# Monitoring the morphological evolution in mixed-

## dimensional lead bromide perovskite film with

## lamellar-stacked perovskite nanoplatelets

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#### **Experimental Methods**

#### Sample preparation

Lead bromide (PbBr<sub>2</sub>) and anhydrous dimethylformamide (DMF) were ordered from Sigma-Aldrich and methylammonium bromide (MABr) was purchased from Dyesol. The salt precursors were used without further purification. Octylammonium bromide (OABr) was synthesized by reacting HBr and octylamine in ethanol and further crystallized in a rotary evaporator. PbBr<sub>2</sub> was dissolved in anhydrous DMF with a mole concentration of 1M and spin-coated on acidic precleaned substrates at 3000 rpm for 15 s under argon atmosphere. Afterwards, the obtained PbBr<sub>2</sub> films were thermally annealed at 80 °C for 10 min under ambient conditions (25 °C, humidity 37 %). MABr and OABr were hand-milled in a mortar with a mole ratio 9:1 and placed in a heating plate at 100 °C.

#### **Characterization methods**

SEM and AFM images were obtained from a Gemini ultra plus filed emission scanning electron microscope and a Keysight 5500 scanning probe microscope, respectively. The UV-vis spectra were recorded by a Lambda 35 PerkinElmer UV-vis spectrometer. The PL measurements were performed on a Fluorolog-3 FL3-22 spectrometer where samples were excited at 365 nm.

The GIWAXS measurements were made using a Ganesha 300XL SAXS-WAXS instrument and the GISAXS measurements were performed at the GALAXI diffractometer.<sup>1</sup> An incident angle of 0.4° were used for both GISAXS and GIWAXS measurements.

In-situ XRR measurements were carried out using a customized X-ray setup at the NREX reflectometer at MLZ, Garching.<sup>2</sup> The sample environment is enclosed by a vacuum tight

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aluminum chamber with Kapton<sup>©</sup> windows for the hard x-rays. To generate precise and stable relative humidity around the sample we employed a feedback-controlled mixture of dry and water saturated nitrogen at constant room temperature (23°C) in enclosed sample chamber. As inert, pressurized und dry gas supply we used the evaporated phase of liquid nitrogen from a storage dewar.



**Figure S1.** AFM surface morphology for MDP film prepared with 60 min vapor exposure time. Line profiles of platelets stacking (position 1) and 2D platelets with lateral size between 120 and 140 nm (position 2 and 3).



**Figure S2.** Shift of the (001) Bragg peak in the GIWAXS data of MDP films upon increasing the organic vapor exposure time as indicated.



Figure S3. a) GIWAXS data integrated intensity over a small q range (covering the (001)-

MAPbBr<sub>3</sub>-Bragg peak) versus the azimuthal angle  $X = \operatorname{atan} \left(\frac{q_r}{q_z}\right)$ . The colored arrow indicates the increased angular range for sample with longer exposure time. b) Color-mapped orientation distribution of MDP film with 5 min vapor treatment.



**Figure S4.** Evolution of the Yoneda peak position (indicated by an orange arrow) in the GISAXS data of MDP perovskite films at different organic vapor exposure times. The black arrow highlights that the very weak specular peak constantly stays at a fixed incident angle ( $a_i$ ) of 0.4°.

Figure S4 shows the vertical line cuts of 2D GISAXS data (Figure 3a-e) at a fixed  $q_y$  window containing 12 pixels. Using a mass density 3.8 g/cm<sup>3</sup> for the neat 3D perovskite bulk crystal<sup>3</sup> and a smaller mass density 3.3 g/cm<sup>3</sup> for 2D (OA)<sub>2</sub>(MA)<sub>3</sub>Pb<sub>4</sub>Br<sub>13</sub> perovskite nanoplatelets, the critical angles for MAPbBr<sub>3</sub> and (OA)<sub>2</sub>(MA)<sub>3</sub>Pb<sub>4</sub>Br<sub>13</sub> are calculated to be 0.224° and 0.215°, respectively. Therefore, the shift of Yoneda peak to smaller  $a_f$  values indicates the formation of quasi-2D nanoplatelets-like system at longer exposure time.



**Figure S5.** Azimuthal integration ( $\mathcal{X}$ ) of the Bragg peak for n = 3 perovskite nanoplatelets from the GIWAXS data.



Figure S6. XRD data for MDP at small q regime.

### REFERENCES

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