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Initial Stages of Photodegradation of MAPbI₃ Perovskite: Accelerated Aging with Concentrated Sunlight

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Initial stages of photo-degradation of CH₃NH₃PbI₃ (MAPbI₃) thin films prior to any significant change in light absorption are studied in experiments with independent control of sample temperature and intensity of concentrated sunlight from 50 to 500 suns. Photo-stability of the MAPbI₃ film is revealed to be extremely sensitive to the sample temperature. Under the combined action of light and heat (either by concentrated sunlight or by external heating), a strong reduction of the film photoluminescence (PL) without changes in the perovskite light absorption can be observed during the initial stages of degradation. On the contrary, illumination of perovskite films (with intensity up to 500 suns) without heating (using chopped concentrated sunlight) induces considerable PL enhancement while the optical absorption spectrum remains unchanged. With accurate temperature control, aging under concentrated sunlight results in similar instability trends as that under 1 sun.

1. Introduction

Metal halide perovskite solar cells (PSCs) have attracted much interest owing to their high power conversion efficiency (increasing from 3.81%^[1] to 24.2%^[2] in the last decade), potentially low-cost fabrication methods^[3,4] and excellent optical and electronic properties^[5-9]. Record efficiencies are already comparable with conventional silicon wafer-based modules.^[10] However, the stability of PSCs is currently far behind the target values of 20-25 years, expected from photovoltaics in power plants.

An extensive search for photo-stable halide perovskite compositions has instigated the development of high-throughput screening methods to identify promising materials and the degradation modes limiting their lifetime. One of the highest acceleration factors can be achieved by exposing the samples to high intensity concentrated sunlight.^[11] However, the relevance of failure modes observed with accelerated aging procedures requires verification, especially in the case of significant heating that typically accompanies exposure to high intensity light and may affect the degradation process and complicate the results' analysis.

Concentrated sunlight has already been used for aging of perovskite films^[12-14] and solar cells.^[15] In particular, it allows screening of perovskite compositions with respect to photo-induced decomposition into PbI_2 and volatile components.^[12] However, only light absorption spectroscopy and structural methods were typically utilized to evaluate material stability in previous studies.^[12-14] In addition, the performance of perovskite-based solar cells can decline significantly before the severe structural changes, such as perovskite decomposition, occur.^[16] Thus, it is important to study the initial stages of material degradation, which we arbitrarily defined here as the time before the onset of the light absorption change. Unlike optical absorption spectroscopy, photoluminescence (PL) is sensitive to electronic processes and, therefore, allows detecting more subtle changes in the material.

In this work we demonstrate that concentrated sunlight is a viable tool for perovskite stability studies, but only under conditions of accurate temperature control. We utilize intermittent

sunlight to allow for independent manipulation of film temperature and light intensity.^[17] In this way, significant heating of the sample can be avoided under light with intensities of up to 500 suns (1 sun = 100 mW/cm²). Even under such extreme conditions aging of encapsulated films resulted in processes qualitatively similar to those observed under 1 sun conditions.

2. Results and discussion

Band-to-band radiative recombination in MAPbI₃ films results in PL peak centered around 770 nm, corresponding to a bandgap of 1.6 eV typically observed in this material. Figure 1 summarizes the effect of light on the PL spectra of encapsulated two-step MAPbI₃ thin films depending on temperature and illumination conditions. All results reported below were repeated for every light intensity and sample temperature with at least three different samples. In addition, for every sample five PL measurements were taken over the exposed area. Data shown in Figure 1 reproduce the average of these five scans.

Naturally, light causes film heating which becomes more severe with increase in light intensity (see Figure 1a). Film temperature is a function of multiple experimental parameters, as it is described in details in Supporting Information (see Figure S1). Under conditions used in this work, continuous sunlight with intensity of 150 suns causes film temperature to rise up to 65 °C at the illuminated area. As we previously demonstrated for inorganic^[18] and organic^[17] photovoltaic materials, the use of chopped concentrated sunlight allows for effective heat dissipation during the dark periods, therefore sample temperature can be controlled with a heating stage independent of the illumination condition. This work confirms the effectiveness of this strategy for perovskite films too. The temperature was found to raise by only few degrees, as observed under intermittent light with 150 suns intensity (see Figure 1a).

Though we occasionally observed films becoming yellow accompanied by a decrease of both perovskite light absorption and PL intensity, in the scope of this study we intentionally limit the discussion to the cases of samples and exposure conditions which resulted in unchanged

film's absorption in the perovskite region to distinguish the “initial” degradation processes from further degradation (Figure S2-S9).

Figure 1b shows the dramatic decrease of PL intensity of a perovskite film subjected to continuous concentrated sunlight of 150 suns ($T = 65\text{ }^{\circ}\text{C}$ at the illuminated area), even though absorbance of MAPbI_3 is kept almost stable within the exposure timeframe (Figure S3). This can be attributed to the generation of non-radiative recombination centers during exposure. Similar results were observed in experiments with various light intensities in the range of 50-150 suns, though the magnitude of the PL decrease was in accord with the light intensity (see Figure 1b and S2b).

To understand if the degradation processes in this accelerated test are reminiscent of processes occurring under realistic light intensities, we performed controlled exposure to simulated sunlight with 1 sun intensity and the same dose of radiation (dose is a product of light intensity and exposure time); we also ensured that the film was kept at $25\text{ }^{\circ}\text{C}$ to distinguish photo- and thermal stability. Surprisingly, the observed trend was opposite to that shown in Figure 1b: perovskite PL increased with time under 1 sun illumination (Figure 1c). Such PL increase of perovskite films under light exposure was previously observed by other groups,^[19,20] and various explanations were suggested including iodine migration^[19] and passivation of deep traps by oxygen^[20]. Considering that the pronounced degradation under our experimental conditions involves perovskite decomposition to PbI_2 , it is possible that the very initial degradation stages can be accompanied by the passivation of non-radiative recombination centers (located at grain boundaries) by PbI_2 ^[21-24].

The processes occurring at 1 sun conditions and in concentrated sunlight experiments are clearly different, which could be due either to variation of temperatures, or light intensities, or their combination. To examine this, we performed MAPbI_3 films exposure to concentrated sunlight with independent control of the light intensity and the sample temperature during the experiment (see Figure 1d and 1e). In these experiments we utilized intermittent concentrated

sunlight, which allowed keeping the sample close to room temperature, even in the area illuminated by 150 suns (see Experimental section and Supporting Information). The PL intensity of these samples demonstrated a significant increase with illumination time (Figure 1d), similar to 1 sun exposure at 25 °C (Figure 1c). The samples illuminated by the chopped light of different intensity (50-150 suns) exhibited similar behavior with the PL enhancement (Figure S5 and S6). It is important to notice that the observed PL enhancement was almost uniform across the whole illuminated area (Figure 2), in contrast to the changes observed in the heated samples (Figure S10).

Photo-induced degradation in perovskite films^[25,26] and devices^[16,27,28] were often shown to be partially or fully reversible in the dark. Therefore, aging with intermittent and continuous light do not necessarily coincide, even if the temperature is kept similar. To confirm the decisive role of heat in our results (as compared to the presence of dark periods), we performed experiments with a home-built temperature control holder in order to study the effect of sample heating during the sample illumination by chopped light. The evolution of PL intensity of the MAPbI₃ film during its exposure to 150 suns and heating to 65°C (Figure 1e) is similar to that observed in the experiment where the sample heating was achieved only by continuous illumination (Figure 1b). In fact, heating in the dark is sufficient to cause a certain drop in PL intensity (Figure 1f).

As can be seen from Figure 1, the evolution of PL trends depends on temperature and not on light intensity, though the magnitude of the increase or decrease might be affected by the latter. Intermittent and continuous illumination resulted in similar changes given the films temperature is controlled at the same level. Concentrated sunlight, therefore, might be a promising tool for high throughput screening of perovskite materials' stability/degradation, if independent control of the temperature is ensured. We conducted aging experiments with light intensities up to 500 suns (see Figure 3) with the results qualitatively similar to those obtained under 1 sun.

It should be noted that the increased solar concentration may result in the change of the recombination mechanism that dominated in perovskite materials under various illumination conditions. Different recombination processes may affect the material degradation. For the best of our knowledge, there are no published experimental data on the effect of sunlight concentration on the recombination mechanisms in metal halide perovskites. However, recent theoretical study predicted that bimolecular and Auger recombination are becoming dominant mechanisms in MAPbI₃ only at solar concentrations significantly higher than those used in our study, above 3,000 and 7,000 suns, correspondently.^[29]

3. Conclusion

In degradation experiments with concentrated sunlight, we demonstrated that the photo-stability of MAPbI₃ films is extremely sensitive to the sample temperature. We successfully recorded initial stages of degradation (without substantial perovskite decomposition) and showed that the combined action of light and heat causes a significant decrease of the perovskite photoluminescence intensity. However, using independent control of light intensity and sample temperature, we have found that illumination of perovskite films without heating by sunlight not only keeps the perovskite light absorption stable but even may result in a considerable PL increase. These results show that photoluminescence spectroscopy is a more sensitive method than UV-Vis light absorption for characterizing the initial stages of perovskite degradation. Aging during 36 hours by intermittent concentrated sunlight of 500 suns allowed us to achieve a dose of ~1000 sun·hours (corresponding to ~0.5 years of outdoor operation in the Negev desert) through only 36 h of illumination, a clear advantage for accelerated stability measurement. However, our results indicate that the temperature needs to be carefully controlled to study perovskite degradation similarly to 1 sun experiments.

Optimistic results on stability of perovskite films under concentrated sunlight is also important in the context of recent suggestion to use perovskite solar cells as concentrated photovoltaics (for low sunlight concentrations).[29, 30] However, further additional research is needed to

study photostability of perovskite solar cells under concentrated sunlight. Generally, it is evident that solar cell can degrade faster than its absorber material itself due to presence of interfaces, degradation of transport layers and/or contacts, interactions between layers, etc.

4. Experimental Section

Film Fabrication and Encapsulation: PbI_2 was dissolved in N, N-dimethylformamide at a concentration of 461 mg/ml (~ 1 M) under stirring at 70 °C for 48 hours. The solution was kept at 70 °C during the whole procedure. Methylammonium iodide was dissolved in isopropanol at a concentration of 40 mg/ml.

The glass substrates were thoroughly cleaned with acetone, deionized water and isopropanol for sequence in ultrasonic bath for 10 min, respectively, dried with nitrogen flow and illuminated under UV light for 10 min. The methylammonium lead iodide (MAPbI_3) films were fabricated by the two-step spin-coating method in a glovebox. The process started by spinning a solution of lead iodide in N, N-Dimethylformamide at 2500 rpm on substrates, following by annealing for 30 min at 70 °C in the glovebox atmosphere. Then the second stage was to spin methylammonium iodide in isopropanol at 2000 rpm on cleaned substrates, annealing them at 110 °C for another 30 min to transform the PbI_2 films into MAPbI_3 films. To avoid reaction with oxygen and water in the air, all samples were encapsulated using cleaned glass with epoxy resin. To prevent reaction between perovskite and the encapsulation agent, the perovskite was removed from the film edges, where the encapsulation was applied.

Measurement and Characterization: The accelerated degradation experiments were implemented through a ‘Solar Furnace’ system and the experimental setup for concentrated sunlight exposure is described in details elsewhere^[17, 18, 31]. Natural sunlight was concentrated outdoors and transmitted indoors. Concentrated sunlight exposure was performed during clear-sky periods around noontime at Sede Boqer (Desert Negev, Israel, Lat. 30.8°N, Lon. 34.8°E, Alt. 475 m), and the solar spectrum delivered to the sample was very close to the standard AM1.5 solar spectrum. To prevent the sample overheating by concentrated sunlight an optical

chopper (open for light during 5.4 % of entire illumination time, Figure S12) was introduced to the system.^[18, 29] For temperature measurements of samples, a thermocouple (T-type) was glued to the inner side of the glass slide. The thermocouple was connected to a multi-meter for temperature reading and displaying. We recorded temperature after the system reach thermal equilibrium (from a few seconds up to 1 minute, depending on the irradiation intensity). The UV–vis absorption spectra of the films were recorded using a Cary 5000 UV–vis–NIR spectrophotometer (Agilent Technologies) in the range of 400-800 nm. Part of photoluminescence measurements were performed with an in-lab-built confocal microscopy system (Figure S11 (a) and (b)).

Photoluminescence mapping experiments were performed using a Renishaw Invia Raman system in backscattering configuration. The samples were attached to a motorized stage with 100 nm step resolution. A laser excitation at 532 nm and a 50x long objective were used (NA = 0.50, spot size $\sim 1 \mu\text{m}$). The maps were acquired at low laser power of 30 nW and acquisition time of 0.5 s to avoid any degradation of the perovskite layers during the measurements. The stage was translated in x and y directions to map the PL spectra from each spot.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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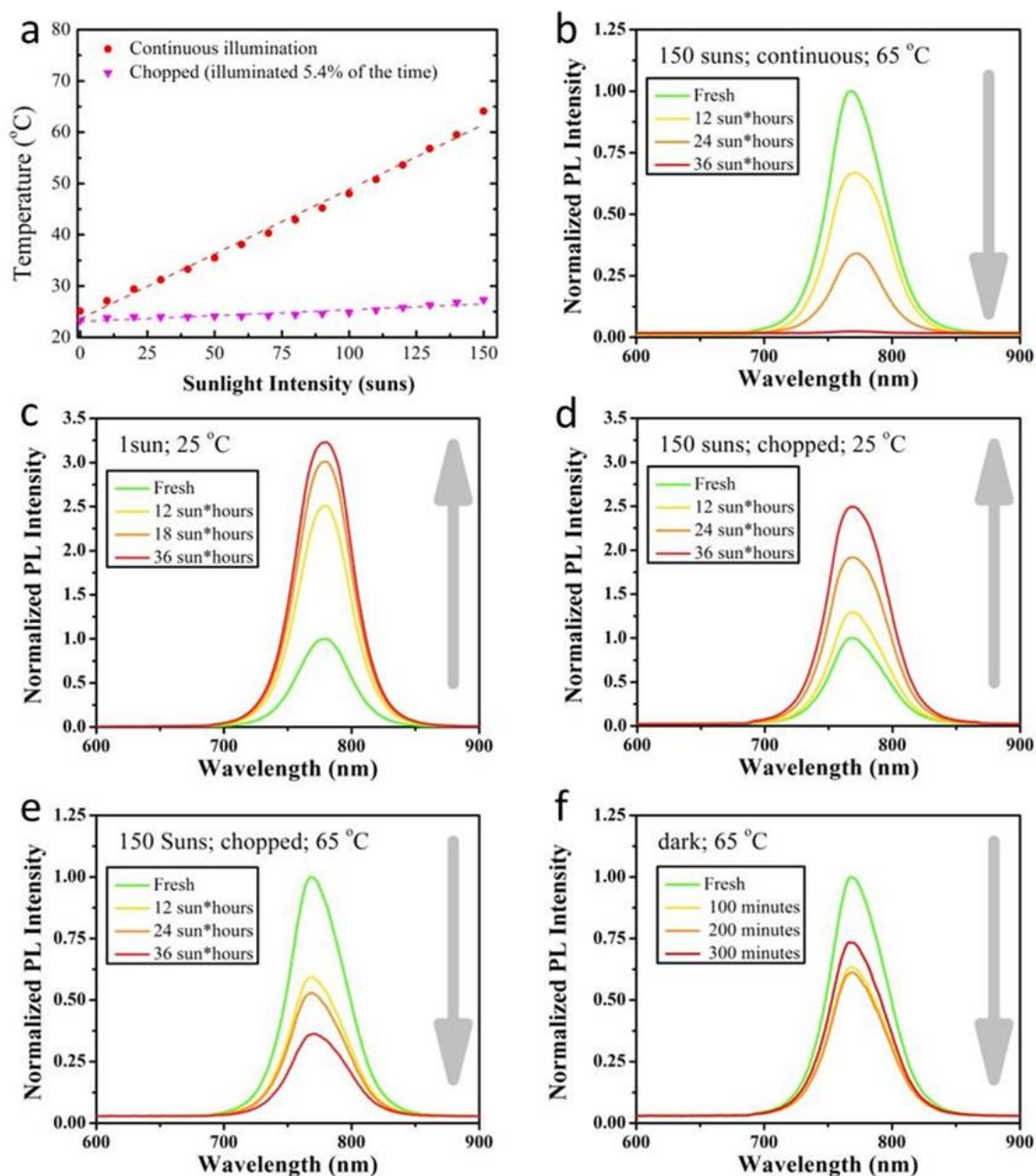


Figure 1. (a) Film temperature as a function of the incident concentrated sunlight intensity with continuous and intermittent illumination. (b)-(e) Normalized photoluminescence spectra of MAPbI₃ films in the fresh state as well as after exposure to (b) concentrated sunlight (150 suns; 65 °C) (c) simulated sunlight (1 sun; 25 °C); (d) intermittent concentrated sunlight (150 suns; 25 °C), (e) intermittent concentrated sunlight (150 suns; 65 °C). The final illumination dose in all photodegradation experiments (b)-(e) was equal to 36 sun·hours. (f) Normalized PL spectra of MAPbI₃ film before and after heating to 65 °C for the time interval equal to the longest photostability experiment. Grey arrows schematically depict trends of PL intensity evolution upon exposure. The spectra shown are the average of 5 measurements over the exposed area.

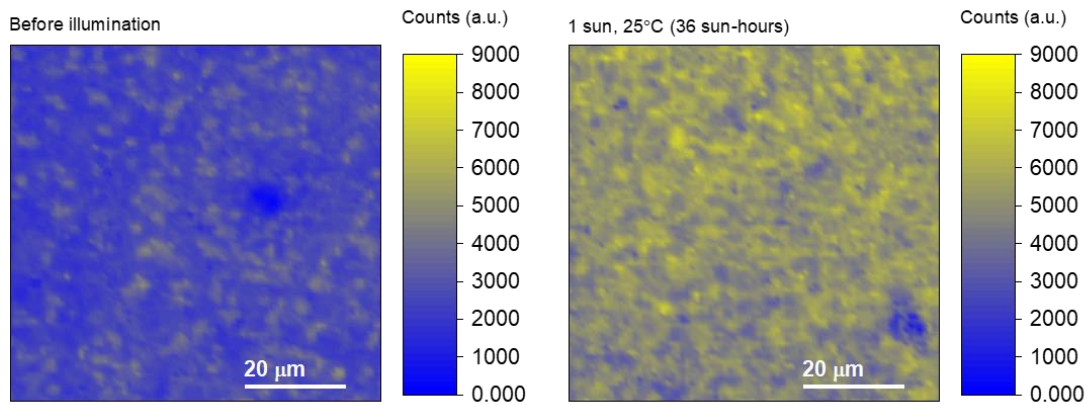


Figure 2. Photoluminescence intensity maps at 775 nm of the sample before and after its continuous exposure to simulated sunlight (1 sun; 25°C) with the dose of 36 sun·hours.

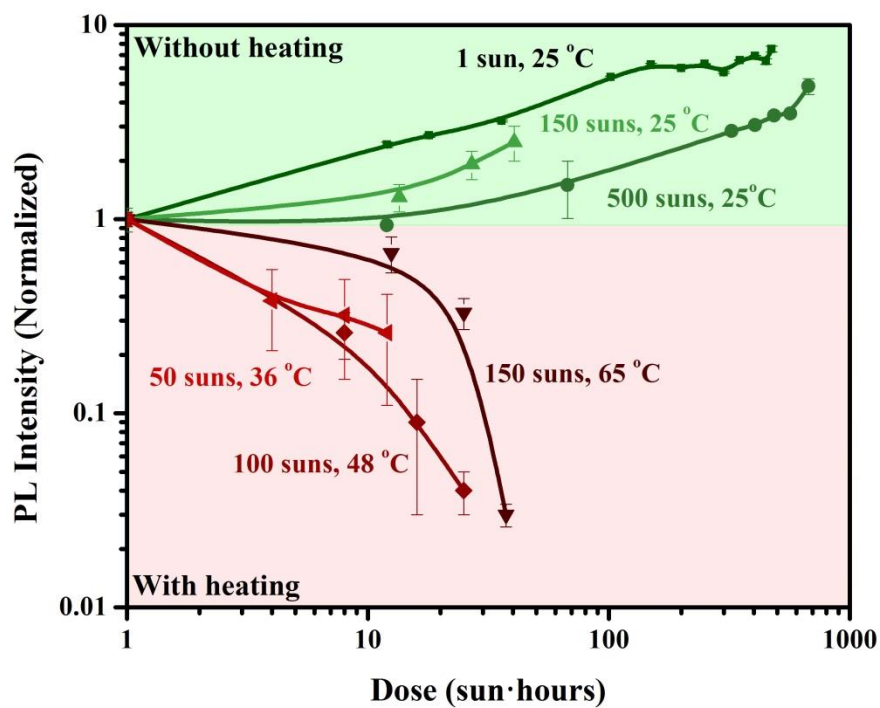


Figure 3. Evolution of normalized peak photoluminescence intensity in MAPI films exposed to concentrated light at different temperatures. The lines are guides for the eye.

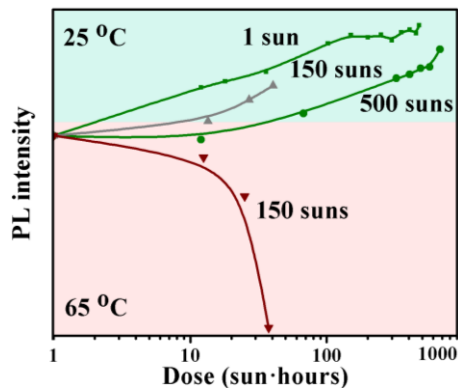
Table of content

Initial stages of MAPbI₃ photodegradation prior to any significant change in light absorption, are studied, with independent control of sample temperature and sunlight intensity (1-500 suns). Under combined action of light and heat, a strong reduction of photoluminescence (PL) was observed. On the contrary, illumination of perovskite films (with intensity up to 500 suns) without heating induces considerable PL enhancement.

Keyword: Perovskite photovoltaic materials

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Initial Stages of Photodegradation of MAPbI₃ Perovskite: Accelerated Aging with Concentrated Sunlight



Supporting Information

Initial Stages of Photodegradation of MAPbI₃ Perovskite: Accelerated Aging with Concentrated Sunlight

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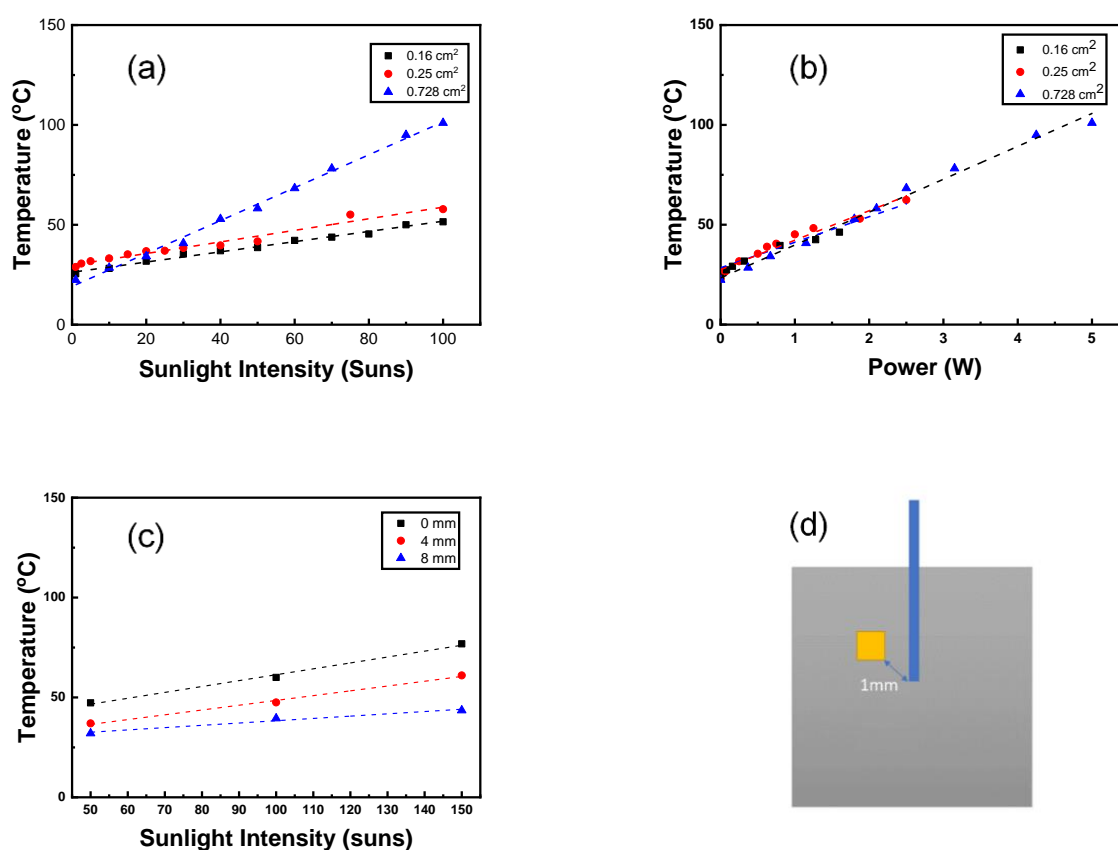
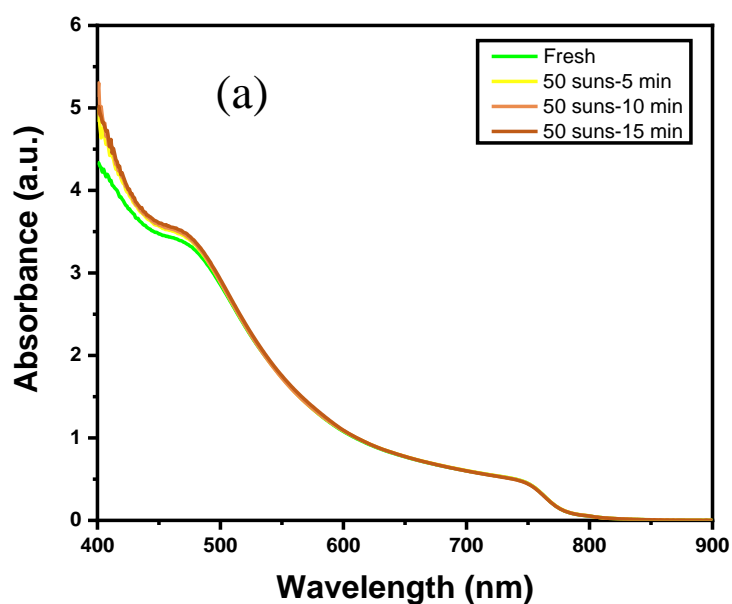


Figure S1 (a) The temperature of the MAPbI₃ film as a function of concentrated sunlight intensity delivered via kaleidoscopes of a different area (0.16, 0.25 and 0.786 cm²); (b) The temperature of the MAPbI₃ film as a function of the power of concentrated sunlight; (c) Temperature of MAPbI₃ films as a function of distance between the thermocouple and the illuminated area; (d) Distance between the illuminated area and the thermocouple.

Figure S1 (a) shows temperature of perovskite film as a function of light intensity for three kaleidoscopes with different area. As can be seen, the sample temperature increases linearly with rising sunlight intensity and the slope increases with kaleidoscope's area. From the other

hand, all three curves merge together if plotted as a function of the total light power (Fig. S1 (b)), proving that total energy per time unit received by the film determines the heating. For the experiments described below, the solar furnace system with the kaleidoscope of 0.16 cm² have been selected.

In the next experiment, we studied the effect of the temperature as a function of the distance between the thermocouple and the illuminated area (Fig. S1 (c)). For the experiments described below, this distance between the kaleidoscope and the thermocouple was set as 1 mm, which showed in Figure S1 (d).



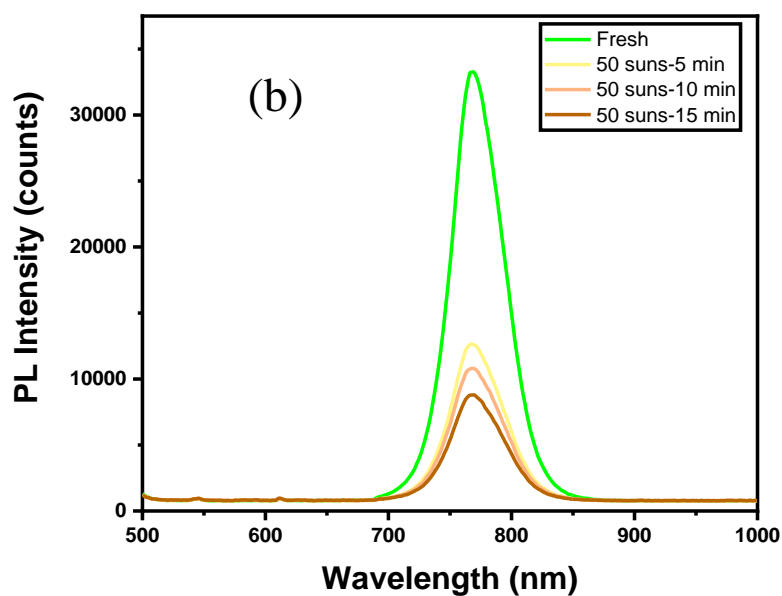


Figure S2. Evolution of (a) UV-visible light absorption spectra; (b) Photoluminescence spectra of the MAPbI₃ film after its exposure to the concentrated sunlight with the intensity of 50 suns.

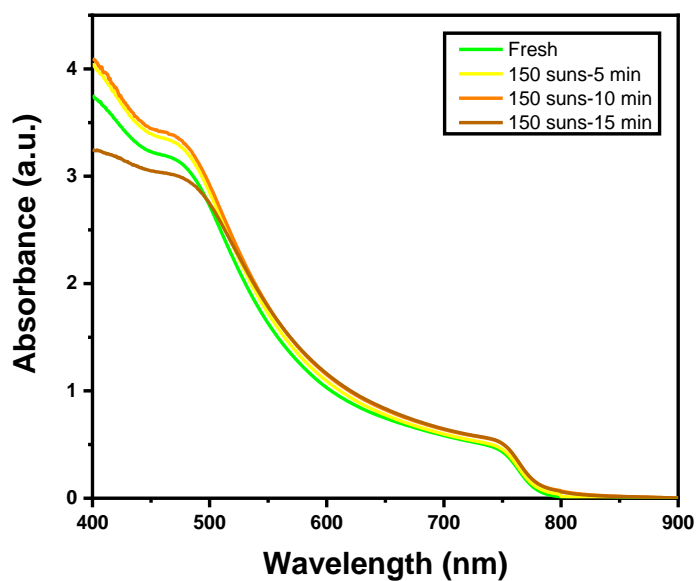


Figure S3. Evolution of UV-visible light absorption spectra of the MAPbI₃ film after its exposure to the concentrated sunlight with the intensity of 150 suns. Evolution of the photoluminescence spectra of this film is shown in the paper (Figure 1b).

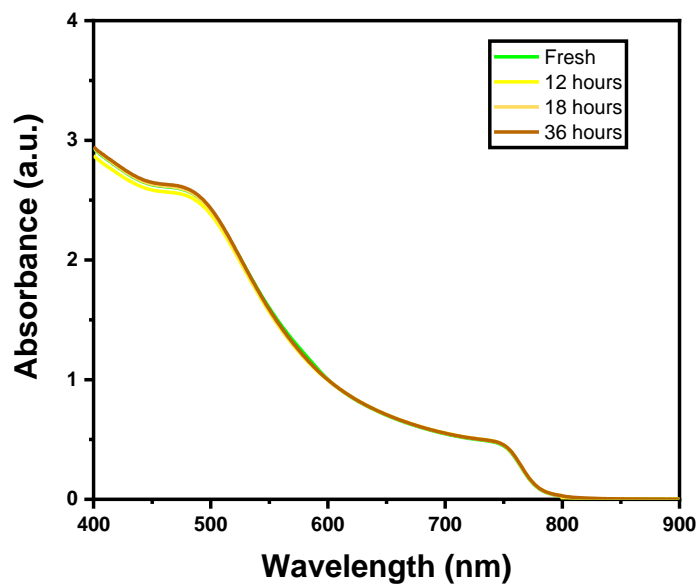
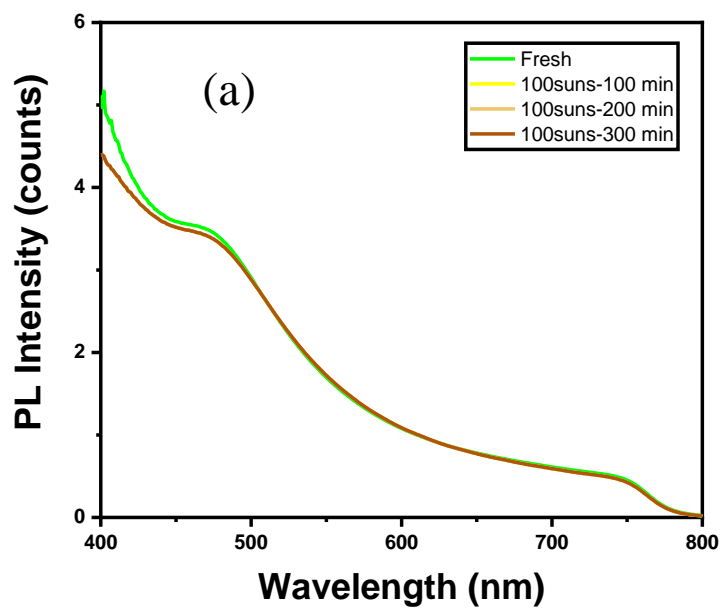


Figure S4. Evolution of UV-visible light absorption spectra of the MAPbI₃ film after its exposure to one sun condition at 25 °C. Evolution of the photoluminescence spectra of this film is shown in the paper (Figure 1c)



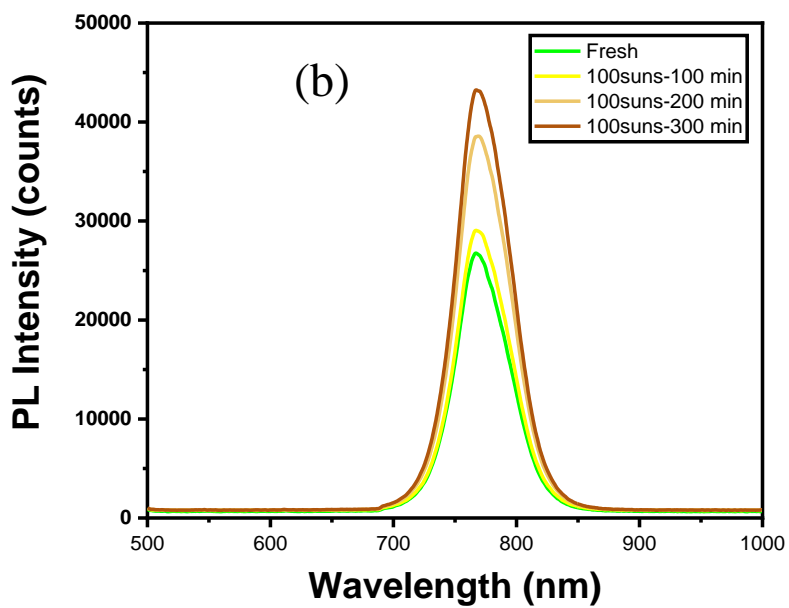
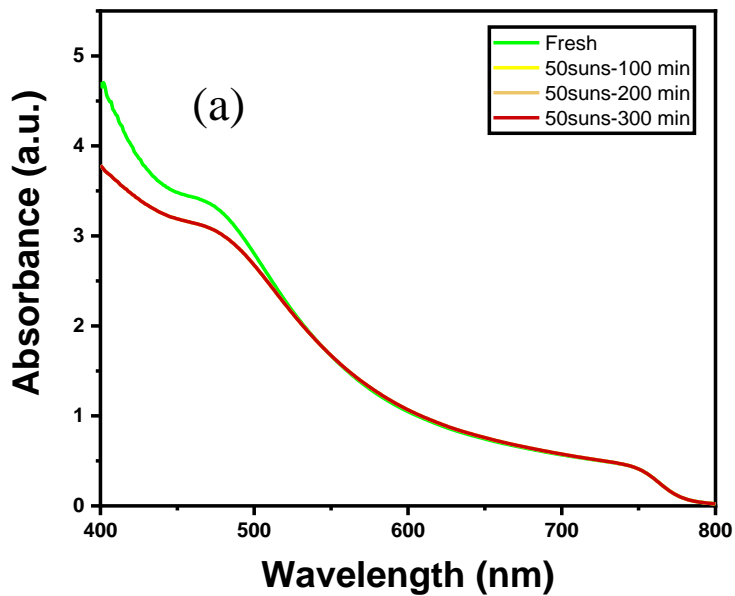


Figure S5. Evolution of (a) UV-visible light absorption spectra; (b) Photoluminescence spectra of the MAPbI₃ film after its exposure to the chopped concentrated sunlight with the intensity of 100 suns.



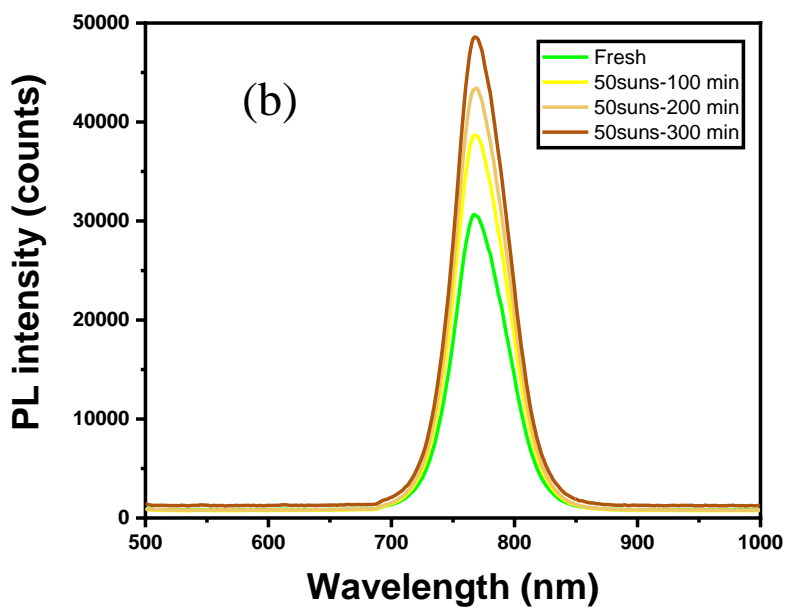


Figure S6. Evolution of (a) UV-visible light absorption spectra; (b) Photoluminescence spectra of the MAPbI₃ film after its exposure to the chopped concentrated sunlight with the intensity of 50 suns.

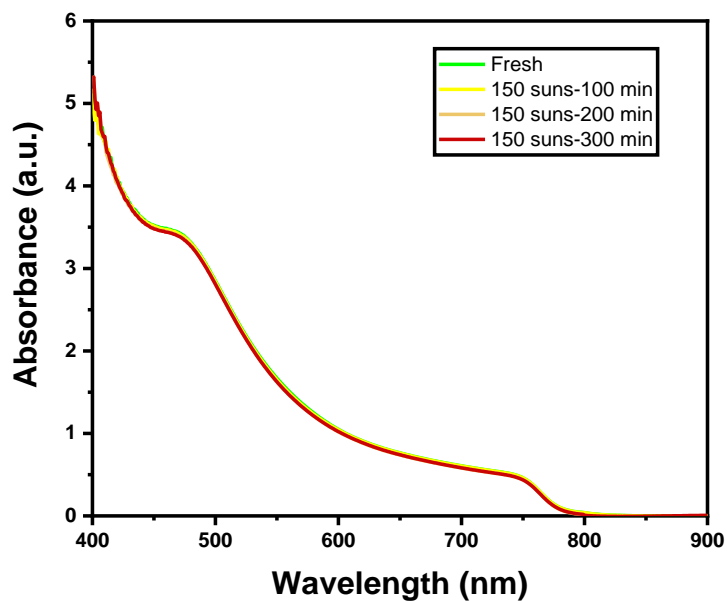


Figure S7. Evolution of UV-visible light absorption spectra of the MAPbI₃ film after its exposure to the chopped concentrated sunlight with the intensity of 150 suns. Evolution of the photoluminescence spectra of this film is shown in the paper (Figure 1d).

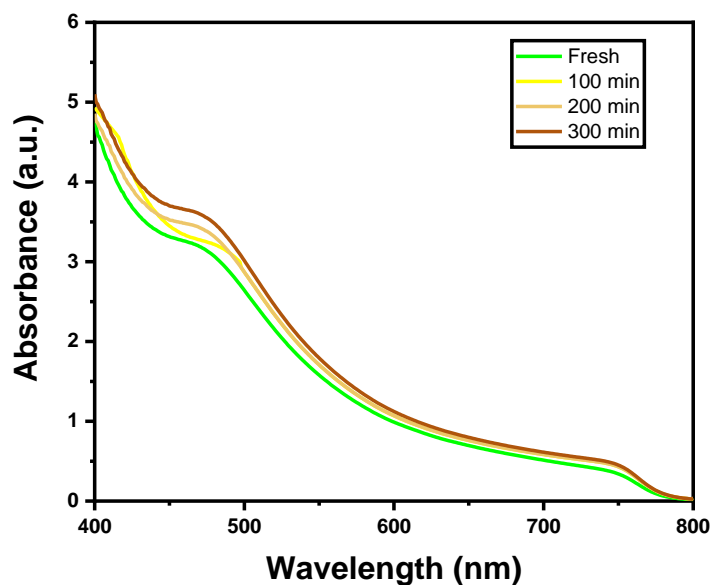


Figure S8. Evolution of UV-visible light absorption spectra of the MAPbI₃ film after its exposure to the chopped concentrated sunlight with the intensity of 150 suns and additional heating to 65 °C. Evolution of the photoluminescence spectra of this film is shown in the paper (Figure 1e).

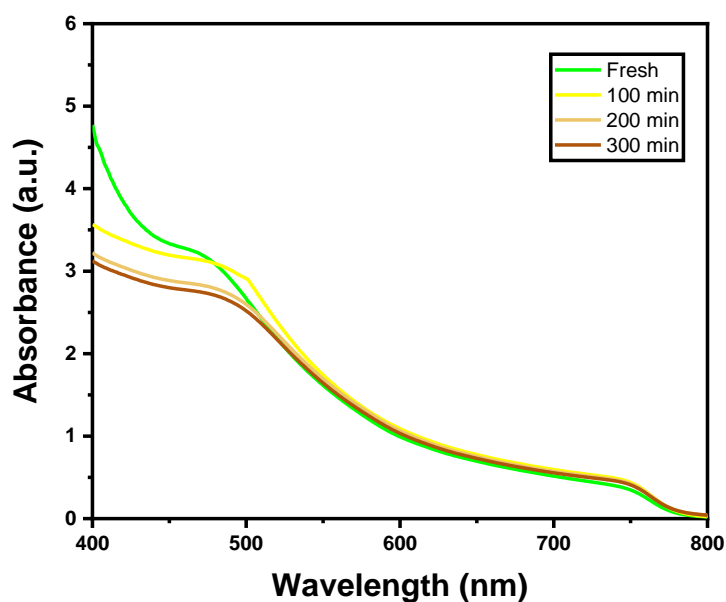


Figure S9. Evolution of UV-visible light absorption spectra of the MAPbI₃ film after the sample heating to 65°C in the dark. Evolution of the photoluminescence spectra of this film is shown in the paper (Figure 1f).

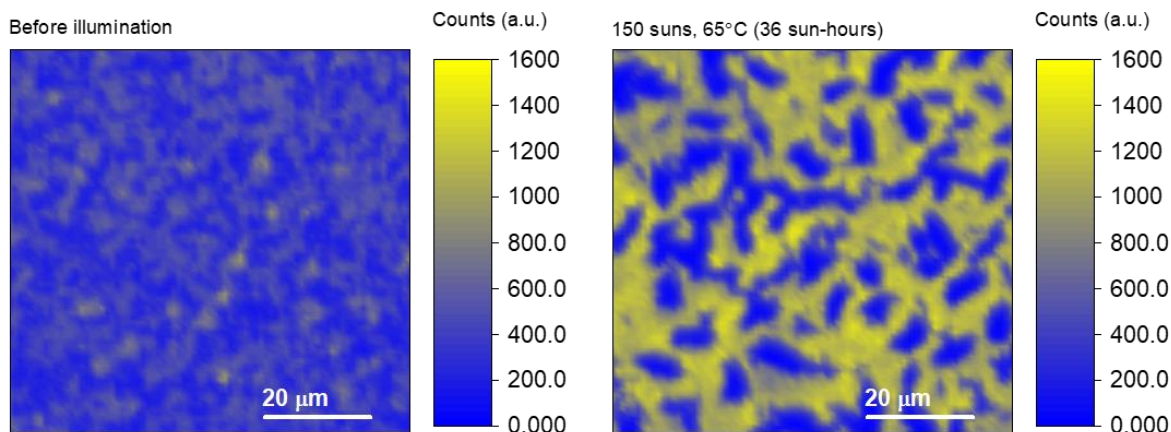


Figure S10. Photoluminescence intensity maps at 775 nm of the sample before (left) and after (right) its continuous exposure to concentrated sunlight of 150 suns (65 °C) with the dose of 36 sun·hours.

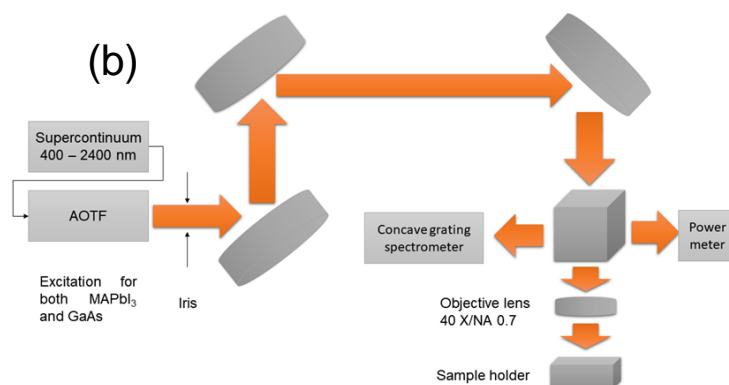
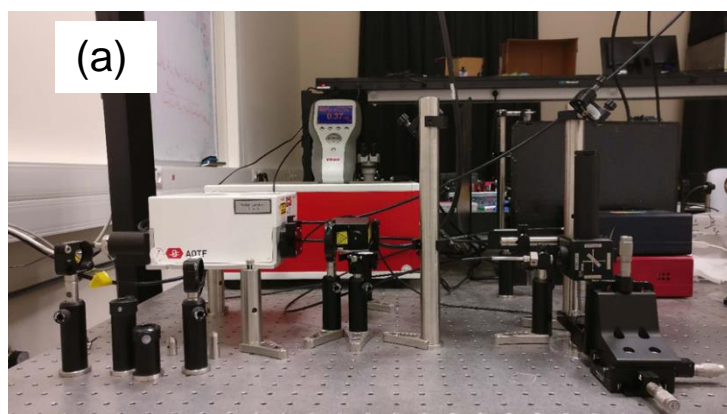


Figure S11. PL spectroscopy setup. (a) The system photograph; (b) Schematics of the beam pathway in the PL spectrometer.

Excitation at 600 nm was used for photoluminescence measurements. Excitation was delivered by a supercontinuum laser (Fianium Whitelase, Model-WL-SC-400-40) filtered by

an Acousto-optic tunable filter system (Fianium, AOTF). Aluminum mirrors guided the laser output of the AOTF to a filter cube (Thorlabs, DFM1) which contains a dichroic beam splitter (Semrock, FF625-SDi01-25x36) and a short pass (Semrock, FF01-650/SP-25) filter. The excitation beam is focused by an objective lens (40 X/NA 0.7) to the sample which three linear translation stages can adjust the position. The same objective lens collects photoluminescence, filtered by a long pass filter (Semrock, FF01-685/LP-25) and coupled via an optical fiber to a concave grating spectrometer (Stellar Net Inc-model- BLK-C-SR). A power meter was set at the first reflection of the dichroic to monitor the stability of the laser.

Two different 4 mm*4 mm square were marked on the samples. One square was chosen as the exposed area, and aluminum paper covered the other spot as the reference spot. UV-visible light absorption of perovskite films and photoluminescence spectra of perovskite films were measured at the gap in every interval.

For analysis of the dynamics of PL intensity (see Figures 31-34 in section 4.6), we measured PL four or five different times on different locations on the each marked spot and calculated the average values. We use error bars in section 4.6 to show how precise our measurements are.

Error bars were calculated using a formula:

$$\sigma = \sqrt{\frac{\sum_i^N (x_i - \bar{x})^2}{N - 1}}$$

where are $\{x_1, x_2, \dots, x_n\}$ the observed PL peak values of the samples, \bar{x} is the mean value of these PL peak observations, and N is the number of observations in the sample.

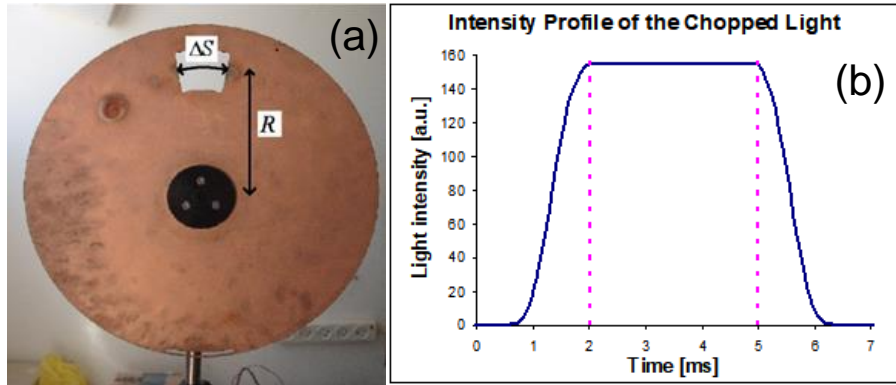


Figure S12. (a) Chopper disk used in the experiments for heating reduction [1]; (b) Light intensity profile with the chopper rotating in our experiment with a frequency of 13.5 Hz ($T = 74$ ms). Three temporal regions can be identified, starting with the sample in the dark: (i) opening (1-2 ms) - the sample is partially irradiated, (ii) constant irradiation (2-5 ms)- the sample is irradiated ($\tau = 4$ ms) and (iii) closing (5-6 ms)- the sample is partially irradiated. $\langle P_{in} \rangle_{chopped} / \langle P_{in} \rangle_{all} = \tau / T = 0.054$.

References

- [1] A. Braun, B. Hirsch, A. Vossier, E. A. Katz, J. M. Gordon, Progress in Photovoltaics: Research and Applications 2013, 21, 202.