Electronic Supplementary Material (ESI) for ChemComm.
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# Supplementary Information

## Visualization of halide perovskite crystal growth processes by in situ heating WAXS measurements

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## Experimental section

### Fabrication process

*N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and γ-butyrolactone (GBL) solutions of $CH_3NH_3PbI_3$ ($MAPbI_3$) (1.0 M) were prepared by dissolving $PbI_2$ + MAI with a molar ratio of 1:1 in the desired solvent. The $TiO_2$ layer was fabricated following the same experimental conditions and protocol given in the previously published literature.[1,2] Each solution of $MAPbI_3$ was spin-coated on the $TiO_2$ layer at 1000 rpm for 10 sec and at 4000 rpm for 30 sec inside a glove box under an argon atmosphere. During the spin-coating process, chlorobenzene was dropped onto the perovskite layer.[3,4] Finally, the resulting film was attached rapidly to the wide-angle X-ray scattering (WAXS) measurement equipment.

### In situ heating WAXS measurements

We performed in situ heating WAXS measurements to evaluate the process of crystallization from the precursor solution of $MAPbI_3$. In situ WAXS patterns were measured at an X-ray incident angle of 5.0º and a photon energy of 12.39 keV using synchrotron radiation at beamline BL46XU of SPring-8, whereby the instrument was equipped with a two-dimensional (2D) X-ray detector (PILATUS300K). During the measurements, the samples were heated from room temperature to 100 °C at a rate of 20 °C/min, and then heated at 100°C for 20 min under a dry $N_2$ atmosphere.

The scattering patterns $I_{2D}(q,\chi)$ measured by the 2D detector were azimuthally integrated to obtain the one-dimensional (1D) intensity profiles $I_{1D}(q)$ as follows:

$$I_{1D}(q) = \frac{1}{2\pi}\int_0^{2\pi} I_{2D}(q,\chi)\, d\chi$$

where $q$ is the magnitude of the scattering vector, and $\chi$ is the azimuthal angle.

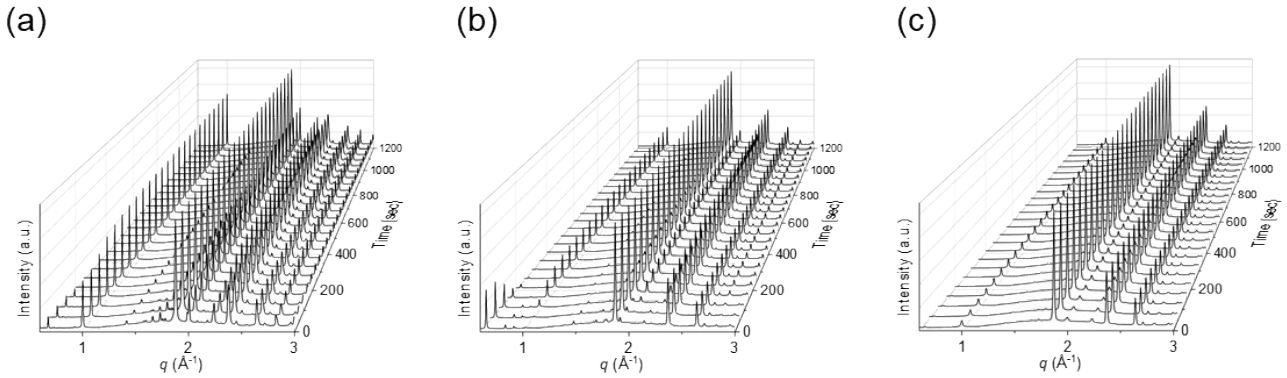


**Fig. S1** Time dependent 1D WAXS profiles up to $q$ = 3 Å$^{-1}$, as obtained by azimuthally integrating the 2D WAXS data. For the (a) DMF, (b) DMSO, and (c) GBL systems.

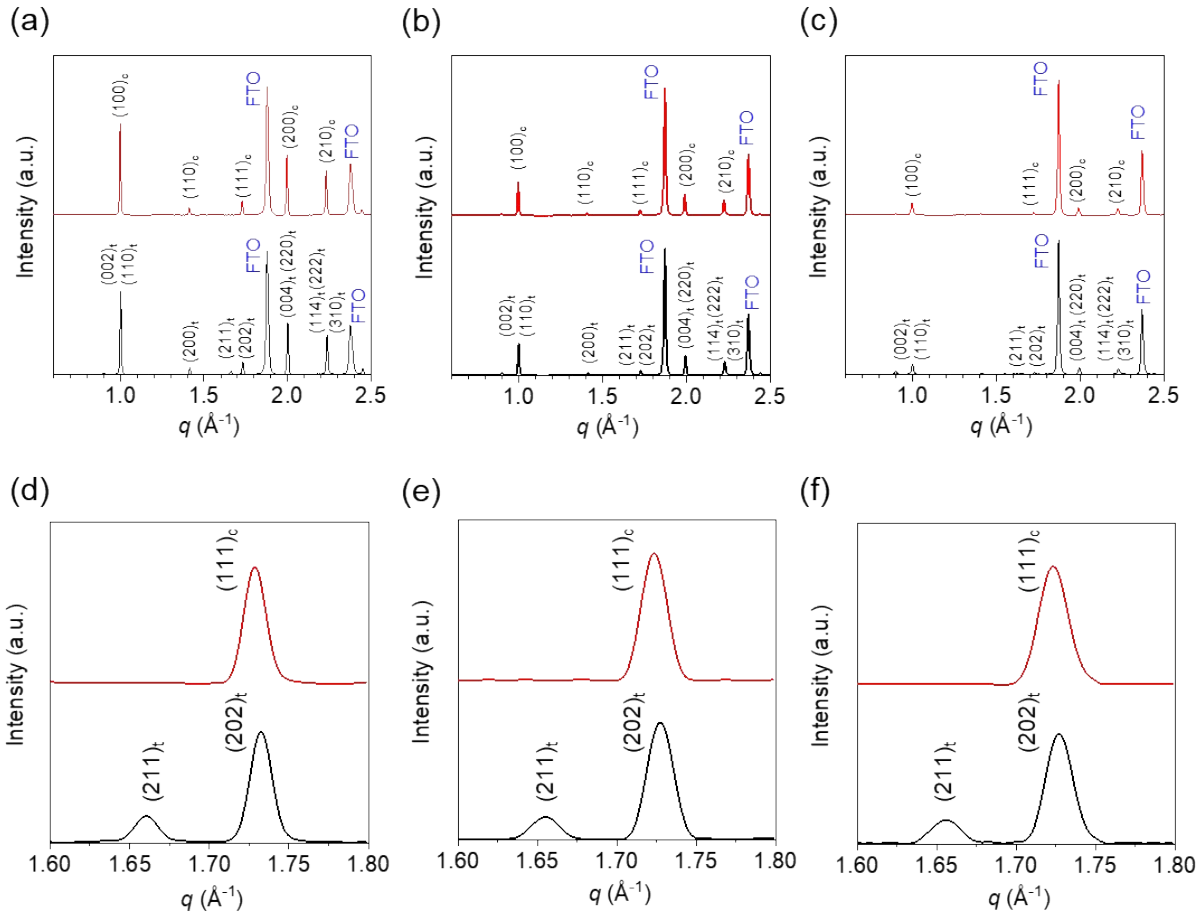


**Fig. S2** 1D WAXS profiles obtained by azimuthally integrating the 2D WAXS data during heating at 100°C (red) and after cooling (black). For the (a) DMF, (b) DMSO, (c) GBL, (d) DMF (near $(211)_t$ peak), (e) DMSO (near $(211)_t$ peak), and (f) GBL (near $(211)_t$ peak) systems.

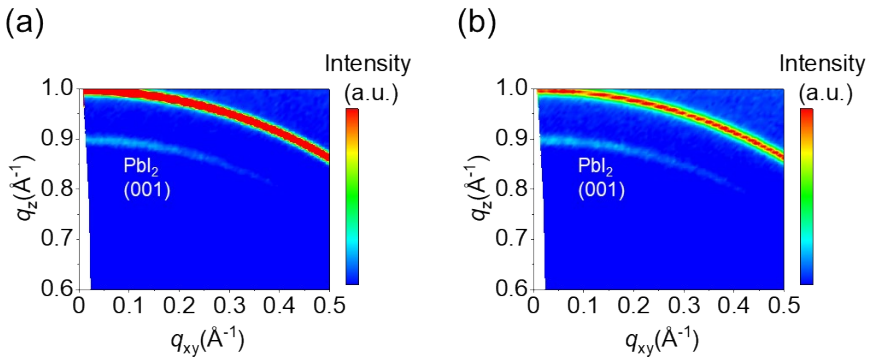


**Fig. S3** 2D WAXS patterns close to the $PbI_2$ (001) diffraction peak after 20 min for the cases of (a) DMSO, (b) GBL.

**Reference**


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