Supplementary Information on

Fast growth of monocrystalline thin films of 2D layered hybrid perovskite

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Experimental Section

1. Synthesis

1.1. Synthesis of $C_6H_5C_2H_4NH_3I$

8 mL (0,064 mol) of phenethylamine $C_6H_5C_2H_4NH_2$ (Alfa Aesar, 99%) were dissolved in 300 mL of dry diethyl ether. 12,6 mL (0,096 mol) of a hydriodic acid solution HI (Sigma-Aldrich, 57% in water) were then added dropwise to the solution in an ice bath. White crystals of $C_6H_5C_2H_4NH_3I$ (called PEAI hereafter) immediately precipitate. The powder was then vacuum filtrated and washed four times with dry diethyl ether. The PEAI white powder was finally recrystallized from a mix of diethyl ether and ethanol and dried in an oven at 60°C overnight.

1.2. Synthesis of PEPI crystals by AVC

2,305 g of PbI_2 (5 mmol) and 2,480 g of PEAI (10 mmol) are dissolved in 5 mL of γ-butyrolactone (GBL) and stirred at 50°C until complete dissolution. The 1 mol/L solution is filtered with a 0,2 μm PTFE syringe filter and poured in a small vial, which is then placed in a bigger Teflon cap vial. 10 mL of dichloromethane (DCM) are finally poured in-between the outer wall the small vial and the inner wall of the big vial. After 48 hours, millimeter-sized rectangle-shaped orange crystals start to grow in the small vial.

1.3. Synthesis of PEPI crystals by AVCC

1,918 g (2 mmol) of the previously AVC grown PEPI crystals are dissolved in 2 mL of GBL and stirred at 50°C until complete dissolution. Two quartz substrates are cleaned with acetone, ethanol and treated with a solution of 10%wt KOH in ethanol in an ultrasonic bath for 15 minutes respectively. The substrates are washed with deionized water and dry in air, then one substrate is placed at the bottom of a big Teflon cap vial. 10 µL of the PEPI solution is deposited on one of the substrate and immediately after capped by the second quartz substrate. Finally 1 mL of DCM in a small vial is placed at the top of the substrates. After only a couple of minutes rectangle-shaped crystals appear in-between the two substrates.

1.4. Spin-coated PEPI thin films

The thin film synthesis protocol is one of those typically used in the literature. 0,175 g of PbI_2 (38 mmol) and 0,189 g of PEAI (0,76 mmol) were dissolved in either 1 mL of N,N-dimethylformamide (DMF) for the DMF film or γ-butyrolactone (GBL) for the GBL film and stirred at 50°C until complete dissolution. Quartz substrates for the deposition were cleaned with acetone, ethanol and treated with a 10%wt KOH solution in ethanol in an ultrasonic bath for 15 minutes respectively. The perovskite solution was then spin-coated in air at 2000 rpm during 30 sec and subsequently annealed at 80°C during 10 minutes for DMF film and 5 minutes for GBL film. The thickness of the as-made DMF film was estimated to be 400 nm and the GBL film 300 nm using a Dektak 8 profilometer.

2. Additional experimental

2.1. Optical micrograph

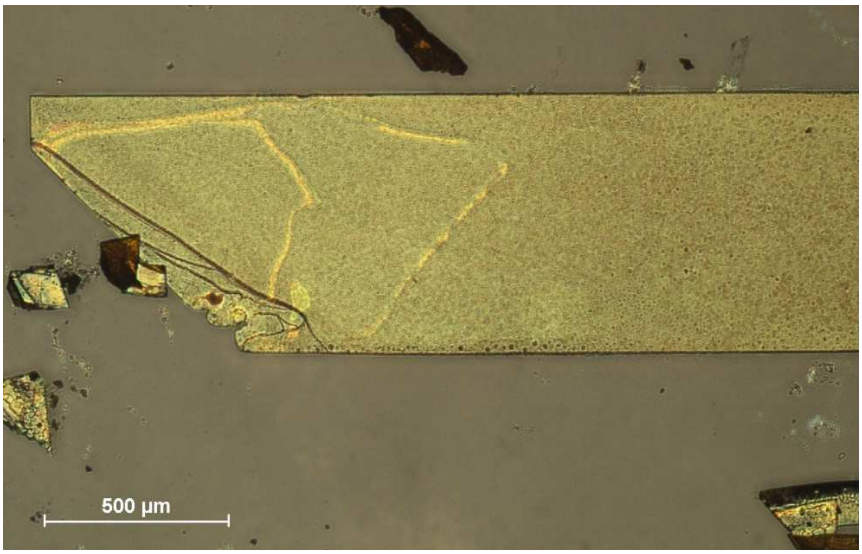

Fig. S1. Optical image of a 2000 x 700 µm² PEPI crystal obtained by AVCC process

2.2. Reflectivity spectroscopy

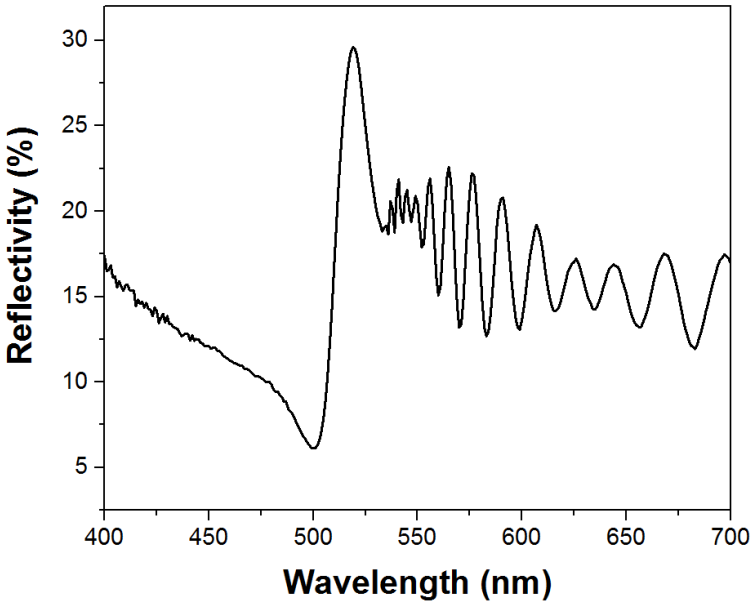

Fig. S2: Specular reflectivity spectrum of a single AVCC crystal performed at incident angle 8°.

The presence of oscillations between 700 and 530 nm in the reflectivity spectrum of the AVCC crystal (Fig. S2) can be interpreted as interference patterns. Assuming the refractive index *n* is

constant between 600 nm and 700 nm and equal to 2, the thickness *e* of the AVCC crystal can be simply deduced from the following formula : $e = \frac{\lambda_1 \lambda_2}{2n\cos(\theta)\Delta\lambda}$ where λ_1 and λ_2 are the wavelengths of two subsequent interference peaks, $\Delta\lambda = \lambda_1 - \lambda_2$ and θ the incidence angle.

2.3. GBL thin film characterization

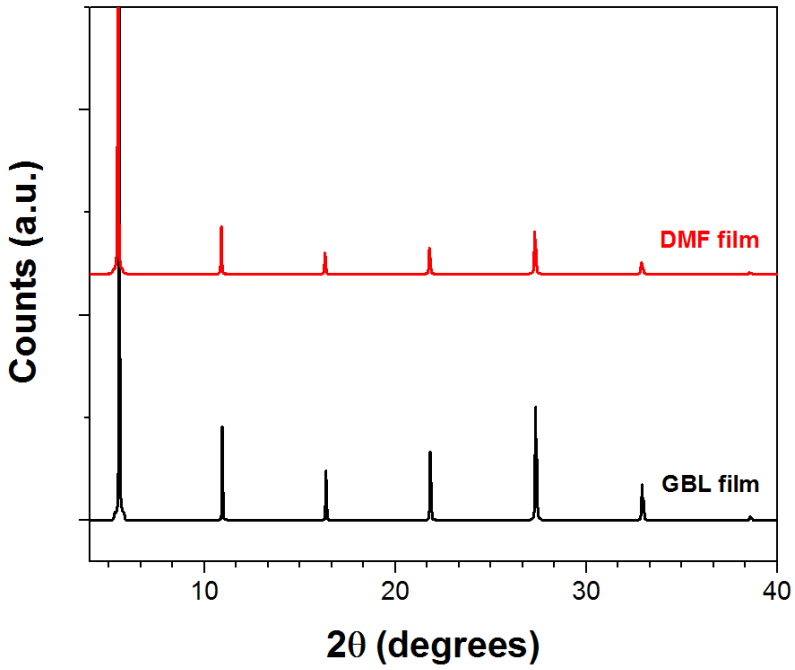

Fig. S3: X-Ray diffraction patterns of PEPI thin films crystallized in DMF (red curve) and in GBL (black curve).

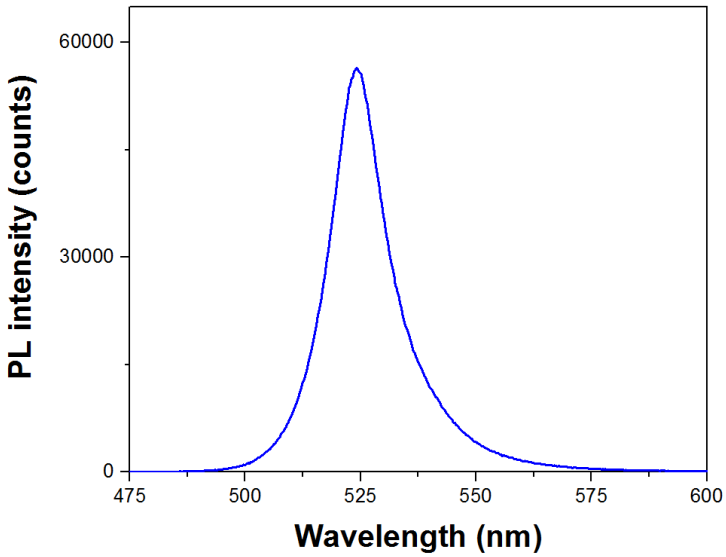

Fig. S4: Photoluminescence spectrum of a PEPI thin film crystallized in GBL.

3. Experimental setup

3.1. Profilometer

The PEPI films and the AVCC crystal thicknesses were measured using a Bruker Dektak 8 Advanced Development profilometer with the software Dektak 32.

3.2. X-Ray Diffractometer

The X-ray diffraction data were collected using a Siemens powder X-Ray diffractometer D5000 (Cu Kα, λ = 1,5418 Å) between 4 and 40° in a 2θ configuration.

3.3. Photoluminescence Spectroscopy

The photoluminescence (PL) spectrum of the AVCC crystal was recorded using a Spectrapro 2500i spectrometer equipped with a Pixis: 100B CCD array detector (Ropers Scientific). The excitation was the second harmonic of a pulse from a Ti:Sapphire Laser (Mai Tai, Spectra-Physics) at 400 nm (8MHz).

3.4. Specular reflectivity

The specular reflectivity spectra were recorded using a Perkin-Elmer lambda 950 spectrometer.