

Supporting Information

Synthesis of Cesium Lead Halide Perovskite Nanocrystals in a Droplet-Based Microfluidic Platform: Fast Parametric Space Mapping

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Materials

Cesium carbonate (Cs_2CO_3 , Aldrich, 99.9%), lead bromide (PbBr_2 , ABCR, 98%), lead chloride (PbCl_2 , ABCR, 99.999%), lead iodide (PbI_2 , ABCR, 99.999%), 1-octadecene (ODE, 90%), trioctylphosphine (TOP, ABCR, 97%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OLA, Acros, $\geq 96\%$), toluene (Fluka, anhydrous, $\geq 99.7\%$), *n*-hexane (Sigma-Aldrich, $\geq 95\%$), potassium iodide (KI, Sigma-Aldrich $\geq 99.99\%$), fluorescein sodium salt (Sigma-Aldrich), Phosphate-Buffered Saline (PBS, ThermoFisher Scientific, pH 7.4, 10x) were used as received. Galden PFPE fluid was purchased from Blaser Swissslube AG.

Batch (flask-based) synthesis of CsPbBr_3 and $\text{CsPb}(\text{Br/I})_3$ nanocrystals

Preparation of Cs-oleate: Cs_2CO_3 (0.407 g, Aldrich, 99.9%), OA (1.3 mL, Sigma-Aldrich, 90%) and ODE (20 mL, Sigma-Aldrich, 90%) were added into a 50 mL 3-neck flask, dried for 1 h at 120 °C and then stored under N_2 . Since Cs-oleate precipitates out of ODE at room-temperature, it must be preheated to 100 °C before injection into reaction flask.

Synthesis of CsPbX_3 NCs: Dried ODE (5 mL) and different amounts of PbX_2 (PbBr_2 , ABCR, 98%; PbI_2 , ABCR, 99.999%) or their mixtures (see Table S1) were loaded into a 25 mL 3-neck flask and degassed at 120 °C for 10 min. Dried OA (1 mL) and OAm (1 mL) were injected at 120 °C under N_2 flow. After complete solubilization of a PbX_2 salt, the temperature was raised to 180 °C and Cs-oleate solution (0.8 mL of stock solution prepared as described above) was swiftly injected and immediately after (about 5 seconds) the reaction mixture was cooled down by a water bath. For PL measurements, the sample was diluted by hexane.

Microfluidic synthesis CsPbX_3 NCs (see also Figure S1)

Cesium oleate precursor solution. In a 100ml three-neck flask, Cs_2CO_3 (0.815 g), ODE (40 mL) and OA (2.6 mL) were dried at 120 °C under vacuum for 2 h to dissolve the cesium salt and to dry the solution. For each subsequent microfluidic synthesis, 5 mL of precursor solution was loaded into a 10-mL gas-tight glass syringe (Hamilton).

Lead halide precursor solution: PbX_2 salts such as PbCl_2 (0.045 g), PbBr_2 (0.089 g) and PbI_2 (0.089 g) were added in a 20 mL Schlenk flask together with dried ODE (5 mL). The mixture was then dried under vacuum for 2 h at 120 °C. After 2 h, 0.8 mL of dried OA and dried OLA were added under argon until all PbX_2 dissolved completely. The solution was then allowed to cool before being loaded into a 10-mL gas-tight glass syringe (Hamilton). For the PbCl_2 precursor solution, a higher temperature (150 °C) and addition of 1 mL TOP were required to solubilize PbCl_2 .

Details of the microfluidic synthesis. Precision syringe pumps (neMESYS, Cetoni GmbH, Germany) were used to inject the dispersed phase (PbX_2 and Cs-oleate precursor solutions) and the carrier fluid (Galden fluorinated fluid, Blaser Swissslube AG, Germany) towards a polyether ether ketone (PEEK) cross-junction (P-729, Upchurch Scientific, Germany) to form a segmented flow of droplets. For the $\text{CsPb}(\text{Br/I})_3$ system, the PbBr_2 and PbI_2 precursor solutions were initially injected into a PEEK T-

junction before being loaded into the PEEK cross-junction for the droplet formation. The injection cross-junction and the syringes carrying the precursor solutions were connected through PTFE tubing (ID 250 μm , OD 1/16", Upchurch Scientific, Germany) using PEEK finger-tight fittings (F-127, Upchurch Scientific, Germany). The carrier fluid was transferred to the PEEK cross-junction through fluorinated ethylene propylene (FEP) tubing (ID 750 μm , OD 1/16", Upchurch Scientific, Germany). Typical flow rates were 10-500 $\mu\text{L min}^{-1}$ for the carrier phase and 0.1-350 $\mu\text{L min}^{-1}$ for the dispersed phase (precursors). The chemical payload of the formed droplets can be tuned precisely and rapidly by a continuous variation of the precursor volumetric flow rates. Particularly, the microfluidic system allowed for independent control of the Pb-to-Cs molar ratio (R_1) and halide ratios (R_2 , I-to-Br and Br-to-Cl) by adjusting the ratio of flow rates at the cross and T-junctions, respectively. The formed droplets containing the reaction mixture were subsequently directed through perfluoroether (PFA) tubing (ID 500 μm , OD 1/16", Upchurch Scientific, Germany) coiled around a copper-heating rod (diameter = 1.5 cm) to allow both the initiation of the NC-forming reaction and on-line detection of the formed perovskite NCs via *in-situ* absorption and PL spectroscopy. The reaction time was controlled either by varying the flow rates of the carrier phase and reagents or through variation of the tubing length, yielding identical results. The heating block was engraved using standard milling procedures to allow the tubing to sit within a defined groove of radius 800 μm . The temperature of the copper rod was controlled using a heating cartridge (6.5x40 mm, 100 W, Farnell, Switzerland), embedded inside the heating rod. The temperature was monitored using a thermocouple (Sensor, Thermoelement Type K - 0.5 mm, Farnell, Switzerland), inserted into the copper block close to the surface. Temperature control was realized using a PID controller (CN7800, Omega, USA), with an observed temperature variation from the set point of less than 0.1 $^{\circ}\text{C}$. The heating rod was placed on top of a motorized rotation stage (CR1/M-Z7E, Thorlabs, Germany), which was also mounted on a motorized linear translation stage (MTS25/M-28E, Thorlabs, Germany). The axial and rotational movement of the heating rod was controlled using in-house Labview software.

On-line photoluminescence. A blue LED (M405L2-Mounted LED, Thorlabs, Germany) was used as an excitation source for all PL measurements. The collimated beam was directed towards a dichroic beam splitter (Multiphoton LP-Strahlenteiler HC 405 LP, AHF, Germany) and then focused into the microfluidic channel using an aspheric lens (A240TM – $f = 8.0 \text{ mm}$ – NA 0.50, Thorlabs, Germany). The emission originating from the microfluidic channel was collected by the same lens, passed through the dichroic beam splitter, and coupled via a 10x objective (RMS10X – NA 0.25, Thorlabs, Germany) to a fiber spectrometer (PPro+, Ocean Optics, UK) through a 2 m long multimode fiber with a core diameter of 400 μm (QP100-2-UV-VIS, Ocean Optics, UK). The spectrometer comprised a 20 μm entrance slit, a 600 lines/mm grating and a detector containing 2048 pixels. The spectrometer was operated between 400 and 1100 nm, and data recorded using 10–100 ms integration times. The entire system was enclosed in a black box to minimize pollution from the stray light.

On-line absorbance. For all absorbance measurements a halogen lamp (HL-2000 HP, Ocean Optics, UK) was used as the illumination source. The output was collimated (F230SMA-C, Thorlabs, Germany) and shaped into a line oriented along the direction of flow via a plano-convex cylindrical lens (LJ4709RM, Thorlabs, Germany) having a focal length of 50 mm. Absorbance detection in droplet microfluidic reactors is challenging due to the limited optical path length, which is determined by the inner capillary diameter. To circumvent sensitivity issues associated with reduced path lengths, we implemented a geometry where a sheet of light propagates in a tangential manner through the curved path of the tubing to approximately match the length of the reaction plugs (2 mm). Such an illumination profile maximizes the incident intensity, maintains illumination uniformity along the tubing and in turn

minimizes contributions from stray light and scattering. A multi-mode fiber was mounted on a 3-axis stage platform and placed along the optical axis of the light sheet to collect the transmitted light. The other end of the fiber was connected to the detector. All collected data were analyzed using an in-house MATLAB® algorithm. Each spectrum was generated from a weighted average of 300-600 scans with an integration time of 100-800 ms. To precisely define the absorption peak, the second derivative of the absorption spectrum was calculated.

Calculation of the reaction time. By moving the heating rod to different positions, we can perform measurements at different points along the tubing. Since the tubing length defines the reaction time then the heating rod rotation provides access to very short reaction times (ms timescales) and linear movement provides access to longer reaction times. The total flow rate is calculated using:

$$Q_{tot} = \frac{dV}{dt}$$

Given a segment of length Δx and cross-sectional area $A = \pi r^2$, where r is the radius of the tubing, the flow rate can be expressed as:

$$Q_{tot} = \frac{dV}{dt} = A \frac{\Delta x}{\Delta t}$$

The time interval Δt indicates the duration of flow through the segment. The reaction time is then given by:

$$\Delta t = \frac{A \Delta x}{Q_{tot}}$$

The length of the tubing, which is wrapped around the heating rod, is determined from the radius of the heating rod R , the helix wave vector k , the winding number N and the rotation angle at the final position φ , *i.e.*

$$\Delta x = (2\pi N + \varphi)R\sqrt{1 + (kR)^2}$$

Temperature calibration. To directly measure the temperature in-situ, during the ramp from 25 °C to the desired reaction temperature at the heating stage, we used a fluorescence-based calibration method. The fluorescence intensity of Rhodamine B continuously decreases with increasing the temperature [Guijt et al. *Lab Chip*. **2003**, 3, 1–4]. To verify that heating of droplets containing the precursor solutions is very fast (*i.e.* ~100 ms for the full temperature ramp), we generated droplets of Rhodamine B in water (100 μ M) and measured the PL spectra (Figure S2). To confirm that the complete temperature ramp

takes no more than 100 ms, we compare PL spectra of droplets at two positions within the heating zone, right after the entrance (*ca.* 100 ms) and after longer residence time (3 seconds), and find these spectra to be undistinguishable.

High-speed imaging of droplets. A high-speed camera (Phantom Miro 320, Vision Research, USA) was used for measuring the droplet velocity and mixing times. For the bright-field measurements, images were acquired at 300 frames-per-second rate and with an exposure time of 20 μ s (Figure S3). Assessment of the mixing time was performed by a quenching assay of fluorescein sodium salt (30 μ M in PBS buffer) with potassium iodide (KI, 1 M in PBS buffer). Fluorescence measurements in droplets were performed with an exposure time of 600 μ s. Static fluorescence measurements using a bench-top fluorescence spectrometer (Fluoromax, Horiba, Germany) were used to assess the percentage of quenching (Figure S4).

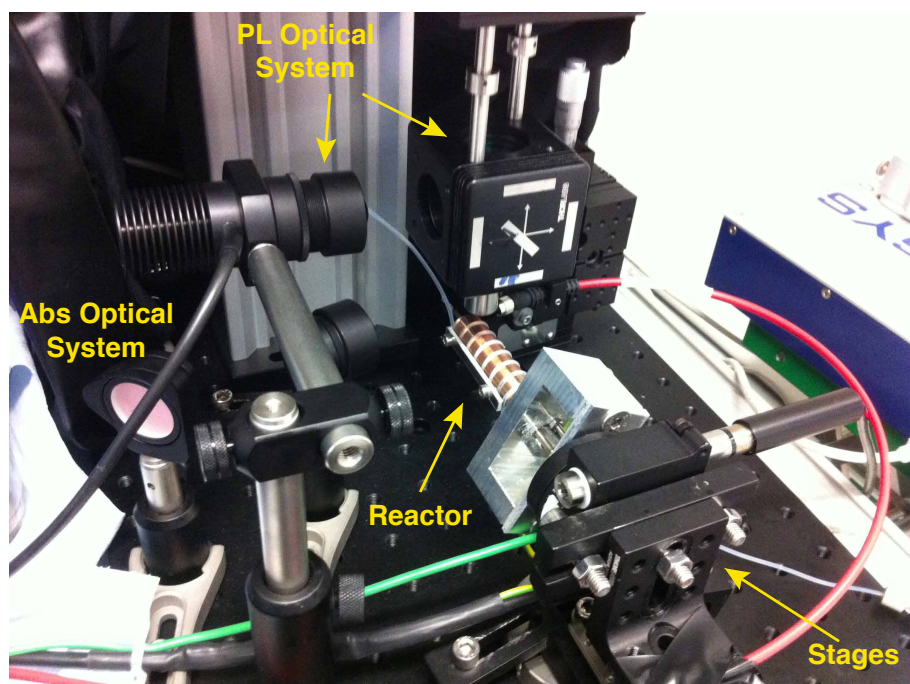


Figure S1: Image of the microfluidic platform with integrated on-line absorbance and photoluminescence detectors.

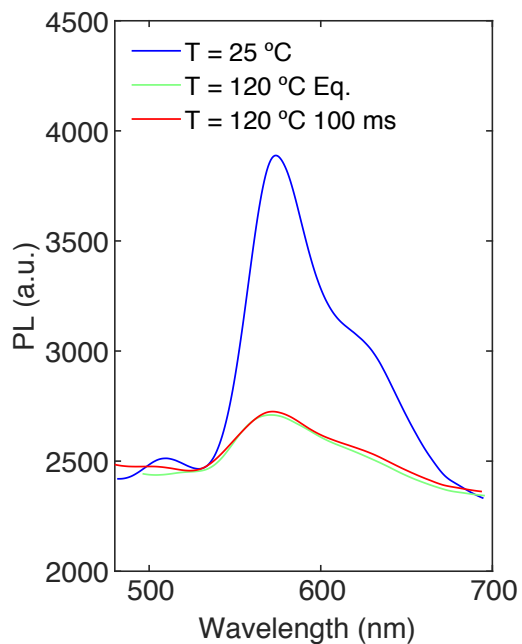


Figure S2: PL spectra of 100 μ M rhodamine B at 25 $^{\circ}$ C and 120 $^{\circ}$ C. The red line illustrates the PL spectrum of Rhodamine B just 100 ms after the droplets have entered the heating zone. Clearly, within such short time span the temperature within the droplet is fully equilibrated, as can be judged by comparing to droplets equilibrated for several seconds (green curve).

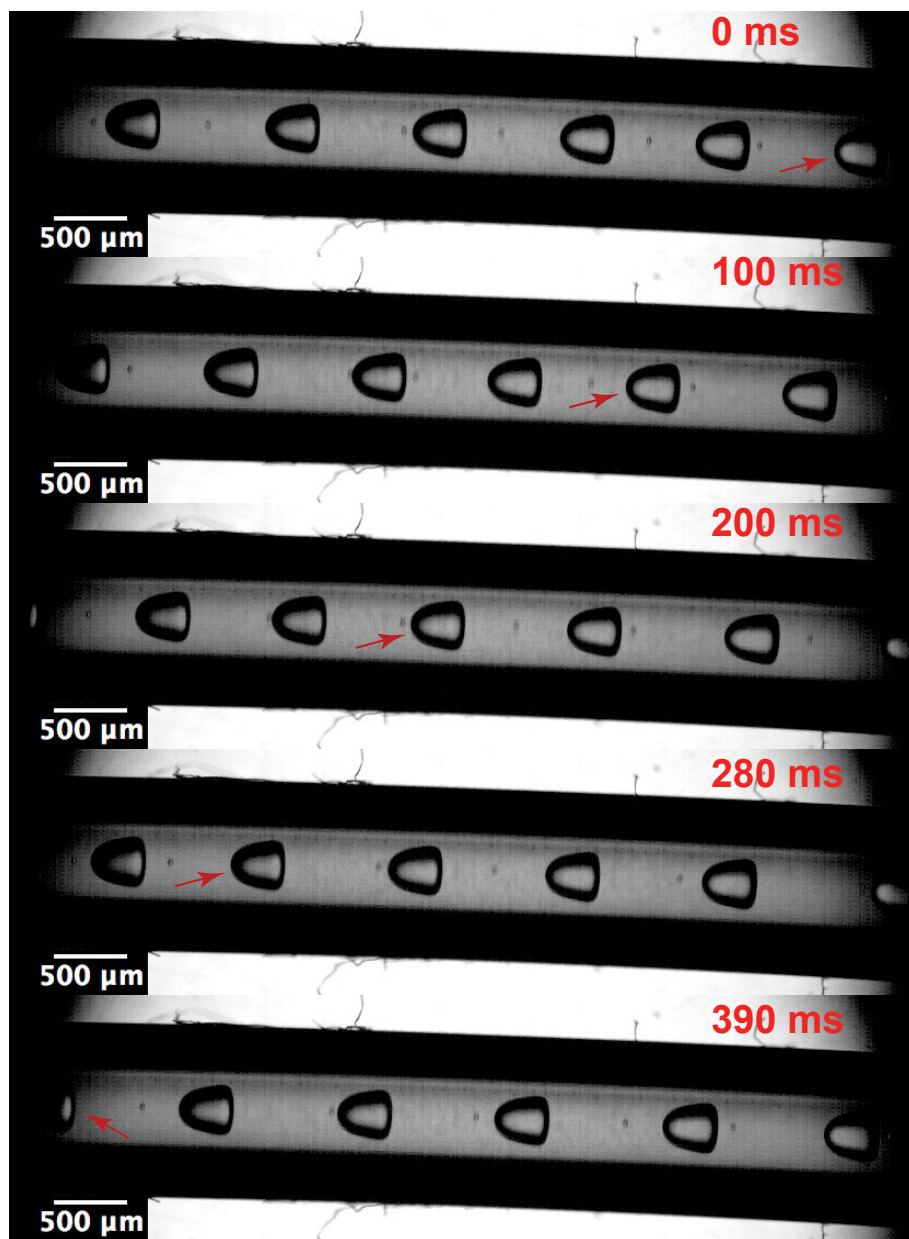


Figure S3: Sequence of images of the generated droplets inside the tube-based reactor, using a high-speed camera. The droplet velocity was equal to 14.5 mm s^{-1} , whereas the superficial velocity was equal to 12.9 mm s^{-1} . The flow rate for the dispersed (reagents) and continuous (carrier fluid) phases were $32 \text{ } \mu\text{L min}^{-1}$ and $120 \text{ } \mu\text{L min}^{-1}$, respectively. The residence time (that is a reaction time) of an individual droplet passing through a 5.66 mm of tubing was equal to 390 ms . The residence time calculated based on the superficial flow rates was equal to 430 ms .

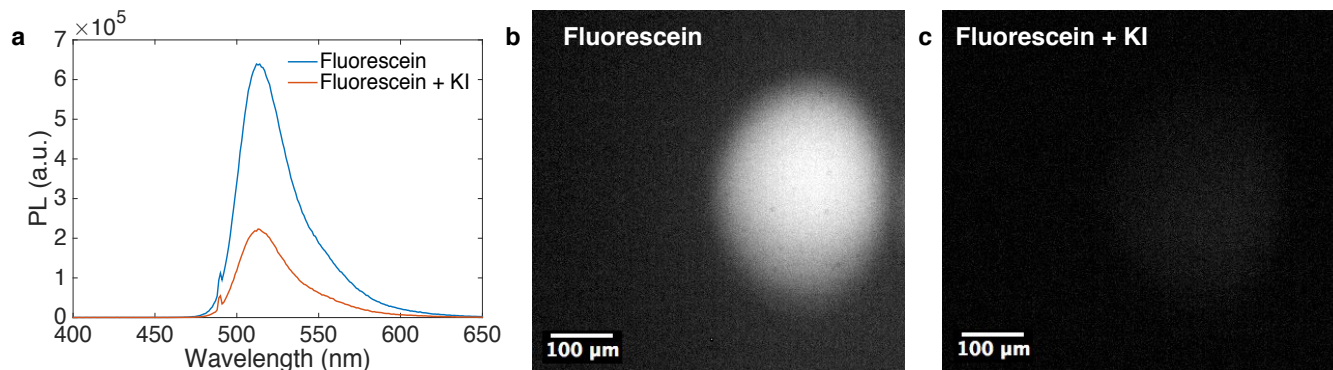


Figure S4: Assessment of mixing times inside the generated droplets by investigating the effect of potassium iodide (KI) on the emission of fluorescein. These two reagents are delivered to a cross-junction separately and hence the subsequent quenching rate indicates the mixing rate. (a) Fluorescence quenching of fluorescein by KI by a factor of 3.3 in a cuvette by adding $1 \mu\text{M}$ of fluorescein sodium salt and 200 mM KI in PBS buffer solution. (b) Droplets of fluorescein in PBS buffer and (c) droplets of fluorescein and KI in PBS buffer. The fluorescence was quenched by a factor of 4.2 in 340 ms . Flow rates for the continuous and dispersed phases were $90 \mu\text{L min}^{-1}$ and $250 \mu\text{L min}^{-1}$, respectively.

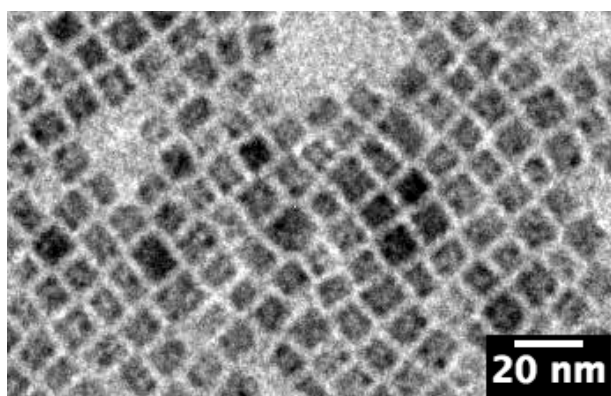


Figure S5: Transmission electron microscopy (TEM) image of CsPbI₃ NCs at $180 \text{ }^\circ\text{C}$ ($R_1 = 7.8$). The sample corresponds to the last experimental datapoint of the red curve in Figure 2b.

Table S1. Reaction parameters for growing CsPbBr₃ and CsPb(Br/I)₃ NCs in a 25mL flask. These PL characteristics are plotted in Figure 8.

R₁	R₂ %PbBr₂ / %PbI₂	mmol PbBr₂ / mmol PbI₂	mmol Cs-oleate	PL (nm)	FWHM (nm)
2.0	100 / 0	0.2 / 0	0.1	514.29	21.80
2.0	90 / 10	0.18 / 0.02	0.1	522.21	22.43
2.0	80 / 20	0.16 / 0.04	0.1	535.96	25.19
2.0	70 / 30	0.14 / 0.06	0.1	557.66	28.01
2.0	60 / 40	0.12 / 0.08	0.1	586.15	33.09
2.0	50 / 50	0.1 / 0.1	0.1	615.50	34.20
2.0	40 / 60	0.08 / 0.12	0.1	636.94	36.74
2.2	80 / 20	0.176 / 0.044	0.1	532.77	25.98
2.2	75 / 25	0.165 / 0.055	0.1	539.93	27.85
2.2	70 / 30	0.154 / 0.066	0.1	545.79	31.80
2.2	65 / 35	0.143 / 0.077	0.1	557.63	32.77
3.76	100 / 0	0.376 / 0	0.1	513	25.59
3.76	80 / 20	0.3 / 0.076	0.1	518.61	30.44
3.76	70 / 30	0.263 / 0.1128	0.1	530.57	31.61
3.76	60 / 40	0.2256 / 0.1504	0.1	556.95	33.37
3.76	50 / 50	0.188 / 0.188	0.1	605	41.79
3.76	40 / 60	0.150 / 0.2256	0.1	635	46.89
3.76	30 / 70	0.1128 / 0.263	0.1	657	44.46
4.7	50 / 50	0.235 / 0.235	0.1	591.64	44.19
4.7	45 / 55	0.2115 / 0.2585	0.1	606.94	52.91
5	50 / 50	0.25 / 0.25	0.1	588.08	45.97
5	45 / 55	0.225 / 0.275	0.1	611.07	50.43