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Organizing and Addressing Magnetic Molecules

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Magnetic molecules ranging from simple organic radicals to single-molecule magnets (SMMs) are intensively investigated for their potential applications in molecule-based information storage and processing. The goal of this Article is to review recent achievements in the organization of magnetic molecules on surfaces and in their individual probing and manipulation. We stress that the inherent fragility and redox sensitivity of most SMM complexes, combined with the noninnocent role played by the substrate, ask for a careful evaluation of the structural and electronic properties of deposited molecules going beyond routine methods for surface analysis. Detailed magnetic information can be directly obtained using X-ray magnetic circular dichroism or newly emerging scanning probe techniques with magnetic detection capabilities.

1. Introduction

The history of molecular magnetism has developed in a circular pathway. At the beginning, attention concentrated mainly on the properties of individual paramagnetic molecules, like simple metal complexes, as a source of structural information.[1] Of course, the investigation was not carried out on individual molecules but rather on large molecular assemblies such as polycrystalline powders or single crystals. Intermolecular interactions were nuisances to be avoided. In a second step attempts were made to use molecular building blocks to design and synthesize bulk magnets.[2,3] In this case, the focus was on promoting a ferro- or ferrimagnetic alignment of the magnetic moments. This required their organization into infinite three-dimensional lattices, but, in fact, there was no direct control over crystal forces that are responsible for the adopted lattice structure. Nevertheless, the arrangement of molecules could be predicted to some extent, and high-T_c molecular magnets were reported.[4−6]

The third step is now leading back to individual molecules hosting a number of magnetic centers.[7,8] The most important results in this area have been obtained working on single-molecule magnets (SMMs), which led to the observation of new physical phenomena at the mesoscopic scale,[9−13]

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thereby setting a milestone in the physics of spin.[14] Because a unique feature of SMMs is the occurrence of molecular magnetic hysteresis, many attempts have been made to organize SMMs into addressable arrays,[15−19] with the final goal of writing and reading information in one molecule. Although SMMs are still far from practical applications, because of the prohibitive temperatures at which the magnetic memory effect is observable, their study is now triggering a new frontier research field.

At the present stage of its pathway, molecular magnetism features, in fact, extensive overlap with the field of spin electronics (or spintronics), which targets information storage and processing by using not only the charge of the electron but also its spin magnetic moment.[20−22] *Spintronics* was born in 1988, with the discovery of giant magnetoresistance, by Peter Grünberg and Albert Fert in metal multilayers.[23,24] This discovery raised tremendous scientific interest and, starting from the 1990s, paved the way to a completely new technology for the realization of reading heads in hard disk drives. It had such a large scientific and technological impact that Fert and Grünberg were awarded the Noble prize in Physics in 2007.

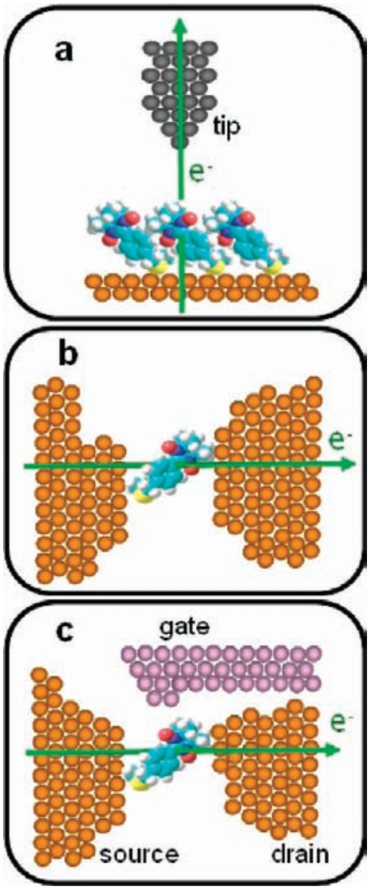

Figure 1. Single-molecule junction architectures: (a) tip−molecule−surface architecture in a scanning tunneling microscopy junction; (b) electrode−molecule−electrode architecture in a break-junction setup; (c) complete single-molecule transistor architecture in a break-junction setup with an additional "gate" electrode.

One of the trends taken by spintronics envisages molecules as possible end points in the race toward miniaturization.[25−29] The newly born area of *molecular spintronics* (MS) now focuses on the reading and manipulation of molecular spin states by electrical currents in miniaturized devices made of one or few molecules.[30] The architecture of the device and the specific molecule to be incorporated are dictated by the required functionality. Arrays of SMMs at surfaces have been suggested as molecule-based memory banks to be electrically and/or magnetically addressed one element at a time using scanning probe microscopy (SPM) techniques[31] (Figure 1a). Devices acting as molecular diodes are best constructed by wiring individual molecules to mechanically controllable break junctions or nanogaps (Figure 1b). The addition of a third electrode (*gate*) allows the external modulation of electron flow, leading to *transistor*-like devices (Figure 1c).[32−34] Even in this simple case, the behavior can be drastically different depending on the electronic coupling between the molecule and the electrodes, which can be tuned by selecting appropriate chemical functional groups.

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MS is certainly an emerging field full of fascinating challenges for experimentalists and theoreticians, chemists and physicists alike. Several features must be improved for applications, like the operating temperature, but the field is extremely rich for basic science. Research activity spans, in fact, from the synthesis of suitable molecules to the construction of devices, from the assessment of a single-molecule response to the development of theoretical models describing the interplay between electrical charge and spin degrees of freedom.[35,36] Major chemical issues remain to be fully addressed: above all, the long-term chemical stability of the molecular units but merely also the chemical stability of molecules during device construction. Polynuclear complexes behaving as SMMs, for instance, are intrinsically very fragile and redox-sensitive and even very small changes in the chemical environment may cause their partial or complete disruption. For this reason, it is essential that the incorporation of SMMs into devices be accompanied by detailed investigations on their stability in environments other than bulk crystals (e.g., metal surfaces). Recent excellent review articles are available that deal with various aspects of the organization of SMMs on surfaces.[37−40] We will herein adopt a slightly different approach, trying to review the most recent literature on magnetic molecules for spintronics rather than focusing on the specific subject of SMMs. We will stress also the many difficulties, which have not yet been definitively overcome, concerning chemical stability and structural intactness during deposition and device fabrication. We will highlight the state-of-the-art for the measurement of the magnetic properties of monolayers of organized molecules and the perspectives for single molecule investigations.

The coverage will not be systematic, but rather we will work out a few examples, taken from our own and other groups' production, in order to show how complex phenomena can now be tackled with success if all the possible precautions are taken.

The organization of the paper is as follows. First, we describe the most common assembly techniques (section 2): examples are taken from recent work on Mn_{12} SMMs but also on organic radicals, magnetic grids, and antiferromagnetic rings. Patterning techniques are also presented, in which magnetic molecules are assembled by taking advantage of lithographic methods. The subsequent section 3 addresses the evolution of strategies to investigate magnetic molecules at surfaces, highlighting the limitations of routine surface analysis by scanning tunneling microscopy (STM), atomic force microscopy (AFM), or X-ray photoelectron spectroscopy (XPS) when applied to complex materials. The ambiguities inherent in using the above techniques can be resolved only by magnetic measurements on monolayers (or submonolayers, i.e., incompletely covered layers), which can be accomplished using a few local-probe techniques like NMR of implanted probes, magnetic circular dichroism (MCD), and its X-ray analogue (XMCD). Examples of the successful magnetic investigation of (sub)monolayers with the above-mentioned techniques are given in section 4. Electrical and magnetic studies on individual molecules are presented in section 5 as a major achievement, before conclusions are drawn and perspectives are suggested.

2. Assembling Magnetic Molecules on Surfaces

Assembling magnetic molecules on surfaces is currently sought as a means for addressing (i.e., probing and manipulating) them as nanoscale magnetic units using SPM techniques. To this aim, the successful deposition of intact molecules into single layers is mandatory, although other important requisites must be fulfilled. In order to fully exploit the storage capability of SMMs, for instance, the periodic structure of the layer and, more importantly, the molecular orientation at the surface must be controlled. In fact, one of the key properties of SMMs is their magnetic anisotropy, which yields greatly different magnetization and coercive fields when the molecule is probed along different axes.

Rather unsurprisingly, many studies have been devoted to the Mn_{12} family of SMMs, $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$.[41,42] The clusters comprise eight Mn^{III} ions with $S = 2$, and four Mn^{IV} ions with $S = {}^3/_2$. The spins of ions with different charges are antiferromagnetically coupled to yield a ground $S = 10$ state, which is subject to a large easy-axis-type magnetic anisotropy.[9] The anisotropy barrier for magnetic moment reversal amounts to ca. 70 K, and at low temperature, the relaxation time becomes on the order of months. Individual Mn_{12} molecules then behave as tiny magnets, displaying a magnetic hysteresis and quantum tunneling effects.[10,11] The acetate ligands in the archetypal Mn_{12} complex (Mn_{12}-acetate, $R = CH_3$) can be easily replaced with a large variety of other carboxylate or noncarboxylate ligands that may convey additional useful properties to the cluster (enhanced solubility, affinity for metal surfaces, etc.) with almost complete retention of magnetic properties.

The first attempts to organize Mn_{12} molecules into low-dimensional arrays were based on the Langmuir−Blodgett (LB) technique.[43] Mn_{12} molecules were embedded within two layers of behenic acid (BA), the lipid that produces the hydrophobic environment required to assemble LB films at the water−air interface. Layers prepared using different ratios BA/Mn_{12} were characterized by IR, X-ray diffraction, and magnetic measurement, which showed that isolated mol-

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ecules are present for BA/Mn_{12} > 10, whereas for lower ratios, the Mn_{12} molecules form a close-packed array. The samples displayed magnetic hysteresis, although with a much smaller coercive field as compared with bulk samples. Attempts to orient the molecules with an external field were unsuccessful. Similar results were also obtained by employing nitronyl nitroxides (NITRs), organic radicals widely used in molecular magnetism,[44,45] and Prussian-blue derivatives.[46] It must, however, be stressed that LB films do not allow a direct approach to individual molecules, nor do they easily permit a stable grafting to surfaces, as required for real devices.

Turning now to the deposition of (sub)monolayers on surfaces, the selection of the substrate to be used for the deposition is not trivial. Conducting supports offer the possibility of carrying out molecular addressing by STM or related techniques. However, many other surface parameters, like roughness, orientation, reactivity, hydrophobicity grade, impurity level, and ease of cleaning, need to be carefully evaluated. Gold(111), silicon (possibly hydrogen-terminated), silicon oxide, and highly oriented pyrolitic graphite (HOPG) are excellent choices because they provide atomically flat surfaces either by fresh cleavage or by following well-established protocols for surface reconstruction and cleaning.

Techniques for assembling monolayers on surfaces are often classified as being based on *physical* methods like evaporation,[47,48] classical lithography,[49] and the LB method[50] or on *chemical* strategies like layer-by-layer deposition,[51] self-assembly,[52] soft lithography,[53] etc.

The key factors that rule deposition are (a) intramolecular interactions, (b) molecule−surface interactions, (c) lateral intermolecular interactions, and (d) external parameters (temperature, pressure, etc.). Factors a−c are strongly (or exclusively) dependent on the molecular structure (shape, conformational flexibility, the presence of specific surface-binding groups or of hydrogen donor/acceptor sites, etc.), which can be largely tailored at the synthetic level. The characteristics of the selected surface (either native or prefunctionalized) influence deposition through factor b. The temperature is often critical for optimal monolayer formation, which is usually achieved when the appropriate interactions between single components are comparable with the thermal energy. In fact, thermal agitation must ensure reversibility of molecule−molecule and surface−molecule interactions, thus providing a mechanism for self-repairing and error correction, two well-known concepts in supramolecular chemistry.[54−56]

The deposition of monolayers of magnetic molecules has been performed following several different approaches: (i) direct deposition of pristine molecules on native surfaces, taking advantage of unspecific molecule−surface interactions; (ii) direct deposition of derivatized molecules on native surfaces through specific molecule−surface interactions; (iii) surface prefunctionalization with chemical groups that provide specific docking sites for pristine molecules; (iv) derivatization of both molecules and surfaces with complementary groups, ensuring an efficient grafting via either covalent or noncovalent interactions. Schemes for approaches (i−iv) are shown in Figure 2.

The easiest way to assemble molecules on a surface is through method (i), whereupon unmodified molecules are physisorbed on a native substrate via nonspecific interactions (e.g., van der Waals forces), as sketched in Figure 2a. This method has been widely employed for structurally simple molecules such as monometallic systems including porphyrins[57] and phthalocyanines.[58] Deposition is carried out either by simply drop casting a very dilute solution on the substrate (followed by solvent evaporation) or by dipping the substrate in a dilute solution (followed by careful cleaning with a fresh solvent and drying). Slight alterations of molecular structure may allow a better assembling on the surface, like in the case of copper(II) phthalocyanines[59] and double-decker [terbium bis(phthalcyaninato)] complexes substituted with alkyl chains that promote a bidimensional ordering.[58]

The same approach has been recently applied to the deposition of more complex multicenter systems such as $[Co_4L_4](BF_4)_8$ (Co_4) where L = 4,6-bis(2′,2″-bipyrid-6′-yl)-2-phenylpyrimidine.[60] The Co_4 compound is a member of the family of gridlike [$n \times n$] polynuclear complexes ($n \leq 4$) assembled through polypyridine-based ligands, which display interesting redox, magnetic, and spectroscopic properties.[61,62] The deposition of these molecules on HOPG is particularly simple: a 10^{-9} M solution of Co_4 in acetonitrile is dropped on HOPG, and the molecules spontaneously assemble on the surface, forming a "grid of grids", as shown by room-temperature STM imaging (Figure 3). By playing with graphite step edges, the authors suggest that it is possible to produce isolated or one-dimensional arrays of Co_4

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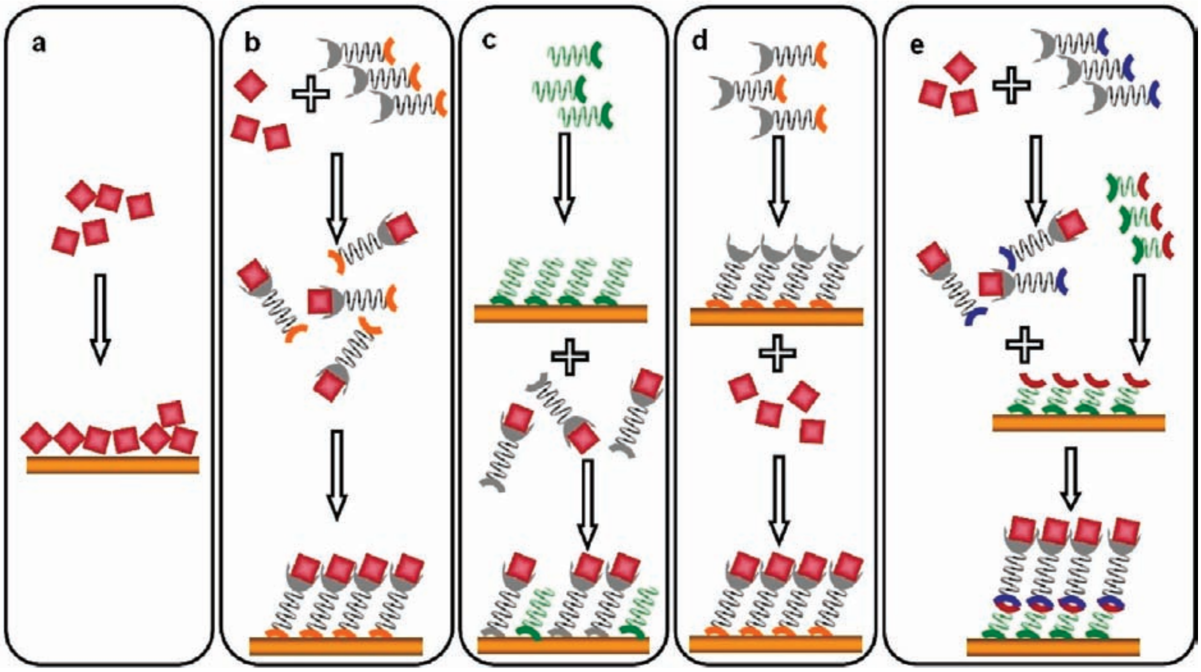

Figure 2. Approaches for deposition of magnetic molecules by (a) drop casting of nonfunctionalized molecules from diluted solutions, (b) self-assembling of prefunctionalized molecules with suitable anchoring groups, (c) insertion of functionalized molecules into a preformed monolayer, (d) functionalization of surfaces with docking groups suitable as molecular receptors, and (e) functionalization of surfaces and molecules with complementary groups.

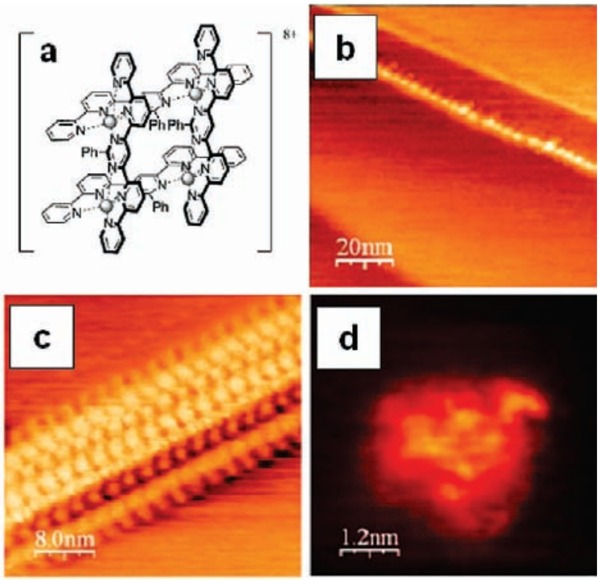

Figure 3. (a) Representation of the $[Co^{II}_4L_4]^{8+}$ complex (L = 4,6-bis(2′,2″-bipyrid-6′-yl)-2-phenylpyrimidine). (b−d) STM images of Co_4 grid complexes deposited onto a HOPG surface at increasing concentrations (b−c) and of an isolated molecule (d). These figures have been adapted from ref 60.

molecules. While this method gives rise to well-ordered areas on the surface, the reproducibility and homogeneity of the deposit are hardly guaranteed by following this strategy.

Method (ii) targets the preparation of chemically stable (sub)monolayers by exploiting specific (covalent or noncovalent) interactions with the surface (Figure 2b). These interactions, in principle, should guarantee a good-quality deposit. Because of the extensive knowledge available on the adsorption of organic thiols and sulfides on gold, S-functionalized magnetic molecules have been designed and employed to be grafted on Au(111) surfaces. For instance, simple organic radicals of the NITR family, functionalized with thiomethyl groups, self-organize on gold surfaces, as indicated by topographic (STM), chemical (time-of-flight secondary ion mass spectrometry, ToF-SIMS; see later), and magnetic (electron paramagnetic resonance, EPR) characterization.[63]

The same approach has been adopted with SMMs of the Mn_{12} family. A derivative containing 16 ligands with R = $AcS(CH_2)_{15}$ (Mn_{12}−C15SAc) was first prepared and deposited on Au(111) as a homogeneous but disordered layer, which showed the chemical composition expected for intact clusters (Figure 4).[15a]

After this pioneering work, other attempts of organizing Mn_{12} clusters have been reported, varying the parameters involved in the deposition.[15c,d,19] For instance, through changes in the nature of the carboxylate to 4-(methylthio)benzoate (R = 4-$MeSC_6H_4$), it was possible to reduce the interaction with the surface and to arrange Mn_{12}−C_6H_4SMe clusters into submonolayers comprising well-separated molecules.[15c] The influence of several experimental parameters (solvent, incubation time, etc.) on the nature of the adsorbate was carefully studied on this particular derivative.[15d] A variant of method (ii) involves the insertion of derivatized molecules into preformed self-assembled monolayers (SAMs) at surfaces (Figure 2c).[15e]

Similar approaches were used to obtain submonolayers of antiferromagnetic $[Cr_7NiF_8(RCO_2)_{16}]^-$ rings on gold surfaces, either using RCO_2^- = 3-thiophenecarboxylate ligands or exploiting host−guest interactions with a thiol-functionalized secondary amine.[64]

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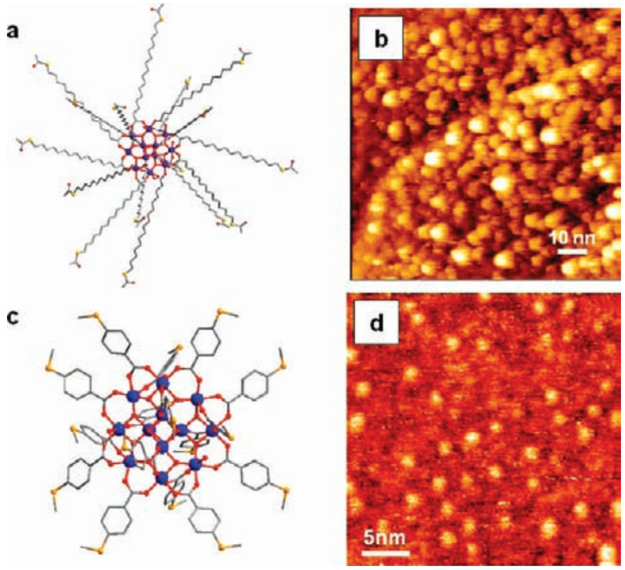

Figure 4. Structure representation of two Mn_{12} derivatives suitable for deposition on a gold surface: Mn_{12}−C15SAc (a) and Mn_{12}−PhSMe (c) and their respective constant-current STM characterization (b and d) (adapted from refs 15a and 15c).

Method (iii) has been used to covalently graft Mn_{12} derivatives on silicon surfaces prefunctionalized with carboxylate groups (Figure 2d). Prefunctionalization was accomplished via a thermal hydrosilylation reaction between H-terminated Si(100) and methyl 10-undecenoate.[16] The methyl-protected ligand was either used in pure form or mixed with 1-decene, thus affording mixed layers with a controllable density of carboxylate receptors. After removal of the protecting groups, the surface was treated with a solution of Mn_{12}-acetate in toluene to accomplish grafting by ligand exchange. In the course of related studies, a Mn_{12} derivative featuring chlorine-marked carboxylate ligands in axial positions was shown to undergo surface binding through equatorial coordination sites,[65] suggesting a preferred orientation of the Mn_{12} molecules with their anisotropy axes parallel to the surface. The same strategy has been very recently used to link SMMs of the Fe_4 family to Si(100) surfaces decorated with trimethylol receptors, which are known to interact site specifically with the propeller-like tetrairon(III) core.[66] The use of a chlorine-marked complex combined with angle-resolved XPS measurements gave clear evidence of a successful oriented grafting of the magnetic complexes with their molecular axes perpendicular to the substrate.

Attempts to use the same strategy to bind Mn_{12} complexes to gold surfaces prefunctionalized with carboxylic groups, featuring both flexible and rigid conjugated spacers, have also been reported.[17,67−71] These monolayers are invariably disordered. The partially ordered layer described in one of the earliest reports[17,67] has been severely criticized and shown to be a likely result of multiple tip artifacts.[69]

Method (iv) entails prefunctionalization of both molecules and surfaces with complementary groups (Figure 2e). It has been applied to accomplish the electrostatic grafting of polycationic Mn_{12} complexes (featuring 16 quaternary ammonium groups) on a Au(111) surface covered by a sodium mercaptoethanesulfonate SAM.[72]

In addition to methods (i−iv), more complex approaches can be envisaged. For instance, sequential reactions provide a convenient route to the functionalization of surfaces with complex molecular architectures[73] and hold great promises for the controlled organization of magnetic molecules.

All of the above-described strategies are based on a “wet approach”, whereupon molecules are transferred to the surface from a liquid phase. Widely used to deposit organic molecules or simple metal−organic complexes on surfaces are thermal evaporation techniques. In this case, a solid sample is heated in high vacuum and transferred to the cold target substrate via the vapor phase. As a major advantage, the preparation chamber can be directly connected to the high-vacuum environment of an XPS spectrometer or of a scanning probe microscope, ensuring the utmost sample cleanliness. Adsorbates of metalloporphyrins and metallophthalocyanines obtained by thermal evaporation were among the first samples investigated by STM techniques[74] and have recently attracted renewed interest in molecular magnetism.[75,76]

So far, the application of thermal evaporation methods to molecular magnetic materials has been severely hampered by the limited thermal stability of most samples, Mn_{12} clusters above all. For this reason, softer variants of the traditional evaporation technique have been proposed, like pulsed-laser deposition,[77] matrix-assisted pulsed-laser evaporation (MAPLE),[49] and vacuum spraying.[78] In the latter approach, used by Moroni et al. to deposit films of Mn_{12}-

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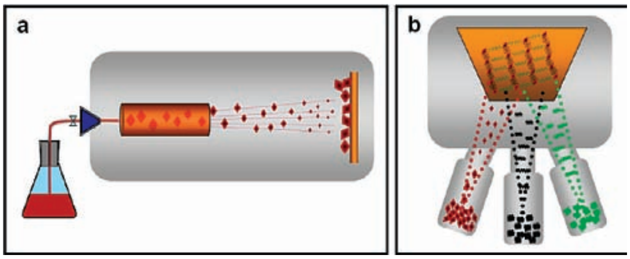

Figure 5. Preparation of molecular adsorbates at surfaces in a vacuum environment using vacuum spraying (a) and surface-assisted coordination chemistry (b).

acetate, a solution of the complex is injected into a high-vacuum chamber through a fast-acting pulsed valve (Figure 5a). Rapid evaporation of the solvents brings clusters to the vapor phase under very mild conditions. Another variant of the evaporation technique is *in situ* "surface-assisted coordination chemistry",[47] which consists of assembling complex molecular structures by starting from the evaporation of their components and playing with the relative concentration as well as with external parameters (Figure 5b). This revolutionary strategy may open new exciting perspectives in surface science.

In addition to the assembly of monolayers or submonolayers, the arrangement of SMMs into stripes or other regular patterns has been realized by exploiting lithographic methods. Thick deposits of SMMs can be obtained by the standard photolithographic approach based on shadow mask evaporation.[77b] On the other hand, less usual approaches have been developed. Cavallini et al. used an approach called lithographically controlled wetting (LCW) to prepare ordered patterns of Mn_{12}-type clusters with sizes and distances controlled at multiple length scales over macroscopic areas.[18] The related technique of microcontact printing (μCP) permitted the deposition of functionalized Mn_{12} clusters as microscale stripes on gold, thus joining together the concepts of monolayer deposition and lithographic patterning.[15b] These SMM stripes or patterns allow a very reliable measurement of the layer thickness by AFM and, as compared with full monolayers, are expected to facilitate the differential reading of magnetic properties by scanning probe techniques like magnetic force microscopy.[79] The confinement of SMMs to specific submicrometric regions of the substrate to afford arrays of molecule-based magnetic dots has also been accomplished using focused ion beam (FIB)[80] lithography or local oxidation nanolithography (LON).[81] These patterning methods are summarized in Figure 6.

3. Not Just Topography

In most examples discussed up to now, the characterization of the layers has relied mainly on the topographical insight provided by SPM techniques. However, surfaces are reactive species, and their chemical interaction with deposited molecules must be anticipated.

Another possible origin of perturbation is represented by the anchoring ligands, when they contain reactive moieties in addition to coordinating groups. As a result, a crucial point is to demonstrate that magnetic molecules remain intact on the surface. This is of paramount importance for SMMs, which are complex, often fragile structures. Indeed, the key message of this Article is the need of sophisticated tools to verify the intactness of molecules in environments other than bulk crystals. Some of these tools, particularly well suited for magnetic molecules, are reviewed below.

The chemical composition of the adsorbates is generally checked by XPS.[15a,c,d] In the case of Mn_{12} clusters, however, an unambiguous determination of manganese oxidation states is difficult using this technique alone, particularly in the case of monolayer deposits on gold.[82]

In a few cases, ToF-SIMS has been usefully employed.[15b] ToF-SIMS is a mass spectrometry technique that can be used to probe surfaces with a penetration depth of about 1 nm. As anticipated earlier, ToF-SIMS was successfully used in the characterization of SAMs of NITR radicals bearing −SMe groups.[63] Besides the two-dimensional order evidenced by STM analysis, the observation of a molecular ion peak in the mass spectra confirmed the chemical integrity of the adsorbed species. Application of the same technique to more complex systems, like the Mn_{12} cluster, has provided less direct but useful information because detection is necessarily limited to low-molecular-weight fragments.[15b]

X-ray absorption spectroscopy (XAS) has only recently been applied to the characterization of SMM monolayers.[82,83] This technique uses synchrotron light to measure the absorption of X-rays at various edges. The advantage of XAS as compared, for instance, to XPS is that it provides direct information on the oxidation state of the transition-metal ion, a crucial issue for SMMs comprising redox-active ions, like in Mn_{12} clusters.

In early XAS investigations performed on bulk Mn_{12}-acetate, the observed absorptions at the Mn $L_{2,3}$ edge ($2p \rightarrow 3d$ transitions) were shown to be consistent with the expected proportions of Mn^{III} and Mn^{IV} ions.[84,85] Similar experiments performed on bulk samples of Mn_{12}−C15SAc and Mn_{12}−PhSMe yielded essentially the same results, indicating that thioacetyl and thioether groups are compatible with the high oxidation state of manganese ions in Mn_{12} clusters.[83] However, when monolayers of Mn_{12}−C15SAc and Mn_{12}−PhSMe were investigated, XAS spectra clearly indicated the presence of Mn^{II} beyond the expected Mn^{III} and Mn^{IV} components (Figure 7). Several attempts were made to obtain intact Mn_{12} clusters by varying the ligand shell

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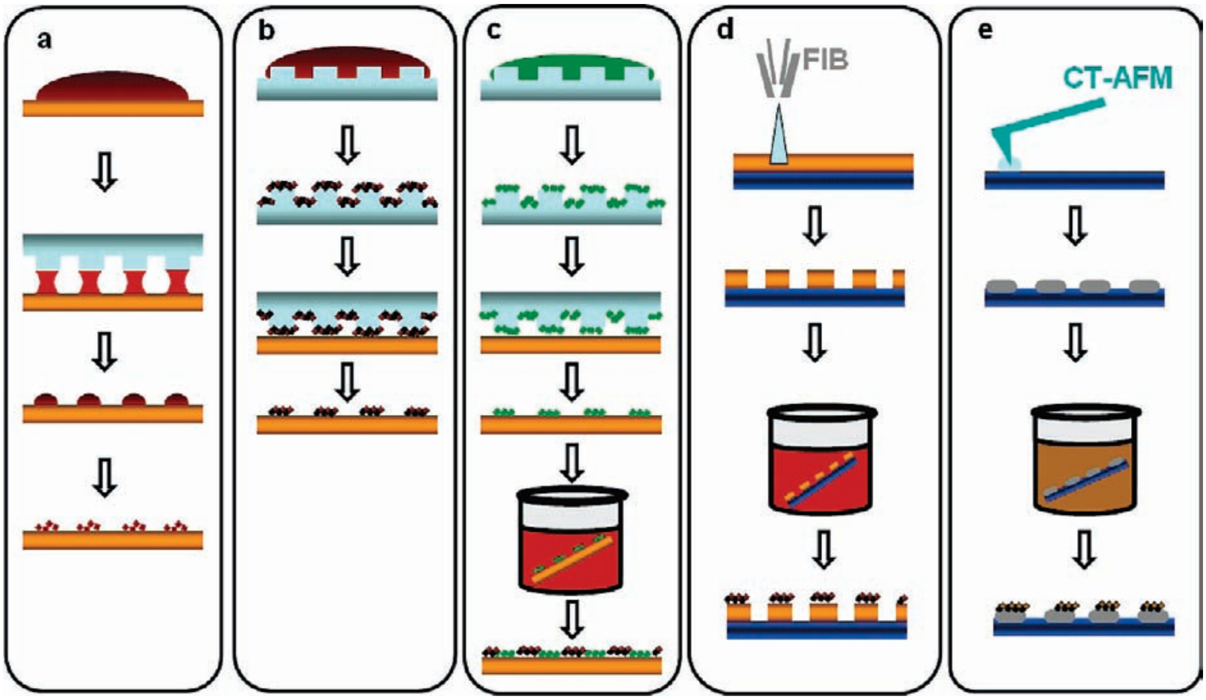

Figure 6. Patterning methods for magnetic molecules by (a) LCW, (b) direct μCP, (c) indirect (back-filling) μCP, (d) FIB lithography, and (e) LON using a conductive-tip AFM (CT-AFM).

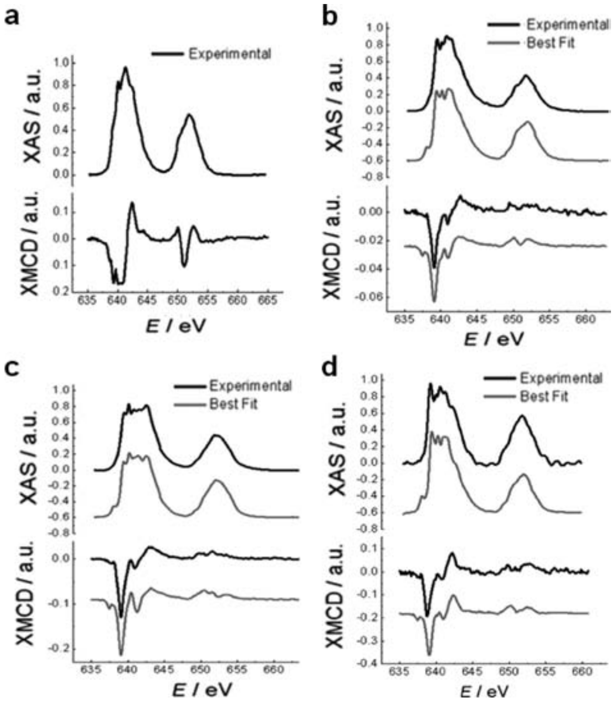

Figure 7. XAS and XMCD characterization of Mn_{12} derivatives: (a) thick film of Mn_{12}−PhSMe; (b) monolayer deposit of Mn_{12}−C15SAc prepared from tetrahydrofuran (THF); (c) monolayer deposit of Mn_{12}−PhSMe prepared from THF; (d) monolayer deposit of Mn_{12}−PhSMe prepared from CH_2Cl_2.

and/or the deposition procedure (e.g., method (iii) instead of method (ii)). Partial reduction to Mn^{II} was invariably observed, and it was impossible to obtain systems containing only Mn^{III} and Mn^{IV}. To get more quantitative information, the experimental XAS spectra $I(E)$ were reproduced through a linear combination of model spectra $I^{\alpha}(E)$, measured on suitable reference compounds containing the Mn ion in the three oxidation states (α = II, III, IV) and in similar chemical environments. The reliability of the method was checked by measuring XAS spectra of a one-electron-reduced Mn_{12} complex (bulk sample), formulated as $Mn^{II}{}_1Mn^{III}{}_7Mn^{IV}{}_4$. In fact, the ratio Mn^{II}:Mn^{III}:Mn^{IV} (5:60:35) obtained by deconvolution of the spectra compared quite well with the expectation (8:58:33). This semiquantitative analysis, when applied to XAS data recorded on (sub)monolayers, always provided a large percentage of Mn^{II} ions (20−30%), showing that the surface itself or the grafting processes have a significant impact on the oxidation states of the metal ions. Moreover, the Mn^{II}:Mn^{III}:Mn^{IV} ratio was found to vary significantly with the adopted deposition procedure.[83]

Several attempts have been made to investigate with density functional theory techniques the stability of SMM species assembled on conducting surfaces. In particular, Barraza-Lopez et al.[36] focused on the interaction of thiol-substituted Mn_{12} complexes with gold surfaces. The calculations evidenced large electronic differences between free and surface-bound Mn_{12} clusters. Assuming an inert surface is therefore not correct, and efforts must be devoted to characterize the chemical and electronic structures of deposited molecules.

4. Addressing Magnetic Properties

The most straightforward way of investigating the magnetic properties of molecular monolayers would consist of measuring their magnetization by SQUID magnetometry or of recording their EPR spectra directly. However, the use of these traditional techniques is seldom viable because of the exceedingly small amount of material that is probed. In the case of NITR radicals, a magnetic investigation through EPR was successful because organic radicals exhibit extremely narrow EPR lines. In fact, the sensitivity of an EPR experiment depends on the inverse square of the line width, which for NITR radicals amounts to only a few gauss. The study revealed the characteristic five-line hyperfine pattern observed for NITR species in solution,[63] though with considerable distortion attributed to anisotropic slow-motion effects. These features can provide a deep insight into the dynamics of magnetic molecules on surfaces and thus deserve further investigation. By contrast, the EPR line width for metal-ion-based complexes like SMMs is about 1000 G, hence 1000 times larger. Furthermore, the large zero-field splitting of the ground state requires the use of high-frequency spectrometers, which often do not possess a resonant cavity and are therefore orders of magnitude less sensitive than traditional X- or Q-band spectrometers. For these reasons, EPR investigations on monolayers of SMMs are totally impracticable.

Several alternative techniques provide the sensitivity required to probe monolayers of magnetic molecules at surfaces and are becoming of increasing importance in this branch of molecular magnetism.

Among magneto-optic techniques, a widely used tool in nanoscale magnetism,[86] the most common is MCD, which measures the difference in absorption of right and left circularly polarized light in the presence of an applied magnetic field. Early MCD measurements on frozen solutions of Mn_{12} were of paramount importance because they provided the first clear evidence that SMM behavior has a molecular origin and does not arise from cooperative phenomena.[87−89]

Systematic use of MCD experiments has recently been made to probe the behavior of Mn_{12} complexes in environments other than bulk crystals, like LB films, dispersions in diamagnetic amorphous matrices, and monolayers on gold.[90] The MCD spectra of LB films and polymer dispersions provided hysteresis curves comparable to those of polycrystalline samples of the same materials, although with a smaller coercive field. Dynamic measurements were also performed that yielded relaxation times orders of magnitude faster as compared with polycrystalline samples. Reference samples suitable for characterization both by traditional magnetometry and by MCD were then used to evaluate the sensitivity of MCD measurements (ca. 3×10^{-11} mol/cm^2), which turned out to be adequate for the detection of a few monolayers. The magnetic signal arising from five superimposed monolayer samples of Mn_{12}−PhSMe was indeed clearly detected. However, simple paramagnetic behavior was observed down to the lowest temperature reached (1.5 K). Such a disappointing result was later confirmed by XMCD. Using X-rays, the sensitivity increases and allows to detect single layers, as we show in the following paragraph.

The XMCD spectra of bulk Mn_{12}−PhSMe, such as those of Mn_{12}-acetate,[84,85] show clear polarization effects, with the Mn^{III} spins aligned along the applied magnetic field and the Mn^{IV} spins antiparallel to the field. The XMCD spectra of monolayers of Mn_{12} derivatives on gold, however, clearly revealed the presence of Mn^{II} ions, as was already reported above in a discussion of the XAS spectra.[83] Using the same approach outlined for the analysis of XAS, the energy dependence of the dichroic signal, $S(E)$, was expressed as a linear combination of model spectra, $S^{\alpha}(E)$, at the same field and temperature values, that is

$$S(E) = \sum_{\alpha} c^{\alpha} \delta^{\alpha} S^{\alpha}(E) \qquad (1)$$

where α runs over the oxidation states, c^{α} is the molar fraction obtained by deconvolution of XAS spectra, and δ^{α} accounts for the orientation of the local magnetic moment in the applied field (positive if parallel to the field). This analysis suggested that the Mn^{II} ions are not present as isolated paramagnetic species and that the magnetic polarization at metal sites is decreased as compared with bulk complexes (Figure 7). Temperatures below 1 K were reached in UHV conditions at the Suisse Light Source synchrotron, in an attempt to search for the opening of an hysteresis loop. However, no magnetic hysteresis was detected down to 700 mK, providing strong evidence that Mn_{12} molecules undergo profound modification of their magnetic properties when deposited on gold surfaces.[83]

XMCD was also used for detecting the magnetic signal arising from layers of a simpler magnetic molecule, namely, (octaethylporphyrinato)iron(II), deposited on cobalt and nickel substrates.[75,76] At variance with all experiments described so far, here the substrate is ferromagnetic. The Fe^{II} ions are in the high-spin state ($S = 2$), and element-specific magnetization measurements through XMCD showed that at low temperature the molecular spins are ferromagnetically coupled to the substrate through superexchange interactions. The magnetization of the porphyrine layer could be rotated, in plane and out of plane, by controlling the magnetization of the substrate. This is indeed regarded as an important step forward in the direction of spin control of electronic transport in molecules.

Another exotic technique called β-detected NMR (β-NMR) has been employed to seek SMM fingerprints in the SAM of a Mn_{12} derivative.[91] β-NMR allows one to gain 13 orders of magnitude in sensitivity as compared with traditional NMR and is based on the implantation of radioactive ^{8}Li in the sample. The energy of implantation determines the depth reached by the nucleus, which can be stopped close to the surface or implanted very deep in the substrate. The precession of the magnetic moment of ^{8}Li nuclei ($I = 2$) in the applied *plus* local magnetic fields can be measured from

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the asymmetry of β decay. In fact, the detection principle is not very dissimilar from that used muon spin resonance, μSR, a sister technique that is widely used in molecular magnetism and entails the implantation of muonium ions.[92] In β-NMR, the emitted electrons are revealed by scintillation counters, which allow an extremely high sensitivity. Experiments were performed on monolayers of Mn_{12} complexes deposited on silicon using method (iii) and showed that magnetic properties of the surface layer are distinct from those of bulk Mn_{12}.

In summary, sophisticated experiments seem mandatory to fully ascertain the intimate electronic structure and magnetism of complex magnetic molecules deposited on surfaces. Even more challenging and demanding is the controlled and reproducible construction of devices incorporating individual molecules, as detailed in the following section.

5. Single-Molecule Device Concepts

Much progress has been made in the past few years toward the electrical or magnetic addressing of single molecules. The electrical addressing of molecular arrays on metal surfaces can macroscopically be realized through a mercury-drop junction[93] or by exploitation of impedance spectroscopy provided that a redox-active center, such as ferrocene, is attached to the free end of the molecule.[94] These techniques do not pose particular problems. By contrast, probing the electron transport properties of *individual* molecules turns out to be extremely challenging. Molecules deposited on conductive surfaces can be investigated using the tip of a scanning tunneling microscope as a movable counterelectrode.[95] In this case, molecules can be organized as monolayers or submonolayers, or inserted within an organic SAM, which provides the required insulation of single molecules from their neighbors and allows a certain control of the molecular orientation.[96,97] A room temperature investigation by scanning tunneling spectroscopy was reported on Mn_{12} complexes grafted by ligand exchange on a prefunctionalized Au(111) surface (method (iii); see section 2). The authors have clearly shown the occurrence of a band gap of ca. 2 V in the $I-V$ spectrum, which can be attributed to the presence of the molecular objects.[69−71] Alternative methods for single-molecule addressing have been proposed in order to overcome the intrinsically asymmetric geometry of STM probes and to allow the addition of a third electrode (gate) to give a transistor-like configuration. An original strategy exploits nanoparticle dimers held together by molecular bridges, which can be directly connected to metal electrodes prepared by e-beam lithography.[98] The direct use of lithographically fabricated nanoelectrodes is, of course, appropriate for molecules with lengths greater than about 10 nm, such as carbon nanotubes or DNA strands.[99] The size of most molecules of interest, however, requires completely different strategies based on mechanically controllable break junctions[100] or on nanogaps prepared by electromigration[101] or electrodeposition.[102] Fabrication techniques nowadays allow one to accurately control the distance between the *source* and *drain* electrodes, as well as to modulate the conductance of the device through an additional *gate* electrode. The incorporation of molecules in such transistor-like devices is usually carried out from solution. This approach was adopted to investigate organic molecules (including fullerenes and endofullerenes[103]) and simple coordination compounds like vanadium dimers[28a] and cobalt terpyridine[28b] complexes. In some cases, functional groups were inserted in the molecular structure to promote robust anchoring to the electrodes. The characterization typically consists of recording differential conductance (dI/dV_b) maps as a function of the bias voltage (V_b) and the gate voltage (V_g). The experiments are usually carried out at very low temperatures to increase the device stability and, in particular, to reduce thermal broadening of the energy levels. In addition, a magnetic field can be applied to distinguish magnetic excitations from nonmagnetic ones. Initial attempts to entrap SMMs of the Mn_{12} family have been described by Heersche et al.,[32] Park et al.,[33] and Del Barco et al.[34] However, considerably more work is required to ensure that these fragile magnetic molecules remain intact and retain their electronic and magnetic properties upon device construction. To this aim, detailed preliminary investigations on molecular arrays deposited on surfaces, as described in sections 3 and 4, seem of paramount importance to ascertain the role of molecule−substrate interactions.

In principle, there are several different approaches that can be used for the magnetic addressing of individual molecules (see Figure 8), like spin-polarized STM (SP-STM), electron spin noise STM (ESN-STM), scanning Hall probe microscopy (SHPM), and magnetic resonance force microscopy (MRFM). The SP-STM method[104] uses a ferromagnetic tip to produce a polarized tunneling

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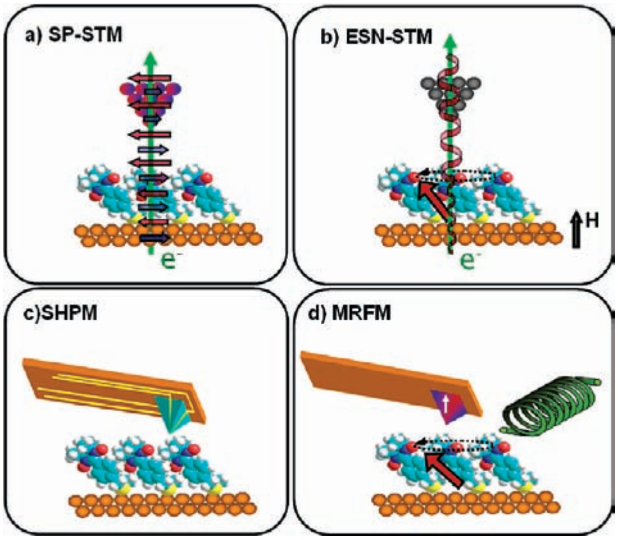

Figure 8. Methods for the magnetic detection of single molecules using SPM: (a) SP-STM; (b) ESN-STM; (c) SHPM; (d) MRFM.

current, which allows one to detect magnetized species with atomic resolution. The magnetic contrast arises from a tunnel magnetoresistance effect[105] (i.e., the transport of polarized electrons through a magnetic species).[106] Up to now, SP-STM has only been rarely applied to magnetic molecules.[107]

A completely different approach is followed in ESN-STM, whereupon the tunneling current is altered by the electron spins of the probed atomic or molecular species, which precess in the presence of a small static magnetic field. The ESN-STM technique was originally devised to observe a single spin of dangling bonds in silicon,[108] while more recently, it has been applied to several organic radicals, such as DPPH, NITR, and poly(chlorotriphenylmethyl) radicals.[109−112]

In SHPM, a miniaturized Hall probe is mounted on the tip of a scanning probe microscope (AFM or STM), thus enabling high-resolution, local magnetic investigations thanks to its sensitivity to the "stray field" of the magnetic objects present on the surface.[113] This technique has never been applied to single molecules but was recently used to study nanoparticles of Prussian-blue analogues.[114]

Finally, MRFM combines the three-dimensional capabilities of magnetic resonance imaging with the high sensitivity and resolution of AFM. Briefly, and in strong analogy with ESN-STM, the magnetic resonance signal coming from the precessing electronic spins in the sample is mechanically detected using a sharpened ferromagnetic tip.[115] Up to now, also this technique has never been applied to molecular materials, but according to recent theoretical work, nice results are expected on organic radicals.[116]

Among alternative techniques that are currently being developed for SMM detection are the nanoSQUIDs reported by Cleuziou et al.[117] In a nanoSQUID, the Josephson junction of the SQUID ring is replaced by a carbon nanotube, thus affording a much enhanced sensitivity, which, in principle, allows one to measure the magnetic response of an individual molecule. Although important issues remain to be solved (reproducible device construction, efficiency of molecule−nanotube interaction, etc.), these revolutionary devices will hopefully soon become available to the chemists' community, as happened a decade ago with their microSQUID counterparts.[118]

6. Conclusions

The field of molecular magnetism is undergoing rapid changes. A major trend now is the investigation of individual magnetic molecules, be they individual spin carriers (e.g., organic radicals and simple metal complexes) or more complex architectures comprising many interacting spins, like SMM. New appealing possibilities are coming into reach for the controlled organization of magnetic molecules on surfaces, for their electric or magnetic addressing using SPM methods and for their wiring into nanodevices. However, much work remains to be done to ensure structural and electronic intactness, to control the interaction with the substrate, and to drive the formation of ordered monolayers or submonolayers comprising isooriented molecules over large areas. Some of the earliest results have been critically reconsidered because more powerful techniques, like XMCD, have been applied to probe the magnetism of monolayer deposits.

In order to efficiently develop MS, the library of molecules and of substrates must now be rapidly enlarged. Furthermore, SPM techniques as well as methods for device nanofabrication and characterization need to be improved in order to allow the (magnetic) addressing of individual molecules in an efficient and reproducible way.

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Finally, theoretical tools must be strengthened, and many groups are already active in this direction.

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