

Identification of linker molecules suited for deposition and study of Mn₁₂ single molecule magnets on Au surfaces

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The authors report on a scanning tunneling microscopy/spectroscopy investigation of the possibility to influence the assembly of monolayers of Mn₁₂ single molecule magnets on a functionalized Au(111) surface by using flexible linker molecules. The results corroborate the general suitability of the deposition via ligand exchange reaction but, on the other hand, reveal the need for a compromise between conductivity and flexibility of the linker molecules. The results are discussed with respect to previous attempts [A. Naitabdi *et al.*, *Adv. Mater. (Weinheim, Ger.)* **17**, 1612 (2005)] to deposit ordered monolayers of Mn₁₂ molecules on Au(111).

The interest in single molecule magnets (SMMs) such as Mn₁₂-acetate¹ has increased considerably since the discovery of their fascinating magnetic properties,²⁻⁴ allowing for the direct observation of quantum effects such as quantum tunneling of magnetization⁵ or quantum phase interference.⁶ Furthermore, there is a promising prospect to both address and manipulate the magnetic state of individual SMMs, allowing for future applications in ultrahigh density data storage or quantum computing devices.⁷

However, studies on the magnetic properties of individual SMMs require the ability to deposit monolayers or spatially isolated molecules on a well-defined surface. With respect to this, there have been a few attempts to deposit Mn₁₂ molecules on Au(111) surfaces either by means of functionalization of the molecule and taking advantage of a strong S–Au interaction^{8,9} or by means of using prefunctionalized surfaces allowing for the deposition of Mn₁₂ via a ligand exchange reaction¹⁰ or electrostatic interactions.¹¹ Moreover, there have been attempts to deposit Mn₁₂ molecules on Si surfaces by related chemical techniques.¹² Nonetheless, after utilizing wet chemical methods for deposition of Mn₁₂ on surfaces no profound evidence for any ordering of the molecular monolayer was obtained so far although a partial ordering of a Mn₁₂ monolayer has been reported.¹⁰

In this work, we present an investigation of two different prefunctionalization layers allowing for the deposition of Mn₁₂ molecules via the ligand exchange reaction.¹³ The functionalization layers as well as the Mn₁₂ molecules deposited on the respective layer have been investigated by means of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). The results demonstrate the general suitability of the deposition via a ligand exchange reaction but, on the other hand, reveal the need for a compromise between flexibility and conductivity of the prefunctionaliza-

tion layer to avoid measurement artifacts. These observations are discussed with respect to a previous attempt to deposit ordered monolayers of Mn₁₂ on the functionalized Au(111) surface.¹⁰

Single crystals of Mn₁₂-parafluorobenzoate [Mn₁₂O₁₂(O₂CC₆H₄F)₁₆(H₂O)₄] (Mn₁₂-pfb), 4'-mercapto-octafluoro-biphenyl-4-carboxylic acid (4-MOBKA), and 4-(mercaptomethyl)-2,3,5,6-tetrafluorobenzoic acid (4-MMTBA) were prepared and the respective monolayers were deposited on a Au(111) single crystal surface as described elsewhere.¹⁴ STM and STS measurements were performed using an Omicron VT AFM/STM incorporated into an Omicron Multiprobe UHV system with a base pressure of 10⁻¹¹ mbar. The STM tips were made of tungsten and had been flash annealed by electron bombardment after electrochemical etching. The tunneling current was set to 6.9 pA for all measurements.

Figure 1 shows a sketch of the linker molecules used in this study as well as a Mn₁₂ molecule grafted to the functionalization layer via ligand exchange reaction. Due to the in-

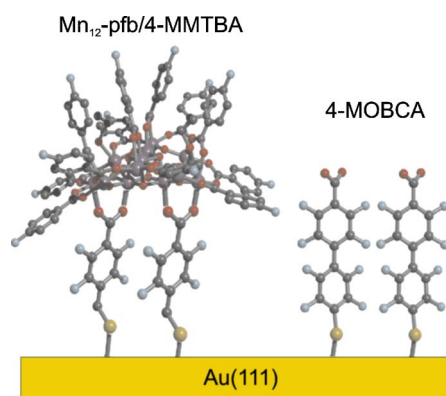


FIG. 1. (Color online) Sketch of a Mn₁₂-pfb molecule grafted to Au(111) via ligand exchange reaction with 4-MMTBA and of 4-MOBKA grafted to Au(111) prior to the deposition of the Mn₁₂ molecule.

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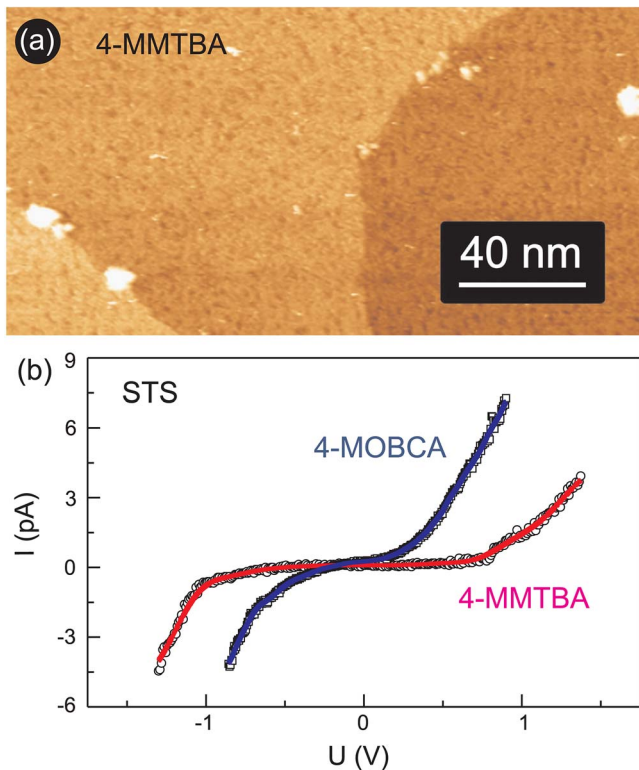


FIG. 2. (Color online) (a) $200 \times 100 \text{ nm}^2$ STM image of 4-MMTBA on Au(111). $U_T = +1 \text{ V}$. (b) Comparison of STS spectra obtained from 4-MMTBA and 4-MOBCA. In contrast to 4-MOBCA, 4-MMTBA displays a pronounced energy gap.

clusion of one alkyl spacer in 4-MMTBA the flexibility of the molecule should be increased what might, in principle, allow for the deposition of ordered Mn_{12} monolayers for sterical reasons. Figure 2(a) shows a STM image obtained from a monolayer of 4-MMTBA deposited on Au(111). The monoatomic steps of Au(111) are visible while very few contaminations are present on the surface. Apparent depressions within the monolayer can be assigned to vacancy islands in the upper layer of gold atoms formed during the self-assembly process.¹⁵ The topography is consistent with a 4-MMTBA layer of high quality allowing for the investigation of Mn_{12} -pfb molecules deposited in the following preparation step. The topography of 4-MOBCA is presented and discussed elsewhere.¹⁴ Figure 2(b) shows STS I - U spectra obtained from monolayers of 4-MMTBA and 4-MOBCA. Each spectrum represents an average of at least 20 measurements at different positions on the surface. The I - U spectrum of 4-MOBCA reveals a conductorlike signature of the conductivity what may be assigned to the delocalized electrons of the phenyl rings. In contrast, the I - U spectrum of 4-MMTBA reveals the presence of a $\sim 1.3 \text{ eV}$ wide energy gap. This result shows that the conductivity of the linker molecules can be significantly altered by the inclusion of a single alkyl spacer group lacking delocalized electrons.

Figure 3 shows STM images of Mn_{12} -pfb molecules deposited on (a) 4-MOBCA and (b) 4-MMTBA. The corresponding height profiles shown in Figs. 3(c) and 3(d) reveal a good agreement between the measured and expected height of the molecules.¹⁶ The topography of Mn_{12} -pfb on

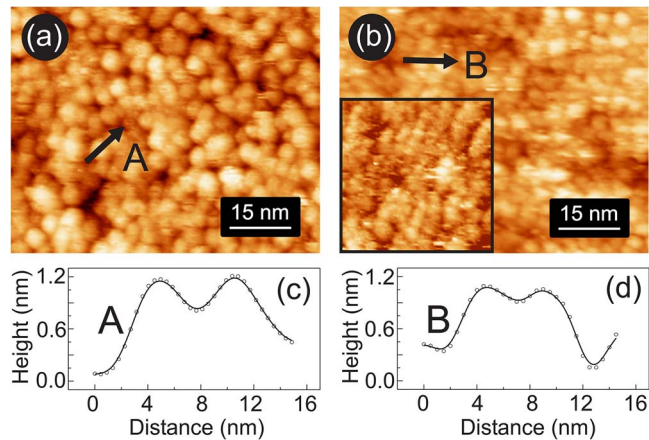


FIG. 3. (Color online) $75 \times 60 \text{ nm}^2$ STM images of Mn_{12} -pfb on (a) 4-MOBCA ($U_T = 2.3 \text{ V}$) and (b) 4-MMTBA. Tip artifacts like in (b) were observed with three different STM tips showing variations of the artifact geometry. The inset of (b) shows a STM image of artifacts obtained from the same sample with a different tip. Bias voltages between 2.3 and 3.7 V were applied, resulting in no significant changes of the topography. Corresponding height profiles are shown in (c) and (d).

4-MOBCA is identical to previous experiments.^{14,16} In contrast, in the case of Mn_{12} -pfb on 4-MMTBA a partial ordering (many groups of molecules in a row) seems to be visible. However, by using different STM tips we found that the apparent ordering of the molecules is a tip artefact. The topography changed with the tip used for the experiment [see inset of Fig. 3(b)]. Such artifacts could rarely be observed for Mn_{12} -pfb on 4-MOBCA with the effect being less distinct. This can be explained by the lower conductivity of the Mn_{12} -pfb/4-MMTBA system (see below).

Figure 4 shows STS I - U spectra obtained from Mn_{12} -pfb/4-MOBCA and from Mn_{12} -pfb/4-MMTBA. Each spectrum represents an average of at least 40 measurements at different positions. The width of the energy gap is slightly increased by $\sim 0.5 \text{ eV}$ in the case of Mn_{12} -pfb/4-MMTBA. However, this is not a sufficient explanation for the tip artifacts observed in Fig. 3(b). The tip artifacts may be explained by the fact that the STM tip approaches the molecular layer prior to any measurement until a fixed set current for a given set voltage is achieved. Since the conductivity of the 4-MMTBA molecule is rather low the STM tip may either touch the Mn_{12} -pfb layer or approach very close to stabilize the set current. This effect cannot be straightforward

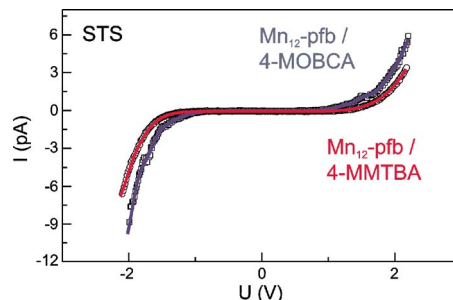


FIG. 4. (Color online) Comparison of STS spectra obtained on top of Mn_{12} -pfb molecules deposited on 4-MOBCA and 4-MMTBA, respectively. Each spectrum represents an average of at least 40 measurements on different molecules deposited on the respective functionalization layer.

overcome by increasing the set voltage because a voltage variation leads to a different distribution of the electrostatic potential between the electrodes¹⁷ but does not necessarily increase the tip-sample distance or the conductivity of the system under investigation significantly. The subsequent STS measurement may thus be quite similar to the spectrum obtained from Mn₁₂-pfb/4-MOBCA due to identical measurement parameters. Albeit this effect does not hamper the ability to perform STS measurements, the topographic STM images will be significantly distorted what results, for example, in multiple imaging of individual molecules what in turn leads to the fake of a partially ordered monolayer because the same tip replica is imaged around the position of each real molecule.

A distinction between real ordering and tip artifacts is not straightforward. However, the different STM tips used for the measurements on Mn₁₂-pfb/4-MMTBA were further investigated by imaging isolated contamination clusters on a Au(111) surface employing high set currents that lead to a close approach of the tip to the surface. All relevant signatures such as number of multiple tips as well as height and diameter distribution of the artificial images were comparable to the ones observed in the measurements on Mn₁₂-pfb/4-MMTBA. Thus a tip artifact simulating an ordered layer is most likely.

The results show similarities to a previous measurement,¹⁰ revealing a partial ordering within a monolayer of Mn₁₂ molecules deposited on a functionalization layer comprising 15 CH₂ spacers in each linker molecule. The presence of an energy gap in both long alkyl chains and Mn₁₂ molecules reveals, however, the possibility that the conductivity of the system under investigation was too low in the previous experiment¹⁰ what may also have resulted in tip artifacts. In principle, the ordering of the Mn₁₂ layer observed in the previous work¹⁰ could also be interpreted as a result of a multiple tip artifact what may be concluded from the groups of clusters with nearly identical diameter and height distribution visible in the STM image of the apparently ordered monolayer. As a consequence, both the new results as well as the previous result¹⁰ indicate that a compromise between flexibility and conductivity of the functionalization layer is necessary to access the real topography as well as the electronic structure of monolayers and individual Mn₁₂ molecules without any influence from STM tip artifacts.

In conclusion, we investigated and compared the topography as well as the electronic structure of Mn₁₂-pfb deposited on 4-MMTBA and 4-MOBCA by means of STM and STS. The topography and electronic structure of the two linker molecules were also investigated. The conductivity of

4-MMTBA is significantly lower than those of 4-MOBCA due to the inclusion of a single alkyl spacer lacking delocalized electrons. In contrast to the successful investigation of Mn₁₂-pfb deposited on 4-MOBCA, the low conductivity of the 4-MMTBA linker molecule resulted in severe tip artifacts during the investigation of Mn₁₂-pfb deposited on 4-MMTBA. Thus the possibility to obtain ordered Mn₁₂ monolayers by using flexible linker molecules could not be unambiguously clarified. However, the results show similarities to a previous result featuring a partial ordering of Mn₁₂ molecules on a functionalized surface. The results indicate the need for a compromise between sterical aspects (flexibility) and electronic properties (conductivity) of functionalization layers used for the deposition of Mn₁₂ molecules to gain access to the topographic and electronic properties of the Mn₁₂ monolayer.

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