Supporting Information

Direct Synthesis of $CsPbX_3$ Perovskite Nanocrystal Assemblies

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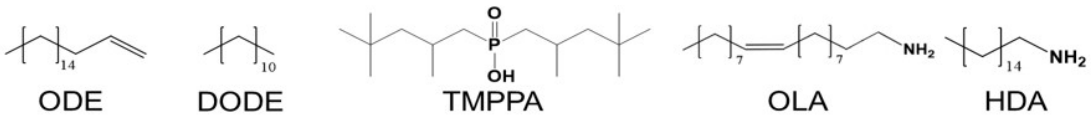

Fig. S1. Chemical structures of the solvents and ligands used in the synthesis of $CsPbX_3$ NCs/SCs.

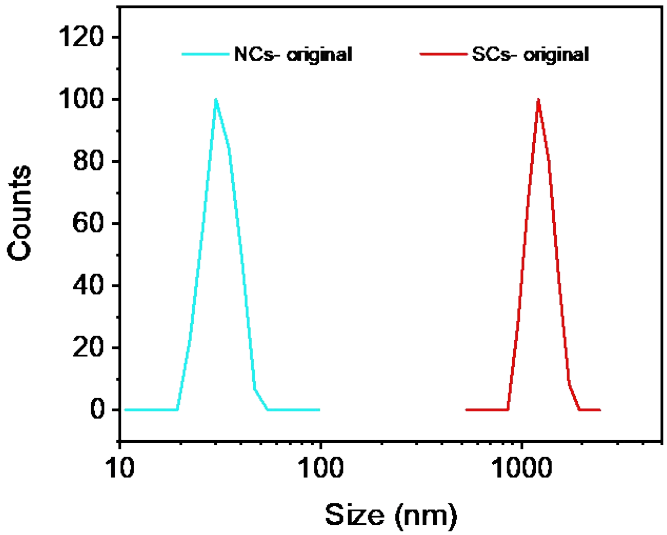

Fig. S2. DLS size measurements for $CsPbI_3$ NCs and SCs.

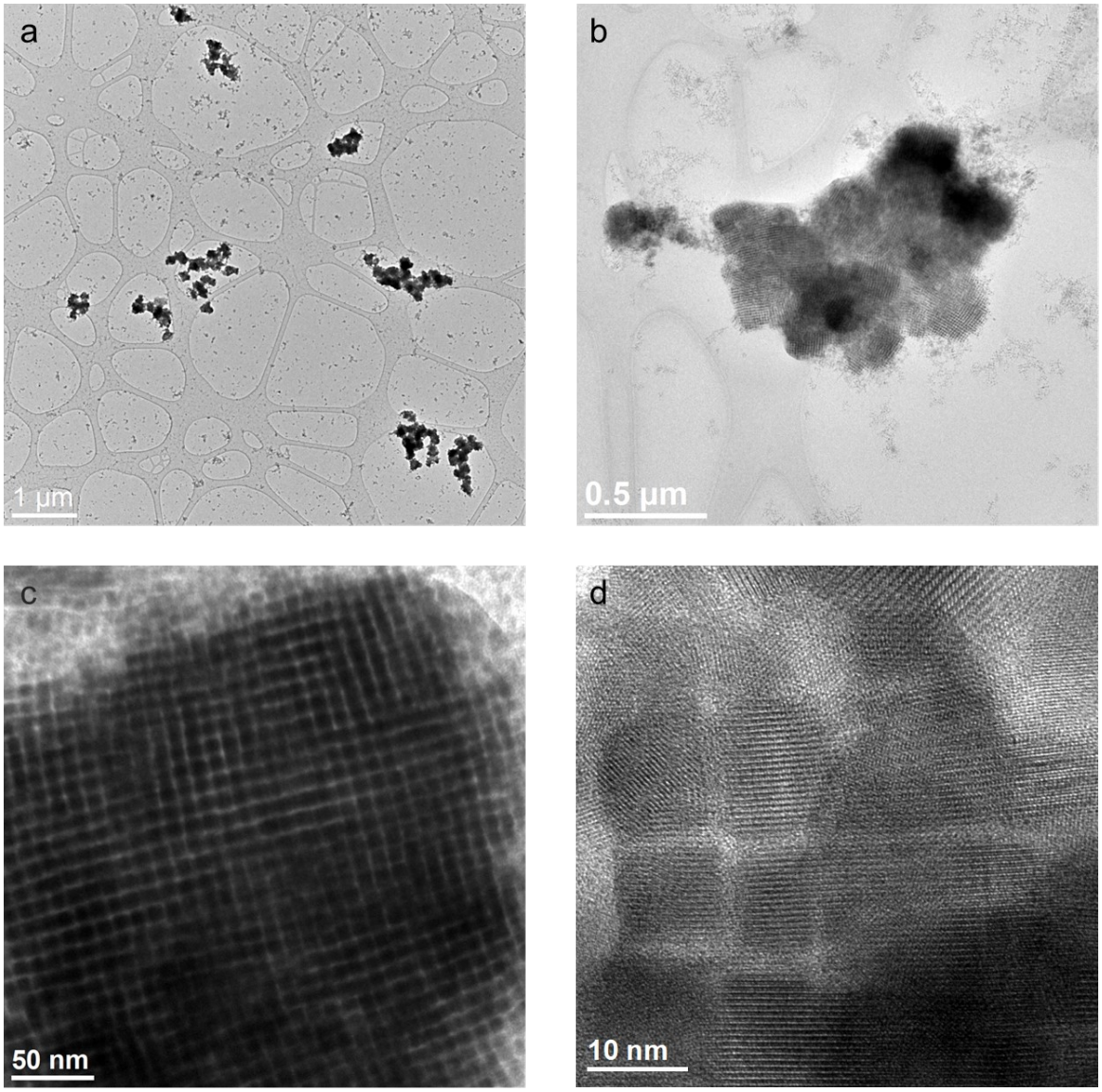

Fig. S3. TEM images for $CsPbI_3$ SCs at a) low, b) medium, c) high and d) highest magnifications.

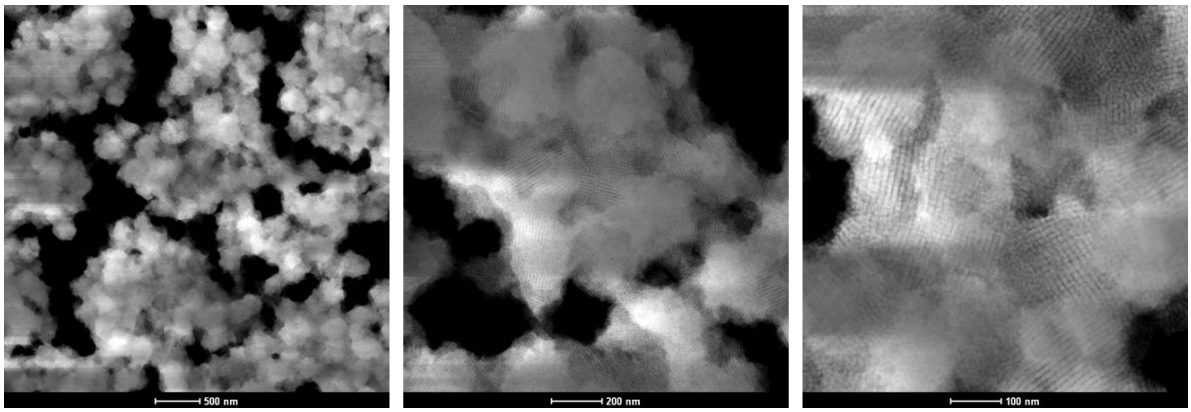

Fig. S4. High-angle annular dark-field imaging (HAADF) images $CsPbBr_3$ SCs.

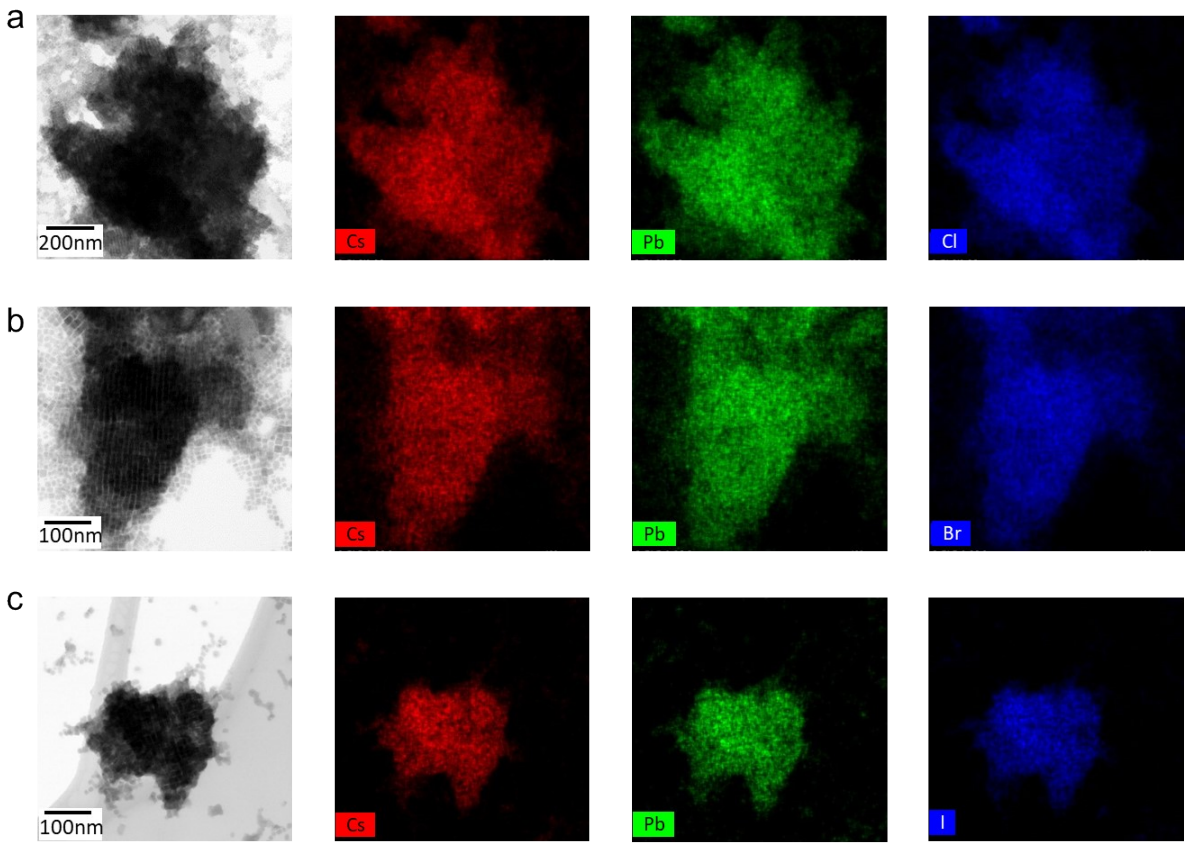

Fig. S5. STEM- EDX mapping of Cs, Pb and halide elements for a) $CsPbCl_3$, b) $CsPbBr_3$ and c) $CsPbI_3$ SCs.

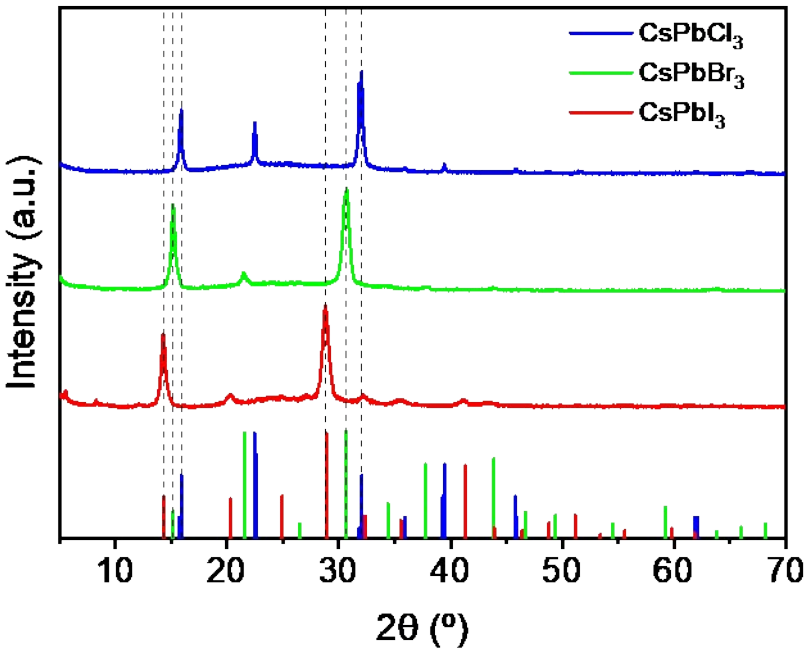

Fig. S6. XRD patterns of $CsPbCl_3$, $CsPbBr_3$ and $CsPbI_3$ super-crystals. Standard PDF numbers for the cubic phases of $CsPbCl_3$, $CsPbBr_3$ and $CsPbI_3$ are 00-018-0365, 00-054-0752, 01-080-4039, respectively.

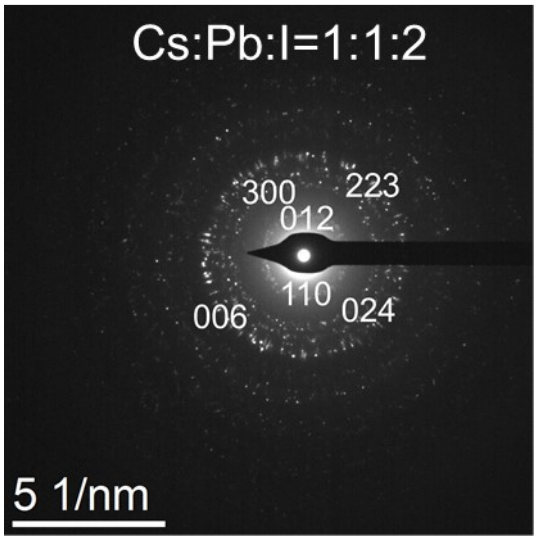

Fig. S7. The SADP of $CsPbI_3$ SCs synthesised at a Cs:Pb:I = 1:1:2 ratio. The pattern is indexed to the Cs_4PbI_6 phase.

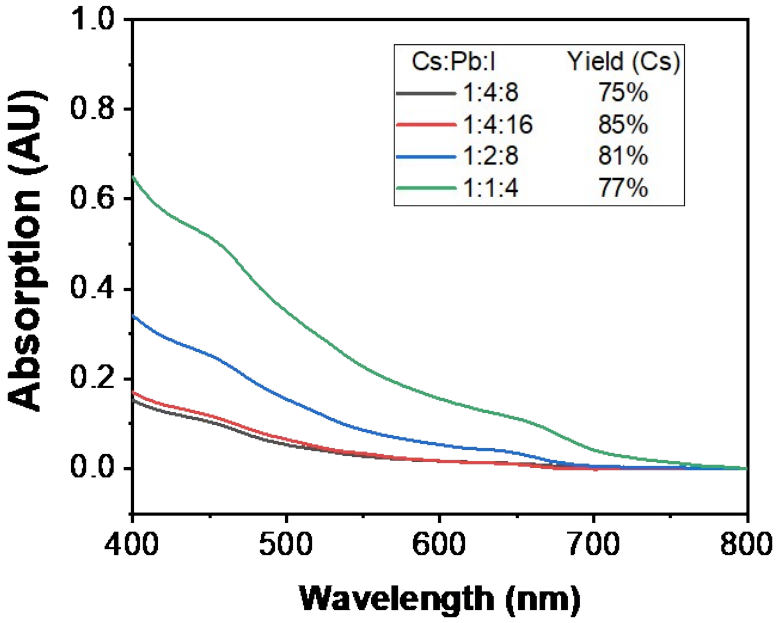

Fig. S8. Absorption spectra of the $CsPbI_3$ SC crude solutions synthesised at different Cs:Pb:I ratios.

The extinction coefficient (ε) for $CsPbI_3$ NCs is 4.07×10^6 M^{-1} cm^{-1} at 400 nm. [1] The absorption spectra was measured by diluting 10 µl of the crude solutions in 3 ml of hexane.

According to the Beer-Lambert law, the concentration of the NCs can be calculated.

$$A = \varepsilon CL$$

In which C is the [NC], L is the path length (1 cm), A is the absorbance.

With the C, the total molar of Cs, and the yield of the synthesis reaction in terms of Cs precursor can thus be calculated.

All the results are summarized in the table below:

Table S1. Calculations of the reaction yield (by Cs content) for different Cs:Pb:I ratios.

Cs:Pb:I	Absorbance at 400nm	Concentration of NC (M)	Concentration of Cs (M)	Total Molar of Cs (Mol)	Total Cs injection (Mol)	Reaction Yield of Cs (%)
1:4:8	0.15	1.1E-6	5.5E-3	3.3E-5	4.4E-5	75
1:4:16	0.17	1.26E-6	6.3E-3	3.7E-5	4.4E-5	85
1:2:8	0.34	2.5E-6	1.2E-2	7.2E-5	8.8E-5	81
1:1:4	0.65	4.8E-6	2.4E-2	1.4E-4	1.8E-4	77

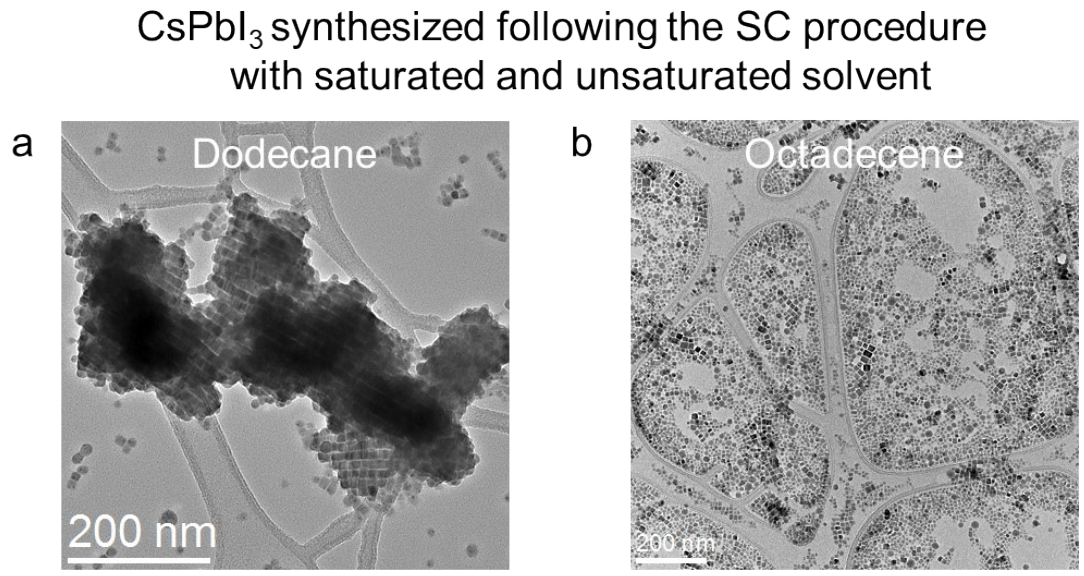

Fig. S9. TEM images for $CsPbI_3$ synthesised at Cs:Pb:I = 1:1:4 with the TMPPA and HDA ligands and a) saturated dodecane solvent and b) unsaturated octadecene solvent

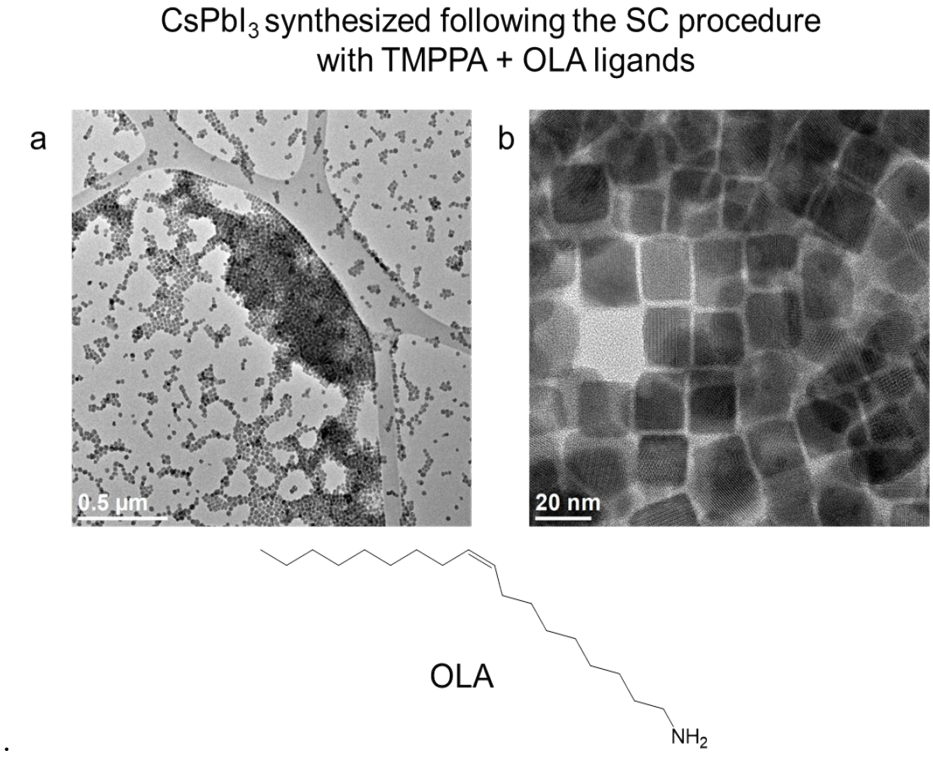

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Fig. S10. a) Low and b) high magnification TEM images for $CsPbI_3$ synthesised at Cs:Pb:I = 1:1:4 with the TMPPA and OLA ligands. Herein, the pre-made

hexadecylammonium iodide is used as the extra iodide source, avoiding the hydroiodic acid being consumed by the alkene of OLA.

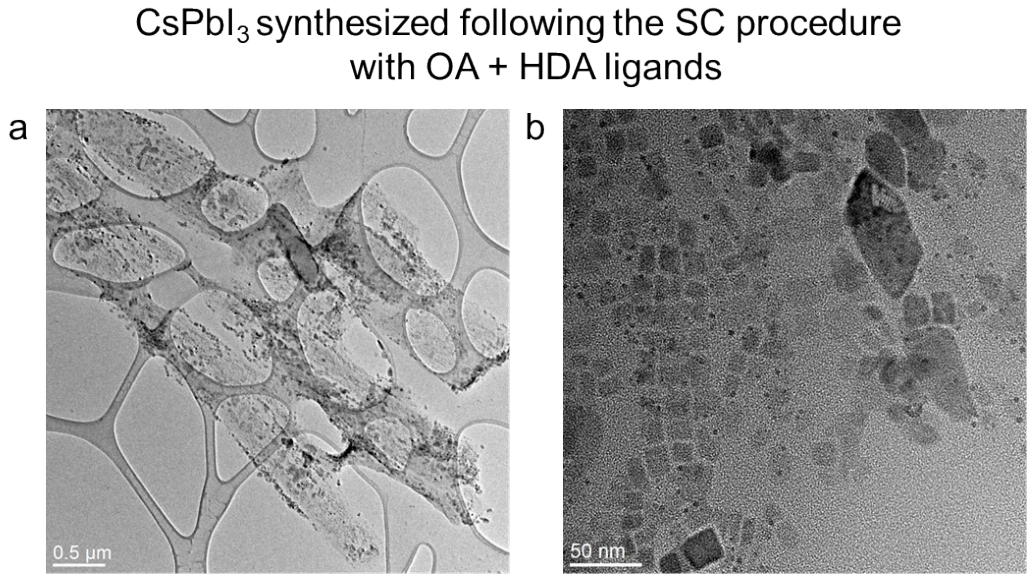

Fig. S11. a) Low and b) high magnification TEM images for $CsPbI_3$ synthesised at Cs:Pb:I= 1:1:4 with OA and HDA ligands.

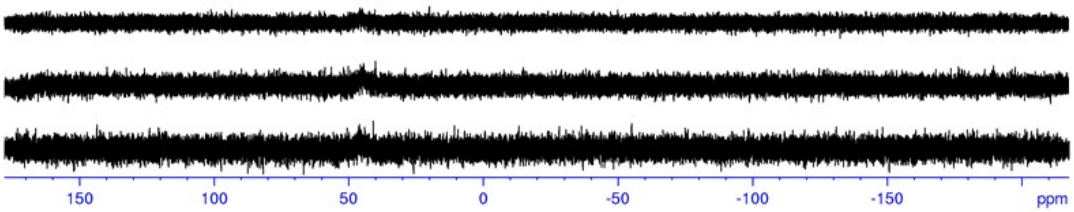

Fig. S12. ^{31}P-NMR spectra of the SC dispersions of (top to bottom) $CsPbCl_3$, $CsPbBr_3$, $CsPbI_3$, which were washed 2 times.

Because TMPPA was the only source of phosphorus in the SC dispersion, ^{31}P NMR spectroscopy can be used to monitor its speciation in solution. After the 2nd wash (centrifuged - redispersed twice), ^{31}P NMR spectra were collected for the $CsPbCl_3$, $CsPbBr_3$, and $CsPbI_3$ SCs, with no phosphorus signals detected with an extended data collection period (10 hr). This indicates that all TMPPA species have been removed. Such a result is consistent with our previous report on the synthesis of $CsPbI_3$ NCs using TMPPA.[2] Hence, it can be confirmed that the TMPPA is not binding to the $CsPbX_3$ SC surface, and the only surface binding ligand is therefore HDA.

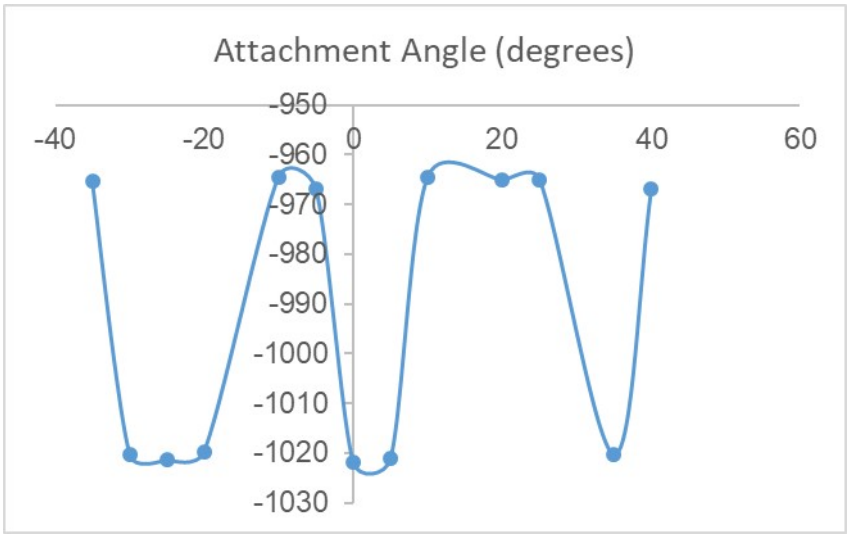

Fig. S13. Plot of NC-ligand energy (in eV) vs attachment angle of the HDA-Br ligand for a single nanoparticle with 3 ligands attached. An attachment angle of 0^{o} indicates the ligand is perpendicular to the surface (see Fig.s 4b-c). Negative and positive angles represent the ligand bend orientation is to the left and right, respectively.

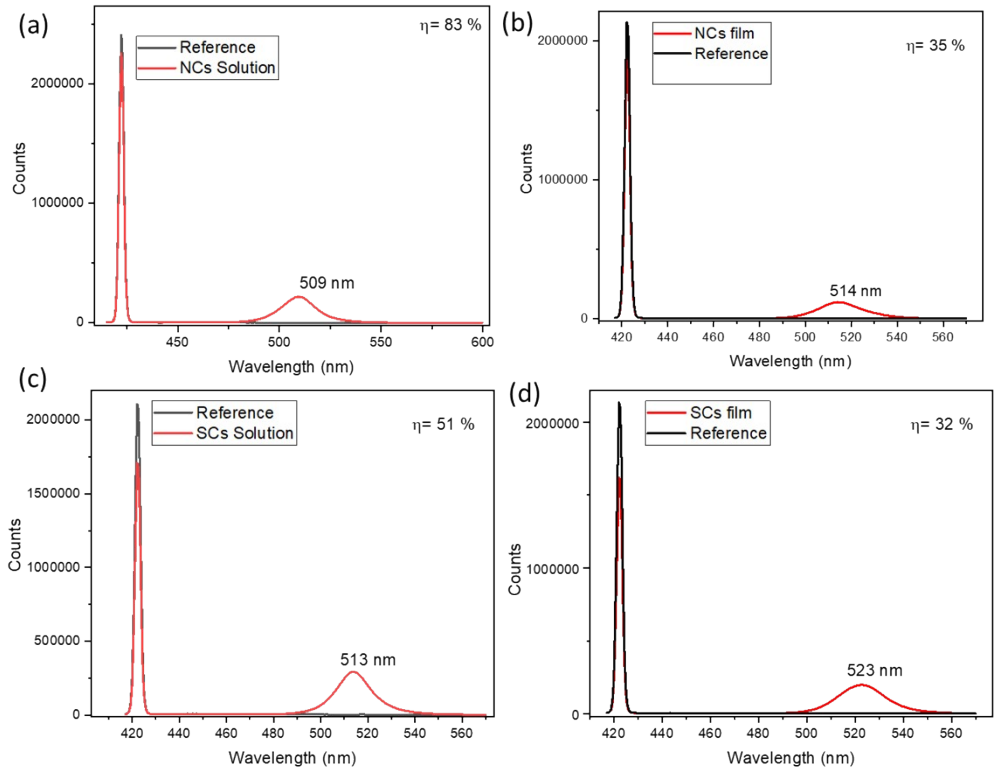

Fig. S14. Absolute PL QYs for $CsPbBr_3$ NCs and SCs.

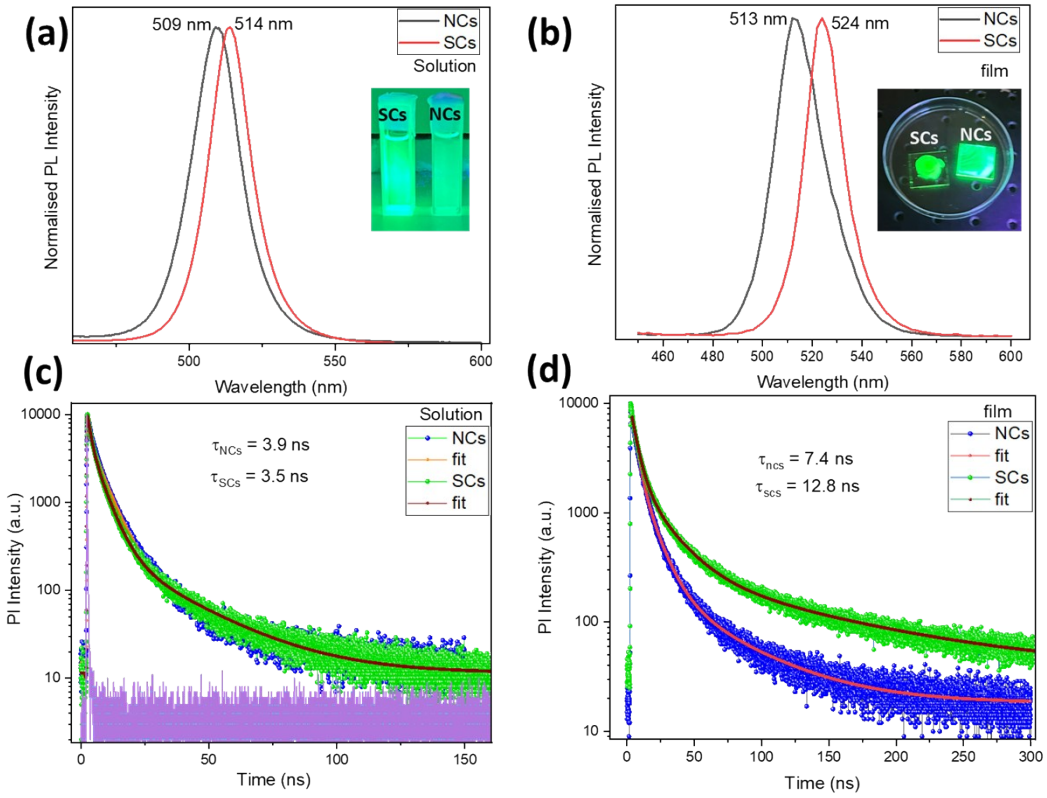

Fig. S15. (a,b) Photoluminescence emission spectra and (c,d) TRPL decay curves of $CsPbBr_3$ NCs and SCs.

Table S2. Fluorescence decay components of the $CsPbBr_3$ NCs and SCs

Sample	**TRF Decay Components**						**Amplitude Average lifetime** $\frac{\sum A_i\tau_i}{\sum A_i}$
	τ_1 **(ns)**	τ_2 **(ns)**	τ_3 **(ns)**	A1	A2	A3	τ_{avg} **(ns)**
SCs solution	1.29	4.80	24.74	6.41	5.17	0.33	3.46
NCs solution	1.24	5.32	20.10	5.45	5.92	0.39	3.92
SCs film	4.91	20.38	110.7	5.371	1.84	0.29	12.82
NCs film	3.83	10.75	50.1	5.69	2.92	0.243	7.37

Table S3. Fractional Emission Contributions of the $CsPbBr_3$ NCs and SCs

Sample	**Fractional Emission Contributions** $\frac{A_i\tau_i}{\sum A_i\tau_i}$		
	$A_1\tau_1$ **(%)**	$A_2\tau_2$ **(%)**	$A_3\tau_3$ **(%)**
SCs solution	20.13	60.00	19.86
NCs solution	14.60	68.28	17.12
SCs film	27.45	38.91	33.64
NCs film	33.34	48.03	18.63

References

1 C. Wang, A. S. R. Chesman, W. Yin, L. Frazer, A. M. Funston, J. J. Jasieniak, *J. Chem. Phys.* **2019**, *151*, 121105.

2 C. Wang, A. S. R. Chesman, J. J. Jasieniak, *Chem. Commun.* **2017**, *53*, 232.