# Advances on the nanostructuration of magnetic molecules on surfaces: the case of single-molecule magnets (SMM)

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SMMs exhibit slow magnetization relaxation rates characteristic of nanodomain particles whose origin is however on individual molecules. For this reason, they have attracted much interest due to their potential applications in high-density information storage devices and quantum computing applications, where for instance, each molecule can be used as a magnetic bit of information. However, for this to become a reality, several basic studies such as their deposition on surfaces are still highly required. Here we will revise all the experimental approximations that have been so far reported for their addressing, nanostructuration and study on surfaces, from the use of stamps as templates to their anchorage to gold surface through the use of thiol-based ligands. It is also important to emphasize that the results and methodologies described along this review are applicable not only to SMMs but to any molecular material.

## Introduction

The rapid growth of high-speed computers and the miniaturization of the magnetic technology have fuelled much interest in the field of nanoscale magnetic materials.[1–3] In the past decade, the data density for magnetic hard disk drives has increased at a phenomenal pace: doubling every 18 months and, since 1997, doubling every year, which is much faster than the Moore's Law for integrated circuits. To maintain such a speedy miniaturization, several methods have been developed. The classical approximation has been the fragmentation of bulk ferro- and ferri-magnetic materials. The main disadvantage of this approach is that the nanoscale magnetic materials exhibit a distribution of particle size, anisotropy and shapes. This situation leads to a distribution of the barrier heights for the inter-conversion of the spins "up" to the spins "down" within the domains, which is not desirable for application in devices. Moreover, from a fundamental point of view, a distribution in barrier heights masks properties such as those associated with resonant magnetization tunnelling. More recently, several other exploratory techniques based on lithographic and scanning probe microscopies, the so-called

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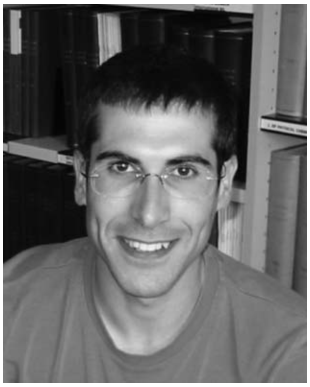

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*top-down* approach, are also being explored. In spite of their enormous success, the main challenge that these new approximations face are: (i) the technological and economical limitations that they find on their way to satisfy the ever-increasing demand of higher area density magnetic storage and (ii) the continuous miniaturization of traditional magnetic materials leads to the observation of new phenomenologies, such superparamagnetic effects or quantum behaviour.

In the last few years, the use of synthetic methodologies, the so-called *bottom-up* approach, has been shown as a complementary alternative to the previously described *top-down* approximations. Among the different materials so far reported, of special interest are *Single-Molecule Magnets* (SMMs).[4] SMMs combine large-spin ground states and high axial magnetic anisotropy, resulting in a barrier for the spin reversal.[5] As a consequence, they exhibit slow magnetization relaxation rates characteristic of nanodomain particles, such as out-of-phase ac magnetic susceptibility signals and hysteresis magnetization loops, whose origin is albeit based on individual molecules. Advantages of these systems are considerable. They exhibit molecular dimensions, enormous monodispersivity, high procesability and interestingly low costs. For all the above mentioned reasons, SMMs have attracted much interest over the last ten years, not only from a scientific point of view but also because their potential use in high-density information storage devices[6] and quantum computing applications,[7] where for instance, each molecule can be used as a magnetic bit of information. However, before SMMs stimulate the realization of a prospective molecular computational device, several basic studies that help us to better understand and control their intricate characteristics are highly required. For instance, an improvement of their usually low blocking temperatures, above which SMMs behave as superparamagnets,[8] will be highly required since they limit their practical utilization to date. They have also been shown to be very dependent on structural and crystalline restrictions.[9] For instance, previous works have shown the influence of dislocations on the resonant spin tunnelling of a crystal of $Mn_{12}$ clusters[10] or the existence of at least two different magnetization relaxation processes, being highly influenced by the network characteristics.[11] But among all these studies, one of the challenges that has attracted more attention over the last few years has been the development of new techniques that allow their nanostructuration and addressing on surfaces.

**Daniel Ruiz-Molina**

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Most of the work so far reported in this direction has been focused on large-metal complexes comprising a dodecamanganese core, the well-known $Mn_{12}$ family.[4] Advantages of this family of clusters are multifold. Among them: (i) they exhibit high thermal and chemical stabilities, (ii) they have one of the highest blocking temperatures so far reported (*ca.* 4–6 K) for a SMM and last, but not less important, (iii) easiness of preparation and their rich synthetic behaviour allows the functionalization of the peripheral organic ligands. Indeed, the metal core $[Mn_{12}(\mu_3\text{-}O)_{12}]$ of this family of molecules comprises a central $[Mn^{IV}{}_4O_4]^{8+}$ cubane structure held within a non-planar ring of eight $Mn^{III}$ ions by eight $\mu_3\text{-}O^{2-}$ ions. The coordination sphere is provided by an outer shell of sixteen peripheral carboxylate groups that are amenable to variation in a simple way by substitution reaction in the presence of the desired carboxylic acid,[12] starting from the precursor $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$ (**1**) ($Mn_{12}$-acetate complex).[13] Thus, maintaining the metal core structure, and therefore, the behaviour as a single-molecule magnet, it is possible to modify the adsorbate–surface affinity or exploit the use of suitable functionalized carboxylates capable to be anchored on the surface. Moreover, such synthetic capabilities also allow us to control their molecular dimensions simply by varying the size of the replacing carboxylate ligands. An example of different molecular dimensions that have been reported for these clusters is shown in Fig. 1.

The first approach to deposit $Mn_{12}$ SMMs on surfaces was attempted by Coronado and co-workers in 1998.[14] By making use of the Langmuir–Blodgett technique,[15] the authors created a surfactant molecular film at the air–water interface where $Mn_{12}$ clusters arrange both in the form of isolated molecules or well-defined monolayers, which may exhibit magnetic anisotropy depending on the orientation of the film with respect to the applied magnetic field. This fact was attributed to the preferential orientation of the complexes with their easy magnetization axis normal to the film surface. After this pioneering work, numerous experimental studies for the deposition and nanostructuration of SMMs on different surfaces have also been reported. In the following, we will review such experimental approaches by grouping them into four different categories: (I) deposition of non-functionalized

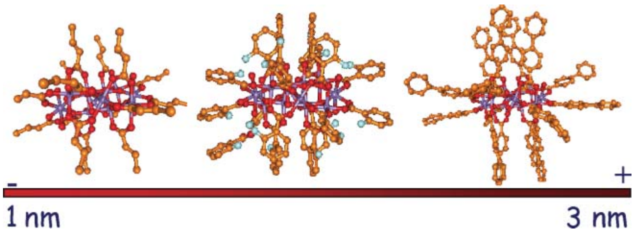


**Fig. 1** Variation of the molecular dimensions of the $Mn_{12}$ cluster according to the use of different peripheral carboxylates. The $Mn_{12}$ core that originates their SMM behaviour remains unaltered in all the cases.

$Mn_{12}$ clusters from solution by non-covalent interactions, (II) functionalization of clusters and/or surfaces to promote stronger ionic or covalent interactions, (III) use of physical approaches, such as laser ablation, and, finally, (IV) incorporation into nanocomposite thin films. By the end, future tendencies for the deposition and study of SMMs magnets on surfaces will be analyzed.

## I Deposition of $Mn_{12}$ complexes from solution by non-covalent interactions

Preliminary experiments evidenced that the first reported $Mn_{12}$ complex, namely $Mn_{12}$-acetate (**1**), does not adhere to non-functionalized surfaces in a stable manner, *i.e.* forming stable molecular layers through van der Waals or π–π interactions. For this reason, in our group we initiated the deposition of clusters such as $[Mn_{12}O_{12}(O_2CC_6H_4Ph)_{16}(H_2O)_4]$ (**2**),[16] which has been functionalized with benzoic carboxylates. The presence of phenyl groups was expected to enhance the interaction with different surfaces and/or intermolecular interactions. First attempts to deposit **2** on HOPG simply by a drop casting from a chlorobenzene solution resulted in the formation of an inhomogeneous layer of molecules of complex **2** over the surface, lacking however any control over their organization and nanostructuration. To solve this situation, two different approaches were used: (i) to make use of water droplets as templates (*breath-figures*), a technique that has been successfully used for the nanostructuration of polymeric materials[17] and (ii) a stamp-assisted deposition (*lithographically controlled wetting—LCW*).[18]

### Breath-figures method

The first of these strategies takes advantage of the well-known *breath-figures* phenomenon, which is based on the condensation of water droplets on a cold surface.[17] Prior to this work, this methodology had been extensively used to fabricate 2D or 3D well-ordered polymeric macroporous materials but never for the nanostructuration of a molecular material on a given surface.[19] Then, following this strategy the self-assembly of complex **2** in the form of magnetic rings on a HOPG surface has been reported.[20] The schematic representation for the formation of the $Mn_{12}$ rings is shown in Fig. 2. Experimentally, a drop of a $CH_2Cl_2$ solution of complex **2** was left to evaporate in a moist atmosphere. Since $CH_2Cl_2$ undergoes cooling evaporation, and it is denser and not miscible with water, such cooling evaporation process promotes the formation of an array of self-assembled water droplets that condense on the organic solvent surface. In the initial stages of solvent evaporation, water droplets start to nucleate and grow whereas the liquid thin film, whose thickness is progressively reduced, undergoes instability and fragmentation according to the well-known dewetting mechanisms.[21] Then, after fragmentation, the solution is confined strategically around the periphery of the water droplets that are acting as templates by the onset of capillary forces.[22] After complete solvent evaporation, the resulting solid deposits replicate exactly the perimeter of each water droplet into monodispersed concentric rings of molecular nanomagnets.

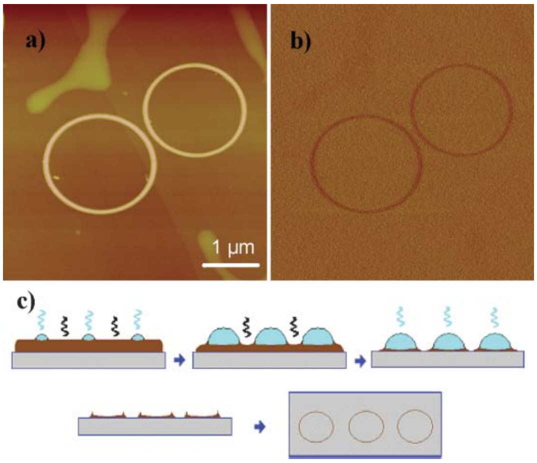


**Fig. 2** $Mn_{12}$ rings of **2** induced by the *breath-figures method* on a HOPG surface: topography (a) and phase-contrast MFM image (b). The rings appear to be relatively uniform in size, with an experimental averaged height that ranges from 119 to 135 nm, averaged diameters ranging from 4.2 to 4.6 μm and ring-thickness at half height of approximately 140 nm.[20]

The confirmation that such ring-like deposits arise from SMMs instead of other impurities came from magnetic force microscopy (MFM) imaging. In this technique, a tip that is covered with a magnetic material is scanned over the sample under study. In a first sweep, the AFM topographic mode is used whereas in the second sweep, which is carried out over the same area but with the tip retracted, the local magnetization of the sample is monitored. The top-view topographical image and the corresponding MFM image of the rings are shown in Fig. 2. As can be seen there, MFM images clearly indicate a magnetic gradient response exactly corresponding to the molecular position found by topographic imaging in spite of the fact that this family of molecules behaves as a paramagnet at room temperature. This fact has been attributed to polarization of the magnetic moment of the molecules by the tip, inducing an apparent magnetic contrast with the diamagnetic substrate, as well as to the large amount of molecules contained within the rings that increment the magnetic response.

### Lithographically controlled wetting method

The second of the approaches used for the nanostructuration of complex **2** is based on a stamp-assisted deposition methodology previously described by Cavallini and Biscarini, the so-called lithographically controlled wetting (LCW) technique.[18] In this technique, a solution of molecules can be confined to the protruding regions of a stamp that is intimately in contact with the liquid surface by capillary forces. Then, after complete evaporation of the solvent, the zones under the protruding regions become enriched at the expense of the surroundings depleted of molecules, resulting in a faithful molecular positive replica of the stamp on the surface.

Surface deposition of complex **2** was assessed on surfaces that differ significantly on their hydrophilicity (*i.e.*, $Si/SiO_2$ and highly oriented pyrolitic graphite, HOPG).[23] On the hydrophilic $Si/SiO_2$ surface, intermolecular interactions are

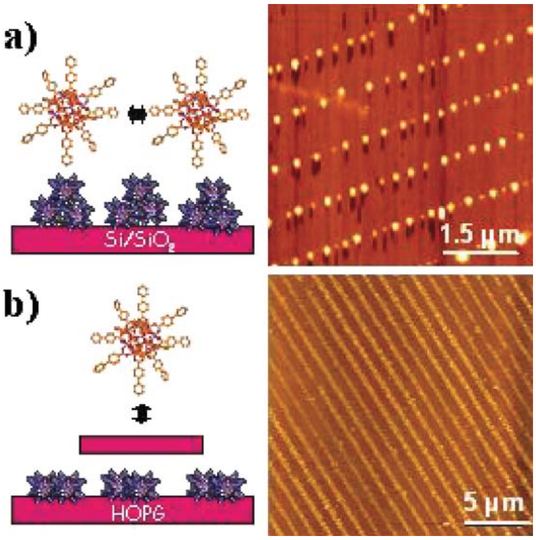


**Fig. 3** AFM images corresponding to spatially distributed arrays of **2** fabricated by LCW: spherically-capped droplets on Si/SiO$_2$ with an average size of 270 nm and interlinear distance of 441 nm dominated by intermolecular interactions (a) and monolayer stripes on the HOPG substrate, 3 nm average high and less than 200 nm width, dominated by adsorbate–surface interactions (b). Reprinted with permission from ref. 23. Copyright 2003, American Chemical Society.

enhanced thanks to the hydrophobic character of complex **2**, thereby allowing the formation of a spatially distributed pattern that consist of droplets of several molecules aligned along the stretching direction. By contrast, on the HOPG surface, the enhanced wettability favours adsorbate–surface interactions to afford monolayer stripes of **2**, as ascribed to their hydrophobic nature (Fig. 3).

## II Deposition of Mn$_{12}$ complexes from solution by covalent interactions

To improve the absorption and stability of the molecular systems on the surface, three different strategies have been mainly followed: (a) modification of the complex with surface-biding functional carboxylates, (b) modification of the surface with functionalities able to coordinate with the Mn$_{12}$ and (c) a combination of both.

### II.a Surface-binding functionalized Mn$_{12}$ complexes

Carboxylate groups containing surface-binding functionalities, such as thiol groups, can be introduced into the Mn$_{12}$ clusters simply by replacing the acetate groups of complex **1**. The presence of the thiol groups is expected to prompt the formation of covalent Au–S interactions, improving the chemical stability of the resulting adsorbates. An schematic representation of a Mn$_{12}$ molecule directly anchored to a gold surface is shown in Fig. 4. However, Mn$_{12}$ complexes may undergo chemical instability (reduction) in the presence of free thiols. For this reason, the first attempt was successfully executed by using an acetyl-protected 16-sulfanylhexadecanoate Mn$_{12}$ derivative (**3**), on a Au(111) surface.[24] Scanning tunnelling microscopy (STM) experiments revealed its self-assembly into a disordered monolayer lacking any epitaxial growth, a fact that was attributed to the presence of disordered long alkyl chains. Moreover, the scanning of the surface plane induced a disruption of the molecular film, allowing the first imaging of individual Mn$_{12}$ molecules by STM.

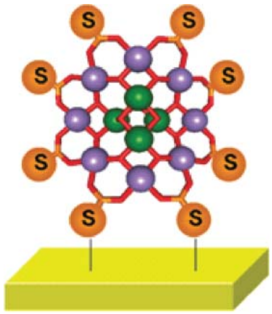


**Fig. 4** Representation of a direct anchoring of a thiol-modified Mn$_{12}$ on a gold surface. The periphery of the cluster features sixteen sulfur atoms, which provide as many surface-binding sites.

The work previously described was successful in such it was the first observation of an isolated Mn$_{12}$ cluster on a surface. However control over the molecular organization and nanostructuration was not achieved. With this aim, Mannini *et al.* applied the microcontact printing (µCP) technique.[25] The µCP technique is based on the faithful replication of a patterned elastomeric "stamp" soaked with the molecular systems or nanoparticles under study on a given surface.[26] Then, following two different variations of this technique, the authors were able to obtain stable monolayers of complex **3** on a Au(111) surface. In the first of the approximations, the gold substrate was prepatterned with stripes of octadecylthiol separated by bare gold regions. Subsequent soaking of the prepatterned gold substrate into a solution of complex **3** induced a selective absorption of **3** onto the bare gold zones within a single monolayer. In the second of the approaches, the stamp was "inked" directly with a dilute solute of complex **3**

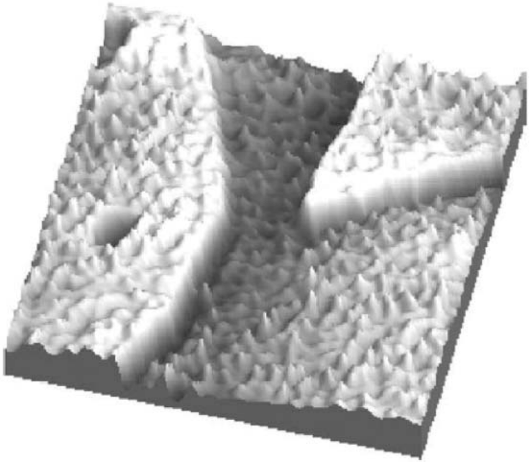


**Fig. 5** 3-D representation (200 × 200 nm$^2$) of a gold substrate soaked into a solution of complex **4** obtained by a constant-current STM technique. In addition to the terraces and the triangular feature typical of a Au(111) reconstruction, molecular motives can also be observed. The size distribution was very narrow (2.7 ± 0.5 nm) and agrees nicely with the size estimated for complex **4** (2.8 × 2.1 nm). Extracted from ref. 27.

and brought into contact with a gold substrate. Transfer of ink occurs only in the contact areas between the stamp and the surface, yielding a molecular replica of the stamp on the surface.

Nanostructuration of complex $[Mn_{12}O_{12}(L)_{16}(H_2O)_4]$ (**4**) (where L stands for the thioether group 4-(methylthio)benzoate), has also been reported by direct soaking of Au(111) substrates.[27] XPS experiments revealed a complete surface coverage for long exposition (soaking) times whereas partial coverage was found for shorter immersion periods. Accordingly, STM measurements evidenced the sub-monolayer coverage of the gold film by quasi-spherical particles, which according with their dimensions may be attributed to individual molecules (see Fig. 5). Since thioether groups do not react with the $Mn_{12}$ core during the ligand exchange reaction, the proposed strategy is also easier than the use of acetyl-protected thiols, which require hydrolysis before grafting to gold.

### II.b Molecule-binding to functionalized surfaces

This experimental approach is based on the functionalization of a given surface with a monolayer of ligands bearing ending carboxylate groups that react with the $Mn_{12}$ clusters. For instance, Bucher and co-workers reported the self-assembly and magnetism of $[Mn_{12}O_{12}(^tBuCO_2)_{16}(H_2O)_4]$ (**5**), on functionalized gold surfaces.[28] The use of complex **5** was justified on the basis of its high solubility and presence of $^t$Bu groups that can be easily replaced by the carboxylate groups linked to the surface.[29] As a model for posterior studies, first they induced the direct deposition of **5** from a dilute solution on native Au(111) (see Fig. 6). In this way, by controlling the amount of solution added, they were able to grow several tens of monolayers at once, which were useful to perform SQUID magnetometry measurements (see bottom of Fig. 6). In a second step, the gold surface was functionalized with a stable self-assembled monolayer of 1,16-mercaptohexadecanoic acid. Covalent immobilization of the $Mn_{12}$ cluster was then achieved by carboxylate-exchange reactions, dipping the functionalized gold substrate into a $CH_2Cl_2$ solution of complex **5**. STM images of the resulting substrates revealed that molecules of complex **5** arrange in domains of ordered monolayers with an intermolecular distance of about 2.0 nm. It is important to emphasize that the rhombus unit cell of sulfur atoms on gold matched quite well the surface spanned by the four axial ligands of complex **5**.

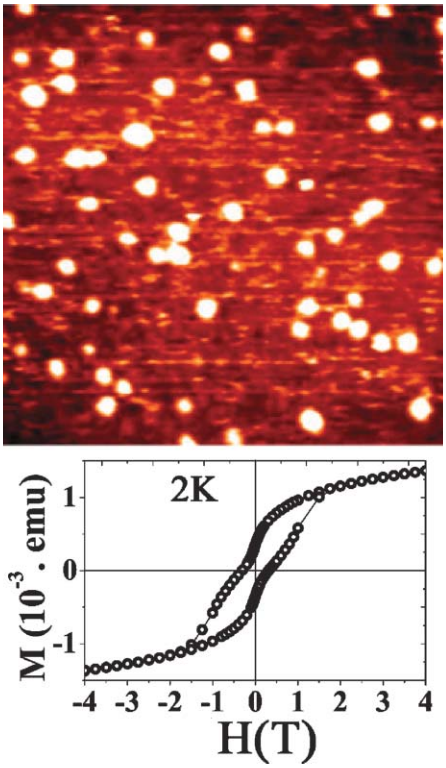
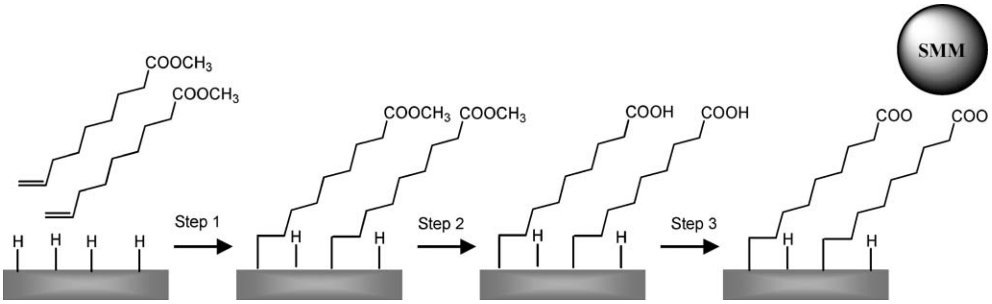


**Fig. 6** STM images of complex **5** directly deposited on Au(111) (top). Hysteresis loop of a thick film of **5** recorded at 2.0 K (bottom). In addition to be characteristic of $Mn_{12}$ clusters, the resulting hysteresis loop was representative of a sample with orientational disorder of the molecules. Image reprinted with permission from ref. 28. Copyright 2005, Wiley-VCH.

Molecule-binding to functionalized surfaces of $Mn_{12}$ clusters has been shown to be practicable not only for gold but also for other surfaces with relevant technological importance, such as Si(100). Following this approach, Fragala and co-workers have reported the anchoring of $Mn_{12}$ clusters on silicon by using undecanoic acid grafted on H-terminated Si(100) surfaces.[30a] For this, the three-step methodology shown in Scheme 1 was followed. First, there is a grafting of the methyl ester of 10-undecenoic acid on the silicon surface. Afterwards, the hydrolysis of the ester groups to render free carboxylic groups on the surface takes place. Finally, the ligand exchange reaction between the $Mn_{12}$ acetate and the grafted undecanoic acid takes place by a ligand exchange reaction to yield the



**Scheme 1** Three-step process used for anchoring SMMs on Si(100). *Reagents and conditions*: step 1: mesitylene, 200 °C; step 2: $H^+$, $H_2O$, 100 °C; step 3: complex **1**, toluene, 60 °C, 100 mm Hg.[31]

molecular layer. The same authors have also reported a synthetic strategy to control the density of $Mn_{12}$ clusters anchored on Si(100) by using mixtures of the reactive methyl 10-undecylenoate precursor ligand (with a terminal carboxylate group) and 1-decene (without any terminal carboxylate group).[30b] XPS and ATR-FTIR spectroscopy showed that the surface density of the $Mn_{12}$ cluster is strictly proportional to the 10-undecylenoate : 1-decene ratio used in the experiment.

Simultaneously, Catala and co-workers also reported the large scale grafting of $Mn_{12}$ derivatives in the form of a homogeneous monolayer on silicon.[31] Although lacking lateral organization, their approach was highly successful to induce a preferred orientation of the $Mn_{12}$ molecules, mainly with their anisotropy axes parallel to the surface of the substrate. This was achieved thanks to the use of $Mn_{12}$ complexes bearing a mix of carboxylate ligands, dichloroacetate groups in the axial positions and *tert*-butyl acetate groups in the equatorial positions. Since the driving force of the substitution reaction is the formation of the weakest acid, *tert*-butyl acid will react first enabling such a preferential orientation.

Finally, Stoll *et al.* demonstrated that the $Mn_{12}$ can be attached not only to functionalized gold and silicon but to potentially any surface covered with carboxylate groups. For this, initially they formed a carboxylate-terminated SAM on a flat surface, and subsequently used adapted layer-by-layer assembly methods to form nanometer thick films of $Mn_{12}$ layers held together using poly(acrylic acid) (PAA).[32]

### II.c Simultaneous molecule- and surface-binding functionalization

This third approach was implemented by Coronado *et al.* and explores both the functionalization of the clusters and the surfaces.[33] Such an approach is based on the electrostatic interaction between a positively charged $Mn_{12}$ derivative and the surface of interest. A schematic representation of this approach is shown in Fig. 7. For this, the $Mn_{12}$ of choice has been the polycationic compound $[Mn_{12}O_{12}(bet)_{16}(EtOH)_4]^{14+}$ (**6**). This cluster comprises 16 quaternary ammonium carboxylates (bet stand for betaine = $^{+}N(CH_3)_3CH_2COO^{-}$) at the periphery, which are expected to favour the ionic immobilization.[34]

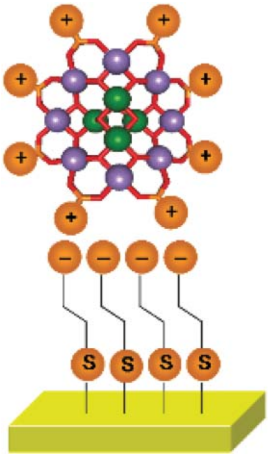


**Fig. 7** Representation of a polycationic $Mn_{12}$ SMM deposited onto a gold surface functionalized with an anionic self-assembled monolayer.

In a preliminary work, ionic immobilization was successfully achieved on a grafted monolayer of sodium mercaptoethanesulfonate ($HS(CH_2)_2SO_3Na$) on Au(111), bearing terminal free $-SO_3^{-}$ groups. After dipping the functionalized substrate into a solution of complex **6**, room-temperature STM images revealed that at short times of immersion a partial coverage of the gold surface is observed whereas longer immersion times induce the formation of 3D aggregates.[33a]

More recently, the same authors have reported an implementation for this technique. Such implementation is based on the deposition of the positively charged complex **6** on a silica templates obtained by local oxidation of a Si(100) surface, either in the form of dots or stripes.[33b] The selective deposition of the molecules on the silica nanopatterns has been explained by the authors as the combination of three factors: (i) the presence of attractive electrostatic interactions between complex **6** and the oxide patterns, (ii) the presence of repulsive interactions between complex **6** and the unpatterned regions, and (iii) the size of the nanopattern.

## III Physical methodologies: laser ablation and photolithography methods

In addition to self-assembly and lithographic techniques, other physical techniques for the deposition of the $Mn_{12}$ complexes have been used. One of these is laser ablation. Laser ablation is the process of removing material from a solid surface by irradiating it with a laser beam. The material is heated by the absorbed laser energy and evaporates or sublimes to be transferred under vacuum to the target substrate surface. Following this approach, Teizer and co-workers have used nitrogen laser ablation at low laser energies for the creation of thin films of complex **1** on glass, mica or $Si/SiO_2$ substrates.[35] XPS data indicates that, while some of the surrounding acetate ligands and water molecules are removed along the ablation process, the cores of the molecules remain intact. Magnetic measurements supported this conclusion. The same authors also obtained films of complex **1** using a variation of this technique—matrix assisted pulsed laser evaporation.[36] In addition to the formation of the molecular films, these experiments were very helpful to confirm the relevance of using low laser energies. Whereas an increase in laser energy and/or pulse frequency leads to fragmentation of complex **1**, the use of lower laser energies favour the deposition of the molecules while preserving their chemical and magnetic integrity.

Another interesting approach was that reported by Dunbar and co-workers, who demonstrated a straightforward route to obtain $Mn_{12}$-acetate thin film patterns on $Si/SiO_2$ surfaces by photolithography methods.[37] For this, a layer of a negative photoresist was spin-coated onto a clean $Si/SiO_2$ substrate and then dried in air. The photoresist layer was then exposed to uniform UV light through a photomask using a mask aligner. After development and rising of the photoresist, a solution of the $Mn_{12}$-acetate was added dropwise to the patterned surface. Finally, a lift-off of the resist material from the substrate resulted in the $Mn_{12}$-acetate film pattern. The resulting micropatterned surfaces were characterized by AFM, XPS and magnetization measurements, confirming the stability of the $Mn_{12}$ clusters along the deposition process.

## IV Nanocomposite thin films

Nanocomposite magnetic materials are interesting because they combine an easy processing and manipulation, low cost and specific mechanical properties. Moreover, the polymeric matrix substantially improves the thermal and chemical stability of the $Mn_{12}$ molecules within the films. For this reason, a substantial research interest was focussed on the development of a reliable and simple methodology to address individual $Mn_{12}$ complex molecules onto a film surface. Such a methodology was reported for the first time in 2003 and relies on a two-step process.[38] In the first step, a solution containing the polymer and the $Mn_{12}$ complex in different ratios is deposited by drop-casting onto a glass substrate, leading to the formation of a thin film containing the $Mn_{12}$ sample once the solvent is evaporated. Although for this different families of polymers can be used, the polymer of choice was poly(bisphenol-A-carbonate) that endows the material with flexibility, crisp-resistance and transparency.[39] In a second step, the resulting nanocomposite thin films are exposed to solvent vapours to induce a swelling of the polymer network,[40] favouring in this way the migration of a small fraction of $Mn_{12}$ molecules (<0.1%) to the film surface. Interestingly, the state of aggregation on the surface can be tailored depending on the nature of the solvent. For instance, whereas the use of a $CH_2Cl_2$–hexanes (1 : 1) mixture induces the formation of semi-globular islands comprising many molecules in each one of them, the use of $CH_2Cl_2$ vapour leads to the formation of small motifs comprising a few molecules, even isolated ones in some cases. It is also worth to mention the successful magnetic characterization of the film surface by MFM. MFM images clearly indicated a magnetic gradient response exactly corresponding to the molecular position found by topographic imaging. This fact has been attributed to the magnetic contrast between the molecules magnetically polarized by the tip and the diamagnetic polymeric substrate.

In addition to the solvent influence, a study of the time exposition on the molecular aggregation at the surface of the polymer has also been reported.[41] Such studies evidenced that in the case of longer exposition times, the molecular islands increase up to a critical diameter above which they transform into circular rings. Afterwards, the rings coalesce with each other, forming larger rings with irregular shape due to a demixing process. It is remarkable that by interrupting the exposure to the solvent the transformation is stopped and the morphology remains frozen in a metastable state.

Although successful in spatial correlation, the previous approaches lack concomitant control over size and distance of the molecular motifs on the thin film surface. With this aim, a modification of the methodology where the films are prepared on a prepatterned master was used (see Fig. 8).[42]

In the first step, a solution containing the polymer and the $Mn_{12}$ complex in different ratios is deposited by drop-casting onto a DVD that acts as a structured master for the formation of the film. Once the solvent is evaporated, the replica is removed from the master. The side of the polymeric film that was in contact with the DVD (blank or recorded) replicates its topographic pattern: a sequence of grooves (blank DVD) or a structured sequence of protrusions (recorded DVD). In a second step, the film is exposed to a saturated atmosphere of solvent vapour that swells the film, leading to the smoothing of the topographic reliefs. Interestingly, during the smoothing process the $Mn_{12}$ clusters concentrate preferentially in the regions where the protrusions were originally formed. Thus, although topographical artefacts were minimized (rms roughness <1 nm) the magnetic response revealed spatially resolved magnetic patterns that faithfully reproduce the domain topography. These results confirmed the validity of this approach to fabricate permanent information storage molecular devices not only with magnetic readout but with potential in optical and electronic responses as well.

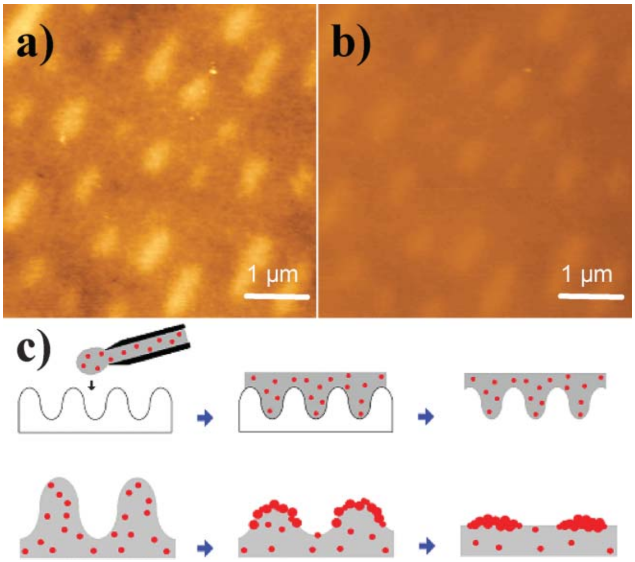


**Fig. 8** $Mn_{12}$ patterns of **4** with size, distance and positional control on the surface of nanocomposite thin films: topography (a) and phase-contrast image (b). Schematic representation (c). A polymer-$Mn_{12}$ solution is cast onto a structured master (*e.g.* DVD). Smoothing and $Mn_{12}$ aggregation processes occur during exposure to $CH_2Cl_2$ vapour.

## V Future trends

In addition to the continuation of the successful achievements previously described, there are two clear prospective areas where future work is expected to evolve, which are: (a) exploration of new SMMs different from the $Mn_{12}$ family and (b) development of new integrated devices to address and study individual SMMs.

### V.a Exploration of new SMMs

As far as the exploration of new SMMs is concerned, one of the candidates is the family derived from the $[(Pc')_2Tb^{III}]^0$ (Pc′ = octa(buthoxy)-substituted phthalocyaninato ligand) (**7**). The advantages of complex **7** over the $Mn_{12}$ family are twofold. First, the flat character together with the presence of long-chain substituted phthalocyanines is expected to favour its self-organization into two-dimensional assemblies.[43] Second, the blocking temperature ($T_B$) of complex **7** has been

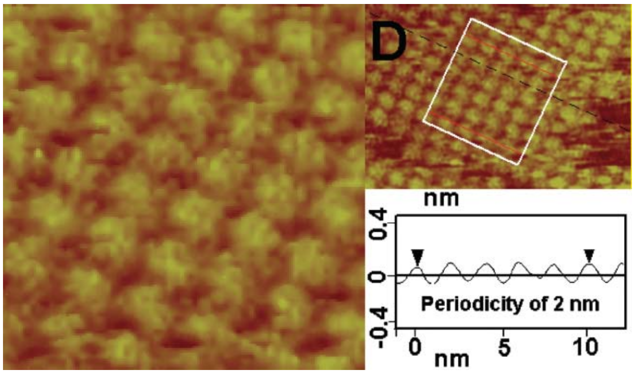


**Fig. 9** (Left) High-resolution STM image of 8 × 8 nm scan area, where the phthalocyanine molecules can be clearly differentiated as bright spots. (Right) Average section of the molecular layer. Obtained from ref. 45.

rated to be one of the highest $T_B$ so far reported for a SMM (36–50 K).[44] Keeping these advantages in mind, very recently the 2-D self-assembly of complex **7** on HOPG directly from a toluene solution was reported.[45] High-resolution STM images of the resulting nanostructured surfaces are shown in Fig. 9.

From these images, three points deserve to be outlined. First, the presence of alkoxyl chains favours the 2-D self-assembly of complex **7** on the surface without the need of supplementary lithographic techniques, as was also demonstrated by DeFeyter and co-workers with non-magnetically active double-decker complexes similar to **7**.[46] Second, clear observation of individual molecules is achieved, a fact that may facilitate their manipulation or analysis. Finally, the adsorption of the double-decker phthalocyaninato molecules with their molecular plane parallel to the graphite surface enables us to control and/or predict the orientation of the preferential magnetization axis on the surface. This fact, together with its relatively larger blocking temperature, is a crucial step on the way for the possible development of SMM-based molecular devices.

### V.b Development of new integrated devices to address and study individual SMMs

The second experimental approach that is going to attract much interest in the following years is the magnetic characterization of individual molecules. The goal is twofold. First, from a scientific point of view the objective is to study and understand the magnetization relaxation at the individual molecular level, and to see how these properties are affected on translation from the macroscopic (crystals or powder) to the nanoscopic (surfaces) world. It is clear that surface deposition will affect such properties. For instance, simply the strong interaction of the molecule with the substrate can modify the molecular geometry, and hence alter the easy magnetization axis of the molecule by comparison with that observed in a macroscopic crystalline environment. The second objective is to convert nowadays prospective ideas into future real market devices.

On the basis of this incipient research line, first electron-transport measurements of individual $Mn_{12}$ molecules attached to metallic contacts have already been obtained. An schematic representation of a $Mn_{12}$ molecule trapped between electrodes is shown in Fig. 10. Heersche *et al.* recently reported $Mn_{12}$ molecules weakly coupled to gold electrodes through thiol groups.[47] Besides ensuring robust tethering of the clusters, the ligands are also believed to serve as tunnel barriers so that the molecule is only weakly coupled electronically to the gold. Experimentally, molecules were deposited on gold wires by a simple soaking process and subsequent electromigration process produced the nanometer-scale gaps in which the molecules were trapped. Afterwards, the samples were cooled down to 4 K, and the junction conductance measured as a function of gate voltage. Interestingly, these studies confirmed the effect of their high-spin ground state on the resulting electron transport.

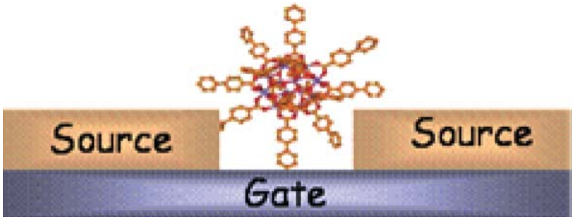


**Fig. 10** Schematic drawing of a $Mn_{12}$ molecule trapped between electrodes.

A related work, giving more emphasis to the magnetic-field dependence of the spectra, has also been reported by Park and co-workers.[48] In such work, the authors were able to distinguish tunneling *via* magnetic molecules from non-magnetic tunneling. However no evidence of magnetic hysteresis was detected. It is important to mention are also the significant variations between devices found by the authors, indicating that the sample fabrication process and the device environment may affect the molecules. Therefore, the developments of more reliable methodologies that allow the reproducibility of the results are prompted to be developed in the near future.

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