KN-9 Crystalline Sponge Method for Absolute Structure Determination

Makoto Fujita[1]

1. Department of Applied Chemistry, University of Tokyo, Tokyo, Japan

email: mfujita@appchem.t.u-tokyo.ac.jp

X-ray single crystal diffraction (SCD) analysis has the intrinsic limitation that the target molecules must be obtained as single crystals. Here, we report a new protocol for SCD analysis that does not require the crystallization of the sample.[1-5] In our method, tiny crystals of porous complexes are soaked in the solution of a target, where the complexes can absorb and orient the target molecules in the pores. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks. As the SCD analysis is carried out with only one tiny crystal, the required sample amount is of the nano-to-microgram order. In this talk, following a general discusson,[6-11] the applications of the method for the absolute structure determination will be discussed. The absolute configurations of elatenyne (1) has still not been unequivocally confirmed because of its almost achiral meso-formed core structure that results in nearly zero [a]D specific rotation. This faint chirality was precisely discriminated by the crystalline sponge and its absolute structure was reliably determined (Fig. 1). [11] We will show a dozen of examples for absolute structure determination in asymmetric synthesis studies as well as in natural product chemistry.

Referenes: 1) K. Biradha and M. Fujita, *Angew. Chem. Int. Ed.* **2002**, *41*, 3392-3395; 2) O. Ohmori, M. Kawano, and M. Fujita, *J. Am. Chem. Soc.* **2004,** *126*, 16292-16295; 3) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita *Nature* **2013**, *495*, 461-466; 4) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, M. Fujita *Nat. Protoc.* **2014,** *9*, 246-252; 5)K. Ikemoto , Y. Inokuma , K. Rissanen , and M. Fujita *J. Am. Chem. Soc.* **2014**, *136*, 6892-6895; 6) T. R. Ramadhar, S.-L. Zheng, Y.-S. Chen and J. Clardy, *Acta Cryst.*, **2015**, *A71*, 46–58; 7) S. Yoshioka, Y. Inokuma, M. Hoshino, T. Sato, M. Fujita *Chem. Sci.* 2015, *6*, 3765-3768; 8) N. Zigon, M. Hoshino, S. Yoshioka, Y. Inokuma, and M. Fujita, A*ngew. Chem. Int. Ed.* 2**015**, *54*, 9033-9037; 9) A. B. Cuenca, N. Zigon, V. Duplan, M. Hoshino, M. Fujita, and E. Fernández, *Chem. Euro J.* **2016**, *22,* 4723-4726; 10) M. Hoshino, A. Khutia, H. Xing, Y. Inokuma, M. Fujita, *IUCrJ* **2016**, *3*, 139-151; 11) V. Duplan, M. Hoshino, W. Li, T. Honda, and M. Fujita, *Angew. Chem. Int. Ed.* **2016**, *55*, 4919-4923.

Keywords: crystalline sponge method, absolute structure, absolute configurations, crystallography, metal-organic frameworks

KN-10 Mechanical properties of nanostructures in the light of synchrotron radiation

Olivier Thomas[1]

1. Aix-Marseille Universite, CNRS IM2NP UMR7334

email: olivier.thomas@im2np.fr

Mechanical properties of nanostructures are different from those of bulk materials. In particular the yield stress is much larger when the size of objects decreases. Many issues are still being debated about the elementary mechanisms at work: what is the role of dislocation sources in these structures? What is the influence of surfaces on dislocation nucleation? … X-ray diffraction is a very powerful tool to investigate mechanics in small dimensions. Indeed X-rays have the distinct advantage of being non-destructive and highly penetrating. Moreover the wavelength of hard X-rays is perfectly matched to lattice spacing, which makes X-ray diffraction very sensitive to strains. In this talk I will give a brief overview of recent developments, which have been made possible thanks to smaller beams (down to few 100 nms) and new 2D X-ray detectors (with high dynamic range and reading frequency). These new features allow for *in situ* mechanical testing of nanostructures. Specific examples will include coherent diffraction imaging of inversion domain boundaries in GaN nanowires and prismatic dislocation loops in Au nanoislands during *in situ* nanoindentation as well as micro-Laue diffraction of Au nanowires during *in situ* three-point bending.

This work is funded by ANR under project MECANIX ANR-11-BS10-01401

Z. Ren *et al.*, Scanning force microscope for in situ nanofocused X-ray diffraction studies, J. Synch. Rad. **21**, 1128 (2014).

C. Leclere *et al.*, In situ bending of a Au nanowire monitored by micro Laue diffraction, J. Appl. Cryst. 48, 291 (2015).

S. Labat *et al.*, Inversion Domain Boundaries in GaN Wires Revealed by Coherent Bragg Imaging, ACS Nano 9 , 9210 (2015).

Keywords: Mechanics, Nanowires, Coherent diffraction, Laue diffraction