Molecular vs. inorganic spintronics: the role of molecular materials and single molecules†

Julio Camarero and Eugenio Coronado

Molecular spintronics is a new and emerging sub-area of spintronics that can benefit from the achievements obtained in molecular electronics and molecular magnetism. The two major trends of this area are the design of molecular analogs of the inorganic spintronic structures, and the evolution towards single-molecule spintronics. The former trend opens the possibility to design cheaper spintronic devices compatible with plastic technology, while the second takes advantage of the possibility to tailor molecules with control down to the single spin. In this highlight these two trends will be compared with the state-of-the-art achieved in the conventional inorganic spintronic systems.

Introduction

Magneto-electronics, spin electronics, or spintronics is a relatively new research field¹,² whose central theme is the active manipulation of spin degrees of freedom of charge carriers (spin memory effect) in solid-state systems, in addition to their electronic charge (charge transport) used in traditional semiconductor electronics. The field has made a major impact on today’s daily life, for instance, by improving hard drive information storage (resulting in the award of the 2007 Nobel Physics prize to Albert Fert and Peter Grünberg for the discovery of ‘giant’ magnetoresistance, GMR³). Future potential applications range from the use of ferromagnetism to incorporate non-volatile memory into conventional electronics,⁴ to the potential use of an individual electron spin as a quantum bit in a quantum computer.⁵ The goals are manipulation of charge by spin (current flow control by magnetic means), as well as manipulation of spin by electronic transport (magnetic information storage by electric means).

Until now spintronics has been almost exclusively based on conventional inorganic metals⁶ and semiconductors.⁷ Still, molecular electronics emerged several decades ago as a promising possibility to complement and even to replace conventional inorganic electronics when it goes nano. In this context, a natural evolution of molecular electronics is that of using magnetic molecules, as well as molecule-based magnetic materials, as components of new spintronic systems. In principle the molecular world has all the ingredients that spintronics needs: molecules and...
molecule-based materials can be designed with the desired electronic properties, and the conductivity of the materials (conjugated polymers, for example) can be changed by more than fifteen orders of magnitude. On the other hand, the spin-relaxation times of magnetic molecules can be exceptionally long—between a few milliseconds and a second—and furthermore molecule-based ferromagnets ordering near room temperature are available. Finally, in this area the molecular world may present some advantages with respect to the inorganic one: thus, the use of molecule-based materials may be preferable, because electron spins can be preserved for longer time periods and distances. Other advantages of the molecular materials are their low density, flexibility, transparency, processability, chemical versatility and novel added functionalities (magnetic switching at the molecular level, emission of light, etc.).

In view of these possibilities, a new area, molecular spintronics, is emerging that benefits from the achievements obtained in two interrelated areas: molecular electronics and molecular magnetism. The two major trends of this area are the design of molecular analogs of the inorganic spintronic structures, and the evolution towards single-molecule spintronics. The former trend opens the possibility to design cheaper spintronic devices compatible with plastic technology, while the second takes advantage of the possibility to tailor molecules with control down to the single spin.

In this highlight article these two trends will be compared with the state-of-the-art achieved in the conventional inorganic spintronic systems, paying particular attention to the materials chemistry aspects.

Inorganic spintronics

Nanomagnetism (i.e., the study of the magnetic properties of magnetic matter at the nanoscale) has been a very active area in modern solid-state physics during recent decades. Magnetic nanostructures exhibit a wide range of fascinating phenomena, such as low dimensional magnetism, induced magnetization in noble metals, electron interference patterns, oscillatory magnetic coupling and giant magneto-resistance (GMR). These advances have been made possible thanks to the parallel development of methods to prepare and to characterize thin films and surfaces. In fact, now one can fabricate ‘designer magnetic solids’ by controlling materials at the atomic scale, that is layer by layer, row by row, and ultimately atom by atom.

Spintronics (including magnetic media) is the most active area within nanomagnetism. It uses the carrier spin degree of freedom to manipulate information in electronic devices. The founding step of spintronics is actually to build magnetic multilayers with individual thicknesses comparable to the mean free paths, so that spin-dependent electron transport can be observed. Typical devices and geometries for the injection/}

![Fig. 1 Basics of spintronics. (a) Multilayered structures used in today’s spintronic devices, consisting of two ferromagnetic electrodes separated by a non-magnetic metallic (spin valve, SV) or insulating (magnet tunnel junction, MTJ) spacer. Their corresponding magnetoresistive effects, called giant magnetoresistance, GMR, and tunneling magnetoresistance, TMR, respectively, are at the heart of spintronics. (b) Schematic representation of the magnetoresistive effects for the antiparallel (top) and parallel (bottom) magnetic configurations. The right Insets show their resistance-circuit analogs. The effective resistances seen by the two spin types of electrons depend on the relative magnetic orientation of the FM layers. For the antiparallel alignment (top), both spin-up and spin-down electrons suffer many scattering processes in some of the FM layers, resulting in a high resistance configuration. For the parallel arrangement (bottom), one of the conduction channels allows one type of electron to travel nearly unscattered, which results in a low resistance configuration acting as a spin filter.](image-url)
Fig. 2  Spin-transfer phenomena in magnetic nanostructures. Schematic representation of current-driven magnetic switching (a), steady precession (b), and domain wall displacement (c). A spin-polarized current, represented as an unscattered smiling spins, is prepared by a first magnetic layer FM1 (or magnetic domain) with an obliquely oriented spin polarization with respect to the magnetization direction of a second layer FM2 (or a domain wall DW). The spin accumulation in the latter results in a spin-transfer torque acting on FM2 (or DW). This can lead to magnetic switching, domain wall displacement, or magnetic oscillations in the microwave frequency range, without any external magnetic field.

accumulation of spin-up or spin-down electrons. However, the large current densities required in such systems mean that the device switching energy is likely to be high compared with that of semiconductor transistors.

On the other hand, the range of applications is expanding from the first read-heads devices used for computer disk drives based on SVs, to new types of non-volatile magnetic memories (MRAM) based on MTJs. The combination of magnetic elements with CMOS (complementary metal oxide semiconductor) components can change the common conception of the architecture of complex electronic components with a much tighter integration of logic and memory. Spin transfer nano-oscillators are promising candidates for applications in future wireless telecommunications when the output power can be increased. In these systems the frequency of the steady precession can be tuned from a few GHz to over 50 GHz by changing the applied magnetic field and/or the dc current, effectively resulting in a current controlled oscillator. This frequency window and their larger agility compared to standard voltage or current controlled oscillators enables their use in practical microwave circuits, as microwave emitters of our cell phones, for example.

Finally, we should notice that today’s spintronic applications using magnetic materials are almost exclusively based on inorganic metallic ferromagnets. A significant breakthrough is the quest for multifunctional materials (see Fig. 3), such as inorganic magnetic semiconductors and multiferroics, allowing control of the magnetization by other means than magnetic fields. The concomitance of several parameters in these materials is attractive to exploit new functionalities in future devices. For example, the ability to exploit the spin degree of freedom in magnetic semiconductors promises new logic devices with enhanced functionality, higher speeds and reduced power consumption. Multiferroic materials display several long-range ferroic orders, such as ferroelectricity, ferromagnetism, and ferroelasticity, bringing interesting additional functionalities. In this case, the coexistence of several long-order parameters brings about novel physical phenomena and offers possibilities for new device functions. For example, magnetoelectric coupling enables the control of the ferroelectric polarization by a magnetic field and, conversely, the manipulation of magnetization by an electric field. In both cases, future spintronic applications need to resort to functional materials with high transition temperatures.

Molecular analogs to inorganic spintronic materials

Spin-dependent phenomena in molecular systems has been a subject of increasing interest in the last few years. Unfortunately, the concepts of spin-transport phenomena for inorganic systems are often not readily transferable to organic ones. Among the reasons one can notice their strong electron–phonon coupling and the absence of an extended Fermi surface. Thus, most of the present efforts focus on understanding how spins can be injected, manipulated and detected in well-controlled molecular materials.

Experimental proofs of spin-dependent transport phenomena through organic spacers in contact with inorganic ferromagnetic electrodes have been recently reported. These include spin injection in π-conjugated molecules and organic tunneling junctions. However, there is a general lack of control over the magnetic response of the devices. Among others, severe temperature and bias dependence found in the magnetotransport properties and large resistances are serious limiting factors for future spintronic applications. In parallel, there are fabrication surface engineering issues that are not well understood and certainly difficult to control.

Notice that the ferromagnetic electrodes used in these spintronic heterostructures are conventional inorganic materials (lanthanum strontium manganites (LSMO) and Co), while the organic material is only used as a spacer. Hence, an open challenge in molecular spintronics is to use molecule-based ferromagnets as spin-injecting electrodes. Such a possibility should be useful to improve the injection of the polarized spins into the organic spacer materials since, due to the electronic similarities between the two molecular materials, the barrier for carrier injection is expected to be small. A promising example in this context is provided by the magnetic semiconductor
V[TCNE]x. Thin films of this material showing ferromagnetic ordering at ca. 220 K have been prepared, which show MR effects three orders of magnitude bigger than those reported in the inorganic analogs. Furthermore, this molecule-based magnetic material has been claimed to be a half semiconductor; thus it is a potential candidate for spin injection as it can be used as a source of spin-polarized charge current.38

Other materials that are of interest in spintronics are those showing granular MR. The inorganic materials of this kind consist of a metallic matrix (copper or silver) with magnetic inclusions. As molecular analogs one can imagine hybrid materials formed by inclusions of magnetic nanoparticles embedded into a conducting polymer.

Magnetic semiconductors are also of interest in spintronics. The typical example is formed by a semiconductor doped with small amounts of ferromagnetic impurities, such as manganese centers (diluted magnetic semiconductors, DMS). This kind of material exhibits both semiconducting properties and ferromagnetism, and has great potential in spintronic devices (spin-light emitting diodes (spin-LEDs) and spin-field effect transistors (spin-FETs), for example). Still, and despite some claims, the maximum $T_c$ reported so far in DMS materials is well below room temperature (173 K in GaAs doped with Mn26). As in the previous case, molecular analogs formed by organic conductors doped with magnetic molecules are feasible. An interesting example is that formed by an organic semiconductor (polyTPD) doped with small amounts of a Mn12 single-molecule magnet (SMM).39 In this case the Mn12 cluster acts as electron acceptor, oxidizing the organic molecule. As a result, the conductivity of the hybrid increases by 8 orders of magnitude, making the films suitable for hole injection layers in organic light emitting diodes (OLED) devices.39

As far as the applications are concerned, an interesting proposal is that of using magnetic electrodes in an OLED device with the aim of modulating the electroluminescence of the device.40 The electrons and holes injected from the electrodes form two types of excitons (singlets and triplets) in a 1 : 3 ratio. As the electroluminescence arises from the singlet excitons only, it is to be expected that a modulation of the singlet : triplet ratio through the application of a magnetic field should lead to a modulation of the electroluminescence. Another finding involving OLED devices has been the observation of a significant magnetic field dependence of current, photocurrent and electroluminescence in OLEDs based on organic $\pi$-conjugated semiconductors.41 Changes of comparable magnitude (up to 10% at 10 mT at 300 K) have been observed in all three experiments, which have been used to develop touch screen devices.

In analogy with inorganic materials, molecular multifunctional materials have also started to be designed which exhibit coexistence or even coupling of properties. In this case a building-block approach has been used. A relevant example in this context is provided by the magnetic molecular conductors and semiconductors.42 These materials are hybrid salts typically formed by organic donor layers, which furnish the electrical properties, separated by inorganic magnetic layers, furnishing the magnetic properties. Interesting physical effects have been observed in a very few cases. Worthy of mention are for example the observation of a coexistence of ferromagnetism and conductivity,43 and the observation of non-linear conductivity and giant negative magnetoresistance.42 Still, these phenomena occur at low temperatures (below 10 K), and in crystalline materials. Therefore, two challenging goals in this area are that of increasing the temperatures at which these phenomena occur, and to prepare these layered materials as organized thin films and multilayers.

**Single-molecule nanospintrons**

One trend in spintronics is to work in reduced dimensions with the aim of discovering new magnetic phenomena and of manipulating spins one by one. When we connect a single nano-object to two magnetic electrodes, the spin-dependent transport is predicted to interplay with single electron physics, i.e., with the Coulomb blockade in the case of weak coupling between the nano-object and the electrodes to give rise to magnet-Coulomb effects, and with the Kondo effect in the case of strong coupling between the nano-object and the electrodes, giving rise to a peak in the conductance at zero bias that splits in the presence of a magnetic field. An excellent review on this topic has been recently published.43

Most works in this area have been devoted to the study of inorganic nanoparticles. Still, some organic nano-objects have also been studied. A significant case is provided by carbon nanotubes. Thus, SVs44 and spin-FETs45 based on carbon nanotubes have been recently reported. One can see here the advantage of using carbon nanotubes for spin transport. Due to both high velocities and very long spin lifetimes (associated with their very small spin–orbit coupling), these organic conductors are promising candidates for future nanospintronic devices presenting very large GMR- or TMR-like effects. Another interesting hybrid nanostructure is that formed by networks of nanoparticles connected with linker molecules. As examples we can mention quantum dots bridged by molecules that show coherent spin transfer,46 and gold nanoparticles connected through an organic spin-polarized molecule that controls the co-tunneling currents in this network.47

Clearly, molecules are also attractive nano-objects to be studied in nanospintronic. In fact, the transport through single molecules (or self-assembled molecular monolayers, SAMs) has been extensively studied in the field of molecular electronics. Since the theoretical proposal of Aviram and Ratner of a molecular rectifier in 1973, this field is still trying to make reliable and reproduducible electrical contacts between inorganic electrodes and the molecules in order to better understand the metal/molecule junction and the intramolecular transport.48 Hence, it is not surprising that the nascent field of single-molecule spintronics has been almost exclusively focused on theoretical proposals.11–14 Very few experiments on single-molecule transport have been reported so far. In a set of experiments a non-magnetic molecule, fullerene C60, is connected to two ferromagnetic electrodes (Ni) and to a gate. In this case a very large negative magnetoresistance effect, together with a Kondo anomaly, is observed.49 The second set of experiments consists of connecting a magnetic molecule, in particular a high-spin SMM, to two
non-magnetic electrodes. This kind of experiment can be done by connecting the molecule through a STM tip and a conducting surface, and often requires ultra-high vacuum and low temperature (<1 K). Another possibility uses the break-junction technique to trap the molecule between two electrodes, acting as current/voltage electrodes, while a third electrode is used as a gate. This last procedure has been recently used to study the electron transport through a Mn\textsubscript{12} SMM.\textsuperscript{50} A Coulomb blockade staircase has been observed, which is typical of the weak coupling of the molecule with the electrodes, together with some additional features, which have been tentatively associated with the interaction between the tunneling electrons with the spin states of the molecule. A discussion on the recent progress made in this area, with a particular focus on SMMs, can be found in ref. 51. As the transport measurements across magnetic molecules are at the very early stage, many problems, which are intrinsic to the molecules, need to be solved to obtain reliable results.

An interesting concern deals with the stability of these magnetic molecules when they are deposited on a metallic surface. In molecular magnetism one usually works with crystals obtained from solutions. These crystals have as building blocks magnetic molecules (SMMs, for example), which are stabilized in the lattice through intermolecular interactions. Typically, these SMMs are poly-nuclear coordination complexes formed by metallic centers connected and surrounded by bridging and terminal ligands. It is difficult to predict if these complex species will survive when they are deposited on a surface. In most cases this process involves the use of a solution containing the magnetic molecule and to deposit it on the surface. Of course, some structural changes, accompanied with changes in the electronic structure, are to be expected when the molecule is transferred from the crystal lattice to the solution and, finally, to the surface. In addition, more drastic changes can also occur. Thus, some labile ligands (coordinated solvent molecules, for example) may dissociate from the metal ions, and furthermore, these metal ions may react with the surface. Such a chemical instability has been found, for example, in some Mn\textsubscript{12} derivatives deposited on gold surfaces. In these SMMs X-ray absorption spectroscopy and X-ray magnetic circular dichroism indicate a redox instability of the complex with a partial reduction of metal ions to Mn\textsuperscript{2+}.\textsuperscript{52} In some cases a molecular species is thermally stable and, therefore, it can be deposited on the surface by sublimation of the solid. This procedure is very convenient as it enables the deposition \textit{in situ} of the molecule and its study by STM in UHV. However, and in contrast with organic crystals, the vast majority of coordination metal complexes cannot be evaporated since they are very often charged species, or thermally unstable neutral species. Alternative methods such as electrospray techniques, which allow the evaporation of charged species, are now starting to be used to solve this problem.\textsuperscript{53}

A second concern is that of controlling, as much as possible, the deposition of the magnetic molecules on the metallic surface. Thus, several approaches have been developed in which in a first step the molecule, the surface, or both have been chemically functionalized. In a second step bottom-up, top-down or a combination of both approaches have been used in the attempt to deposit SMMs on the surface with nanoscale accuracy,\textsuperscript{54} to organize them taking advantage of the self-assembling processes,\textsuperscript{55} and, even, to orient them on the surface.\textsuperscript{56} Still, this control is very limited and the study of the magneto-transport properties of these single molecules remains largely unexplored.

Notice that control of the deposition of magnetic molecules on surfaces can be important to produce self-assembled ordered arrays of magnetic “dots” of the smallest size—nanometer size—for their use in information storage devices, which is one of the current challenges in nanomagnetism.\textsuperscript{57} The complexity and cost of the traditional top-down lithographic methods rises exponentially at the nanometer range, and the use of self-organization processes for patterning technologies\textsuperscript{58,59} is becoming particularly appealing thanks to its low cost and high production efficiency. For this aim, it is mandatory to ensure all the components of the array are identical, a fact that perhaps can only be possible by using magnetic molecules, identical by definition.

In the perspective of using magnetic molecules for developing nanospintronics devices, besides the conventional applications (spin valves, spin transistors or magnetic bits), we can imagine applications in quantum computing and in nanoscale oscillators and resonators. In quantum computing a possible advantage of these molecules is the long quantum-coherence times they exhibit compared with semiconducting materials\textsuperscript{60} and the possibility of scalability. In this context a theoretical proposal based on molecular nanospintronics has already been developed. It involves an all-electrical scheme for the implementation of a two-qubit gates and readout which is within reach of current technology.\textsuperscript{61} This scheme involves the use of molecules formed by two localized spins whose interaction can be switched on and off by means of a redox-active central unit. The change between on and off states can be achieved by injection or extraction of a single electron in the redox unit using a STM tip or a three electrode setup (Fig. 4). The other application where the SMMs can be attractive is in the production of nanoscale oscillators and resonators with THz frequencies. As we have seen before (Fig. 2), this recent spintronic application has been used to switch an inorganic magnet without applying a magnetic field and to generate microwaves (the steady precession of the oscillator ranges from a few GHz to over 50 GHz). A SMM becomes attractive in this context since,\n
![Fig. 4 Quantum computing using magnetic molecules. A polyoxometallate molecule formed by two localized spins and a central redox cluster is electrically contacted by a STM setup to act as a two-qubit gate (adapted from ref. 61).](image-url)
due to its small magnetic moment, the reversal of the magnetization is very easy; at the same time its strong anisotropy might enable the production of nanoscale oscillators and resonators with frequencies as high as 0.5 THz.

Outlook

Molecular spintronics is only in its infancy and requires careful and quantitative research to establish a physical picture of many important and general issues. Research focused on the elaboration processes at the nanometer scale has to be performed to get the atomic level control required to tailor the molecular analogs of the conventional inorganic spintronic nanostructures. In this context, advances in processing techniques leading to improvement of material properties are desired. The field of single-molecule spintronics is at an even earlier stage with more questions than answers and very few experiments on transport through magnetic molecules.

As far as the molecular spintronic nanostructures are concerned, particular attention is needed for issues related to molecular engineering of hybrid organic and inorganic materials, surfaces, interfaces (organic/organic, organic/inorganic) and structures.64 For instance, detailed understanding of growth mechanisms in organic thin-film deposition is crucial for tailoring growth morphologies,63 which in turn determine the physical properties of the resulting films. Although plastic electronics have started to enter the consumer market with devices like organic FETs and OLEDs, there is still a severe lack of understanding of the basic growth mechanisms in molecular materials. This is in sharp contrast with what happens with the epitaxy of metal films where, apart from the thermodynamic aspects of growth, single atom diffusion can substantially determine growth morphologies. In organic thin-film growth, a wide variety of growth morphologies can appear due to the complexity of the building blocks and their interactions.64 In fact, a richer spectrum of growth mechanisms is expected in organic film growth because molecules are anisotropic and have internal degrees of freedom that open novel diffusion channels accompanied by changes in the molecular conformations.

From the point of view of the physical properties, several fundamental questions need to be investigated. i) What controls spin injection from ferromagnetic contacts to the molecule? ii) What is the role played by an external bias voltage? iii) How is spin transport related to chemical details? iv) Can the molecular spin state of a magnetic molecule be manipulated through an electrical current? v) To what extent can the state-of-the-art theory compare with the experiments?

From the point of view of possible applications, it is to be noticed that even if molecular spintronic systems with suitable performance characteristics are available, nanotechnology solutions will find practical use only if they are economically viable. We will need hence to develop methods for the controlled mass fabrication of functional molecular spintronic nanostructures and their integration into usable macroscopic systems and devices. This general approach should also result in new materials and devices that might find use beyond the applications traditionally targeted by miniaturization efforts and, particularly, by new insights into the physics of small systems, in this case combined with chemical methods. The most interesting devices will probably be those that we have not even contemplated here!

Acknowledgements

We thank the Spanish Ministerio de Ciencia e Innovación for financial support (projects MAT2006-13470, MAT2007-61584 and CSD 2007-00010, Consolider-Ingenio in Molecular Nanoscience), the Comunidad de Madrid (project Nanomagnet S-0505/MAT/0194) and the Generalidad Valenciana (Project PROMETEO/2008/128). Financial support was also provided by EC through NoE MAGMANet.

References
