

A comparative study on the deposition of Mn₁₂ single molecule magnets on the Au(111) surface†

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Different approaches to the deposition of Mn₁₂ single molecule magnets on the Au(111) surface and their characterization by a broad variety of techniques are investigated with respect to their suitability for a profound corroboration of the integrity of the Mn₁₂ core. In this context, the most recent improvements in the experimental approaches are presented and the latest results on the electronic properties of Mn₁₂ are linked to each other. The results confirm the high instability of Mn₁₂ single molecule magnets on surfaces and reveal the need for an amendment of the requirements to define the structural integrity of Mn₁₂ molecules on surfaces.

Introduction

Single molecule magnets, like the famous Mn₁₂-acetate^{1a} [Mn₁₂O₁₂(O₂CCH₃)₁₆(H₂O)₄] and its derivatives, have attracted significant interest during the past decade due to their unique magnetic properties^{1b-d} like hysteresis of pure molecular origin and the possibility to observe quantum tunneling of magnetization.^{1c} Since the ligand shell of Mn₁₂ molecules can be tailored according to the needs of specific experiments or applications,² this material class is a favoured choice for future basic studies on quantum effects of magnetism on the molecular scale like quantum phase interference³ and is furthermore a promising candidate for preliminary studies aiming at molecular ultrahigh density data storage devices or quantum computing applications.^{4a-d}

With respect to applications it is necessary to deposit both spatially isolated Mn₁₂ molecules and homogeneous monolayers of Mn₁₂ on well-defined surfaces to provide access to the electronic and magnetic properties of individual molecules by means of different experimental techniques. Since the first identification of individual Mn₁₂ clusters on a Au(111) surface^{5a} there have been many additional attempts to deposit Mn₁₂ on Au(111) taking advantage of S–Au interactions, electrostatic interactions or a well-known ligand exchange reaction.^{5b-f} Furthermore, the possibility to deposit Mn₁₂ molecules on Si surfaces has been investigated.^{5g,h} Most of these studies employed scanning probe techniques like STM (scanning tunneling microscopy) as well as spectroscopic techniques like XPS (X-ray photoelectron spectroscopy) to determine the topography and the composition of the surface, respectively. There have also been attempts to deposit Mn₁₂ layers by means of laser ablation,⁵ⁱ matrix-assisted pulsed laser evaporation,^{5j} photolithography^{5k} or patterning on a polymer surface.^{5l} However, profound evidence for the deposition of intact Mn₁₂ monolayers is still lacking.

Recently, we have shown by means of a combined STM, XPS, XAS (X-ray absorption spectroscopy) and RPES (resonant

photoelectron spectroscopy) study^{6a} that the Mn₁₂ core is degraded during certain deposition procedures. A fragmentation of Mn₁₂-thiophenecarboxylate (Mn₁₂-th) molecules was observed after direct deposition on Au(111) while a pre-functionalization of the Au(111) surface with a subsequent ligand exchange reaction was found to be suited for the deposition of Mn₁₂-th molecules. Furthermore, by means of a series of XAS measurements we provided evidence that the spectroscopic investigation of Mn₁₂ molecules using X-ray radiation has to be considered critically especially in the case of monolayers that were initially intact since radiation damage effects were observed on a relatively short time scale.^{6b} However, different signatures from monolayers damaged during the deposition or by different external influences and by X-ray radiation, respectively, indicate a possibility to examine the success of the deposition by a straightforward XAS measurement. On the other hand, the detection of clusters with approximately the diameter of Mn₁₂ molecules by means of STM in combination with the detection of a Mn signal in XPS spectra cannot corroborate the presence of intact Mn₁₂ molecules on a surface.

In this work, we present a comparison of different wet chemical deposition techniques for Mn₁₂ as well as their characterization by means of STM and XPS. We show that artefacts both from the chemical preparation of Mn₁₂ monolayers and from the STM measurements affect some of the experiments. The results are discussed with respect to both previous and the most recent results on Mn₁₂ monolayers.

Results and discussion

Deposition of Mn₁₂/Scanning tunneling microscopy

Fig. 1 shows sketches of the procedures used for the deposition of Mn₁₂ single molecule magnets on the Au(111) surface. In Fig. 1a the direct deposition of suitably functionalized Mn₁₂ molecules *via* self-assembly from solution due to a strong S–Au interaction is shown. The Mn₁₂ derivatives Mn₁₂-thiophenecarboxylate⁷ ([Mn₁₂-(O₂CC₄H₃S)₁₆(H₂O)₄]) and Mn₁₂-methylthiobenzoate^{5b} ([Mn₁₂-(O₂CC₆H₄SCH₃)₁₆(H₂O)₄]; Mn₁₂-mtb) were deposited using this technique. The experimental conditions used for the deposition of Mn₁₂-mtb were different from a previous work^{5b} where different

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† The HTML version of this article has been enhanced with colour images.

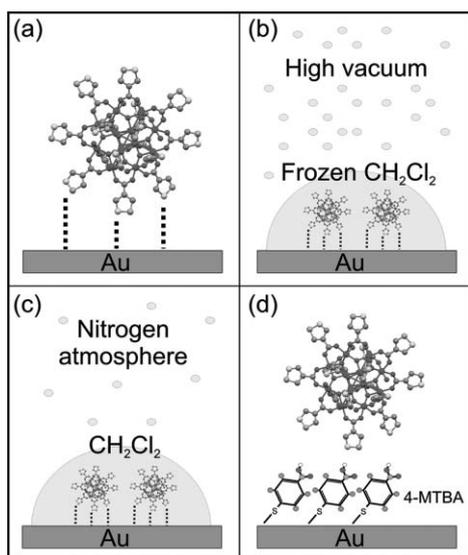


Fig. 1 Sketches of the procedures used for deposition of Mn_{12} molecules *via* (a) direct deposition (b) drop–freeze–sublimation technique (c) drop–evaporation technique and (d) ligand exchange reaction.

solvents and Au substrates were used (see Experimental). Fig. 1b shows the direct deposition of Mn_{12} -mtb in combination with a drop–freeze–sublimation technique (see Experimental) using a frozen layer of Mn_{12} -mtb solution to cover the molecules prior to sublimation of the solvent under high vacuum conditions. Fig. 1c shows a third direct deposition technique with the Mn_{12} solution dropped onto the Au surface before evaporation of the solvent. This technique was investigated for Mn_{12} -mtb. In Fig. 1d the deposition of Mn_{12} molecules *via* a ligand exchange reaction with a 4-mercapto-2,3,5,6-tetrafluorobenzoic acid⁸ (4-MTBA) functionalization layer is presented. This technique was implemented for Mn_{12} -th.

In the following the characterization of the different techniques by means of STM is presented. The comparison of the respective XPS spectra will be presented afterwards.

Fig. 2 shows an STM image of clusters on the Au(111) surface detected after direct deposition of Mn_{12} -mtb. Clusters with diameters ranging from 1.5 to 3 nm are visible. The shape of the large clusters is highly inhomogeneous. The measured height ranges from 0.3 to 0.8 nm which is smaller than the real

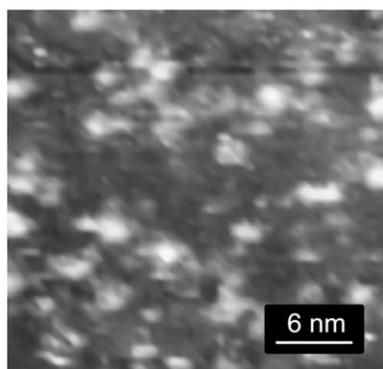


Fig. 2 STM image ($30 \times 30 \text{ nm}^2$) obtained after direct deposition of Mn_{12} -mtb on Au(111). The properties of the clusters could not be assigned to intact Mn_{12} molecules.

height of Mn_{12} -mtb ($>1.5 \text{ nm}$). Since STM probes rather the electronic structure of the sample than the real topography a lower measured height could in principle be explained by a low conductivity of the possibly intact Mn_{12} molecule. However, the possibility to influence the apparent height of Mn_{12} molecules by tuning the STM bias voltage has been demonstrated in a previous work^{9b} while no voltage-dependent changes of the topography were observed for the present sample. Furthermore, scanning tunneling spectroscopy (STS) measurements showed a comparable electronic structure of the surrounding area and the clusters. Although the spectra were extremely noisy what can be attributed to tip contaminations possibly due to fragments or contaminants, no hints of an energy gap^{9b} were found. In addition, intact Mn_{12} molecules should exhibit a comparable shape since the aspect ratio of spatially isolated Mn_{12} -mtb molecules would result in a resolution-limiting effect due to the STM tip shape rather than allowing observation of the molecular shape^{9b} which is not the case for the clusters shown in Fig. 2. As a consequence of the results, the clusters that were observed after deposition of Mn_{12} -mtb on Au(111) are not intact Mn_{12} -mtb molecules.

A possible approach to avoid the destruction of the Mn_{12} core may be to cover the molecular layer with frozen solvent prior to introduction into an ultrahigh vacuum (UHV) chamber. This technique might reduce a possible ligand diffusion during the deposition procedure and protect the molecules from atmospheric influences. Fig. 3a shows an STM image obtained after deposition of Mn_{12} -mtb on Au(111) *via* the drop–freeze–sublimation technique.

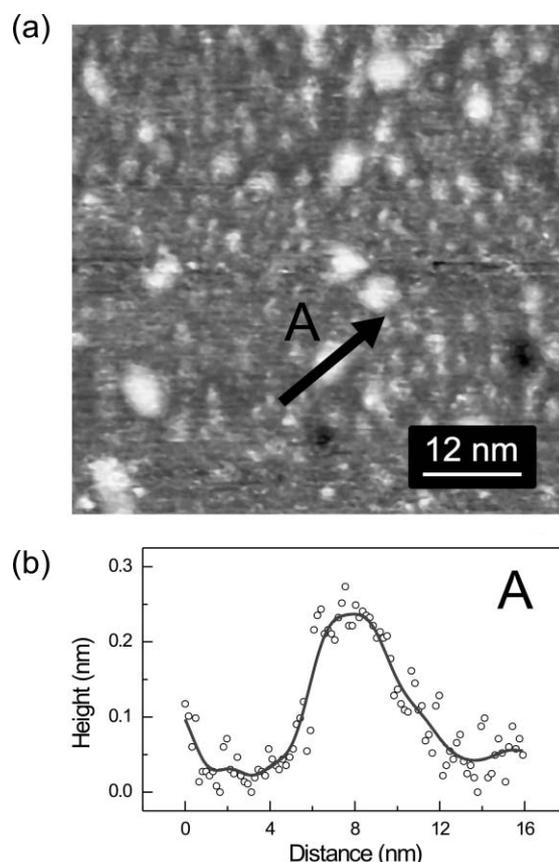


Fig. 3 STM image ($60 \times 60 \text{ nm}^2$) obtained after direct deposition of Mn_{12} -mtb on Au(111) *via* drop–freeze–sublimation technique.

A layer of different-sized clusters is visible (large clusters: 2–4 nm, small clusters: 1–1.5 nm edge-to-edge). The height profile in Fig. 3b shows that the measured height of the clusters is below 0.3 nm. Furthermore, smaller clusters are visible in the surrounding area of the larger ones clearly indicating the presence of contaminants or molecular fragments. When using STM tips with a lower resolution (tested on multi-atomic Au steps generated by high-energy sputtering or on clusters generated on bare Au(111) by voltage pulses), the smaller clusters could not be resolved any more and the surface seemed to be covered solely with the larger clusters. Again, attempts to identify a complex electronic structure by STS failed with the spectra being highly instable. However, the electronic structure of clusters and surrounding area was comparable and thus the cluster height cannot be assigned to intact Mn_{12} -mtb molecules for the reasons described above.

Finally, there have been attempts to directly deposit Mn_{12} -mtb monolayers on Au(111) by dropping Mn_{12} -mtb solution onto the Au(111) substrate and waiting for evaporation of the solvent. Comparable techniques have been used for the deposition of different molecules on highly-oriented pyrolytic graphite (HOPG).¹⁰ Although the underlying binding mechanisms are different, this approach seems reasonable at least for spectroscopic investigations of Mn_{12} . During the deposition, an inhomogeneous brown film forms on the surface with most material being located at the edge of the solvent drop (diameter: 5 mm) that evaporated. Fig. 4 shows an STM image obtained about 1 mm from the drop edge position (inner part) where no macroscopic residuals were detected. Even though the image quality is reduced possibly due to a contamination layer the monoatomic steps of Au(111) are still visible. No signature of Mn_{12} -mtb molecules was found by means of STM. In contrast, shapeless clusters with different heights showing the same signature as in the previous attempts were observed.

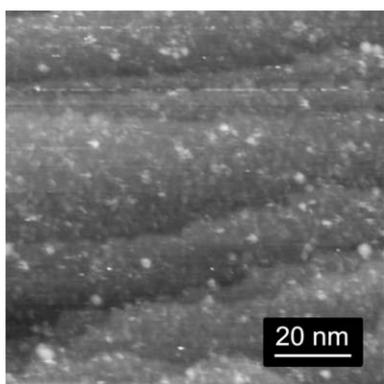


Fig. 4 STM image ($100 \times 100 \text{ nm}^2$) obtained after direct deposition of Mn_{12} -mtb on Au(111) *via* drop-evaporation technique.

As a result the direct deposition of Mn_{12} -mtb by using the investigated deposition techniques on Au(111) seems to have failed. Molecular fragments or contaminants are visible in STM images instead of intact Mn_{12} -mtb molecules. However, a Mn peak in XPS spectra (see below) was observed for all of the samples investigated. According to the results, a fragmentation of the molecules resulting in adsorption of Mn containing fragments on the surface is likely. Nonetheless, the large set of parameters possibly affecting the deposition has to be emphasized

(*e.g.* solvents, substrates, rinsing, atmosphere *etc.*). Consequently, general conclusions on the possibility to deposit Mn_{12} molecules by direct deposition methods can hardly be drawn since a systematic study of many possibly relevant parameters is lacking. In principle, intact molecules might also have been removed or destroyed by the STM tip during the investigation. However, this effect is unlikely since tip changes or spikes were rarely observed.

Due to the failure to directly deposit Mn_{12} -mtb on Au(111) the possibility to directly deposit Mn_{12} -th on Au(111) was investigated. Fig. 5 shows an STM image obtained after direct deposition of Mn_{12} -th on Au(111). No clusters that might be assigned to Mn_{12} -th molecules could be observed. The corrugation of the surface is below 0.3 nm with very small clusters being visible.^{6a} Thus the direct deposition of Mn_{12} -th has also failed for this specific technique. Nevertheless, there is a significant Mn peak in XPS spectra (see below) which is consistent with the high coverage of small clusters. Thus a large amount of molecular fragments seems to be present on the Au(111) surface after direct deposition of Mn_{12} -th. In a previous work,^{5c} STM images obtained from a sample prepared in a different solvent indicated a successful deposition. However, due to the large set of additional parameters a direct comparison with the present work is difficult.

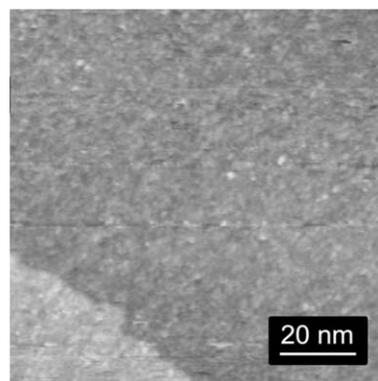


Fig. 5 STM image ($100 \times 100 \text{ nm}^2$) obtained after direct deposition of Mn_{12} -th on Au(111). No signature of any Mn_{12} molecule was found over the whole surface of the Au single crystal.

Apart from additional possible effects, the inability to directly deposit Mn_{12} -mtb or Mn_{12} -th molecules on Au(111) by utilizing the investigated procedures might be attributed to the strong S–Au interaction in combination with the mobility of the ligands in a solvent environment. The molecule might either be distorted and as a consequence fragmented or it might bind in an incomplete ligand configuration and thus fragment due to reduction of the Mn core ions after absorbing electrons from the metallic substrate. These problems might be overcome by decoupling the Mn_{12} molecule from the surface. This can be achieved either by using long chain ligands or pre-functionalization layers. The use of long chain ligands^{5a} seems to be suited for the deposition of intact molecules on Au(111) as will be discussed below. Different approaches utilizing functionalization layers for the deposition of Mn_{12} on Au(111) have also been investigated.^{5c,d} However, it is important to keep in mind the necessity of conductive linker molecules and ligands. Thus the use of short linker molecules and ligands with delocalized electrons appears as a prerequisite for STM/STS studies. This will also be discussed below.

Fig. 6a shows an STM image of Mn_{12} -th on the Au(111) surface pre-functionalized with 4-MTBA. Comparable images have been obtained for Mn_{12} -parafluorobenzoate (Mn_{12} -pfb) and are presented in a previous publication.^{9a} A dense homogeneous layer of clusters is visible. The height profile in Fig. 6b shows that the measured height (1.1 nm in average) is in good agreement with the expected height of about 1.2 nm (given that the bottom ligands have been exchanged with 4-MTBA). The presence of an energy gap in individual clusters as well as the possibility to influence the apparent height of the molecules by tuning the STM bias voltage was substantiated recently.^{9b} In this work, a further experiment on the stability of the above system is presented. Ar^+ sputtering was used to investigate the stability of the monolayer. The sputtering rate was optimized on a bare Au(111) sample to obtain 5 Ar^+ impacts (1700 eV) on a 200×200 nm² area within 2 s with the diameter of the emerging craters being below 10 nm. If the monolayer presented in Fig. 6a would be due to fragmented Mn_{12} -th molecules the stability of the clusters imaged by STM should be high and thus about 5 craters within a 200×200 nm² area should be expected also for the molecular layer. However, after sputtering the surface for 2 s at 1700 eV no signature of any cluster could be detected by means of STM any more. In contrast, the STM tip changed every 5–10 lines probably due to contamination desorption avoiding to record any STM image. This result is a strong indication that the clusters visible in Fig. 6a are highly fragile and can be destroyed by secondary processes

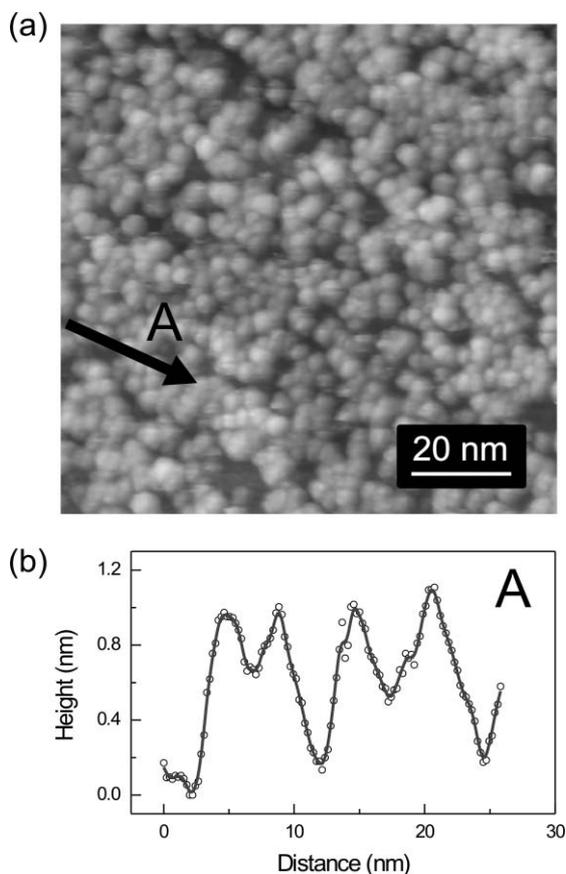


Fig. 6 (a) STM image (100×100 nm²) obtained after deposition of Mn_{12} -th on 4-MTBA/Au(111). (b) Height profile along 4 molecules as depicted in (a).

after the Ar^+ impact. This observation is consistent with previous results revealing the possibility to affect the stability of individual molecules by high STM currents.^{9b} The further investigation of the presumably intact Mn_{12} -th layer will be described below.

During the investigation of pre-functionalization layers an experiment on artefacts due to the deposition procedure was performed. Fig. 7 shows an STM image of a 4-MTBA functionalization layer that was immersed in CH_2Cl_2 for 5 min without any Mn_{12} molecule being present. Isolated clusters with diameters between 2 and 5 nm are visible. The apparent height of the clusters is comparable to those of the clusters observed during the experiments on direct deposition of Mn_{12} on Au(111). No contamination of the surface due to elements not present in 4-MTBA could be revealed by means of XPS. The formation of clusters was observed for any functionalization layer investigated when immersed in CH_2Cl_2 . Since the diameter of the clusters is of the same order as the diameter of Mn_{12} molecules this result corroborates the need for advanced investigation techniques for Mn_{12} layers since a misinterpretation of STM images is possible.

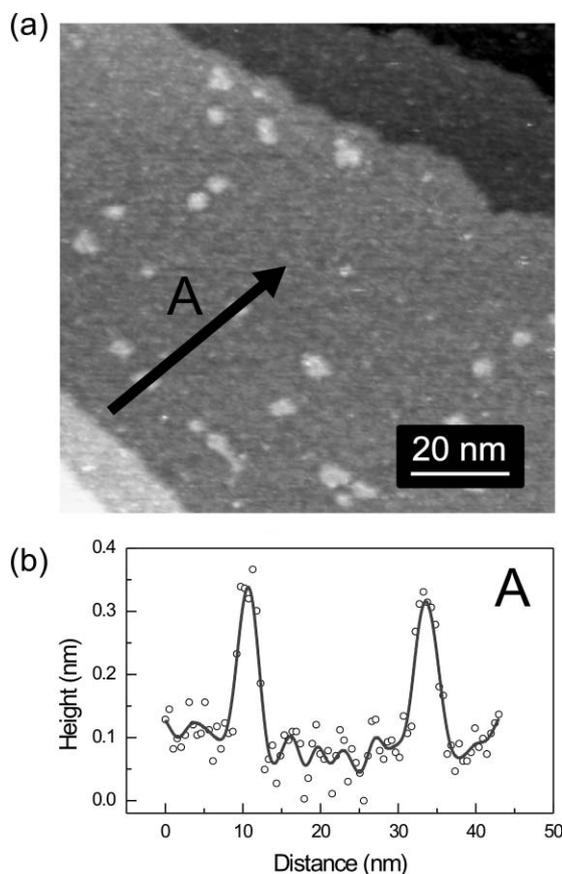


Fig. 7 (a) STM image (100×100 nm²) obtained after dipping 4-MTBA/Au(111) in CH_2Cl_2 for 5 min. (b) The height profile shows contaminants with diameters on the order of the expected diameter of Mn_{12} .

Fig. 8 shows an STM image of Mn_{12} -pfb on 4-MTBA displaying a multiple tip effect that results in faking of a partially ordered monolayer. Due to the Mn_{12} aspect ratio of about 1 : 1 the apparent cluster shape is dominated by the STM tip curvature even when relatively sharp STM tips are used. If a multiple STM tip with all individual tips on the same length scale is used the

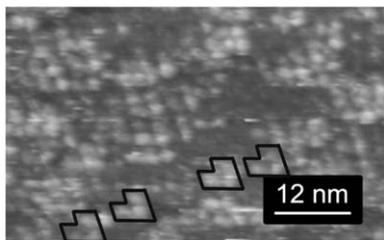


Fig. 8 STM image ($60 \times 30 \text{ nm}^2$) obtained after deposition of Mn_{12} -pfb on 4-MTBA/Au(111). The apparent partial ordering of molecules is an artefact of a multiple STM tip as depicted in the image.

molecules are imaged according to the number and shape of the tips rather than to the shape of the molecules. The tip used for the image in Fig. 8 was a triple tip [tested on isolated contamination clusters on bare Au(111)] as is clearly visible from the identical groups of three clusters with nearly identical height and diameter distribution depicted in Fig. 8. As a consequence, a layer of ordered clusters is faked even though individual clusters such as in Fig. 6a are present on the surface what has been investigated with two different STM tips. In further experiments,^{9c} longer functionalization molecules such as 4'-mercapto-octafluorobiphenyl-4-carboxylic acid or 4-(mercaptomethyl)-2,3,5,6-tetrafluorobenzoic acid were used. With the size of the functionalization molecule we observed an increasing sensitivity for tip artefacts during imaging deposited Mn_{12} molecules. Especially for 4-(mercaptomethyl)-2,3,5,6-tetrafluorobenzoic acid that includes one alkane spacer multiple tip artefacts showed up for nearly all STM tips used. This can be assigned to the decreased conductivity of the linker molecule which leads to a smaller distance between STM tip and Mn_{12} monolayer. If the overall conductivity of the system is too low, the STM tip may even touch the surface which results in severe artificial distortions of STM images.

X-Ray photoelectron spectroscopy

Since it was shown in a previous work^{6b} that Mn_{12} molecules are damaged by X-ray radiation even in the crystalline environment the investigation of Mn_{12} monolayers with standard X-ray sources usually present in surface science setups is limited to the sole detection of elements or stable fragments. Furthermore, in contrast to the synchrotron based techniques employed in ref. 6a, b and 11, XPS is a technique with low sensitivity to different oxidation states of Mn ions. As a conclusion, the sole presence of Mn peaks in XPS spectra along with traces of other elements being present in the respective Mn_{12} molecule is not a sufficient proof for the presence of intact Mn_{12} clusters on a surface.

For corroboration, XPS Mn 2p spectra (Al K α) of the systems investigated by STM (see above) are presented in Fig. 9. Within experimental resolution there is no difference in the peak positions and thus the significance of such spectra for studies on the integrity of Mn_{12} molecules seems to be extremely limited since apparently damaged molecules or Mn containing contaminants yield spectra comparable to those from probably intact molecules. However, differences in the Mn peak intensity with respect to the Au 4p_{1/2} peak intensity are visible in Fig. 9 that can be assigned to a different coverage. For Mn_{12} -th no significant change of the Mn peak intensity was obtained when changing the preparation parameters. This correlates perfectly with the observation made

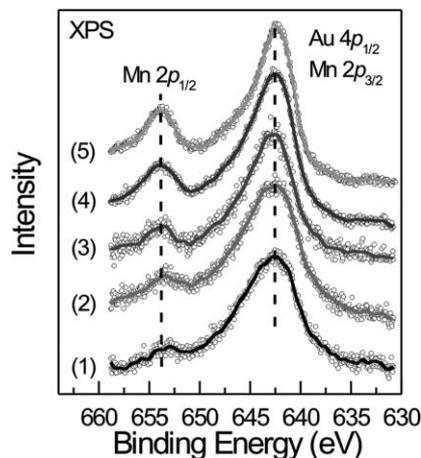


Fig. 9 XPS spectra of Mn_{12} -mtb (1) directly deposited on Au(111), (2) deposited *via* drop–evaporation technique, (3) deposited *via* drop–freeze–sublimation technique, and of Mn_{12} -th deposited (4) directly on Au(111) and (5) on 4-MTBA/Au.

by STM that a homogeneous layer forms even for very short preparation times. On the other hand, the peak intensity changed as a function of preparation parameters for Mn_{12} -mtb. For longer preparation times (direct deposition), yielding a stronger Mn peak intensity, the formation of up to 0.8 nm high clusters was observed in STM measurements. Thus the change in intensity might be assigned to a larger amount of fragments forming clusters during longer deposition procedures.

Comparison with previous studies

Since there seems to be no straightforward laboratory-based experiment for proving the structural integrity of Mn_{12} molecules on a surface the investigation might be focused on indications obtained from advanced techniques like X-ray absorption spectroscopy (XAS). The previous synchrotron-based study on different Mn_{12} derivatives revealed significant similarities between XAS spectra obtained from radiation-damaged single crystals and from monolayers deposited *via* a ligand exchange reaction.^{6b} Fig. 10 shows a comparison of the typical XAS line shapes obtained from (1) single crystals of Mn_{12} -pfb showing degradation due to X-ray radiation as well as (2) Mn_{12} -pfb monolayers on 4-MTBA/Au that look like those in Fig. 6 and (3) Mn_{12} -pfb single crystals that have been Ar⁺ sputtered as well as (4) Mn_{12} -th monolayers that have apparently been damaged during the deposition procedure and look like those in Fig. 5. The validity of the effects has been demonstrated for Mn_{12} -th, Mn_{12} -pfb and Mn_{12} -biphenylcarboxylate,^{6b} hence a comparison of different Mn_{12} derivatives is feasible. The shape of spectrum (4) indicates a degradation of the molecules during the deposition due to the sole Mn²⁺ contribution^{6a} while the spectrum (2) allows the interpretation that an intact layer of molecules has been damaged under the influence of X-ray-radiation.^{6b} This interpretation is supported by the results showing that the molecules can be damaged by low-intensity Ar⁺ sputtering (see above) or high STM currents.^{9b} The spectrum obtained from the Mn_{12} -pfb monolayer deposited *via* ligand exchange reaction with 4-MTBA was nearly identical to a spectrum obtained for $[\text{Mn}_{12}\text{O}_{12}(\text{L})_{16}(\text{H}_2\text{O})_4]^{5a,11}$ with L including a long alkyl chain. Assuming that the spectral shape is a consequence

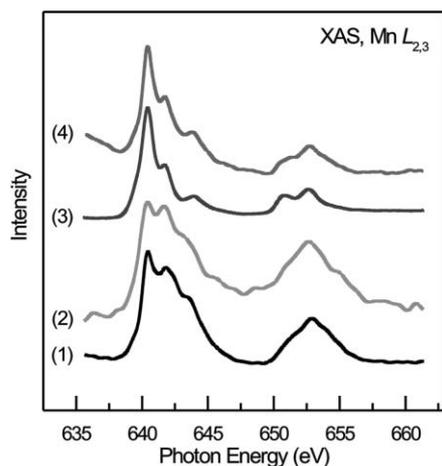


Fig. 10 XAS spectra obtained from (1) radiation-damaged Mn_{12} -pfb single crystals and (2) Mn_{12} -pfb/4-MTBA monolayers that look like those in Fig. 6 in STM images, (3) Ar^+ -sputtered Mn_{12} -pfb single crystals and (4) Mn_{12} -th monolayers that look like those in Fig. 5 in STM images.^{6a,b}

of radiation-induced degradation rather than degradation during the deposition, the need for functionalization layers or long-chain ligands corroborates the necessity to decouple the molecule from the substrate to avoid a possible distortion or reduction due to an incomplete ligand configuration. This would, however, hamper the direct deposition of functionalized Mn_{12} molecules with small ligands on bare Au substrates.

Albeit two different approaches seem to allow the deposition of intact monolayers of Mn_{12} , the use of functionalization layers might be advantageous for future STS studies on the electronic properties of individual molecules. Long alkyl chain ligands are expected to display a low conductivity¹² as well as a large energy gap and thus access to the properties of the Mn_{12} core by means of STM or STS is complicated. On the other hand, Mn_{12} derivatives with highly conductive ligands like Mn_{12} -th or Mn_{12} -pfb may allow straightforward access to the properties of the Mn_{12} core. Furthermore, the possibility to deposit a broad variety of derivatives may facilitate a detailed comparison of the respective electronic and magnetic properties in subsequent studies in the future.

Conclusions

In conclusion, different approaches to the deposition of Mn_{12} monolayers on the Au(111) surface have been investigated by means of scanning tunneling microscopy and X-ray photoelectron spectroscopy. The results have been linked to previous X-ray absorption spectroscopy measurements. The feasibility of direct deposition of functionalized Mn_{12} molecules with small sulfur containing ligands onto Au(111) has to be considered critically since the clusters that can be observed after deposition show no signature of intact Mn_{12} molecules. A possible degradation might be assigned to a Mn_{12} core distortion or to reduction of the core due to an incomplete ligand configuration during the deposition procedure. However, due to the large set of parameters possibly affecting the wet chemical preparation of Mn_{12} monolayers, the possibility to directly deposit suitably functionalized derivatives cannot be generally ruled out. Mn_{12} clusters deposited *via* a ligand

exchange reaction seem to conserve their structural integrity since no proof for a degradation of the molecules during the deposition procedure could be achieved. In contrast, the molecules could be damaged by low-intensity Ar^+ sputtering or high STM currents. The comparison with previous results corroborates the necessity of a strong decoupling of the Mn_{12} molecule from the surface *via* pre-functionalization layers or long chain ligands. The deposition *via* ligand exchange reaction may be advantageous for future STS investigations since a broad variety of Mn_{12} derivatives can be studied using this deposition technique.

Finally, an amendment of the requirements to define the structural integrity of Mn_{12} molecules on surfaces is suggested. Beside the identification of clusters by means of STM and the detection of a Mn peak in XPS the electronic structure of the molecules should be investigated by means of STS and/or XAS.

Experimental

Chemical synthesis, deposition on surfaces

Mn_{12} -ac, Mn_{12} -mtb, Mn_{12} -th, Mn_{12} -pfb and 4-MTBA were synthesized as described elsewhere.^{1a,5b,7-9a} Perfect-shaped Mn_{12} single crystals were carefully selected for the experiments. CH_2Cl_2 *p.a.* was used for solving the Mn_{12} single crystals and ethanol *p.a.* was used to solve 4-MTBA. Carefully cleaned glass beakers were used for the deposition of Mn_{12} -mtb while PFA (perfluoroalkoxyalkane) beakers were used for the deposition of Mn_{12} -th and 4-MTBA. This was especially necessary to avoid a contamination of 4-MTBA with Na or K, that was observed by means of XPS when glass beakers were used. Direct deposition of the molecules was performed by dipping an Au(111) single crystal (upside down) into the respective Mn_{12} solution (Mn_{12} -mtb: 0.3 mmol, 30 min; Mn_{12} -th: 0.03 mmol, 240 min). After immersion the single crystal was thoroughly rinsed with CH_2Cl_2 and dried with dry N_2 . The deposition *via* drop-freeze-sublimation technique was performed by dropping Mn_{12} -mtb solution (2.8 μ mol) onto an Au(111) single crystal placed in a nitrogen atmosphere. The sample was then immediately placed onto a metal cube placed in liquid nitrogen leading to immediate freezing of the solvent. A possible crystallization of water was avoided due to the nitrogen atmosphere. After 2 min the sample was introduced into the ultra-fast load lock (flushed and filled with nitrogen) of the UHV chamber. The load lock was immediately evacuated by opening the valve of a running turbo pump resulting in sublimation of the solvent due to the high vacuum conditions. The deposition *via* a drop-evaporation technique was performed by dropping Mn_{12} -mtb solution (0.03 mmol) onto an Au(111) single crystal placed in nitrogen atmosphere. After full evaporation of the solvent the sample was immediately transferred into the UHV chamber. The deposition of Mn_{12} -th *via* a ligand exchange reaction with 4-MTBA was performed as described elsewhere.^{6a}

Scanning tunneling microscopy/spectroscopy, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy

The STM/STS and XPS measurements were performed in an Omicron Multiprobe system including the Omicron VT AFM/STM, a dual-anode X-ray source and an EA 125 hemispherical

energy analyzer. Electrochemically etched tungsten tips, flash-annealed by electron bombardment, were used for the measurements. The tunneling current was set to 6.9 pA for all measurements. The bias voltage was varied between +0.3 V and +1.8 V for Mn₁₂-mtb to investigate possible voltage-dependent height variations, set to +1 V for recording images 2, 3, 4, 5, 7 and set to +2 V to record images 6, 8. XAS measurements were performed at the D1011 beamline at MAX-lab (Lund) as well as at the PM3 and the RGLB beamline at BESSY (Berlin). Further details of the XAS measurements are described elsewhere.^{6a,b}

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