ESRF	**Experiment title:** Solid state and solution X-ray Natural, Magneto-Circular and Magneto-Chiral dichroism of the nonanuclear Mn(III) chiral single molecule magnet, Mn_9.	**Experiment number**: CH-5014
Beamline: ID12	**Date of experiment**: from: 28.04.2017 to: 30.04.2017	**Date of report**: 07.09.2017
Shifts: 6	**Local contact(s)**: Andrei Rogalev, Fabrice Wilhelm	*Received at ESRF:*

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Report:

Scientific backround

This proposal was devoted to the study of local magneto-chiral properties in a chiral single-molecule magnet (SMM). In molecular multifunctional materials, multiple physical properties can coexist independently or interact with one another to create new physical properties, or the opportunity to tune one property by modulation of the other. In chiral molecular nanomagnets the simultaneous breaking of parity and time-reversal symmetries, associated to natural circular dichroism (NCD) and birefringence and to magneto-circular dichroism (MCD) and birefringence, respectively, can result in the material displaying magnetochiral dichroism (MChD) and birefringence.[i] MChD offers the opportunity to address and/or manipulate the magnetic moment of a molecular nanomagnet by illuminating it with unpolarised light, which is one of the most sought-after targets in the field of molecular magnetic materials. Furthermore, the magnetic bistability associated with SMMs will result in an hysteresis, with respect to the direction of an external magnetic field, of the absorption of unpolarised light in chiral SMMs. This optical, magnetic-field-induced, bistability would allow for the reading of information stored on SMMs in form of magnetic polarisation. Writing of binary information in the form of magnetic polarisation on chiral SMMs can, in principle, be achieved by taking advantage of the 'inverse' MChD effect. As recently theorised by Sessoli and Rogalev,[ii] though experimentally unproven, 'inverse' MChD can be used to induce magnetic polarisation to a chiral medium by irradiation with unpolarised light. The overarching goal of the work in this proposal was to experimentally prove this theory using a chiral SMM, work that has never been reported previously. Recently we have synthesized a new Mn^{III}-based single-molecule magnet, $[Mn_9O_4(Me\text{-}sao)_6(LipO)_3(MeO)_3(MeOH)_3](Cl)$ (**1**) (Figure 1A) (Me-saoH$_2$ = methylsalicylaldoxime, LipOH = lipoic acid). **1** displays SMM behaviour, with magnetic hysteresis both in the solid state, in solution and when deposited on Au nanoparticles (AuNPs). The NCD spectra of the two enantiomers of **1** in solution (Figure 1B) confirm the enantiopure nature of the single crystals of **1** and show that it does not racemise in solution. **1** is an excellent candidate for the observation of XNCD and XMChD since the MChD response is proportional to the magnetisation of the sample and requires the medium to display NCD.

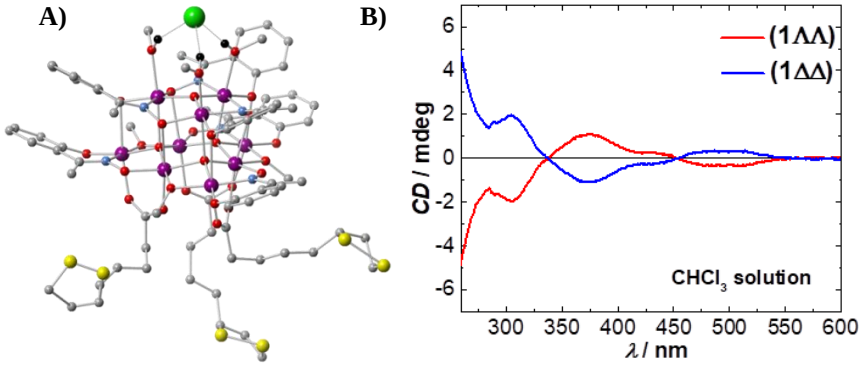

Figure 1. (A) Molecular structure of **1**. (B) CD spectra of enantiomers of **1** in chloroform solutions.

Experimental details

We were able to measure 2 samples, racemic polycrystalline mixture of **1** and racemic mixture of **1** deposited on gold nanoparticles. Following the suggestion of the ESRF proposals reviewing panel, most of the experiment time was dedicated to verify the stability of **1** under the X-ray flux. Grinded racemic polycrystalline mixture of **1** in a very small amount of immersion oil was placed in the cavity of the sample holder and covered with kapton film to avoid desolvation under UHV conditions. After the sample was cooled to 2.1 K, XANES spectra at the Mn K-edge were collected after certain periods of exposure to the synchrotron beam. After 4 hours of measurements the beam flux was reduced by 33 times and measurements were continued. The second sample was pressed in a pellet, placed in the cavity of the sample holder and covered with kapton film.

During the allocated beamtime we were able to measure:

a) XANES at 2 K at Mn K-edge of the racemic polycrystalline mixture of **1** under normal beam flux at various periods of exposure to the beam;
b) XANES and XMCD at 2 K at Mn K-edge of the racemic polycrystalline mixture of **1** under 33 times less intense beam flux at various periods of exposure to the beam;
c) XANES and XMCD at 2 K at Mn K-edge of the racemic mixture of **1** deposited on gold nanoparticles under reduced beam flux.

In order to investigate the presence of XNCD and XMChD, as well as to follow the field dependence of XMCD in **1**, we will require additional beamtime, since long acquisition time is necessary.

Results

The investigations under normal flux (Figure 1) have showed sample damage. The XANES spectra spectra collected would not supperpose after certain periods of exposure to the synchrotron beam.

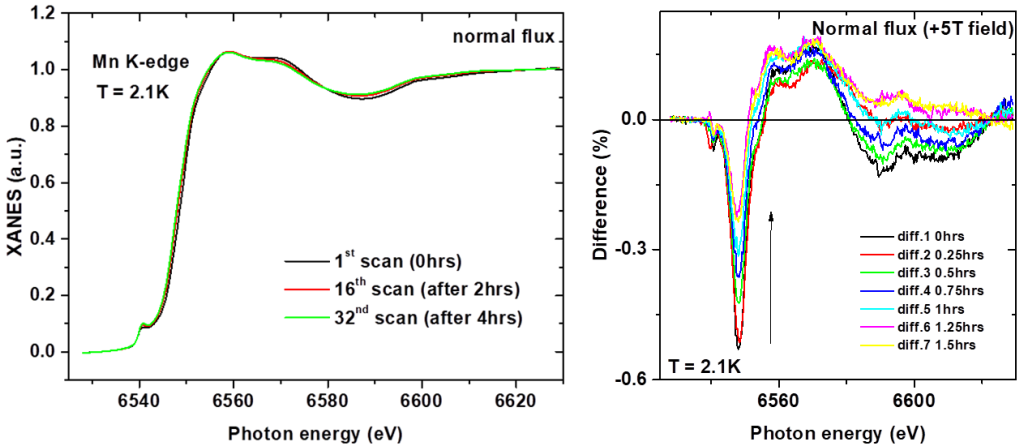

Figure 2. (left) XANES spectra at Mn K-edge of the racemic polycrystalline mixture of **1** under normal beam flux at various periods of exposure to the beam. (right) Difference between the initial XANES spectrum of **1** and XANES spectra of 1 collected under normal beam flux at various periods of exposure to the beam.

After the reduction of the beam flux intensity by 33 times no sample damage was observed after a long exposure time, as confirmed by both XANES and XMCD spectra (Figure 3).

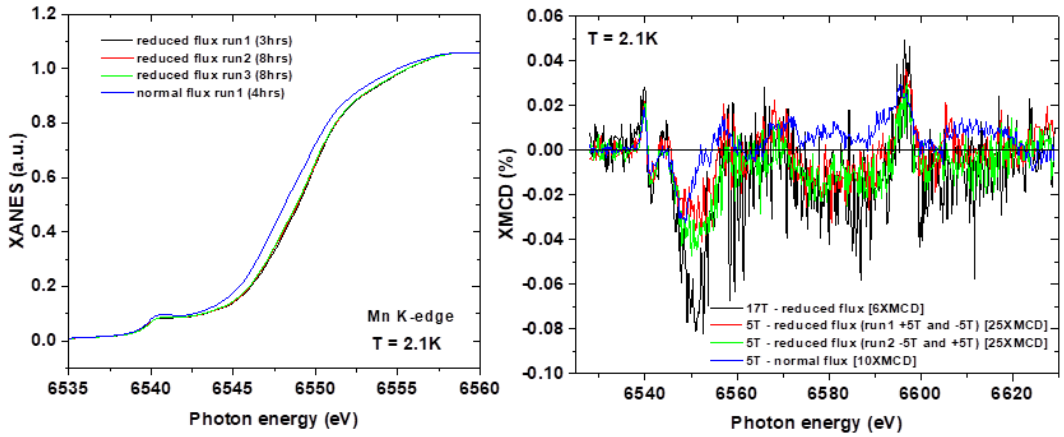

Figure 3. (left) Comparison between the XANES spectra at Mn K-edge after exposure to the normal flux beam and after the exposure to the reduced beam. (right) XMCD spectra at Mn K-edge collected under various conditions.

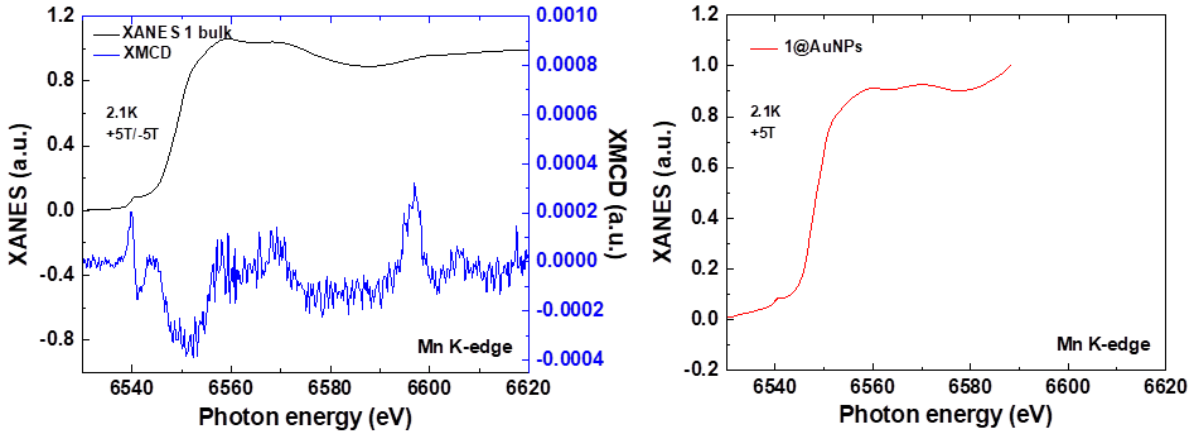

Figure 4. (left) XANES and XMCD spectra of the bulk sample of **1**. (right) XANES spectra of **1** deposited on gold nanoparticles.

Collected XANES spectra have shown that the oxidation state of Mn in **1** deposited on gold nanoparticles is +III, same as in the bulk sample (Figure 4). This observation is particularly important since it confirms the stability of **1** upon deposition on gold surface. Moreover, this result is included in an article that is under preparation at the moment.

Performed experiments have showed that it is possible to control the beam damage of the sample. The acquisition of qualitative spectra (Figure 4) requires long acquisition time. After the discusion with ID12 beamline scientists it was established that the observation of XNCD and XMChD in **1** will require single crystal measurements on a goniometer along crystal axes since **1** crystallizes in orthorombic $P2_12_12_1$ space group. It was impossibele to perform such measurements in the allocated number of shifts.

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[i] Train, C.; Gruselle, M.; Verdaguer, M. *Chem Soc Rev* **2011**, *40*, 3297.

[ii] Sessoli, R.; Boulon, M. E.; Caneschi, A.; Mannini, M.; Poggini, L.; Wilhelm, F.; Rogalev, A. *Nat Phys* **2015**, *11*, 69.