Supporting Information for:

# Colloidal Synthesis of Quantum Confined Single Crystal $CsPbBr_3$ Nanosheets with Lateral Size Control up to the Micrometer Range

*Javad Shamsi,[†&] Zhiya Dang,[†] Paolo Bianchini,[‡] Claudio Canale,[‡] Francesco Di Stasio,[†] Rosaria Brescia,[†] Mirko Prato[†]* and Liberato Manna[†]*.*

[†] Nanochemistry Dept., Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

[&] Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso, 31, 16146, Genova, Italy

[‡] Nanophysics Dept., Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

**Corresponding Authors:** mirko.prato@iit.it, liberato.manna@iit.it

**Materials:**

Lead(II) bromide ($PbBr_2$, 99.999% trace metals basis), cesium carbonate ($Cs_2CO_3$, reagentPlus, 99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OlAm, 70%), oleic acid (OlAc, 90%), Octanoic acid (OctAc, 99%), Octylamine (OctAm 99,5%), Hexane (anhydrous, 95%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

**Methods:**

**Preparation of Cesium-oleate solution:**

0.032 g $Cs_2CO_3$ and 10 mL OlAc were loaded into 25 mL 3-neck flask, dried for 1h at 120 ºC under vacuum, and then heated under $N_2$ to 140 ºC until all $Cs_2CO_3$ reacted with OlAc.

**Synthesis of $CsPbBr_3$ NSs**:

10 mL ODE, 0.013g $PbBr_2$, 250 µL OlAc, 250 µL OlAm, and a proper volume of OctAm and OctAc (e.g. 400 µL to obtain nanosheets – NSs – of lateral size close to 1 µm, see main text for details) were loaded into a 25 mL 3-neck flask and dried under vacuum for 20 minutes at 100 ºC. After complete solubilization of the $PbBr_2$ salt, the temperature was increased to 150 ºC under $N_2$ and 1 mL of Cs-oleate solution (prepared as described above) was swiftly injected. After 5 minutes, the reaction mixture was slowly cooled to room temperature using a water bath.

**Isolation and purification of $CsPbBr_3$ NSs**:

To collect the NSs, 10 mL of hexane was added to the crude solution and then the mixture was centrifuged at 700 RPM for 5 min. After centrifugation, the supernatant was discarded and the NSs were redispersed in hexane. It has to be noted that, due to the large area of our nanosheets, they show a natural tendency to aggregate in solution over time, and we observed a gradual shift of the PL wavelength from blue to green (i.e. towards the emission value of non-confined bulk-like $CsPbBr_3$ structures). This effect is even stronger on cleaned samples, where the centrifugation step is likely responsible for a not-negligible loss of surface ligands, thus facilitating the aggregation of nanosheets and their evolution to thicker assemblies. It is nonetheless interestingly to remark that, if fresh diluted solutions are used to prepare films of these NSs,

either by spin coating or drop casting, followed by gentle dipping in pure solvent to remove the excess of organics (as done in the preparation of the samples for AFM characterization, see main text), the quantum confinement can be preserved.

**Characterization:**

Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. HRTEM and SAED analyses were performed on a JEOL JEM-2200FS microscope equipped with a Schottky emitter operated at 200 kV, a CEOS spherical aberration corrector of the objective lens, and an in-column energy filter (Omega-type). The background of FFT for the HRTEM images was subtracted using ImageJ. Samples were prepared by dropping diluted NSs suspensions onto holey carbon film-coated 400 mesh copper grids. The UV-Vis absorption spectra were recorded on a Varian Cary 5000 UV−vis−NIR spectrophotometer. The PL spectra were collected by Varian Cary Eclipse Fluorescence Spectrophotometer. The NSs solutions were prepared by diluting in Hexane (20 μL in 1 mL), in 1 cm path length quartz cuvettes. PLQY and time-resolved PL lifetime measurements were carried out with an Edinburgh Instruments fluorescence spectrometer (FLS920) equipped with a Xenon lamp with monochromator for steady-state PL, and a time-correlated single photon counting unit coupled with a pulsed laser diode ($\lambda$ = 405 nm, pulse width = 50 ps) for time-resolved PL. PLQY values were obtained from $CsPbBr_3$ NSs toluene solutions in a quartz cuvette and diluted to 0.1 optical density at the excitation wavelength ($\lambda$ = 450 nm) using a calibrated integrating sphere. AFM images were acquired employing a Nanowizard III (JPK Instruments, Germany) in intermittent contact mode, in air. Single-beam uncoated silicon cantilevers (OMCL-AC160TS-W, Olympus) with a nominal tip radius of curvature of 10 nm and typical cantilever resonance frequency of 300 kHz were used. Quantitative Imaging mode (QI – JPK Instruments) was used in order to determine simultaneously sample topography, adhesion and elasticity (Young's Modulus). QI is based on the acquisition of a large set of force-distance curves and on the reconstruction of the sample topography from the tip position at the specific force load. Local mechanical properties of

the sample can be extracted from the analysis of the acquired curves. QI images deriving from 128x128 force-distance (FD) curves, with maximum force load of 4 nN. For each curve, tip speed was 20 µm/s and curve length was 100 nm. For the determination of the absolute value of Young's Modulus each single FD curve was fitted with the Hertz model, the tip was approximated as spherical and with a radius of 30 nm. The fluorescence imaging has been carried out by a Nikon A1 MP confocal microscope (Nikon Instruments, Tokyo, Japan). For all the images we excited the sample with a pulsed laser at 405nm and 40 MHz of repetition rate (LDH-D-C-405, PicoQuant GmbH, Berlin, Germany). We used a 100x 1.4 NA oil immersion objective and we kept the pinhole size at 1 Airy unit. The pixel dwell time was 5 µs and 8 line averages. The fluorescence was acquired over two channels, in the 425 - 475 nm and in the 500 - 550 nm spectral windows, by two GaAsP photomultipliers tubes respectively. The sample was prepared by dropcasting 20 µl of nanosheets in Hexane solution. In order to reduce the evaporation, we sealed the coverslip onto a glass slide.

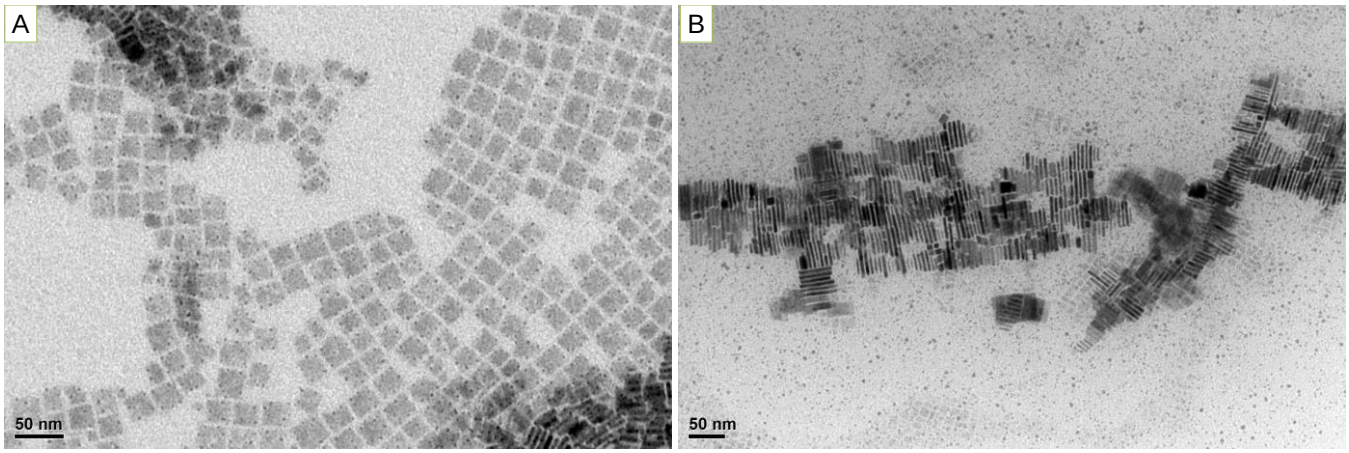


***Figure S1:*** *TEM images of NPLs prepared by using the solution of Cs-oleate in OlAc instead of hot solution of Cs-oleate in ODE. Reaction conditions: 0.013 $PbBr_2$, 10 mL ODE, 500µL OlAc, 500µL OlAm. Reaction temperature, (A) 50°C, (B) 150 °C.*

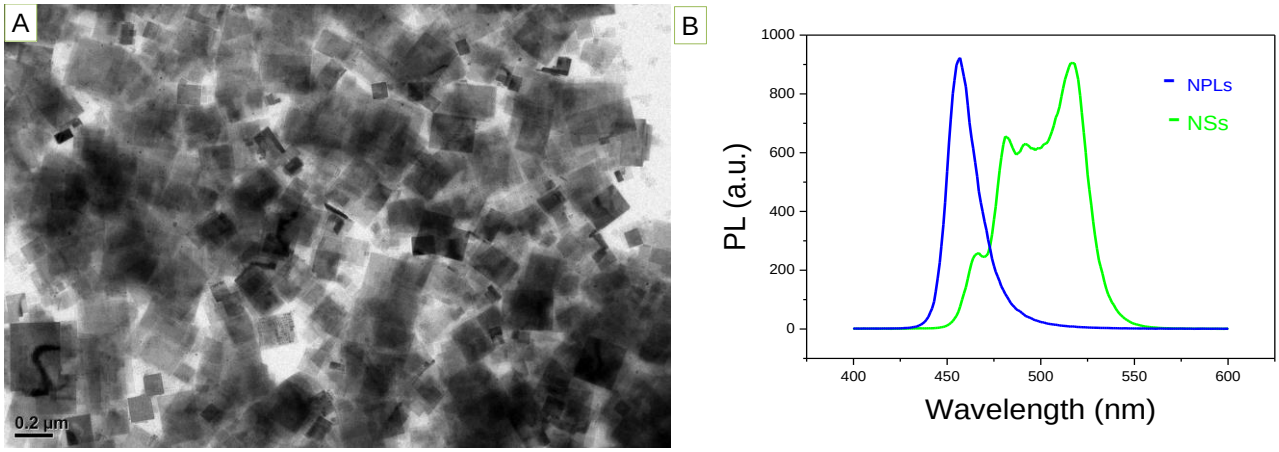


***Figure S2:*** *Promoting the growth in lateral size by increasing reaction time from few seconds up to two minutes. Reaction conditions: 0.013 $PbBr_2$, 10 mL ODE, 500µL OlAc, 500µL OlAm, reaction temperature: 150 ˚C. (A) TEM image of NSs synthesized by increasing the reaction time; (B) Comparison of the PL spectra of NPLs (figure S1B) with that of as-prepared NSs.*

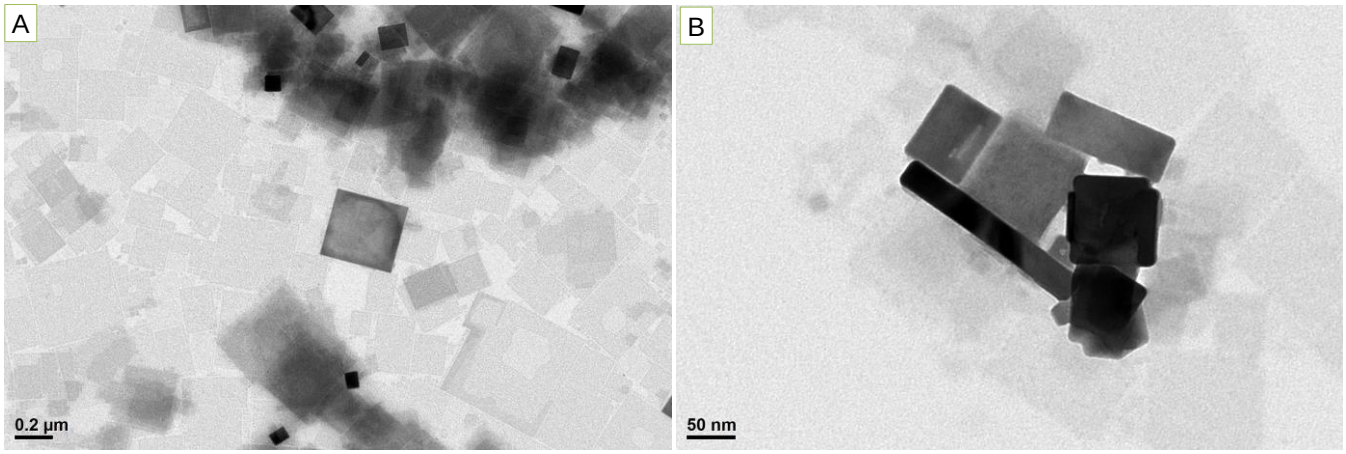


***Figure S3:*** *Role of short ligands. TEM images of products which were synthesized by adding only (A) 500 µL OctAc or (B) 500 µL OctAm. Reaction conditions: 0.013 $PbBr_2$, 10 mL ODE, 250µL OlAc, 250µL OlAm, reaction temperature: 150 ˚C, reaction time: 5 min.*

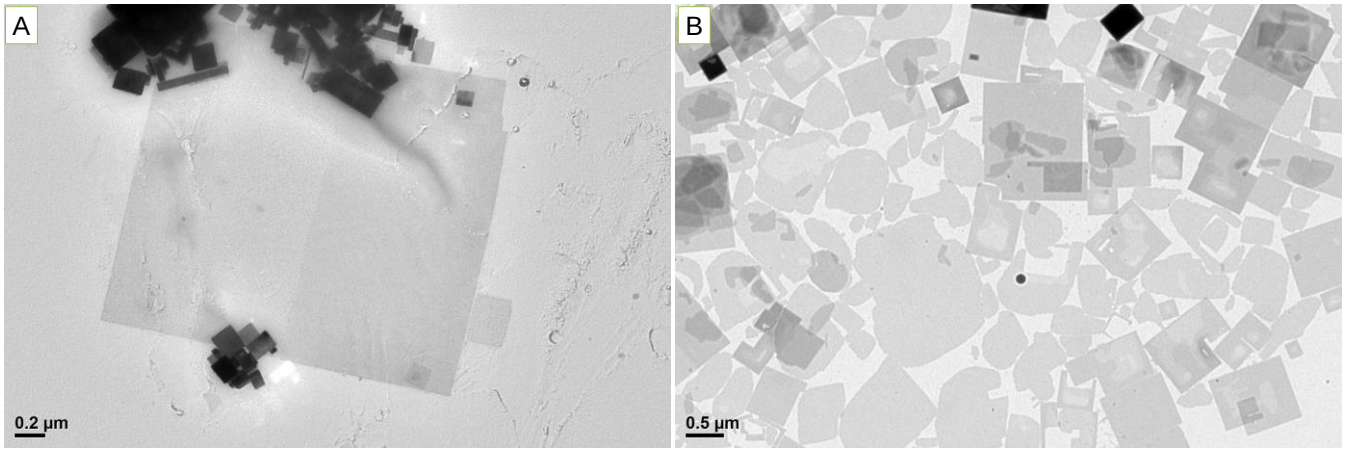


***Figure S4:*** *The effect of reaction temperature. TEM images of products at (A) 160˚C (B) 140˚C. Reaction condition: 0.013 $PbBr_2$, 10 mL ODE, 250µL OlAc, 250µL OlAm, 500 µL OctAc, 500 µL OctAm, , reaction time: 5 min.*

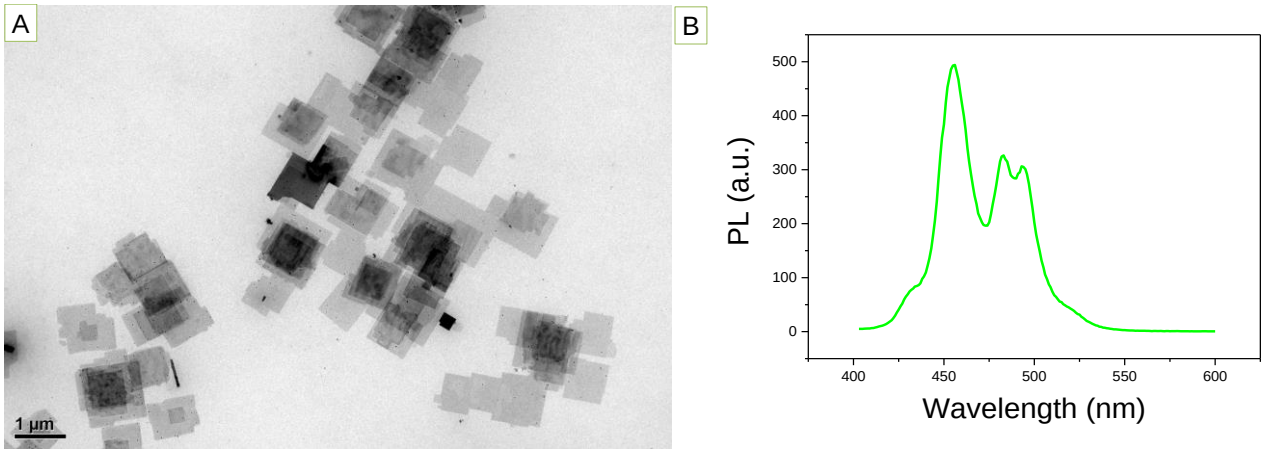


***Figure S5:*** *The result of increasing reaction time up to 6 min. (A) TEM image and (B) PL spectrum of aggregated NSs. Reaction conditions: 0.013 $PbBr_2$, 10 mL ODE, 250µL OlAc, 250µL OlAm, 500 µL OctAc, 500 µL OctAm, , reaction temperature: 150 ˚C.*

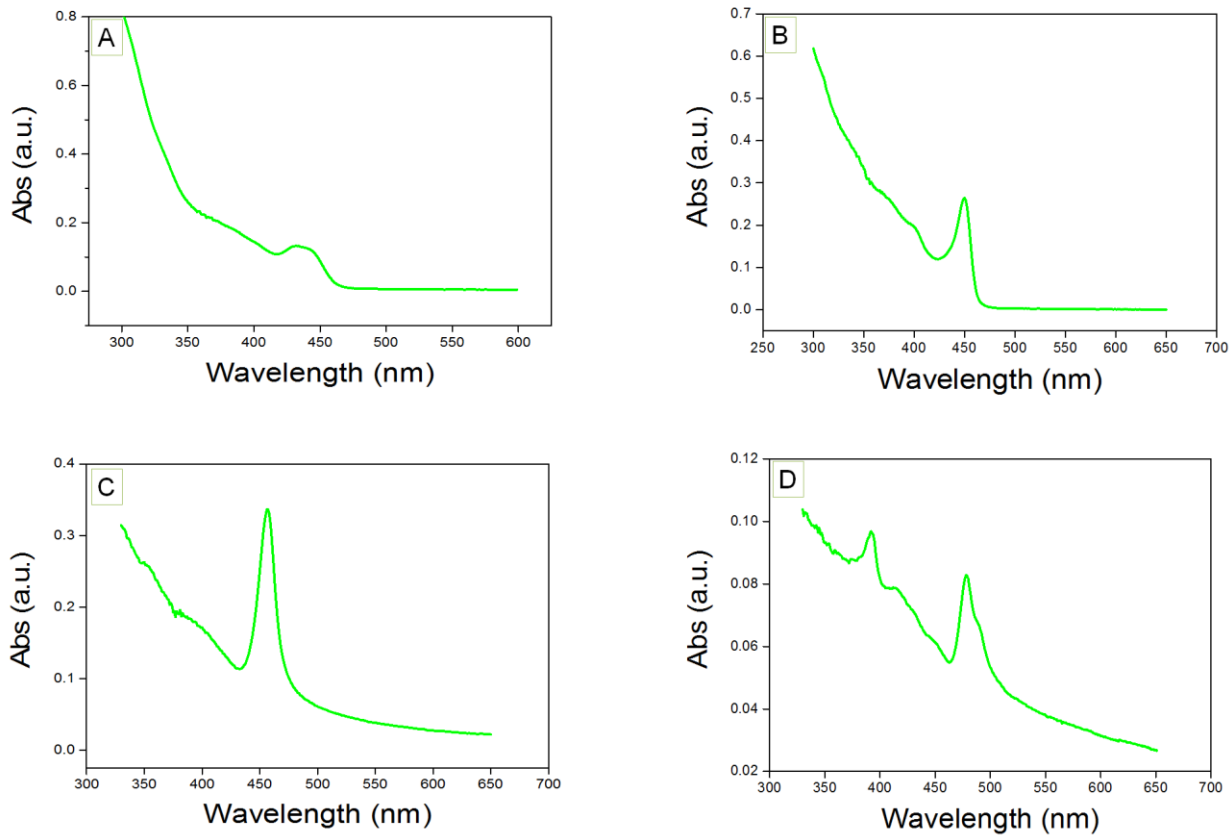


***Figure S6:*** *Absorption spectra of samples of $CsPbBr_3$ NSs of different lateral sizes prepared with different amounts of short ligands. Reaction conditions: 0.013 $PbBr_2$, 10 mL ODE, 250µL OlAc, 250µL OlAm, reaction temperature: 150 °C, reaction time: 5 min, (A) 250 µL OctAc, 250 µL OctAm, (B) 300 µL OctAc, 300 µL OctAm (C) 400 µL OctAc, 400 µL OctAm (D) 500 µL OctAc, 500 µL OctAm.*

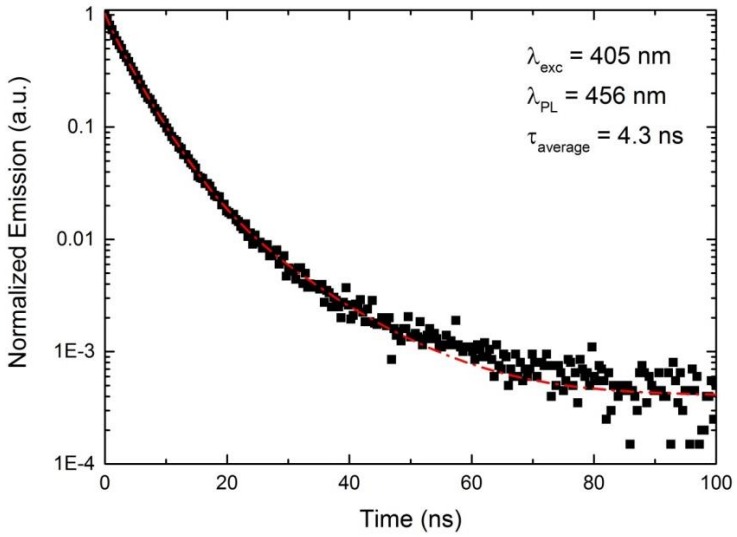


***Figure S7:*** *PL decay measured at the PL peak ($\lambda_{PL}$= 456 nm) for a diluted toluene solution of $CsPbBr_3$ nanosheets. The PL decay fitting was carried out with a three-exponential function:* $\boldsymbol{I = I_1 e^{(-t/\tau_1)} + I_2 e^{(-t/\tau_2)} + I_3 e^{(-t/\tau_3)}}$*. The results of the fitting procedure are summarized in Table S1. Importantly the 4.12 ns component ($\tau_2$, see table S1) accounts for more than 80% of the PL decay, while an initial fast decay ($\tau_1$ = 1.16 ns) represents only the 10% of the total decay. The time-resolved PL measurement was carried out using a time-correlated single photon counting unit and a pulsed laser diode as excitation source ($\lambda$ = 405 nm, pulse width = 50 ps).*

**Table S1**

| | **Value** | **Std. error** |
|---|---|---|
| $\mathbf{I_1}$ | 0.10 | 0.01 |
| $\boldsymbol{\tau_1}$ **(ns)** | 1.16 | 0.1 |
| $\mathbf{I_2}$ | 0.835 | 0.008 |
| $\boldsymbol{\tau_2}$ **(ns)** | 4.12 | 0.08 |
| $\mathbf{I_3}$ | 0.065 | 0.012 |
| $\boldsymbol{\tau_3}$ **(ns)** | 11.6 | 0.8 |

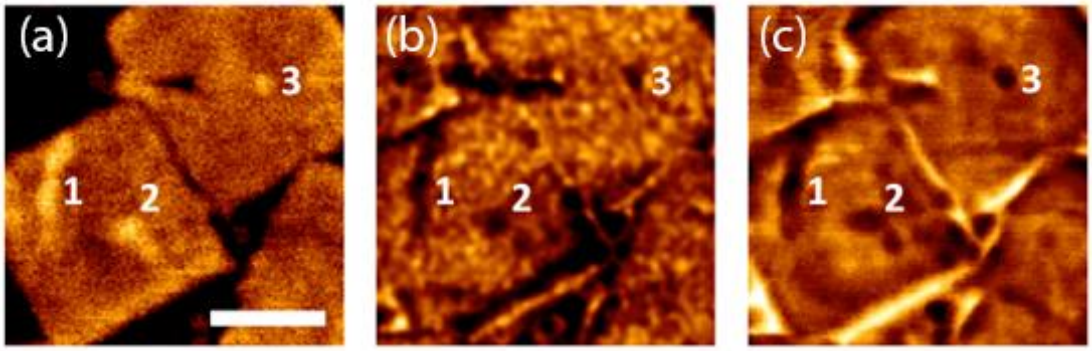


***Figure S8:*** *Few protruding features (indicated with 1, 2, 3) are displayed on the flat NSs surface in AFM topographical image acquired in QI mode (a). The adhesion between the AFM tip and the sample is significantly reduced on these spots, appearing as darker areas in the high-resolution adhesion map (b). At the same time, the same areas are also characterized by smaller Young's moduli (c). These observations suggest that the protruding regions are the residue of the organic molecules, originally capping the nanosheets. Scale bar: 300 nm. Data scale: 2 nm (a), 1.5 nN (b), 800 MPa (c).*

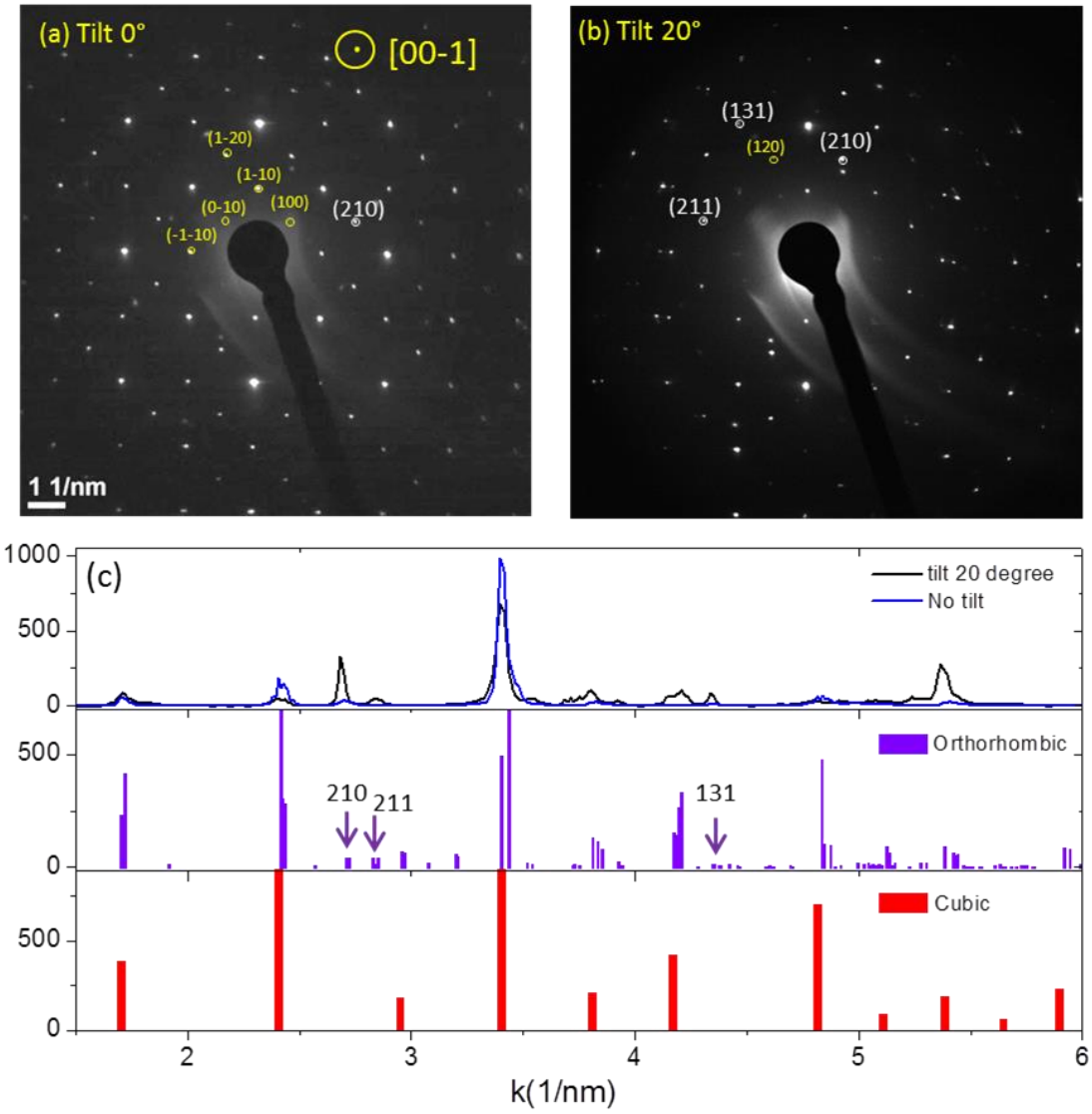


***Figure S9:*** *1. SAED patterns from the thin area of NS of Fig 1a in the manuscript with (a) no tilt and (b) 20° tilt. (c) Corresponding azimuthally integrated patterns in comparison with the powder XRD data for an orthorhombic phase (ICSD 97851) and a cubic phase (ICSD 29073). The distinctive peaks for orthorhombic are labelled by arrows and marked in the diffraction patterns.*

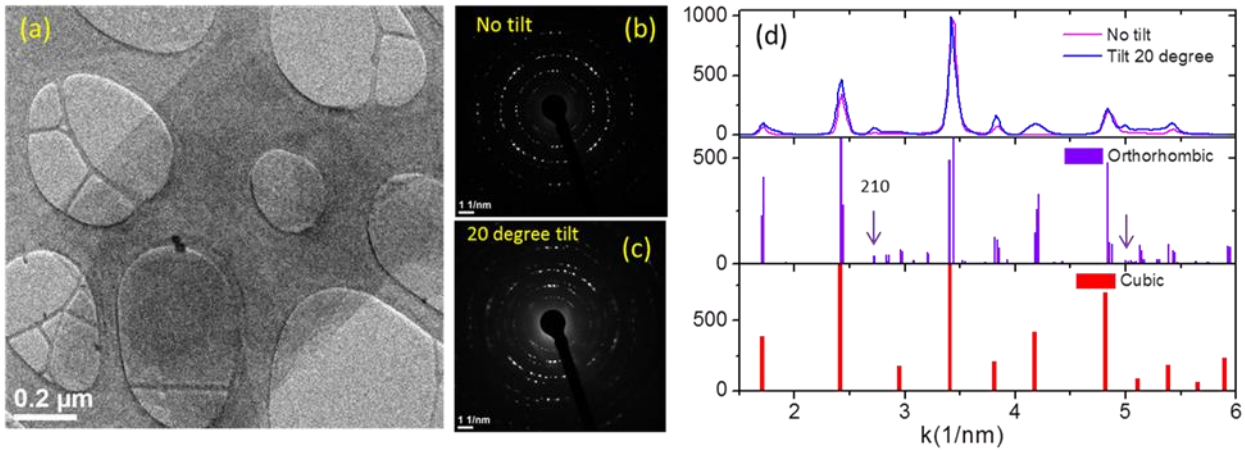


***Figure S10:*** *(a) TEM image of a region including multiple NSs and (b,c) SAED pattern with (b) no tilt and (c) 20° tilt. (d) Corresponding azimuthally integrated patterns in comparison with the XRD data for orthorhombic and cubic phases from database.*

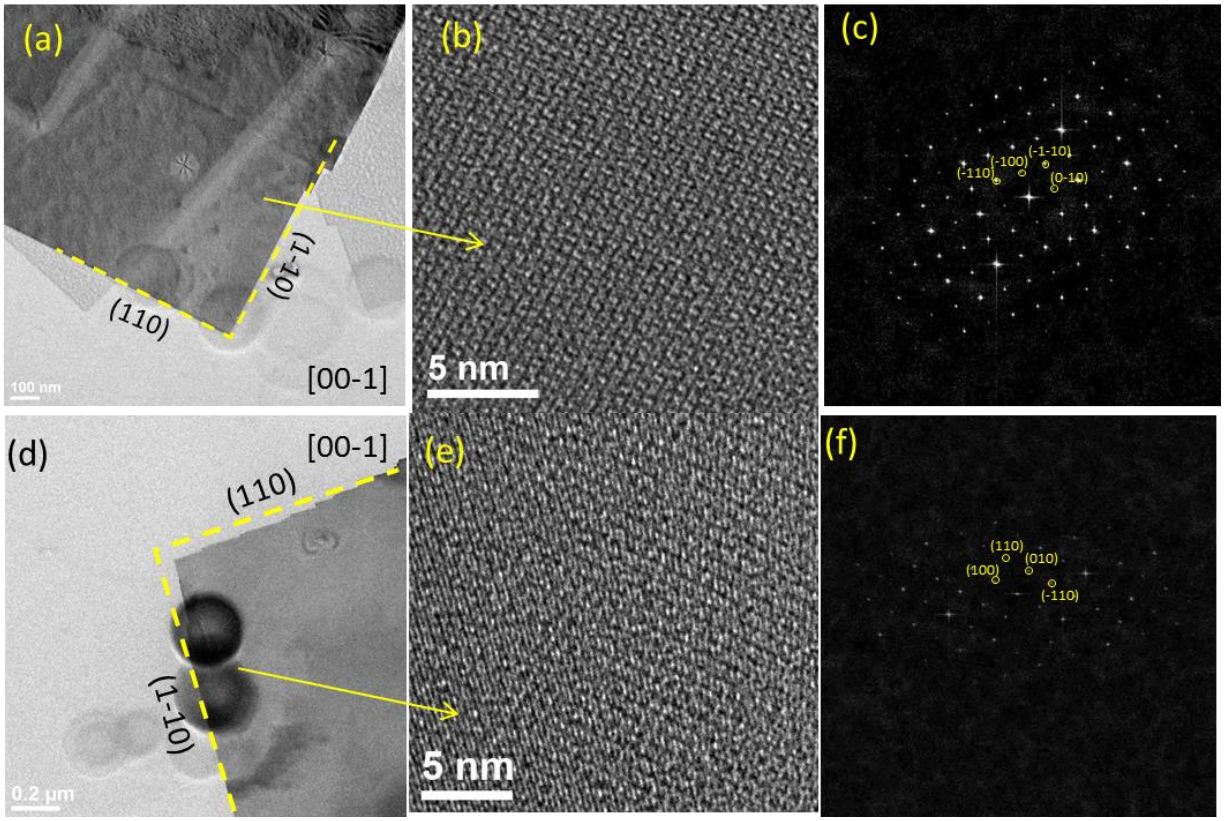


***Figure S11:*** *Low magnification TEM image,(b) HRTEM and (c) corresponding FFT showing orthorhombic phase; 5μm NS: (d) low magnification TEM image,(e) HRTEM and (f) corresponding FFT showing orthorhombic phase.*

**Anion exchange on Nanosheets**

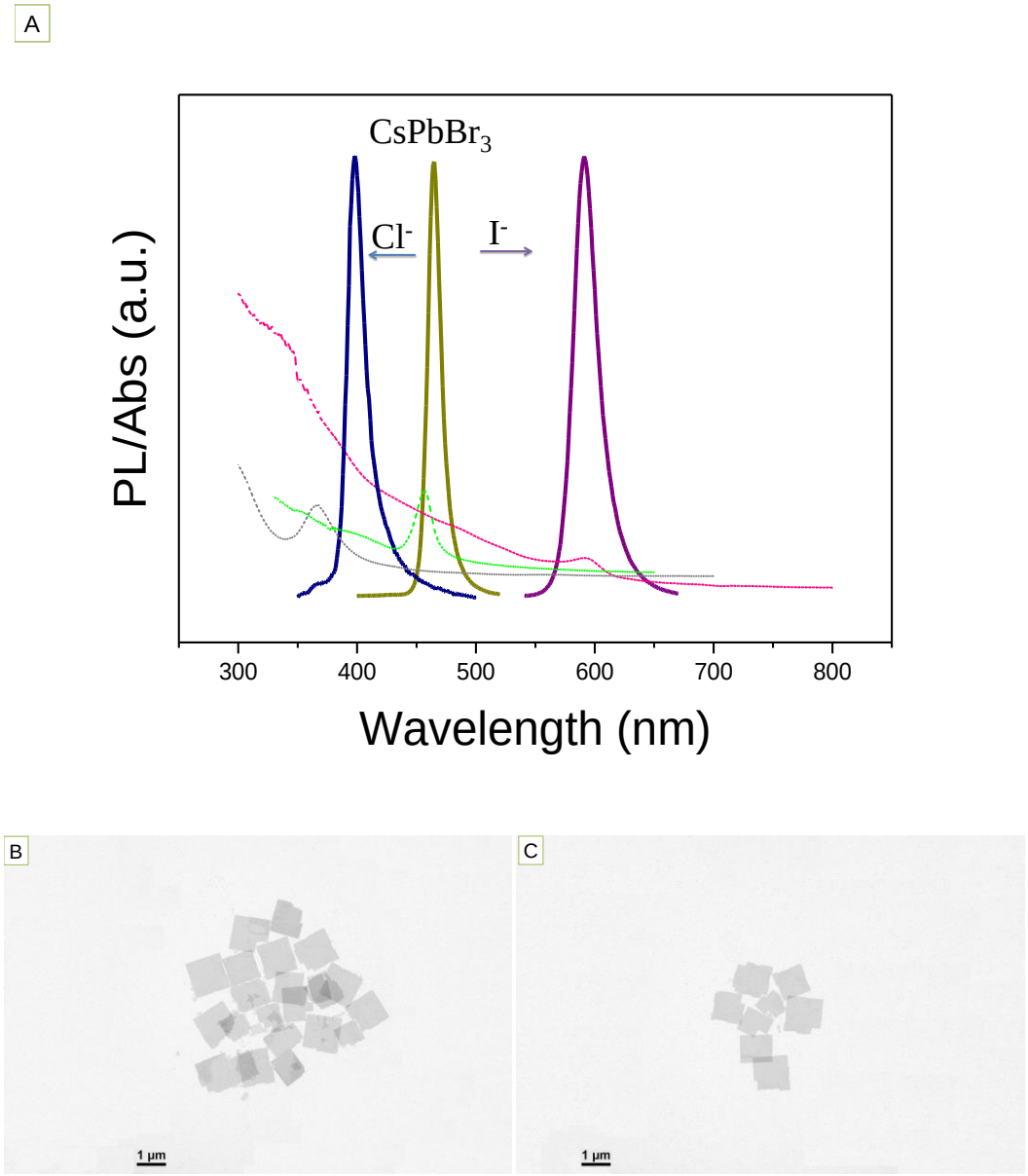


***Figure S12:*** *Results of anion exchange reactions on the NSs: (A) PL and absorption spectra of the initial $CsPbBr_3$ NSs, and of the corresponding samples after exchange with $Cl^-$ and $I^-$; TEM images of (B) $CsPbCl_3$ NSs (C) $CsPbI_3$ NSs. These exchange reactions were carried out in air as described in our previous work[1]: briefly, 50µL of crude $CsPbBr_3$ NSs solution was dispersed in 3 mL of toluene and different amount of oleyl ammonium iodide or tetrabutyl ammonium chloride were added[1].*

***Supplementary References:***

*Akkerman, Q. A.; D’ Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. J. Am. Chem. Soc. 2015, 137, 10276−10281.*