

Supporting information

Chloride Incorporation Process in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskites via Nanoscale Bandgap Maps

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Table S1: Summary of annealing history for MAPbI_{3-x}Cl_x sample: The text with the light red background highlights the extra annealing treatment with respect to the previous step.

<i>Annealing cycle</i>	<i>A0, “as prepared”:</i> T (°C), t (min)	<i>A5:</i> T (°C), t (min)	<i>A20:</i> T (°C), t (min)	<i>A30:</i> T (°C), t (min)
Cycle 1	60°C, 60 min	60°C, 60 min	60°C, 60 min	60°C, 60 min
Cycle 2	-	95°C, 5 min	95°C, 5 min	95°C, 5 min
Cycle 3	-	-	95°C, 5 min 110°C, 10 min	95°C, 5 min 110°C, 10 min
Cycle 4	-	-	-	110°C, 10 min

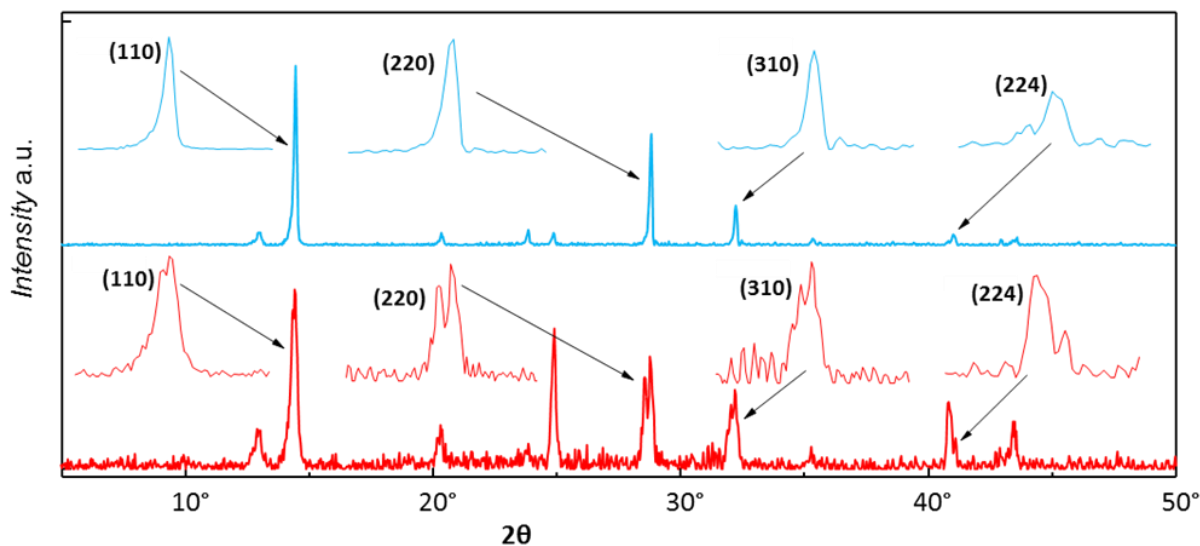


Figure S1. XRD patterns of a MAPbI_{3-x}Cl_x film dried in air (red) and after annealing 110 °C 150 min (blue). The data are normalized with respect to the strongest peak intensity and are displayed with an offset for clarity

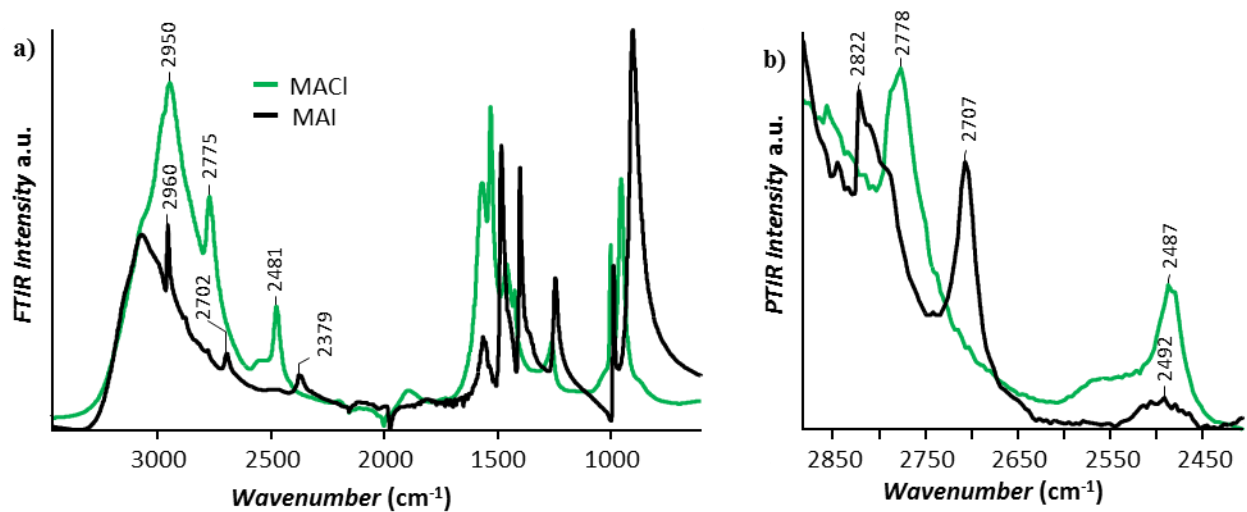


Figure S2. (a) FTIR spectra of the MAI and MAI precursor powders obtained using a diamond attenuated internal reflection accessory. (b) PTIR spectra of the MAI and MAI precursor films.

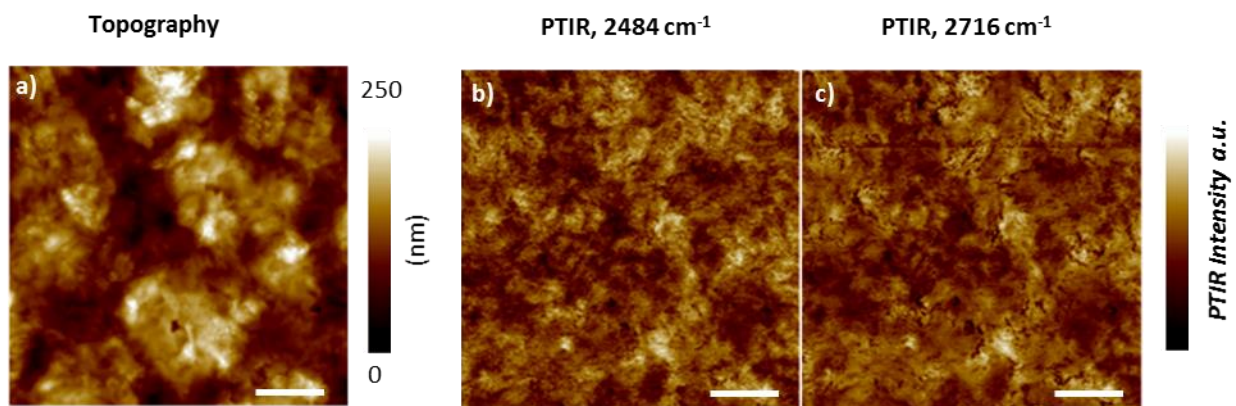


Figure S3. a) AFM topography image of as prepared $\text{MAPbI}_{3-x}\text{Cl}_x$ film; b, c) corresponding PTIR maps obtained by illuminating the sample at 2484 cm^{-1} and 2716 cm^{-1} respectively. The PTIR maps are plotted in a common full scale and all scale bars are $2.0\text{ }\mu\text{m}$.

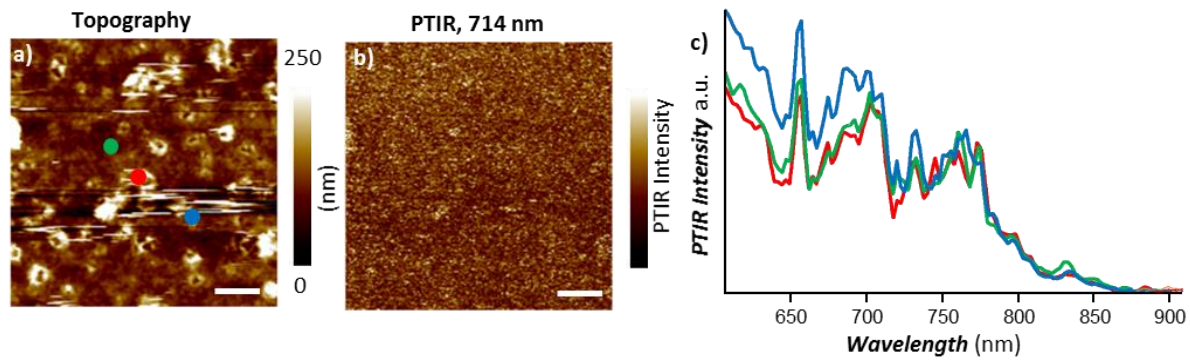


Figure S4. a) AFM topography image of the as prepared MAPbI₃ reference sample; b) corresponding PTIR absorption map obtained by illuminating the sample at 714 nm (1.74 eV) All scale bars are 2.0 μm . (c) PTIR electronic absorption spectra obtained at the marked color-coded locations in panel a.

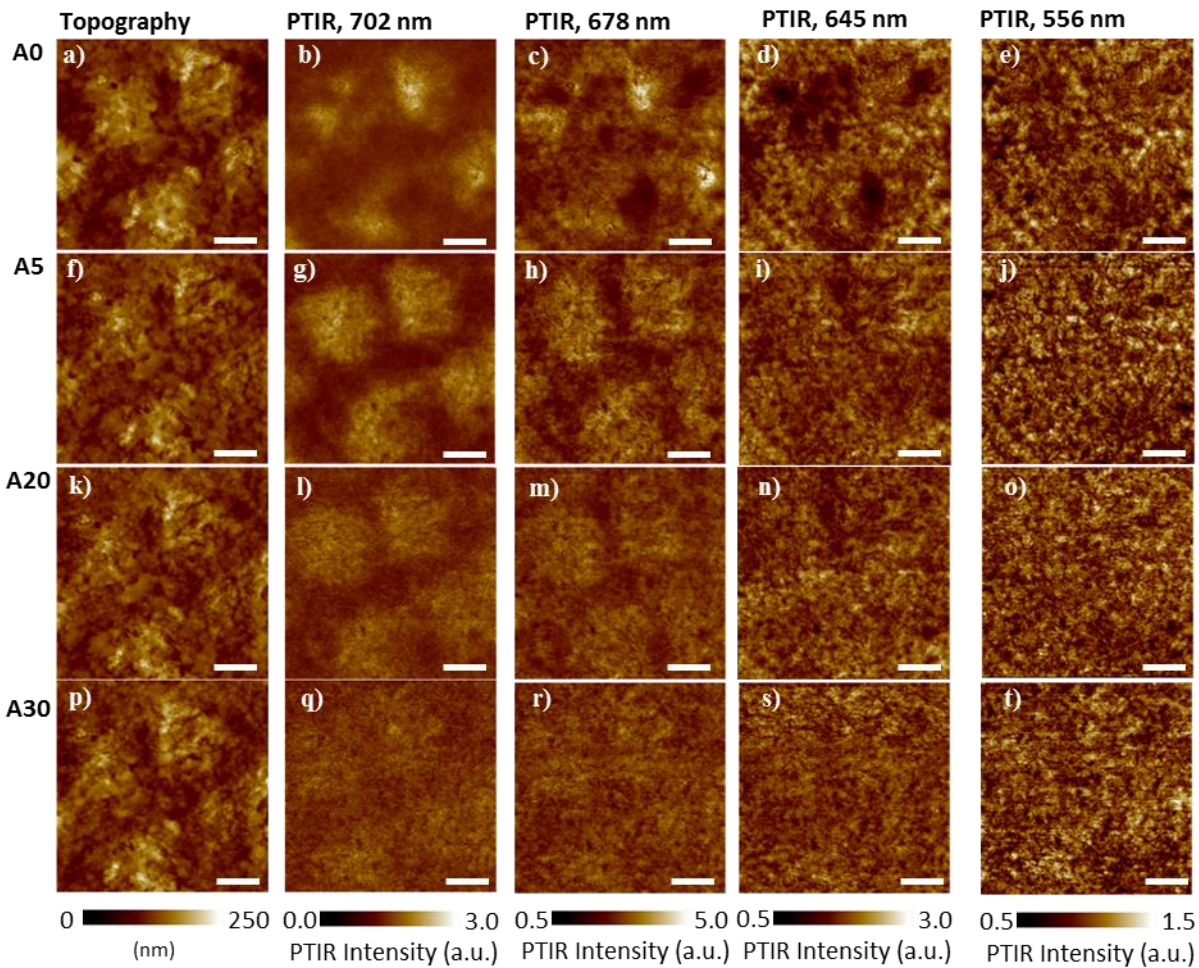


Figure S5. AFM height images (first column) and PTIR maps recorded by illuminating MAPbI_{3-x}Cl_x film at 702 nm (1.77 eV, second column), at 678 nm (1.83 eV, 3rd column), at 645 nm (1.92 eV, forth column), and at 556 nm (2.23 eV, fifth column). The data are displayed in rows as a function of the annealing: *A0*, as prepared sample (first row), *A5*, after annealing at 95 °C for 5 min (second row), *A20*, after additional annealing at 95 °C for 5 min and at 110 °C for 10 min (third row), and *A30*, after additional annealing at 110 °C for 10 min (fourth row). All scale bars are 2.0 μm.

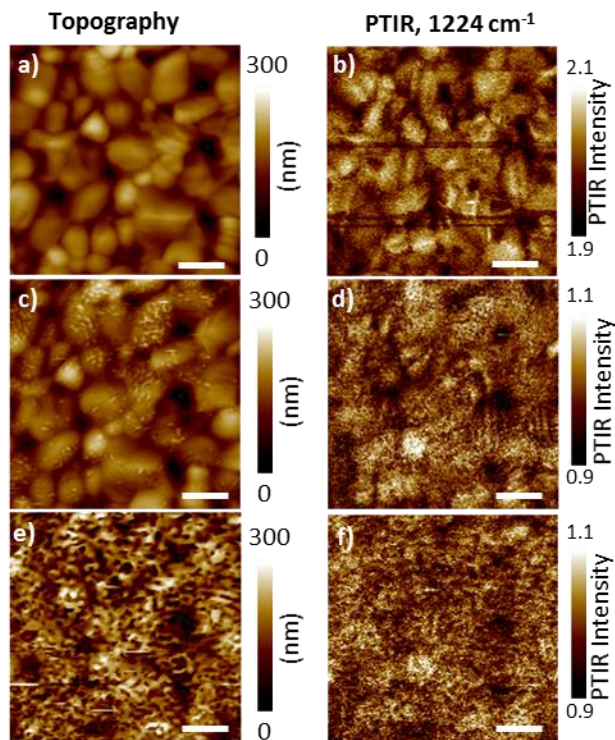


Figure S6. Pairs of AFM topography and PTIR absorption map (1224 cm^{-1} corresponding to NH_3 rocking mode of the methylammonium ion) of the MAPbI_3 sample before annealing (a and b), after 10 minutes annealing at 140° C (c and d) and after additional 50 minutes annealing (e and f) at 140° C , respectively. The intensity of the PTIR maps are plotted with the same scale range and all scale bars are $1.0\ \mu\text{m}$. Substantial material degradation is evident in both the topography and PTIR maps.