

Supporting Information

Role of Acid-Base Equilibria in the Size, Shape and Phase Control of Cesium Lead Bromide Nanocrystals

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S1. Experimental details and further photo-physical characterization of nanoplatelets

Table S1. Synthesis conditions used to prepare CsPbBr₃ nanoplatelets (NPLs) and (RNH₃)₂PbBr₄ nanosheets (NSs, 1 ML), and their photoluminescence (PL) properties (T: synthesis temperature; [Cs]_i: concentration of Cs⁺ in injection solution; hν: photon energy at PL maximum; FWHM: PL full width at half maximum; φ: PL quantum yield; τ: PL lifetime; “-“: data not collected). *formed during cooldown.

NPL / NS thickness nm	Reaction conditions					Photoluminescence (PL)			
	T (°C)	[OIAm] (mM)	[OA] (mM)	[Cs] _i (mM)	t min	hν (eV)	FWHM (meV)	φ (%)	τ (ns)
2.4	90	250	500	300	5				
1.8	90	250	500	23	5				
2.4	140	250	500	150	5	2.67	78	20	6.2
1.8	140	250	500	23	5	2.84	81	-	-
1 ML	140	250	500	0	*	3.08	130	3	2.6
2.4	190	250	500	23	5				
1.8	190	250	500	15	1				

S2. Re-precipitation of PbBr_2

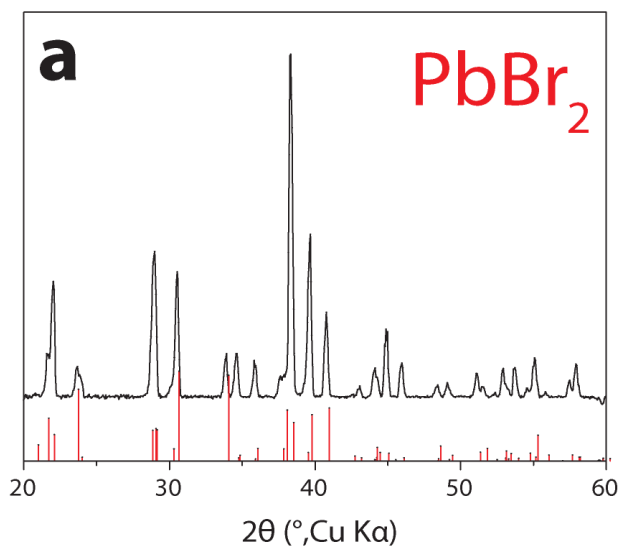


Figure S1 . XRD pattern of PbBr_2 precipitated out of an oleylamine, oleic acid, 1-octadecene mixture at ca. 195-200 $^\circ\text{C}$.

S3. Synthesis of nanocubes over 100 nm

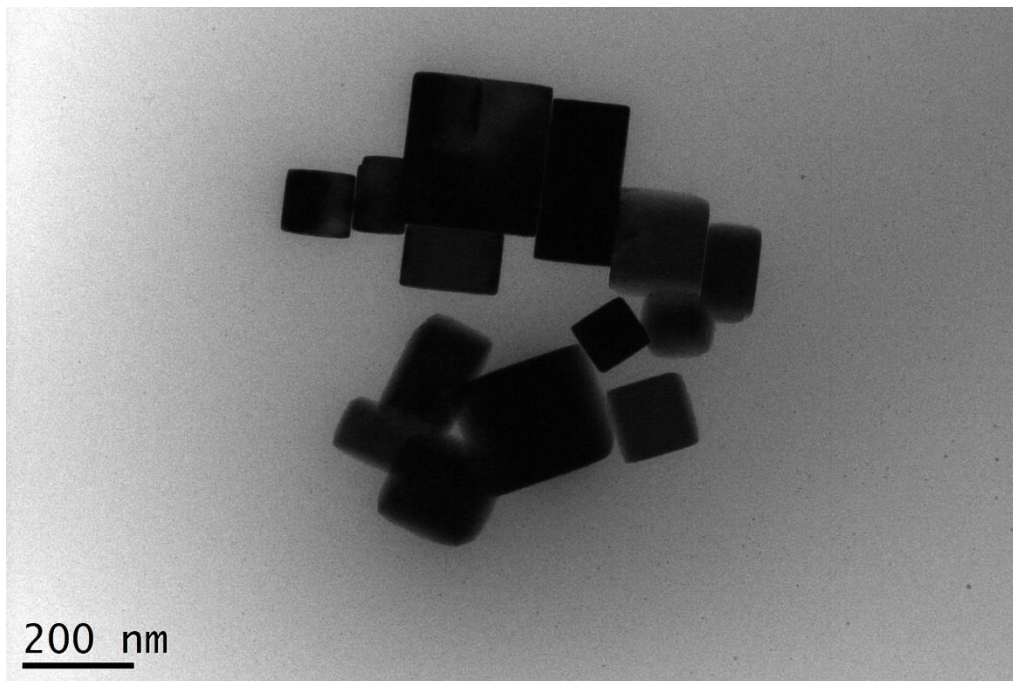


Figure S2 . CsPbBr₃ nanocubes over 100 nm in size, synthesized at 240 °C with [OlAm] = 1.5 M, [OA] = 1.5 M and grown for 5 minutes.

S4. Effect of [OA] on Nanocrystal size and shape

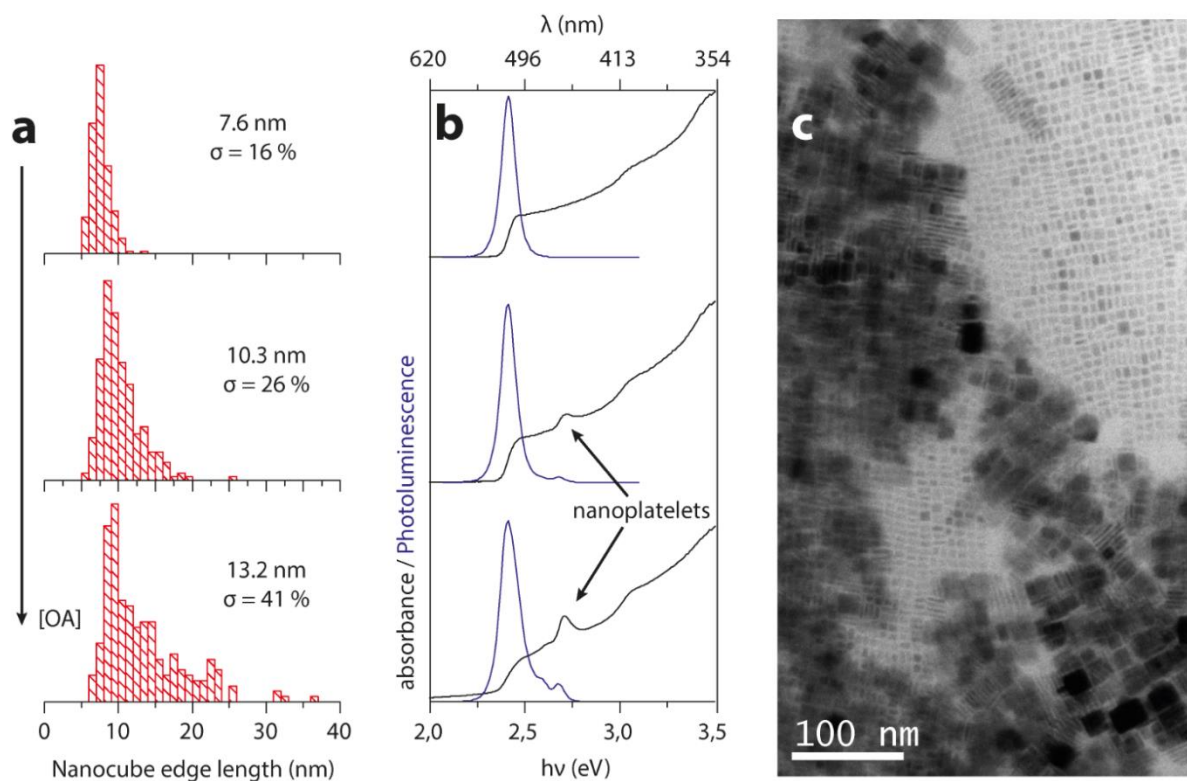


Figure S3. Effect of oleic acid concentration on the size and shape of CsPbBr₃ nanocrystals synthesized at 190 °C. (a) Size-distribution histograms and (b) optical spectra of nanocrystals synthesized with increasing concentrations of oleic acid ([OA] = 0.25, 0.50 and 1.00 M, [OlaM] = 0.25 M). (c) TEM image of nanocrystals synthesized with [OA] = 1.00M and [OlaM] = 0.25M. Note the presence of nanoplatforms.

S5. Effect of [OA] and reaction time on Nanocrystal size and shape

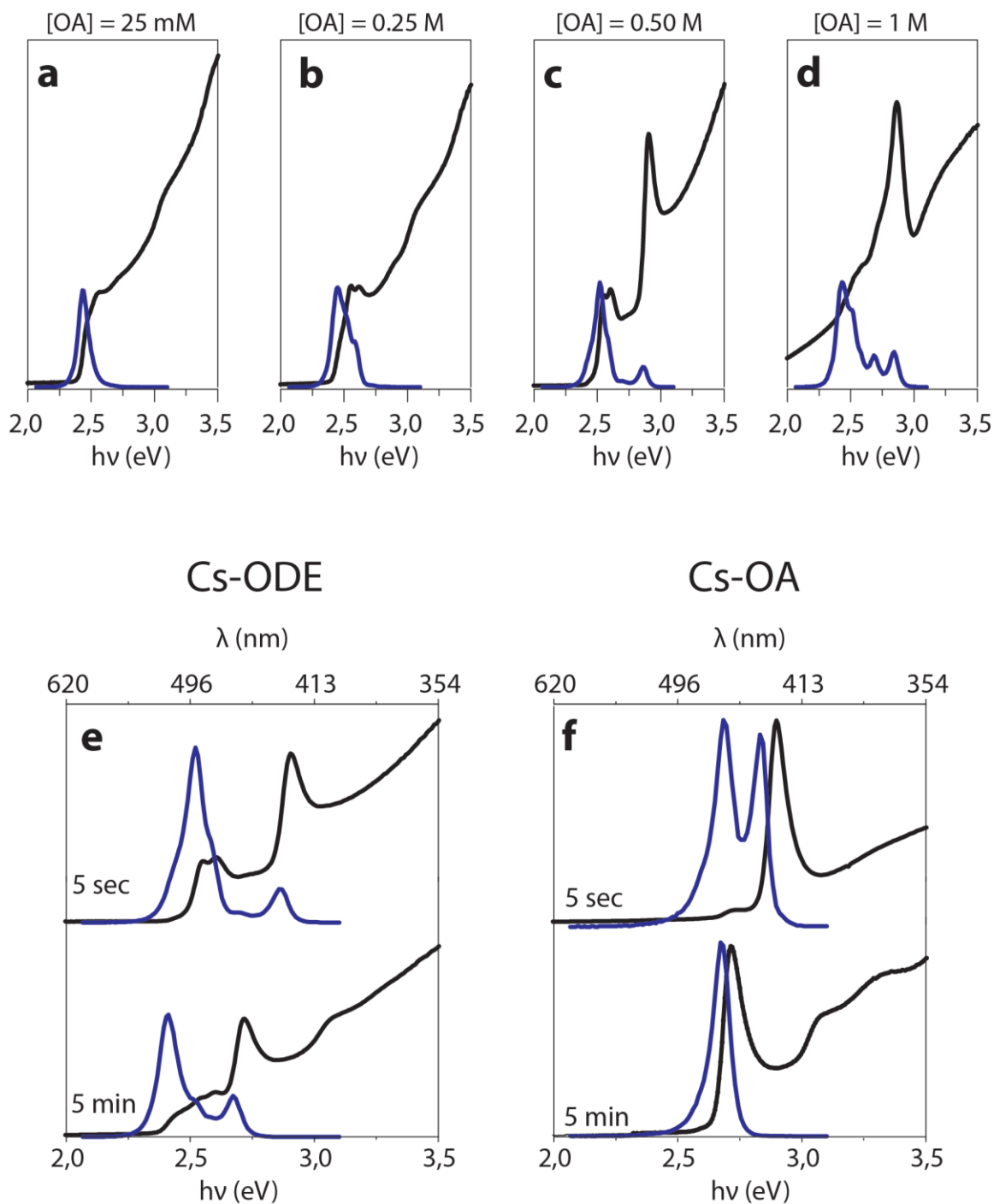


Figure S4. (a-d) absorption (black) and photoluminescence (blue) spectra of CsPbBr₃ nanocrystals synthesized for 5 s at 140 °C with increasing amounts of oleic acid ([OIAm]=0.25M) using Cs-oleate in ODE. (e-f) Absorption (black) and photoluminescence (blue) spectra of CsPbBr₃ nanocrystals synthesized at 140 °C for 5 secs and 5 minutes using Cs-ODE and Cs-OA, respectively, as a Cs-precursor.

S6. HRTEM characterization of CsPbBr₃ nanoplatelets

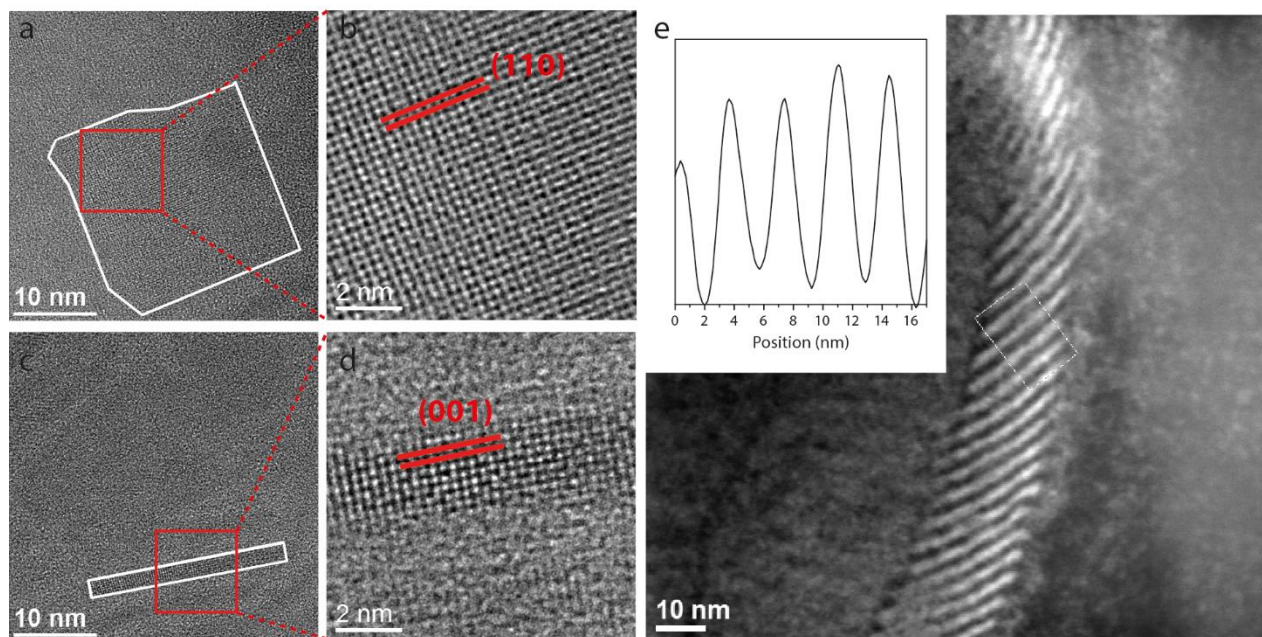


Figure S5. (a-b) top- and (c-d) side-view STEM and HRTEM images of 2.4 nm thick CsPbBr₃ nanoplatelets, respectively. (e) side-view HAADF image of stacks of 1.8 nm thick CsPbBr₃ nanoplatelets (inset: contrast line-scan of the region is delimited in the image)

S7. NMR characterization of a solution containing oleylamine (0.5M) and oleic acid (1M) in toluene-d₈

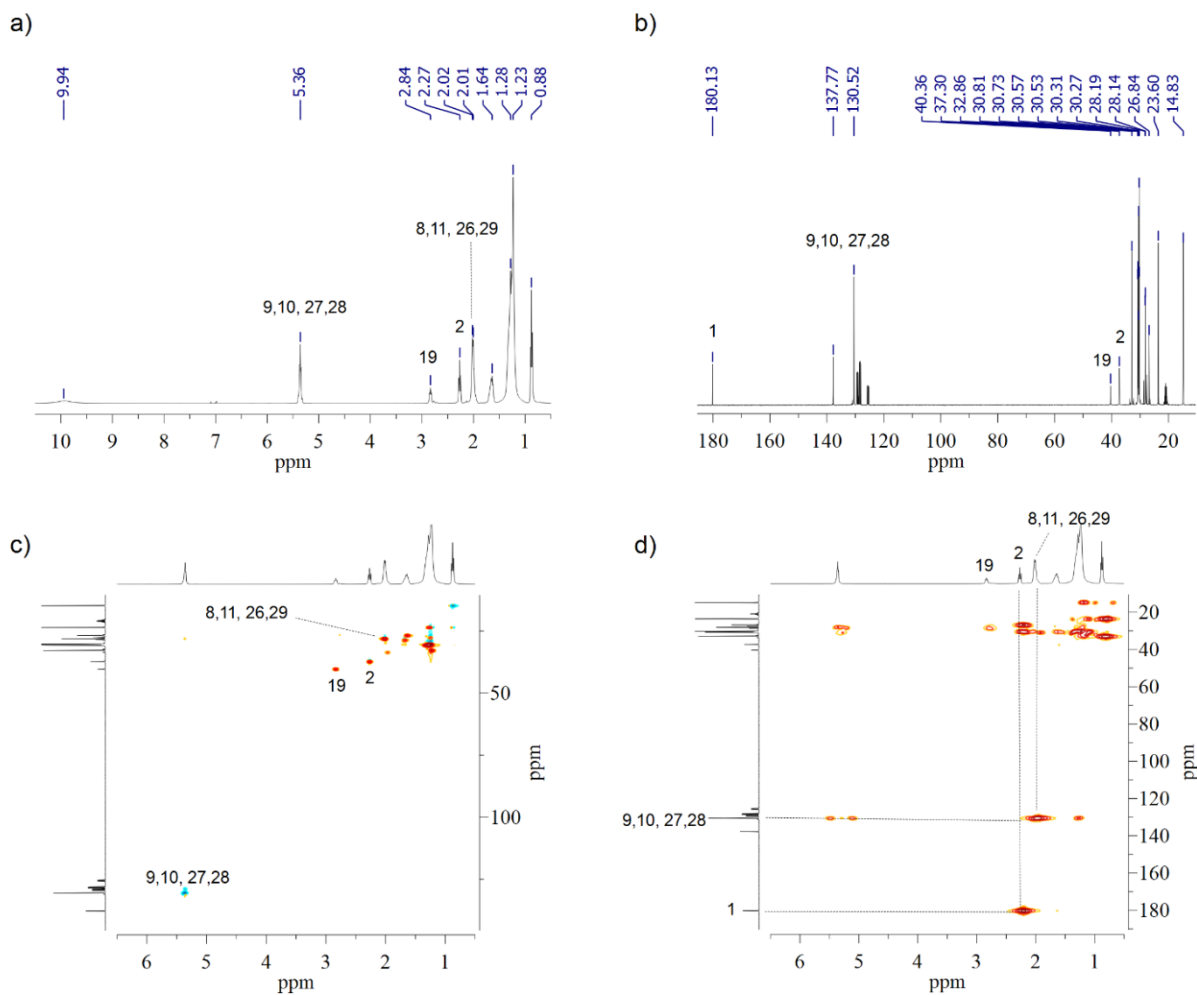
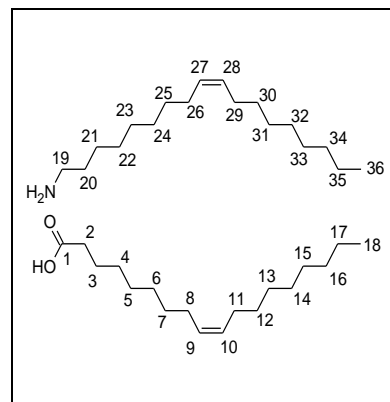


Figure S6.1 a) ¹H, b) ¹³C, c) edited ¹H-¹³C-HSQC and d) ¹H-¹³C-HMBC NMR spectra of an OlAm : OA solution in toluene-d₈. Diagnostic signals have been embedded in the figures.

Table S3 Assignment of resonances

Assignment	¹ H	<i>J</i> (Hz)		¹³ C
-	9.94	-	<i>br s</i>	-
9,10, 27 and 28	5.36	-	<i>m</i>	130.5
19	2.84	-	<i>ps t</i>	40.4
2	2.27	7.65	<i>t</i>	37.3
8, 11, 26 and 29	2.11-2.91	-	<i>m</i>	28.2 and 28.1
20	1.67	-	<i>m</i>	28.6
3	1.64	-	<i>m</i>	26.8
4-7,12-15, 21-25, 30-33	1.45-1.05	-	<i>m</i>	30.8-20.3
17 and 35	1.26	-	<i>m</i>	23.6
16 and 34	1.23	-	<i>m</i>	32.9
18 and 36	0.88	6.9	<i>t</i>	14.8
1	-	-	CO	180.1



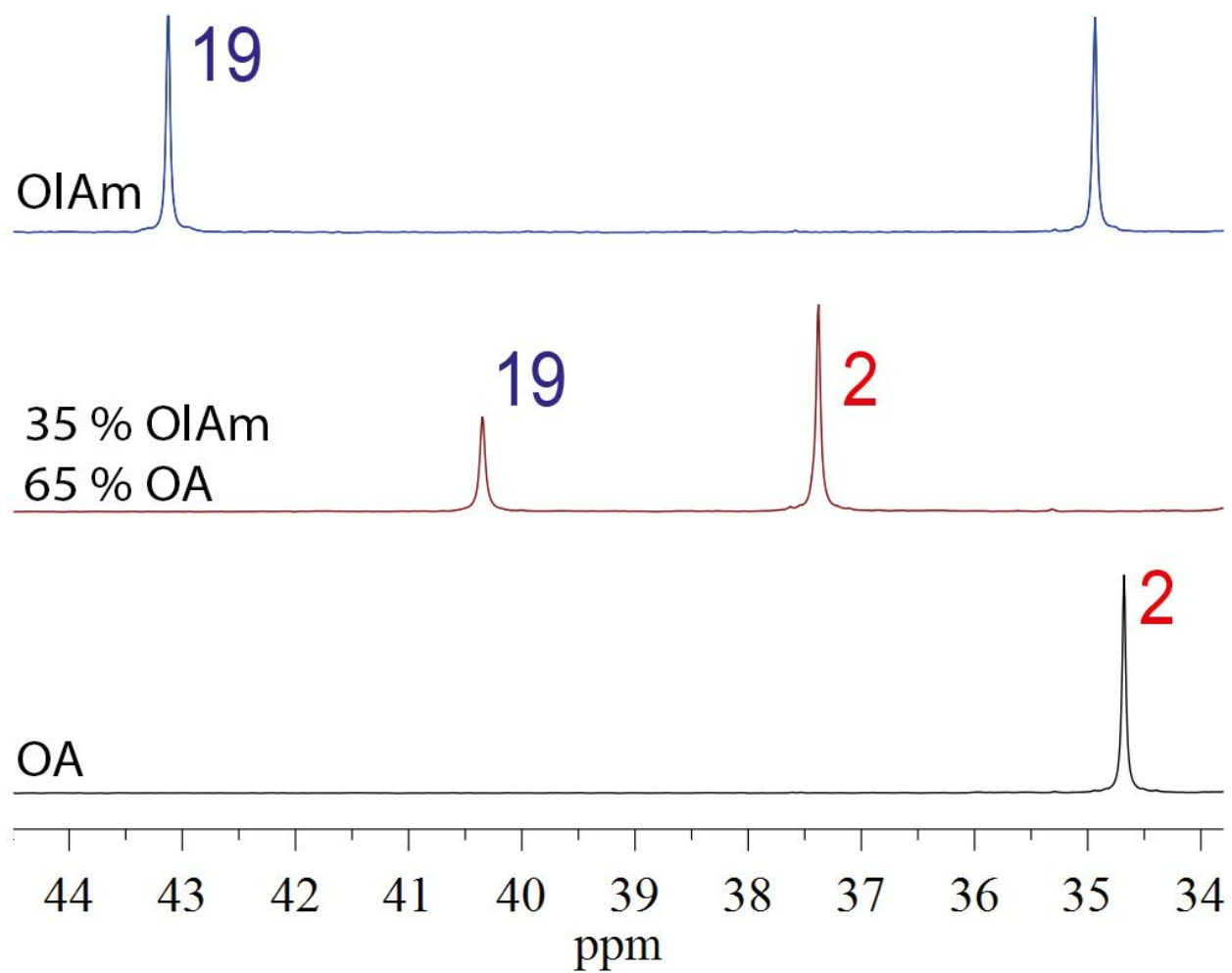


Figure S6.2 ^{13}C -NMR spectra of oleylamine and oleic acid solutions in toluene- d_8

S8. Nanoplatelets synthesized at 90 and 190 °C

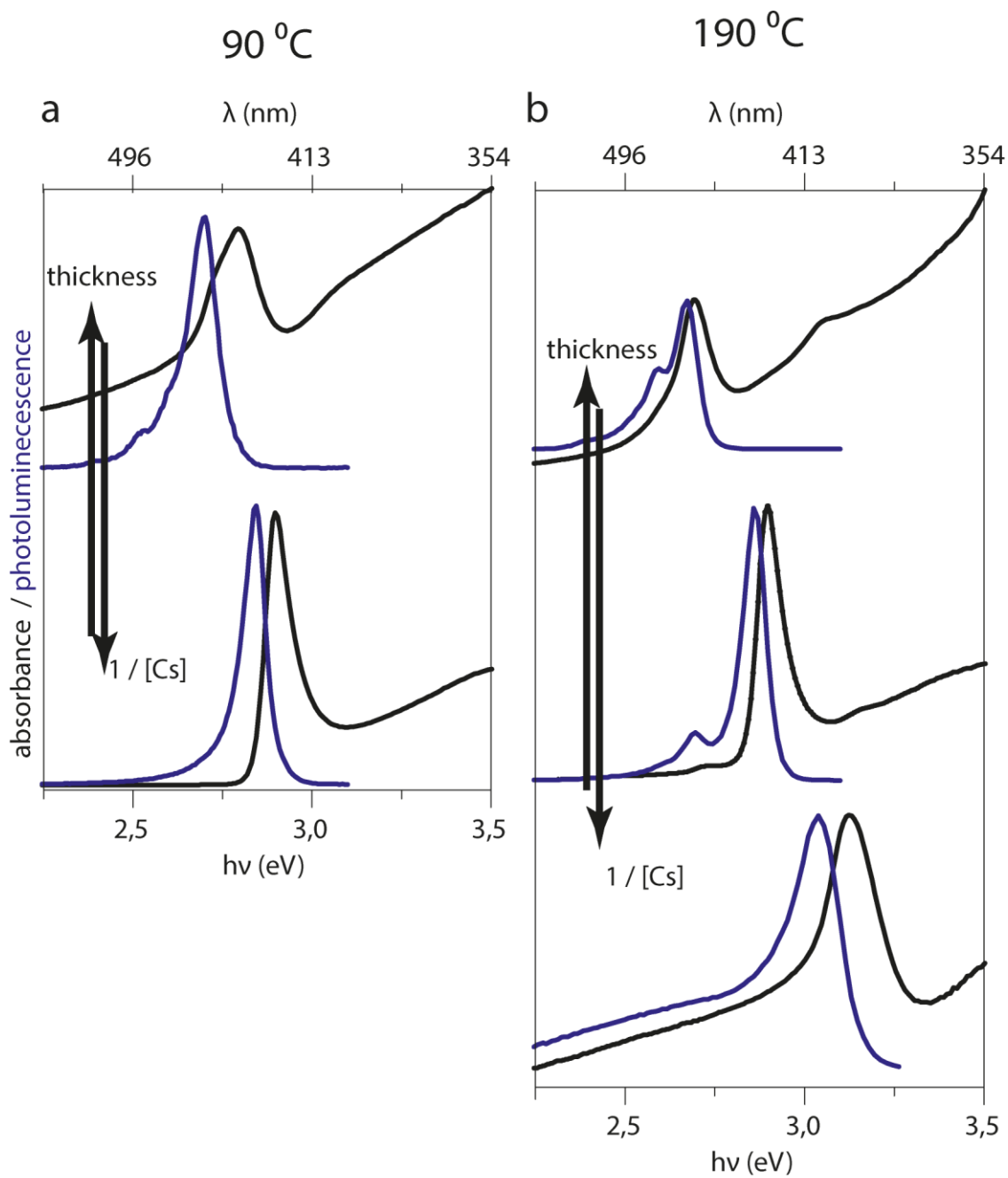


Figure S7. Absorbance and photoluminescence spectra of nanoplatelets synthesized at (a) 90 and (b) 190 °C.

S9. Formation of nanoplatelets in presence of Bronsted acids

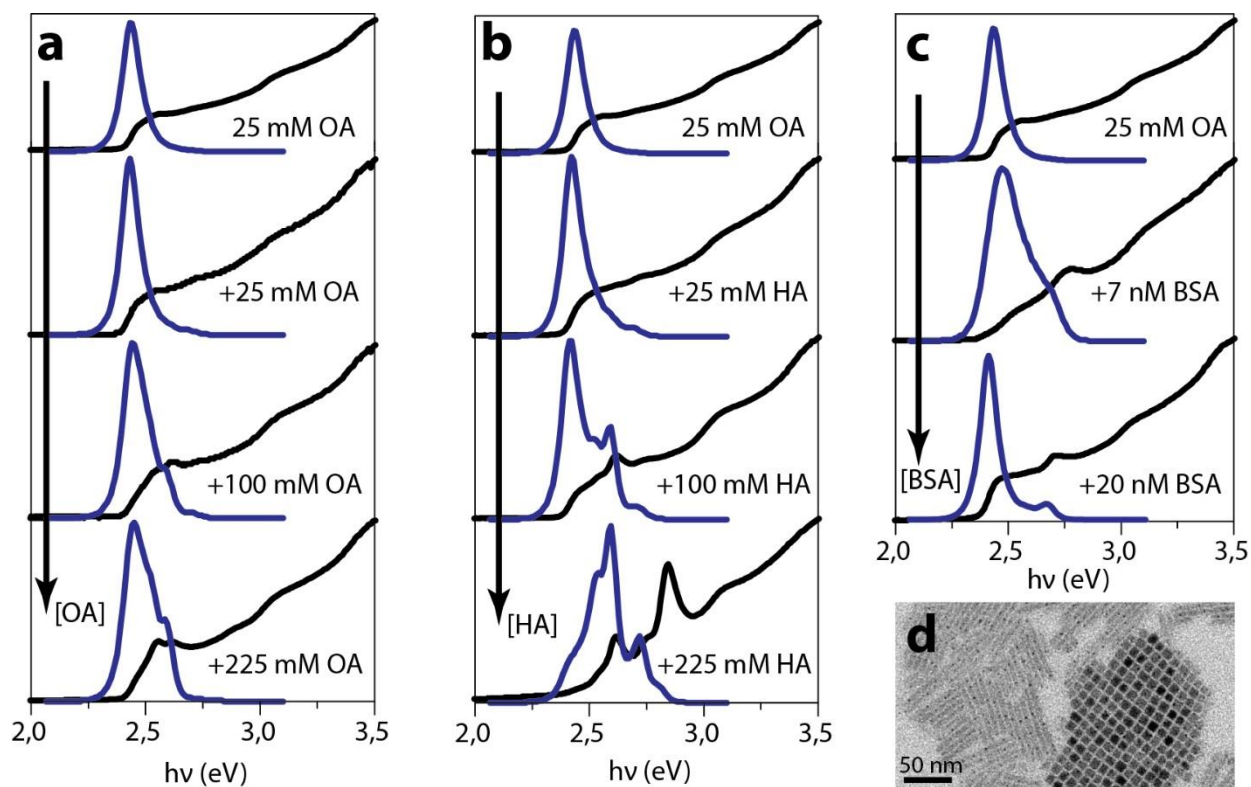


Figure S8. Absorbance (black) and photoluminescence (blue) spectra of nanocrystals synthesized with increasing amounts of (a) oleic acid (OA), (b) hexanoic acid (HA) and (c) benzylsulfonic acid (BSA). Increasing the amount of acid causes extra peaks appear in the absorption and photoluminescence spectra of the nanocrystal product, which is attributed to the presence of nanoplatelets (deduced from the peak position and the narrow width of these peaks at high intensities, which is to be expected of a two-dimensional semiconductive system). (d) TEM image of nanocrystals (cubes + stripes) obtained in the presence of BSA.

S10. CsBr nanocrystals

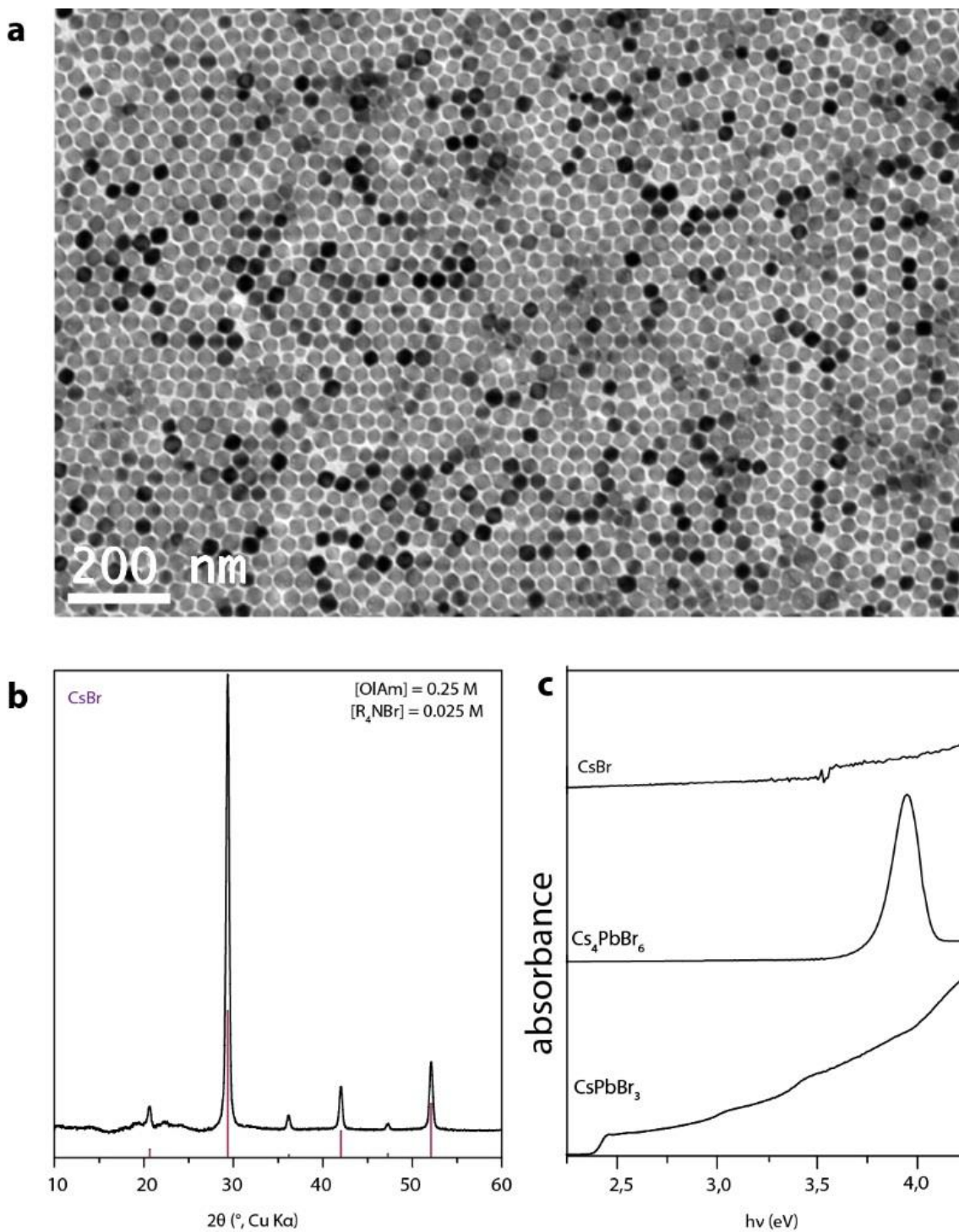


Figure S9. Monodisperse CsBr nanocrystals could be synthesized by reacting a tetralkylammonium bromide (DDAB) with Cs-oleate at 150 °C for 5 minutes in the presence of oleylamine. (a) TEM image and (b) XRD pattern (ICSD 98-005-3848) of CsBr nanocrystals. (c) absorbance spectra of CsBr, Cs₄PbBr₆ and CsPbBr₃ nanocrystals.

S11. Nanowire formation upon treating CsPbBr₃ nanocrystals (< 4.0 nm) with polar solvents

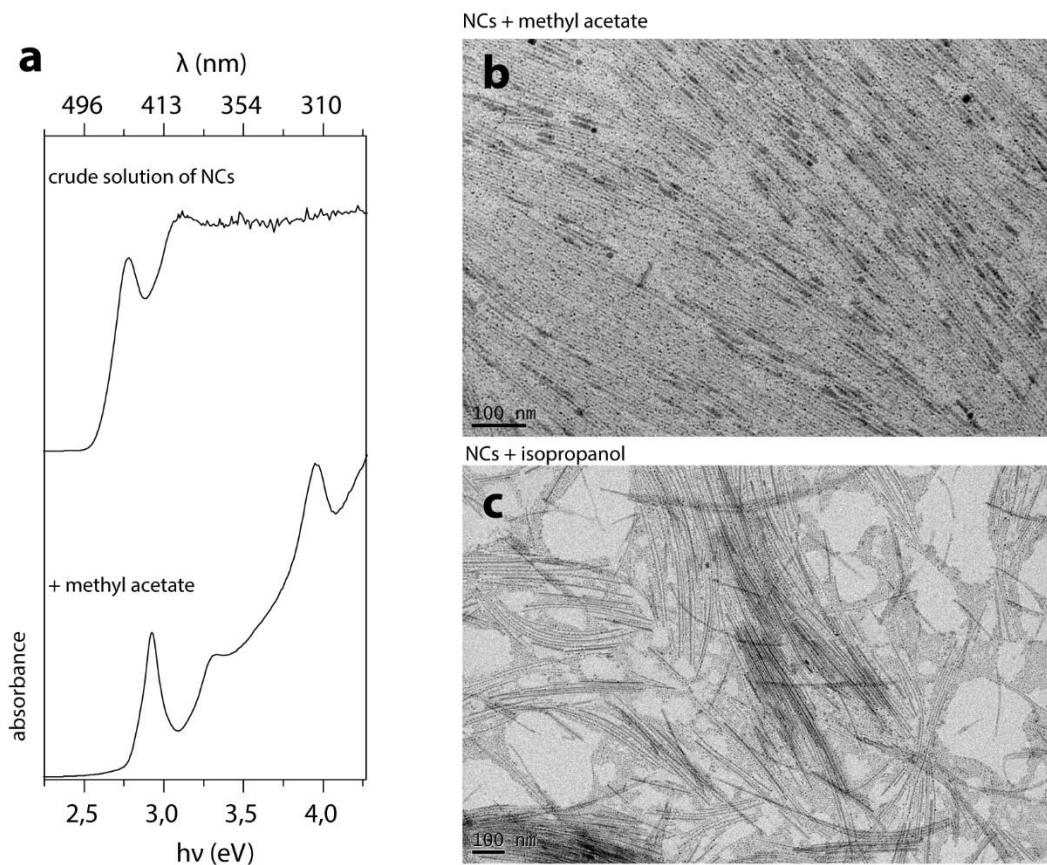


Figure S10. Effect of anti-solvents on CsPbBr₃ nanocrystals synthesized at 100 °C ([OIAm] = 0.25 M, [OA] = 0.025 M). (a) Absorbance spectra of the crude solution containing CsPbBr₃ nanocrystals (< 4.0 nm) and of the nanocrystals precipitated by the addition of methyl acetate. TEM images of nanocrystals precipitated with (b) methyl acetate and (c) isopropanol show the presence of a large quantity of nanowires.

S12. Extension of the work to other halide systems

Methods: The syntheses of CsPbX_3 nanocubes, Cs_4PbX_6 nanocrystals and $[\text{RNH}_3]\text{PbX}_4$ nanosheets ($X=\text{Cl}, \text{I}$) were conducted in the same way as reported for the bromides in the main text. All the materials were synthesized in 6.0 mL solutions with $[\text{PbX}_2] = 33 \text{ mM}$. CsPbX_3 NCs were synthesized at $165 \text{ }^\circ\text{C}$ with $[\text{OIAm}] = [\text{OA}] = 0.25 \text{ M}$. Cs_4PbX_6 NCs were synthesized at $165 \text{ }^\circ\text{C}$ with $[\text{OIAm}] = [\text{OA}] = 1.0 \text{ M}$ for $X = \text{I}$ and 1.5 M for $X = \text{Cl}$. $(\text{RNH}_3)_2\text{PbX}_4$ nanosheets were obtained by adding oleic acid to a solution of PbX_2 heated at $100 \text{ }^\circ\text{C}$. In these latter syntheses, $[\text{OIAm}] = [\text{OA}]_i = 0.25 \text{ M}$ (with $[\text{OA}]_i$ denoting the initial concentration of oleic acid).

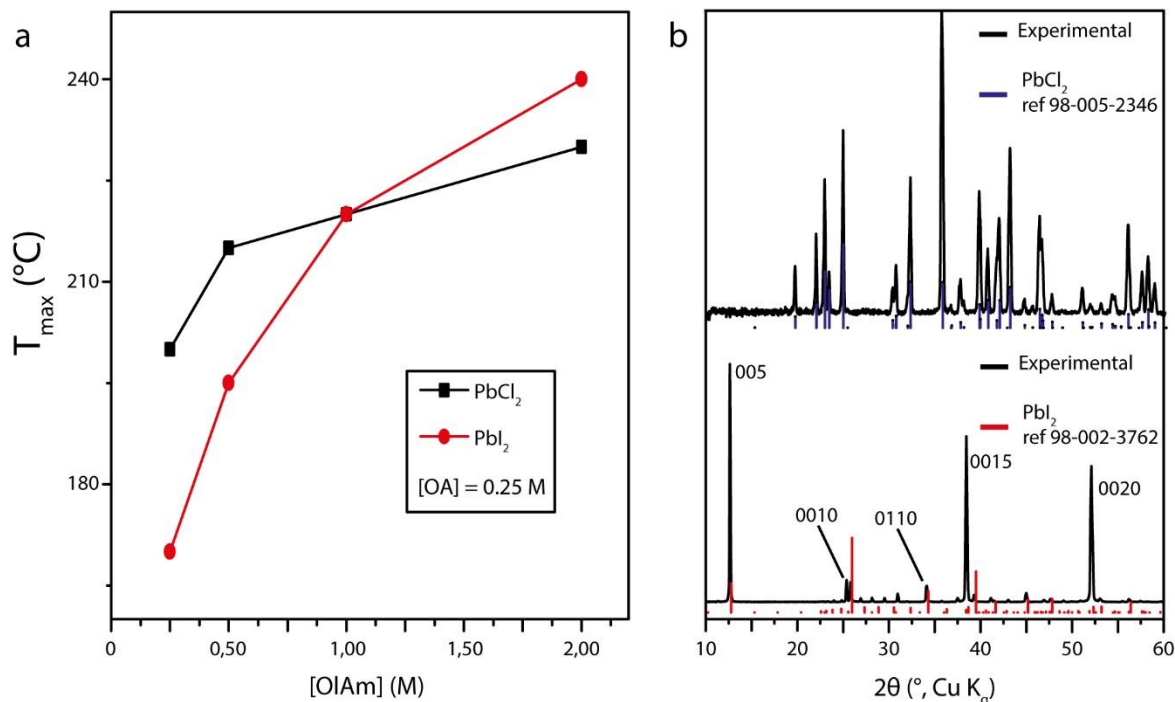


Figure S11. (a) Maximum reaction temperature T_{max} as a function of ligand concentration; at T_{max} , PbX_2 ($X = \text{Cl}, \text{I}$) precipitates from the reaction medium (33 mM of PbBr_2 solution in 1-octadecene with $[\text{OA}]$ set at a constant 250 mM), as confirmed by (b) x-ray diffraction.

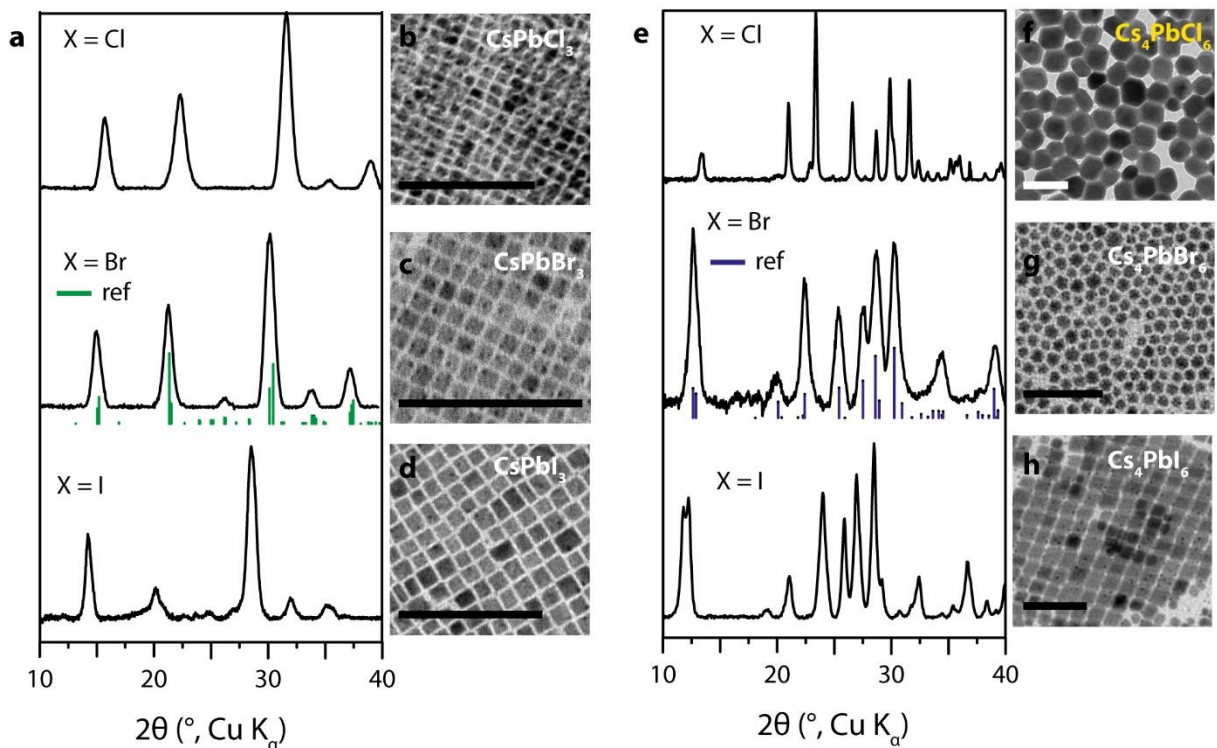


Figure S12. (a) x-ray diffraction patterns and (b-d) respective transmission electron microscopy images of CsPbX₃ (X = Cl, Br, I) nanocubes synthesized at 165 °C in the presence of [OlAm] = [OA] = 0.25 M. (e) x-ray diffraction patterns and (f-h) respective transmission electron images of Cs₄PbX₆ nanocrystals synthesized at 165 °C in the presence of [OlAm] = [OA] = 1.0 M (when X = Br, I) or 1.5 M (when X = Cl). All scale bars represent 100 nm.

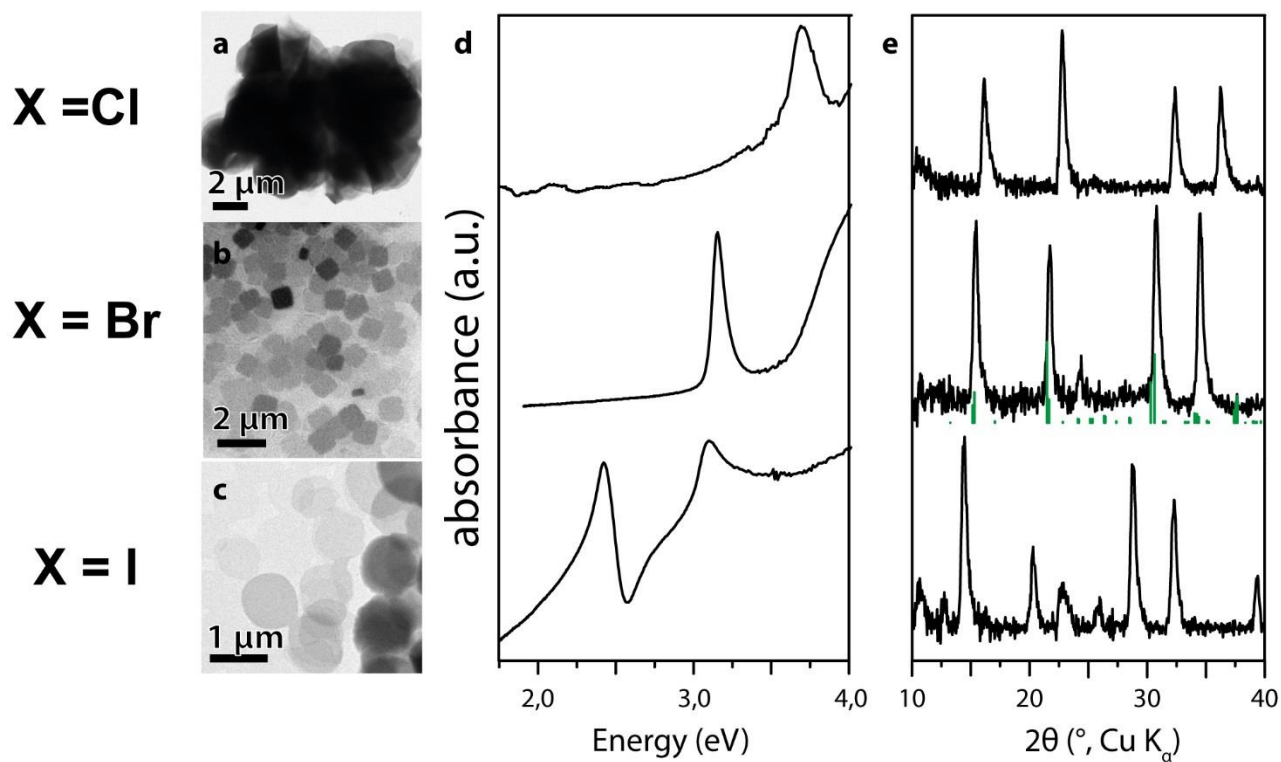


Figure S13. (a-c) transmission electron microscopy images, (d) absorbance spectra and (e) x-ray diffraction patterns of $(\text{RNH}_3)_2\text{PbX}_4$ nanosheets (green lines correspond to the CsPbBr_3 reference pattern) obtained by adding oleic acid to a hot solution of PbX_2 ($[\text{OIAm}] = [\text{OA}]_i = 0.25 \text{ M}$, $[\text{OA}]_i$ denotes the initial concentration of oleic acid).