## **Supporting information**

# Ligand-assisted monolayer thickness tailoring of highly luminescent colloidal CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (X=Br, I) perovskite nanoplatelets

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#### Materials and methods.

**Materials.** Methylamine (CH<sub>3</sub>NH<sub>2</sub>, 40% in methanol) was purchased from ABCR GmbH & Co KG. Lead (II) iodide (PbI<sub>2</sub>, 99.999% trace metals basis), lead (II) bromide (PbBr<sub>2</sub>, 99.999% trace metals basis), N,N-Dimethylformamide (DMF, anhydrous, 99.8%), hydroiodic acid (57% in water), hydrobromic acid (48% in water, 99.99%), acetonitrile anhydrous (CH<sub>3</sub>CN, 99.8%) and hexane anhydrous (95%) were purchased from Sigma-Aldrich. Chloroform (>99%) and toluene (>99%) were purchased from Merck Millipore. Oleylamine (approximate C18-content 80-90%) was purchased from Acros Organics. Oleic acid (97%) was purchased from VWR Chemicals.

**Methylammonium iodide synthesis.** Briefly, in a 500 ml flask, 27.86 ml CH<sub>3</sub>NH<sub>2</sub>, 40% in methanol, was mixed with 100 ml of ethanol. Then, at room temperature, 30 ml 57% water solution of the HI was added dropwise with continuous stirring. Obtained solution was placed in rotary evaporator at 60°C for removing all solvents. Then after several time washing with diethyl ether, MAI was dissolved in ethanol and precipitated with diethyl ether twice. Then, for obtaining highly pure crystals, MAI was dissolved in 80 ml of hot ethanol and placed in refrigerator at -3°C for re-crystallization.

**Methylammonium bromide synthesis.** In 500 ml flask, 27.86 ml CH<sub>3</sub>NH<sub>2</sub>, 40% in methanol, was mixed with 100 ml of ethanol. Then8.5 ml 48% water solution of the HBr was added dropwise with continuous stirring at room temperature. Obtained solution was placed in rotary evaporator at 60°C for removing all solvents. After several times of washing with diethyl ether, MABr was dissolved in ethanol and precipitated with diethyl ether twice.

#### Nanoplatelets (NPLs) synthesis.

All syntheses were carried at room temperature in air with average room humidity ~45%.

CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs. CH<sub>3</sub>NH<sub>3</sub>Br (0.0112g, 0.1 mmol) and PbBr<sub>2</sub> (0.0367, 0.1 mmol) were dissolved in 1 ml DMF forming 0.1 mM solution. Then, 200  $\mu$ l of the Oleic acid and different amount of the Oleylamine for different thicknesses of NCs were added. Next, 100  $\mu$ l of this mixture was injected into 3ml toluene or chloroform. Bright emitting (PL = 447-520 nm) NPLs were formed within seconds (*See supplementary video*). For purification, obtained NPL solution was precipitated once with acetonitrile/toluene (1:1) mixture followed by centrifugation at 9000 rpm for 2 min. Thus obtained NCs were fully dispersible in nonpolar solvents such as hexane, toluene, chloroform etc. Detailed synthesis procedure presented in Table S1:

DMF,	Oleic	Oleylamine,	Perovskite	Toluene,	PL peak,	Volume of	Thickness,	Lateral
ml	acid, µl	μΙ	precursor, µl	ml	nm	Acetonitrile/Toluen	nm	size, nm
						e mixture for		
						washing, ml		
1	200	16	100	3	514	2	2.6±0.2	13.8±1.8
1	200	18	100	3	511	2	-	-
1	200	21	100	3	488	2.5	2±0.1	11.6±2.4
1	200	24	100	3	473	2.5	-	-
1	200	28	100	3	452	3	-	-
1	200	30	100	3	447	3.5	1.6±0.1	10.7±1.5
1	200	60	100	3	447	3.5	1.6±0.1	5.4±0.8

Table S1. Parameters of synthesis of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs with different thicknesses

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs. CH<sub>3</sub>NH<sub>3</sub>I (0.0159g, 0.1 mmol) and PbI<sub>2</sub> (0.0461, 0.1 mmol) were dissolved in 1 ml of DMF forming 0.1 mM solution. Then, 200  $\mu$ l of the Oleic acid and corresponding amounts of the Oleylamine for different thicknesses of NPLs were added. Next, 100  $\mu$ l of this mixture was injected into anti-solvent (chloroform, toluene and chloroform-toluene mixture) media. Obtained NC solution (only for NCs with 722 nm 630 nm PL) and was precipitated by centrifugation with 15400 rpm at -10° for purification. Obtained precipitate was re-dissolved in hexane. Detailed synthesis procedure presented in Table S2:

DMF,	Oleic acid,	Oleylamine, µl	Perovskite	Chloroform,	Toluene,	Chlorofor	PL peak,	Lateral
ml	μΙ		precursor,	ml	ml	m	nm	size, nm
			μl			+		
						Toluene,		
						ml		
1	200	50	100	3	-	-	722	22.3±6
1	200	100	100	3	-	-	683	Wide
								distribution
1	200	150	100	3	-	-	628	-
1	200	200	100	3	-	-	592	-
1	200	250	10	-	-	2 + 1	578	-
1	200	250	10	-	3	-	549	-

Table S2. Parameters of synthesis of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs with different thicknesses

#### **Material characterization**

**Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM).** TEM and HRTEM images were recorded using a PHILIPS CM 300 UT high-resolution transmission electron microscope (300 kV acceleration voltage, 0.17 nm point resolution at Scherzer defocus), equipped with a LaB<sub>6</sub> filament and a CCD camera with an image size of 2048×2048 pixels. Samples for TEM were prepared by casting one drop of the NC solution in hexane or toluene onto a standard copper grid coated with a continuous amorphous carbon film. The size distribution and thicknesses of NCs were obtained from the TEM image with ImageJ software.

X-ray Powder Diffraction (XRD). X-ray diffraction analysis was performed by classical ex situ Bragg – Brentano geometry using a Panalytical X'pert powder diffractometer with filtered Cu-K $\alpha$ radiation and an X'Celerator solid-state stripe detector. Hexane solution of nanocrystals was drop casted onto glass and dried in glove box at 60°C for further measurements.

**Optical measurements.** The absorption spectra of the NC dispersions were taken on a Perkin-Elmer Lambda 950 spectrometer and emission spectra on a Jasco spectrofluorometer FP-8500. The emission spectra were corrected for the wavelength-dependent spectral responsivity of the fluorometer.

**Lifetime measurements**. The photoluminescence decay curves were measured by exciting the dispersed nanoparticle samples using a 405 nm laser diode, driven by a pulse generator, and creating a flux density of  $0.1 \mu J/cm^2$ . The emission was dispersed using an H10 monochromator (Jobin-Yvon), detected by a 9816 photomultiplier (EMI) and recorded using a digital oscilloscope TDS540 (Tektronix).

Absolute measurement of the **photoluminescence quantum efficiency** was carried out according to the method described by de Mello et al<sup>1</sup>. The samples were mounted in an integrating sphere, connected to an iHR 320 monochromator (Jobin-Yvon) with an optical fiber. The spectra were recorded with a Si CCD (Syncerity, Jobin-Yvon) camera and corrected for the spectral sensitivity of the setup, determined with the help of a calibrated Xe lamp (Hamamatsu).



**Figure S1.** PL spectra of the blue (447 nm) emitting NPLs with two different lateral size (5 nm and 11 nm) but same thickness of 1.6 nm.



**Figure S2.** The lateral size statistics of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs. a, d) blue (447 nm), b) cyan (488 nm) and c) green (514 nm) emitting CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs; e) statistical thickness distributions with respect to optical emission; f) NIR (722 nm) emitting CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs



**Figure S3.** Electron diffraction analysis of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs: a) exemplary diffraction pattern for NPLs with PL peak at 514 nm. b) Line profile obtained by radial averaging of the diffraction pattern and expected peak intensities for random orientation of the NPLs (red lines). The analysis confirms the perovskite crystal structure and points to a preferred <001> orientation of the NPLs on the carbon support grid.



**Figure S4.** Self-assembled superstructure of blue emitting (447 nm) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs. a) Bright-field TEM image. The marked areas (red and blue squares) and corresponding Fourier transformations indicate a 2D platelet superstructure b) Sketch of a possible OAm ligand overlapping. c) Proposed sketch of NPLs assembling with average distances between individual NPL measured from the TEM image.



Figure S5. a) Quantum size effect in CdTe quantum dots (QDs)<sup>2</sup>.
b) Quantum size effect in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> nanoplates (NPLs).



**Figure S6.** Additional TEM picture of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs. a) Red NPLs with PL peak at 683 nm; white dashed square indicated non-destroyed NPLs; yellow circles marks destroyed NPLs under high energy beam irradiation b) NIR NPLs with PL peak 722 nm. Differences in contrast of the NPLs display different thicknesses obtained nanocrystals.



Figure S7. Radiative ( $k_{rad}$ ) and non-radiative ( $k_{non-rad}$ ) rate for CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs (a) and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs with different PL emission peaks.

**Table S3.** PLQY, PL decay time, radiative  $(k_{rad})$  and non-radiative  $(k_{non-rad})$  rate for CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NPLs with different PL emission peaks.

PL Peak , nm	513	509	488	474	452	447
PLQY,%	89	-	50	-	-	35
Decay time T <sub>1/e</sub> , ns	11.9	8.4	5.8	6.6	5.7	5.6
k <sub>rad</sub> , s <sup>-1</sup>	$7.5 \times 10^{7}$	-	$8.6 \times 10^{7}$	-	-	$6.3 \times 10^{7}$
k <sub>non-rad</sub> , s <sup>-1</sup>	$0.9 \times 10^{7}$	-	$8.6 \times 10^{7}$	-	-	$11 \times 10^{7}$

**Table S4.** PLQY, PL decay time, radiative  $(k_{rad})$  and non-radiative  $(k_{non-rad})$  rate for CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NPLs with different PL emission peaks.

PL Peak , nm	722	683	628	592	578	549
PLQY,%	31	47	36	-	21	19
Decay time T <sub>1/e</sub> , ns	19.7	14.2	15.6	8.4	6.8	7.2
k <sub>rad</sub> , s <sup>-1</sup>	$1.5 \times 10^{7}$	$3.3 \times 10^{7}$	$2.3 \times 10^{7}$	-	$3.1 \times 10^{7}$	$2.6 \times 10^{7}$
k <sub>non-rad</sub> , s <sup>-1</sup>	3.5×10 <sup>7</sup>	$3.7 \times 10^{7}$	$4.1 \times 10^{7}$	-	$11 \times 10^{7}$	11.3×10 <sup>7</sup>

### Reference

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