

STRUCTURE, DISORDER AND FUNCTION IN METAL-ORGANIC FRAMEWORKS

C. Tschense,¹ T. W. Kemnitzer,¹ J. Wack,¹ Y. A. Avadhut,¹ C. D. Keenan,² J. Senker¹

¹ Inorganic Chemistry III, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany

² Chemistry Department, Carson-Newman University, Jefferson City, Tennessee 37830, USA

E-mail: juergen.senker@uni-bayreuth.de

ABSTRACT

Porous materials offer potential for applications like drug delivery, gas storage and separation as well as sensor design. In particular, within the context of current efforts for the realization of a sustainable energy future, porous materials are of relevance. Most applications rely crucially on the interactions between framework and incorporated guests, which in turn are influenced by the framework flexibility and the disorder of introduced anchor groups. The lecture will provide an overview of our recent results about introducing and analyzing selective host-guest interactions in series of functionalized metal-organic frameworks based on the MIL-53 topology based on NMR crystallographic strategies. Postsynthetic modification (PSM), allows us further to introduce amino and amid functionalities and thus make use of supramolecular principles to vary the host guest interactions with small molecules^[1]. Using xenon, carbon dioxide and acetone as local probes we have been able to study the porosity and inter pore connectivities, the structural and dynamical disorder of anchor groups and guest molecules as well as preferred binding sites. This requires an integral approach combining different techniques like powder X-ray diffraction, sorption measurements, solid-state NMR spectroscopy and computational chemistry. We make use of techniques to hyperpolarize ¹²⁹Xe gas^[2] to speed up the NMR experiments and apply modern multinuclear and multidimensional NMR techniques to unravel homo- and heteronuclear connectivities and distances. In this way, we could follow the reversible breathing mode of MIL-53 as a function of temperature and Xe partial pressure (Fig. 1a), which includes a volume change of about 30 %. The adsorption of carbon dioxide and acetone in MIL-53-X with X= NH₂ and NHCHO was shown to be correlated to strong preferred alignments of the guest molecules based on Rietveld refinements, ¹³C-¹³C spin-diffusion and double-quantum correlation experiments (Fig. 1b). Additionally, a two-step gate opening was observed for MIL-53-NHCHO upon water adsorption which is accompanied by an ordering process of the anchor groups (Fig. 1c).

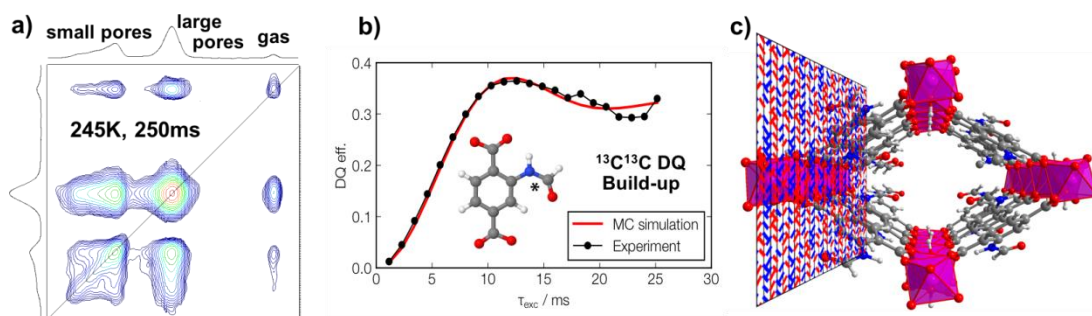


Fig. 1: a) ¹²⁹Xe EXSY spectrum of MIL-53; b) ¹³C-¹³C DQ build-up of MIL-53-NHCHO; c) Resulting anchor group alignment within MIL-53-NHCHO.

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