Single-Molecule Magnets on Gold

Direct Observation of Single-Molecule Magnets Organized on Gold Surfaces[**]

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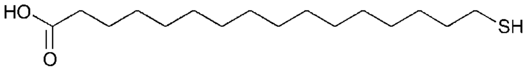
An aim of molecular electronics is to use single (or a few) molecules as active components of electronic devices, based on the idea that a small number of molecules, or even a single molecule, can perform basic electronic functions, that is, rectification, amplification, and storage.[1,2]

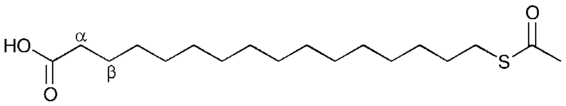
In the last decade, it was discovered that single molecules can, in principle, be used to store magnetic information. The research in this field started from the observation that a dodecamanganese(III,IV) cluster, $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 4\,H_2O\cdot 2\,AcOH$ ($\mathbf{1}\cdot 4\,H_2O\cdot 2\,AcOH$),[3] exhibits a hysteresis cycle under cryogenic conditions.[4] This compound is considered to be the prototype of a class of materials referred to as single-molecule magnets (SMMs), so-called because their magnetic behavior is strongly reminiscent of bulk magnets.[4b] Magnetic hysteresis in SMMs arises from a purely molecular mechanism rather than from bulk magnetic interactions, a fact firmly established by magnetic dilution experiments.[5] Practical applications of SMMs as molecular-scale units for information storage or "qubits" for quantum computation[6] require the addressing of individual molecules, that is, imaging, probing, and eventually manipulating individual molecules. This goal can be realized most easily by depositing target molecules on a suitable substrate with monolayer[7a,b] or submonolayer[7c] coverage, and by addressing them individually using scanning probe microscopy techniques, such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), and magnetic force microscopy (MFM). The first technique is particularly attractive for the study of the interplay between charge transport and the magnetic properties of the clusters. Partially ordered Langmuir–Blodgett films of Mn_{12} clusters have been prepared,[8] but no successful attempt to deposit SMMs on conducting substrates (for example, on gold) has been reported to date.

We present herein a method to deposit suitably derivatized Mn_{12}-type clusters on a gold film, and to observe them directly at the single-molecule level using STM. This result, which has been achieved for the first time, opens exciting perspectives for the storage of magnetic information in an individual cluster.

Since the clusters **1** do not adhere to gold surfaces in a stable fashion, suitable variants need to be designed that contain surface-binding functionalities, such as thiol or thioether groups. In particular, we have attempted to introduce 16-sulfanylhexadecanoate ligands (L′) around the Mn_{12} core by exploiting a well-known ligand-exchange reaction.[5b] However, treatment of $\mathbf{1}\cdot 4\,H_2O\cdot 2\,AcOH$ with HL′ in toluene or CH_2Cl_2 affords intractable solids, presumably as a result of the oxidative instability of free thiols in the presence of Mn_{12} centers.[9] In contrast, the use of the corresponding acetyl-protected acid HL yields a fully-substituted derivative $[Mn_{12}O_{12}(L)_{16}(H_2O)_4]$ (**2**) which is highly soluble in organic solvents (See Experimental Section).



HL′



HL

The composition of **2** has been established by elemental analysis, FT-IR and ^1H NMR spectroscopy, and MALDI-TOF mass spectrometry. Mass spectrometry is emerging as a powerful new tool for the characterization of molecular clusters in a noncrystalline form.[11] Mass spectra collected in positive and negative mode show isolated molecular peaks at $m/z = 6125$ and 6123, which correspond to $[M+H]^+$ and $[M-H]^-$, respectively, for the species $[Mn_{12}O_{12}(L)_{16}]$ ($M = 6124$). Neither the positive nor the negative mode spectra exhibit peaks that correspond to a cluster with H_2O ligands; these ligands are presumably lost under the experimental conditions used.[11b] Satellite peaks for the partially substituted species $[Mn_{12}O_{12}(OAc)_n(L)_{16-n}]$ with molecular weight $M' = M - 270n$ are not observed (Figure 1). Infrared spectra are dominated by a very strong band at $1695\ cm^{-1}$, which arises from the stretching vibration of the acetyl C=O group.

The magnetization dynamics studied by variable-frequency ac susceptibility measurements on a polycrystalline sample exhibits the distinctive features of Mn_{12} derivatives.

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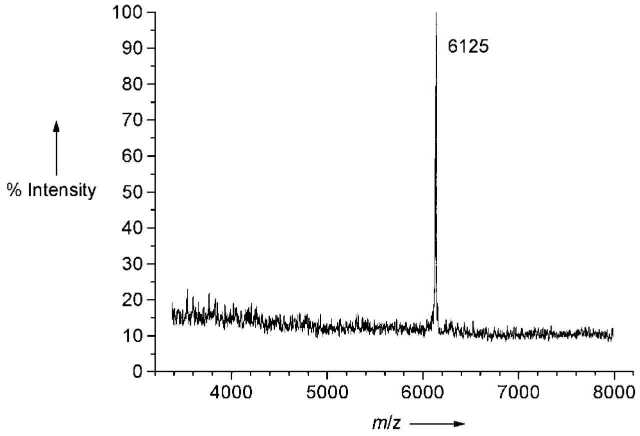

Figure 1. Positive-mode MALDI-TOF spectrum of **2**.

The relaxation time of the magnetization (τ) is plotted in Figure 2 as a function of the inverse blocking temperature $1/T_{\mathrm{max}}$ (that is, the temperature at which the out-of-phase susceptibility reaches a maximum at each frequency). An Arrhenius-type behavior is observed [Eq (1)] with $\tau_0 = 2.4 \pm 0.4 \times 10^{-8}$ s and $\Delta/k_B = 55.1 \pm 0.8$ K, which suggests a thermally activated mechanism for magnetization reversal. The energy barrier (Δ/k_B) is close to that found for **1**$\cdot 4\,H_2O \cdot 2\,AcOH$ (61 K),[4a] which confirms that the Mn_{12} core remains intact during the ligand-exchange reaction.

$$\tau = \tau_0 \exp(\Delta/k_B\, T) \qquad (1)$$

Deposition of the nanoclusters on a Au(111) surface was carried out by incubating gold substrates[12a] in diluted solutions of **2** in THF, together with aqueous NH_4OH to facilitate deprotection of the thiol groups and to promote robust anchoring to the gold surface through Au–thiolate bonds. This technique has proved to be very effective in circumventing the oxidative instability of organic thiols in the deposition of self-assembled monolayers.[12b]

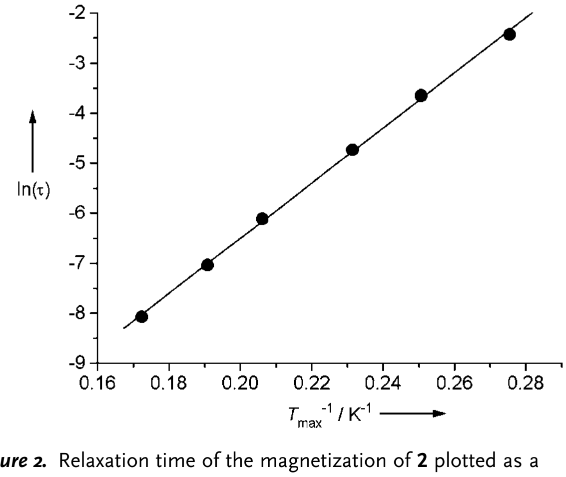

Figure 2. Relaxation time of the magnetization of **2** plotted as a function of inverse blocking temperature.

X-ray photoelectron spectroscopy (XPS) measurements reveal the presence of all the elements expected from the molecular structure of **2** and atomic proportions in excellent agreement with the calculated composition (Table 1). In particular, two different oxygen signals, labeled as O(1s)′ and O(1s)″ in Table 1, can be resolved at binding energies (BEs) of approximately 530 and 532 eV, respectively. The two peaks have been assigned to the 12 oxygen atoms of the $\{Mn_{12}O_{12}\}$ core, and to the remaining 52 oxygen atoms from carboxylate and water ligands, respectively. This interpretation is in agreement with that suggested in a recent XPS investigation of **1**$\cdot 4\,H_2O \cdot 2\,AcOH$[13a] and is supported by a comparison with the BEs found in Mn_2O_3 and MnO_2 (529–530 eV).[13b]

Table 1: Experimental XPS data and expected composition of the layers of **2**.

	Binding energy [eV][a]		Atom % (exp)		Atom % (calcd)[b]
	$Mg_{K\alpha}$	$Al_{K\alpha}$	$Mg_{K\alpha}$	$Al_{K\alpha}$	
Mn(3p)	48.8	48.8	3.1	2.6	3.2
S(2p)	162.6	162.6	4.0	4.2	4.2
C(1s)	285.1	285.0	75.2	76.1	75.8
O(1s)′	530.3	530.2	3.2	3.1	3.2
O(1s)″	532.3	532.3	14.5	14.1	13.6

[a] Relative to Au($4f_{7/2}$) = 84.0 eV. [b] Values for a mono-deprotected cluster are within 0.1 % of those reported for all of the elements.

Decomposition of the O(1s) spectra yields a 1:4.5 intensity ratio for the two oxygen types, which is in good agreement with the expected ratio in **2** (1:4.3).

It is well-known that the BE of S(2p) electrons can be used to discriminate between free (163.4 eV) and Au-bound (161.9 eV) sulfur atoms in simple thiols.[13c] The width of the S(2p) signal at 162.6 eV is indeed larger than the experimental resolution, and decomposition of the peak suggests that the free and the Au-bound sulfur atoms exist in a 1:2 ratio with BEs of 163.3 and 161.8 eV, respectively, for the $S(2p_{3/2})$ electrons. Considering the conformational flexibility of the alkyl chains, such a large fraction of Au-bound sulfur atoms is not surprising. Although further studies are needed to clarify the details of the interaction, it is likely that thioacetyl end-groups may contribute significantly to cluster adsorp tion.[13d]

STM analysis of the sample (Figure 3) shows complete coverage of the gold substrate by a disordered layer of round particles with an apparent lateral size of approximately 5.8 nm, which is in reasonable agreement with the size of **2** obtained from molecular-modeling studies (5.0–5.6 nm). Disorder may originate from the specific arrangement of the alkyl chains of the deposited molecules, which prevents pairing for steric reasons and an epitaxial growth of the layer.[7b] In addition, the conformational flexibility of the chains may prevent the formation of the hexagonal or cubic arrangements that have been previously reported, for instance, for gold clusters.[14] Prolonged scanning of the surface under the adopted experimental conditions (0.8–1.3 V, 5–10 pA) causes extensive motion of the mole-

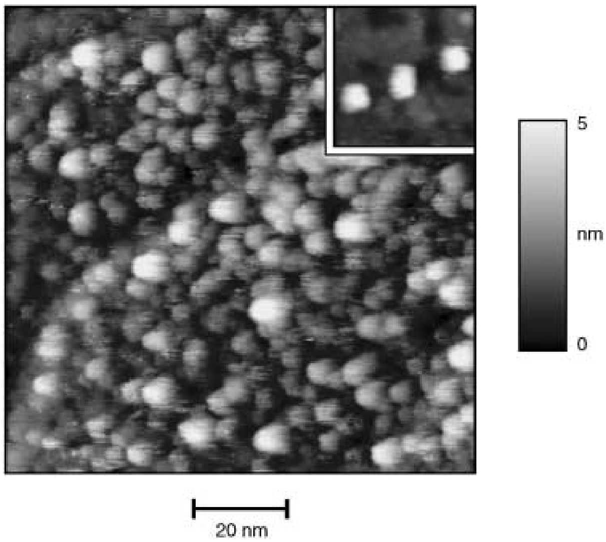

Figure 3. Constant-current STM image of Au-bound Mn_{12} clusters (setpoint = 5 pA, bias = 1.3 V, scan size = 100 nm, scan rate = 3 Hz). The inset shows three isolated molecules (setpoint = 10 pA, bias = 0.8 V, scan size = 30 nm, scan rate = 3 Hz).

cules at the surface and progressive disruption of the layer. Well-isolated molecules can then be imaged, as shown in the inset of Figure 3.

Given the small quantities of available material, a magnetic proof of the existence of SMMs on the surface cannot be obtained from bulk measurements,[8] and requires techniques such as the surface magneto-optical Kerr effect,[15a] spin-polarized STM,[15b] or MFM.[15c] Our experiments, however, show that it is indeed possible to address single molecules of Mn_{12}, and that the idea of storing information in one molecule has considerable credibility.

Experimental Section

16-(acetylthio)hexadecanoic acid was obtained by reacting 16-sulfanylhexadecanoic acid with acetyl chloride, as described elsewhere.[16] Compound **2** was synthesized by a modified ligand-exchange method.[5b] A slurry of freshly-prepared **1**·$4H_2O$·2AcOH[3] (304 mg, 0.147 mmol) in anhydrous toluene (10 mL) was treated with 16-(acetylthio)hexadecanoic acid (819 mg, 2.478 mmol) and the solvent was distilled off under reduced pressure (50 mmHg). Additional azeotropic distillations were performed with toluene (10 mL, 80 mmHg; 2 × 10 mL, 100 mmHg). The residue was dissolved in CH_2Cl_2, the solution was centrifuged, and the solvent was evaporated to give **2** as a black lustrous solid (765 mg, yield 84 %).

Elemental analysis (%) calcd for $C_{288}H_{536}Mn_{12}O_{64}S_{16}$: C 55.83, H 8.72, S 8.28; found: C 55.72, H 8.72, S 7.98; FT-IR (KBr pellet): $\tilde{\nu}$ = 2920 (CH), 2852 (CH), 1695 (C=O), 1588 (OCO), 1422 (OCO), 1112, 953, 720, 629 cm^{-1}; ^1H NMR (200 MHz, [D_8]toluene, 25 °C, TMS): δ = 47.5 (8H; CH_2 (α, axial, $Mn^{III}Mn^{III}$)), 46.2 (8H; CH_2 (α, equitorial, $Mn^{III}Mn^{III}$)), 43.1 (8H; CH_2 (α, equitorial, $Mn^{III}Mn^{III}$)), 13.9 (8H; CH_2 (α, axial, $Mn^{III}Mn^{IV}$)), 8.8 (8H; CH_2 (β, axial, $Mn^{III}Mn^{III}$)), 5.1 (8H; CH_2 (β, axial, $Mn^{III}Mn^{IV}$)), 2.8 (32H; CH_2S), 2.0 (48H; CH_3), 1.3 (384H; CH_2), −3.9 (8H; CH_2 (β, equitorial, $Mn^{III}Mn^{III}$)), −4.7 ppm (8H; CH_2 (β, equitorial, $Mn^{III}Mn^{III}$)). For the assignment of ^1H NMR signals, see ref. [5b].

Mass spectra were collected using a Voyager-DE-RP MALDI-TOF mass spectrometer (Applied Biosystems/PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction.[17] A 337-nm UV nitrogen laser was used and the mass spectra were obtained in both linear and reflection modes. Samples were prepared by mixing a solution of the sample in CH_2Cl_2 (10 μL) with a solution of the matrix (dihydroxybenzoic acid in CH_2Cl_2, 30 μL, 1 mgL^{-1}). 1 μL of the solution was loaded on to a gold-sample plate, the solvent was removed in warm air, and the sample transferred to the mass spectrometer for analysis.

A Cryogenic S600 SQUID magnetometer was used to perform ac magnetic measurements. Gold films (150-nm thick) on freshly cleaved muscovite mica were prepared using standard procedures;[12a] the films exhibited a preferred orientation in the (111) direction. The substrates were immersed for at least 5 min in a solution of **2** (0.3 mM) in THF that contained a catalytic amount of aqueous NH_4OH, then rinsed thoroughly with THF and dried in a nitrogen stream.

XPS measurements were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of 7×10^{-9} Pa. Photoemission spectra were excited by a non-monochromated X-ray source equipped with two anodes (K_α lines; Al = 1486.6 eV and Mg = 1256.6 eV) and measured by means of a hemispherical electron-energy analyzer with a multichannel detection system and an angular acceptance of ± 8°. Electrons were collected at a take-off angle of 55° with respect to the surface normal of the samples, to enhance the sensitivity to the surface; the overall energy resolution was 1.7 eV. The Au($4f_{7/2}$) signal was used as a reference for the XPS energy scale, and was set at 84 eV of BE. The integrated intensities were corrected for the angular asymmetry of electronic levels and for the analyzer transmittivity, and directly used to evaluate the atomic percentages from tabulated photoionization cross-sections. Since the electron attenuation length (approximately 0.5–0.7 nm) is shorter than the cluster dimensions (5–6 nm), the XPS intensities should also reflect the electron signal attenuation, which depends, in turn, on the location of the emitting atoms and on the adsorption geometry. Nevertheless, given the low electronic density of the ligand shell the corrections to the measured intensities are expected to be small.

Constant-current STM images were recorded in air at room temperature using a Digital Instruments Nanoscope III equipped with mechanically sharpened Pt/Ir tips.

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