

Supporting Information

Ligand-free template-assisted synthesis of stable perovskite nanocrystals with near-unity photoluminescence quantum yield within pores of vaterite spheres

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1. Materials

Lead(II) bromide (PbBr_2 , 99.998% trace metals basis, TCI Chemicals), dimethyl sulfoxide (DMSO, $\geq 99\%$, ECOS), sodium carbonate (Na_2CO_3 , $\geq 99.0\%$, Sigma-Aldrich), calcium bromide (CaBr_2 , 99.98% trace metals basis, Sigma-Aldrich), ethanol (EtOH, technical grade, 95%, Vecton), ethylene glycol (EG, anhydrous, 99.8%, Sigma-Aldrich), Ytterbium(III) bromide hydrate ($\text{YbBr}_3 \cdot x\text{H}_2\text{O}$, Sigma-Aldrich) were used as received without additional purification. Milli-Q water with a resistance of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was employed for all experiments (Millipore, Bedford, MA, USA)

2. CaCO_3 synthesis

2.1. Synthesis of micrometric CaCO_3

CaCO_3 microspheres (*Mic*) that were further used as templates for CsPbBr_3 PNCs were fabricated in a co-precipitation reaction by mixing CaBr_2 and Na_2CO_3 solutions.¹ For this, $615 \mu\text{L}$ of CaBr_2 solution (1 M) were mixed with 2.5 mL of Milli-Q water. Then $615 \mu\text{L}$ of Na_2CO_3 solution (1 M) were rapidly added under magnetic stirring at 1000 rpm. After 30 s the synthesized microsized CaCO_3 spheres ($4.7 \pm 2 \mu\text{m}$) were washed once with Milli-Q water by centrifuging at 4000 rpm for 10 s to remove residual salts. Consequently spheres were washed one more time with EtOH and once again with DMSO. Finally, the obtained *Mic* were resuspended in 0.5 mL of DMSO and were further used as a template for PNCs synthesis.

2.2. Synthesis of submicrometric CaCO_3

CaCO_3 submicrospheres (*Sub*) that were further used as templates for CsPbBr_3 PNCs were fabricated in a co-precipitation reaction by mixing CaBr_2 and Na_2CO_3 solutions in ethylene glycol: water mixture (5:1 in volume) under magnetic stirring.¹ To 2 mL of CaBr_2 solution (0.33 M in a 5:1 (v/v) ethylene glycol (EG): water solution) solution was rapidly added $386 \mu\text{L}$ of Na_2CO_3 solution (0.33 M in a 5:1 (v/v) EG: water solution) and left under magnetic stirring at 1000 rpm for 30 min at room temperature. Formed CaCO_3 submicrospheres ($0.4 \pm 0.2 \mu\text{m}$) were washed once with Milli-Q water by centrifuging at 9000 rpm for 3 min to remove residual salts. Consequently, *Sub* were washed one more time with EtOH and once again with DMSO. Finally, the obtained *Sub* were resuspended in 0.5 mL of DMSO and were further used as a template for PNCs synthesis.

3. Synthesis of CsPbBr₃ PNCs in CaCO₃ (different CsPbBr₃ to CaCO₃ ratio)

To fabricate PNCs within the pores of *Sub* and *Mic*, 50 μ L of freshly prepared CaCO₃ spheres dispersed in DMSO were mixed with various amounts of perovskite precursor solutions (CsBr and PbBr₂, 0.05 M). After mixing, vaterite particles were centrifuged at 13000 rpm (60 s). Then part of the supernatant was removed, so that only 30 μ L of it remained. Afterwards the residual pellet of CaCO₃ spheres were resuspended in the remaining supernatant. This suspension was then deposited on glass substrates using a spin coater. Afterwards, the spheres were slowly dried at 30 °C for 20 min. As the result of solvent evaporation PNCs crystallized in the pores of *Sub* and *Mic*. Overall 31 samples were synthesized according to the conditions described in **Table S1**. In this experiment only the amount of perovskite precursors was varied, whereas the quantity of template vaterite spheres remained a constant. Each sample contained either 0.79 mg of *Sub* or 2.14 mg of *Mic* spheres dispersed in 50 μ L DMSO.

Table S1. Synthesis conditions of PNCs obtained in CaCO₃ templates by varying PbBr₂ and CsBr.

Sample name	CaCO ₃ dispersion (μ L)	PbBr ₂ solution 0.05 M (μ L)	CsBr solution 0.05 M (μ L)	DMSO (μ L)	CsPbBr ₃ weight (mg) / quantity (μ mol)
α 1Sub/ α 1Mic	50	125	125	0	3.632 / 6.3
α 2Sub/ α 2Mic	50	117.5	117.5	15	3.416 / 5.9
α 3Sub/ α 3Mic	50	110	110	30	3.199 / 5.5
α 4Sub/ α 4Mic	50	102.5	102.5	45	2.983 / 5.1
α 5Sub/ α 5Mic	50	95	95	60	2.758 / 4.8

α 6Sub/ α 6Mic	50	87.5	87.5	75	2.542 / 4.4
α 7Sub/ α 7Mic	50	80	80	90	2.325 / 4
α 8Sub/ α 8Mic	50	72.5	72.5	105	2.108 / 3.6
α 9Sub/ α 9Mic	50	65	65	120	1.899 / 3.3
α 10Sub/ α 10Mic	50	57.5	57.5	135	1.683 / 2.9
α 11Sub/ α 11Mic	50	50	50	150	1.466 / 2.5
α 12Sub/ α 12Mic	50	42.5	42.5	165	1.242 / 2.1
α 13Sub/ α 13Mic	50	35	35	180	1.017 / 1.8
α 14Sub/ α 14Mic	50	28	28	194	0.809 / 1.4
α 15Sub/ α 15Mic	50	20	20	210	0.576 / 1
α 16Mic	50	12	12	226	0.359 / 0.6

4. Synthesis of CsPbBr₃ PNCs in CaCO₃ (different CsPbBr₃ to CaCO₃ ratio and different Cs to Pb ratio)

In the similar fashion as described in the previous paragraph 3, a set of samples (50) was synthesized. Here we varied the amount of PbBr₂ and the ratio between PbBr₂ and CsBr (**Table S2**).

Table S2. Synthesis conditions of PNCs obtained in CaCO₃ templates by varying the amount of PbBr₂ and PbBr₂:CsBr ratio.

Sample name	CaCO ₃ dispersion (μL)	PbBr ₂ solution 0.05 M (μL)	CsBr solution 0.05 M (μL)	DMSO (μL)	PbBr ₂ (μmol)	PbBr ₂ :CsBr ratio
<i>α</i> ₁₃ Sub1/ <i>α</i> ₁₃ Mic1	50	35	35	180	1.8	1:1
<i>α</i> ₁₁ Sub1/ <i>α</i> ₁₁ Mic1	50	50	50	150	2.5	1:1
<i>α</i> ₉ Sub1/ <i>α</i> ₉ Mic1	50	65	65	120	3.3	1:1
<i>α</i> ₇ Sub1/ <i>α</i> ₇ Mic1	50	80	80	90	4	1:1
<i>α</i> ₄ Sub1/ <i>α</i> ₄ Mic1	50	102.5	102.5	45	5.1	1:1
<i>α</i> ₁₃ Sub1.2/ <i>α</i> ₁₃ Mic1.2	50	35	42	173	1.8	1:1.2
<i>α</i> ₁₁ Sub1.2/ <i>α</i> ₁₁ Mic1.2	50	50	60	140	2.5	1:1.2
<i>α</i> ₉ Sub1.2/ <i>α</i> ₉ Mic1.2	50	65	78	107	3.3	1:1.2
<i>α</i> ₇ Sub1.2/ <i>α</i> ₇ Mic1.2	50	80	96	74	4	1:1.2
<i>α</i> ₄ Sub1.3/ <i>α</i> ₄ Mic1.3	50	102.5	123	24.5	5.1	1:1.2

<i>a13Sub1.3/ a13Mic1.3</i>	50	35	45.5	169.5	1.8	1:1.3
<i>a11Sub1.3/ a11Mic1.3</i>	50	50	65	135	2.5	1:1.3
<i>a9Sub1.3/ a9Mic1.3</i>	50	65	84.5	100.5	3.3	1:1.3
<i>a7Sub1.3/ a7Mic1.3</i>	50	80	104	66	4	1:1.3
<i>a4Sub1.3/ a4Mic1.3</i>	50	102.5	133.25	14.25	5.1	1:1.3
<i>a13Sub1.4/ a13Mic1.4</i>	50	35	49	166	1.8	1:1.4
<i>a11Sub1.4/ a11Mic1.4</i>	50	50	70	130	2.5	1:1.4
<i>a9Sub1.4/ a9Mic1.4</i>	50	65	91	94	3.3	1:1.4
<i>a7Sub1.4/ a7Mic1.4</i>	50	80	112	58	4	1:1.4
<i>a4Sub1.4/ a4Mic1.4</i>	50	102.5	143.5	4	5.1	1:1.4
<i>a13Sub1.5/ a13Mic1.5</i>	50	35	52.5	162.5	1.8	1:1.5
<i>a11Sub1.5/ a11Mic1.5</i>	50	50	75	125	2.5	1:1.5
<i>a9Sub1.5/ a9Mic1.5</i>	50	65	97.5	87.5	3.3	1:1.5

$\alpha 7_{Sub1.5}/$ $\alpha 7_{Mic1.5}$	50	80	120	50	4	1:1.5
$\alpha 4_{Sub1.5}/$ $\alpha 4_{Mic1.5}$	50	102.5	153.75	0	5.1	1:1.5

In the similar way as described in paragraph 3 and in previous **Table S2**, a set of samples (18) was synthesized. In this series we additionally varied the amount of $PbBr_2$ the ratio between $PbBr_2$ and CsBr (**Table S3**).

Table S3. *Synthesis conditions of PNCs obtained in $CaCO_3$ templates by varying the $PbBr_2:CsBr$ ratio.*

Sample name	$CaCO_3$ dispersion (μL)	$PbBr_2$ solution 0.05 M (μL)	CsBr solution 0.05 M (μL)	DMSO (μL)	$PbBr_2:CsBr$ ratio
$\beta 1_{Sub}/ \beta 1_{Mic}$	50	65	65	120	1:1
$\beta 2_{Sub}/ \beta 2_{Mic}$	50	65	84.5	100.5	1:1.3
$\beta 3_{Sub}/ \beta 3_{Mic}$	50	65	97.5	87.5	1:1.5
$\beta 4_{Sub}/ \beta 4_{Mic}$	50	80	80	90	1:1
$\beta 5_{Sub}/ \beta 5_{Mic}$	50	80	104	66	1:1.3
$\beta 6_{Sub}/ \beta 6_{Mic}$	50	80	120	50	1:1.5
$\beta 7_{Sub}/ \beta 7_{Mic}$	50	100	100	50	1:1
$\beta 8_{Sub}/ \beta 8_{Mic}$	50	100	130	20	1:1.3
$\beta 9_{Sub}/ \beta 9_{Mic}$	50	100	150	0	1:1.5

5. Synthesis of CsPbBr₃ PNCs in CaCO₃ (different CsPbBr₃ to CaCO₃ ratio and addition of Yb)

A set of samples with a ratio between PbBr₂ and CsBr equal to 1:1.5 was selected as optimal for this experiment. Thus, 0.05 M solution of YbBr₃ in DMSO was prepared. After this, to 3 chosen samples were added 6 different mol% of Yb³⁺ (**Table S4**). In total 36 samples were obtained in this part.

Table S4. Synthesis conditions of PNCs obtained in CaCO₃ templates by varying Yb³⁺ ions concentrations.

Sample name	CaCO ₃ dispersion (μL)	PbBr ₂ solution 0.05 M (μL)	CsBr solution 0.05 M (μL)	DMSO (μL)	YbBr ₃ solution 0.05 M (μL)	Yb (mol%)
β9Yb1Sub/ β9Yb1Mic	50	100	150	0	0.5	0.5
β9Yb2Sub/ β9Yb2Mic	50	100	150	0	1	1
β9Yb3Sub/ β9Yb3Mic	50	100	150	0	2	2
β9Yb4Sub/ β9Yb4Mic	50	100	150	0	4	4
β9Yb5Sub/ β9Yb5Mic	50	100	150	0	6	6
β6Yb1Sub/ β6Yb1Mic	50	80	120	49.6	0.4	0.5
β6Yb2Sub/ β6Yb2Mic	50	80	120	49.2	0.8	1
β6Yb3Sub/ β6Yb3Mic	50	80	120	48.4	1.6	2

$\beta 6\text{Yb}_3\text{Mic}$						
$\beta 6\text{Yb}_4\text{Sub}/$ $\beta 6\text{Yb}_4\text{Mic}$	50	80	120	46.8	3.2	4
$\beta 3\text{Yb}_5\text{Sub}/$ $\beta 3\text{Yb}_5\text{Mic}$	50	80	120	45.2	4.8	6
$\beta 3\text{Yb}_1\text{Sub}/$ $\beta 3\text{Yb}_1\text{Mic}$	50	65	97.5	87.2	0.325	0.5
$\beta 3\text{Yb}_2\text{Sub}/$ $\beta 3\text{Yb}_2\text{Mic}$	50	65	97.5	86.9	0.65	1
$\beta 3\text{Yb}_3\text{Sub}/$ $\beta 3\text{Yb}_3\text{Mic}$	50	65	97.5	86.2	1.3	2
$\beta 3\text{Yb}_4\text{Sub}/$ $\beta 3\text{Yb}_4\text{Mic}$	50	65	97.5	84.9	2.6	4
$\beta 3\text{Yb}_5\text{Sub}/$ $\beta 3\text{Yb}_5\text{Mic}$	50	65	97.5	83.6	3.9	6

6. Photoluminescence properties evaluation

Photoluminescence (PL) measurements (Figures S1) of PNCs fabricated in CaCO_3 spheres were carried out with Axio Imager A2m microscope combined with the OceanOptics QE Pro spectrometer. The samples were deposited on glass substrates, the PL measurements were performed with 10 \times objectives (Carl Zeiss EC EpiplanNEOFLUAR). A mercury lamp HBO-100 with 360 nm wavelength excitation source was used coupled with a long-pass filter with a cut-on wavelength of 420 nm. PL intensity was measured in 9 different regions of interest for each substrate containing PNCs in CaCO_3 . Afterwards the PL spectra were integrated and averaged. Each sample was synthesized in triplicates to ensure the reproducibility of the data.

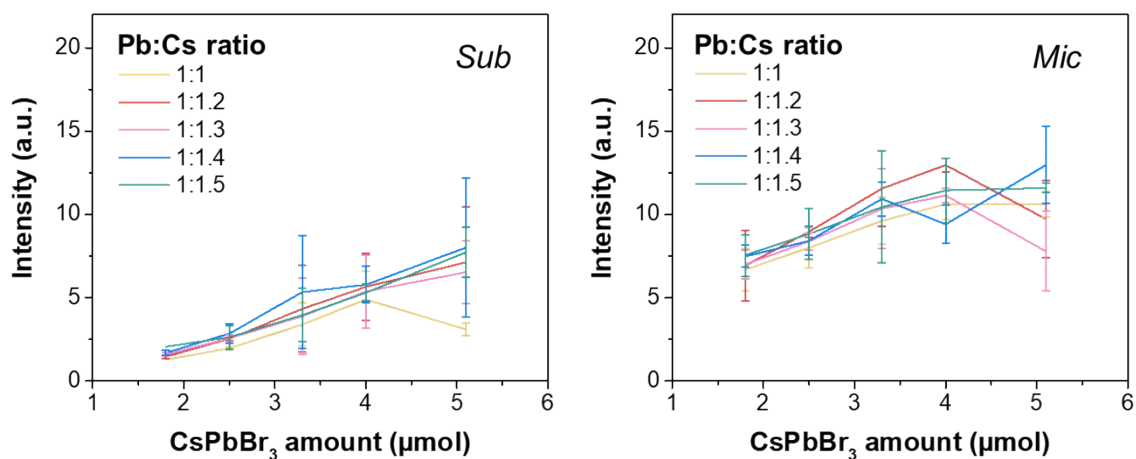


Figure S1. The PL intensity of CaCO_3 spheres with different ratios between Cs and Pb.

7. Measurements of fluence-dependent photoluminescence

The measurements were performed with a femtosecond laser 450 nm (Pharos, Light Conversion) with adjustable laser intensity. The adjustment was conducted with two filter wheels equipped with ND filters (FW212CNEB). The maximal pump fluence was chosen not to damage the sample. The PL was measured with a spectrometer.

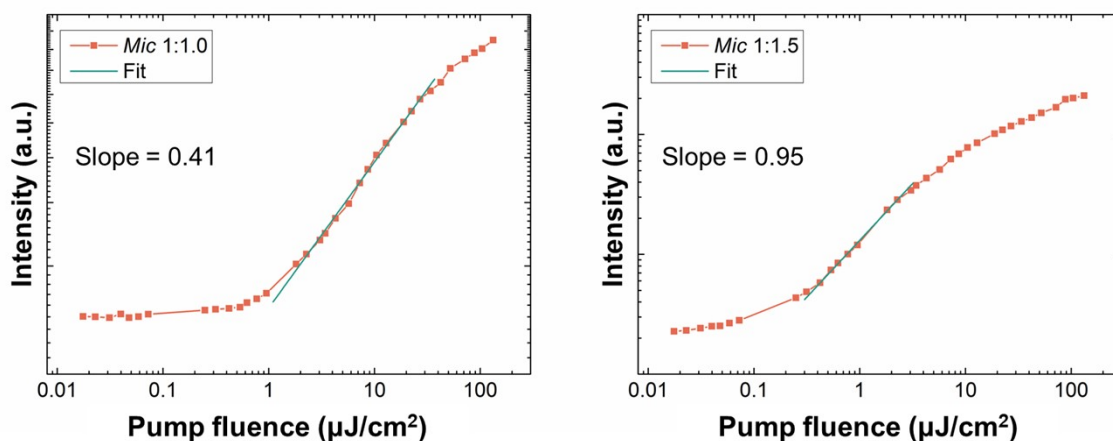


Figure S2. Single-photon PL intensity dependence on excitation fluence at 450 nm wavelength.

8. PLQY measurements

Photoluminescence quantum yield (PLQY) measurements for *Sub* and *Mic* vaterite spheres with PNCs were carried out as described in the article by de Mello et al.² Briefly, experimental setup consisted of an integrating sphere (Labsphere), which through the optical fiber was connected to the fiber spectrometer QE Pro. The baffle was placed between the fiber and the sample to prevent the direct illumination of the fiber by the pump laser. Prior to the PLQY measurements the whole measurement system (integrating sphere, fiber and spectrometer) was calibrated by measurement of the spectrum of quasi blackbody irradiation. Obtained spectrum was compared with mathematical approximation according to the temperature of the quasi blackbody. As a result, an instrument response function (IRF) was obtained that allows direct comparison of photoluminescence amplitudes. During any PLQY measurements there was no replacement of the fiber, spectrometer or integrating sphere. The power attenuation was performed with filter wheels equipped with absorptive ND filters FW212 (Thorlabs). CW laser with an excitation wavelength 405 nm was utilized as a laser pump.

To obtain the PLQY of CaCO₃ with PNCs three kinds of measurements were performed. Firstly, the spectrum (a) of a laser pump was measured in the absence of the sample. Then, the sample was placed into the integrating sphere in such a way that the laser did not irradiate the sample directly and the second spectrum (b) was measured. Lastly, the sample was positioned in such a way that it was directly irradiated by the pump laser and the final spectrum (c) was obtained. The PLQY was then calculated using the following formula:

$$\eta = \frac{P_c - (1 - A)P_b}{L_a A}$$

where L is area under curve of the laser profile and P is area under curve of the emission profile with indexes referring to the corresponding spectra (a, b or c), A is the absorption coefficient, which is equal to:

$$A = 1 - \frac{L_c}{L_b}$$

9. SEM measurements

Scanning electron microscopy (SEM). To perform SEM measurements, *Sub* and *Mic* vaterite spheres with PNCs synthesized on silicon substrate instead of previously used glass substrate. Afterwards, SEM images were obtained with the Merlin-Zeiss microscope at the accelerating voltage of 1.5 kV. PNCs were visualized via a backscattered electron detector.

10. TEM measurements

High-resolution transmission electron microscopy (HRTEM) images of CsPbBr_3 PNCs fabricated in CaCO_3 spheres were obtained using Zeiss Libra 200FE microscope with an accelerating voltage of 200 kV. For HRTEM analysis, samples dispersed in toluene were dropped ($1.5 \mu\text{L}$) onto a copper TEM grid (200 mesh) and dried for a few minutes. Microphotographs show PNCs at the edge of spheres, in only region that can be transmitted.

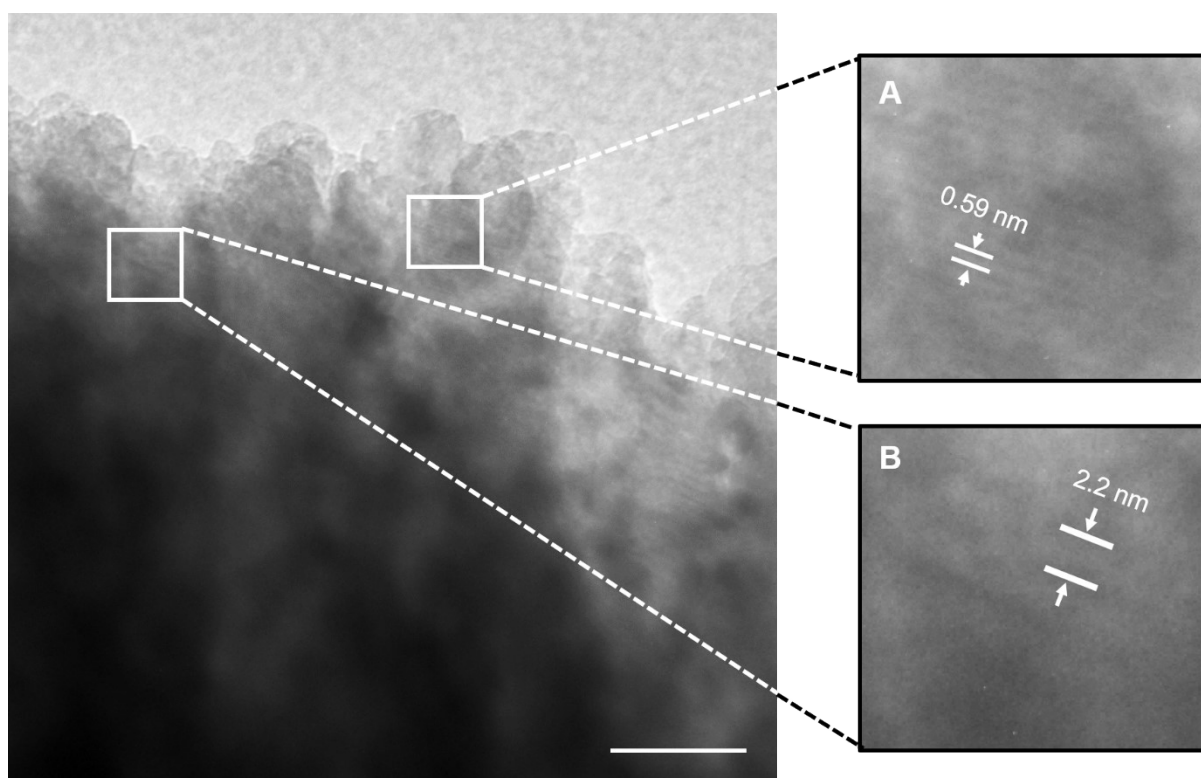


Figure S3. CsPbBr_3 PNCs (a) at the edge of the CaCO_3 microsphere and Moiré patterns (b) corresponding to $\text{CsPbBr}_3/\text{CsPb}_2\text{Br}_5$ PNCs. Scale bar corresponds to 50 nm.

11. EDX measurements

Energy-dispersive X-ray spectroscopy (EDX) spectra of CsPbBr₃ synthesized in *Sub* and *Mic* templates were obtained using the JEOL Centurio energy-dispersive X-ray spectrometer (EDXS). The EDX spectra were processed using JEOL Analysis Station software.

12. BET and BJH measurements

Surface area, average pore diameter and total pore volume were measured from N₂ adsorption isotherms at liquid nitrogen temperature (-196 °C) using the Quantachrome Nova 1200 analyzer. All the samples were degassed under vacuum at 415 K for 12 h. The surface area was calculated using the *Brunauer-Emmett-Teller (BET)* equation (39.2 m²/g for *Sub*, 13.6 m²/g for *Mic*), the average pore diameter was calculated using the *Barrett-Joyner-Halenda (BJH)* (3.5 nm for *Sub*, 14.4 nm for *Mic*) equation.

13. ICP-AES measurements

To confirm the presence of ytterbium in the obtained samples, the inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed. ICP-AES analysis was made with the ICPE-9000 Shimadzu spectrometer. For this, the synthesized CaCO₃ vaterite spheres with PNCs from a single substrate were washed out from the substrate and dissolved in 5 mL of a HNO₃/HCl (5/3 v/v) mixture. Then acid decomposition was carried out at a temperature of 200 °C and a pressure of 55 bar for 15 min in a MARS 6 (CEM) microwave system.

Table S5. ICP-AES measurements of ytterbium in *Mic*.

	Yb (µg/mL)
<i>Mic</i>	-
<i>Mic</i> (1:1.5) + 6% Yb	5.1

14. XRD measurements

To perform XRD measurements, *Sub* and *Mic* vaterite spheres with PNCs were obtained on silicon substrate instead of previously used glass substrate. XRD measurements of CsPbBr₃ fabricated in CaCO₃ templates were performed using a Shimadzu 7000-maxima X-ray diffractometer with a 2 kW characteristic Cu-K α (K α 1 $\lambda = 1.54059$ Å) X-ray radiation source and a Bragg-Brentano goniometer geometry. The angular resolution during the analysis was 0.01 degree at a scanning speed of 1.5 degrees/min.

15. XPS measurements

The elemental composition and chemical state of the obtained CsPbBr₃ PNCs fabricated in CaCO₃ templates were studied using the *X-ray photoelectron spectroscopy (XPS)*. To perform XPS measurements, *Sub* and *Mic* vaterite spheres with PNCs synthesized on a silicon substrate instead of previously used glass substrate. In our case, the XPS analysis was carried out in an ultra-high vacuum ($1.8 \cdot 10^{-9}$ mbar) using K-Alpha Thermo Scientific spectrometer with monochromatic Al-K α X-rays source (1486.6 eV). A flood gun was used to neutralize the surface charge, the C1s position of the adventitious carbon was at the binding energy (BE) = 284.8 eV. For high-resolution spectra (0.1 eV resolution) of a photoelectric signal collected from a spot area $\sim 300 \times 200$ nm in size, the analyzer's constant energy mode (CAE) with a pass energy of 20 eV and a number of scans equal to 10 was chosen. Shirley/Tugard background was used to deconvolute the spectra. The shape of the spectrum components was obtained at a 20% Gauss/Lorentz function mixture ratio. The XPS data were recorded twice: once from the surface of the *Sub* and *Mic* vaterite spheres and again from the same region of interest after 50 nm ion etching. The energy of the Ar⁺ ion beam was set to 1000 eV, which approximately corresponded to an etching rate of 2 nm/s.

16. Up-conversion measurements

Custom 10W Pharos single-unit integrated femtosecond laser system and high power optical parametric amplifier Orpheus-F were used for excitation of samples. The excitation femtosecond laser was focused on a sample from behind with an x10 objective (Mitutoyo Plan APO NIR, NA = 0.28). Signal was collected by x10 objective (Mitutoyo M Plan APO, NA = 0.26). The collected signal through the long-pass filter

was guided to the imaging spectrograph Andor Kymera 328i with CCD camera Andor iDus (**Figure S3**).

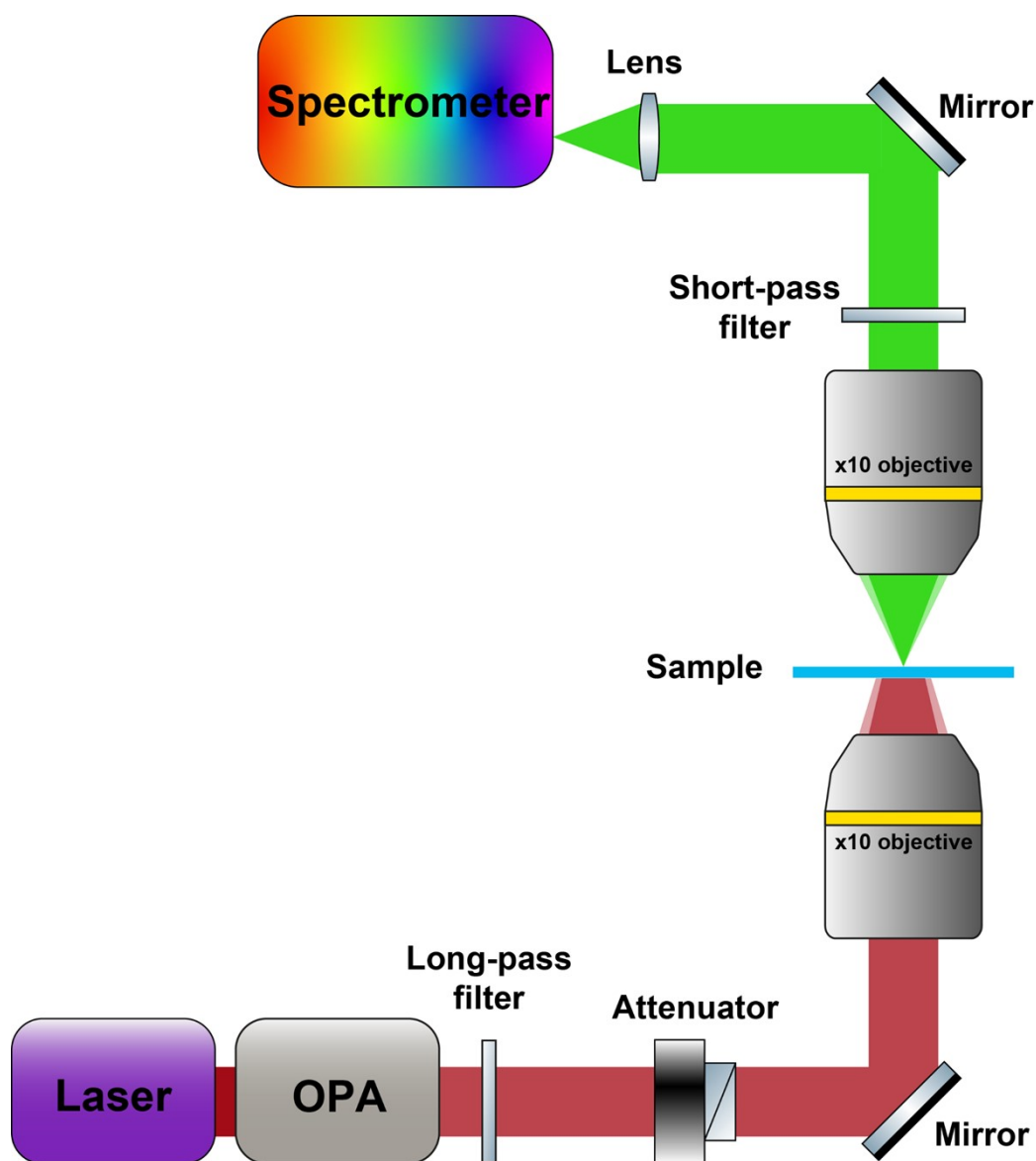


Figure S4. Scheme of up-conversion measurements set-up.

17. Preparation of IR visualizer

To prepare the visualizer, it was necessary to concentrate vaterite spheres on the substrate to increase light-matter interaction volume. For this a glass substrate coated with either *Mic* or *Sub* was washed out with 1 mL of toluene to obtain the solution of vaterite spheres in a nonpolar solvent in a centrifuge tube. Then, the obtained suspension was centrifuged at 13000 rpm (60 s) and the 990 μ L of supernatant were removed and the remaining pellet was resuspended. This resulted in a milky-white

solution with high concentration of CaCO_3 with PNCs. Afterwards 3 μL of this solution was applied on another glass substrate as a single drop. After the evaporation of the toluene the visualizer was ready to use.

18. References

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- 2 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230–232.