



Experiment title:

X-Ray Dichroism of a Mn12 monolayer on Au

Experiment number:

HE-1962

Beamline:

Date of experiment:

from: *March 11th* to: *March 15th 2006*

Date of report:

Shifts: 9

Local contact(s): *Julio Cezar*

Received at ESRF:

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Report:

We had planned to investigate the grafting of Mn12-bet clusters [bet = +N(CH₃)₃-CH₂-COO-] onto the Au(111) surface prefunctionalized with a Self Assembled Monolayer (SAM) of MercaptoEthaneSulphonate (MES) (see fig. 1) in order to verify the retaining of the cluster main magnetic properties and their preferential orientation with respect to the surface, by using circular and linear dichroism.

First of all, in order to set-up the best experimental conditions to avoid radiation damage, we started by taking XAS and XMCD measurements at the Mn L_{2,3} edges in a Mn12-bet thick film. As a reference sample, besides the Mn12-bet, also the non-functionalized cluster (Mn12-ac) was measured.

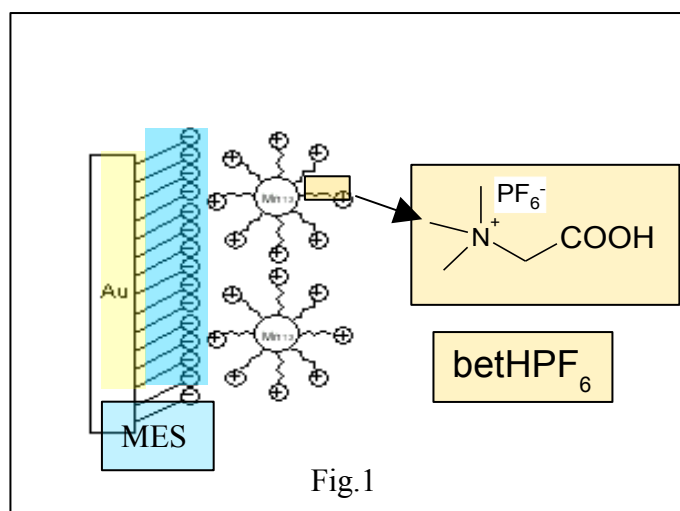
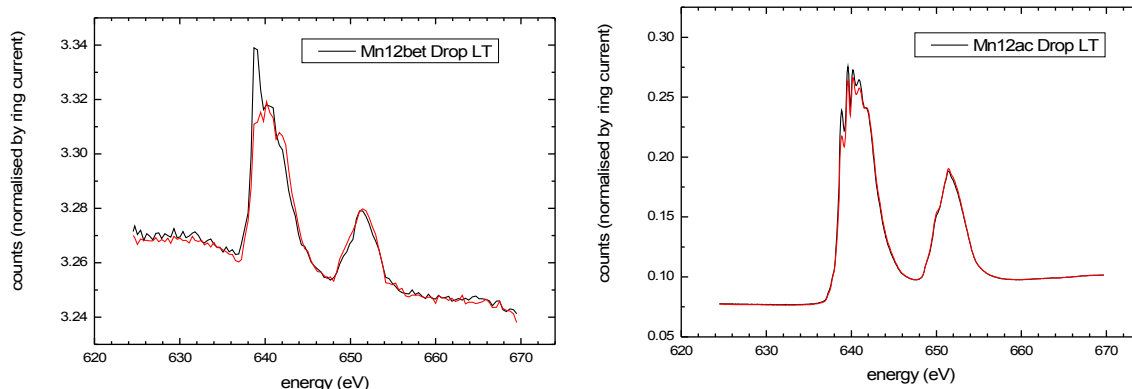


Fig.1



In Fig.2 the XAS spectra of Mn12-ac and Mn12-bet **thick films** taken at 10 K, H=5T, with both photon helicities, are compared.

The Mn12-ac XA spectrum compares very well with the literature, whereas the Mn12-bet adsorption spectrum, to our knowledge measured for the first time, shows a new interesting feature: a quite strong component characteristic of Mn²⁺ which is absent in the Mn12-ac spectrum. This finding is in agreement with the reducing action of the cation ligands, which is expected to lower the oxidation state of four Mn atoms from +3 to +2.5 [1]. If confirmed, this would be the first spectroscopic evidence of the Mn12-core reduction.

A second interesting result, to be better investigated, is the much stronger dichroism of this Mn^{2+} component with respect to that of the Mn^{3+} and Mn^{4+} components.

The system of main interest, however, consisted in isolated clusters of Mn12-bet grafted on a MES-SAM grown on Au(111) (both single crystal and films evaporated on mica). Here the XA spectra evidenced a potential problem due to the presence of a very strong Mn^{2+} component (see Fig. 3). As a matter of fact, whilst a small Mn^{2+} component is expected, the strong decrease in the other components related to higher oxidation state is an indication of cluster damaging.

In order to investigate the source of damage we deposited isolated clusters directly on the gold surface, without interposition of the MES layer. The spectra relative to Mn12-bet e Mn12-ac are shown in Fig.4. For both

derivatives, the spectra of the isolated clusters and that of the corresponding thick film are very similar, whereas they are completely different from

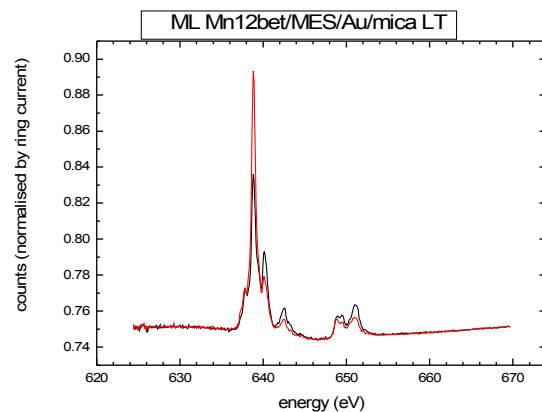
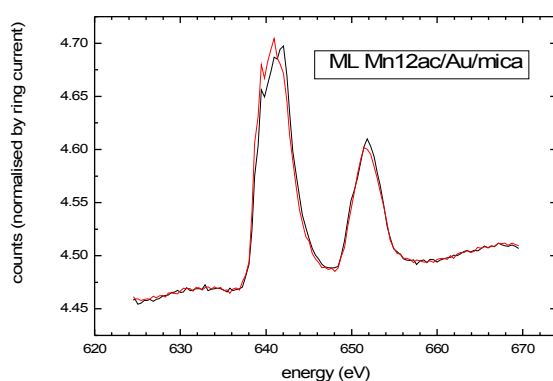


Fig. 3

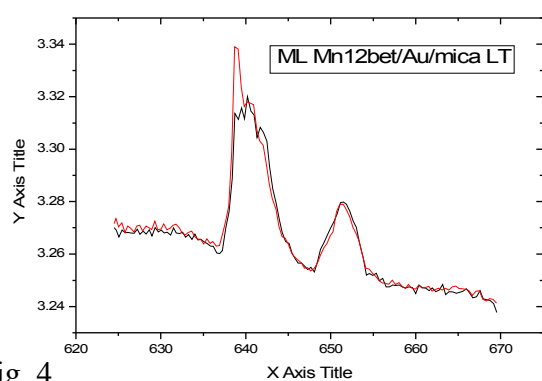


Fig 4

that of the isolated clusters deposited on the MES layer (Fig.3). The conclusion is that the probably the interaction of the Mn12-bet derivative with the MES is strong enough to seriously affect the Mn12-core. On the contrary, the interaction with the bare gold surface is weaker and does not affect the clusters.

A deeper analysis of the XMCD data of all the measured sample will be carried out in the next future and the Mn12-bet and Mn12-ac dichroic signals will be compared with theoretical simulations in progress.

In the very last part of the run we were also able to perform a preliminary study of Cr7Ni heterometallic rings directly grafted on the gold surface by sulphur containing functionalizations. In fact two different derivatives (Cr7Ni-thiobutane $[HS(C_2H_4)NH_2Bu]$ $[Cr_7NiF_8 Piv_{16}]$ and Cr7Ni-3tpc $[(C_3H_7)_2NH_2][Cr_7NiF_8L_{16}]$) have been deposited from liquid phase on Au(111) and characterized by means of XAS. By comparing the Cr-2p and Ni-2p X-ray absorption edges we have confirmed the STM and X-ray photoemission spectroscopy (XPS) results performed in our lab, indicating a higher coverage for the Cr7Ni-3tpc system (about 20-25%) with respect to Cr7Ni-thiobutane (about 5-7%). However the possibility of having an STM directly connected to the beamline experimental chamber would have been of great relevance to check the quality of the SMM two-dimensional distribution.

For what concern the sample degradation, we have verified that the Cr7Ni clusters are more stable than Mn12 clusters, allowing a ten times higher beam flux and a faster acquisition time.

For each derivative, the absorption spectrum is essentially the same for both monolayer and thick film, showing a negligible inner clusters interaction with the gold substrate.

We have also verified the possibility of performing a full XMCD characterization of the monolayers compared with the thick film, in order to clarify if the low dimensionality significantly affects the magnetic properties of the Cr7Ni rings.

As the XMCD technique enables the identification of the single Cr and Ni magnetic contributions their actual values and the total spin of the ring will be extracted and compared with macroscopic results, though the Ni signal is quite low and requires long acquisition times.

Moreover, by exploiting X-ray Linear Dichroism (XLD), we expect to be able to get information on the orientation of such SMM's grafted on gold.