Molecular nanomagnets for information technologies†

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Nanomagnets will play a crucial role for the storage and processing of magnetic information in the future, so we may wonder to what extent molecular systems will contribute to this game. In this Feature Article, I’ll briefly review the basic requirements for information technology and some of the recent achievements in the field, as well as some ideas that can be further pursued.

Introduction

Information storage by means of magnetic media is one of the oldest technologies for data recording, since the early prototype of magnetic wire recorder, the “telegraphone”, was made by the Danish engineer Valdemar Paulsen in 1898. Magnetic media became very popular in the mid-1900s, with analog recording on audio and video tapes being developed; a milestone was the first digital device for magnetic recording, the RAMAC, made by IBM in 1956. At that time, 5 megabytes could only be stored in a device weighing several tons taking up a whole laboratory, whereas today, portable devices fitting into a pocket can store hundreds of gigabytes! However, the basic principles of digital storage in magnetic media have remained essentially unchanged, and an engineer working on the IBM projects in the 1950s would not have any problem in understanding how a modern device works. Yet, the size of an elementary register (bit) has shrunk from a few mm to about 1000 nm², thus allowing magnetic storage densities of ~50 Gbit per square inch in the hard disks commercially available today. At present, industries are developing devices at 1 Tbit per square inch, implying a bit size of ~100 nm². Part of this success is due to the non-volatile character of magnetic storage and the robustness of magnetic media. This growth of storage density will soon face fundamental limitations, since the reduction in size of magnetic bits implies a drastic reduction of the anisotropy barrier ΔE. For commercial applications, a register is required to hold information for longer than 10 years, and this implies a stability ratio C⁺ = ΔE/kₜ₁ > 50 at room temperature (this condition defines somehow the super-paramagnetic limit).

Extraordinary progress has been made in the production of inorganic nanoparticles with improved control in size and dispersion. Just to have some reference values for comparison, FePt nanoparticles have high chemical stability, are resistant to high temperatures and they have very high magnetocrystalline anisotropy (10⁶ erg/cm³). This implies that 3 nm FePt particles are able to retain magnetic information for 10 years at room temperature! To be competitive, features of molecular nanomagnets should be compared with these numbers. However, molecular nanomagnets have been – and will continue to be – a test bed for studying magnetic phenomena at the nanoscale, searching for alternative solutions to the superparamagnetic limit. Moreover, they will contribute to the development of molecular spintronics.

Information technologies also need new ideas on information processing. Smaller and faster processors are continuously required, and top-down semiconductor technology will probably dominate down to ~10 nm. Carbon-based and molecular electronics may provide alternative solutions, starting from niches of specialized applications. However, novel approaches for information processing are appealing, and required for the medium and long term. In this context, quantum computation certainly provides revolutionary ideas.

The next generation of computers probably won’t be much different from the computing machine depicted in Fig. 1, but its components will have sizes of one or a few nm: at this scale, molecules, and in particular spin clusters, can play their role. The molecular approach may indeed provide scalable structures by means of relatively cheap bottom-up approaches. Two...
fundamental steps are essentially required: control in positioning molecules on specific portions of the surface, and the chemical stability of individual molecules on surfaces. As a basic prerequisite, the superposition of quantum states is required for the manipulation of quantum bits (qubits). While in simple bistable systems, information may have the form of magnetization up (\( \uparrow \)) or down (\( \downarrow \)), a quantum bit, like a spin \( \frac{1}{2} \), has the form of \( |\Psi>| = \alpha|\uparrow> + \beta|\downarrow> \), so that any superposition (couple of \( \alpha \) and \( \beta \) values) of the \(|\uparrow>\) and \(|\downarrow>\) states carries a specific piece of information, thus increasing enormously the capability of encoding information in a single device. In order to achieve a quantum gate, the quantum system must be sufficiently decoupled from the environment in such a way that its dynamics is coherent. A further requisite to achieve quantum gates with multiple qubits is the entanglement of quantum states in different molecular systems. These aspects will be explained and discussed in the following paragraphs. The choice of examples is arbitrary, and this review is far from being exhaustive.

Molecular nanomagnets for information storage

Molecular nanomagnets, or magnetic nanoparticles, are new terms that identify both ferro- and antiferro-magnetic intramolecular coupling. Thus they can have a high- or low-spin ground state, and they comprise both molecules and nanoparticles of molecular origin.

Magnetic molecules essentially have no dispersion in size and shape, and their shell can be controlled at the synthetic level. These are critical points for metal nano-particles fabricated by top-down methods. Conversely, the chemical stability and the influence of the environment can be critical for molecules.

The starting idea is to have a magnetic molecule \(~1\text{ nm}\) in size able to retain magnetic information. To do this, its magnetization potential should exhibit a double well with an energy barrier \( \Delta E \) that separates the up and down directions of the magnetization. The most common situation is an energy barrier given by magnetic (uniaxial or more complex) anisotropy. If we consider only the thermally activated mechanism for the magnetization reversal, one molecule magnetized along the direction of an external magnetic field will retain its magnetization for days/years only if kept at a temperature, the so-called blocking temperature \( T_B \), which is much lower than \( \Delta E \). The true novelty of molecular nanomagnets – with respect to metal nanoparticles – resides in the fact that the magnetic anisotropy can be engineered through the ligands bridging and/or chelating the metal centres. From this viewpoint, the molecular approach appears very promising in order to overcome the superparamagnetic limit. In principle, complex information (more than a single bit) can be stored in molecules by exploiting the splitting between and within multiplets.

In practice, \( \text{Mn}_{12} \) has held the record of the highest anisotropy barrier for a magnetic molecule for several years. Several attempts have been made to slightly modify the ligand shell and/or the chemical environment of single ions in order to enhance the anisotropy barrier, but in spite of the fact that more than 60 derivatives of \( \text{Mn}_{12} \) have been synthesized, the record for the anisotropy barrier \( \Delta E/k_B \) has not exceeded \(~74\text{ K} \), i.e. far below room temperature. On top of that, it should be pointed out that \( \text{Mn}_{12} \), like most molecules, has an excited state populated at room temperature, but this is a common problem for most of the quantum devices studied nowadays. It has also been clear since the mid-1990s that quantum tunnelling is an additional – and detrimental – mechanism for magnetization reversal, and it may well speed up the loss of information. This aspect is comprehensively discussed in ref. 4. A further weak point of \( \text{Mn}_{12} \) was encountered during the several attempts to graft individual \( \text{Mn}_{12} \) molecules onto a surface and then checking their properties. Whilst some measurements by sensitive magnetometers (SQUIDs, Hall probes, magneto-optical) gave evidence for the opening of a small hysteresis loop on thick films of \( \text{Mn}_{12} \) (Fig. 2), the magnetic signal detectable (muon scattering, XMCD) from a monolayer of individual \( \text{Mn}_{12} \) molecules depended on the preparation and irradiation conditions.\(^5\)\(^6\) The lesson we learn is that \( \text{Mn}_{12} \) molecules are extremely sensitive to the environment and to the measuring probe.

Much effort has been devoted to “engineer” the anisotropy barrier at molecular level. The complete list of all the attempts and strategies deserves a special review, well beyond the scope of this article. One successful example worth mentioning is the case of \( \text{Fe}_{12} \), which seems to be more stable than \( \text{Mn}_{12} \) when deposited on a surface.\(^7\) Recently, a new record for the anisotropy barrier was established at \(~86\text{ K} \) by the \( \text{Mn}_6 \) molecule \( [\text{Mn}^{11}\text{II}O_2(\text{Etsao})_6(O_2\text{CPh(Me)}_2)_2(\text{EtOH})_6] \) comprising two \( \text{Mn}^{11}\) triangles ferromagnetically coupled to give a total molecular spin \( S = 12 \).\(^8\) This situation of high spin and high anisotropy barrier seems to
arise from Mn–N–O–Mn torsion angles. However, this derivative presents excited states quite close in energy to the ground state with \( S = 12 \), and this reduces the effective anisotropy barrier, thus the magnetization blocking is observable only at liquid helium temperature.\(^9\)

The fact that \( \text{Mn}_6 \) comprises Mn ions with only one valence state promises for more stability of isolated molecules but the functionalization and grafting of this molecule on surface just started to be investigated.\(^1\)

A broader outlook on the field should also comprise achievements in the synthesis of magnetic nanoparticles (~3 to 8 nm in size) by molecular routes. Nanoparticles of Prussian Blue analogues have been successfully synthesized\(^12\) and grafted on to an Si surface,\(^13\) yet it is not clear how to increase the blocking temperature since the single ion anisotropy is expected to be rather weak in this class of materials. Alternative routes to encapsulate magnetic ion(s) in nonmagnetic (or antiferromagnetic) molecules like ferritene,\(^14\) endo-fullerene\(^15\) or nanotubes have been successfully explored, and these may provide interesting test beds.

**Alternative solutions to the superparamagnetic limit**

The field of molecular magnetism provides not just a plethora of single-molecule magnets but it is also extremely rich for testing novel mechanisms that may provide alternative solutions to the superparamagnetic limit. In this context it is worth mentioning the observation of slow dynamic in magnetization in one-dimensional systems like CoPhOMe recently reported by R. Sessoli and co-workers.\(^16\)\(^17\) This Ising spin chain is made of Co\(^{2+}\) ions (anisotropic effective \( s = 1/2 \) spins) alternated with nitronyl-nitroxide radicals (isotropic \( s = 1/2 \) spins), and the mechanism of slow relaxation of the magnetization is well accounted for by the Glauber model.

An alternative mechanism for the blocking of magnetization has been recently proposed and observed in highly degenerate molecule – the Ni\(_{10}\) family of derivatives.\(^18\) The Ni\(_{10}\) molecule comprises ten Ni\(^{2+}\) ions (\( s = 1 \)) in a supertetrahedron structure forming essentially a non-magnetic core of six Ni\(^{2+}\) ions plus four weakly coupled Ni\(^{2+}\) ions at the vertexes giving rise to an \( s(2s + 1)^9 = 81\)-degenerate ground state well separated from the first band of excited states. For temperatures smaller than the energy gap between the ground and the excited band, a few branches of phonons are available in the systems and these phonons may well be trapped by magnetic molecules, thus drastically reducing the probability of magnetization reversal. As a matter of fact, the magnetization results blocked at temperatures smaller than the energy gap separating the two lowest bands without any significant anisotropy barrier (see Fig. 3). Recently a Co\(_{10}\) derivative\(^19\) with a supertetrahedron structure analogous to that of Ni\(_{10}\) has been reported and similar slow magnetization dynamics were observed, thus supporting the key idea. This mechanism was observed, almost fifty years ago, in spin impurities dispersed in a crystal at very low temperature, and was called resonant phonon trapping. The new idea is that it can be enhanced in molecular systems. So, although it won’t be straightforward to increase the blocking temperature, there are hints that alternative mechanisms may be able to store information in magnetic molecules without the need for magnetic anisotropy.

**Molecules for quantum devices**

Molecular spin clusters have great potential for encoding quantum bits (qubits), and they are considered to be emerging candidates among solid-state electron spin systems for the development of quantum architectures. It is worth recalling the basic requirements for a quantum device, which can be summarized by the so called DeVincenzo criteria:\(^2\)

1. Identification of a well-defined qubit: the quantum states of the candidate system must be well described and well separated from other possible states not directly involved in computation. The hardware and the possibility of error correction should scale not more rapidly than the complexity of the problem (scalability).

2. Initialization: a reliable experimental procedure must be defined in order to set the qubit in a well-defined initial state.

3. Accurate quantum gate operations. A quantum gate operation corresponds to the motion (coherent time evolution) of the system from an initial quantum state to a final state. This dynamics must be described by the Schrödinger equation, that is, eventually, by a well-defined unitary transformation.

4. Low decoherence: gate operations occur in finite time and the coherent time evolution should not be perturbed by other agents. For solid state quantum devices this is a crucial aspect since the device is embedded in the environment made of nuclear and electronic spins, lattice vibrations, charge carriers and electromagnetic radiation. For a reliable qubit, the gate rate would have to be \( 10^4 \) times more rapid than the time at which the system loses coherence. In practice this is quite hard to achieve with solid state systems but it should be taken as a reference goal.

5. Readout: a method to read the final state should be defined and experimentally realized.

From this perspective, molecular nanomagnets have specific features that reveal their potentialities: 1) they have well defined electron spin states with a well defined pattern of energy levels; 2) in principle scalable architectures can be implemented with molecular building blocks; 3) the coherence time is sufficiently long and controllable at the molecular level. Here below I discuss some examples.

Single-molecule magnets like Mn\(_{12}\) derivatives have shown that the main phenomena can be described by the spin
Hamiltonian and the ground multiplet $S = 10$ (high spin). On this basis, a specific scheme for quantum computation was originally proposed by Leunberger and Loss.\textsuperscript{20} They proposed to exploit the differently spaced energy levels of the ground multiplet as registers and to use a multi-frequency sequence of electromagnetic pulses to address them and to create quantum superposition of the states in a way that allows one to perform Grover’s algorithm. This pioneering work was the first to highlight a possible parallelism between the spin dynamics of molecular magnets and quantum algorithms, although the scheme is limited to the number of levels of the specific molecule and it is, therefore, not scalable. From an experimental point of view, this proposal also presents challenges in implementing multi-frequency pulses with sufficient spectroscopic resolution.

More recently, interest was directed to low spin ($S = 1/2$) clusters, looking for two-level systems (true quantum bits) suitable for scalable and universal architectures of quantum computation. In principle, single molecular units such as Cu monomers, VO$^{2+}$ or organic radicals, like nitronyl nitroxides and iminonitrooxides, constitute $S = 1/2$ centres that can be embedded in more sophisticated molecular structures. For instance, vanadyl groups containing two localized $S = 1/2$ and capable switchable polyoxometalates were used to develop the $\sqrt{\text{SWAP}}$ gate proposed in ref. 21.

A finer strategy can be developed by using antiferromagnetic spin clusters. The basic idea is well represented by antiferromagnetic spin triangles, examples of which exist in a plethora of molecular triizers.\textsuperscript{22} Let’s consider an equilateral triangle of three $S = 1/2$ spins, antiferromagnetically coupled, for instance a molecular Cu$_3$ trimer.\textsuperscript{23,24} The ground state is a degenerate doublet whose degeneracy can be lifted by making the triangle isoceles, i.e. by introducing a different Heisenberg exchange coupling in one of the bonds ($J_1 \neq J_{12}$). In this case, two doublets separated by a gap $|J_3 - J_{12}|$ can be obtained as the lowest lying states. This situation can be found in other trimers with half-integer spin centres and also in heterometallic trimers. A case of Cr$^{3+}$ ($S = 3/2$) trimer, namely $[\text{Cr}_3\text{O(O}_2\text{C}_6\text{H}_5)_6(\text{C}_5\text{H}_{10}\text{NH}_3)_3]\text{ClO}_4$, is shown in Fig. 4: the low temperature Schottky anomaly evidences the split between the two lowest doublets. The scheme of the lowest level is represented in the inset.

As compared to monomers, molecular systems with a higher number of metal centers have some advantages. For instance, the presence of well-defined excited states can be used as resources for the implementation of gates with two or more qubits.\textsuperscript{25} The most common situation indeed involves two molecules linked by a permanent (i.e. unswitchable) linker. Let’s consider a situation in which the coupling (superexchange, for instance) between two molecules is vanishingly small when both of them are in their ground state but it is finite when one of them is in a specific excited state. This is the case, for instance, for two antiferromagnetic spin triangles such that the vertex of the first one is coupled to the basis of the second one, as described in ref. 26. By exciting one molecule to its excited state with an electromagnetic pulse, the interaction is switched on, and two-qubit gates can be performed between both molecules even when they are in their ground state carrying the resulting information.\textsuperscript{26}

The strategy of using antiferromagnetic spin clusters to create two-level ($S = 1/2$) quantum systems can be further developed. The key idea\textsuperscript{27} was implemented in ref. 28, where we proposed to engineer the Cr octa-nuclear wheel at a molecular level by substituting one of the Cr$^{3+}$($S = 3/2$) with one divalent Ni$^{2+}$ ($S = 1$). This introduces an extra spin to the otherwise non-magnetic octa-nuclear ring whose ground state thus results in a non-degenerate doublet ($S = 1/2$) (see Fig. 5).

The strategy can be extended to larger rings as well.\textsuperscript{29} All these systems turn out to have an $S = 1/2$ ground doublet well separated from the excited states, as required by one of the above-mentioned DeVincenzo criteria. Other molecular systems with dominant antiferromagnetic interactions, like V$_{15}$, also have a low spin ground state but the presence of interactions, like the Dzyaloshinski-Moriya interaction, introduces further low-lying levels.

**Quantum coherence**

The basic logic operation for an $S = 1/2$ electronic spin system is a precession of the $S = 1/2$ spin. Under realistic experimental conditions, a magnetic pulse of $\approx 10$ Oe to an electronic spin $S = 1/2$ (g-factor $\approx 2$) gives rise to a switching time of $\approx 10$ ns. To avoid information dropout during the gate (switching) operation, a molecular system must have a coherence time much longer than this. Thus, the relevant feature here is the ‘figure of merit’ $Q$, defined as the ratio between the switching time $T_\text{s}$ and the coherence time $T_2$, i.e. $Q = \pi T_2$. $Q$ represents the number of operations performed before losing phase coherence.
Determination of $T_2$ in molecular spin clusters has therefore a central role to establish whether a molecular spin cluster is suitable for quantum computation. For Cr$_7$Ni a first attempt to determine an upper limit of decoherence was made by measuring the resonant absorption of microwaves. These experiments were probably limited by dipolar interactions and inhomogeneities within the single crystal. Subsequently ESR pulses were used in diluted and deuterated Cr$_7$Ni and a coherence time of 3 $\mu$s at 2 K was estimated. In the case of Cr$_7$Ni, the figure of merit $Q > 100$ at 2 K, and this is comparable to other solid-state systems. For single rare-earth impurities, $T_2$ was found to be $\approx 50$ $\mu$s. In the case of V$_{15}$, Rabi oscillations were recently observed with an estimated coherence time of 0.8 $\mu$s at 4 K.

The control of the decoherence mechanisms in molecular spin cluster is quite instructive. Firstly, in order to neglect dipolar interaction in measurements performed on ensemble, it is necessary to work on diluted systems, either molecules in solutions or “diluted” crystals containing non-magnetic molecules. Whilst magnetic molecules generally do not contain free electric charge (possible sources of decoherence), they contain a large, but finite, number of nuclear spins that are quite often the main source of decoherence for the electron spins at low temperatures. It is therefore important to identify nuclear spin centres in specific molecules to make the problem soluble, at least in principle, from chemical, experimental and theoretical point of views. The case of Cr$_7$Ni was, again, paradigmatic. For the pulsed-ESR experiments of the Oxford group, it was clear that protons affects the coherent electron spin dynamics and $T_2$ was significantly increased in deuterated samples. Parallel NMR experiments showed that nuclei in the bridging F ions induce a broad peak, revealing a strong super-hyperfine interaction with these nuclei as showed that nuclei in the bridging F ions induce a broad peak, increased in deuterated samples. Parallel NMR experiments in molecules.

Entanglement in (supra-)molecular structures

Entanglement between quantum states is a fascinating problem of quantum physics, and it is considered a fundamental resource for quantum information processes. Indeed, when the states of two systems A and B are entangled, by measuring the state of A one can get information on the quantum states of B – this is the basis for controlled logic gates. By definition, entanglement is created when the states $|\Psi\rangle$ of a composite system cannot be written as simple products of states of its components. The definition of entanglement given by Schrödinger may further clarify this concept: “When two systems, of which we know the states by their respective representatives, enter into temporary physical interaction due to known forces between them, and when after a time of mutual influence the systems separate again, then they can no longer be described in the same way as before, viz. by endowing each of them with a representative of its own. I would not call that one but rather the characteristic trait of quantum mechanics, the one that enforces its entire departure from classical lines of thought. By the interaction the two representatives [the quantum states] have become entangled.” In bipartite spin systems, a Bell state $|\Psi\rangle = (|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle)/\sqrt{2}$ is the typical example of a highly entangled state.

Translated into molecular language, we should firstly identify two (or more) spin systems for which we know exactly the original quantum states. In order to create entanglement, a functional linker must be introduced, such that the states of the separate systems can no longer be represented as before. Within a single molecule, single spins are linked through (super-)exchange coupling, yet one should keep in mind that each subsystem needs to be well separated from the others so, if not spatially far apart, sub-systems must be at least individually addressable. So the challenge here is to create supra-molecular structures with entangled molecular spin states. The basic idea is sketched in Fig. 6. Of course more complex supra-molecular structures – comprising more spin centers – can be obtained starting from this, but the basic features need to be proved first.

The first case of supra-molecular entanglement was shown for a pair of Mn$_4$ molecules linked through C–H···Cl hydrogen bonds to give rise to an (Mn$_4$)-dimer. The ground $S = 9/2$ state of the single Mn$_4$ molecules were proved to be entangled with each other by a permanent link.

Further examples of supra-molecular structures, based on antiferromagnetic Cr$_7$Ni wheels, have been reported: two Cr$_7$Ni rings have been linked through metal centers. In the first report, the link was obtained through amines at the centre of the rings.
and this was found almost magnetically ineffective in most of the cases. More recently the functional link was attached through a nicotinic group at one of the carboxylate bridges of the ring; this was shown to be magnetically active, and, even more interestingly, could be changed at will, paving the way to the implementation of several schemes.

In most of the cases, the magnetic link is permanent but several switchable linkers can also be introduced (see Fig. 6). From the perspective of the realization of logic gates, this situation was described in ref. 21, where the case of polyoxometalates was considered. In this work the implementation of a √2SWAP gate was proposed as well as the possibility to use a STM tip to read out information. A Ru$^{2+}$–Ru$^{3+}$ dimer with redox properties has been also introduced into supra-molecular Cr$_7$Ni–M$_x$–Cr$_7$Ni structures. Very interesting also are optically switchable linkers like organic diarylethenes. In this case, however, the derivatives appear to be stable only when deposited on surfaces, thus limiting the number of measurements and applications. Further constraints in this kind of scheme appear to be the switching time of the functional linker, which needs to be comparable with that of the single molecular qubit. Moreover, the switching process should not alter the coherence of the single qubit. This poses tough requirements, and it has yet to be tested whether these can be met.

Molecules on surfaces

The discussion presented so far has essentially been based on our knowledge of the magnetic properties measured on bulk samples, but some studies mentioned above suggest that isolated molecules on surfaces may well behave differently. It is clear that proving that the magnetization can be retained in a single molecule is certainly a challenging goal for the future. From the examples mentioned, we have learnt that the environment – in particular for the case of an isolated molecule on a surface – can change the magnetic properties substantially. This is not necessarily detrimental but, if controlled, it can be used as a resource. A few examples – certainly not representative of the whole effort devoted to this emerging field – may help to explain the concept. Single Fe and Mn atoms have been placed on a CuN surface and their magnetization studied by inelastic electron tunnelling spectroscopy. Experimental results show that the magnetic anisotropy can be efficiently increased by the surface molecular network. This is very encouraging and complementary to the initial idea to tune the magnetic anisotropy by the molecular environment. A further example is the case of Fe-porphyrin deposited on ferromagnetic Ni or Co films on a Cu(100) surface. In this case the magnetization of the underlying Ni or Co layer was proved to control that of the Fe-porphyrin via a superexchange interaction. This adds a further tool to control and eventually to switch the magnetization of individual molecules on surfaces.

A clear advantage of molecules, with respect to single impurities implanted in a solid-state system, is the possibility to position molecules on specific parts of the surface by exploiting specific functional groups of procedures. Positioning single nano-objects on specific parts of a surface is actually required for any applications in information technology. Patterning of surfaces by self-organization assisted by stamps on the μm-scale was probably one of the first attempts to organize monolayers of Mn$_{12}$ molecules. Also worth mentioning is the selective deposition of Mn$_{12}$ onto the SiO$_2$ surface based on the electrostatic interaction of a positively charged Mn$_{12}$ derivative. In order to position single molecules, however, scanning probes or dip-pen techniques, combined with functionalization of derivatives, will be probably the highest performing.

Finally we would like to observe that – at least in principle – larger objects should be addressable more easily than single ions, and this also puts large molecular objects in a more favourable position with respect to monomers.

Conclusions

Fortunately, many early concerns regarding the technological challenges facing the field of information technology were revealed to be unfounded, and goals previously believed to be beyond fundamental limits have been achieved by alternative routes. Therefore, there is probably little point in being concerned whether or not the quantum computing machine of Fig. 1 will actually be achieved – the point is to keep searching for ways to make it.

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