Scanning tunneling spectroscopy on Mn$_{12}$ single molecule magnets grafted on Au(111)

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Abstract.

We report on the electronic properties of Mn$_{12}$ molecules chemically grafted on the functionalized Au(111) surface studied by means of scanning tunneling microscopy/spectroscopy at room temperature. Reproducible current-voltage curves were obtained from Mn$_{12}$ molecules showing a large region of low conductance around the Fermi energy. In agreement with the tunneling spectroscopy results the bias voltage variation upon scanning leads to apparent height changes of the Mn$_{12}$ clusters. We discuss these findings in the light of the recent band structure calculations and electronic transport measurements on single Mn$_{12}$ molecules.

Single molecule magnets (SMMs) [1] attract considerable attention due to their unique magnetic properties such as quantum tunnelling of magnetization (QTM) [2] and hysteresis of pure molecular origin [3, 4, 5] making them potential candidates for future spintronic applications [6]. The most widely investigated and first discovered SMM [7] is Mn$_{12}$ acetate [8] which allows for the exchange of the ligand shell thus facilitating the synthesis of a broad variety of derivatives [9]. To date, experiments on the magnetic and electronic properties of SMMs have been performed mostly on crystals and powders while the magnetic as well as the electronic properties of individual molecules or SMM monolayers on surfaces remain to a large extent unknown. Two possible experimental approaches to the investigation of the fundamental physical properties of individual Mn$_{12}$ molecules are feasible: transport measurements in a single-molecule transistor geometry [10, 11] or scanning tunneling spectroscopy (STS).

Very recently, investigations of the electronic properties of Mn$_{12}$ derivatives bound to Au surfaces by means of x-ray absorption spectroscopy and x-ray photoemission spectroscopy have been reported [12, 13]. The results presented in Ref.[13] showed a good agreement with the recent LDA+$U$ calculations on the valance band structure of Mn$_{12}$ molecules for $U$=4eV indicating the presence of intact Mn$_{12}$ molecules on a suitably functionalized Au(111) surface. However, no evidence for an energy gap in a chemically intact and spatially isolated Mn$_{12}$ cluster has been presented although it has been predicted theoretically [12, 14] and was observed in resonant photoemission spectroscopy measurements on Mn$_{12}$ monolayers [13].

In this work, we address the electronic properties of sub-monomers of Mn$_{12}$ molecules chemically grafted on a functionalized Au(111) surface studied by scanning tunneling microscopy/spectroscopy (STM/STS) at room temperature (RT).
Figure 1. (a) top and (b) side view of a Mn$_{12}$-pfb molecule. Violet spheres represent manganese ions, red - oxygen ions, blue - carbon, green - fluorine, yellow - hydrogen.

Mn$_{12}$-parafluorobenzoate [Mn$_{12}$O$_{12}$O$_2$C$_6$H$_4$F)$_{16}$(H$_2$O)$_4$] (see Fig. 1) referred to as Mn$_{12}$-pfb was prepared according to the procedure reported by Burgert et al. [15]. The 4-mercapto-2,3,5,6-tetrafluorobenzoic acid (4-MTBA) and 4'-mercapto-octafluorobiphenyl-4-carboxylic acid (4-MOBCA) functionalization layers as well as the Mn$_{12}$ layers were prepared according to the procedure reported elsewhere [15]. STM and STS measurements were performed in ultra-high vacuum (UHV) with an Omicron VT AFM/STM at RT using electrochemically etched tungsten tips that were flash-annealed by electron bombardment. The ± sign of the bias voltage denotes the voltage applied to the sample.

Figure 2 shows STM images of the Au(111) surface functionalized by 4-MOBCA (a) and 4-MTBA (c) as well as of Mn$_{12}$-pfb clusters on the functionalized Au(111) surface (b and d). The deposited Mn$_{12}$ clusters have a diameter of 2.4±0.2 nm full width at half maximum and an average apparent height of 1.2±0.1 nm measured with respect to the functionalization layer. The apparent diameter of the molecules is slightly larger than the expected diameter of about 2 nm derived from the crystal structure, that can be explained by the apex geometry of the STM tip used in this experiment. In addition, Mn$_{12}$ clusters deposited on the functionalized Au(111) surface could not be moved by the STM tip over the surface during scanning that indicates a successful chemisorption of the Mn$_{12}$-pfb clusters. Along with the STM images of Mn$_{12}$-pfb monolayers we also performed STS measurements on the individual Mn$_{12}$ clusters grafted on the functionalized Au(111) surface. Lower panels of Fig. 2 show $I-V$ characteristics recorded on the 4-MOBCA (a) and on the 4-MTBA (c) functionalized Au(111) surface as well as at center of the Mn$_{12}$-pfb molecules deposited on 4-MOBCA/Au(111) (b) and 4-MTBA/Au(111) (d). The $I-V$ curves presented here were obtained by averaging over at least thirty (4-MOBCA) or six (4-MTBA) curves recorded at different locations of the sample surface. The $I-V$ characteristics recorded on the functionalized surfaces [Fig. 4 (a) and 4 (c)] show the features typical for aromatic thiols with an asymmetry between positive and negative bias voltages [16].

Both $I-V$ curves obtained at the center of Mn$_{12}$-pfb clusters deposited on the 4-MOBCA functionalized Au(111) surface show a line shape revealing a broad region of low conductivity. In case of Mn$_{12}$-pfb deposited on the 4-MTBA functionalized surface [Fig. 2 (d)] we found that increasing the bias voltage beyond -1.2 V during STS measurements leads to large instabilities in the $I-V$ spectra. In contrast to 4-MTBA, the use of 4-MOBCA was found to be more advantageous since no instabilities in the STS spectra in both positive and negative bias voltage ranges were observed. This allows for the investigation of a broader energetic region around
Figure 2. 150 × 150 nm² STM images of (a) the 4-MOBCA functionalized surface, (b) Mn₁₂-pfb deposited on the 4-MOBCA functionalized Au(111) surface, (c) the 4-MTBA functionalized surface, and (d) Mn₁₂-pfb deposited on the 4-MTBA functionalized Au(111) surface. STM scanning parameters for the images shown in (a) and (c) were $U_T = 1$ V and $I_T = 6.9$ pA; in (b) and (d) $U_T = 2$ V and $I_T = 6.9$ pA. Lower panels of (a) and (c) show the corresponding $I − U$ characteristics for each functionalized surface. Lower panels of (b) and (d) show the corresponding $I − U$ curves measured on top of the Mn₁₂ clusters. $I − U$ curves in (b) correspond to different set voltages (1.7 V and 2.3 V), $I − U$ curve in (d) was recorded at 2.7 V set voltage.

the Fermi energy compared with the previous studies [17]. Moreover, STS measurements at different set voltages were possible on Mn₁₂-pfb deposited on the 4-MOBCA functionalized Au(111) surface [see Fig. 2 (b)].

Figure 3 shows STM images of Mn₁₂-pfb on 4-MTBA/Au(111) obtained at +2 V and +0.5 V. The higher bias voltage corresponds to the band onset whereas the lower value corresponds to the energy gap region. When imaging within the broad gap region (+0.5 V), the Mn₁₂-pfb molecules are almost “invisible” for the STM tip and thus the characteristic monoatomic steps of Au(111) can be observed [Fig. 3 (b)]. At +2 V bias voltage the Mn₁₂-pfb molecules are visible with an apparent height of [1.2±0.1] nm measured with respect to the functionalization layer that is consistent with the expected height of 1.5 nm for a free standing molecule.

The $I − U$ characteristics in the region of the positive bias voltage [Fig. 2 (b)] are comparable to that presented in Fig. 2 (d) showing a slightly smaller region of low conductivity due to the smaller set voltage. The width of the latter region was determined to be about 2 eV [Fig. 2 (b)] that is close to the value measured for another Mn₁₂ derivative bound to the Au(111) surface [17]. The STS spectrum obtained at a set voltage of 1.7 V [Fig. 2 (b)] is nearly symmetric. This symmetry indicates that the electrostatic coupling between molecule and substrate is comparable to the coupling between tip and molecule [18]. In previous studies this condition was used to estimate the $E_F$-HOMO difference, which is one-fourth of the measured energy gap width [18]. Assuming a negligible contribution from the ligands as well as from the linker molecules because of their expected conductor-like behavior in STS measurements, application of this formalism to Mn₁₂-pfb yields a value of 0.5±0.2 eV. This value would be in reasonable agreement with the electronic structure found in the combined experimental and theoretical study of Mn₁₂-acetate [14].

In conclusion, we performed STM/STS measurements at RT in order to determine the electronic structure of spatially isolated Mn₁₂-pfb molecules chemically grafted on the
Figure 3. 120 × 70 nm² STM images of Mn₁₂-pfb clusters recorded at the same area at +2 V (a) and +0.5 V (b) bias voltage. Corresponding height profiles are shown in the lower panels.

functionalized Au(111) surface. Reproducible current-voltage curves were obtained from Mn₁₂ molecules showing a well defined wide energy gap. In agreement with the tunneling spectroscopy results the bias voltage variation upon scanning leads to apparent height changes of the Mn₁₂ clusters. Although the full electronic structure of Mn₁₂-pfb cannot be determined from our results we showed that chemically intact Mn₁₂ clusters exhibit an energy gap in STM studies. These results represent a key step towards addressing the magnetic properties of individual Mn₁₂ molecules by means of STM/STS.

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