

## Isolated Mn<sub>12</sub> Single-Molecule Magnets Grafted on Gold Surfaces via Electrostatic Interactions

Eugenio Coronado,<sup>\*†</sup> Alicia Forment-Aliaga,<sup>†</sup> Francisco M. Romero,<sup>†</sup> Valdis Corradini,<sup>\*‡</sup> Roberto Biagi,<sup>‡</sup> Valentina De Renzi,<sup>‡</sup> Alessandro Gambardella,<sup>‡</sup> and Umberto del Pennino<sup>‡</sup>

*Instituto de Ciencia Molecular, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Spain, and INFN-S3, Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via G. Campi 213A, 41100 Modena, Italy*

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Electrostatic interactions drive the adsorption of polycationic single-molecule magnets onto anionic monolayers self-assembled on gold surfaces. Well-isolated magnetic clusters have been deposited and characterized using scanning tunneling microscopy and X-ray photoemission spectroscopy.

The discovery that certain magnetic clusters of only a few metal atoms, like the family of dodecanuclear manganese complexes (Mn<sub>12</sub>), exhibit magnetic bistability at low temperature makes these compounds very attractive as components in high-density magnetic memories.<sup>1</sup> Another remarkable feature of these single-molecule magnets (SMMs) is the observation of quantum tunneling effects of the magnetization.<sup>2</sup> Recently, it has been predicted that these quantum effects can be also of interest in spintronics because they should strongly affect the electron transport properties through an individual molecule attached on a metallic surface.<sup>3</sup>

To investigate the properties of an individual molecule using scanning probe microscopy techniques or to develop nanomagnetic devices based on SMMs, the design of appropriate Mn<sub>12</sub> derivatives and the implementation of procedures to graft them onto suitable substrate surfaces become crucial. In this context, Mn<sub>12</sub> molecules have been processed as Langmuir–Blodgett films<sup>4</sup> or obtained as aggregates on thin-film-patterned surfaces upon exposure of

a Mn<sub>12</sub>-containing polycarbonate matrix to different solvent vapors.<sup>5</sup> Deposition of Mn<sub>12</sub> on surfaces has been attempted using several strategies: (i) Organized arrays using stamp-assisted or photolithography methods on oxidized silicon.<sup>6</sup> (ii) Direct attachment on gold using sulfur-functionalized derivatives. The main difficulty of such a method is that thiol groups cannot be prepared for this purpose because they immediately react with the manganese core. This problem has been overcome using Mn<sub>12</sub> compounds bearing acetyl-protected thiol groups.<sup>7</sup> (iii) Attachment on gold or silicon surfaces previously functionalized with carboxylate groups via a ligand-exchange reaction.<sup>8</sup> In general, these procedures lead to the formation of a layer of densely packed Mn<sub>12</sub> clusters bound to the surface through covalent bonds. Only in one case have well-separated clusters been deposited on gold using Mn<sub>12</sub> functionalized with bulky thioether benzoate groups.<sup>9</sup>

In this Communication, a simple procedure to graft individually accessible Mn<sub>12</sub> molecules on gold surfaces is proposed (Scheme 1). It involves a two-step procedure in which polycationic SMMs are deposited onto a gold surface

\* Authors to whom correspondence should be addressed. E-mail: eugenio.coronado@uv.es (E.C.); valdis@unimo.it (V.C.).

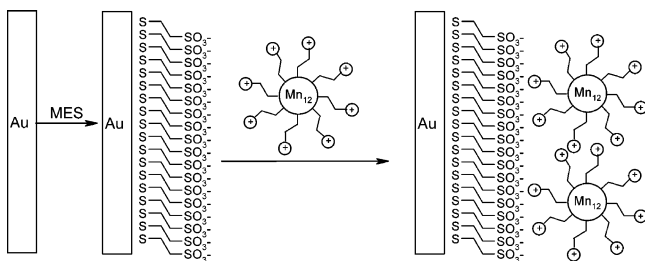
<sup>†</sup> Universidad de Valencia.

<sup>‡</sup> Università di Modena e Reggio Emilia.

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Scheme 1

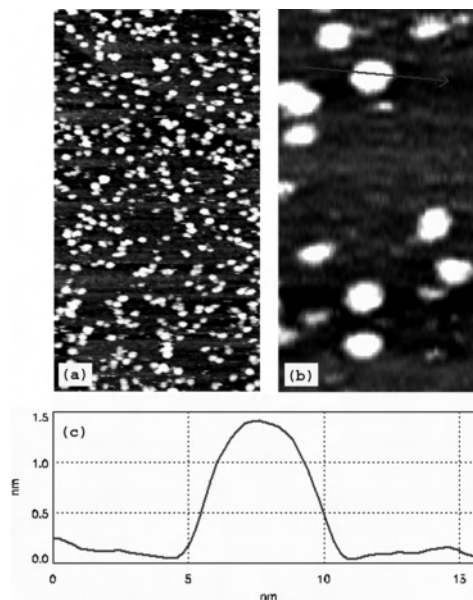


previously functionalized with an anionic self-assembled monolayer (SAM).

As a source of polycationic SMM, we have employed the hexafluorophosphate salt of the two-electron-reduced cluster  $[\text{Mn}_{12}\text{O}_{12}(\text{bet})_{16}(\text{EtOH})_4]^{14+}$  (bet = betaine =  $^+\text{N}(\text{CH}_3)_3\text{CH}_2\text{COO}^-$ ), with 16 quaternary ammonium substituents in the periphery and a  $S = 11$  ground spin state.<sup>10</sup> This salt exhibits the typical features of a SMM, namely, a slow relaxation of the magnetization with an effective energy barrier of 34 K and quantum effects in the magnetization (steps in hysteresis loops and observation of temperature-independent loops below 0.25 K). The compound is soluble and stable in an acetonitrile solution.

In the first step, an Au(111) surface was treated with sodium mercaptoethanesulfonate ( $\text{HS}(\text{CH}_2)_2\text{SO}_3\text{Na}$ ; MES) to achieve a highly packed SAM functionalized with negative  $-\text{SO}_3^-$  headgroups.<sup>11</sup> Good-quality (degree of coverage 100%) SAMs are obtained by soaking the gold substrate in a diluted solution (1 mM) of MES for 10 min. In a second step, ionic immobilization of the cationic magnetic molecules onto this anionic MES-SAM has been obtained by immersion of the above gold substrate in a diluted solution (1 mM) of  $[\text{Mn}_{12}]^{14+}$ . Room-temperature scanning tunneling microscopy (STM) images of these surfaces prove that short times of immersion (3 min) lead to partial coverage of the gold-functionalized surface, with isolated  $\text{Mn}_{12}$  molecules (Figure 1a,b). The average area occupied by a single molecule is  $39 \pm 7 \text{ nm}^2$ . We emphasize two aspects of this two-step deposition process: (i) SMMs are homogeneously distributed over wide extended terraces (up to 1000 nm) with no 3D aggregates, and (ii) they are strongly grafted to the MES-SAM because they are not removed or damaged by the interaction with the STM tip.

The analysis of the overlayer height profile (Figure 1b) shows a uniform distribution of the diameter ( $3.0 \pm 0.5 \text{ nm}$ ) and of the height ( $1.4 \pm 0.2 \text{ nm}$ ) of the clusters. These dimensions agree with those expected for the  $[\text{Mn}_{12}]^{14+}$  molecule ( $2.2 \times 1.6 \text{ nm}$ ) assuming the orientation of the  $S_4$  axis to be perpendicular to the surface.<sup>12</sup> The preferred “flat” orientation of clusters on the surface can be induced by the



**Figure 1.** Constant-current (30 pA and 2 V) STM images of  $[\text{Mn}_{12}]^{14+}$  isolated molecules grafted onto a MES-functionalized Au(111) surface:  $110 \times 190 \text{ nm}^2$  (a);  $23 \times 42 \text{ nm}^2$  (b). STM height profile of a single  $\text{Mn}_{12}$  cluster (c).

maximization of the number of ionic interactions between  $\text{Mn}_{12}$  cationic ligands and MES anionic headgroups. Indeed, electrostatic potential calculations show that this orientation lies in a potential energy absolute minimum. The larger value of the diameter compared to the expected value derives from the convolution with the non-negligible curvature radius of the tip. For this reason, to extrapolate the correct molecular coverage, we consider the expected value of the molecular diameter (2.2 nm) rather than the STM-measured one (3.0 nm), deriving a coverage of about 8–12%.<sup>13</sup> For longer immersion times (10 min), the formation of 3D aggregates is observed, while the ratio of surface covered by a first layer of isolated  $\text{Mn}_{12}$  clusters does not increase appreciably.

The surface coverage derived from the STM investigation can be confirmed by X-ray photoemission spectroscopy (XPS) experiments. Mn 2p core levels related to the MES/Au(111) sample after 3 and 10 min of immersion in a  $\text{Mn}_{12}$  solution are reported in Figure 2. The Mn  $2p_{3/2}$  core-level signal is superimposed onto a gold substrate feature (Au  $4p_{1/2}$ ), while the peak at higher binding energies corresponding to the Mn  $2p_{1/2}$  core level is totally related to the Mn present in the adsorbed overlayer.

A quantitative analysis<sup>14</sup> of the 3-min core-level intensities leads to an area for each  $\text{Mn}_{12}$  molecule ranging from 20 to  $36 \text{ nm}^2$ . Supposing a molecular diameter of 2.2 nm, coverage of about 10–20% can be derived, a value quite in agreement with the one derived from STM analysis. The 10-min core-level intensity is about twice that of the 3-min signal. This increment can be explained by the formation of 3D aggregates as already underlined in the STM discussion.<sup>15</sup>

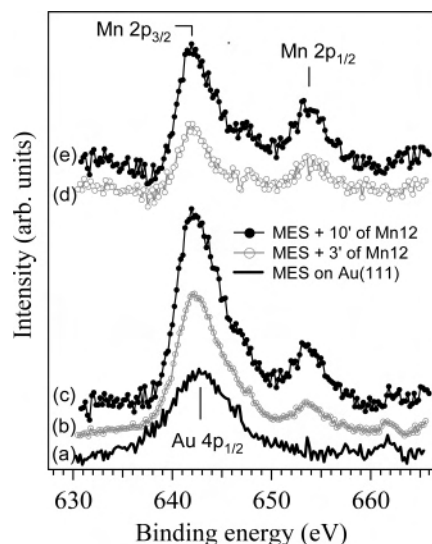
To check the strength of the ionic interactions between the magnetic cation and the anionic functionalized SAM,

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(12) Across a very large area, only two different height values have been observed: 1.4 nm (which corresponds to the  $\text{Mn}_{12}$  expected value) and 0.6 nm (which equals the value expected for the MES monolayer). This indicates that, in this case, STM is a good method to probe both topography and density of states. This is due to the small dimensions and rigidity of the organic shell around the  $\text{Mn}_{12}\text{O}_{12}$  core.

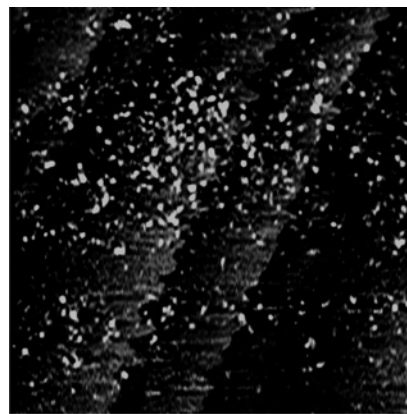
(13) Small aggregates of MES (1–2% coverage) are also observed. These particles have a height of ca. 0.6 nm. They are clearly distinguishable from the  $\text{Mn}_{12}$  clusters.



**Figure 2.** Core-level Mn 2p XPS spectra of MES/Au(111) samples before (a) and after 3 min (b) or 10 min (c) of immersion in a 1 mM solution of  $[\text{Mn}_{12}]^{14+}$  in  $\text{CH}_3\text{CN}$ . The MES/Au(111) contribution in part a has been subtracted from those in parts b and c to obtain the pure contribution of the Mn 2p core levels for 3 min (d) and 10 min (e) of immersion.

$[\text{Mn}_{12}]^{14+}$  clusters have been directly deposited on a gold surface. In this case (Figure 3), the  $\text{Mn}_{12}$  clusters are much less evenly distributed, with regions depleted and regions where  $\text{Mn}_{12}$  clusters are accumulated.

By comparing consecutive STM images of the same region, we have also observed that  $\text{Mn}_{12}$  clusters can be easily shifted or removed by the STM tip, suggesting that they are only weakly bound to the gold surface, at variance with the adsorption on the MES–SAM. Further, the exposure of the



**Figure 3.** Constant-current (30 pA and 2 V) STM image of  $[\text{Mn}_{12}]^{14+}$  molecules deposited directly on a Au(111) surface:  $200 \times 200 \text{ nm}^2$ .

sulfonate monolayer to a solution of  $\text{Mn}_{12}\text{Ac}$  leads to a deposition of aggregates of these neutral magnetic clusters exclusively along the steps of the gold substrate.  $\text{Mn}_{12}\text{Ac}$  has then a poor affinity for the MES–SAM. This clearly indicates that ligand exchange is irrelevant in the adsorption mechanism and that electrostatic interactions play a key role in this process.

In summary, the proposed two-step ionic approach has shown to be very efficient to immobilize cationic SMMs on gold surfaces. Compared with the direct attachment of neutral derivatives on gold using thiol groups, this procedure is intrinsically safer with respect to the redox stability of the manganese cluster. The main characteristic, derived from the electrostatic mutual repulsion of polycationic clusters, is the very uniform distribution of the single molecules and the absence of clustering. In addition, the small size of betaine, as compared to other carboxylate ligands, makes this  $[\text{Mn}_{12}]^{14+}$  derivative more accessible to the probe tip for investigating the magnetic or conducting properties of the core. Furthermore, SMMs anchored to the surface using this two-step approach seem to reveal a preferential orientation of their magnetic axis perpendicular to the surface.

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(14) The estimation of the  $\text{Mn}_{12}$  coverage proceeds as follows: the Mn  $2p_{1/2}$  peak area of the MES/Au(111) is quantitatively compared to the S 2p peak area of a previously measured methylthiolate SAM on Au with known packing, using the ratio between the tabulated sensitivity factors of the two lines. The  $\text{CH}_3\text{S}/\text{SAM}$  surface density is about  $21 \text{ \AA}^2/\text{molecule}$ ; therefore, the Mn 2p intensity corresponds to one Mn atom per  $200 \text{ \AA}^2$ ; i.e., a single  $\text{Mn}_{12}$  molecule occupies  $2400 \text{ \AA}^2$ . So, in the hypothesis that the sulfur atom of methylthiolate presents an attenuation factor similar to that of the Mn atom in the  $\text{Mn}_{12}$  cationic cluster, a surface density of about  $2400 \text{ \AA}^2/\text{molecule}$  can be derived. The expected area (assuming a molecular diameter of  $22 \text{ \AA}$ ) for a single  $\text{Mn}_{12}$  molecule is  $380 \text{ \AA}^2$ . This yields a coverage factor of ca. 15%.

(15) Additional evidence that the  $\text{Mn}_{12}$  complex is deposited without chemical change comes from the parallel increase of the Mn and N XPS signals with time.