# Isolated single-molecule magnets on native gold†

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**The incorporation of thioether groups in the structure of a $Mn_{12}$ single-molecule magnet, $[Mn_{12}O_{12}(L)_{16}(H_2O)_4]$ with L = 4-(methylthio)benzoate, is a successful route to the deposition of well-separated clusters on native gold surfaces and to the addressing of individual molecules by scanning tunnelling microscopy.**

A central issue in the area of current information technology is the development of molecule-based devices for data storage. The discovery that certain transition metal clusters like $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 2AcOH\cdot 4H_2O$ (**1**) and its derivatives act as single-molecule magnets (SMMs), has introduced exciting perspectives in this field.[1] The involvement of such SMMs in information storage requires an individual addressing of the clusters. The simplest strategy to do so is to organize SMMs on surfaces and use modern techniques such as scanning probe microscopy (SPM) for single-molecule addressing.

In a previous contribution, we reported the self-assembly of a sulfur-functionalized $Mn_{12}$ derivative, $[Mn_{12}O_{12}(O_2C(CH_2)_{15}\text{-}SAc)_{16}(H_2O)_4]$, on Au(111), and the observation of a layer of densely-packed clusters by scanning tunnelling microscopy (STM).[2] Other routes toward addressable arrays of $Mn_{12}$-type clusters have also been explored, including dispersion in polycarbonate matrices,[3] stamp-assisted self-organization into aggregates on oxidized silicon,[4] and grafting on Au(111)[5] or Si(100)[6] surfaces functionalized with carboxylate groups. However, a technique for the direct deposition of isolated $Mn_{12}$ clusters is not yet available.

We wish to fill this gap by reporting a route to extended arrays of isolated SMMs on a native gold surface. The approach devised involves $Mn_{12}$ clusters containing 4-(methylthio)benzoate groups (L) that promote a weaker and more reversible interaction with the gold substrate as compared with the corresponding thiol functionalities.[7]

The cluster $[Mn_{12}O_{12}(L)_{16}(H_2O)_4]$ (**2**) was synthesized‡ and isolated as **2**$\cdot 8CHCl_3$. The molecular structure§ of **2** at 193 K (Fig. 1) exhibits crystallographic $S_4$ symmetry, which is comparatively rare in $Mn_{12}$ derivatives.

The periphery of the cluster features sixteen sulfur atoms, which provide as many surface-binding sites. In order to confirm retention of SMM behavior in the presence of the thioether groups, the field dependence of the magnetization has been recorded at different temperatures on an oriented single crystal. At 4 K, a saturation value of 20 $\mu_B$ is reached, which is the value expected for an $S = 10$ ground spin state.

Below 4 K, a stepped hysteresis appears (Fig. 2), characteristic of thermally-assisted quantum tunneling of the magnetization. However, two relaxation processes seem to be present since half of the magnetization suddenly reverses when crossing $H = 0$, whereas the other half exhibits a wide hysteresis and steps separated by 4.5 kOe.

The presence of a second relaxation process, which is confirmed by the observation of two peaks in the out-of-phase ac magnetic susceptibility (Fig. 2), is rather common in $Mn_{12}$ derivatives and has been associated with species with a smaller magnetic anisotropy due to tilting of the elongation axis of a manganese(III) ion.[8] As no evidence of this type of disorder has been found in the crystal structure of **2** we may ascribe its presence to the partial desolvation of the crystals used for the measurements.

The dynamic parameters obtained for the high temperature relaxation ($\tau_0 = 1.6(2)\ 10^{-9}$ s and $\Delta/k_B = 65.4(4)$ K) are

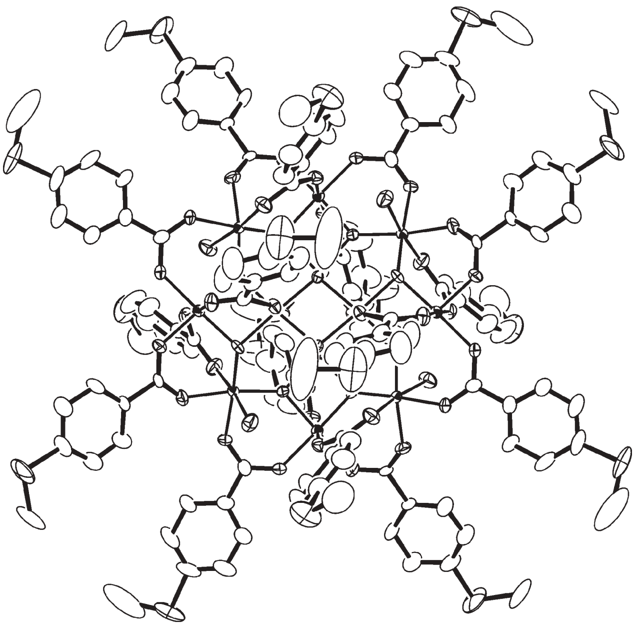

**Fig. 1** ORTEP representation of **2** viewed along the tetragonal axis (*c*). The sulfur atoms of the 4-(methylthio)benzoate ligands are drawn using cross-hatched ellipsoids.

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† Electronic supplementary information (ESI) available: detailed synthetic procedure, FT-IR, MALDI-ToF data, detailed X-ray crystal structure, $^1$H-NMR spectra, electrochemical data of **2**, ToF-SIMS spectra and profile analysis on STM images of **2** grafted on gold. See http://www.rsc.org/suppdata/cc/b4/b418072k/

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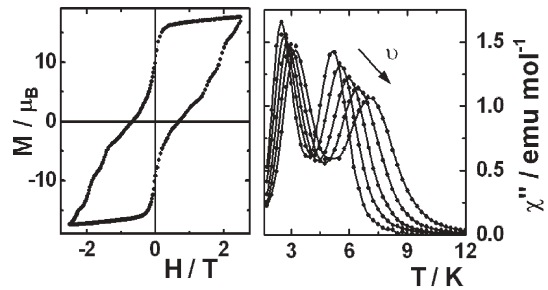

**Fig. 2** (Left) Hysteresis loop at 1.6 K recorded on a single crystal of **2** with the magnetic field along *c*. (Right) Temperature dependence of $\chi''$ at different frequencies (0.3–10 kHz).

comparable with those of **1** ($\tau_0 = 1.2 \times 10^{-9}$ s and $\Delta/k_B = 86.5$ K extracted from measurements taken in the same frequency range, given the marked dependence of these parameters on the investigated frequencies).[9]

Since solutions of **2** are used in the deposition step, we have checked the stability of the clusters in solution. $^1$H-NMR and electrochemical studies confirm a full retention of the structure observed in the solid state (see ESI†). Deposition was then carried out by soaking flame-annealed Au(111) substrates (a film of 150 nm evaporated on mica) in a 0.3 mM solution of **2** in anhydrous THF for 30 min and 24 h. Our preliminary XPS measurements¶ of this deposition reveal a Mn 2*p* signal, which is just visible after the 30 min immersion but appears quite distinctly for longer times (Fig. 3). The binding energy (653.7 eV for Mn $2p_{1/2}$) agrees closely with that observed on a bulk deposit obtained by drop-casting (curve (c)), as well as on solid **1**[10] and $[Mn_{12}O_{12}(O_2CtBu)_{16}(H_2O)_4]$.[5a] The similar intensities of the Mn 2*p* signals in (b) and (c) strongly suggest complete surface coverage after 24 h immersion, whereas the much weaker Mn 2*p* band observed in (a) points to only partial surface coverage.

Preliminary Tof-SIMS data show characteristic peaks assigned as molecular ion fragments of **2**. In addition, parent molecular ion peaks representative of the intact ligand molecule and fragment peaks at lower mass values were detected (see ESI†).

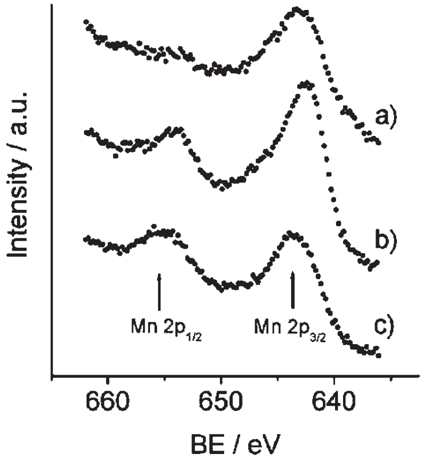

**Fig. 3** Core-level Mn 2*p* XPS¶ spectra of Au(111) films after 30 min (a) and 24 h (b) of immersion in THF solution of **2**, and of a bulk deposit obtained by drop-casting using a saturated solution of **2** in $CH_2Cl_2$ (c). The spectra are on the same absolute scale. The intense peak in (a) is the Au $4p_{1/2}$ signal.

STM measurements were carried out at room temperature, under $N_2$ atmosphere.|| Fig. 4 presents an image of the 30 min immersion sample obtained in constant-current mode and evidences sub-monolayer coverage of the gold film by quasi-spherical particles.

The size distribution is very narrow (2.7 ± 0.5 nm, see top of Fig. 4) and agrees nicely with the size estimated for **2** (2.8 × 2.1 nm from X-ray structure§).

Moreover, the particles appear for the first time well isolated (nearest-neighbour distance ~5 nm, see ESI†). This feature is retained even on a large scale, as can be seen in Fig. 5. The deposited particles appear to be stable in time as no differences in shape and size were observed over a 24 h period.

STM investigations thus demonstrate the validity of our approach based on the incorporation of thioether groups to address the formation of a submonolayer of individually-accessible clusters. Since thioether groups do not react with the $Mn_{12}$ core

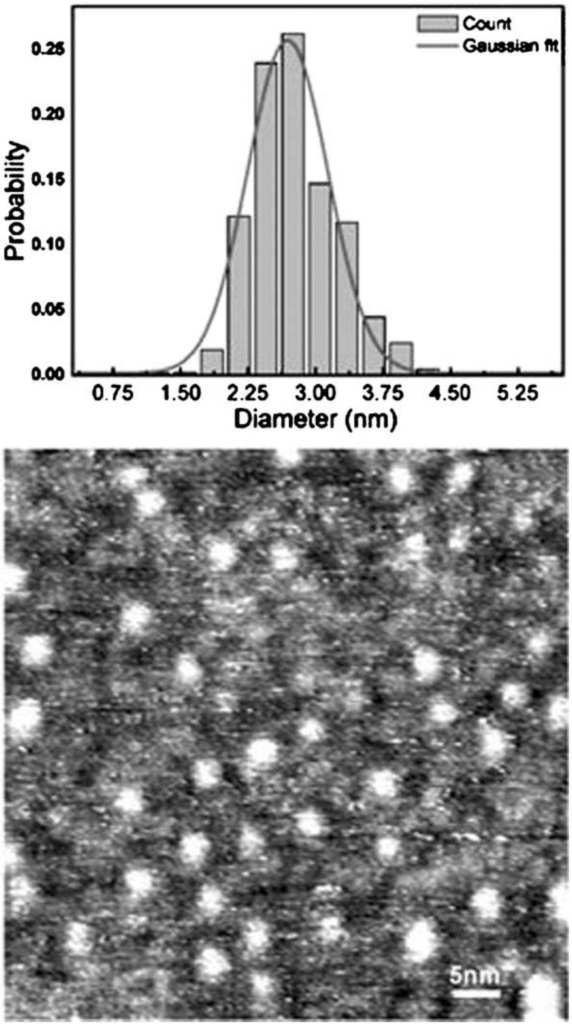

**Fig. 4** (Bottom) Constant-current STM image of **2** assembled on the Au(111) surface (scan area 60 × 60 nm$^2$). (Top) The distribution of diameters extracted from 400 measurements.** The best-fit gaussian distribution is shown as a light gray curve ($R^2 = 0.97$, $x_c = 2.7$ nm, $\sigma = 0.5$ nm).

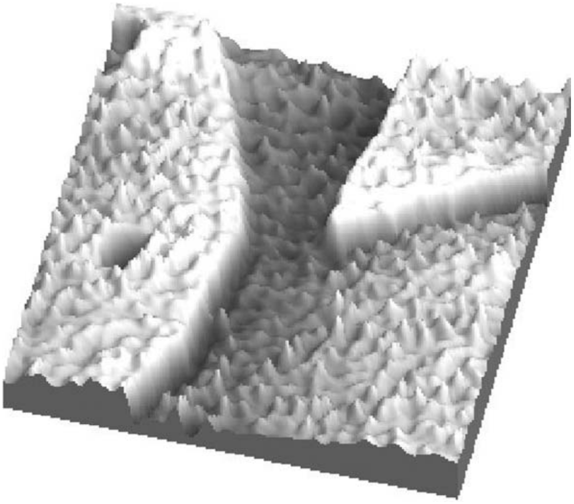

**Fig. 5** 3-D representation of a constant-current STM image (200 × 200 nm$^2$) of **2** assembled on gold showing terraces and a triangular feature typical of Au(111) reconstruction.

during the ligand-exchange reaction, the proposed strategy is also easier than previously-reported protocols based on acetyl-protected thiols, that require hydrolysis before grafting to gold.[2]

Direct attachment of the clusters to a metallic surface may now provide straightforward access to electron transport measurements using the STM tip as a second, movable electrode. The experiment has been invoked by very recent theoretical studies, which anticipate a strong interplay between quantum tunneling of the magnetization and molecular conductance.[11]

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## Notes and references

‡ *Synthesis*: A slurry of complex **1** (204 mg, 0.0990 mmol) in anhydrous toluene (10 mL) was treated with 4-(methylthio)benzoic acid (333 mg, 1.98 mmol). The mixture was concentrated at reduced pressure to remove acetic acid as the toluene azeotrope. Several treatments with 10 mL portions of toluene and a final recrystallization from $CHCl_3$ afforded large blocks of $\mathbf{2}\cdot 8CHCl_3$ that were collected and dried *in vacuo*. Yield 0.220 g (62%) (C, 42.58; H, 3.14; S, 13.78%. Calc. for **2**: C, 42.72; H, 3.36; S, 14.23%). X-EDS (single crystal): S/Mn atomic ratio = 1.35(3).

§ *Crystal data*: $C_{136}H_{128}Cl_{24}Mn_{12}O_{48}S_{16}$: $M_r = 4553.42$, tetragonal, space group $I\bar{4}$, $Z = 2$, $a = 19.934(1)$, $c = 25.343(3)$ Å, $U = 10070.4(14)$ Å$^3$, $T = 193(2)$ K, $D_c = 1.502$ g cm$^{-3}$, $F(000) = 4584$, $\mu$(Mo-K$\alpha$) = 1.276 mm$^{-1}$, 6172 reflections collected on a Siemens P4-RA diffractometer ($\theta \leqslant 25.99°$) and corrected for absorption, 5988 independent reflections ($R_{int} = 0.0193$) used for refinement on $F_o^2$; all nonhydrogen atoms treated anisotropically, hydrogen atoms added in idealised positions, merohedral-twinning (twinning matrix: 1 0 0 0 −1 0 0 0 −1); final $R$ values $R1 = 0.0499$ [$I > 2\sigma(I)$] and $wR2 = 0.1339$ (all data) for 563 parameters and 37 restraints; largest peak and hole in the final $\Delta F$ map: 1.014 and −0.432 e Å$^{-3}$. CCDC 257821. See http://www.rsc.org/suppdata/cc/b4/b418072k/ for crystallographic data in .cif or other electronic format.

¶ XPS spectra were taken in a UHV chamber ($1 \times 10^{-10}$ mbar) with a double-pass cylindrical analyser and excited by a conventional X-ray source ($h\nu = 1253.6$ eV). The analyser energy resolution was of 1.6 eV at 100 eV pass energy.

|| STM measurements were performed with a Solver P47pro system (NT-MDT, Zelenograd, Moscow, Russia; www.ntmdt.com) equipped with a customized low-current STM head and Pt/Ir mechanically-etched tips prepared immediately before use (bias voltage = 50 mV for small scans, 350 mV for large scans; constant current mode with a set point of 5 pA). Image analysis has been done with WSxM free software downloadable at http://www.nanotec.es.

** The particle-size distribution has been evaluated from a set of 6 images obtained independently but in identical conditions. The software for data fitting is Origin (version 7.5, 2003) supplied by OriginLab Corp.

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