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Electronic transport properties and orientation of individual Mn_{12} single-molecule magnets

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Individual Mn_{12} single-molecule magnets have been investigated by means of scanning tunneling spectroscopy at room temperature. Current-voltage characteristics of a Mn_{12} derivative are studied in detail and compared with simulations. A few-parameter scalar model for ballistic current flow through a single energy level is sufficient to describe the main features observed in scanning tunneling spectra of individual Mn_{12} molecules and offers a deeper insight into the electronic transport properties of this class of single-molecule magnets. In addition, distance-voltage spectroscopy performed on individual Mn_{12} molecules reveals a possibility to identify the orientation of the molecular easy axis. The results indicate a preferential orientation of the easy axis of the molecules nearly perpendicular to the surface.

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I. INTRODUCTION

Mn_{12} single-molecule magnets (SMMs) have attracted considerable interest since the discovery of their fascinating magnetic properties.[1,2] During the past two decades, crystalline SMM samples have been intensively studied, unveiling the ability to directly observe quantum tunneling of magnetization or quantum phase interference effects.[3–7] Most of the observed effects are ascribed to properties of individual molecules rather than an interaction between the molecules.[8] Hence, significant effort is under way to study SMM monolayers or the individual molecules experimentally as well as theoretically.[9–19] For this purpose, Mn_{12} acetate[20] and its derivatives are a preferred material class because the high ground-state spin ($S=10$) (Ref. 21) combined with a large magnetic anisotropy results in relatively high blocking temperatures (~3.5 K) and very long relaxation times possibly allowing an investigation of the magnetic properties of individual molecules at experimentally accessible temperature. Furthermore, the ligand shell of Mn_{12} can be tailored[22] to meet specific requirements for experiments. Recent results indicated that Mn_{12} molecules can be deposited on conductive surfaces despite their redox instability.[23–25] This was achieved by using either long-chain ligands or prefunctionalization layers to ensure a sufficient decoupling of the molecules from a metallic substrate or by using appropriate solvents. Electronic transport characteristics of a Mn_{12} derivative obtained by means of scanning tunneling spectroscopy (STS) revealed a large conductance gap.[26] However, future magnetic-field-dependent STS studies require novel theoretical as well as experimental approaches as current-voltage (I-U) characteristics of Mn_{12} molecules obtained by means of STS cannot be assigned to electronic structure calculations[10] in a straightforward manner. Furthermore, knowledge of the orientation of the molecular easy axis is required for magnetic-field-dependent studies.

In this paper, we show that STS spectra obtained from Mn_{12} molecules reflect signatures of pure highest occupied molecular orbital (HOMO)-mediated[27] transport. This finding is discussed with respect to calculations on electronic transport through Mn_{12} molecules. Furthermore, distance-voltage (z-U) spectra[28] obtained from individual Mn_{12} molecules indicate a preferential orientation of the molecular easy axis approximately perpendicular to the surface. The results are further corroborated by macroassisted I-U spectroscopy and represent an important step toward future magnetic-field-dependent STS studies.

II. EXPERIMENT AND SIMULATION

Single crystals of Mn_{12}-thiophene-3-carboxylate $[Mn_{12}O_{12}(O_2CC_4H_3S)_{16}(H_2O)_4]$ (further referred to as Mn_{12}-th) were prepared according to the procedures reported by Lim *et al.*[29] A sketch of the molecule is shown in Fig. 1. Mn_{12}-th monolayers on a functionalized Au(111) single-crystal surface were prepared via ligand exchange reaction with 4′-mercapto-octafluorobiphenyl-4-carboxylic acid (4-MOBCA) as described elsewhere.[25] STS measurements were performed with an Omicron VT AFM/STM scanning tunneling microscope (STM) incorporated into an Omicron multi-

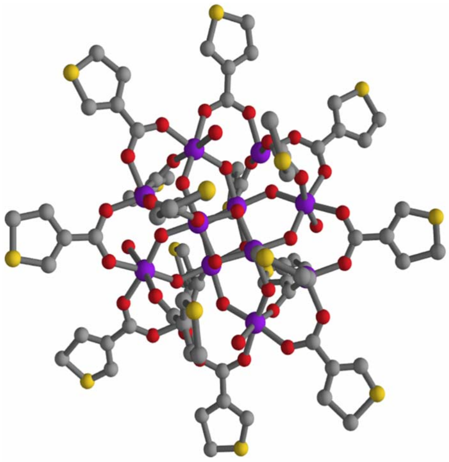

FIG. 1. (Color online) Sketch of a Mn_{12}-th molecule viewed along the easy axis. Mn: violet, O: red, S: yellow, and C: gray.

probe UHV system (base pressure of 10^{-11} mbar) at room temperature. The sign of the bias voltage corresponds to the voltage applied to the sample. Electrochemically etched tungsten tips flash annealed by electron bombardment were used.

Simulations of STS *I*-*U* spectra were obtained via the MOLCTOY code which is a few-parameter scalar model for ballistic current flow through a single energy level.[30,31] This code couples a minimal model for the molecular electronic states with a Landauer theory of transport with a few adjustable parameters. The only parameters used were Γ_1: coupling to electrode 1, Γ_2: coupling to electrode 2, U_C: single-electron charging energy, and E_F-ϵ: difference between the Fermi level and the nearest molecular orbital [HOMO or lowest unoccupied molecular orbital (LUMO)]. In the experiments, electrode 1 corresponds to the Au(111) substrate while electrode 2 corresponds to the STM tip. The model takes into account that conductance gaps in STS *I*-*U* (*dI*-*dU*) spectra of many molecules on surfaces do not reflect the HOMO-LUMO gap but a signature of either pure HOMO- or pure LUMO-mediated transport for both polarities.[32] The one-level model is appropriate in the case of STS measurements on Mn_{12}-th at room temperature because of the large conductance gap with no hints of multiple levels being visible in the conductance onset region. It is worth noticing that a signature of the HOMO-LUMO gap may be visible in STS measurements for extremely asymmetric tunneling conditions;[30] that is, however, not realized in the present experiment due to the decoupling of the Mn_{12} core from the Au(111) substrate via the 4-MOBCA linker molecules. Additional details of the MOLCTOY code are described elsewhere.[30,31,33]

Due to the simplification of the model, few real parameter values can be derived by fitting the simulated to the experimental *I*-*U* spectra. Nevertheless, the nature of the molecular level participating in the electronic transport (occupied or unoccupied) can be identified.[34] Furthermore, the difference between the Fermi level and HOMO or LUMO can be estimated.

III. RESULTS AND DISCUSSION

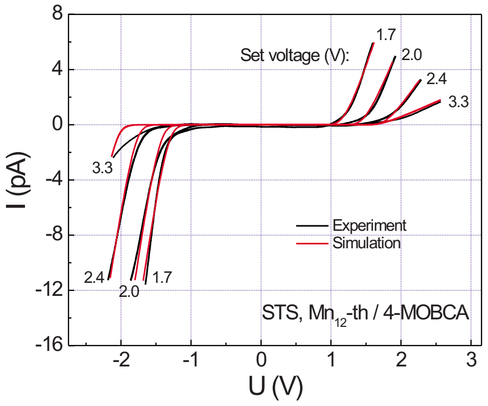

FIG. 2. (Color online) STS spectra obtained from Mn_{12}-th at different set voltages (black) and corresponding spectra obtained from the simulations (red). A higher set voltage in STS measurements corresponds to a larger distance between tip and molecule.

Figure 2 shows STS *I*-*U* spectra (black) obtained from Mn_{12}-th molecules on 4-MOBCA/Au(111). As demonstrated previously,[26] the spectra reveal a large conductance gap that can be assigned to the Mn_{12} core because neither 4-MOBCA nor the ligands exhibit a conductance gap. Under variation in the set voltage applied between tip and sample, the width of the conductance gap changes from about 2.3 to nearly 4 eV. The red curves in Fig. 2 represent *I*-*U* spectra simulated with the MOLCTOY code[30,31] for $T=300$ K. The charging energy was set to 1.5 eV for all calculations. The other parameters are listed in Table I. The total values for U_C and $\Gamma_{1,2}$ were arbitrarily chosen as the resulting currents were multiplied by a constant factor (10^{-6}) to adjust the theoretical to the experimental curves. Nevertheless, the ratio between these values was carefully optimized to achieve the best fit. In particular, the ratio of the coupling parameters (Γ_2/Γ_1) provides an insight into the electronic transport through the molecule. The asymmetry of the *I*-*U* spectra which changes as a function of the set voltage can be explained as follows: an increase in the set voltage results in a larger distance between molecule and tip that reduces the coupling parameter Γ_2 while the coupling between molecule and substrate Γ_1 remains unchanged.[35] As shown in Table I, the coupling between tip and molecule is always weaker than the coupling between molecule and substrate ($\Gamma_2<\Gamma_1$). Although the real values of $\Gamma_{1,2}$ are presumably significantly different, the correct ratio can be derived from the simulations. Based on this result, the asymmetric variation in the spectral shape can be used to determine the molecular level participating in the electronic transport. Assuming transport via the HOMO level, the stronger coupling between molecule and substrate Γ_1 compared with the weaker coupling between tip and molecule Γ_2 results in an effective depletion of the HOMO level for positive bias voltage (electrons tunneling from the tip toward the substrate) which causes a self-consistent charging energy that lowers the HOMO level with respect to E_F.[34] Consequently, the onset of the current in *I*-*U* spectra is shifted to higher bias voltage in the positive range and thus the slope of the *I*-*U* curve decreases. For transport via the LUMO, the asymmetry would be vice versa. As a result, the transport through Mn_{12}-th in STS measurements in the voltage range of (at least) 1.7–3.3 V occurs via the HOMO level. This finding may be taken into account for future calculations and field-dependent measurements because the applied

TABLE I. Parameters used for the simulations in Fig. 2. The corresponding set voltage for the respective STS measurement is also listed. $T=300$ K and $U_C=1.5$ eV.

Set voltage (V)	E_F-ϵ (eV)	Γ_1 (eV)	Γ_2 (eV)	Γ_2/Γ_1
1.7	0.72	0.5	0.21	0.42
2.0	0.82	0.5	0.17	0.34
2.4	0.98	0.5	0.10	0.20
3.3	1.02[a]	0.5	0.03	0.06

[a] Value estimated due to instabilities in experimental spectra at high negative voltage.

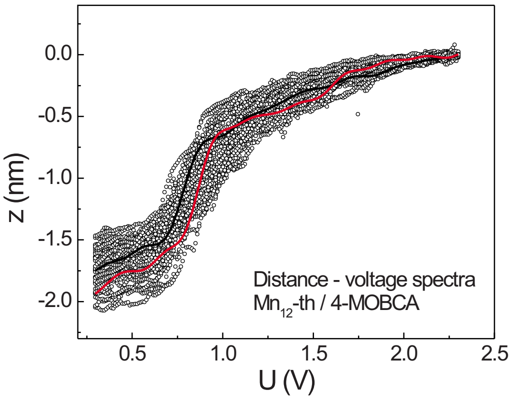

FIG. 3. (Color online) Forty distance-voltage (z-U) spectra obtained from different Mn_{12}-th molecules (unfiltered raw data) revealing two distance ranges separated by a distinct descent around 1 V. The two spectra shown as a straight line demonstrate that the step height is nearly identical for different curves while there are variations in the tunneling contact range.

voltage range corresponds to the values usually used for the investigation of Mn_{12} molecules by means of STM/STS. Instead of considering tunneling through the Mn_{12} molecules and pure scattering on a $S=10$ spin, the occupation of the HOMO level may have to be included in the calculations. In addition, the difference between the Fermi level and HOMO was estimated. Although additional tunable parameters as well as details of the measurement geometry and the electronic structure of the molecules have to be included in future experiments and more advanced simulations, the order of magnitude of the E_F-HOMO difference required to adjust the simulated to the experimental spectra is in good agreement with calculations on the electronic structure of Mn_{12} molecules.[10,11,36]

As demonstrated for different molecules,[28] the presence of a conductance gap in molecules can be used for distance-voltage spectroscopy. Here, we show that this is also valid for Mn_{12}-th and that there is a signature of a preferred orientation of the molecular easy axis with respect to the surface.

Figure 3 shows z-U spectra obtained from 40 different Mn_{12}-th molecules on 4-MOBCA/Au(111). The spectra were obtained by measuring the z position of the STM piezotube as a function of the voltage applied between tip and substrate. The feedback loop remained operating. Two distance ranges separated by a distinct descent are visible. This can be assigned to the conductance gap of Mn_{12}-th. Above 1 V, electronic transport occurs via the HOMO level of Mn_{12}-th. The tip approaches slightly with decreasing voltage. Around 1 V, a conductance gap sets in. This value cannot be directly assigned to signatures in the I-U spectra because it corresponds to a set voltage below the range of stable STM/STS measurements on Mn_{12}-th. In the range of the descent the tip is rapidly extended with decreasing voltage and penetrates the molecule. Around 0.7 V, another stable distance range sets in which corresponds to a normal tunneling contact with the 4-MOBCA substrate as the linker molecules are sufficiently conductive at low bias voltage.[25] The average height of the step separating the two distance ranges is 1 ± 0.2 nm. As visible in Fig. 3, the step height varies only slightly for different spectra while significant variations are visible in the tunneling contact range. The step height can be used as an estimation of the real height of the molecules.[28] A small uncertainty arises from the fact that the tunneling distance between tip and Mn_{12}-th as well as 4-MOBCA is slightly different due to the different electronic structure.[25] Nonetheless, the small spread of the measured height values indicates a preferential orientation of the molecules either with the easy axis perpendicular or parallel to the surface. For an orientation with the easy axis perpendicular to the surface, the comparison with the structural x-ray data obtained from Mn_{12}-th single crystals yields diameters in the 0.9–1.2 nm range (taking into account the ligand exchange reaction with 4-MOBCA) which is in good agreement with the measured heights. For an orientation with the easy axis parallel to the surface, the structural x-ray data yields heights in the 1.4–1.6 nm range while in the case of random orientation a larger spread (± 0.4 nm) would be expected. The comparison indicates that the molecules are oriented with the easy axis perpendicular to the surface. A preferred orientation can be explained by a higher probability for exchange of axial ligands.[22] Nevertheless, a small uncertainty remains due to the lack of knowledge about the exact state of the STM tip after penetrating the Mn_{12}-th molecule.

For corroboration of the z-U spectra, macroassisted I-U spectroscopy was performed. Two different measurement modes were used to consecutively record I-U spectra from Mn_{12}-th and 4-MOBCA molecules. In the "z-U approach" mode, the STM tip was regularly approached (2.8 V and 6.9 pA) to obtain STS spectra from a Mn_{12}-th molecule. In the next step, the bias voltage was reduced to 0.3 V (corresponding to the conductance gap region) while the feedback loop remained operating and the set current was unaltered. After a delay time of 0.2 s the feedback loop was switched off and an I-U spectrum was recorded. On the other hand, the "forced approach" was achieved by extending the STM tip by 1.2 nm (Ref. 37) (feedback loop off) after recording the STS spectrum of Mn_{12}-th. Subsequently, another STS spectrum was recorded. According to the z-U spectra (Fig. 3), both operating modes are expected to result in STS spectra obtained from Mn_{12}-th and from 4-MOBCA (with a tunneling distance of a few angstrom in both cases). Figure 4 shows a comparison of the spectra. In agreement with the previous measurements, Mn_{12}-th features a broad conductance gap. In contrast, the spectrum obtained after approaching the tip shows no gaplike features and is comparable to previous spectra obtained from 4-MOBCA.[25] The current measured after the forced approach was slightly smaller than after z-U approach due to the larger tip-molecule distance in the former case. The total current in both measurements on 4-MOBCA is higher compared to previous measurements[25] due to the smaller tip-molecule distance. The similarity between the spectra recorded in the two different modes demonstrates their equivalence. Consequently, the features visible in the z-U spectra (Fig. 3) correspond to a monolayer of Mn_{12}-th molecules grafted to 4-MOBCA.

The results show that z-U spectroscopy can be applied to estimate the height of Mn_{12} molecules. An estimation of the real height of different Mn_{12} molecules within a monolayer is

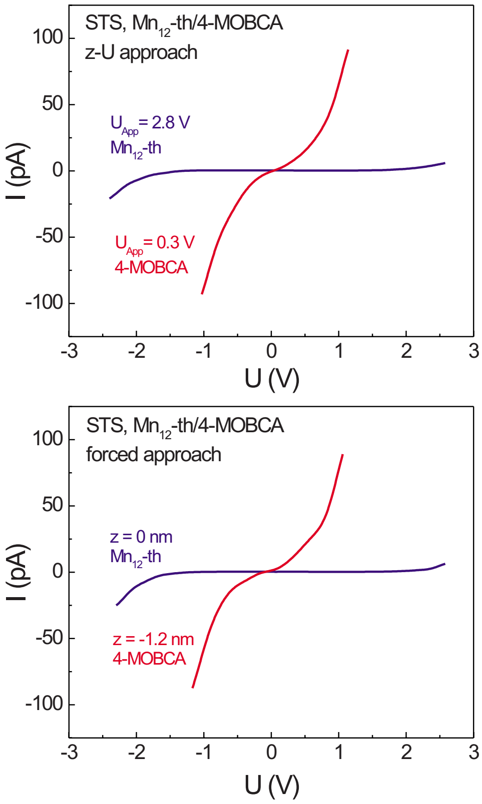

FIG. 4. (Color online) STS *I-U* spectra obtained from Mn_{12}-th and from 4-MOBCA in two different operating modes.

an important prerequisite for future magnetic-field-dependent STS studies. The knowledge of the relative heights can be used to estimate the orientation of the molecular easy axis with respect to the surface. Furthermore, the results corroborate the success of the ligand exchange reaction by providing evidence that a monolayer of Mn_{12} molecules is grafted to the surface rather than, for example, a multilayer or a layer of small molecular fragments. Consequently, future magnetic-field-dependent STM/STS measurements can be performed on individual Mn_{12} molecules in awareness of the orientation of the easy axis without any influences from bulk effects.

IV. CONCLUSIONS

In conclusion, individual Mn_{12}-th single-molecule magnets have been deposited on Au(111) via ligand exchange reaction with 4-MOBCA. Comparison of experimental STS *I-U* spectra obtained at different set voltages with simulations obtained via a one-level model shows that the electronic transport through Mn_{12}-th molecules in STS measurements occurs via the HOMO. Furthermore, the applicability of *z-U* spectroscopy to Mn_{12} molecules has been demonstrated. The results indicate a preferential orientation of Mn_{12}-th molecules with the easy axis perpendicular to the surface. An estimation of the orientation of individual Mn_{12} molecules within a monolayer will allow well-defined magnetic-field-dependent STS measurements in the future.

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