

## SLS Symposium on Molecules

Tuesday, April 9, 2013

10:00 to 12:15, WBGB/019

### 10:00 Single-Ion Magnets: Playing with Molecule-Substrate Interactions

*Jan Dreiser, C. Piamonteze, F. Nolting, Ch. Wäckerlin, T. A. Jung, F. Donati, L. Gragnaniello, A. Cavallin, S. Rusponi, H. Brune, K. S. Pedersen, J. Bendix*

### 10:30 Steric Control at the Active Site in Organocatalysis by Phosphine Metal-Organic Frameworks

*Xiaoying Xu, S. M. Rummelt, F. L. Morel, M. Wörle, M. Ranocchiari, J. A. van Bokhoven*

### 11:00 Coffee

### 11:15 Time-resolved X-ray absorption spectroscopy of copper-mordenite during methane to methanol conversion

*E.M.C. Alayon, M. Nachtegaal, J.A. van Bokhoven*

### 11:45 High-resolution NEXAFS to probe electronic excitations in “larger” organic molecules

*N. Schmidt, Rainer Fink*

# Single-Ion Magnets: Playing with Molecule-Substrate Interactions

Jan Dreiser,<sup>1</sup> Cinthia Piamonteze,<sup>1</sup> Frithjof Nolting<sup>1</sup>, Christian Wäckerlin,<sup>2</sup> Thomas A. Jung<sup>2</sup>, Fabio Donati,<sup>3</sup> Luca Gragnaniello,<sup>3</sup> Alberto Cavallin,<sup>3</sup> Stefano Rusponi,<sup>3</sup> Harald Brune<sup>3</sup>, Kasper S. Pedersen,<sup>4</sup> Jesper Bendix<sup>4</sup>

<sup>1</sup>Swiss Light Source, Paul Scherrer Institut, CH 5232 Villigen, Switzerland, <sup>2</sup>Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland, <sup>3</sup>Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland, <sup>4</sup>Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark.

Single-Ion Magnets (SIMs) [1-3] contain a single transition metal or rare-earth ion embedded in an organic ligand. In contrast to many other mononuclear molecular magnets, SIMs exhibit long magnetization relaxation times rendering them good candidates for future molecular spintronics or information processing applications. In order to exploit their properties they should be organized and addressable one-by-one [4], and one way to achieve this goal is to deposit submonolayers of SIMs on to surfaces. Interestingly, the properties of SIMs can be strongly modified upon adsorption on a surface with respect to the bulk crystalline phase because of molecule-substrate interactions [5]. It is thus important to understand how these interactions can be employed to control magnetic and structural properties of the SIMs.

In this talk I will report on recent results obtained on submonolayers of SIMs deposited on single-crystalline metallic substrates mainly using X-ray magnetic circular dichroism and scanning tunneling microscopy.

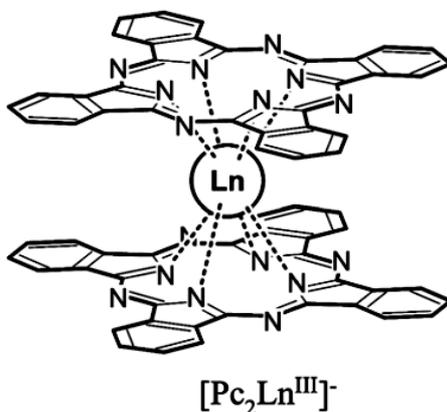


Figure 1: Example of a SIM taken from Ref. [1].

## References:

- [1] Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.-y.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694.
- [2] AlDamen, M. A.; Clemente-Juan, J. M.; Coronado, E.; Marti-Gastaldo, C.; Gaita-Arino, A. *J. Am. Chem. Soc.* **2008**, *130*, 8874.
- [3] Westerström, R.; Dreiser, J.; Piamonteze, C.; Muntwiler, M.; Weyeneth, S.; Brune, H.; Rusponi, S.; Nolting, F.; Popov, A.; Yang, S.; Dunsch, L.; Greber, T. *J. Am. Chem. Soc.* **2012**, *134*, 9840.
- [4] Gatteschi, D.; Cornia, A.; Mannini, M.; Sessoli, R. *Inorg. Chem.* **2009**, *48*, 3408.
- [5] Domingo, N.; Bellido, E.; Ruiz-Molina, D. *Chem. Soc. Rev.* **2012**, *41*, 258, and references therein.

# Steric Control at the Active Site in Organocatalysis by Phosphine Metal-Organic Frameworks

Xiaoying Xu,<sup>a,b</sup> Stephan M. Rummelt,<sup>a</sup> Flavien L. Morel,<sup>a,b</sup> Michael Wörle,<sup>a</sup> Marco Ranocchiari,<sup>\*b</sup> Jeroen A. van Bokhoven<sup>\*a,b</sup>

<sup>a</sup> ETH Zürich, Department of Chemistry and Applied Biosciences, 8093 Zürich, Switzerland;

<sup>b</sup> Paul Scherrer Institute, Department of Synchrotron Radiation and Nanotechnology, CH-5232, Villigen PSI, Switzerland

xiaoying.xu@psi.ch; +41 (0)56 310 21 48

Metal-organic frameworks (MOFs) with large porosity and high crystallinity are ideal candidates for heterogeneous catalysts.<sup>1</sup> Soluble phosphines are Lewis-base organocatalysts<sup>2</sup> and they are mostly employed as “almost universal” ligands in homogeneous catalysis, with industrial applications from hydrogenation and hydroformylation of olefins to oligomerization and hydrocyanation.<sup>3</sup> MOFs with free phosphine sites can be therefore useful both as basic catalyst and as a-what we call-solid porous ligand (SPL) to coordinate single atoms through post-synthetic modification (PSM). We report here a rationally designed, crystalline, and porous P-functionalized MOF featuring IRMOF-9 topology (Figure 1).

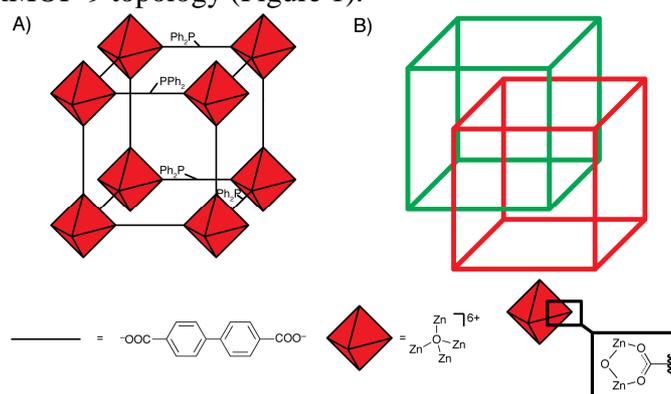


Figure 1. Structure of LSK-3

LSK-3 performed phosphine organocatalysis with a unique reaction selective behavior, which has been rationalized by means of molecular modeling. The crystalline nature of the framework provides additional steric hindrance and new unexplored ways to modify the local environment of the active site. Analogously to enzymes, it is not only the size of the pores that determines the behavior of the catalyst, but it is how the active site is located in the MOF pocket that selects which substrates can and cannot react. This opens new avenues for structural control and understanding of heterogeneous catalyst fully exploiting the unique MOF properties.

<sup>1</sup> Ranocchiari, M. and van Bokhoven, J. A. *Phys. Chem. Chem. Phys.*, 2011, 13, 6388–6396.

<sup>2</sup> Ye, L.-W., Zhou, J. & Tang, Y. *Chem. Soc. Rev.*, 2008, 37, 1140-1152.

<sup>3</sup> Sadimenko, A. P. *Advances in Heterocyclic Chemistry*, Elsevier Inc., 2011, 104, 391-475.

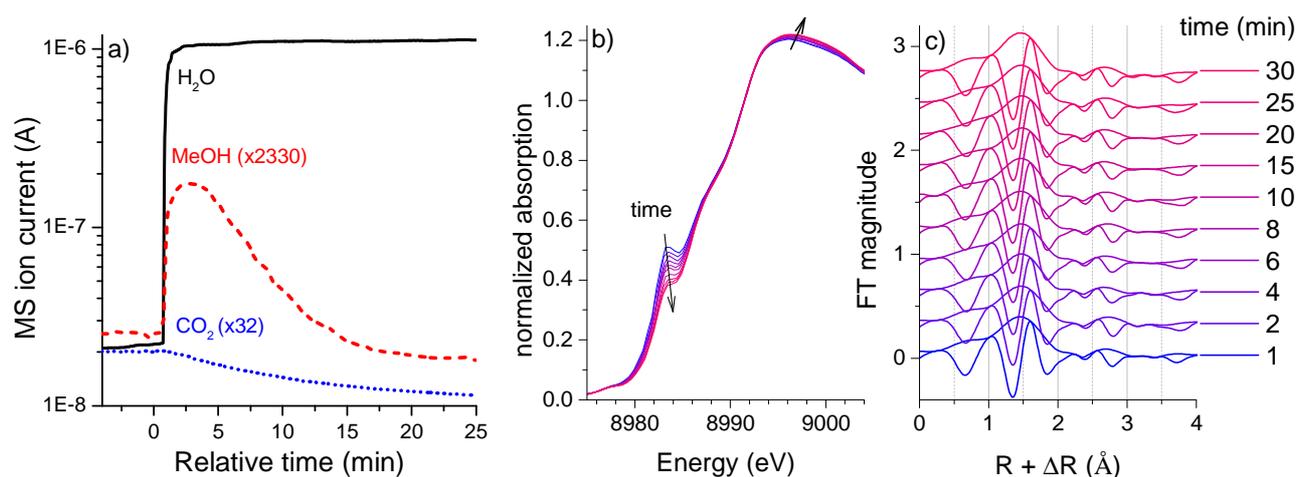
# Time-resolved X-ray absorption spectroscopy of copper-mordenite during methane to methanol conversion

E.M.C. Alayon,<sup>a,b</sup> M. Nachtegaal,<sup>b</sup> J.A. van Bokhoven<sup>a,b</sup>

<sup>a</sup>Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang Paulistrasse 10, CH-8093 Zurich

<sup>b</sup>Laboratory for Synchrotron Radiation and Sustainable Chemistry, Paul Scherrer Institute, CH-5232 Villigen  
evalyn.alayon@chem.ethz.ch

Developing a process route for the low-temperature partial oxidation of methane to methanol offers an attractive opportunity to utilize vast reserves of methane that are otherwise stranded or flared. Conventional technology converts methane to CO and H<sub>2</sub>, through steam reforming at  $\geq 700^\circ\text{C}$ , followed by methanol synthesis at  $\geq 50$  bars. Since the energy input for steam reforming comprises a major cost of a gas to liquid plant, there is significant incentive to operate at milder conditions. Copper-exchanged zeolites convert methane to methanol at mild conditions (130–200°C) with excellent selectivity to methanol [1] but the methane conversion intermediate strongly sorbs to the Cu-zeolite, preventing a catalytic process. Further, from the amount of methanol that was extracted and on the premise of a dicopper site converting methane,[2] only 5% of the total Cu sites were estimated to be active. We have shown that introducing a wet stream of helium at 200°C after methane conversion releases methanol into the gas phase and allows multiple turnovers in a batch-wise operation.[3] By X-ray absorption spectroscopy (XAS) at the Cu K-edge, we found that a large fraction of Cu reacts with methane,[4] contrary to the reported minority in the literature. Therefore, the identity of the Cu sites associated to the reaction pathway remains ambiguous.



**Figure 1.** a) Mass spectrometer profile of H<sub>2</sub>O, MeOH and CO<sub>2</sub> recorded during water-assisted desorption of the methane conversion intermediate, together with the time-resolved XAS spectra of Cu-MOR displaying the b) XANES and c) Fourier transform of the EXAFS.

Time-resolved XAS provides access to both electronic and geometric structural information at short time scales, which are relevant for identifying structural information at transient conditions. Here, we report our use of time-resolved XAS to follow the structural changes to the Cu sites during methane conversion and desorption of the activated intermediate (Figure 1). We observed that a large fraction of Cu<sup>II</sup> reacts with methane undergoing reduction to Cu<sup>I</sup> and hydration. During desorption in H<sub>2</sub>O/He as methanol, there was a corresponding decrease in the fraction of Cu<sup>I</sup> component and a small increase of a Cu<sup>II</sup> oxide, without large geometric changes. Bound activated methane appeared to be associated to Cu<sup>I</sup> sites.

## References

- [1] M.H. Groothaert, P.J. Smeets, B.F. Sels, P.A. Jacobs, R.A. Schoonheydt. *J. Am. Chem. Soc.* 127 (2005) 1394.
- [2] J.S. Woertink, P.J. Smeets, M.H. Groothaert, et al., *Proc. Nat. Acad. Sci. USA* 106 (2009) 18908.
- [3] E.M.C. Alayon, M. Nachtegaal, M. Ranocchiaro, J.A. van Bokhoven, *Chem. Commun.* 48 (2012) 404.
- [4] E.M.C. Alayon, M. Nachtegaal, E. Kleymenov, J.A. van Bokhoven, *Microporous Mesoporous Mater.* 166 (2013) 131.

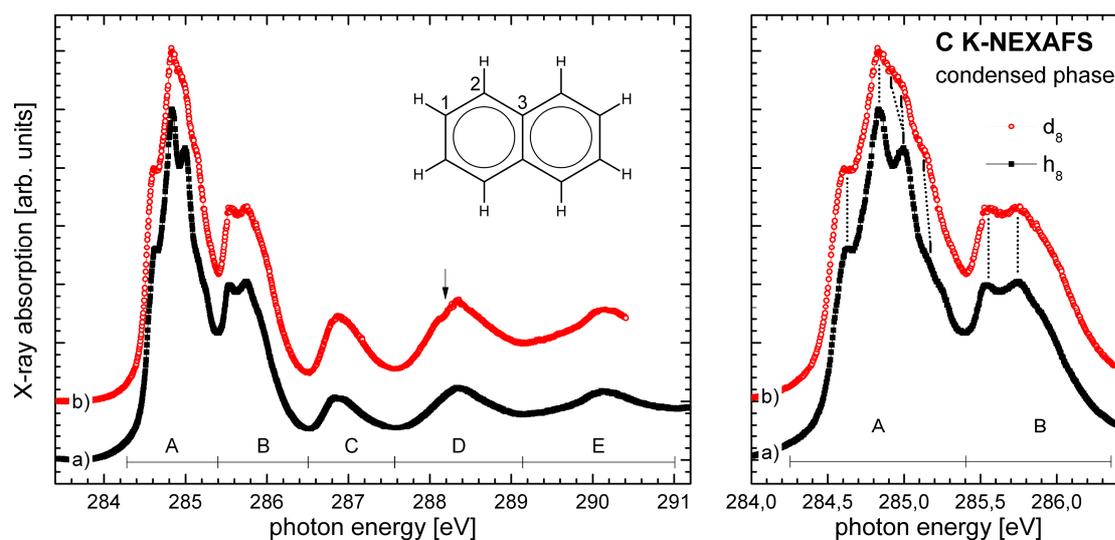
## High-resolution NEXAFS to probe electronic excitations in “larger” organic molecules

Norman Schmidt, Rainer Fink

*Interdisciplinary Center of Molecular Materials (ICMM), Physikalische Chemie II, FAU Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany*

Near-edge x-ray absorption spectroscopy is an extremely valuable tool to investigate organic molecules. The resonant excitation of core electrons serves as spectroscopic fingerprint which can be used to assess both initial and final state effects. Beamlines operating in the soft x-ray regime offer a resolving power  $> 10.000$ . Thus, energy resolution is sufficient to probe the vibronic excitations in organic molecules [1, 2].

In this contribution we will discuss some aspects of high-resolution NEXAFS based on two model systems, naphthalene [3,4] and NTCDA [5]. In order to fully understand the spectroscopic features, theoretical calculations are required. Furthermore, the direct comparison of spectra recorded from the gas or condensed phase offers better insight into the involved molecular orbitals, e.g., Rydberg states can be quenched leading to spectral broadening or energetic shifts.



*Comparison of the C K-edge NEXAFS spectra of condensed multilayer films of naphthalene-h<sub>8</sub> (a) and naphthalene-d<sub>8</sub> (b). The isotope effect indicates excitations that efficiently couple to vibronic states.*

### References:

- [1] A. Schöll, Y. Zou, D. Hübner, S. G. Urquhart, Th. Schmidt, R. Fink, and E. Umbach, *J. Chem. Phys.* 123(4) (2005) 044509
- [2] A. Schöll, D. Hübner, Th. Schmidt, S. G. Urquhart, R. Fink, E. Umbach, *Chem. Phys. Lett.* 392 (2004) 297-302.
- [3] D. Hübner, F. Holch, M.L.M. Rocco, K. C. Prince, S. Stranges, A. Schöll, E. Umbach and R. Fink, *Chem. Phys. Lett.* 415 (2005) 188
- [4] G. Tsvetkov, N. Schmidt, T. Strunskus, Ch. Wöll, R. Fink, *Surf. Sci.* 601 (2007) 2089
- [5] A. Schöll, Y. Zou, L. Kilian, D. Hübner, D. Gador, C. Jung, S. G. Urquhart, Th. Schmidt, R. Fink, and E. Umbach, *Phys. Rev. Lett.* 93(14) (2004) 146406.