Synthesis of highly calibrated CsPbBr₃ Nanocrystals perovskites by soft Chemistry

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Experimental sections

<u>Materials</u>. Lead(II) bromide (PbBr₂, 99.99%), cesium carbonate (Cs₂CO₃, 99.99%), oleic acid (OA, 90%), phenylethylamine (PEA, C₈H₁₁N, \leq 100 %), dimethylformamide (DMF, 99.8% anhydrous), toluene (\geq 99.9%), tetra-octylammonium bromide (TOABr, 98%) were sourced from Sigma-Aldrich.

<u>Characterizations.</u> NCs were observed and analyzed by a transmission electron microscopy with a Microscope JEM 2100 Plus (JEOL) and an accelerating voltage of 200 kV. High resolution TEM (HRTEM), high-angle annular dark field scanning TEM (HAADF-STEM) images, and energy-dispersive X-ray (EDX) spectroscopy were taken with a Microscope Titan3 G2 80-300 (FEI ThermoFisher) operating at 200 kV. Thin film of NCs were characterized by applying an X-ray diffractometer (D8 ADVANCE, Bruker, Germany) with a Cu K α radiation source (λ = 0.15418 nm) at a rate of 2°/min in the scanning angle (2 θ) range from 3° to 60°. The UV-vis absorption spectra of NCs were recorded using a UV-vis spectrometer (Perkin-Elmer LAMBDA 950 UV/Vis/NIR Spectrophotometer) over the wavelength from 300 to 700 nm. The PL and TRPL spectra were recorded using a homemade micro-PL setup (See scheme SI-1). The laser source was a PDL 800-D Picosecond Pulsed Diode Laser from PicoQuant (λ = 405nm, rep. Rate 5MHz, power 1.86 μ W). The spectrometer was an Acton SP-2500i from Princeton Instrument. The microscope objective was a Plan Fluor ELWD 40x/0.60 DIC M from Nikon. The detection was performed using a ID100 Visible Single-Photon Detector from IDQ, and the signal was acquired using a TimeHarp 260 acquisition card from PicoQuant. The homemade setup was controlled using a homemade script based on the Qudi framework.¹

Synthesis.

Colloidal perovskite CsPbBr₃ NCs were fabricated by an adapted LARP technique but instead of using a pure toluene solution to fabricate NCs, a toluene solution containing CsPbBr₃ NCs precursors stabilized by TOABr was used.

The method to get highly calibrated $CsPbBr_3 NCs$ described in this communication, consists of two main steps. In the first one, a toluene solution of $CsPbBr_3 NCs$, so-called **PVK-TOA** is prepared. In

¹ J. M. Binder, A. Stark, N. Tomek, J. Scheuer, F. Frank, K. D. Jahnke, C. Müller, S. Schmitt, M. H. Metsch, T. Unden, T. Gehring, A. Huck, U. L. Andersen, L. J. Rogers and F. Jelezko, SoftwareX, 2017, 6, 85–90.

parallel, a **pre-SB** solution is synthesized, containing $PbBr_2$, OA, Cs_2CO_3 , and PEA. Then, in the second step, a small volume of **pre-SB** solutions (2,5 % in volume of **SA**) is added to **SA** at RT to form the final monodisperse perovskite-NCs (**SB** solutions).

CsPbBr₃ NCs precursors stabilized by TOABr (PVK-TOA, SA): NCs were prepared by following the procedure reported by Wei *et al.*² PbBr₂ (0.1 mmol) and TOABr (0.1 mmol) were mixed in toluene (10 mL) and stirred until the full dissolution of reagents by slightly heating (45°C) – vial A. In parallel, Cs_2CO_3 (2.5.10⁻⁵ mol) was dissolved in OA (1 mL) – vial B. Then vial B was poured out vial A in one shot at room temperature and stirred for 5 min. Then NCs precursors were recovered after centrifugation at 10000 rpm for 10 min and redispersed in toluene (PVK-TOA).

Pre-SB solutions in DMF vial :

- Pre-SB 1-8 : PbBr₂ (0.1 mmol) and OA (0.122 mL) were solubilized in DMF (1mL) at 35°C vial C. Cs₂CO₃ (2.5.10⁻⁵ mol) and OA (0.122 mL) were solubilized in DMF (1mL) vial D. Vial C and D were mixed together at room temperature. Then, PEA (pre-SB 1: 12.5 μL; pre-SB 2: 25 μL; pre-SB 8: 100 μL) was added to the mixture and the solution was stirred for 5 min to homogenize the solution.
- **Pre-PEA** : PEA (12.5 μ L) and OA (0.122 mL) was solubilized in DMF (1mL).
- **Pre-Pb** : PbBr₂ (0.1 mmol) and OA (0,122 mL) was solubilized in DMF (1mL).

Final CsPbBr₃ NCs (SB solutions at different ratios) were used without other treatments :

• **Pre-SB** solutions (0.125 mL) were poured onto **SA** (5 mL) and stirred for a minimum of 10 min to complete the reaction and to get the final **SB solutions (SB 1-8)**.

Alternative final CsPbBr₃ NCs:

- **Pre-PEA** solution (0.125 mL) was poured onto **SA** (5 mL) and stirred during 10 min to get the final solution named **PEA** solution.
- **Pre-Pb** (0.125 mL) was poured onto **SA** (5 mL) and stirred during 10 min to get the final solution named **Pb** solution.

Sample	Description	Miscellaneous
PVK-TOA (SA)	Pristine CsPbBr₃ solution.	Polydisperse NCs, with
	(TOABr and PbBr ₂ in Toluene +	average size 40μm.
	Cs₂CO₃ in Oleic acid	
	centrifugated)	
Pre-SB solutions		
pre-SB 1	Precursor solution with PbBr ₂ ,	
	Oleic acid, Cs ₂ CO ₃ and PEA in	
	DMF.	
pre-SB 2	Precursor solution, similar to	
	pre-SB 1 but with twice the	
	amount of PEA.	
pre-SB 8	Precursor solution, similar to	
	pre-SB but with eight times	
	the amount of PEA.	
SB solutions		

²Homogeneous Synthesis and Electroluminescence Device of Highly Luminescent CsPbBr₃ Perovskite Nanocrystals. S. Wei, Y. Yang, X. Kang, L. Wang, L. Huang, D. Pan, *Inorg. Chem.* **2017**, *56*, 2596–2601; DOI: 10.1021/acs.inorgchem.6b02763

Sample	Description	Miscellaneous
SB 1	PVK-TOA (SA) + pre-SB 1	Highly calibrated NCs, average
		size 10nm
SB 2	PVK-TOA (SA) + pre-SB 2	Highly calibrated NCs, average
		size 10nm
SB 8	PVK-TOA (SA) + pre-SB 8	Highly calibrated NCs, average
		size 10nm

Table SI-1 – Names and descriptions of the solutions synthesized in this communication



Scheme SI-1 – Homemade micro-PL setup for PL and TRPL measurements.



Scheme SI-2 – Schematic illustration of the action of PEA as a scissor on **PVK-TOA**. HR-STEM of intermediate structure highlighting the role of PEA. The white arrows shown the cutting line



Figure SI-1 – TEM (200 KeV) pictures of – (a) PVK-TOA (scale bar 100 nm) – (b) SB 1 (scale bar 1μ m) – (c) SB 1 (scale bar 200 nm) – (d) SB 1 (scale bar 100 nm) – (e) SB 1 (scale bar 50 nm) and HR-STEM picture in HAADS mode (XX KeV ?) of SB 8 with scale bar – (f) 500 nm – (g) 100 nm and – (h) 10 nm.

NCs sizes and distance separations estimate. NCs size was estimated from TEM pictures using the Julia programming language³, the ImageSegmentation. jl library and a watershed algorithm⁴. Briefly, the raw image (figure SI-3 (a)) was thresholder to distinguish the NCs from the background (figure SI-3 (b)). Then, we applied the inverse distance transform to calculate the distance from each pixel to the nearest pixel belonging to the background (figure SI-3(c)). Therefore, we could identify the 10% pixels that were further away from the background as belonging to a NC, and group pixels that were direct neighbors to form NC markers (figure SI-3(d)). This also allowed partial removal of the noise. We applied the watershed algorithm to determine the pixels belonging to each NC from these defined markers and the inverse distance transform. It consisted of growing each region starting from the markers and adding pixels with the lowest inverse distance transform. To picture how the algorithm work, one can imagine that the inverse distance transform defines a set of ridges and valleys and that markers define a set of water sources that flood the valleys, creating lakes. When two lakes meet we have found the delimitation between two NCs. We could then apply the binary mask defined by figure SI-3(a) to remove any pixel belonging to the background and obtained figure SI-3(e). From there it was straightforward to estimate the area of each NC by counting the number of pixels belonging to the NC. The histogram from figure SI-3(g) was obtained by taking the square root

³ J. Bezanson, A. Edelman, S. Karpinski and V. B. Shah, *SIAM Review*, 2017, **59**, 65–98. 4 R. C. Gonzalez and R. E. Woods, in *Digital Image Processing*, Prentice Hall, 2nd edn., 2002, pp. 567–642.

of the estimated area of the NCs (that is, assuming NCs are cubic). To compute the distance between NCs, we computed each NC barycenter and calculated the Delaunay triangulation of the resulting cloud of points (figure SI-3(f)). Finally, we plotted the histogram of edges lengths whose maximum gave an estimate of the average distance between centers. Delaunay triangulation is imperfect because some edges correspond to diagonals instead of direct neighbors, which explains the asymmetry of the histogram in figure SI-3(h). Plots in figures 1, 2, 3, SI-2 SI-3, SI-13, SI-14 and SI-15 were produced using the Makie.jl library⁵.



Figure SI-2 – Triangulation of TEM picture of SB 1 and histogram of size distribution of NCs . (a) Raw TEM image. (b) Thresholder image. (c) Inverted distance transform. (d) Identified NCs markers. (e) Identified NCs areas. (f) Identified NCs centers and triangulation giving closest neighbors. (g) Histogram of NCs sizes and Gaussian fit. (h) Histogram of triangulation edges lengths, the maximum gives the average distance between NCs centers.

⁵ S. Danisch and J. Krumbiegel, Journal of Open Source Software, 2021, 6, 3349.



Figure SI-3 – Triangulation of TEM picture of SA and histogram of size distribution of NCs . (a) Raw TEM image. (b) Thresholded image. (c) Inverted distance transform. (d) Identified NCs markers. (e) Identified NCs areas. (f) Histogram of NCs sizes and Gaussian fit.



Figure SI-4 – HR-STEM pictures of (a) PVK-TOA NCs with a lattice spacing of 0.582 nm and (b) of SB-8 with a similar lattice spacing of 0.582 nm.



Figure SI-5 – (a) DRX of SA (PVK-TOA) in blue Line and SB samples for SB-2 in black line, (b) DRX Data for Structure monoclinic (5.827 x 5.891 x 5.827, beta=89.65) of CsPbBr₃, Reference ICSD 18-364, (c) DRX of SA (PVK-TOA) and (d) SB-2 samples.



Figure SI-6 – TEM picture of resulting solution of PVK-TOA after addition of a mixture of – (a) OA in DMF and – (b) PbBr₂ in DMF, named **Pb** solution.



Figure SI-7 – TEM images of solution of PVK-TOA after addition of pre-PEA (PEA 1) recorded on (a) JEOL (200 Kev) with a scale bar of 200 nm and HR-STEM picture in HAADS mode (XX Kev ?) with a scale bar (b) 10 nm and (c) 100 nm.



Figure SI-8 – TEM picture of SB 8 (a) after synthesis and (b) after 3 weeks with the same scale bar 100 nm (200 KeV).



Figure SI-9. HR-STEM pictures in HAADS mode of PEA-1 after 1 min showing the different formation of final NCs from PVK-TOA NCs and the different zone of cutting -(a) - scale bar 20 nm -(b) - amplified zone of (a) and -(c) - scale bar 10 nm.



Figure SI-10. HR-STEM pictures of **SB-2** after 1 min in HAADS mode – (a) Scale bar 100 nm – (b) 50 nm – (c) zoom of a zone showing the connection between NCs in current formation scale bar 50 nm, showing the presence of an extended RP n = 2 zone to the base of NCs and RP n = 1 at the limit of NCs.



Figure SI-11 – TEM picture of SB-2 after 10 min of stirring (a) recorded on TEM (200 Kev), scale bar 200 nm and – (b) in HAADS mode recorded in HR-STEM (XX KeV), scale bar 5 nm.



Figure SI-12 – TEM picture of SB-1 after 10 min – (a) scale bar 100 nm – (b) scale bar 20 nm and (c) - (e) of three different zone with a HR-STEM in HAADS mode, scale bar 5 nm.



Figure SI-13 – Optical properties of PVK-TOA NCs (**SA**). (a) Absorption spectra (solid lines) and PL spectra (dashed lines) of NCs in solution (blue lines) and in film (yellow lines). (b) TRPL trace of NCs in solution (blue line) and in drop-casted with (yellow line). The signal is much weaker in film, hence the difference in the baseline of the normalized decay curves.



Figure SI-14 – Optical properties of calibrated NCs (**SB**). (a) Absorption spectra (solid lines) and PL spectra (dashed lines) of NCs in solution (blue lines) and in film (yellow lines). (b) TRPL trace of NCs in solution (blue line) and in drop-casted with (yellow line). The signal is much weaker in film, hence the difference in the baseline of the normalized decay curves.



Figure SI-15 – Determination of the PLQY of samples using an integrating sphere. (a) Spectrum near excitation region to determine absorption of **SB 2** films. (b) PL spectrum near emission region to determine emission of **SB 2** films. (c) Spectrum near excitation region to determine absorption of **SB 2** solutions. (d) PL Spectrum near emission region to determine emission of **SB 2** solutions. PLQY is determined by the ratio between the number of emitted photons and the number of absorbed photons.