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A new approach to grafting a monolayer of oriented Mn_{12} nanomagnets on silicon†

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The functionalisation of a Si(100) silicon wafer allows for the oriented grafting of a monolayer of Mn_{12} nanomagnets using a two-step procedure.

The discovery of the blocking and the quantum tunnelling of the magnetization in molecular systems was a major breakthrough in the area of molecular magnetism.¹ The first complex where these phenomena were observed is $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ (Mn_{12} -ac), described by Lis in 1980.² The blocking of magnetization is due to the high spin ground state of the molecule ($S = 10$) and the uniaxial magnetic anisotropy responsible for a relatively high barrier to the reorientation of the magnetization below 8 K.³ Such behaviour leads to a magnetic bistability that may be utilised to store information (even if it occurs below 4 K in the case of Mn_{12} derivatives), where a bit of information has the size of one molecule (around 1.2 nm).

One of the very first steps for reaching such a goal is to organize the molecules as a monolayer on a substrate in order to address a single molecule. Different approaches have been reported recently: (i) using the Langmuir–Blodgett technique;⁴ (ii) grafting on a gold substrate by using a thiol modified Mn_{12} complex;⁵ (iii) deposition of the biphenyl derivative of Mn_{12} and nanopatterning on polycarbonate films;⁶ and (iv) deposition of monolayer and multilayers on gold.⁷ Very recently, grafting Mn_{12} -ac on Si(100) has been reported.⁸

The next step is to conceive an approach where grafting leads to an orientation of the molecules on the substrate. We show here that by using a mixed Mn_{12} complex (*i.e.* containing two different carboxylate groups) it is possible to graft a monolayer in an oriented manner on a silicon substrate. Mn_{12} -ac is made of a $\text{Mn}_{12}\text{O}_{12}$ (4 Mn(IV) and 8 Mn(III)) core which has a disk-like shape surrounded by 16 acetate groups: 8 in equatorial and 8 in axial positions and 4 water molecules (see Scheme 1).

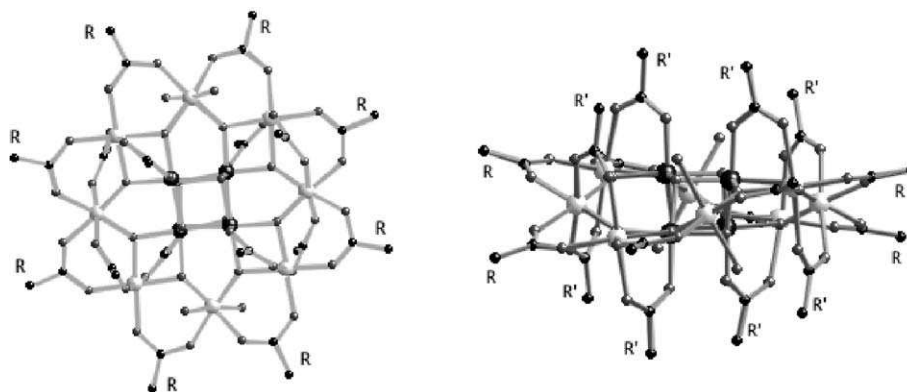
The Mn(III)-O long distances (Jahn–Teller effect) are those with the axial ligands. Christou and co-workers elegantly demonstrated that due to pK_a differences between carboxylic acids it is possible (i) to substitute the acetate groups by other carboxylates in solution keeping the oxide core intact, and (ii) to prepare mixed complexes from the selective substitution of the axial or the equatorial carboxylates.^{9,10} We took advantage of this particular reactivity and selected a Mn_{12} complex possessing dichloroacetate groups in axial positions and *tert*-butyl acetate groups in equatorial positions, *i.e.* $\text{Mn}_{12}\text{O}_{12}(\text{CHCl}_2\text{COO})_8(\text{tBuCH}_2\text{COO})_8(\text{H}_2\text{O})_3$ (**1**).^{10†} Reacting **1** with a carboxylic acid-functionalised silicon wafer induces a selective substitution of either axial or equatorial carboxylates of the molecule by carboxylic acid groups originating from the substrate. The choice of axial chlorinated carboxylates allows to probe the ligands exchange by X-ray photoelectron spectroscopy (XPS).

Direct immersion of a Si–H(100) surface§ in neat distilled undecylenic acid (110 °C, 12 h under Ar) leads to thermal grafting of the acid *via* its alkene end.^{11,12} The hypothesis of formation of silyl esters emitted in the case of this coupling agent, was discarded by complementary experiments.¹³ Attenuated transmission reflection infra-red (ATR-FTIR) spectroscopy shows that most of the available Si–H functions have reacted as the intensity of the

† Electronic supplementary information (ESI) available: Spectroscopic data of deposited and grafted Mn_{12} sample (Figs. S1–S6). See <http://www.rsc.org/suppdata/cc/b419271k/>

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Scheme 1

2111 cm^{-1} peak (Si–H stretching vibrations) decreased (see ESI).[†] Indeed, only 50% of the Si–H functions may react for steric reasons.¹⁴ Furthermore, the spectrum showed the presence of methylene stretching vibrations at 2855 and 2927 cm^{-1} (see ESI)[†] as well as the carbonyl stretching of the carboxylic acid at 1718 cm^{-1} (see ESI).[†] No C–H vibration due to terminal alkene groups could be observed, thus ascertaining the absence of grafting *via* silyl ester groups.

Grafting of **1** was achieved by immersion of the previous modified substrate in a degassed 10^{-4} M toluene solution of the complex for 1 h.[¶] The obtained wafer was thoroughly sonicated three times (3×10 min) in 30 ml of distilled toluene to remove any physisorbed molecules. ATR-FTIR spectra show that the band at 1718 cm^{-1} almost vanishes after the immersion of the substrate in the Mn_{12} solution which is the first evidence for the grafting of molecules by carboxylate substitution (see ESI).[†]

XPS studies were carried out^{||} on: (i) native silica where free molecules of **1** were merely deposited by evaporation of a droplet (10^{-3} M in toluene) on the substrate to serve as a reference; (ii) the acid-functionalised Si(100) substrate with grafted Mn_{12} . The XPS spectra of the references show all the expected characteristics (see binding energies in Table 1) already reported elsewhere.¹⁵ The Mn2p spectrum has two peaks at 653.8 and 642.2 eV, corresponding to the excitation from the $2p_{1/2}$ and $2p_{3/2}$ levels, respectively. Since the Mn2p excitations are generally not sensitive to the oxidation state of the Mn atoms, the Mn3s spectrum was registered (native silica). The spectra obtained for the grafted Mn_{12} sample reveal the same features as the reference sample (Table 1). The energy difference (ΔE) between the Mn3s peaks of the reference and the grafted sample are equal to 5.4 and 5.5 eV, respectively (Fig. 1), close to the value reported for manganites with the average oxidation state of 3.3.¹⁶ This is the best evidence for the integrity of the grafted complex.

The ATR-FTIR and XPS data insure that **1** has been grafted on the substrate but do not give evidence that the sample analyzed is a monolayer of Mn_{12} molecules (some physisorbed molecules may be present on top of the first grafted monolayer despite the sonication process). In order to give such a proof we performed two additional studies. The first one consists in repeating exactly the same chemical process used for the grafting experiment on a substrate functionalised by undecane instead of undecanoic acid (*i.e.*, carboxylic groups from the surface were replaced by methyl groups). The XPS spectra of a sample obtained without the sonication process show all the signals expected for Mn_{12}

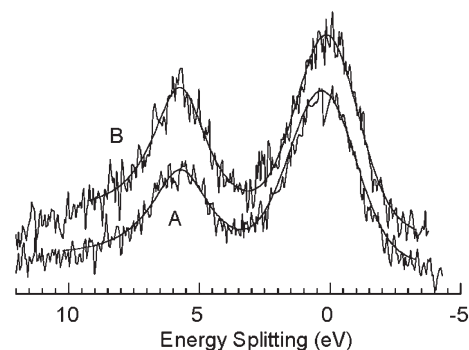


Fig. 1 Energy splitting of the Mn3s multiplet for deposited Mn_{12} on native silica (A) and grafted on Si(100) (B).

demonstrating that the molecules can be physisorbed. However, after sonicating the substrate no XPS signal is present anymore. This is the best evidence that sonication leads to the complete removal of physisorbed molecules while molecules linked by coordination bonds are still present. Thus, only one monolayer of **1** is present on the acid functionalised Si substrate. The definitive evidence comes from X-ray reflectivity studies before and after the grafting of the Mn_{12} . From the surface electronic density modification observed by X-ray reflectivity, we deduced an average value of 1.5 nm for the thickness of the Mn_{12} layer. (see ESI).[†]

Atomic force microscopy (AFM) imaging was performed on the acid functionalised and on the Mn_{12} grafted substrates (Fig. 2).^{**} Fig. 2 shows that the average roughness of the acid functionalised Si substrate is lower than 0.5 nm on a large scale which is consistent with a very flat organic monolayer.

For the Mn_{12} grafted substrate, the topological image shows a homogeneous layer on a large scale (see ESI)[†] with a roughness between 1 and 1.5 nm. One cannot exclude that the tip measures a thickness corresponding to the length of the organic layer and the grafted Mn_{12} . Indeed, the presence of the Mn_{12} monolayer may well perturb the underlying organic part and create some holes.

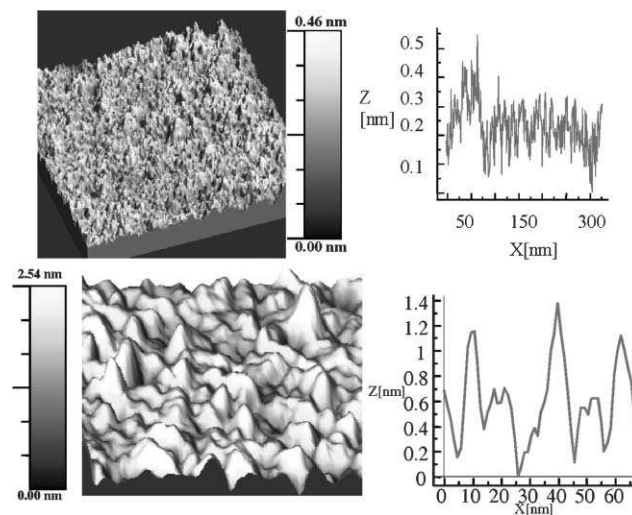


Fig. 2 (Top) AFM image (400×400 nm) of grafted undecanoic acid on Si(100) wafer and topological profile, (down) AFM image (70×70 nm) of grafted Mn_{12} on Si(100) wafer and topological profile.

Table 1 Binding energies (eV) obtained from X-ray photoelectron spectroscopy

	Peaks attribution	Deposited Mn_{12} ^a	Grafted Mn_{12}
O 1s	COO-/COOH	532.0	532.0
	Mn–O	530.3	530.0
C 1s	CH ₂ , CH ₃	284.3	284.5
	C–Cl	287.6	287.6
	C···O	288.7	288.8
Cl 2p	$2p_{1/2}$	201.8	201.9
	$2p_{3/2}$	200.2	200.3
Mn 2p	$2p_{1/2}$	654.6	653.8
	$2p_{3/2}$	642.8	642.2
Mn3s (ΔE)	3s multiplet	5.4 eV	5.5 eV

^a All spectra have been recorded on a silicon wafer.

In order to check the orientation of the grafted molecules, a quantitative analysis of the Mn2p and the Cl2p XPS signals was performed. The Mn/Cl ratios extracted from the XPS data (see ESI)† provide information on the nature of the substituted carboxylates:†† if only equatorial *tert*-butyl acetates were exchanged upon grafting on the acid-functionalised Si surface, no difference in the Mn/Cl ratio should be observed between the free and grafted Mn₁₂ clusters (theoretical value Mn/Cl = 0.75), whereas axial substitution should lead to a minimum of four remaining dichloroacetates (Mn/Cl = 1.5) out of the eight present on the non-grafted cluster. If substitution occurred in a random way, an average value of 6 remaining dichloroacetates would be expected, thus leading to a ratio Mn/Cl = 1. Hence, the value of Mn/Cl = 0.74 ± 0.04 obtained on the grafted substrate means that the substitution proceeds only through replacement of equatorial *tert*-butyl acetate groups. Such a result may be at a first glance surprising because one may expect a substitution of the axial carboxylate groups less tightly linked to the Mn atoms because of the Jahn–Teller effect. However, this cannot actually be the case because the substrate is functionalised by carboxylic acid groups and not carboxylate groups. As already stated by Christou,¹⁰ the driving force of the reaction is the formation of the weakest acid, hence *tert*-butylacetic acid rather than dichloroacetic acid. Furthermore, the thermodynamically most stable bonds should form, *i.e.* those corresponding to the strongest Mn–carboxylate bonds which are the equatorial ones where no Jahn–Teller effect is present.

In this communication, we have shown the feasibility of grafting on a large scale a homogenous monolayer of Mn₁₂ derivative on silicon even though no lateral organisation could be observed. The Mn/Cl elements ratios obtained from the analysis of the XPS spectra are in line with a preferred orientation of the Mn₁₂ molecules with their anisotropy axes parallel to the substrate's surface. This is the first example which shows that orientation of the molecules may be achieved by chemical means. The next step is mastering the orientation of the Mn₁₂ molecules with their anisotropy axes perpendicular to the 2D substrate.

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Notes and references

† NMR studies in solution show species where equatorial and axial carboxylates have been exchanged. The main species in solution is **1**, since the axial *tert*-butyl resonances are so relatively weak compared to the equatorial *tert*-butyl resonance.

§ Generation of the Si–H functions proceeds through etching the wafers in a piranha bath (30% H₂O₂/70% H₂SO₄, 20 min, 120°) followed by immersion in a 10% HF solution. This procedure is repeated three times.

¶ Mn₁₂O₁₂(CHCl₂COO)₈(*t*BuCH₂COO)₈(H₂O)₃ was synthesized as previously described¹⁰ and single crystals, checked by X-ray diffraction and elemental analysis, were used in all experiments.

|| XPS spectra were recorded on a Vacuum Generator ESCALAB 210 using an Al K α source monochromatized at 1486.6 eV. The radiations were generated (20 mA, 15 kV) under UHV at 10^{−10} mbar. Spectra were recorded at a take-off angle of 90° with respect to the sample plane.

** Lateral resolution is limited by the curvature of the tip (2 nm curvature at the apex). The AFM images were taken in tapping mode (Nanoscope III, Si supersharptip, Nanosensor at a resonance frequency of 236 KHz).

†† Mn/Cl ratios were calculated using the Mn2p_{3/2} spectrum because of much better S/N ratio. The reproducibility of all experiments has been checked (see ESI).†

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