

Supporting information for:

# **Super-Resolution Luminescence Micro-Spectroscopy Reveals Mechanism of Photo-Induced Degradation in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Nanocrystals**

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# I. Experimental setup and analysis procedure

The experimental setup used is the same as reported in<sup>1</sup> (Figure SI-1).

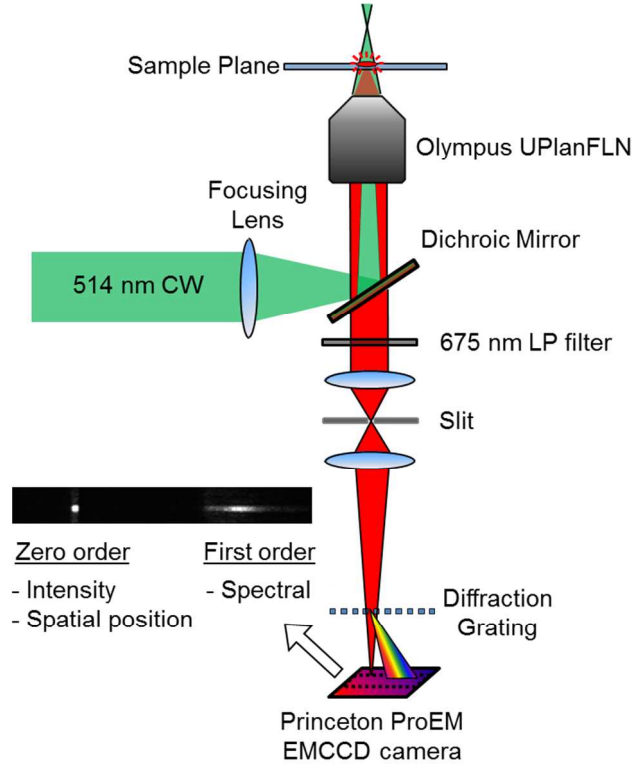


Figure SI-1. Experimental setup where a diffraction grating is used to spatially separate the zero order diffraction (image) and 1<sup>st</sup> order diffraction (spectrum) onto the CCD chip, which enables the SuperLuMS method

Images were acquired at 100 ms exposure time and each acquisition consisted of 1000 frames. A slit was placed at the image plane formed by the objective. The slit was then passed through a diffraction grating before being imaged on the camera. The zero and first order diffraction were imaged with spatial separation onto the chip so that intensity features in the image (zero order) and spectral features (first order) could be observed separately yet simultaneously of individual objects. The data was then analyzed using MatLab where the emission profile individual emitting objects in the zero order were fitted with a 2D Gaussian function according to Equation SI-1 in each frame.

$$G(x, y, \theta) = A \exp(-(a(x - x_0)^2 + 2b(x - x_0)(y - y_0) + c(y - y_0)^2)) \quad \text{Eq. (SI-1)}$$

$$a = \frac{\cos^2 \theta}{2\sigma_x^2} + \frac{\sin^2 \theta}{2\sigma_y^2}, \quad b = \frac{\sin 2\theta}{4\sigma_x^2} + \frac{\sin 2\theta}{4\sigma_y^2}, \quad c = \frac{\sin^2 \theta}{2\sigma_x^2} + \frac{\cos^2 \theta}{2\sigma_y^2}$$

where  $\theta$  is the orientation at the main axis of the Gaussian profile in the x-y plane.

## II. Additional results: Blinking and nano-domains on degradation

In this section we present additional results in support of our model. Each spectral evolution map in Figure SI-2 represents an example discussed in detail below. We emphasize two of the observed phenomena discussed in the main article: (1) blinking suspends degradation and (2) the existence of multiple nano-domains that degrade independently.

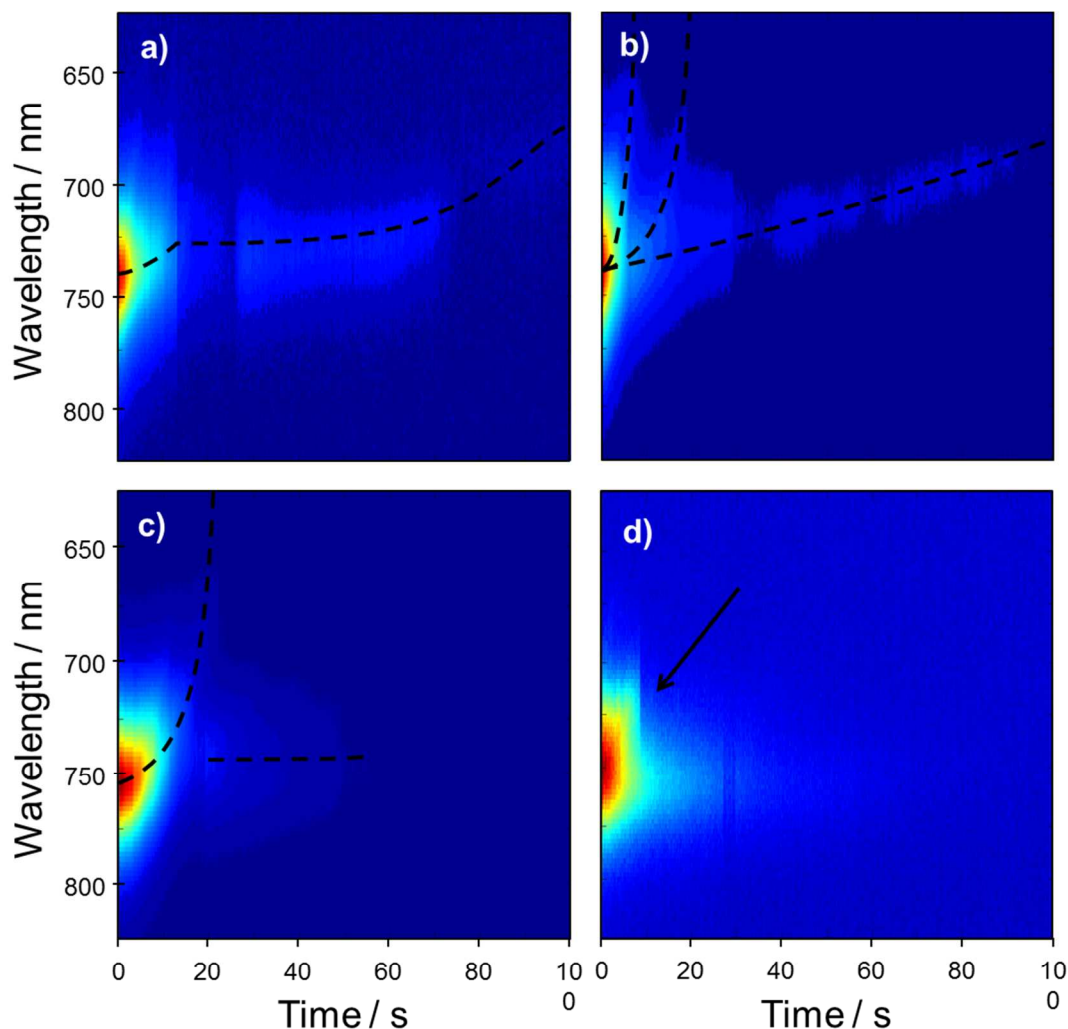


Figure SI-2. Additional examples in support of the model discussed in the main article. (a) shows blinking suspending degradation. (b) shows multiple domains degrading at different rates. (c) shows at least 2 domains that blink and degrade independently. (d) shows one domain blinking off (marked with an arrow) while the other remains emitting.

In Figure SI-2a the emission blinks down (not completely off) significantly around 18 s prior to which a spectral shift is observed from around 745 nm to 725 nm. As the intensity blinks down, for roughly 10 s,

degradation is halted and after slowed down when it blinks on again. Figure SI-2b shows an example of multiple domains degrading at different rates. Figure SI-2c shows an example where degradation first occurs in the time frame of 20 s. After 20 s we also see that one part blinks on that is only slightly blue shifted from its original peak. This domain must have blinked off at some point in the first couple of seconds and then blinked on again as the remaining domain degraded. Figure SI-2d shows the presence of multiple domains as we can see after 10 s that a part of the spectrum abruptly disappears. This is due to the quenching of one domain while the other(s) remain emitting. This example also supports the broadening of the spectrum as it blue-shifts during degradation.

### III. Number of excitations estimation

In this section we provide the calculation of the number of excitations ( $N$ ) present an excitation power density ( $I_0$ ) of  $10 \text{ W/cm}^2$ , which is equivalent to 100 Sun. We assume the Napierian absorption coefficient ( $\alpha$ ) of  $\text{MAPbI}_3$  is  $0.9 \times 10^5 \text{ cm}^{-1}$  (at  $514 \text{ nm}$ )<sup>2</sup> and the radiation penetration depth ( $\delta_p$ ) is estimated at 100 nm.  $\delta_p$  is the depth at which the intensity inside the material has fallen to  $1/e$  of the radiation (Figure SI-3). With these we can estimate the number of excitations per seconds using Equation SI-2 in the volume defined by the surface area ( $S$ ) and sample thickness ( $d$ ).

$$N = \frac{I_0 S}{h\nu d} (1 - e^{-\alpha d}) \quad \text{Eq. (SI-2)}$$

where  $h$  is Planck's constant ( $6.626 \times 10^{-34} \text{ J s}$ ) and  $\nu$  is the frequency of the excitation ( $5.84 \times 10^{14} \text{ s}^{-1}$ ). We estimate the number of excitations to be  $N = 10^{24} \text{ s}^{-1} \text{ cm}^{-3}$ . Since we are using a CW light source we the next assumption that all excited species live out their lifetime within 100 ns which reduces the number of excitations to  $N = 10^{17} \text{ cm}^{-3}$  within that given time period.

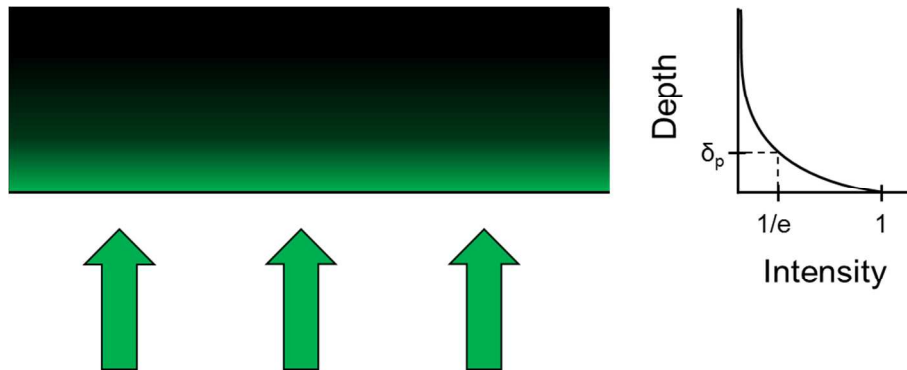


Figure SI-3. Schematic showing how the intensity falls off according to Beer-Lambert's law inside of the material.  $\delta_p$  (penetration depth) is defined at the depth where intensity is  $1/e$  of the initial light intensity.

## IV. $\text{PbI}_2$ vs $\text{MAPbI}_3$ PL spectra

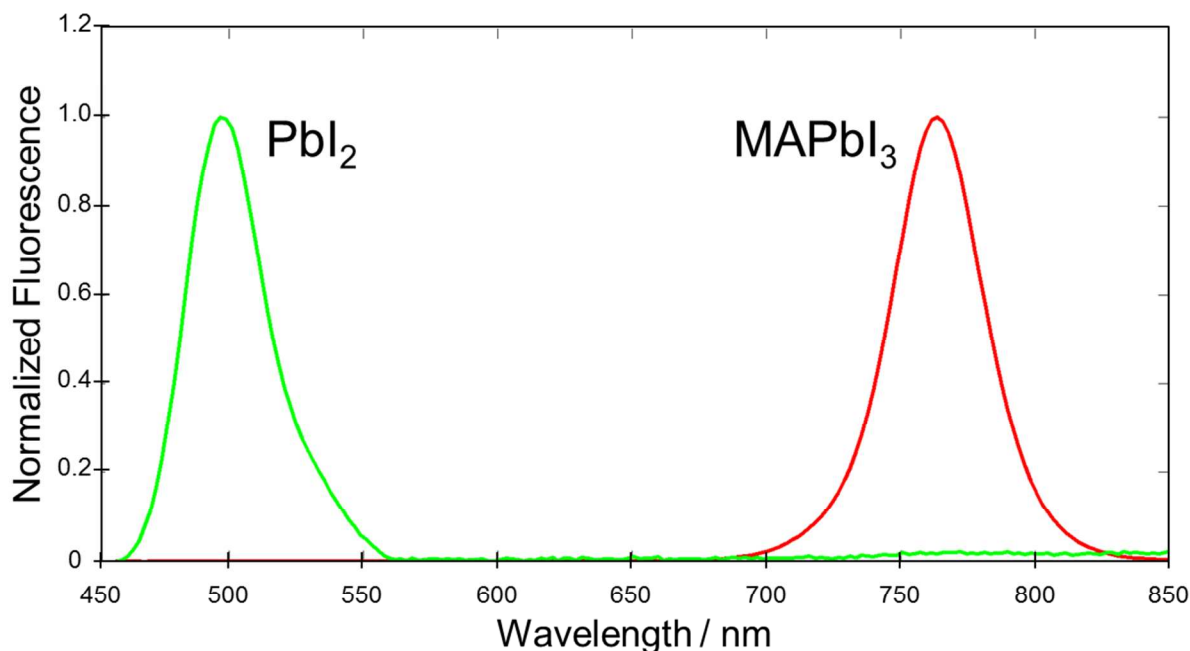


Figure SI-4. Fluorescence spectra of  $\text{PbI}_2$  and  $\text{MAPbI}_3$  from a thin film. Both spectra are taken from the same region of the sample where a band-pass filter was used to separate the  $\text{PbI}_2$  spectrum from the  $\text{MAPbI}_3$  spectrum.

Figure SI-4 shows the emission spectra of an  $\text{MAPbI}_3$  bulk sample that has been exposed to low intensity light for 10 days. We used a bandpass filter so the  $\text{PbI}_2$  peak (centered around 500 nm) could be seen without saturating the camera with emission from the  $\text{MAPbI}_3$  peak (centered around 765 nm). Each peak was then normalized so that the bands can be clearly seen.

## V. References

- (1) Merdasa, A.; Jiménez, Á.; Camacho, R.; Meyer, M.; Wu, F.; Scheblykin, I. G. Single Lévy States - Disorder Induced Energy Funnels in Molecular Aggregates. *Nano Lett.* **2014**, *14*, 6774–6781.
- (2) Xing, G.; Mathews, N.; Lim, S. S.; Lam, Y. M.; Mhaisalkar, S.; Sum, T. C. Long-Range Balanced Electron and Hole-Transport Lengths in Organic-Inorganic  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . *Science* **2013**, *342*, 344–347.