

Magnetic memory of a single-molecule quantum magnet wired to a gold surface

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In the field of molecular spintronics¹, the use of magnetic molecules for information technology is a main target and the observation of magnetic hysteresis on individual molecules organized on surfaces is a necessary step to develop molecular memory arrays. Although simple paramagnetic molecules can show surface-induced magnetic ordering and hysteresis when deposited on ferromagnetic surfaces², information storage at the molecular level requires molecules exhibiting an intrinsic remnant magnetization, like the so-called single-molecule magnets³ (SMMs). These have been intensively investigated for their rich quantum behaviour⁴ but no magnetic hysteresis has been so far reported for monolayers of SMMs on various non-magnetic substrates, most probably owing to the chemical instability of clusters on surfaces⁵. Using X-ray absorption spectroscopy and X-ray magnetic circular dichroism synchrotron-based techniques, pushed to the limits in sensitivity and operated at sub-kelvin temperatures, we have now found that robust, tailor-made Fe₄ complexes retain magnetic hysteresis at gold surfaces. Our results demonstrate that isolated SMMs can be used for storing information. The road is now open to address individual molecules wired to a conducting surface^{6,7} in their blocked magnetization state, thereby enabling investigation of the elementary interactions between electron transport and magnetism degrees of freedom at the molecular scale^{8,9}.

The observation of a magnetic memory effect³ in single-molecule magnets (SMMs) has represented a breakthrough in nanomagnetism¹⁰. It has opened the exciting perspective of exploiting the information storage capability of individual SMMs, made even more appealing owing to their rich quantum behaviour^{4,11}. In fact, the combination of a large spin of the molecule with an easy-axis magnetic anisotropy results in an energy barrier that hampers the reversal of the magnetization, although the barrier can be cross-cut by a tunnelling mechanism for some particular values of the magnetic field⁴. Anchoring SMMs on conducting surfaces is required to make them individually addressable by scanning probes⁸, which enable both high-resolution morphological studies and local spectroscopic investigations¹². Moreover, the proposed scheme provides access to electron transport through the magnetic molecules, the target of a field that is referred to as molecular spintronics^{1,9}. Despite the successful efforts to organize SMMs on various substrates¹³ and the reported possibility to detect magnetic features of atoms^{14–16} or molecules

on surfaces^{17–20}, evidence that SMMs retain molecular magnetic hysteresis when wired to metallic surfaces is still lacking. Without such evidence, one of the pillars of this emerging field would break down.

Demonstration that SMM behaviour is not destroyed on interaction with the surface can be achieved by using synchrotron radiation at very low temperature. In fact, X-ray magnetic circular dichroism²¹ (XMCD) is a unique tool to provide a detailed magnetic characterization down to sub-monolayers of magnetic atoms²² or molecules^{2,5}.

Previous investigations have mainly focused on the archetypal dodecamanganese family of SMMs (Mn₁₂; refs 3,4), but adsorbates of Mn₁₂ complexes on gold undergo systematic reduction, with concomitant disappearance of magnetic hysteresis⁵. Moreover, even the surface layers of bulk Mn₁₂ samples show no magnetic hysteresis, probably owing to structural deformations²⁰. In contrast, we have found that a different class of SMMs comprising four high-spin iron(III) ions, Fe₄, exhibits the sought redox stability and structural robustness. Studies on bulk samples have revealed that Fe₄ clusters in the layers closer to the surface–vacuum interface retain both their static and dynamic magnetic features²⁰ and are therefore good candidates to investigate the existence of magnetic hysteresis in molecules grafted onto conducting surfaces.

In the propeller-like molecular structure of Fe₄ (see Fig. 1a), the outer individual $s = 5/2$ spins interact antiferromagnetically with the inner one, to give a ground $S = 5$ spin state characterized by an anisotropy barrier of about 16 K to be overcome for magnetization reversal^{23–25}. The ligands lying above and below the plane of the iron ions are derivatives of 2-hydroxymethyl-1,3-propanediol, which can be functionalized to promote interactions with different substrates as well as to enhance magnetic anisotropy^{23,24}. For deposition on gold surfaces, we have designed the sulphur-functionalized derivative [Fe₄(L)₂(dpm)₆] with H₃L representing 11-(acetylthio)-2,2-bis(hydroxymethyl)undecan-1-ol and Hdpm representing dipivaloylmethane²⁵. The compound can be isolated in pure, crystalline form and is completely stable in solution (see Supplementary Information).

A monolayer of Fe₄ molecules on a Au(111) surface was obtained by self-assembly from solution. Its scanning tunnelling microscopy (STM) characterization (Fig. 1b) carried out at room temperature in air confirms the surface coverage by a homogeneous layer of objects with size 2.5 ± 0.4 nm (see Fig. 1c and Supplementary Information), in good agreement with the molecular size

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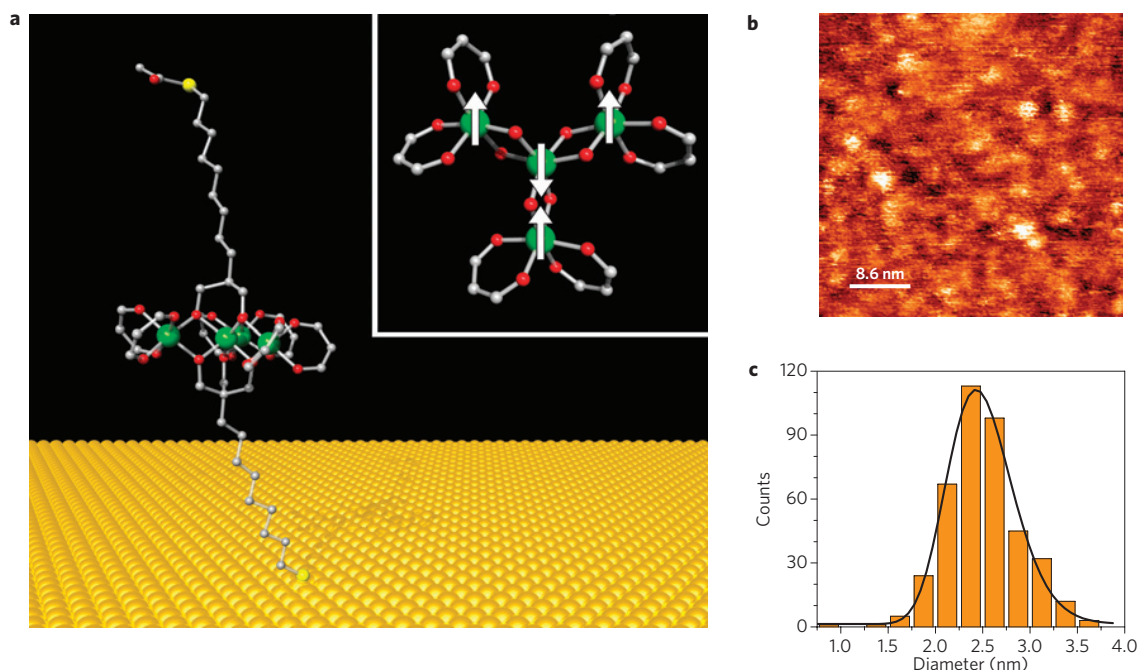


Figure 1 | Monolayer of Fe₄ on gold. **a**, Schematic diagram of the anchoring on a gold surface of the Fe₄ derivative studied in this work through its thiolate-terminated aliphatic chains. A view along the plane of the four metal atoms with the chains fully stretched has been chosen for the sake of clarity. Iron atoms are drawn as large green spheres, oxygen in red, carbon in grey and sulphur in light yellow. Inset: A view of the magnetic core structure of Fe₄, with the ground-state spin arrangement (white arrows). **b**, Room-temperature constant-current STM image of the Fe₄ monolayer obtained on a scan area of 55 × 55 nm² (bias voltage $V_b = 350$ mV, tunnelling current $I_t = 9$ pA). **c**, Statistical distribution of molecular diameters extracted from five images obtained in the same experimental conditions as in **b**. The diameters follow a log-normal distribution centred at 2.50 nm with a standard deviation of 0.14 nm (solid curve).

determined by X-ray diffraction. The gold–sulphur chemical affinity enables the selective formation of a single-layer-thick deposit, but no bidimensional order comparable to that observed in self-assembled monolayers of aliphatic thiols²⁶ can be detected in the STM topographic images. In fact, the shape of the molecule and the strong steric hindrance of the equatorial ligands are expected to prevent significant interactions between the aliphatic chains of adjacent molecules, a key factor in the formation of organic self-assembled monolayers.

The electronic structure of the layer has been investigated through X-ray absorption spectroscopy (XAS) with an endstation capable of reaching sub-kelvin temperatures^{27,28}. In Fig. 2a, we show the XAS spectra recorded at the Fe L_{2,3}-edge ($2p \rightarrow 3d$) on the Fe₄ monolayer with left- (σ_+) and right- (σ_-) hand circular polarization. The average spectra, calculated as $(\sigma_- + \sigma_+)/2$, coincide over the entire energy range with those recorded on a thick film of the same compound prepared by drop-casting (see Supplementary Information)²⁰, showing that the electronic structure of the molecule is fully preserved on grafting. However, the signal-to-background intensity ratio is about 30 times smaller in the monolayer as compared with the thick deposit and has been found reproducible over five different preparations. As the total-electron-yield mode used to detect X-ray absorption probes only the first few layers in bulk samples²⁹, the observed intensity fully confirms that we are actually monitoring a monolayer deposit.

Element- and surface-selective magnetometry has then been carried out by recording the dichroic component, that is, the difference between the XAS signals obtained using right-hand and left-hand circularly polarized X-rays, in an applied field of 3 T at 0.50 ± 0.05 K. The XMCD features (see Fig. 2b) and the XMCD/XAS intensity ratio (0.25–0.30) are identical to those observed in bulk samples. The XMCD/XAS ratio has to be regarded as a reliable fingerprint of the spin alignment within the tetra iron(III) core. In fact, owing to the very similar

coordination environment of the central and peripheral iron ions, an antiferromagnetic interaction is expected to afford an approximately halved XMCD/XAS ratio as compared with full polarization induced by the magnetic field (see Supplementary Information). Fragmentation into simple paramagnetic units or marked alterations of the core structure would then be accompanied by significant changes in the XMCD/XAS ratio as compared with the bulk, not observed here.

As the presence of hysteresis is directly related to the magnetic anisotropy, we have first investigated the field dependence of the XMCD signal at 709.2 eV at two different temperatures ($T = 1.5 \pm 0.1$ and 4.5 ± 0.1 K). Interestingly the magnetization isotherms so obtained do not rescale on a unique curve when plotted versus H/T (Fig. 2c), in agreement with what is expected for an anisotropic paramagnet. The field dependence of the XMCD signal compares well with the magnetization curve calculated using the spin Hamiltonian that describes the magnetic behaviour of bulk samples.

The encouraging results prompted us to explore the field-dependent magnetic response of the sample down to the very low temperatures required to observe magnetic memory effects in SMM materials. We have therefore exploited the assets of the X11MA-SIM beamline (beam stability and fast switching of X-ray polarization) and further optimized the endstation so as to achieve the lowest possible level of iron contamination in the thermal shields required to reach sub-kelvin temperatures (see Supplementary Information for details). The recorded hysteresis curves are shown in Fig. 3a–c.

Whereas simple paramagnetic behaviour is found at 1.0 K, a gradual opening of the hysteresis loop is detected at sub-kelvin temperatures. At $T = 0.50 \pm 0.05$ K, the loop has the typical butterfly shape resulting from fast magnetization tunnelling in zero field^{23,24}, showing unambiguously that SMM behaviour is observable on gold-wired molecules. Even though XMCD has recently been

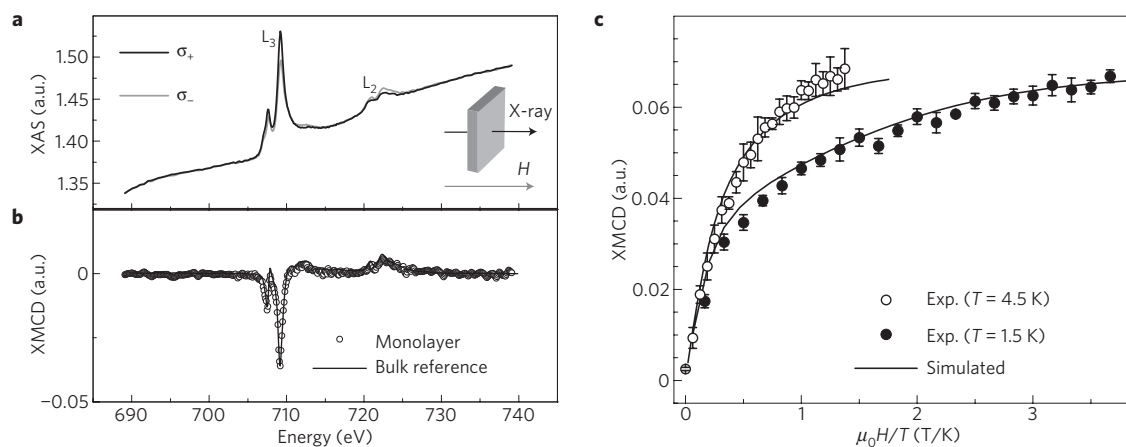


Figure 2 | XAS/XMCD of Fe₄ monolayer. **a**, Iron L_{2,3}-edge XAS spectra recorded on the Fe₄ monolayer at $T = 0.50 \pm 0.05$ K using left- (σ_+) and right- (σ_-) hand circularly polarized light in a field induction of 3.0 T. **b**, XMCD spectrum (open circles) obtained as ($\sigma_- - \sigma_+$) and compared to the bulk reference spectrum (solid line) recorded in similar experimental conditions on a thick film on the same substrate. **c**, Field and temperature dependence of the XMCD signal at 709.2 eV (multiplied by -1) recorded on the Fe₄ monolayer. The data have been taken by scanning the field up to 5.5 T at two different temperatures, and the standard deviation (bars) has been evaluated by averaging four data sets. The lines correspond to the calculated magnetization by using the spin Hamiltonian $H = DS_z^2 + g\mu_B\mu_0\mathbf{H}\cdot\mathbf{S}$, where D is the axial anisotropy parameter, g is the Landé factor, μ_B is the Bohr magneton and \mathbf{H} is the applied magnetic field. Taking into account a random orientation of the molecular z axes with respect to the magnetic field, an acceptable agreement is obtained assuming $D/k_B = -0.62$ K and $g = 2.00$, as found in bulk samples²⁵.

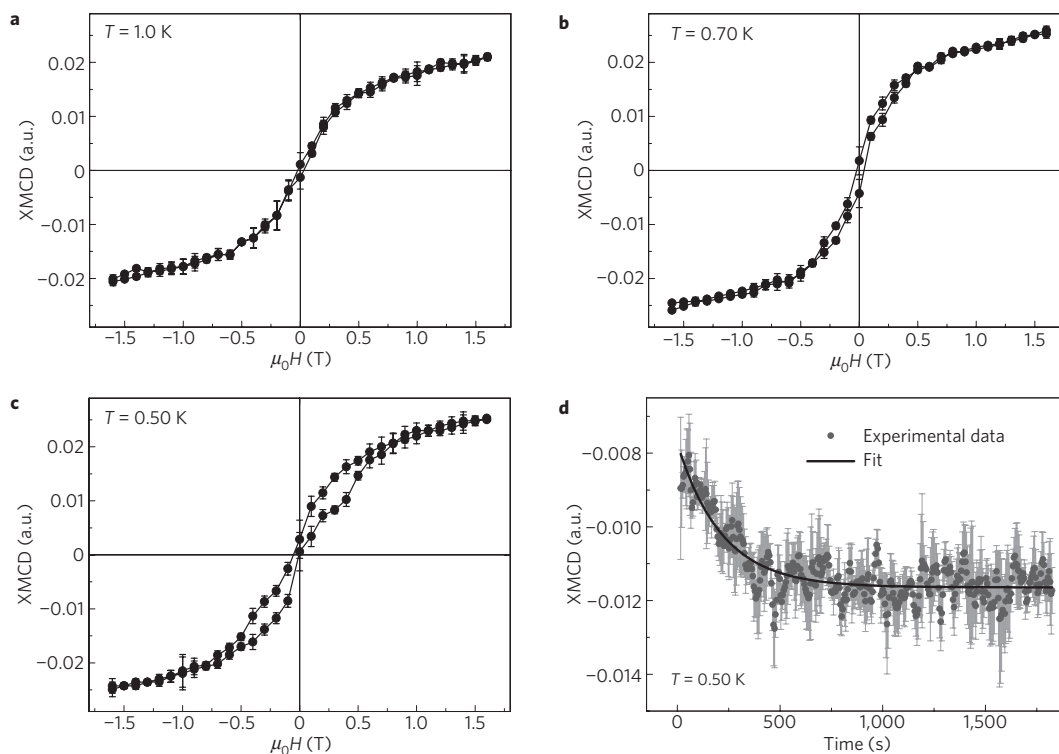


Figure 3 | Hysteresis and magnetization dynamics of Fe₄ monolayer. **a–c**, Temperature dependence of the magnetic hysteresis for the Fe₄ monolayer, monitored through the XMCD intensity (multiplied by -1) at 709.2 eV obtained from XAS signals normalized to the pre-edge intensity (704.0 eV). The error bars represent the standard deviations estimated by averaging over three field cycles. A sweeping rate of 2 mT s^{-1} has been used. **d**, Time dependence of the dichroic signal (multiplied by -1) at 709.2 eV for the Fe₄ monolayer at $T = 0.50 \pm 0.05$ K. The sample was first magnetized in a strong positive magnetic field ($+2.0$ T), then the field was rapidly ramped to a moderate negative value (-0.25 T) and the time dependence of the dichroic signal was measured. The procedure was repeated four times and the grey error bars represent the standard deviation. The black line provides the best-fit to experimental data using a mono-exponential decay.

used to detect the substrate-driven magnetism of paramagnetic (octaethylporphyrinato)iron(II) complexes deposited on a ferromagnetic surface², this is the first observation of a magnetic hysteresis of purely molecular origin in monolayers.

Further evidence that the deposited Fe₄ complexes retain slow magnetic relaxation was gained by measuring the time dependence of the XMCD signal after magnetizing the sample in a strong magnetic field and then rapidly reducing the field to a small

value in the opposite direction. As reported in Fig. 3d, even if the XMCD signal is significantly noisier than in thick films²⁰, a time dependence of the magnetization is distinctly observed at $T = 0.50 \pm 0.05$ K. Fitting of the data using a mono-exponential decay law provided a characteristic time $\tau = 220 \pm 15$ s, which is comparable to that observed²⁰ at the surface of thick films ($\tau = 285 \pm 10$ s at $T = 0.55 \pm 0.05$ K).

Despite the very low blocking temperature of Fe₄ and its low remnant magnetization due to resonant tunnelling in zero field, both consequences of the relatively small spin of this SMM, the present results give a positive answer to a key question, that is, there are no fundamental reasons that preclude the observation of magnetic hysteresis when SMMs are wired to a conducting substrate. This conclusion is not at all trivial given the peculiar origin of magnetic bistability in SMMs: geometrical distortions as well as changes in the environment and in the effectiveness of spin-phonon coupling are indeed known to have a profound influence on the spin dynamics of SMMs (ref. 4). Furthermore, SMMs are intrinsically fragile systems and previous attempts to demonstrate slow magnetic relaxation in Mn₁₂ adsorbates most probably failed owing to redox and structural rearrangement phenomena^{5,20}. Clearly emerging from our studies is also the potential of XMCD for the characterization of monolayers of magnetic molecules, which are even more demanding than inorganic nanostructures.

Although extra efforts to increase the blocking temperature are required before SMMs can be realistically incorporated into storage devices, the present results already pave the way to fundamental developments in the emerging field of molecular spintronics such as the possibility to control magnetization reversal by conduction electrons in a metal–molecule–metal nanojunction. This approach would mimic at the molecular scale the current-induced motion of domain walls confined to nanostructures, which was revealed to be particularly useful for memory storage applications³⁰.

Methods

A flame-annealed polycrystalline Au substrate, showing triangular reconstruction of Au(111) (see Supplementary Information), was plunged into a 0.5 mM dichloromethane solution of Fe₄ (the synthesis of which is described elsewhere²⁵) for 20 h so as to afford monolayer coverage. Overlayers of physisorbed molecules not directly grafted to the gold surface were removed by repeated washings with pure dichloromethane. Samples dried under nitrogen atmosphere were investigated by room-temperature low-current STM in a controlled atmosphere. Identical samples for XAS/XMCD investigations were transferred to the ultrahigh vacuum chamber through a portable glove box inflated with nitrogen gas.

The XAS/XMCD investigations were carried out at BESSY (Berlin, Germany) and SLS (Villigen, Switzerland). For the experiments, we used the same TBT-XMCD endstation, working under strong applied magnetic fields with both a pumped ⁴He cryostat and a ³He–⁴He dilution set-up^{27,28}, connected to the UE46-PGM (BESSY) and X11MA-SIM (SLS) beamlines. The absorbance was measured in the total-electron-yield mode²⁹ and magnetization and hysteresis curves were recorded by monitoring the field dependence of the dichroic signal at the energy of its maximum amplitude. Time-dependent XMCD measurements were obtained by monitoring the evolution of the dichroism after a rapid switching of the magnetic field from $\mu_0 H = +2.0$ to -0.25 T and continuously switching the polarization of the light. The required light stability was achieved by the fast switching mode available at SLS, which uses a couple of undulators with opposite polarizations rapidly tuned and detuned, respectively.

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Additional information

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