ESRF	**Experiment title:** XMCD study of magnetism of Co-based single chain magnets assembled on HOPG	**Experiment number**: CH-4462
Beamline: ID32	**Date of experiment**: from: 22/09/2015 to: 29/09/2015	**Date of report**:
Shifts: 18	**Local contact(s)**: Emilio Velez-Fort	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Matteo Mannini*, Andrea Caneschi, Lorenzo Poggini*. Roberta Sessoli*, Michele Serri*:

University of Florence, Laboratory of Molecular Magnetism Department of Chemistry & INSTM RU Via della Lastruccia 3 Sesto Fiorentino IT -50019 FIRENZE

Maria G. F. Vaz*, Miguel Novak*:

Universidade Federal do Rio de Janeiro Instituto de Fisica da Materia Condensada BR - 21945-970 RIO DE JANEIRO

Report:

The objective of the experiments was to use XMCD to characterize the magnetism of micro/nanocrystals assemblies of cobalt based single chain magnets (SCM)[1,2] $[Co(hfac)_2(PyrNN)]_n$ and $[Co(hfac)_2NaphNN]_n$, exhibiting large coercivity and high blocking temperatures in conventional bulk phase magnetometry measurements.

Magnetisation hysteresis measurements through soft x-rays is a well established technique however for the characterization of molecular systems specific experimental conditions are required including an optimal control of the photon-flux, an appropriate sweep rate of the magnet and low temperatures.

For this reason, prior to start with the SCM based experiment, we evaluated the capabilities of ID32 beamline performing a standard characterization of thin films of the single molecule magnet Terbium (III) bispthalocyaninato ($TbPc_2$) that, in line with previous experiments on the former ID08 beamline[3] was expected to be easily studied. The results (Figure 1a,b), which have been partially shown in a recent research paper[4] and are included in a submitted publication and in another manuscript in preparation by our group, show low temperature XMCD hysteresis measurements with a wider magnetization loops compared to the ID08 measurements thanks to the faster field sweep rate (2.6T/min) achievable after the upgrade to ID32.

These measurements have been performed by using the "on the fly mode" developed by the ID32 team in collaboration with our group specifically for this experiment.

In the following we moved to the investigation of Co-based chains. The samples were studied as single crystals, powders deposited on copper and microcrystals deposited on graphite. The measurements, performed at the lowest temperature achievable (nominal value T=5K, measured on sensor D), showed magnetic dichroism at the Co L_3 edge but, contrary to the magnetometry measurements,[1,2] none of the cobalt chains samples exhibit an open magnetic hysteresis, as illustrated in Figure 1 c,d. It was later shown by magnetometry measurements on some of the samples studied at ESRF that the material had not lost its single chain magnet behaviour after the X-ray study, and still exhibited low temperature hysterisis loops similar to the pristine material.

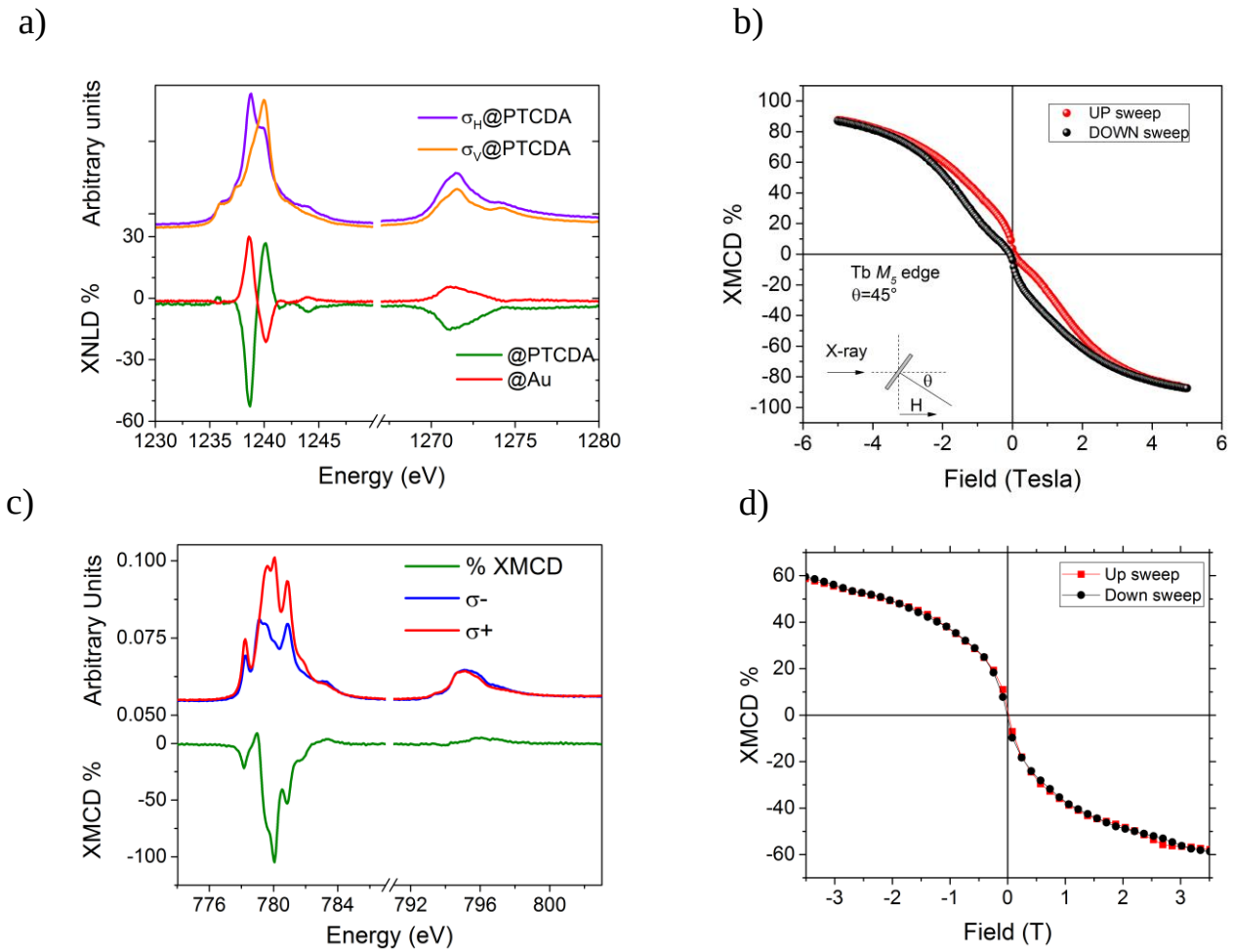

Figure 1 a) Top: XAS at the Tb M_5 edge of a 20nm $TbPc_2$ film deposited on a layer of perylene tetracarboxylic dianhidride (PTCDA) using linearly polarized light at an angle of 45° between the beam and the sample. **Bottom:** XNLD spectrum of a thick $TbPc_2$ film deposited on PTCDA and on policrystalline gold. **b)** XMCD hysteresis of a 100nm $TbPc_2$ film on polycrystalline gold at T=5K (nominal temperature of sensor D, nearest to the sample) and an angle of 45° between the beam and the sample. **c) Top:** XAS at the Co L_3 edge of $[Co(hfac)_2NaphNN]_n$ powders deposited on copper foil using circularly polarized light, at T=5K nominal temperature (sensor D, nearest to the sample). Bottom: XMCD spectrum of the same sample. **d)** XMCD hysteresis of $[Co(hfac)_2NaphNN]_n$ powders deposited on copper foil, measured at T=5K nominal temperature.

We attribute the discrepancy between magnetometry and XMCD to different sampling volumes of the two techniques and to a likely temperature difference between the measured one and the real temperature of the sample due to the imperfect thermal contact between the sample holder and the cold finger through the Stycast epoxy layer.[4]

1. Vaz, M. G. F. *et al.* A Cobalt Pyrenylnitronylnitroxide Single-Chain Magnet with High Coercivity and Record Blocking Temperature. *Chem. Eur. J.* 5460–5467 (2014). doi:10.1002/chem.201304852
2. Cassaro, R. A. A. *et al.* A Single-Chain Magnet with a Very High Blocking Temperature and a Strong Coercive Field. *Inorg. Chem.* **54,** 9381–9383 (2015).
3. Margheriti, L. *et al.* X-ray detected magnetic hysteresis of thermally evaporated terbium double-decker oriented films. *Adv. Mater.* **22,** 5488–93 (2010).
4. Kummer, K. *et al.* The high-field magnet endstation for X-ray magnetic dichroism experiments at ESRF soft X-ray beamline ID32. *J. Synchrotron Radiat.* **23,** 464–473 (2016).