

# Lack of Photon Antibunching Supports Supertrap Model of Photoluminescence Blinking in Perovskite Sub-Micrometer Crystals

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Antibunching effect is typically observed in individual systems possessing photoluminescence (PL) blinking and vice versa. Contrary to this common perception, absence of antibunching in strongly blinking methyl ammonium led tri-iodide (MAPbI<sub>3</sub>) perovskite crystals of sizes from tens to hundreds of nanometers regardless of the excitation power density is observed. Antibunching effect does not appear even when photon statistics are analyzed for bright and intermediate PL intensity levels independently. This shows that there is no directional energy funneling and accumulation of charge carriers in the small local regions in MAPbI<sub>3</sub> crystals where an Auger recombination can potentially suppress the simultaneous emission of two photons. This result allows for the exclusion of the PL blinking mechanism based on the idea of emitting sites previously hypothesized for perovskites. Therefore, the model of PL blinking in perovskite crystals based on the presence of a metastable non-radiative recombination center (the supertrap) is the only one proposed so far which explains blinking without conflicting with the absence of photon correlations.

# 1. Introduction

The fascinating phenomenon of luminescence blinking was discovered soon after the single molecule spectroscopy field was started by W.E. Moerner and M. Orrit in the end of 1980s (Nobel Prize in Chemistry in 2014)<sup>[1,2]</sup> It turned out that photoluminescence (PL) of a small object like an individual dye molecule or an artificial atom (a small semiconductor nanocrystal or so-called quantum dot (QD) 1–10 nm in size)

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shows irregular fluctuations looking like a random "telegraph signal."<sup>[3-7]</sup> Commonly accepted blinking mechanisms in a semiconductor QD or a dye molecule assume that a single quantum system (single emitter) is jumping between different configurations having either different PL excitation cross sections or different PL quantum yields (PLOYs) resulting in different PL brightness at a given excitation rate. For example, when a QD becomes charged (one charge is inside the QD while the opposite charge is trapped outside the QD's core), photo excitation leads to formation of a trion state, which has a low radiative yield due to Auger recombination. Therefore, charging/discharging of the OD leads to PL blinking.<sup>[8]</sup> In addition, other mechanisms of PL blinking of QDs related to a fluctuating non-radiative (NR) rate are also possible, see, for

example, the so-called multiple recombination centers (MRC) model and others.  $^{\left[ 9-12\right] }$ 

However, PL blinking is not an exclusive property of a single quantum system. It was observed in large, definitely multichromophoric ensembles like  $\pi$ -conjugated polymers,<sup>[13,14]</sup> lightharvesting complexes,<sup>[15]</sup> molecular J-aggregates,<sup>[16]</sup> large organic nanoparticles,<sup>[17,18]</sup> and ensembles of germanium vacancy color centers in diamond microcrystals.<sup>[19]</sup>

For explanation of PL blinking in extended systems energy migration (exciton or charge diffusion) over the whole system volume is absolutely essential.<sup>[13]</sup> There are two accepted mechanisms: i) Emitting site mechanism postulates that excitons funnel to just one or a very small number of low energy chromophores.<sup>[20]</sup> These chromophores are essentially single emitters (working as emitting sites) and they can be easily quenched by a nearby switchable quencher or by switching themselves to a dark state in the same way as a single dye molecule or a QD; ii) Trapping mechanism assumes that the emission of the whole system can be quenched by a metastable quencher which can be reached by excitations because of their efficient diffusion over the whole volume of the system. Appearing/ disappearing of a quencher (a metastable NR center or a supertrap<sup>[21]</sup> as we will call it below) at any spatial location can drastically change PL intensity causing PL blinking.<sup>[13]</sup> Emission can occur from any spatial location in the system www.advancedsciencenews.com



**Figure 1.** Schematic illustration of the two models of PL blinking of perovskite crystals. a,b) Emitting site model. Blinking is originated from reversible quenching of the emitting site. (a) Bright PL state: a substantial part of the total PL comes from a QD-like emitting site due to the radiative recombination of the electrons and holes funneled to it. (b) The emitting site is quenched and works as a non-radiative recombination center. It leads to the dim PL state where PL originates only from charge recombination in the bulk. c,d) Trapping or Supertrap model. Blinking occurs due to reversible switching of an efficient non-radiative (NR) center (supertrap) from an active to a passive state. The NR center in its active state has a large charge capturing cross section and gives fast NR recombination. (c) NR-center is passive and bright PL is observed. (d) NR center is active. Due to the efficient diffusion of charge carriers it quenches PL in a substantial part of the crystal leading to the dim PL state. The picture illustrates diffusion limited quenching.

and energy funnels to the quencher only when the quencher is active. This is contrary to the emitting site mechanism where energy always funnels to the special site regardless whether it is luminescent or quenched. The emitting site and trapping mechanisms are illustrated in **Figure 1**.

Recently, a class of low-temperature solution-processed semiconductors, metal halide perovskites (MHP),<sup>[22,23]</sup> gained enormous attention due their high performance in photovoltaics and optoelectronics.<sup>[24]</sup> The success of MHPs is based on high absorption coefficient and a benign character of the majority of the defect states, which are shallow electron or hole traps.<sup>[25]</sup> MHPs are often referred to as defect tolerant semiconductors where the presence of high concentration of defects does not really eliminate radiative recombination completely.<sup>[26,25]</sup> Nevertheless, NR charge recombination is still the dominant processes at low excitation conditions.

Methyl ammonium led tri-iodide (MAPbI<sub>3</sub>) and other MHPs show a pronounced photoluminescence blinking effect. Moreover, PL blinking is inherent not only to MHPs colloidal QDs (which was expected),<sup>[27]</sup> but also to sub-micrometer crystals,<sup>[28,29]</sup> local regions of thin films,<sup>[30]</sup> and even micrometersized crystals.<sup>[21,31]</sup> Because the crystals are so large, adding one more charge does not lead to Auger recombination (contrary to QDs) and therefore, Auger recombination cannot be the reason of PL blinking.<sup>[21]</sup> To account for PL blinking in large MHP individual crystals the same mechanisms as discussed above for extended multi-chromophoric systems were proposed (Figure 1): emitting site mechanism and trapping mechanism (where the metastable quencher is the supertrap<sup>[21]</sup>).<sup>[28]</sup>

Although the supertrap model is widely used in the literature and seems to work for MHPs, strictly speaking its validity has not been proven yet. The assignments of the switching processes to ion migration due to the temperature,<sup>[32]</sup> environmental<sup>[33–35]</sup> and electric field<sup>[36]</sup> dependences of the blinking phenomenon can work not only for the supertrap but also for the activation of NR recombination in the emitting site. How to make a choice between the two mechanisms? Blinking itself obviously cannot tell the difference. Also, correlation between PL lifetime and PL intensity can be similar for these two cases (see Section 3). The difference is in the presence or absence of local emitting sites, which are essentially single emitters. Light coming from a single emitting site must obey the sub-Poisson photon statistics and possess so-called photon antibunching effect. Obviously, photon-correlation experiments can be used to support or reject one of the blinking mechanisms.

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Luminescence photon antibunching is a phenomenon discovered in luminescence of single quantum systems (individual atoms,<sup>[37]</sup> dye molecules,<sup>[38,39]</sup> and QDs of many semiconductors including perovskites<sup>[27,40–42]</sup>) and in extended systems like clusters of QDs,<sup>[43]</sup> light-harvesting complexes,<sup>[44]</sup> and single conjugated polymer molecules.<sup>[45,46]</sup> Antibunching implies that two or more photons cannot be emitted at the same time. In all noted extended systems, the reason for antibunching is the funneling of excitations to a small volume of which size is smaller than the characteristic radius of a process preventing radiative decay of two excitations at the same time. For inorganic semiconductors, this process is Auger recombination, for organic systems it is exciton–exciton annihilation with typical interaction radii up to 10 nm.

To the best of our knowledge, there are only very few publications discussing photon-correlation experiments on sub-micrometer sized crystals of MHPs. In the work by Wen et al.<sup>[47]</sup> it was briefly mentioned that a photon antibunching effect was present neither in the PL of individual crystals (which also showed no ADVANCED SCIENCE NEWS \_\_\_\_\_



**Figure 2.** A sub-micrometre MAPbI<sub>3</sub> crystal (crystal #1), its photoluminescence transients and the second order cross-correlation functions  $g_{norm}^{(2)}(t)$ : a) PL image of the sample area with crystal #1 marked, scale bar is 2 µm. b) The AFM profile of the crystal #1 covered by a PMMA film. The size of crystal #1 was estimated to be 70 (height) × 210 × 115 nm, see SI. c) PL transients obtained at different excitation power densities (c1 – 0.9; c2 – 0.09 and c3 – 0.009 W cm<sup>-2</sup>). d)  $g_{norm}^{(2)}(t)$  calculated for the corresponding PL transients shown in (c).  $g_{norm}^{(2)}(0) = 1$  for all excitation powers (no photon antibunching).

PL blinking) nor in PL of local areas of perovskite films (which actually showed some PL blinking). The second work we know is Tong et al.<sup>[48]</sup> where micrometers long but very thin (12 nm) nanowires of CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> showed no blinking and no antibunching until they were chemically cut into much smaller nanorods which readily showed both phenomena.

In this work we present a detailed and careful check for the presence of the photon antibunching effect in  $MAPbI_3$ perovskite crystals with sizes big enough (tens to hundreds of nanometers) to ignore quantum confinement and Auger recombination at the moderate excitation conditions. We will use the obtained results for selecting one of the PL blinking models proposed for these materials.

#### 2. Experimental Results

We prepared  $MAPbI_3$  sub-micrometer crystals (Figure 2a,b) using the diluted precursor solution method. The crystals

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were covered by a thin layer of PMMA to increase their photostability (see Supporting Information). For each individual sub-micrometer crystal we measured AFM surface profile, PL spectrum, PL decay, PL transient, and the second order crosscorrelation function  $g^{(2)}(t)$  (see Figure 2c,d and also Supporting Information). The PL spectra were found to be typical for bulk MAPbI<sub>3</sub> as expected for sub-micrometer crystals of sizes exceeding tens of nanometers (Figure S1, Supporting Information). Also, a pronounced PL blinking (Figure 2c) was observed in accordance with the previous studies.<sup>[28]</sup> A PL lifetime analysis showed a correlation between PL intensity and the average PL lifetime<sup>[21]</sup> (see examples Figure S3f,g, S7c,d, and S9c,d, Supporting Information). The PL spectra of individual MAPbI<sub>3</sub> crystals in their bright and dim states were the same within the limit of our accuracy (Figure S1, Supporting Information). Note that inhomogeneity of PL spectrum of MAPbI<sub>3</sub> at room temperature was reported in some publications and was associated with a radiative recombination of shallowly trapped charges.<sup>[49]</sup> We did not observe this effect in our samples or at least the contribution of this emission (if it existed in our samples at all) did not change during the PL intensity fluctuations.

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We utilized the Hanbury-Brown and Twiss (HBT) scheme with two signal channels to measure the second-order photon cross-correlation function  $g^{(2)}(t)$  of PL of individual MAPbI<sub>3</sub> crystals. In the case of pulse excitation, when the time T between the two laser pulses is larger than PL decay time,  $g^{(2)}(t)$ looks like a periodical peak-like function with the period T (Figure 2d). The central peak in this function (near zero delay,  $g^{(2)}(0)$  is proportional to the probability to detect more than one PL photon per one laser pulse exciting the individual crystal. The side peaks give information about the probability for two detected PL photons to originate from two different laser pulses. It is convenient to represent such a function in a normalized form:  $g_{\text{norm}}^{(2)}(t) = g^{(2)}(t)/g^{(2)}(T)$ . Thus,  $g_{\text{norm}}^{(2)}(0)$  is the ratio between the central peak and the first side peak which gives a simple and the most indicative and widely used parameter to characterize photon statistics of the emitter.  $g_{norm}^2(0) = 0$  for an ideal single emitter (sub-Poisson statistics) and  $g_{norm}^2(0) = 1$  for an emitter with Poisson photon statistics.

 $g_{norm}^{(2)}(t)$  was measured for 15 MAPbI<sub>3</sub> crystals of different sizes and blinking dynamics under varied excitation power density. Figure 2d shows  $g_{norm}^{(2)}(t)$  for crystal #1 calculated from the data obtained in the experiment shown in Figure 2c. The differences between the zero and the side band peak amplitudes in  $g_{norm}^{(2)}(t)$  were smaller than the statistical error for all excitation powers (Figure 2d, see also Supporting Information). For the smallest excitation power, we had to compare the peak integral counts instead of the amplitudes, as the latter were subjected to larger fluctuations due to a small statistics. Thus, regardless of the excitation power density used, the integrated PL did not show antibunching effect within the accuracy of the measurements.

We used three excitation power density values: 0.009, 0.09, and 0.9 W cm<sup>-2</sup> at 1 MHz repetition rate. These values correspond to the charge carrier concentrations of the order of 10<sup>15</sup>, 10<sup>16</sup>, and 10<sup>17</sup> cm<sup>3</sup> respectively. These numbers roughly translate to 2.5, 25, and 250 photoexcited electron-hole pairs per laser excitation pulse for crystal #1 which was approximately 210 nm  $\times$  115 nm  $\times$  80 nm in size, see Supporting Information for details. We observed a 10 times increase of PLOY upon increasing the excitation power over this range (100 times increase) which agrees with the square root dependence of PLQY on excitation power in the case of photodoping.<sup>[50-52]</sup> A PLOY increase is accompanied with an acceleration of the PL decay (see Section 9 in Supporting Information) which is usually explained by a non-linear dependence of the radiative recombination rate of free charges on their concentration, however, an accurate quantitative explanation of this effect in MAPbI<sub>3</sub> is still missing.<sup>[52]</sup> Increasing PLQY also means that our measurements were carried out under conditions when NR Auger recombination was not dominant as is also expected from low photogenerated charge concentrations, which in our experiments were from 10 to 1000 times lower than needed for an efficient Auger recombination to occur.[50,53,54]

We also studied  $g^{(2)}$  functions for different intensity levels of PL blinking transients by calculating cross-correlation functions for photons which match their corresponding intensity levels. **Figure 3**a shows four examples of  $g_{norm}^{(2)}$  functions calculated for three dim and three bright levels in the PL transient of crystal #1 for 0.9 W cm<sup>-2</sup> excitation power (see more examples for different excitation powers in the Supporting Information). These data also do not show antibunching. Thus, despite our careful and extensive search for the effect among nanocrystals of different sizes, blinking dynamics, blinking amplitudes, and among different PL intensity levels for each crystal, we did



**Figure 3.** a) Normalized second order cross-correlation functions  $g_{norm}^{(2)}(t)$  calculated for different intensity levels (indicated by colour strips) of the PL transient shown in (b). b) The PL transient measured for perovskite crystal #1 at excitation intensity 0.9 W cm<sup>-2</sup> ( $n_{e-h} = 1.5 \times 10^{17}$  cm<sup>-3</sup>). Different intensity levels (indicated by colour strips) correspond to  $g_{norm}^{(2)}(t)$  functions shown in (a).  $g_{norm}^{(2)}(0) = 1$  for all PL transient intensity levels which shows absence of photon antibunching for both dim and bright PL intensity states.

not find any example of the antibunching phenomenon. Can this result be useful for understanding the charge dynamics in MAPbI<sub>3</sub> in the presence of quenchers and rationalizing the origin of PL blinking in perovskite semiconductors?

#### 3. Discussion

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For an ideal single photon source the photon statistics is sub-Poisson with  $g_{norm}^{(2)}(0) = 0$ . This is called photon antibunching, because it is not possible for a true single emitter to emit a "bunch" of photons. Obviously, a two-level system (the simplest model of a chromophore, a single emitter) cannot be double excited and therefore, can emit only one photon at a time. The second most common reason for antibunching is Auger charge recombination. For example, a semiconductor QD, contrary to an ideal two-level system, can absorb two photons, and potentially emit two photons too. However, the double excitation creates an extremely high concentration of the excited electron and holes because the QD is very small. Even for a quite large 10 nm cubic QD this corresponds to an excited state concentration as large as 10<sup>18</sup> cm<sup>-3</sup>. At such concentrations, two charge carriers in the presence of a third one will recombine non-radiatively via Auger recombination. Auger recombination occurs in bulk semiconductors at similar concentrations.<sup>[54]</sup> So, the reason for antibunching in QDs (see an example measured at our setup in Figure S2a, Supporting Information) is the de-activation of the second excitation by Auger recombination.[41]

Sub-micrometer sized MAPbI<sub>3</sub> crystals we study here are not single chromophores in terms of their absorption. Many electron-hole pairs can be created in any part of the crystal at the same time without them "feeling each other" because the crystal size is significantly larger than the delocalization length of the electron wave function. Radiative recombination can happen in any location of the crystal leading to an emission with Poisson statistics. It is because the number of excited electronhole pairs obeys Poisson statistics and there are no restrictions for the emission of two or more photons at the same time. Indeed, Auger recombination does not create an antibunching effect here because: i) Auger recombination does not happen in the bulk of the studied crystal since even the maximum concentration of charge carriers used (1017 cm-3) is still 10 times less than required for the Auger processes to be important. We also directly see that Auger nonradiative losses are not dominant because PLQY increases 10 times upon changing the excitation density from 1015 to 1017 cm-3; ii) Even reaching an excitation density above the Auger threshold will not help. Indeed, for crystal #1 Auger recombination can be important if it contains N > 2000 excited electron-hole pairs. However, even if a half of them will be deactivated by Auger recombination, it will still not make any difference to the Poisson photon statistics determined by the other half of the excitations. The same situation is with PL blinking. Auger recombination cannot lead to a substantial abrupt PL quenching upon adding/removing one charge (charging of the crystal) because to reach the conditions for Auger losses one needs the number of charge carriers N >> 1, so, plus or minus one charge does not really influence PL intensity much. Thus, neither antibunching nor blinking can occur in large MAPbI<sub>3</sub> crystals via the Auger mechanism.

The only way to create conditions when emission of two photons is suppressed via the Auger process is to "force" the charge carriers somehow to be collected in a small volume inside the large crystal. This is exactly the idea of an emitting site which has been also proposed to explain both antibunching and PL blinking in extended systems (the emitting site model, see Section 1).

The emitting site model (Figure 1a,b) implies that PL blinking is the result of the existence of one or a small number of local regions, which can effectively capture charge carriers and where they recombine radiatively (Figure 1a). Let us consider the simplest case of only one emitting site for simplicity. Transformation of the emitting site to a nonradiative recombination center (Figure 1b) leads to an abrupt drop of PL intensity and a decrease of PL lifetime, because of the enhancement of the total charge recombination rate. Reversibility of this process results in PL blinking with two intensity levels and correlated changes in PL lifetime (as was found experimentally). Realization of the emitting site mechanism for a semiconductor is illustrated in Figure 1a,b. Charge carriers can radiatively recombine in the crystal bulk and in the local emitting site. The latter can be seen as a QD imbedded into the bulk semiconductor of a slightly larger bandgap. Thus, the emitting site is excited via charge or energy transfer from the bulk, which works as a light-harvesting antenna. Let us compare a bulk crystal with the hypothetical emitting site and a QD. If the excitation conditions are such that the emitting site is not saturated, the expected emission count rate for both systems should be proportional to their absorption cross section (or, more precisely, PL excitation cross section). Since the absorption cross section of the crystal is several orders of magnitude larger than of the QD, a proportionally larger count rate is expected from the emitting site. On the other hand, to obtain a similar count rate from the QD and the emitting site in the bulk crystal, a proportionally larger excitation power density should be used to excite the single QD. Figure S2, Supporting Information, shows similar counts rates from a MAPbI3 crystal and a QD measured at 400 times different excitation power densities. Like a QD, the emitting site cannot emit two photons at the same time, because as soon as three or more charge carriers meet there, Auger recombination occurs (see Figure 4a). Therefore, the emission from the emitting site should exhibit photon antibunching. Note however, the emitting site is still able to emit several photons "one by one" per excitation pulse and even exceed the PL count rate from the bulk recombination, while keeping photon antibunching. It is possible in the case of fast radiative recombination rate (≈20 ns like observed in QDs) compared to bulk charge recombination (≈100 ns) and efficient charge transfer from the bulk "reservoir" (which still does not saturate the emitting site). Such an excitation regime for the hypothetical emission site is something between the pulse and CW excitation regimes and it does not contradict to the experimentally observed PL transient parameters such as bright/dim PL intensity ratios and absolute count rates, see Figures 2c,5b and others in Supporting Information.

The total emission of a large bulk crystal with an emitting site is the sum of photons which resulted from a radiative recombination of charge carriers in the bulk and photons emitted by the emitting site. These two components must exhibit differing photon statistics properties: Poisson and sub-Poisson







**Figure 4.** Expected photon statistics for PL of a perovskite sub-micron crystal in the framework of the emitting site model. a) Fast Auger processes inside the emitting site prevent simultaneous emission of two or more photons. It leads to photon antibunching for PL arising from the emitting site  $(g^2(0) \text{ is close to zero—sub-Poisson statistics})$ . The rest of PL emission is due to the electron–hole recombination events in the bulk of the crystal. Since the crystal size is much larger than the electron–hole Bohr radius and recombination events occur in different parts of the crystal independently, bulk recombination has no restriction for multiphotonic emission. So, the bulk emission exhibits Poisson statistics (no antibunching,  $g_{norm}^{(2)}(0) = 1$ ). b) PL transient and expected difference in  $g_{norm}^{(2)}(t)$  for the bright and dim states. The total emission for the bright state is a sum of PL photons with sub-Poisson and Poisson statistics. So the bright PL state is expected to show a partial antibunching effect with  $g_{norm}^{(2)}(0) < 1$ . The antibunching dip magnitude depends on the ratio between the bulk and the emitting site PL (see Figure 5).

respectively (Figure 4a). This must lead to a partial antibunching effect for the whole crystal with  $g_{norm}^{(2)}(0)$  depending on the relative intensities of the two contributions as described by Equation S1, Supporting Information; which derivation was inspired by Ref. [55] (**Figure 5**a). In the emitting site model the emitting site can be totally quenched, therefore we should not see antibunching for the low PL intensity level (when an emitting site is quenched, radiative recombination occurs in the bulk of the crystal only) and a partial antibunching for the high PL intensity level according to Figures 4,5a. The expected extent of the antibunching effect for the experimentally observed PL transients (e.g., Figure 5b) should be easily resolved with our accuracy. However, the analysis of the experimental data (e.g., Figure 5c and all others) did not show any evidence of antibunching. It means that our experimental results contradict the emitting site model.

By changing the emitting site to a metastable NR recombination center we convert the emitting site model to the trapping or supertrap model. The crystal is assumed to be uniform in a sense that it does not possess any emitting centers or local energy funnels. So, the radiative recombination can occur anywhere in the bulk (Figure 1c). However, when the NR center (the supertrap) is activated, it collects and recombines non-radiatively a large fraction of charge carriers generated within the diffusion length from the NR center (Figure 1d), which leads to PL intensity and a lifetime correlated decrease observed experimentally (see Supporting Information).<sup>[21]</sup> PL intensity drop is determined by the fraction of







**Figure 5.** a) Expected dependence of  $g_{norm}^{(2)}(0)$  for a hypothetical mixed emitter consisted of a single photon source (sub-Poisson statistics) and an emitter exhibiting Poisson statistics (e.g. charge recombination in the crystal bulk), calculated using Equation S1. The green rectangular shows the  $g_{norm}^{(2)}(0)$  expected for the bright intensity level of the crystal which PL transient is shown in (b) if the blinking of this crystal occurred according to the emitting site model. The blue circle marks the value of  $g_{norm}^{(2)}(0)$  expected for the PL transients shown in Figure 2 (c2, c3) if the emitting site model was valid. b) PL transient with a large blinking amplitude obtained for MAPbI<sub>3</sub> single crystal #2 at excitation power 0.1 W cm<sup>-2</sup>. c)  $g_{norm}^{(2)}(t)$  for the bright state of the PL transient shown in (b).

charge carriers collected by the NR center which is dependent on: effective diffusion length of electron and holes (including energy transfer and photon reabsorption/recycling terms,<sup>[56,57]</sup> capturing cross-section,<sup>[58,59]</sup> and the NR recombination rate of the NR center itself. The cartoon in Figure 1d shows the case of the diffusion-limited quenching. In the case of the recombination rate limited process, the emission distribution should be uniform over the whole crystal.<sup>[21]</sup> The nature of the metastable NR centers is not established yet. One idea is that it is a defect complex providing an efficient trapping of both electrons and holes and their NR recombination. Then the metastability is a result of dissociation/formation of the complex due to ion migration.<sup>[32]</sup> Within this framework, the concentration of supertraps should be orders of magnitude smaller than the concentration of the usual point defects in perovskites<sup>[25]</sup> which seems to be the case. Regardless of the state of the NR center (active or passive) charge carriers can radiatively recombine in the bulk of the crystal without any restriction on the emission of two photons simultaneously. Therefore, PL photon statistics should not show any signs of antibunching effect for any PL intensity level. This is exactly the situation observed in our experiments.

To summarize, the origin of both PL blinking and photon antibunching phenomena is in the excitation and charge dynamics in spatially limited systems and it does not need to be the same. If we look at the literature data on both organic and inorganic emitting nano- and micro-objects, the phenomena of PL blinking and photon antibunching seems to be always observed at the same time. If antibunching was missing, blinking was usually missing as well. Thus, the common perception is that these two phenomena are essentially coupled to each other, however, they do not need to be. Let us look at the crossover from a semiconductor QD to a large sub-micrometer crystal in relation to blinking and antibunching. An Auger blinking mechanism can efficiently work only for small nano crystals since it requires the presence of three or more charges within less than a few nanometers distance. An MRC/supertrap mechanism is much less sensitive to the size, it requires the crystal to be smaller than the charge carrier diffusion length, which for perovskites is of the order of 1000 nm.<sup>[60-62]</sup> While for small nanocrystals (QDs) probably both mechanisms are relevant,<sup>[10,63]</sup> upon increasing the size, the contribution of the Auger mechanism goes down. Therefore, large crystals without local energy funnels (emitting sites) cannot blink by the Auger mechanism and, therefore also cannot possess antibunching while an MRC/supertrap mechanism can still give PL blinking. This is exactly the case for MAPbI<sub>3</sub>. So, contrary to many other systems, PL blinking and PL antibunching in a MAPbI<sub>3</sub> semiconductor originate from the different physical mechanisms (trapping versus Auger) and that is why these phenomena do not need to be present at the same time.

#### 4. Conclusion

Contrary to most known emitting nanoparticles where PL blinking and an antibunching phenomena accompany each other,  $MAPbI_3$  perovskite sub-micrometer crystals do not show this correlation. We performed a comprehensive study of the g2 correlation function for photons emitted from different intensity levels in PL blinking transients. However, no fingerprints of even a partial antibunching were found, meaning that all intensity levels possess the Poisson-like photon statistics. This contradicts the emitting site model





hypothesized previously to explain PL blinking in MAPbI<sub>3</sub>. In this model PL blinking is assigned to the reversible quenching of a single emitter which could possess non-Poisson statistics due to a local Auger process. Nevertheless, our experimental results fit the supertrap model, which implies that a reversible switching between the active and passive state of the supertrap (an efficient NR recombination center) is the reason for the PL blinking of the whole crystal. Note that all other experimental data like PL blinking itself and its correlation with PL lifetime can be readily explained by both models. Thus, a photon correlation experiment was absolutely necessary to exclude the presence of emitting sites in individual microcrystals of MAPbI<sub>3</sub>.

# 5. Experimental Section

MAPbI<sub>3</sub> perovskite crystals were prepared by the single-step deposition method using *p*-butyrolactone as a solvent for the precursor and the unimolar ratio of PbI<sub>2</sub> and MAI salts (1:3 ratio of Pb (or MA) and I). In order to obtain individual MAPbI<sub>3</sub> sub-micrometer crystals instead of a film, the stock precursor solution was further diluted before spin casting on a glass substrate. After annealing in the ambient air environment the sample was covered by a PMMA layer for improving its stability, see Supporting Information for details. The glass slide contained crystals of very different sizes ranging from several micrometers to tens of nanometers. In this study we concentrated on small-size crystals (from tens to hundreds of nanometers) demonstrating pronounced PL blinking.

Morphological and luminescence properties of the samples were studied by a custom built combined atomic-force (NanoScanTech) and fluorescence microscope equipped with an imaging spectrometer (SOL instruments), Andor Ixon, EMCCD camera for wide-field imaging and a free space HBT-scheme for time-correlated single photon counting.<sup>[64]</sup> The fluorescence microscope was able to work in the scanning confocal (SPAD detector) and epi-fluorescent wide-field (EMCCD detector) regimes. Optical cross-talk due to the SPAD emission in the HBT-scheme was negligible since all back reflections were prevented by avoiding cubic beam splitters and by tilting all critical optical elements to the optical axis. The sample was excited by a pulsed laser light (Avesta) at 525 nm with pulse duration of 1.8 ps and repetition rates 1 and 0.5 MHz.

# **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.

# Keywords

antibunching, Auger recombination, charge trapping, luminescence blinking, metal halide perovskites, semiconductors

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