Presence of Maximal Characteristic Time in Photoluminescence Blinking of MAPbI$_3$ Perovskite

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Photoluminescence (PL) blinking is a common phenomenon in nanostructured semiconductors associated with charge trapping and defect dynamics. PL blinking kinetics exhibit very broadly distributed timescales. The traditionally employed analysis of probability distribution of ON and OFF events suffers from ambiguities in their determination in complex PL traces making its suitability questionable. Here, the statistically correct power spectral density (PSD) estimation method applicable for fluctuations of any complexity is employed. PSDs of the blinking traces of submicrometer MAPbI$_3$ crystals at high frequencies follow power law with excitation power density dependent parameters. However, at frequencies less than 0.3 Hz, the majority of the PSDs saturate revealing the presence of a maximal characteristic timescale of blinking in the range of 0.5–10 s independently of the excitation power density. Super-resolution optical microscopy shows the characteristic timescale to be an inherent material property independent of polycrystallinity. Thus, for the first time the maximum timescale of the multiscale blinking behavior of nanoparticles is observed demonstrating that the power law statistics are not universal for semiconductors. It is proposed that the viscoelasticity of metal-halide perovskites can limit the maximum timescale for the PL fluctuations by limiting the memory of preceded deformations/re-arrangements of the crystal lattice.

1. Introduction

During the last decade metal-halide perovskites (MHPs) have been one of the most celebrated optoelectronic materials in the field of energy research. While all-inorganic compositions have evolved to be efficient emitting material, organic–inorganic halide perovskites achieved striking efficiency in photovoltaic devices.[1–4] Practical utility of these materials is largely dependent on the density and nature of defects which can trap photo-generated charge carriers and lead to their nonradiative recombination. Studies based on combined PL and electron microscopy methods have revealed heterogeneous distribution of trap states in the films.[5–8] These traps are associated not only with vacancies, interstitials, and surfaces, but also with the crystal strain and local compositional variations.[7,9,10] Additionally, defect states in MHPs can be influenced by photoexcitation resulting in both formation of new defects and removal/passivation of already existing defects.[11–13] Moreover, defects created by light can spontaneously disappear when the sample is kept in dark.[13,14] These effects are often referred to the self-healing properties of MHPs.[15] Thus, at least some of the defect states crucial for electronic properties of MHPs possess a transient or metastable nature. That is why there is no surprise why intermittency or blinking of the PL intensity under constant photoexcitation is a commonly observed phenomenon when emission of an individual micrometer and smaller sized MHP crystal is monitored.[16–21] Moreover, when thin polycrystalline films are observed via PL microscope, local PL intensity fluctuations are often clearly visible.[16,18] It is interesting that PL blinking of large crystals[21,24] was reported even before the same phenomenon in MHP colloidal quantum dots (QDs) was observed.[25–27] The nature of these fluctuations lay in the presence of strong metastable nonradiative recombination centers with a very large recombination cross section (so-called supertraps).[19,23] Thus, PL yield depends on the actual number of metastable nonradiative recombination centers per crystal which fluctuates in time and depends on other conditions.[14] Conceptually, this model is same as the multiple recombination center (MRC) model proposed a decade ago as one of the explanations

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for QD blinking.\textsuperscript{[15]} PL blinking phenomenon was used to estimate charge transport in MHPs, find the spatial location of the metastable defects using super-resolution optical imaging and spectroscopy, assess their charge recombination across sections, and to unravel the nature of the nonradiative recombination centers.\textsuperscript{[16–23,34,36]}

Rationalizing PL intensity fluctuations in individual emitters is an active research field for the last 25 years where the largest body of literature is devoted to PL blinking of colloidal semiconductor QDs.\textsuperscript{[35,37–44]} Blinking of semiconductor QDs, nanorods, nanoplates, and nanowires usually show a wide range of timescales from milliseconds to hours.\textsuperscript{[19,45–47]} The most popular way to characterize blinking statistics is to calculate probability distributions of ON and OFF times ($P_{\text{ON}}$ and $P_{\text{OFF}}$). Since ON/OFF time distributions have some shortcomings (see Note S10, Supporting Information, for details) alternative methods of the blinking process characterization are applied. There are several studies which use autocorrelation function\textsuperscript{[46,48–51]} and power spectral density (PSD)\textsuperscript{[48,52,53]} where the latter being Fourier transformation of the former (see Note S3, Supporting Information, for details). PSD is a better method of analysis considering the difficulty in interpretation of the slowly varying autocorrelation function. Although analysis of PSD is common for characterizing noise in electrical circuits, its application to PL fluctuations is still quite rare.\textsuperscript{[48,52–54]} Note that this method can be used for analysis of PL fluctuations in any system regardless whether they are caused by charging–discharging processes or carrier trapping on metastable defects or anything else. PL blinking in MHPs is very complex and only very seldomly resembles two-level switching.\textsuperscript{[36–38]} Even though there are several studies on large nano- or micro-crystals of MHPs where some aspects of PL fluctuation kinetics were discussed, thorough statistical data and analysis of PL fluctuations in these systems are missing.\textsuperscript{[17–21,36]}

In the current contribution we investigated properties of PL fluctuations in MAPbI$_3$ submicrometer crystals of 100–500 nm in size resembling grains in a standard MAPbI$_3$ polycrystalline film used for solar cell fabrication. Contrary to the majority of studies, we measured very long PL traces, up to 75 min and analyzed them using the PSD method.\textsuperscript{[55,56]} We found that most of the PL fluctuation traces among all the studied crystals possess a clear maximal characteristic timescale in the range of 0.5–10 s which limits the low frequency part of the PSD. This characteristic time is independent of excitation light intensity. High frequency region shows a power law behavior with the exponents in the range 1.6–1.9 and these high frequency fluctuations are partially light induced. Applying super-resolution luminescence microscopy, we demonstrate that the observed features of the PSD are intrinsic to the material and not caused by polycrystalline nature of the microcrystals. Connections between the blinking characteristic times, self-healing phenomena, and mechanical properties of the perovskites are discussed.

2. Results

To cover a broad range of frequencies, we measured PL traces as long as 75 min with 30 ms time resolution resulting in 150 000 data points covering at least one order of magnitude larger frequency range than the currently available data for MHPs.\textsuperscript{[26–32]} One can see that PL fluctuations are very complex consisting of jumps between multiple intensity levels and semigradual undulations (Figure 1a–f and Figure S2.1 and Note S2, Supporting Information). Often the lowest PL intensity level is not close to zero. Some crystals show continuous increase of PL intensity of the brightest level when continuously exposed to the laser excitation over a long time (the PL enhancement effect,\textsuperscript{[11]} Figure 1c and Figure S2.1 and Note S2, Supporting Information). To characterize such complex blinking traces, we employed the PSD estimation method. The algorithm of the calculation of the PSD estimator and its confidence interval is given in the Experimental Section and Note S3, Supporting Information.

The high frequency part of the PSDs (Figure 1g–i) for all MAPbI$_3$ crystals in the double logarithmic scale follow a straight-line featuring the power law dependence. However, at the low frequency range, below 0.3 Hz, all crystals showed a quasi-saturation behavior (Figure 1g–i). Formally we can fit the spectrum consisting of a constant at the low frequency range ($PSD = A$, $f \ll f_0$) and a power law at high frequencies ($PSD = f^{-\beta}$, $f \gg f_0$) by a stretched Lorentzian function:

\[ PSD(f) = \frac{A}{1+(f/f_0)^\beta} \]  

This formal fitting allows us to determine two important parameters of the spectrum: characteristic frequency $f_0 = 1/(2\pi\tau)$, which shows the crossover point of the saturation and the power law, and the power law exponent $\beta$. Here, $\tau$ is the characteristic timescale of the PL fluctuations. Details are discussed in Note S3, Supporting Information. Note that for $\beta = 2$, Equation (1) gives a Lorentzian function which is the PSD expected for a stochastic two-level system (TLS) with defined total switching rate $2\pi f_0 = 1/\tau$ (Figure 2 and Note S4, Supporting Information), which we will use as a reference point in further discussions. We found that PSDs of many studied crystals become constants in the low frequency range (Figure S5.1, Supporting Information) and thus can be well approximated by Equation (1). The other crystals demonstrate deviations of different extent in their PSDs from constant levels in the low frequency region (Figure S5.2, Supporting Information). We need to stress that the longer the correlation times probed, the smaller the number of data points become. This results in a large statistical uncertainty of the estimated PSD in the low frequency region. To understand if the observed deviations from constant levels have any significance, one needs to compare them with the statistical deviations in the PSDs of TLSs where spectrum must be constant at low frequency. For this purpose, we generated intensity traces of TLSs using Monte Carlo simulations with the same bin time, trace length, and characteristic time as in our experiments and then calculated their PSDs using the same algorithm as for the experimental data (Figure 2 and Notes S6 and S7, Supporting Information). We found that PSDs of TLSs, similarly to the experimentally observed PSDs for our crystals, also often show some “wavy saturation” shape in the low frequency range instead of a constant. However, these deviations are as large as expected from the confidence intervals calculated by our algorithm (Figure 2c,d). Thus, considering the error bars, we can classify most of the recorded PSDs (75%) as possessing
saturation and hence exhibiting well-defined maximum fluctuation correlation times in the range from 0.5 to 10 s (Note S7, Supporting Information). Thus, only 25% of the studied crystals possess even slower fluctuation dynamics with times in the range of 100 s or longer (Figure 2e,f).

We extracted \( \tau \) and \( \beta \) from 37 PSDs by fitting them with the stretched Lorentzian function. The corresponding PL traces were 25–75 min long and acquired at the excitation power of 0.3 W cm\(^{-2} \) (≈3 Sun). Figure 3 shows the distribution of \( \tau \) and \( \beta \). The characteristic time \( \tau \) varies from 0.5 to 10 s from crystal to crystal. The average value of the exponent \( \beta \) is 1.66, with a few crystals possessing \( \beta = 1.8–1.9 \), which is very close to \( \beta = 2 \) (the pure Lorentzian function). Note that for nanocrystals of traditional semiconductors like CdSe and others, \( \beta \) is much smaller, ranging from 0.7 to 1.3.\(^{[48,52,53]} \) Thus, we can conclude that, in comparison with most of the other individual semiconductor emitters, the spectra of PL fluctuations for MAPbI\(_3\) submicrometer crystals are much closer to the spectrum of a system having a single switching rate.

Small \( \beta \) values in power laws are usually attributed to system heterogeneities. It is well known that charge dynamics, trap concentration, and other properties can substantially vary from grain to grain in a MAPbI\(_3\) film.\(^{[5–8]} \) SEM images of our sample show that many objects visible as single spots in the PL images must be polycrystalline aggregates consisting of several merged crystallites of 100–500 nm in size (Figure 4a,b and Figure S1.1, Supporting Information). Therefore, the observed complexity of the PSDs could potentially be a consequence of an inhomogeneity when each crystallite belonging to the same aggregate exhibits a different PSD spectrum.

To verify this possibility, we employed a super-resolution localization analysis (2D Gaussian fit of the individual objects in PL images, see Note S8, Supporting Information, for details) to the individual PL spots.\(^{[19,57]} \) This approach allows distinguishing between individual crystals and polycrystalline objects. When PL blinking does not lead to any spatial shift of the centroid position of the Gaussian fit, we consider such object consisting of a single domain, over which free diffusion of charge carrier occurs. When a metastable non-radiative recombination center appears in such domain, PL intensity is reduced, but the radiative recombination still can happen in any location inside of the domain resulting in no shift of the centroid position (see “trap-capacity-limited” blinking case discussed in ref. [19]). To the contrary, spatial hindered...
A shift in correlation with a PL intensity change is a clear indication that the object consists of several domains with a limited transfer of charge carriers between them (a polycrystalline object). [19] Number of crystallites in a polycrystalline object can be roughly estimated from the number of clusters in the distribution of the centroid coordinates, see Note S8, Supporting Information. Figure 4c,d demonstrates the localization analysis of four distinct blinking traces along with their respective PSDs obtained from 75 min long traces. Using the classification given above, traces 1 and 2 belong to single crystallites, while trace 3 and 4 are definitely convolutions of PL signal coming from at least three and four merged crystallites, respectively. However, we do not observe any correlation between the number of crystallites and the features of PSDs (Figure 4e): all PSDs show the power law at high frequencies with similar β around 1.6 and a quasi-saturation for $f < 0.3 \text{ s}^{-1}$ (characteristic time $\tau = 0.5$ s). Thus, we conclude that the observed spectral features are inherent to processes at the level of an individual crystallite reflecting properties of the MAPbI$_3$ material itself.

Figure 2. a) Schematic illustration of a two-level system (TLS) with the respective transition rate constants, b) simulated time-trace of a TLS, c,e) magnified experimental PL traces of spots 4 and 5, and d,f) corresponding PSDs obtained from experimental and simulated TLS traces. For spot 4, small variation of PSD from the constant level in the saturation is observed for both experimental and simulated traces; however, the variations are within the confidence interval. For spot 5, however, the variations are significant and fall out of the estimated confidence interval.

Figure 3. Distribution of the stretching exponent $\beta$ and the characteristic time $\tau$ extracted from 37 PL intensity traces measured at 0.3 W cm$^{-2}$ excitation power. Semitransparent black lines indicate the respective average values ($<\beta> = 1.66$, $<\tau> = 2.6$ s).
Often PL blinking processes are partially photo-activated.\textsuperscript{36,58} To evaluate the effect of excitation power density on the blinking traces and PSDs, we varied the excitation power over three orders of magnitude: $W_1 = 0.025 \text{ W cm}^{-2}$ or $6.5 \times 10^{16} \text{ photons s}^{-1} \text{ cm}^{-2}$; $W_2 = 0.3 \text{ W cm}^{-2}$ or $7.9 \times 10^{17} \text{ photons s}^{-1} \text{ cm}^{-2}$; and $W_3 = 3.25 \text{ W cm}^{-2}$ or $8.5 \times 10^{18} \text{ photons s}^{-1} \text{ cm}^{-2}$.

Figure 5a (Figures S9.1–S9.7, Supporting Information) shows 25-min-long traces of the same MAPbI\textsubscript{3} crystal at these three excitation power densities.

First of all, the relative blinking amplitude $\Delta PL/PL_{\text{max}}$ decreases with the increase of the excitation power density in agreement with the previous report.\textsuperscript{21} The decrease of the relative amplitude correlates with decreasing of the saturated PSD values (Equation S10 and Note S4, Supporting Information) calculated for the normalized PL traces (Figure 5d). Distributions of $\tau$ and $\beta$ for several crystals at three different excitation powers are shown in Figure 5e. Most interestingly, increasing of the excitation power results in decreasing of the exponent $\beta$ (Figure 5c) which becomes more and more different from 2 at higher excitation power (compare the average values shown in the Figure 5e). At the same time, the saturation behavior was observed for all excitation powers.
used without any systematic change in the characteristic frequency $f_0$.

### 3. Discussion

For colloidal semiconductor and perovskite QDs, the cause of the PL intensity fluctuations is the nonradiative decay of the photoexcited state, the rate of which fluctuates with time. There are three basic microscopic mechanisms of the fluctuating nonradiative recombination proposed in the literature. The first one is the Auger mechanism introduced by Efros and Rosen.[59] This mechanism which is also called charging mechanism,[60] A-type blinking mechanism,[61] Auger-blinking,[62] AC blinking,[63] and Type I blinking[64] is based on fast Auger recombination of the photoexcited state of the ionized nanocrystal. Thus, in the Auger mechanism, blinking is a result of ionization-neutralization cycles. The second one is the trapping mechanism (TM) suggested by Frantsuzov and Marcus.[65] In literature it is also called BC-blinking,[62] NBC blinking,[63] Type II blinking,[64] and “cold” carrier trapping mechanism because of the trapping of band edge carriers.[66] This mechanism is similar to the well-known Shockley–Read–Hall charge recombination where electrons get trapped in the band gap states for a certain time and successively recombine nonradiatively with holes. If the trapping state is metastable, the nonradiative rate fluctuates leading to fluctuating PL intensity. The third one, the hot carrier trapping mechanism by Galland et al.[61] is also known as B-type or HC blinking.[62,63] This is a modified trapping mechanism where a hot carrier (instead
of a relaxed carrier) is being trapped in a metastable trap. Over the years, it has been found that combination of two\textsuperscript{62,67,68} or even three\textsuperscript{69} of these mechanisms can work simultaneously in one blinking object.

PL blinking in large nanocrystals of MAPbI$_3$, from the very moment of its discovery was assigned to the presence of a metastable efficient nonradiative recombination center, so-called super trap.\textsuperscript{69} Thus, it is the same as the trapping mechanism suggested by Frantsuzov and Marcus for QDs.\textsuperscript{85} To support this hypothesis, photon correlation experiments recently showed that Auger mechanism cannot be of any importance for PL blinking of large MAPbI$_3$ crystals.\textsuperscript{69} We believe that the properties of PL blinking in bulk perovskite nanocrystals can be quantitatively described by a model similar to the supertrap or MRC models. However, it is to be noted that MRC model be imagined as a superposition of many Lorentzian-like spectra result in a power law shape of the PSD. In this case, the PSD can be unreliable for finding characteristic timescale. The threshold dependence makes applicability of the threshold method truncation times in a multiscale blinking trace is quite rare for metal chalcogenide semiconductors\textsuperscript{31,73} and observed only in few cases for halide perovskite QDs.\textsuperscript{31,73} Figure 6 shows that the truncation times $T_{ON}$ and $T_{OFF}$ depend strongly on threshold value, as was mentioned before. The threshold dependence of $T_{ON}$ in semiconductor nanocrystals was first found by Frantsuzov et al.\textsuperscript{35} and later justified by Crouch et al.\textsuperscript{55} Presence of such dependence makes applicability of the threshold method unreliable for finding characteristic timescale. The $T_{ON}$ and $T_{OFF}$ dependencies cross at the value of $2\tau$, where $\tau$ is the characteristic time found from the PSD. It is interesting that this result agrees with the limiting case of a pure TLS (Note S4, Supporting Information), for which $1/\tau = 1/T_{ON} + 1/T_{OFF}$. So, when truncation times coincide, $2\tau = T_{ON} = T_{OFF}$. For the discussion on the mathematical connection of ON/OFF distributions and PSD, see Notes S4 and S10, Supporting Information. Therefore, we conclude that the appearance of a characteristic time in PL fluctuations of a semiconductor nano/micro-object is an unexpected and unique observation. It means that the physical processes in MAPbI$_3$ leading to nonradiative decay must have some features unique for this material.

The exponent $\beta$ determining the high frequency part of the PSD spectrum clearly decreases with increasing of the excitation light intensity. The smaller the $\beta$ relative to 2, the stronger the fluctuations at high frequencies in comparison with that expected for an exponential process. To appreciate quantitatively the deviation from the TLS with the same characteristic time, let us compare the PSD with $\beta = 1.64$ and $\tau = 2.01$ s and the Lorentz function with $\tau = 2.01$ s shown in the same plot of Figure 1g. At the frequency of 10 Hz, PL of this crystal

Reports studying autocorrelation function or PSD for PL fluctuations in MHP semiconductors are missing, therefore, we cannot directly compare our results with any published study. However, we can compare them with other systems where PSD or autocorrelation function were measured, although the number of such studies is limited.\textsuperscript{46,48–53} We are aware of only one report where a Lorentzian PSD of a PL trace was depicted for a self-assembled InP QDs.\textsuperscript{53} It was found that autocorrelation function of the blinking colloidal QDs does not reach an asymptotic value and often the decay occurs on a timescale of measurement time. This fact implies absence of any characteristic timescale of blinking (discussed in detail in Note S10, Supporting Information).\textsuperscript{42,49–51}

We can also look at the probability distributions of ON and OFF times widely discussed in literature for many, if not all, blinking systems. Unfortunately, use of $P_{ON}$ and $P_{OFF}$ distributions has important limitations. These limitations concern to the fact that most of the individual emitters lack well-defined ON and OFF states making application of this approach questionable due to dependence of parameters on experimental/fitting conditions. To illustrate it, we conducted the conventional analysis of ON/OFF duration times probability density distributions at different threshold values for the trace of spot 2 (Figure S1b, Supporting Information). It is observed that both ON time and OFF time distributions show exponential truncations at long times which is quite an unusual result (Note S10, Supporting Information). In literature, presence of both ON and OFF truncation times in a multiscale blinking trace is quite rare for metal chalcogenide semiconductors\textsuperscript{31,73} and observed only in few cases for halide perovskite QDs.\textsuperscript{31,73}
fluctuates about three times more in terms of the fluctuation spectral density than what is expected from the exponential processes. Thus, we conclude that there is a clear photo-induced component in the fluctuations which is visible at timescales much shorter than the characteristics time $\tau$.

Despite of this excitation power dependence, the characteristic frequency $f_0 = 1/2\pi\tau$ of the transition representing the window of quasi-saturation at low frequency to the power law behavior at high frequency does not show any obvious excitation power dependence. Hence, the maximum characteristic time $\tau$ is independent of excitation power density. Therefore, it must be determined by properties of the material which are not related to electronic excitations.

Regarding all these observations, a question arises: how broad can the timescale of the fluctuations in principle be? If the shortest timescale of fluctuations is limited by the timescale of intermolecular motion or/and electron transfer (picoseconds), is there any physical mechanisms limiting the maximum length of the correlation time? Apparently, we observe this limitation in MAPbI$_3$ crystals.

Today, there is more and more evidence that the apparent defect tolerance and self-healing properties of MAPbI$_3$ and other MHPs in general originate from the softness of the crystal. This means that the material can easily re-assemble to its local structure when disturbed by a defect or another stimulus.\cite{NoteS4,NoteS6} Transient phenomena related to this are, for example, recovery of PL and even solar-less performers after degradation, PL enhancement, and PL blinking which occur at timescales from seconds to hours.\cite{NoteS4,NoteS6,NoteS7}

One of the connections between structural re-arrangement and electronic properties lays in ion migration which can create and annihilate charge trapping states. All the constituent ions (H$^+$, MA$^+$, and I$^-$) except lead ions (Pb$^+$, Pb$^{2+}$, and Pb$^{0}$) can easily diffuse inside the MAPbI$_3$ crystal.\cite{NoteS8,NoteS7,NoteS6} Substantial ion mobility and the ease of crystal lattice reorganization at room temperature agree well with the mechanical properties of MHPs exhibiting low shear modulus leading to lability in the crystal.\cite{NoteS8,NoteS9,NoteS10} While diffusion of atoms and molecules can be connected to material viscosity, its ability to hold the strain while stretching and to relax back to its original state is the elastic response of the solid. Both viscosity and elasticity are inherent to MHPs making them so-called viscoelastic materials. Nanoindentation experiments support the viscoelastic nature of MAPbI$_3$ crystals and demonstrate that the creep deformation and stress relaxation occur at the timescale of tens of seconds.\cite{NoteS8,NoteS7} Since strain and ion migration largely control the defect activity and charge recombination in MAPbI$_3$, we propose that viscoelasticity of MAPbI$_3$ and MHPs in general could be important to rationalize their transient optical responses including PL blinking with timescales from seconds to hours.

Diffusion coefficients of the various ionic defects are found to be on the order of $10^{-30}$–$10^{-6}$ cm$^2$ s$^{-1}$ at room temperature.\cite{NoteS8} Thus, the characteristic timescale for the ion-diffusion-assisted change of a 100 nm crystal can be estimated as $T \approx L^2/D$, which gives the values in the interval from $10^{-4}$ to 1 s and agrees with the timescale of fluctuations observed experimentally.

We propose that the material fluidity sets the fundamental limit to the maximum characteristic time observed in the spectra of the fluctuations. One can see the origin of this limit as that the system loses the memory of a deformation as soon as it is mechanically changed by transformation and re-organization of the lattice. The higher the fluidity the shorter the maximum characteristic timescale is expected to be.

Indeed, hard crystals possess the longest mechanical memory (years), while a characteristic memory of a liquid is in a millisecond range.\cite{NoteS8,NoteS6} Mechanical memory (or memory of the shape) requires elasticity and, is therefore, limited by the fluidity of the material. Contrary to hard crystals, MHPs in terms of some of their mechanical properties are closer to liquids rather than to solids.\cite{NoteS4,NoteS6} This is probably at least one of the reasons why many phenomena with the characteristic time of around 1–100 s are observed in MHPs.

It will be interesting to see if similar saturation of PSD exists for smaller perovskite nanocrystals (10 nm or smaller) with quantum confinement. Upon decreasing, the size charging–discharging process due to surface trapping becomes an additional, and sometimes dominant mechanism of PL fluctuations.\cite{NoteS4,NoteS6,NoteS7} In our future studies we will apply PSD analysis to small perovskite nanocrystals to find out if there is any longest characteristic time of this Auger blinking mechanism in perovskites.

The origin of very slow fluctuations observed in 25% of the studied crystals is not clear for us. One could argue that this deviation is a result of photobrightening or photobleaching of the crystals during the long measurements. However, we modeled photobrightening on the trace corresponding to spot 2 and found a very negligible effect of this process on PSD (Note S11, Supporting Information). We speculate that these fluctuations reflect collective dynamics of the whole crystal and its environment, rather than switching of a single nonradiative recombination center(s) from an active to a passive state. Note that, smooth slow changes of PL intensity of large microcrystals have been reported in several studies and can be related to the change of the environmental conditions (e.g., humidity fluctuations).\cite{NoteS2}

From the above discussion, the following picture of the fluctuating nonradiative recombination in MAPbI$_3$ submicrometer

Figure 6. Dependence of ON and OFF truncation times on the intensity threshold which separates ON and OFF states in the PL intensity trace. PL trace corresponds to spot 2 in the PL image shown in Figure S1b of Note S1, Supporting Information. Solid black line indicates 2 $\pi$ value, where $\tau$ is the characteristic time obtained from the PSD for this trace. The intensity threshold level can be compared with the overall PL intensity distribution shown in the bottom.
crystal arises: i) fast, photo-activated switching processes with timescales <0.5 s; ii) light-independent exponential-like switching process with a clearly visible characteristic time in the range 0.5–10 s; and iii) in some cases even slower fluctuations at timescale of the order of 100–1000 s are possible. If we relate the first two processes to activation and de-activation of individual nonradiative recombination centers which is hypothetically limited by viscoelasticity, the longest timescale could reflect collective slow dynamics of the whole crystal.

4. Conclusions

PSD analysis of very long PL blinking traces of MAPbI \(_3\) nanocrystals presented presence of a characteristic timescale in the range of 0.5–10 s contrary to the usually observed power law statistics. This timescale has a striking similarity with the timescales of other transient effects in MHP assigned to ion migration and lattice re-arrangement. We propose that the mechanisms limiting the maximum timescale of the PL fluctuations are related to mechanical properties of the material such as viscoelasticity, rather than to the presence of electronic excitation and light irradiation. We can clearly distinguish this slowly switching nonradiative charge recombination channel from the photo-induced metastable channels responsible for the power law statistics in the high frequency part of the PSD. Connecting the mechanical properties with nonradiative recombination and defect metastability can potentially lead to new ideas for controlling and manipulating nonradiative charge recombination in soft semiconductors and utilizing self-healing effects in opto-electronic devices.

5. Experimental Section

Sample Preparation: The precursor solution of 0.8 m MAPbI\(_3\) was prepared by mixing 461 mg of PbI\(_2\) (99% from Sigma-Aldrich) and 159 mg of MAI (99% from Sigma-Aldrich) into 1.25 mL γ-butyrolactone (GBL, ≥99% from Sigma-Aldrich). The mixture was heated at 60 °C and stirred for 2 h to obtain a clear solution.

For the desired MAPbI\(_3\)-GBL nanocrystal crystals, the MAPbI\(_3\)-GBL precursor solution was diluted 2000 times to obtain the concentration of 4 × 10\(^{-4}\) m. Then, 20 µL of this solution was drop-casted onto a prewashed glass substrate. The sample was annealed at 80 °C for 20 min. Once the particles were formed, the film was coated with a poly(methyl methacrylate) (PMMA) by spin coating. The used polymer solution was prepared by dissolving 1 mg of PMMA (996 000 by GPC, Sigma-Aldrich) in 1 mL of toluene (Sigma-Aldrich). All preparations were carried out in ambient air.

Photoluminescence Microscopy: Measurements were performed using a home built wide field inverted fluorescence microscope equipped with Olympus IX-71 microscope body, a 40x (NA = 0.6, Olympus LUCPLANFL) objective, argon-ion laser, and EMCCD camera as the main components. The samples were excited with 514 nm line of the argon-ion laser giving the excitation spot size of 50 µm in diameter at the sample plane. One pixel at the EMCCD detector corresponded to 200 nm × 200 nm region of the sample. A set of neutral density filters was used to vary the excitation power density from 0.025 to 3.25 W cm\(^{-2}\). To block the excitation light and collect only the PL signal, two long pass filters from 25 to 75 nm.

Blinking Data Analysis: First, the recorded movies for the sample drift were corrected, which was usually less than two pixels (400 nm). In the next step, the authors employed a localization algorithm on the time-averaged data to identify and mark well-separated PL emitting spots on the image. PL intensity traces were obtained from each marked spot. Here, the authors integrated the intensity over the whole spot and subtracted the averaged background. Background was obtained from the area around the respective spots. Resultant traces were used for further analysis. Further details of the blinking trace extraction procedure could be found elsewhere.[21]

Power Spectral Density and Confidence Interval Estimation: PSD of the blinking traces were calculated by the Welch method. In this method, a spectral window needs to be selected. The Hamming window was chosen. The confidence interval was calculated as 95% using the chi squared distribution. (For details see Note S3, Supporting Information).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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