Influence of the ligand shell on the surface orientation of Mn₁₂ single molecule magnets

M. Fonin^{a,*}, S. Voss^a, S. Herr^{a,b}, G. de Loubens^b, A.D. Kent^b, M. Burgert^c, U. Groth^c, U. Rüdiger^a

^a Department of Physics, University of Konstanz, 78457 Konstanz, Germany

^b Department of Physics, New York University, 4 Washington Place, New York, NY 10003, USA

^c Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany

ABSTRACT

Here we report the synthesis, investigation as well as surface deposition of a truly axial symmetry Mn₁₂-diphenylphosphinate (Mn₁₂-phn) single molecule magnet. Out of 16 acetate ligands encapsulating the Mn₁₂O₁₂ core, 12 ligands were exchanged by diphenylphosphinate in this compound. Mn₁₂-phn shows well-defined magnetic hysteresis curves indicating a very high crystal quality. A monolayer of Mn₁₂-phn was chemically grafted on a functionalized Au(111) surface via ligand exchange reaction and studied by means of scanning tunneling microscopy and spectroscopy. Via distance-voltage spectroscopy we determine the real-space height of the Mn₁₂-phn molecules with high accuracy. A large spread in the measured molecular heights obtained from the distance-voltage spectra indicates the absence of preferential orientation of Mn₁₂-phn molecules with respect to the surface which we attribute to the equal anchoring probability of all diphenylphosphinate ligands in Mn₁₂-phn while none of the four acetate ligands are exchanged. These results are compared with the experimental data obtained from a different Mn₁₂ derivative containing 16 thiophenecarboxylate ligands. In general, we show that the substitution of the ligand shell may have a major impact on the surface orientation of the Mn₁₂ clusters deposited on Au, i.e. on the orientation of the easy magnetization axis.

Keywords:
Single molecule magnets
Mn₁₂

1. Introduction

During the past decade single molecule magnets (SMMs) [1,2] have attracted much attention due to their unique magnetic properties such as quantum tunneling of magnetization (QTM) or quantum phase interference making them potential candidates for future applications as basic units in information technology devices [3,4]. The Mn₁₂ family ([Mn₁₂O₁₂(O₂CL)₁₆(H₂O)₄] with L – various ligands) with a S = 10 ground state and relatively high blocking temperatures (about 3.5 K) represents the first discovered and to date best investigated class. Moreover, by tailoring of the ligand shell of Mn₁₂ its magnetic, mechanical, optical and electrical properties can be altered to meet a broad variety of requirements for possible applications. The combination of these favourable properties makes Mn₁₂ derivatives the preferred SMMs for deposition and characterization of individual molecules or monolayers on surfaces. With respect to this, several investigations regarding the ability to deposit Mn₁₂ molecules on surfaces have been performed [5–11]. Despite several setbacks due to an extraordinary redox-instability of Mn₁₂, recent results indicate a possibility to

reliably obtain monolayers of intact molecules on Au(111) surfaces [5,11,12]. Electronic transport characteristics of a Mn₁₂ derivative obtained by means of scanning tunneling spectroscopy (STS) revealed a large conductance gap [13]. However, future magnetic field dependent STS studies require not only the knowledge of the electronic structure but also of the orientation of the molecular easy axis with respect to the surface. To this end, the influence of the tailored ligand shell of Mn₁₂ derivatives on the orientation of clusters deposited via ligand exchange reaction on different surfaces remains to be tested.

Here we report the synthesis, investigation as well as surface deposition of a new Mn₁₂ derivative, namely [[Mn₁₂O₁₂(O₂PC₁₂H₁₀)₁₂(O₂CCH₃)₄(H₂O)₄][Mn₁₂O₁₂(O₂PC₁₂H₁₀)₁₂(O₂CCH₃)₄]] (Mn₁₂-diphenylphosphinate, Mn₁₂-phn). Magnetic hysteresis measurements on Mn₁₂-phn confirm its single molecule magnet properties. Mn₁₂-phn was chemically grafted on a Au(111) surface functionalized with 4'-mercapto-octafluorobiphenyl-4-carboxylic acid (4-MOBICA) and studied by means of scanning tunneling microscopy (STM) and spectroscopy at room temperature. We determine the real-space height of the molecules grafted on the functionalized Au surface with high accuracy by implementing the distance-voltage (*z*-*U*) spectroscopy. An observed large spread in the measured molecular heights obtained from *z*-*U* spectra indicates no preferential orientation of the molecules on the surface.

* Corresponding author. Tel.: +49 7531 883106; fax: +49 7531 883789.
E-mail address: mikhail.fonin@uni-konstanz.de (M. Fonin).

2. Experimental

2.1. Compound preparation

All chemicals and solvents were used as received. The complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]$ ($\text{Mn}_{12}\text{-ac}$) was prepared as described elsewhere [14]. $\text{Mn}_{12}\text{-phn}$ was prepared as described below. A solution of diphenylphosphinic acid (0.79 g, 3.2 mmol) in CH_2Cl_2 (80 ml) was dropped into a solution of $\text{Mn}_{12}\text{-ac}$ (0.50 g, 0.24 mmol) in acetonitrile (50 ml) within 1 h. The solvent was evaporated under reduced pressure to complete dryness. The remaining solid was redissolved in CH_2Cl_2 (70 ml) and filtered through kieselguhr. Hexane was added and the solution was allowed to stand undisturbed at 4 °C for 12 h. The resulting black crystals were collected by filtration, washed with hexane and dried in vacuo. A crystallography sample was grown slowly from CH_2Cl_2 /hexane at 4 °C and maintained in mother liquor to avoid solvent loss. Selected IR bands (ATR, cm^{-1}): 3053 (w), 1570 (m), 1541 (m), 1485 (w), 1437 (m), 1384 (m), 1332 (m), 1124 (vs), 1046 (vs), 1014 (vs), 994 (vs), 751 (m), 723 (vs), 701 (vs). MALDI-TOF-MS (m/z): 3693.2 $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{PC}_{12}\text{H}_{10})_{12}(\text{O}_2\text{CCH}_3)_4]^+$; 3633.8 $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{PC}_{12}\text{H}_{10})_{12}(\text{O}_2\text{-CCH}_3)_3]^+$; 3475.7 $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{PC}_{12}\text{H}_{10})_{11}(\text{O}_2\text{CCH}_3)_4]^+$. Details of the synthesis and the characterization of 4-MOBPA can be found elsewhere [12].

2.2. X-ray crystallography

Crystal data of $\text{Mn}_{12}\text{-phn}$: $\text{C}_{314.87}\text{H}_{264}\text{Cl}_{21.55}\text{Mn}_{24}\text{O}_{92}\text{P}_{24}$, $M_r = 8345.58$, tetragonal, $I41/a$, $a = 34.7178(9)$ Å, $b = 34.7178(9)$ Å, $c = 28.8662(10)$ Å, $V = 34793.2(18)$ Å³, $Z = 4$, brown block, $\rho_{\text{calc}} (\text{g}/\text{cm}^3) = 1.593$, $\mu(\text{MoK}\alpha) (\text{cm}^{-1}) = 1.192$, $T = 100$, empirical absorption correction, $T_{\text{max}}/T_{\text{min}} = 0.650/0.699$, 124,917 reflections collected, 18,049 unique ($R_{\text{int}} = 0.133$), $R_1 = 0.0639$, $wR_2 = 0.1610$, using 17,930 reflections with $I > 2\sigma(I)$ to refine 1067 parameters. The crystallography data collection was performed at a STOE IPDS-II diffractometer equipped with a graphite monochromated radiation source ($\lambda = 0.71073$ Å) and an image plate detection system. The selection, integration and averaging procedure of the measured reflex intensities, the determination of the unit cell by a least-squares fit of the 2θ values, data reduction, LP correction, and the space group determination were performed using the X-Area software package delivered with the diffractometer. An empirical absorption correction method was implemented after indexing of the crystal faces. The structure was solved by direct methods (SHELXS-97) [15] and standard Fourier techniques against F^2 with a full-matrix least-squares algorithm using SHELXL-97 [15] and the WinGX (1.70) [16] software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined with a riding model.

2.3. Physical measurements

The magnetic measurements were performed by using a micro-Hall effect magnetometer to detect the magnetic dipolar field of a $\text{Mn}_{12}\text{-phn}$ single crystal placed on top of the sensor. The field was aligned with the easy axis of magnetization using the transverse field method.

$\text{Mn}_{12}\text{-phn}$ was deposited on the functionalized Au(111) surface via ligand exchange reaction with 4-MOBPA as described elsewhere [12]. STM and STS measurements were performed in an Omicron Multiprobe UHV system at room temperature. For the STM/STS measurements, electrochemically etched tungsten tips, flash-annealed by electron bombardment were used. The $\pm$ sign of the bias voltage denotes the voltage applied to the sample.

3. Results and discussion

$\text{Mn}_{12}\text{-phn}$ crystallizes in the space group $I41/a$ with the two different complexes $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{PC}_{12}\text{H}_{10})_{12}(\text{O}_2\text{CCH}_3)_4]$ (complex **1a**) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{PC}_{12}\text{H}_{10})_{12}(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_4]$ (complex **1b**) per asymmetric unit. The structure of the $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ core is similar to other Mn_{12} complexes (see Fig. 1). The central $[\text{Mn}_4\text{O}_4]^{8+}$ cubane is surrounded by a ring of eight Mn^{III} ions that are held together via eight $\mu_3\text{-O}^{2-}$ ions. The residual free sites of the Mn^{III} ions are occupied with eight axial and four equatorial μ_2 -bridging diphenylphosphinate molecules.

The axial $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ -bridging molecules are four acetate molecules. The last four free sites of the Mn^{III} ions are occupied by four water molecules in the case of complex **1b**, in case of complex **1a** the free sites keep unoccupied. The ligand exchange reaction remains incomplete as only 12 of the 16 acetate molecules were exchanged. The first four of the equatorial acetate ligands and four of the axial acetate ligands are exchanged [17] as well as four of the equatorial acetate ligands afterwards. In this state the direct coordination sphere around the $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ core is packed tightly and no further ligands can be exchanged. Only the acetate molecules are small enough to fill the free axial sites bridging the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ ions.

Magnetization hysteresis measurements were carried out on a well-shaped $\text{Mn}_{12}\text{-phn}$ single crystal in the temperature range from 0.4 to 3.2 K, at a sweep rate of 1 T/min. Fig. 2a represents the temperature dependence of the hysteresis loops showing a series of steps, separated by plateaus. As the temperature is lowered, the hysteresis increases because there is a decrease in the transition rate of thermally assisted tunneling. The hysteresis loops become temperature independent below 0.6 K, demonstrating quantum tunneling at the lowest energy levels. The steps in the hysteresis loops are very sharp due to low solvent/ligand disorder in the crystals [18–20]. The field between two resonances allows an estimation of the anisotropy constant D , yielding for the difference between two steps at high fields a value of $D = 0.49$ K (assuming $g = 2$). Additional measurements were performed in the presence of a constant transverse field. The results of these measurements are presented in Fig. 2b showing oscillations of the tunneling probability at zero field as a function of the magnetic field applied approximately along the hard magnetization axis.

Fig. 3 shows STM images of $\text{Mn}_{12}\text{-phn}$ clusters on the 4-MOBPA/Au(111) surface obtained at +2.8 V (a) and +0.4 V (b), respectively.

Fig. 1. The structure of $\text{Mn}_{12}\text{-phn}$ viewed along the c -axis: Mn – violet, O – red, P – green, C – gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. (a) Hysteresis loops of a Mn_{12} -phn single crystal measured at different temperatures and a constant field sweep rate indicated in the figure. The loops display a series of steps, separated by plateaus. As the temperature is lowered, there is a decrease in the transition rate due to reduced thermally assisted tunneling. The hysteresis loops become temperature independent below 0.6 K. (b) ΔM at zero field as a function of transverse field measured at 0.4 K.

The higher bias voltage corresponds to the region of high conductance, whereas the lower value corresponds to the conductance gap region. The molecules are invisible for the STM operated at +0.4 V bias voltage, and thus the characteristic monoatomic steps of the 4-MOBKA covered Au(111) surface can be observed. At +2.8 V bias voltage the Mn_{12} -phn molecules are visible.

For the determination of molecular heights we utilized the z - U spectroscopy method described elsewhere [21,22]. The principle of z - U spectroscopy implemented in this study is shown in an idealized sketch in Fig. 4. An STM tip is brought into tunneling contact with a Mn_{12} molecule. This corresponds to a tip-molecule distance of about 0.5 nm. z - U characteristics of Mn_{12} -phn are obtained by varying the bias voltage and measuring the z -position of the tip. The feedback loop of the STM remains operating and a fixed set current is selected so that the tip position is altered whenever a variation of the tunneling current is detected. Since Mn_{12} molecules reveal a broad conductance gap in STS I- U measurements [12,13] no molecular states can be occupied by electrons at low bias voltage, thus the tunneling current rapidly decreases around the onset of the conductance gap. As a result, the tip is extended until the fixed set current is restored. STM images and STS spectra [22] show that this is the case for a tunneling contact with the 4-MOBKA functionalized substrate. In a previous work, [12] STS I- U spectra of 4-MOBKA also showed that the conductance is relatively

Fig. 3. $150 \times 150 \text{ nm}^2$ STM images of Mn_{12} -phn clusters measured at +2.8 V (a) and +0.4 V (b) bias voltage. Mn_{12} -phn molecules are "invisible" for the STM tip at +0.4 V (within the conductance gap) and thus the characteristic steps of the 4-MOBKA covered Au(111) surface are visible. The two STM pictures were obtained from the same sample area.

Fig. 4. Schematic representation of the z - U spectroscopy measurements on Mn_{12} -phn.

low at low bias voltage. Consequently, the STM tip approaches the 4-MOBKA layer very closely and the difference H between the positions of (tunneling) contact with the Mn_{12} molecule and the substrate is a good estimation of the real height of the molecular layer.

Fig. 5a shows z - U spectra obtained from different Mn_{12} -phn clusters. The set current was 6.9 pA. In the z - U spectra, a distinct step is visible around 1 V, corresponding to -0.5 nm with respect to the 0 nm position for 2.8 V. The step separates two distance ranges which correspond to a tunneling contact with the Mn_{12} -phn molecule (high bias voltage) and with the 4-MOBKA functionalization layer (low bias voltage). To demonstrate that the step is not a measurement artifact, a z - U spectrum obtained from bare Au(111) in the bias voltage range between 0.4 V and 1.4 V is shown for comparison. The absolute z position is not directly comparable to the measurement on Mn_{12} -phn due to the different starting positions. Nonetheless, no hint of any step is visible in the z - U spectrum obtained from Au(111), clearly showing that the signatures obtained from Mn_{12} -phn are due to the molecule.

The evaluation of 40 z - U spectra obtained from Mn_{12} -phn yields an average step height of 1.4 nm with the individual step heights ranging from 1.1 to 1.7 nm. These values are in very good agreement with the diameter of the Mn_{12} -phn molecules derived from the X-ray structure, assuming random orientation and ligand exchange with 4-MOBKA. A broad spread of the measured molec-

Fig. 5. (a) Representative distance–voltage characteristics obtained from different individual Mn_{12} -phn molecules (open circles) and from bare Au(111) (black line, upper corner, same scale). Three curves marked with different colors (red, orange, blue) are presented to demonstrate the different step heights. (b) Sketches of two orientations of Mn_{12} -phn molecules resulting in the minimum and maximum height values of 1.1 nm and 1.7 nm (measured with respect to the 4-MOBKA layer due to the exchange of ligands). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ular heights can be attributed to a random orientation of different molecules which can be explained by the equally high acidity of the diphenylphosphinic acid and of 4-MOBKA with no site-specific ligand exchange reaction being expected. The bulky diphenylphosphinate ligands effectively suppress the ligand exchange of the axial acetate ligands thus leading to the higher ligand exchange probability of the diphenylphosphinate ligands. Contrary to that, in the case of Mn_{12} -thiophenecarboxylate (Mn_{12} -th) a smaller spread of the measured molecular heights was observed. [22] Moreover, the comparison of the measured molecular heights with the structural X-ray data obtained from Mn_{12} -th single crystals indicated that the Mn_{12} -th molecules are oriented with the easy axis perpendicular to the surface. A preferred orientation was explained by a higher probability for exchange of axial ligands due to the higher acidity of 4-MOBKA compared to thiophenecarboxylate ligands. [23] Thus, we show that the substitution of the Mn_{12} ligand shell may have a major impact on the surface orientation of the Mn_{12} clusters deposited on Au, i.e. on the orientation of the easy magnetization axis. Moreover, the possibility to determine the orientation of individual Mn_{12} molecules is an important prerequisite for future well-defined magnetic field dependent cryogenic STS measurements. For such measurements, the orientation of the molecular easy magnetization axis with respect to an external magnetic field has to be known. According to the results of the z - U spectroscopy, the orientation can be identified by means of STS. Beyond the estimation of the real height, the z - U spectra also demonstrate the presence of a single Mn_{12} -phn monolayer on 4-MOBKA, thus confirming the success of the ligand exchange reaction.

4. Conclusion

The synthesis, investigation as well as surface deposition of a truly axial symmetry Mn_{12} -diphenylphosphinate (Mn_{12} -phn) single molecule magnet has been reported. Out of 16 acetate ligands encapsulating the $\text{Mn}_{12}\text{O}_{12}$ core, 12 ligands were exchanged by diphenylphosphinate in this compound. Mn_{12} -phn shows well-defined steps in the magnetic hysteresis loops indicating that the crystals possess a very high quality. A monolayer of Mn_{12} -phn was chemically grafted on a functionalized Au(111) substrate and studied by means of STM/STS. The presence of a conductance gap in Mn_{12} molecules was used for distance–voltage (z - U) spectroscopy that, in the present case, allows the determination of the real-space height of the molecules with high accuracy. A large spread in the measured molecular heights obtained from the z - U spectra indicates the absence of a preferential orientation of the Mn_{12} -phn molecular easy axis with respect to the surface which we attribute to the equally high acidity of the diphenylphosphinic acid and of 4-MOBKA. These results are compared with the data obtained from another Mn_{12} derivative containing 16 thiophenecarboxylate ligands which shows a preferential orientation of the clusters on the Au surface with the easy magnetic axis perpendicular to the surface plane. In general, we show that the substitution of the ligand shell may have a major impact on the surface orientation of Mn_{12} clusters deposited on Au, i.e. on the orientation of the easy magnetization axis. This represents a crucial step towards addressing the magnetic properties of individual Mn_{12} molecules in the future. The possibility to identify the orientation of individual molecules will allow measurements with a well-defined orientation of the easy magnetization axes with respect to an external magnetic field.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) via the Collaborative Research Center (SFB) 767, Project C5.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.11.028.

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