ESI for "Perovskite Processing for Photovoltaics: a Spectro-Thermal Evaluation"

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Figure ESI1 shows typical XRD pattern for CH₃NH₃I annealed at 100 °C.



Figure ESI1: XRD data from CH₃NH₃PbI₃ showing the annealed perovskite material (*); reflections at *ca.* 14, 28 and 43° correspond to (110), (220) and (330) planes respectively. Other peaks correspond to the substrate. No PbI₂ is seen, indicating full conversion to the final perovskite material.

Figure ESI2 shows the evolved gas FTIR spectra for CH₃NH₃Cl and CH₃NH₃I at 100 °C.



Figure ESI2: FTIR of gases evolved from CH₃NH₃Cl and CH₃NH₃I at 100 °C. (*N.B.* the features seen are an actually 'inverse' background caused by insufficient venting prior background measurement, resulting in negative water vapour and CO₂ signals.)

Figure ESI3 shows the evolved gas FTIR spectra from annealed $CH_3NH_3PbI_{3-x}Cl_x$ and $CH_3NH_3PbI_3$ *ca.* 230 °C. DMF and decomposition products can be observed.



Figure ESI3: FTIR spectra of gases evolved from (a) CH₃NH₃PbI_{3-x}Cl_x and (b) CH₃NH₃PbI₃ around 230 °C.

Figure ESI4 shows FTIR of CH₃NH₃Pbl_{3-x}Cl_x during 30 °C pre-drying at *ca*. 0 h, *ca*. 8 h and *ca*. 11 h:



Figure ESI4: intensity of evolved gas FTIR peak at 1720 cm-1 for MAPbI3-xClx undergoing slow solvent loss at 30 °C under N₂. It must be noted that the presence of water vapour and CO₂ in the t=0 spectrum (solid line) are a result of insufficient venting time prior to run.

Figure ESI5: FTIR spectra of $CH_3NH_3PbI_{3-x}CI_x$ during 100 °C annealing step <u>after</u> pre-drying at *ca.* 10, 15, 30 and 80 min



Figure ESI5: selected evolved gas FTIR spectra during 100 °C annealing of pre-dried CH₃NH₃Pbl_{3-x}Cl_x

Figure ESI6 shows evolved gas FTIR spectra of $CH_3NH_3I_{3-x}CI_x$, which had previously been been pre-dried at 30 °C then annealed at 100 °C, during T scan 100 – 250 °C, and $FTIR_{1720}$ profile of a sample that had only been subjected to annealing at 100 °C



Figure ESI6: STA-FTIR analysis over the temperature range 100 – 250 °C for sample of CH₃NH₃I_{3-x}Cl_x that had been subjected to 30 °C for 900 minutes and 100 °C for 90 minutes. (a) evolved gas spectra at 110 and 187 °C; (b) evolved gas spectrum at 236 °C; (c) evolved gas spectrum at 240 °C (d) FTIR₁₇₂₀ evolved gas from sample prep by 100°C, 80 min annealing only (no pre-drying) showing spikes at increasing T

Figure ESI7 shows evolved gas FTIR during T scan following 'annealing' at different T / t combinations



Figure ESI7: Post-anneal evolved gas FTIR spectra of CH₃NH₃I_{3-x}Cl_x 'annealed' at (a) 30 °C for 900 min; (b) 100 °C for 10 min; (c) 100 °C for 80 min. Selected spectra across the temperature scan range.

Figure ESI8 shows Evolved gas FTIR spectra for sample of $CH_3NH_3I_{3-x}CI_x$ 'annealed' at RT in silica gel desiccant. Y-axis merely shows what's being measured; scale at bottom RHS is appropriate for all 3 spectra



Figure ESI8: FTIR evolved gas spectra obtained during T scan of a sample of CH₃NH₃I_{3-x} Cl_x 'annealed' at room temperature under silica gel desiccant. Spectra (baseline corrected)