

Electronic Supplementary Information

A New Metric to Control Nucleation and Grain Size Distribution in Hybrid Organic-Inorganic Perovskites by Tuning the Dielectric Constant of the Antisolvent

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1 Solvent-Antisolvent Interactions

ϵ	DMF-ATS	Binding Energy	Same solvents	Binding Energy
36.7	DMF-DMF	-1.95	DMF-DMF	-1.95
28.54	DMF-DCM	-2.86	DCM-DCM	-2.29
26.64	DMF-THF	-0.80	THF-THF	-1.92
24.38	DMF-CB	-3.45	CB-CB	-2.44
23.73	DMF-ANS	-3.60	ANS-ANS	-3.88
22.66	DMF-TOL	-3.96	TOL-TOL	-3.46

Table 1 Intermolecular binding energies (in kcal/mol) of solvent pairs used in perovskite precursor solution processing as a function of the dielectric constant (column 1), arranged in decreasing value of the pair. Columns 2 and 3: Binding energy results for DMF interacting with five different antisolvents. Columns 4 and 5: Binding energy results for same-solvent pairs, for comparison.

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2 Solvent-HOIP Precursor Interactions

ϵ	Solvent-MAPbI ₃ Interaction	Binding Energy	MA ⁺ -PbI ₃ -solvent Interaction	Binding Energy
36.7	DMF-MAPbI ₃	-6.58	MA ⁺ – (PbI ₃ DMF)	-6.70
28.54	DCM-MAPbI ₃	-4.07	MA ⁺ – (PbI ₃ DCM)	-6.72
26.64	THF-MAPbI ₃	-7.33	MA ⁺ – (PbI ₃ THF)	-7.74
24.38	CB-MAPbI ₃	-7.38	MA ⁺ – (PbI ₃ CB)	-7.60
23.73	ANS-MAPbI ₃	-8.59	MA ⁺ – (PbI ₃ ANS)	-7.86
22.66	TOL-MAPbI ₃	-8.88	MA ⁺ – (PbI ₃ TOL)	-8.19

Table 2 Comparison of the intermolecular binding energy of a variety of solvents to a MAPbI₃ monomer (column 3) to the binding energy of a MA⁺ cation to a complex formed by PbI₃[−] and a solvent molecule (column 5) in the perovskite precursor solution. Intermolecular binding energies are given in kcal/mol.

3 Effect of Changing PbI_2 Concentration

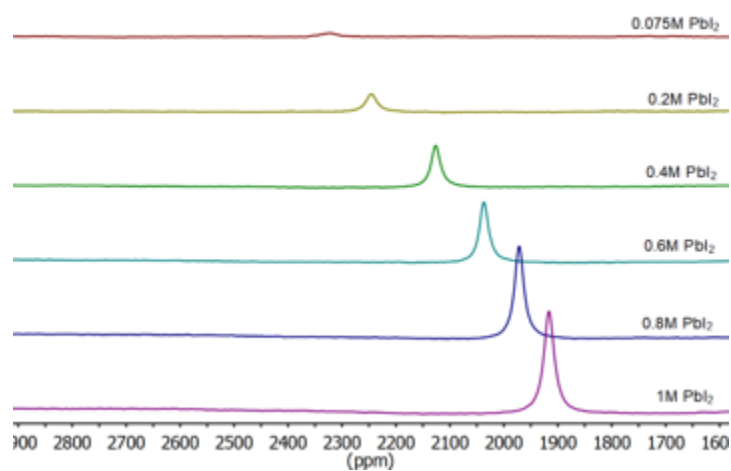


Fig. 1 Solution-state ^{207}Pb -NMR spectra for various concentrations of PbI_2 ranging from 0.075 M to 1 M. An upfield shift and stronger peak intensity were observed with increasing PbI_2 concentration.

4 Effect of Changing MAI Concentration

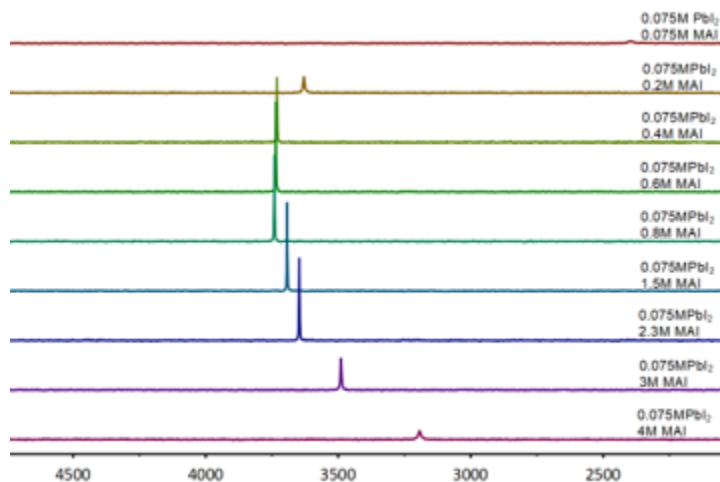


Fig. 2 Solution-state ^{207}Pb -NMR spectra of 0.075 M PbI_2 with varying MAI concentration from 0.075 M (equimolar) to 4 M. Initially, a downfield shift was observed until the molar ratio is 0.075 M PbI_2 :0.8 M MAI; MAI concentrations greater than 0.8 M resulted in an upfield shift. The presence of considerable excess MAI also yielded a significant decrease in peak intensity.

5 Effect of Antisolvents of Varying Dielectric Constant and Increasing MAI Concentration

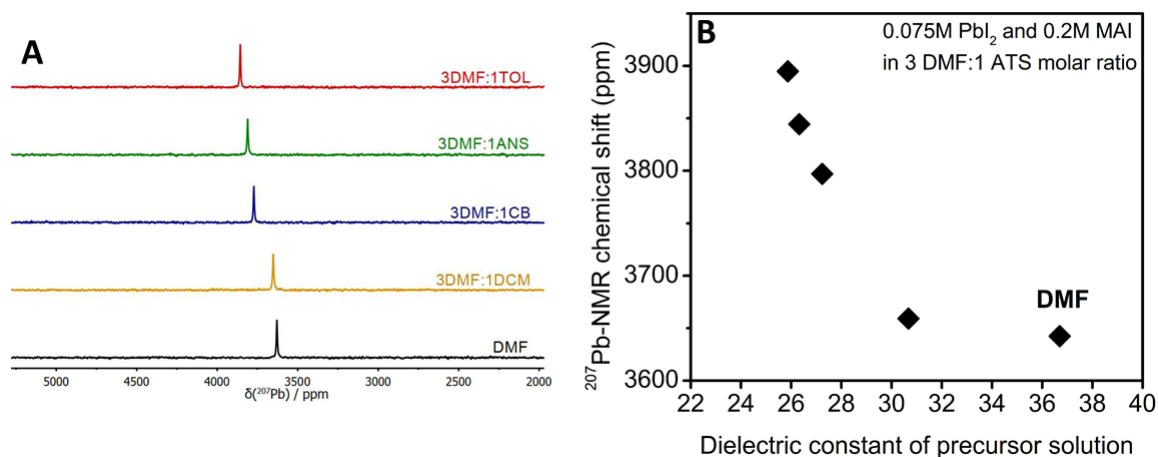


Fig. 3 (A) Solution-state ^{207}Pb -NMR spectra of 0.075 M PbI_2 and 0.2 M MAI in pure DMF and in a 3:1 molar ratio of DMF to antisolvents with varying dielectric constants. (B) ^{207}Pb -NMR chemical shift as a function of the dielectric constant of the precursor solution. A clear trend in downfield shift is observed when an antisolvent with a lower dielectric constant is incorporated into the precursor solution.

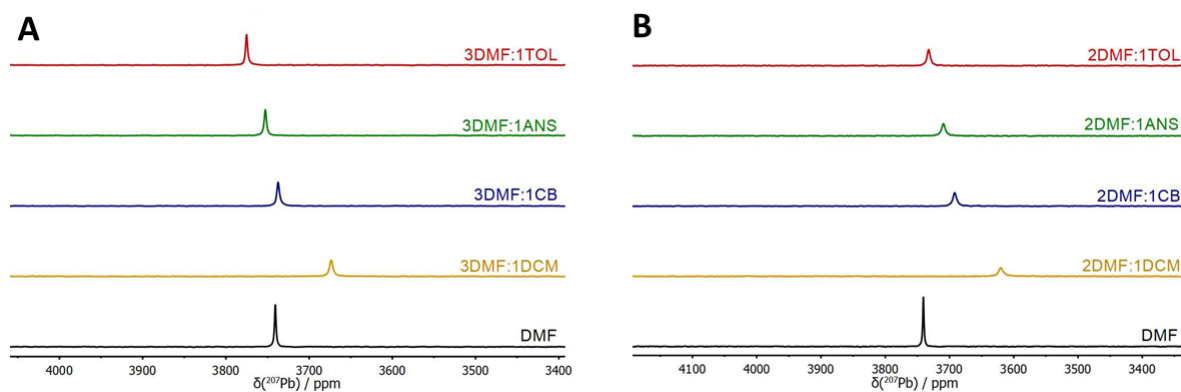


Fig. 4 Solution-state ^{207}Pb -NMR spectra of 0.075 M PbI_2 and 0.8 M MAI in pure DMF and in a (A) 2:1 molar ratio and (B) 3:1 molar ratio of DMF to antisolvents with varying dielectric constants.

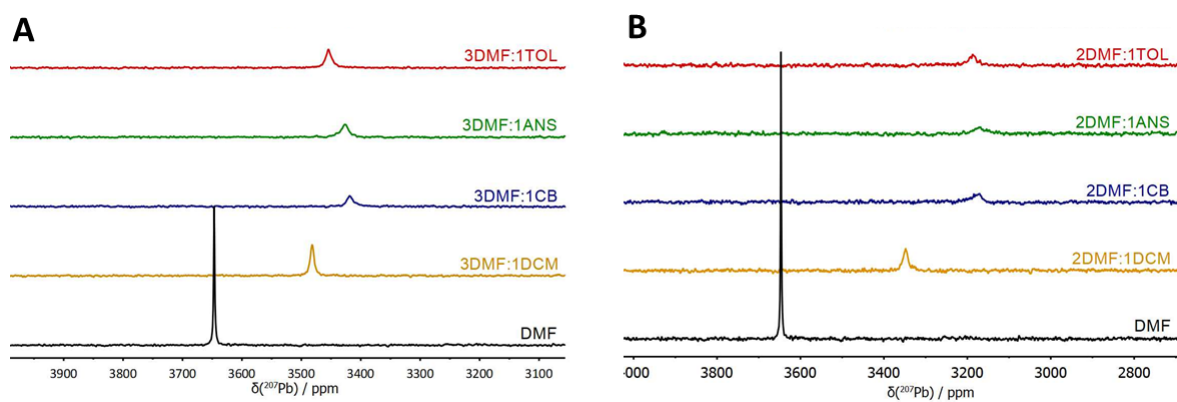


Fig. 5 Solution-state ^{207}Pb -NMR spectra of 0.075 M PbI_2 and 2.3 M MAI in pure DMF and in a (A) 2:1 molar ratio and (B) 3:1 molar ratio of DMF to antisolvents with varying dielectric constants.

6 Fabricated Thin Films

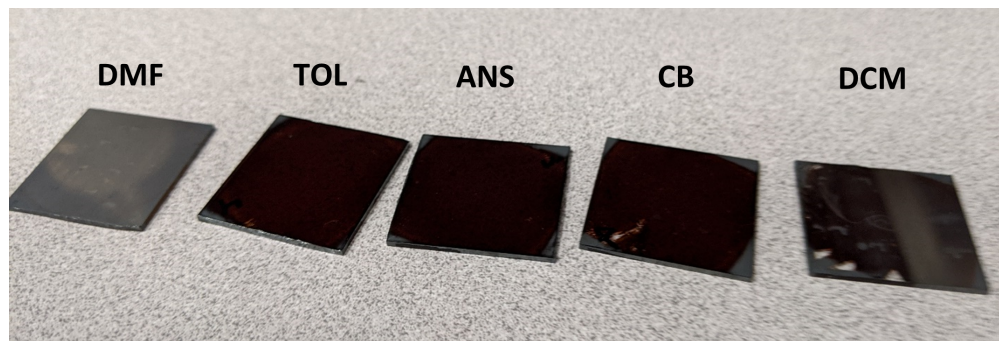


Fig. 6 Images of thin films fabricated using 1 M MAPbI_3 in DMF prepared using an antisolvent dripping method. The film denoted as DMF (leftmost image) was prepared with no antisolvent. The surfaces of the films prepared with DMF (leftmost) and DCM (rightmost) show significant dullness and roughness compared to those of the other films.

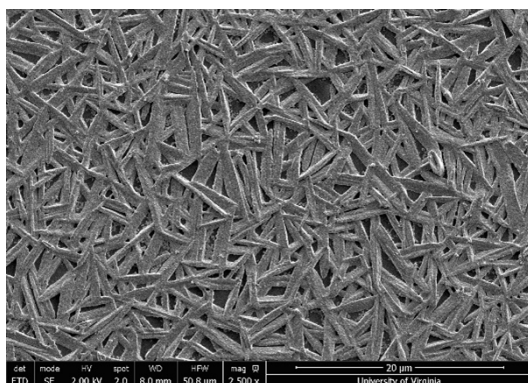


Fig. 7 SEM image of a film fabricated using 1 M MAPbI_3 in DMF with no antisolvent. The film shows a needle-like morphology with pinholes. A magnification of 2.5k was used with a scale bar of 20 μm .

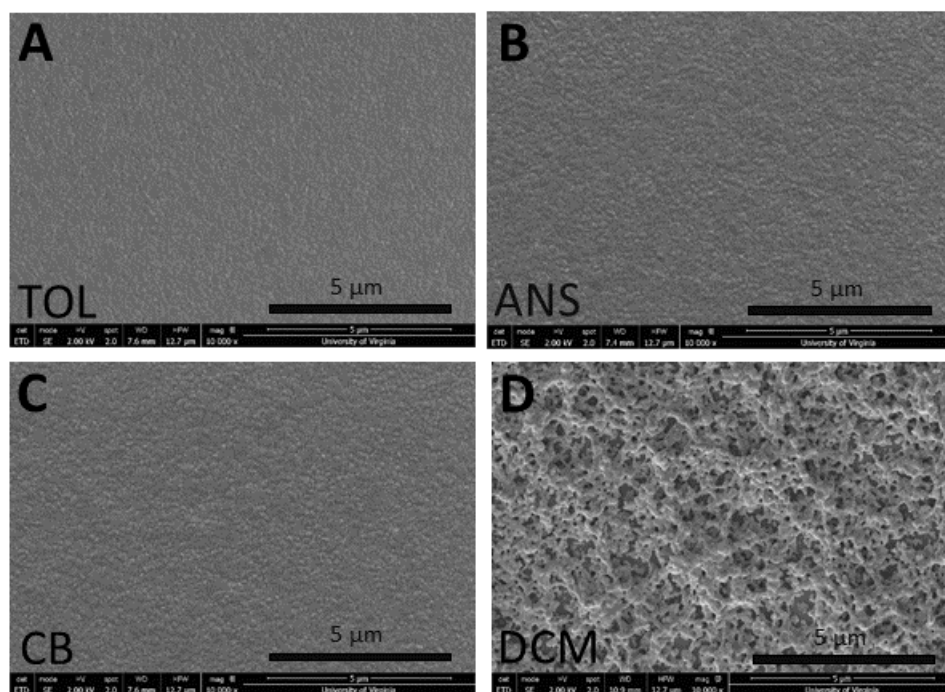


Fig. 8 SEM images of the films fabricated with 1M MAPbI₃ in DMF using antisolvent dripping method with the antisolvent (A) TOL (B) ANS (C) CB and (D) DCM. 10 k magnification was used with the scale bar 5 μm.