Angewandte
Chemie

Single-Molecule Magnets on Silicon

Anchoring Molecular Magnets on the Si(100) Surface[**]

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The continuous scaling down of device size in integrated circuits (ICs) has led to many questions about the limitations (lithographic, physical, or economic) of top-down developments of microelectronic devices. On the other hand, bottom-up technologies using molecules as single data-processing devices are enormously promising in terms of storage and data-handling density, and there are reports on molecular wires, switches, rectifiers, and storage elements which, in principle, could form the basis of future molecular electronics.[1] Nevertheless any synthetic strategy towards such molecules remains useless for molecular devices unless they are ordered in a suitable and accessible way so that their state can be probed. The most promising architecture in molecular electronics is a hybrid system in which a dense array of molecular devices is hosted on a silicon-based microelectronic circuit.[2]

In the last decade, it was discovered that single molecules can be used to store magnetic information. The prototype of this class of materials, referred to as single-molecule magnets (SMMs), is the dodecamanganese(III,IV) cluster $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2AcOH$ ($\mathbf{1}\cdot 4H_2O\cdot 2AcOH$).[3] A recent paper showed the possibility of anchoring a thiol-substituted Mn_{12} cluster on a gold substrate.[4] However, no reports have appeared to date on the possibility of anchoring the Mn_{12} cluster on a surface of technological importance, such as Si(100). Very recently, patterned Mn_{12} aggregates were deposited from solution on a silicon oxidized surface, but no indication of suitable bonding between the Si surface and the Mn_{12} cluster was reported.[5]

The Mn_{12} cluster **1** itself is not suited for direct anchoring on silicon, and therefore two different strategies can be adopted, based either on modification of the cluster with suitable functionalities capable of surface binding, or on modification of the surface with a layer capable of cluster coordination. The first approach has severe drawbacks due to the thermal instability of the Mn_{12} core, which is not well suited to classical protocols for silicon grafting.[6] In contrast, preliminary modification of the silicon surface allows anchoring of the cluster under mild conditions and thus precludes degradation of the core.

Herein we report on the anchoring of Mn_{12} SMMs on silicon by using undecanoic acid grafted on H-terminated Si(100) surfaces. Hydrosilylation of the double bond with formation of a robust Si–C bond is well documented.[6] We describe a three-step process (Scheme 1) consisting of 1) grafting of the methyl ester of 10-undecenoic acid on the silicon surface, 2) hydrolysis of the ester group, and 3) ligand exchange between $\mathbf{1}\cdot 4H_2O\cdot 2AcOH$ and the grafted undecanoic acid to anchor the Mn_{12} SMMs to the organic layer. The presence of free COOH groups atop the grafted monolayer is the key to successful anchoring of the Mn_{12} clusters.

X-ray photoelectron spectroscopy (XPS), especially in angle-resolved mode, proved to be an ideal tool for characterization of the nanoscale layer and probing the depth distribution of elements and their bonding states. Therefore, each reaction step was monitored by XPS, and in all cases it provided evidence for all the expected elements in the grafted layers with associated binding energies (BEs) in excellent agreement with the expected bonding states. An XPS BE scale was calibrated by centering the Si $2p_{3/2}$ peak at 99.0 eV.[7] Thus, the weak C 1s signal of the adventitious carbon observed on the freshly HF etched Si(100) surface has a BE value of 284.5 eV, in close agreement with 284.6–285.0 eV commonly reported in the literature.[8] The Si 2p region of the samples grafted with methyl 10-undecenoate is a reliable indicator of the grafting efficiency. There is evidence of the well-resolved Si $2p_{3/2-1/2}$ spin–orbit doublet of elemental silicon, and the absence of any signal around $BE = 103$ eV for oxidized Si, even after several days of exposure to air, points unequivocally to efficient passivation of the surface by the ester monolayer.

Spectral features due to Si 2p after hydrolysis of the ester (step 2) and anchoring of the Mn cluster (step 3), do not

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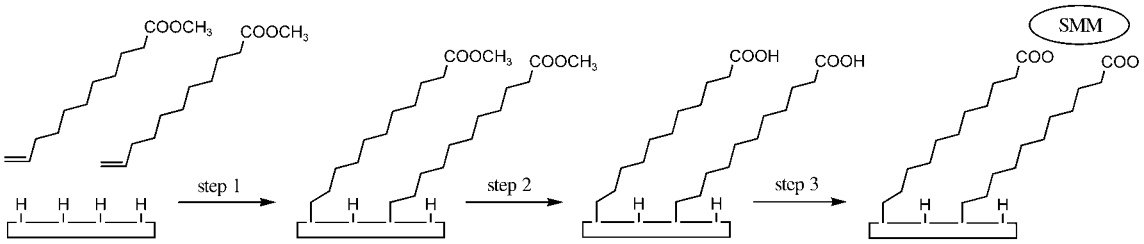
[**] The authors thank Dr. A. Cornia for stimulating discussions and the MIUR (FIRB 2001 and PRIN 2003 research programs) for financial support.

DOI: 10.1002/ange.200453933



Scheme 1. Three-step process used for anchoring SMMs on Si(100). Conditions: step 1) mesitylene, 200°C; step 2) H^+, H_2O, 100°C; step 3) **1**·$4\,H_2O\cdot 2\,AcOH$, toluene, 60°C, 100 mm Hg.

reveal appreciable surface oxidation, even though the hydrolysis reaction (step 2) requires a highly oxidizing environment (boiling water).

The relative intensity of the C 1s signal in the grafted ester is strongly enhanced relative to the freshly HF-etched surface (Figure 1a and b), and thus corresponds to the increased amount of carbon due to the organic layer. Moreover, the spectrum shows a rich structure, clearly due to the presence of several bonding states. It consists of four main components, centered at 283.5 eV (the carbide Si–C bond), 284.8 eV (the aliphatic backbone), 287.2 eV (the OCH_3 groups), and 289.4 eV (the C=O groups). All these features are entirely consistent with an Si–C-grafted monolayer of methyl undecanoate. A further component at 285.8 eV is due to slightly oxidized carbon surface contaminants. This feature is apparent in all the recorded spectra and it is likely due to the chemical manipulations. The contribution of adventitious carbon to the component centred at 284.8 eV can be neglected, since it is present in small amounts on freshly HF-etched surfaces and is usually of even less relevance on organic compounds.[9]

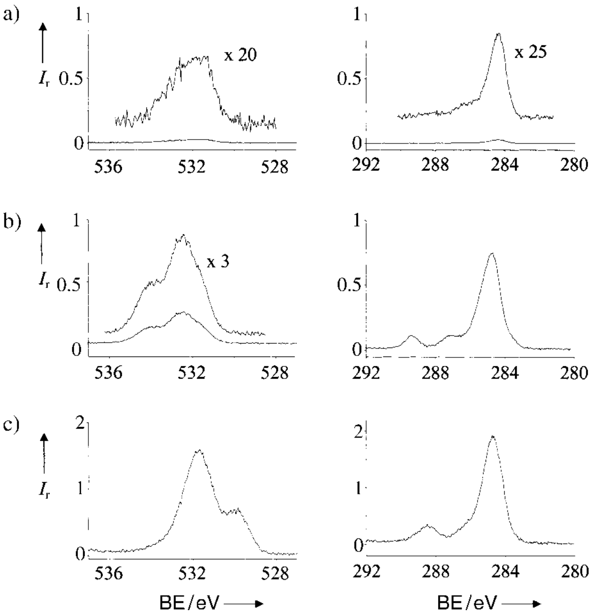


Figure 1. High-resolution XPS spectra of a) HF-etched Si(100) substrate, b) after grafting of 10-methyl undecenoate on the silicon surface, c) after hydrolysis of the ester groups followed by anchoring of Mn_{12} SMMs. Left: O 1s; Right: C 1s. The relative intensities I_r are normalized to the total Si signal.

Anchoring of the Mn cluster causes remarkable changes to the C 1s spectral region (Figure 1c) relative to the grafted ester layer. The C 1s band has an increased intensity and shows a clear shift of the carboxy component (289.4 eV) toward lower binding energies (288.5 eV), as expected for the COO^- groups present both in coordinated acetate and undecanoate ligands. However, broadening of this band might hide any low-intensity component at 289.4 eV still present because of partial ligand exchange. Finally the shoulder at 283.6 eV is no longer visible because of the increased thickness of the grafted layer.

Similar to the C 1s peaks, the intensity of the O 1s envelope is markedly higher in the grafted layer compared to the freshly HF-etched Si(100) surface (Figure 1). In particular, in the grafted ester (Figure 1b) the O 1s band consists of three overlapping signals. The two main components, centered at 532.7 and 534.1 eV, represent C=O and $COCH_3$ groups, respectively. Their intensity ratio is 1:1, as expected for the grafted ester. A low-intensity shoulder at 531.6 eV is due to oxygen in Si–O bonds.

In the SMM layer, the O 1s feature is resolved into three components. The bands centered at 530.1 and 531.7 eV are assigned to the $Mn_{12}O_{12}$ core and to the remaining 36 O atoms of the ligand framework.[4] Their intensity ratio of 1:3 is in agreement with the expected efficiency of substitution. The third component (at 531.6 eV) is associated with oxidized silicon.

The O:Mn atomic ratio inferred from the O 1s (530.1 eV) and Mn $2p_{3/2}$ (641.7 eV) signals, evaluated by using Wagner sensitivity factors[10] and corrected for the instrument transmission function, is 1:1, as required for the $Mn_{12}O_{12}$ core.

Moreover, the valence state of manganese in the SMM layer was obtained from the Mn 3s spectral region. The Mn 3s band splitting that originates from exchange coupling between the 3s hole and the 3d electrons is the best indicator for the Mn valence state.[11] The observed value of 5.1 eV is consistent with a formal valency of 3+ to 3.3+, as expected for complex **1**.

Deeper insight into the structure of the grafted layer was obtained by angle-resolved XPS spectra measured at takeoff angles of 10, 45, and 80° (relative to the surface), which provide information on the depth distribution of elements in the grafted layers (Figure 2 and Table 1).

In the case of the ester monolayer, these data are of great relevance, since it acts as the bridge between the silicon

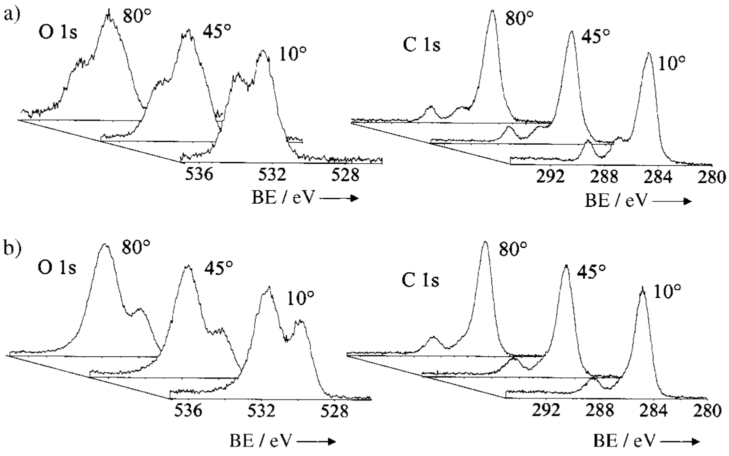


Figure 2. Spectra determined at takeoff angles between 10 and 80° for samples obtained a) after grafting of methyl 10-undecenoate on the silicon surface, and b) after anchoring of the Mn_{12} cluster.

Table 1: Dependence of elemental composition on takeoff angle for grafted methyl 10-undecenoate before and after anchoring of the Mn_{12} cluster.

Takeoff angle	Atomic fraction [%] before Mn_{12} anchoring			
	Si	C	O	Mn
80°	60.7	29.2	10.1	–
45°	49.7	37.2	13.1	–
10°	13.4	66.3	20.3	–
Takeoff angle	**Atomic fraction [%] after Mn_{12} anchoring**			
	Si	C	O	Mn
80°	29.8	33.8	32.6	3.7
45°	20.7	41.0	33.0	5.3
10°	4.0	33.0	35.8	9.9

substrate and the magnetic cluster. The C 1s spectral region (Figure 2a) shows a progressive increase in the components at 289.4 and 287.2 eV upon decreasing the takeoff angle (i.e., for shorter sampling depths). By contrast, the component associated with the Si–C carbon (283.5 eV) almost disappears at lower angles. These results are consistent both with Si–C bond grafting and with terminal ester groups atop the layer.

At smaller takeoff angles, the O 1s features have reduced intensity of the band at 531.6 (SiO_x) relative to components at 532.7 and 534.1 eV due to C=O and OCH_3. This observation is compatible with carboxylic termination on the topmost region of the layer.

The anchored Mn_{12} cluster does not show significant changes in the C 1s feature at different takeoff angles (Figure 2b). This is a consequence of the approximately spherical distribution of the alkanecarboxylato ligands (undecanoato and acetato).

By contrast, in the O 1s region the observed increased intensity at lower grazing angle of the signal due to Mn-bonded oxygen (530.1 eV) points to the Mn_{12} cluster lying atop the layer. In addition, as expected for an Mn-containing overlayer homogeneously distributed on the substrate, the Mn:Si atomic ratio progressively increases with decreasing takeoff angle (Table 1). The Mn:C atomic ratio is slightly higher for smaller takeoff angles, as expected for an Mn-containing layer mainly located above the grafted carbon chains.

To show the importance of the coordination bond between the grafted undecanoic acid and Mn_{12} cluster **1**, some experiments were performed to determine whether **1** could stick to surfaces on which no ligand exchange takes place. The acetato ligands in the cluster form a slightly hydrophobic sphere around the $Mn_{12}O_{12}$ core, as suggested by the insolubility of the cluster in water and its solubility in organic solvents such as acetonitrile. Therefore, a hydrophobic methyl-terminated monolayer (1-decene grafted on Si) and a less hydrophobic methyl ketone-terminated monolayer (5-hexen-2-one grafted on Si) were chosen to evaluate the physisorption of cluster **1**.[12]

Negligible cluster sticking was detected in XPS spectra on both 1-decene and 5-hexen-2-one monolayers (< 0.1 and 0.8 % Mn, respectively) subjected to the same treatment for cluster anchoring as the acid-terminated surface. These results indicate that significant irreversible physisorption does not occur, and cluster anchoring requires acid-terminated compounds to exchange with acetato ligands and coordinate the $Mn_{12}O_{12}$ core.

The roughness and homogeneity of the Mn-containing layer were determined by AFM analysis. Figure 3 compares the AFM images of the ester layer before and after anchoring the Mn_{12} cluster. The layer before cluster anchoring appears very flat and homogeneous with a roughness of less than 0.1 nm, comparable to that of a freshly etched Si(100) surface. The thickness of the grafted layer was estimated by atomic force lithography using the AFM tip. Thus, grafted molecules

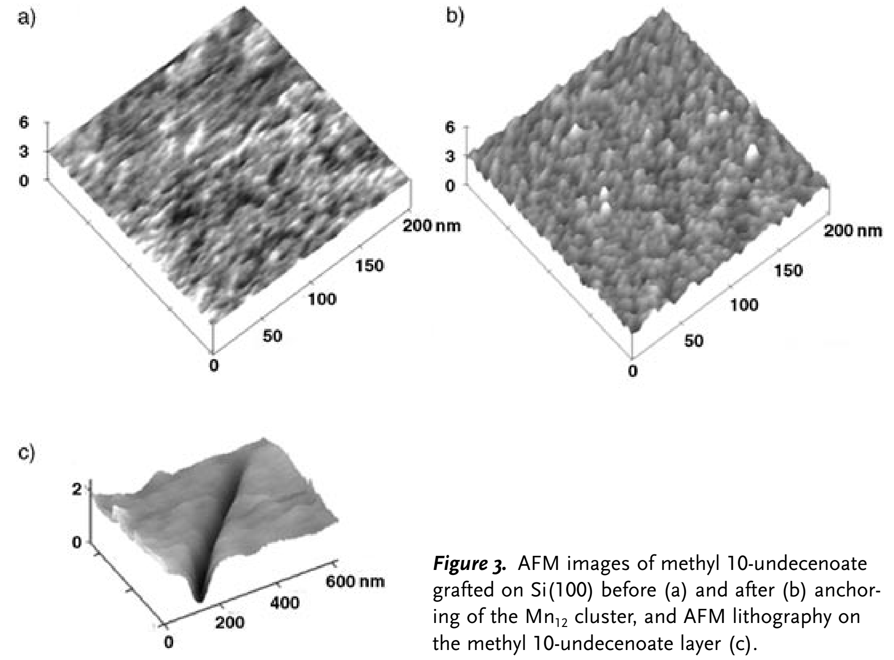


Figure 3. AFM images of methyl 10-undecenoate grafted on Si(100) before (a) and after (b) anchoring of the Mn_{12} cluster, and AFM lithography on the methyl 10-undecenoate layer (c).

were removed along a straight line by rastering the AFM tip on the surface under a suitable constant force. The depth of the scratch obtained in the ester layer was about 1.1 nm, a value slightly lower than the total length (ca. 1.5 nm) of the linear chain of methyl 10-undecenoate. Therefore, an inclined (ca. 45°) grafting geometry must be assumed to account for the observed value. After grafting of the Mn_{12} clusters, the surface is much more structured than that of the host surface. The typical vertical size of the observed features of about 1 nm is consistent with the expected height of cluster **1**. There is evidence of poorly ordered particles, almost homogeneously distributed over the surface. Their apparent lateral size is about 5–15 nm, which is greater than the expected value for isolated Mn_{12} clusters. This difference could be explained by the limited lateral resolution of the AFM analysis, but also by possible cluster aggregates not resolved by AFM. Similarly to what was observed for Mn_{12} SMMs anchored on Au,[4] the disordered arrangement might be due to the long alkyl chains of the grafting units, whose conformational flexibility prevents the formation of regular arrangements.

In conclusion, this study has shown a viable route for anchoring Mn_{12} SMMs on Si(100), that is, on surfaces suited to integration with well-established silicon technologies. This novel bottom-up approach represents a promising perspective for information storage with SMMs.

Experimental Section

1·4 H_2O·2 AcOH was synthesized according to the literature procedure[3a] and crystallized by diffusion in acetone/acetic acid solution. Elemental analysis (%) calcd for $C_{36}H_{72}O_{56}Mn_{12}$: C 20.97, H 3.52; found: C 21.01, H 3.24. ^1H NMR (500 MHz, CD_3CN, 25 °C, TMS): $\delta =$ 47 (12 H, axial $Mn^{III}Mn^{III}$), 40 (24 H, equatorial $Mn^{III}Mn^{III}$), 14 ppm (12 H, axial $Mn^{III}Mn^{IV}$).

Methyl 10-undecenoate was synthesized according to the method reported by Sieval et al.[6a] Briefly, a mixture of 10-undecenoic acid (10 g, 54 mmol), methanol (65 mL), and sulfuric acid (0.14 mL) was refluxed for 3 h. The excess methanol was removed in vacuum, and the resulting material was dissolved in diethyl ether. The product was distilled under vacuum to obtain a transparent liquid. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.83–5.78$ (m, 1 H), 5.00–4.91 (m, 2 H), 3.66 (s, 3 H), 3.31–2.84 (m, 2 H), 2.06–2.01 (m, 2 H), $\delta = 1.63–1.9$ (m, 2 H), 1.38–1.29 ppm (m, 10 H).

Monolayer preparation: 10 mL of alkene solution (60 % v/v) in mesitylene was placed in a small, three-necked flask fitted with a nitrogen inlet and a condenser. The solution was deoxygenated with dry nitrogen for at least 1 h. Subsequently, a Si(100) substrate was etched in 2.5 % hydrofluoric acid for 2 min and immediately placed in the solution. The solution was then refluxed at 200 °C for 2 h with slow N_2 bubbling to prevent bumping. After cooling to room temperature, the sample was removed from the solution and sonicated in dichloromethane for 10 min.

The methyl ester was hydrolyzed by boiling according to a modification of the method reported by Sieval et al.[6a]

The Mn_{12}-funtionalized silicon surface was synthesized by a modified ligand-exchange method.[13] The silicon surface was rinsed in a slurry of freshly prepared **1**·4 H_2O·2 AcOH in anhydrous toluene, and the solvent was distilled under reduced pressure (100–150 mbar). Additional azeotropic distillations were performed with toluene (3 × 10 mL, 100–150 mbar). The modified substrate was removed from the solution and sonicated in acetonitrile and dichloromethane for 10 min to remove unanchored Mn_{12} clusters.

1-decene and 5-hexen-2-one monolayers were prepared and characterized by XPS similarly to the methyl 10-undecenoate monolayer. In both cases, the Si 2p XPS region showed only the Si $2p_{3/2-1/2}$ spin–orbit doublet of elemental silicon. The absence of significant signals around BE = 103 eV due to oxidized Si pointed to efficiently passivated surfaces. Similarly, the C 1s region was consistent with the presence of organic monolayers. The C 1s region of grafted 1-decene consisted of two main components centered at 283.5 (carbide Si–C bond) and 284.8 eV (aliphatic backbone). The C 1s region of grafted 5-hexen-2-one also showed a third main component centered at 286.1 eV (C=O group).

The XPS spectra were recorded on a PHI ESCA/SAM 5600 Multy technique spectrometer equipped with a monochromated $Al_{K\alpha}$ X-ray source. The analyses were carried out at various photoelectron angles (relative to the sample surface) in the range 10–80° with an acceptance angle of ± 7°.

AFM images were obtained in high-amplitude mode (tapping mode) by a Digital Instrument Multimode apparatus. The noise level before and after each measurement was 0.01 nm. AFM lithography was performed with an NT-MTD instrument.

Received: February 4, 2004
Revised: April 20, 2004 [Z53933]

Keywords: cluster compounds · monolayers · photoelectron spectroscopy · single-molecule magnets · surface chemistry

[1] G. P. Lopinsky, D. D. M. Wayner, R. A. Wolkow, *Nature* **2000**, *406*, 48.
[2] G. F. Cerofolini, G. Ferla, *J. Nanopart. Res.* **2002**, *4*, 185.
[3] a) T. Lis, *Acta Crystallogr. Sect. B* **1980**, *36*, 2042; b) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141; c) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *Mater. Res. Bull.* **2000**, *35*, 66.
[4] A. Cornia, A. C. Fabretti, M. Pacchioni, L. Zobbi, D. Bonacchi, A. Caneschi, D. Gatteschi, R. Biagi, U. del Pennino, V. De Renzi, L. Gurevich, H. S. J. Van der Zant, *Angew. Chem.* **2003**, *115*, 1683; *Angew. Chem. Int. Ed.* **2003**, *42*, 1645.
[5] M. Cavallini, F. Biscarini, J. Gomez-Segura, D. Ruiz, J. Veciana, *Nano Lett.* **2003**, *3*, 1527.
[6] a) A. B. Sieval, A. L. Demirel, J. M. Nissink, M. R. Linford, J. H. van der Maas, W. H. de Jeu, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **1998**, *14*, 1759; b) G. F. Cerofolini, C. Galati, S. Reina, L. Renna, *Mater. Sci. Eng. C* **2003**, *23*, 253.
[7] G. F. Cerofolini, C. Galati, S. Lorenti, L. Renna, O. Viscuso, C. Bongiorno, V. Raineri, C. Spinella, G. G. Condorelli, I. L. Fragalà, A. Terrasi, *Appl. Phys. A* **2003**, *77*, 403.
[8] I. L. Swift, *Surf. Interface Anal.* **1982**, *4*, 47.
[9] D. Briggs in *Practical Surfaces Analysis*, *Vol. 1*, 2nd ed. (Eds.: D. Briggs, M. P. Seah), Wiley, New York, **1995**, p. 440.
[10] C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. H. Raymond, L. H. Gale, *Surf. Interface Anal.* **1981**, *4*, 211.
[11] a) V. R. Galakhov, M. Demeter, S. Bartkowski, M. Neumann, N. A. Ovechkina, E. Z. Kurmaev, N. I. Lobachevskaya, Ya. M. Mukovskii, J. Mitchell, D. L. Ederer, *Phys. Rev. B* **2002**, *65*, 113102; b) V. Di Castro, G. Polzonetti, *J. Electron Spectrosc. Relat. Phenom.* **1989**, *48*, 117.
[12] Note that the methyl ketone-terminated surface is expected to have comparable hydrophobicity to that grafted with methyl 10-undecenoate, but the latter monolayer was not suited to evaluate cluster physisorption since it is partially hydrolyzed during the anchoring process due to the presence of water and acetic acid in the starting material **1**·4 H_2O·2 AcOH.
[13] H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301.