Luminescence blinking scales up: non-radiative recombination via super-traps in organo-metal halide perovskites semiconductors

Aboma Merdsa[1], Alexander Dobrovolsky[1], Eva Unger[1], Yuxi Tian[2], Marina Gerhard[1], Rafael Camacho[3], Elke Debroye[3], Johan Hofkens[3], Ivan G. Scheblykin[1]

[1] Chemical Physics, Lund University, PO Box 124, 22100, Sweden

[2]School of Chemistry & Chemical Engineering, Nanjing University, 22 Hankou Rd, Nanjing 210023, China

[3]Department of Chemistry, KU Leuven, Celestijenlaan 200F, B-3001 Leuven, Belgium

E-mail: ivan.scheblykin@chemphys.lu.se

Organo-metal halide perovskites are very promising materials for new generations of low-cost solar cells and light-emitting devices. Their solution processability is a beneficial feature, although it leads to a great spatial inhomogeneity of films, spatial variation of the trap state density and a great sensitivity of the properties to the environment. Due to the sample inhomogeneity, unraveling the fundamental physical processes by traditional spectroscopy methods is difficult, calling for their combination with microscopy techniques in order to see beyond the ensemble-averaged response.

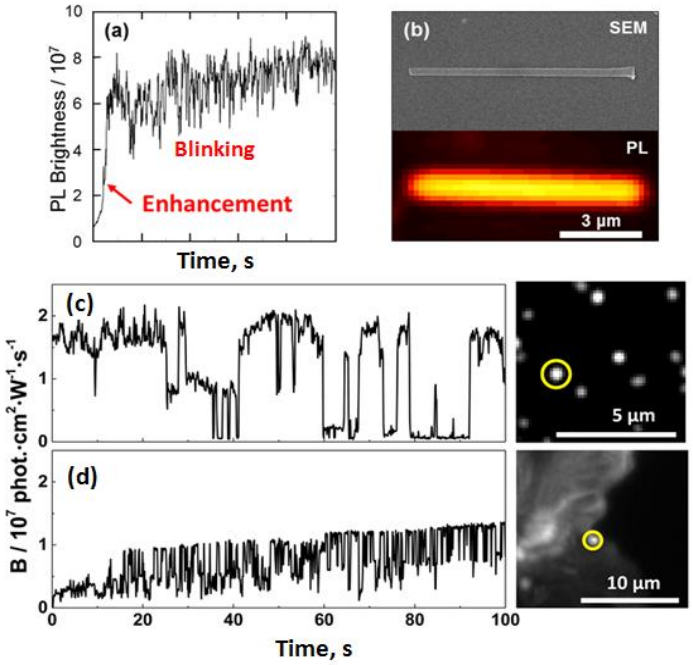

Figure 1. a) PL enhancement and PL intensity fluctuations of a large microrod of $MAPbI_3$ which PL and SEM image is shown in (b), adapted from ref. 5. c) On/off blinking of sub-micrometer $MAPbI_3$ crystals, d) – PL blinking of a small grain in a large $MAPbI_3$ polycrystal, adapted from ref. 1.

Fluorescence microscopy and single molecule spectroscopy approaches including optical super-resolution have found to be very useful to study this interesting semiconductor.[1],[2],[3] Among several interesting phenomena, in this presentation we will concentrate on such a fascinating phenomenon as photoluminescence (PL) blinking of individual nano- and even micro crystals of methylammonium lead tri-iodide.[1],[4] If excited at the same excitation power, a blinking individual perosvkite crystal can be 10^6 times brighter than a dye molecule.

Photoluminescence blinking reports on efficient charge migration over the crystal volume and the ability of just one trapping state to control the fate of all photoexcited charge carriers in the whole volume of the microcrystal. The nature of such "super-trap", as we call it, is not known. Recently we proposed[5] that it might be a donor-acceptor pair formed by a hole and electron trap located in close spatial proximity able to immobilize diffusing charges of both signs resulting in very efficient non-radiative recombination. Defects in perovskites (donor and/or acceptor defect in our case) are able to diffuse through the material. Therefore, blinking can then occur due to association and dissociation of the complex occurring at the time scale of seconds.[5]

Photoluminescence blinking allowed application of optical super-resolution methods based of luminescence intensity fluctuations. Combining super-resolution localization imaging and super-resolution optical fluctuation imaging (SOFI) we were able to detect and quantify preferential emitting regions exhibiting different types of blinking in polycrystals and correlate them with the structural details observed by scanning electron microscopy.[5]

We found that super-traps are most efficient in structurally homogeneous and large $MAPbI_3$ crystals due to efficient carrier diffusion in $MAPbI_3$. Super-traps may therefore pose limitations on the efficiency of perovskite based solar cells. The main challenge now is to understand the chemical nature of the super-trap.

Funding: Knut and Alive Wallenberg, Swedish Research council, Tryger foundation

References:

[1] Tian, Y.; Merdasa, A.; Peter, M.; Abdellah, M.; Zheng, K.; Ponseca, C. S.; Pullerits, T.; Yartsev, A.; Sundström, V.; Scheblykin, I. G., *Nano Lett.* **2015**, *15* (3), 1603–1608.

[2] Tian, Y.; Merdasa, A.; Unger, E.; Abdellah, M.; Zheng, K.; McKibbin, S.; Mikkelsen, A.; Pullerits, T.; Yartsev, A.; Sundström, V., Scheblykin I.G., *J. Phys. Chem. Lett.* **2015**, *6* (20), 4171–4177.

[3] Merdasa, A.; Bag, M.; Tian, Y.; Källman, E.; Dobrovolsky, A.; Scheblykin, I. G., *J. Phys. Chem. C* **2016**, 120, 10711.

[4] Zhu, F.; Men, L.; Guo, Y.; Zhu, Q.; Bhattacharjee, U.; Goodwin, P. M.; Petrich, J. W.; Smith, E. A.; Vela, J. *ACS Nano* **2015**, *9*, 2948–2959.

[5] Merdasa, A. et al, "Super-Trap" at Work: Extremely Efficient Non-Radiative Recombination Channels in MAPbI3 Revealed by Luminescence Super-Resolution Imaging and Spectroscopy. *ACS Nano* **2017**, in revision.