



	Experiment title: Tuning magnetism and magnetochemical response of surface-supported metallocsupramolecular architectures by control of dimensionality and topology	Experiment number: HE 1747
Beamline: ID08	Date of experiment: from: 17/11/2004 to: 26/11/2004	Date of report:
Shifts: 24	Local contact(s): Dr. P. Bencok	<i>Received at ESRF:</i>
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The design of molecule-based clusters, polymers and networks with novel electronic and magnetic properties has become a major goal in the area of nanostructured materials. Recent efforts have focused on transferring concepts derived from supramolecular chemistry to the fabrication of low-dimensional molecular architectures on metal and semiconducting substrates. The original approach developed by our group relies on the sequential deposition of polyfunctional organic molecules (terephthalic acid, hereafter indicated as TPA) and transition metal atoms (Fe) on atomically clean metal substrates (Cu, Au). Scanning tunneling microscopy (STM) images (Fig. 1) show that supramolecular architectures self-assemble at elevated substrate temperatures, forming highly-ordered two-dimensional metallocsupramolecular arrangements [1]. Experiment HE1747 aimed at characterizing the nature of the chemical bonds between organic linkers and metal centers in metal-organic complexes, formed *in situ* at a metal substrate, and at controlling the magnetic response of the metal centers via ligand coordination. Here we report on the electronic and magnetic properties of the mononuclear Fe(TPA)₄ configuration, constituted by four TPA molecules linked via oxygen ligands to a central Fe atom [Fig. 1 (c) and (e)], compared to those of the O-Fe(TPA)₄ configuration, where the Fe ions are bound to four oxygen atoms in the surface plane and an on-top additional oxygen [Fig. 1 (d) and (f)]. The investigations of di-nuclear Fe complexes performed during the same experiment will be described in a forthcoming publication for reasons of space.

The preparation of mono- and di-nuclear Fe-TPA compounds was carried out *in-situ* at the ESRF taking advantage of the dedicated STM chamber connected to the high-field magnet of the ID08 beamline. The STM images acquired prior to the XAS measurements, shown in Fig. 1 (a) and (e), allowed us to optimize the self-assembly parameters of the supramolecular structures (order of the molecular precursor layer, Fe-TPA stoichiometry, annealing temperature) and to ensure the homogeneity of the samples by probing different regions of the surface. XAS and XMCD spectra were measured at the $L_{2,3}$ Fe edges in total electron yield mode using circularly polarized light with 99% polarization in magnetic fields of up to 6 T. The data were recorded at temperatures spanning from 5 to 300 K. To probe the out-of-plane and in-plane magnetization the sample was rotated between normal incidence ($\theta = 0^\circ$) and grazing incidence ($\theta = 70^\circ$) with respect to the direction of the photon beam.

Figure 2 shows the total XAS spectra of the Fe(TPA)₄ and O-Fe(TPA)₄ networks, compared to that of a comparable amount (0.025 monolayers) of Fe deposited on clean Cu(100). The narrowing of the spectral features and the multiplet structure in the Fe(TPA)₄ XAS compared to Fe/Cu(100) reveals that strong coordination bonds exist between the central Fe atoms and the carboxylate ligand groups of TPA, which significantly affect the configuration of the Fe electrons. The strength of the lateral coordination bonds is at the origin of the increased thermal stability of Fe(TPA)₄ (up to $T = 500$ K) compared to the more common hydrogen bond stabilized supramolecular surface structures studied up to this date. The additional oxygen

ligand in the O-Fe(TPA)₄ phase further modifies the Fe electronic configuration relative to Fe(TPA)₄, as shown by the sharpening of the multiplet structure and by the shift of the spectral weight at the *L*₃ edge in Fig. 2. While the Fe(TPA)₄ XAS is similar to those previously published high-spin monomeric and dimeric ferrous complexes [2], the O-Fe(TPA)₄ XAS spectrum can be simulated by the exact diagonalization of an atomic many-body Hamiltonian for a Fe²⁺ ion involving the onsite energies of the Fe 2*p* and 3*d* states, full multiplet Coulomb interaction within the Fe 3*d* manifold and between the 2*p* and 3*d* manifolds and spin-orbit interaction in the 3*d* and 2*p* levels [3]. Crystal field of appropriate symmetry (D_{4h}, 10Dq = 0.5 eV, δ₁ = 0.25 eV, δ₂ = 0.19 eV) was also included and the spectra from the first six initial eigenstates were averaged with appropriate Boltzmann weights at the experimental temperature of 5 K. The good agreement between the calculated and experimental XAS shows that the ligand field dominates over the charge transfer with the substrate in determining the valence state of the metal centers in the supramolecular networks. The similarity between the Fe XAS of Fe(TPA)₄ assembled on Cu(100) and Au(111), not shown here, lends further support to this result. This is a very important point since it proves that genuine coordination architectures have been obtained and shows that the design principles of coordination chemistry can be generally employed at surfaces to develop molecule-based materials with tunable electronic and magnetic properties.

Low-temperature XMCD measurements (Fig. 3) show that both phases present a sizeable dichroism indicating that the Fe *d*-states are exchange-split in the presence of the ligand field and possess a nonzero magnetic moment. There are however remarkable differences between Fe(TPA)₄ and O-Fe(TPA)₄ brought about by the different ligand configuration. First, the magnitude of the Fe moment is significantly larger in O-Fe(TPA)₄ compared to Fe(TPA)₄, as shown by the amplitude of the XMCD intensity relative to the total XAS signal in the two cases. Second, the magnetic anisotropy easy axis changes abruptly from in-plane in Fe(TPA)₄ to out-of-plane in O-Fe(TPA)₄, as given by the comparison of the XMCD at θ = 0° and 70° for each phase. The sum-rule derived magnetic moments obtained after subtraction of the substrate background signal and the step-like contribution of 2*p*-4*s* transitions are reported in Table I. The spin configuration appears to be intermediate with respect to the low-spin (S=0) and high-spin (S=2) states of an Fe²⁺ ion. This can be attributed to the strength and symmetry of the ligand field as in planar Fe²⁺ compounds (e.g., Fe-phthalocyanines where S=1 [4]) but also to the presence of covalent interactions between the Fe atoms and the Cu substrate leading to noninteger spin values. We note also that the reported magnetic moments, measured at 6 T and 5 K, do not represent the full saturated values (see the magnetization curves in the insets of Fig. 3) and that the saturation moments might differ in the in-plane and out-of-plane directions, as in single-crystals of high-spin Fe²⁺ tetragonal compounds [5]. The magnetic anisotropy energy changes sign but is significant in magnitude for both Fe(TPA)₄ and O-Fe(TPA)₄ and could be exploited to stabilize the Fe magnetic moment by either going to lower temperatures or designing similar compounds with even larger anisotropy fields.

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 multiplet structure observed in the *L*_{2,3} XAS of Fe in Fe(TPA)₄ and O-Fe(TPA)₄ self-assembled on Cu(100) and Au(111) compared to the relatively featureless spectra of Fe deposited on the bare substrates indicates the dominant influence of the ligand bonds on the electronic ground state of the metal centers, and its ferrous valence. XMCD data demonstrate the presence of a sizeable magnetic moment localized on the Fe atoms in Fe(TPA)₄. The modification of the ligand field in the O- Fe(TPA)₄ phase significantly enhances the magnitude of the Fe magnetic moment and causes the reversal of the magnetic anisotropy axis from in-plane to out-of-plane. These results show that the intrinsic magnetization parameters of supported supramolecular networks can be effectively tuned by controlling the number and symmetry of organic linkers.

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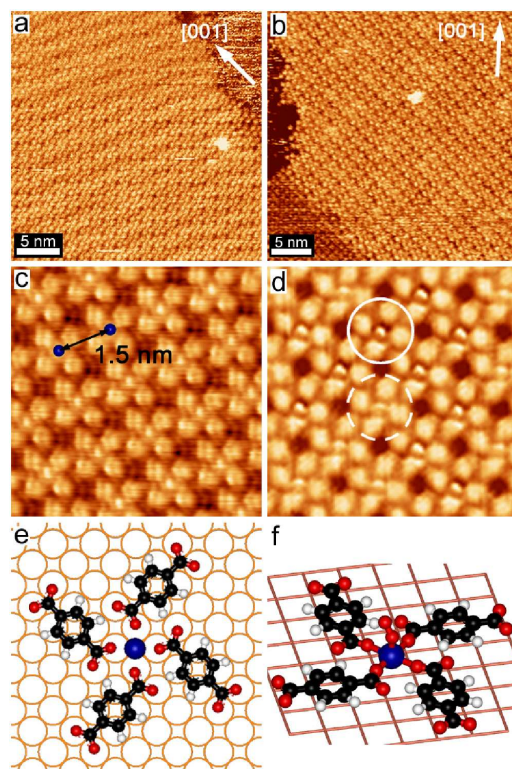


Fig. 1. STM images of (a) $\text{Fe}(\text{TPA})_4$ and (b) $\text{O-Fe}(\text{TPA})_4$ complexes arrays self-assembled on $\text{Cu}(100)$. (c) High-resolution topograph of $\text{Fe}(\text{TPA})_4$ array with Fe atoms marked by blue spheres. (d) High-resolution topograph of a mixed $\text{Fe}(\text{TPA})_4$ and $\text{O-Fe}(\text{TPA})_4$ phase. The presence of an additional oxygen linker in $\text{O-Fe}(\text{TPA})_4$ configuration (marked by solid circle) comparing to $\text{Fe}(\text{TPA})_4$ (marked by dashed circle) is evidenced by the presence of a dark feature at the Fe site. (e,f) Tentative structural models of the two configurations.

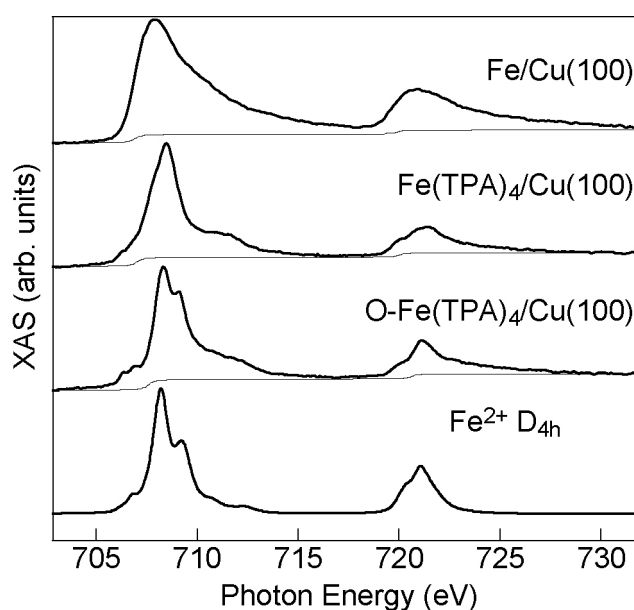


Fig. 2. Comparison between the Fe XAS spectra of 0.025 monolayers $\text{Fe}/\text{Cu}(100)$, $\text{Fe}(\text{TPA})_4$, $\text{O-Fe}(\text{TPA})_4$, and Fe^{2+} calculated spectrum in D_{4h} symmetry. The experimental spectra are shown after subtraction of the Cu background. The thin solid lines represent the intensity attributed to $2p-4s$ transitions.

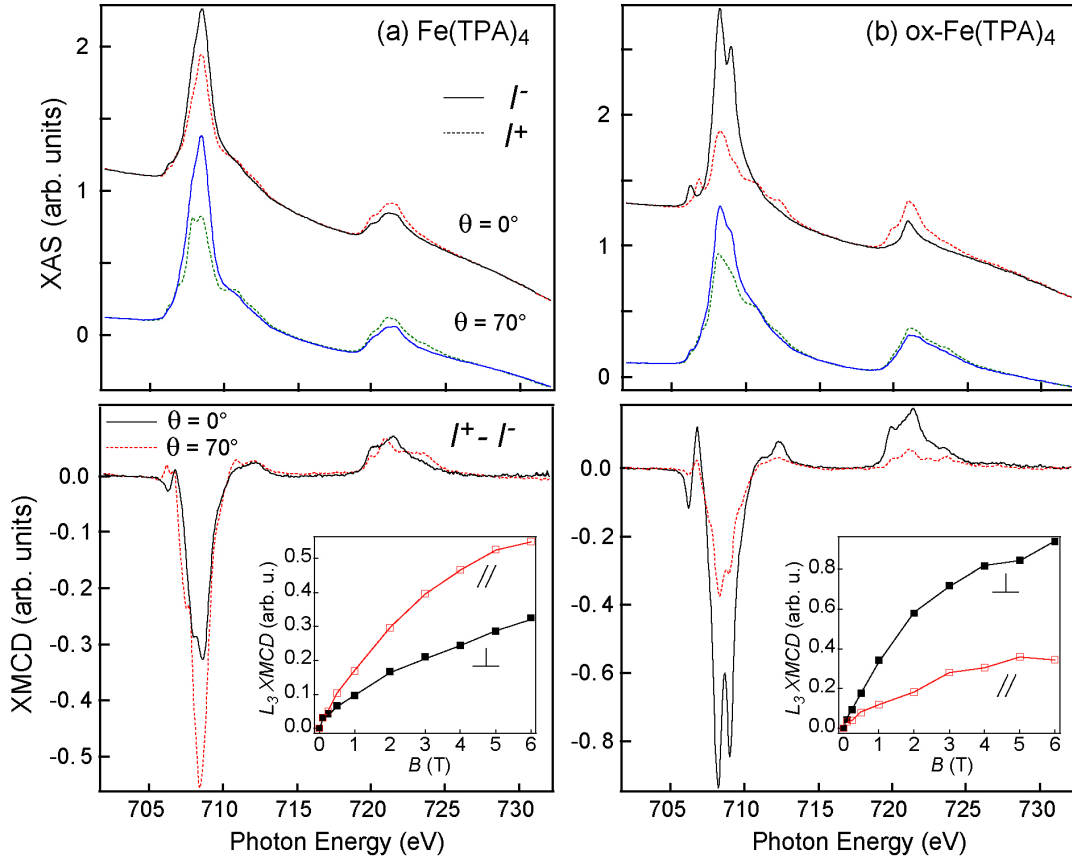


Fig. 2. XAS spectra recorded for parallel (I^+ , dotted line) and antiparallel (I^- , solid line) alignment of the photon helicity with applied field $B = 6$ T at $\theta = 0^\circ$ and 70° , $T = 5$ K for (a) $\text{Fe}(\text{TPA})_4$ and (b) $\text{O-Fe}(\text{TPA})_4$ coordination networks. The corresponding XMCD ($I^+ - I^-$) is shown in the bottom panels. The magnetization curves in the insets are obtained by recording the L_3 XMCD intensity at 708.3 eV as a function of B , for $\theta = 0^\circ$ (full squares) and $\theta = 70^\circ$ (open squares).

	$(m_S + m_T) / n_h [\theta = 0^\circ]$	$(m_S + m_T) / n_h [\theta = 70^\circ]$	$m_L / n_h [\theta = 0^\circ]$	$m_L / n_h [\theta = 70^\circ]$
$\text{Fe}(\text{TPA})_4$	0.29 ± 0.03	0.34 ± 0.03	0.05 ± 0.02	0.10 ± 0.02
$\text{O-Fe}(\text{TPA})_4$	0.64 ± 0.04	0.22 ± 0.04	0.13 ± 0.02	0.06 ± 0.02

Table I. Magnetic spin (m_S), dipole (m_T), and orbital (m_L) moment of Fe in the coordination network per number of unoccupied d -states (n_h) as derived by application of the XMCD sum rules to the data shown in Fig. 2. The values are given in Bohr magnetons, $n_h = 4$ in Fe^{2+} .