Unravelling the microscopic details of the “gate-opening” in ZIF-8 upon gas adsorption.

R. Boada(1,2), M. Amboage(1), A. Freeman(1), S. Hayama(2), L. Keenan(1), and S. Diaz-Moreno(1)
(1) Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom
(2) Department of Chemistry, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain
roberto.boada@uab.cat

The vast compositional and structural diversity of metal–organic frameworks (MOFs), which goes beyond conventional solid-state matter, has made MOFs one of the most versatile class of materials available nowadays. Zeolitic imidazolate frameworks (ZIF) are a subclass of MOFs formed by the combination of imidazolate linkers and metal cations which forms zeolitic topologies. Their outstanding surface area and tunable porosity, together with their structural flexibility, attracts interest for potential applications based on the separation and storage of molecules in a large variety of fields ranging from energy storage and environmental science all the way to biology and medicine. Thus, a full understanding of the mechanisms governing the gas adsorption processes is needed in order to develop new optimized porous materials suitable for real applications.

Within the ZIF family, ZIF-8 with the sodalite (sod) topology and chemical formula $Zn(mim)_2$, where mim=2-methylimidazolate, has become the benchmark for many studies. Several of them have highlighted that ZIF-8 exhibits some flexibility of its framework which allows the diffusion of gas molecules larger than the pore itself. This phenomenon is explained as a torsional motion of its methylimidazole linkers when going from low to high gas loadings.

In this work we have exploited the element selectivity of the X-ray absorption and emission spectroscopies to study the modification of the local geometry and electronic structure properties of the Zn metal site in ZIF-8 during this so called “gate-opening”. The results from our in-situ extended X-ray absorption fine structure (EXAFS) and high energy resolution X-ray absorption near edge spectroscopy (XANES) experiments offers a novel insight into the process taking place upon gas adsorption. XANES ab-initio calculations using full multiple scattering theory have allowed us to model the spectral changes happening closer to the absorption edge which is most sensitive to stereochemical details (coordination geometry, bond angles and oxidation state). This study provides a better understanding of the microscopic details of the host–guest interactions that we believe is very valuable for a molecular understanding of the metal organic frameworks. These findings could further drive the applications in guest molecule separation, and the future tailoring and development of improved compounds.

Acknowledgments: R.B. acknowledges funding support from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 665919.