Electronic Supplementary Material (ESI) for Nanoscale.

# Revisiting the nontemplate approach for the synthesis of highly green emissive hybrid perovskite nanocrystals: platelets or spheres?

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## Supporting Information

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| **Figure S8:** Comparative X-ray diffraction patterns of $LHP_{OLA}$ nanoplatelets, before ($MAPbBr_3$ NPLs, emission centered at 515 nm) and after the halide exchange with chloride (emission centered at 495 nm and 476 nm), and iodide (emission centered at 570 nm and 648 nm). Samples were measured using a parallel beam geometry in the symmetric reflection mode under ambient conditions. | **S9** |
| **Figure S9:** TEM images of LHP NPLs before ($MAPbBr_3$) and after the anion exchange with chloride (emission centered at 411 nm), and iodide (emission centered at 570 nm). Scale bar: 200 nm. | **S10** |

## Experimental Section

### Precursors and solvents:

All the reagents used in the synthesis of the perovskites and the alkyl ammonium bromides were purchased from Aldrich and used as received. The organic solvents were of spectroscopic grade (from Scharlab, Alfa Aesar and Acros Organics).

The precursors, methylammonium bromide ($CH_3NH_3Br$) and octylammonium bromide ($CH_3(CH_2)_7NH_3Br$), were synthesized by reaction of the corresponding amine in water/HBr, accordingly to the previously reported procedure.[1] In the case of octadecylammonium bromide ($CH_3(CH_2)_{17}NH_3Br$), it was prepared by using a similar methodology but the amine was previously dissolved in acetonitrile at 60°C and then HBr was added. In all cases, the precipitate was washed several times with diethyl ether, dried under vacuum and used without further purification.

**Synthesis of LHP nanoplatelets:** A solution of oleic acid (OLA, 0.30 mmol, 85 mg) was stirred and pre-heated to 80 $^0$C in a beaker, and then octylammonium bromide (OABr, 0.106 mmol, 22,4 mg) was added. Once, it was completely dissolved in the oleic acid solution, methylammonium bromide (MABr, 0.24 mmol, 26.4 mg, dissolved in 100 $\mu$L of DMF) and lead(II) bromide (0.10 mmol, 36.7 mg, dissolved in 200 $\mu$L of DMF) were added simultaneously, observing the formation of a yellow pale solution. Immediately, after setting a vigorous stirring, it was added acetone (5 mL) to induce the precipitation of a greenish-yellow precipitate. Finally, after 10 seconds of reaction, the LHP nanoplatelet dispersion was placed in an ice-water bath for 5 minutes.

**Purification of LHP nanoplatelets:** The unreactive material was separated by several steps of centrifugation. After the synthesis, the dispersion was firstly centrifuged at 5000 rpm, 5 min, and 5 $^0$C. The supernatant was discarded and the precipitate, dissolved in 5 mL of a mixture of methyl acetate:hexane (1:1), was washed by a second centrifugation step at 2000 rpm, 5 min, and 5 $^0$C. Finally, the supernatant was further characterized.

**UV-visible spectroscopy:** UV-Vis absorption spectra were performed on a spectrophotometer UV/VIS/NIR Lambda 1050, equipped with software PerkinElmer UV Winlab.

**Steady state and time-resolved photoluminescence (PL):** Steady-state emission spectra of all dissolutions were recorded in a FLS1000 photoluminescence spectrometer (Edinburgh Instruments) equipped with a 450 W ozone free xenon arc lamp and coupled with a 375 nm picosecond pulsed diode laser (EPL-375, Edinburgh Instruments). The Fluoracle software was used to register the data.

**Quantum yield:** The quantum yields were recorded with Quantaurus QY Plus C13534-11, equipped with Xenon lamp for excitation in visible~~.~~

**X-ray Diffraction:** The PXRD analyses were performed in a powder diffractometer Panalytical Empyrean X-ray platform (equipped with a 1.8 kW Cu Kα ceramic X-ray tube) and with a PIXcel3D detector (2 × 2 area detector, operating at 45 kV and 40 mA). The diffraction patterns were measured using a parallel beam geometry in the symmetric reflection mode under ambient conditions. For preparing XRD samples were dropped several droplets of the NCs dispersions into a silicon zero-diffraction single crystal substrate. The PXRD pattern of Figure S3 was obtained in a Panalytical Empyrean X-ray platform with a capillarity platform and copper radiation (Cu Kα = 1.541 78 Å). The capillary tube used is made of special glass nº 0140, with a diameter of 0.5 mm.

**Transmission electron microscopy.** Transmission electron microscopy (TEM) was performed on a HITACHI HT7800 microscope with a filament of $LaB_6$ operated at 100 keV. High resolution images were performed on a FEI TECNAI G2 F20 operated at 200 keV.

**Scanning transmission electron microscopy high-angle annular field (STEM-HAADF)** images were acquired using a FEI Titan 80-300kV transmission electron microscope (TEM) operated at 300 kV. This microscope is equipped with a condenser lens Cs corrector (CETCOR Cs-condenser CEOS Company) and a high brightness field emission gun (XFEG). The convergent semi-angle was 25 mrad and particular care has been considered for avoiding electron beam damage.

**Halide ion exchange reaction:** At first, the halide (Cl and I) precursor solutions were prepared by dissolving 0.1 mmol of $PbCl_2$ or $PbI_2$ powder in a mixture of 5 ml of toluene, 0.1 mL of oleylamine and 0.1 mL of oleic acid at 100 $^0$C under continuous stirring. Then, the appropriate amount of precursor was added to the $MAPbBr_3$ NCs dispersion to initiate the halide ion exchange. The amount of the halide source was varied from 10 to 200 $\mu$L to tune the composition of the NCs and the resultant photoluminescence. The reaction mixtures were kept under stirring for 30-40 min at 40 $^0$C and the dispersions obtained was characterized.[2]

**Preparation of LHP nanoplatelets Solid Film:**

**- Centrifugal casting method:** The $MAPbBr_3$ NPLs (5 mL) were added to a conical centrifuge tube (25 mL), which contain the quartz slide substrate (0.5 x 0.8 mm) at its bottom, and the mixture was centrifuged for 4 min at 12500 rpm. The supernatant was pipetted out and the quartz substrate with the deposited $MAPbBr_3$ NPLs was allowed to slowly dry inside the closed conical centrifuge tube, at room temperature.

**- Dip coating method:** A quartz slide substrate (0.5 x 0.8 mm) was placed inside a vial that contained 5 mL dispersion of $MAPbBr_3$ NPLs. Then, it was slowly dry in a toluene atmosphere.

- **Drop casting method:** A dispersion of $MAPbBr_3$ NPLs (ca. 1 mL) was deposited, drop by drop, onto a quartz slide substrate (0.5 x 0.8 mm) and the solvent was slowly evaporated at room temperature.

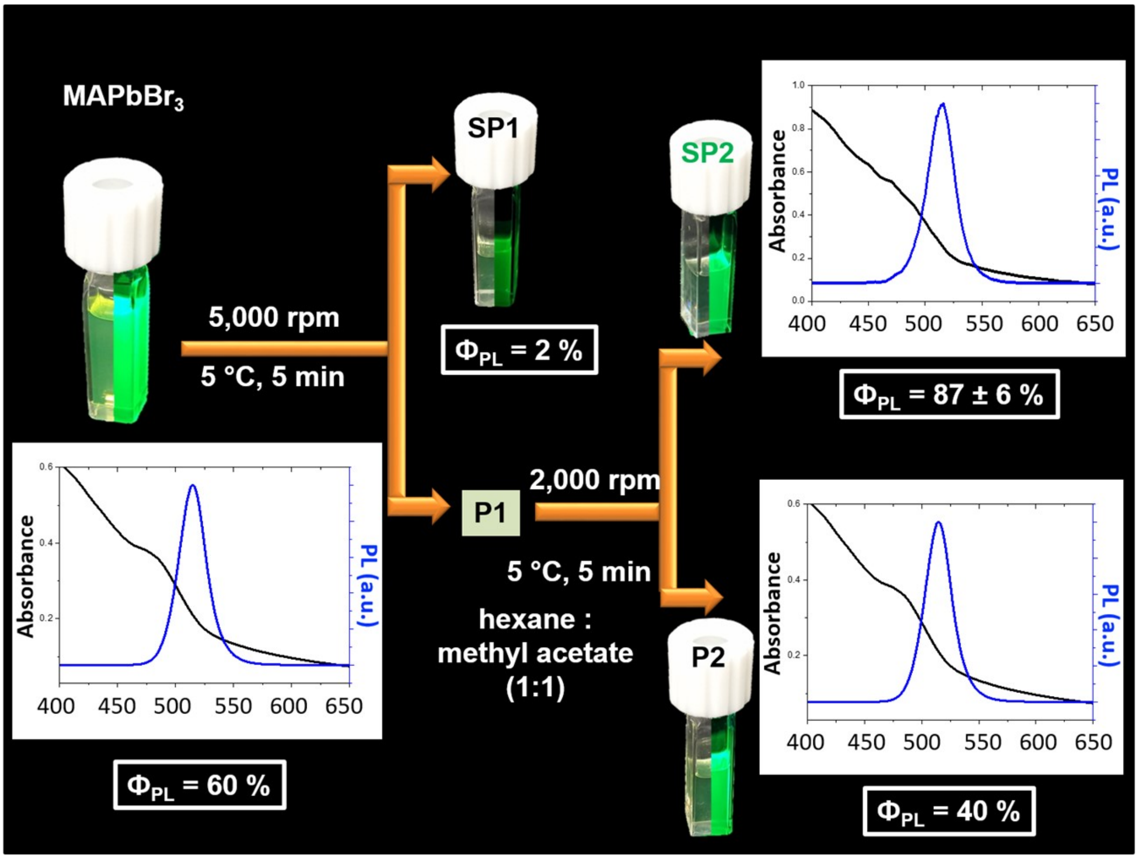

**Figure S1:** Purification steps of hybrid LHP nanoplatelets.

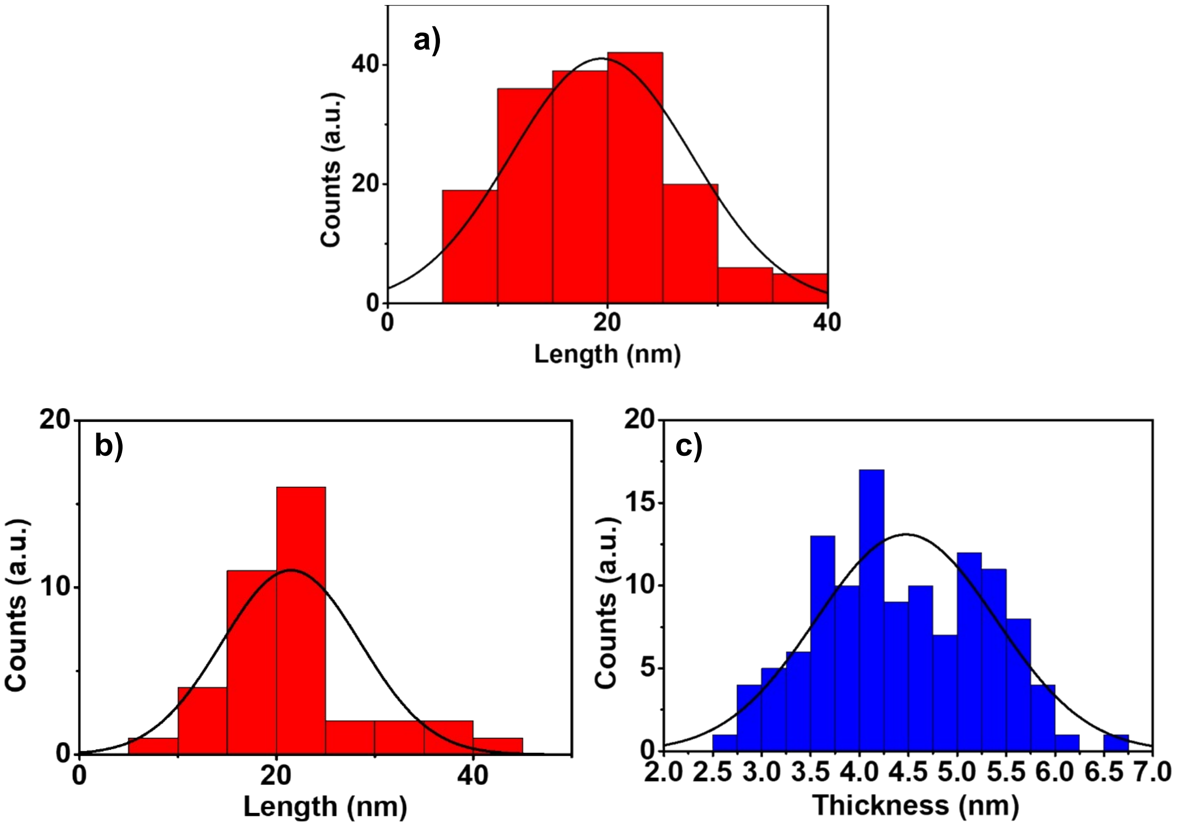

**Figure S2:** Histograms of $\mathrm{LHP}_{\mathrm{OLA}}$ (a) TEM image and (b-c) HAADF-STEM image.

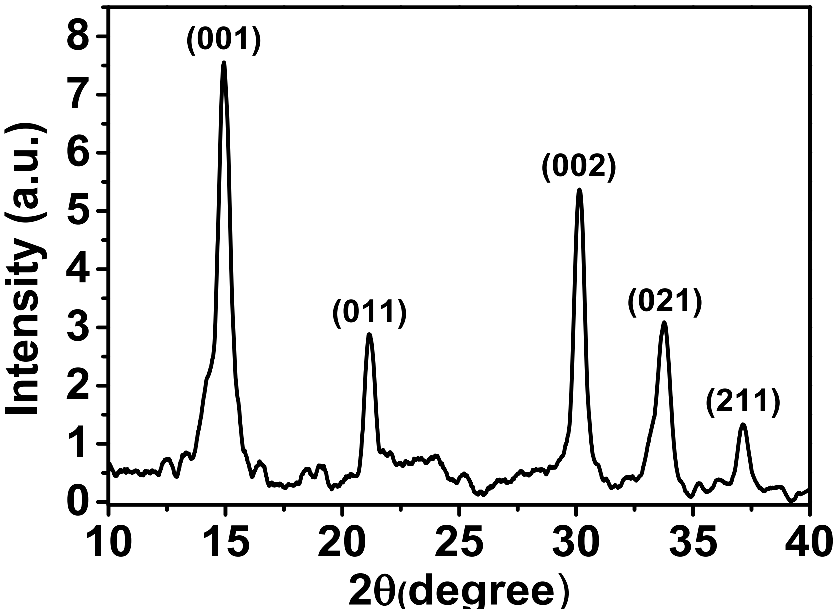

**Figure S3:** X-ray diffraction pattern of $MAPbBr_3$ nanoplatelets, measured in a capillary tube with a diameter of 0.5 mm.

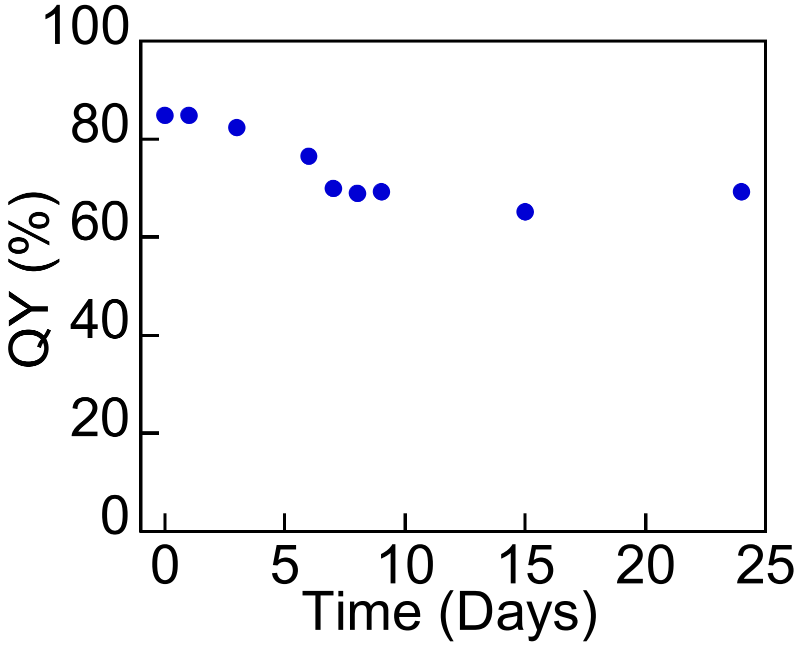

**Figure S4:** Chemical stability of the $LHP_{OLA}$ colloid; the photoluminescence quantum yield was recorded for 25 days.

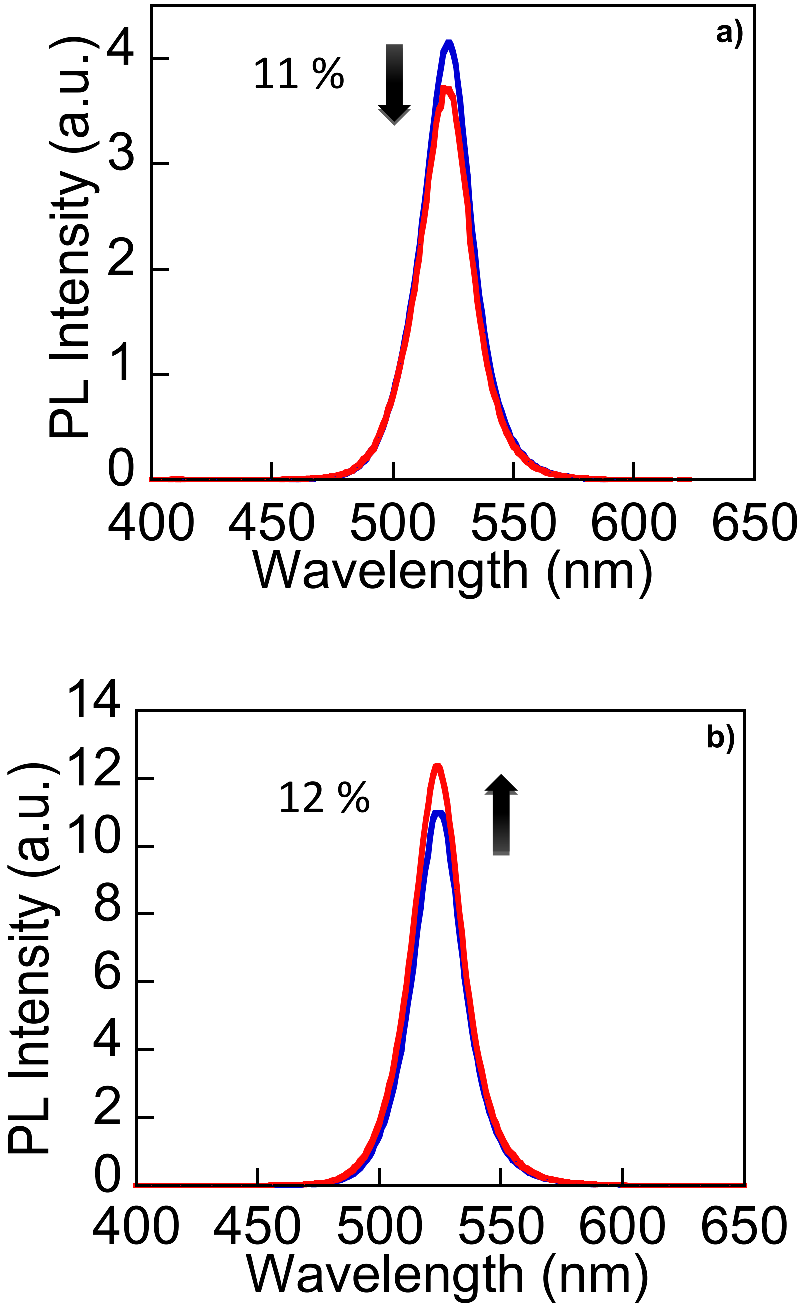

**Figure S5:** Photostability of the $LHP_{OLA}$ colloid, before (blue line) and after irradiation (red line) with (a) xenon lamp ($\lambda_{ex}$=365 nm; irradiation time = 4 hours) and (b) picosecond pulse laser (0.15 mW, 20 MHz; $\lambda_{ex}$=375 nm; irradiation time= 2 hours).

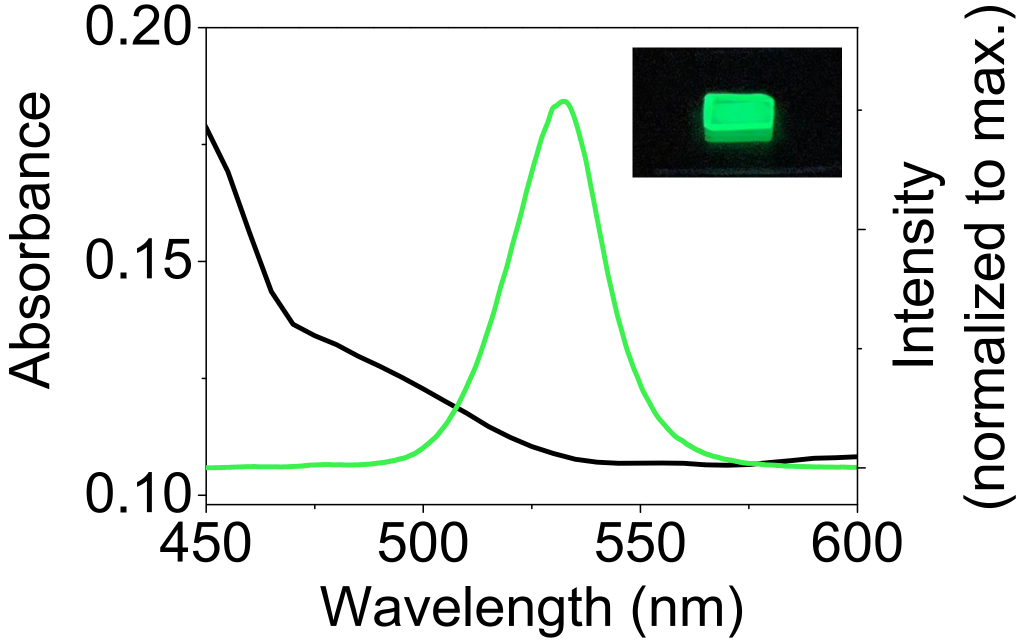

**Figure S6:** Absorption and emission spectra of a $LHP_{OLA}$ thin film prepared by drop casting.

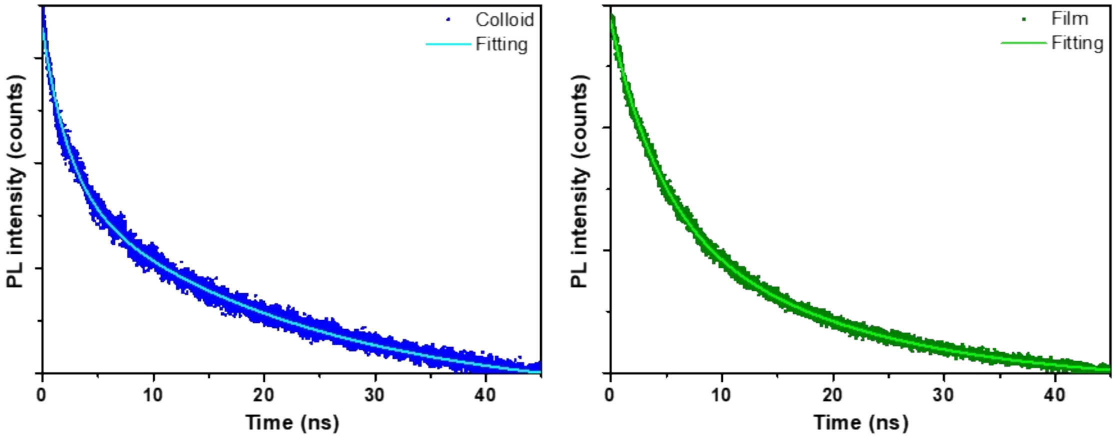

**Figure S7:** Time-resolved photoluminescence lifetime of $LHP_{OLA}$ colloid (left) and b) $LHP_{OLA}$ thin film (right).

**Table S1:** Rate decays of the photoluminescence lifetime of $LHP_{OLA}$ colloid and $LHP_{OLA}$ thin film.

| *Sample* | $\chi^2$ | $\tau$ (ns) | $\tau_1$ ($A_1$) | $\tau_2$ ($A_2$) |
|---|---|---|---|---|
| ***Colloid*** | 1.2 | 20.1 | 2.3 (7.16%) | 22.2 (92.84%) |
| ***Thin Film*** | 1.1 | 13.8 | 4.1 (21.16%) | 16.5 (78.84%) |

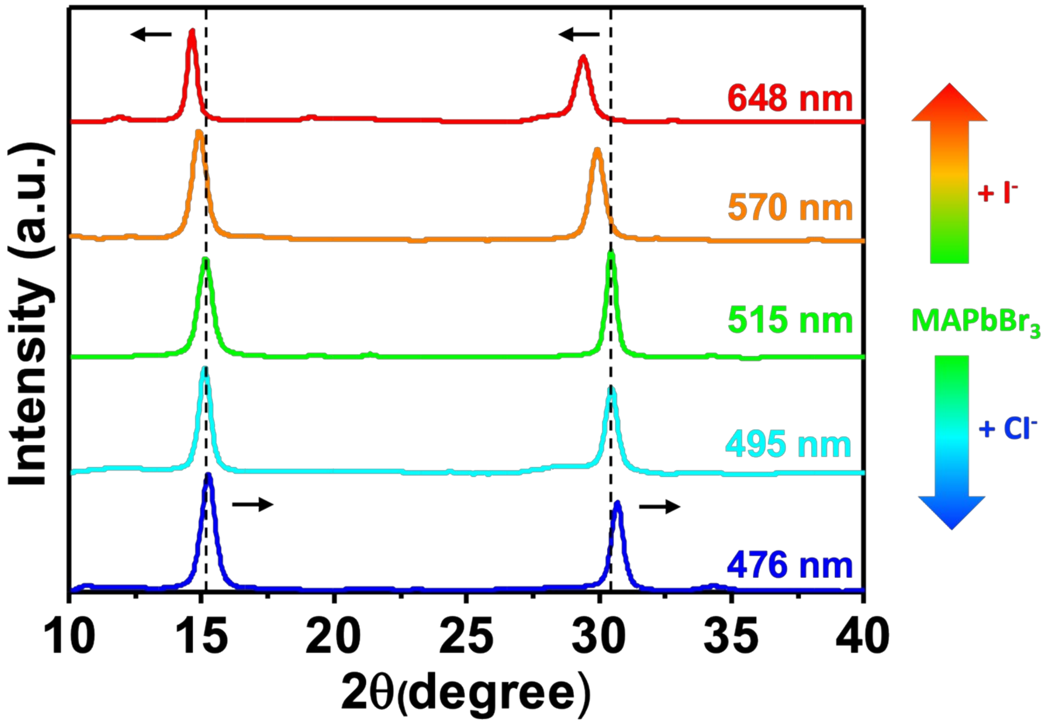

**Figure S8:** Comparative X-ray diffraction patterns of $LHP_{OLA}$ nanoplatelets, prepared before (MAPbBr3 NPLs, emission centered at 515 nm) and after the halide exchange with $Cl^-$ (emission centered at 495 nm and 476 nm), and $I^-$ (emission centered at 570 nm and 648 nm). Samples were measured using a parallel beam geometry in the symmetric reflection mode under ambient conditions.

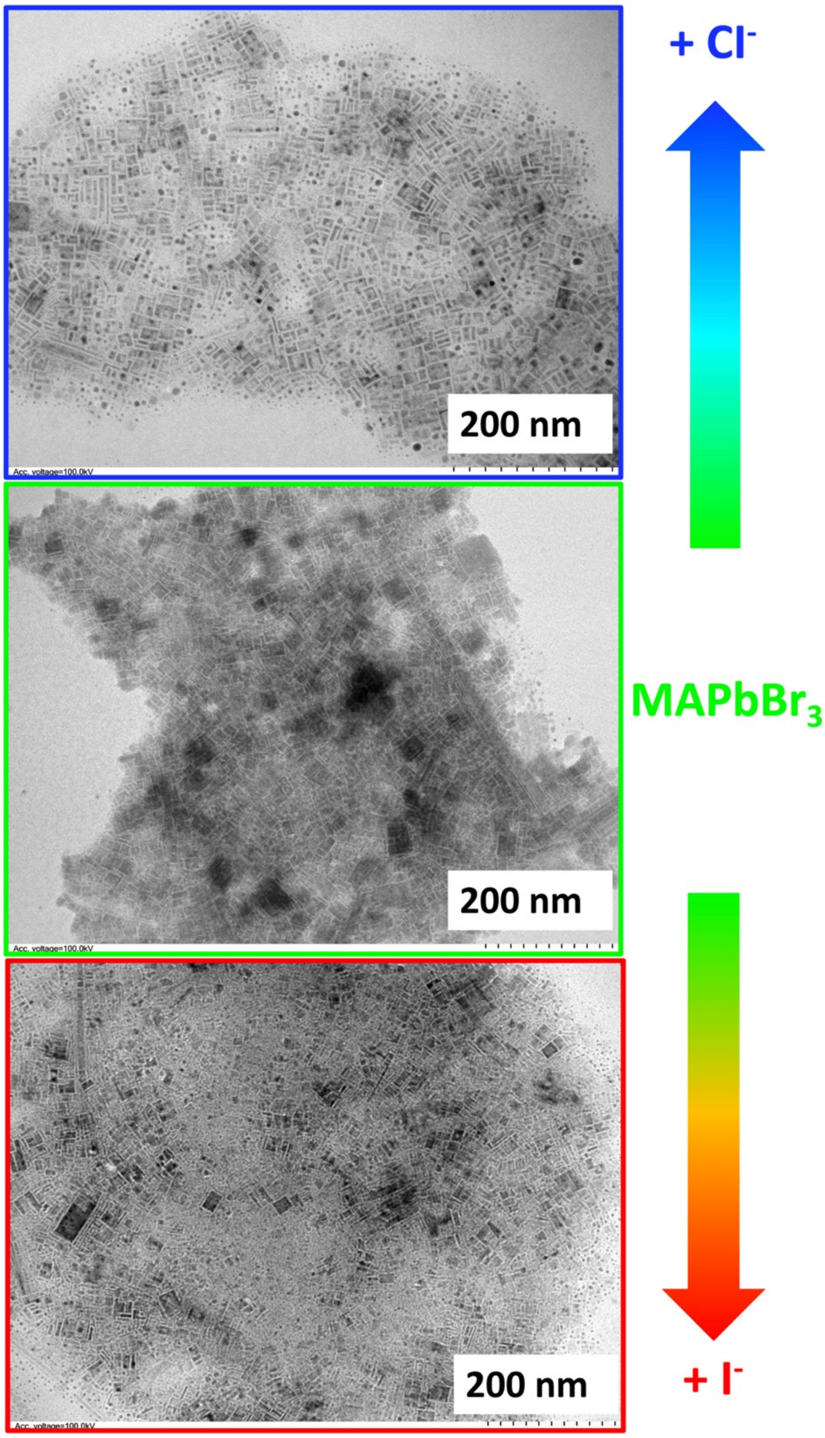

**Figure S9:** TEM images of $LHP_{OLA}$ NPLs before ($MAPbBr_3$) and after the anion exchange with chloride (emission centered at 411 nm), and iodide (emission centered at 570 nm). Scale bar: 200 nm.

## References:

1. Papavassiliou, G. C.; Pagona, G.; Karousis, N.; Mousdis, G. A.; Koutselas, I.; Vassilakopoulou, A., Nanocrystalline/microcrystalline materials based on lead-halide units. *Journal of Materials Chemistry* **2012,** *22* (17), 8271-8280.

2. Tong, Y.; Bohn, B. J.; Bladt, E.; Wang, K.; Müller-Buschbaum, P.; Bals, S.; Urban, A. S.; Polavarapu, L.; Feldmann, J., From Precursor Powders to CsPbX3 Perovskite Nanowires: One-Pot Synthesis, Growth Mechanism, and Oriented Self-Assembly. *Angewandte Chemie International Edition* **2017,** *56* (44), 13887-13892.