



	Experiment title: Tailoring the magnetism of 4f rare-earth atom lattices formed by metal-organic coordination	Experiment number: HC-4830
Beamline: ID32	Date of experiment: from: 24/03/2022 to: 03/04/2022	Date of report: 06/09/2022
Shifts: 18	Local contact(s): Roberto Sant	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Marina Pivetta - EPFL Lausanne Stefano Rusponi - EPFL Lausanne		

Report:

A single atom with long spin lifetime represents the prototype of the smallest bit for data storage. So far, single atom magnets have been obtained by adsorbing a 4f rare-earth atom onto well-defined sites at surfaces [1-3], or by inserting it into custom-designed molecular frames [4-7]. Here, we aim at combining the two approaches and use surface-adsorbed rare-earth atoms coordinated with organic ligands to realize 2D self-assembled metal-organic networks with tunable magnetic properties. As compared with the isolated adatom case, a 2D metal-organic network has the advantage of providing an ensemble of periodically spaced single atom magnets, all with identical environment and structurally robust against thermal disordering, whose magnetic properties are determined by the choice of the rare earth element, supporting substrate and coordinating molecules. For the present proposal, coordination with tetraphenyl-dicarbonitrile (NC-Ph₄-CN) molecules provides high-symmetry C_{5v} crystal field, while the use of graphene as substrate minimizes spin-electron and spin-phonon scattering. The choice of the rare earth species, with oblate or prolate 4f charge distribution and different total angular momentum J, is expected to determine the orientation of the magnetization easy axis upon coordination [8].

All the samples were prepared *in-situ*. The metal-organic structures were grown at room temperature by successive deposition of molecules and rare earth (RE) atoms onto the graphene/Ir(111) surface. We used NC-Ph₄-CN molecules as organic ligand, and Tb, Dy, Ho, Er as RE elements. For each RE, several samples have been prepared for coverage calibration purposes. Ideally, a surface completely covered by the metal-organic structures corresponds to a RE coverage of the order of 0.5% of ML, with 1 ML defined as 1 RE atom per graphene unit cell. XAS and XMCD were acquired at the RE M_{4,5} edges in order to access the electronic state of the RE and the L and S moments. We acquired XMCD spectra as a function of the incidence angle to investigate the easy magnetization axis and the magnetic field dependence of the XMCD intensity to investigate the magnetization reversal mechanism. Further, XMLD spectra provide additional information on the effect of the ligand field on the RE 4f charge distribution. The measurements were carried out at the lowest reachable temperature of ~6 K and magnetic fields up to 7 T.

As mentioned in our feedback form, at least 4 out of the 18 allocated shifts were lost because of technical problems (computer failure, end station problems with cryogenic parts). In addition, the quality of the signal was not always satisfactory. In some cases, many more spectra had to be acquired to try to compensate for that.

A preliminary analysis of the data obtained for the metal-organic structures formed by NC-Ph₄-CN molecules and the RE atoms has been carried out. The results are summarized below.

a) When included in the metal-organic structures, all the investigated elements display 4fⁿ⁻¹ electronic configuration, where the 4fⁿ configuration is the one corresponding to the atom in the gas phase. This is in contrast with what has been observed for most of the RE as isolated adatoms on the same surface: in fact, only Tb was found in the 4fⁿ⁻¹ configuration as adatom, while Dy, Ho and Er displayed 4fⁿ configuration [9]. Therefore, coordination with the organic ligands promotes a change in the 4f occupation, with one 4f electron likely transferred to the outer 6s5d shell or farther to the molecular ligand.

b) To highlight the magnetic anisotropy of each species, we have performed angular dependent XMCD measurements. Figure 1 displays the normalized XMCD intensity as a function of the incidence angle. These data show that Tb, Dy and Ho display in-plane magnetization easy axis, while Er displays out-of-plane easy axis. This behavior can be understood considering the 4f spatial distribution of the different species. In the presence of equatorial charge, Tb, Dy, and Ho, classified as oblate, tend to low-J_z ground states corresponding to in-plane magnetization easy axis. For Er, being prolate, equatorial coordination promotes high-J_z states corresponding to an out-of-plane magnetization easy axis.

c) No magnetic hysteresis could be detected, for any of the investigated elements.

d) Multiplet calculations will be carried out to determine the exact J_z ground state as well the energy splitting of the excited spin states responsible for the different strength in the observed anisotropy, and to identify the relaxation pathways for all the investigated elements.

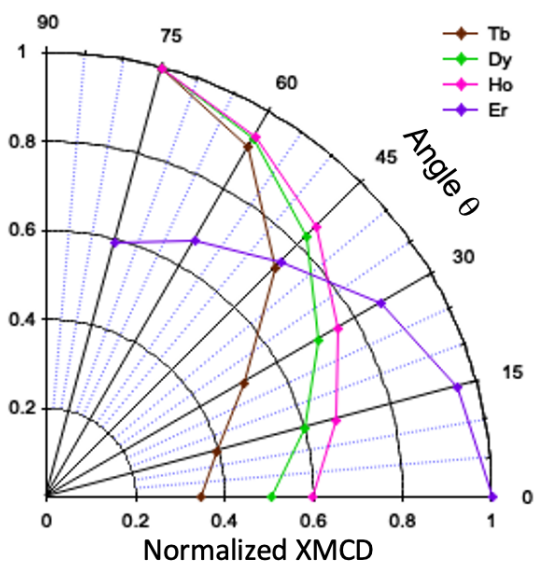


Fig. 1: Normalized XMCD intensity measured as a function of the incident angle θ ($\theta = 0$ corresponds to normal incidence). Tb, Dy, Ho display in-plane magnetization easy axis, while Er displays out-of-plane easy axis. Among the investigated elements, Tb shows the strongest anisotropy.

- [1] R. Baltic, M. Pivetta, F. Donati, *et al.* Nano Lett., **16**, 7610 (2016)
- [2] F. Donati, S. Rusponi, S. Stepanov, *et al.* Science, **352**, 318 (2016)
- [3] A. Singha, P. Willke, T. Bilgeri, *et al.*, Nat. Commun., **12**, 4179 (2021)
- [4] N. Ishikawa, M. Sugita, T. Ishikawa, *et al.*, J. Am. Chem. Soc. **125**, 8694 (2003)
- [5] C. A. P. Goodwin, F. Ortu, D. Reta, *et al.*, Nature **548**, 439 (2017)
- [6] F.-S. Guo, B. M. Day, Y.-C. Chen, *et al.*, Science **362**, 1400 (2018)
- [7] C. A. Gould, K. R. McClain, J. M. Yu, *et al.*, J. Am. Chem. Soc. **141**, 12967 (2019)
- [8] J. D. Rinehart and J. R. Long, Chem. Sci. **2**, 2078 (2011)
- [9] R. Baltic, F. Donati, A. Singha, *et al.*, Phys. Rev. B **98**, 024412 (2018)