Striking the Balance between the Capping Ligands for $CsPbBr_3$ Nanocrystal Synthesis via Emulsion LARP Approach

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Supporting Information

Experimental Details:

Chemicals:

CsBr (99.9%, Sigma-Aldrich), $PbBr_2$ (≥98%, Sigma-Aldrich), Dimethyl sulfoxide (≥99.9%, Sigma Aldrich), Hexane fraction (ACE Ltd., South Africa), Oleic Acid (≥99%, Sigma-Aldrich), Oleylamine (Acros Organics), Acetone (ACE Ltd., South Africa) were used in this study. All the reagents were used as received without further purification.

Synthesis:

$CsPbBr_3$ nanocrystals were synthesized using emulsion ligand-assisted reprecipitation (Emulsion-LARP) method. In a 100 ml round-bottom three-necked flask, 10 ml hexane was introduced and kept on a magnetic stirrer. A specific quantity of oleic acid (OA) and oleylamine (OLA) were added to the flask and allowed to stir using a magnetic needle. Briefly, 3 mmol CsBr and 3 mmol $PbBr_2$ were dissolved in 3 ml doubled-distilled water and 3 ml dimethyl sulfoxide (DMSO), respectively, to produce Cs-precursors and Pb-precursor solutions. 0.3 ml Pb-precursor solution was then injected into the hexane solution and allowed to stir vigorously. The solution turned slightly turbid with this injection. This was followed by the gradual injection of 0.3 ml Cs-precursor solution. 6 ml acetone was added to the solution, which precipitated yellow nanocrystals from the solution. The nanocrystals from the crude solution were separated by centrifuging at 6000 rpm for 10 mins, and the supernatant was discarded. The nanocrystals were redispersed in 5 ml hexane and centrifuged again for 5 mins at 6000 rpm. Bright green colloidal solution was obtained after the centrifugation, which was collected and used for further characterizations.

The synthesis was conducted in two phases. In the first phase, the quantity of OA was fixed at 0.5 ml, and the quantity of OLA was varied (0, 0.02, 0.05, 0.1, 0.2, 0.5, and 1 ml). In the second phase, the quantity of OLA was fixed at 0.1 ml and the quantity of OA was varied (0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 1 and 2 ml). Apart from these, one sample was prepared without adding either OA or OLA.

Instrumentation:

A D8 Advance X-ray diffractometer (Bruker, Germany) was employed to acquire the X-ray diffraction (XRD) patterns using a Cu-anode, ceramic X-ray tube source and Lynx Eye detector. The diffractometer was operated at 40 mA current and 40 kV voltage. The XRD patterns were obtained in the diffracting angle ranging from 10°-60° with a step-size of 0.02° using the Cu-K_α radiations (λ = 1.5406 Å). The high-resolution transmission electron microscopy (HRTEM) images and elemental mapping using energy dispersive spectroscopy (EDS) were obtained on a JEOL JEM-F200. A PerkinElmer 950 lambda spectrophotometer was used for recording the absorption spectra in the ultraviolet (UV) and visible (Vis) regions. The X-ray photoelectron spectra (XPS) were recorded on a PHI Quantes Scanning Dual X-ray Photoelectron Microprobe and the peak fitting analysis of the XPS spectra was performed using XPS Peak 4.1 software. The XPS survey scans were recorded in energy steps of 1 eV/step and dwell time of 50 ms/step with a pass energy of 280 eV. The binding energy (BE) charge correction for C 1s was achieved by correcting the reference BE value to 284.8 eV. The Fourier Transform Infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS10 FTIR spectrophotometer using the Attenuated Total Reflectance (ATR) mode. The samples were analysed in their liquid form, wherein the NCs were dispersed in hexane. The background correction was performed for the hexane solvent. An Edinburgh FS5 spectrofluorometer attached with a xenon lamp source was used to record the photoluminescence (PL) spectra. Edinburgh FLS980 spectrofluorometer was used to record the PL decay curves and the PL quantum yield (PLQY). The temperature-dependent PL emission spectra were recorded using a 325 nm He-Cd laser via a Horiba iHR320 monochromator.

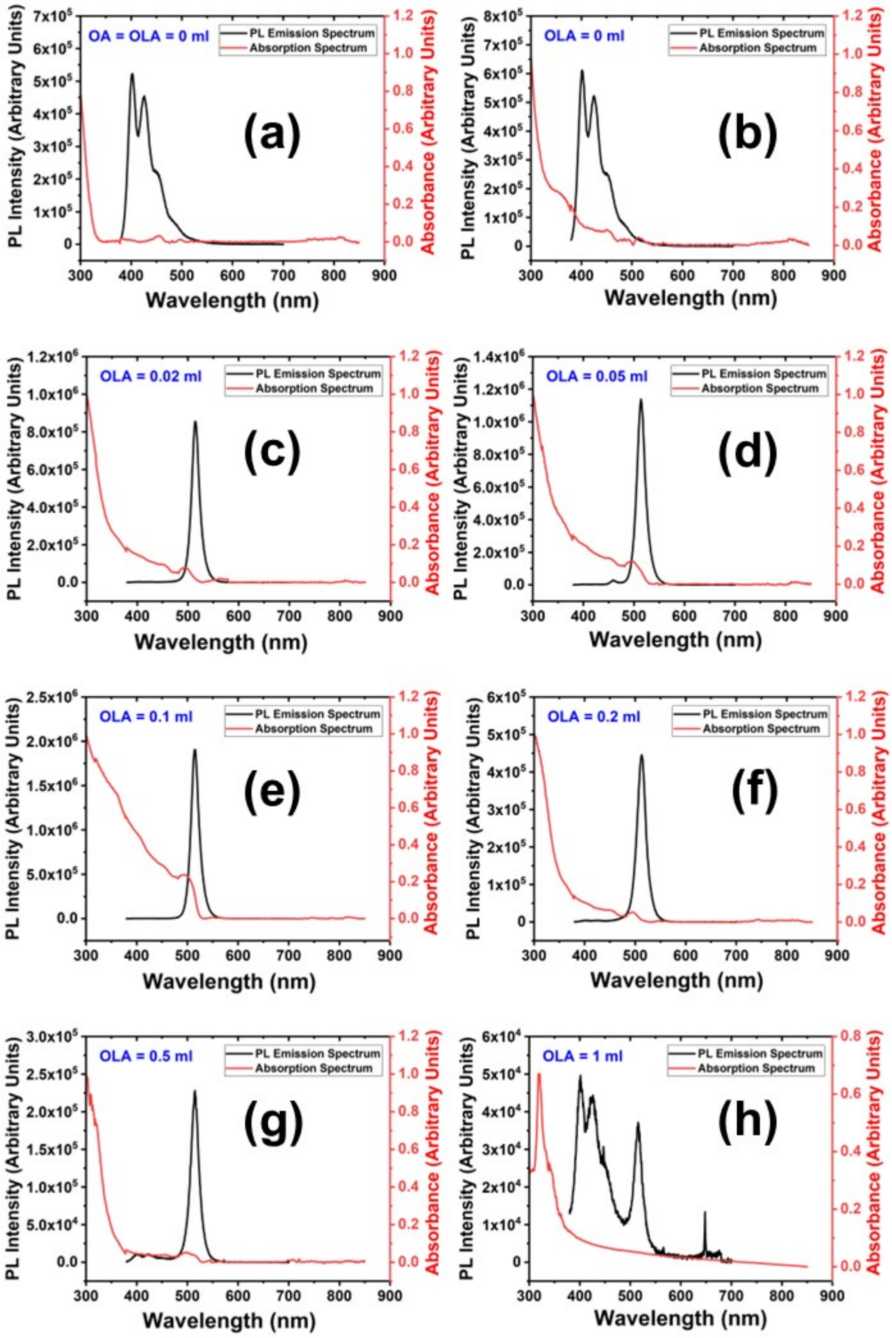

Fig. S1 UV-Visible absorbance and PL emission spectra of $CsPbBr_3$ NCs. (a) NCs prepared without using OA or OLA during the synthesis. (b-h) NCs prepared with a fixed amount of OA (0.5 ml) and varying amounts of OLA ranging from 0 to 1 ml: (b) OLA = 0 ml, (c) OLA = 0.02 ml, (d) OLA = 0.05 ml, (e) OLA = 0.1 ml, (f) OLA = 0.2 ml, (g) OLA = 0.5 ml, and (h) OLA = 1 ml.

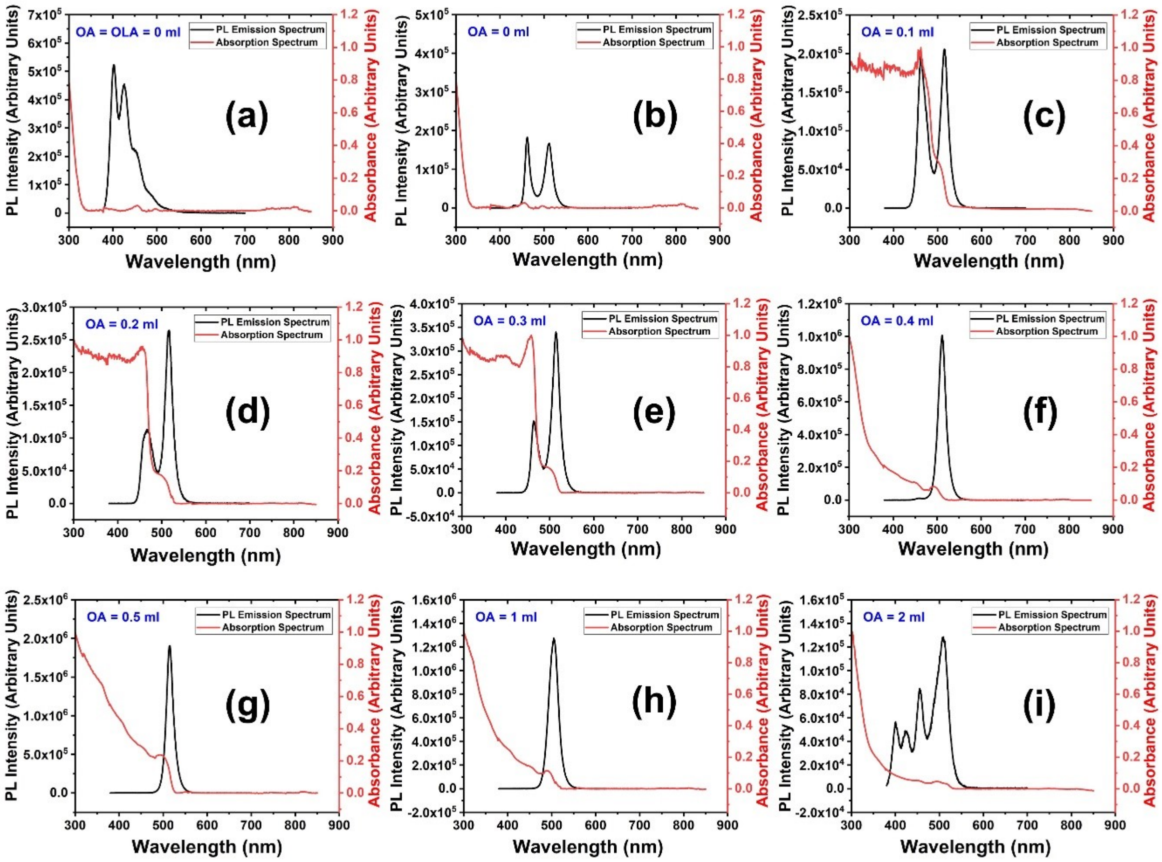

Fig. S2 UV-Visible absorbance and PL emission spectra of $CsPbBr_3$ NCs. (a) NCs prepared without using OA or OLA during the synthesis. (b-i) NCs prepared with a fixed amount of OLA (0.1 ml) and varying amounts of OA ranging from 0 to 2 ml: (b) OA = 0 ml, (c) OA = 0.1 ml, (d) OA = 0.2 ml, (e) OA = 0.3 ml, (f) OA = 0.4 ml, (g) OA = 0.5 ml, (h) OA = 1 ml, and (i) OA = 2 ml.

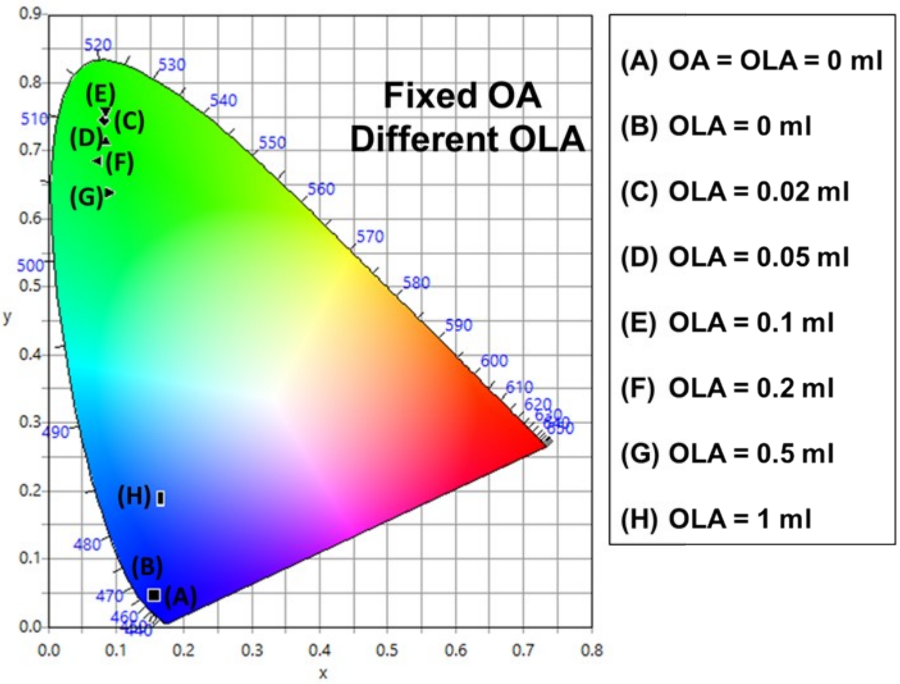

Fig. S3 CIE 1931 chromaticity diagram showing the variation of color emission from $CsPbBr_3$ NCs under 365 nm excitation for fixed OA and varying OLA concentrations.

Table S1 CIE chromaticity coordinates for the color emission from $CsPbBr_3$ NCs under 365 nm excitation for fixed OA and varying OLA.

Sr. No.	Sample	x	y
(A)	OA = OLA = 0 ml	0.1576	0.0454
(B)	OLA = 0 ml	0.1576	0.0449
(C)	OLA = 0.02 ml	0.0828	0.7447
(D)	OLA = 0.05 ml	0.0852	0.7129
(E)	OLA = 0.1 ml	0.0838	0.7593
(F)	OLA = 0.2 ml	0.0748	0.6849
(G)	OLA = 0.5 ml	0.0897	0.6388

(H)	OLA = 1 ml	0.1669	0.1877

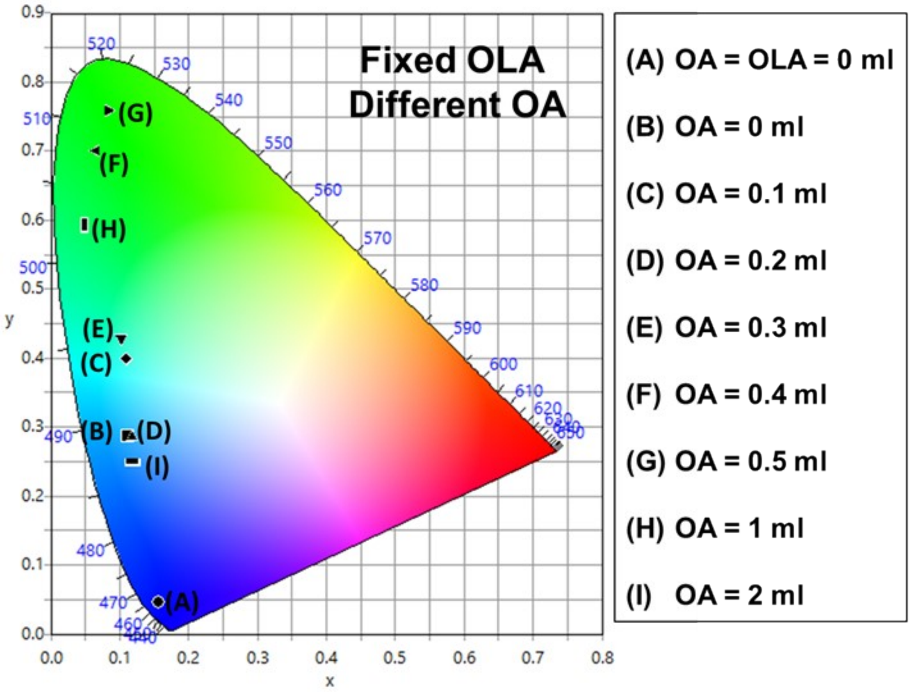

Fig. S4 CIE 1931 chromaticity diagram showing the variation of color emission from $CsPbBr_3$ NCs under 365 nm excitation for fixed OLA and varying OA concentrations.

Table S2 CIE chromaticity coordinates for the color emission from $CsPbBr_3$ NCs under 365 nm excitation for fixed OLA and varying OA.

Sr. No.	Sample	x	y
(A)	OA = OLA = 0 ml	0.1576	0.0454
(B)	OA = 0 ml	0.1114	0.2858
(C)	OA = 0.1 ml	0.0080	0.2858
(D)	OA = 0.2 ml	0.1103	0.3990
(E)	OA = 0.3 ml	0.1080	0.4302

(F)	OA = 0.4 ml	0.0660	0.7002
(G)	OA = 0.5 ml	0.0838	0.7593
(H)	OA = 1 ml	0.0498	0.5927
(I)	OA = 2 ml	0.1199	0.2487

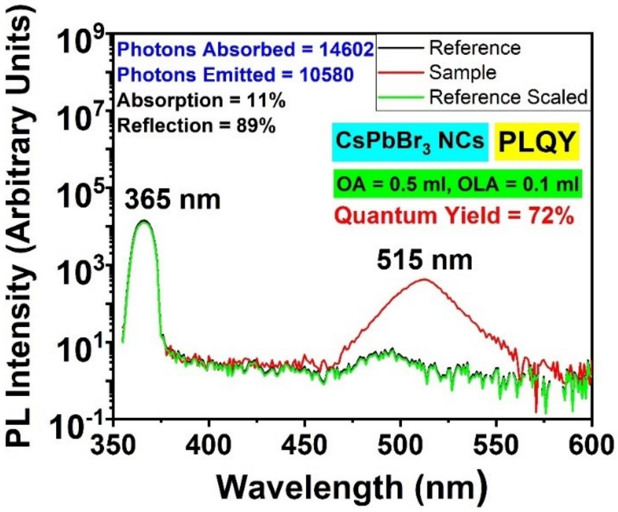

Fig. S5 Emission spectra for the determination of PLQY for $CsPbBr_3$ NCs prepared using 0.5 ml OA and 0.1 ml OLA.

Table S3 Best fit parameters of PL decay curves for the green emission of $CsPbBr_3$ NCs prepared with fixed OA and different OLA concentrations.

Sr. No.	**OLA Concentration**	**Decay time Parameters**	**Decay time Values (ns)**	**Coefficients**	**Coefficient values**	**Average lifetime (ns)**	**Goodness of Fitting**
1.	0.02 ml	τ_1	6.26	A_1	22002.87	22.5	1.056
		τ_2	17.38	A_2	24122.49		
		τ_3	44.44	A_3	4513.42		
2.	0.05 ml	τ_1	6.21	A_1	22513.87	23.5	1.150
		τ_2	17.14	A_2	22902.01		
		τ_3	46	A_3	4747.62		

3.	0.1 ml	τ_1	6.16	A_1	22958.56	30.4	1.054
		τ_2	16.89	A_2	22327.26		
		τ_3	56.23	A_3	5847.75		
4.	0.2 ml	τ_1	5.54	A_1	26644.74	22.1	1.120
		τ_2	15.5	A_2	19537.82		
		τ_3	48.46	A_3	3463.74		
5.	0.5 ml	τ_1	5.88	A_1	26261.86	18.7	1.034
		τ_2	14.91	A_2	19145.58		
		τ_3	41.88	A_3	3190.4		
6.	1 ml	τ_1	1.9	A_1	38969.58	18.7	1.183
		τ_2	9.66	A_2	9644.48		
		τ_3	36.79	A_3	3117.61		

Table S4 Best fit parameters of PL decay curves for the green emission of $CsPbBr_3$ NCs prepared with fixed OLA and different OA concentrations.

Sr. No.	OA Concentration	Decay time Parameters	Decay time Values (ns)	Coefficients	Coefficient values	Average lifetime (ns)	Goodness of Fitting
1.	0 ml	τ_1	3.22	A_1	14723.29	17.0	1.109
		τ_2	10.44	A_2	17813.98		
		τ_3	41.36	A_3	1855.15		
2.	0.1 ml	τ_1	5.22	A_1	25148.63	20.9	1.144
		τ_2	12.97	A_2	22748.46		
		τ_3	40.32	A_3	5654.05		
3.	0.2 ml	τ_1	6.26	A_1	32191.85	21.5	1.148
		τ_2	15.22	A_2	16027.09		
		τ_3	44.14	A_3	4634.83		
4.	0.3 ml	τ_1	4.61	A_1	29356.83	21.7	0.962
		τ_2	13.45	A_2	22599.79		
		τ_3	40.24	A_3	6490.85		
5.	0.4 ml	τ_1	5.31	A_1	29583.95	22.8	1.028
		τ_2	11.35	A_2	15297.31		
		τ_3	41.25	A_3	6227.09		
6.	0.5 ml	τ_1	6.24	A_1	26404.61	29.2	1.089
		τ_2	18.36	A_2	18920.06		

		τ_3	54.26	A_3	5559.99		
7.	1 ml	τ_1	6.35	A_1	33569.93	26.4	1.126
		τ_2	17.58	A_2	18996.38		
		τ_3	51.65	A_3	5518.09		
8.	2 ml	τ_1	4.51	A_1	24600.67	9.7	1.210
		τ_2	12.4	A_2	10675.18		
		τ_3	33.82	A_3	272.78		

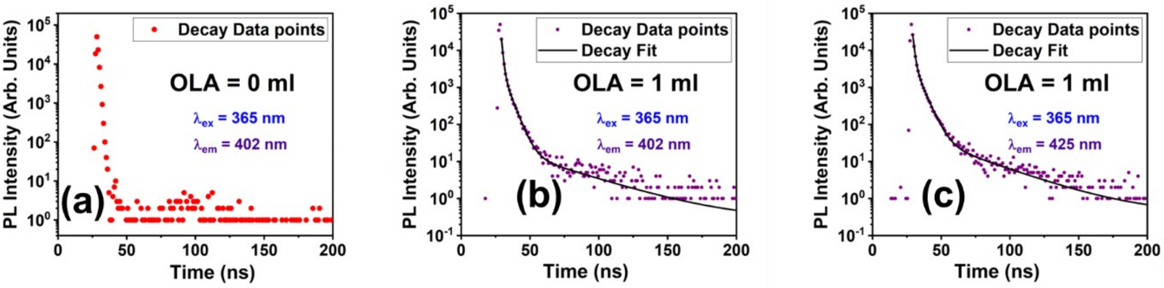

Fig. S6 PL decay curves for the blue emissions of $CsPbBr_3$ NCs excited at 365 nm showing the variation of the decay kinetics for fixed OA concentration and different OLA concentrations: (a) OLA = 0 ml for 402 nm, (b) OLA = 1 ml for 402 nm, and (c) OLA = 1 ml for 426 nm.

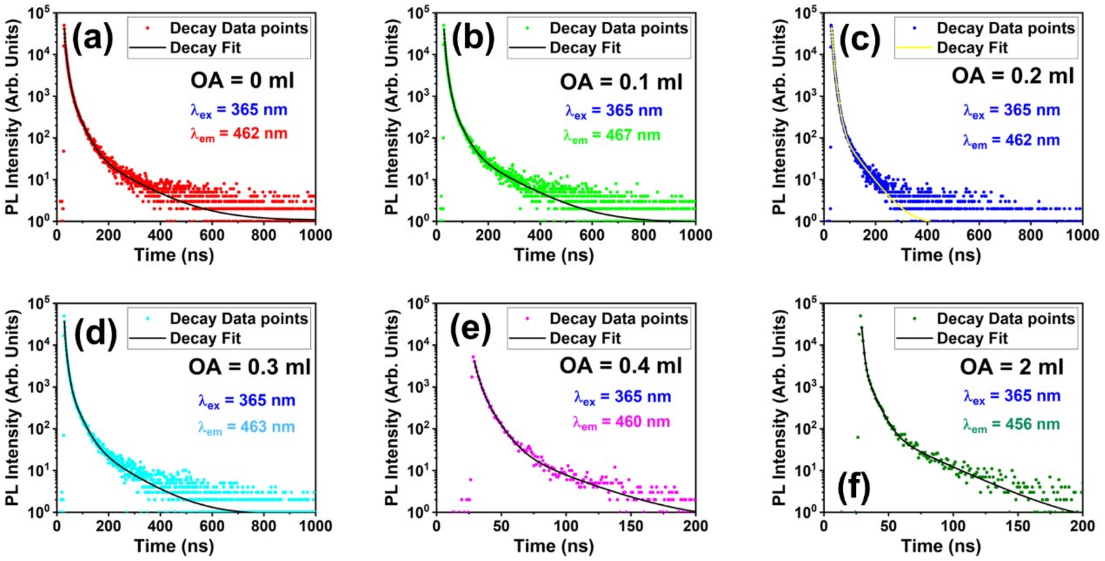

Fig. S7 PL decay curves for the blue emissions of $CsPbBr_3$ NCs excited at 365 nm showing the variation of the decay kinetics for fixed OLA concentration and different OA concentrations: (a) OA = 0 ml for 462 nm, (b) OA = 0.1 ml for 467 nm, (c) OA = 0.2 ml for

462 nm, (d) OA = 0.3 ml for 463 nm, (e) OA = 0.4 ml for 460 nm, and (f) OLA = 2 ml for 456 nm.

Table S5 Best fit parameters of PL decay curves for the blue emission of $CsPbBr_3$ NCs prepared with fixed OA and different OLA concentrations.

Sr. No.	OLA Conc.	Emission Wavelength (nm)	Decay time Parameters	Decay time Values (ns)	Coefficients	Coefficient values	Average lifetime (ns)	Goodness of Fitting
1.	0 ml	402 nm	Fitting was not possible				-	-
2.	1 ml	402 nm	τ_1	4.38	A_1	3541.99	4.7	1.038
			τ_2	36.66	A_2	22.99		
3.	1 ml	426 nm	τ_1	4.90	A_1	5508.58	6.6	0.985
			τ_2	32.85	A_2	52.09		

Table S6 Best fit parameters of PL decay curves for the blue emission of $CsPbBr_3$ NCs prepared with fixed OLA and different OA concentrations.

Sr. No.	OA Conc.	Emission Wavelength (nm)	Decay time Parameters	Decay time Values (ns)	Coefficients	Coefficient values	Average lifetime (ns)	Goodness of Fitting
1.	0 ml	462 nm	τ_1	8.08	A_1	20207.20	13.7	0.997
			τ_2	28.20	A_2	2239.99		
2.	0.1 ml	467 nm	τ_1	7.88	A_1	639.71	15.7	0.990
			τ_2	28.23	A_2	111.95		
3.	0.2 ml	462 nm	τ_1	10.15	A_1	11375.14	14.1	0.985
			τ_2	52.27	A_2	230.77		
4.	0.3 ml	463 nm	τ_1	7.43	A_1	16994.76	12.8	1.052
			τ_2	28.07	A_2	1605.19		
5.	0.4 ml	460 nm	τ_1	8.08	A_1	1379.94	12	1.086
			τ_2	35.85	A_2	51.86		
6.	2 ml	456 nm	τ_1	5.66	A_1	3895.59	9.3	0.933

			τ_2	30.83	A_2	119.62		

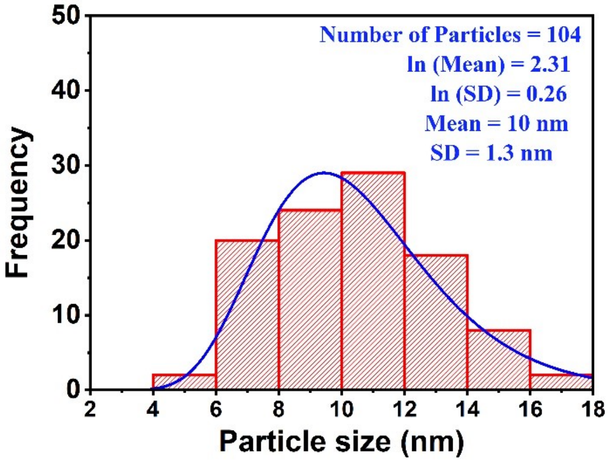

Fig. S8 Particle-size distribution of the $CsPbBr_3$ NCs prepared using the optimized quantities of both OA and OLA.

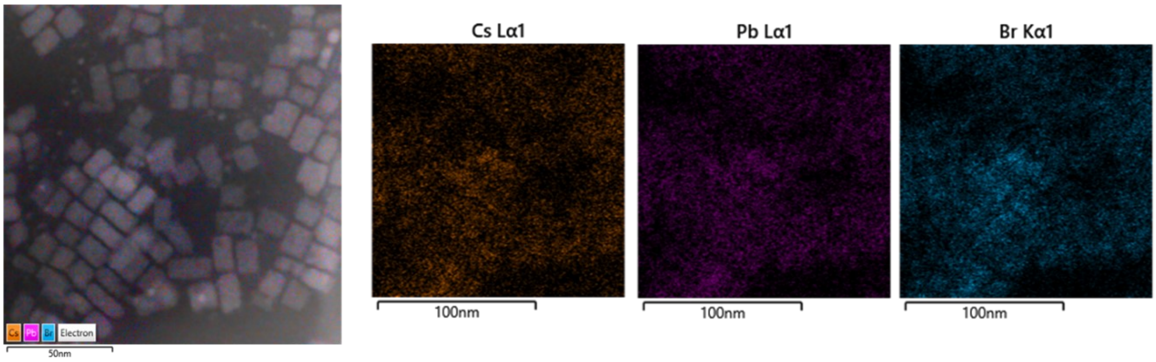

Fig. S9 Elemental map obtained from the EDS showing the distribution of the constituent elements in $CsPbBr_3$ NCs prepared using the optimized quantities of both OA and OLA.

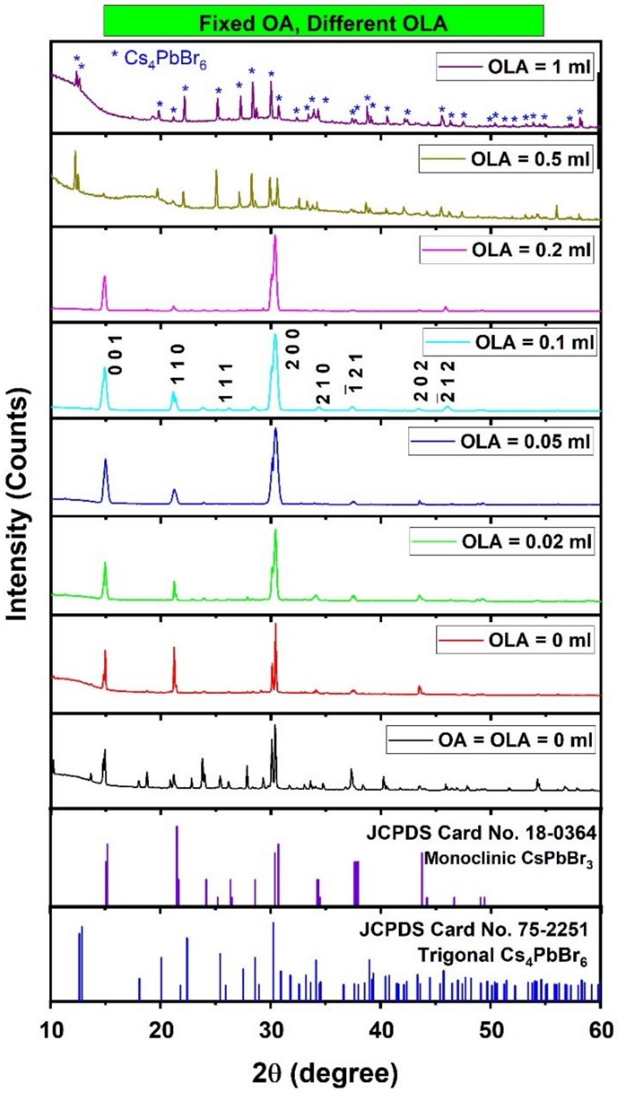

Fig. S10 XRD patterns of CsPbBr$_3$ NCs prepared with a fixed OA and varying OLA concentration.

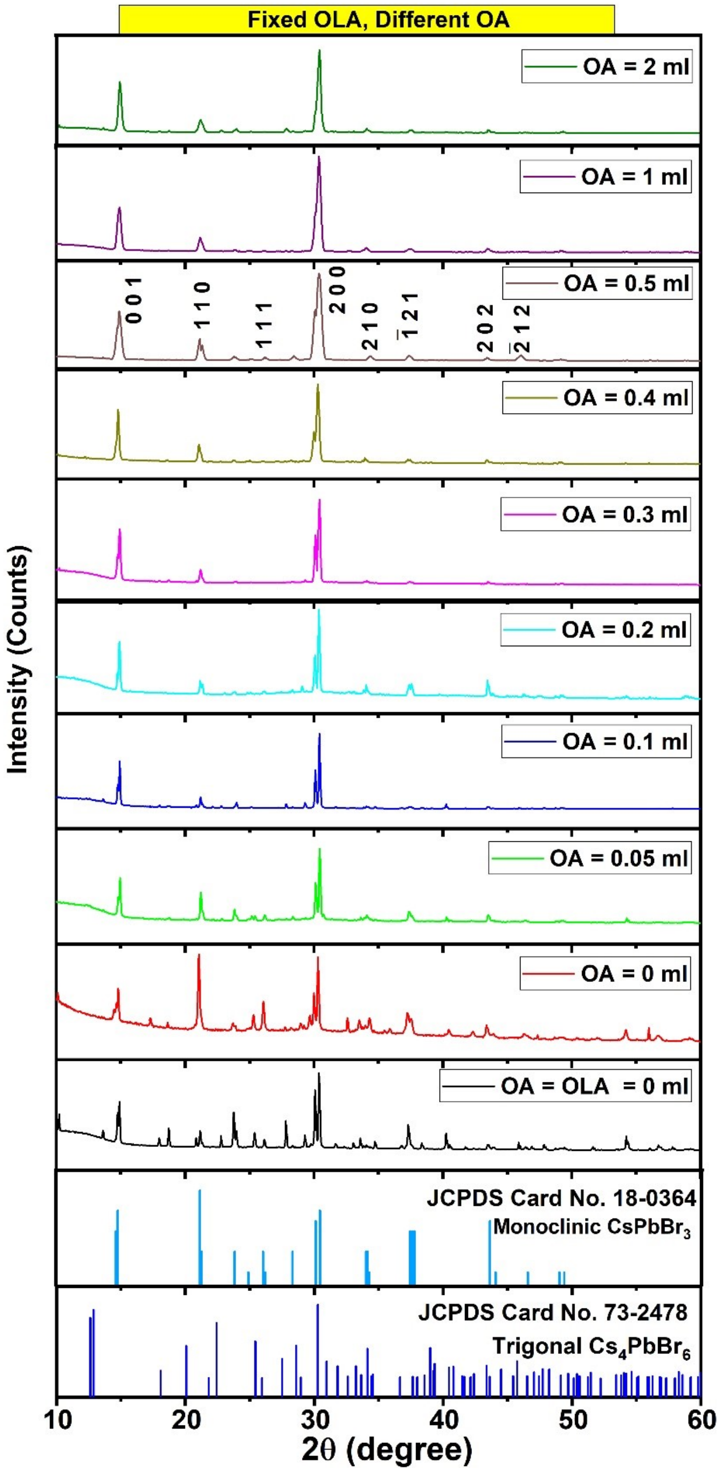

Fig. S11 XRD patterns of $CsPbBr_3$ NCs prepared with a fixed OLA and varying OA concentration.

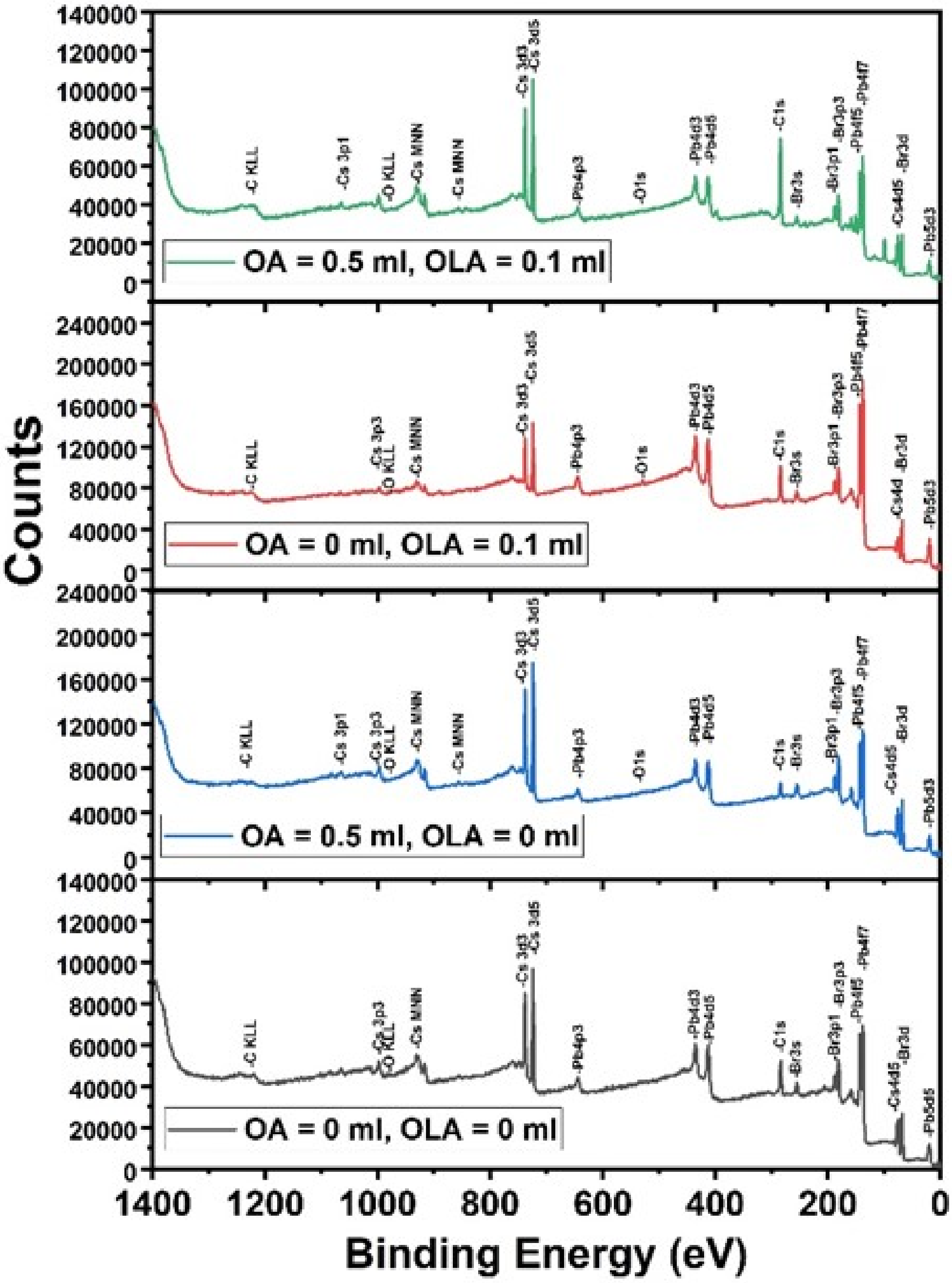

Fig. S12 XPS full-survey scan for the $CsPbBr_3$ samples prepared without adding any ligands, prepared by adding either OA or OLA, and prepared using the optimized quantities of both OA and OLA.

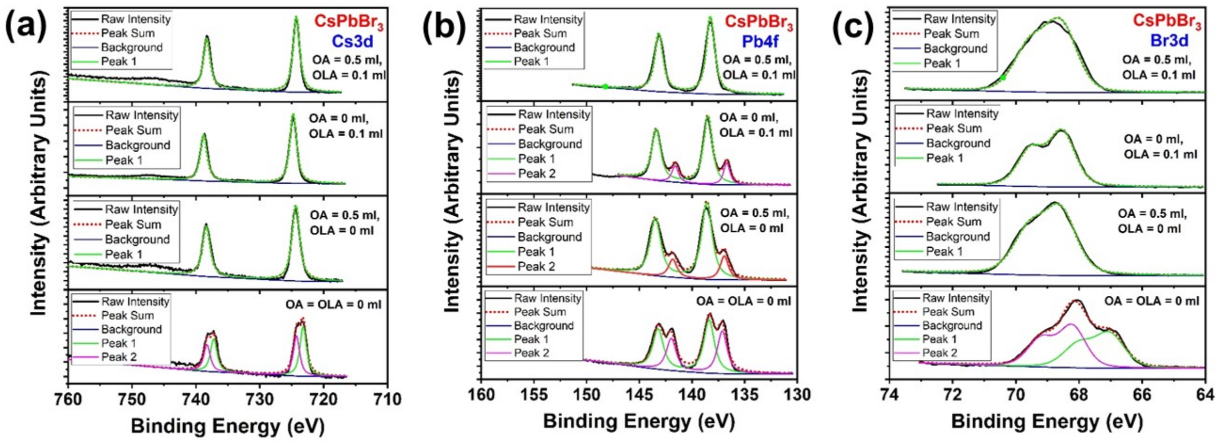

Fig. S13 High-resolution XPS spectra for (a) Cs 3d, (b) Pb 4f, and (c) Br 3d, for the $CsPbBr_3$ samples prepared without adding any ligands, prepared by adding either OA or OLA, and prepared using the optimized quantities of both OA and OLA.

Table. S7 The chemical states and the corresponding binding energies for the different core-levels in the high resolution XPS scans performed for the $CsPbBr_3$ samples prepared without adding any ligands, prepared by adding either OA or OLA, and prepared using the optimized quantities of both OA and OLA.

Sr. No.	**Core-Level**	**Peak**	**Spin-Orbit Slitting**	**Binding energy (eV)**			
				For samples prepared with both OA and OLA	**For samples prepared with only OLA**	**For samples prepared with only OA**	**For samples prepared without any ligands**
1.	Cs 3d	1	Cs $3d_{5/2}$	724.2	724.7	724.5	723.1
			Cs $3d_{3/2}$	738.3	738.7	738.4	737.2
		2	Cs $3d_{5/2}$	-	-	-	724.1
			Cs $3d_{3/2}$	-	-	-	738.2
2.	Pb 4f	1	Pb $4f_{7/2}$	138.2	138.5	138.6	138.3
			Pb $4f5_{/2}$	143.1	143.4	143.5	143.1
		2	Pb $4f_{7/2}$	-	136.7	136.9	137.0
			Pb $4f5_{/2}$	-	141.5	141.8	141.9
3.	Br 3d	1	Br $3d_{5/2}$	68.7	68.6	68.8	67.0

			Br 3d$_{3/2}$	69.5	69.5	69.7	68.0
		2	Br 3d$_{5/2}$	-	-	-	68.2
			Br 3d$_{3/2}$	-	-	-	69.2

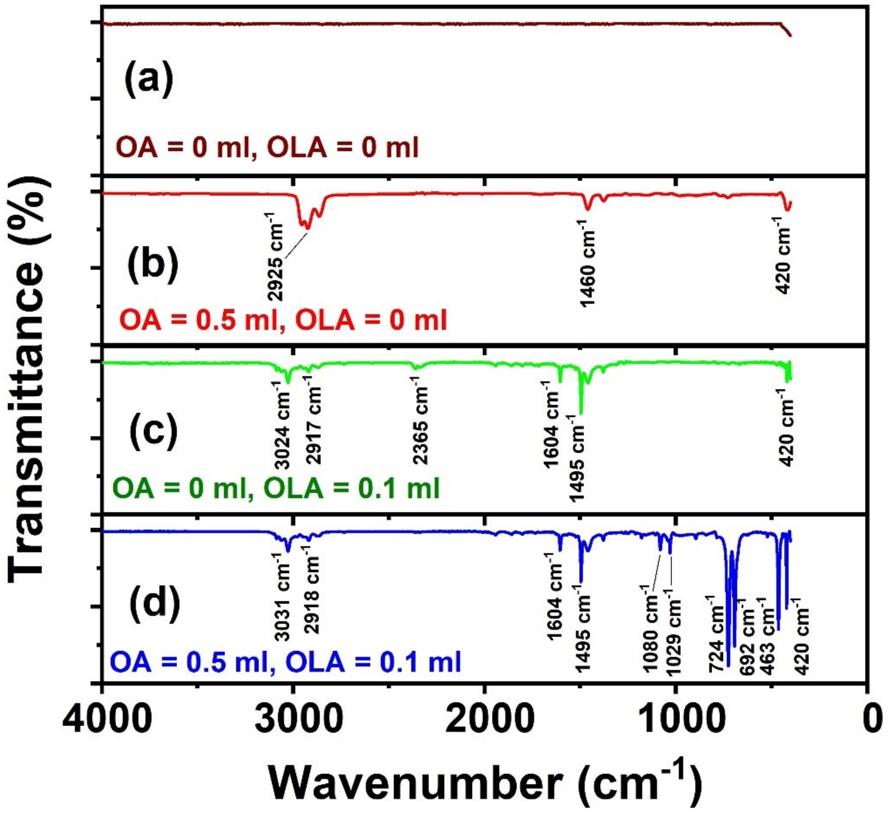

Fig. S14 FTIR spectra of the $CsPbBr_3$ NCs prepared: **(a)** without OA or OLA, **(b)** with only OA, **(c)** with only OLA, and **(d)** with both optimized quantities of OA and OLA.

Table. S8 The vibrational modes responsible for the absorption peaks in the FTIR spectra recorded for the $CsPbBr_3$ NCs prepared without OA or OLA, with only OA, with only OLA, and with both optimized quantities of OA and OLA.

Sr. No.	**Peak Positions of $CsPbBr_3$ NCs**				**Vibrational Modes responsible for the absorption**
	Without OA or OLA (OA = 0 ml, OLA = 0 ml)	**With only OA (OA = 0.5 ml, OLA = 0 ml)**	**With only OLA (OA = 0 ml, OLA = 0.1 ml)**	**With both OA and OLA (OA = 0.5 ml, OLA = 0.1 ml)**	
1.	-	-	3024	3031	N-H stretching vibrations
2.	-	2925	2917	2918	Asymmetric C-H stretching vibrations
3.	-	2862	2861	2865	Symmetric C-H stretching vibrations
4.	-	-	2365	-	Asymmetric O=C=O stretching vibrations
5.	-	-	1604	1604	C=C stretching vibrations
6.	-	1460	1495	1495	Asymmetric stretching of O-C-O bond of the carboxylic (COO^-) group
7.	-	-	-	1080	C-O-C stretching vibrations
8.	-	-	-	1029	Out-of plane bending vibrations of methylene ($-CH_2-$) groups
9.	-	-	-	724	In-plane rocking vibrations of methylene ($-CH_2-$) groups
10.	-	-	-	692	In-plane bending of O-C-O bond of the carboxylic (COO^-) group
11.	-	-	-	463	Pb-Br stretching vibrations
12.	-	420	420	420	

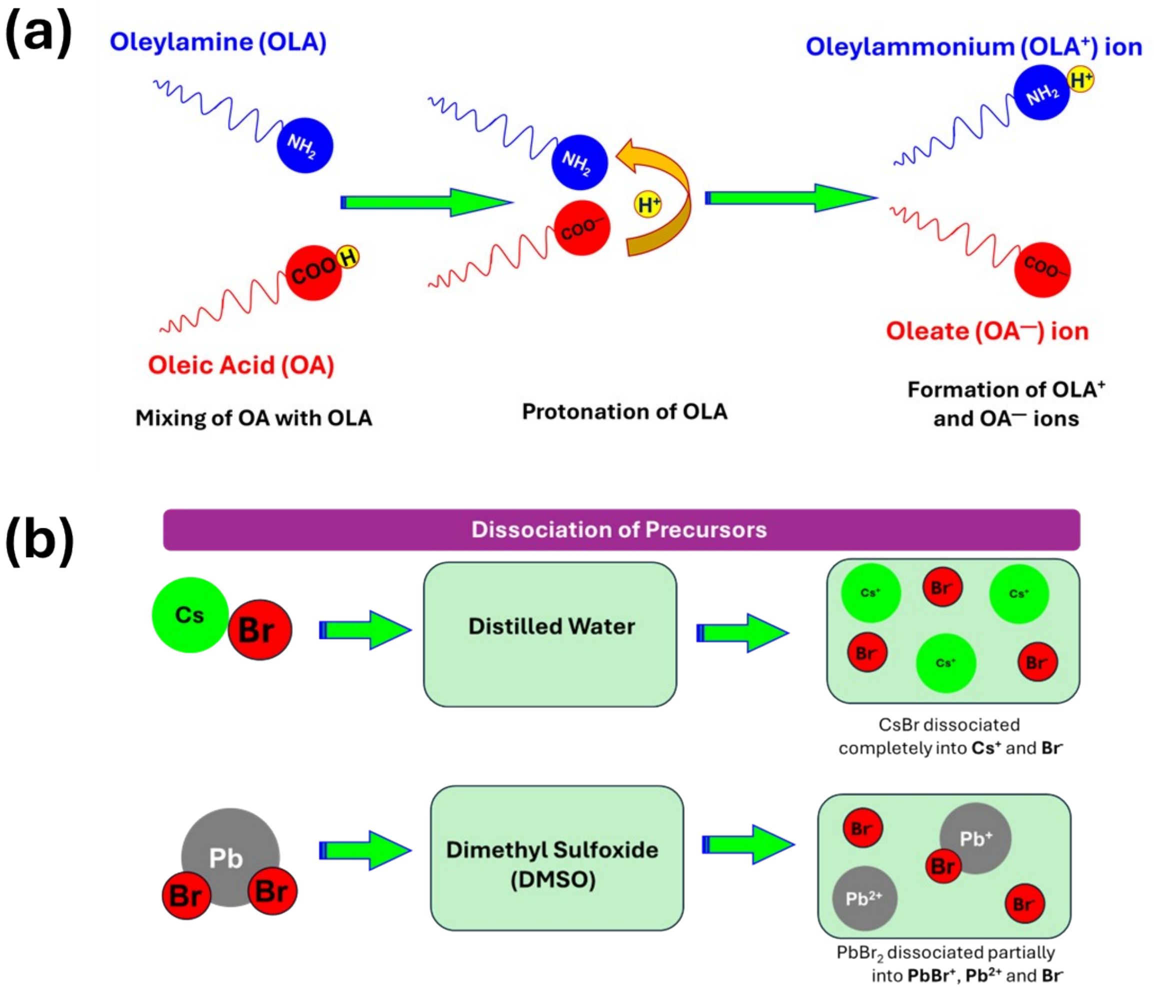

Fig. S15 Graphical representation showing: **(a)** Protonation of oleylamine by oleic acid in a non-polar organic solvent, **(b)** Dissociation of CsBr and $PbBr_2$ precursors in distilled water and DMSO media, respectively.