Electronic and Magnetic Properties of Mn$_{12}$ Molecular Magnets on Sulfonate and Carboxylic Acid Prefunctionalized Gold Surfaces

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**ABSTRACT:** Structural, electronic, and magnetic properties of [Mn$_{12}$O$_{12}$(bet)$_{16}$(EtOH)$_4$](PF$_6$)$_{14}$·4CH$_3$CN·H$_2$O (in short Mn$_{12}$bet, bet = betaine = N(CH$_3$)$_2$CH$_1$−COO$^-$) single-molecule magnets (SMMs) deposited on previously functionalized gold surfaces have been investigated. Self-assembled monolayers (SAMs) either of sodium mercaptoethanesulfonate (MES) or mercaptopropionic acid (MPA) are used as functionalization to avoid the direct interaction between the Mn$_{12}$bet molecules and the Au surface with the aim of preserving the main functional properties of the molecules. Scanning tunneling microscopy (STM) and X-ray photoemission spectroscopy (XPS) analysis show deposited Mn$_{12}$bet SMMs well-isolated from each other and uniformly distributed on both MES and MPA SAMs. X-ray absorption spectroscopy (XAS) studies show that the oxidation state of the mixed-valence Mn$_{12}$bet core is largely reduced to Mn$^{2+}$ when molecules are deposited on MES-SAM, whereas in the case of MPA-SAM the relative weights of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ in the Mn$_{12}$bet core are preserved. Despite the substantial retaining of their electronic properties, the magnetization of Mn$_{12}$bet molecules deposited on MPA-SAM measured by X-ray magnetic circular dichroism (XMCD) is perturbed with respect to the pristine molecules. When Mn$_{12}$Ac molecules were anchored at surfaces,$^{14,15}$ that is because of the relatively weak stability of these compounds that leads to a large fragmentation and a reduction of the oxidation states of the magnetic ions when deposited on surfaces. As a result, the main functional properties of Mn$_{12}$Ac SMMs are lost.

Recently, the direct deposition of transition-metal SMMs on gold surfaces through covalent bond was partially successful only in particular cases of sulfur-functionalized robust magnetic molecules including Fe$_4$,$^{16,17}$ and Cr$_7$Ni$^{18,19}$ Conversely, sulfur-functionalized Mn$_{12}$Ac and Mn$_{16}$$^{20,21}$ complexes, which possess the highest anisotropy energy barrier temperatures reported so far for SMMs (61 and 86 K, respectively), showed structural modification of the molecular environment accomplished with a modification of the Mn oxidation states and a large decrease in the molecular magnetization when deposited on bare gold surfaces.$^{14,15,22}$ Overall, these findings suggest that although the

1. **INTRODUCTION**

It has been envisaged that ordered arrays of self-assembled monolayers (SAMs) of single-molecule magnets (SMMs)$^{1−9}$ would allow information to be stored at the single molecular level with a density of the order of 100 Tbit/in$^2$, which is far beyond the capability of modern hard disk drives (HDDs). This will represent a breakthrough in data storage technology, which will permit us to overcome the limitations imposed by the modern miniaturizing processes (top-down approach) in terms of increasing costs and reaching of the quantum super-paramagnetic limit. SMMs combine large spin-ground state (S) with large and negative zero-field splitting (D) to give rise to an anisotropy energy barrier (U) for the reversal of the magnetization. Therefore, SMMs could potentially be used to encode the basic unit of information for data storage devices,$^9$ spintronics,$^{2,10}$ and quantum computing.$^{11−13}$ The observation of the hysteresis loop at cryogenic temperatures in the first discovered SMM, Mn$_{12}$Ac,$^*$ suggested the possibility to use these molecules as magnetic HDD bits if properly deposited on surfaces. Unfortunately, no magnetic hysteresis was observed when Mn$_{12}$Ac molecules were anchored at surfaces.$^{14,15}$ That is because of the relatively weak stability of these compounds that leads to a large fragmentation and a reduction of the oxidation states of the magnetic ions when deposited on surfaces. As a result, the main functional properties of Mn$_{12}$Ac SMMs are lost.

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sulfur-functionalization is particularly suited to stabilize molecules at gold surfaces, it turns out to be inconvenient for Mn-based SMMs (Mn$_{12}$Ac and Mn$_{6}$) because it either reacts on its own with the redox-active Mn-core or facilitates the reactivity of the Mn-core with gold surfaces, yet the direct deposition of the as synthesized SMMs (without sulfur functionalization) on gold surfaces is detrimental for Mn-based SMMs.\textsuperscript{15} Remarkably progresses have recently been done on the deposition of Mn$_{12}$ SMMs by electrospray ion beam, which has been shown to be a soft method, compatible with the deposition of such fragile molecules. Indeed, the quantum properties of Mn$_{12}$ molecules have been demonstrated to be preserved if deposited on metallic and thin-insulating surfaces.\textsuperscript{23} The same deposition technique has also been used to study the self-assembled aggregation mechanism of Mn$_{12}$ SMMs on gold surface, but no proof of the preserved properties of the molecules was provided.\textsuperscript{24} Apparently, less problematic is the case of rare-earth SMMs, such as the bis(phthalocyaninato)terbium, which retain their magnetic properties almost unaltered when deposited onto bare graphite,\textsuperscript{25} gold,\textsuperscript{26} or copper.\textsuperscript{27} Therefore, the mechanism leading to alteration of the SMMs properties upon reacting with any surface is still far from being understood. Moreover, the implementation of suitable protocols for the deposition of 2D arrays of SMMs, which retain their main functional properties for data storage devices, is still challenging.

A quite interesting and promising route is the deposition of properly functionalized SMMs onto a prefunctionalized surface, which has the advantage of preventing the direct interaction of the molecules with the metallic surface. Eventually, this approach exploits the electrostatic interactions established between SMMs and the interface.\textsuperscript{28,29} In this approach, followed for the first time by some of us,\textsuperscript{30} the cationic [Mn$_{12}$O$_{12}$(bet)$_{16}$]($\text{EtOH}$)$_4$ (Scheme 1) of the Mn$_{12}$bet molecule,\textsuperscript{31} was electrostatically grafted on a Au(111) surface functionalized with a SAM of a sodium salt of mercaptoethanesulfonate (HS(CH$_2$)$_2$SO$_3$Na$^+$; MES) (Scheme 1). In contrast to Mn$_{12}$Ac, which contains 4 Mn$^{4+}$ and 8 Mn$^{3+}$,\textsuperscript{32} this cationic Mn$_{12}$ derivative contains two Mn$^{3+}$ sites coming from the reduction of two Mn$^{4+}$ ions.\textsuperscript{33} By combining scanning tunneling microscopy (STM) and X-ray photoemission spectroscopy (XPS) it was found that well isolated Mn$_{12}$bet SMMs were deposited on MES functionalized gold surfaces. However, poor information was given on the oxidation state of the Mn$_{12}$bet molecules because of the low spectral resolution of XPS. Most importantly, their magnetic properties after the deposition on the surface were not investigated.

Herein, we aim to study the topography, electronic and magnetic properties of Mn$_{12}$bet SMMs deposited on gold surfaces previously functionalized with MES or mercapto-propionic acid (HSCH$_2$CH$_2$COOH = MPA) ligands. Both MES and MPA ligands bind to a gold surface through thiol head-groups. The end-groups are SO$_3^-$/Na$^+$ and COOH, respectively. We first analyze the topography and core level spectra of MES and MPA SAMs and the deposited Mn$_{12}$bet by means of STM and XPS. Then, we investigate the valence of the Mn ions and magnetization curves at low temperature of the obtained SMM submonolayers (sub-MLs) with respect to the thick films (TFs) by X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD).

### 2. EXPERIMENTAL SECTION

#### 2.1. Synthesis

The synthesis of the Mn$_{12}$bet has already been reported.\textsuperscript{28} MES and MPA ligands were purchased from Aldrich and used without further treatments.

#### 2.2. Preparation of the Samples

Au(111) substrate was cleaned by repeated cycles of Ar$^+$ sputtering-annealing in ultrahigh vacuum (UHV) environment. Flame-annealed gold on mica substrates was also used for spectroscopic studies. For both MES and MPA, the functionalization of the gold substrates was achieved by dipping the substrates into a 1 mM ethanol solution of organic ligands for 10 min. Finally, the surface was washed out with ethanol to remove the excess of ligands that may form multiple layers and dried with nitrogen gas. The deposition of Mn$_{12}$bet SMMs on the formed SAMs of MES and MPA was achieved by dipping the substrates into a 1 mM solution of Mn$_{12}$bet in acetonitrile. TFs of Mn$_{12}$bet were achieved by casting a drop of a saturate solution of Mn$_{12}$bet on a gold surface and letting it to dry. It is worth noting that the choice of the MES and MPA length (~0.5 nm) has been done on the basis of two competing requirements: decoupling the molecules from the gold substrate and guaranteeing the conductivity between the molecules and the surface necessary for STM analysis.

#### 2.3. Magnetometer

Variable temperature magnetization data were collected on polycrystalline samples of Mn$_{12}$bet molecules by a calibrated commercial magnetometer.

Figure 1. Views of Mn$_{12}$bet molecular structure along (a) and perpendicular (b) to the main axis. Mn, purple; O, red; N, blue; C, black. H atoms and PF$_6^-$ counterions are omitted for clarity.

Scheme 1\textsuperscript{4}$^{4}$

"Top: the structures of the protonated betaine, MES, and MPA molecules. Bottom: scheme of the Mn$_{12}$bet grafted on a previously MES-functionalized gold surface."
magnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

2.4. Scanning Tunneling Microscopy. STM measurements were performed with an Omicron UHV STM system. The tips used were electrochemically etched from tungsten wires. The ad-layer morphology and SMMs size distributions were evaluated from a set of images obtained under identical experimental conditions. Room-temperature STM acquisitions were carried out in constant-current mode with typical imaging conditions of 2.0 V and 30 pA. We found that these reference values ensure good and very reproducible topographic contrast, whereas they minimize the mechanical interaction between the tip and the sample, preventing the soft organic material to be dragged or damaged during the scan operations.

2.5. X-ray Photoemission Spectroscopy. XPS measurements were performed with an Omicron hemispherical analyzer (EA125) and Mg Kα X-ray source (hν) 1253.6 eV.

2.6. X-ray Absorption Spectroscopy and X-ray Magnetic Circular Dichroism. XAS spectra at the Mn L\textsubscript{2,3} and L\textsubscript{1,2} edges of Mn\textsubscript{12}bet as TF and as sub-MLs on MPA/Au and MES/Au samples freshly prepared on site have been collected at the ID08 Dragon beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), in the total electron yield detection mode (TEY) and normalized by the incident photon flux. The degree of circular polarization was \sim 100\%, and no correction of polarization was necessary. The photon source was an Apple II undulator that delivers a high flux (10\textsuperscript{15} photons/s) of polarized light. The samples were fixed to a molybdenum sample holder by means of tantalum wires to ensure a proper thermal and electrical contact and readily transferred to a UHV (10\textsuperscript{−10} mbar) He magnetocryostat with base temperature of 10 K and maximum magnetic field of 5 T. In our geometry, the direction of both the impinging X-ray beam and the magnetic field is perpendicular to the sample surface. The \(σ^{↑↓}\) absorption spectrum is measured as the average of spectra collected with the photon helicity parallel (antiparallel) to the magnetic field direction. XMCD spectra are then derived as the difference between \(σ^{↑↑}\) and \(σ^{↑↓}\). The beam flux was attenuated by more than one order of magnitude to avoid sample degradation induced by radiation exposure. Under these conditions, the spectra did not show any sign of degradation during the time required to collect a complete set of XMCD spectra.

3. RESULTS AND DISCUSSION

3.1. Topography. First, we studied the topography of MES and MPA on Au(111), reported in Figure 2a,c, respectively, to verify the formation of homogeneous SAMs. The black regions, 0.20 ± 0.02 nm deep and large few nanometers, which are typical depressions of the gold surface, referred to us as vacancy islands (VIs). The presence of VIs confirms the occurrence bonding of the gold surface and the thiol head-groups of MES and MPA ligands as well as the formation of a homogeneous SAM\textsuperscript{32,33}. A few white spots are also visible with average height lower than 0.4 nm and diameter smaller than 3 nm (Figure 2c). We ascribe these entities to a partial second layer of residual solvents and organic ligands deposited on top of the SAM. The presence of these molecules does not prevent the identification of the Mn\textsubscript{12}bet SMMs we deposited on top of MES- and MPA-SAMs (Figure 2b,d). We observe a random and uniform distribution of larger white spots for both samples. The diameter of 3.0 ± 0.5 nm and height of 1.4 ± 0.2 nm, reported in Figure 2d, are comparable to those of the Mn\textsubscript{12}bet clusters (2.2 and 1.6 nm, respectively). The overestimation of the diameter of the Mn\textsubscript{12}bet molecules by STM is well known and is due to the finite curvature radius of the tip, whereas the under-estimation of the height is due to the difference of conductivity between the molecule and the substrate.\textsuperscript{34} The surface coverage of the larger white spots, supposed to be the Mn\textsubscript{12}bet SMMs, is estimated by statistical analysis of STM images. Taking into account the real diameter of the molecules of 2.2 nm, rather than that measured of 3 nm, we find that the average substrate area occupied by each single molecule is 39 ± 7 nm\textsuperscript{2}, which corresponds to a surface coverage of 8−12\% for both Mn\textsubscript{12}bet on MES and MPA samples. Smaller white spots are still visible and are ascribed to residual organic ligands and impurities.

3.2. Chemical Composition. The sulfur 2p core levels of the Mn\textsubscript{12}bet-MPA and Mn\textsubscript{12}bet-MES SAMS samples are reported in Figure 3a,c, respectively. The spectrum of the Mn\textsubscript{12}bet-MES sample is characterized by two broad peaks centered at about 162.2 and 168.0 eV binding energies. The peak at lower binding energies (162.2 eV) could be fitted with two spin−orbit doublets components, S1 and S2, with Voigt profiles. S1 doublet is assigned to the sulfur atoms covalently bonded to the gold atoms of the surface, whereas the S2 doublet is assigned to unbounded thiol groups of the MES ligands whose presence is also suggested by the STXM analysis. The ratio of the S1 and S2 integrated intensity gives an estimation of the partial second layer formed, which is \sim 15\%.
The peak at higher binding energy (168.5 eV) is assigned to the sulfonate group. The sulfur 2p core levels of the Mn$_{12}$bet-MPA sample has only one broad peak centered at 162.2 eV, which, by analogy to the Mn$_{12}$bet-MES sample, could be fitted with two components S1 and S2 characteristic of the sulfur atoms bonded and unbonded to the gold surface, respectively. In this case, the amount of second layer of MPA estimated is ∼20%. These results are in qualitative agreement with the presence of a partial second layer of ligands observed by STM on the same samples.

As far as the manganese is concerned, the observed XPS peaks at about 643 and 654 eV for both Mn$_{12}$bet-MES and Mn$_{12}$bet-MPA (Figure 3b,d) are assigned to Mn-2p$_{3/2}$ and 2p$_{1/2}$ core levels, respectively. This suggests the presence of Mn$_{12}$bet molecules, as also inferred from the analysis of the STM images. The contribution of the Au-4p$_{1/2}$ core level at about 641.5 eV is expected to be superimposed on the Mn-2p core level peak. Since the energy resolution of XPS is not sufficient to resolve the Mn oxidation states and chemical environment of Mn$_{12}$bet on MES and on MPA, this analysis will be carried out by XAS.

3.3. Electronic Properties. Figure 4 shows the XAS spectra of Mn$_{12}$bet on MES (d) and MPA (b) compared with that of the TF (c). The spectrum of the TF is assumed to give the fingerprint of the intact Mn$_{12}$bet, hence any differences observed in the sub-MLs spectra will give insight into the effects of the 2D configuration of the Mn$_{12}$bet molecules as well as of the substrate–molecules interactions. We clearly observe that the Mn$_{12}$bet on MPA spectrum overall resembles the TF spectrum even though slight modifications are present, such as an increased intensity of the feature at ∼642.5 eV and a shoulder at high energy at the L$_2$ edge, which are ascribed to the apparent increased contribution of Mn$^{3+}$ and Mn$^{4+}$. Both Mn$_{12}$bet on MPA and TF spectra are characterized by an intense feature at the L$_3$ edge at ∼639.6 eV. Conversely, the spectrum of the Mn$_{12}$bet on MES is dramatically different from the TF spectrum. Although the feature at 639.6 eV is still present at the L$_3$ edge of the Mn$_{12}$bet on MES spectrum, at higher photon energies, most of the features observed in the TF disappear, whereas the L$_2$ edge appears flattened and shifted to lower energies.

To facilitate the analysis of these spectra, we also report in Figure 4 the reference XAS spectrum (e) of the MnO containing Mn$^{2+}$ species only. This spectrum is clearly characterized by a peak at ∼639.6 eV, which is also present in the TF spectrum. This result confirms the expected partially reduced core structure of the Mn$_{12}$bet derivative, as already discussed in the Introduction. Interestingly, we observe that the XAS spectrum of the Mn$_{12}$bet on MES (spectrum d) is almost identical to that of MnO, suggesting that the magnetic cores of the Mn$_{12}$bet molecules are full reduced to Mn$^{2+}$.

From this analysis, we conclude that Mn$_{12}$bet on MPA is much less modified, in terms of oxidation state and crystal field, than on MES. Because the main difference between the MES and MPA functionalization consists of the presence of a sulfonate group in the MES and of a carboxylic acid in the MPA, this suggests that an electron charge transfer to the SMM molecules is favored by the sulfonate group. This could be due to the fact that the sulfonate group is bulkier and has a negative charge with respect to MPA so that there will be anionic repulsions between MES molecules and more steric problems in the SAM formation, albeit from the STM images, the final appearance of both kinds of SAMs seems quite similar. It could be, however, that due to the steric and charge problems mentioned above, the MES monolayer has a lower density than the MPA monolayer, and the Mn$_{12}$bet molecules can interact more with the Au surface affecting the Mn$_{12}$bet integrity. It appears, therefore, that the decoupling from the surface is more efficient with an MPA than with an MES monolayer.

Finally, we recorded the XAS spectrum of Mn$_{12}$bet molecules directly deposited on gold surface, spectrum (a) of Figure 4, starting from the same batch of diluted Mn$_{12}$bet samples used.
for the preparation of the sub-MLs. We already know from our previous work that under such conditions Mn$_{12}$$\text{bet}$ molecules tend to form bi- and tridimensional structures. The results show that the XAS spectrum (a) of the Mn$_{12}$$\text{bet}$ directly deposited on the gold surface resembles very well the spectral line shape of the TF, spectrum (c), suggesting that the electronic properties of the Mn$_{12}$$\text{bet}$ molecules are the same as those of the TF. In view of the above results, we restrict the investigation of the magnetic properties to Mn$_{12}$$\text{bet}$ SMMs deposited on MPA/Au substrate.

### 3.4. Magnetic Properties

Figure 5a,b (top panel) show representative $\sigma^{\uparrow\uparrow}$ and $\sigma^{\uparrow\downarrow}$ XAS spectra measured at 10 K and 5 T for Mn$_{12}$$\text{bet}$ as TF and sub-ML on MPA. The corresponding XMCD spectra are also reported in the bottom panel of Figure 5a,b. The dichroic signal is dominated by the Mn$^{2+}$ contribution at ~639.6 eV for both TF and sub-ML samples being more intense for the former. The sign of this peak is negative for both samples, which means that the Mn magnetic moments are aligned with the external field. The blue and thick lines are the integrals of the XMCD signals. The orbital sum moments are responsible for such differences in the corresponding XAS spectra that we ascribed to an increased contribution of the Mn$^{3+}$ and Mn$^{4+}$ valences (Figure 5c). These results suggest that the sub-ML magnetization is significantly lower and qualitatively different with respect to the TF. The causes responsible for such differences are discussed in the following. Figure 6 shows the magnetic field dependence of the XMCD signal % measured at 639.6 eV at 10 K for Mn$_{12}$$\text{bet}$ as TF and as sub-ML on MPA-SAM. The magnetization of a bulk polycrystalline sample measured at 10 and 20 K are also reported along with the fit of the magnetization calculated from the diagonalization of the spin Hamiltonian: $\hat{H} = D\hat{S}_z^2 + g\mu_B B \cdot \hat{S}$, where $S$ is the molecular spin, $D$ is the molecular zero-field splitting, $g$ the isotropic spectroscopic splitting factor, $\mu_B$ the Bohr magneton, and $B$ the magnetic induction. The best fit gives: $S = 11$, $D = -0.29$ K, and $g = 2.05$. The negative sign of $D$ means that the Mn$_{12}$$\text{bet}$ molecule possesses uniaxial anisotropy, and hence it behaves as a SMM. The XMCD signal has been rescaled to the bulk curve to compare directly its behavior with the magnetization curve. Indeed, the XMCD signal of the TF nicely overlaps with the magnetization curve, proving that the XMCD signal is proportional to the magnetization. The XMCD intensity of the Mn$_{12}$$\text{bet}$ sub-ML on MPA is much lower than that corresponding to the TF sample and its field dependence is significantly different, being more linear and without any trace of saturation at the highest fields. Therefore, although the electronic properties of Mn$_{12}$$\text{bet}$
as deduced from XAS spectra) seem to be almost retained, its magnetic properties seem to be perturbed by the deposition on the MPA prefunctionalized gold surface. Several causes can produce these differences, for example, structural changes of Mn₁₂bp SMMs grafted on surfaces due to the interaction with the SAM and orientation effects due to the Mn₁₂bp easy axis that lays preferentially in the plane of the surface (and hence perpendicular to the direction of the magnetic field) in the sub-ML rather than randomly oriented as in the case of the TF. Another possible reason for the different magnetic response between the TF and su-ML samples could be related to the incident beam overheating the grafted molecules with respect to the cold substrate. A very recent work demonstrates that heat flow across the interface is not favored by linking the molecules to the substrate through other than covalent bonds.

4. CONCLUSIONS

We have deposited Mn₁₂bp SMMs on MES- and MPA-functionalized gold surfaces, wishing to minimize the perturbations of the SMMs pristine properties induced by the interaction with the gold surface and to understand their origins. The analysis of the XAS spectra reveals that the interaction with the MES functionalization completely reduces the Mn₁₂bp core to Mn²⁺. Conversely, the MPA functionalization leaves almost unchanged the relative weights of the Mn³⁺, Mn⁴⁺, and Mn⁵⁺ valence states in the Mn₁₂bp. These findings emphasize that the (redox) stability of the Mn₁₂ core and hence its magnetism is strongly dependent on the nature of the interfacial molecular layer. Indeed, MPA-SAM seems to be a promising route for a deposition of SMMs on gold surfaces that preserves their electronic and magnetic properties. Still, the analysis of the XMCD spectra of Mn₁₂bp deposited on MPA-SAM in comparison with those characteristic of a TF shows significant changes in its magnetic properties. We suggest that the use of longer chains of carboxylic acid based ligands might lead to an effective decoupling of the Mn₁₂bp molecules and in general of molecular magnets from the substrate finally offering the possibility to retain their functional properties. However, whether these changes are due to small structural changes of the Mn₁₂ upon deposition on the MPA-SAM, to interactions with the functionalized substrate, or to a poor thermal conductivity of the MPA ligands are still open questions that deserve further investigations.

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