

Supplementary material

Solvent engineering for fast growth of centimetric high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite single crystals

Zhiliang Ku,^a Nguyen Huy Tiep,^{a,b} Bo Wu,^a Tze Chien Sum,^a Denis Fichou,^{a,c,d}

and Hong Jin Fan.^{a,*}

^a School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore. Email: FANHJ@ntu.edu.sg

^b Interdisciplinary Graduate School, Nanyang Technological University, 639798, Singapore.

^c CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire, F-75005 Paris, France.

^d Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, Institut Parisien de Chimie Moléculaire, F-75005, Paris, France.

Experimental details

Synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite

$\text{CH}_3\text{NH}_3\text{PbI}_3$ was prepared according to the previous report.¹ Typically, 27.8 mL methylamine (40% in methanol, Aldrich) was added into 30 mL hydroiodic acid (57 wt.% in water, Aldrich) at 0 °C for 2 h with stirring. After removing the solvent by evaporation at 50 °C, the product was washed with diethyl ether and then recrystallized in ethanol. The obtained white crystals were dried in a vacuum box.

Growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films and single crystals

$\text{CH}_3\text{NH}_3\text{PbI}_3$ films were prepared according to a previous procedure.³⁸ For the growth of single crystals, PbI_2 (572.8 mg, 99%, Aldrich) and as-prepared $\text{CH}_3\text{NH}_3\text{I}$ (195.5 mg) were mixed and stirred in 1 mL of γ -butyrolactone at 60 °C. Then, 1 mL of acetonitrile (Aldrich) was added into the solution and a clear pale yellow solution was obtained. After that, the solution was

transferred into a vial and the vial was kept in an oven at 70°C for 20 min. After this step, deposition of small crystals in the bottom of the vial would be observed. One of these small crystals was picked out and transferred into another flask with the same mother solution for continuous growth. The crystals used for measurement were grown for 6 h and have a diameter of 1.0 cm. TGA was performed on a TA SDT-Q600 V20.9 setup.

X-ray diffraction

Powder XRD patterns were collected using Rigaku D/Max-2550 with Cu K α radiation and the pole figures were characterized using Bruker D8 Discover. Microstructure of the samples was observed by field emission scanning electron microscopy (FESEM, FEI Sirion).

Photoluminescence

PL spectra were recorded using a spectrophotometer (Acton, Spectra Pro 2500i) equipped with a charge-coupled device detector (Princeton Instruments Pixis 400B). Time-integrated and time-resolved PL measurements were performed by exciting the samples with femtosecond laser pulses ($\lambda=600$ nm). The laser pulses were generated from an optical parametric amplifier (OPerA Solo) that was pumped by a 1-kHz regenerative amplifier (Coherent Libra, 800 nm, 50 fs, 4 mJ). A mode-locked Ti-sapphire oscillator (Coherent Vitesse, 80MHz) was used for seeding the amplifier. The time-integrated PL from the samples were recorded using the same spectrophotometer and a CCD camera (Princeton Instruments, Pixis 400B). The time-resolved PL was collected using an OptronisOptoscope streak camera system which has an ultimate temporal resolution of 6 ps. For all collections, the excitation fluence was kept low ($\sim 1 \mu\text{J cm}^{-2}$) to avoid high-order recombination effects.

Solubility tests

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ powder used for the solubility tests was obtained by grinding the prepared crystals. The 200 μl vials of GBL/ACN solvent were heated under stirring while the perovskite

powder was added in small amount of 0.01 g by 0.01 g. Saturation conditions were obtained when the perovskite powder did not dissolve completely after 30 mins in the solvent. The process was repeated at different temperatures in the range 25–100°C and various GBL/CAN solvent ratio from 1/0 to 1/1 (v/v).

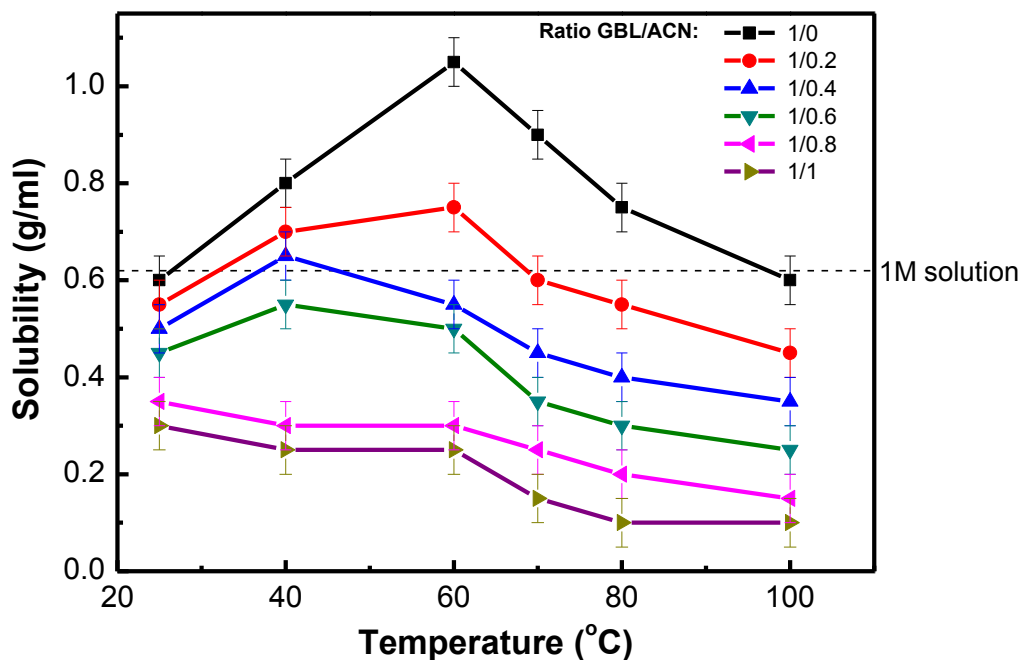


Figure S1 Temperature-dependent solubility of MAPbI₃ in mixed GBL/ACN solvents having different ratio (v/v). The error bars correspond to ± 0.05 g.

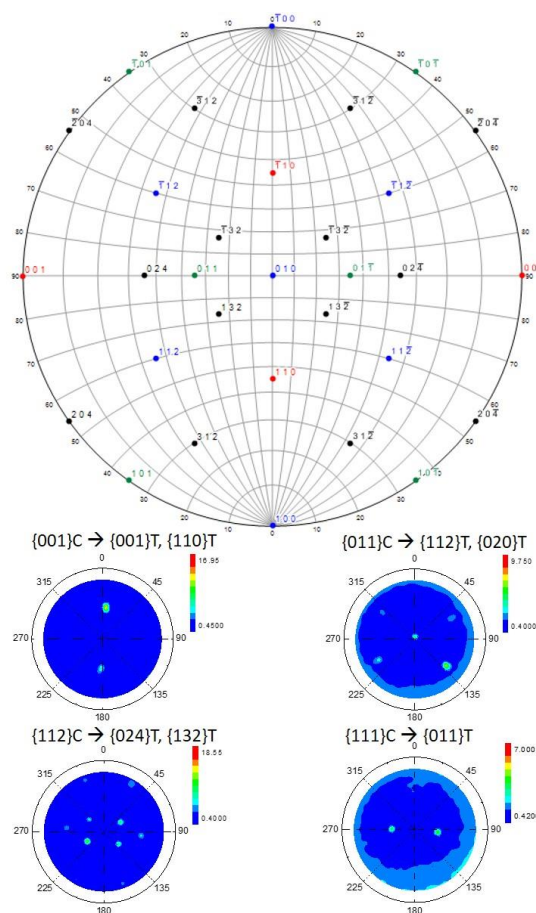


Figure S2 Pole figures of the natural facets of a centimetric $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal. Top: expected pattern for the $\{010\}$ front facet. Bottom: corresponding experimental patterns.

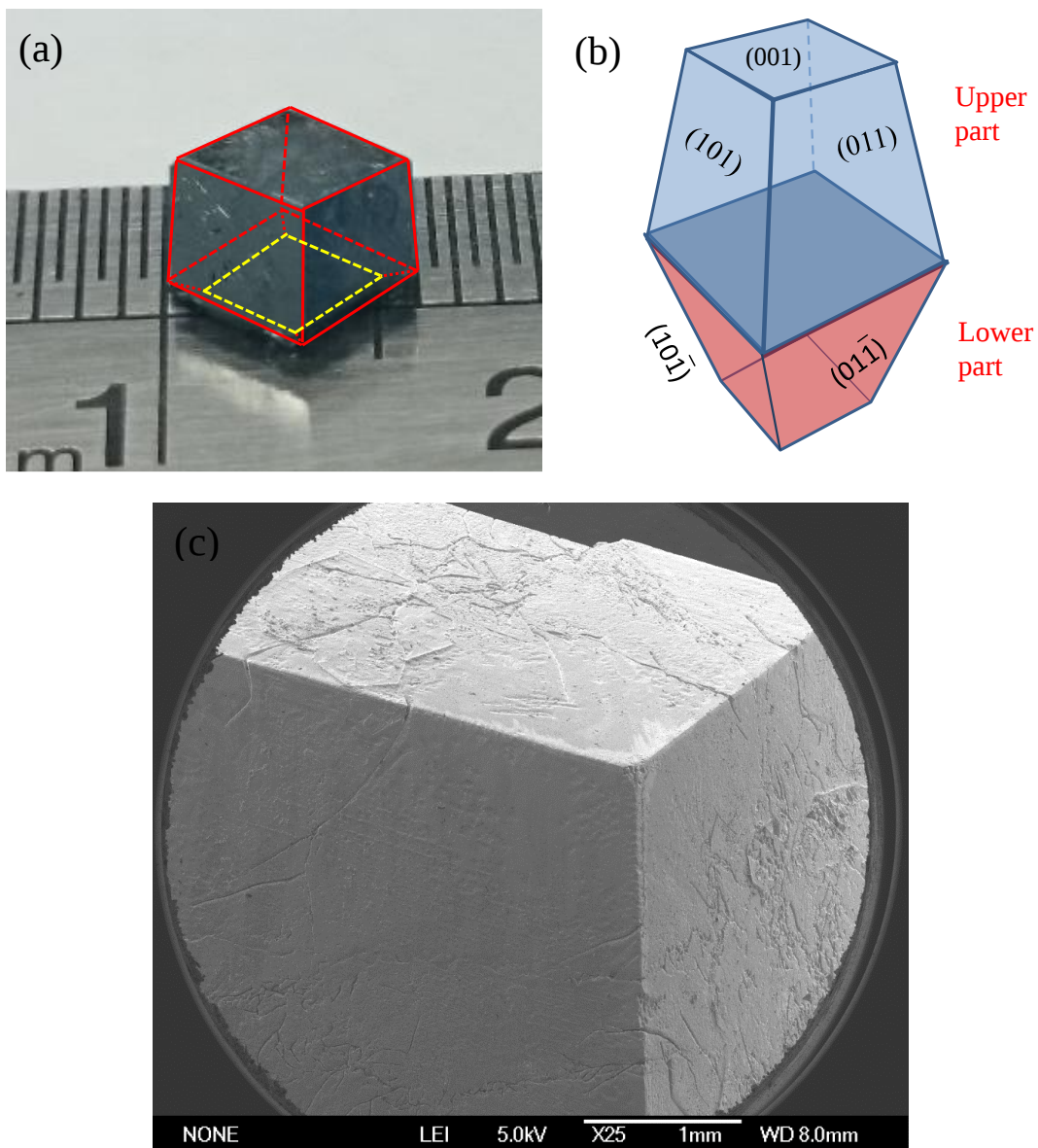


Figure S3 (a) Photograph of a non-perfect tetragonal crystal due to imbalanced growth rates between the upper part and lower part of the crystal. The outline of the crystal is indicated. (b) Schematics of a perfect tetragonal crystal. The upper part of the crystal in contact with solution grows faster than the bottom part that is in touch with the flask bottom. (c) An enlarged view of the image shown in Figure 5b.