



	<b>Experiment title:</b> Magnetism in Novel Low-Dimensional Metal-Organic Coordination Systems at Surfaces	<b>Experiment number:</b> HE 1538
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<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Stefan Stanescu	
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Molecule-based magnetic materials have unique properties unavailable in conventional metal, alloy or metal-oxide magnets [1]. The novel approach developed by our group [2] allows the controlled assembly of organic molecular building blocks and transition metal atoms on single crystal surfaces into highly organized, low-dimensional metallosupramolecular architectures. The flexibility in the rational design of such systems provides prospects for the design of novel materials whose basic electronic and magnetic properties can be manipulated by tuning the symmetry and strength of the coordination bonds, the coupling to the substrate, and the system topology [2]. Experiment HE 1538 aimed at characterizing electronic structure and magnetism of Fe centers incorporated in metallosupramolecular systems, fabricated *in situ* by controlled sequential deposition of the organic linker 1,2,4-benzenedicarboxylic acid (terephthalic acid, TPA) and Fe atoms on an atomically clean Cu(001) substrate [3]. We are pleased to report here a number of significant results obtained in the experiment.

1) Thanks to the new sample preparation facility and scanning tunneling microscope (STM) installed at beamline ID8, we were able to carry out *in-situ* the growth and characterization of homogeneous, well-ordered metallosupramolecular architectures (Fig. 1). This achievement is of primary importance for studying this class of compounds with synchrotron radiation and was decisive for the success of our experiments. Moreover, the sample preparation and STM analysis were carried out in parallel with x-ray magnetic circular dichroism (XMCD) experiments on multiple substrates, thus maximizing the use of the photon beam.

2) X-ray absorption spectroscopy (XAS) and XMCD were combined to gather, for the first time, detailed information on the valence character of transition metal centers in coordination architectures synthesized at surfaces. A fundamental question that STM and other methods are unable to target is the relative influence of metal substrate and ligands in the electronic ground state (and corresponding magnetic moment) of the metal center. The rich multiplet structure observed in XAS and corresponding XMCD over the Fe  $L_{2,3}$  edges (Fig. 2 a, b) for mononuclear Fe-(TPA)<sub>4</sub> compounds compared to the relatively featureless spectra of Fe atoms adsorbed on Cu(001) (Fig. 2 b, inset) indicates the dominant influence of the ligands on the metal center ground state. This striking result proves that the genuine coordination architectures have been obtained and suggests that the rich variety of motifs and design principles for coordination architectures can be in general employed at surfaces, thus opening a novel approach to effectively tune the valence state and magnetic moment of transition metal centers at surfaces by an appropriate choice of the ligands and assembly protocols.

3) XMCD data allowed to determine the existence of a magnetic moment localized on the Fe atoms in Fe-(TPA)<sub>4</sub>. A preliminary analysis reveals partial quenching of the orbital moment, as expected for a square-planar ligand field. The magnetization curves show paramagnetic behavior, signaling a negligible or weak magnetic coupling between adjacent Fe centers.

The experiment took advantage of the high radiation flux at the ID8 beamline and of the high magnetic field (7 T) and variable temperature range (6-300 K) available at the experimental station. Metal-organic architectures were prepared by sequential evaporation of TPA (0.6-1 ML) and Fe (0.03-0.06 ML) on Cu(001) at 450 K [3], followed by *in situ* characterization by STM at room temperature. Subsequently exclusively well-defined phases were transferred into the cryo-magnet chamber. XAS at the L<sub>2,3</sub> edges was performed in total electron yield mode using circularly polarized light. XMCD was recorded by switching both light polarization and sample magnetization in magnetic fields up to 6 T.

Exemplaric STM data for disordered and well-defined metal-organic arrangements obtained in the present experiment are shown in Figs. 1a and b, respectively. STM was crucial to select only the homogeneous phases for XMCD analysis. In Fig. 1 b, extended well-ordered arrays of metal-organic complexes develop on the surface, occupying whole terraces on a mesoscopic scale. The complexes are constituted of cloverleaf arrangements comprising mononuclear iron centers, coordinating in a square-planar unidentate fashion four surrounding TPA ligands (cf. inset of Fig. 1b) [3]. The packing of individual Fe-TPA coordination complexes results in an extended long-range ordered superstructure, where the Fe atoms span a square array with a 15.3 Å stride along the high-symmetry substrate directions (i.e., a (6x6) unit cell, cf. inset in Fig. 1b).

XAS spectra at the L<sub>2,3</sub> Fe edges for the structure shown in Fig. 1b are depicted in Fig. 2a. They were recorded in the out-of-plane geometry, with the photon helicity parallel ( $\leftarrow^+$ ) and antiparallel ( $\leftarrow^-$ ) to the substrate normal. The spectra were taken in a field of 6T applied along the incident beam and at a temperature of 10 K. Both the L<sub>3</sub> and L<sub>2</sub> white lines show a pronounced substructure which is absent in simple Fe/Cu(100) at comparable coverages indicating the dominant influence of ligand-fields in the electronic configuration of the iron caused by carboxylate coordination. Preliminary calculations within a cluster model suggest that the Fe centers are predominantly of  $d^6$  character. Notably, Fe-TPA XAS is similar to that known for biologically relevant mono- and di-nuclear iron complexes [4]. Moreover, the out-of-plane and in-plane XAS and XMCD (Fig. 2b) present significant differences, which are not observed in bulk Fe compounds with similar coordination [4]. These differences are associated with the square-planar Fe-carboxylate coordination in the present system and are currently being investigated to gain more detailed information about the symmetry of the Fe  $d$  orbitals in the TPA complexes. Oxygen K-edge XAS also present a remarkable difference between in-plane and out-of-plane spectra (not shown here).

The XMCD (fig. 2b) provides information about the magnetization state of the iron atoms. We observe that the dichroism disappears when the magnetic field is switched off, proving paramagnetic behavior for the studied system. The weak magnetic coupling between the Fe centers in the structure is explained by their substantial separation (15.3 Å in Fig. 1b), with the TPA molecules not being able to couple adjacent Fe moments. The possibility of employing smaller linker molecules, and/or fully 2-D reticulated architectures to mediate a ferromagnetic or antiferromagnetic interaction between the transition-metal centers is of great interest for future studies. Comparing the XMCD spectra with the field parallel and perpendicular to the surface reveals a further important point, namely the anisotropy of the Fe moment. A quantitative evaluation of the XMCD data is currently underway to derive the spin and orbital moment for Fe-TPA depending on the direction of the applied field.

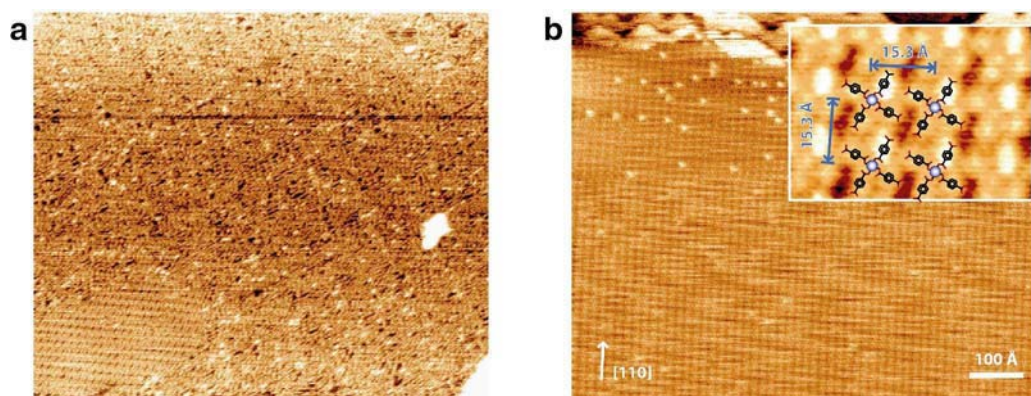
In conclusion, our results represent the first characterization of the electronic and magnetic properties of transition metal centers in metallosupramolecular compounds synthesized at surfaces. The results are extremely promising and suggest that the controlled fabrication of metallosupramolecular architectures at surfaces offers a great potential to develop novel molecule-based magnetic materials, which can be comprehensively characterized by synchrotron radiation spectroscopy. We are indebted to the staff of beamline ID8 for the excellent working conditions of the STM and XMCD set up.

[1] *MRS Bull.* 2000, 25(11), Guest Editor: J. S. Miller and A. J. Epstein; E. Coronado et al., *Nature* **408**, 447 (2000); S.S.Y. Chui et al., *Science* **283**, 1148 (1999).

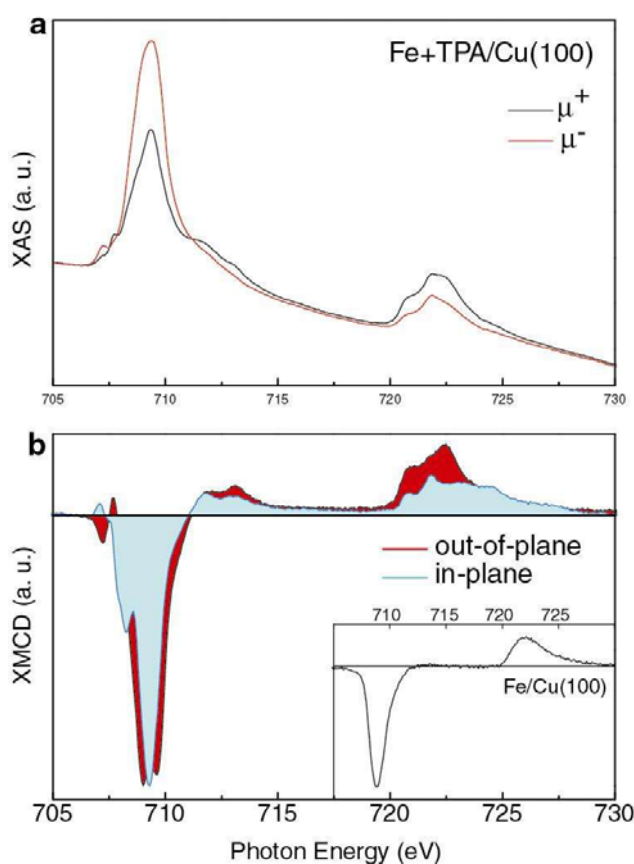
[2] N. Lin et al., *Angew. Chem. Int. Ed.* **24**, 4779 (2002); A. Dmitriev et al., *Angew. Chem. Int. Ed.* **115**, 2774 (2003); H. Spillmann et al., *J. Am. Chem. Soc.* **125**, 10727 (2003); S. Stepanow et al., *Nature Mat.* in press (2004).

[3] M. Lingenfelder, H. Spillmann, A. Dmitriev, S. Stepanow, N. Lin, J.V. Barth and K. Kern, *Chem. Eur. J.* in press

[4] S. J. George et al., *J. Am. Chem. Soc.* **114**, 4426 (1992); J. van Elp et al., *Proc. Natl. Acad. Sci. USA* **90**, 9664 (1993); G. Peng et al., *J. Am. Chem. Soc.* **117**, 2515 (1995); H. Wang et al., *J. Am. Chem. Soc.* **119**, 4921 (1997); E. C. Wasinger et al., *J. Am. Chem. Soc.* **125**, 12894 (2003).



**Figure 1:** STM images of the Cu(001) surface covered with Fe-TPA coordination compounds. (a) Inhomogeneous aggregates. (b) Well-ordered homogeneous phase comprising a regular  $\text{Fe}(\text{TPA})_4$  array with mononuclear Fe centers. The inset shows details of the corresponding Fe-TPA coordination. STM imaging followed *in situ* preparation of the metallosupramolecular system prior to XMCD analysis.



**Figure 2:** (a) Out-of-plane XAS and (b) XMCD spectra recorded over the Fe  $L_{2,3}$  edges for the  $\text{Fe}(\text{TPA})_4$  arrays shown in Fig. 1b. The XMCD is reported also for the in-plane geometry ( $70^\circ$  off normal) revealing clear changes depending on the direction of the light propagation vector and magnetic field. The spectra were taken in a field of 6 T at a temperature of 10 K. The inset shows the Fe XMCD obtained for an equal amount of Fe atoms deposited on the pristine Cu(100) substrate.