

Review

Magnetic molecules on surfaces: SMMs and beyond

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ABSTRACT

In this critical review we cover the state of the art of surface deposition of complex magnetic molecules. Deposition methods are reviewed, as well as the most used types of surfaces, including the use of nanoparticle supports. The relevant characterization methods for molecules on surfaces are reviewed along with the molecules deposited and their most relevant examples. The perspectives of the field close the review article, the reader will get an overview of what has been done in the field of surface deposition of magnetic molecules and will acquire the tools to design their own experiments.

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1. Introduction

Technology is extensively present in all areas of modern life. Portable electronic devices are widespread. Progress requires these devices to be smaller, faster and more energy-efficient every day. However, the limitations of silicon electronics and magnetic materials used today for information storage and processing are now clearer than ever. One cannot use as bits in computers particles that are smaller than a magnetic domain: the magnetic domain limit of the materials cannot be overcome. Molecules are much smaller, however a transition to molecular electronics might never arrive if we understand this transition as a simple substitution of classical inorganic magnets for molecules while ignoring the quantum mechanical nature of the latter. Nevertheless, molecular electronics and information storage or processing devices might be envisioned if we learn to control the surface deposition of molecules to fabricate hybrid molecular/inorganic systems that can be integrated in devices. Molecules can offer much more than classical magnets since quantum properties can be exploited in a molecular/inorganic device.

In 1992, slow relaxation of the magnetization, the basic characteristic of a classical magnet, was found for the first time as a molecular property.[1] A dodecanuclear manganese molecule was the first reported to exhibit these properties. These molecules were called single-molecule magnets (SMMs) because each single molecule could behave as a nanosized magnet and it displayed quantum tunneling of the magnetization (QTM). Since then, the synthesis of new, better SMMs and nanomagnets has been an important field of research resulting in thousands of publications.[2–7] The state-of-the-art and record functional temperature for a SMM is set at 80 K by a remarkably simple dysprosium metallocene complex reported by Layfield.[8] This publication followed the dysprosium metallocene with hysteresis at 70 K reported simultaneously by Layfield [9] and Mills.[10] The discovery of SMMs also fueled the study of the magnetic properties of single molecules with a strong emphasis in the possibility of exploiting QTM in quantum technologies.

Magnetic molecules gained additional relevance since the electronic spin was put forward as the potential realization of the qubits for quantum information processing (QIP).[11] While organic radicals have demonstrated conditions for realizing 2 qubit quantum gates,[12,13] most of the efforts have focused on spin carriers consisting on transition metal or rare earth complexes.[14–16] Addressing, quantum state preparation and readout has been achieved by gating electronic transport through a single molecule located between gold nanoelectrodes, using however the nuclear spin states for information encoding [17].

Magnetization hysteresis in a single molecule, QTM or the ability to coherently manipulate spin states open very attractive possibilities of using single molecules in technological devices. Of course, the use of single molecules requires a proper organization of these on a surface as a previous step to reaching the limit of addressing one of them individually. Examples of proposed applications are the use of SMMs to store magnetic information, the use of single molecules as qubits for quantum computation or the use of them for molecular spintronic devices. For each one of these applications, surface deposition of the magnetic molecule is a key step. Even the implementation of the simplest proposition of a single-molecule device depends on the interaction of the molecule with the surface of an electrode or a scanning tunneling microscopy (STM) tip.[18] Therefore, this research is a multidisciplinary field where the synthetic chemist that prepares and functionalizes the molecules (or surfaces) needs to collaborate with the physicists that study the properties of these materials and the new physical phenomena observed for a single molecule or

with material scientists and nanotechnologists to prepare and characterize ordered arrays of molecules on surfaces.

The deposition of magnetic molecules on surfaces and the understanding of the interaction of the molecule with the substrate is non-trivial. To fully control the deposition, three key factors must be understood: i) the molecular stability in the deposition conditions, ii) the surface's stability in the deposition conditions, and iii) the nature of the molecule surface-interaction. One factor that becomes crucial for exploiting molecular nanomagnets on surfaces is the control of the dynamic behavior of the molecular magnetic properties. It is established that this is heavily dependent on the interaction of their spin magnetic moment with the phonons surrounding them. Upon deposition, a completely new set of phonons come into play, these associated to the substrate. An extensive knowledge of the chemical and physical properties of all parts of the system is necessary to choose the right deposition technique for the specific molecule/surface system. The organization of organic molecules on surfaces is a well-studied topic that shall benefit the task of depositing magnetic molecules: a key observation is that molecular shape and intermolecular interactions play an important role on the way the molecule will interact with the surface and the properties of a monolayer.[19,20].

It is worth to point out that most interesting SMMs or nanomagnets synthesized are structurally complex coordination compounds, in many cases containing more than one metal center (usually called high-nuclearity complexes when the number of metal centers exceeds 4) and most of the times are heteroleptic (i.e. they contain different types of ligands in the same molecule). The metallic core provides the magnetic properties, while the ligand envelope can be used to fine tune the latter or provide other properties like solubility, luminescence, or grafting ability. Thus, even though the possibilities for intermolecular interactions and molecule/surface interactions are many, the lessons learned from the organization of simple organic molecules on surfaces are still very useful. After all, the outer surface of a coordination complex is formed by the organic ligands that can be chemically modified, in most cases without affecting the magnetic properties of the metallic core.

The implementation of devices employing magnetic molecules poses at least two unique challenges that require a multidisciplinary team. First, the deposition of said molecules onto surfaces without disrupting the properties that make them interesting. Second, the characterization of the composite system with the state-of-the-art techniques.

In this review, we address deposition techniques, types of surfaces and characterization methods used for preparation and characterization of monolayers and submonolayers of magnetic molecules. Finally, we review the literature on surface deposition of the most relevant magnetic molecules and discuss future perspectives in the field.

2. Deposition techniques

2.1. Chemisorption vs physisorption

From the point of view of the molecule-surface interaction, the deposition can occur either through chemisorption or physisorption, as illustrated in Fig. 1. In physisorption the electronic structure of the molecule is barely perturbed in the process, while for chemisorption the electronic structure of the molecules changes, as new bonds are created. For chemisorption, a new chemical bond will be formed between the molecule and the surface, shown in green in the Fig. 1 (a) and (b). There are two ways to achieve this

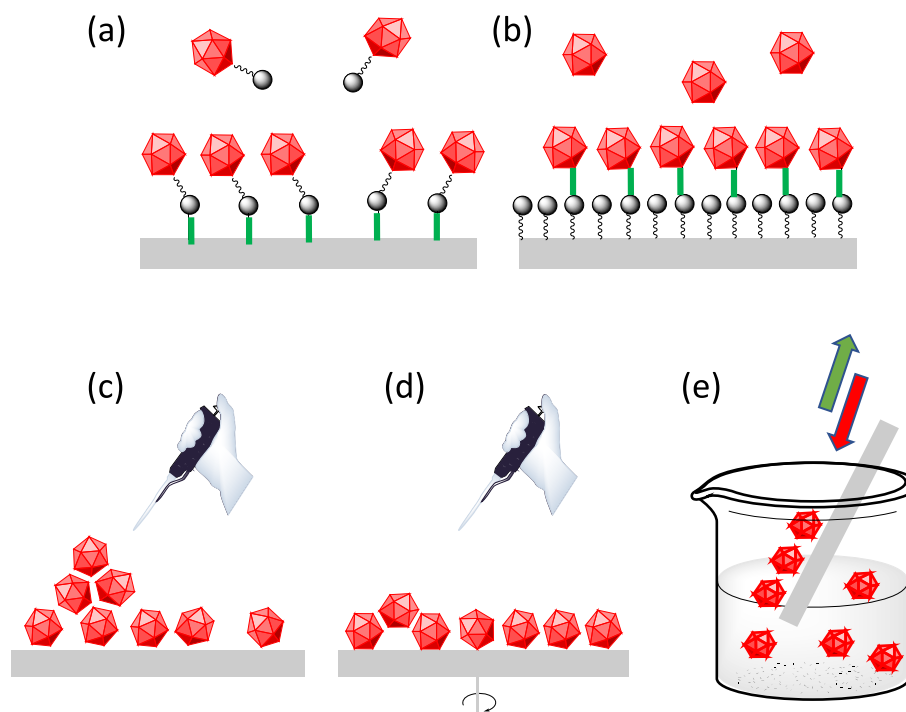


Fig. 1. (a) and (b) show examples of chemisorption: a new covalent bond (green) is formed between the molecules (red) and the substrate via a linker (grey) attached to the molecule (a) or to the surface (b). (c), (d) and (e) show examples of physisorption by (c) drop casting, (d) spin coating and (e) dip coating. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

new molecule-surface bond: molecule functionalization with grafting ligands that bind to the surface (Fig. 1(a)) or surface functionalization with a functional group X (a grey circle in Fig. 1(b)) that will react with the molecule. The reaction with the molecule can entail a reaction with a functional group on a ligand or a ligand-substitution reaction. Commonly used functional groups are depicted in Fig. 2. Direct deposition of magnetic molecules is usually achieved with the first method, since molecule functionalization is, a priori, the simplest procedure given the ability of chemists to play with ligands and add any desired functionality to a magnetic molecule. The formation of this new bond will drive the grafting of the molecule on the surface. Intermolecular interactions on the newly formed layer will also be important to achieve

an organized layer of molecules on the surface. The most used strategy for chemisorption by direct deposition is the use of ligands with S-containing group terminal groups that will form a chemical bond with a gold surface, resembling the formation of self-assembled monolayers (SAMs) of long-chain aliphatic S-containing groups on Au (Fig. 2 (b)). This method takes advantage of gold's particular affinity to soft donor atoms like sulfur.[21] The S-functionalized molecule is dissolved in an appropriate solvent and the gold surface is immersed in the solution. After some time, the gold substrate is removed and rinsed thoroughly to eliminate any physisorbed material, leaving a grafted monolayer of magnetic molecules on the substrate. For simple S-derivatives, the cooperative Van der Waals interactions between the long aliphatic chains

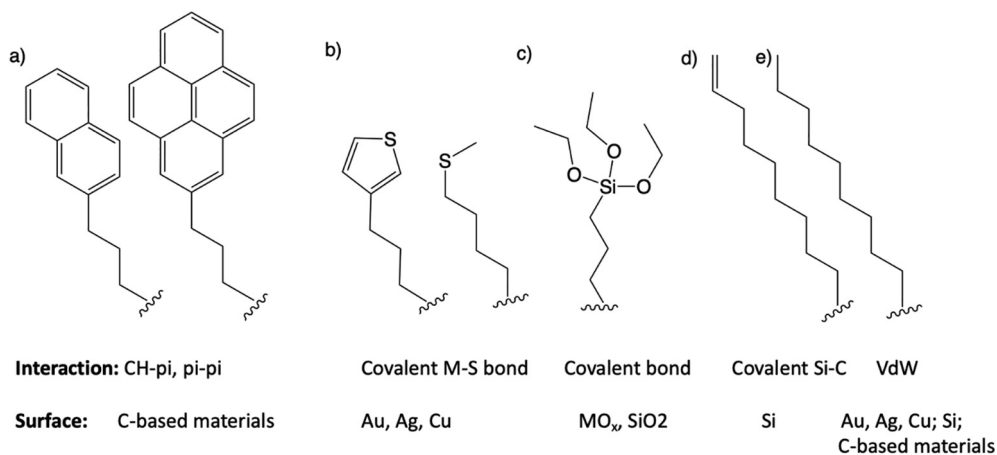


Fig. 2. Common functional groups. (a) aromatic groups are used for physisorption, (b) S-containing group derivatives are used for chemisorption on soft metals, (c) tris-alkoxysilanes are used for oxides, (d) unsaturated bonds are used in hydrosilylation with Si-H activated Silicon and (e) long aliphatic chains are used for physisorption and self-assembly exploiting VdW forces between chains.

of the S-containing group directs the SAM organization on the surface. For magnetic molecules with complex and/or voluminous structures, this self-organization may not be possible, and the grafted molecules might form a disordered layer. One must also consider the possibility of several thioesters or thiols in the molecule that will fail to direct a unique orientation of the molecule in a surface. This last point should be avoided by precise chemical control that should allow a single functionalized ligand in the molecule, as illustrated in Fig. 1(a).

The functionalization of the surface is also a good roadmap for chemisorption (Fig. 1(b)). Gold surfaces can be first functionalized with a thiol that contains a terminal donor group X (alcohol, carboxylic acid, amine, pyridine, etc.). The chemical knowledge on the ligand exchange properties of the magnetic molecule must be used to choose the appropriate X group placed on the surface to then carry out the grafting. In this way, SH-(CH₂)_n-X organic groups can be used to functionalize gold surfaces while X-silanes can be used to functionalize Si/SiO₂ or metal oxide surfaces. Following the functionalization, the surface exposes the reactive X groups that can react with the desired magnetic molecule so as to graft it on the substrate. Again, rinsing becomes an important step to remove material that has not been grafted or chemisorbed onto the surface.

Physisorption, on the other hand, relies on Van der Waals, H-bond, π - π stacking or even electrostatic interactions between the molecules to be deposited and the surface. This is harder to control but at the same time may facilitate the self-organization of self-assembled molecular layers on a surface, since the molecules are not strongly anchored to a fixed spot on the surface by a chemical bond. Like for chemisorption, the possibility to obtain an ordered array of molecules on the surface depends on the deposition method and on the possible intermolecular interactions among the chosen molecules that might allow the self-assembly on the surface. Table 1 shows the most common deposition methods with the interactions involved and selected examples.

2.2. Wet methods vs vapor deposition

The classification of the deposition based on the molecule-surface interaction is not the most used by chemists. From a chemist's point of view, the deposition methods are classified according to the treatment required for the molecule to be deposited. One refers to wet methods when the molecule is dissolved in a solvent prior to the deposition and vapor deposition when the molecule is deposited from the gas phase. Wet methods or vapor deposition

methods can lead to both chemisorption or physisorption. The main problem when depositing complex molecules onto surfaces is their possible decomposition, as already pointed out in 2009 by Sessoli, Gatteschi *et al.* [35] Wet methods require molecular stability in solution. This can be established for most systems, for example by NMR characterization. Furthermore, wet methods are easy to implement in a chemical laboratory. Wet methods include drop casting, spin coating or dip coating illustrated for physisorption in Fig. 1 (c), (d) and (e), respectively. Drop casting is the simplest of methods, since a drop of a diluted solution of the molecule is casted onto the surface and the solvent is evaporated.[36] The key parameter for drop casting is the concentration of the solution. By using drop casting it is extremely unlikely to obtain ordered monolayers, since material accumulates in some areas as the solvent evaporates. Dip coating consists in immersion of the substrate in a solution of the molecule and removal of the substrate from the solution after a time.[37] The key parameters here are immersion time and concentration. Longer immersion times or very concentrated solutions may lead to multilayer coverage, while very diluted solutions or very short dipping times might result in submonolayers. Dip coating can be used for both chemisorption or physisorption. Rinsing after deposition is necessary to eliminate all the molecules not directly attached to the surface and obtain a clean layer.

Spin coating is a wet deposition technique that requires a specific but simple instrument: a spin coater. The substrate is held on a spinner that can be programmed to spin at different rotational velocities. A drop of solution is casted onto the center of the resting or spinning substrate. As the substrate spins, the drop is evenly distributed on the surface of the substrate by the centrifugal force, evaporating in a controlled manner. Any excess material is expelled by the same centrifugal force. Spin coating can be used to obtain uniform thin films, by precisely controlling the spinning time and velocity. In addition to the molecular properties, for spin coating the viscosity of the solution as well as the superficial tension of the droplet are factors that must be considered. For typical organic solvents and diluted solutions of magnetic molecules these properties approximate those of the pure solvent.[37] Velocities between 500 and 5000 rpm are commonly used to obtain uniform coverage. Spin coating can be performed to obtain thin films on large surfaces such as a typical silicon wafer. For large volumes, fume exhaust and drying times must also be considered as an important parameter to control.

More complex wet deposition techniques have also been used for magnetic molecules. An example is the preparation of thin films

Table 1

Summary of most common deposition methods, interaction involved and surface and molecule type with selected examples. Wet methods = drop casting, dip casting or spin coating.

	Deposition methods	Surfaces	Interaction	Molecules	Selected examples
Physisorption	vapor deposition	Metals (Au, Cu, Ag)	Van der Waals	molecules with aliphatic groups	Cr ₇ Ni [22]
	wet methods or vapor deposition	Carbon-based materials (HOPG, graphene, CNTs); oxides (mica, manganites)	CH- π , π - π	molecules with aromatic groups	Co ₂ [23] TbPc ₂ [24]
Chemisorption	vapor deposition	HOPG; C-based materials; Si; SiO ₂ ; metals (Au, Ag, Cu...); oxides	electrostatic	Molecular ions	Ni ₁₂ [25]
	wet methods	functionalized Si/SiO ₂ or oxides (i.e. X-Silane) metals (Au, Cu, Ag...)	Van der Waals	sublimable molecules with a preferred orientation on the surface	Cr ₇ Ni [22] Fe ₄ , [26] [DyPyNO] ₂ [27] Ln-Pc [28,29] Fe ₄ [30]
	vapor deposition	metals (Au, Cu, Ag...)	covalent or coordination bond	molecules with a ligand that is reactive towards group X functionalized molecules with a grafting group (i. e. SR) functionalized, sublimable molecules with a grafting group (i.e. SR)	Fe ₄ [31–33]; Cr ₇ Ni [34] Cr ₇ Ni [22]

of molecules over a substrate using Langmuir-Blodgett films. This exploits the well-known Langmuir-Blodgett trough to transfer a monolayer of a molecular species onto a substrate that is immersed or emerged into or from the trough. This method requires the molecules to organize and form a Langmuir film on the surface of the solvent (typically water) to be then physisorbed on the substrate.

Vapor deposition methods consist of transferring the molecules from the gas phase to the surface. They require volatile molecules that can be sublimated and are thus stable at the necessary conditions (pressure and temperature). Sublimation is done in ultra-high vacuum (UHV), which requires specific apparatus for proper implementation. Since not all substances can be evaporated, vapor deposition methods cannot be implemented with many molecular candidates for deposition. While some species have an easily achievable sublimation point, more often sublimation temperatures require extremely low pressures only achieved through an ultra-high vacuum set up. For evaporable or sublimable molecules, one can exploit this property for surface deposition with great advantages over wet methods. Direct evaporation/sublimation in a closed environment with the substrate can be used to achieve thin films, monolayers or submonolayers of the molecule on the substrate as the molecules reach the substrate via the vapor phase. In this manner, usually the molecules will be physisorbed to the surface, but adequate molecule or substrate functionalization can also result in chemisorption. UHV guarantees the absence of possible pollutants. Key factors that can be controlled for UHV evaporation of molecules onto surface are the substrate/crucible distance, the evaporation time and temperature and the amount of sample used. The distance between the evaporator and the substrate must be controlled because it is highly desirable to attain an evaporation cone that will cover the substrate but will not contaminate the UHV chamber. Evaporation in UHV is the cleanest way to deposit molecules on a substrate. In order to obtain submonolayers, or isolated molecules this is indeed the technique of choice if the material can be evaporated. Thus, even though evaporation or sublimation is limited to a handful of materials that can withstand sublimation and it requires very specific equipment, it is still the reference technique to attain ultra-clean, non-polluted specimens.

Since many species cannot be evaporated without losing their integrity, researchers have adapted the use of electrosprays to surface deposition (ESD). Electrospray is a widely used technique to produce nano- or micro-droplets used in the mass spectrometry of coordination compounds that fragment very easily with more strenuous ionization methods. ESD consists of the formation and deposition of atomized precursor droplets of a solution of the molecule to be deposited onto a conductive substrate using electrostatic forces. The generated droplets are in the order of tens of nanometers of size, and high-quality thin films of different substances can be obtained. For non-volatile molecules, electrospray deposition (ESD) has become a reliable technique since it allows to transfer this kind of molecules to substrates without being damaged or fragmented, as has been demonstrated in several experiments.[38–41] Recently, electrospray deposition (ESD) has been coupled to STM in order create monolayers or submonolayers of molecules that cannot be deposited by vapor deposition. The first ESD deposition studies of nanomagnets were done using the archetypical SMM, Mn_{12} .[42,43] Besides ESD, related techniques such as vacuum-spraying[44], pulsed-laser deposition[45], and matrix-assisted pulsed-laser evaporation (MAPLE)[46] have also been employed with different degrees of success. All of these techniques require specific instrumentation and their application to large substrate areas is not always straightforward.

Techniques that allow to have the molecules arranged following nano or microscopic patterns have also been developed. These techniques include microcontact printing (μ CP),[47] dip pen,

[48,49] standard photolithography,[50] electron beam lithography,[51] focused ion beam (FIB)[52] and local oxidation nanolithography (LON).[53].

3. Characterization techniques

The main challenges for the characterization of molecules on surfaces are related with the detection limits of current technology. Addressing and detecting a single molecule, a submonolayer or a monolayer on a surface is still a very challenging task. In this section, we will briefly review the most usual characterization techniques and the information that they provide. We must distinguish between topographic, compositional and property-related characterization of the molecular layer (Fig. 3). The latter is the most difficult of the three. Indeed, the characterization of the molecular properties on a surface is key to the possible implementation of molecules in devices, since one main goal is to exploit molecular properties such as slow relaxation of the magnetization of SMMs, the coherent manipulation of quantum states for quantum computing or the interplay between spin and electron transport for molecular spintronics.

A typical monolayer of molecules like Mn_{12} or $TbPc_2$ will contain approximately 10^{13} molecules/cm². This calculation can be performed with more accuracy using the single-crystal X-ray crystal structure dimensions, since molecular dimensions can be extracted from crystallographic data. The small number of molecules involved makes it extremely difficult with standard characterization techniques like SQUID magnetometry to detect the properties of the monolayer. The number of molecules is even smaller in an uneven coverage of the surface, as depicted in the cartoon in Fig. 3. If the layer formed is large enough and covers the macroscopic substrate, simple techniques like ellipsometry and contact angle can give valuable information. With ellipsometry-one can assess the thickness of the molecular layer by analyzing how light is reflected by the film. This technique is useful for films as thin as 1 nm. It is important to previously characterize the bare substrate. For example, silicon wafers have a native SiO_2 layer if not treated with HF: the thickness of the SiO_2 layer must be considered in the mathematical model used to

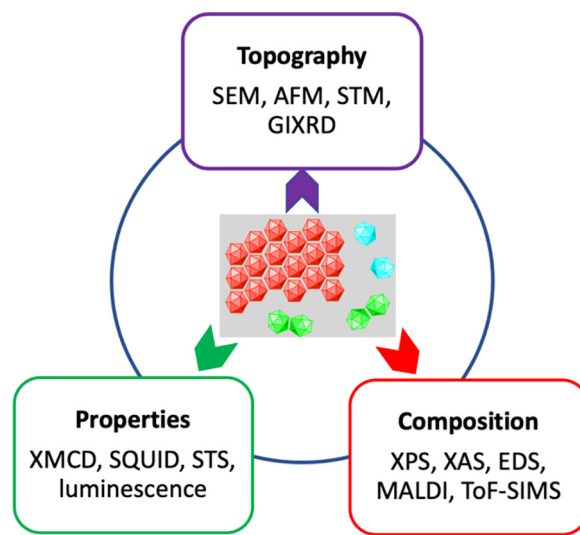


Fig. 3. Most common characterization techniques for magnetic molecules on surfaces, grouped by the information they provide. In the center, a cartoon representation of a functionalized substrate where the red objects represent an ordered array of molecules, and green and blue objects represent dimers (green) and isolated (blue) molecules respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

obtain the thickness. Ellipsometry can be nicely combined with contact angle measurements. The contact angle is defined as the angle formed by a drop of liquid on a solid surface at the boundary where liquid, gas, and solid intersect. Most of the times, a droplet of water is used. In this case, the contact angle will readily inform of the hydrophilicity of the surface. Changes in hydrophilic character are expected after surface functionalization with a nanomagnet, and the changes will depend on the exact nature of the molecule used.

Time of flight secondary ions mass spectroscopy (ToF-SIMS) is a surface-sensitive technique that provides elemental, chemical state, and molecular information from surfaces of solid materials. In this sense, it is ideal to study molecules deposited on surfaces. A focused primary ion beam is used to sputter the surface of the specimen studied and ejected secondary ions are collected and analyzed using a ToF detector. The system is coupled to a microscope so that a surface mapping can be obtained for any mass of interest on a sub-micron scale. Secondary ions (in example, the metal present in the molecules deposited), molecular fragments or whole molecular ions can be detected and mapped. This technique is extremely powerful to ascertain molecular integrity on a surface. Molecules that can be characterized by conventional mass spectroscopy are ideal candidates for ToF-SIMS on a substrate. Examples are TbPc₂ SMMs [54] Fe₄ SMMs, [32] or Schiff-base lanthanoid complexes.[55] Although a conductive substrate is preferred, it is not a requirement for the technique. ToF-SIMS can be applied to any molecule/substrate combination. Some examples are shown in Fig. 4.

When molecules are chemisorbed or physisorbed on a surface, a topographical observation of the resulting hybrid system can help understand whether there are one or more molecular orientations on the surface or if the molecules are ordered following a pattern, if nanocrystals form on the surface or if the molecules reorganize by supramolecular interactions. Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) are the techniques used to obtain topographical information on a substrate. Fig. 5 shows a compar-

ison of the scales that can be imaged using SEM, AFM and STM images.

SEM is a technique that allows to observe the surface topography by scanning it with a focused electron beam. This beam interacts with the sample and different signals, depending on the working mode, are collected. In the most common mode of SEM, secondary electrons emitted by the excited atoms from the sample are collected. Then, depending on the intensity of these electrons, an image is produced. SEM microscopes can be equipped with Energy-dispersive X-ray spectroscopy (EDS) capabilities so that a compositional analysis and quantitative element mapping can be achieved along with the sample's image. The main limitation of SEM is the low spatial resolution, so single molecules or nanometer sized islands cannot be imaged. High-resolution state of the art SEM can reach resolution of several nanometers. Thus, SEM can be helpful to establish homogeneous coverage of large areas of substrate or the formation of large aggregates or nanocrystals on the surface of the substrate, but it must always be accompanied with AFM or STM. Additionally, SEM can be very useful to characterize devices prepared using molecular layers in hybrid systems, as shown in Fig. 5 for a ITO/LnPraNO/Cu²⁺@PEO/Pt device.[56] An advantage is the fact that non-conductive samples can be imaged, since specimens for SEM can be covered by a conductive layer of material (usually gold or carbon, deposited by sputtering or vapor deposition).

From the family of scanning probe microscopies (SPM), AFM and STM are the most relevant. In SPM, a sharp probe tip scans the surface of a sample, sensing different properties at the nanoscale. Which specific technique is employed depends on what property-one wants to measure. In AFM, a tip on a cantilever scans the surface of a sample, measuring the attractive and repulsive forces between them. A laser is focused over the cantilever and its deflection is measured with a photodiode. From this signal, topography images and/or force-distance curves are obtained. Non-contact AFM methods avoid tip-contamination and degradation and the height of objects (molecules or submonolayers) can be measured with great accuracy with respect to the substrate.

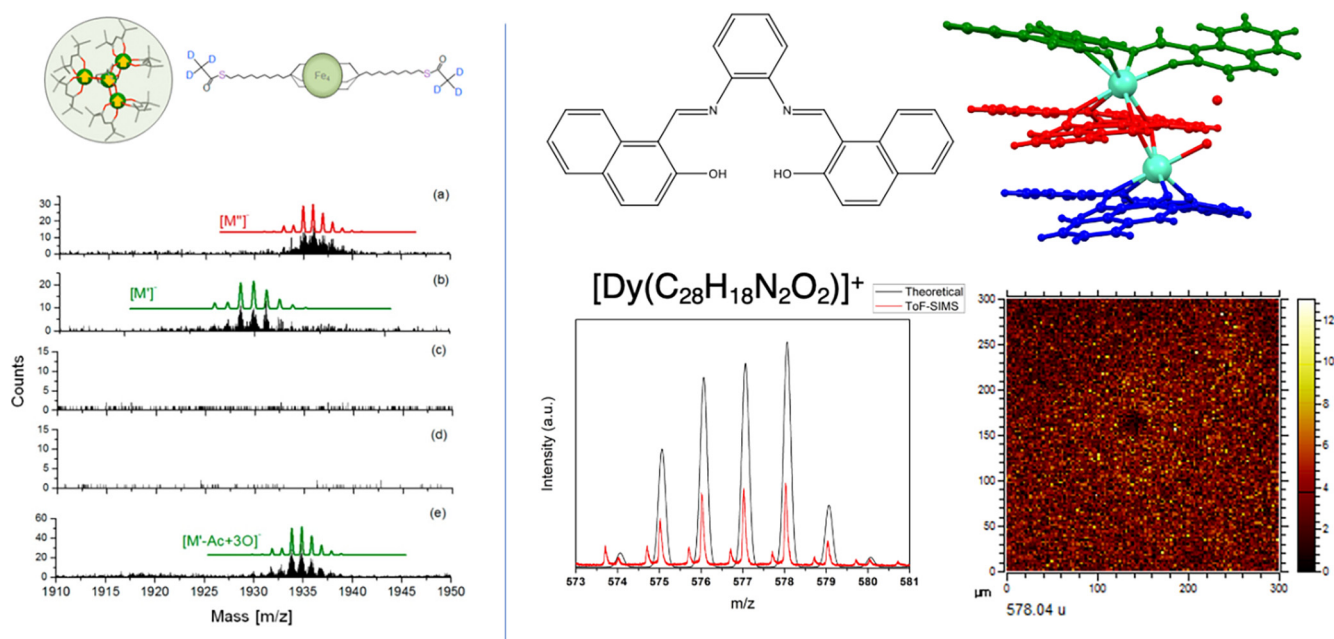


Fig. 4. Examples of the use of ToF-SIMS to detect molecular fragments and a mapping of such fragments on the surface. Left panel: Structure of derivatives of Fe₄ and ToF-SIMS of the bulk of Fe₄ SMMs (a, b) and monolayers on Au (c, d and e). The calculated peak in green is plotted over the experimental spectra. Reprinted (adapted) with permission from [32]. Copyright© 2014 American Chemical Society. Right panel, ToF-SIMS spectra and surface mapping for the [DySYML]⁺ fragment. Reprinted (adapted) from [55] with permission from the Chinese Chemical Society (CCS), Peking University (PKU), and the Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

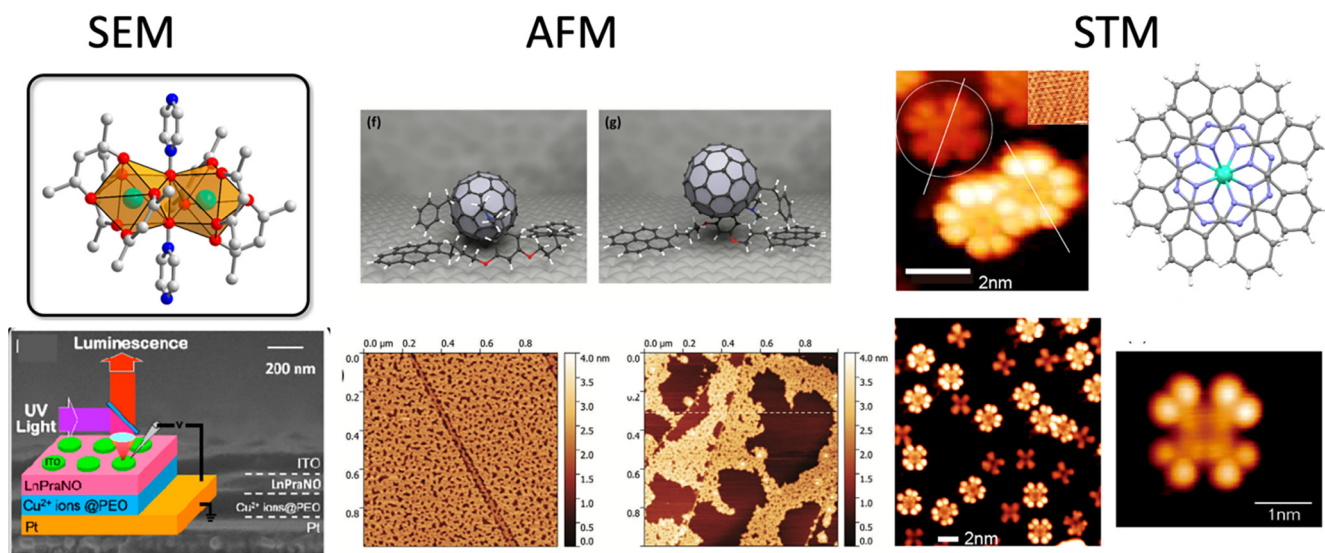


Fig. 5. Comparison of images obtained by SEM, AFM and STM that highlight the different resolution that can be obtained with each of these imaging techniques. With SEM one can image large areas of several micrometers, while AFM can obtain detailed topographical information of small areas of several nm and STM can be used to image molecules with direct observation of the molecular orbitals. SEM: Crystal structure of LnPr₄NO and cross-section SEM image of a device using the luminescent and magnetic molecular material. Reprinted (adapted) with permission from reference [56]. Copyright© 2021 American Chemical Society; AFM: molecular dynamics computed structures of functionalized EMF and AFM images of a sub-monolayer on HOPG, adapted with permission from reference [57]; STM: structure of TbPc₂ and STM images of TbPc₂ (eight-lobe moieties) TbPc (circled in the first image) and Pc (cross shaped in the bottom image) on NbSe₂. Adapted with permission from reference [58].

Patterning and microcontact printing techniques have been very useful to accurately determine the presence of ordered or grafted molecules on a surface. One early example is a 2007 paper by Coronado *et al.* that reports patterning of Si wafers and accurate positioning of Mn₁₂ SMMs on the patterned surface.[53].

For AFM, the substrate must be atomically defined so highly oriented pyrolytic graphite (HOPG), mica (muscovite), Au or Cu monocrystals or atomically defined Silicon are the preferred deposition substrates. Additionally, the substrates are much harder than the molecular arrays, so that the height of a monolayer can be characterized with accuracy by performing a nanoindentation experiment. In a nanoindentation experiment the tip of the AFM is pushed through the molecular layer until the substrate offers enough resistance, and then it drags some material for a few nanometers. The result is a well where one can determine with accuracy the height of the molecular layers covering the substrate. The main limit of AFM is the lateral spatial resolution related to the radius of the tip is usually of the order of several nanometers and thus this tip size limits the accuracy of lateral distances. In recent years great advances have been made in AFM and AFM tips. State of the art research on functionalized tips can reach atomic resolution. Functionalized tips can be used to obtain atomic resolution images of single molecules, for example flat molecules with aromatic groups like perylene derivatives can be imaged with atomic resolution with CO-functionalized tips.[59].

AFM tips can also be used to probe electric or magnetic properties but this is limited to room temperature and to large objects like nanoparticles, not to the study of the magnetic properties of a single-molecule on a substrate.[60] AFM cannot be combined with an elemental analysis technique like EDS, but it can be combined with Raman spectroscopy, an example is the work on spin crossover films[61] or on the archetypical TbPc₂ SMMs.[62].

For single molecules or sub-monolayers of molecules that can be deposited in vapor phase STM is still the reference technique. STM measures the tunnel current between the sample and the tip, which is exponentially related to the tip-sample distance, the surface must be conductive and atomically flat for STM imaging. Atomically defined Au or Cu single crystals are readily available, and these are the preferred substrates for STM. Scanning a certain

area of the substrate allows to obtain a representation of the local density of states (LDOS).[63] STM permits visualization of a single molecule on a surface with much better resolution than AFM (in the three spatial directions) and these data can be used to ascertain a molecule's dimensions and position on a surface, for example by using the ratio between height and lateral size as done by Affronte *et al.* for Cr₇Ni nanomagnets on Au.[22].

Of course, to obtain high resolution images, specific conditions of the molecule, the substrate and for the measurement are required. Ideally, the molecules must be anisotropic in shape, so that only one orientation is possible on the surface and the molecules must sublime in order to deposit them by evaporation to avoid the presence of impurities or undesired products from side-reactions that can happen in solution. Finally, high resolution images will also require specific conditions like ultra-high vacuum (UHV) and low temperatures to avoid the thermal motion of the molecules on the surface. Thus, it is not easy that a particular surface/molecule system satisfies all the required conditions to obtain good STM images. However, many astounding high-resolution images have been reported on simple metalloporphyrins[64] or metallophthalocyanines.[65] In the field of nanomagnets and SMMs, Affronte and Winpenny have extensively used STM to characterize monolayers of complex Cr₇Ni nanomagnets on Au(111).[22] However, it is in the characterization of TbPc₂ SMMs on a variety of surfaces that high resolution images have been obtained using STM to image and characterize SMM, as shown in Fig. 6. Bucher and Ruben report the manipulation of single molecules of TbPc₂ by the STM tip and a combined STM/STS (STS: scanning tunneling spectroscopy) study at low temperature to characterize the isolated molecules and an ordered 2D array of TbPc₂ on Au(111).[66] In this study the authors are able to identify the molecular orbital lobes of single molecules, as well as the orbital overlap in the self-assembled monolayer and compare it with the STM-tip manipulated ensembles.

STM can be coupled to STS (or dI/dV spectroscopy) to electronically characterize the surface deposited molecules and this spectroscopic technique can yield very valuable information. In particular for SMMs, the Kondo peak can be observed using STS. One example is a thorough STS study of the Kondo peak on TbPc₂ SMMs monolayers as a function of the substrate.[68].

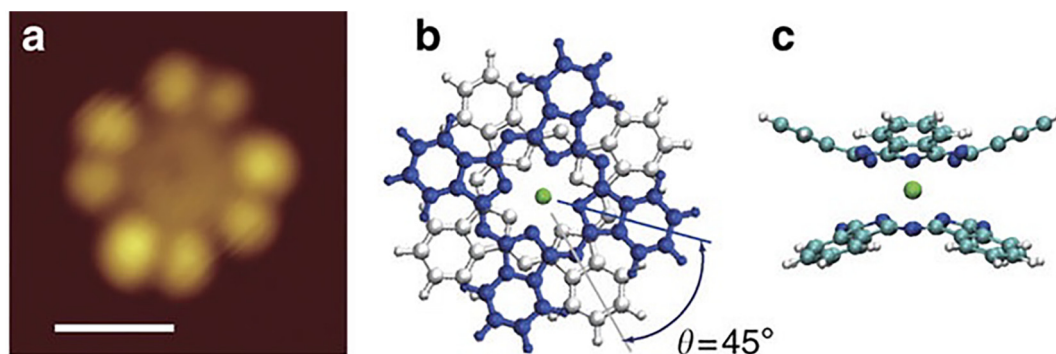


Fig. 6. (a) TbPc₂ orbital lobes imaged by STM, (b) and (c) show the crystal structure of TbPc₂, highlighting the 45° angle between Pc ligands, as observed by STM. Reprinted (adapted) with permission from [67].

X-ray absorption and spectroscopies can be used to probe the electronic states of atoms. These techniques can provide compositional information of the monolayer or sub-monolayer and different kinds of relevant data related to the molecular properties. X-rays can be generated in a synchrotron facility with extremely high flux, so very small amounts of matter can be detected. The most used techniques to characterize molecules in surfaces using X-rays are X-ray Photoelectron Spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and XMCD. These and other techniques like X-ray absorption near-edge structure (XANES) spectroscopy or X-ray natural linear dichroism (XNLD) are reviewed in detail by Cornia *et al.*[69].

In XPS, a substrate is irradiated by a focused X-ray beam. Electrons from the elements present on the surface are excited and emitted with a certain kinetic energy (KE) that is measured by a detector. This kinetic energy depends on the element specific binding energy (BE) of these electrons in their orbitals. From XPS one can obtain compositional information of the layer and oxidation states of the elements present. A comparison with the XPS spectra of the bulk crystals of the molecular sample can lead to the clear identification of intact molecules on a substrate. XPS is ideal to characterize molecules deposited on a substrate since the sample penetration of the X-rays is limited to a few nanometers. The substrate must be conductive or else the XPS peaks can appear shifted by charging effects, hindering the measure of correct BE values, but there are strategies to improve the spectra of insulators and overcome charging issues.[70] When hard-X-rays are used in a synchrotron source the technique is called HAXPES, hard-X-rays photoelectron spectroscopy. With HAXPES the core levels of elements can be addressed, and coupled to other techniques mapping of an element, including depth mapping can be done.

XAS is coupled to magnetic fields and high-flux polarized X-rays in order to obtain X-ray magnetic circular dichroism (XMCD) spectra. XMCD has become instrumental to characterize the magnetic properties of SMMs and nanomagnets on surfaces.[71] XAS collects absorption data at the L_{2,3} edges of transition metals and at the M_{4,5} edges of lanthanoid ions. When the high-flux X-rays are polarized with positive (I⁺) and negative (I[−]) circular polarization the XMCD signal is calculated as the difference between XAS spectra at positive (I⁺) and negative (I[−]) circular polarization recorded in a magnetic field. The experimental XAS and XMCD spectra can be used to calculate the effective magnetic moment considering the dipolar transition rules. With this, one can calculate the expectation values of the projection of the orbital <L_z> and spin <S_z> magnetic moments, which in turn can be used to obtain the effective moment, M_z. [71] For transition metals, <S_z> can be approximated to the effective spin value, S_{eff}. [72] The XAS spectra of transition metals can be simulated using CTM4XAS software (<http://https://www.anorg.chem.uu.nl/CTM4XAS/>) considering spin-orbit

coupling and crystal field. Thus, XMCD is one of the most useful techniques to obtain magnetic properties of molecules on surfaces. XAS can be used to obtain compositional, electronic and magnetic information of a thin layer or submonolayer of molecules. Fitting of XAS data can be used to obtain crystal field and anisotropy values for transition metals and this information can be used to ascertain molecule integrity on the surface, or even, molecular distortions caused by grafting or chemisorption. The different detection modes available in most beamlines are total electron yield (TEY) or fluorescence electron yield (FEY), which allow for probing a few nm of the sample (TEY) or the bulk material (FEY). This makes XMCD unique to obtain information of molecules on a surface. XAS and XMCD will give element specific magnetic properties, spin–spin coupling information and if sum-rule analysis can be performed, direct information on the orbital magnetic moments. Most XAS and XMCD beamlines are currently equipped with low temperature and high magnetic field magnets (down 4 K and up to 5 T). In these conditions hysteresis plots for SMMs can be obtained. XMCD addresses the element specific magnetic behavior, thus it can be exploited for surface-deposited heterometallic 3d-4f SMMs to obtain spin–spin coupling information.[73] Rosado *et al.* showed that the magnetic coupling between Ni and Tb in a heterometallic SMM was maintained when a Ni₄Tb SMM was chemisorbed in the surface of iron oxide nanoparticles (IONPs). Fe₃O₄ was used as a magnetic substrate and the relative orientation of the spins on the Ni₄Tb with respect to the different types of Fe in the Fe₃O₄ iron oxide were also determined by XMCD.[74] XNLD, using linearly polarized X-rays, is sensitive to the orientation of molecules with respect to the surface. Very often it is used in combination with angular dependence of the XMCD signal. For Co₂, with large heterocyclic aromatic groups, the angular dependence of the XNLD at N-edge was used to ascertain a particular molecular orientation with respect to a HOPG surface. [23] XNLD can also be used to probe molecular orientation on a surface. XNLD was used to establish that TbPc₂ SMMs adsorb with the same orientation on MgO and Ag(100) and this is the same as the molecular orientation reported for these SMMs on metal surfaces. [75] An example of endohedral metallofullerenes was reported by Popov *et al.* in 2018.[76] In this case, the lack of angular dependence of the XMCD signal suggested randomly oriented molecules, and this was confirmed by with the negligible XNLD signal. Fig. 7 shows XAS, XMCD spectra and hysteresis loop obtained from XMCD data for an EMF containing Dy ions.

XMCD has also been coupled to ESD, for example to obtain and characterize anisotropic Fe₄ arrays.[77] Sessoli, Saintavit and co-workers have pioneered the application of XMCD to the study of SMMs on surfaces, and they reviewed the state of the art in a book chapter.[78] In this book chapter, they mostly review the XAS and XMCD spectra of Mn₁₂ on surfaces. One of the more puzzling observations in the field was the fact the Mn₁₂ lost its SMM prop-

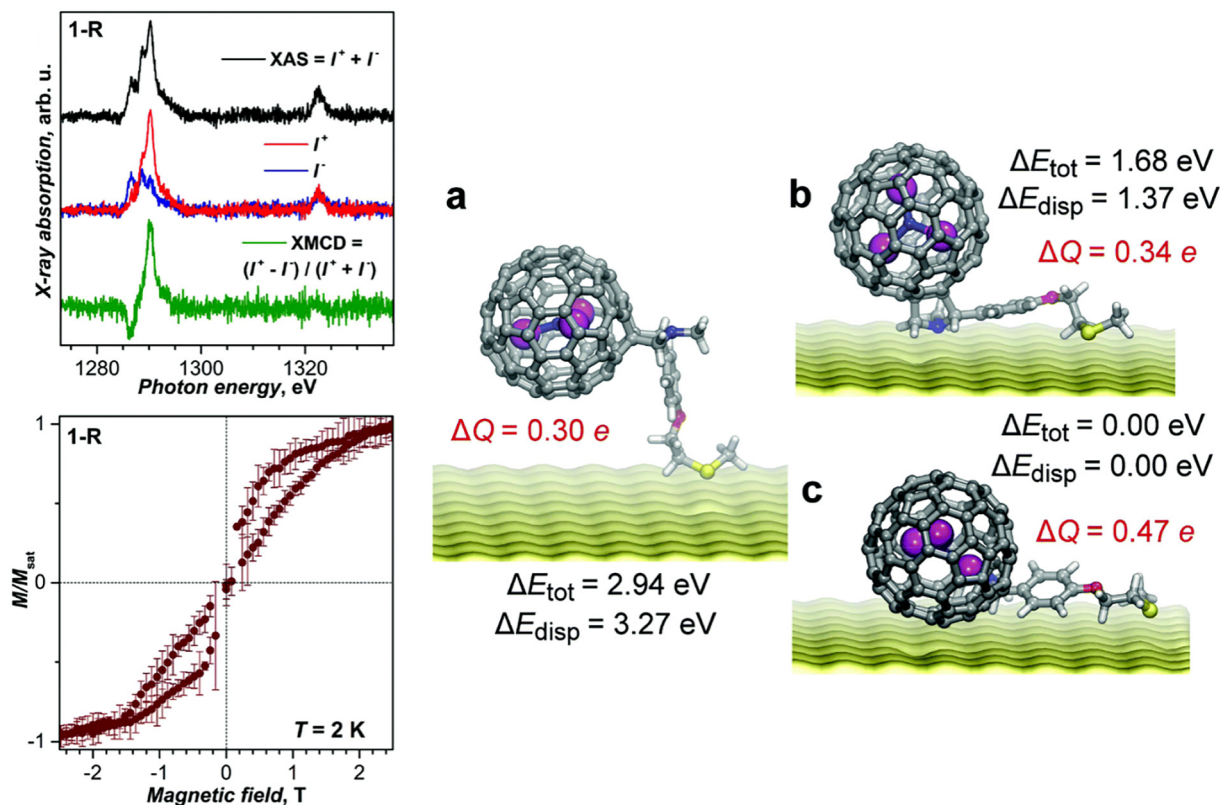


Fig. 7. XAS and XMCD spectra for Dy-EMF at the Dy-M_{4,5} absorption edge measured at 2 K in the magnetic field of 6.5 T. Magnetization curves of sub-monolayers of Dy-EMF obtained from XMCD data at 2 K. (a, b, c) Cartoons of the DFT calculated dispositions of functionalized EMF on a surface. Adapted from reference [76] with permission from the Royal Society of Chemistry.

erties when deposited on a surface. This hampered many proposals of molecular-based devices. XAS and XMCD data on surface deposited Mn₁₂ could finally explain this fact: most of the data show that Mn₁₂ is reduced on the surface, as XAS and XMCD data unambiguously show presence of Mn(II). The lack of SMM behavior of Mn₁₂ on surfaces is ascribed to the reduction of part of the Mn(IV) and/or Mn(III) to Mn(II). Sessoli *et al.* also review their most significant work with Fe₄ SMMs, and it is using XMCD that they unambiguously show that SMM behavior is possible after surface deposition by measuring at millikelvin temperatures the hysteresis loop of an Fe₄ SMM deposited on a surface.[31] More recently, Dreiser *et al.* showed using XMCD the hysteresis loop of a single TbPc₂ molecule on a MgO/Ag surface.[75].

For the particular case of Fe(II) spin crossover (SCO) complexes, where the Fe(II) ion transitions reversibly between an $S = 2$ high-spin (HS) state and an $S = 0$ low-spin (LS) state due to an external stimulus like a change of temperature, XMCD can be very useful; the fitting of the XAS and XMCD spectra can lead to the relative proportion of HS and LS states and thus can be used to follow the transition. Other techniques, like near-edge X-ray absorption fine structure (NEXAFS) have also been used in the specific case of SCO molecules. NEXAFS is a synchrotron-based technique that has been commonly employed to determine the spin state of spin crossover complexes on surfaces. Like XAS, NEXAFS is based on electronic transitions from core states to unoccupied states. In Fe (II) complexes, the Fe L₂ ($2p^{1/2} \rightarrow d$) and L₃ ($2p^{3/2} \rightarrow d$) edges are characteristic and the resultant absorption spectrum depends on the unoccupied orbitals, which in turn depends on the spin state. Moreover, X-ray photons can induce the switch from LS to HS in a process called soft X-ray induced spin-state trapping (SOX-IESTT),[79] analogous to the well-known light-induced excited spin-state trapping (LIESST).[80].

4. Types of surfaces

4.1. Deposition on conventional substrates

Device design must consider the choice of substrate as of crucial relevance for the properties needed for the envisioned application. In this context, characteristics like conductivity or magnetism must be taken into consideration. Thus, the most interesting substrates for magnetic molecules are conductive, semiconductive and magnetic substrates, with an atomically defined surface. For several years, metallic substrates have been the most studied, the most usual being noble metals that can be obtained as single crystals like Cu or Au. Au (111) is a gold single crystal that is cut along the crystallographic (111) plane or metallic gold deposited on a flat substrate like mica or glass and annealed to reconstruct the (111) plane. This provides an ordered and known surface.[81] Single crystals of gold and other metals are conductive and thus can be used for techniques such as STM. Nevertheless, deposition on bare metal substrates is not the only option. Indeed, pre-functionalized metallic surfaces have also garnered attention due to the possibility of anchoring molecules by intermolecular interactions like hydrogen bonds,[82] by electrostatic forces [83] or by forming covalent bonds.[84] This last method has been broadly used, since Au surfaces can be prepared for molecule deposition with SAMs of functionalized thiols, which expose a functional group that can bind to the desired magnetic molecule. Additionally, single crystals of copper, silver and other metals have also been widely employed for the deposition of Fe₄ SMMs [85] or simple metal porphyrins.[86] One of the main advantages to using these sorts of materials is their resistance to oxidation. Important questions to elucidate are whether the deposited molecules form self-assembled structures, whether their structure is kept intact

after contact with the surface and most importantly, if their magnetic properties are not perturbed once they are attached to the surface. Simple flat molecules like metal phthalocyanines are known to couple strongly to a magnetic and metallic surface. [87,88].

For specific applications, semiconductor or magnetic surfaces might be needed. Silicon is one of the most versatile materials for this purpose, as it is already the most used substrate in current electronic devices. Apart from that, it is cheap and can be obtained with an atomically defined surface that can be easily functionalized, or the outermost layer thermally oxidized to SiO₂ creating a layer of a few nm of SiO₂ over the Si wafer. This oxide layer can be easily removed by treatment with diluted HF to obtain pristine silicon.[89] The two main routes for functionalization are well understood and are based on the formation of Si-H or Si-OH motifs on the surface of the wafer. Hydrosilylation, the addition of a Si-H bond to an insaturated C=C bond, is used to anchor molecules that have been functionalized with a terminal C=C bond on silicon wafers.[90] For silica or SiO₂/Si, the surface is activated by O₂ plasma or treatment with freshly prepared piranha solution (an aqueous solution of H₂SO₄ and H₂O₂). This renders the surface rich in Si-OH and reaction with a suitable molecule can result in chemisorption of the molecular species on the surface. Other Si-based materials can also be used: quartz is suitable for molecular deposition, for example of thin films of spin-crossover (SCO) molecules.[91].

In specific research fields like spintronics, it is relevant to study the properties of magnetic molecules deposited onto ferromagnetic electrodes. Several studies have been conducted using cobalt [92] and nickel[88] or other magnetic materials like epitaxially grown Fe₃O₄. [93] One main issue is the uncontrolled atmospheric oxidation of the metal surface, but this can be avoided by working in UHV or in a controlled inert atmosphere. Surfaces like Co and Ni are usually generated by sputtering the metal on a silicon wafer or a similar flat surface. The thickness of the resulting metal layer can range from several nanometers to micrometers. Uncontrolled surface oxidation may give rise to a surface that is not atomically defined and this can hinder the study and characterization of the resulting system. The molecular interaction with a surface, magnetic or not magnetic, must be controlled when one wants to develop a device where single molecular properties are to be exploited, since strong coupling between the surface and the molecule is often observed and therefore molecular properties are altered. In particular, for magnetic substrates the magnetic properties of the substrate must be carefully considered when the molecule's magnetic properties on the surface are assessed [87,88].

Alternatively to the aforementioned substrates, carbon allotropes such as HOPG, carbon nanotubes (CNTs) and graphene have also been employed as substrates for functional molecules. Advantages of HOPG are its low cost and its conductivity while it allows for weak Van der Waals, CH- π and π - π interactions with the deposited molecules, providing an interesting approach for nanostructuring of molecules rich in aromatic groups.[23,94] Regarding CNTs, the molecular-CNT hybrid materials investigated arise from ligand functionalization of the molecule of interest with aromatic groups to form π - π stacking interactions with the CNTs and they are of great interest for fields such as molecular spintronics or single-molecule electronics.[95] CNTs have also been used to encapsulate magnetic molecules.[96] Graphene, on the other hand, has been used as an intercalating layer between a metallic substrate and the magnetic molecule, with the purpose of dampening their interaction and therefore maintaining the molecule's properties [77,97].

In addition, less common surfaces like semi-metallic Bi (1 1 1), [98] hexagonal boron nitride (h-BN),[99] or chalcogenides [100] have also been used as substrates for the deposition of magnetic

molecules. Superconducting substrates have gained a lot of attention over the last few years, like superconducting Pb [101] or superconductor NbSe₂. TbPc fragments on NbSe₂ have been deposited to study the magnetic coupling between the Tb angular momentum and the radical Pc spin [58].

4.2. Deposition on nanoparticles

Nanoparticles (NPs) are considered useful surface models. Over the last years, several reliable procedures have emerged for the synthesis of different size and shape nanoparticles [102] in a very reproducible manner. These may be crystalline materials and can exhibit crystalline facets. The magnetic iron oxides maghemite (Fe₂O₃) or magnetite (Fe₃O₄) form nanoparticles that are superparamagnetic and monodomain, and are generally called superparamagnetic iron oxide nanoparticles (SPIONs) or simply IONPs. Metal NPs are also well-known but their surface oxidation is enhanced by the NPs' high surface/bulk ratio. Noble metals Au and Ag can be prepared as NPs with extensive control of size and shape. Nanoparticle decoration with molecules on their surface, called surfactants or ligands, has been widely studied and reproducible routes have been reported. NPs can be treated and functionalized in solution but they can also be obtained as a bulk material by centrifugation, magnetic separation or precipitation. The solids obtained are homogenous materials formed by individual NPs covered by a regular layer of surfactants or ligands: these ligands can be a magnetic molecule of interest. Thus, the problems of detection inherent to monolayers of molecules on a surface, even to state-of-the art detectors can be overcome by preparing large quantities of the molecule/NP material, this is particularly helpful for magnetic characterization using SQUID magnetometry. Functionalized NPs are really easy to manipulate in a chemical laboratory and the materials prepared can be readily characterized, using techniques like electronic spectroscopy or luminescence of a dispersion of NPs, elemental analyses, IR or solid-state SQUID magnetometry. Thus, the decoration of nanoparticles with magnetic molecules is a good alternative to study the interaction of said molecules with certain surfaces. The studies of NP functionalization or decoration for drug delivery [103,104] or catalysis [105] are really numerous, however research devoted to NP functionalization with magnetic molecules is still limited to a few papers that we will review here. IONPs are a great choice to gain insight on the magnetic interaction between isolated molecules or monolayers of magnetic molecules with a magnetic surface. Sañudo *et al.* showed that the SMMs grafted onto magnetite NP can retain their magnetic properties like QTM or intermolecular magnetic coupling in the hybrid system.[74,106] Zoppellaro and co-workers showed how the local magnetic field of the NPs can be used to change the properties of a softer magnetic shell, in which they are embedded.[107] The layer of molecules that decorate the NPs, often called shell in an analogy to core-shell magnetic NPs, can also affect the properties of the core material. In 2015 Prado and coworkers showed how the Fe₂O₃ NP magnetic properties were altered by surface modification with a paramagnetic system: a hysteresis enhancement was observed for Fe₂O₃ NPs with Co(II) paramagnetic complexes covalently grafted to the surface.[108] A similar hysteresis enhancement was observed for IONPs decorated with Dy(III) SMMs that displayed hysteresis at temperatures as high as 30 K for the hybrid system but not for the isolated parts.[109] A organic SAM in the previous and in the Co₄Dy SMMs case [110] results in the magnetic integrity of the SMMs while on the magnetic surface, while it is also effective to allow synergy between the properties of the SMM that affect the magnetic substrate magnetization hysteresis.

After IONPs, the most used system are Au NPs. In 2013, Murugesu *et al.*, showed that the coordination bond between the NP sur-

face and the SMM affected the magnetization relaxation properties of the SMM, this emphasized the necessity to control the magnetic interaction between a magnetic molecule and the surface.[111] In 2014, Sessoli and co-workers observed a change in the relaxation dynamics of Fe_4 SMMs grafted onto Au NPs.[112] Piligkos and coworkers combined a surface deposition study on Au with the decoration of Au NPs with a chiral SMM and demonstrated the retention of the magnetic behavior and optical activity for the surface deposited species.[113].

Surface-confined coordination chemistry is a great tool that can lead to unprecedented low coordination-number environments for the metal ions, leading to in theory exceptional magnetic properties. Silica nanoparticles can be prepared easily and afford a very suitable platform for on-surface chemistry. Exploiting carboxylato-exchange reaction of Mn_{12} -esterate Mn_{12} SMMs have been chemisorbed on spherical silica NPs. The energy barrier and mean relaxation time are found to be comparable to the bulk compound.[114] Isolated Dy(III) ions can be immobilized on silica NPs [115] and be used as a starting material for on-surface chemistry. On surface synthesis of Dy(III)-Cp* and Dy(III)-COT derivatives that are magnetically isolated from the neighbors have been prepared with success. However, the sought-after high-temperature hysteresis of the magnetization has not yet been achieved [116–118].

5. Deposition of magnetic molecules on surfaces

Molecules with interesting magnetic properties as SMMs, spin crossover (SCO) molecules or qubits are interesting candidates for surface deposition and implementation of spintronic devices, information storage or information processing devices. For surface deposition, the molecules should have shape anisotropy to favor one single orientation of the molecule on the surface and either be soluble (for wet deposition methods) or sublimable (for vapor deposition). In some instances, ligand modification, for example with large aliphatic groups like *tert*-butyl or by fluorination can be done in order to improve ease of sublimation of a particular compound. Good knowledge of the phase diagram of the molecular material is thus necessary to find a good candidate for evaporation. It is often possible to make the sublimation conditions less strenuous by reducing the pressure and increasing the vapor pressure of the solid using functional groups that lead to weaker intermolecular interactions like the aforementioned *tert*-butyl groups or fluorines.

Chemical flexibility is desirable to achieve molecular functionalization for chemisorption. If good magnetic properties coexist with shape anisotropy and either solubility or sublimation capacity in one molecule, we have a good candidate for surface deposition, as depicted in Fig. 8. The most studied molecules, Mn_{12} , Fe_4 and Cr_7Ni families all have these characteristics, their shape anisotropy can be observed in Figs. 9, 10 and 11.

5.1. Mn_{12} SMMs

A dodecanuclear manganese carboxylate with formula $[\text{Mn}_{12}\text{O}_{12}(\text{Ac})_{12}(\text{H}_2\text{O})_4]$, where Ac = acetate, CH_3COO^- , was the compound for which SMM properties were described for the first time.[1] Its synthesis and structure had been reported several years earlier by Lis.[122] The crystal structure of $[\text{Mn}_{12}\text{O}_{12}(\text{Ac})_{12}(\text{H}_2\text{O})_4]$ is shown in Fig. 9. The compound can be described as a central $[\text{Mn}(\text{IV})_4\text{O}_4]$ cubane surrounded by a $[\text{Mn}(\text{III})_8\text{O}_8]$ ring. All Mn ions display octahedral coordination completed by 4 H_2O molecules and 16 carboxylato ligands. The R group of the carboxylato ligands can be changed practically at will.[123] In this paper, we call Mn_{12} any derivative of the original complex. This complex, with a large spin ground state of $S = 10$, was found to exhibit magnetic hysteresis with coercive fields up to 1.5 T at 2 K from pure molecular origin.

Each single molecule of Mn_{12} behaves as a nanosized magnet. Apart from its interesting magnetic properties and facile synthesis, its molecular structure and chemical properties allowed chemists to develop Mn_{12} derivatives via ligand-exchange reactions, producing a large family of compounds.[123] The solution equilibria related to the carboxylato ligands on the Jahn-Teller axes of Mn (III) are responsible for the chemical versatility of Mn_{12} SMMs and allow the ligand exchange reactions to obtain heteroleptic compounds. Additionally, exploiting the low-boiling point azeotrope acetic acid/toluene, the substitution can be total to afford new Mn_{12} species with 16 new carboxylato groups. Mn_{12} has been one of the most studied molecular species regarding the deposition of thin films of molecules on surfaces. The same mixed-valent nature of Mn_{12} is however at the core of the shortcomings for surface deposition: Mn_{12} can be easily reduced and oxidized, as shown by Christou.[123] The availability of several oxidation states for Mn_{12} with potentials that depend on the R group of the carboxylato ligands originates the instability of Mn_{12} on surfaces. Nevertheless, the studies on Mn_{12} deposition have pioneered the way towards depositing and addressing single-molecules on surfaces in a controlled manner.

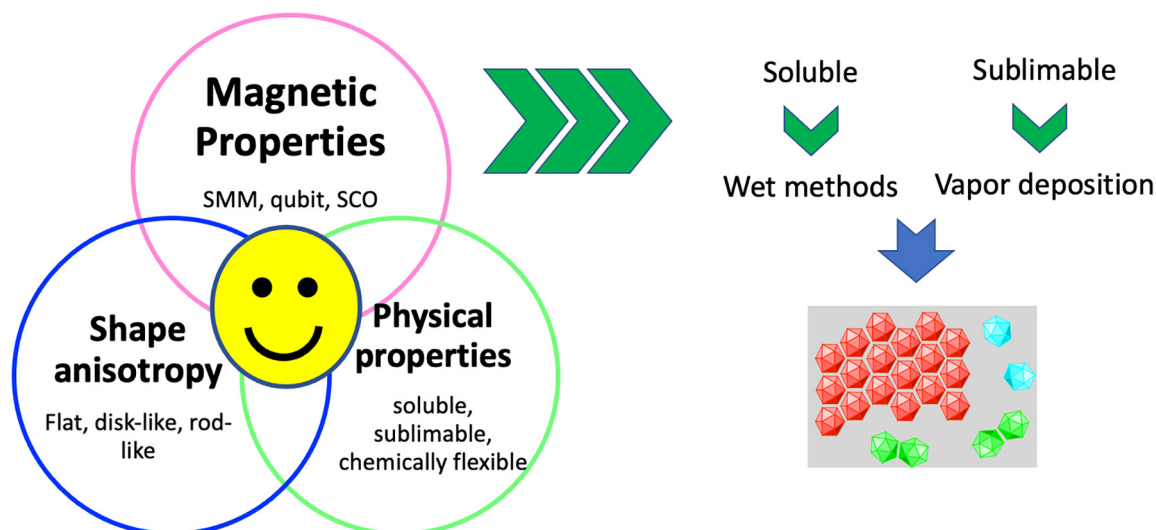


Fig. 8. Schematic representation of the desired molecular characteristics to achieve optimal surface deposition.

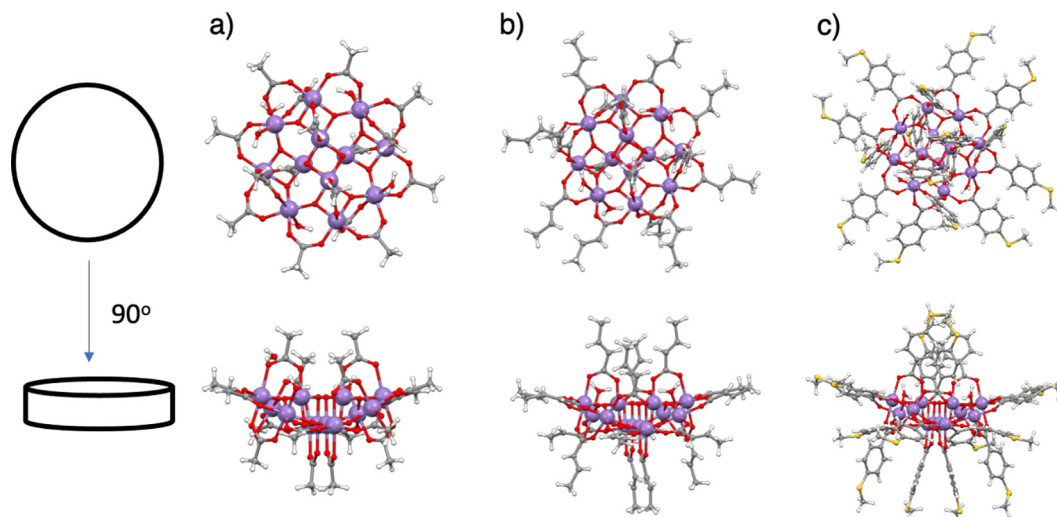


Fig. 9. Crystal structure of several Mn_{12} derivatives, compared to the disc-shape of the molecule. $[Mn_{12}O_{12}(L)_{16}(H_2O)_4]$, with L =(a) acetate, CH_3COO^- ; [119] (b) 2-butenate, $CH_3CHCHCOO^-$; [120] and (c) 4-(methylthio)benzoate, $CH_3SC_6H_4COO^-$; [121].

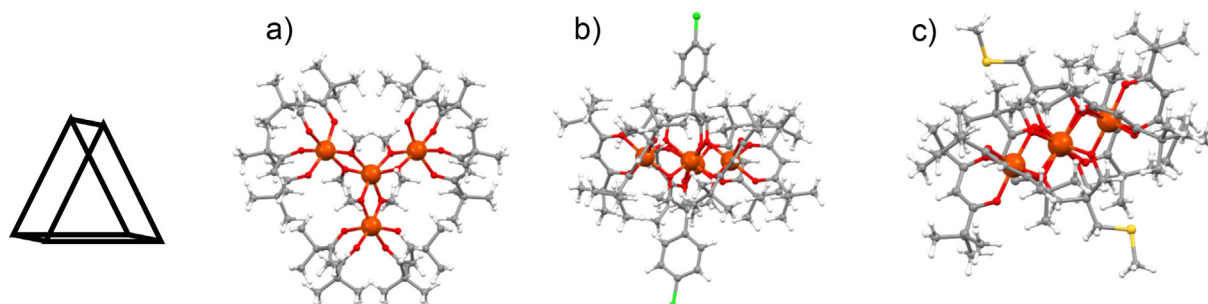


Fig. 10. Crystal structure of several $[Fe_4(L)_n(dpm)_6]$ derivatives, where Hdpm = dipivaloylmethane, $(CH_3)_3CCOCH_2COC(CH_3)_3$. (a) Top view of $[Fe_4(L)_6(dpm)_6]$, HL = methanol, CH_3OH ; [136] (b) side view of $[Fe_4(L)_2(dpm)_6]$, H_3L = 2-(4-chloro-phenyl)-2-hydroxymethyl-propane-1,3-diol; $Cl(C_6H_4)C(CH_2OH)_3$ [137]; (c) side view of $[Fe_4(L)_2(dpm)_6]$, H_3L = $CH_2SCH_3C(CH_2OH)_3$; [101].

The first achievement on preparation of a Mn_{12} thin film was published in 1998 by Coronado and coworkers. About 300 layers of the Langmuir-Blodgett film were deposited on a mylar substrate to study the magnetic properties of the film. The thin films of ordered Mn_{12} molecules presented magnetic anisotropy of the orientation of the film with respect to the external magnetic field. [124] Five years later, the deposition of Mn_{12} on Au(111) was reported by Cornia and coworkers. [125] Many different attempts have been made since then on the same surface by exploiting the chemical flexibility of Mn_{12} to obtain gold-sulfur bonds [121,126,127] or electrostatic interactions [83] by ligand functionalization. Mn_{12} complexes have also been deposited on crystalline Si (100), [90] silica nanoparticles, [128] semi-metallic Bi (111), [129] polymeric thin films, [130,131] Cu (001) or BN on Rh(111). [132].

Due to the thermal instability of Mn_{12} , sublimation is not viable since the molecule degrades. Therefore, alternatives such as electrospray deposition, [42,43,132] low energy laser ablation, [45] pulsed laser evaporation [46] and vacuum spray deposition [44] have been tested for Mn_{12} . Deposition of single Mn_{12} molecules has also been achieved by using an STM tip [129] and surface arrangements have also been performed by microcontact printing [47] and electron beam lithography. [51] Most of the early studies of surface deposition were performed using Mn_{12} or a suitably functionalized derivative. [133–135] Unfortunately, the fragility of Mn_{12} did not allow researchers to observe the desired molecular properties once the Mn_{12} was deposited on a surface, but the

knowledge gained from deposition of such a complex molecule as Mn_{12} on surfaces paved the way for many of the more successful efforts that were to come.

5.2. Fe_4 SMMs

After the interest that Mn_{12} produced among the scientific community, many groups directed their research towards the synthesis of new examples of compounds with SMM properties. The complexes known as “iron stars” became relevant due to the chemical flexibility towards functionalization, and their robustness. $[Fe_4(-CH_3O)_6(dpm)_6]$, where Hdpm = dipivaloylmethane, $(CH_3)_3CCOCH_2COC(CH_3)_3$, is a tetranuclear Fe(III) complex that presents single-molecule magnet behavior reported for the first time in 1999. This compound consists of a cluster of four Fe(III) ions with the shape of a star, featuring one Fe(III) in the center linked to the other three *via* alkoxide bridges, as shown in Fig. 10. [136] The methoxido ligands can be substituted by tripodal ligands, leading to a large family of complexes that in this review will be called Fe_4 . Some examples are shown in Fig. 10 (b) and (c), where tripodal alkoxides with functional groups provide a unique binding mode for the molecule on a surface. In this way, when a chemisorbed layer forms, all the molecules should have the same orientation with respect to the surface.

Since it is possible to tune the terminal and bridging ligands, many derivatives of the original molecule have been reported. Thus, it is possible to choose the appropriate ligands to favor

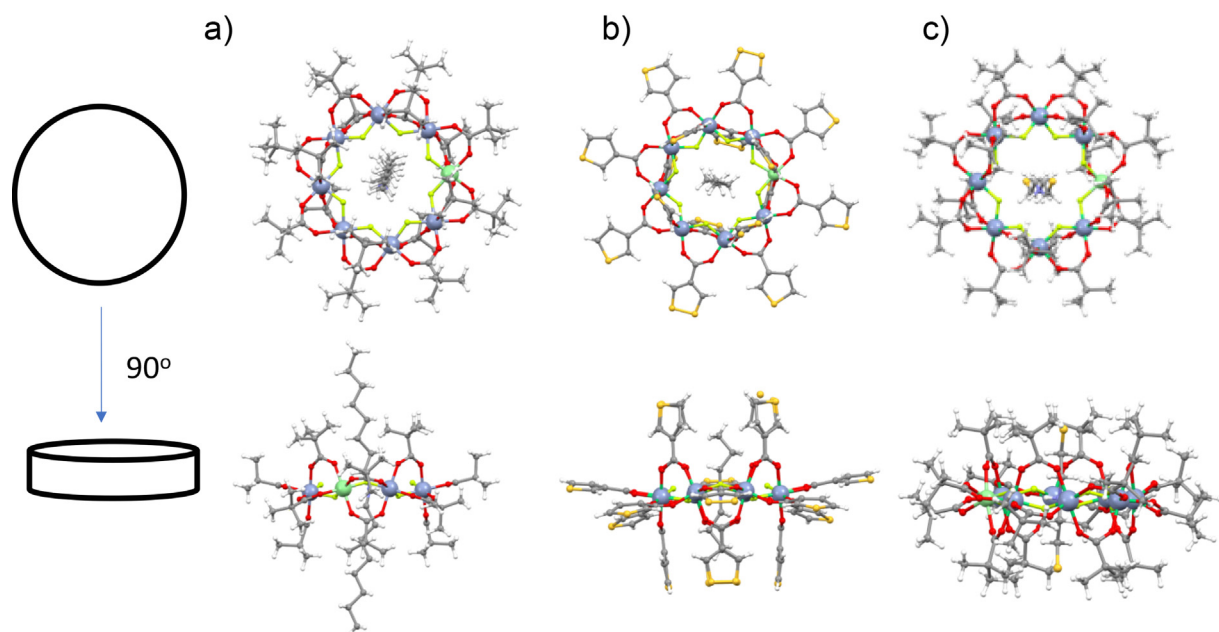


Fig. 11. Crystal structure of several Cr_7Ni complexes that show the disc-like nature of the compound. (a) A long ammonium chain to induce VdW interactions (R_2NH_2) [$\text{Cr}_7\text{NiF}_8(\text{tBuCOO})_{16}$] where $\text{R} = n\text{-octyl}$, C_8H_{16} ; [143] (b) a S-containing group functionalized carboxylato ligand derivative for chemisorption on $\text{Au}(111)$ (NH_2Pr_2)[$\text{Cr}_7\text{NiF}_8(3\text{-tpc})_{16}$], where 3-Htpc = 3-thiophenecarboxylic acid, $\text{C}_5\text{H}_4\text{O}_2\text{S}$; [144] (c) a derivative with a thiol-functionalized ammonium ($\text{tBuNH}_2\text{CH}_2\text{CH}_2\text{SH}$)[$\text{Cr}_7\text{NiF}_8(\text{tBuCOO})_{16}$]; [144].

desired molecule–substrate interactions (i.e. chemisorption or physisorption), to obtain molecules that can be sublimated and to induce a preferred orientation on the substrate. The spin ground state of Fe_4 ($S = 5$) is highly populated at 20 K and displays axial magnetic anisotropy. These features produce the slow relaxation of the magnetization of the molecule at temperatures below 1 K. The blocking temperature (T_B) of these compounds is much lower than the current record of 80 K [8] and at the time it was reported, the magnetic properties were not an improvement with respect to the standard SMM Mn_{12} . The work on Fe_4 allowed to demonstrate that slow relaxation of the magnetization can be still be observed upon deposition on metal surfaces [31] and also allowed the observation of the characteristic field dependence of the relaxation rate due to resonant QTM for SMMs wired to a surface. [33] These two key results were a significant stimulus to the field, since the work on Mn_{12} had put into question whether SMMs could be deposited intact on surfaces while at the same time retaining their magnetic properties. These results showed that, indeed, nanomagnets and SMMs could retain their individual magnetic properties upon surface deposition.

Following the work done on Mn_{12} , functionalization of Fe_4 with S-containing group containing ligands and alkenes were studied to target chemisorption on gold substrates [31,138–140] and on H-terminated silicon [30,137], respectively.

Unlike Mn_{12} , which decomposes at high temperatures, there are some derivatives of Fe_4 that can be sublimated under UHV conditions directly over a substrate. These derivatives are [$\text{Fe}_4(\text{Ph-C}(\text{CHOO})_3)_2(\text{dpm})_6$] [26] and fluorinated variants. [141,142] For Fe_4 derivatives that are not thermally stable, electrospray deposition (ESD) has been successfully used [77,99].

5.3. Cr_7Ni complexes

The family of molecules with general formula $(\text{R}_2\text{NH}_2)[\text{Cr}_7\text{NiF}_8(\text{RCOO})_{16}]$ has been extensively studied over the last years. These compounds will be called Cr_7M in this review. The Ni derivatives, Cr_7Ni , have been proposed and studied as qubits for quantum com-

putation. [145,146] The parent molecule of this family is [$\text{Cr}_8\text{F}_8(\text{tBuCOO})_{16}$]. It is a regular ring of 8 Cr(III) ions organized in a regular octagon with one fluoride bridge between each pair of Cr(III) ions. [147] Timco and Winpenny showed that it is possible to selectively substitute one of the Cr(III) ions for a M(II) ion forming a negatively charged Cr_7M compound with a threaded secondary ammonium as a counterion, also serving as template of the selective formation of the heterometallic species. Fig. 11 shows the crystal structure of several Cr_7M derivatives. The divalent metal M(II) could be Ni(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II) or Cd(II). Thus, the total spin of the ground state can be tuned depending on M(II). Cr_7M where $\text{M} = \text{Ni(II)}$ has been the most widely studied system because it has a ground state of $S = 1/2$, rendering them potential qubit realizations [143,148].

The richness of the chemistry of the Cr_7Ni rings makes them excellent candidates for functionalization and further deposition on surfaces: the M(II) can be selected, tuning the spin; the carboxylate can be chosen to afford solubility, the possibility of sublimation or a grafting group; the Cr(III) can be substituted by other M(III) ions, like Ga(III), In(III) or V(III), to tune the magnetic properties. [149] Additionally, the stability in solution in non-coordinating solvents of the Cr_7M rings had been demonstrated by paramagnetic NMR studies on the Co(II) derivative [150], thus making these compounds ideal candidates for deposition from solution, while not limited to wet deposition techniques. The family of Cr_7M compounds are also thermally stable and thus amenable to deposition by sublimation. To graft and address single Cr_7Ni molecules on surfaces, specific derivatives were required in order to enhance the interaction with the substrate and the chemical versatility of these compounds made this possible. In a study comparing the deposition by sublimation of a Cr_7Ni with a thiol-functionalized dibutylammonium to the original dibutylammonium Cr_7Ni , Affronte and Winpenny showed that monolayers of Cr_7Ni of the original complex were ordered as weak Van der Waals forces allowed the molecules to self-assemble on the surface, while the thiol derivative formed disordered monolayers. The strong Au-S bond precluded the reorganization of the monolayer on the gold

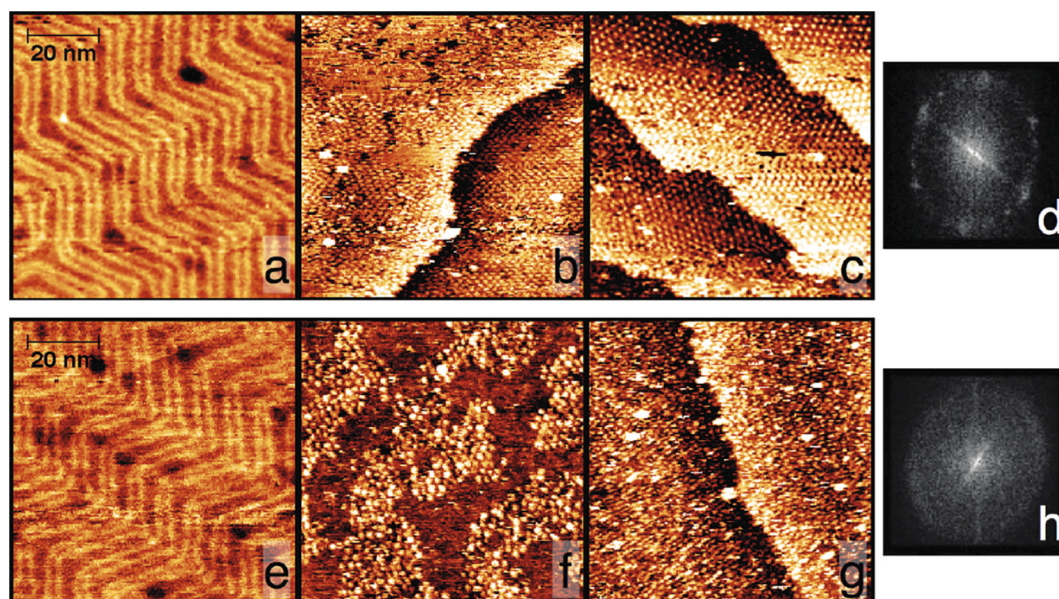


Fig. 12. STM images showing the SAM of Cr₇Ni molecules (top panel) as compared to the more disordered, covalently linked Cr₇Ni-SH complexes on Au(111) (bottom panel). Reprinted (adapted) with permission from [22]. Copyright© 2011 American Chemical Society.

surface, STM images are shown in Fig. 12. The magnetic properties upon deposition were confirmed by means of STM, XPS, XAS and XMCD.[22].

The deposition on Au surfaces of derivatives with S-containing groups built on the carboxylato ligands was also investigated. The compound (NH₂^{Pr})[Cr₇NiF₈(3-tpc)₁₆] (where tpc = tiophene carboxylate) was synthesized and deposited onto Au(111) by immersion of the substrate into a THF solution of the said molecule, taking advantage of the strong affinity between sulfur and gold. Clusters of Cr₇Ni were observed by means of STM and XPS. The compound (tBuNH₂CH₂CH₂SH)[Cr₇NiF₈(O₂C^tBu)₁₆] was also reported in the same paper. In this case, the only sulfur moiety present was the counterion that is held in the center of the Cr₇Ni ring by electrostatic forces—as demonstrated in NMR studies for Cr₇Co.[150] In both cases, despite observing 2D distributions of isolated molecules, low coverage of the surface by Cr₇Ni occurred while SAMs of free thiolammonium species were found. This highlighted the necessity to understand the stability of the compound in the deposition conditions.[144] Following this line of work, the compound Cr₇Ni-4mtpp (Et₂NH₂)[Cr₇NiF₈(O₂CCH₂tBu)₁₅(O₂CCH₂CH₂-C₆H₄SCH₃)] was synthesized in order to attain chemisorption on a gold substrate. In this derivative, one of the sixteen pivalato ligands to the Cr₇Ni ring was substituted by a thiol-bearing derivative and it led to coverages of up to 35 % of the total surface of the gold substrate. Additionally, the pivalato derivatives were also deposited on gold. In this case, Van der Waals interactions are responsible for the physisorption of the Cr₇Ni rings to the Au surface thus, resulting in lower coverages. XAS and XMCD were performed to study the chemical and magnetic properties of the deposited Cr₇Ni molecules, indicating that the electronic properties were not affected with respect to those in the bulk, whereas the magnetic properties presented a slight variation in the exchange coupling but without affecting the possibility to exploiting them as qubits.[34].

The deposition of the Cr₇Ni nanomagnets on surfaces is a story of success. A good part of this success can be attributed to the chemical versatility of the system that allows practically “at-will” functionalization and also to the molecular stability in a wide variety of deposition conditions, from solution to vapor phase deposition. Winpenney and co-workers opened up new technological uses

of surface-deposited nanomagnets by recently reporting the deposition of a 5 nm layer of [Cr₈F₈Piv₁₆] and its use as a resist to obtain sub-10 nm structures in silicon and tungsten[151] using an ion beam lithography and etching process.

5.4. Double-decker lanthanoid phthalocyanine (LnPc₂) complexes

The complexes known as double-decker lanthanoid phthalocyanines LnPc₂ consist of two phthalocyanine (C₃₂H₁₈N₈) ligands with a lanthanoid ion bonded to the two ligands in a sandwich or double-decker complex, shown in Fig. 13. The general formula of these complexes is [Ln(III)Pc₂]ⁿ (n = 0, -1) where n is the charge of the complex.[152] The structure of the ligand is shown in Fig. 13, it can display two states, -2 fully deprotonated or a radical -1 state. The radical is stabilized by the aromatic system of the Pc. The planar nature of the ligand is one great asset for surface deposition. The Pc ligand has four aromatic groups and, in the complex, the two ligands are rotated with respect to each other by 45°, as shown in Fig. 13 (c). If both Pc ligands are completely deprotonated the compound is an anion LnPc₂⁻. On the other hand, the compound can be neutral when one Pc is a radical, stabilized through conjugation. The most studied lanthanoid in these complexes is terbium(III), which, by Hund's rules, has magnetic momenta L = S = 3 and J = 6. In the anionic compound, both phthalocyanines are double negatively charged and thus have closed-shell configuration. The magnetism, then, arises strictly from the terbium ion. In the neutral TbPc₂, the unpaired electron provides an additional S = 1/2 center.[153].

Although phthalocyanine complexes had been thoroughly studied in the past, it was not until 2003 that their dynamic magnetic properties were investigated in detail. Ishikawa and coworkers studied the family of phthalocyanine molecules (TBA)[LnPc₂], where Ln = Tb, Dy, and TBA⁺ = N(C₄H₉)₄⁺. These were found to exhibit SMM behavior at temperatures much higher than that previously seen for transition metal SMMs.[154] Apart from being the first lanthanoid SMMs, they represented the first mononuclear species showing SMM properties and thus they were called single ion magnets (SIMs) or mononuclear SMMs. Ishikawa *et al.* reported the magnetization hysteresis at 1.7 K and detailed ac susceptibility measurements for (TBA)[TbPc₂] and (TBA)[DyPc₂] and discussed

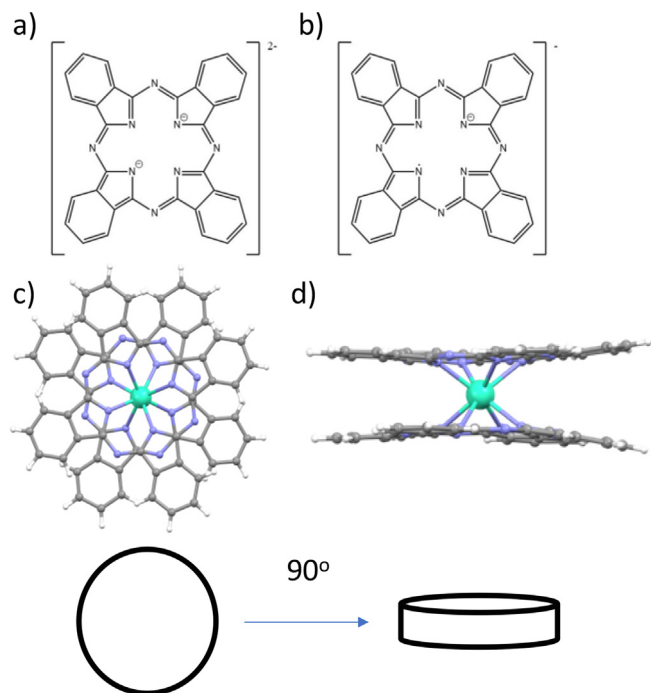


Fig. 13. The structure of the (a) Phthalocyanine dianion and its (b) deprotonated phthalocyanine radical form. (c) Top view of the crystal structure of TbPc₂ with the alternated position of the phenyl rings of the top and bottom Pc ligands. (d) shows a 90° rotation from (c), where the sandwich or double-decker structure of the complex is clearly appreciated. Below (c) and (d) a cartoon disk-like shape of the molecule.

the mechanisms of the magnetization relaxation, concluding that this was dominated by a Raman process below 25 K and an Orbach process at 25–40 K.[155] Later on, Ishikawa and Wernsdorfer reported the observation of quantum tunneling of the magnetization for the same Dy and Tb compounds, resulting from the coupling between the electronic and the nuclear spin of the metal ion.[156] In 2009, Kyatskaya *et al.* reported the anchoring of a heteroleptic Tb(PcPc) complex on single walled carbon nanotubes (SWCNTs). The fast relaxation of the magnetization at zero field due to quantum tunneling was still observed, but the hysteresis loop was more open due to the reduced intermolecular interactions in the TbPc₂ complexes on the nanotubes conjugate.[24] The properties of lanthanoid-phthalocyanine complexes and their coupling to magnetic surfaces [157] and the magnetic properties of surface confined TbPc₂ SMMs have been extensively reviewed.[54].

The well-known chemistry of phthalocyanine ligands leads to excellent examples of tailored Pc functionalization for surface deposition. Ligand design was exploited to chemically bond TbPc₂ to a silicon substrate [158] and to an oxide.[159] A very nice example of surface modification and ligand modification with complementary H-bonding groups was reported in 2018, where functionalized TbPc₂ complexes were deposited on functionalized silicon exploiting multiple H-bonding. A submonolayer was obtained and studied by XAS, XMCD and XNLD. The anchoring of TbPc₂ molecules is robust and the organic linker ensures that the TbPc₂ molecules can be used in spintronic devices independent of the substrate.[82].

The high blocking temperatures observed in the ac data for these compounds imply large energy barriers for the relaxation of the magnetization. It is known that dipolar interactions like those found in the bulk material trigger QTM so the opening of hysteresis loops of the magnetization vs field expected for these spe-

cies from the ac data at the high temperatures were not observed. The double-decker type of structure places the ligands above and below the lanthanoid. Rinehart and Long established in their 2011 paper [160] using a quadrupole approximation of the 4f-shell electron distribution that such a ligand arrangement is the most favorable to attain large anisotropies for Dy and Tb. Thus, these compounds are ideal candidates for surface deposition where isolated molecules should display M vs H hysteresis at high temperatures. By drop casting, two-dimensional ordered assemblies of neutral TbPc₂ and DyPc₂ were observed on HOPG by means of STM.[161] Even though the TbPc₂ molecule displays a clear disk-like shape, molecules in different orientations have been observed by STM. To further favor the ordering on the substrate, long-chain alkane substituted phthalocyanines were employed. This strategy presented in prior studies relies on the supramolecular interactions between aliphatic chains.[162,163] TbPc₂ molecules were deposited onto Cu(111) in order to study their electronic structure when supported on a substrate. Deposition was performed by a dry imprinting technique, which consists of stamping fine-grained TbPc₂ crystals onto the copper substrate using a soft applicator. By means of STM, single molecules and clusters were observed and in turn their stability in UHV was corroborated. ST showed that the TbPc₂ molecules lie flat on one of the Pc ligands without any specific order, even if the sample was heated up to 550 K, indicating a strong molecule-substrate interaction. Experimental dI/dV spectra suggested that the electronic structure of the molecules was not affected by the copper substrate.[164] Thermal stability was also verified, indicating that LnPc₂ molecules can be sublimated without degradation.[165,166] This can explain why so many studies are reported on these molecules on surfaces: the possibility of creating clean sub-monolayers by evaporation has been crucial in the attention LnPc₂ complexes have received by the community.

A detailed study on the magnetic properties via XMCD and XAS of TbPc₂ on HOPG was reported by Biagi *et al.*[94] In this paper, both anionic and neutral molecules were deposited (in two different experiments) by drop casting. Depending on the concentration, submonolayers (~0.7 nm) or thick films consisting of several monolayers were obtained and observed by STM and AFM. The measured properties were independent of the film's thickness and similar to the bulk, indicating that these were not affected upon deposition. However, no magnetic hysteresis was observed, a key property for the potential use of these compounds in real devices. Narrow hysteresis loops were observed in different non-magnetic substrates such as Au(111)[167] or Cu(111)[168]. In 2011, Veciana and coworkers reported a narrow magnetic hysteresis for TbPc molecules deposited by drop casting onto HOPG.[169] An important breakthrough was published in 2016, when Ruben and Dreiser reported the observation of giant hysteresis of isolated adsorbed TbPc₂ molecules.[75] To achieve this, an insulator MgO layer was deposited onto Ag(100) to act as a tunnel barrier between the SMM and the metal substrate. The magnetic properties were studied by means of XAS, XMCD and X-ray linear dichroism (XLD). The submonolayer of isolated TbPc₂ molecules on MgO was compared to monolayers and thick layers of TbPc₂ directly on the Ag(100) substrate and to a submonolayer of isolated TbPc₂ molecules on h-BN/Ag(100). The results indicated that hysteresis was observed for submonolayers when an insulating MgO layer was present, as it suppressed the electron scattering and protected the SMM from weak interactions with the substrate. This is a clear example of surface-enhancement of the properties of the well-known SMM TbPc₂. In the case of h-BN, the observed hysteresis was significantly narrower than for MgO, as this oxide could be grown in several layers whereas h-BN forms a single monolayer that was deemed too thin to actually decouple the molecules from the substrate. In 2019, the hysteresis loop on MgO/Ag for the DyPc₂

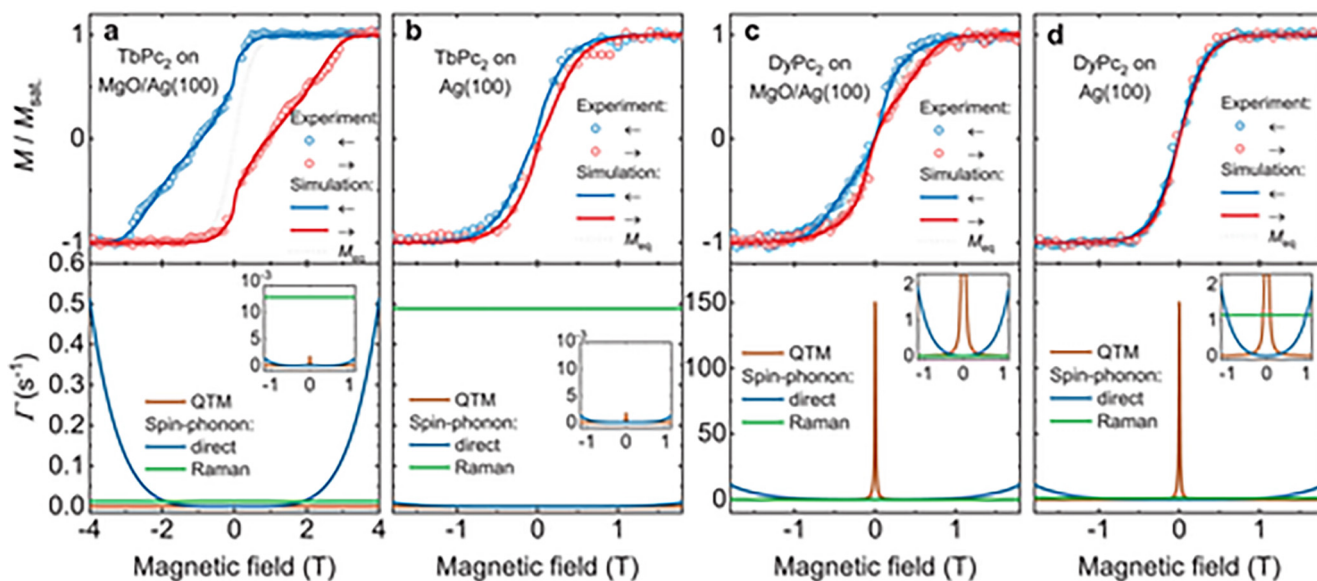


Fig. 14. Reprinted (adapted) with permission from [170]. Comparison of M/M_{sat} vs H hysteresis loops obtained from XMCD data for TbPc₂ and DyPc₂ on Ag and MgO/Ag (top panels), with the different contributions to the relaxation rate (bottom panels).

analogue was reported, shown in Fig. 14. Thus, the combination MgO/Ag might be also useful for other SMMs.[170].

Deposition on ferromagnetic substrates gathered a lot of attention because of its potential applications in molecular spintronics or memory devices. Several papers presented the adsorption and magnetic characterization of TbPc₂ on these substrates.[88,92].

Besides the aforementioned substrates, deposition on Si (100), [82] Au(111),[171] HOPG,[169] graphene,[172] and CNTs[173] have been reported. Apart from the double-decker lanthanide phthalocyanines, multiple-decker compounds have also been reported on surfaces, for example, Tb₂Pc₃ on Ag (111)[28].

5.5. Spin crossover complexes

In this review, our intention is to give only a general overview on the advances of spin-crossover complexes deposition on surfaces. For more detailed information about this topic, the reader is advised to check specific literature reviews that have been published recently.[174–176].

Some transition metal complexes, mostly within a pseudo-octahedral environment in the d⁴-d⁷ configuration present spin interconversion between low spin (LS) and high spin (HS) states that can be triggered in a controlled manner by external stimuli such as changes in temperature or pressure, or light irradiation, [179–182] leading to reversible changes of the physical properties of the carrier materials, like color, magnetic properties and size. The property of SCO continues to stimulate great research efforts because it is a switching phenomenon with a local, molecular origin, therefore with great potential for spintronics applications at the nanoscopic scale.[183] Among all, iron(II) complexes are, by far, the most studied ones.[184] Fe(II) has an electronic configuration of d⁶ and presents a LS state of $S = 0$ (diamagnetic) and a HS state of $S = 2$ (paramagnetic). The spin transition from HS to LS happens in many instances around room temperature and it entails a thermal hysteresis loop. This means that at certain temperatures, the compound can be frozen in either of the two states, HS or LS. The thermal hysteresis of SCO compounds depends mainly on cooperative effects, that is the intermolecular interactions established between molecules in the solid. The main drawback when it comes to processing this sort of complexes to exploit their prop-

erties of bistability is their high sensitivity to the environment. Small modifications in the surroundings may drastically change the cooperativity that leads to the thermal hysteresis needed for bistability. One important question to elucidate is whether cooperativity, which as we said is essential for bistability, may be preserved upon deposition of SCO complexes on surfaces, since this feature is a direct consequence of intermolecular interactions between the active species. This explains the fact that many SCO materials with thermal hysteresis are coordination polymers (1D, 2D or 3D). Several interesting studies have focused on the deposition of multi-layer molecular based SCO coordination polymers from solution.[185–187] Moreover, over the last few years, the implementation of SCO compounds in devices has been studied. [188] Thin films of Fe(II)-based spin crossover complexes have been embedded in junctions to study whether the spin crossover is still present in these structures, and whether temperature can affect the charge transport along the device.[189–191] However, these are out of the scope of this review, which is focused on the deposition of individual magnetic molecules. Many of the reported experiments are carried out under ultra-high vacuum conditions, as it allows to obtain well defined molecule–substrate interfaces. [176] In 2009, the first SCO to be sublimated onto surfaces was reported. The complex was [Fe(phen)₂(NCS)₂] (Fig. 15 (a))[192]

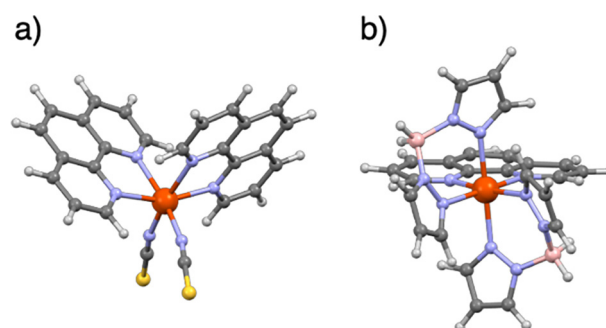


Fig. 15. Crystal structure of two SCO complexes that have been grafted on surfaces. Structure a) [Fe(phen)₂(NCS)₂];[177] b) [Fe(H₂B(pz)₂)(phen)].[178] Phen = phenanthroline, C₁₂H₈N₂, and (H₂B(pz)₂) = dihydrobis(pyrazolyl)borate, C₆N₄BH₈.

and it was deposited on silicon and glass substrates.[193] After this publication, many derivatives of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ have been sublimated, obtaining either thin films or even single SCO molecules on substrates.[176] For molecules which do not withstand sublimation, electrospray deposition has yet again demonstrated to be a powerful tool to deposit molecules on substrates.[194–196].

Metallic substrates are known to interact strongly with SCO molecules adsorbed onto them. This often results in the loss of the molecular property of SCO and therefore, the loss of the switching between HS and LS states.[197] This phenomenon evidences the important role that surfaces play for the integrity of the complexes. To maintain their functionality, the molecules must be electronically decoupled from the substrate.[195,198–200] The compound $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phen})]$, where $([\text{H}_2\text{B}(\text{pz})_2])_2$ = dihydro bis(pyrazolyl)borate and phen = 1,10-phenanthroline, (Fig. 15 (b)) [201] was reported to lose its integrity upon deposition on gold. By means of NEXAFS, it was observed that the first layer of molecules did not exhibit electron-induced switching, whereas the second and outer layers did. This clearly evidenced that even an inert Au(111) substrate could have strong interactions with the adsorbed molecules, resulting in integrity loss or deformation, to such extent that the molecular properties were lost.[199,202] For this reason, only a few studies have reported the reversible switching of SCO complexes in direct contact with metallic substrates. [194,195] Mayor et al. reported [194] the structural modification of a SCO complex to prevent the strong surface-molecule interactions expected for metallic substrates, that often results in the loss of molecular integrity. While spin switching of individual complexes has been evidenced on partially insulating layers, this is one of few examples where switching is fulfilled on a metallic substrate. Chemical modification of the two terpyridine ligands of this complex was achieved by linking the two binding terpy units into a rigid macrocycle, in this way the metal is encapsulated by the ligand to prevent integrity loss when adsorbed on a substrate. For the classic SCO complex $[\text{Fe}(\text{phen})_2(\text{SCN})_2]$ the use of substrates that are metallic and non-magnetic Cu(111), Cu(100) [174] results on the coexistence of the HS and LS forms, but no SCO. Authors claim this is due to a strong chemisorption of the SCO complex. The introduction of an intermediate layer as in $\text{Cu}_2\text{N}/\text{Cu}(100)$ or an extra monolayer of the same SCO complex [174] leads to the recovery of the SCO switching. For a similar complex, $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phenme}_4)]$, authors showed that it remains

intact and retains SCO on Bi(111) but it breaks up and SCO is lost when deposited on Au(100), as illustrated in Fig. 16.[203].

Efficient light-induced spin switching was observed for the SCO complex $[\text{Fe}(\text{pyrpyr}(\text{CF}_3)_2)_2(\text{phen})]$ on HOPG and semiconducting substrates (WSe_2 and HfS_2). When deposited on Au(111) and Co/Cu(100), fragmentation and loss of SCO occurs.[197] It seems quite common to observe fragmentation and chemisorption on metallic substrates like Au(111) or Cu(100) and loss of SCO switch, while non-metallic or semimetallic substrates help to efficiently retain the SCO property.

5.6. Other molecules

Many magnetic molecules different from the archetypical and ubiquitous Mn_{12} , Fe_4 , Cr_7Ni or TbPc_2 have also been deposited on surfaces. Very simple molecules like metal porphyrins or transition metal phthalocyanines have been widely studied. A wealth of knowledge has been acquired in these studies, in particular regarding the hybridization or interaction between the adsorbed molecule and the substrate. These results were reviewed in 2015 by Barth et al.[204] Metal porphyrins or transition metal phthalocyanines differ from other more complex magnetic molecules in one clear feature: due to the same nature of the ligand the metal lies in the square-planar ligand coordination pocket of the ligand leaving the axial positions open to other interactions. This lays in the fundamental chemistry of these species, evidenced by their biological role as small molecule transport vehicles in living organisms or charge transfer co-enzymes.[205] However it is a drawback for possible exploitation of their magnetic properties adsorbed on a surface. Surface interactions have important consequences to their electronic, magnetic, or chemical properties since the coordinating sphere of the metal is affected. A very promising compound in this family is the vanadyl analogue, [VOPc]. This molecule has been proposed as qubit for quantum information processing[206] and several surface deposition studies show very promising results. In 2018 deposition on a superconductive surface was reported. [207] The authors found two adsorption geometries for this molecule shown in the cartoon in Fig. 17, and that the spin–superconductor interactions could be tuned with molecular orientation. It is worth to point out that even in this case, with such a simple molecule with a clear shape anisotropy as [VOPc], it is very difficult to control the molecular disposition on the surface. On other

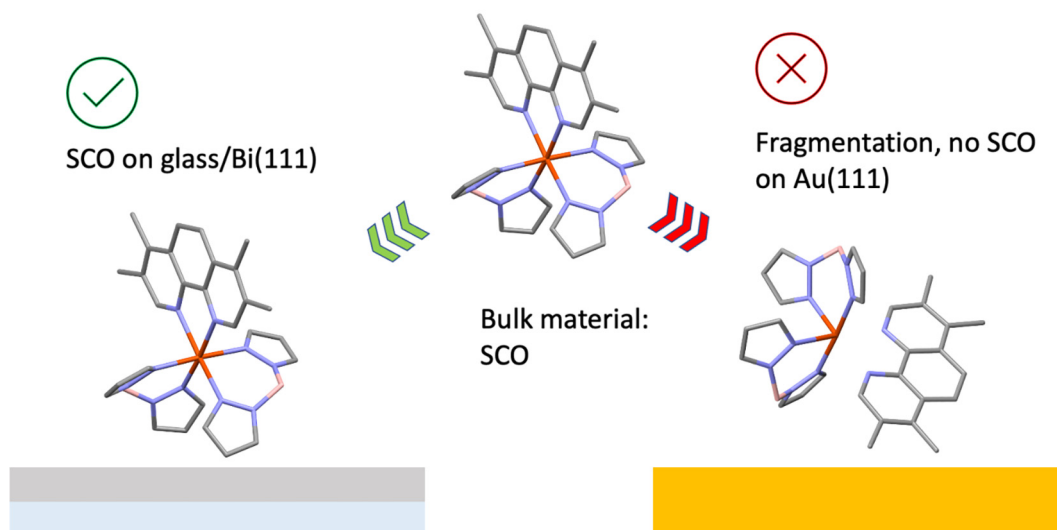


Fig. 16. Illustration of the deposition of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phenme}_4)]$ on Bi(111) and Au(111), SCO is maintained on Bi(111) but lost on Au(111) due to fragmentation.[203].

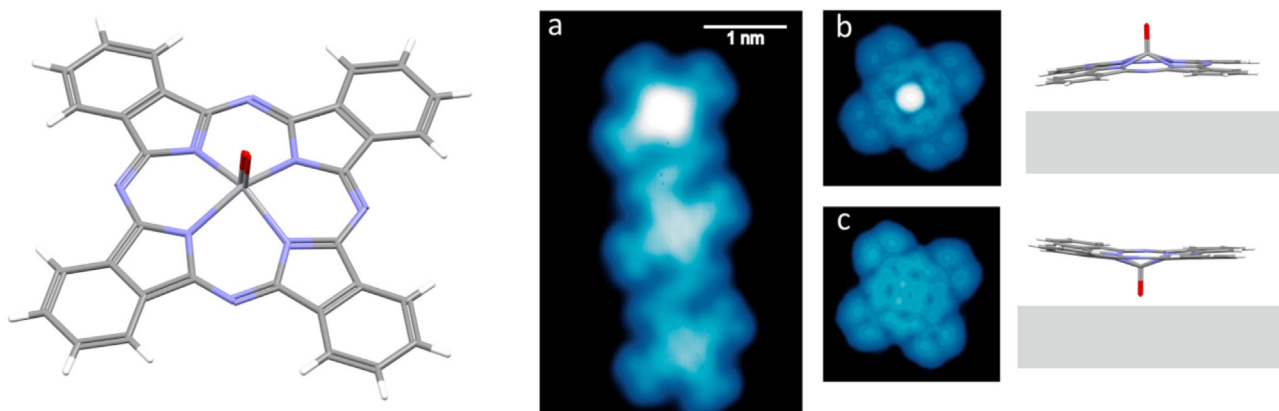


Fig. 17. The crystal structure of [VOPc], and the two possible orientations (oxygen up (b) and oxygen down (c) imaged by STM. (Adapted with permission from [207]. Copyright©2018 American Chemical Society).

metallic substrates such as Au(111)[208], Si(111) and Ag(111) [209] or Ni(111)[210], the strong interaction between the [VOPc] and the substrates was found to disrupt the electronic structure of the molecules. In the latter, graphene was placed as an intermediate layer which prevented the molecules to suffer such alterations. This was corroborated on graphene/SiC(0001). Again, [VOPc] interacted weakly with graphene, which enabled deposition of intact molecules on the substrate, in a flat-lying orientation with the vanadyl group pointing out. [97]

More complex magnetic molecules like the ones reviewed above Mn_{12} , Fe_4 , Cr_7Ni or $TbPC_2$ are characterized by having the metal centers “buried” into a ligand shell. Therefore, the interaction with a substrate when adsorbed on a surface is in principle already minimized by the same nature of these more complex structures. Most of the complexes reported in the literature either

show clear shape anisotropy like (a), (d) or (f) or have a clear reactive group like (b), (c), (f) or (g). The reactive group is usually a S-containing group that will force chemisorption by formation of a covalent bond with the substrate. Fig. 18 shows the crystal structure of several magnetic molecules that have been deposited on surfaces, as discussed here.

As mentioned earlier, one of the main concerns regarding surface deposition of magnetic molecules is the molecular stability in the deposition conditions. In this respect, using molecules that have not been thoroughly studied is not ideal because of the reduced amount of reference data against which to compare the information extracted from the characterization on surface. There are however many examples in the literature where the molecular stability on surface of established SMMs has been demonstrated (see below).

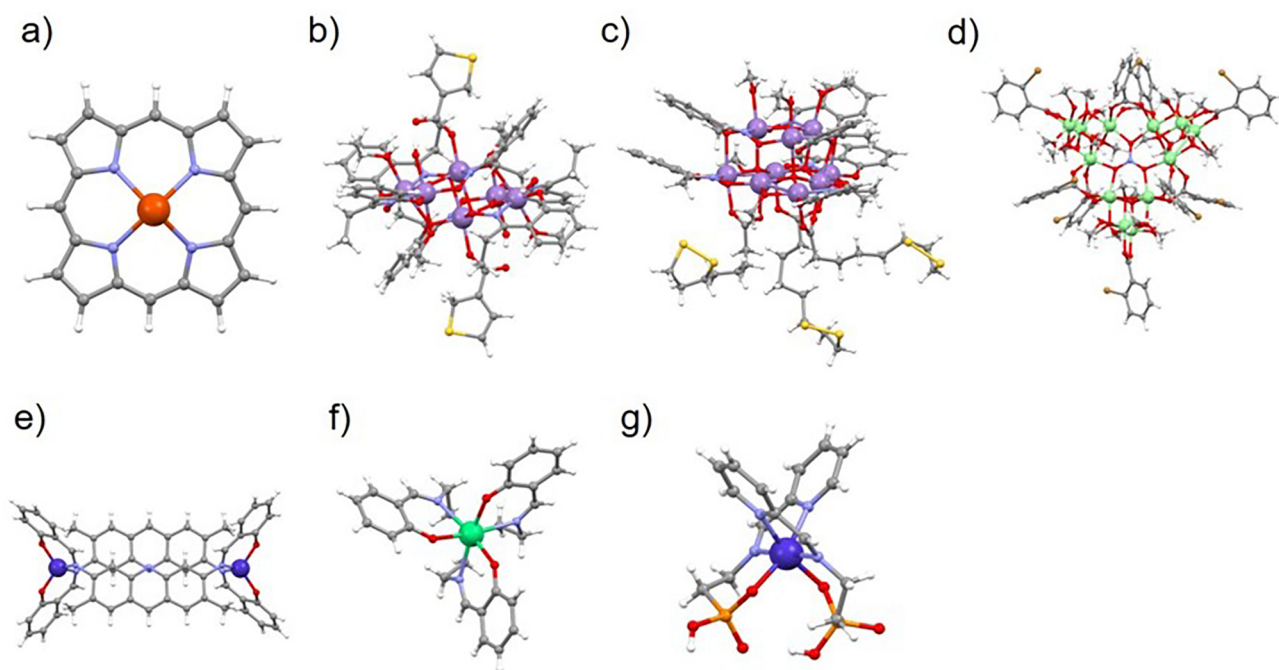


Fig. 18. Crystal structure of several magnetic molecules that have been deposited on surfaces. They either show clear shape anisotropy like (a), (d) or (f) or have a clear reactive group like (b), (c), (f) or (g). Structure of a) Copper metalloporphyrin[211]; b) $[Mn_6^II O_2(Et-sao)_6(O_2C-th)_2 L_{4.6}]$, where $HO_2C-th = 3$ -thiophene carboxylic acid, $L = EtOH$, H_2O and $saoH_2$ is salicylaldoxime; c) $[Mn_9 O_4(Me-sao)_6(L)_3(MeO)_3(MeOH)_3]Cl$ ($Me-saoH_2 =$ methylsalicylaldoxime, $HL =$ lipoic acid) d) $[Ni_{12}(NO_3)(MeO)_{12}(BrC_6H_4CO_2)_9(-MeOH)_{10}(H_2O)_2][ClO_4]_2$; e) $[Co_2(C_{29}H_{23}O_2)_2]$; f) $[Er(trensal)]$, where $H_3trensal = 2,2',2''$ -tris(salicylideneimino)triethylamine; g) $Co(Pyipa)_2$ where $Pyipa = 2$ -[(Pyridin-2-ylmethylene)amino]ethyl phosphonic acid.[93].

Apart from the huge family of Mn_{12} SMMs, manganese ions have also been employed to synthesize a huge collection of molecules of different nuclearity, such as the well-studied Mn_6 SMMs. [212,213] Several derivatives were deposited on Au(111) substrates with the formula $[Mn_6O_2(R-sao)_6(O_2C-th)_2L_{4-6}]$, where $R = H$ or Et , and $th-COOH = 3$ -thiophene carboxylic acid, $L = EtOH, H_2O$ and $saoH_2 =$ salicylaldehyde. In the bulk, the dynamic magnetic properties and spin state of the complex were highly dependent on the R group of the ligands, however, no magnetic data on the surface deposited complexes were reported. XPS data showed possible decomposition and the presence of free thiophene ligand on the surface, highlighting the importance of complex stability in the deposition conditions. In 2012, a well-known SMM containing four Mn ($Mn^{III}Mn^{II}$) ions, $[Mn_4(CH_3COO)_2(pdmH)_6]^{4+}$ ($pdmH =$ deprotonated pyridine-2,6-dimethanol), was anchored to multi-walled carbon nanotubes (MWCNTs) functionalized with carboxylate groups via electrostatic interactions. Although the authors could observe the functionalized nanotubes, the SQUID data evidenced the loss of the magnetic properties. [214] Mitcov *et al.* recently showed that an enneanuclear Mn(III) chiral magnet could be grafted on Au by ligand functionalization: the authors showed the preservation of both SMM behavior and chirality on the surface. [113].

Pons-Balagué *et al.* reported the nanostructuring of dodecanuclear Ni_{12} complexes on mica by exploitation of electrostatic interactions. The functionalized surfaces were studied by AFM and grazing-incidence X-ray diffraction, which revealed the formation of polycrystalline thin layers. [25] π - π stacking combined with molecular shape anisotropy and intermolecular interactions served to achieve ordered arrays of Co_2 dinuclear complexes on a HOPG surface. The molecules were luminescent and the preservation of magnetic properties was established by XMCD. [23] Aliaga-Alcalde and coworkers have studied surface deposition of complexes containing curcuminoid ligands on several substrates. For curcuminoids, chemical flexibility on the ligand synthesis can be exploited to facilitate the physisorption of the molecules onto the surface. [215].

In order to understand how the nature of the magnetic ion affects the exchange coupling of the molecules with magnetic substrates, Mallah and coworkers studied simple monomers with different metal centers on a ferromagnetic substrate. The compounds $[M(Pyipa)_2]$ ($M = Ni$ and Co , $Pyipa =$ pyridin-2-ylmethyleneaminoethyl phosphonic acid; Co analogue shown in Fig. 18(g)) were attached by chemisorption to epitaxial $Fe_3O_4(111)$. The magnetic properties of the system were characterized by XMCD. For the Co compound, they observed a strong ferromagnetic coupling with the surface, whereas the analogous Ni compound was either not coupled or weakly antiferromagnetically coupled to the substrate. These results were corroborated by DFT calculations. [93] Thin

films of 10 nm of the SMMs $Na[Ln(5,7Cl_2q)_4]$ with 5,7-dichloro-8-hydroxyquinoline ($5,7Cl_2q$) ligands were deposited on permalloy (NiFe), a ferromagnetic substrate. The authors show the importance of the molecule/substrate spin-interface: the SMMs are magnetically blocked at low temperatures due to the interface coupling between the Ln spins of the SMM and the ferromagnetic substrate. [216] Fig. 19 shows the specific magnetic behavior observed for the thin film on permalloy compared to a diamagnetic substrate. This highlights the importance of studying the spin-interface between molecule/substrate for molecular spintronic applications.

$[Er(trenal)]$ single-ion magnet (Fig. 18 (f), $H_3trenal = 2,2',2''$ -tris(salicylideneimino)triethylamine) has attracted a lot of attention in the last decade due to its excellent optical properties, strong magnetic anisotropy and a trigonal pyramidal structure that allows for several possible adsorption conformations. [217] Another key feature of this species is that it can be sublimated and it withstands UHV. $[Er(trenal)]$ was sublimated in UHV on Au(111) and on Ni/Cu(100). The molecules were physisorbed on Au(111) whereas they were chemisorbed on the Ni/Cu(100) surface. This was evidenced by the high diffusion of the molecules on the gold substrate that led to ordered 2D arrays, whereas a stronger interaction on the nickel substrate led to random placing of the molecules. The integrity of the molecules upon deposition was corroborated by XPS. XMCD measures showed that the easy axes of magnetization were randomly oriented on the surface because of the lack of shape anisotropy of the molecules, and that at zero magnetic field the molecules were antiferromagnetically coupled to the Ni substrate. [218] It was found that a graphene layer between the $[Er(trenal)]$ molecules and the metallic substrate allowed molecules to self-assemble having the easy axes of magnetization perpendicular to the substrate, as the molecule-metallic substrate interaction was reduced. [217] In 2021, the island formation of $[Er(trenal)]$ molecules adsorbed on graphene/Ru(001) was reported. The resultant system was characterized by bright-field low-energy electron microscopy (LEEM) and synchrotron-based X-ray photoemission electron microscopy (X-PEEM). [219].

Lanthanoid compounds can present luminescence and great magnetic properties, thus they are great candidates for multifunctional devices. In 2021, Bernot and coworkers reviewed their excellent work on lanthanoid dimers with pyridine-*N*-oxide ligands chosen due to their chemical tunability, luminescence and robustness toward deposition. They report luminescent devices with thick films of the lanthanoid dimers with possible application in optical information storage. [56].

Endohedral metallofullerenes (EMFs) are fullerenes that encapsulate metallic species inside the fullerene cavity. These compounds provide an excellent platform to study exotic metallic species that are stabilized by the fullerene cage. Interested readers might find the mini-review published in 2019 useful. [220] The

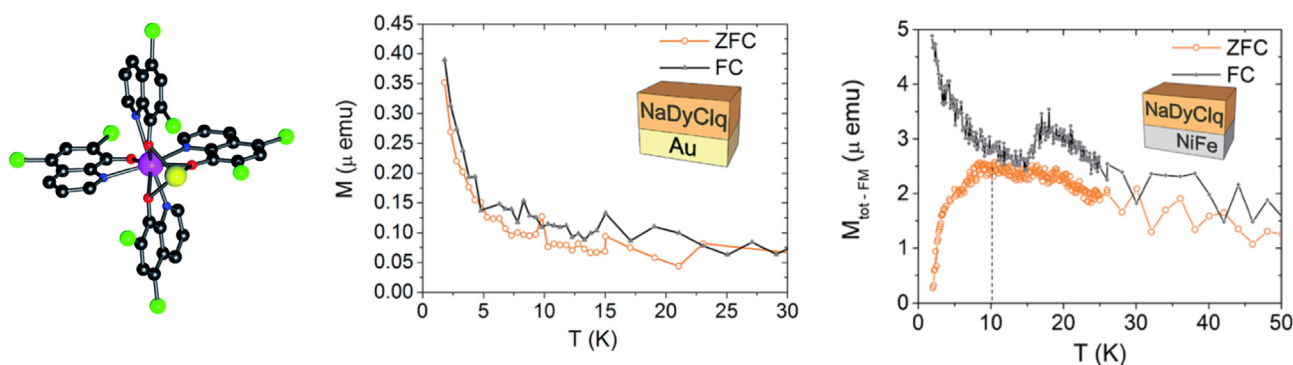


Fig. 19. Reprinted (adapted) from reference [216] with permission from the Royal Society of Chemistry. Crystal structure of $Na[Dy(5,7Cl_2q)_4]$ ($NaDyClq$) and ZFC/FC curves for a thin film of $NaDyClq$ SMMs that show paramagnetic behavior on Au and magnetic blocking on NiFe.

general comments that start Section 5 do not apply to EMFs, since these are not classic coordination or organometallic complexes. In particular, lanthanoid and actinoid species have been stabilized in fullerenes, leading to some outstanding SMMs that have also been deposited on surfaces. The nature of fullerene derivatives makes EMFs ideal candidates for deposition on HOPG or graphene. The outstanding SMMs $\text{Dy}_2@C_{80}(\text{CH}_2\text{Ph})$ and $\text{Tb}_2@C_{80}(\text{CH}_2\text{Ph})$ can be deposited on graphene to form monolayers with high hysteresis temperatures. The Dy analogue shows hysteresis up to 17 K.[221] A pyrene functionalized analogue of $\text{Tb}_2@C_{80}(\text{CH}_2\text{Ph})$ displays the opening of the hysteresis loop up to 28 K.[57] The host fullerene molecule plays a key role stabilizing the metallic fragment and isolating it from the surface. STM/STS has been used to study the single-electron metal-metal bond of isolated $\text{Dy}_2@C_{80}(\text{CH}_2\text{Ph})$ and $\text{Er}_2@C_{80}(\text{CH}_2\text{Ph})$ on graphene/Ir(111) substrates.[222].

6. Perspectives

Undoubtedly, a lot has been learned since the first attempts to deposit Mn_{12} SMMs on surfaces. Those first attempts by Coronado, Sessoli and co-workers were key pieces of work that served as inspiration for many scientists after that. Even though the expected SMM properties of Mn_{12} were not observed after surface deposition, valuable lessons were learnt by the community and have been applied to many other systems. This led to the achievement of great milestones, such as the observation of Fe_4 hysteresis grafted on Au by a long-chain S-containing group or the giant hysteresis of TbPc_2 on Ag/MgO. These two milestones showed that SMMs can be deposited intact on surfaces while retaining their magnetic properties, and that coupling to the surface must be controlled in order to achieve the full potential of these molecules.

Right now, the large number of papers reporting successful surface deposition of magnetic molecules shows a huge interest and research efforts in the topic but at the same time, the variety of possible magnetic molecules is overwhelming. Advances in STM imaging have been key to understand how molecules are deposited on a surface. A lot has to be done to make STM imaging more readily available to interested researchers that have no access to such facilities, in particular imaging at low temperatures to obtain good resolution images of complex magnetic molecules. This is very important to properly image single molecules and monolayers on surfaces and reach relevant conclusions regarding how a molecule is positioned on a surface. AFM with functionalized tips also holds a lot of promise in this aspect. If the technique is developed to be widely available, many more systems can potentially be imaged with atomic resolution than those that can be imaged by STM, since AFM has no requirements as to conductive properties of the substrate or molecule deposited. Furthermore, AFM will not be affected by a diamagnetic decoupling layer between molecule and substrate, such as MgO or an organic molecule SAM. Research towards effectively decoupling the magnetic molecules from the phonons of the surface and achieving large area coverages with homogenous orientation of all the molecules on the layer is one of the hot-topics in the field. Positive results in this matter will prove to be fundamental for the advance of molecule-based electronics and information storage and processing devices. The evidence gathered so far mostly in metal porphyrins and phthalocyanines, Cr_7Ni and TbPc_2 SMMs shows that molecular position on a substrate is a factor difficult to control. Even with highly shape-anisotropic systems such as [VOPc], different orientations of the isolated molecules on surfaces have been imaged by STM, with vanadyl groups up or down with respect to the surface. Strategies like on-surface coordination chemistry, or surface-supported MOFs, will become more important in the near future to achieve ordered chemisorbed monolayers like the Dy-

carboxylato 2D networks with strong anisotropy reported in 2021.[223].

Furthermore, to fully exploit magnetic molecules on surfaces, methods have to be developed to attain large surface area coverage. This can be done exploiting supramolecular interactions between the magnetic molecules and their self-assembly on the surface. Winpenny and Affronte showed this for a Cr_7Ni qubit on a Au surface, or by using on-surface chemistry, as mentioned above. The 2D organization of magnetic molecules on different substrates is thus a challenge that will be tackled in the next few years. It is likely that this will entail the study of 2D metal-organic nanosheets or 2D MOFs that can address 2-dimensional organization of a magnetic (SMM or qubit) unit into a diamagnetic 2D network to ensure the necessary conditions to retain the SMM or qubit properties of the magnetic unit while placing it in an organized 2D layer. Roubeau and coworkers have already taken steps in this direction by reporting a 2D array of vanadyl qubits with diamagnetic Zn linkers, they are able to build a bidimensional metal-organic framework (MOF) in which the vanadyl qubits have all a controlled orientation and retain their magnetic properties. Their results provide the basis for developing a viable hybrid quantum computing architecture by integrating the 2D qubit MOF into a superconducting resonator.[224,225].

It is remarkable that the breakthrough in hysteresis temperatures, pushed up to 80 K for organometallic dysprosium SMMs, has not resulted yet in surface deposition of these species. [8–10] The instability of these and other organometallic SMMs like [Ti(COT)Cp] [226] complexes might greatly hinder the surface deposition of the intact molecules. Derivatives of the dysprosium SMMs have been obtained by surface-confined coordination chemistry. This is a great tool that can lead to unprecedented low coordination-number environments for the metal ions, leading to in theory exceptional magnetic properties. However, the high-temperature hysteresis of dysprosium SMMs has not been reproduced by the surface Cp^*Dy centers on silica NPs.[116–118].

The challenge of preparing new SMMs or qubits with better performance relies on synthetic chemists and it is clear that advances are slow but very positive in this regard. However, the greater challenge of using these molecules in molecular spintronics, quantum computing or information storage is a multidisciplinary task that requires great understanding of synthetic chemistry. A lot of emphasis is put on the molecular properties that we want to exploit to be retained on a surface, however one must not forget the real possibility of synergy between the molecule's magnetic moment and the spins on the surface, in particular if ferromagnetic substrates are used. The study and possible exploitation of the spin-interface for spintronic applications will surely be one of the areas where researchers will find impressive results. In the next few years, advances in imaging and 2D organization of magnetic molecules on surfaces while retaining the desired magnetic properties will be a hot-topic. If advances are positive, multidisciplinary work involving synthetic chemists, physicists and engineers might yield the predicted molecular-based devices for a better, faster, lower-energy use technology.

Data availability

Data from the authors is available on request. Other data is available as indicated in the reviewed articles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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