

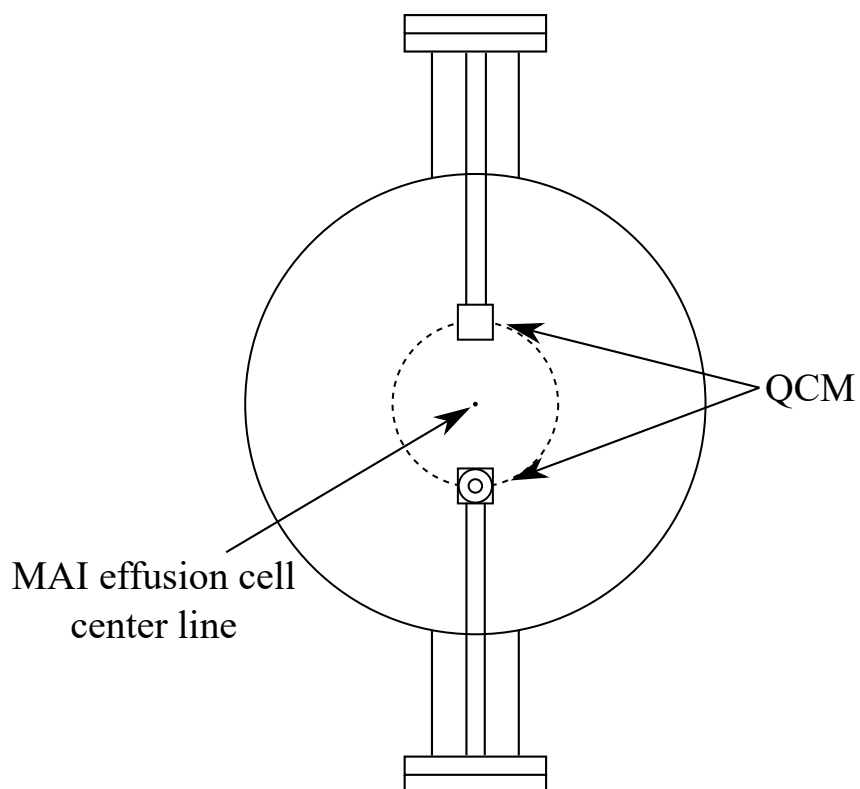
# Deposition of Methylammonium Iodide via evaporation - combined kinetic and mass spectrometric study

## Supporting information

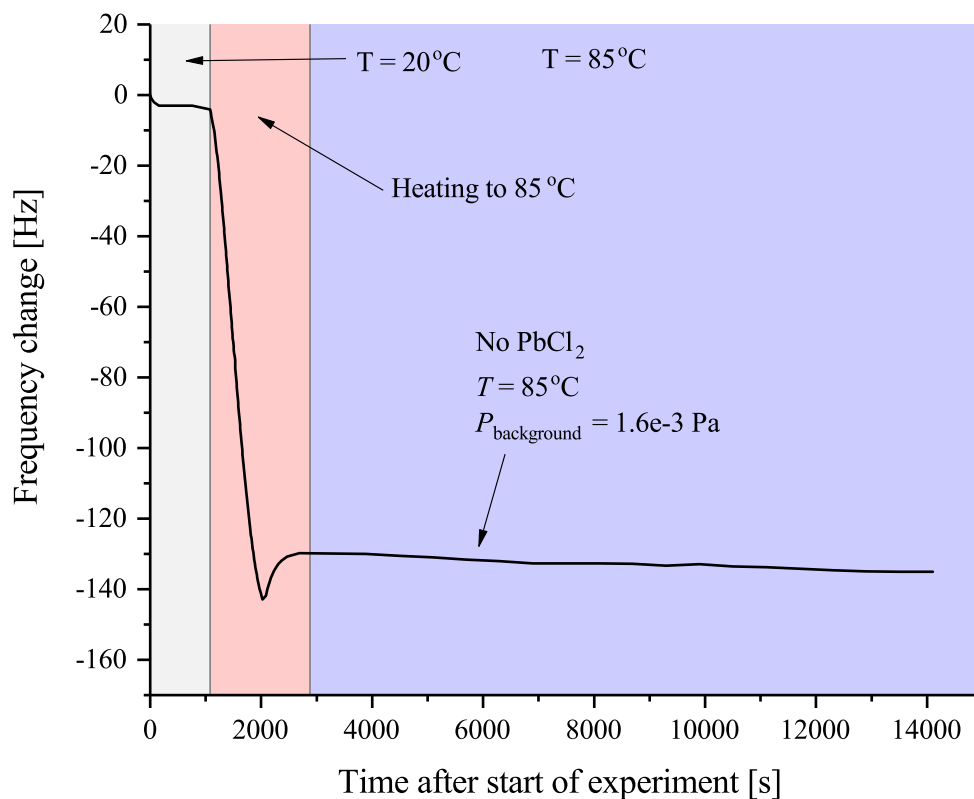
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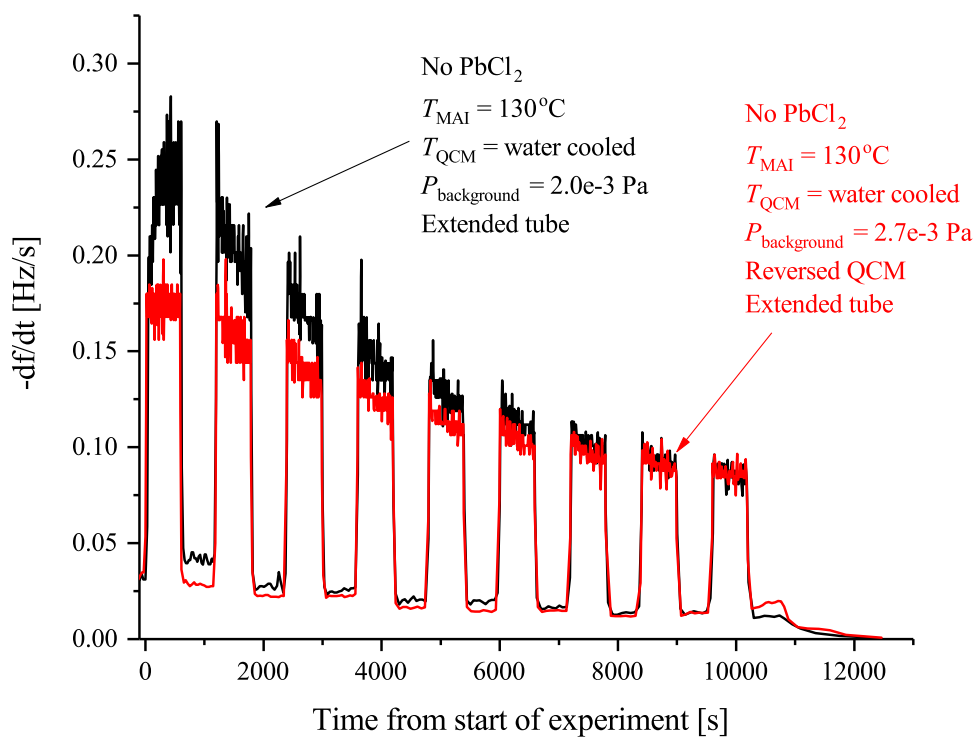
### 1 Additional figures



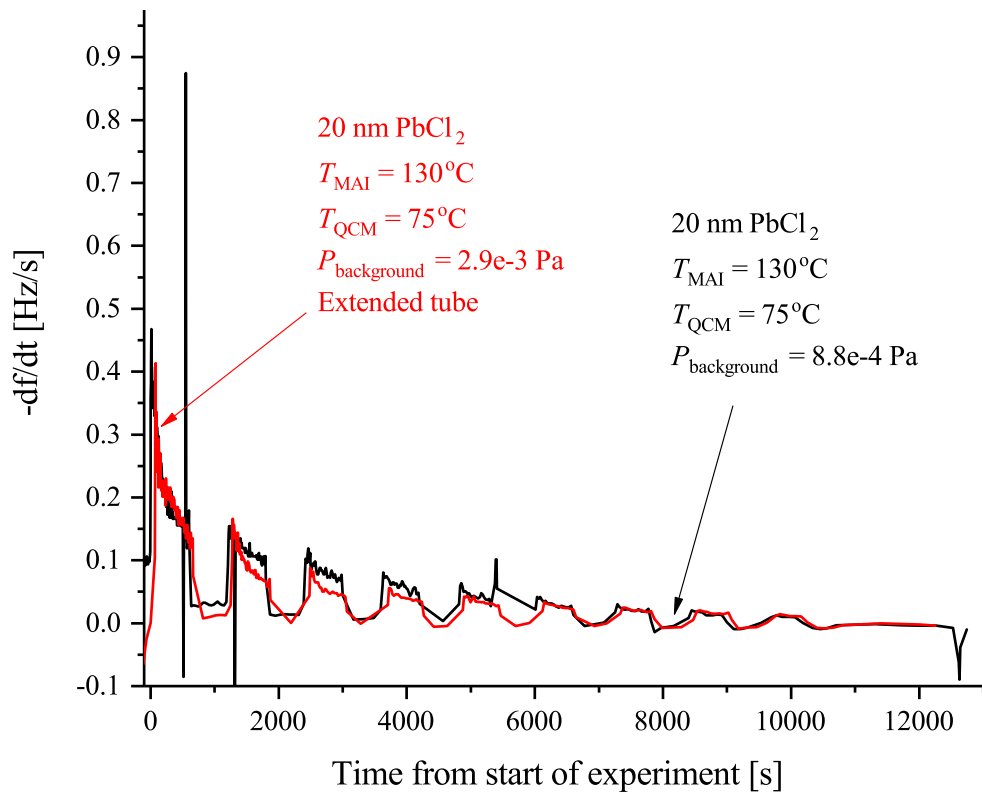
**S 1** Schematic drawing of the QCM set up shown from a different angle compared to Figure 1.



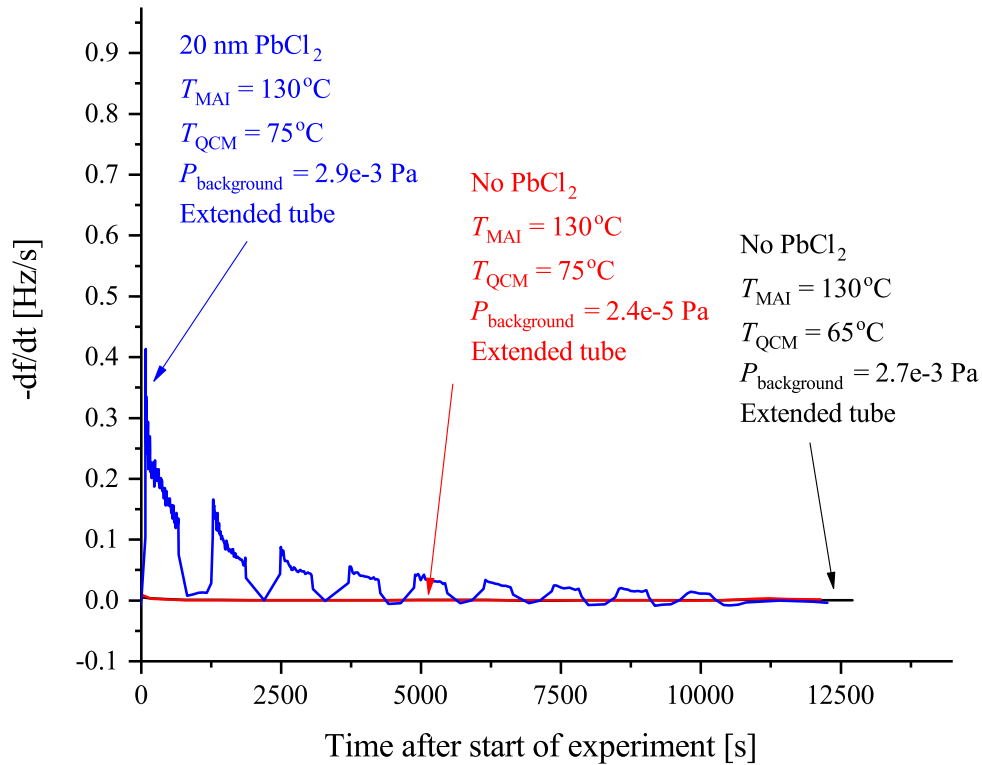
**S 2** QCM experiment using the forward QCM in which a blank crystal was heated to  $85^{\circ}\text{C}$  without any MAI being deposited. The different zones define different temperature regions: the gray is  $20^{\circ}\text{C}$ , the red is heating to  $85^{\circ}\text{C}$  and the blue is  $85^{\circ}\text{C}$ . Like the experiments in the main paper the temperature was controlled using a heat bath.



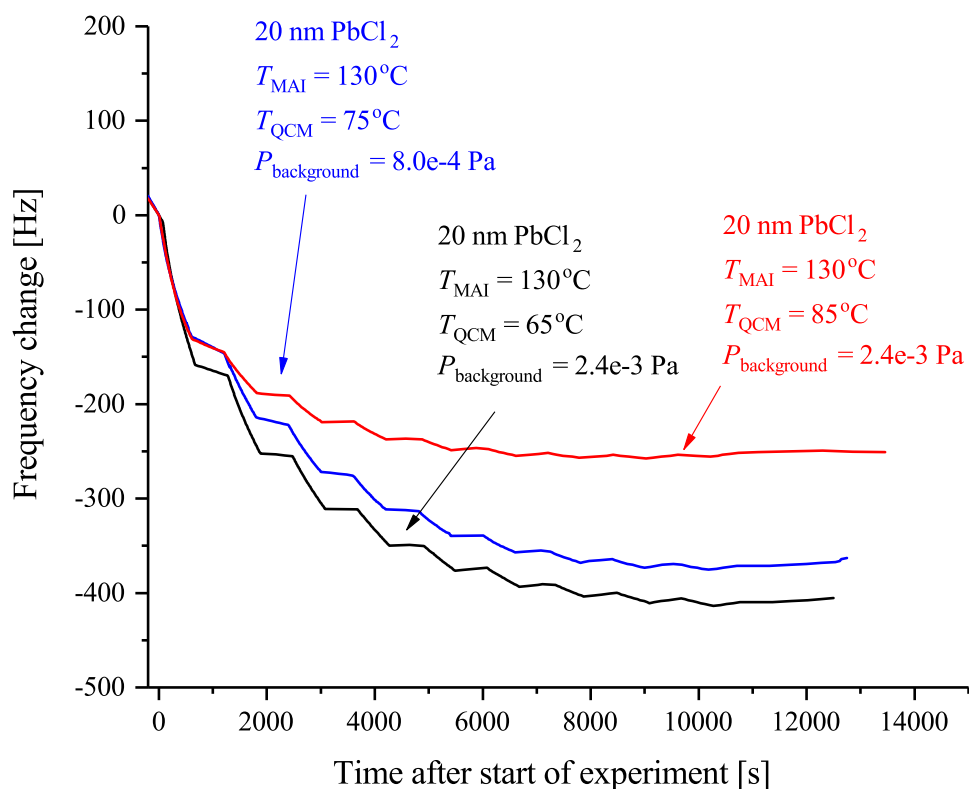
**S 3** QCM experiment using the reverse QCM showing the effect of having line of sight from the MAI effusion cell and the sensor.  $T_{\text{MAI}}$  is the MAI source temperature,  $T_{\text{QCM}}$  is the QCM temperature,  $P_{\text{background}}$  is the background pressure. The signal was again chopped in 10 min intervals using the shutter on the MAI source.



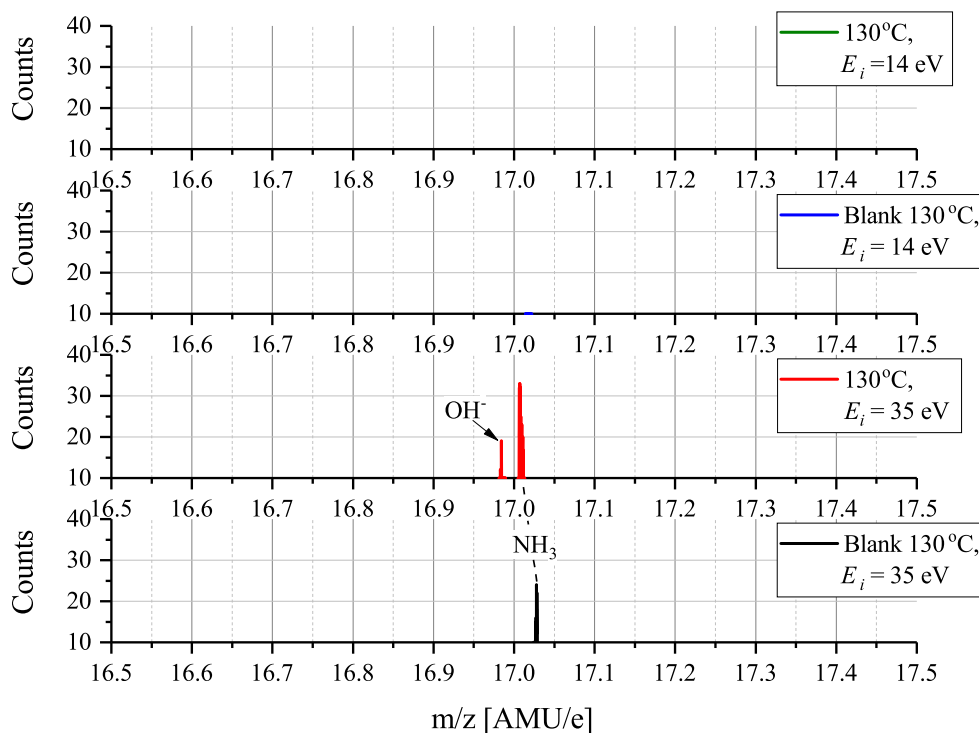
**S 4** QCM experiment using the forward QCM showing the effect of moving the MAI effusion cell 10 cm further away from the sensor.  $T_{\text{MAI}}$  is the MAI source temperature,  $T_{\text{QCM}}$  is the QCM temperature,  $P_{\text{background}}$  is the background pressure. The signal was again chopped in 10 min intervals using the shutter on the MAI source.



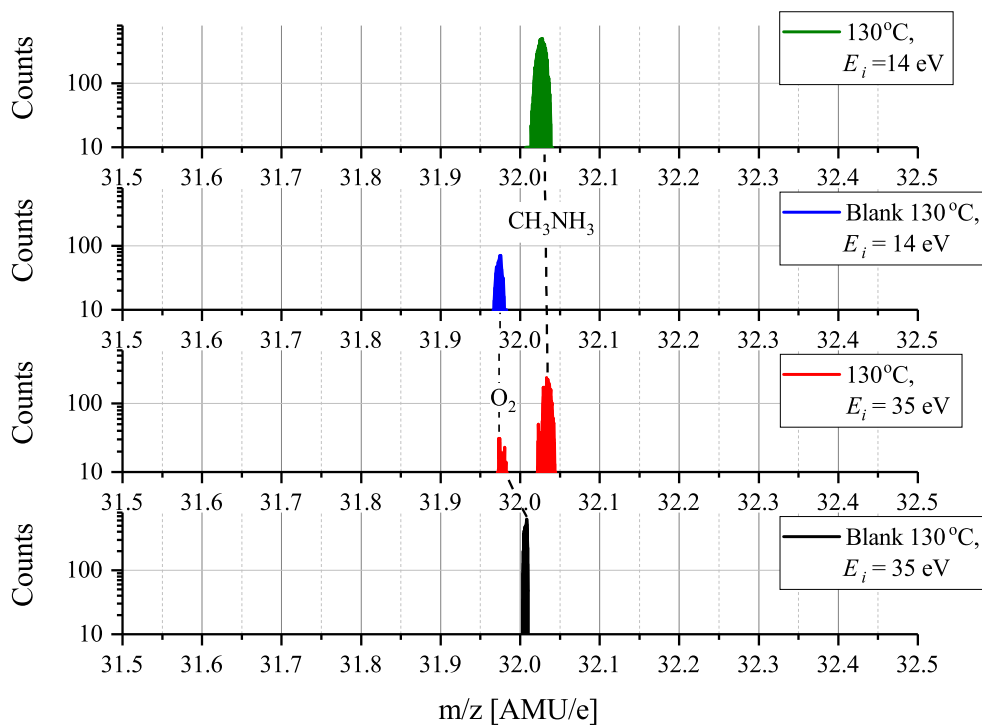
**S 5** QCM experiment using the forward QCM showing the effect of having  $\text{PbCl}_2$  predeposited on the QCM crystal. The  $65^\circ\text{C}$  and  $75^\circ\text{C}$  blank plot are hard to distinguish as they are more or less identical.  $T_{\text{MAI}}$  is the MAI source temperature,  $T_{\text{QCM}}$  is the QCM temperature,  $P_{\text{background}}$  is the background pressure. The signal was again chopped in 10 min intervals using the shutter on the MAI source.



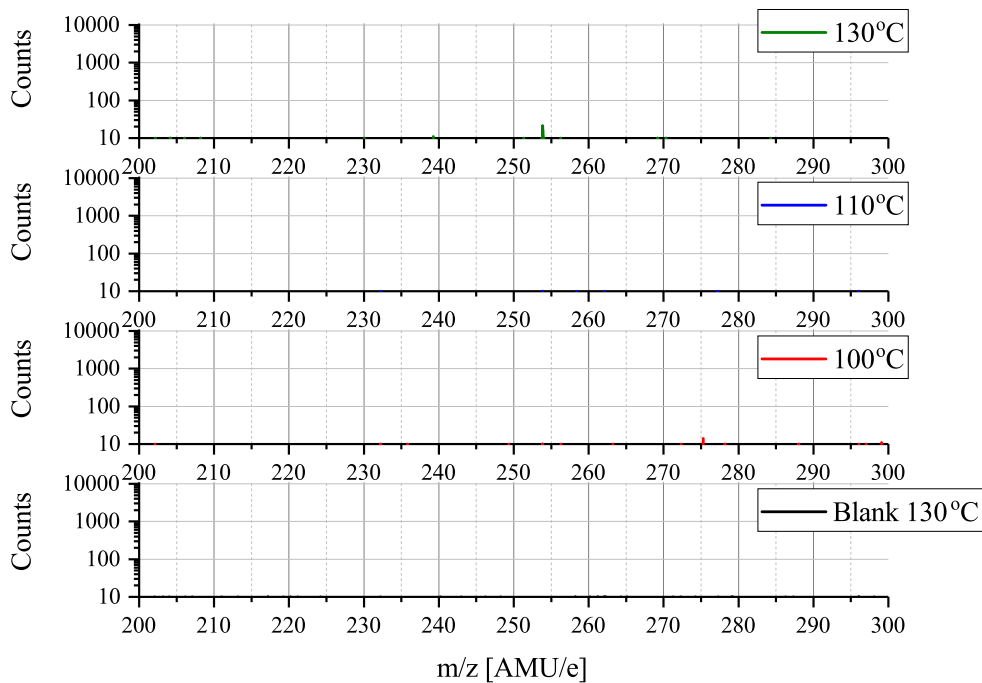
**S 6** QCM experiment using the forward QCM showing the corresponding frequency change of the observed rate shown in Figure 3 of the main paper.  $T_{\text{MAI}}$  is the MAI source temperature,  $T_{\text{QCM}}$  is the QCM temperature,  $P_{\text{background}}$  is the background pressure. The signal was again chopped in 10 min intervals using the shutter on the MAI source.



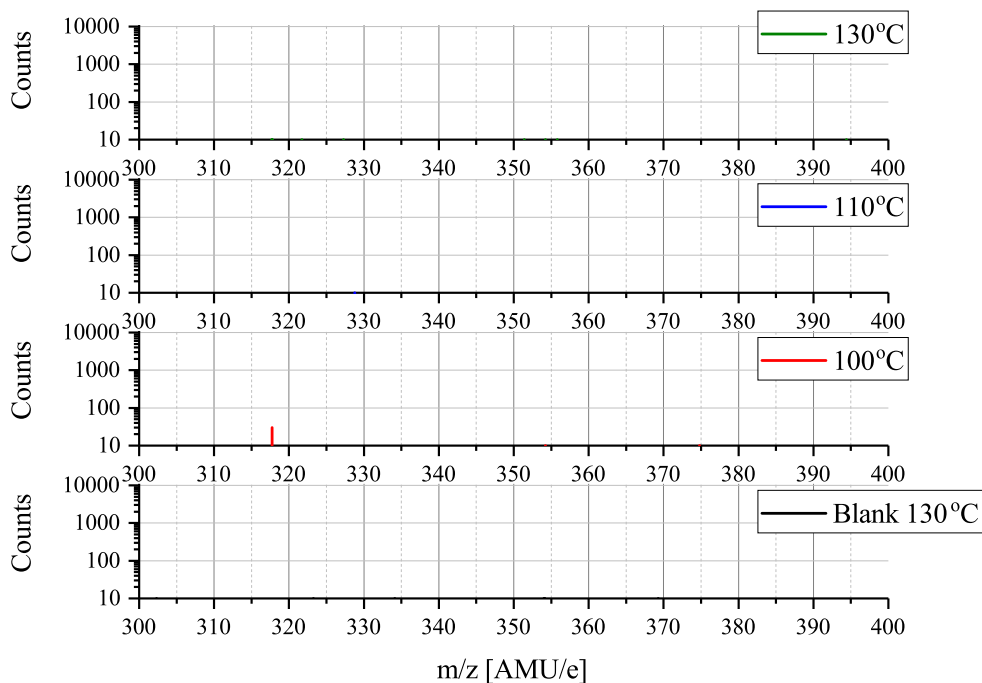
**S 7** Mass scans in the  $m/z = 16.5\text{-}17.5$  range for MAI evaporated at  $130^{\circ}\text{C}$  recorded using an ionization energy,  $E_i$ , of 35 eV or 14 eV. The dashed lines indicate peaks originating from the same species (OH<sup>-</sup> or NH<sub>3</sub>) indicated in the label. The Counts axis starts from 10 counts as everything below is designated as noise.



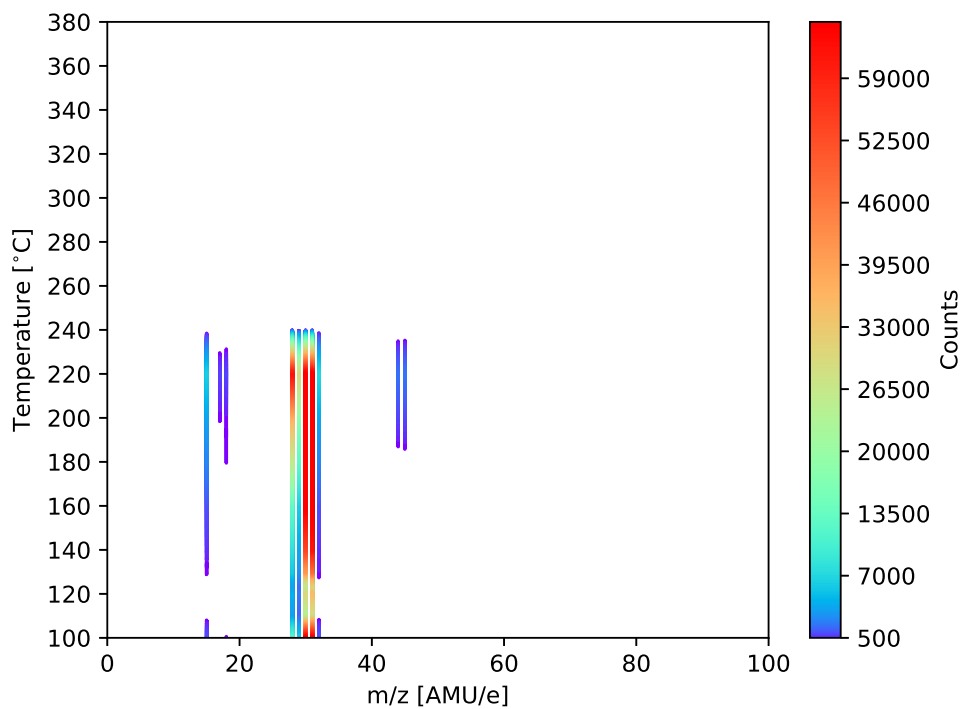
**S 8** Mass scans in the  $m/z = 31.5\text{-}32.5$  range for MAI evaporated at  $130^\circ\text{C}$  recorded using an ionization energy,  $E_i$ , of 35 eV or 14 eV. The dashed lines indicate peaks originating from the same species ( $\text{O}_2$  or  $\text{CH}_3\text{NH}_3$ ) indicated in the label. The Counts axis starts from 10 counts as everything below is designated as noise.



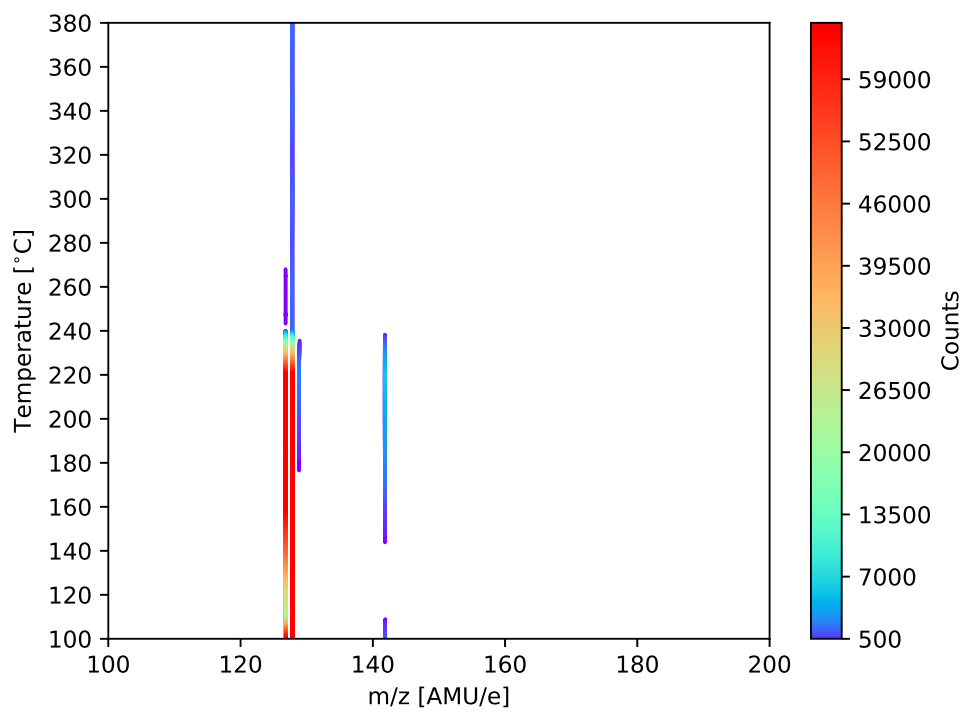
**S 9** Mass scans in the  $m/z = 200\text{-}300$  range for MAI evaporated at  $130^\circ\text{C}$  recorded using an ionization energy,  $E_i$ , of 14 eV. The Counts axis starts from 10 counts as everything below is designated as noise.



**S 10** Mass scans in the  $m/z = 300-400$  range for MAI evaporated at  $130^{\circ}\text{C}$  recorded using an ionization energy,  $E_i$ , of 14 eV. The Counts axis starts from 10 counts as everything below is designated as noise.



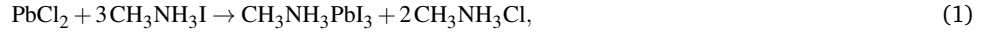
**S 11** Intensity plot of the significant peaks ( $> 500$  counts) in the  $m/z = 0-100$  range for MAI evaporated at temperatures of up to  $380^{\circ}\text{C}$ . The data was recorded using an ionization energy of 14 eV.



**S 12** Intensity plot of the significant peaks (> 500 counts) in the  $m/z = 100$ - $200$  range for MAI evaporated at temperatures of up to  $380^{\circ}\text{C}$ . The data was recorded using an ionization energy of 14 eV.

## 2 PbCl<sub>2</sub> depletion calculations

The reaction expected to take place is



from which one would anticipate that the amount of MAI that needs to be deposited is 3 times the amount of PbCl<sub>2</sub>. The amount of PbCl<sub>2</sub> per area can be estimated by using that the density of PbCl<sub>2</sub> is  $5.85 \frac{\text{g}}{\text{cm}^3}$  which yields

$$20 \text{ nm} \times 5.85 \frac{\text{g}}{\text{cm}^3} = 1.17 \times 10^4 \frac{\text{ng}}{\text{cm}^2}. \quad (2)$$

From this the mass of the fully converted perovskite can be estimated by using the molar masses of PbCl<sub>2</sub> =  $278 \frac{\text{g}}{\text{mol}}$  and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> =  $620 \frac{\text{g}}{\text{mol}}$  which yields

$$\frac{620}{278} \times 1.17 \times 10^4 \frac{\text{ng}}{\text{cm}^2} = 2.61 \times 10^4 \frac{\text{ng}}{\text{cm}^2}. \quad (3)$$

The mass increase that one would expect for full conversion if all the MAI reevaporates is thus

$$2.61 \times 10^4 \frac{\text{ng}}{\text{cm}^2} - 1.17 \times 10^4 \frac{\text{ng}}{\text{cm}^2} = 1.44 \times 10^4 \frac{\text{ng}}{\text{cm}^2}. \quad (4)$$

To estimate the highest amount of MAI deposited we use that the maximal frequency change observed in Figure 6 is about -405 Hz (the 65°C plot). From equation (1) in the main paper one gets

$$\Delta f = -C_f \Delta m \Leftrightarrow \Delta m = -\frac{\Delta f}{C_f}. \quad (5)$$

By using that  $C_f$  is given by<sup>1</sup>

$$C_f = \frac{2nf_0^2}{(\rho_q \mu_q)^{1/2}}, \quad (6)$$

where  $n$  is the number of the harmonic at which the crystal is driven,  $f_0$  is the resonant frequency of the fundamental mode of the crystal,  $\rho_q = 2.648 \frac{\text{g}}{\text{cm}^3}$  is the density of quartz,  $\mu_q = 2.947 \times 10^{-11} \frac{\text{g}}{\text{cm}^2 \text{s}^2}$  is the shear modulus of quartz, that  $n = 1$ ,  $f_0 = 6 \times 10^6$  Hz and inserting the  $\Delta f = -405$  Hz one gets

$$C_f = 8.15 \times 10^7 \frac{\text{cm}^2 \text{Hz}}{\text{g}} \Rightarrow \Delta m = \frac{405 \text{ Hz}}{8.15 \times 10^7 \frac{\text{cm}^2 \text{Hz}}{\text{g}}} = 4.97 \times 10^3 \frac{\text{ng}}{\text{cm}^2}. \quad (7)$$

This is obviously a much lower number than what one would expect and the PbCl<sub>2</sub> would need to be no thicker than 6.90 nm for full conversion. As suggested by equation (1) the Cl of the PbCl<sub>2</sub> is exchanged with I from the MAI during the reaction through



Given that the I is heavier than the Cl the reaction will give rise to a frequency change, which could be interpreted as deposition of MAI though the entire molecule does in fact not stick. The MAI deposition rate might thus be overestimated slightly though the error is mitigated by the fact that the I carries roughly 80% of the MAI mass. In any case the same chain of reactions need to take place when doing the actual CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> deposition and the shown rates thus serve as "effective" rates though it is not clear which specific reaction the MAI is part of.

## 3 Sticking coefficient calculations

To estimate the sticking coefficient,  $S_c$ , from the pressure one can use the concept of Langmuir (L) where one Langmuir corresponds to an exposure of  $1.33 \times 10^{-4}$  Pa of gas for one second. By assuming a  $S_c$  of 1 one can show that an exposure of 1 L corresponds to a deposition of about 1 monolayer per second and since a monolayer is roughly 0.3 nm one expects a deposition rate of 0.3 nm/s for a 1 L exposure. The number of Langmuir scales with pressure meaning that a deposition pressure of  $1.33 \times 10^{-3}$  Pa gives rise to an exposure of 10 L or a rate of 3 nm/s. The chamber pressure during a typical experiment is shown in Figure 7 from which one can deduce that the partial pressure associated with MAI evaporation is roughly  $2 \times 10^{-3}$  Torr or a rate of 6 nm/s when the pressure change stabilizes.

Using a MAI density of  $2.22 \frac{\text{g}}{\text{cm}^3}$  one can calculate the amount of MAI that would have been deposited during the approximately 11000 s the experiments shown in Figure 6 takes which is given by

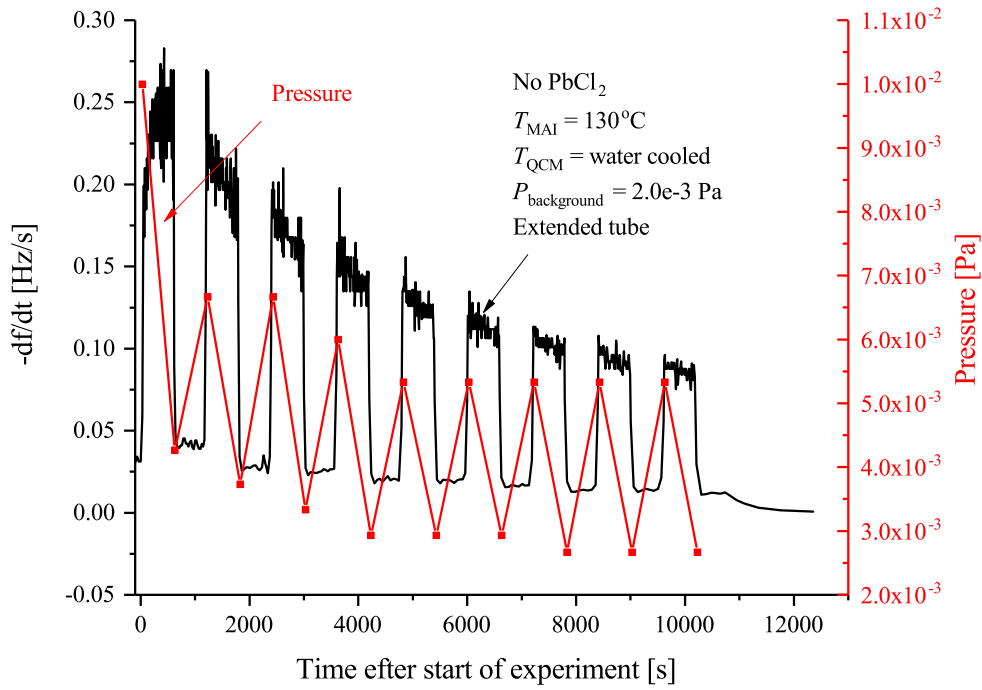
$$\Delta m = S_c R t \rho_{\text{MAI}}, \quad (9)$$

where  $R$  is the rate,  $t$  is the exposure time,  $\rho_{\text{MAI}}$  is the MAI density and  $S_c$  is assumed to be 1. This yields

$$\Delta m = 6 \times 10^{-7} \text{ cm/s} \times 11000 \text{ s} \times 2.22 \frac{\text{g}}{\text{cm}^3} = 1.47 \times 10^{-2} \frac{\text{g}}{\text{cm}^2} = 1.47 \times 10^7 \frac{\text{ng}}{\text{cm}^2}. \quad (10)$$

By using equation (7) and that the frequency change observed in Figure 6 is  $\Delta f = -250$  Hz,  $-360$  Hz and  $-405$  Hz for the 85°C, 75°C and 65°C case, respectively one can calculate the deposited mass per area to be





**S 13** QCM experiment showing the change in chamber pressure observed when operating the shutter together with the observed deposition rate on a blank crystal.  $T_{\text{MAI}}$  is the MAI source temperature,  $T_{\text{QCM}}$  is the QCM temperature,  $P_{\text{background}}$  is the background pressure. The signal was again chopped in 10 min intervals using the shutter on the MAI source.

$$\Delta m_{85^\circ\text{C}} = 3.07 \times 10^3 \frac{\text{ng}}{\text{cm}^2}, \Delta m_{75^\circ\text{C}} = 4.42 \times 10^3 \frac{\text{ng}}{\text{cm}^2} \text{ and } \Delta m_{65^\circ\text{C}} = 4.97 \times 10^3 \frac{\text{ng}}{\text{cm}^2}. \quad (11)$$

From this one gains the sticking coefficients

$$S_{c,85^\circ\text{C}} = 2.095 \times 10^{-4} \simeq 2.1 \times 10^{-4}, S_{c,75^\circ\text{C}} = 3.017 \times 10^{-4} \simeq 3.0 \times 10^{-4} \text{ and } S_{c,65^\circ\text{C}} = 3.392 \times 10^{-4} \simeq 3.4 \times 10^{-4}, \quad (12)$$

in the 85°C, 75°C and 65°C case, respectively.

## References

- [1] Stanford Research Systems, *QCM100- Quartz Crystal Microbalance Theory and Calibration*, <http://www.thinksrs.com/downloads/PDFs/ApplicationNotes/QCMTheoryapp.pdf>.
- [2] L. K. Ono, M. R. Leyden, S. Wang and Y. Qi, *J. Mater. Chem. A*, 2016, **4**, 6693–6713.