Supporting Information

The Phosphine Oxide Route towards Lead Halide Perovskite Nanocrystals

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S0. Abbreviations and Experimental Details

Abbreviations

Nanocubes = NCs
Oleic Acid = OA
Cesium-Oleate = Cs-oleate
1-Octadecene = ODE
Trioctylphosphine Oxide = TOPO
Deuterated Toluene = d-toluene
n-Tetradecylphosphonic acid = TDPA
Diisooctylphosphinic acid = DOPA
Temperature = T
Photoluminescence = PL

Table S1. Synthesis parameters used in preparation of $CsPbBr_3$ NCs. Resulting PL peak, full width half maxima (FWHM) and their size are recorded, total reaction volume is constant at 7.5 mL using ODE

Entry	**$PbBr_2$**	**TOPO**	**OA**	**Cs-oleate in OA (solution 1)**		**Cs-oleate in ODE (solution 2)**		**T**	**PL**		**Size**
	(mg)	(g)	(mL)	(mL)	[Cs] (M)	(mL)	[Cs] (M)	(°C)	Peak (eV)	FWHM (eV)	(nm)
i	60	1	0	0	-	1	0.15	75	2.42	0.10	32 ± 19
ii	60	1	0.4	0	-	1	0.15	75	2.42	0.12	20 ± 15
iii	60	1	0	1	0.15	0	-	75	2.41	0.08	-
iv	60	1	0.4	1	0.15	0	-	75	2.44	0.11	6.8 ± 1.1
v	60	1	0.4	2	0.075			75	2.45	0.10	5.3 ± 0.8
vi	60	1	1.3	0	-	1	0.15	75	2.49	0.21	-
vii	60	1	0.4	1	0.1	0	-	75	2.42	0.07	9.0 ± 0.9
vii	60	1	0.4	1	0.2	0	-	75	2.44	0.09	7.0 ± 0.6
ix	60	1	0.4	1	0.3	0	-	75	2.46	0.12	7.9 ± 0.8
x	60	1	0.4	1	0.4	0	-	75	2.44	0.12	8.8 ± 0.8
xi	30	0.5	0.2	1	0.15	0	-	25	2.65	0.23	3.4 ± 0.4*
xii	60	1	0.4	2	0.075	0	-	50	2.43	0.07	6 ± 0.6
xiii	60	1	0.4	2	0.075	0	-	140	2.39	0.08	10.7 ± 1.1
xiv	60	0.72	0.4	1	0.15	0	-	75	2.46	0.11	-
xv	60	4	0.4	1	0.15	0	-	75	-	-	-

S1. Precipitation of Lead Bromide

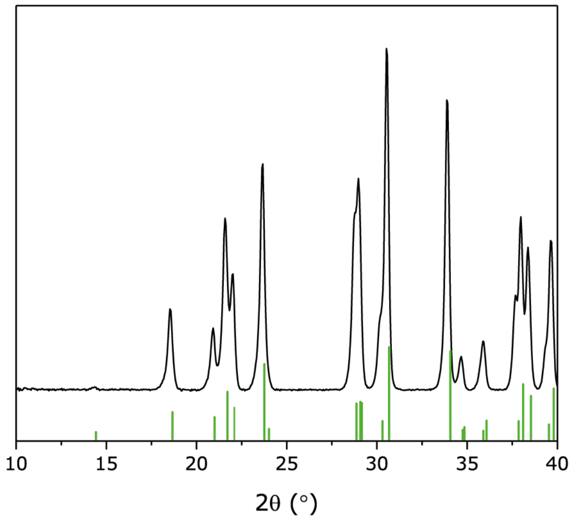


Figure S1 XRD pattern of $PbBr_2$ precipitated out of TOPO and OA in ODE at 75°C, reference pattern for $PbBr_2$ (shown in green) is taken from ICSD 98-003-6170.

S2. ^{1}H NMR OA Concentration Dependence

In order to ascertain that our shift in the α-CH_2 in OA is due to interactions with TOPO (Figure 2a of the main text) and not due to concentration, we perform ^{1}H NMR on OA alone at the same concentrations as the solutions containing TOPO : OA. As can be seen in Figure S2, the gap between the α-CH_2 of OA and that of TOPO : OA widens with increasing TOPO : OA ratios (i.e. decreasing OA concentrations). Therefore, we can conclude that the shift we report in Figure 2a is an effect which the interactions with TOPO contribute towards.

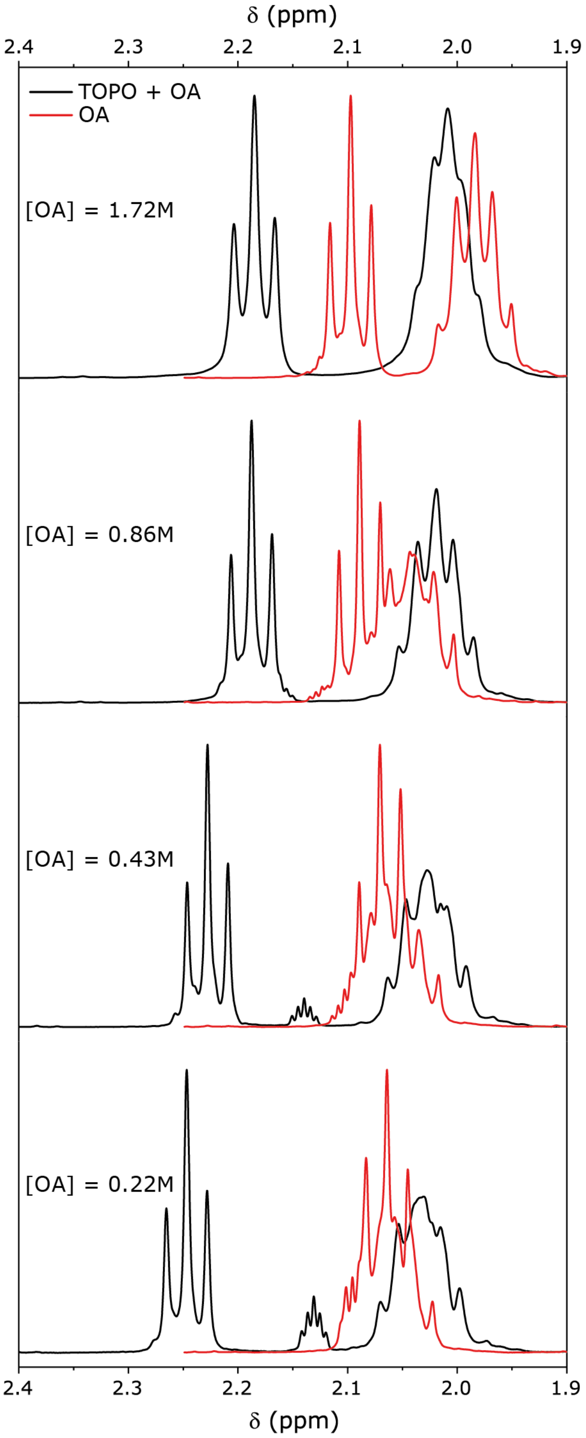


Figure S2 ^{1}H NMR spectra of TOPO:OA mixtures ([TOPO] = 0.43 M) and oleic acid alone both in d-toluene over increasing concentration of OA. Chemical shift range shown is for α-CH_2 in OA.

S3. ^{1}H NMR Temperature Dependence

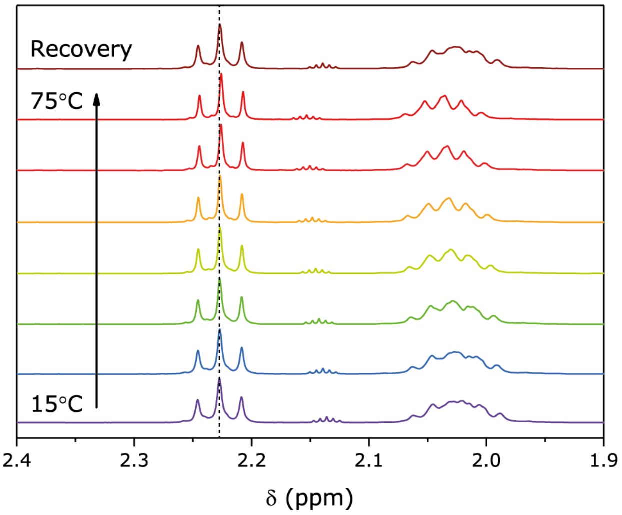


Figure S3 ^{1}H NMR spectra of TOPO:OA mixture (1:1) in d-toluene over temperatures ranging from 15 to 75°C, chemical shift range shown is for α-CH_2 in OA.

S4. Effect of Acid Content on the Synthesis of NCs

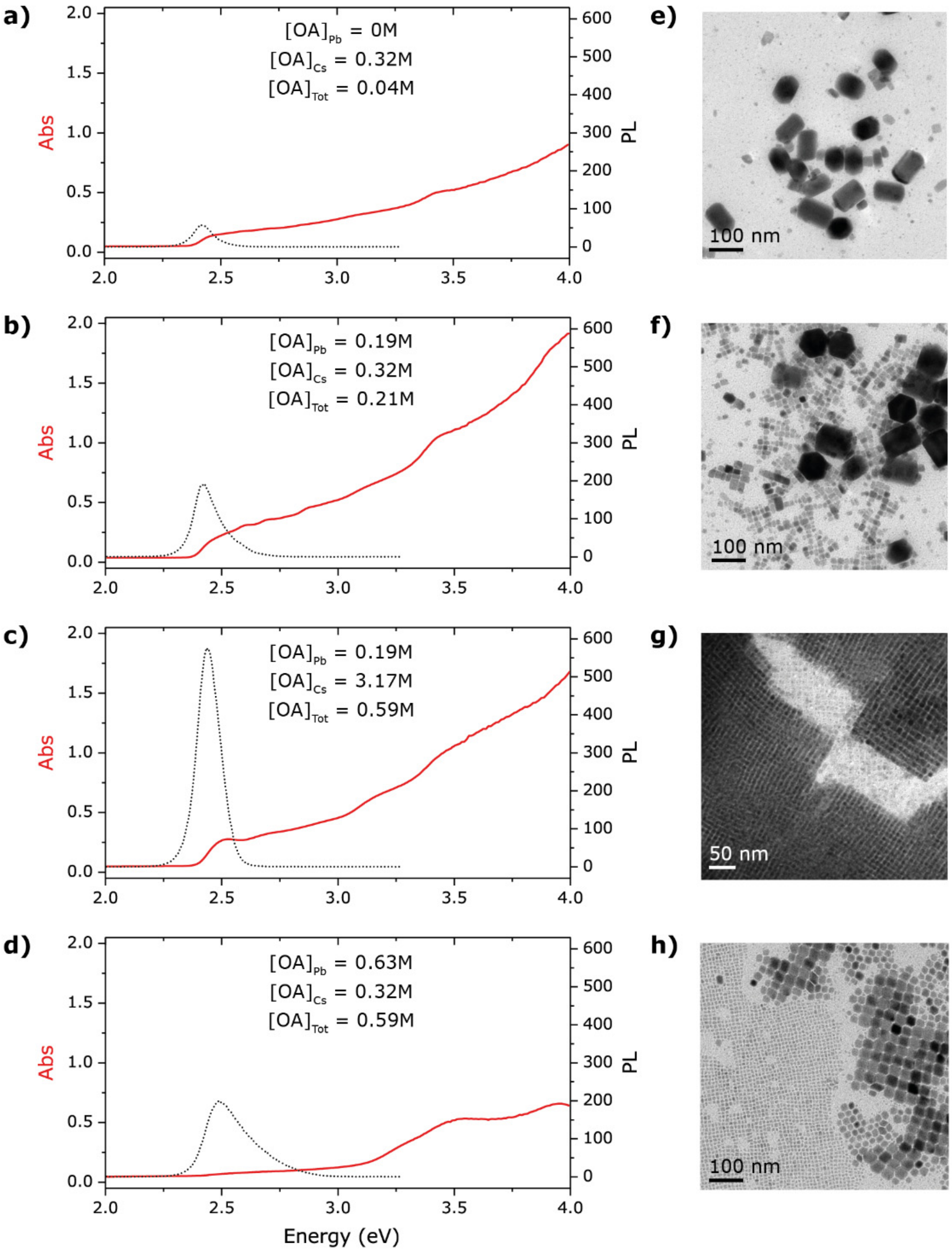


Figure S4 (a)-(d) PL (dotted) and absorption (red) spectra of NCs synthesized at differing OA content. OA added to the reaction mixture is denoted as $[OA]_{Pb}$, OA added on injection of Cs-Oleate is denoted as $[OA]_{Cs}$ and their combined total in the reaction flask is denoted as $[OA]_{Tot}$. (e)-(h) corresponding TEM images. These results show that a higher $[OA]_{Tot}$ is required for monodisperse NCs but a balance between $[OA]_{Pb}$ and $[OA]_{Cs}$ must be reached to obtain such NCs.

S5. Effect of Reaction Time on the Synthesis of NCs

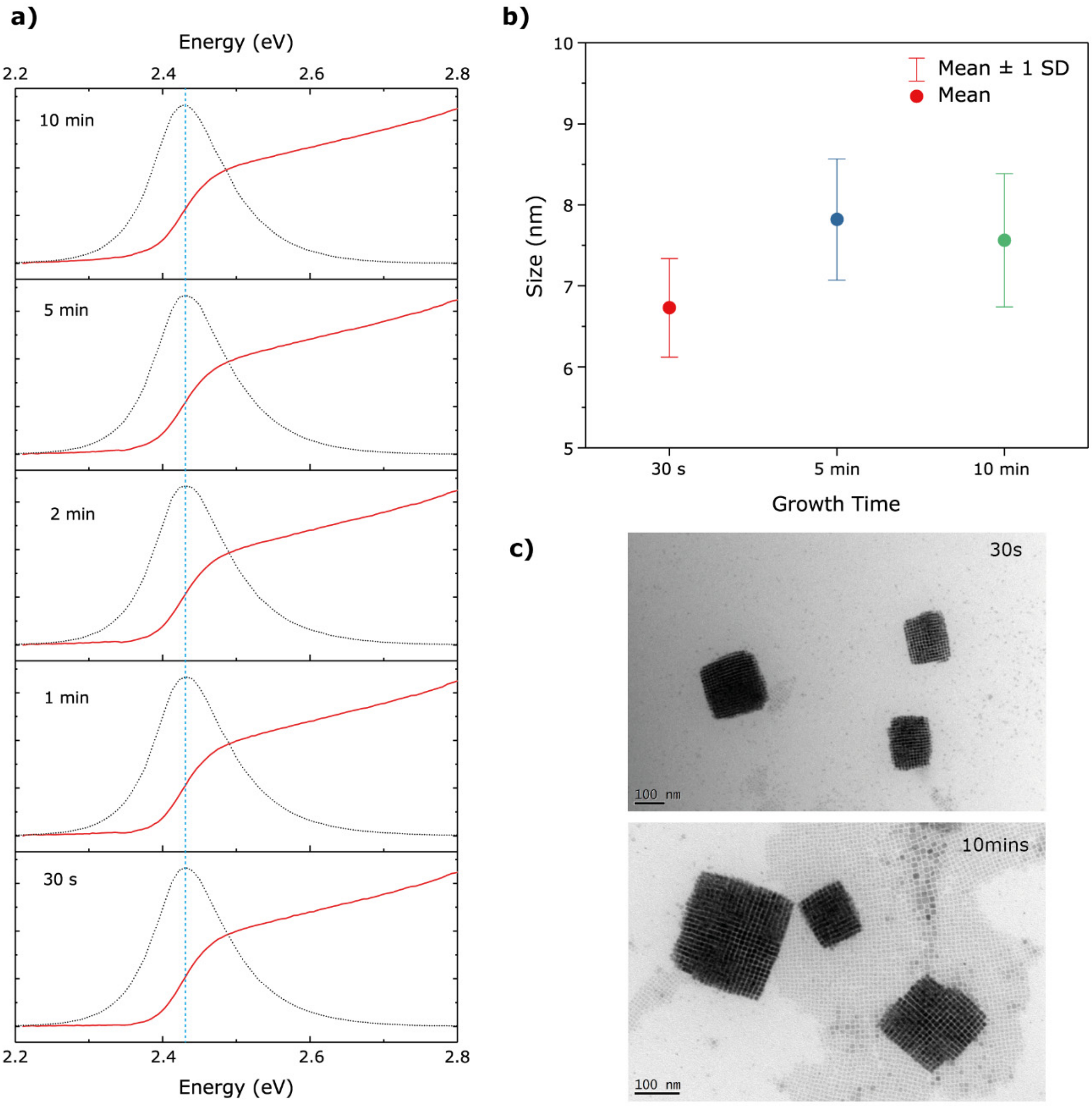


Figure S5 (a) PL (dotted) and optical absorption spectra (red) of NCs with increasing reaction times, (b) particle size and size distribution of NCs reacted for 30 seconds, 5 minutes and 10 minutes, (c) example TEM images of NCs reacted for 30 seconds and 10 minutes. We define reaction time as the time between the injection of Cs-oleate and the quenching in an ice bath.

S6. Synthesis of $CsPbBr_3$ NCs via the Amine Route

We follow the procedure reported in a previous paper from our group.[1] In short, 72 mg of $PbBr_2$ (0.2 mmol, 33 mM), 500 µL of oleylamine, 50 µL of oleic acid and 5.45 mL of 1-octadecene are mixed and degassed for 15 minutes at 100 ^{0}C in order to obtain a colorless solution. Thereafter, the temperature is ramped to 140 ^{0}C under a dry nitrogen flow and 0.5 mL of a 0.15 M Cs-oleate solution in 1-octadecene (previously heated for 10 minutes on a hot-plate set at 200 ^{0}C) is swiftly injected. The reaction mixture is immediately cooled after injection with an ice bath and diluted with 5 mL of toluene. The dispersion is centrifuged at 2500 rpm (for 3 minutes) and the NCs are re-dispersed in 2.0 mL of hexane

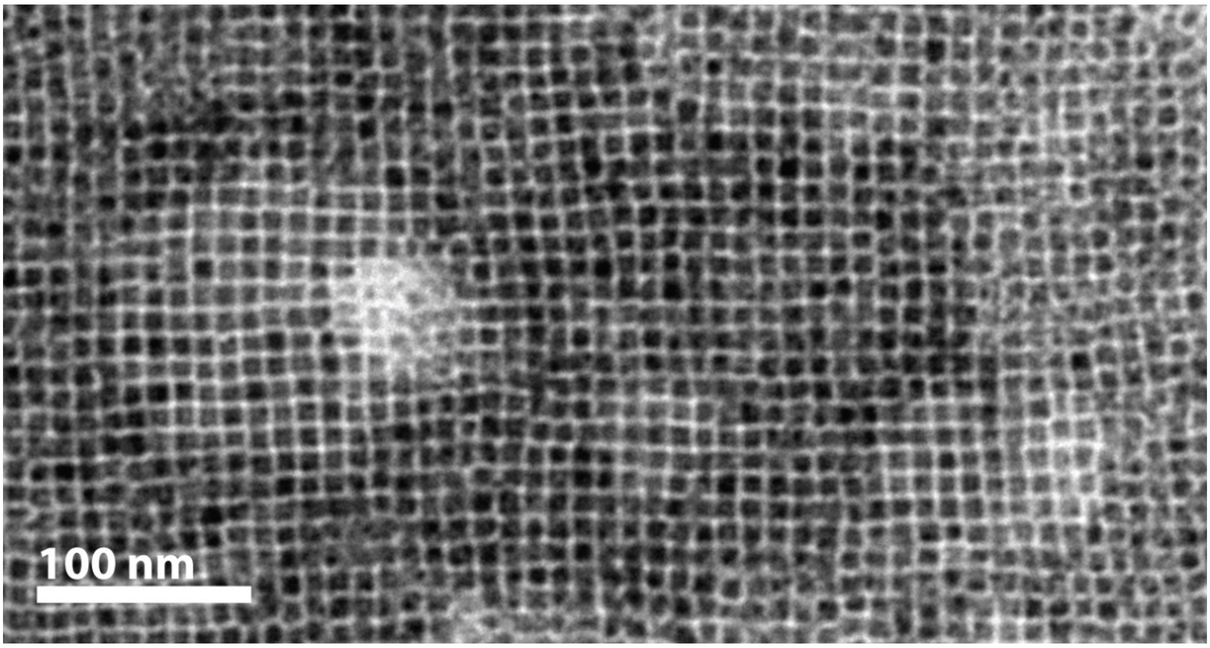


Figure S6 TEM image of 6 nm NCs synthesized via the amine route with a composition of $Cs_{0.9}PbBr_{2.8}$ and a N / Cs ratio of 0.33 (as determined by XPS).

S7. Synthesis of $CsPbBr_3$ and Cs_4PbBr_6 NCs

Synthesis of Cs_4PbBr_6 NCs. The same standard procedure employed for the $CsPbBr_3$ NCs is used here, but with 4.0 g TOPO (10.36 mmol) and 2.36 mL ODE instead. To separate the NCs, we add toluene to the reaction mixture prior to centrifuging to avoid the excess TOPO from solidifying.

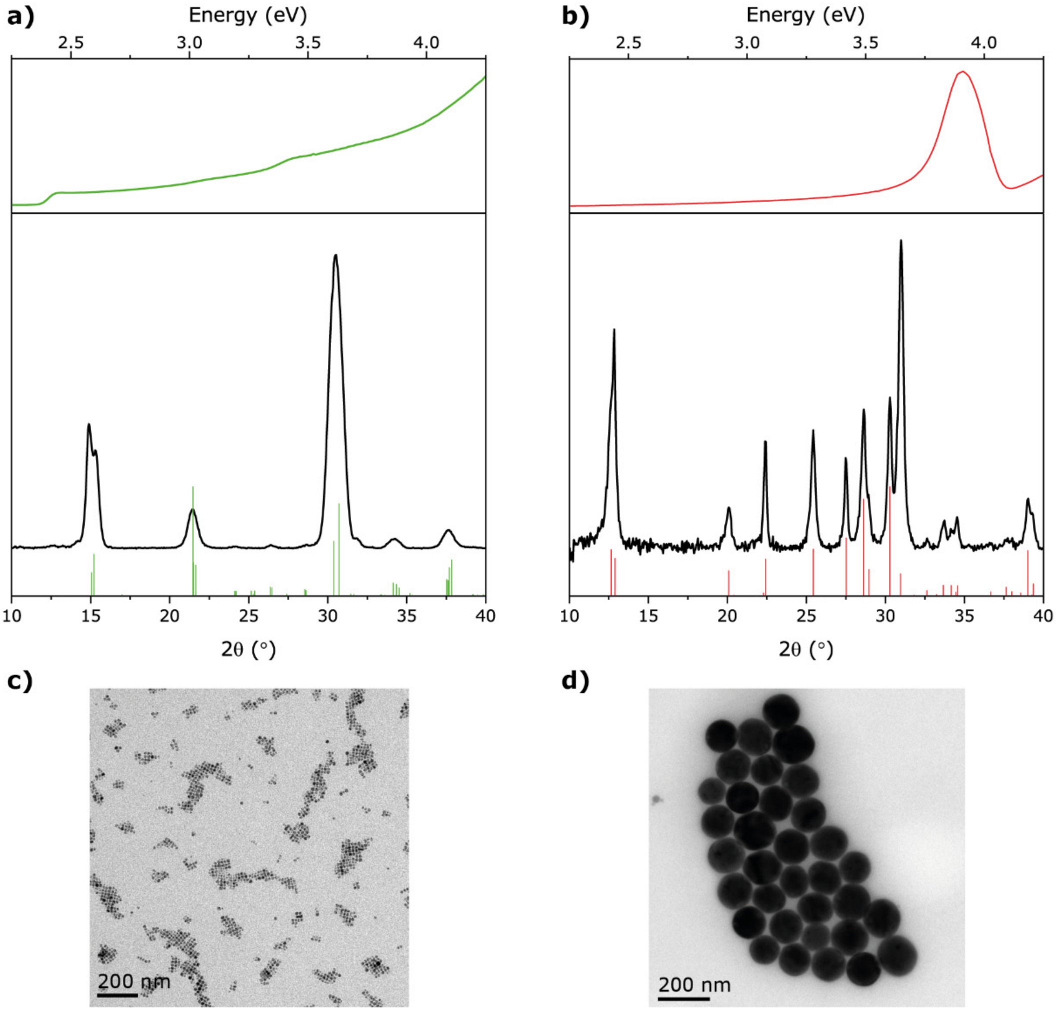


Figure S7 (a) Optical absorption (top) and XRD patterns (bottom) of $CsPbBr_3$ NCs (Table S1, Entry iv), (b) Absorption (top) and XRD (bottom) of Cs_4PbBr_6 NCs (modified version of Table S1, Entry iv, requiring 4 g of TOPO) (c)-(d) corresponding TEM images. XRD reference pattern for $CsPbBr_3$ is given in green and is from COD 4510745, reference pattern for Cs_4PbBr_6 is given in red and is from ICSD 98-009-7851.

S8. Transformation of NCs

$CsPbBr_3$ ↔ Cs_4PbBr_6 transformation reactions.

3D to 0D. In this transformation, 100 µL of a NC dispersion ([Pb] = 0.025 mM, as measured by ICP) is mixed with 100 µL of toluene and stirred at room temperature. A 0.96 M TOPO in toluene solution is added, 10 µL at a time with stirring intervals, until the solution turns from a bright green suspension to white, indicating the formation of Cs_4PbBr_6. The total added was 150 µL over 30 minutes. We can achieve the same transformation by adding 50 µL of NCs to a 0.58 M TOPO solution in toluene and stirring for 15 minutes. The transformation does not occur in the presence of oleic acid.

0D to 3D. To reverse the previous transformation, we add 100 µL of oleic acid to the white Cs_4PbBr_6 solution with stirring, and a yellow-green solution forms. We attribute this to $CsPbBr_3$ but note the loss in confinement of the NCs, as shown by the colour change.

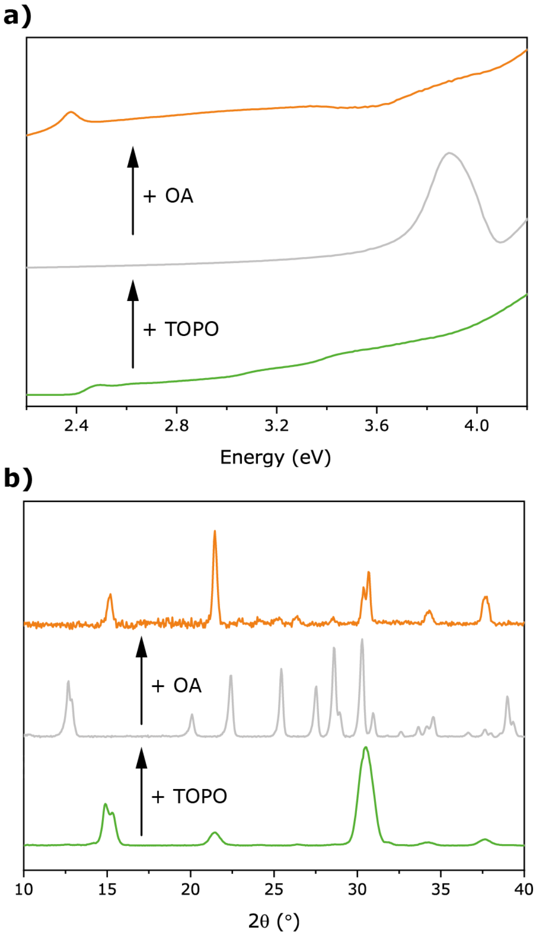
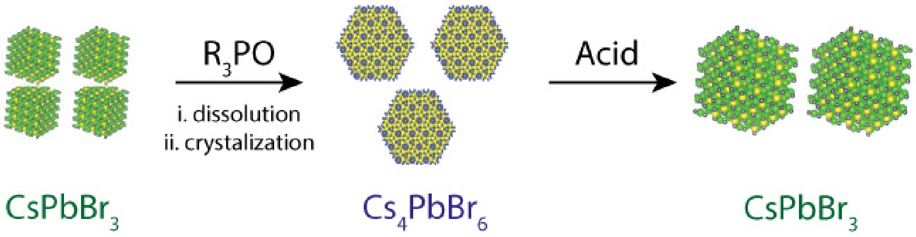


Figure S8 (a) Absorption spectra and (b) XRD patterns of $CsPbBr_3$ NCs being transformed to Cs_4PbBr_6 via the addition of TOPO and then back to $CsPbBr_3$ via the addition of OA. Back transformed $CsPbBr_3$ NCs exhibit narrower XRD with respect to the starting ones and is indicative of larger grain size.

Scheme S1. The quasi-reversible $CsPbBr_3$ to Cs_4PbBr_6 transformation



S9. Effect of Cs Concentration on the Synthesis of NCs

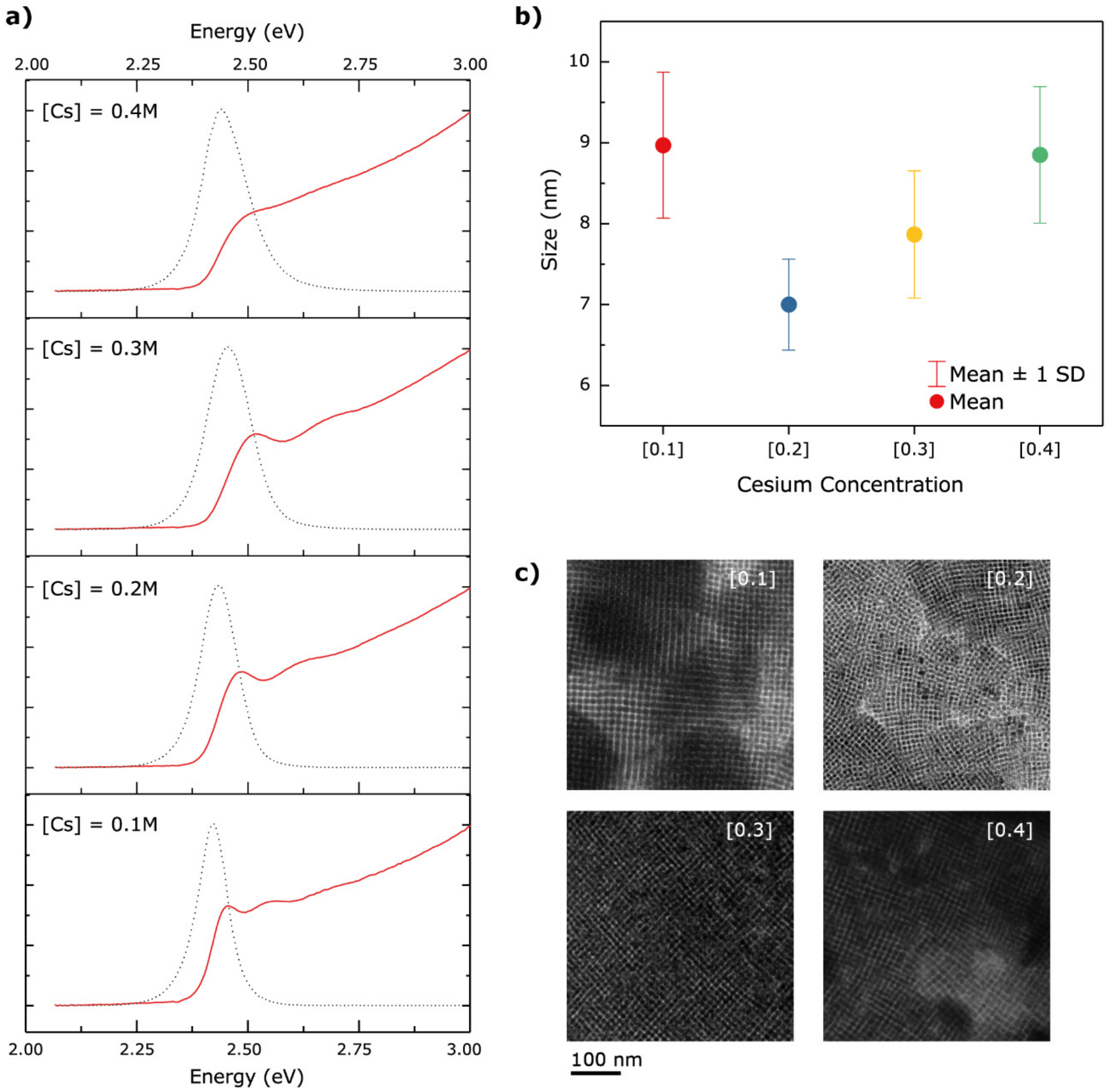


Figure S9 (a) PL (dotted) and absorption spectra (red), (b) particle size and size distribution, and (c) TEM images of NCs synthesized at different concentrations of cesium in Cs-oleate.

S10. Computational Experimental Details

A model of a $CsPbBr_3$ NC with edge size of about 2.4 nm was built by cutting a cubic bulk structure along the (100) facets, leaving Cs and Br on the surface. This NC presents a stoichiometry of $Cs_{125}Pb_{64}Br_{240}$, with an excess positive charge when each ion is considered in its more stable thermodynamic electronic configuration (i.e. Cs^+ , Pb^{2+} and Br^-). This excess was compensated by randomly removing 13 Cs ions from the surface, resulting in the following stoichiometry $Cs_{112}Pb_{64}Br_{240}$. We model four reactions to calculate the stability of the ligands proposed, where each ligand, formed of a cation and an anion, is considered to replace a CsBr pair of adjacent atoms on a facet of the NC:

1: NC(o)_Br_TOPOH <-> NC(o) + TOPO + HBr

2: NC(o)_Oleate_TOPOH <-> NC(o) + TOPO + OA

3: NC(o)_Oleate_Cs <-> NC(o) + Cs-Oleate

4: NC(o*)_Oleate_H <-> NC(o*) + OA

Here the underscore before the ion indicates it is bound to the NC surface, and NC(o) and NC(o) refer to the NC described in the second paragraph of this section but with one and five CsBr pairs of atoms extracted from its surface respectively. The energies -21.34, -9.72, -26.24 and -2.54 kcal/mol are found, respectively, for the four reactions, a negative number indicating a more stable configuration of the left side of the equilibrium.

To study the electronic properties of the NC at different Cs concentrations, we consider different degrees of surface passivation of our NC with Cs-oleate ligands. We start from an ideal fully passivated NC, with Oleate ions substituting all Br^- on the surface, yielding 16 Cs-oleate ligands per face. From this point we add and subtract Cs-oleate ligands, in order to see its effect on the density of states. Adding two Cs-oleate ligands on the surface is enough to induce two clear trap levels localized at the added extra ligands.

To study the removal of Cs-oleate ligands from the surface of the initial NC, we first calculate the most stable ligand removal sequence. In the structure we can find vertex ligands, where a Pb^{2+} cation is bound to three oleate anions; edge ligands, where a Pb^{2+} cation is bound to two oleate anions, and finally facet ligands, where a Pb^{2+} cation is bound to an oleate anion. We find that the higher the oleate coordination around Pb, the easier it is to remove a Cs-oleate ligand. Hence, we respect this order for ligand removal. Here, we find that, when about 55 % of the ligands are removed, trap states localized at ligands start to reduce the band gap. This last structure presents the stoichiometry of $Cs_{65}Pb_{64}Br_{144}$.

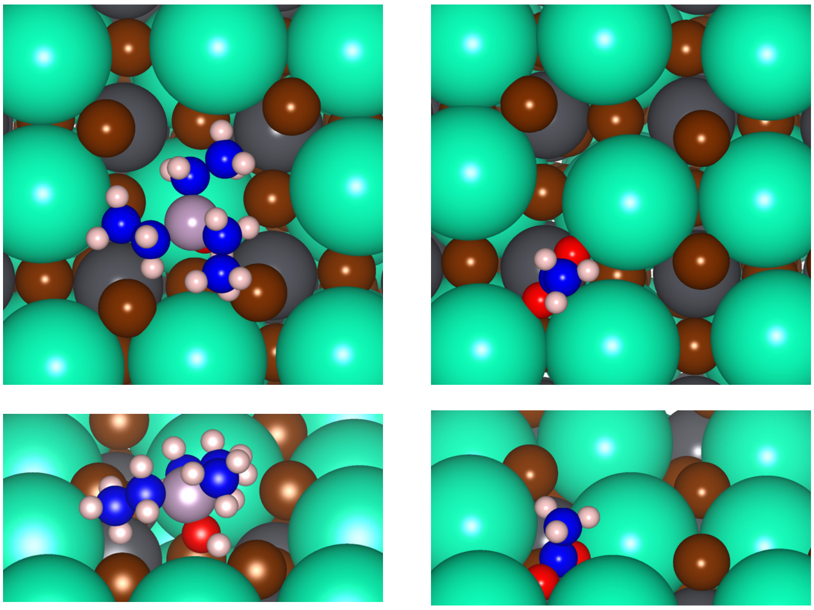


Figure S10 Relaxed structures with the Cs-oleate and TOPOH..Br attached to the NC surface. In the left, $TOPOH^+$ substitutes Cs^+ and Br^- occupies a Br^- site. On the right side, Cs^+ enters a Cs^+ site and the oleate anion substitutes Br^-

S11. NMR Study of Ligands

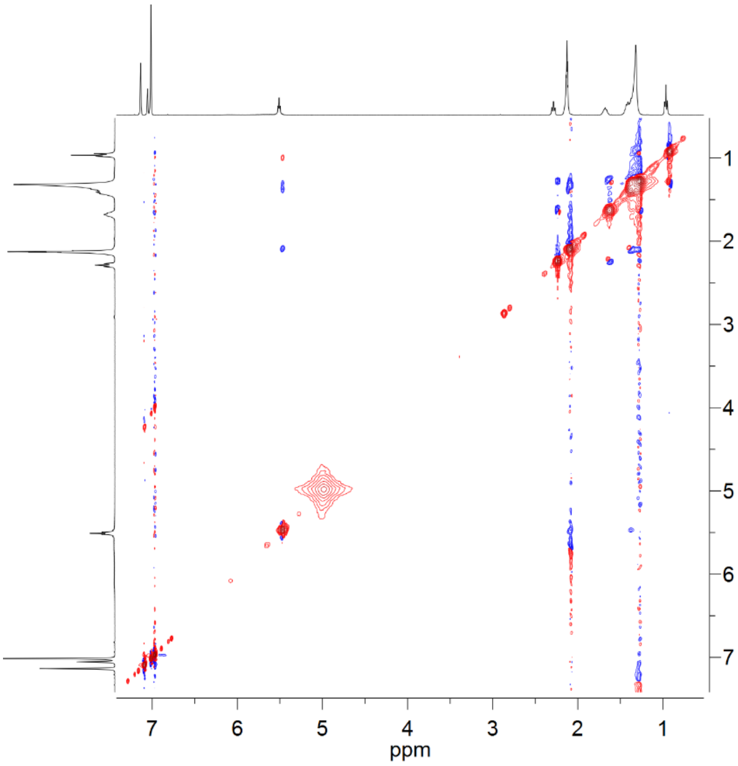


Figure S11.1 ^{1}H NOESY spectrum of Cs-oleate in d-toluene. The experiment has been acquired with the aim to compare with the NOESY recorded on the samples A and B, in the same experimental conditions (same NMR sequence and mixing time = 300 ms). In this case, the cross peaks are, as expected, positive (blue) in opposite phase (red) compared to the diagonal, indicating a fast movement of the molecules in solution, enabling a building up of positive NOE.

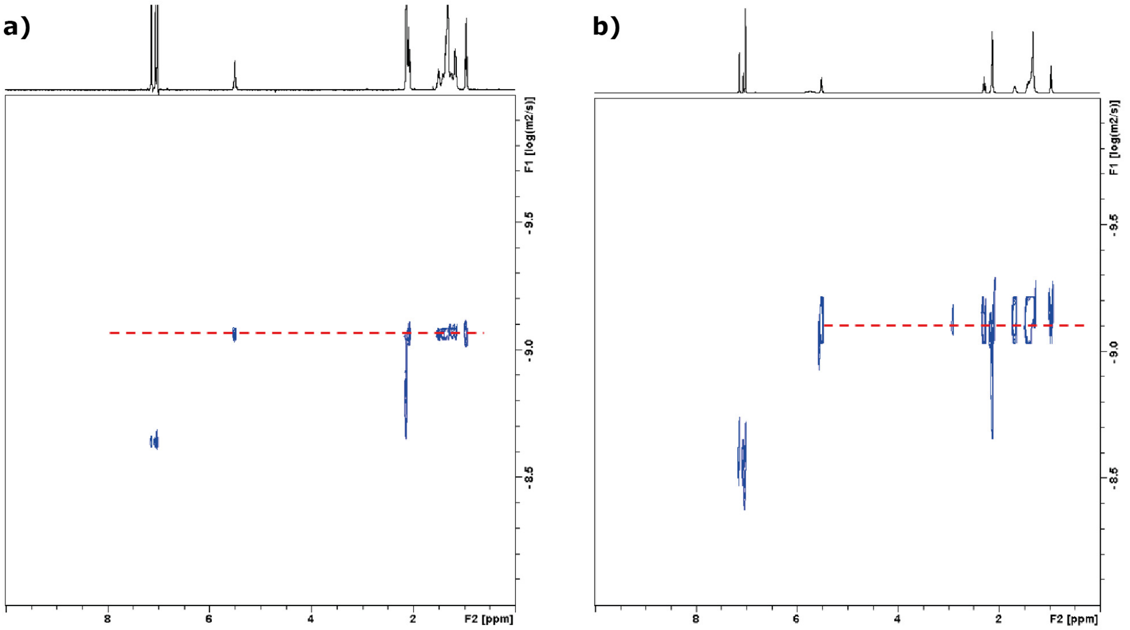


Figure S11.2 ^{1}H DOSY spectrum of (a) Oleic Acid (0.2 M, 725 μm^2/s) and (b) Cs-oleate (0.2 M, 726 μm^2/s) in d-toluene.

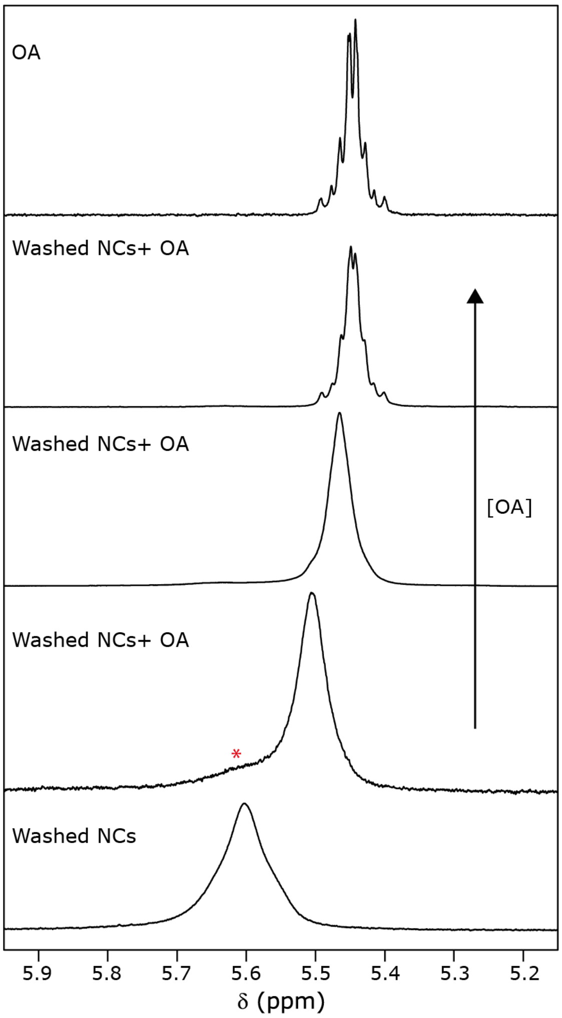


Figure S11.3 ^{1}H NMR spectra (double bond region) of washed NC dispersions in d-toluene containing increasing amount of OA_{free} in the final suspensions and of neat OA (0.22 M) for comparison. When no additional OA is present (Washed NCs) the right part of the resonance slightly shows a shoulder, which is attributable to the percentage of OA_{free} in exchange with OA_{bound} to NC. When OA is added, the peak of OA_{bound} fractions (indicated by the red asterisk, *) partially overlaps the intense OA_{free} signal. On adding more OA, this shoulder becomes less visible, but is still present and accounts for the line broadening which is affected by the relative populations of the two exchanging sites. Full details of the washing procedure of NCs can be found in the Experimental Section of the main text. Briefly, NCs are washed by adding an equal volume of acetone and centrifuging. The NCs are re-dispersed in toluene and OA is added, if being used. This process is repeated twice to obtain washed NCs.

S12. Colloidal Stability of Nanocrystals

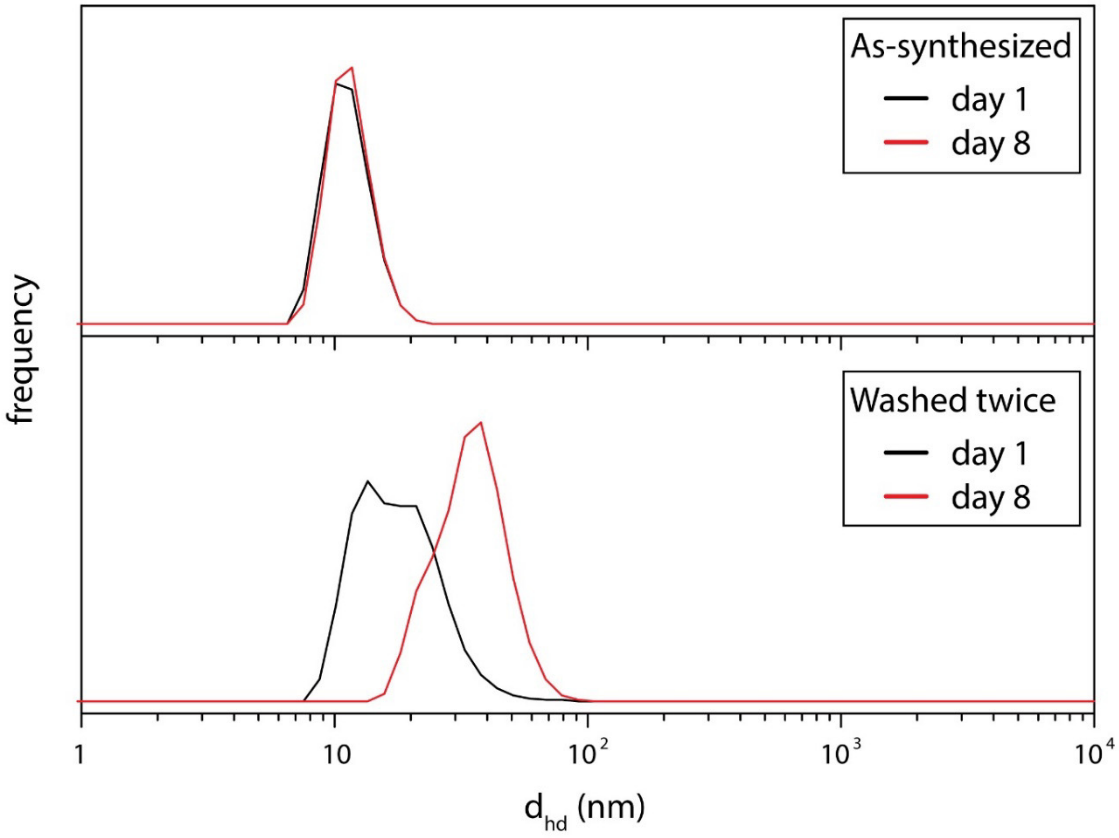


Figure S12 Dynamic light scattering measurements of as-synthesized and washed (with added OA) $CsPbBr_3$ NC dispersions over an eight day period, related to the NCs in Figure 6 of the main text where their PLQY stability is presented.

S13. Alternative Acids Study

We are able to expand our NC synthesis to use acids other than OA. We synthesize NCs using TDPA and DOPA with modifications to the TOPO-acid ratios to reflect the affinity of the acid to TOPO, which we establish by using ^{31}P NMR.

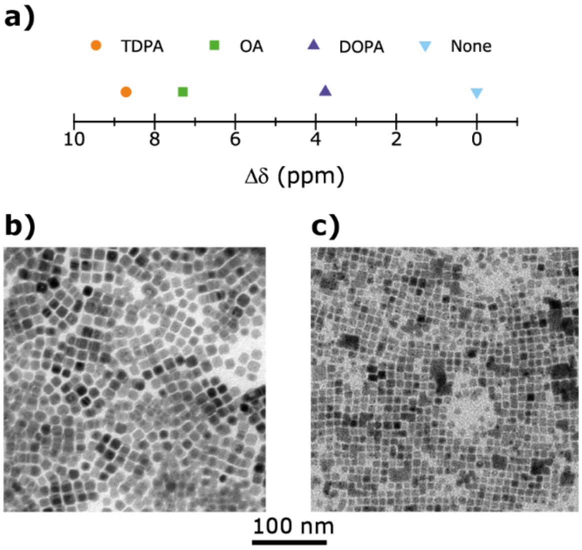


Figure S13 a) Differences of ^{31}P chemical shift of TOPO with acids TDPA, OA and DOPA, all in a 1:1 ratio with TOPO, b) TEM image of NCs made with TDPA instead of OA (10 nm, $\sigma = 10$ %). c) TEM image of NCs made with DOPA instead of OA (7 nm, $\sigma = 28$ %).

References

(1) Almeida, G.; Goldoni, L.; Akkerman, Q.; Dang, Z.; Khan, A. H.; Marras, S.; Moreels, I.; Manna, L. *ACS Nano* **2018**, *12*, 1704–1711.