PL spectra, and photographs of CsPbBr_3 NCs under ambient and UV light. These nanocrystals were synthesized with a,c) dodecylamine and b,d) didodecylamine (DDDAm), respectively.

8. XRD patterns of CsPbBr_3 NCs prepared by using primary amines

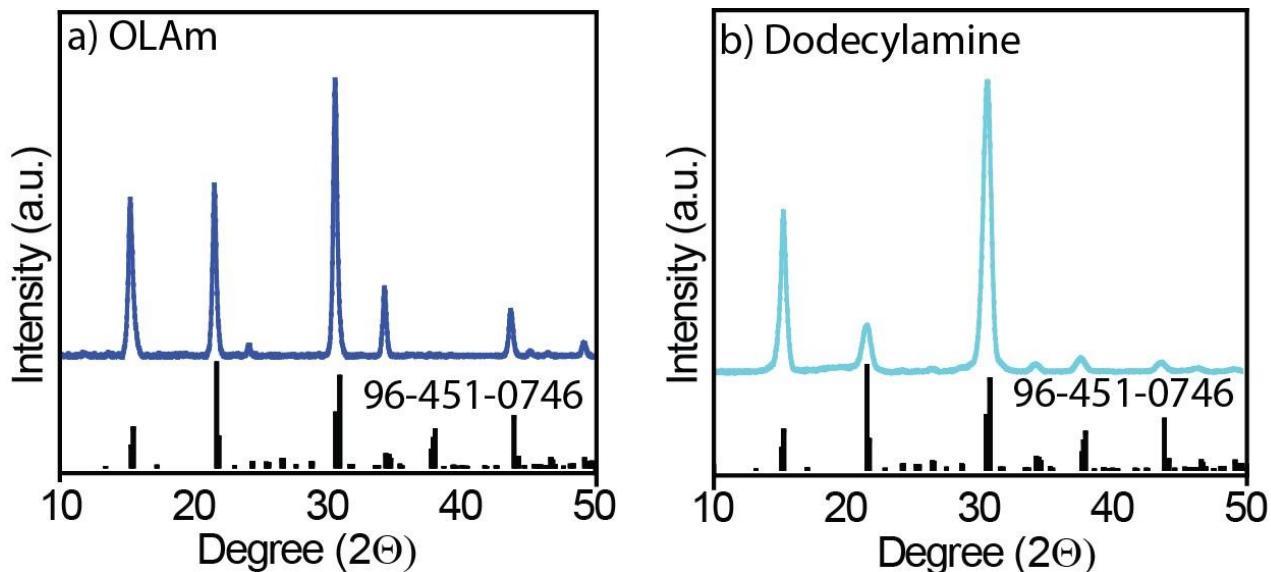


Figure S8. XRD patterns of CsPbBr_3 NPLs synthesized using primary amines: a) oleylamine and b) dodecylamine.

9. Synthesis carried out with dodecylamine and didodecylamine in the absence of Cesium carbonate

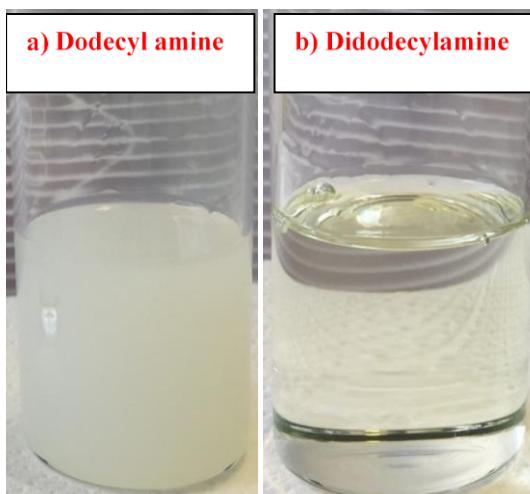


Figure S9. Photographs of vials containing the crude solution of syntheses carried out using either dodecylamine (a) or didodecylamine (DDDAm) (b) in the absence of a Cs^+ precursor, while all other reaction conditions were kept the same: the syntheses were carried out using 0.2 mmol of $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$, 4.75 mmol OA, and 1.25 mmol of corresponding primary or secondary amines, at an injection temperature of 100 °C. No precipitate was collected in vial (b) and the reaction mixture remained clear and colorless.

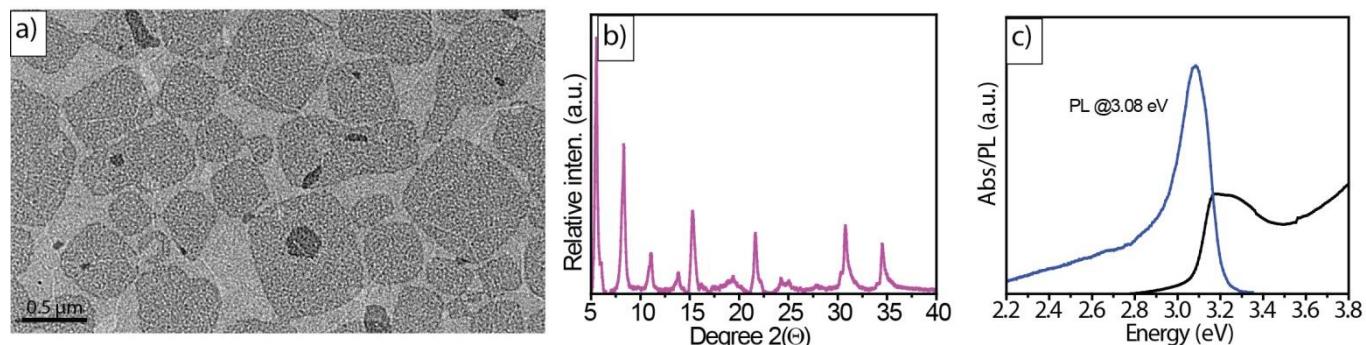


Figure S10. a) TEM image of layered lead bromide perovskite, b) XRD pattern, and c) absorbance and PL spectra.

10. Control syntheses of CsPbBr₃ carried out under secondary amine-rich conditions

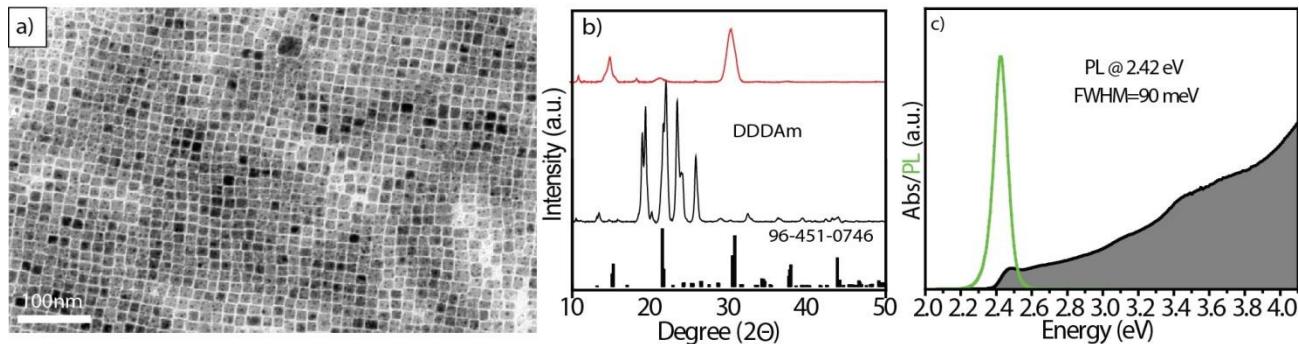


Figure S11. The synthesis was carried out by using 0.2 mmol PbAc₂·3H₂O, 0.05 mmol Cs₂CO₃, 3 mmol of oleic acid (OA), 5 mmol (a four-fold excess compared to the standard procedure) of didodecylamine (DDDAm) and an injection temperature of 80 °C. a) TEM image of the resulting CsPbBr₃ nanocubes, b) XRD pattern showing the absence of other cesium lead bromide phases, and c) absorbance and PL spectra. The additional peaks other than orthorhombic CsPbBr₃ perovskite phase in the XRD patterns are due to an excess of unreacted DDDAm in the sample and can be indexed accordingly.

11. Stability of CsPbBr₃ nanocubes against conversion to Cs₄PbBr₆ in the presence of excess of didodecylamine as compared with the excess of oleylamine

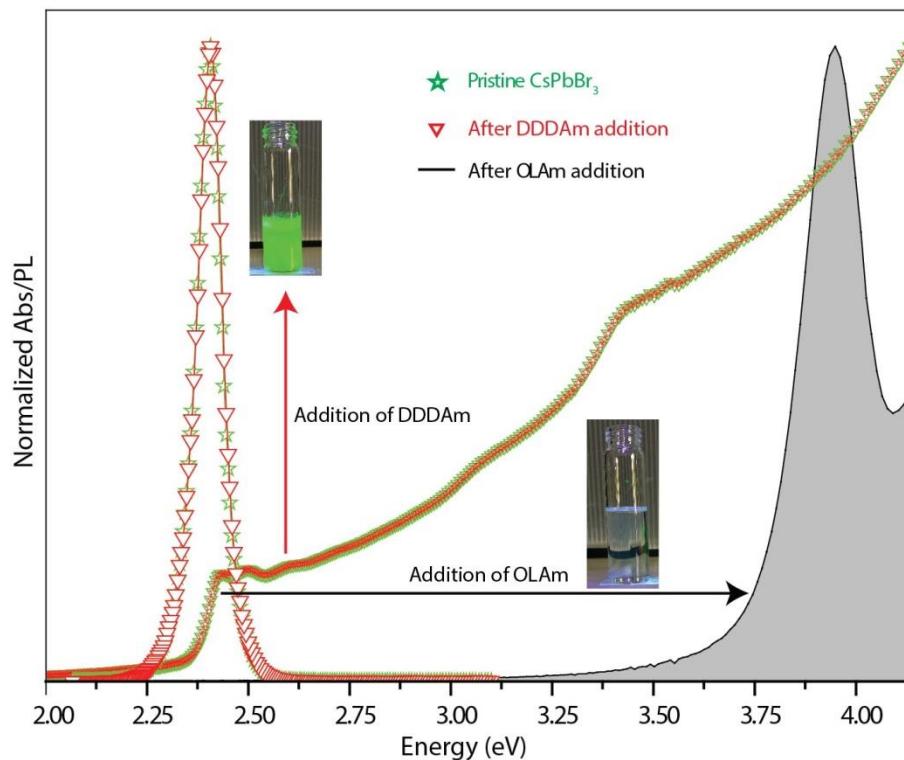
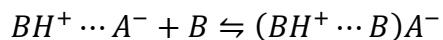


Figure S12. Absorption and PL spectra of the CsPbBr₃ nanocubes synthesized in the presence of didodecylamine (DDDAm) are shown in green. The overlaid red absorption and PL spectra were measured after an excess of DDDAm was added to the toluene dispersion of the nanocubes. The black shaded absorption spectrum was measured after an identical toluene dispersion of initially CsPbBr₃ nanocubes was mixed with an excess of oleylamine. The photographs in the insets show the resulting mixtures under UV light. An excess of oleylamine triggers the complete conversion of emissive CsPbBr₃ nanocubes to non-emissive Cs₄PbBr₆ phases, while DDDAm is inactive for that transformation.

12. Solubility of lead (II) bromide in the presence of primary and secondary amines

It should be noted that the solubility of PbX_2 salts in the mixture that contains both acid (oleic acid) and a primary amine (oleylamine), which is typically used for the synthesis of CsPbX_3 NCs, is highly limited by the formation of the ammonium carboxylate salt, as discussed in a previous work from our group.¹ For primary amines in the presence of excess amine, this salt can undergo dissociation by homoassociation (i.e. hydrogen bonding between a base and its conjugate acid),² which can be described as:



in which $\text{BH}^+ \cdots \text{A}^-$ is the ammonium carboxylate salt, formed by the acid AH (oleic acid in this case) and the base B (the primary amine in this case). Homoassociation (the formation of $\text{BH}^+ \cdots \text{B}$), in turn, promotes the solvation of PbX_2 . Homoassociation cannot take place with secondary aliphatic amines when substituents are bulkier than the methyl groups.² In the figure below is can be seen how PbBr_2 , for example, is easily dissolved in an oleic acid-octylamine mixture, but not in an oleic acid-dioctylamine mixture or in oleic acid alone.

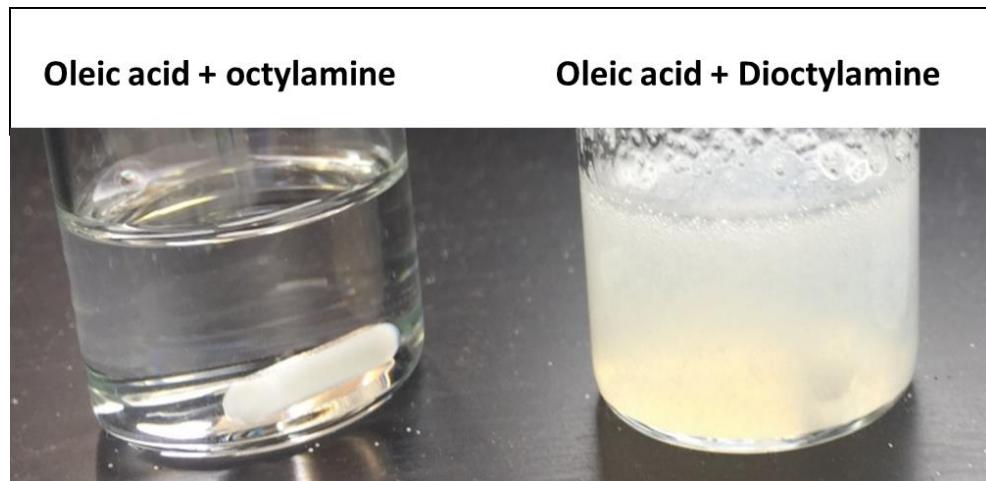


Figure S13. Solubility of lead bromide in primary (left vial) and secondary (right vial) amines with the same hydrocarbon chain length. Experimental details: 72 mg of PbBr_2 , 3 mmol of amine (octylamine or dioctylamine), 3 mmol of oleic acid, 5 ml of octadecene were combined in a 20 mL vial, heated up to 130 °C on a hotplate and kept at that temperature for 30 minutes.

13. ^1H NMR spectra of the mixtures of oleic acid and dodecylamine

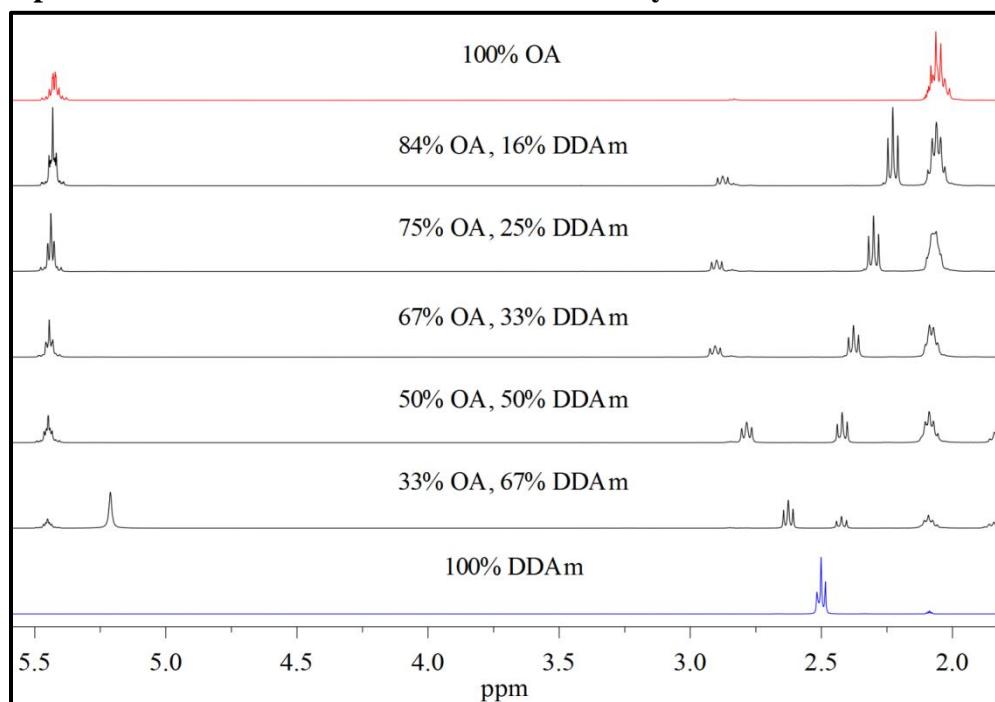


Figure S14. Selected regions of the ^1H NMR spectra of dodecylamine (DDAm), oleic acid (OA) and their various mixtures in toluene-d8 at various molar %.

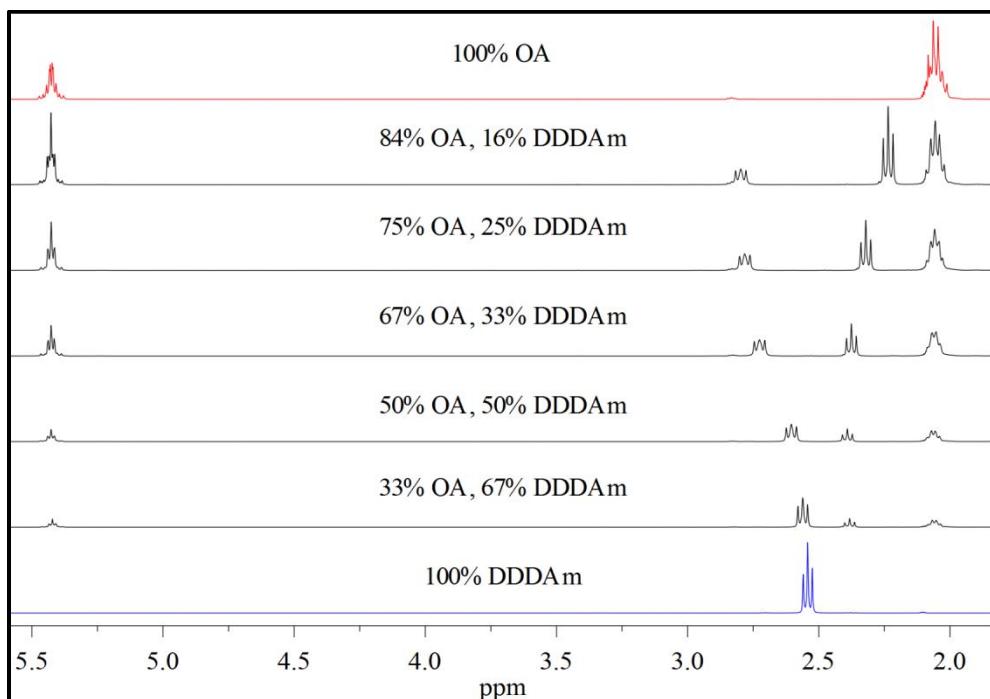


Figure S15. Selected regions of the ^1H NMR spectra of didodecylamine (DDDAm), oleic acid (OA) and their various mixtures in toluene-d8 at various molar %.

14. Chemical shift of $\alpha\text{-CH}_2$ for primary and secondary amines in the presence of oleic acid

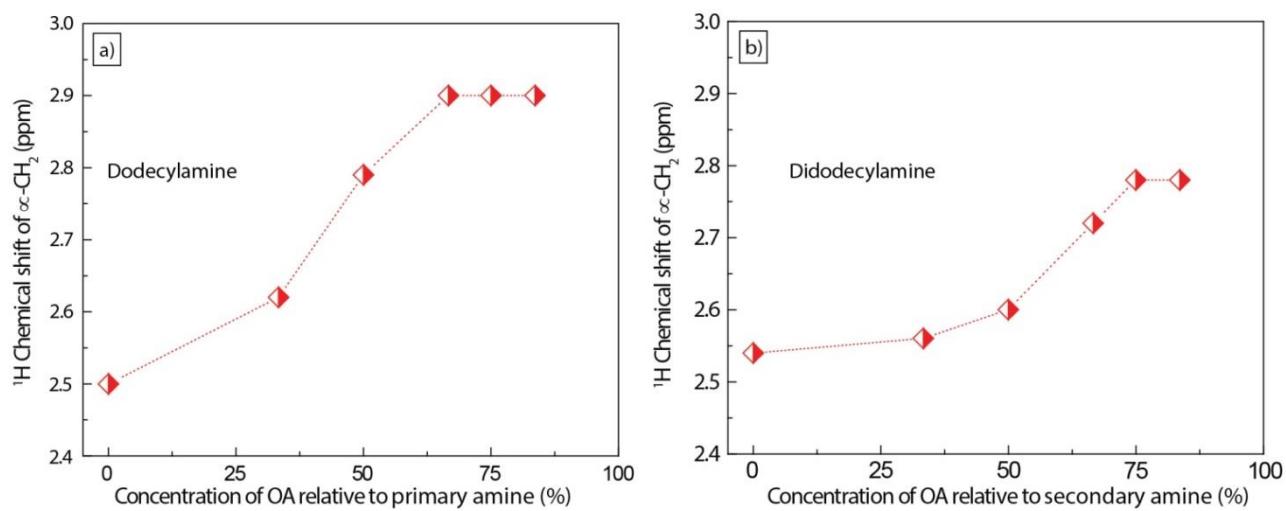


Figure S16. Comparison of ^1H chemical shifts of $\alpha\text{-CH}_2$ for (a) primary and (b) secondary amines as a function of the relative amount of OA(oleic acid).

15. NMR analysis on CsPbBr₃ nanocubes synthesized by using secondary amine

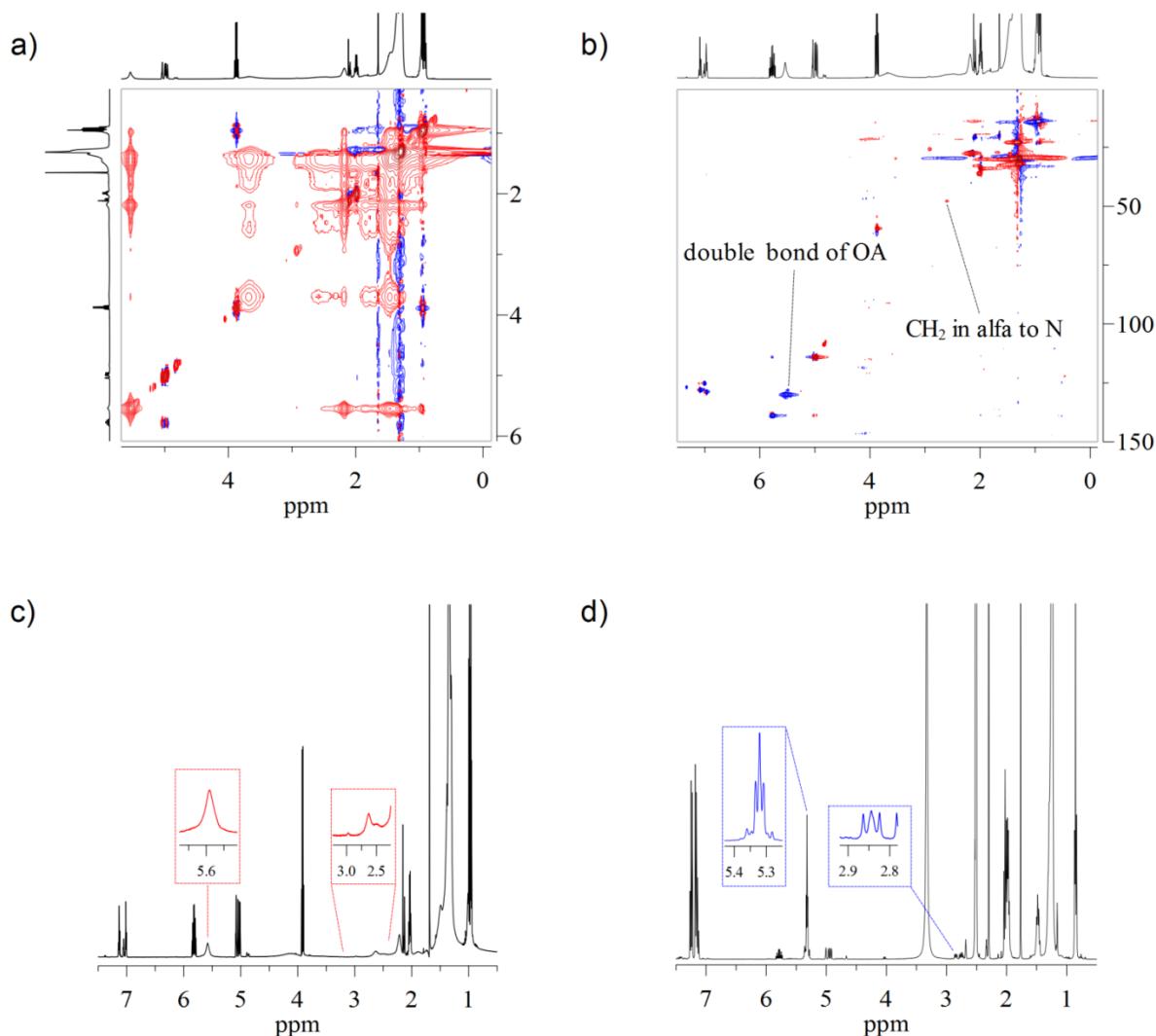


Figure S17. a) ^1H - ^1H NOESY, b) ^1H - ^{13}C HSQC and c) ^1H -NMR spectrum on washed CsPbBr₃ nanocubes synthesized using DDDAm (didodecylamine), in toluene-d8; d) ^1H NMR on a washed NC sample dissolved in deuterated DMSO.

16. XPS analysis of CsPbBr_3 nanocubes synthesized by using primary and secondary amine

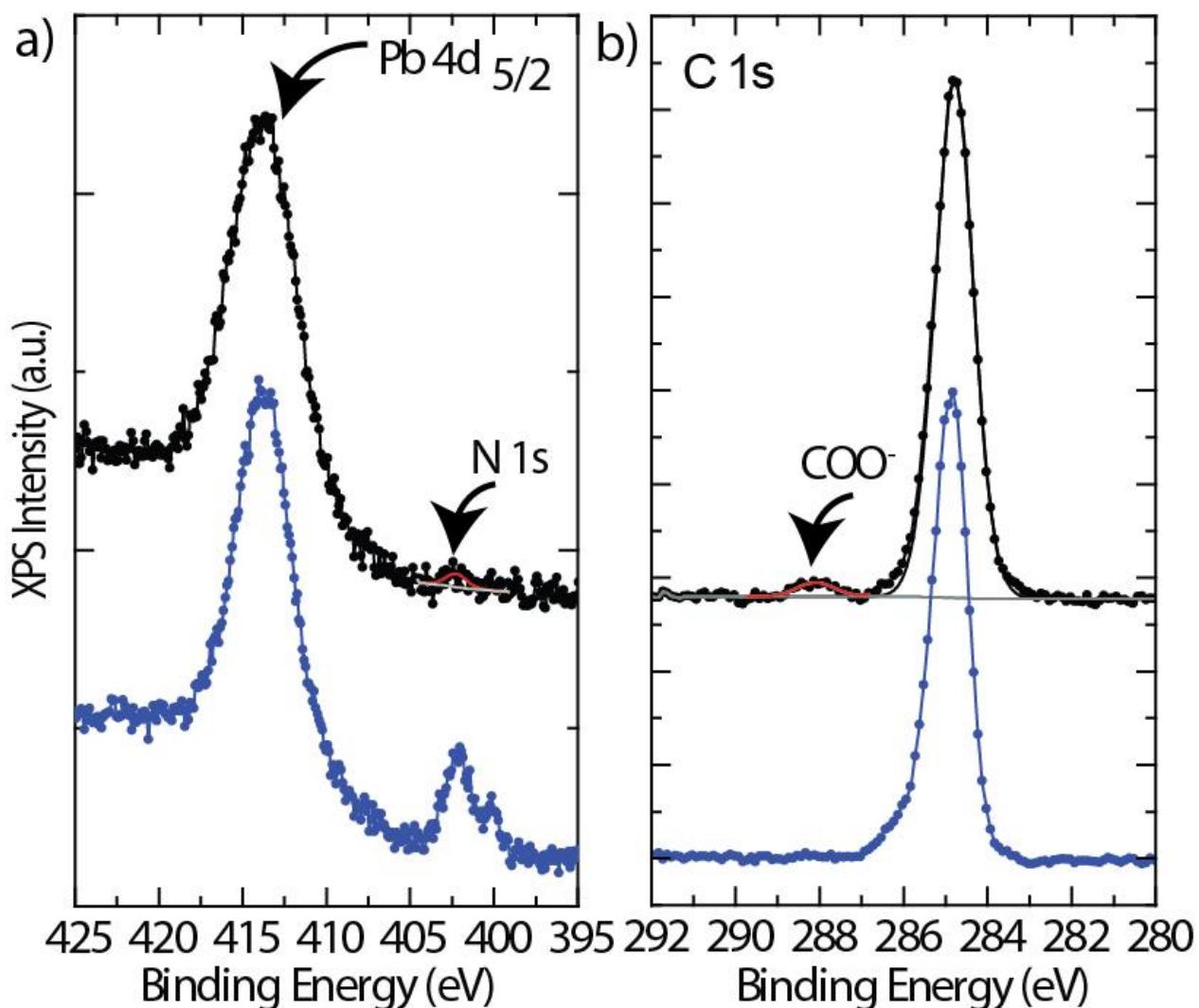


Figure S18. Quantitative XPS analysis of ligand composition on the surface of CsPbBr_3 nanocubes synthesized by using DDDAm (black) and OLAm (blue). Panel a) refers to the Pb 4d5/2 and N 1s regions, while panel b) refers to the C 1s region.

17. HRTEM analysis of CsPbBr₃ Nanocubes prepared by didodecylamine

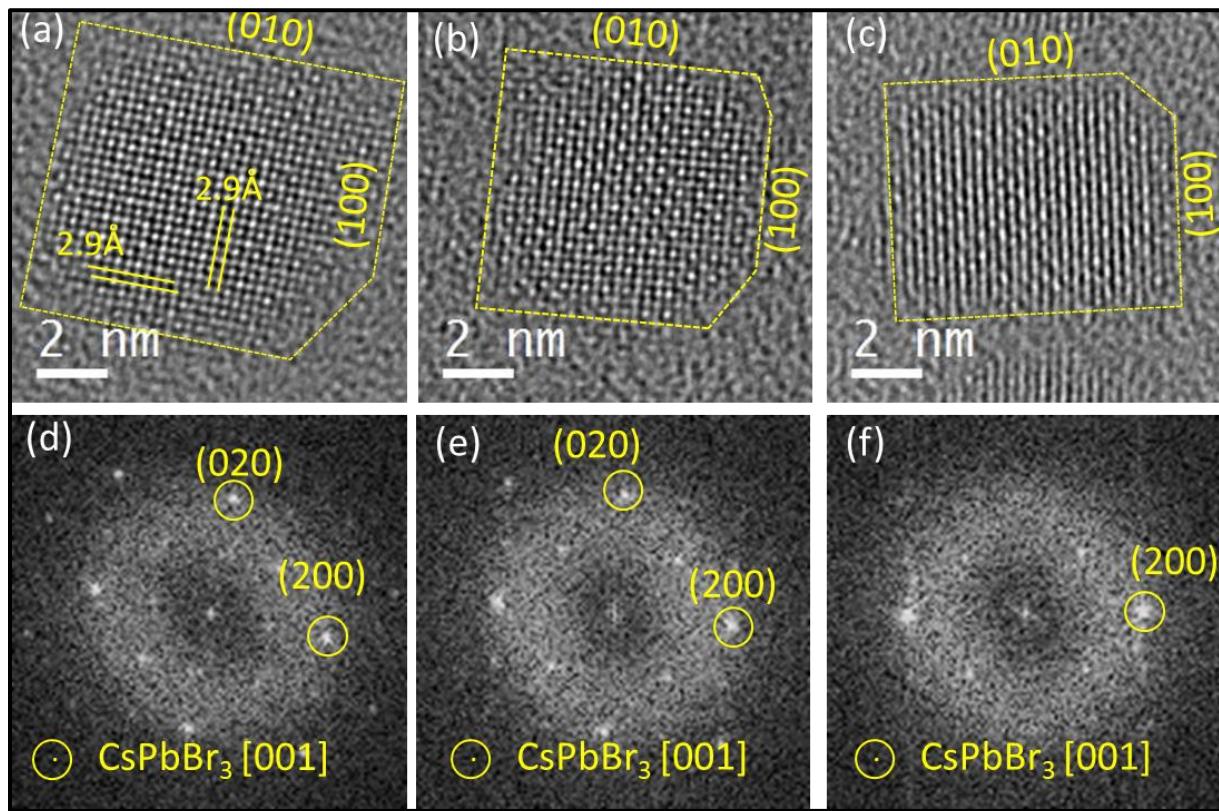


Figure S19. (a-c) HRTEM images of three CsPbBr₃ nanocubes enclosed by {100} facets with corresponding fast Fourier transform (FFT), shown in (d-f).

18. Ligand surface coverage with secondary amines

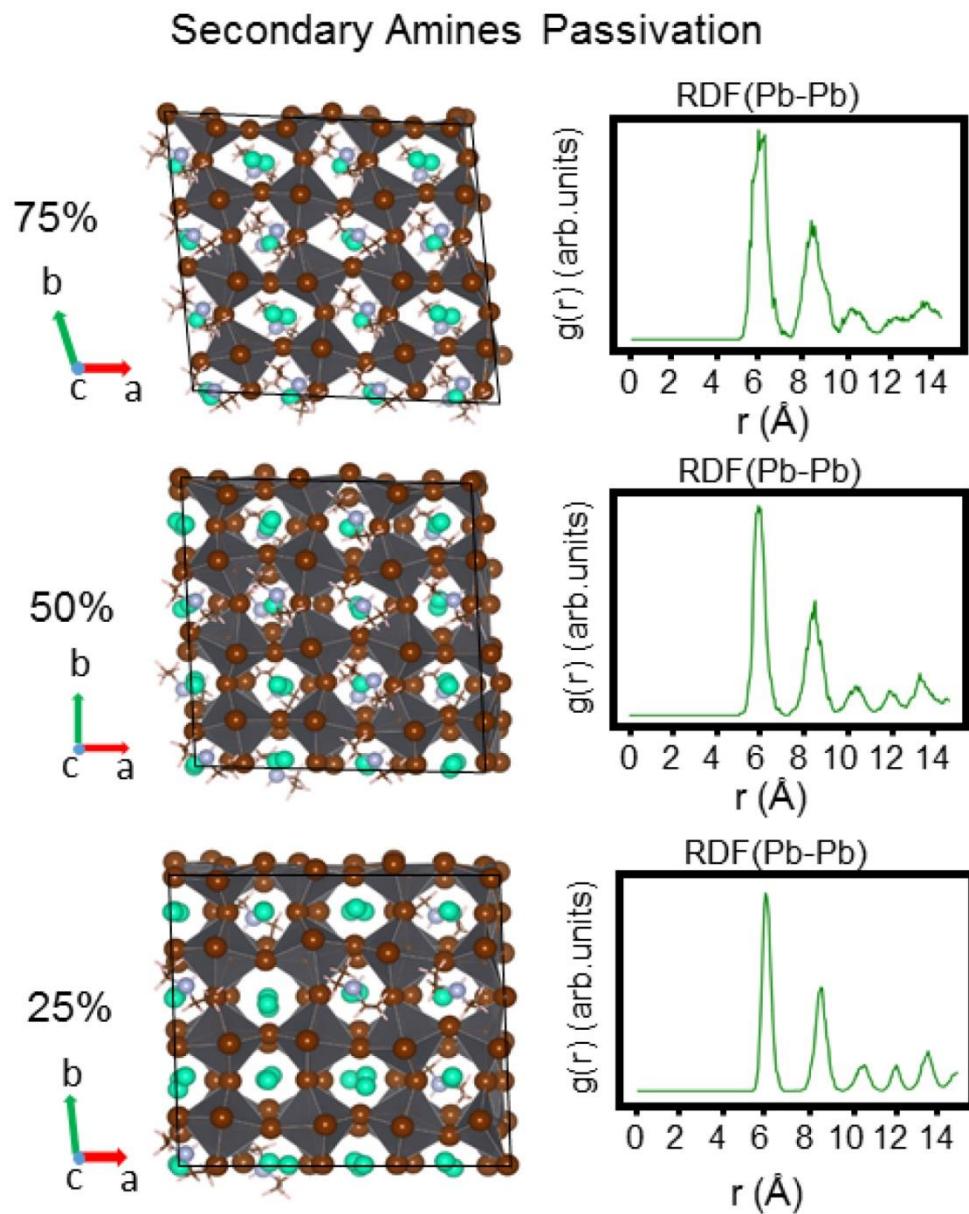


Figure S20. Structures and radial distribution functions for the slabs in which the ligand surface coverage of secondary amines has been reduced to 75-50-25%.

19. CsPbBr₃ nanocubes used for self-assembly experiment in glove box

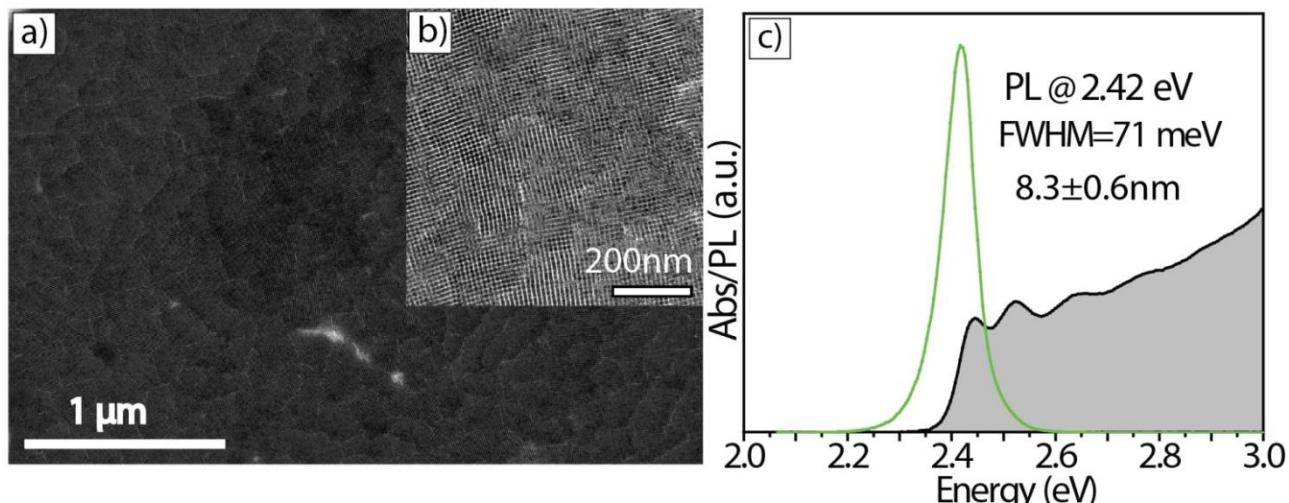


Figure S21. TEM images of the CsPbBr₃ nanocubes synthesized by using DDDAm under standard synthetic conditions (Figure a, b) and their optical properties c).

20. Size distribution for a sample of ~8.5 nm CsPbBr₃ nanocubes used for self-assembly under ambient conditions

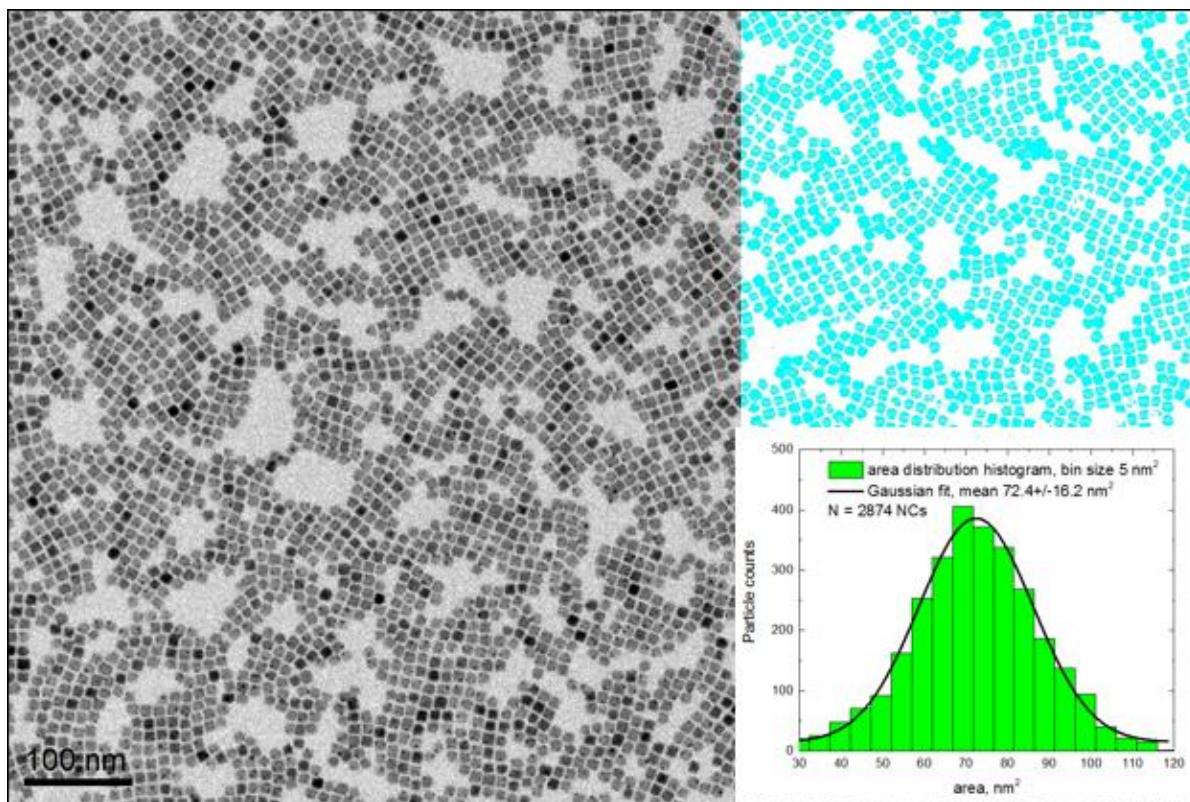


Figure S22. TEM image of nanocubes with results of the threshold size analysis in ImageJ.^{3,4} (top right) an overlay of the cyan outlines of the NCs identified in the image. (bottom right) the histogram of the nanocrystal areas from the entire image (N = 2874 nanocrystals). Assuming a square NC outline, the average NC area of 72.4 ± 16.2 nm² corresponds to an edge length of 8.5 ± 0.9 nm.

21. Self-assembly of 8.5 nm CsPbBr₃ nanocubes and optical microscopy imaging

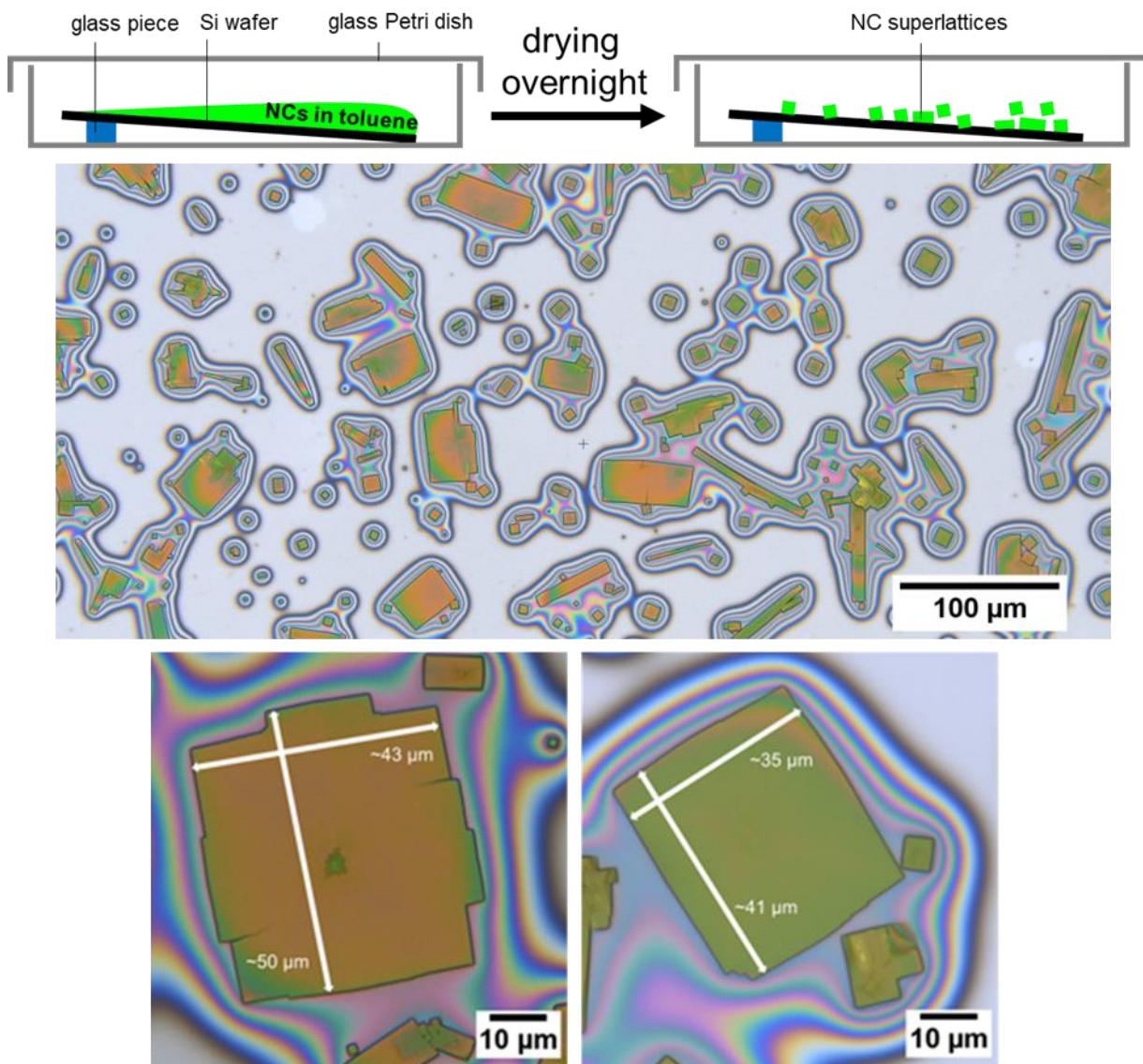


Figure S23. Sketch of the self-assembly experiment and optical microscopy images of $\sim 50 \mu\text{m}$ NC superlattices.

22. Synthesis of CsPbCl_3 NCs by using secondary amines

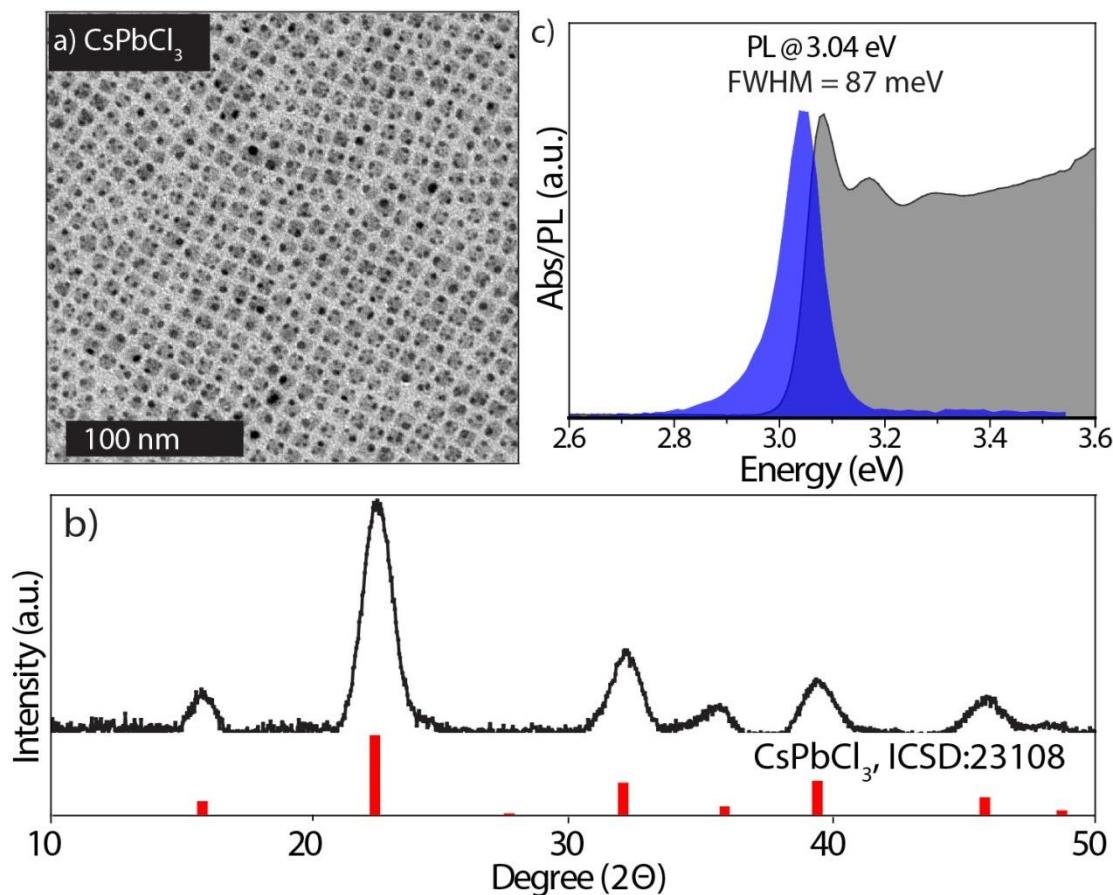


Figure S24. a) TEM image, b) XRD pattern, c) absorption and PL spectra of CsPbCl_3 NCs synthesized with didodecylamine (DDDAm). The synthesis was carried out as follows: The amount of each precursor used was 0.2mmol of $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$, 0.05mmol of Cs_2CO_3 , 4.75mmol of OA, and 1.25mmol of dialkylamine; the reaction temperature was 80°C ; 50 μl of benzoyl chloride was diluted in 0.5ml of octadecene; the reaction time was 30 seconds.

23. Caption of Supporting Video 1

The video displays two experiments in which a colloidal suspension of CsPbBr_3 NCs in toluene is mixed with a toluene solution containing either a large excess of a primary amine (oleyleamine, left vial) or a secondary amine (didodecylamine, right vial).

24. References

- (1) Almeida, G.; Goldoni, L.; Akkerman, Q.; Dang, Z.; Khan, A. H.; Marras, S.; Moreels, I.; Manna, L. *ACS nano* **2018**, *12*, 1704.
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