XAS and XMCD investigation of Mn$_{12}$ monolayers on gold

Matteo Mannini,[a] Philippe Sainctavit,[b] Roberta Sessoli [a], Christophe Cartier Dit Moulin,[c] Francesco Pineider,[a] Marie-Anne Arrio, [b] Andrea Cornia,[d] and Dante Gatteschi* [a]

[a] La.M.M., Department of Chemistry and INSTM Research Unit
Università di Firenze
Via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy.

[b] Institut de Minéralogie et de Physique des Milieux Condensés, UMR7590
Université Pierre et Marie Curie
Case 115, 4, place Jussieu, 75252 Paris cedex 05 France.

[c] Laboratoire de Chimie Inorganique et Matériaux Moléculaires
Université Pierre et Marie Curie
Case 42, 4, place Jussieu 75252 Paris cedex 05, France.

[d] Department of Chemistry and INSTM Research Unit
Università di Modena e Reggio Emilia
Via G. Campi 183, 41100 Modena, Italy.
1 – Experimental Setup

The experiments were done at BESSY II synchrotron in the UE46-PGM insertion device beamline. The X-ray source is an Apple II undulator delivering elliptically polarized X-rays. For the energy range of Mn L\text{2,3} edges, the undulator’s third harmonic is monochromatized by a plane grating mirror. Since the samples were known to be potentially sensitive to radiation damage and photo-reduction, the various optical elements of the beamline have been set so as to reduce the photon density on the sample. The cooled apertures downstream the undulator have been set to 0.2x0.2 mm\text{2}. The monochromator exit slit has been set to 20 µm and a defocusing toroidal mirror has been installed to deliver a parallel X-ray beam on the sample. Closing the cooled aperture and the exit slit reduced the flux by a factor 500 and the parallel beam toroidal mirror lowered the photon density on the sample by an extra factor 400. With this specific set-up, no radiation damage and no photo-reduction have been observed for accumulation time longer than 10 hours.

The beamline end-station is a UHV cryostat that can cool a sample down to 1.5 K thanks to a pumped 4He stage. Alternatively sub-Kelvin region can be achieved with a dilution 3He-4He setup widely described in reference 27 of the main text. The full-option endstation is described also in the following website: http://www.impmc.jussieu.fr/impmc/Recherche/equipement.php.

The cryostat is equipped with a superconducting coil delivering ±7 T. XAS and XMCD can be measured in Total Electron Yield by recording the drain current with Keithley 617 electrometers.

Thanks to the UHV pressure in the sample chamber (below 2x10^{-10} mbar) and a high resistive insulation of the sample (better than 500 GO), excellent signal/noise ratio can be achieved for photocurrents in the pA range.
XMCD signals have been measured by sets of four spectra corresponding to XAS measurements with the two directions (parallel and anti-parallel to the x-ray propagation vector) of the magnetic induction and the two helicities (left and right) of the x-ray beam.

2 - Analysis of the XAS and XMCD signals.

The analysis of the XAS and XMCD spectra have been performed by linear combinations of experimental spectra of reference compounds. XAS and XMCD signals have been taken from Ref. 23 for Mn\textsuperscript{II} ions, and from Ref. 21 for Mn\textsuperscript{III} and Mn\textsuperscript{IV} ions with magnetic polarization parallel to the external magnetic field.

The spectra have been pre-normalized in order to stick to the present experimental conditions: 80% circularly polarized X-rays, T=4.2K (and T=0.5K), H=4T and H=2T (assuming the field and temperature dependence of the dichroic signal to be described by a Brillouin function). XMCD were consequently normalized in order to keep intact the information related to the percentage of dichroic component.

Alternatively XAS and XMCD reference spectra for Mn\textsuperscript{III} have been extracted in accordance to the sum rules method (see reference 28) from signal in Fig.2 of the main text for Mn\textsubscript{12} subtracting the contribution of Mn\textsuperscript{IV}. This procedure is in agreement with the electronic structure of Mn\textsubscript{12} that has been demonstrated to be accessible with XAS and XMCD in reference 21. Our method to calculate the alternative XAS/XMCD can be summarized by the following equations:

\[
I^{\text{III}}(E) = \frac{(12*I^{12}(E) - 4*I^{\text{IV}}(E))}{8}
\]

\[
S^{\text{III}}(E) = \frac{(12*S^{12}(E) + 4*S^{\text{IV}}(E))}{8}
\]

where \(I^{12}\) and \(S^{12}\) are respectively the experimental XAS and XMCD spectra of 3 bulk.

In figure S1 are presented the standards spectra employed in the analysis. All the spectra have been normalized to the number of free-electrons (holes) present: this number has been estimated for Mn12 as:

\[
h^{12} = (8*h^{\text{III}} + 4*h^{\text{IV}})/12 = 6.33.
\]

This is the particular case of the more general expression that we used also to provide the final normalization for all the experimental spectra:

\[
h = S^{\alpha}h^{\alpha} / S^{\alpha}
\]

where \(h^{\alpha}\) is the number of holes corresponding to the \(\alpha\) oxidation state of Mn.
Figure S1. XAS and XMCD normalized spectra used to form the two set of standards in fitting calculations
3 - Sensitivity of XMCD to the antiferromagnetic coupling between Mn\textsuperscript{III} and Mn\textsuperscript{IV} inside Mn\textsubscript{12} molecules.

The sensitivity of XMCD on the antiferromagnetic coupling between Mn\textsuperscript{III} and Mn\textsuperscript{IV} inside Mn\textsubscript{12} molecules is best seen by comparing the experimental XMCD signal constructed for 8 Mn\textsuperscript{III} ions antiparallel to 4 Mn\textsuperscript{IV} ions with the one constructed for 8 Mn\textsuperscript{III} ions parallel to 4 Mn\textsuperscript{IV} ions (see figure below).

These data are obtained using the standard presented in figure S1 (b) and (d).

![XMCD Signal Comparison](image)

*Figure S2.* Experimental XMCD signal of 3 bulk (black line) and the as reproduced signals considering an antiferromagnetic coupling (8 Mn\textsuperscript{III} - 4 Mn\textsuperscript{IV}, red line) and a ferromagnetic coupling (8 Mn\textsuperscript{III} + 4 Mn\textsuperscript{IV}, blue line).

From the above figure, the most prominent sign for AF coupling is the shape of the positive XMCD signal in the energy range between 642 and 645 eV. The signature of the ferrimagnetic spin structure is the sharp positive XMCD signal in the energy region between 641.5 eV and 645 eV. XMCD spectra expected for ferro- and antiferro-magnetic coupling are compared in order to support this analysis. Our data indicate that replacement of acetate ligands in 1 with different carboxylates does not alter the observed XMCD.
4 - Fits of XAS spectra

The XAS spectra have been fitted for compound 4 bulk (Figure S3, panel a), for 2 deposited from THF (Figure S3, panel b), for compound 3 deposited from THF (Figure S3, panel c) and for compound 3 deposited from CH₂Cl₂ (Figure S3, panel d). The experimental spectra are drawn as black solid lines and the reconstructed spectra are given as colored thin lines. The spectra have been fitted as a weighed sum of the XAS spectra given in Fig.S1 using two set of standards within those presented in Figure S1:

Set A: Mn£II (Fig. S1a), Mn£III (Fig. S1b), Mn£IV (Fig. S1d),
Set B: Mn£II (Fig. S1a), Mn£III (Fig. S1c), Mn£IV (Fig. S1d).

The best-fit percentages of manganese ions in the different oxidation states are given in table T1.

Figure S3. Experimental XAS spectra (black lines) and the best fits obtained with “set A” (blue lines) and “set B” (red lines). The better agreement provided by set B is evident.
5 - Fits of XMCD spectra.

The XMCD spectra and the reconstructed spectra (figure S3) have been obtained following the same procedure adopted for XAS fitting. The polarization contributions from Mn$^{II}$, Mn$^{III}$ and Mn$^{IV}$ extracted using both Set A and Set B have been given explicitly in the table T1.

Figure S4. Experimental XMCD spectra (black lines) and the best fits obtained with “set A” (blue lines) and “set B” (red lines). The better agreement provided by set B is evident.
Is important here to evidence that an acceptable agreement is not achieved when considering fully ferromagnetically polarized contributions of Mn$^{\text{II}}$, Mn$^{\text{III}}$, Mn$^{\text{IV}}$ ($\delta^{\text{II}}, \delta^{\text{III}}, \delta^{\text{IV}} = +1$) as represented in figure S5.

**Figure S5.** Comparison of experimental XMCD spectra with calculated XMCD ones obtained for all ions with a magnetic moment parallel to the applied field (green line) and for $\delta^{\text{II}}, \delta^{\text{III}}, \delta^{\text{IV}}$ values given in the paper (red line).
Table T1. Summary of XAS and XMCD composition evidences for the two sets of standard spectra (set A and B). Reported percentages are extracted from XAS spectra while arrows indicate the average polarization of each component deduced from XMCD spectra. Up-pointing arrows (red) correspond to a polarization parallel to the applied magnetic field, and blue pointing down arrows to the antiparallel case. The length of the arrows corresponds to the approximate polarization intensity \( d \) in eq. 2 where the unit polarization \( d = \pm 1 \) corresponds to the length of the arrows for \( d \) in the bulk phase.

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Sample</th>
<th>SET A (Mn\textsuperscript{II}, Mn\textsuperscript{III}, Mn\textsuperscript{IV})</th>
<th>SET B (Mn\textsuperscript{II}, extractedMn\textsuperscript{III}, Mn\textsuperscript{IV})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn\textsuperscript{II}</td>
<td>Mn\textsuperscript{III}</td>
<td>Mn\textsuperscript{IV}</td>
</tr>
<tr>
<td></td>
<td>XAS</td>
<td>XMCD</td>
<td>XAS</td>
</tr>
<tr>
<td>3 bulk\textsuperscript{[a]}</td>
<td>n.d.</td>
<td>n.d.</td>
<td>66 %</td>
</tr>
<tr>
<td>4 bulk\textsuperscript{[b]}</td>
<td>5%</td>
<td>60%</td>
<td>35%</td>
</tr>
<tr>
<td>2 monolayer from THF</td>
<td>25%</td>
<td>55%</td>
<td>20%</td>
</tr>
<tr>
<td>3 monolayer from THF</td>
<td>20%</td>
<td>35%</td>
<td>45%</td>
</tr>
<tr>
<td>3 monolayer from CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>30%</td>
<td>50%</td>
<td>20%</td>
</tr>
</tbody>
</table>

[a] Oxidation states percentages and polarizations for 3 bulk are imposed as demonstrated in Ref.21. [b] The Mn\textsuperscript{II}:Mn\textsuperscript{III}:Mn\textsuperscript{IV} ratio in 4 is 8:58:33.