

**Experiment title:**

"Investigation of ultra-thin film deposit of evaporated Single Molecule Magnet by XMCD and XNLD"

**Experiment number:**

HE-2984

**Beamline:**

ID08

**Date of experiment:**

from: 01/07/2009 to: 14/07/2009

**Date of report:**

25/08/2009

**Shifts:**

21

**Local contact(s):**

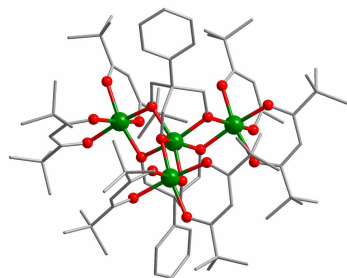
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## Report

Single Molecule Magnets (SMM)[1] are a class of magnetic molecular materials which hold great promises in molecular spintronics and data storage. For this reason, a number of recent studies have targeted their organization into nanostructured architectures at solid surfaces[2]. Using X-ray Circular Dichroism, we have demonstrated that a properly-functionalized tetra-iron(III) SMM, Fe<sub>4</sub>, can be anchored to surfaces as a monolayer from solution and that the deposit so-obtained maintains the SMM features typical of the bulk phase[3]. We have also demonstrated that a differently functionalized Fe<sub>4</sub> cluster (see figure 1), behaving as Single Molecule Magnets in bulk, can be transferred to surfaces as a thick film by thermal evaporation in UHV, with full retention of magnetic properties as evidenced by standard magnetometry and EPR studies [4].

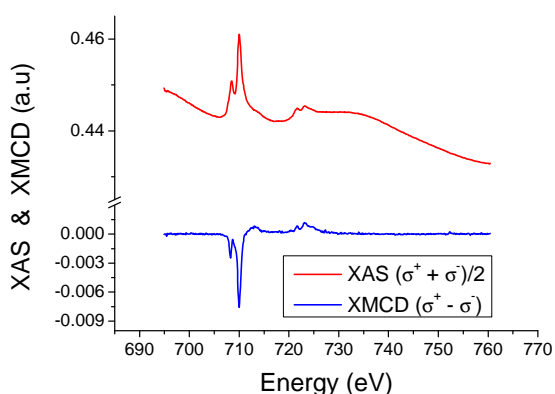


**Figure 1.** Structure of the first evaporable Fe<sub>4</sub> cluster, as determined by single-crystal X-ray diffraction. Color code: iron(III) = green, oxygen = red, carbon = gray.

The aim of this proposal was: i) to confirm that the electronic and magnetic structure of Fe<sub>4</sub> is preserved upon evaporation down to the monolayer level, (using XMCD and the temperature dependence of the dichroic contribution); ii) to reveal any long-range structural ordering of the evaporated deposit (using XNLD); iii) to explore the influence of the substrate on the Fe<sub>4</sub> properties.

In order to accomplish these tasks we required first of all to adapt the ID08 capabilities to our needs: we took care of the installation and the optimization of a proper molecular evaporator suitable to control the

deposition process down to the monolayer dose. For this reason, the assigned time at ID08 was divided in two parts. In a preliminary part, which extended from July 1<sup>st</sup> to the beginning of the official beamtime, we installed evaporators for metals (provided by ID08 staff) and for molecules (provided by the users), we fully baked the UHV chambers, and we prepared Cu(100) and Au(111) single crystals, which were immediately characterized using STM, LEED and Auger facilities. In the same timeframe, we were also able to optimize the evaporation processes for metals and molecules. This part of the experiment was completed before the starting of the beamtime. The second part corresponded to the real experiment with X-ray light. First of all we repeated a characterization of a bulk deposit in order to verify and optimize the experimental conditions as well as to acquire reference spectra (we followed the strategy already successfully used in our previous beamtime HE-2692 to avoid radiation damage and to optimize the detection of very weak signals). Then we prepared a first thick deposit of Fe<sub>4</sub> by evaporation and recorded its XAS and XMCD spectra, which were found identical with those taken on the bulk phase and on a monolayer deposit prepared by wet chemistry [3].



**Figure 2.** XAS and XMCD spectra of the evaporated thick film of the Fe<sub>4</sub> cluster on Au(111) recorded at 6K with an induction of 3T.

Subsequently identical results were achieved by diminishing the thickness of the deposit down to the monolayer level and by switching to different surfaces.

In particular we obtained the same spectroscopic features evaporating Fe<sub>4</sub> on Cu(100) and on a Co/Cu(100) support. Unluckily, we verified that a long-range structural ordering of the evaporated deposit was absent. On the other hand we successfully demonstrated that the electronic and spin structure of the cluster is not destroyed upon interaction with a non-innocent magnetic surface like Co. Detailed data analysis and simulations are currently in progress to fully describe the observed dependence of the dichroic contribution upon the applied magnetic field at several temperatures.

The results so obtained are of primary relevance for further development of this research area and justify a continuation of this kind of investigation. In particular, having demonstrated the stability of Fe<sub>4</sub> upon evaporation, it is now essential to clarify in detail the impact of magnetic substrates on the magnetic properties of SMMs. To this aim, both substrates and molecules need to be engineered in order to tune the electronic and magnetic coupling at the surface.

## References

- [1] D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets* (Oxford University Press, Oxford, UK, 2006).
- [2] D. Gatteschi, et al. *Inorg. Chem.* 48 (2009) 3408.
- [3] M. Mannini, et al. *Nature Mater.* 8 (2009) 194.
- [4] L. Margheriti et al. *Small* 5 (2009) 1460.