ESRF	**Experiment title:** Magnetic signatures of coordinating atoms in monodomain metal-organic nanoporous networks.	**Experiment number**: HC-3596
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Shifts: 18	**Local contact(s)**: Emilio Velez-Fort and Nicholas Brooks	*Received at ESRF:*

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Report:

General evaluation of the beamtime

We are quite satisfied by the outcome of this experimental run and the support received by the local staff. The measurements that we carried out point towards very interesting results that must be analysed in depth. During this beamtime we were able to measure different samples. The obtained data was in some cases enough to finish previous studies, while for other systems the results can only be considered preliminary.

Carried measurements and sample preparations

The core of our measurements consists in linear dichroism at normal (0º) and grazing (70º) incidence as function of the magnetic field. In parallel to these single dichroic spectra, we also recorded hysteresis loops of the prepared systems. Each sample measured took roughly a day because the signal of interest was weak with respect to the large bulk background as it came from the surface and the amount of material is scarce (only a few tenths of a monolayer). As a matter of fact, we required the repetition of every single spectrum (generally 8 times per light polarization and magnetic field applied) to obtain an acceptable signal to noise ratio.

Given the long acquisition times and in order to reduce dead times by sample preparation and sample exchange, we worked in parallel with three different substrates: two Cu(111) crystals and one Au(111). The sample preparations and characterizations by means of STM and LEED were carried out simultaneously to the XAS/XMCD measurement of a prepared sample. Moreover, to have a reference of metal magnetic signal without molecular coordination, all the measurements were repeated without molecules. To save time, we used in some cases a mask when evaporating metals in order to have two different metal coverage regions within the same crystal.

The samples that we measured (in chronological order) were the following:

i) Fe (islands)/Cu(111). The Fe was deposited with the substrate at RT and used as reference for sample ii). Two different Fe coverage regions were obtained using the mask.

ii) Fe (nanodots)/DCA/Cu(111). The Fe was deposited with the substrate at RT. Two different Fe coverage regions were obtained using the mask (similar Fe amounts to i) were deposited).

iii) Fe (dendritic islands)/Cu(111). The Fe was deposited with the substrate at LT (110 K) and used as reference for sample iv). Two different Fe coverage regions were obtained using the mask.

iv) Fe (nanodots)/DCA/Cu(111). The Fe was deposited with the substrate at LT (110 K). Two different Fe coverage regions were obtained using the mask (similar Fe amounts to i), ii) and iii) were deposited).

v) Sm(single atoms)/DCA/Cu(111). Two different Sm quantities were evaporated on two different molecular phases: more quantity in a compact phase and less in the porous one.

vi) Clean Au(111) for data treatment of sample viii).

vii) Sm(clusters)/Cu(111). The same Sm quantities than in sample v) was deposited and used as reference, as well as the measurement of clean Cu(111) signal for data treatment.

viii) Fe coordinated with DCA (half of the sample) and Co coordinated with DCA (on the other half) /Au(111). Mask was used to evaporate Fe or Co in both regions.

Results from this beamtime

Our first goal was to study the magnetic fingerprints of Fe clusters when the molecular network was present on the surface. In our home lab, we had previously studied the variation of Fe clusters size as a function of Fe coverage and deposition temperature. We have observed that there is a correlation between the Fe nanodot size and the XMCD signal, which leads to a correlation between size, orbital moment and coercive field. Particularly clear are the hysteresis loops, which exhibit larger coercive fields as the cluster size is reduced (which occurs for the lowest deposition temperature). A paper communicating these results is drafted and to be submitted in the following month.

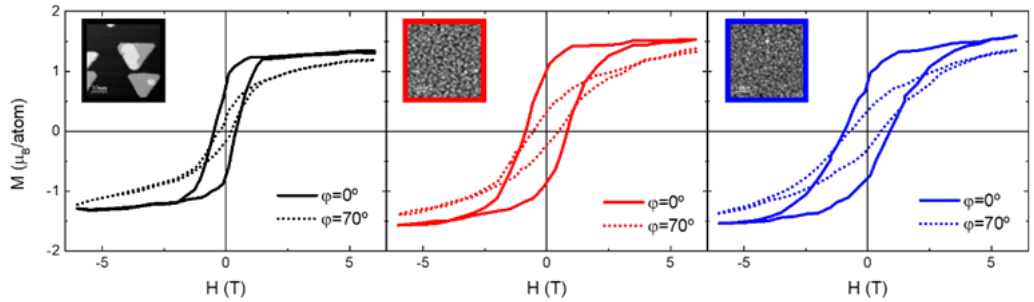

Figure 1. *Hysteresis cycles normalized for the total magnetic moment obtained with the 3d rules for three samples: i) Fe islands on Cu(111); and Fe clusters on DCA network deposited at ii) RT and iii) LT.*

The second goal was to study the magnetic behaviour of single Sm atoms deposited on the DCA network. We reproduced the systems we did in our home lab that show by STM that the evaporated Sm atoms adsorb on top of the coordinating Cu adatoms. Importantly, these Sm atoms follow the geometry of the Cu adatoms array in the underlying molecular layer. We have performed XAS/XMCD measurements of Sm deposited on two different phases: a compact phase (where the Sm interatomic distance is lower) and a porous phase (where this distance is higher). Preliminary results show that the normalized XMCD spectra show a dominant peak for the case of the porous phase, where the Sm interatomic distance is larger, especially for normal incidence.

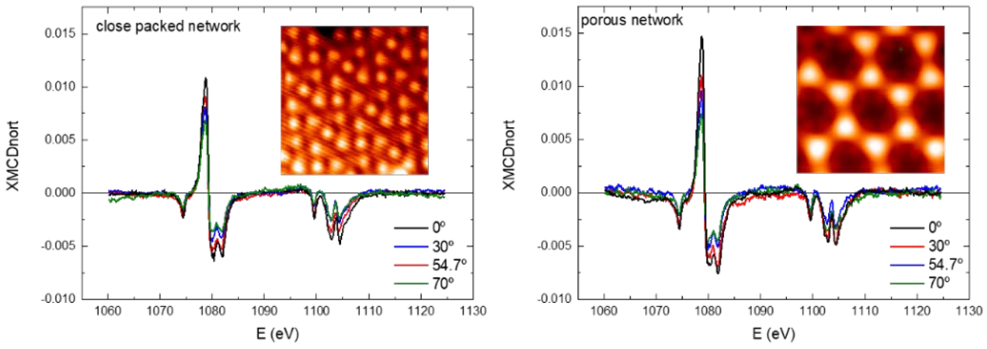

Figure 2. *XMCD spectra of Sm as a function of angle for compact and porous DCA network phases. Inset images: 5x5nm^2. Close packed image: 50pA; 1V. Porous image: 50pA; -1V.*

Finally, we studied the magnetic signal of Fe and Co atoms when these elements coordinate the metal-organic network of DCA molecules. To avoid spontaneous formation of DCA-Cu bonds we required the use of a different substrate than Cu(111). In particular we studied Co,Fe+DCA on Au(111) although we could not achieve a high-quality network with few defects. We obtained a very weak Co and Fe signals in the XAS/XMCD spectra, so many scans to increase the statistics was required. The results remain inconclusive and better sample quality is mandatory to achieve proper XMCD and hysteresis datasets. These results must be repeated.

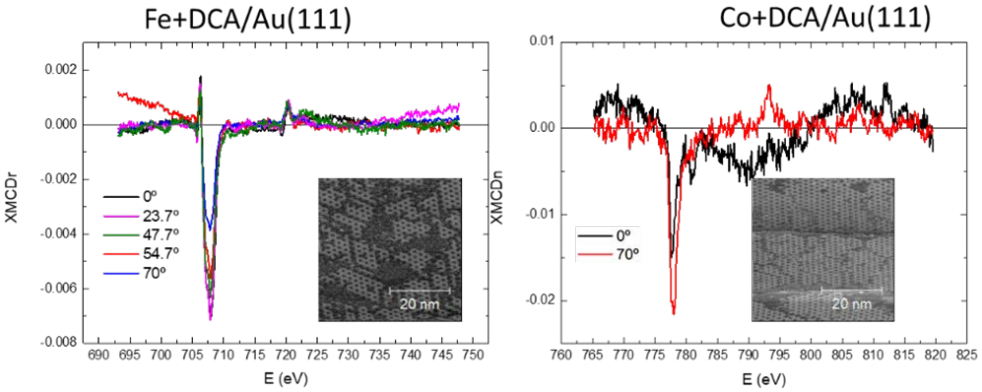

Figure 3. *Angle-dependent XMCD spectra for Fe and Co atoms co-deposited with DCA molecules that form the sought nanoporous metal-organic networks. The XMCD spectra show different behaviour with respect to isolated atoms or small clusters. Further measurements are necessary in this system.*

Outlook

In this beamtime, we could complete two of three goals we pursued. However, the case of Co and Fe as coordination atoms remains to be studied. In particular we must improve the sample quality to obtain better signal to noise ratios. We have performed further work at our home institution and have obtained high-quality networks both on Au(111) and on Ag(111). Another proposal will be submitted in order to carry out angle dependent XMCD spectra and hysteresis cycles measurements.