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Thermodynamic and kinetic modulation of methylammonium lead bromide crystallization revealed by *in situ* monitoring

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Abstract: Elucidating microscopic crystal growth mechanisms requires observing dynamic, molecular-level surface features during growth by *in situ* monitoring. Herein, fluid-cell atomic force microscopy (AFM) was used to determine how formic acid (FAH) modulates the thermodynamics and kinetics of the crystal growth of $CH_3NH_3PbBr_3$ ($MAPbBr_3$), a model hybrid organic-inorganic perovskite (HOIP) with promising optoelectronic properties. The growth of $MAPbBr_3$ in dimethylformamide (DMF) proceeds through the spreading of atomic crystal steps generated at screw dislocations on the {100} surface. Temperature-dependent step velocity measurements demonstrate that with increasing concentration, FAH decreases both the solubility of $MAPbBr_3$ and the kinetic coefficient (β) of step movement. Moreover, solution ^1H-NMR measurements provide insight into molecular-level changes in solution speciation caused by FAH. FAH increases the lifetime of the methylammonium (MA^+) ions and promotes the association of $MAPbBr_3$, thus tuning the solubility of the perovskite. FAH also alters the molecular tumbling motion and bulk diffusion of the MA^+ ions, possibly via H-bonding. Our findings establish a direct correlation between the mesoscale crystal growth kinetics and the molecular-scale interactions between organic additives and constituent ions, providing unprecedented insights for developing predictive syntheses of HOIP crystals with defined size, crystal habit and shape, and defect distribution.