Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Self Limiting Atomic Layer Deposition of Al_2O_3 on Perovskite surfaces: A Reality?

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FIGURES:

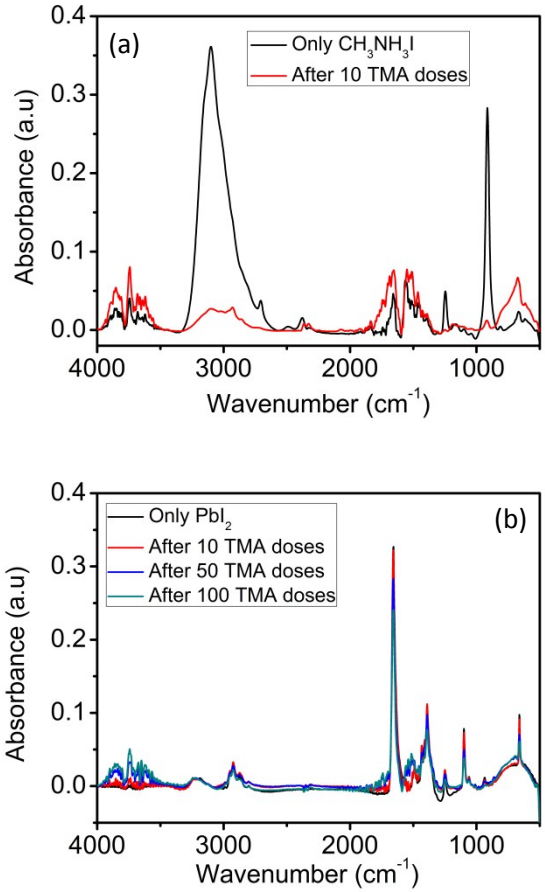


Figure S1: FTIR spectra comparison of (a) only methylammoniumiodide (MAI) and after exposure to 10 TMA doses, (b) pure PbI2 film and after continuous exposure to TMA.

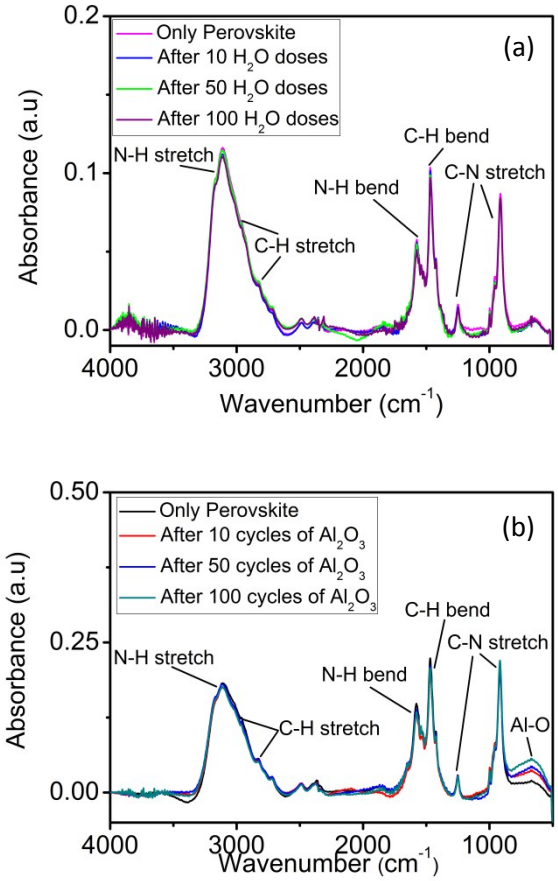


Figure S2 : FTIR spectra of perovskite deposited on KBr pellet and exposed to (a) repeated H_2O exposure, (b) sequential (1,1) exposure of TMA-H_2O.

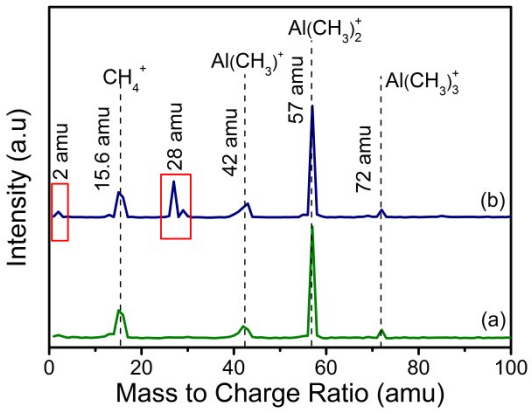


Figure S3: Comparison of mass spectrum of the byproducts released after reaction of TMA on (a) hydroxylated Si surface, (b) $CH_3NH_3PbI_xCl_{3-x}$ film surface

As seen from Figure S3b, byproducts corresponding to mass to charge ratio of 2, 16, 28, 42, 57 and 72 amu are recorded during the TMA exposure on perovskite surface. Of them, 16,

42, 57 and 72 amu are the byproducts formed during the base line measurement of TMA exposure on –OH terminated surface during deposition of Al_2O_3 (shown in fig. S3a). These correspond to the byproduct $CH4^+$ and unreacted $Al(CH)^+$, $Al(CH_3)_2^+$ and $Al(CH_3)_3^+$ respectively and are in agreement with earlier reports.[1, 2] The additional mass recorded at 2 and 28 amu as seen from fig. 3a can be attributed to H_2^+ and N_2^+/CH_3N^+ ions which can be obtained from the breakdown of the CH_3NH_2 byproduct. Thus the elimination of CH_4 and CH_3NH_2 from the perovskite surface definitely throws light on the probable reaction between TMA and the perovskite structure resulting in the formation of only PbI_2.

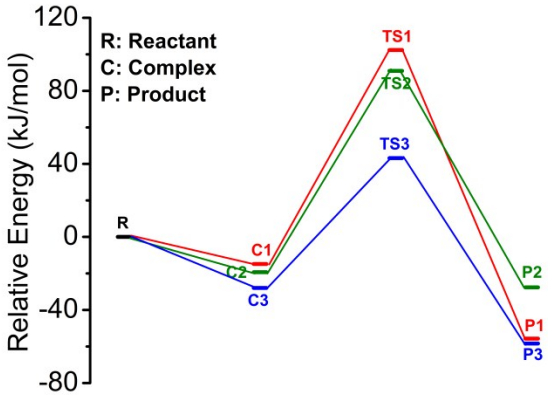
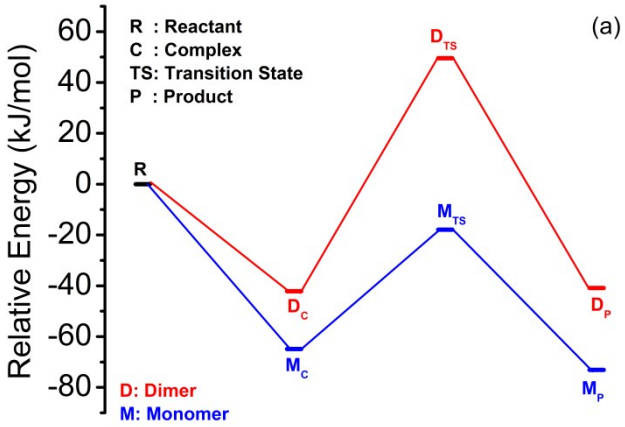


Figure S4: Reaction pathways and calculated energies for reactions between $CH_3NH_3PbI_3$ and (1), (2) TMA dimer, and (3) TMA monomer using UB3LYP functional, basis sets LanL2 for Pb and I, and 6-311++G(d,p) for all the other atoms.



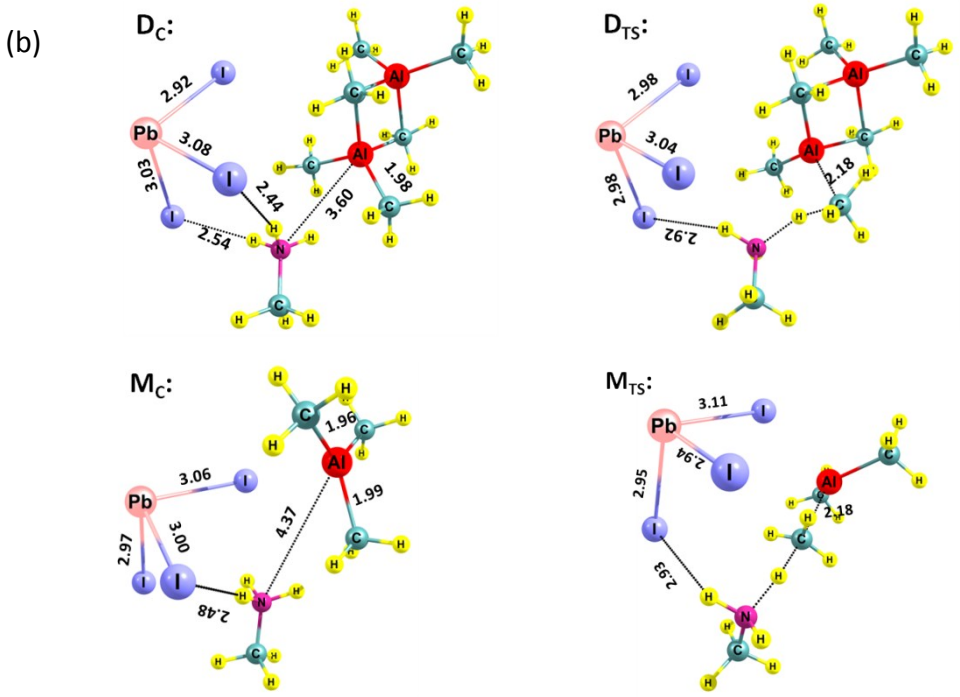


Figure S5: (a) Another reaction pathway and calculated energies for reactions between $CH_3NH_3PbI_3$ TMA dimer (D) and TMA monomer (M) using M06 functional, basis sets LanL2 for Pb and I, and 6-311++G(d,p) for all the other atoms, (b) optimised complex and transition state structures. The reactants and products were kept the same as in the main paper.

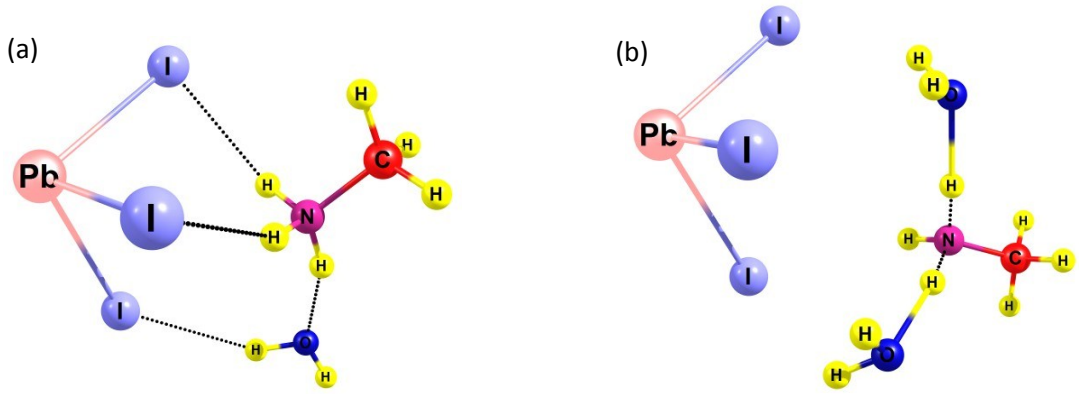


Figure S6: Optimized structures obtained by DFT calculations for (a) one and (b) two H_2O molecule interacting with perovskite.

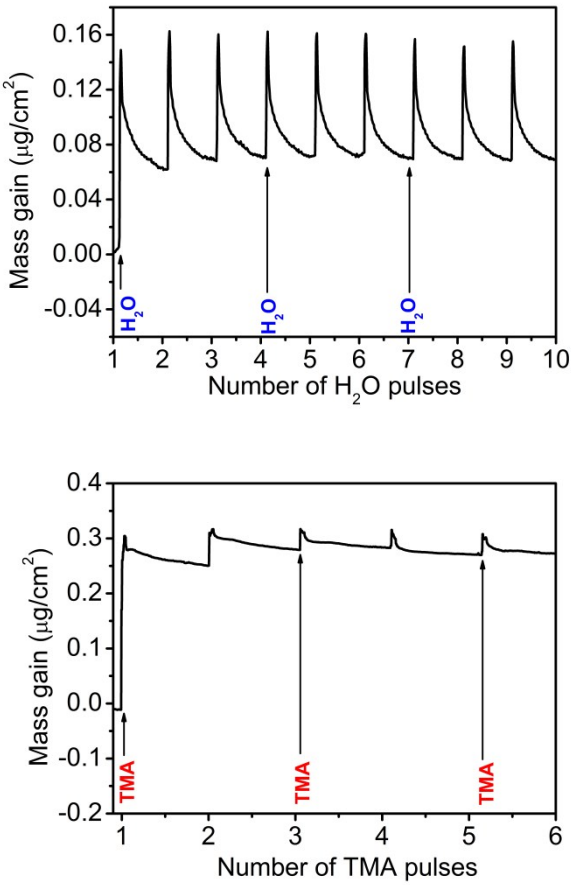


Figure S7: (a) Self-saturation H_2O studied on perovskite surface as observed by *in-situ* QCM, (b) Mass change observed after subsequent TMA exposure.

References:

1 R. E. Winters and R. W. Kiser, *J. Organomet. Chem*, 1967, **10**, 7-14.
2 J. Tanaka and S. R. Smith, *Inorg. Chem*, 1969, **8**, 265-270.