

## Fluorescence Blinking Beyond *Nano*-Confinement: The Curious Case of Perovskite *Micro*-Crystals

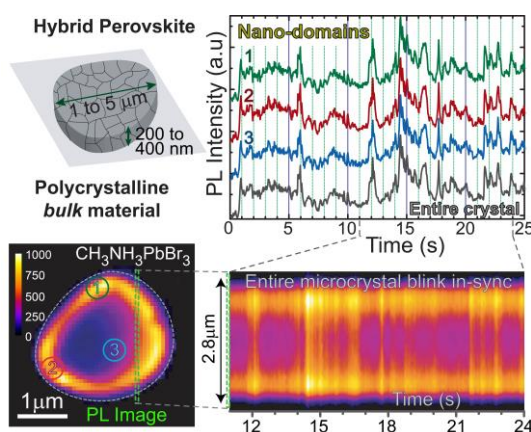
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**Abstract:** Temporally random, discrete photoluminescence (PL) intermittency between bright and dark intensity level (PL blinking) has been long recognized to be a signature of single quantum-emitters. Apart from single fluorescent molecules, proteins and conjugated polymers, a variety of quantum-confined semiconductor nanocrystals also exhibit PL blinking, generally attributed to Auger ionization-recombination leading to charging-discharging of NCs, or to long-lived carrier trapping in surface traps. However, luminescence intermittency is seldom reported beyond nanoscale dimensions because (i) spatiotemporally uncorrelated intensity fluctuations average out over the ensemble, and (ii) contributions of surface-states in radiative-recombination become far less significant compared to that of the bulk. While there are a few rare examples of PL intermittency in spatially extended ( $\sim\mu\text{m}$ ) yet nano-confined (1 or 2-D) systems [1-2], such blinking is spatiotemporally heterogeneous.

We investigated various organo-metal (hybrid) halide perovskite microcrystals (MCs), and some of which were found to exhibit PL blinking in local nanodomains [3]. Here, we present a highly unusual phenomenon, where entire individual methylammonium (MA) lead bromide ( $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ) MCs, bulk polycrystalline materials (volume  $\sim 0.1\text{--}3\ \mu\text{m}^3$ ) with no dimensional confinement, undergo discrete and prominent intensity fluctuations between multiple levels on top of a slow ( $>\text{sec}$ ) time-varying base [4]. More importantly, blinking is found to be spatially-synchronous across each MC (**Figure 1**), which implies extremely long-range ( $>\mu\text{m}$ ) communication amongst majority of photogenerated carriers at distal locations in each crystal. We explain this intriguing observation using a phenomenological model which invokes the slow formation and removal of few non-radiative traps (quenchers). Highly mobile charge carriers in hybrid perovskite crystal can recognize their presence and efficiently migrate to quenching sites, leading to abrupt and transient intensity fluctuations over *entire* individual MCs. This presentation will elaborate on likely causes and possible mechanisms as well as implications of such long-range spatially-correlated blinking dynamics in microcrystals.



**Figure:** Spatially-synchronous PL blinking of entire micron-sized crystals of  $\text{MAPbBr}_3$  perovskite (reproduced from reference 4)

### References and Notes:

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2. Si, J.; Volkán-Kacsó, S.; Eltom, A.; Morozov, Y.; McDonald, M.P.; Kuno, M.; Jankó, B. *Nano Lett.* **2015**, *15*, 4317–4321
3. Halder, A.; Chulliyil, R.; Subbiah, A.S.; Khan, T.; Chattoraj, S.; Chowdhury, A.; Sarkar, S.K. *J. Phys. Chem. Lett.* **2015**, *6*, 3483–3489
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**Invited Lecture**  
**Inter-Disciplinary Explorations in Chemistry (I-DEC 2018)**

**Bio-Sketch of Speaker**

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Dr. Arindam Chowdhury obtained his BSc in Chemistry from University of Calcutta (1995) and a Masters in Chemistry from IIT Kanpur (2007), followed by a PhD (Chemistry) from Carnegie Mellon University, Pittsburgh in 2002. His doctoral dissertation involved Stark Spectroscopy of dyes in low temperature glassy matrices to characterize electronic states of dyes, molecular aggregates and proteins. During post-doctoral research at Columbia University, he developed an evanescent-field microscopy setup for high-throughput single-molecule fluorescence detection/imaging, and used super-resolution (localization) methods to visualize the interactions and dynamics of DNA-repair proteins.

With a keen interest in teaching and education, Dr. Chowdhury joined IIT Bombay in 2006 as an Assistant Professor, where he established one of the first single-molecule fluorescence spectroscopy laboratories in India. Here, his research focus has been to understand spatiotemporal heterogeneity in soft-matter matrices (such as polymer thin-films/gels) and semiconductor nanomaterials (such as quantum-dots/quantum-wells) using single-molecule translational/rotational dynamics and single-emitter luminescence spectroscopy. He is also involved in development of new methodologies for sensing applications in biological media using polarization-/spectrally-resolved fluorescence microscopy. Over the last few years, Dr. Chowdhury's research has ventured into the study of optoelectronic properties and carrier-recombination dynamics in solar photovoltaic materials, with special interest in organo-metal halide perovskite nano-/micro-crystals/films. Dr. Chowdhury is affiliated with the National Centre for Photovoltaic Research and Education (NCPRE) and the Wadhwani Research Center for Bioengineering (WRCB) at IIT Bombay.