Electronic Supplementary Information

Insights into the Role of Lead/Surfactants Ratio on Formation and Passivation of Cesium Lead Bromide Perovskite Nanocrystals

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Supporting TEM data



Figure S1. (Top) Large area TEM photograph of as-prepared $CsPbBr_3(4)$ sample evidencing the simultaneous presence of lead-poor Cs_4PbBr_6 NCs and tick perovskite nanoparticles. (Bottom) Large area TEM photograph of purified $CsPbBr_3(4)$ sample.

Supporting EDX data

Sample	Element concentration (atomic %)							Mc	Molar ratios		
	Cs		Pl	Pb		Br		Cs	Pb	Br	
	Conc	SD	Conc	SD		Conc	SD				
1	21.80	0.36	19.97	0.10		58.21	0.15	1.1	1.0	2.9	
2	24.27	0.61	19.02	0.49		56.73	0.08	1.3	1.0	3.0	
3	25.93	0.52	18.74	0.60		55.73	0.24	1.4	1.0	3.0	
4	36.17	1.10	13.01	0.38		50.81	0.74	2.8	1.0	3.9	

Table S1. Element concentration (atomic %) and obtained molar ratios of the studied samples analyzed via FEG-SEM-EDX (n=3).

Conc = average concentration

SD = standard deviation



Figure S2. EDX profiles of as-prepared NCs.

Table S2. Element concentration and molar ratios (n=3) of purified samples analyzed via FEG-SEM-EDX.

Sample	Eleı	nental	Molar ratios						
	Cs		Pb		Br		Cs	Pb	Br
	Conc	SD	Conc	SD	Conc	SD			
CsPbBr ₃ (1)	25.01	0.17	19.13	0.06	55.87	0.19	1.3	1.0	2.9
$CsPbBr_3(4)$	29.21	0.03	16.03	0.40	54.44	0.23	1.8	1.0	3.4

Conc = average concentration SD = standard deviation

Supporting X-ray data

The preferred orientation of the NCs and size-induced broadening effects of diffraction peaks make hard the unambiguous assessment of the crystalline phase, among the commonly expected ones for CsPbBr₃ (*i.e.*, cubic, orthorhombic, monoclinic, tetragonal), only differing from each other basically for tiny distortions of the unit cell, while often keeping very similar periodicities of the crystal lattice. Moreover, in the presence of shape anisotropy, which implies different numbers of unit cells along different crystallographic directions in the crystal, peak intensity ratios can further dramatically change, being for each reflection (diffraction "peak") the integral intensity (area) proportional to the crystal volume and the maximum intensity proportional to the square of the number of unit cells in the crystalline domain along the direction of the scattering vector.¹ Therefore only the coupled sample/detector scan mode ($\theta/2\theta$), keeping the orientation of the scattering vector constant with respect to sample surface, allows to reliably compare the intensity ratio between different diffraction orders originated from the very same lattice planes (hence, for a given crystal orientation and from the same crystals as long as the beam illuminates the same sample region while changing the incidence angle), even in the case of crystals with different size/shape and non-random orientation (the intensity ratio will be also independent of crystal volume).

Finally, some variability in the Powder Diffraction Files from the crystallographic databases (for example the expected A_2/A_1 ratio for the cubic Pm-3m can range from 1.3 in JCPDS #18-0464 to 2.3 in ICSD #01072-7930) carries further uncertainty in the assessment of the crystalline phase, probably due to the intrinsic difficulty in obtaining stable CsPbBr₃ NCs featuring actually pure phases leading to unambiguous X-ray intensity ratios.



Figure. S3. Experimental and fit XRD profiles as solid grey and dotted red lines, respectively, for (from the top left) the CsPbBr₃ (purified and as deposited 1, 2,3, purified and as deposited 4) samples. The interpolated and subtracted background profile is represented by the orange solid line; the difference profile by the green line; peak positions for the cubic and orthorhombic phases included in the fit for samples CsPbBr3 (1 as deposited, 2, 3) are reported at the bottom of each panel as red and green vertical bars, respectively. For the purified CsPbBr₃ (1) sample, only the orthorhombic phase (space group Pbnm) is considered. For samples CsPbBr₃ (4) as deposited and purified, both orthorhombic (CsPbBr₃) and Cs₄PbBr₆ are considered. The horizontal axis is in units of 2-Theta degrees.

All expected peak positions for the different phases were obtained from the Cif files data_1533063 (Pm-3m) and data_4510745 (Pnma) of the COD [http://www.crystallography.net/] database, and data_97851 (Pbnm) of ICSD, and recalculated based on the unit cell returned by the Le Bail fit, reported below.

----- $CsPbBr_3(1)$ Pbnm, Cell : a = 8.12644 8.32792 11.72450 alpha = 90 beta = 90 gamma = 90 _____ $CsPbBr_3(2)$ Pm-3m, Cell : a = 5.96561 b = 5.96561 c = 5.96561 alpha = 90 beta = 90 gamma = 90 Pbnm, Cell : a = 8.17844 b = 8.21733 c = 12.13965alpha = 90 beta = 90 gamma = 90_____ $CsPbBr_3(3)$ Pm-3m, Cell : a = 5.86 b = 5.86 5.86 alpha = 90 beta = 90 gamma = 90 Pnma, Cell: a = 8.26895 b = 11.75376 c = 8.18101alpha = 90 beta = 90 gamma = 90_____ $CsPbBr_3(4)$ Pbnm, Cell : a = 8.28721 b = 8.09229 c = 12.27811 alpha = 90 beta = 90 gamma = 90 Cs₄PbBr₆ R-3c, Cell : a = 13.6587 b = 13.6587 c = 17.2487; alpha = 90 beta = 90 gamma = 120

The Le Bail approach, only relying on the experimental intensities and peak positions, was used to assess the possible crystalline phases in each sample, together with a direct comparison of the experimental intensity ratio between the second and first diffraction orders of the main reflection relative to the expected ratio in the relevant Powder Diffraction Files (Pdf), taken as the main references in the text. As a consequence, due to the unreliability of peak intensity quantitative fitting in the Le Bail approach, no estimation is reported about the actual fraction of any phase in the mixture.

Supporting NMR data



Figure S4. 2D-NOESY spectrum of mixture(1), i.e. the reaction mixture leading to $CsPbBr_3(1)$ NCs before injecting cesium oleate, in C_6D_6 .



Figure S5. 2D-NOESY spectrum of as-prepared $CsPbBr_3(2)$ NCs in C_6D_6 .



Figure S6. 2D-NOESY spectrum of as-prepared $CsPbBr_3(3)$ NCs in C_6D_6 .



Figure S7. 2D-NOESY spectrum of purified $CsPbBr_3(2)$ NCs in C_6D_6 .



Figure S8. 2D-NOESY spectrum of purified $CsPbBr_3(3)$ NCs in C_6D_6 .

Supporting optical data



Figure S9. Absorption spectra of as-prepared and purified $CsPbBr_3(4)$ NCs in cyclohexane evidencing the optical transition at 313 nm ascribable to the presence of $CsPbBr_6$ NCs only in the case of the as-prepared sample.



Figure S10. Normalized PL spectra of as-prepared and aged (10 days) CsPbBr₃(1) NCs in cyclohexane.



Figure S11. Normalized PL spectra of as-prepared and aged (10 days) CsPbBr₃(4) NCs in cyclohexane.

REFERENCES

¹ C. Giacovazzo, H. L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti and M. Catti, Fundamentals of Crystallography. Oxford University Press Inc., New York, 1992, Reprinted 1995. Chap. 3, pag. 152, 163, 178.