Spatially correlated photoluminescence blinking and flickering of hybrid-halide perovskite micro-rods

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A B S T R A C T

Temporally stochastic, abrupt photoluminescence (PL) intermittency (blinking) has been long recognized to be characteristic of single quantum-emitters as intensity fluctuations average out over the ensemble. While there are a few rare examples of PL blinking in spatially extended (−μm) yet quantum-confined (1 or 2-D) nanostructures, such phenomenon is in general spatiotemporally uncorrelated. However, recent investigations on organo-metal iodide perovskite nano-/micro-rods have revealed that blinking is plausible even in larger structures. Here, we report abrupt and discrete PL instability of entire individual methylammonium lead bromide (MAPbBr3) single-crystal rods of dimensions between 1 and 2 μm. Intriguingly, similar to bulk polycrystalline disks of MAPbBr3, these dimensionally unconfined micro-rods exhibit spatially-synchronous multi-level PL intermittency, on top of a slow time-varying base emission intensity. Here, we find two dominant intermittency characteristics, one of which is more abrupt (discrete) while the other is relatively gradual, designated as ‘blinking’ and ‘flickering’ respectively. One of the two intermittency behaviors is found to dominate in each micro-rod in the ensemble; however, both flickering and blinking have an extremely high spatial correlation of intensity fluctuations at short distances (<−1 μm). As opposed to micro rods which mostly “blink”, the tendency of spatially homogeneous intermittency is relatively less for micro rods which mostly “flicker”, especially over longer distances, as revealed by a correlation analysis used to quantify the extent of spatiotemporally concerted PL intermittency. We propose that the observed blinking and flickering behaviors owe to transient non-radiative traps; measurements on the same crystals under varied photoexcitation powers and under controlled atmospheric conditions suggest the existence of two distinct non-radiative traps with varying quenching efficiency, which leads to the observed diversity in the PL intermittency of entire MAPbBr3 crystals.

1. Introduction

Photoluminescence (PL) or fluorescence intermittency with time, commonly referred to as blinking, is ubiquitous for single-emitters such as single molecules, fluorescent proteins, and quantum-confined semiconductor nanocrystals (NCs) [1–3]. Further, conjugated polymers and molecular aggregates are also known to exhibit blinking [4–6], where the emission intensity fluctuates between multiple bright and dark states in a seemingly random yet discrete manner. For semiconductor materials, till recently, the general perception had been that quantum confinement of carriers in more than one dimension is necessary for PL intermittency, such as for 3D confined quantum-dots (QDs) [7,8]. The primary reason for such a notion is because of the high density of surface defects in nanostructures, and blinking mechanisms typically involve dark (low quantum yield) surface-states where charge carriers can be trapped for relatively long durations [7,9,10]. Although rare, spatially extended semiconductor NCs confined in 2- or 1-dimension(s) (such as quantum-wires) have also been reported to exhibit spatially heterogeneous PL intermittency [11,12]. Off late, there has been considerable interest in the all-inorganic and organo-metal (hybrid) halide perovskites (OHPs), the optoelectronic properties of which have been explored extensively for both photovoltaic and LED applications [13,14]. Over the last few years, it has been revealed that various individual nano/micro-crystals of perovskites also undergo extensive blinking and other photo-induced processes such as photo-activation (curing) and photo-degradation [15,16,23]. Since these processes may pose a problem in terms of device applications, there is a general interest in understanding what are the factors lead to PL intermittency in perovskite materials.

More recently, an interesting spatially-extended blinking phenomenon has been reported for OHP nano-/micro-structures such as for methylammonium lead iodide (MAPbI3) rods, which extend beyond the diffraction limit [17,21]. In these systems, where there is nominal quantum-confinement, blinking has been most often found to be spatially heterogeneous. Interestingly, for even bigger micrometers sized (“bulk”) methylammonium lead bromide (MAPbBr3)
poly-crystalline disks/films without any dimensional confinement, both spatially heterogeneous (localized) as well as entire-crystal (homogeneous, spatially concerted) multi-state intermittency on top of a base emission has been discovered [19]. All these observations dispel the long-standing belief on the relationship of PL intermittency and involvement of surface states (in effect, quantum-confinement); however, such phenomenon remains poorly understood due to lack of systematic investigations and thorough analyses.

One of the propositions is that blinking of the entire MAPbI₃ single crystal nano-rods is associated with the presence of metastable non-radiative traps, which can effectively funnel the charge carriers through a non-radiative channel [21]. Moreover, the blinking of micron-sized MAPbI₃ single crystal rods has been attributed to efficient non-radiative pathway(s) being transiently established [17,18], perhaps owing to mobile, charged (ionic) species which can lead to the formation of highly efficient quenchers of emission in OHP crystals [22]. Here, the concept of “supertraps” with exceptional quenching ability was introduced, which can abruptly change the radiative recombination efficiency over extended regions. However, the question remains whether this is the only mechanism via which entire micrometers sized crystal-line OHPs can exhibit spatially synchronous PL intermittency. For instance, heterogeneously distributed photoactive traps have been invoked to explain the spatially correlated PL intermittency of MAPbI₃ rods of length 1–2 μm [18]. It is also unclear whether only OHP of certain materials or morphology exhibit synchronous blinking, and there have been few efforts to explore in detail the PL intermittency of bulk crystals and understand possible origins of such phenomenon.

In this work, we report the multi-level, spatially-synchronous PL intermittency in MAPbBr₃ single crystal micro-rods (MRs) of lengths up to few microns, which do not have any quantum-confinement of charge carriers (effectively bulk). In contrast to earlier measurements, acquisition of PL intermittency data at a much faster time scale (100 Hz) enabled us to identify two distinct intermittency behaviors for individual single-crystals, namely, abrupt “blinking” and gradual “flickering”. Here, we present PL intermittency data and analyses of mostly blinking and mostly flickering MRs in terms of their spatial synchronicity, quantified using correlation of intensity trajectories over the entire MRs. We provide insights on why the extent of spatial correlation in intermittency can vary for different MRs, and propose plausible mechanisms involving transient non-radiative traps and long diffusion length of photo-generated carriers, a combination of which can result in sudden yet partial quenching/brightening of PL emission for entire MRs. Our measurements further reveal that photo-excitation, as well as environmental constituents such as oxygen and nitrogen, are involved in the formation/annihilation of at least two distinct transient non-radiative defects, which can lead to both abrupt blinking and gradual flickering of entire MAPbBr₃ single-crystal MRs.

2. Materials and methods

2.1. Materials

Methyl amine (CH₃NH₂, 33 wt% in absolute alcohol, Aldrich), hydrobromic acid (HBr, 48 wt% in H₂O, sigma-aldrich.com), ethanol (99.9%, changshu shenghq fine chemicals Co. Ltd.), oleic acid (OA, >90%, Aldrich), n-octylamine, dimethylformamide (DMF, >99.9%, spectrochem. Pvt.Ltd), toluene (for analysis, >99.5%, merckilipore.in), lead (II) bromide (PbBr₂, for synthesis, >99%, Lobachemie. Pvt.Ltd). All the chemicals were used as received without any further purification.

2.2. Syntheses

The synthesis of MABr and MAPbBr₃ 1-D rods is reported elsewhere [19,24], which we followed with nominal modifications. In brief, the equimolar mixture of MABr and lead bromide (PbBr₂) was mixed in dimethylformamide (2 mL) solvent. Oleic acid (0.5 mL) and n-octylamine (30 μL) were added to the mixture solution as capping groups, and the solution was stirred for 5 min till the precursors get dissolved. Further, toluene (8 mL) was added dropwise to the precursor solution. The complete reaction was carried out at room temperature and under ambient conditions. The final solution was stirred for ~24 hrs at room temperature (~298 K) for the growth of MAPbBr₃ 1-D rods. The sample was then washed and centrifuged with toluene at 5000 rpm for 10 min and kept under vacuum for further characterizations.

2.3. Characterisation

The microstructure morphology of the synthesized 1-D MAPbBr₃ rods was examined by drop cast solution on aluminium foil (5 mm × 5 mm) under field emission scanning electron microscope (FESEM, JEOL JSM-7600F). Because of the high sensitivity of the sample towards the electron beams, palladium (Pd) was sputtered over it for 60 s at 10 mA current to minimize the charging effect. Further, the surface topography was explored with atomic force microscopy (AFM, Asylum Research MFP 3D). For AFM measurements, a AC-240TS tip was used in AC-mode (tapping mode) at 70 kHz drive frequency. Powder X-ray diffraction (pXRD) analysis was performed for the identification of crystal phases of the MRs on an X-ray diffractometer (Smart Lab), equipped with Cu-Kα source (wavelength ~ 1.54 Å). Moreover, the crystallinity nature of the material was investigated with transmission electron microscopy (TEM) (JEOL, JEM-2100F model). The UV-visible absorption spectra were collected between 400 and 700 nm by using JASCO V530 absorption spectrophotometer, whereas the PL emission spectra in solution phase was collected by using Cary Eclipse fluorimeter. The lifetime measurements were performed using time-correlated single-photon counting (TCSPC) setup (Jobin Yvon Horiba (IBH corporation)). The sample was excited at 440 nm, and emission was collected over 530 nm.

2.4. PL imaging and blinking measurements

The spatially resolved PL of MRs were measured with the help of a home-built inverted wide-field epifluorescence microscope [25]. The dilute solution of MRs (~1 mM) in toluene was spin-cast onto a coverslip at 2000 rpm for 1 min, which was excited with a continuous wave 488 nm laser via a 60X objective lens (1.49 NA, 60X, APO-TIRF), and the emitted light was collected with the same objective lens, passed through a dichroic mirror and a 515–570 nm bandpass filter and eventually detected using an air-cooled (−10 °C) sCMOS camera (Hamamatsu Digital Camera, C13440). The intermittency data was collected at 100 Hz. Unless otherwise mentioned, all measurements were performed under ambient conditions (295K with ambient relative humidity (RH) of 55%) with laser power density (measured before objective lens) of 0.7 Wcm⁻². The environment dependent PL imaging was performed using an enclosed chamber with gas inlet and outlets, which was sealed on top of the microscope stage [20]. The sample was kept under a constant flow of respective gases in the dark for 30 min before subsequent measurements on the same MRs.

2.5. Correlation analyses

For the extraction of temporal intensity trajectories of different nano-domains or even of entire MR, ImageJ (NIH) was used. The extent of cross-correlation among different nano-domains was calculated by using Pearson Correlation Coefficients (PCC), a method employed recently to probe spatial synchronicity of blinking [19]. The following expression was used to calculate the PCC among the intensity trajectories using a MATLAB code.

\[
PCC = \frac{N \sum (I(t) \cdot F(t)) - (\Sigma I(t))(\Sigma F(t))}{\sqrt{\left[N \sum (I(t))^2 - (\Sigma I(t))^2\right] \left[N \sum (F(t))^2 - (\Sigma F(t))^2\right]}}
\]
where \( N \) is the total number of frames, \( I_i \) and \( I_j \) are two different data sets, \( I_i(t) \) and \( I_j(t) \) are intensities at time at \( t \)-th frame of the two-intensity trajectory data sets respectively. We constructed a cross-correlation matrix by correlating the intensity trajectories of each pixel with that of every other pixel of a single-pixel line-strip taken along the major axis of MR. The diagonal elements represent the self-correlation, thus, having the highest \( PCC = 1 \). The off-diagonal elements correspond to the inter-pixel correlation along the strip.

3. Results and discussions

3.1. Characterization of MAPbBr\(_3\) crystals

The morphological and optoelectronic characterization of the prepared samples are provided in Fig. 1. A typical SEM image (Fig. 1a) reveals the formation of rigid MAPbBr\(_3\) rods of \( \sim 50-100 \) nm diameters and varying lengths between \( \sim 250 \) nm and few microns. The formation of unbranched rigid rods with sharp edges was further corroborated by TEM measurements (Fig. 1a, inset) and is consistent with prior literature \([24]\). The AFM image of a typical micro-rod (MR) is shown in Fig. 1b, the cross-section topographic analyses of which (insets) reveal uniform heights of \( \sim 40 \) nm across the length a MR; however, the difference in the widths at two locations suggest a few MRs may be associated laterally, the evidence for which is visible in the SEM image. In effect, both electron microscopy and AFM suggest that the MRs are bulk crystalline materials. The high crystalline nature of the MRs is evidenced from XRD measurements (Fig. 1c), which show characteristic diffraction peaks corresponding to perovskite formation with a cubic phase \([24,26,27]\). HR-TEM images (Fig. 1d) further establish the high crystallinity of the MRs, with homogeneous crystal growth which extends at least up to several tens of nanometers. Both XRD and HR-TEM images, reveal a lattice parameter of 5.94 Å, in accordance with the existing literature for organolead halide perovskites \([24]\). The AFM image of a typical micro-rod (MR) is shown in Fig. 1b, the cross-section topographic analyses of which (insets) reveal uniform heights of \( \sim 40 \) nm across the length a MR; however, the difference in the widths at two locations suggest a few MRs may be associated laterally, the evidence for which is visible in the SEM image. In effect, both electron microscopy and AFM suggest that the MRs are bulk crystalline materials. The high crystalline nature of the MRs is evidenced from XRD measurements (Fig. 1c), which show characteristic diffraction peaks corresponding to perovskite formation with a cubic phase \([24,26,27]\). HR-TEM images (Fig. 1d) further establish the high crystallinity of the MRs, with homogeneous crystal growth which extends at least up to several tens of nanometers. Both XRD and HR-TEM images, reveal a lattice parameter of 5.94 Å, in accordance with the existing literature for organolead halide perovskites \([24]\). Moreover, the X-Ray, as well as electron diffraction patterns, are suggestive of the formation of high-quality single-crystals \([24]\), similar to that reported for other organolead halide perovskites \([26]\).

The absorption and PL spectrum (Fig. 1e) of the MRs in toluene solution shows a clear excitonic absorption feature at \( \sim 525 \) nm (2.36 eV) and a nominal stoke shifted intense PL emission spectrum centered at 532 nm (2.33 eV) with a line width of 97 meV. Similar results have also been reported for other bulk structures of MAPbBr\(_3\) \([19,29]\), which suggest that excitons/carriers are not quantum-confined in any dimension, as expected of their morphology. We then probed the carrier recombination dynamics using TCSPC, which exhibit a multi-exponential decay (Fig. 1f). The time-resolved PL decay could be re-convoluted with a tri-exponential function with lifetime components of 12.85 ns (64.87%), 63.30 ns (29.56%), and 325.65 ns (5.55%). We find that the average radiative lifetime \( (\tau_{avg}) \) to be \( \sim 45 \) ns, slightly less than that reported for MAPbI\(_3\) MRs of similar morphology \([18]\). While we find that the majority of carriers recombine within few tens of nanoseconds, it is important to mention that radiative recombination processes can continue even after several hundred nanoseconds following photoexcitation, which will be relevant to explain possible reasons for the intermittency of the MAPbBr\(_3\) MRs.

3.2. Blinking and flickering of MAPbBr\(_3\) MRs

To probe the PL intermittency behaviors of individual MRs, a dilute solution was spin-cast onto glass coverslips which allowed for imaging spatially segregated MRs under ambient conditions (295 K, RH \( \sim 55\% \)) using a wide-field laser epifluorescence setup. Immediately following the identification of an isolated MR, we collected PL intensity movies at 100 Hz using a laser (488 nm) at low excitation power density of 0.7 Wcm\(^{-2}\) to minimize adverse photo-induced effects (photo-curing or degradation) commonly observed in hybrid halide perovskites \([22]\). Fig. 2a and b (left panels) show the PL intensity images of two typical MRs of \( \sim 1 \) μm (MR-1) and \( \sim 2 \) μm (MR-2) in length. The intensity line profiles (Fig. 2a and b) of both these MRs show that the emission is diffusion-limited (\( \sim 210 \) nm) along the minor axis, as expected for...
lateral dimensions being less than 200 nm, while there is a gradation of PL intensity along the major axis of each MR.

We have imaged and studied several tens of isolated MAPbBr$_3$ MRs of lengths between 0.5 and 2.5 $\mu$m all of which were found to undergo PL instability with acquisition time. Here we present the intermittency data and thorough analysis for two representative MRs of two different lengths (Fig. 2a and b), the dynamic behaviors of which are analogous to that for other MRs. Fig. 2c and d show sequential time-lapse snapshot images of MR-1 and MR-2, which represent the intermittency features typically observed for MRs of comparable dimensions. It is interesting to note that the spatial PL intensity gradient (along the major axis) is not uniform over time, and while entire MRs undergo intermittency, fluctuations do not originate from localized domains within each individual MR (vide infra). Further, each isolated MR in a movie exhibits PL intensity fluctuations in an independent and stochastic fashion, ruling out the possibility of external factors such as excitation power fluctuations or focus drifts as the cause of intermittency. It is worth mentioning that barring the emission intensity, the PL emission spectral profiles of all MRs remain unaffected throughout the course of measurements (data not shown), implying spectral diffusion is also not responsible for the observed PL intermittency.

The spatially integrated PL intensity trajectories of entire MR-1 and MR-2 collected over the first 1 min is shown in Fig. 2e and f, respectively. While intermittency is always found to occur on top of a base intensity (i.e., never non-emissive) for all MRs of comparable dimensions (0.5–2.5 $\mu$m), we generally find two contrasting behaviors in terms of intensity fluctuations. The nature of intermittency exhibited by MR-1 is typical of one of the situations, being mostly in a highly emissive (bright or on) state with intermittent (and infrequent) abrupt transitions to a lower emissive state which lasts for relatively short-time durations (categorized as "blinking"). The alternate behavior is similar to that observed for MR-2, where intensity fluctuations occur over several seemingly random shades of grey levels, with no well-defined bright or dark state (categorized as "flickering"). While the former (blinking) pattern has been recently reported for MAPbI$_3$ MRs of similar dimensions [17,18], the latter (flickering) is reminiscent of PL fluctuations in micron-sized MAPbBr$_3$ polycrystalline discs [19]. It should be further noted that "blinking" and "flickering" are not necessarily specific to the length of the MRs (up to ~ 2.5 $\mu$m), i.e., we find either of the behaviors to be dominant in MRs of different lengths.

Careful inspection of the PL intensity traces, exemplified using temporal blow-up of 10 and 1 s durations (Fig. 2e and f, middle and bottom panels), reveal the existence of at least four distinct intensity levels for both MR-1 and MR-2 (shown using horizontal dashed lines). Although the typical dwell-times for these various intensity levels typically lie between few tens to hundreds of milliseconds, the number

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Fig. 2. PL blinking of MAPbBr$_3$ MRs: False colour average PL images and intensity profiles of two MAPbBr$_3$ rods MR-1 (a) and MR-2 (b) with lengths ~1 and ~2 $\mu$m, respectively. The FWHM of radial line profiles of MR-1 are FWHM$_1$ = 220.63 nm and FWHM$_2$ = 213.20 nm whereas for MR-2, the FWHMs are FWHM$_1$ = 226.81 nm and FWHM$_2$ = 213.48 nm. The time lapse sequential PL image snapshots of MR-1 (c) and MR-2 (d) and their corresponding intensity-time trajectories (e and f) using the PL emission of entire MRs. The horizontal dotted lines represent the different intensity levels for multi-state PL intermittency. Some gradual and abrupt intensity jumps between these levels are marked using dashed ovals. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
of grey states between which intensity jumps occur for a single MR is found to vary over different time-windows in entire trajectories of each MR. Intriguingly, for all the MRs, we observe two distinct temporal characteristics of intermittency even within a single trace (see marked ovals in the bottom panel, Fig. 2e and f). The intensity jump from one grey/bright/dim level to another most often occurs over a few tens of milliseconds, while abrupt (~10 ms) fluctuations in PL are relatively less frequent. It is important to emphasize that none of these above characteristics are analogous to conventional two-state (telegraphic noise) quantum-jump like intermittency typically exhibited by single-emitters [3,30,31], and therefore suggests a very different origin than that for quantum-confined semiconductor nanocrystals.

Another intriguing feature worth mentioning is that, apart from high frequency (50–100 Hz) PL intermittency over few tens of milliseconds, we always find a lower frequency (~0.1–1 Hz) intensity modulation over the entire trajectories, the timescales of which strongly depend on the MR being investigated. For instance, MR-1 remains in a reasonably stable bright state over tens of seconds, while MR-2 undergoes more frequent gradual oscillations over seconds timescale. While the origins of such fluctuations remain unclear, this gradual intensity variations may arise from a combination of photo-induced curing and degradation processes known to occur in hybrid perovskites [22]. Due to the presence of such low-frequency modulations and large variation in the amplitudes of fluctuations over various MRs, the quantification of

Fig. 3. Spatially synchronous blinking of entire MR-1. (a) PL intensity image of MR-1. (b) Normalized intensity-time traces of three different nano-domains (I-III), marked in (a), along with the average intensity trajectory of entire MR-1, which shows near identical blinking patterns. (c) Spatially-resolved time trajectory (kymogram) of MR-1 over the course of 100 s depicting the synchronicity of blinking of the entire rod. The x- and y-axes labels represent the time difference and the starting time of the corresponding row, respectively. The width of each row bound within the white lines is the same as the length of the rod, marked with a dotted white rectangle in (a). (d) PL intensities of II and III against I for each frame and corresponding PCC. (e) Correlation coefficient matrix for each pair of pixels, along the strip represented by a dotted rectangle in (a). The decay of correlation coefficients along the dotted green and blue lines is shown in the inset of (e). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
timescales of transitions during blinking or flickering processes is not straightforward; however, an intuitive understanding of intermittency behaviors could be obtained by inspecting each PL trajectory in detail.

3.3. Spatial synchronicity in PL intermittency

Intriguingly, entire individual MRs undergo spatially homogeneous PL intermittency, as demonstrated in Fig. 3 (for MR-1) and Fig. 4 (for MR-2) (also see Movies M1 and M2, supporting information). To probe the spatial dependence of blinking, we plotted the PL intensity traces from three different locations of MR-1 (Fig. 3a) as well as MR-2 (Fig. 4a). We first focus on the spatial dependence of blinking in MR-1, the average intensity trajectory of which is plotted in Fig. 3b, along with spatially-resolved intensity traces (designated I, II, and III). We find that the normalized PL trajectories from I, II, and III are nearly indistinguishable; every blinking event of these three locations as well as for the entire MR-1 is almost exactly temporally superimposable. For the entire trajectory duration, even small fluctuations in these local domains and the entire MR are found to occur simultaneously; however, there are minute differences in the amplitudes of intensity fluctuations. To verify whether blinking is indeed spatiotemporally correlated over the entire MR, we plot the intensity profile along the major axis of MR-1 as sequential image strips over the entire 100s (Fig. 3c). This spatiotemporally resolved PL intensity image (Kymogram) conveys that the entire MR-1 undergoes spatially synchronous PL intermittency. Similar behaviour is observed for MR-2 for even larger spatial distance; however, the occurrences of large amplitude abrupt intensity fluctuations (as seen in MR-1) are relatively less frequent.

To quantify the extent of spatial correlation in blinking, we evaluated the Pearson Cross-correlation Coefficient (PCC) between the intensity time-series for the three spatial locations within MR-1 (I, II, and III).

Fig. 3d shows the scatter plot of the emission intensities for 10,000 data points, which reveal an extremely high value of PCC \( (r_{1-II} = 0.984; r_{1-III} = 0.945) \), and thus, indicates spatiotemporally synchronous intensity fluctuations (blinking) for these three distal locations (≥500nm apart). Such correlation analysis performed on most other MRs (including MR-2) yielded very similar results, however the PCC values were slightly lower over longer distance (vide infra). It is interesting to note that \( r_{1-II} \) (as well as \( r_{2-III} = 0.976 \)) is slightly higher than that for \( r_{1-III} \), which prompted us to probe the spatial variation (distance dependence) of correlated blinking propensity in the MRs. Hence, we evaluated the PCC for the time-series of each pair of pixels along the major axis of MRs. Fig. 3e depicts the correlation-coefficient matrix \( (r_{ij}) \) for MR-1, considering a single-pixel wide and 18 pixel (1.2 μm) long strip along the rod (Fig. 3a, dashed rectangle). The off-diagonal elements in \( r_{ij} \) (Fig. 3e) represent the spatial correlation of blinking \( r_{ij} \) between \( i^{th} \) and \( j^{th} \) pixels. We find extremely high values of \( r_{ij} \) (~0.95), and further, the correlation for domains I and II is slightly lower (~0.85) than for an equivalent distance between II and III (0.95), and further, the correlation for domains I and III (~2 μm apart) falls off to ~0.7. To quantify the extent of spatial-correlation in flickering, we performed PCC analyses over the entire length of MR-2,
the intermittency correlation matrix \( (I_{ij}) \) for which is shown in Fig. 4c. While we do observe that the values of \( n \) are remarkably high (mean \( \sim 0.9 \)) at short distances, the spatial dependence of the PCC (Fig. 4c, inset) exhibits a gradual decay to \( \sim 0.7 \) beyond \( \sim 1 \) \( \mu \)m, suggesting a progressive weakening of the extent of long-range spatio-temporal correlation in intermittency. A closer inspection of the intensity trajectories (Fig. 4b) reveals that nearly all the flickering events occur in a concerted manner over these three locations of MR-2, however, there are prominent differences in the corresponding amplitudes of fluctuations at certain instances. Several such time-points are indicated in Fig. 4b (arrowheads), where such stark and systematic variations of flickering amplitudes is possible. Could such a heterogeneity in the flickering amplitudes be the cause for the weaker spatial correlation in flickering at longer distances in MR-2?

In order to better visualize these events and identify systematic trends, if any, we constructed and subsequently inspected the spatially-resolved time evolution of the absolute intensities along the entire length of MR-2. Representative such kymograms at different time-windows (Fig. 4d) reveal several features different from that for MR-1, which are obscured in the normalized intensity trajectories (Fig. 4b). For instance, here we notice that the intensity gradient along MR-2 is more pronounced compared to MR-1, for the majority of the time-course. Barren lesser occurrence of synchronous high frequency (50–100 Hz) intensity fluctuations (Fig. 2), the most prominent difference is that, lower frequency intensity jumps (over a few tens of ms) from a bright to a dim level (or vice versa) does not always occur at the exactly same instance across the entire length of MR-2. These features, i.e., spatially modulated intensity changes with time, are often visible in the kymograms (dashed rectangles, Fig. 4e). In fact, we find that there is a significant temporal variation of such intensity gradients along the length of MR-2, the extent of which is also non-uniform over different time windows. This suggests that the relative emission intensity over different spatial locations in a MR gets altered with time; however, there is a clear gradient over space rather than emission (or intermittency) being spatially heterogeneous. As we do not observe such behaviors at relatively smaller distances, it is reasonable to conclude that the lowering of the blinking PCC at distances beyond \( \sim 1 \) \( \mu \)m is essentially a consequence of temporally varying intensity gradient along the MRs.

3.4. Origins of PL intermittency of entire crystals

What are the possible reasons for spatially-correlated PL intermittency over such large distances in a bulk crystalline object? In recent literature, there are a few reports of a similar phenomenon, which include both rods and disks of MA lead halide perovskites [17–19]; however, there is no full-proof explanation of why this is observed. It is important to emphasize that without invoking the formation of transient traps with very high efficiency to deactivate carriers non-radiatively (quencher), PL intermittency in these systems cannot be explained. There have been several propositions on the nature and origin of such traps, which can, in effect quench a very large density of photo excited carriers before getting saturated. For instance, it has been suggested that the transient quenchers can be some sort of “super-traps” which are donor-acceptor pairs [17], and further, such ions/charged species can be highly mobile within OHP crystals leading to partial quenching of entire crystals [22]. In addition, the short-lived NR traps can be induced by excitation light and via adsorption-desorption of atmospheric constituents [20,32]. Besides, light soaking can lead to both photo-curing and photo-degradation, which can significantly alter the photo-physical properties of hybrid perovskites [33,34]. To understand how transient NR traps/quenchers may be generated, we first performed the excitation power dependence of PL intermittency characteristics of entire individual MAPbBr\(_3\) MRs under ambient conditions. To minimize the photo-degradation, measurements were performed on MAPbBr\(_3\) rods by sequentially increasing excitation powers, the data for one of which (MR-3) is shown in Fig. 5a. At low excitation powers (\( \sim 0.3 \) Wcm\(^{-2}\)), MR-3 has few large-amplitude abrupt PL fluctuations typical of blinking; however, with the increase in the power density leads to the reduction of such sudden intensity jumps with concomitant increase multi-frame lower frequency fluctuations. At \( \sim 9.5 \) Wcm\(^{-2}\), we find that intermittency of MR-3 effectively transforms into flickering type (dominant) with a few sporadic blinking events (Fig. 5a). These observations are qualitatively similar to most other MAPbBr\(_3\) MRs that we studied, which reveal that the occurrences, amplitudes and nature of the intermittency of individual MRs are indeed affected by photon irradiation density. As flickering behaviors likely owes to a relatively higher density of NR traps, our results suggest that a photo-induced process is responsible, albeit partially, for the formation/annihilation of non-radiative transient quenchers. In essence, it is more likely to observe flickering behaviors at higher excitation powers.

Further, to probe the environmental effects on the PL blinking and flickering, we investigated individual MRs under ambient conditions (air, RH \( \sim 55\%) \) and subsequently, the intermittency characteristics of the same crystals under oxygen and nitrogen environments. The effect of different atmospheric constituents on the PL intermittency of a single MR (MR-4) is depicted in Fig. 5b, where a rather dramatic yet reversible change of temporal fluctuations in the emissivity is observed. We find that MR-4 exhibits abrupt multi-state intermittency (flickering) propensity under ambient conditions; however, in oxygen environment, gradual low-frequency oscillations (flickering) becomes predominant with intermittent blinking events with short “off-/dim-time” durations. In the presence of light, oxygen is not only known to form NR defects in perovskites [35,36], but also can passivate certain defects leading to photo brightening [16,37,38]. It is therefore likely that, the change in intermittency behaviors (from ambiance to oxygen) owes to the interplay between both these effects. In stark contrast, however, MR-4’s emissivity is reduced dramatically in a nitrogen atmosphere, and abrupt blinking events with very short “on-/bright-time” durations become prevalent. The dominance of low-intensity levels in nitrogen atmosphere points to the enhancement of non-radiative recombination processes, likely due to the higher density of certain NR quenchers, or the reactivation of non-emissive sites upon the removal of oxygen. It is important to further note that upon re-introduction of MR-4 to oxygen environments, the intermittency characteristics is completely reversed (Fig. 5b). Therefore, our results suggest the possibility of two different types of transient quenchers formed under ambient conditions, wherein moisture can also play a role in their creation or annihilation.

It is intriguing that PL intermittency, which is a relatively slow process spanning over millisecond-second timescales, is spatially correlated over extremely long distances (microns) [18,19]. In order for this to occur, the photo-generated carriers at distal locations of a single micron-sized perovskite must recombine with the same efficiency at each instance. This essentially implies that a communication channel needs to be active between a large population of carrier photo-generated simultaneously. It is possible that like metals, electrons, and holes are basically delocalized over the entire crystal, which can lead to efficient correlation and communication between them. Alternatively, owing to the extremely high (\( \sim 10^7 \) mm\(^2\) S\(^{-1}\)) [28] carrier diffusivity as well as long carrier recombination lifetimes (Fig. 1e), which effectively leads to diffusion lengths of several microns, a considerable fraction of photo-generated electrons and holes can efficiently encompass the entire crystal in timescales less than microseconds. Therefore, if a NR quencher is created for time durations of more than milliseconds, it can funnel a large number of carriers from over the entire crystal leading to PL intermittency.

Our measurement have revealed that for any MR, PL intermittency between bright and dim levels can either occur within 10 ms (blinking) or it may take several tens of milliseconds (flickering). We propose, based on our environmental and excitation power dependence measurements (Fig. 5), that there are likely to be at least two distinct types of transient quenchers that can be formed in the crystal, under ambient conditions and in the presence of light. One of these category of
quenchers act as highly efficient yet unstable NR traps, although their density is low, leading to abrupt intermittency (blinking) events of entire crystals. Another type of transient NR trap(s), which have higher number density, serves as a relatively less efficient quencher, which produces low-amplitude and low-frequency intensity fluctuations (flickering) of entire MAPbBr$_3$ MRs. It is important to note that blinking is observed under all measurement conditions, while flickering is highly dependent on the ambient conditions. This indicates that abrupt blinking of a crystal likely involves photoinduced NR traps, while transient NR quenchers generated by adsorption of atmospheric constituents predominantly lead to the flickering phenomenon. However, further experiments need to be performed to not only understand the exact nature of these transient NR quenchers, but also elucidate on the exact mechanism via which entire MRs undergo synchronous intermittency.

4. Conclusions

We have presented observations on spatially synchronous PL intermittency of entire micron-size crystalline rods of a hybrid perovskite, which is intriguing because of the absence of any dimensional confinement of photogenerated carriers in these systems. While similar findings at slower time scales have been reported recently for other hybrid halides, we provide a detailed correlation analysis of the extent of spatial synchronicity over entire single-crystals, hitherto not performed earlier. Moreover, our measurements and analyses reveal the existence of distinct categories of PL intermittency, namely, abrupt “blinking” and relatively gradual “flickering” events, one which dominates in each crystal irrespective of its size. We show that the spatial correlation of PL intermittency varies between the two processes, especially at longer distances (beyond \( \sim 1 \mu m \)). The base background intensity on top of which both blinking and flickering events occur can be explained by fast (within \( \sim 50 \) ns) radiative recombination dynamics in local regions. Based on long carrier diffusion lengths (\( \sim \mu m \)) and high diffusivities reported for hybrid lead halide perovskites, we propose that collective carrier migration to a few non-radiative traps dispersed within the crystal is responsible for spatially homogenous synchronous intermittency. Photoexcitation power dependence of PL-intermittency and measurements performed on individual MRs under controlled environmental conditions further suggest the existence of two distinct transient NR traps with different origins and diverse quenching efficiency, leading to blinking and flickering phenomenon of MAPbBr$_3$ crystals.

Declaration of competing interest

The authors declare no conflict of interest.

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