Supporting Information

Unveiling the Shape Evolution and Halide-Ion-Segregation in Blue Emitting Formamidinium Lead Halide Perovskite Nanocrystals using an Automated Microfluidic Platform

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Materials

Lead(II) acetate trihydrate (≥ 99.99% trace metals basis, Aldrich), formamidine acetate salt (99%, Aldrich), lead(II) bromide (98%, ABCR), lead(II) chloride (ultradry, 99.999%, ABCR), trioctylphosphine (99 %, Strem), oleic acid (90%, Aldrich), oleylamine (95%, STREM), 1-octadecene (90%, Sigma-Aldrich), ethanol (≥ 99.8%, Fluka), toluene (≥ 99.7%, Fisher Scientific UK), acetonitrile (≥ 99.9%, Merck KGaA), methyl acetate (99%, Sigma-Aldrich), diethyl ether - Et_2O (≥ 99.8%, Sigma-Aldrich), HBr (48%, for analysis, Acros Organics), HCl (37%, Sigma-Aldrich, puriss. p. a.), cumarin (97%, Aldrich).

Precursor preparation

Method 1: $PbBr_2$ and $PbCl_2$ solutions

In a 20 mL Schlenk flask 0.069 g $PbBr_2$ (0.188 mmol) and 6 mL octadecene (ODE) were added and the mixture was dried under vacuum for 30-60 mins at 120 °C. In a second Schlenk flask (20 mL) 0.052 g $PbCl_2$ (0.188 mmol) and 5 mL ODE were added and the mixture was dried under vacuum for 30-60 mins at 130°C. After heating, 1 mL of degassed oleic acid (OA) and 0.5 mL of degassed oleylamine (OLA) were added to both mixtures under nitrogen. Additionally, 1 mL trioctylphosphine (TOP) was added to the chloride solution. Formamidinium precursor was prepared by adding 0.130 g formamidinium acetate (FAAc, 1.25 mmol) together with 16 mL ODE and 4 mL degassed oleic acid into a 50 mL Schlenk flask. The mixture was degassed at room temperature for 30 min under vacuum and then heated to 120 °C for another 30-60 mins under nitrogen yielding a clear (sometimes yellowish) solution. After the precursors were cooled down to room temperature, they were loaded into 10 mL glass syringes (Hamilton, Gastight-1010).

Method 2: OLAmX (X=Br, Cl) solutions

The synthetic procedure is adapted by Protesescu *et al.*[1] ethanol (100 mL) and OLA (37.5 mL) were combined in a 250 mL 3-neck flask and stirred vigorously. The reaction mixture was cooled in an ice-water bath and 27 mL HBr (20 mL HCl in case of OLAmCl precursor) was added. The reaction mixture was left to react overnight under nitrogen flow. Then the solution was dried under vacuum and the obtained product was purified by rinsing multiple times with diethylether. The product (a white powder) was obtained after vacuum-drying at room temperature. 0.111 g OLAmBr (0.32 mmol) and 9 mL dried OA were added to a Schlenk flask and the mixture was dried under vacuum for 30-60 mins at 120 °C. After heating, 1 mL dried OLA was added to the mixture. OLAmCl precursor was prepared following the same procedure, using 0.097 g OLAmCl (0.32 mmol). Formamidinium precursor preparation was identical to the one described in synthetic *method 1*. Lead precursor was prepared by adding 0.076 g lead acetate ($PbAc_2$, 0.20 mmol) together with 10 mL OA into a 20 mL Schlenk flask. The mixture was degassed at 120 °C for 30-60 mins under vacuum. After the precursors were cooled down to room temperature, they were loaded into 10ml glass syringes. (Hamilton, Gastight-1010).

Flask-based synthesis of $FAPb(Cl/Br)_3$ nanocrystals

Method 1: $Pb(Br,Cl)_2$ (0.185 mmol) and 5 mL ODE were combined in a 3-neck flask and dried at 120 °C under vacuum for 1 h. OA (1 mL), OLA (0.5 mL) and TOP (1 mL) ligands were injected under nitrogen atmosphere. After heating to the desired hot injection temperature (*e.g.* 155 °C) the FA-oleate (65 mg,

0.625 mmol, in 2.5 mL OA) precursor solution was injected. After 30 s the reaction mixture was cooled using a water bath.

Method 2. FAAc (119 mg, 1.14 mmol), $PbAc_2$ (76 mg, 0.20 mmol) and a mixture of OA (2 mL) and ODE (8 mL) were combined in a 3-neck flask and dried at 60 °C under vacuum for 30 min. The mixture was then heated to the desired hot injection temperature (*e.g.* 130 °C) under nitrogen atmosphere, followed by injection of OlAm(Br,Cl) (0.8 mmol) precursor dissolved in toluene (2 mL). After 30 s the reaction mixture was cooled using a water bath.

Offline Characterization

Washing procedure for XRD measurements. For XRD measurement are accessible by washing the crude reaction mixture 3 times with 10 mL toluene and 2 mL acetonitrile (AcCN), followed by filtration of the NC dispersion using a 200 nm pore size filter.

Washing procedure for QY measurements. For QY measurements we washed the NCs either with toluene/methyl acetate or toluene/AcCN, and higher QYs were generally obtained for the latter solvent combination. We observed decreasing QYs when going to higher chloride contents and no PL for the pure chloride NCs.

Absorbance and photoluminescence measurements. UV-Vis absorption measurements were carried out using a Jasco V670 in transmission mode. PL spectra were recorded with a Fluorolog iHR 320 Horiba Jobin Yvon spectrofluorimeter equipped with a PMT detector. Cumarin was used as a standard to measure QY.

Microfluidic synthesis $FAPb(Cl/Br)_3$ NCs

Details of the microfluidic synthesis. Precision syringe pumps (neMESYS, Cetoni GmbH, Germany) were used to inject the dispersed phase (PbX_2 or OLAmX, FA-oleate, Pb-Oleate precursor solutions) and the carrier fluid (Galden fluorinated fluid, Blaser Swisslube AG, Germany) towards a polyether ether ketone (PEEK) 7-port manifold (0.5mm thru hole, Upchurch Scientific, Germany) to form a segmented flow of droplets. The 7-port manifold and the syringes carrying the precursor solutions and the carrier fluid were connected through PTFE tubing (ID 250 μm, OD 1/16", Upchurch Scientific, Germany) using PEEK finger-tight fittings (F-127, Upchurch Scientific, Germany). Typical flow rates were 30-300 μL min^{-1} for the carrier phase and 0.5-150 μL 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. 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 PL spectroscopy. The reaction time was controlled either by varying the flow rates of the carrier phase and reagents. 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, Thermolement 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 °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 (M375L2-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 365 LP, AHF, Germany) and then focused into the microfluidic channel using an aspheric lens (A240TM – f = 8.0 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 (PRo+, 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 350 and 1100 nm, and data recorded using 50-100 ms integration times. The entire system was enclosed in a black box to minimize pollution from the stray light. Using a home-made Matlab script we manage to remove all the photoluminescence spectra generated from the oil carrier phase and extract only those which are generated by the droplets containing the synthesized nanocrystals. Then, the collected PL spectra are weighted with their overall variance (summed over all wavelengths). For calculating the PL peak and FWHM, we calculated the first and second derivative of the spectra. The peak wavelength is identified as the location of the minimum of the second derivative and the FWHM is not determined from the turning points of the curve but as the true full width at half maximum with respect to the maximum of the peak (minimum and maximum of first derivative to the right and left of the minimum of second derivative, respectively).

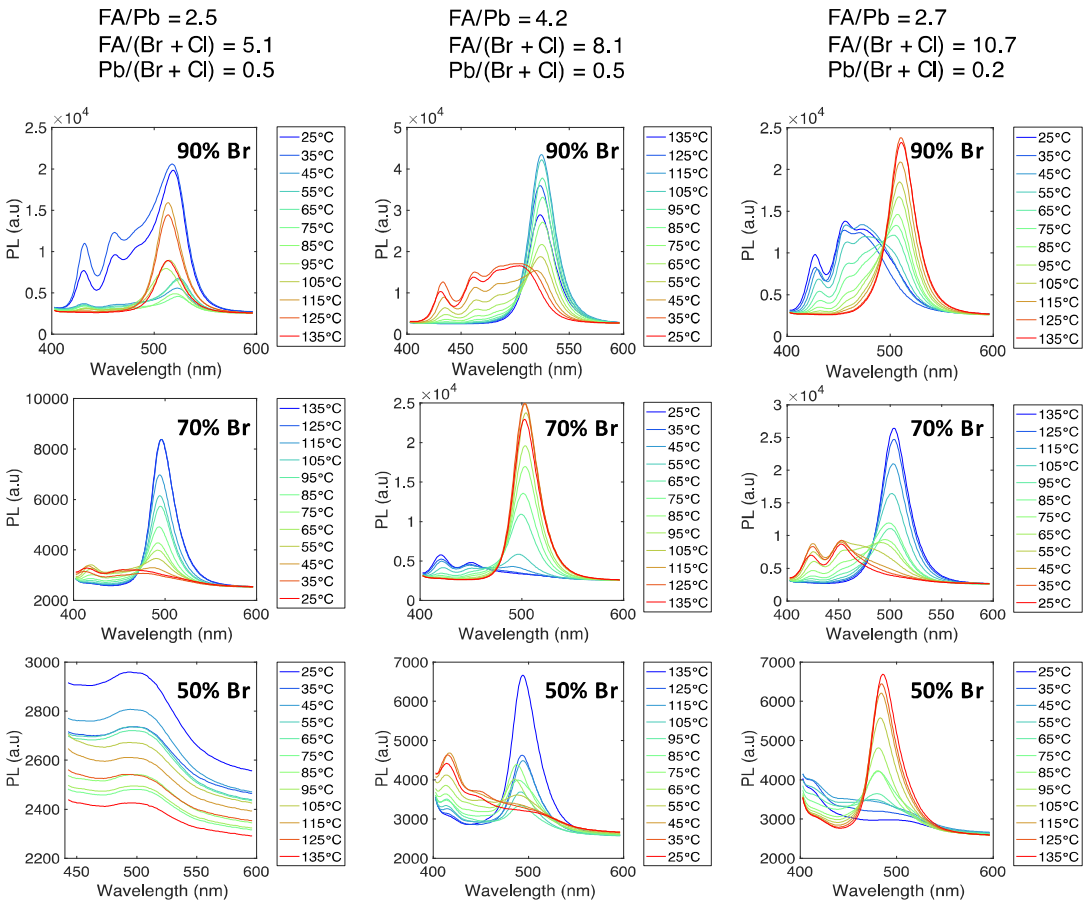

Figure S1: Evolution of PL spectra of $FAPb(Cl/Br)_3$ NCs for different temperatures at fixed combinations of of FA/Pb, FA/(Br + Cl) and Pb/(Br + Cl) and at various Br loadings; 90% (top), 70% (middle) and 50% (bottom). Synthetic method 2 was used for the formation of $FAPb(Cl/Br)_3$ NCs.

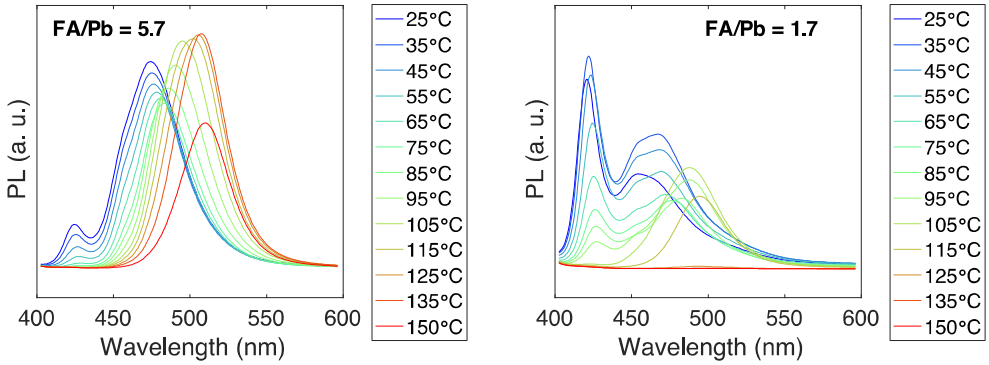

Figure S2: Effect of temperature on the PL spectra of $FAPb(Cl/Br)_3$ NCs for two different FA-to-Pb molar ratios, 5.74 (left) and 1.70 (right). The Br content was fixed at 90%. Performing the synthesis at temperatures in the range of 65-135°C and high excess of FA (5:1) favors the formation of NCs with cubic phase. On the other hand, lower temperatures in the range of 25-65°C and FA to Pb ratio being close to 1:1 favors the formation of NPLs together with the coexisting NCs.

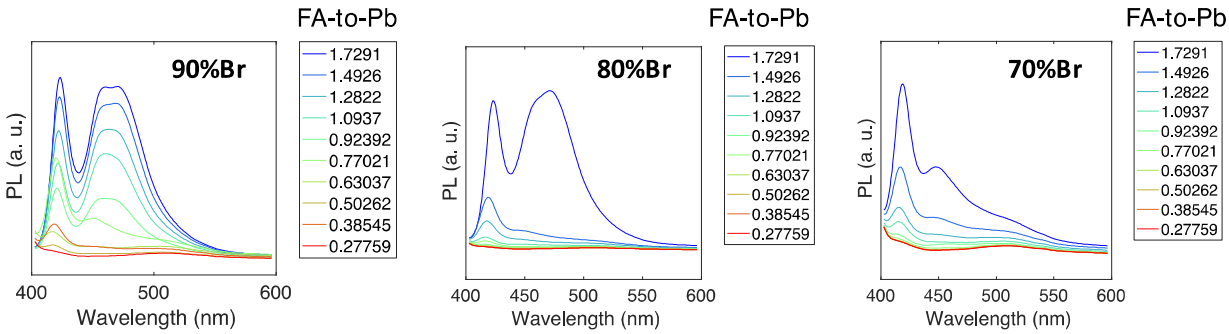

Figure S3: PL spectra of $FAPb(Cl/Br)_3$ NCs for FA-to-Pb molar ratios lower than 1.72 at given Br loadings (90%, 80%, 70%). The temperature (25 °C) and reaction time (7 s) were maintained constant.

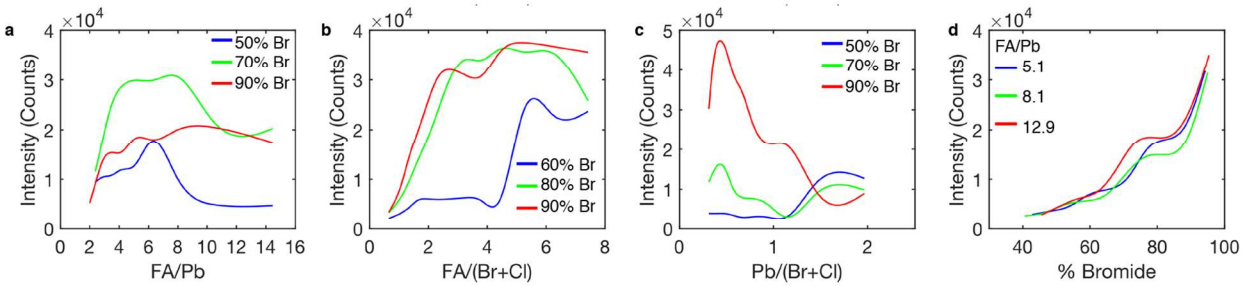

Figure S4: Effect of (a) FA-to-Pb molar ratio, (b) FA to total halide ratio, (c) Pb to total halide ratio, and (d) Br loading on PL intensities of $FAPb(Cl/Br)_3$ perovskites. Colors in the PL spectra displayed in Figures 3a-d to various Br loadings and FA-to-Pb molar ratios indicated in the corresponding legends. The temperature (130 °C) and reaction time (7 s) were maintained constant.

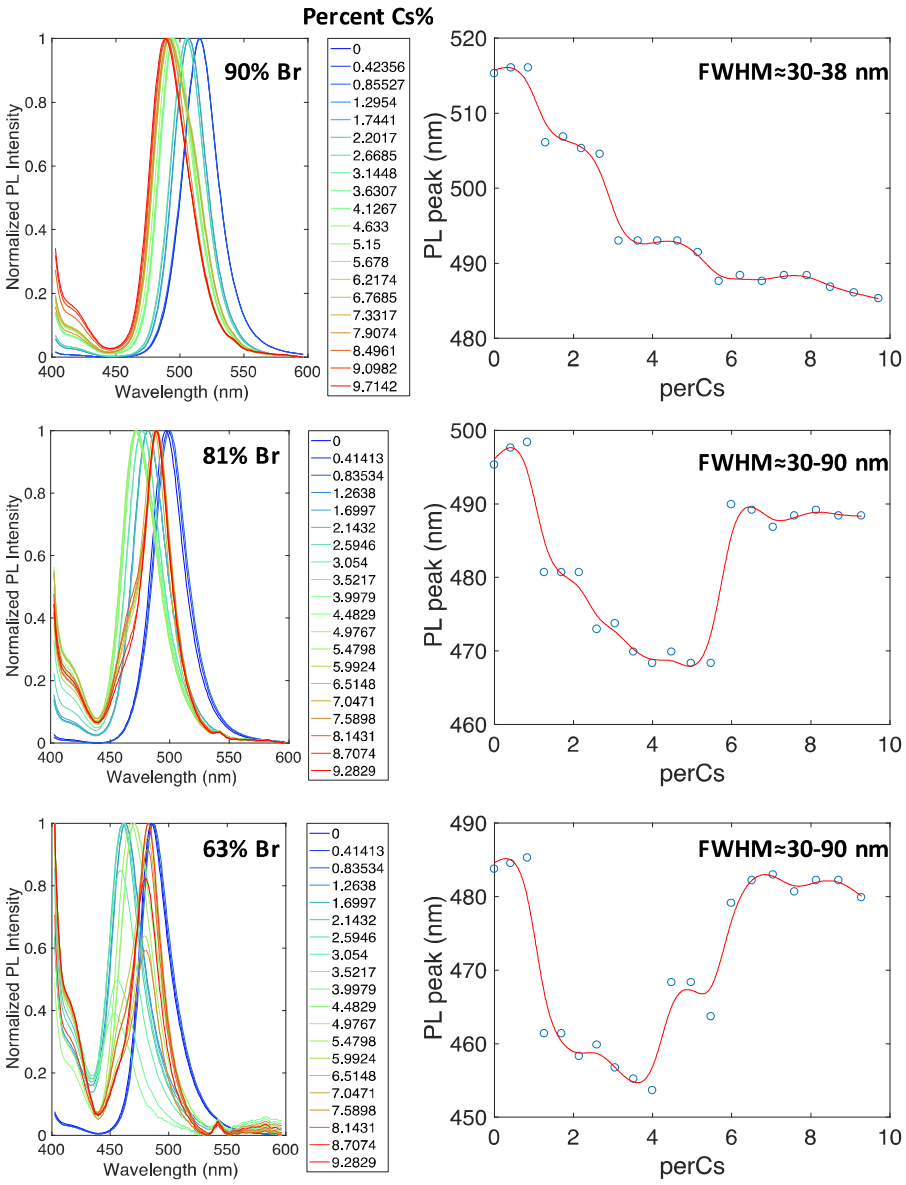

Figure S5: PL Spectra of $FAPb(Cl/Br)_3$ NCs after the addition of Cs cation. The amount of Cs loaded in the microfluidic setup is expressed as Cs% (provided in the legend, relative to FA content) at various Br loadings. The other molar ratios were kept fixed at FA/(Br+Cl) = 3.1, FA/Pb = 6.3 and T=130°C.

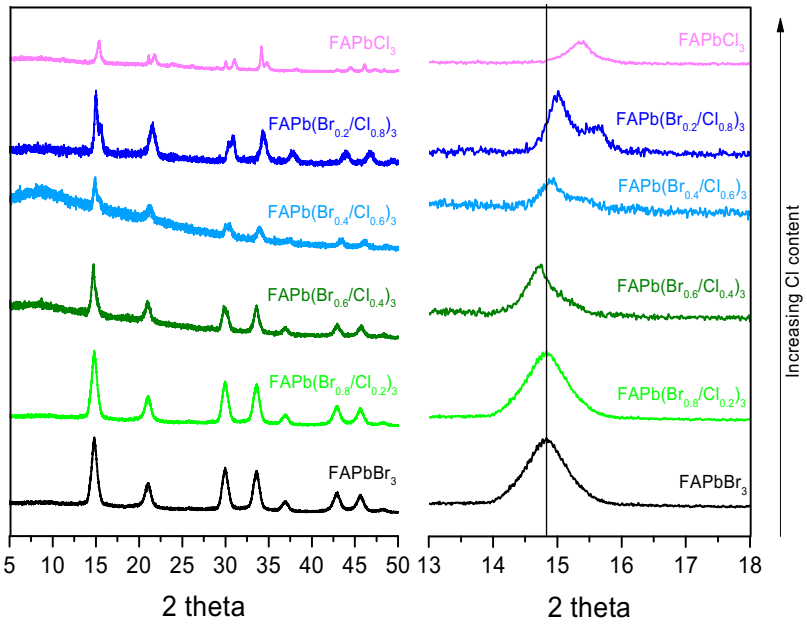

Figure S6: XRD spectra of $FAPb(Cl/Br)_3$ NCs with varying compositions (20 %, 40 %, 60 %, 80 % of Cl related to the total halide content). High purity samples for XRD measurements were obtained by washing the crude reaction product 3 times with 10 ml toluene + 2 ml AcCN. After redispersing in toluene the washed NCs were obtained upon filtration using a 200 nm pore size filter. Decomposition of the particle is revealed for compositions higher than 60% Cl.

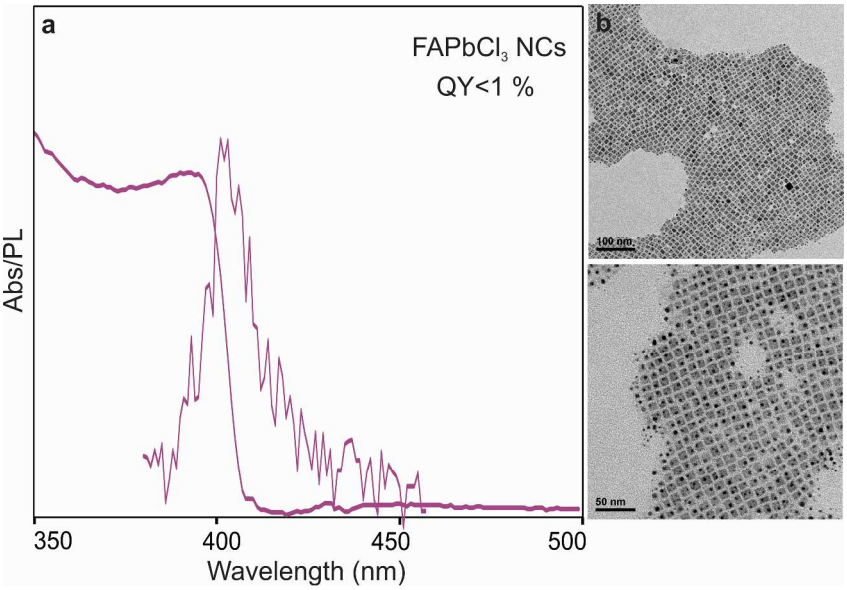

Figure S7: (a) PL and absorption spectra for $FAPbCl_3$ NCs, (b) the TEM images for $FAPbCl_3$ NCs.

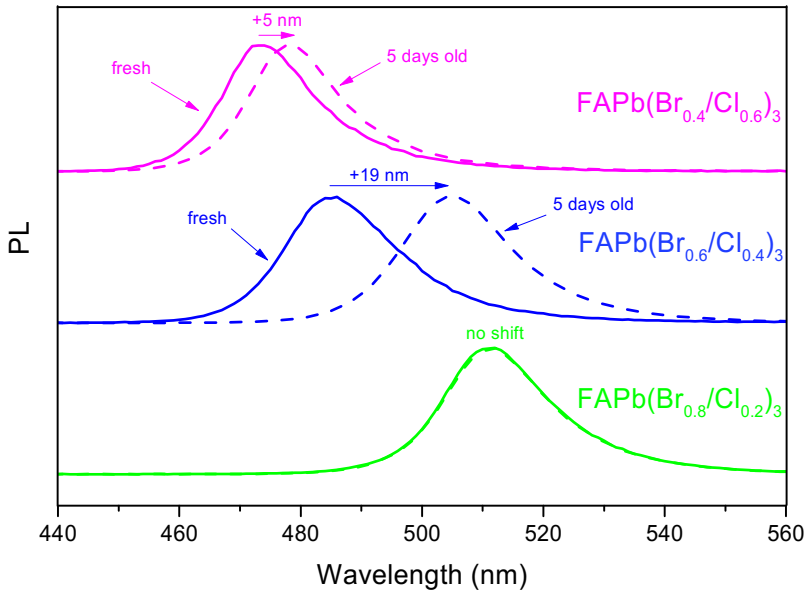

Figure S8: Comparison of PL spectra from freshly synthesized $FAPb(Cl/Br)_3$ NCs (solid lines) and 5-day-old NCs (dashed lines). The chloride content is between 20 to 60% related to the total halide content.

Table S1: QY values of $FAPb(Cl/Br)_3$ NCs synthesized using method 2 - OlAmX (X = Cl, Br) precursors.

Sample	Washing procedure	QY
20% Cl	2 washing steps with 10 ml toluene + 2 ml Acetonitrile	56%
40% Cl	2 washing steps with 10 ml toluene + 2 ml Acetonitrile	50%
60% Cl	2 washing steps with 10 ml toluene + 2 ml Acetonitrile	34%
80% Cl	2 washing steps with 10 ml toluene + 2 ml Acetonitrile	28%

References

1. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Bertolotti, F.; Masciocchi, N.; Guagliardi, A.; Kovalenko, M. V. *J. Am. Chem. Soc.* **2016,** 138, 14202-14205.