

Supplementary Information

Microfluidic synthesis of monodisperse and size-tunable CsPbBr₃ supraparticles

Julia Nette ^a, Federico Montanarella ^{b,c}, Chenglian Zhu ^{b,c}, Taras V. Sekh ^{b,c}, Simon C. Boehme ^{b,c}, Maryna Bodnarchuk ^{b,c}, Gabriele Rainò ^{b,c}, Philip D. Howes ^d, Maksym Kovalenko ^{b,c}, Andrew J. deMello ^{a*}

^a Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland

^b Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland

^c Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland

^d Division of Mechanical Engineering and Design, London South Bank University, 103 Borough Road, London SE1 0AA, UK

Materials and Methods

Materials

008-Fluorosurfactant in FC-40 5 wt% (RAN Biotechnologies), Fluorinert FC-40 (3M), toluene (>99.5%, AnalR Normapur), acetone (>99.8%, Sigma-Aldrich), Cs_2CO_3 (99.9%, Sigma-Aldrich), oleic acid (OA) (90%, Sigma-Aldrich), 1-octadecene (ODE) (90%, Sigma-Aldrich), PbBr_2 (98%, ABCR), hexadecane (99%, Acros), oleylamine (OLA) (97%, Strem), toluene (anhydrous, 99.8%, Sigma-Aldrich; for NP synthesis and sample dilution), ethyl acetate (99.9%, Sigma-Aldrich).

Synthesis of Cesium Oleate (Stock Solution 1)

Cs_2CO_3 (0.2 g), oleic acid (0.6 mL), and 1-octadecene (7.5 mL, distilled) were loaded into a 25 mL flask, dried under vacuum for 20 minutes at 100°C, and then heated under N_2 to 120°C until all the Cs_2CO_3 reacted with OA. The solution was stored in a glovebox.

Synthesis of CsPbBr_3 NCs

The 8.0 - 8.5 nm NC synthesis was adapted from¹. In a 25 mL three-neck flask, a 55 mg/5 mL PbBr_2 in hexadecane (or ODE) was prepared, after the PbBr_2 was degassed three times. The solution was again degassed three times at room temperature. The following procedure relates to a total volume of 15 mL for the PbBr_2 precursor solution. The suspension was quickly heated to 180°C, when the temperature reached 120°C, OA (1.5 mL) and oleylamine (1.5 mL) were injected. At 180°C, cesium oleate solution in ODE (Stock Solution 1, 1.8 mL, preheated to 100°C), was injected. The reaction mixture was cooled immediately to room temperature in an ice bath. The crude solution was centrifuged at 12,100 rpm for 5 minutes, the supernatant discarded, and the precipitate dispersed in toluene (0.9 mL). The solution was centrifuged again at 10000 rpm for 3 minutes, and the precipitate discarded. Next, OLA/OA ligands were exchanged by DDAB/ PbBr_2 treatment. 0.9 mL of anhydrous toluene and didodecyldimethylammonium (DDAB)/ PbBr_2 (0.33 mL, 0.067 M DDAB, 0.033 M PbBr_2 in toluene) were added to the supernatant and stirred for 1 hour, followed by destabilization with ethyl acetate (4.8 mL), centrifugation at 12,100 rpm for 3 minutes, and redispersing in 2.0 mL of anhydrous toluene.

Synthesis of CsPbBr₃ SPs

The CsPbBr₃ SPs were synthesized based on the flask-based method published by Tang et al.². A prepared solution of CsPbBr₃ NCs in toluene at the desired concentration (2–7 mg/mL) and a 5% 008-fluorosurfactant in FC-40 solution were transferred into Gas tight Luer Lock syringes (Hamilton Bonaduz AG, Bonaduz, Switzerland) of 0.25 mL volume and 1 mL volume, respectively. The syringes were connected to PTFE tubing (clear) of 1/16 inch OD, 0.01 inch ID (Sigma Aldrich, Burlington, USA), with Precision Dispensing Needle straight 30 (Distrelec, Nänikon, Switzerland), and all bubbles were removed from syringes and tubing. The tubing was subsequently connected to the connector of the microfluidic chip. A commercial, Small Droplet Junction Chip (Quartz, 5 μm, fluorophilic coating) (Dolomite Microfluidics, Royston, UK) was used with a linear connector (4 way), a top interface (4 way) and a linear connector seal (black). A 1 mL glass vial was prepared with 0.3 mL of 5% 008 fluorosurfactant in FC-40 and a magnetic stir bar. A short piece of outlet tubing was prepared, connected to the microfluidic chip, and secured to the prepared vial with adhesive tape and parafilm. Syringes were mounted to a rack of Nemesys Low Pressure S pumps (Cetoni GmbH, Korbussen, Germany) and controlled using the Cetoni Nemesys and Cetoni Qmix suite software. Droplet generation was performed at flowrates between 20 and 100 nL/min for the NCs in toluene solution, and 70–400 nL/min for the two 008 fluorosurfactant in FC-40 solutions. This allowed for a droplet generation of approximately 20,000 droplets per second, and produced droplets with diameters between 2 and 6 μm. This emulsion was collected into the outlet vial under gentle stirring. The collection time typically extended over 12 hours (overnight). After collection, the emulsion was gently stirred at room temperature under ambient conditions for 48 hours in the outlet vial. The solid SPs had diameters between 267 and 708 nm. After evaporation, the SP solution was precipitated by centrifugation (9000 rpm for 15 minutes). The precipitate was redispersed in FC-40 and precipitated again (9000 rpm for 15 minutes). The precipitate was redispersed in FC-40 and the particles were analyzed using TEM, SEM and STEM. For further storage, 5% 008 fluorosurfactant in FC-40 was reintroduced into the solution to a total concentration of 2.5% surfactant in oil. For SEM measurements the SP solution was deposited on a silicon substrate (5 x 5 mm precut chip, TedPella, Redding, USA) and left to dry in open air. For TEM and STEM measurements the same was performed on a TEM support made of CF400-CU carbon film with 400 mesh copper (Electron Microscopy Sciences, Hatfield, USA). For optical measurements, the SP solution was

transferred into a cuvette and both absorption and photoluminescence spectra were recorded. For single particle spectroscopy, the SP solution was deposited on a silicon substrate with a SiO₂ layer, and dried.

Characterization

Characterization of the droplet flow was performed using an Eclipse Ti-E inverted microscope (Nikon Corporation, Tokyo, Japan) equipped with a motorized stage (Mad City Labs Inc., Madison, USA) and a MotionPro Y-series high speed camera (Integrated Design Tools, Pasadena, USA) using Motion software. Droplet sizes were measured using ImageJ³ (Wayne Rasband and contributors, National Institutes of Health, USA).

SPs were characterized optically and structurally. The optical characterization was performed in a Fluoromax-4 spectrofluorometer (Horiba, Kyoto, Japan). Structural characterization was performed in a HT 7700 Hitachi EXALENS TEM (100.0 kV), a Talos F200X TFS TEM (100.0 kV), and a FEI Magellan 400 TFS SEM (2.00 kV). For single particle optical characterization and confocal PL imaging, a 5 times in FC-40 diluted solution of SPs was used.

Single Particle Optical Characterization

For single-SP spectroscopy, a custom-built μ -PL setup was used. Samples were mounted on x-y-z nano-positioning stages inside an evacuated liquid-helium closed-loop cryostat (Montana Instruments, Bozeman, USA) with temperature control between 4.6 K and 300 K. Single SPs were excited by means of a fiber-coupled excitation laser at 480 nm with a repetition rate of 5 MHz and pulse width < 50 ps (Toptica Photonics, Munich, Germany), which was focused ($1/e^2$ diameter = $2.4 \mu\text{m}$) on to the sample using a microscope objective (NA = 0.8, $100\times$ magnification). The emitted light was collected by the same objective and passed through a dichroic mirror (long-pass, cut-on wavelength 488 nm) (Semrock Inc., Rochester, USA) and a long-pass filter at 500 nm (Thorlabs Inc., Newton, USA). A monochromator coupled to an EMCCD (0.75 m, 1 s binning time, Princeton Instruments, Trenton, USA) with a grating of 300 lines/mm, blaze 500 nm was used for spectroscopy measurements, yielding a spectral resolution of about 1 meV. A single APD (Micro Photon Devices, Bolzano, Italy) with a time resolution of 50 ps was used to measure PL decays.

Confocal PL imaging

Confocal PL images were obtained using a SP8 confocal microscope (Leica, Wetzlar, Germany). Samples were excited with a pulsed laser (405 nm, 5 MHz repetition rate) via an oil-immersion objective (NA = 1.4, $63\times$ magnification) and the emission was collected via the same objective, recorded using a HyD SMD hybrid detector (Leica, Wetzlar, Germany) and a PicoHarp 300 time-correlated single-photon counting (TCSPC) module (Picoquant, Berlin, Germany). The PL intensity was obtained after spectral filtering (collecting light only between 450 and 650 nm) and temporal integration of all TCSPC events. PL images with a pixel size of 180.55 nm were obtained by raster scanning and analysed via the Picoquant SymPhoTime 64 software.

Supplementary Figures

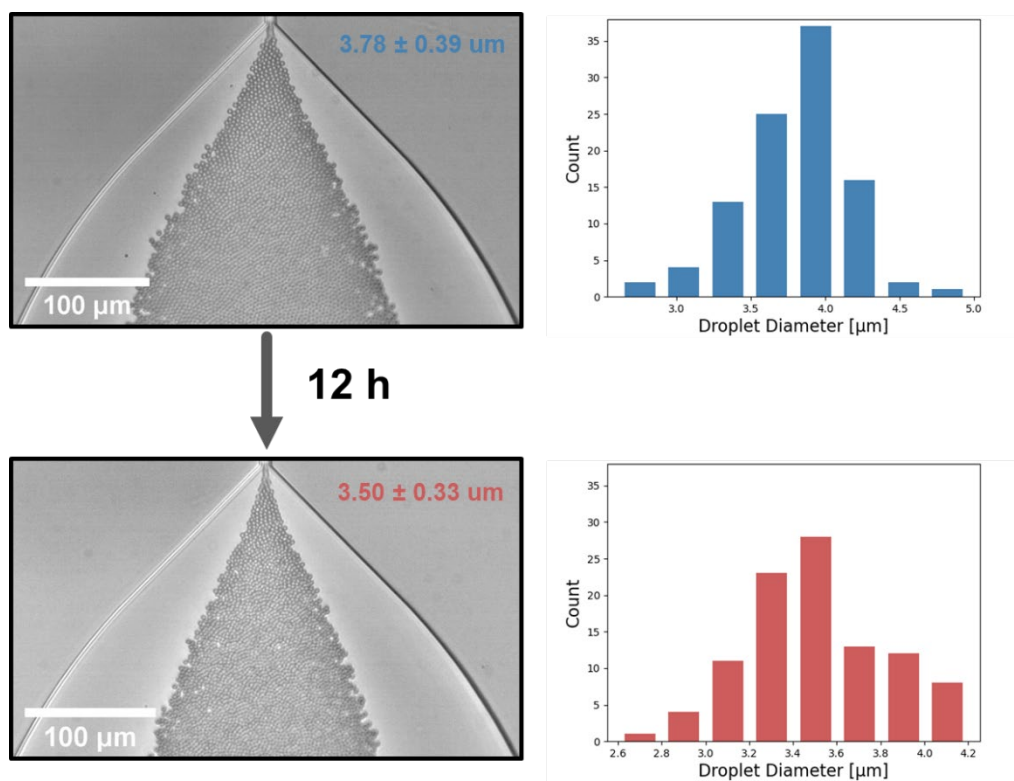


Figure. S1. Assessment of droplet stability in the microfluidic chip over a period of 12 hours. Top: 0 hours, bottom: 12 hours.

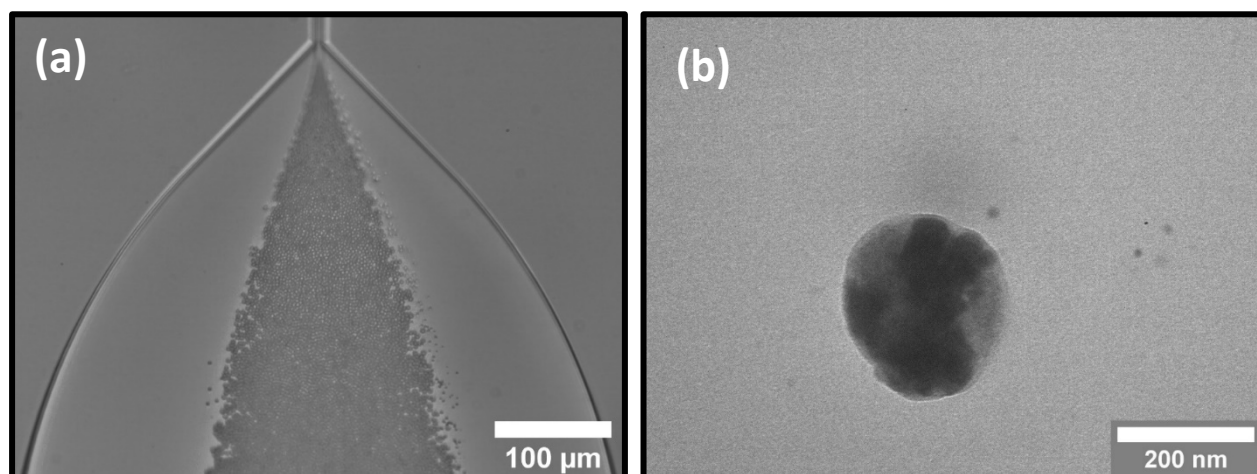


Figure. S2. Supraparticle formation at low NC concentration in toluene (1.5 mg/mL CsPbBr₃ in toluene). (a) Image of droplet generation at 20,000 Hz. (b) A representative SP containing different ordered domains of nanocrystals (black and light grey shading) indicating variable thickness.

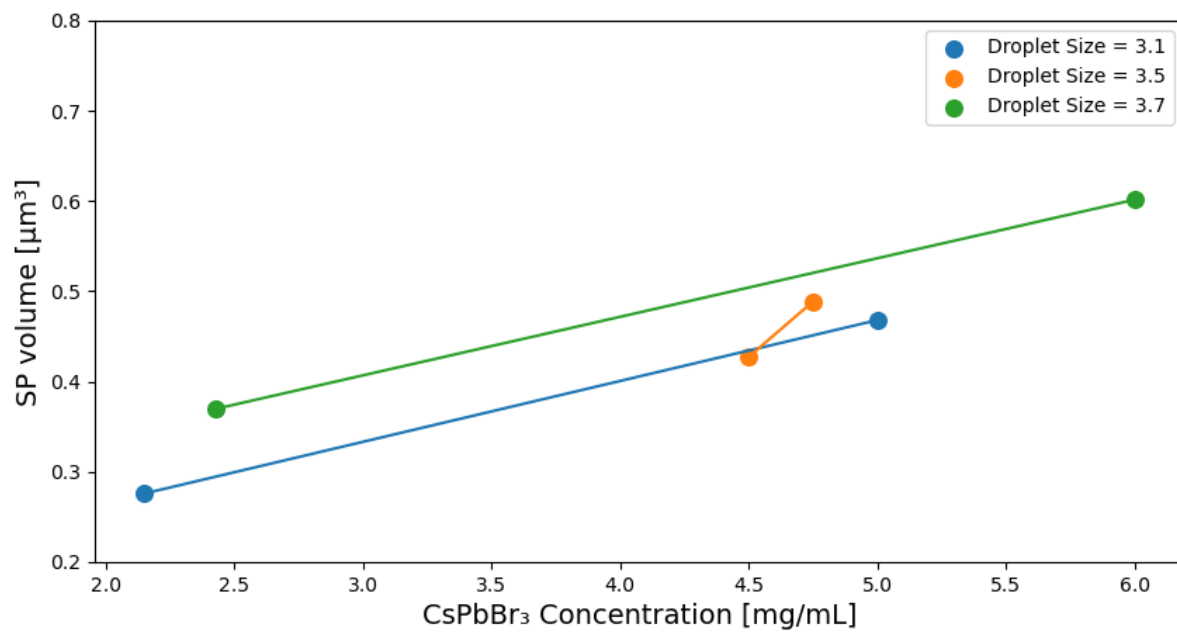
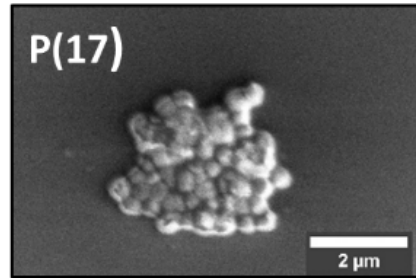
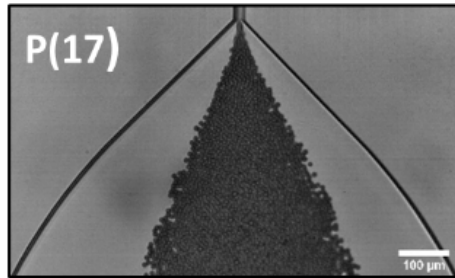
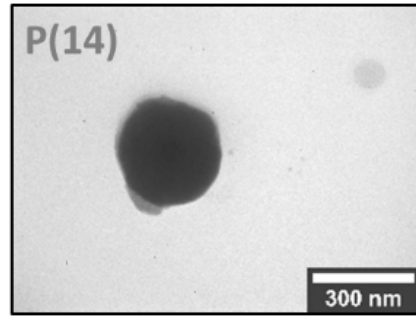
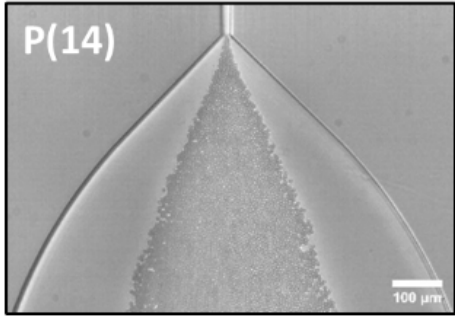
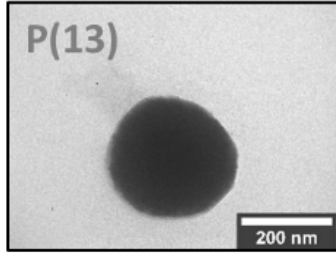
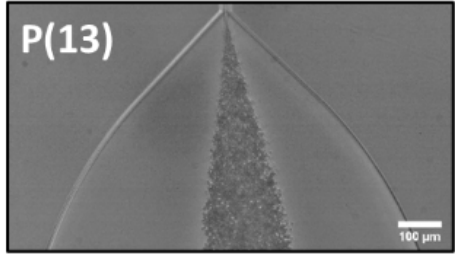
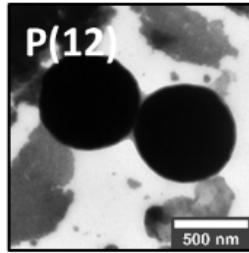
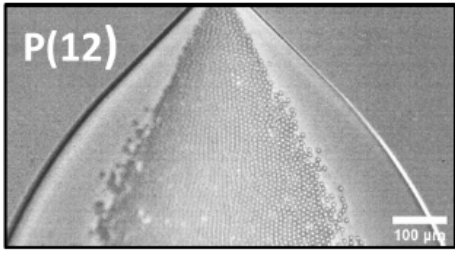


Figure S3. Comparison of different CsPbBr₃ concentrations ranging from 2.15 mg/mL to 7.3mg/mL at fixed droplet sizes: 3.1 μm (blue), 3.5 μm (yellow), 3.7 μm (grey), and 4.7 μm (orange).



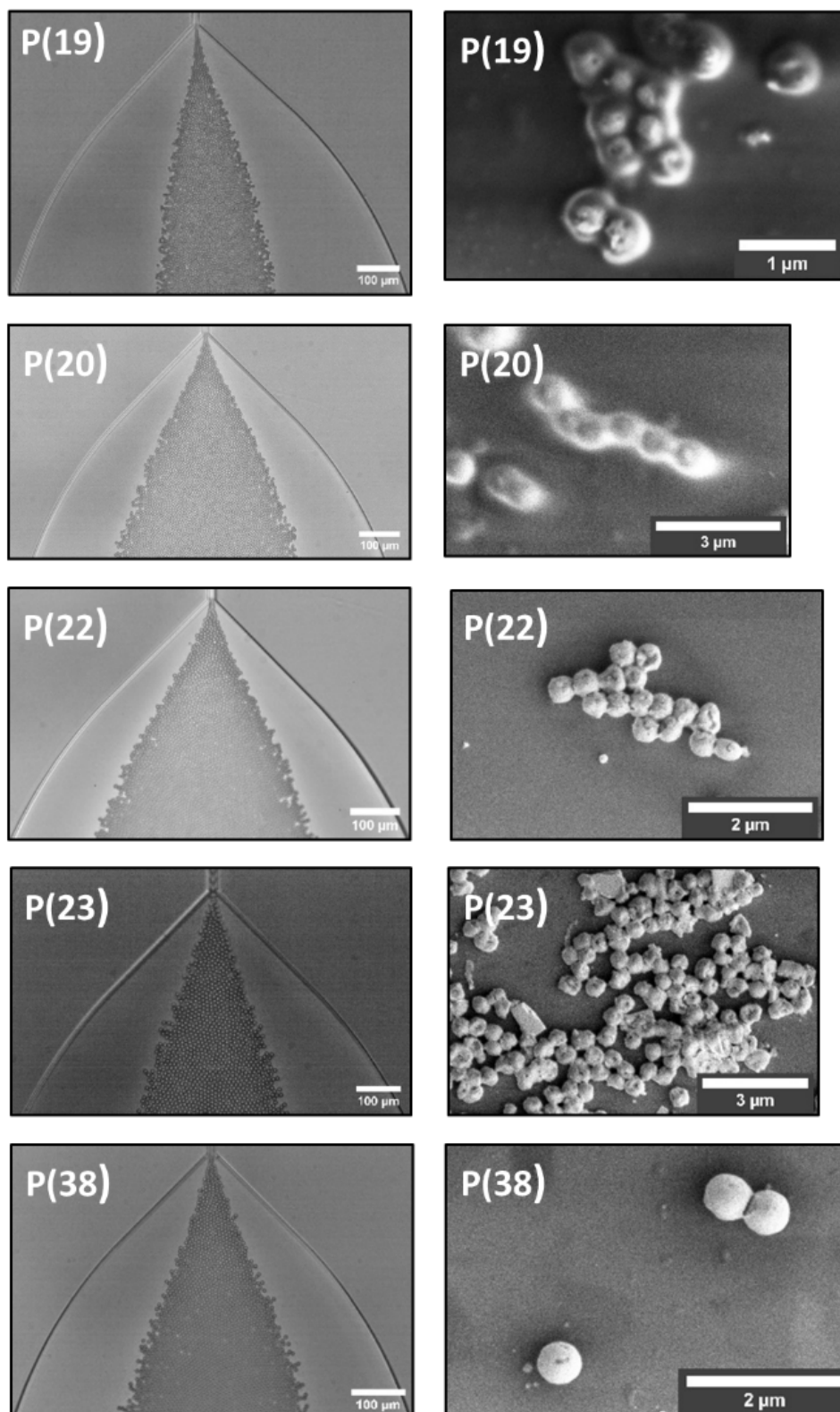


Figure S4. Right: Highspeed camera images of the droplet formation process for the experiments described in **Table S1**. Left: Corresponding TEM or SEM images of solid SPs after evaporation of the solvent.

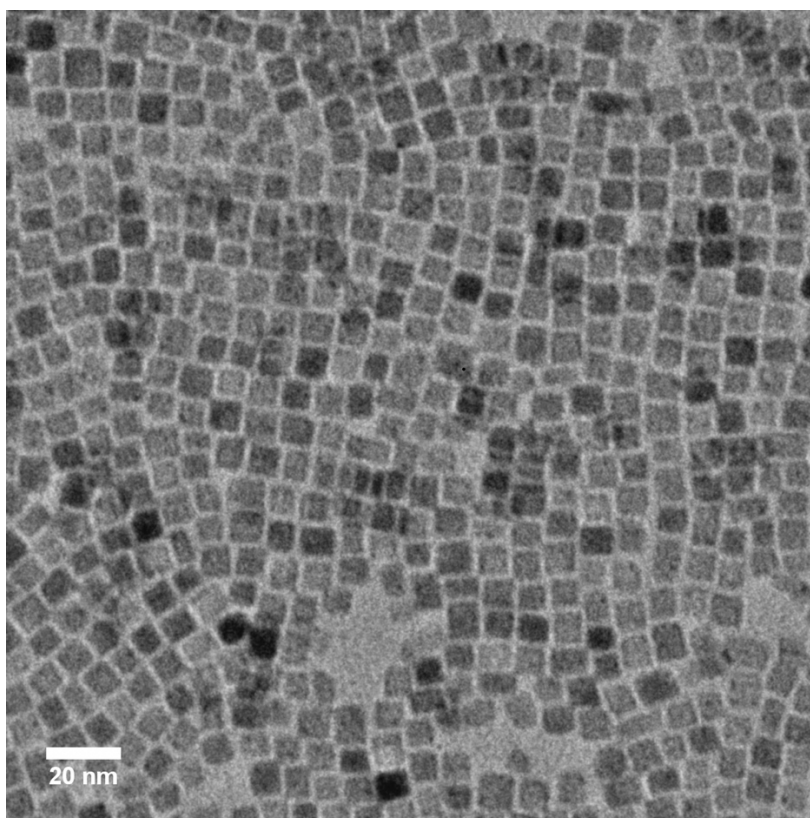


Figure S5. TEM image of the monodisperse CsPbBr₃ NCs from a colloidal suspension (6 mg/mL) in toluene, with an average diameter of 8 nm.

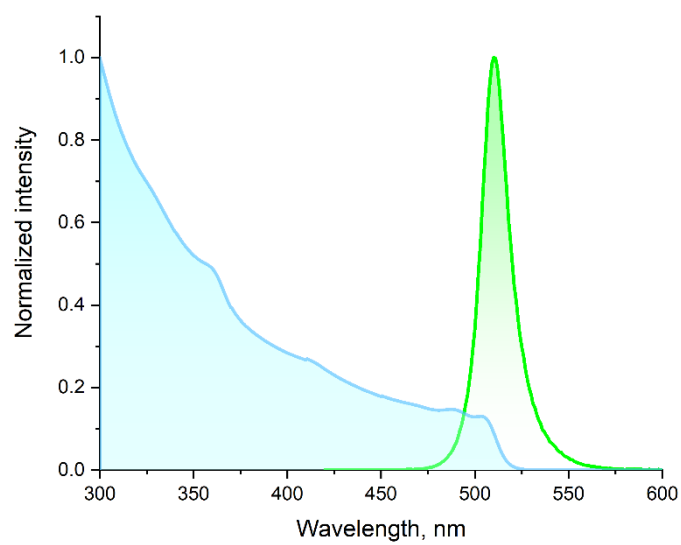


Figure S6. Absorption (blue) and PL (green) spectra of a colloidal solution of 8.0 nm CsPbBr₃ NCs in toluene.

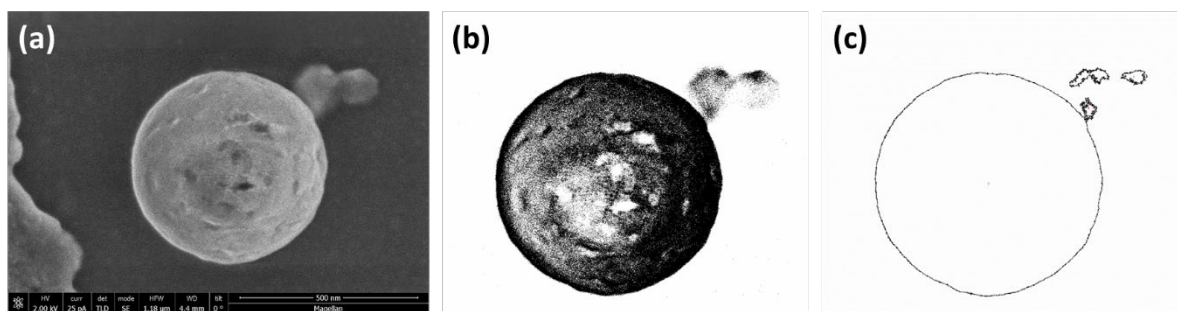


Figure S7. Circularity and roundness analysis of a single SP from sample P(38) with the SEM image in (a), a binary version of the SEM image in (b) and an outline used to measure the circularity and roundness in (c), with a measured circularity of 0.356 and a measured roundness of 0.978. Here, circularity is defined as $4\pi \cdot (\text{area}) / (\text{perimeter}^2)$ and roundness as $4 \cdot (\text{area}) / (\pi \cdot \text{major_axis}^2)$.

Supplementary Table

Sample	P(12)	P(13)	P(14)	P(17)	P(19)	P(20)	P(22)	P(23)	P(38)
Concentration [mg/mL]	7.3	2.2	2.4	2.2	5	6	4.5	4.8	5
Droplet Size [μm]	4.78	3.11	3.72	3.26	3.1	3.68	3.5	3.52	4.58
Droplet Size dispersity [%]	8%	11%	12%	12%	10%	11%	9%	11%	7%
Droplet Size dispersity [μm]	0.38	0.34	0.45	0.39	0.31	0.40	0.32	0.39	0.32
SP size [μm]	0.708	0.276	0.369	0.359	0.468	0.602	0.427	0.489	0.624
SP size dispersity [%]	13%	10%	9%	10%	12%	8%	8%	10%	9%
SP size dispersity [μm]	0.092	0.0276	0.033	0.036	0.056	0.048	0.034	0.049	0.056
No. of SPs counted	27	19	19	23	13	6	53	58	71

Table S1. Experimental conditions for datapoints presented in **Figure 2**, with the concentration of NCs in toluene, the droplet size (diameter), droplet size dispersity in μm and %, the SP size and dispersity in μm and % and the number of counted SP to determine size and size dispersity.

Bibliography

- 1 M. I. Bodnarchuk, S. C. Boehme, S. Ten Brinck, C. Bernasconi, Y. Shynkarenko, F. Krieg, R. Widmer, B. Aeschlimann, D. Günther, M. V. Kovalenko and I. Infante, *ACS Energy Lett.*, 2019, **4**, 63–74.
- 2 Y. Tang, L. Gomez, A. Lesage, E. Marino, T. E. Kodger, J. M. Meijer, P. Kolpakov, J. Meng, K. Zheng, T. Gregorkiewicz and P. Schall, *Nano Lett.*, 2020, **20**, 5997–6004.
- 3 C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 2012, **9**, 671–675.