

# The Role of Excitation Energy in Photobrightening and Photodegradation of Halide Perovskite Thin Films

## – Supporting Information –

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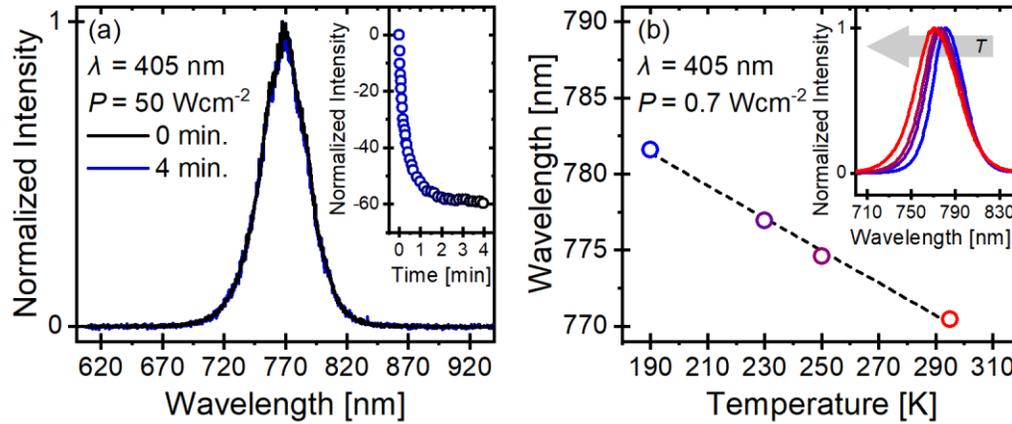
Figure S3: Temporal evolution of the perovskite emission during excitation with a) a green and b) a blue excitation source at different excitation powers.

Figure S4: Excitation wavelength dependent evolution of the PL intensity of unencapsulated  $\text{MAPbI}_3$  films processed by different routes.

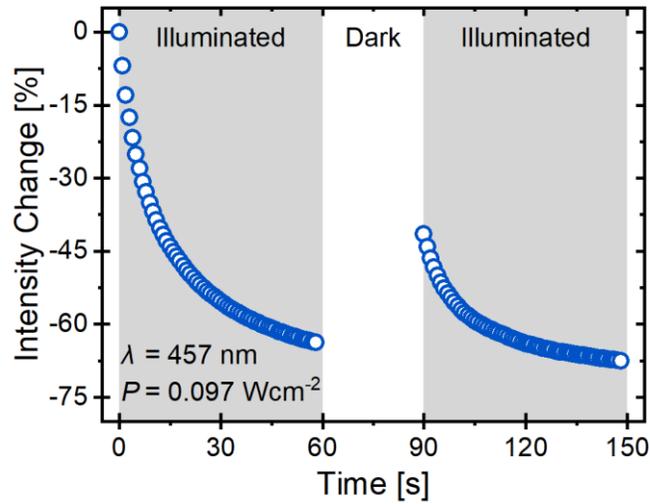
Figure S5: Excitation wavelength dependent evolution of the PL intensity of an encapsulated  $\text{MAPbI}_3$  film processed from a  $\text{PbI}_2$  precursor.

Figure S6: PL time traces of an unencapsulated  $\text{MAPbI}_3$  film in different atmospheres for a,b) 532 nm excitation and c,d) 405 nm excitation.

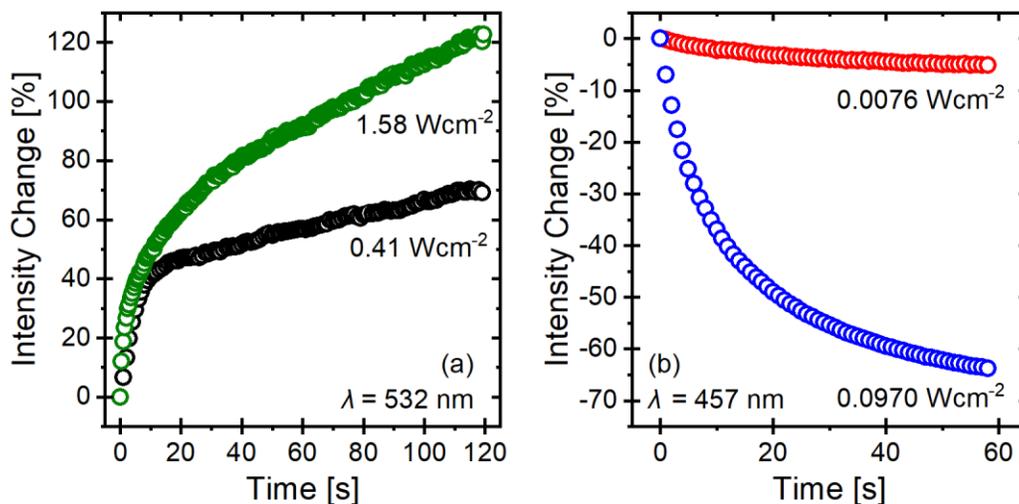
Figure S7: Time-resolved PL measurements of the samples presented in Figure S4.



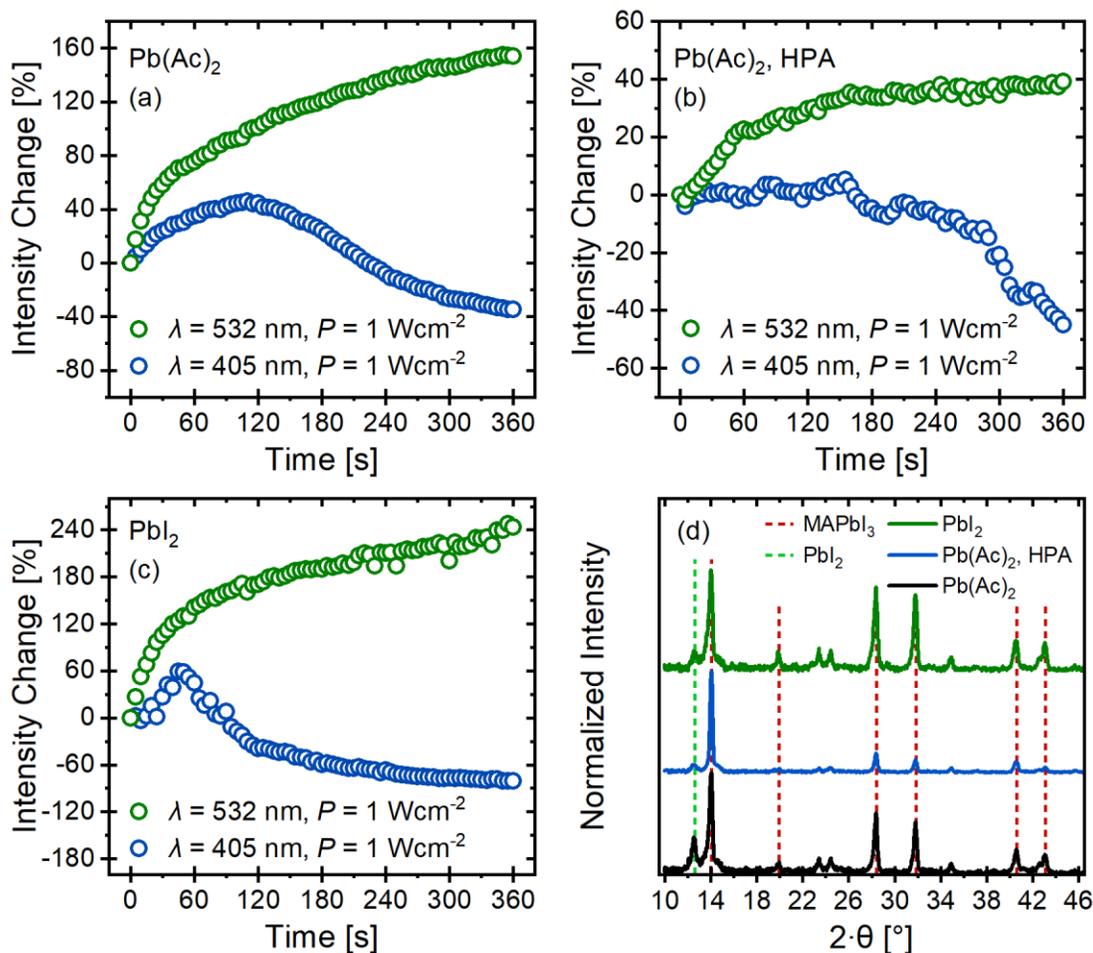
**Figure S1.** Study of sample heating during illumination. a) Normalized photoluminescence spectra after a torture test of the perovskite film for an illumination time of 240 s at a high power density of  $50 \text{ W cm}^{-2}$  with a blue 405-nm diode laser. The absence of any spectral shift within our spectral resolution of  $\sim 0.5 \text{ nm}$  suggests sample heating of less than 5 K. Inset: Drop of PL intensity during the 240-s heating test. b) Shift of the spectral position of the perovskite emission with temperature under blue excitation ( $\lambda = 405 \text{ nm}$ ). The measured data were fitted with a linear function, revealing a spectral shift of  $\sim 0.1 \text{ nm/K}$ . Inset: Perovskite PL spectra for temperatures between 190 K and 300 K.



**Figure S2.** Partial recovery of the MAPbI<sub>3</sub> PL intensity after blue illumination by storage in the dark. Time traces of a MAPbI<sub>3</sub> film sample during two illumination periods of 60 s each with a blue LED (457 nm) and an excitation intensity of 0.097 W cm<sup>-2</sup>. The sample was kept in the dark for 30 s in between the measurements. During the first illumination period, the PL intensity of the film is reduced to ~35% of its initial value. At the beginning of the second illumination period, it is recovered to ~60% of the initial value. This behavior indicates a partial reversibility of the underlying degradation mechanism.

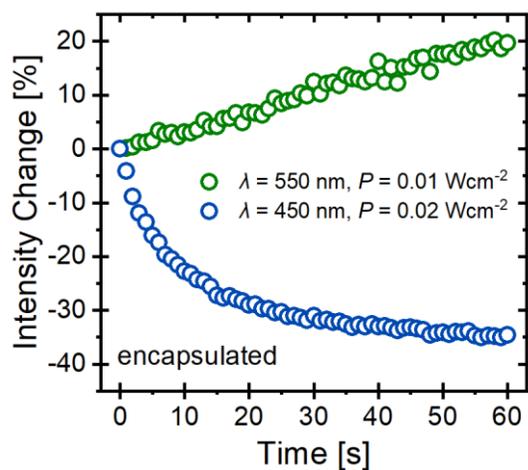


**Figure S3.** Temporal evolution of the perovskite emission during excitation with different wavelengths and varying power in air. Time traces of the PL intensity for a) green laser excitation ( $\lambda = 532$  nm) with excitation power densities of  $0.41 \text{ W cm}^{-2}$  (black) and  $1.58 \text{ W cm}^{-2}$  (green) and b) blue LED excitation ( $\lambda = 457$  nm) with  $0.0076 \text{ W cm}^{-2}$  (red) and  $0.097 \text{ W cm}^{-2}$  (blue). In the case of green light excitation, photobrightening dominates the transient PL intensity even at high power excitation, while during blue light illumination, photodegradation is observed even for low excitation powers.

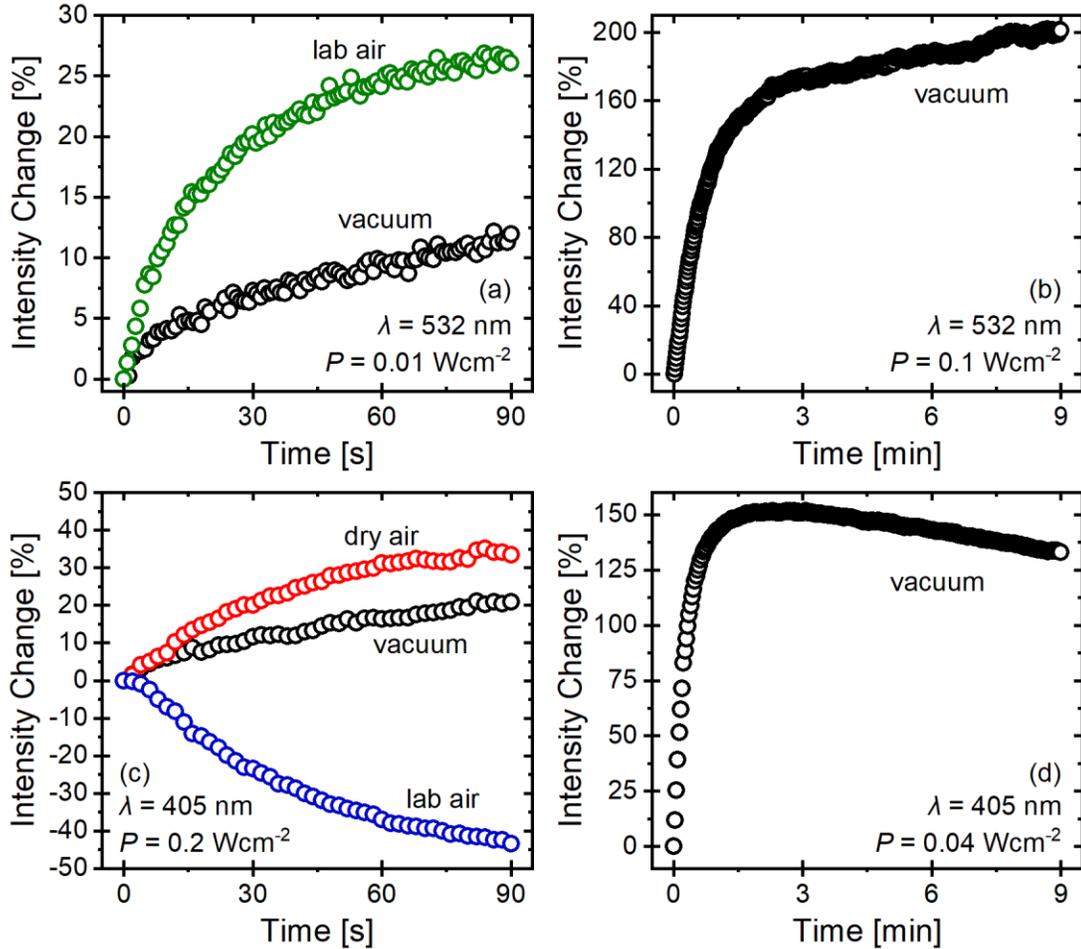


**Figure S4.** PL evolution of unencapsulated MAPbI<sub>3</sub> film samples processed by different routes during continuous laser excitation with different wavelengths in lab air (relative humidity (42±2)%). Illumination-time-dependent PL intensity of films processed from a lead acetate (Pb(Ac)<sub>2</sub>) precursor with and without the stabilizer hypophosphorous acid (HPA) (a,b) and from a lead(II) iodide (PbI<sub>2</sub>) precursor (c) during laser excitation of the samples with 405 nm and 532 nm. (d) XRD patterns of the as prepared samples shown in (a-c). The differently processed films show the same overall wavelength-dependent behavior as observed for PbCl<sub>2</sub>-based samples in the main text: While green light excitation only leads to photobrightening of the perovskite, blue light excitation eventually results in a decrease of the PL intensity with time. Interestingly, in contrast to the results shown in the main text, all samples show a short photobrightening effect during the

first 1-2 min of 405-nm excitation, before photodegradation dominates the further evolution of the PL. This behavior further affirms the concurrent nature of photobrightening and photodegradation of the perovskite during blue illumination, as postulated in the main text and also supported by Figure S6. The different behavior compared to the results shown in the main text can be interpreted in the framework of the proposed degradation mechanism, as the samples examined in (a-c) exhibit a smaller fraction of residual  $\text{PbI}_2$  compared to the samples presented in the main text (see Figure 3b).

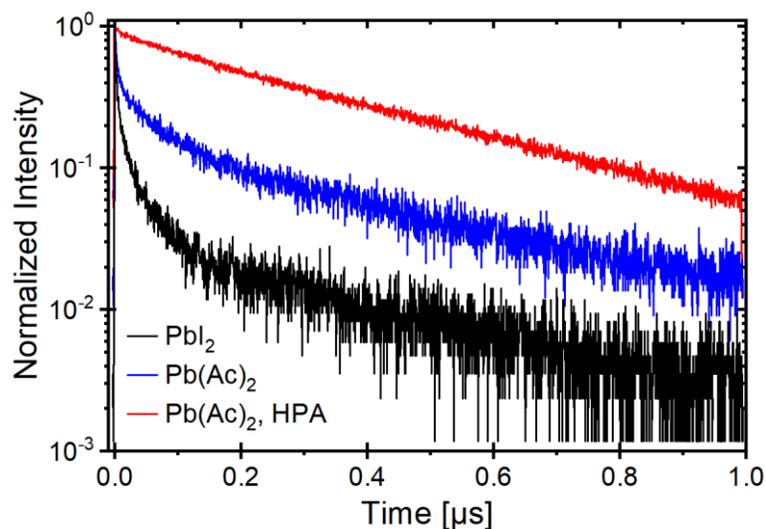


**Figure S5.** Relative change of the PL intensity of a MAPbI<sub>3</sub> film capped with a ~300 nm PMMA layer during illumination with light of (550±5) nm (green) and (450±5) nm (blue) in lab air (relative humidity (42±2)%). The PL intensity traces reveal the same trend for the sample encapsulated with a PMMA capping layer as shown for unencapsulated samples in the main text. Excitation with 450 nm leads to a transient decrease of the PL intensity while excitation with 550 nm only induces photobrightening. The shown PL spectra and traces were measured with the same setup as in Figure 2 of the main text.



**Figure S6.** PL intensity of an unencapsulated MAPbI<sub>3</sub> film versus time under different atmospheres for green light (532 nm) and blue light (405 nm) illumination. a) PL intensity time traces at  $0.01 \text{ W cm}^{-2}$  excitation power density in vacuum ( $<5 \cdot 10^{-6}$  mbar, black), and lab air (relative humidity  $(42 \pm 2)\%$ , green) for an excitation wavelength of 532 nm and b) long term intensity time trace at  $0.1 \text{ W cm}^{-2}$  in vacuum. For green light excitation, degradation cannot be observed in any of the examined atmospheres and does also not occur after long time illumination, indicating the importance of the excitation wavelength on the existence of photodegradation. c) PL intensity time traces at  $0.2 \text{ W cm}^{-2}$  excitation power density in vacuum ( $<5 \cdot 10^{-6}$  mbar, black), dry air (20% O<sub>2</sub>, 80% N<sub>2</sub>, red) and lab air (blue) for an excitation wavelength of 405 nm and d) long term intensity time trace at  $0.04 \text{ W cm}^{-2}$  in vacuum. In contrast to green illumination, the

short-term transient PL intensity during blue light excitation clearly depends on the measurement atmosphere. While in dry environments (i.e. dry air and vacuum conditions) photobrightening similar to the effect of green light excitation can be observed, in humid conditions, photodegradation occurs as described in the main text. These results hint towards a competition between photobrightening and photodegradation processes during blue light excitation, whereas degradation effects seem to be heavily promoted by humid surroundings. The idea of concurrent photoinduced effects is further supported by the long-term behavior of the sample during blue light excitation under vacuum conditions shown in (d). While the PL intensity increases during the first  $\sim 90$  s of the experiment, on longer timescales, the PL evolution is reversed to photodegradation even in the absence of humidity. Thus, both photobrightening and photodegradation are expected to occur during excitation of the perovskite with wavelengths  $< 520$  nm. Photodegradation dominates the observed PL intensity evolution in humid environments but can be overcompensated on short timescales by photobrightening effects in dry surroundings. Note, that despite the high vacuum conditions applied in (b) and (d), traces of atmospheric molecules might still be present in the films.



**Figure S7.** Time-resolved PL decays of  $\text{MAPbI}_3$  films fabricated by different routes (see Figure S4). The perovskite films exhibit long PL lifetimes in the order of a few hundred ns. While the film processed from lead  $\text{Pb(Ac)}_2$  with HPA shows monoexponential behavior, an additional short component is observed for the films prepared without HPA and from  $\text{PbI}_2$ , indicating the superior quality of the former. Time-resolved PL decays were measured using 470 nm excitation wavelength pulsed at 1 MHz using a PicoHarp 300 time-correlated single photon counting (TCSPC) apparatus and a PDL 800-B driver.