

# Supplementary information

## Fermi-level pinning in methylammonium lead iodide perovskites

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### Synthesis of the hybrid perovskites samples

All chemicals used were purchased from Sigma Aldrich except for PbAc<sub>2</sub>, which was synthesized. The perovskite films were processed on 8 x 8 mm<sup>2</sup> indium tin oxide (ITO) coated substrates (10 Ohm/sq., Präzisions Glas & Optik GmbH, Germany). The substrates were cleaned and afterwards ozone-treated before use. The solution for the perovskite layer was prepared by dissolving 0.8 mmol of PbAc<sub>2</sub>, 0.2 mmol of PbCl<sub>2</sub> and 3 mmol of methylammonium iodide (MAI) to 1.66 ml of DMF. The solution was stirred at 70 °C for 30 mins and then filtered (0.45 μm PTFE) before use. The films were formed via spin coating at 4000 rpm for 60 s and subsequently annealed at 80 °C for 10 mins. The samples were then

stored inside a glovebox (0.4 ppm of H<sub>2</sub>O and <0.1 ppm of O<sub>2</sub>) where they were mounted on a custom made sample holder suitable for an Omicron VT SPM machine (Fig. 1). They were then transferred under inert gas inside a "suitcase", consisting of a UHV gatevalve and a wobblestick. The final step was the transfer of the sample from the latter suitcase to the SPM under ultra-high vacuum.

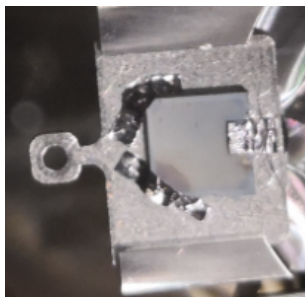
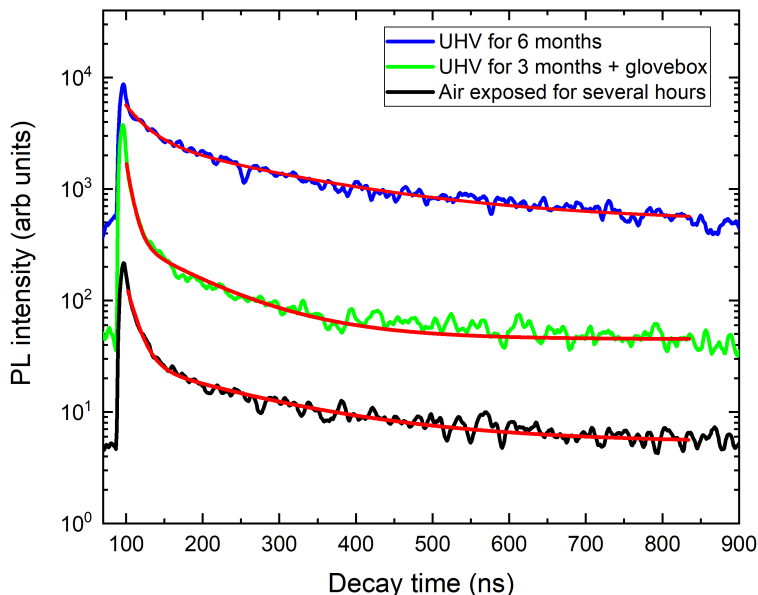


Figure 1: Omicron VT SPM sample holder with a mounted glass substrate.

## Time resolved photoluminescence

The TRPL measurements (Fig. 2) were carried in air using a LifeSpec II (Edinburgh Instruments) fluorescence lifetime spectrometer equipped with a Time Correlated Single Photon Counting (TCSPC) system. The samples were mounted on a sample holder, which was tilted 30° from the vertical position to ensure that the directly reflected light was not collected by the optics of the emission channel. A pulsed diode laser (EPL-640, Edinburgh Instruments), with a nominal wavelength of 638 nm and a typical pulse width of less than 100 ps, served as excitation source. The repetition frequency used here was of 1 MHz. The size of the laser spot diameter was 30  $\mu\text{m}$  and the injection level of  $3 \cdot 10^{15} \text{ cm}^{-3}$  (calculated using the laser power, repetition frequency and a reasonable absorption coefficient). We measured three different samples. One was kept inside our SPM machine under UHV for 3 months before storing it in our glovebox. The second one was exposed to air for several hours as it was used for SEM and XRD measurements. The third one was kept in UHV for more than 6 months in order to see if the sample deteriorates in vacuum.

All samples were measured the same day with the same TRPL settings. We then fitted the obtained curves with a two-exponential decay function to extract two decay times. Both decay times are similar and we do not see a strong deviation between the samples. The sample that has been stored in vacuum for 3 months exhibits the lowest lifetimes, whereas the one that was stored in UHV for 6 months exhibits the longest decay times.



Exposed to air for several hours		In UHV for 3 months + glovebox		In UHV for 6 months	
t1 (ns)	t2 (ns)	t1 (ns)	t2 (ns)	t1 (ns)	t2 (ns)
10	107	6	65	9	133

Figure 2: (a) Time-Resolved Photoluminescence for three samples stored under different conditions. The red curves display the fitted transients whereas the other ones are the experimentally measured curves. The experimental curves were smoothed in order to improve the visibility.(b) Decay times obtained by fitting the curves with a two-exponential decay function. The fits have been done on the raw data without smoothing.

# Photoluminescence

The photoluminescence measurements were done in the same equipment as the TRPL ones. We switched the illumination source to a cw-laser (MRL-III-640 Red Diode Laser, Ready Laser) with a wavelength of 640nm and a beam diameter of approximately 3mm. The three PL spectra are displayed on Fig.3. We observed a clear shift of the PL maximum peak from 1.58 eV to 1.63 eV for the sample stored in UHV for 6 months. This shift was not visible for the sample stored in UHV for 3 months. However, both of the latter samples displayed a lower PL intensity than the sample exposed to air, which is in agreement with other reports where an enhancement of the PL due to oxygen exposure has been observed.<sup>1</sup> The shift of the PL peak position indicates that the sample that was stored in UHV for 6 months is substantially different. We attribute this shift to higher energies to a partial decomposition of the films due to the long storing period of the sample in UHV. The sample that was stored only 3 months in vacuum does not show this shift. We therefore conclude that our measurements (which have been done during the first weeks after introducing the sample into UHV did not suffer from severe decomposition).

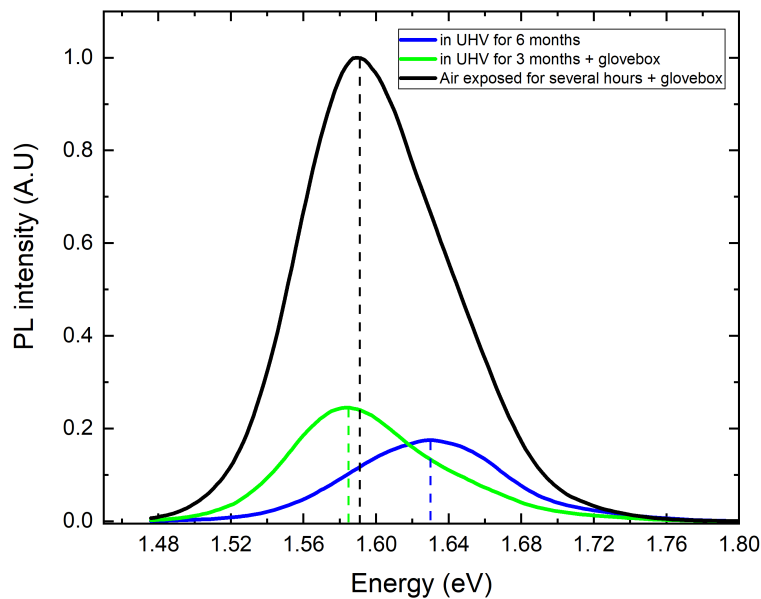


Figure 3: Photoluminescence for three samples stored under different conditions.

# XRD

X-Ray Diffraction was performed on the sample exposed to air for several hours (Fig. 4) in a Bruker D8 Discover XRD apparatus. The diffractogram displays a clear MAPbI<sub>3</sub> tetragonal crystal structure and no PbI<sub>2</sub> secondary phases, showing that the samples are both of good quality and stability.

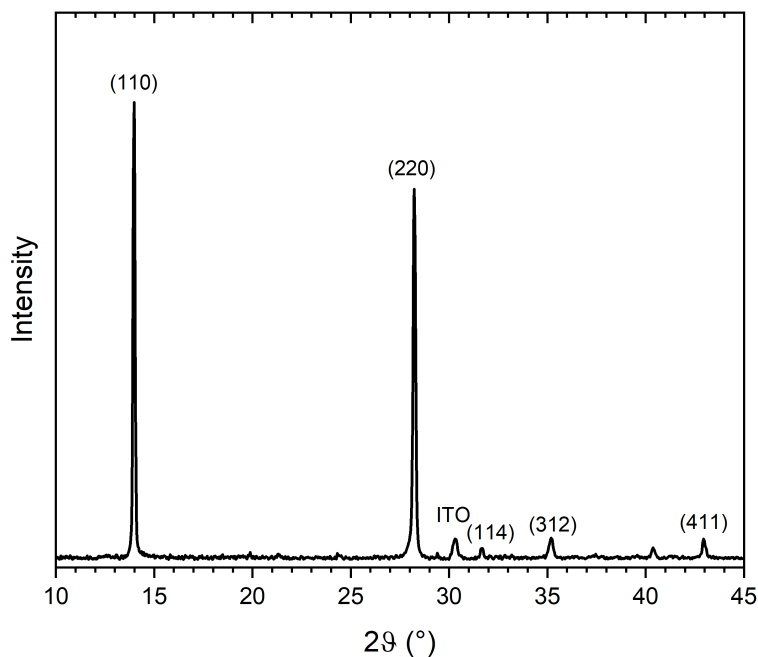


Figure 4: X-ray Diffractogram of the MAPbI<sub>3</sub> sample with the associated crystallographic planes taken from.<sup>2</sup>

## References

- (1) Brenes, R.; Guo, D.; Osherov, A.; Noel, N. K.; Eames, C.; Hutter, E. M.; Pathak, S. K.; Niroui, F.; Friend, R. H.; Islam, M. S.; Snaith, H. J.; Bulović, V.; Savenije, T. J.; Stranks, S. D. Metal Halide Perovskite Polycrystalline Films Exhibiting Properties of Single Crystals. *Joule* **2017**, *1*, 155–167.
- (2) Luo, S.; Daoud, W. Crystal Structure Formation of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> Perovskite. *Materials* **2016**, *9*, 123.