

Self-Healing and Light-Soaking in MAPbI₃: the effect of H₂O

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The future of Halide Perovskites, HaPs, which are of enormous interest for light ↔ electrical energy conversion, is beclouded by limited scientific understanding of their long-term stability. While HaPs can be altered by absorbed radiation that induces multiple processes, remarkably, they can also return to their original state by “self-healing”. Here we use 2-photon absorption to effect light-induced modifications within single crystals of MAPbI₃, the prototypical HaP. We then follow the changes in the photo-damaged region by measuring the photoluminescence, resulting also from 2-photon absorption, but with 2.5 orders of magnitude lower intensity than that used for photodamaging the MAPbI₃. We find, immediately after photo-damage, two brightening and one darkening process, all of which recover but on different timescales. The first two are attributed to trap-filling (the fastest) and to proton-amine related chemistry (the slowest), while photodamage is attributed to the lead-iodide sub-lattice. Surprisingly, while after 2-photon-irradiation of crystals that were stored in dry, inert ambient, photo-brightening (or “light-soaking”) occurs, mostly photodarkening is seen after photodamage in humid ambient, showing for the first time an important connection between the self-healing of a halide perovskite and the presence of H₂O. In either case, though, for long-term steady-state illumination practically no difference remains between samples kept in dry or humid environment. This result suggests that photo-brightening requires a chemical reservoir, that is sensitive to the presence of H₂O or, possibly other proton-related, particularly amine, chemistry, for which we give some conjectures.

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Halide perovskites, HaPs, have been studied widely in recent years as active materials in thin film solar cells and light-emitting diodes and as radiation detectors. The most striking characteristic of these materials is the ease with which they can be synthesized and the high quality of devices made with them. This feature can be related to the materials' lattice dynamics, which, in turn can be related to the nature of their chemical bonding.^[1–4] These dynamics are expressed in low frequency Raman spectra^[5] and in their stability.

Usually, when a material for electronics is synthesized, it is necessary to take particular care to avoid the formation of (non-equilibrium) defects which affect the material's function negatively. However, if the bonding framework is sufficiently dynamic, the material can effectively “clean” itself from defects^[6]. Because of this, the material will not require particular care in the synthesis, because it transforms rapidly into its most stable form with defect densities that can approach the thermodynamically dictated ones.

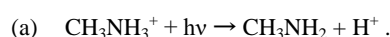
In the case of the MAPbI₃, this “dynamicity” was identified, and experimentally observed^[2,7] and finally confirmed by DFT calculations^[8]. This dynamic nature implies that one should not consider classic, *static* defects but rather a more complicated dynamic state.^[4,9,10] Having the material in such a state could help explain phenomena such as the blinking^[11,12] of large halide perovskite clusters (>10³ nm³), which cannot be explained by direct Auger recombination, with a particular electron/hole trap physically moving, changing dynamically its energy. Its energy state would flicker continuously between inside and outside the band gap with a randomized probability, thus changing it from an efficient to an ineffective trap.^[4] These dynamics also affect performance efficiency and stability of the devices made with MAPbI₃.

Here we show that a MAPbI₃ single crystal can self-heal, i.e., it can return to its original state after photo-damage, implying that its dynamic behavior leads the material to eliminate non-equilibrium defects. In general, light-induced modifications can cause the optoelectronic properties of the perovskite to degrade or to improve. The first process is commonly called *photo-damage* and corresponds to the formation (or activation) of defects. The second process corresponds to the passivation or annihilation of defects and has been given various names such as “light soaking”,^[13,14] “photo-brightening” and “photo-enhancement”. Hereafter we will use the term *photo-brightening* as it corresponds to an increase of the photoluminescence, PL, and *photo-darkening* for a decrease in PL. In general, we call the process that leads to light-induced modifications in the material, as a result of exposure to strong (laser) light, *photo-bleaching*. In MAPbBr₃ we associated *photo-darkening* with (transient) tri-halide interstitials^[15,16] and a similar effective scheme may be involved in photo-darkening of MAPbI₃.

Because PL efficiency is repressed by the presence of defects with in-gap energy levels, we pose that the stronger the PL recovery after photo-damage, the lower the density of optically active defects that remain in the material. While in complete cells with small-grain, poly-crystalline thin films of halide perovskites, other mechanisms that increase the PL could take place (for example, reduction of carrier mobility so as not enabling photo-generated carriers to reach the selective contacts), in single crystals, we do not identify any alternative mechanism modifying the PL. Defect densities in thin polycrystalline films is known to be relatively low (even if some orders of magnitude less so than in single crystals), ever since the early days of PV-driven research on halide perovskites.^[11,17,18]

The present work is distinguished from others, done on polycrystalline films (made up of crystallites of 0.5 μm average size or less), where O₂ can diffuse into the thin films during light treatment causing *photo-brightening*.^[11,17–19] The reason is that in our case the bleaching happens on a timescale that is too short for diffusion of chemicals from the exterior of the crystal and any effect has to be attributed to the chemicals already present in the crystal structure. We therefore study a sub-set of all the phenomena that can happen in a thin polycrystalline film, as found in photovoltaic and light-emitting devices. Nevertheless, our work on single crystals, is directly relevant to thin films, because it describes effects that are present *within the grains* that make up these films, and as such it constitutes the benchmark for further studies with polycrystalline material.

Earlier we reported the occurrence of self-healing of photo-damage in MAPbBr₃, FAPbBr₃ and CsPbBr₃, where all experiments were done in air with ~ 45 % RH.^[15,16] Of the three Pb bromide perovskites, only MAPbBr₃ showed, under certain conditions, *photo-brightening* of PL in the bulk. We explained that observation by the effect of methylamine, which will, for any given steady-state, light-induced modification, be present as a result of photolysis of methylammonium, according to



Illuminating MAPbI₃ with high, pulsed laser intensities a similar *photo-brightening* effect is obtained. We note that in a few cases *photo-brightening* effects have been reported also for CsPbBr₃ samples. However, as those films always were obtained from either DMSO (dimethyl sulfoxide)- or DMF (N,N-dimethylformamide)-containing solutions, the likely cause is solvent-HaP interactions. DMF can degrade to dimethylamine and formic acid, forming dimethyl-ammonium, which can substitute partially the Cs⁺ in the lattice and have a proton chemistry similar to methylammonium.

DMSO is known^[21] to form adducts with PbBr₂ and can be found in CsPbBr₃ (as explained in the *supplementary information* SI-0). We speculate that DMSO bound to Pb²⁺ acts like a defect, which could be passivated by photolysis breaking the Pb²⁺-DMSO bond. Light-induced passivation (sometimes together with oxygen) has been often invoked previously for HaPs (including Cs-based HaPs)^[17,20] We note that in samples obtained from fused salts, *photo-brightening* has not been reported for CsPbBr₃.^[22]

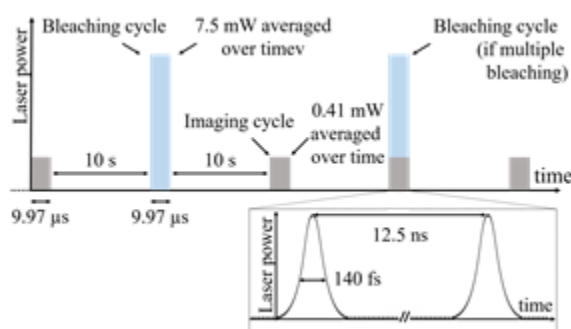
Methodology

How we visualize damage and track self-healing in the perovskite samples is particularly important for understanding the present study. For this reason, we discuss the experimental method in some detail before reporting and discussing the results.

We use the PL generated by 2-photon (2P) photoexcitation, ~45 μm inside the material, thus avoiding surface-related effects. This approach is particularly important to eliminate different surfaces, due to grain boundaries, grain shapes (which can be tuned by changing the kinetics of crystallization through temperature and solvents) and due to grain and film surface defects (which can be passivated with ligands). The PL signal serves to assess the state of the material after the crystal is exposed to a high-intensity laser, similar to how we monitored self-healing in the bromide Pb perovskites^[15,16]. The changes in PL, generated by the 2-photon up-conversion of sub-bandgap radiation, reflect both damage inflicted to the MAPbI₃ and recovery from the damage. The experiments are done with freshly cleaved MAPbI₃ single crystals^[23] (see below) with 2P confocal microscopy. In such microscopy a pulsed laser, emitting photons with sub-bandgap energy, 950 nm (1.305 eV) in our case, as MAPbI₃ has a ~ 1.6 eV band gap, which translates into an absorption onset at ~ 775 nm,^[24] is focused at a spot inside the crystal to reach densities sufficient to excite 2-photon absorption. The resulting 475 nm (2.610 eV), supra-bandgap photons generate electron-hole pairs in the MAPbI₃; the recombination of these photogenerated electron-hole pairs results in the PL that is measured. To calculate the energy (density) deposited during each bleach cycle in our 2P-experiments and the penetration depth we use the same method that is detailed in the main text and supplementary information of our earlier report^[25] (using the vectorial Debye theory)^[26,27].

Cleaving the crystals assures having an almost flat surface through which the photons can enter and escape during measurement. The external surfaces of as-grown single crystals are not optically flat because of the imperfect drying process (small crystallites form from micro-droplets drying on the surface of the single crystals, even if these are carefully wiped with absorbing paper). This causes “shadowing” effects inside the crystal which modify the laser intensity at the focus in the crystal, and the PL that reaches the detector.

The energy deposited at the focus inside the crystal to generate photodamage is 330 times larger than the one used for imaging (via PL excitation). The power of the damage-causing laser pulse corresponds to LP 90 % (see Table S1; LP = Laser Power). The experiment is done with the crystal (synthesis in SI-1) either in dry or 45% humid N₂ ambient. An energy equivalent to 10 sec exposure of the surface to AM 1.5 is deposited in the 10 μs of the ~800 pulses that make up the bleaching cycle. The energy calculation was done with the method, explained in the Supplementary Information (SI-2, 3, 4) of refs.^[16,28], adapted to the values of 2-photon absorption in MAPbI₃ from ref.^[29]. We kept 10 sec between bleaching cycles to have, on average, a treatment energy equivalent to the AM1.5 solar one. Scheme 1 illustrates all the critical parameters.



Scheme 1. Explanation of imaging and bleaching conditions: TOP: gray squares represent imaging cycles, light blue ones bleaching cycles. In both cases the cycles are composed of 798 pulses. BOTTOM: Time parameters for laser pulses to image or bleach.

The energy deployed in this experiment is sufficient to modify the defect density in MAPbI₃, but does not cause a strong increase in the local temperature. This conclusion can be intuitively evaluated considering that no modification is obtained at the low laser power (used for imaging) and that there is no material decomposition at higher laser powers, because the material eventually heals. In the supplementary information (see *Charge Density and Temperature Supplementary Document*) we perform calculations about the expected rise in temperature and charge density at the end of the bleaching cycle. Taking into account the diffusion of the electronic charges and of heat, we find that the temperature cannot increase by more than 100 °C (i.e., up to a temperature commonly reached in the annealing steps for thin films) and that the charge density reaches a maximum of 100 x that under continuous 1 sun illumination. Such density is insufficient to induce any process other than those that can be expected to happen *in operando* conditions: at worst, the probability of charge recombination (induced by trap filling) is increased, which is not detrimental for the crystal and happens, even, if with lower probability, *in operando*. At the same time such density is not sufficient to promote Auger recombination, which also does not happen *in operando*; further details are provided in the SI.

The bleaching processes happen deep inside the crystal and, therefore, *photo-brightening*, *photo-damage* and self-healing can directly be attributed to the chemistry of MAPbI₃ (and of already existing, dissolved chemicals,^[30,31] such as H₂O).

Noticeably other works done on thin films reported effects on the material characteristics and/or device performance of the ambient atmosphere as, for example, O₂. However, there O₂ actually diffuses in thin polycrystalline films (with < 1 μm grain sizes) during light treatment, increasing the *photo-brightening* effect.^[11,17–19] In our case, the bleaching happens on a time-scale that is insufficient for diffusion of chemical species from the exterior (which would take several hours) implying that the effect of H₂O that we find is due to the H₂O already in the crystal structure.

Variability of the data.

In our experience MAPbI₃ crystal growth results are much more variable than those for MAPbBr₃. In films this effect of variability in properties is even stronger, as reported by Fassl et al.^[32] They showed how small changes in the concentration of the precursors can affect the optoelectronic properties of MAPbI₃ thin films as well as the evolution of those properties under light. In the study of Fassl et al. the differences are exacerbated by possible effects of passivation and nucleation-crystallization due to passing from under- to over-stoichiometric ratio of the reagents.

Our single crystal synthesis method is the one that is most commonly used for MAPbI₃ and the one that is least influenced by solvent or other molecules that may enter the crystal. While there are crystallization techniques that are different from the one employed here (such as progressive degradation of NMF, N-methylformamide, by HI to form MA⁺ *in situ*, causing the precipitation/crystallization^[33] of MAPbI₃), their use would not change the degradation and healing (chemical) mechanisms studied here as these are independent from the specific doping/defects of the crystals even if these can modify their kinetics (see SI-5).

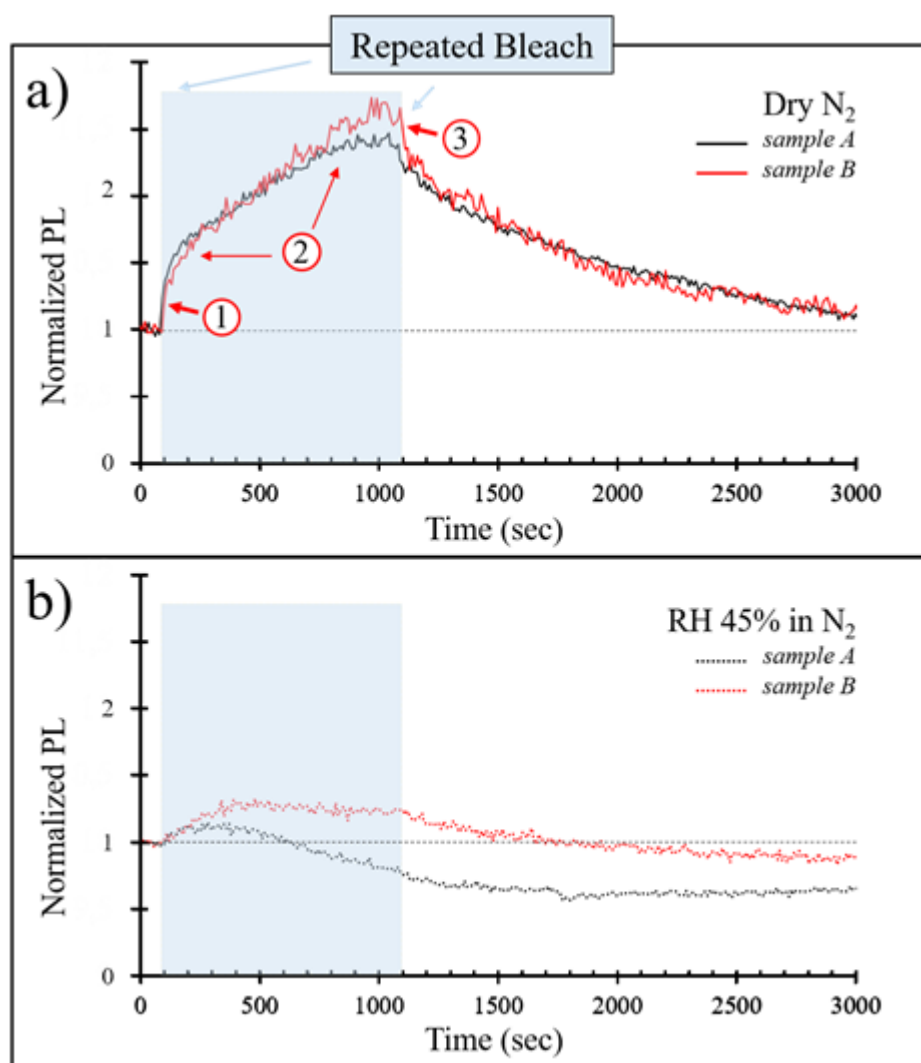


Figure 1. Photobleaching-induced variations of the PL from within two MAPbI₃ single crystals (red and black curves, normalized to the initial, i.e., pre-bleaching PL) in (a) dry N₂ and (b) 45 % RH in N₂. Both plots show the time dependence of the PL as a result of up to 100 bleaching cycles (data taken in between the bleaching cycles; show in the blue-shaded areas). Comparing plots (a) and (b) shows that water reduces the effect of photo-brightening in MAPbI₃. The numbers in (a) refer to stages of the PL changes, discussed in the text.

We report the results from two crystals to give an idea of the variability between samples, and so as to allow adequate comparison of our results with literature data. We also analyzed a further 10 samples briefly, with less accurate optical alignment and shorter equilibration time with the atmosphere. The reason is a very practical one, limitations on instrument availability for an extended continuous period of days and nights. Even so, those experiments showed the samples' variability by comparing the responses to the first bleaching cycles and the initial speeds of recovery. The behavior of these 10 samples was intermediate between that of the two samples reported here, and for which the accurate measurements were performed and are reported. Furthermore, and importantly, *grosso modo* these two MAPbI₃ samples show qualitatively similar behavior. We note that there is no difference in PL emission spectra between the two crystals.

In general, our bleaching results are reproducible for any given sample in N₂ and each sample yields consistent results by repeating the experiment in other regions of interest in the crystal. This means that the variability is only from sample to sample and does not occur in any one sample. In a humid N₂ atmosphere (below 50% RH), it is necessary to wait at least 3

hours to have reproducible results. For shorter times, intermediate results were found just after the bleaching which do not provide useful information for the present discussion. Drying of the crystals takes much longer than their humidification and the results continue to evolve even after 12 hours (see SI-6-7 for further details).

As a conjecture to explain the variability between the samples we note that the doping of each crystal (which determines the Fermi level position in the bandgap) need not be the same, even for crystals, grown in the same batch. This can happen because it is unlikely that all crystals nucleate at the same time in the solution. During crystallization some I⁻ oxidizes to I₂ in the solution, which leads to variation of the electrochemical (redox) potential of the solution and, therefore, of the electrochemical potential of the electrons (Fermi level) of the crystals, over time. Thus, they may have different doping densities, impacting^[10] the crystal's Fermi level, especially given their relatively low doping. While normally such differences should not matter, for samples with very low doping densities as the MAPbI₃ crystals,^[34,35] this can be an issue. If the photodamage and self-healing kinetics are influenced by the densities of free electrons and/or holes in the crystals, then this will affect the crystals' behavior after bleaching. Further details on this conjecture are provided in Supplementary Information (SI-5).

Experimental results, Fig. 1

In Fig. 1 we show the evolution of the 2P-generated PL of two MAPbI₃ single crystals (1st in black and 2nd in red) synthesized together (for the synthesis of MAPbI₃ single crystals see (SI-1)). The PL evolutions in Figure 1 are obtained after performing 100 bleaching cycles (see Scheme 1). The shaded areas indicate the time interval during which the 100 bleaching cycles occur. Each data point in the plots is obtained from a PL signal excited by 330 times lower energy than that used for photodamage. As shown in Scheme 1, the imaging cycles occur between the bleaching cycles and after the 100 bleach cycle period is over. Bleaching was under N₂ flow in inert environment (Fig. 1a) or under flow of humid (45% RH) N₂ over the same sample that was previously imaged in dry N₂ (Fig. 1b).

Fig. 1a shows that the results in N₂ are quite similar for the two crystals (black and red plots). Several features, which can be attributed to different processes, are:

- rapid initial increase (marked (1)) to ~1.3 x the pre-bleach value after the first bleach cycle;
- successive bleach cycles (marked (2)) during which the PL efficiency continues to increase, up to ~2.4 x the pre-bleaching value after 90-100 bleaching cycles (3);
- when bleaching is stopped there is a rapid, modest PL drop to ~2.1 x the initial PL;
- after that the PL intensity drops slowly towards its original value with a half time of ~600 seconds.

Because the long time for this stage, the main healing one, fits with a (diffusive) chemical origin, the slow PL increase (often-reported as "light-soaking" effect) has to be also of chemical origin. Our working hypothesis is that the chemical process is photolysis of MA⁺ in MAPbI₃ to methylamine and H⁺ (reaction (a)). Earlier DFT calculations showed that methylamine can bind to Pb²⁺ in the perovskite structure, possibly donating electrons to the I-Pb-I electronic network, which defines the energies of the valence band maximum and conduction band minimum, as well as of electronically and optically active defect states.^[16] In the language of electrically active defects, this process is relevant for trap filling. This effect persists until the proton re-binds to the methylamine. In this scenario, the observed effects of light-soaking and self-healing are due to acid-base, methylammonium-methylamine chemistry. While consistent with multiple results reported in the literature,^[36-38] this process remains a hypothesis, direct (dis)proof of which will be hard: identifying Pb:N(H₂CH₃) bonds at very low concentrations (normal doping densities) during light-soaking seems beyond presently known analytical capabilities.^[39] However, the results presented in the following paragraphs corroborate our hypothesis, because water is known to affect the proton chemistry in MAPbI₃ crystals.^[40]

If, after the experiments in dry N₂ (Fig. 1a), the MAPbI₃ crystals are kept in N₂ with 45 % RH for at least 3 h before starting the experiments, the results are quite different. Fig. 1b shows that pre-exposure to humidity has a very strong effect on both photo-brightening and PL recovery *in the bulk*, even though the crystals maintain their integrity. Not only do they not change to the known yellow mono-hydrates (as happens after prolonged exposure to RH > 50 % around RT),^[40] also no change could be seen within our resolution, in the normal and polarized Raman spectra, PL emission spectra or X-ray diffraction rocking curves.^[41]

In humid ambient we do not observe the rapid initial PL increase (1) as in Fig. 1a. While as in (2) in Fig. 1a the subsequent bleach cycles increase the PL, they do so to a very limited extent. After ~12 bleach cycles, the photoluminescence of the “black” sample peaks at ~1.15 x the original while the PL of the “red” sample peaks after ~30 bleach cycles at ~1.25 x the original PL. Beyond that, the PL decreases for both samples (photo-darkening). This behavior fits a strongly decreased photo-brightening, which allows, as the photo-brightening effect decreases, photo-darkening to show up.

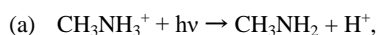
Ignoring, for the moment, the difference in extent-time behavior of the PL change between the two samples, shown in Fig.1b, in both cases the presence of water in the ambient strongly reduces the effect of photo-brightening, and that effect occurs tens of microns inside the crystal. This implies that water affects the internal chemistry of MAPbI₃ that acts against the photo-brightening. During the 800 seconds following the end of the bleaching period both samples show similar trends. The data show that pre-exposure to humid ambient strongly inhibits the process that leads to photo-brightening, which, as discussed later, might be one of the reasons why water can be so detrimental for HaP-based devices. From past reports, it can be deduced that water *absorption* (to be distinguished from surface *adsorption*^[42]) in MAPbI₃ could be significant, from 1 H₂O per~ 50-100 MAPbI₃ formula units to 1 H₂O per 3-10.^[30,31,40,43–45] It is therefore quite reasonable that water can interact, directly or indirectly with any photo-induced process and/or its product(s).

In the SI (SI-6 Fig. S2) data for multiple laser powers are reported showing the same qualitative trends and differences between data collected in dry and humid N₂. Samples that were pre-exposed to humidity show, after re-drying, partial recovery of the phenomena and kinetics observed under the original dry conditions (Fig. S2). Further details are provided in the SI-6 section.

A further look at Fig. 1b shows that the “black” sample accumulates more photodamage, reaching a minimum of PL (~0.6 of the original) at around 1800 seconds, ~700 sec after the last photobleaching cycle. This fits with the photo-brightening effect still persisting after the end of the bleach and being healed during the post-bleaching period. Besides this, a second, slow healing of the photodamage is present and the sample recovers part of its PL over the next 1200 sec (1800-3000 sec).

In humid ambient, the “red” sample, however, accumulates only some photo-damage. Photodarkening shows after ~1500 sec and has not yet healed after 3000 sec. In both samples the processes associated with both photo-damage and photo-brightening take place during photobleaching. After bleaching, in both samples the products of these processes slowly react again (self-healing) to revert the material to its original state and opto-electronic properties. Even if the amount of photo-damage differs between the samples, both appear to tend to a similar final state during recovery (a small recovery of the photo-darkening is present in the red sample at the longest times). This shows that the processes related to photo-damage, photo-brightening and self-healing of both the darkened and brightened material are relevant, regardless of the original state of the sample.

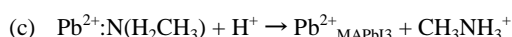
Proposed chemical explanation To explain the effect of water we recall the working hypothesis to explain photo-brightening (reactions (a-d) below) and we add the contribution of water to the over-all picture. We attribute the photo-brightening to the defect-passivating coordination of Pb to the N lone-pair on CH₃NH₂ (to form Pb:N(H₂CH₃)). The process starts with the above postulated photolysis of CH₃NH₃⁺ in the HaP:



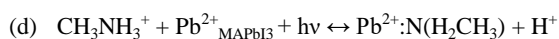
followed by the formation of a Pb-N bond



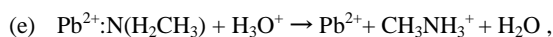
healing happens, because, if the products cannot escape or diffuse away, (a) + (b) can be reversed by H⁺, to re-form CH₃NH₃⁺:



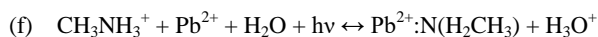
in this way a steady-state is established during illumination:



Consistent with our earlier work^[40,46] where we found that H⁺ migration in the bulk is enhanced in the presence of H₂O, we find that the self-healing reaction is more rapid in more humid than in drier ambient (cf. Fig. 1b with 1a). This is probably because of the reaction:



and the corresponding steady-state during illumination:



If we assume that the steady-state for (d) is more to the right than for (f), we can explain why the maximum PL in dry ambient is higher than in humid ambient. This assumption can be tested by finding the energy of each configuration in the absence and presence of H₂O (possibly by future DFT calculations). One should notice that, in dry conditions, the concentration of CH₃NH₂ is related to the amount of free H⁺ in the lattice. Therefore, following reaction (c), if for some reason H⁺ accumulates in the lattice, we expect the concentration of CH₃NH₂, determining the concentration of passivating Pb:N(H₂CH₃), to be lower than without such H⁺ accumulation.

Experimental results, Fig. 2

We now focus on the photo-damage of the material that could not be properly observed in Fig.1 because of the dominating effect of photo-brightening during successive bleaching cycles. To that end we look at the effects of just one bleach cycle. In Fig. 2a we show the effect on MAPbI₃ in dry N₂. The PL increases to ~1.3 its original value, as was the case after the first bleach cycle in the 100 bleaching cycles experiment (Fig. 1a, label “1”) in both black and red samples. The PL then decreases rapidly to its original value over ~20 seconds (Fig.2a, label “a”) with a decrease parallel to what happens at the end of the 100th bleaching cycle (Fig. 1a, label “3”). The 2 samples, in black and red, differ somewhat in their behavior after that point. While the PL of the black sample decreases to ~0.60 its original value after 600 sec the red sample the minimum is reached after 1500 seconds with a PL of ~0.70 its original value. Considering that the PL was still decreasing (healing of the photo-brightening) after 2000 seconds from the end of the 100th bleaching in Fig.1a, the results of Fig.2a show that, for both samples, the recovery of the photo-brightening is faster after a single bleaching cycle.

We can now draw some conclusions about the photo-brightening, comparing the results from Fig.1a and Fig.2a: in Fig. 1a we see a rapid increase (label “1”) and then a drop of around ~0.3 times the original PL (the sharp drop, labelled “3”) respectively after the first and after the 100th bleaching cycle. Based on the results of Fig. 1a and Fig.2a, we conclude that two different processes of photo-brightening exist having different half-life times. The rapid one (~20 sec), with a PL increase of ~0.2-0.3x the original PL, may have a physical origin (trap filling). The slow one, which can accumulate and heals more slowly (>2000 sec after 100 bleach cycles and ~600 or ~1500 for the black and red sample respectively after 1 bleach cycle), is most probably of chemical origin.

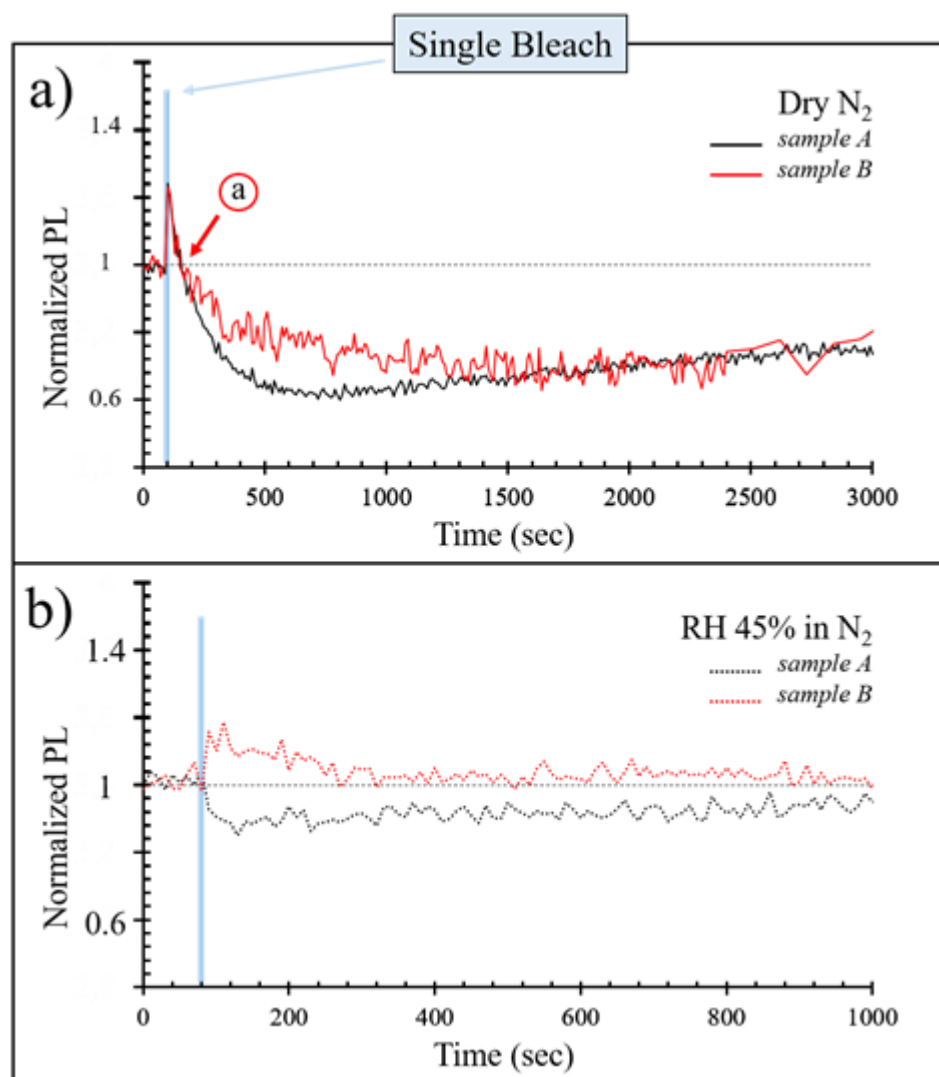


Figure 2. Photobleaching-induced variations of the PL from within two MAPbI₃ single crystals (red and black curves, normalized to the initial, i.e., pre-bleaching PL) each in (a-b) dry N₂ and (c) 45 % RH in N₂. All plots show the time-dependence of the effect of 1 bleaching cycle.. The time reported on the x axis of (b) is shorter than that for (a), to allow a better view of the data.

As shown in both Figs 2a and 2b, and similar to what is seen in Fig. 1b, the “black” sample is more affected by photodamage than the “red” one. Comparing Fig.2a and 2b shows that in a more humid ambient, MAPbI₃ is less susceptible to photodamage than in a less humid one. From these results we deduce that H₂O is involved in both the photodamage process and in self-healing after photodamage.

The apparent protection that H₂O conveys can be explained by considering that H₂O provides extra stabilization of the Pb-I structure via H-bonds. Alternatively, H₂O might deform the structure, increasing the energy needed to create (poly-)iodide interstitials. These hypotheses can be tested by DFT as formation energies of interstitials defects^[4,16] and the H-bond energies can be calculated. Experimentally, if H₂O deforms the structure it would exert internal pressure; therefore, one would expect the structure to become more elastic, increasing its Young’s modulus. Indeed, after exposure to humid ambient, Buchine^[41] found a small modulus increase for MAPbI₃ (and most other Pb-HaPs),.

Notably, the effect of H₂O does not only affect resilience to damage of MAPbI₃, but also its self-healing kinetics. If the lattice is more elastic because of the presence of H₂O, it can drive photo-generated distortions or defects to revert toward their original location, resulting in the healing of the material.

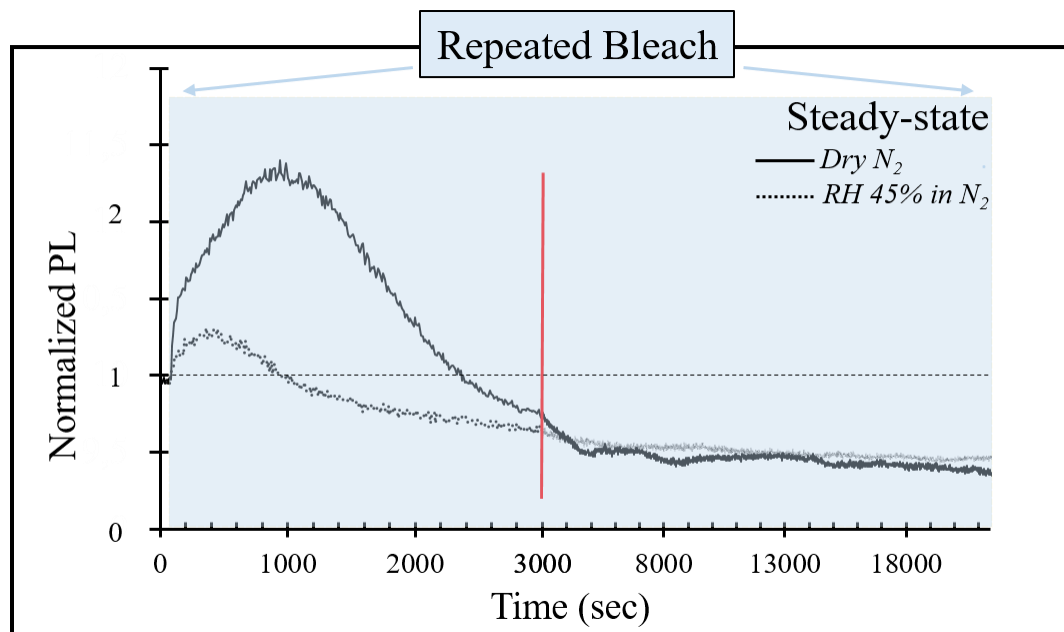


Figure 3. Photobleaching-induced variations of the PL of a MAPbI₃ single crystal, normalized to the initial, i.e., pre-bleaching PL, in dry N₂ (full line) and in 45 % RH in N₂ (dotted line). The bleaching is repeated 2200 x to get to a quasi-steady-state. In this state (right hand side, long times) the behavior of the sample is mostly independent of humidity. The oscillations in esp. the dry N₂ trace correspond to small alignment deviations due to slight variations of the laboratory ambient temperature during the experiment, which changes the focal point in the crystal. The red line shows the approximate border between the compressed (right-hand side) and extended (left-hand side) ordinate axis.

Putting our results and their interpretations in perspective, we note that an irradiated HaP solar cell (sealed like any (opto)electronic device) can always be considered in a steady-state (on the time scale of chemical reactions) and the multiple processes that that we presented will happen inside it simultaneously. Photo-brightening and photo-damage will be induced continually, by solar radiation, as well as the tendency of the material to attain its lowest energy state. The steady-state properties of the material can then be very different from the material's properties just after its preparation and will likely depend on the type and extent of external inputs.

Experimental results, Fig. 3

To get an idea of the behavior of dry and humid MAPbI₃ at the steady state, we checked the response of our crystals to photo-bleaching every 10 sec causing photo-damage/photo-brightening over a long period of time. To that end we continued to bleach samples, up to 2200 times. In this way, the excitation and the internal chemical environment in the crystal approach to some extent a steady-state. Indeed, the PL does not substantially vary over time anymore, despite the continuing cyclic illumination. Obviously, such an experiment cannot measure the PL in a real steady-state because bleaching occurs periodically and not continuously. This is a condition imposed by both the scanning of the microscope and, especially by the use of 2P excitation, which requires a very high sub-bandgap intensity to suffice for enough non-linear frequency doubling to get good S/N in the PL. For the same reason the laser has to be focused in the smallest possible volume. Still, our experimental settings can be viewed as a quasi-steady-state given that the time of the experiment is much longer than that of a single bleaching cycle.

Analyzing the data sheds further light on the role of water. In Fig. 3 we show the normalized PL of the first sample (black traces in Figs.1 and 2), bleached in dry N₂ (full line) or in humid N₂ (dotted line) with the same intensity of Figs. 1 and 2. Up to the 100th bleach (1000 s) the results fit those shown in Fig. 1. As the number of bleaches is increased further, the differ-

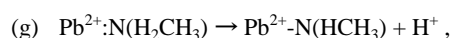
ence between the sample in dry N₂ and in humid N₂ decreases almost converging by the 300th bleach cycle (3000 s). At longer times (note that after 3000 s in Fig. 3a the scale of the x axis changes - indicated by the red vertical line) the difference between the traces approaches zero. This shows that in this quasi-steady-state for cyclic bleaches, the external environment no longer affects the final PL, which is reduced to ~0.45 times the original intensity.

This last result is of marked importance as it shows that some (encapsulated) samples might show very good efficiencies at short times only because of the light-soaking effects that are present in the absence of water. These will, however, eventually disappear because, as seen in Fig. 3, because the chemical process at the basis of photo-brightening is limited in terms of how much passivation (from reaction(d)) can balance the photo-damage causing a decrease of PL. Evidently, in the quasi-steady-state this process becomes less effective than initially. One interpretation of this finding is an interaction between chemical species involved in photo-brightening and products of photodamage or some slowly-forming photo-brightening products. Actually, in the end, after the 2200th bleach, the sample in humid N₂, retains a slightly higher PL than the one in dry N₂, consistent with faster self-healing of photo-damage that leads to a lower (steady-state) density of defects (cf. data for multiple laser powers in SI-8, Fig.S4).

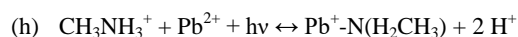
We note that the patterns we show in Figs. 1, 2 and 3 are reproduced also for a range of deployed energies between 1/20 and 1.5 times the energy reported. The corresponding data can be found in Supplementary Information, SI-6, 7, 8, Figs. S2, S3, S4.

Further chemical mechanistic explanation To explain these quasi-steady-state observations, we look at possible reactions that were not previously considered, but can affect the defect equilibrium in MAPbI₃. Our results can be interpreted by assuming that, over time, photo-bleaching produces a specie that is more effective than H₂O in inhibiting photo-brightening. While we could not find an obvious candidate species in the literature, we can propose a plausible mechanism.

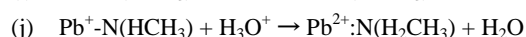
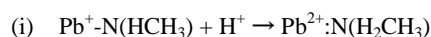
Kerner et al. showed how, in solution^[47,48], after binding to Pb, an amine can react to form a stable amide bond releasing a H⁺ and that the process is likely to happen also in MAPbI₃ to form methylamide^[49]:



which builds up to a steady-state during illumination:



Such a steady-state will not change substantially by the likely change in H⁺ diffusion kinetics in the presence of H₂O. The reason is that reaction (g) can be reversed, possibly with H₂O:



and that (i) and (j) have probably similar activation energies, related to the breaking of the Pb⁺-N bond. If both (i) and (j) are much slower than (c) and (e) which re-form methylammonium, then (i) and (j) determine the steady state. Kerner et al. found reaction (g) to be slow^[47], which implies that the steady state can be reached after a long time only; this can explain why convergence of the PL signals of the dry and humid sample is obtained only after hours (Fig. 3). Examining the results equivalent to the ones shown in Fig. 3, using lower and higher laser powers (Fig. S4), we could find only small differences between the data collected in humid and dry environments in the semi-steady state confirming that our observation are not power or charge concentration dependent.

Summary We analyzed the effect of photobleaching in the bulk of MAPbI₃ single crystals using PL in a 2P confocal microscope setting. Using this strategy, we avoid any material loss, allowing us to identify two types of photo-brightening (light-soaking), each of which show self-healing (recovery from higher intensity to the *status quo ante*), with half-times around 20 and 600 seconds. We discovered that H₂O, absorbed in low concentrations in the perovskite bulk, hinders photo-brightening, which implies that H₂O influences what is called in the literature “light-soaking” (a process that is mostly used to improve the photo-conversion efficiency of halide perovskite solar cells and contributes to reaching record efficiencies in cells that always contain some small fraction of MA). We attribute the effect of H₂O to the modification of the proton chemistry in the MA halide perovskite, linked to the equilibrium between methylammonium and methylamine (which

can bind to Pb²⁺). We propose a chemical mechanism involving the formation of methylamide, covalently bound to (Pb_{MAPbI₃})²⁺, which will be affected by the proton concentration in the HaP.

We also found that H₂O modifies the process that causes photo-darkening in MAPbI₃, reducing the extent of damage due to the illumination and increasing the rate of the self-healing.

These results are very relevant and significant for explaining the effect of H₂O on MAPbI₃. While H₂O is commonly thought to damage halide perovskites, in a few cases it has been reported to improve the performance of devices made with HaPs.^[45,50,51]

H₂O “damages” samples which are more prone to experience photo-brightening. We found that H₂O increases the rate of self-healing, thus acting against photo-brightening. The photo-brightening is therefore reduced and the material has a lower PL compared to a sample without H₂O. At the same time, in samples where the photo-brightening is weaker and photo-darkening dominates, H₂O appears to improve the material, because increasing the rate of self-healing acts against photo-darkening, i.e., the samples have a higher PL than if H₂O is absent. Differences between samples in the literature are probably due to different processing procedures *that result, among other things, in differences in the proton chemistry between samples*.

We conclude by noting that repeating the bleaching >2000 times (with an energy deposited on the sample, on average, similar to one sun) over 20,000 seconds (~5.5 hr), the material reached a quasi-steady-state, where, despite the fact that the light exposure is not continuous, no further change in PL emission over time is observed. The final state is, however, almost independent of the presence of H₂O, which we explain by the formation of a chemical steady state, based on the presence of (Pb⁺-amide) species, which is not affected by H₂O.

Experimental details

MAPbI₃ single crystals were grown, by modifying established procedures, as follows: CH₃NH₃I and PbI₂ were dissolved in GBL at 1.1 M and 1.0 M concentration respectively at 60 °C. The solution was then placed in an open crystallizer and its temperature was slowly increased to 110 °C over 3 hours. Maintaining the same temperature, the solution was evaporated over time (depending on the size of the crystallizer). It is extremely important to stop the crystallization process before the complete drying of the solutions. If this is not done, multiple small crystals form on the surface of the earlier-formed large (~1 cm) size ones. Also, trying to redissolve and recrystallize these crystals becomes impossible, because they partially degrade. Indeed, upon redissolution in γ -butyrolactone (GBL) a reddish solution is obtained that does not produce crystals with the aforementioned procedure. The identity of the species that give the reddish color to these solutions was not investigated further.

Details on the 2P imaging in the crystal and on the evaluation of the quantification of the energy deployed locally by the light beam can be found in our earlier report^[28] and in the Supplementary Information (SI-2-3). Refer to SI-9 for the settings of the current experiments. The laser power was modulated between the imaging (5% of the maximum laser power (LP 100% = 8.2 mW) and the bleaching (90% of the maximum laser power for the data in the main text) with an increase of deployed energy of ~325 times ($= (90/5)^2$). Importantly, we note that the bleaching procedure does not cause heat damage inside the crystal and the effects that we analyze are photo-effects. In this study, 2P measurements were performed either in dry or in humid N₂ with a relative humidity (RH) of 45 % that was achieved by bubbling N₂ through a saturated K₂CO₃ solution in H₂O. The temperature was maintained around 25 °C by the facility temperature control where the microscope is placed. We quantified the amount of H₂O effectively absorbed by the single crystals in another work currently submitted to publication^[43] with values around 1 H₂O molecule every 3 MAPbI₃ unit cells.

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