

Oral Contributions

[MS37-04] **Ultrafast Electron Microscopy: a New Tool to Study Chemical Dynamics at the Nanoscale.** Renske M. van der Veen

California Institute of Technology, 91101, Pasadena, USA (now at: Max Planck Institute for Biophysical Chemistry, Göttingen, Germany)
Email: renske.vanderveen@alumni.ethz.ch

4D ultrafast electron microscopy (4D UEM) combines the time resolution of conventional optical spectroscopy with the excellent spatial resolution of electron microscopy techniques [1, 2]. The structural and electronic changes are initiated by short (fs, ps, ns) laser pulses, which are followed by similarly short electron pulses for probing the dynamics by means of imaging, diffraction, or energy-loss spectroscopy within the electron microscope. The inherent spatial resolution and imaging capabilities of transmission electron microscopy (TEM) are ideal to pinpoint individual nanostructures and to investigate size effects and the influence of the surroundings. Here we apply 4D UEM to visualize the photoswitching dynamics of individual spin-crossover Fe(pyrazine)Pt(CN)₄ nanocrystals [3]. It is shown that the metal-organic framework nanoparticles are largely influenced by the frictional and thermal characteristics of the interface, which are unique on the level of a single nanoparticle, while averaged out in conventional studies on nanoparticles ensembles. Theoretical modeling allows describing the non-equilibrium thermoswitching dynamics as a trajectory in the phase diagram of the spin transition. In addition, we demonstrate the in situ irreversible transformation of very thin spin-crossover nanoparticles resulting in a material with an exceptionally large negative thermal expansion coefficient, which is revealed by time-resolved electron imaging and diffraction [4]. Negative thermal expansion is a unique property exhibited by only few materials. Here we show that the increased flexibility of the metal–cyanide framework after the removal of the bridging

pyrazine ligands is responsible for the negative thermal expansion behavior of the new material. This in situ visualization of single nanostructures should be extendable to other classes of chemical systems.

[1] A. H. Zewail, “Four-dimensional electron microscopy,” *Science*, vol. 328, no. 5975, pp. 187–193, 2010.

[2] D. J. Flannigan and A. H. Zewail, “4D Electron Microscopy: Principles and Applications”, *Acc. Chem. Res.*, vol. 45, no. 10, pp. 1828–1839, Oct. 2012.

R. M. van der Veen, O.-H. Kwon, A. Tissot,

Hauser, and A. H. Zewail, “Single-nanoparticle phase transitions visualized by four-dimensional electron microscopy”, *Nature Chemistry*, vol. 5, no. 5, pp. 395–402, Apr. 2013.

[4] R. M. van der Veen, A. Tissot, A. Hauser, and A. H. Zewail, “Unusual molecular material formed through irreversible transformation and revealed by 4D electron microscopy”, *Phys. Chem. Chem. Phys.*, vol. 15, no. 20, pp. 7831–7838, 2013.

Keywords: dynamics; electron microscopy of crystals; metal-organic complexes