



Experiment title:

XAS/XMCD study of a new sublimable spin crossover molecular system

Experiment number:

CH5180

Beamline:

ID32

Date of experiment:

from: 25/10/2017 to: 31/10/2018

Date of report:

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Shifts:

18

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Report:

The aim of our experiment was to study by X-ray absorption spectroscopy the SCO transition down to the nanoscale of a new Fe(II) sublimable complex based on a mixed scorpionate-type ligand. Spin Crossover (SCO) metal complexes are molecular systems able to swap spin states under a variety of stimuli, amongst which temperature, magnetic and electric fields, light irradiation. This switchability makes them promising building blocks for spintronics, data storage and sensing devices.^[1,2] Sublimable derivatives were shown to enable assembly of the pristine complex onto different substrates, with controlled thicknesses from micrometers down to sub-monolayer coverage. Nevertheless several details on the behavior of these molecules at the nanoscale are still missing, in particular the point whether a monolayer of these molecule can maintain the reversible switching between the two spin states being strongly debated. Among this class of complexes, many iron based complexes were investigated with synchrotron based technique, following the SCO transition by x-ray absorption spectroscopies.^[3-6] We indeed performed one the pioneering studies on submonolayers of a scorpionate derivative at the former ID08 beamline (see He-3754 report). This series of experiments explored the behaviour of a new sublimable complex, with a switching temperature close to room temperature, making it thus a promising candidate for being incorporated in devices and for the study of transport properties switching.

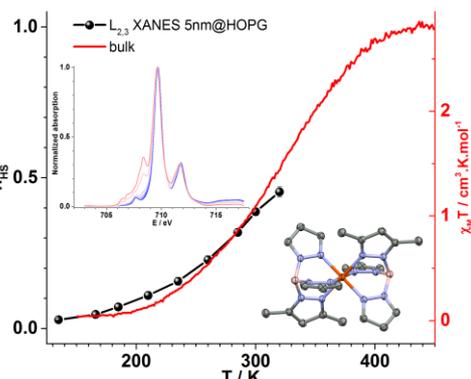


Figure 1 Fe L₃ edge XANES spectra for a 5 nm film on HOPG and extracted HS fraction vs. T compared to bulk behaviour

The molecules were deposited *in situ* on either an Au(111) single crystal or high-quality HOPG, by thermal sublimation in UHV. We studied a 5nm thick sample on HOPG (Figure 1) and submonolayer (0.5ML) samples on both HOPG (Figure 2) and Au (Figure 3). All spectra

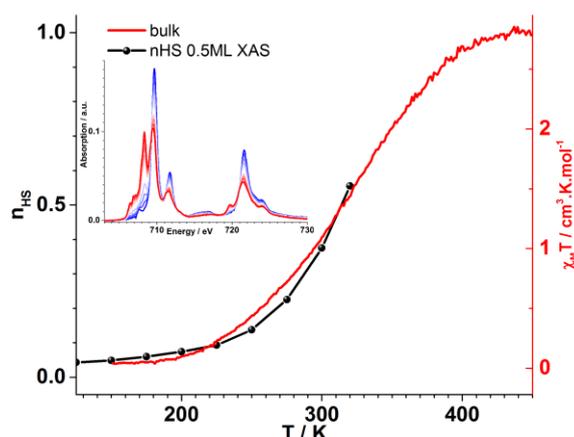


Figure 2. Fe L_{2,3} edge XANES spectra for 0.5ML on HOPG from 160 to 320 K, and corresponding extracted HS fraction vs. T compared to bulk behaviour

show a clear conversion from the low spin (LS) state to the high spin (HS) state by increasing the temperature, in remarkable agreement with the properties of the bulk. This is all the more surprising considering that previous results reported in the literature always resulted in much more gradual, often incomplete, conversions for such ultrathin layers as compared to the bulk. Complete switching could not be observed due to the maximal temperature reachable by the XMCD end-station at ID32 of 320K. The submonolayer on HOPG behaviour (Fig. 2) is very much similar to the thicker film and the bulk. This is in sharp contrast with the submonolayer on Au(111) (Fig. 3): even at 2 K there is a sizeable fraction of the molecules locked in the HS state ($\approx 55\text{-}60\%$), but the remaining molecules undergo spin crossover which is essentially complete at 300 K, that is with a transition curve that is significantly shifted to low temperatures as compared to the bulk. This feature points out to a possible interaction of the molecules with the substrate, that affects their SCO transition efficiency.

Further experiments were realized to assess the LIESST effect, *i.e.*

the SCO transition induced by illumination of the molecules with an appropriate wavelength,^[7-8] supplied by a ThorLabs laser diode fiber coupled to a reflective collimator insuring a focalized spot on the sample, with irradiation powers in the 10s of mW/cm^2 . XANES spectra were monitored while measuring at 45° incidence at low temperature for different wavelengths in the visible range. Some photoconversion from the LS state to the HS state was seen to take place but relaxation kinetics of the HS metastable state were so fast as to prevent any further measurement.

In the remaining time of the experiment, we also profited from the irradiation setup to try to characterize by X-ray absorption spectroscopy the coexistence of two distinct photoexcited metastable states with distinct relaxation behaviours for one complex. We had previously tried this characterization on other XMCD endstations at other synchrotron facilities, but the results were always inconclusive. Thanks to the exceptional stability and high signal/noise ratio shown by the beamline during the whole measurement period, we could evidence the very subtle back-and-forth photoconversion at low temperature controlled by the wavelength used (Fig. 4).

References

- [1] P. Gütllich, H. A. Goodwin, *Spin Crossover in Transition Metal Compounds I-III*, Springer-Verlag, Berlin/Heidelberg, **2004**.
- [2] M. A. Halcrow, *Spin-Crossover Materials: Properties and Applications*, John Wiley & Sons Ltd, Oxford, UK, **2013**.
- [3] M. Bernien, D. Wiedemann, C. F. Hermanns, A. Krüger, D. Rolf, W. Kroener, P. Müller, A. Grohmann, W. Kuch, *J. Phys. Chem. Lett.* **2012**, *3*, 3431.
- [4] B. Warner, J. C. Oberg, T. G. Gill, F. El Hallak, C. F. Hirjibehedin, M. Serri, S. Heutz, M. A. Arrio, P. Sainctavit, M. Mannini, G. Poneti, R. Sessoli, P. Rosa, *J. Phys. Chem. Lett.* **2013**, *4*, 1546.
- [5] X. Zhang, T. Palamarciuc, J.-F. Létard, P. Rosa, E. V. Lozada, F. Torres, L. G. Rosa, B. Doudin, P. A. Dowben, *Chem. Commun.* **2014**, *50*, 2255.
- [6] K. Bairagi, A. Bellec, C. Fourmental, O. Iasco, J. Lagoute, C. Chacon, Y. Girard, S. Rousset, F. Choueikani, E. Otero, P. Ohresser, P. Sainctavit, M.-L. Boillot, T. Mallah, V. Repain, *J. Phys. Chem. C* **2018**, *122*, 727.
- [7] S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* **1984**, *105*, 1.
- [8] S. Decurtins, P. Gutlich, K. M. Hasselbach, A. Hauser, H. Spiering, *Inorg. Chem.* **1985**, *24*, 2174.

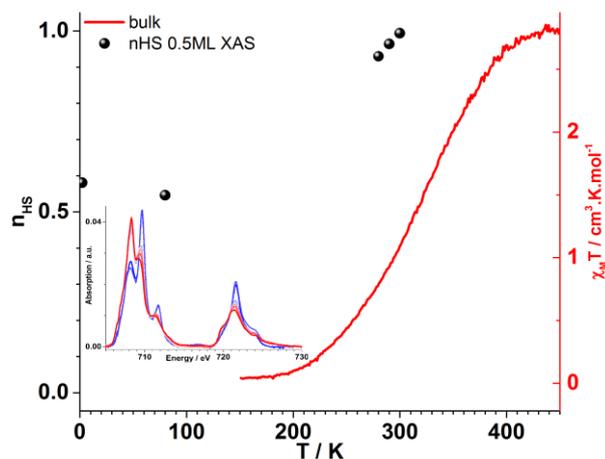


Figure 3. Fe $L_{2,3}$ edge XANES spectra for 0.5ML on HOPG from 2 to 320 K, and corresponding extracted HS fraction vs. T compared to bulk behaviour

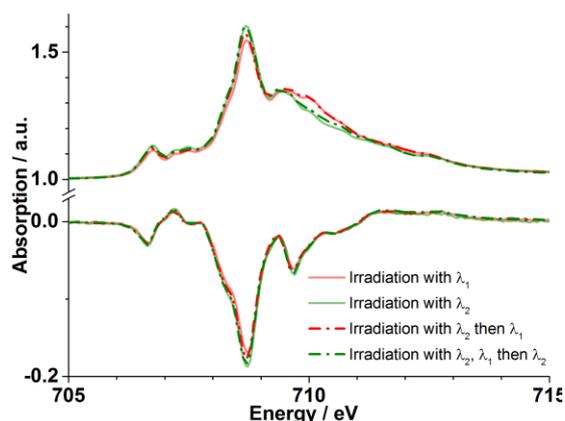


Figure 4. Interconversion between two different photoexcited states seen by the Fe L_3 edge XANES and XMCD spectra.