

Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface

The control of magnetic anisotropy is important for the development of metal-organic materials for magnetic applications, both at the single molecule and extended film level [1]. In so-called single molecule magnets, this is achieved by chemical modification of the environment and variations in the number of metal ions that carry the magnetic moment. For metal-organic layers in contact with a metal substrate or electrode, however, it was unclear whether such a strategy would be effective and whether these layers would display electronic and magnetic properties that are typical of molecules or metals. Experiments at beamline ID08 using a combination of scanning tunnelling microscopy (STM), X-ray magnetic circular dichroism (XMCD), and charge transfer multiplet calculations have provided a response to these questions.

Co-deposition of transition-metal ions and organic ligands on single-crystal surfaces offers the potential to design supramolecular metal-organic grids with programmable structural features, where the interaction with the substrate is used to stabilise a planar geometry [2]. This approach was favoured over the deposition of magnetic molecules synthesised in solution, since it allows a more direct comparison of the electronic configuration of the magnetic sites depending on the ligand and metallic environment. Figure 80 shows the supramolecular assembly of Fe and terephthalic acid (TPA) molecules on a Cu(100) surface. Each Fe atom is

coordinated to four TPA molecules through Fe-carboxylate bonds, with supramolecular $\text{Fe}(\text{TPA})_4$ units organised in a square lattice with $15 \times 15 \text{ \AA}^2$ periodicity. STM images indicate that, despite the 4-fold lateral coordination to the carboxylate ligands and the residual interaction with Cu, Fe centres are chemically active, forming an array of open coordination sites that may selectively bind other ligands, for example O_2 forming pyramidal-like $\text{O}_2\text{-Fe}(\text{TPA})_4$ complexes.

Pristine and O_2 -saturated $\text{Fe}(\text{TPA})_4$ monolayers were prepared and characterised *in situ*, exploiting the UHV STM facility connected to the XMCD end-station. X-ray absorption spectra (XAS) were recorded at the $L_{2,3}$ edges of Fe and K-edge of O, in magnetic fields of up to 6 T with the sample held at 8 K. The results (Figure 81), interpreted with the aid of charge transfer multiplet calculations, show that the Fe *d*-orbitals interact mainly with the O ligands and are only weakly perturbed by the metallic substrate. Furthermore, both $\text{Fe}(\text{TPA})_4$ and $\text{O}_2\text{-Fe}(\text{TPA})_4$ constitute high-spin Fe^{2+} complexes, against the tendency of the Cu electrons to reduce the Fe moment via *4s-3d* hybridisation and Kondo screening.

Angle-dependent XMCD measurements revealed strong in-plane magnetic anisotropy of $\text{Fe}(\text{TPA})_4$ complexes opposite to Fe/Cu(100) (Figure 81d) and that the easy axis direction can be controlled by the symmetry of the ligand bonds,

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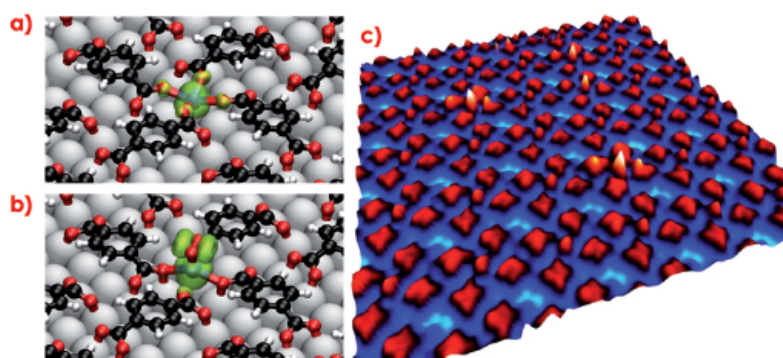


Fig. 80: Planar supramolecular layers of Fe-TPA complexes self-assembled on Cu(100). a) ball and stick model of $\text{Fe}(\text{TPA})_4$ array as calculated by density functional theory. Blue dots indicate the position of Fe atoms, red O, black C, white H; the green halo represents the spin density. b) $\text{O}_2\text{-Fe}(\text{TPA})_4$ array. c) STM image of a $\text{Fe}(\text{TPA})_4$ monolayer grown on Cu(100). Selective uptake of O_2 by Fe sites is indicated by a change of STM contrast (white spots). Lateral image size is $84 \times 84 \text{ \AA}^2$.

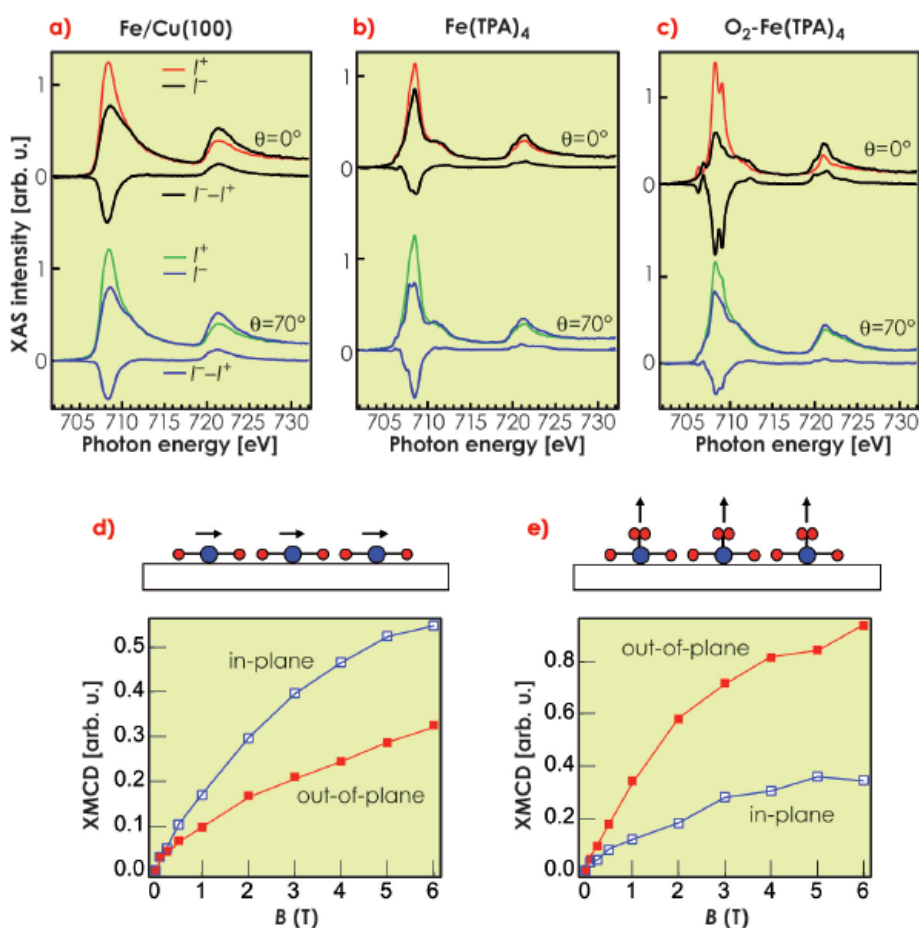


Fig. 81: Circularly polarised XAS of a) 0.025 monolayers Fe/Cu(100), b) Fe(TPA)₄, and c) O₂-Fe(TPA)₄ for parallel (+) and antiparallel (-) orientation of the photon helicity with field-induced magnetisation. Spectra were recorded in the electron-yield mode at normal ($\theta = 0^\circ$) and grazing incidence ($\theta = 70^\circ$), d) Field-dependent magnetisation of Fe(TPA)₄, and e) O₂-Fe(TPA)₄.

independently from the metal substrate. Apical O₂ ligands at Fe sites drive an abrupt spin reorientation transition, rotating the Fe easy axis out-of-plane and favouring the formation of an unusually strong orbital moment of about $0.55 \pm 0.07 \mu_B$ per Fe atom. With respect to bulk molecular crystals, the planar and open coordination structure of the self-assembled Fe array makes such a system extremely sensitive to chemisorption, providing straightforward control of the preferred Fe spin orientation.

In conclusion, we have demonstrated that it is possible to construct planar metal-organic networks and to control their magnetic properties at the interface with a metal substrate. This constitutes an essential step towards the inclusion of molecular materials into heterogeneous magnetoelectronic devices.

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Emerging magnetic moment in Pt₁₃ nanoparticles

A fascinating property of matter at the nanosize scale is the appearance of new physical phenomena which do not exist in the bulk. For example, bulk Pt has a very weak magnetic response, only present if a magnetic field is applied since it is a Pauli paramagnet. It is known that the presence of a magnetic material such as cobalt may induce a magnetic moment on Pt, this has been evidenced by X-ray magnetic circular dichroism (XMCD) of Pt covering a Co nanoparticle [1]. However, it has recently been found

that small Pt₁₃ clusters may develop a magnetic moment when embedded in NaY zeolite [2]. A number of questions remained open after this exciting report, based on conventional magnetisation measurements: what is the contribution to the spontaneous moment coming from the orbital moment, and whether the observed magnetic moment could have arisen from a spurious source such as Fe contamination of the zeolite.