Single-Particle Emission Imaging of Stimulus-Induced Structural Changes

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Crystalline materials that change their structures and properties in response to environmental stimuli such as mechanical force are of great interest both from basic and technical viewpoints.[1] However, fundamental mechanisms of structural changes remain unresolved. Recently, we have developed the fluorescence microscope system for investigating the structural and functional changes of a single particle induced by external stimuli. By monitoring emission behaviors in real time, we could capture elementary steps such as structural transitions that are masked in bulk samples. In this presentation, we will discuss the following two topics.

1) Structural transition during halide Exchange on a single perovskite nanocrystal.[2] In this study, transformation from red-emitting metal halide perovskite $CH_3NH_3PbI_3$ nanocrystals to green-emitting $CH_3NH_3PbBr_3$ nanocrystals was achieved without significant morphological changes and loss of photoluminescence (PL) efficiency via a controlled halide exchange reaction. Single-particle PL measurements revealed that sudden cooperative transitions between two light-emitting states via intermediate dark states with >100 s durations during halide exchange originate from two distinct defect-mediated reconstruction processes with different activation energies.

2) Structural transition on mechanochromic organic dyes. Mechanochromic luminescence refers to mechanical-stimuli-responsive reversible color changes of solid-state emissive dyes. Recently, phenanthroimidazolylbenzothiadiazoles (PBs) have been developed as a new class of highly emissive solid-state fluorophores that exhibit versatile mechanochromic properties.[3] For instance, emission color of the crystalline powder of PBs changes from green to orange during the mechanical stimulus, suggesting a transition from crystalline phase to amorphized structures. In this study, we monitored the structural changes of mechanochromic dyes under the fluorescence microscope with a mortaring system.

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1) M. Kato, H. Ito, M. Hasegawa, K. Ishii, *Chem. Eur. J.* **2019**, *25*, 5105. 2) I. Karimata, T. Tachikawa, *Angew. Chem., Int. Ed.* in press. 3) S. Nagai, M. Yamashita, T. Tachikawa, T. Ubukata, M. Asami, S. Ito, *J. Mater. Chem. C* **2019**, *7*, 4988.