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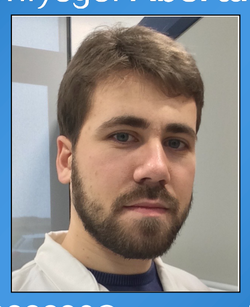

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Shining a light on the photoluminescence behaviour of methylammonium lead iodide perovskite: investigating the competing photobrightening and photodarkening processes

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Thanks to their ideal band-gap and high absorption coefficient[1], perovskite materials are good candidates for the next generation of solar cells with an impressive certified 22.1% power conversion efficiency[1]. In particular, $CH_3NH_3PbI_3$ (MAPI) solar cells presents a simple solution processing alongside an easy deposition method by spin coating. However, the development of perovskite based solar cells is impeded by two main obstacles: degradation through reaction with air and moisture[3,4] and hysteretic behaviour[5]. Here, we will show how the atmosphere affects its photoluminescence (PL).

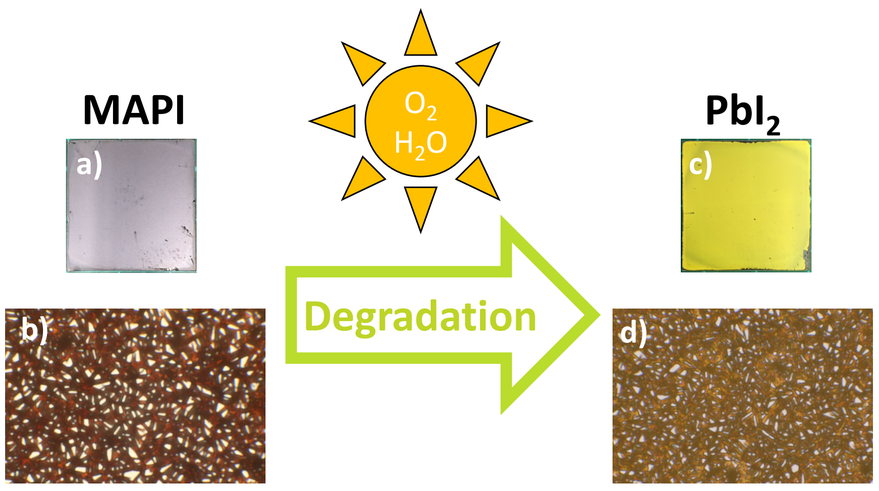

Figure 1: **a)** & **c)** Photographs and **b)** & **d)** optical microscopy images (40X) of a MAPI thin film respectively before and after degradation.

Summary

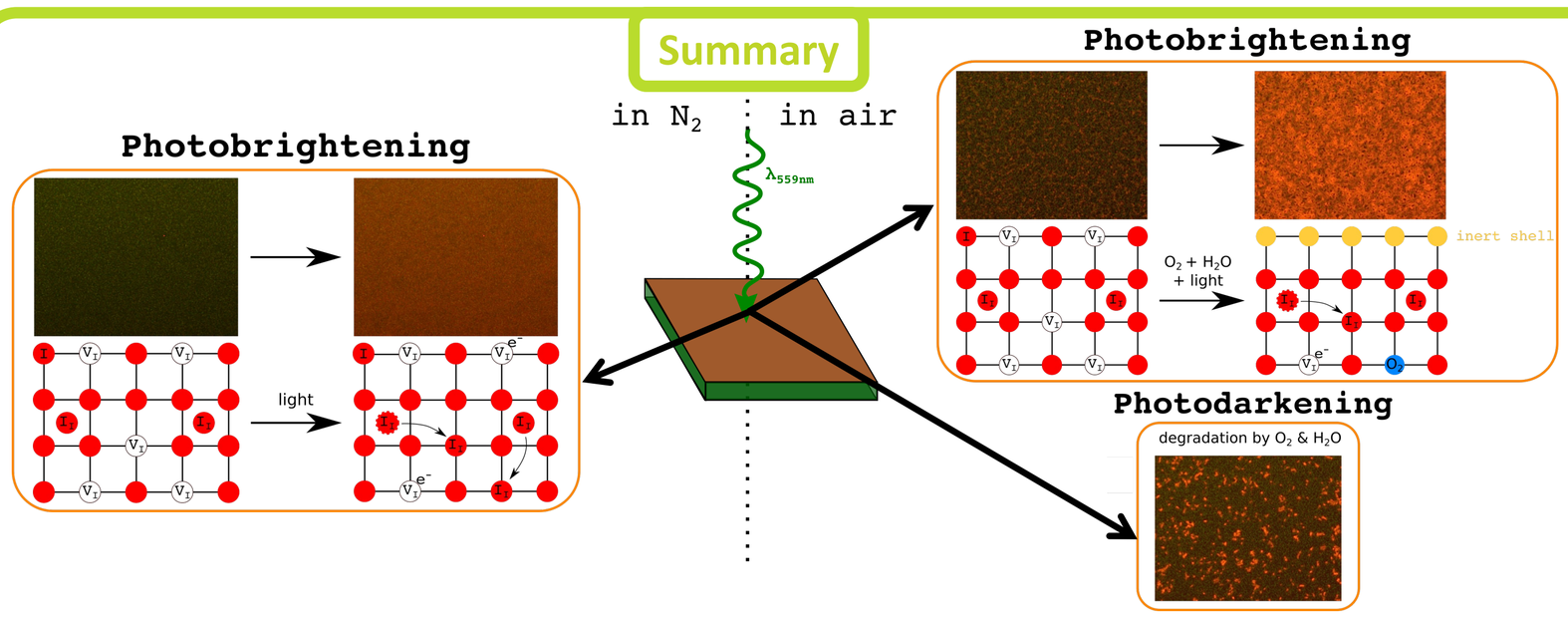

Figure 2: Summary of the processes happening in MAPI under illumination in air and N_2.

Methodology

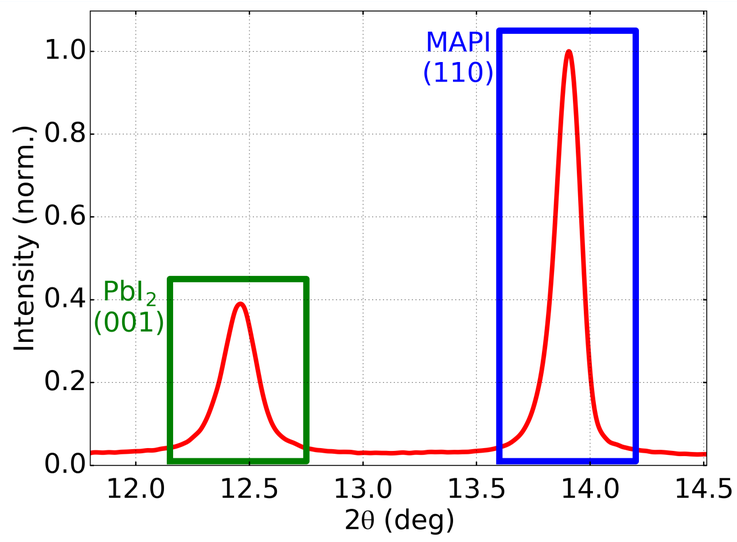

Figure 3: X-ray diffraction pattern of a partially degraded MAPI thin film.

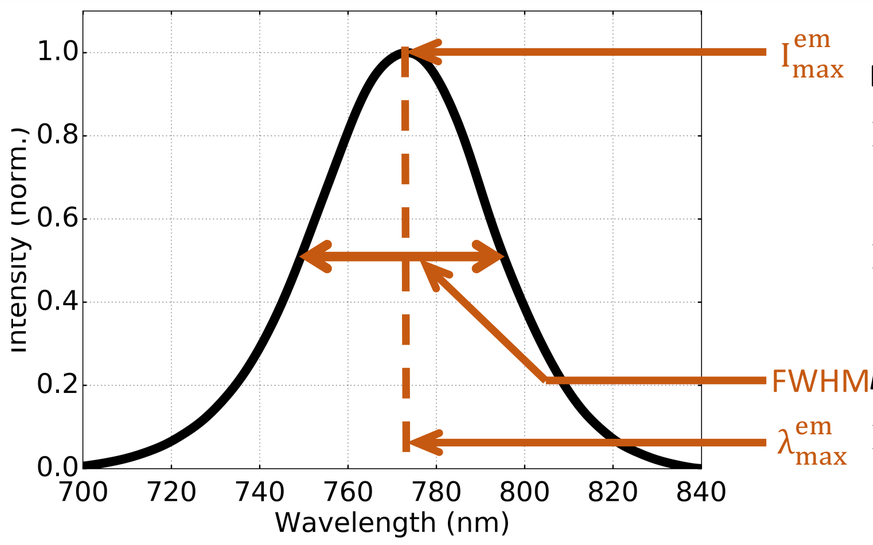

Figure 4: PL spectra (λ_{exc} = 559 nm) of a MAPI thin film.

Fluorescence microscopy

- The PL of MAPI thin film on glass was measured under continuous illumination (λ_{exc} = 650 nm).
- Samples were measured in air (~50% RH) and in N_2 atmospheres.

***In situ* X-ray diffractometry**

- The fluorescence and X-ray diffraction pattern of a sample was measured under continuous white light illumination in air.

Results

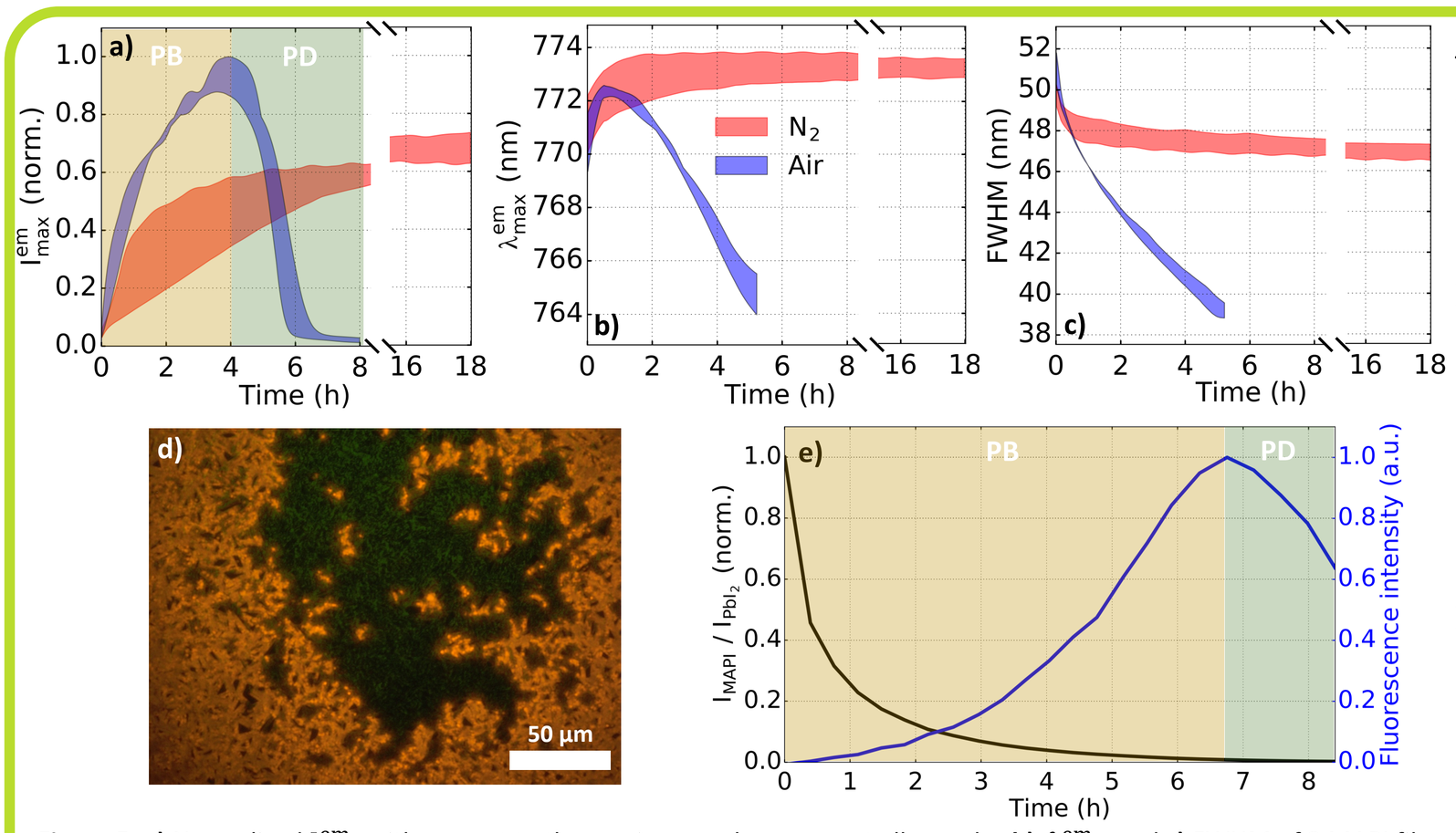

Figure 5: **a)** Normalised I^{em}_{max} with respect to the maximum value amongst all samples **b)** λ^{em}_{max} and **c)** FWHM of 3 MAPI films measured under air (blue area) and 3 MAPI films measured under N_2 (red area) vs time. PB and PD processes are outlined for air samples in **a)**. **d)** Fluorescence image (λ_{exc} = 559 nm) of a MAPI film in air after ~6 h. **e)** Ratio of the intensity of the MAPI (110) and PbI_2 (100) diffraction peaks (black) and Fluorescence intensity (blue) of a MAPI thin film over time.

The PL measured presents large variations over time:

- Samples measured under air display photobrightening (PB) over 4 hours and photodarkening (PD) over 3 hours. At contrary, samples measured under N_2 show a softer PB and no PD due to the absence of degradation.
- Samples under N_2 quickly red-shift which could be caused by the recrystallisation of the perovskite, due to the passivation of trap states by light and ion migration. Samples under air also show this red-shift in the first 30 minutes however, λ^{em}_{max} decreases after, which is probably linked to lattice changes induced by degradation. It is likely that these shifts are competing events;
- The FWHM decreases for all samples, however it reaches a much lower value for samples measured in air consistently with the presence of oxygen passivating trap states[6] resulting in a higher I^{em}_{max};
- *In situ* XRD shows degradation of the perovskite as soon as it is illuminated. However, this is masked by the photobrightening of the sample. The maximum PL intensity is measured while the sample is mostly converted to PbI_2.

Conclusion

- Photodarkening and Photobrightening both induce changes in the perovskite electronic properties;
- These two processes are competitive in air with the photobrightening masking the photodarkening at the start of the illumination;
- After a certain time, the degradation balances the photobrightening, leading to a photodarkening of the perovskite;
- These competing processes needs to be carefully considered when measuring the properties of perovskite solar cells under illumination.

References

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