Supplemental Material:

Directly Imaging the Structure-Property Correlation of Perovskites in Crystalline Microwires

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1. Growth of MAPbI₃ microwires.

Methylammonium iodide (MAI) is synthesized by slowly mixing 60 mL of methylamine (33 wt% in ethanol, Sigma-Aldrich) and 65 mL of hydroiodic acid (HI) (57 wt% in water, Sigma-Aldrich) under continuous stirring at 0 °C for 2 h. The MAI precipitates after evaporation of the solvent at 50 °C for 2 h. The obtained product is washed with diethyl ether, collected by filtration, and then dried in a vacuum oven for 24 h.

The MAPbI₃ microwires are synthesized via an antisolvent-assisted one-step solution method by using dichloromethane (DCM) as untisolvent. DCM has been demonstrated to be an effective antisolvent to grow high-quality perovskite single crystals with low trap state densities [1-3], which is attributed to that DCM is an extremely poor solvent for both MAX and PbX₂ and lacks the ability to form hydrogen bonds, thus minimizing asymmetric interactions with the ions during their assembly into crystal form [3]. Just prior to synthesis, the glass substrates $(18 \times 18 \text{ mm}^2)$ are washed sequentially with acetone, deionized water and ethanol, and then dried with nitrogen gas flow. MAI (0.1 mol) and PbI₂ (0.1 mol) (99.999%, Sigma-Aldrich) are dissolved in anhydrous N,N-dimethylformamide (DMF, 1 mL) under ultrasound to obtain a clear precursor solution. The MAPbI₃ microwires are synthesized by dripping 70 µL of the precursor solution on a glass substrate over a Teflon stage in a beaker, followed by an addition of the antisolvent of DCM (1.5 mL) at the bottom of the beaker with a liquid level below the stage [Fig. 1(a)]. Subsequently, the beaker is sealed by a porous Parafilm (3M) to control the evaporation rate of the solution. The MAPbI₃ microwires used for measurements are grown for 12 h.

2. PL spectra evolution of the initial microwires.



Figure S1. PL spectra evolution of the initial microwires with continuous structural/compositional variations to a stable state. (a) In-situ PL spectra over time along with the color change of the initial perovskite microwires after taking out from the sealed beaker within 50 minutes. The sample was placed in a watch glass covered with a transparent glass sheet to avoid the influence of the surrounding environment and facilitate the observation of the materials. PL excitation wavelength was 532 nm (50× objective, 2 KW cm⁻²). (b, c) The corresponding FWHM (b) and PL intensity (c) extracted from the real-time PL emission spectra. The lines are a guide to the eye.

3. The effect of precursor concentration on the material quality of the as-grown





Figure S2. Optical images of the as-grown MAPbI₃ microwires synthesized with different precursor concentrations. (a)-(f) correspond to a precursor concentration of 0.8 M, 0.4 M, 0.2 M, 0.1M, 0.05 M and 0.025 M, with corresponding diameter of about 7~8 μ m, 5~6 μ m, 3~4 μ m, 2~3 μ m, 0.5~1 μ m and 0.1~0.5 μ m, respectively.

4. FTIR spectra of the as-grown microwires and pure DMF.

FTIR spectra are analyzed using a Nicolet 6700 spectrometer. Fig. S3(a) shows the FTIR spectrum of the as-grown microwires, the existence of the ammonium and methyl groups in CH₃NH₃⁺ cation are verified by N-H stretching (3111 and 3169 cm⁻¹), NH₃ bending modes (1459 and 1580 cm⁻¹), C-H stretching (2919 and 2964 cm⁻¹), CH₃ bending vibrations (1381 and 1420 cm⁻¹), C-N stretching mode (956 cm⁻¹) and CH₃NH₃⁺ rocking modes (902 and 1247 cm⁻¹) [4, 5]. It must be mentioned that the stretching vibration of C=O (v(C=O)) of the as-grown microwires appeared at 1637 cm⁻¹ indicates the existence of DMF [6, 7], which is shifted to a lower wavenumber compared with that of pure DMF [1670 cm⁻¹ for v(C=O), Fig. S3(b)]. The decreased C=O stretching frequency is due to the decrease in bond strength between carbon and oxygen as a consequence of the intermediate formation [6]. The FTIR result further illustrates the existence of the intermediate phase in the as-grown microwires.



Figure S3. FTIR spectra of the as-grown microwires (a) and pure DMF (b). The FTIR absorption peak at 1637 cm^{-1} is ascribed to the stretching vibration of C=O in DMF.

5. Growth of bulk MAPbI₃ crystals.

As a control, bulk MAPbI₃ crystals are synthesized via an inverse temperature crystallization method [8]. In the typical process, one molar MAPbI₃ solution was prepared by dissolving equimolar amounts of PbI₂ and MAI in γ -butyrolactone (GBL). The above mixture was contained in a flask and stirred at 60 °C in an oil bath to obtain a clear solution, and then filtered using PTFE. 2 mL of the filtrate was transferred into a vial and the vial was kept in an oven with a heating temperature of 110 °C. After reaction for 4 hours, the millimeter-sized bulk MAPbI₃ crystals were obtained.

6. Growth of MAPbI₃·DMF intermediate crystals.

MAPbI₃·DMF is well accepted as an intermediate state [6, 9, 10], which is relatively stable in air and converts very slowly to the MAPbI₃ phase. The atomic configuration of MAPbI₃·DMF consists of one dimensional $\{PbI_3\}^-$ inorganic chains isolated from one another by MA⁺ cations and DMF molecule crystallizing in the monoclinic $P2_1/m$ space group [10].

The preparation of MAPbI₃·DMF intermediate crystals are based on a previously reported one-step crystallization process [9, 10]. Typically, 1 M precursor solution of PbI₂ and MAI with a molar ratio of 1:1 dissolved in DMF was prepared. MAPbI₃·DMF intermediate crystals were synthesized by dripping 20 μ L of the above precursor solution on a Si/SiO₂ substrate and dried under ambient conditions.

7. Raman spectra of the possible components.



Figure S4. (a) Raman spectra of the purchased PbI₂ powder (blue curve), assynthesized PbI₂·DMF crystals (red curve), as-synthesized MAI crystals (black curve), as-synthesized MAPbI₃·DMF (pink curve) and MAPbI₃ (green curve) for comparison. (b) PL spectrum of PbI₂.

According to the previous reported method [11], PbI₂·DMF crystals are synthesized by dripping 1 M precursor solution of PbI₂ in DMF on a Si/SiO₂ substrate and dried under ambient conditions. Raman spectra of the purchased PbI₂ powder, assynthesized PbI₂·DMF crystals, as-synthesized MAI crystals, as-synthesized MAPbI₃·DMF (pink curve) and MAPbI₃ (green curve) (Figure S4) are collected using a HORIBA XploRA PLUS Raman spectrometer attached to a confocal microscope with a 50× objective and a 532-nm laser for the excitation. Laser power density is minimized to ensure that no degradation of the sample is induced. The PL spectrum of PbI_2 is pumped by a 325 nm laser with power density of 200 KW cm⁻².

8. First-Principle Calculations.

Table S1. Calculated properties of the MAPbI₃·DMF, MAPbI₃ and monolayer MAPbI₃.

Formula	Structure	a (Å)	b (Å)	c (Å)	α	β	γ	V (Å ³)
					(deg)	(deg)	(deg)	
MAPbI ₃ ·DMF	monoclinic	4.576	25.493	12.219	90.00	96.07	90.00	1417.39
MAPbI ₃	monoclinic	8.563	8.844	12.592	90.00	90.00	90.00	953.61
Monolayer MAPbI ₃	monoclinic	8.563	8.844	35.000	90.00	90.00	90.00	2650.59

Geometry optimization and electronic structure calculations are performed based on the density functional theory (DFT) in conjunction with the projector-augmented wave (PAW) pseudopotential [12, 13], as implemented in the Vienna ab initio simulation package (VASP) code [14-16]. The exchange-correlation functional is treated under the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) form [17]. The van der Waals density functional (vdW-DF) of optPBE are considered for all simulations [18, 19]. A plane wave cutoff energy of 500 eV is used for the plane-wave expansion of the wave function. A centered grid of $5 \times 3 \times 5$, $3 \times 3 \times 3$ and $3 \times 3 \times 1$ k-points were used to sample the Brillouin zone [17] in the structural optimization of the MAPbI₃·DMF, MAPbI₃ and monolayer MAPbI₃, respectively. A centered grid of 9 \times 3 \times 5, 5 \times 5 \times 5 and 5 \times 5 \times 1 k-points were used to sample the Brillouin zone [20] in electronic property calculations of the MAPbI₃·DMF, MAPbI₃ and monolayer MAPbI₃, respectively. To obtain reliable optimized structures, the maximum force is less than 10^{-2} eV/Å per atom and energies are converged to within 10⁻⁵ eV between two successive steps. The optimum configurations of the MAPbI₃ DMF, MAPbI₃ and monolayer MAPbI₃ are shown in Fig. 3(d) and Fig. 6. The parameters of them are listed in Table S1.



9. Characterization of transmission electron microscope.

Figure S5. TEM (a, b), HAADF-STEM (c) and HRTEM (d) images of the as-grown perovskite microwire.

To gain further insights into the microscopic mechanisms of the structure-property correlations, we perform the transmission electron microscope (TEM) characterization. As shown in Figure S5a and 5b, the microstructure differences of the as-grown MAPbI₃ mircowire are difficult to be observed from the TEM images. Since there are density differences between MAPbI₃ and MAPbI₃·DMF, it is expected for us to observe a different contrast in the as-grown microwire by using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), a direct probe of density variations in the material (Figure S5c). Unfortunately, the contrast between MAPbI₃

and MAPbI₃·DMF is not observed, and the HRETM lattice fringes (Figure S5d) of the as-grown microwire are indexed to a tetragonal crystal structure of the perovskite phase. However, it is reasonable not to observe the phase separation, because the MAPbI₃·DMF intermediate phase is difficult to stably exist under the high energy electron beam of the transmission electron microscope.

10. Stability of MAPbI₃·DMF under ambient conditions.



Figure S6. PL spectra of the pristine MAPbI₃·DMF crystals that have just completed the crystallization process (black curve) and the same sample after 2 hours' (blue curve) and 24 hours' storage in air, respectively (green curve). Pumped by a 325 nm laser with power density of 20 KW cm⁻².

11. Formation of the dark domains at wire junctions.

During the formation process of the bright and dark domains, we found an interesting phenomenon: the dark regions tend to form at wire junctions, which we infer is related to the rate of the solvent volatilization during the growth of the microwires. At the earlier stage of the solvent evaporation process, the PbI₂ forms a $[PbI_6]_4^-$ octahedral layer and accelerates the formation of a three-layer structure of PbI₂-MAI-DMF [21-23]. Under further evaporation of DMF, the dangling parts of the microwires have a larger exposed surface, which results in faster solvent evaporation. Thus it leads

to the earlier formation of the perovskite layer on the outer surface of the microwires, and the formed compact perovskite layer outside the microwires can prevent the further evaporation of DMF in the internal intermediates, and results in the bright domains with the intermediate phase as the dominant component. On the contrary, the solvent at the wire junctions is less volatile, and the large amount of residual solvent can inhibit the formation of the compact perovskite crust and leads to a more moderate phase transition process, thus resulting in the formation of a thicker layer of the black MAPbI₃ perovskite composition at wire junctions.



12. Thermal annealing treatment.

Figure S7. Thermal annealing treatment showing remaining local differences in PL efficiency. (a) Optical images of a single microwire before (left) and after 80 °C annealing (right), and the solid squares represent the PL spectra collected regions, scale bar: 10 μ m. (b,c) The corresponding PL spectra collected from the dark domain (white square in a) and bright domain (blue square in a) before (b) and after annealing (c).

13. Laser illumination treatment.

MAPbI₃ microwires were illuminated under continuous-wave laser at 532 nm. A $50\times$ objective lens was used to focus the beam to a ~1 µm diameter spot on the microwires with the power density of about 2 KW cm⁻². To achieve a uniform treatment, the laser spot was scanned along microwires continuously. During the treatment, samples were kept in a N₂-filled chamber. MAPbI₃·DMF intermediate crystals were illuminated under continuous-wave laser at 325 nm with the power density of about 2 KW cm⁻².

14. Room-temperature preservation.

Figure S8. Room-temperature preservation resulting in inhomogeneous morphology and material degradation. (a-c) Bright-field optical images of one single microwire just after a fresh synthesis (a), after room-temperature preservation in a N₂-filled glovebox for 7 days (b) and 40 days (c). (d) The corresponding normalized PL spectra of the transferred microwire collected from the regions highlighted by white dashed rectangle in (a)-(c). PL excitation wavelength was 532 nm with power density of 2 KW cm⁻² (black and red curves) and 2600 KW cm⁻² (blue curve). (e) Raman spectrum of the microwire after 40 days' preservation collected from the highlighted region in (c).

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