ESRF	**Experiment title:** In depth investigation of Ln-based Single Ion Magnets by Hard X-ray	**Experiment number**: HE-3896
Beamline: ID12	**Date of experiment**: from: 19/02/2013 to: 25/02/2013	**Date of report**: 1st September 2013
Shifts: 18	**Local contact(s)**: A. Rogalev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Roberta Sessoli, Matteo Mannini, Andrea Caneschi, Marie-Emmanuelle Boulon*
Laboratory University of Florence Laboratory of Molecular Magnetism Department of Chemistry & INSTM RU Firenze, Italy.

Kevin Bernot*, INSA - Rennes, France

Philippe Sainctavit*, CNRS IMPMC Université Pierre et Marie Curie Paris, France

Report:

Single-molecule magnets (SMMs) exhibit a magnetic bistability due to the presence of an anisotropy barrier that, at low temperature, opposes the reversal of the molecular giant spin leading to a memory effect.[1] Among these systems lanthanide-based ones are gaining a remarkable role. Thanks to the large magnetic moment and large anisotropy of lanthanides ions these kinds of SMMs show higher blocking temperatures and coercivity than transition-metal-based ones, this is the case of the single lanthanide ion based SMM that we have investigated during last ID12 beamtime. In the specific case of Ln-based systems, the soft X-ray based investigation (at M edges) cannot provide a complete overview of the molecular properties of those systems because the spectral features related to 4*f* states are almost not affected by crystal field that can only change the intensity of XMCD, XMLD or XNLD signals. That is why we decided to employ a hard X-ray -based characterization approach; we started from a bulk analysis of Ln-based systems which properties are known to be sensitive to the molecule organization in order to understand the origin of alterations in lanthanide-based single ion magnets properties by investigating their $L_{2,3}$ edges.

Effect of a thermal treatment on theXMCD signal in the $TbPc_2$ Single Ion Magnet

The magnetic properties of the Terbium(III) bis-phthalocyaninato neutral complex have been found to be promising featuring almost the highest barrier for a SMM however its dynamics of the magnetization is strongly influenced by the molecular packing as recently observed in evaporated samples.[2] Two samples were measured during this beam time: the first one is a freshly prepared powder and the second sample was thermally treated at ≈ 400°C in hight vacuum (10^{-7} mba) which corresponds to its the evaporating temperature, used for deposition of surface. It have previously been observed that the hysteresis disappears when the powder is heated, but, if the same powder is used to be deposited a thick film, this film possesses the hysteresis. [3] By measuring the XMCD signal, we observe that the butterfly shaped hysteresis loop of the fresh sample is instead totally closed for the thermally treated one. The XMCD signal is strictly identical at Tb L_3 edge for both of the compounds as shown on figure 1.

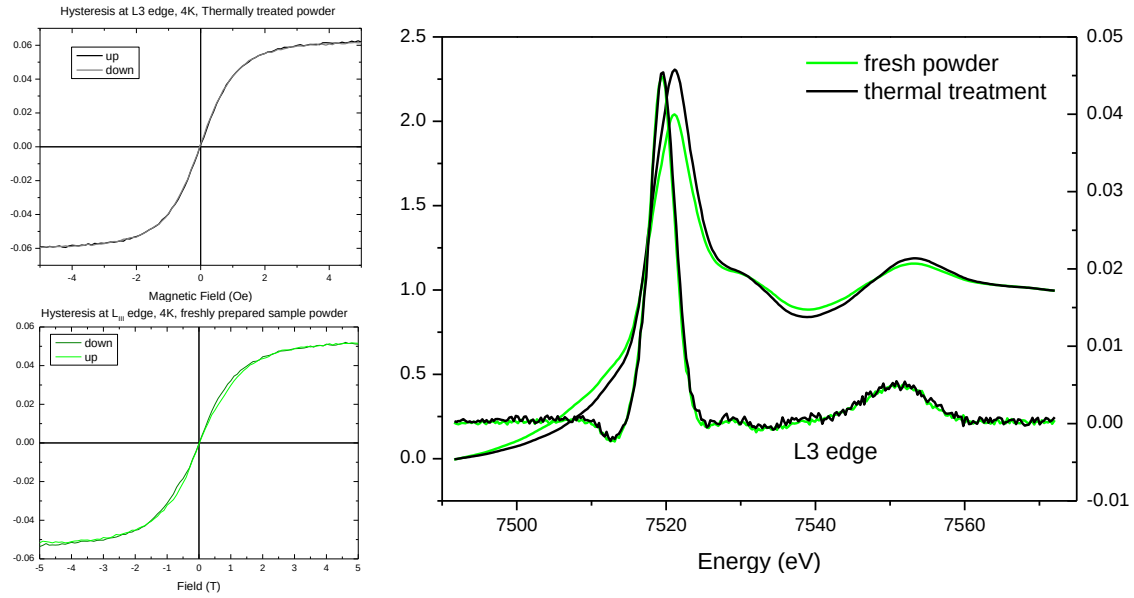

Figure 1: Comparison between the XMCD of $TbPc_2$ powder freshly prepared and thermally treated

LnDOTA Series, effect of the nature of the ion

The XMCD of the complex of Na[LnDOTA(H2O)]•$4H_2O$, where $DOTA^{4-}$ is the anion of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid.[4,5] In order to investigate the influence of the nature of the lanthanide ion with a given ligand field we investigated the three derivatives with Ln = Tb, Dy and Yb, i.e. both prolate and oblate ions; moreover, Dy-based derivative exhibits a giant field dependence of the magnetic relaxation time[4]. Powder samples were prepared as cellulose pallet. The hysteresis cylcles are closed for each derivatives , we report in figure 2 the XMCD signal of each derivative.

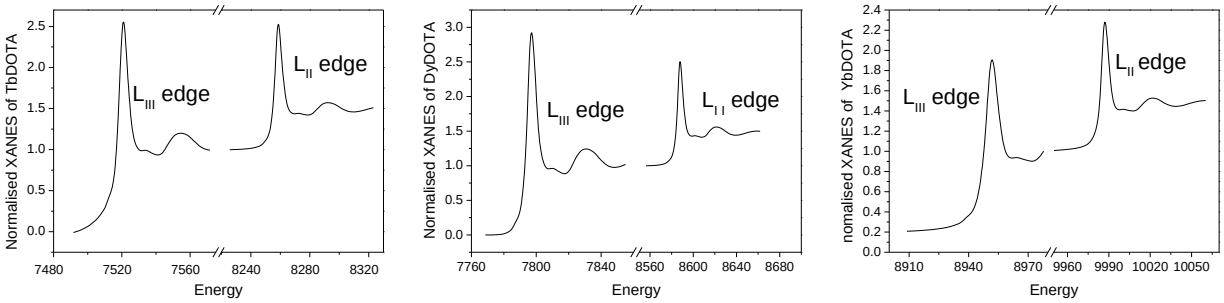

Figure 2: XMCD of Tb (left) Dy (center) and Yb (right) derivatives

References

1. Gatteschi, D., Sessoli, R. & Villain, J. *Molecular nanomagnets*. (Oxford University Press, 2006).

2. Car, P.-E. *et al*. Giant field dependence of the low temperature relaxation of the magnetization in a dysprosium(III)-DOTA complex. *Chem.Commun.* **47,** 3751–3 (2011).

3. Malavolti, L. *et al*. Erratic magnetic hysteresis of TbPc2 molecular nanomagnets. *J. Mater. Chem. C* **1,** 2935–2942 (2013).

4. Cucinotta, G. *et al*. Magnetic Anisotropy in a Dysprosium/DOTA Single-Molecule Magnet: Beyond Simple Magneto-Structural Correlations. *Angew. Chem. Int. Ed.* **51,** 1606–1610 (2012).

5. Boulon, M.-E. *et al*. Magnetic anisotropy and spin-parity effect along the series of lanthanide complexes with DOTA. *Angew. Chem. Int. Ed.* **52,** 350–4 (2013).