Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

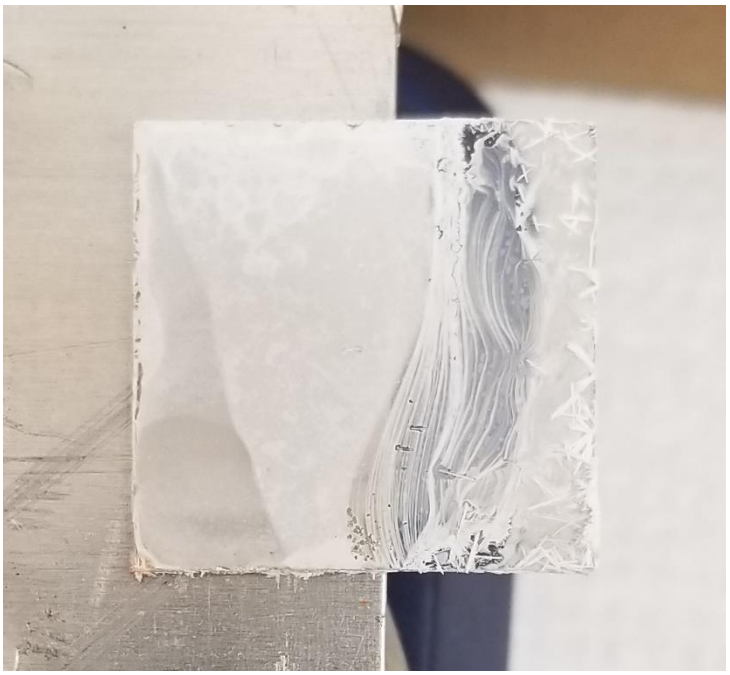


Figure S1: Temperature gradient using aluminum metal as the heat-conducting material for one attempt at directional $PbBr_2$ crystal growth (21 ℃ in the air to 30 ℃ on aluminum)

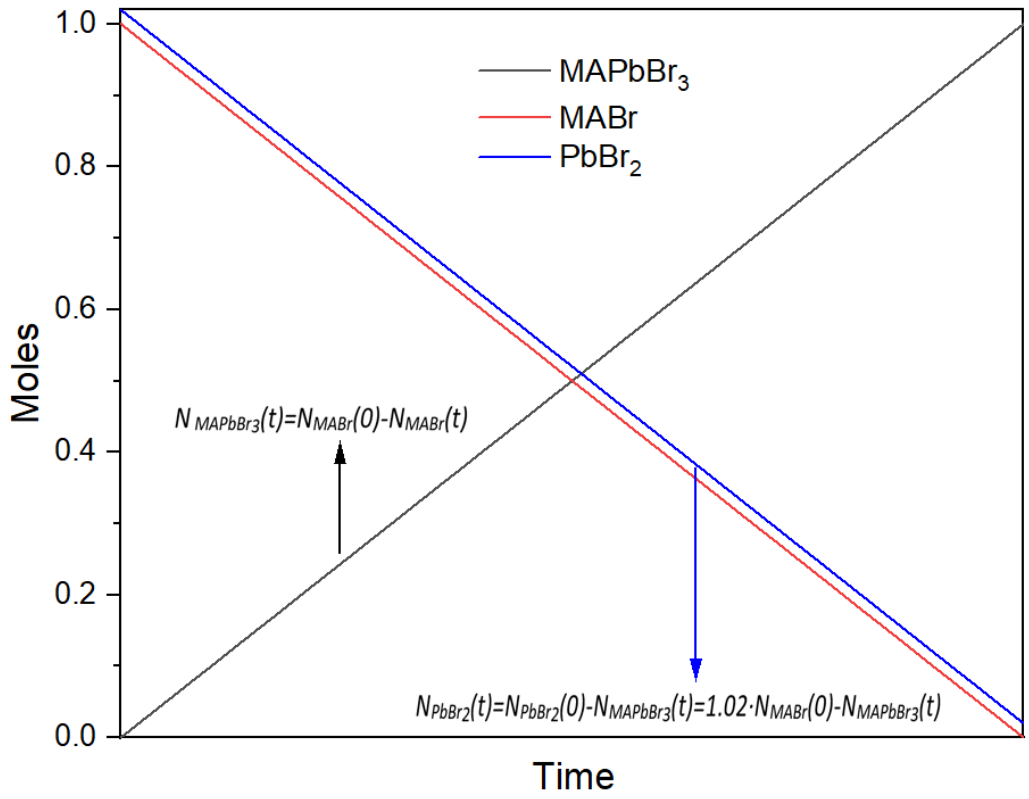


Figure S2: Visualization of the mathematical model of $MAPbBr_3$ formation, and MABr (1 mole initially) and $PbBr_2$ (1.02 mole initially) depletion.

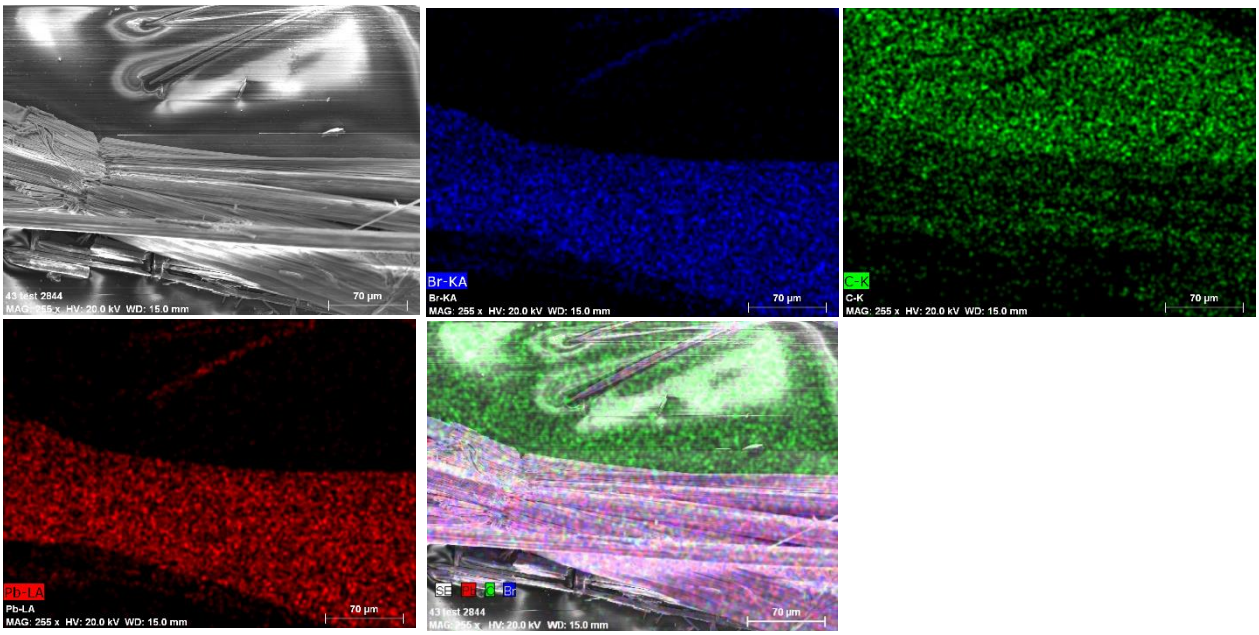


Figure S3: SEM and EDS images indicating 1:2 ratio Pb:Br of $PbBr_2$ microwires.

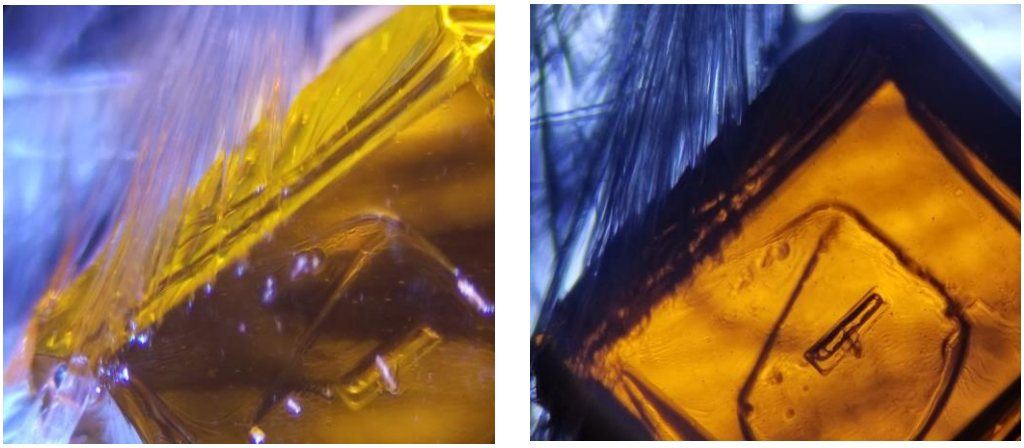


Figure S4: Optical microscope images of $PbBr_2$ growth near perovskite single crystals in transmission (left panel) and reflection (right panel) modes.

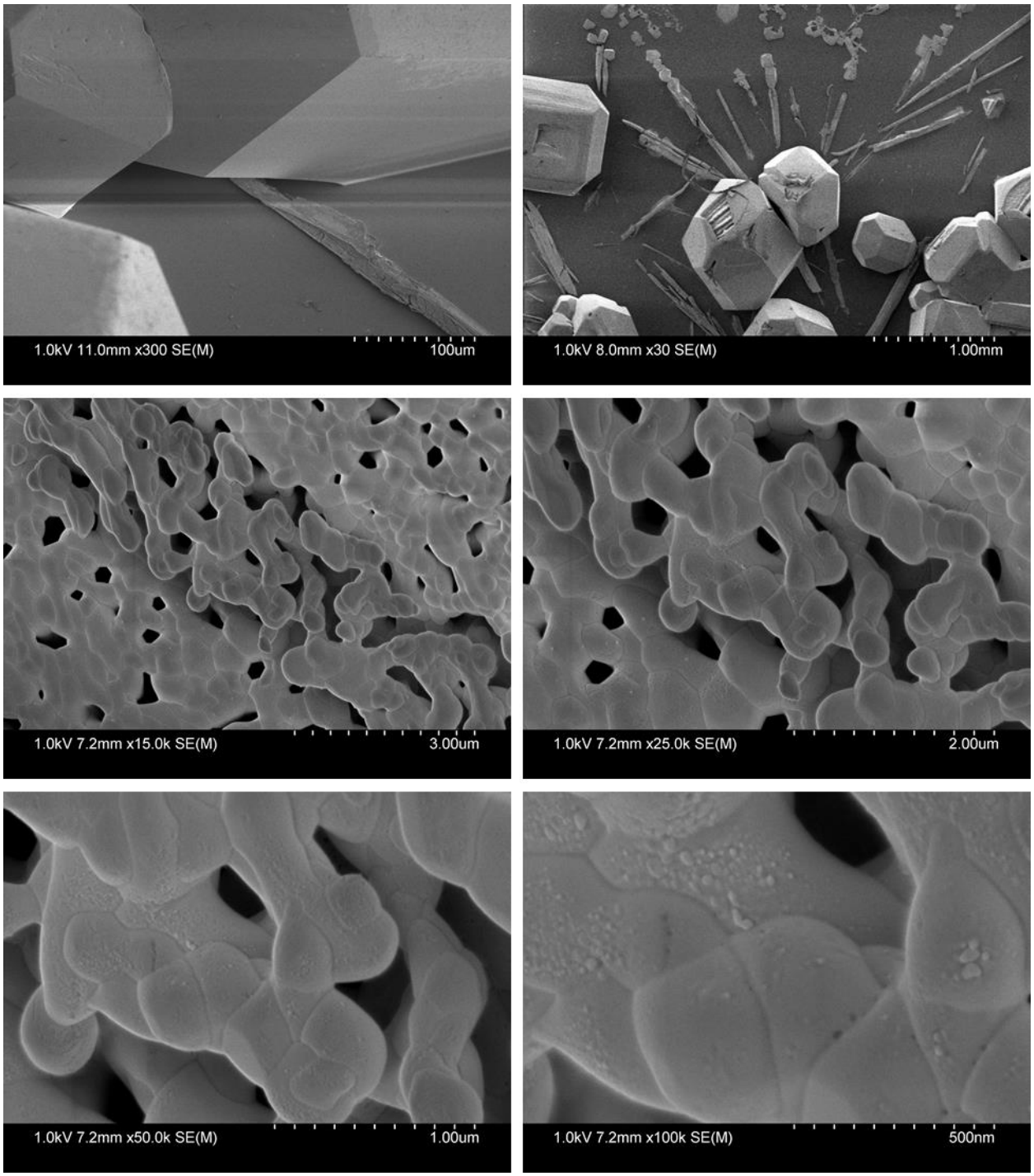


Figure S5: SEM images of off-stoichiometry $MAPbBr_3/PbBr_2$ films. High magnification shows porous nature of $PbBr_2$ crystals likely due to precipitation of $PbBr_2$ from leftover solution.

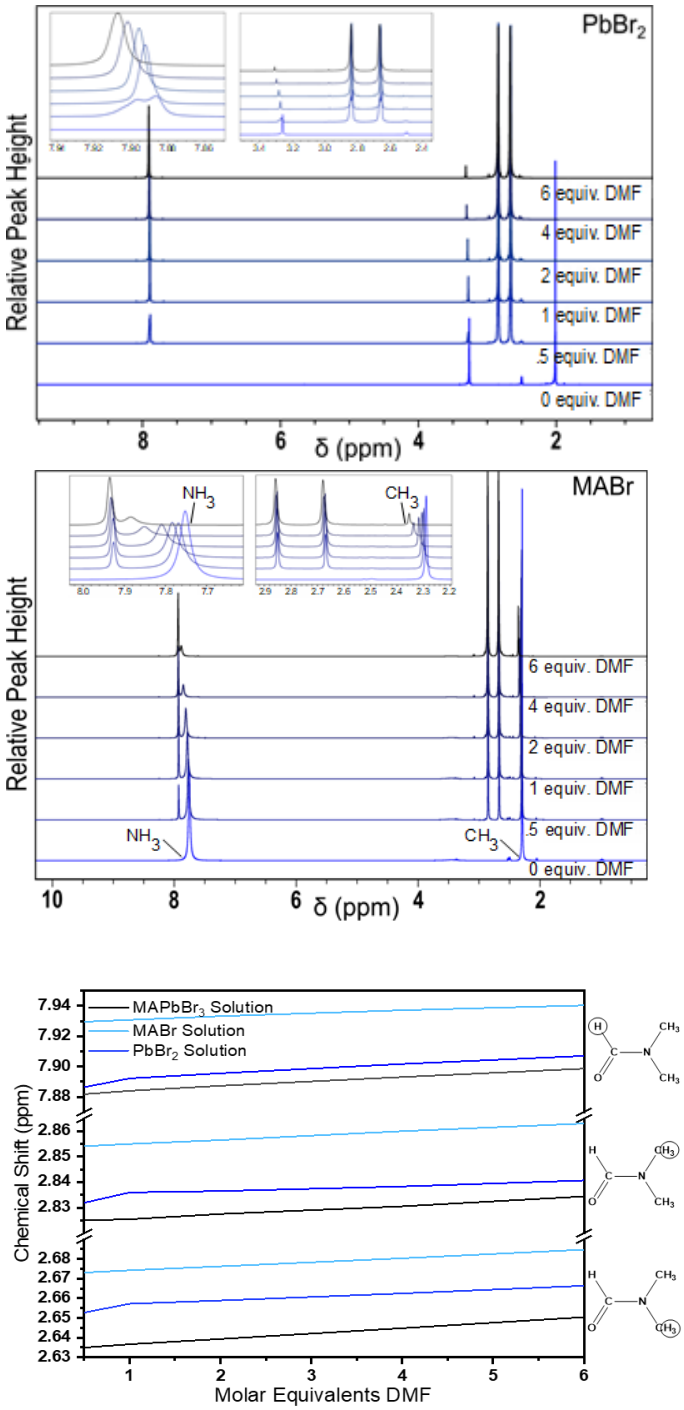


Figure S6: Top: ^{1}H NMR spectra in deuterated DMSO with 0-6 molar equivalents DMF titrated in of MABr and $PbBr_2$**.** Bottom: ^{1}H NMR spectra showing DMF hydrogen chemical shifts in $MAPbBr_3$, $PbBr_2$ and MABr solutions.

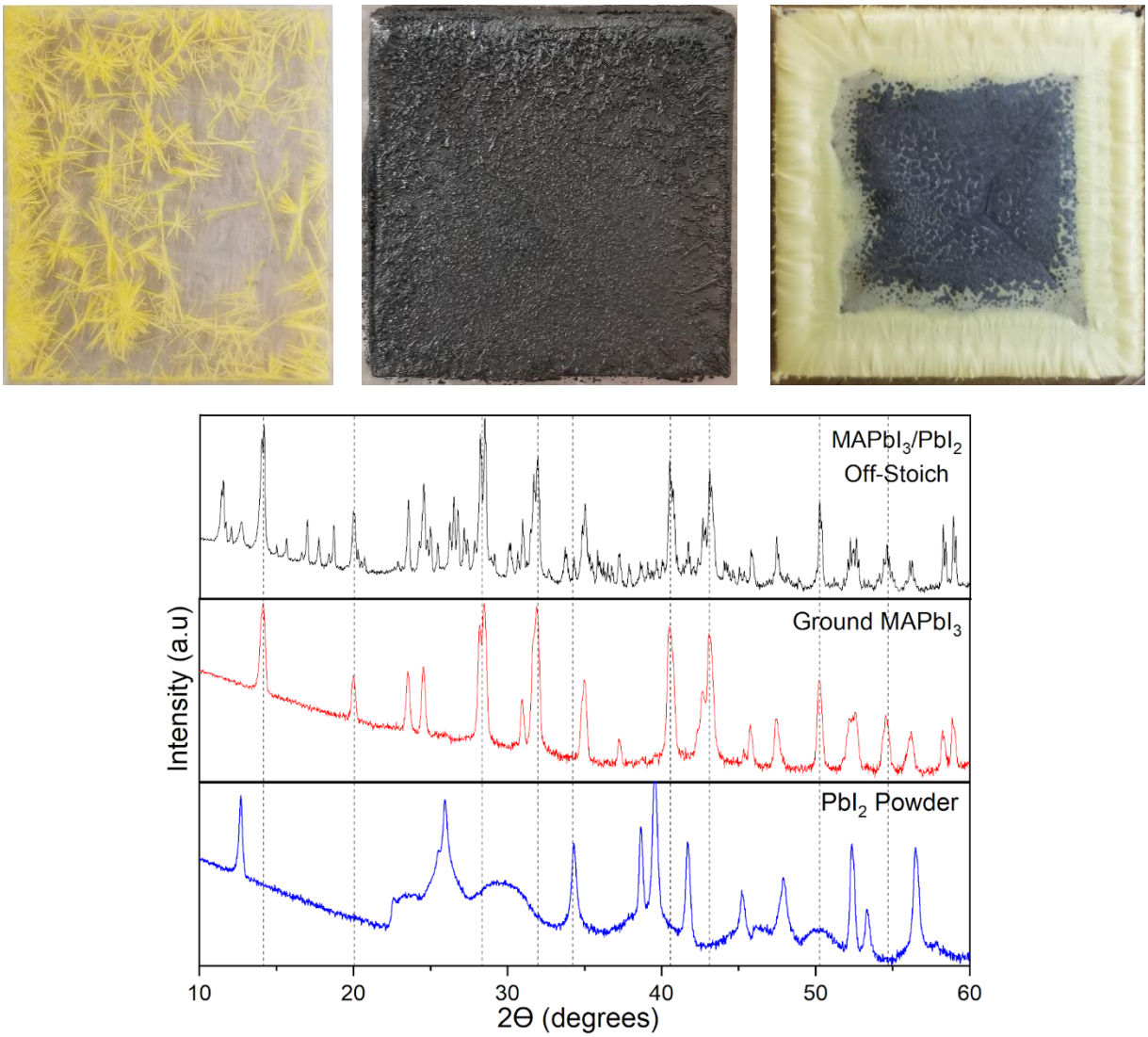
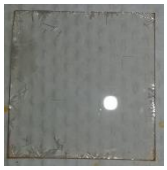
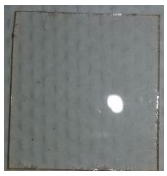
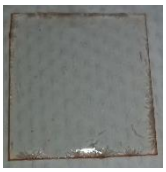
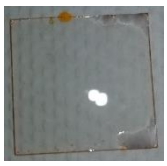
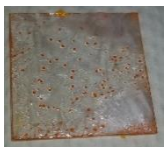


Figure S7: Random orientation of PbI_2 crystals from pure PbI_2 solution, $MAPbI_3$, and oriented PbI_2 crystals grown from off-stoichiometry precursor solution. Bottom: off-stoichiometry $MAPbI_3$ XRD pattern (black), ground $MAPbI_3$ single crystals (red) and PbI_2 powder (blue) for peak analysis.

Table S1: Photographs of the crystallization process with different $PbBr_2$:MABr ratios

Ratio $PbBr_2$: MABr	20 min	30 min	40 min	50 min	60 min	2 hours
1:1						
2:1						
1.5:1						
1.36:1						
1.25:1						
1.02:1