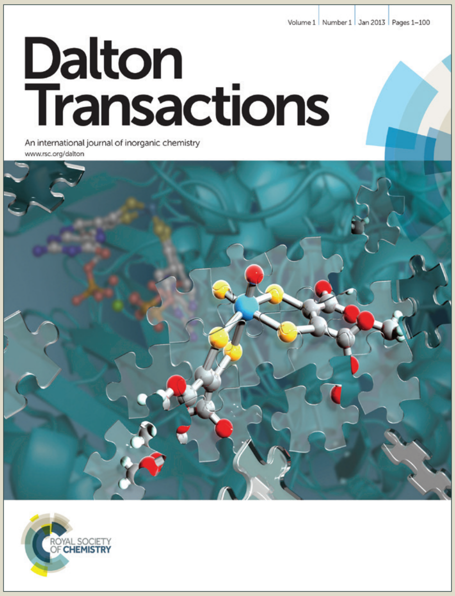
Dalton Transactions

Accepted Manuscript



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Dalton Transactions

Cite this: DOI: 10.1039/c0xx00000x

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Perspective

Interweaving spins with their environment: novel inorganic nanohybrids with controllable magnetic properties.

Christian Cervetti,[a†] **Eric Heintze,**[a†] **and Lapo Bogani***[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We discuss current developments in the synthesis and characterization of magnetic nanohybrids made of molecular magnets and nanostructured materials. We first review several novel approaches that have recently been attempted to combine magnetic coordination complexes with differently-obtained inorganic systems. Special focus is given on how the altered environment can affect the magnetic properties of single molecules, providing new routes to multifunctional devices based on hybrid magnetic nanosystems. We then show how this approach is opening new outlooks towards the control of nanomagnets using external stimuli (e.g. photons, electrons, etc...) and for the creation of ultra-sensitive devices. Eventually we provide a unified vision of the area, with a personal perspective of the main goals currently at stake and of possible future developments.

1. Introduction

The development of novel magnetic materials has been one of the mainstays of inorganic chemistry[1]. Magnetic systems were initially restricted to three-dimensional inorganic solids, and much of early research concentrated on understanding the properties of structurally-simple metals, semiconductors and insulators. The development of complex oxides opened several new fields, introducing intriguing effects such as high-temperature superconductivity, multiferroics, and ferroelectricity, to name just a few[2]. Such systems remain challenging for both synthesis and characterization and constitute very fertile research grounds for physicists and chemists alike. Likewise, the chemistry of metal complexes and supramolecular adducts unlocked whole new perspectives in the synthesis of inorganic materials. Among other possibilities, it allowed linking a controlled number of metal centres together using multidentate or bridging groups, adding tailored functionalities via rational molecular design, and engineering the properties of extended structures via tuning the weak interactions among their building blocks.

In magnetism, the application of these methodologies has led to a new research area, called molecular magnetism[1]. The systematic investigation of metal complexes has offered a much deeper understanding of the magnetic properties of metal ions, the exchange pathways offered by ligands and intermolecular interactions. While the field initially focused on obtaining three-dimensional magnetic ordering at high temperatures (a task eventually achieved, after decades of attempts), it was soon realized that molecular magnetic materials are better suited for the creation of low-dimensional structures, rather than extended systems. It is on this background that the first single-molecule magnets (SMMs) were created: molecular magnetic systems with nanoscale dimensions that can retain their magnetization for extremely long times at low temperatures[3]. The resulting magnetic hysteresis allows storing information at the molecular level, and the clean observation of macroscopic quantum effects[4,5] has made SMMs a veritable multidisciplinary

Christian Cervetti obtained his Master in Physics at the University of Modena and Reggio Emilia, Italy, in 2010. He is PhD student in Stuttgart, Germany, at the International Max Planck Research School for Advanced Materials by the Max Planck Society, focusing on nanoscale magnetism and spin transport in carbon nanomaterials.

Eric Heintze obtained his Master in Physics at the University of Stuttgart, Germany, on optical effects in SCMs. Since years, he is member of the Lacrosse German National Team. He is currently completing his Ph.D. work, focusing on ESR on optically-switchable magnetic structures and molecules.

Lapo Bogani, after a PhD in Florence (IT) and an individual Marie Curie fellowship, is now ERC and Sofja Kovalewskaja group leader in Stuttgart, Germany. His work on single nanomagnets, and functional nanostructures has led to several awards, including the G. Semerano, R. Nasini, Burghen and N. Kurti prizes playground for physicists and chemists. Such results were then extended to magnetic chains, for which slow dynamics of the magnetization could also be obtained, albeit with a different mechanism[6]. These systems, called Single Chain Magnets (SCMs) in analogy to SMMs, showed quantum and finite-size effects[7], and a somehow more complex phenomenology. A whole research area then developed around the synthesis and functionalization of SMMs and SCMs, leading to rationally-designed structures and functionalizations.

Concurrently, new forms of nanostructured inorganic materials have appeared, establishing the new quest for nanoscale functional devices. Carbon nanostructures, such as nanotubes[8] and graphene[9], have emerged as key elements in the fabriacation of superior electronic nanodevices and ultra-sensitive detection in the liquid and gas phases[10]. Their transport and mechanical properties, intimately linked to their structural features, constitute a rich ground of materials research that lead to ultra-high electron mobilities[11,12], Coulomb blockade[13] and high quality mechanical resonators[14]. Non-carbon based structures, such as nanowires[15] and quantum dots, keep on attracting attention as promising systems for quantum computation and to investigate novel physics, such as Majorana fermions[16]. The application of improved nanostructuring techniques to noble metals has also opened the way to the field of plasmonics[17], where light and evanescent waves are guided and manipulated via aptly-designed nanostructures. The combination of these systems with magnetic functionalities, and molecular materials in particular, holds great promises[18]. The very last few years have seen several steps forward in this direction, as the fundaments of this area are being built up. Nevertheless much remains to be done, and both the creation and study of such hybrid devices are challenging tasks, involving ingenious chemical solutions, rigorous physical investigations and new theoretical treatments. A minority of specialized papers cover a few of the areas, almost no reviews exist covering the full field and a unified perspective is still somehow lacking. Here we provide such a unified perspective, highlighting the correlation between structure and functionality, the connected fabrication methods and showing the main results obtained. We particularly stress the relevance of the interactions between the magnetic molecules and the altered environment of the hybrids, which often constitutes a major difference with the crystalline surroundings of molecular materials. As many of the properties of the novel hybrid devices depend exactly on this altered environment, the successful hybrid systems will be those in which the environment-spin interplay is efficiently harnessed and controlled.

2. Magnetic nanomaterials

In this section we provide the background necessary to understand the synthesis and properties of the hybrids, in a language accessible to both physicists and chemists. Two alternative well-known approaches have been used to create nanoscale materials: a top-down or a bottom-up strategy (Fig.1). The former approach is used to create functional parts of nanodevices and constitutes one of the main ways to obtain graphene, carbon nanomaterials, quantum dots and plasmonic devices. It has the advantage of allowing the use of purely inorganic materials, easier integration in devices and structuring on surfaces. The main drawback lies in a resulting dispersion of sizes and properties, which has to be either considered in large samples, or overcome by characterizing one single nanosystem. The latter approach, on the contrary, is the main strategy employed to create SMMs and has the advantage of producing molecular systems with exactly the same structure and shape, where the position and nature of each atom is known.

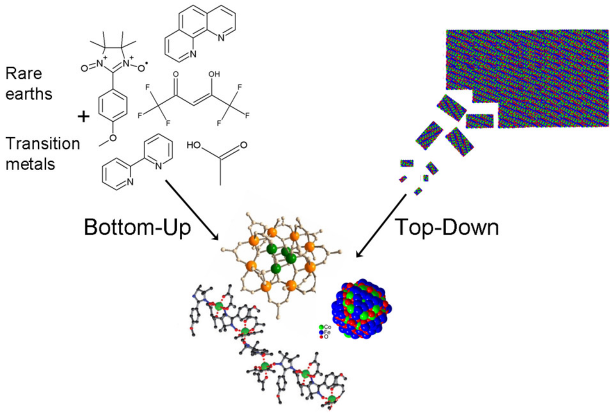

Fig.1 Schematic representation of bottom-up and top-down processes. (here represented by processes used to make magnetic nanomaterials). Hybrid nanosystems often stem from the union of both methodologies, so as to combine the advantages of both.

A characteristic of hybrid magnetic systems is that they include functional parts made with each strategy, so as to combine the advantages of the two approaches. For example, spin valves can be created out of a carbon nanostructure, often obtained via top-down methods, to which a functional spintronic element is added in the form of a molecular compound; the resulting system combines the electronic functionality of the carbon nanotube with the magnetic behaviour of the molecule.

As the functional magnetic elements are typically SMMs, it is useful to briefly review their properties here, stressing the ones that can be most influenced by the environment[19]. SMMs consist of a core of magnetic ions bridged by chemical groups and shielded by an outer shell of organic ligands (e.g. acetate in the archetypal $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ cluster[3,4]). The core spins interact strongly with each other, typically via ligand-mediated superexchange interactions, so that they produce a total spin ground state well-separated from the higher ones. As only this state is populated at sufficiently low temperatures (T), the whole cluster can be considered as a giant spin system. This whole molecular spin can also have anisotropic properties, resulting from the anisotropy and disposition of its individual components[19], that can be described using Stevens equivalent operators[20]. Stevens' formalism allows describing the effect of the electric field of the crystal as an expansion in tesseral harmonics of progressively lower symmetry, thus allowing to visualize the origin of the anisotropy components and the symmetry effects of the environment (Fig.2a). In SMMs the axial anisotropy term ($B_2^0 \hat{O}_2^0$ in Stevens formalism) is dominant (Fig.2b) and has a negative coefficient, leading to a double well-potential landscape for the spin levels. The spin-up and spin-down configurations are then separated by an anisotropy barrier ΔE (Fig. 2c) so that the relaxation time τ of the magnetization diverges exponentially with temperature T, following the Arrhenius law: $\tau = \tau_0 e^{\Delta E / k_B T}$.

At sufficiently low T, the relaxation becomes slower than the measuring time of the experiment, giving rise to a magnetic hysteresis loop of molecular origin. Non-axial anisotropy terms (i.e. all those outside the first column, in Fig. 2a) lead to mixing of the quantum states at opposite sides of the barrier. This enables a faster spin relaxation via resonant quantum tunnelling (QT) for the magnetic field (H) values at which mixed states become degenerate[21,22]. QT produces steps in the hysteresis loop, which in some cases can be considered a fingerprint of SMM behaviour.

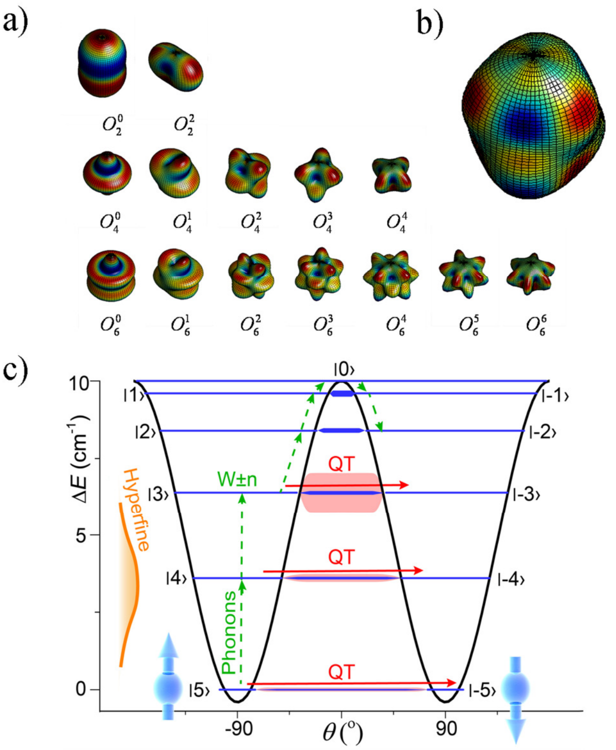

Fig.2 a) Geometric representation of the anisotropy elements in spherical coordinates, described by the first Stevens operators, showing the progressive addition of the tesseral harmonic terms. b) Geometric representation of the magnetic anisotropy of the Fe_4 SMM. The dominant axial term is reduced by a factor of 500, for clarity reasons. c) Resulting energy level diagram for the Fe_4 SMMs, with environmental effects highlighted (Scales are exaggerated for clarity). The underbarrier quantum tunnelling (QT) processes, made possible by higher order Stevens operators, are highlighted in red; Hyperfine and dipolar effects are shown as a distribution of energies around the single molecule levels (yellow); transitions due to phonon absorptions are shown as dashed arrows (green).

The quantum tunnelling properties are very sensitive to many different forms of perturbation arising from interaction with the surroundings[22]. Neighbouring spins, be they other molecules (via dipolar interactions) or the nuclear spin bath of the molecule itself (via hyperfine interactions), produce a distribution of effective magnetic fields, around the value of the externally applied one, which broadens the QT steps. Moreover, these interactions are responsible for the destruction of coherence in the molecular system, a fundamental problem for any quantum computing scheme. In this sense, hybrid devices implementing only one or a few SMMs can thus help creating systems with improved quantum properties.

By exciting the system into higher energy levels of the double well potential via interaction with the phononic (or vibrational) bath, the steps of the barrier can be climbed up.[19,23,24] This relaxation mechanism is the most important one at high temperatures or when tunneling is suppressed, e.g. by applying an external magnetic field. If the density of available phononic modes is changed, e.g. by embedding the SMM in different structures, the system will thus show altered thermal-relaxation dynamics[23]. The main repercussion of this is expected to be an appreciable variation of the spin-flip attempt rate τ_0 , predicted to depend on the fifth power of the sound velocity in the material[24].

3. Engineering the interactions

The interaction of a molecular spin with its surroundings plays an essential role in the design of new complexes and their integration into devices. The chemistry of SMMs enables designing this interaction by equipping the magnetic units with bridging ligands that can promote or lower dipolar and intermolecular interactions. Specific supramolecular arrangements can be produced (Fig. 3a), to obtain weakly exchange-interacting dimers, trimers and tetramers that are the first step towards entangled spin states[26] and other complex quantum features. The first exchange-coupled molecular systems was created via multiple C–H···Cl hydrogen bonds in the $[Mn_4O_3Cl_4(O_2CEt)_3(py)_3]$ dimer[25]. Nevertheless, the tailoring of the coupling in this case results to be rather problematic. A thorough investigation has been carried out, both theoretically and experimentally, for dimers of general formula $[\{Cr_7NiF_3(Etglu)(O_2C^tBu)_{16}\}_2L]$, where the Ni site allows changing the linking group L systematically[27]. The studied dimers included different hetero-aromatic linkers, such as pyrazine (*pyr* in short), bidimethylpyrazolyl (*bipz*), 4,4'-bipyridyl (*bipy*), trans-1,2-bipyridylethene (*bipyet*) and bipyridyltetrazine (*bipytz*), as in Fig.3a. These groups differ primarily in: length, ranging from 7 Å for pyrazine to 15 Å of bipyridyltetrazine, dihedral (torsional) angle between the aromatic cycles, from 28° in *bipytz* to 56° in *bipz*, and number of simple covalent σ bonds between the heteroaromatic groups. DFT calculations[28] revealed that, in general, the magnetic interaction is maximum when the overlap (both spatial and in energy) between the spin-polarized orbitals of the Ni site and the orbitals of the N linker atoms is maximized. Moreover, the π orbitals are found to propagate the spin-polarization along the linker group more effectively than σ orbitals. Comparing the different linkers evinced that the spin polarization propagates though them following a few general criteria. First of all, the spin polarization alternates moving from each atom to the next along the linker. This implies that it is possible to impose either ferromagnetic (FM) or antiferromagnetic (AFM) coupling between the two molecular spins by simply choosing a linker which structure allows bond pathways containing only an odd or even number of atoms respectively. Furthermore, when the linker structure (e.g. *bipz*) allows both even and odd numbered bond pathways, supporting AFM and FM coupling simultaneously, destructive interference between the two paths reduces considerably the spin polarization in the middle of the linker. This explains why the cross-talking between the two molecular spins is weaker for *bipz*, despite it being shortest. For the case of linkers containing more than one aromatic ring, the dihedral angle θ_d between the conjugated rings is found to play an important role in tuning the spin coupling. The

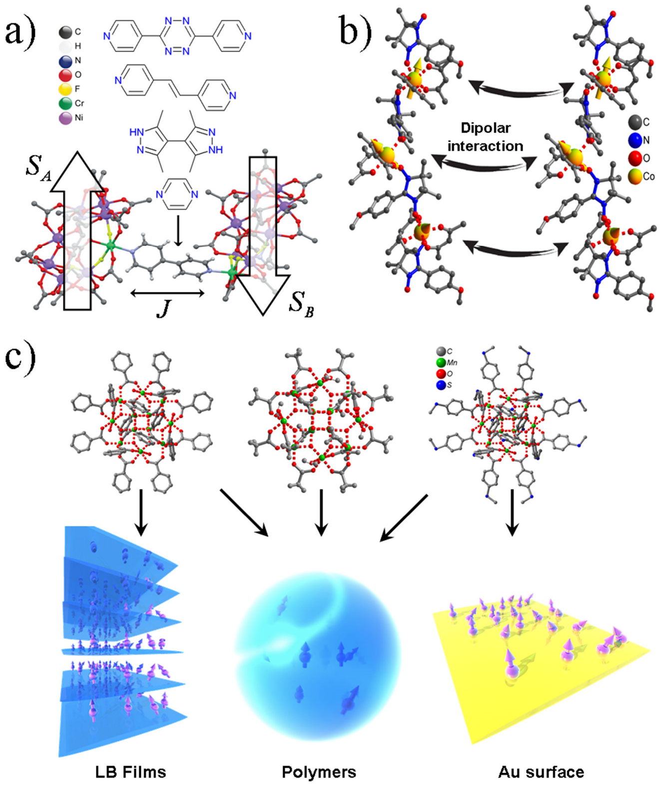

Fig.3 a) Tailored intermolecular interactions in SMMs, exemplified by Cr_7Ni compounds), in which the bridging group (here hetero-aromatic linkers) can be tuned and the interactions along with it.[28] b) Dipolar interactions affecting SCMs (here CoNIT-PhoMe, see text), which can be controlled by chemically changing the spacing ligands.[32] c) Chemical tailoring of the clusters of the Mn_{12} family, so as to include them into different environments such a Langmuir-Blodgett films (left), polymers (center) and Au surfaces (right)[33]. Figure subpanel a adapted with permission from Ref. 28.

exchange coupling constant between two molecular spins is found to obey a $\cos^2(\theta_d)$ trend, reaching the maximum value for coplanar rings. Importantly, the conductance of biphenyl junctions was found to follow the same angular behaviour[29], establishing a fundamental parallel between electron transfer mechanisms and magnetic coupling. These studies, in addition to the fundamental insight that they provide on interacting quantum systems, are also valuable for the study of hybrids where the interaction is mediated by linkers. In particular, as we will see later on, the overlap of delocalized π orbitals may provide useful correlations with the covalent functionalization of graphene using nitrophenyl radicals[52].

The suppression of dipolar interactions can be mimicked in crystals, showing the dramatic effect that the environment can have before any hybrid is made. An illustrative example is given by rare-earth-based SCMs[31]. Here the surroundings consist of identical spins belonging to the different chains packed in the crystal. In order to observe SCM behaviour, intra-chain interactions have to be dominant, despite the fact that the development of magnetic correlation along the chains enhances inter-chain interactions. In the rare-earth-based compound [Dy(hfac)$_3${NIT(Et)}] (hfac=hexafluoroacetylacetonate, NITEt=2-ethyl-4,4,5,5- tetramethyl-4,5-dihydro-l*H*-imidazolyl-1-oxyl 3-oxide), the high magnetic anisotropy of Dy^{3+} ions, combined with the short interchain distances, makes the dipolar interaction large enough to produce three-dimensional magnetic order[31]. Using the NIT(C_6H_4OPh) radical in place of NIT(Et) allowed increasing the interchain distance while keeping the intrachain parameters unaltered. This reduces the dipolar interaction between different chains, suppressing the 3D magnetic order and promoting the desired dynamic properties[32].

The tailoring of the ligands also allows incorporation of SMMs into different environments and in truly hybrid systems. One of the first studies on environmental effects[33] considered the archetypal Mn_{12} cluster, with a substitution of the peripheral acetate ligands so as to accommodate it into Langmuir-Blodgett films, amorphous polymeric matrices, and on metal surfaces such as Au(111) (Fig. 3c). The following investigation required the development of dedicated, high-sensitivity magneto-optical instrumentation, so as to detect the small quantities of SMMs in such structures. This lead to the observation of a gradual shrinking of the hysteresis cycle going towards softer environments.[33] While several explanations have been proposed for this phenomenon, a large part of the observation can be attributed to the presence of different phononic environments, which can considerably increase the spin-flip attempt rate of Mn_{12} clusters. This was one of the first evidences of the importance of the environment and spin-phonon coupling for the relaxation of the magnetization.

The strategy of using tailored organic ligands to tune different interactions can be exploited to integrate molecular spins in spintronics and multifunctional devices. This task requires establishing a coupling between the magnetic response of the molecular unit and other parts of the device, ensuring, at the same time, that all elements retain their significant features. Two main methods are usually followed. One is to change the SMM peripheral groups with appropriate ligands whose reactivity promotes a selective incorporation. A second approach is to pre-functionalise the target material either with groups that can undergo substitution with the SMM peripheral moieties[34] or with self-assembled monolayers that can trap the SMM both by ionic or van der Waals interactions,[35] with this last method having the potential of producing templating effects[36]. Devices of different dimensionality, such as single-molecule junctions (0D), nanotubes and nanowires (1D), metallic surfaces and two-dimensional materials (2D) generate radically different architectures enabling at the same time alternative strategies to study and tailor the interactions present in the system. Examples of systems that have thus been anchored to conducting inorganic substrates are given in Fig.4.

Anchoring magnetic molecules to an extended magnetic or non-magnetic surface offers the opportunity to study several environmental effects such as spin-phonon coupling, magnetic interactions and charge transfer processes. A major difficulty in this widely explored scenario is the poor redox stability of some SMMs, such as the Mn_{12}, that, once in contact with the metal, can lose their magnetic features due to either charge transfer or structural deformations[37]. Positive results were only achieved recently[38] employing a functionalized [$Fe_4(OMe)_6(dpm)_6$] (Hdpm =dipivaloylmethane) (Fe_4 in short) cluster with improved structure[39] anchored to a gold surface via a sulphur terminated alkyl chain. The magnetic response addressed via X-ray magnetic circular dichroism revealed the opening of a hysteresis loop characterized by QT steps at sub-Kelvin temperatures[40]. The system was shown to follow altered dynamics, with the presence of additional transverse Stevens operators, and, in particular, of a B_4^3 contribution. In addition, these experiments also hinted at a different spin-phonon coupling for molecules wired to metallic surfaces, as compared with the bulk case. Nonetheless, a full treatment and clear-cut evidence could not be extracted. The first complete theoretical and experimental studies of the influence of a different spin-phonon coupling on the spin dynamical response of conducting hybrids are expected to appear soon[23].

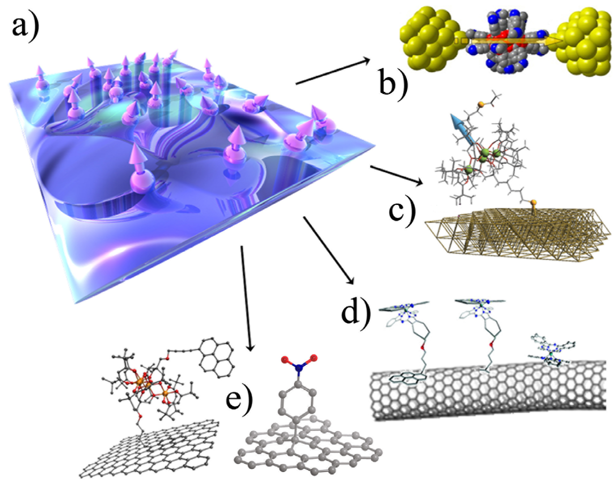

Fig.4 a) Schematic representation of spins interacting with a sea of delocalized electrons, and several systems that lead to this situation. b) used in Single molecule Junctions, c) Functionalized Fe_4 clusters linked to a metal surface[40]; d) A_3B-Tb-Pc, modified with three different functional groups, so as to graft it on carbon nanotubes; e) Functionalization of graphene surfaces using molecular clusters with pyrene[23] ligands (left) or nitrophenyl[52] radicals (right), as used to bind magnetic systems on a graphene surface. Figure subpanels c and e adapted with permission from Ref.s 40 and 52.

The same scheme has been exploited to investigate the magnetic interactions between a molecular spin and a ferromagnetic layer[41]. A mononuclear Tb double-decker complex ($TbPc_2$) was evaporated in situ on thin Ni films with different orientations of their easy-axis. The molecule and film magnetic moments, M_{Tb} and M_{Ni} respectively, were monitored selectively as function of an external magnetic field by probing the X-ray magnetic circular dichroism at the Tb and Ni absorption edges. The $TbPc_2$ easy-axis points perpendicular to the phthalocynines plane and, owing to the compact molecular structure, is coupled to the M_{Ti} via strong super-exchange interactions. The molecular spin couples antiferromagnetically with the substrate magnetization and the presence of the substrate does not seem to modify the molecule anisotropy. By sweeping the magnetic field it was possible to study the super-exchange interaction in film/molecule system and its effect on the hysteresis loop of the $TbPc_2$. The Pc ligand that separates the Tb ion from the substrate is found to mediate the super-exchange coupling. Moreover, the insertion of Li as electron donor or O as acceptor, at the interface, created charge-transfer effects visible on the super-exchange coupling. An increase of electron occupancy of the Pc ligand causes an increase the super-exchange interaction and moreover overcomes the hyperfine interaction increasing the relaxation time M_{Tb} up to 10^3 s at 100 K.

The rich chemistry of carbon-based nanostructures, such as CNT and graphene, offers a wider range of strategies to engineer and study the interactions between the SMM and extended conducting channels. Similar to the single molecule junction case, reported in detail in the following paragraph, the specific binding ligand is responsible for the coupling with the conducting element of the device. Covalent and non-covalent bindings represent the two main routes for the control of the interaction with molecular spins.

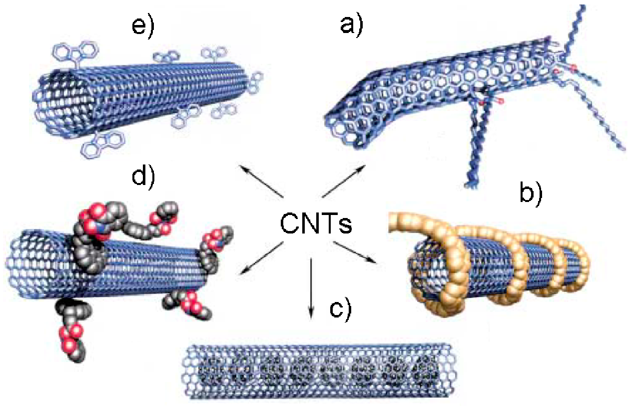

Fig.5 Schematic description of different methods of functionalization of CNTs. a) Covalent binding on defects, here shown for chains. b) Non-covalent exhohedral functionalization, here shown for polymers wrapped around the CNT. c) Endohedral functionalization, as shown for fullerenes in the inner CNT cavity. d) Non-covalent functionalization with van-der Waals and π-stacking interactions. e) Covalent functionalization with molecular groups. Adapted with permission from Ref. 42.

One route for non-covalent functionalization of carbon-based materials relies on π-π staking interactions of aromatic groups, such as pyrene or porphyrin ones, with the graphene/CNT conjugated structure. Widely used for the functionalization of CNTs, π-π staking interactions with pyrene are strong enough to immobilize proteins[43] and nanoparticles[44] permitting further processing in solution[42]. Following this approach, a detailed modification of the tripod ligand $R'–O–CH_2C(CH_2OH)_3$ binding a terminal pyrene group via an alkyl chain was performed. The tripod is then bound to the Fe_4 compound, which can then be successfully grafted to CNTs[45] and graphene[46]. The grafting process allowed a particularly clean control over the number of SMMs in the hybrids and offered a new view on the reactivity of single CNTs with pyrene. The sequential grafting of a number of SMMs also allowed using CNT-based field effect transistors to detect single grafting events. Moreover, by tailoring the number alkyl chain atoms[47], this approach can be exploited to tune the coupling between the magnetic centre and the conducting carbon channel. The one-dimensional structure of CNTs offers an alternative route for non-covalent binding that makes use of long alkyl chains. Exploiting weaker Van der Waals interactions with the hydrophobic wall of the CNT, the alkyl groups can either wrap the tube around its diameter (Fig.5), or lay along its axis. In this case, the lack of delocalized π orbitals in the grafting group is likely to make the interaction with the SMM weaker, preserving the tube electronic structure to a greater extent. Nevertheless, the selectivity of these two different groups for CNTs seems to depend on several details such as the tube diameter, the number of grafting groups attached to the magnetic unit and the specific conditions in which the hybrid material is produced, such as processing in solution or on either pre-functionalized or non-pre-functionalized surfaces[44]. Similar strategies were also used to create CNT hybrids containing Tb-based double-deckers[48], which possess a large spin density on the phtalocyanine ligands, and can thus produce a considerable interaction with the CNT electrons.

Covalent functionalization of CNTs can only take place at defective sites present in the tube sidewalls (Fig.5). These are often naturally present, as no current growth method is able to yield perfect CNTs without any defect. Moreover, oxidative treatments (often performed in order to purify the tubes from growth contaminants[42]) as well as ultrasonication (used to untangle the CNT bundles) can create additional defects, sometimes in large amounts. The removal of the metal catalyst, e.g. with HNO_3, results in local openings of the carbon structure that favour the addition of organic groups, such as carboxyl ones, which can act as valuable anchor groups for further functionalization. These chemical possibilities remain unexplored in the creation of SMM-CNT hybrids.

Eventually, CNTs offer the possibility of endohedral encapsulation of magnetic clusters. Encapsulation of endohedral fullerenes, which possess intriguing magnetic properties, has been performed[49]. The magnetic and spectroscopic properties of such systems, which look particularly promising for quantum computation and spintronics, remain to be investigated in detail. For the purposes of molecular spintronics, this approach might show some advantages and disadvantages. The main advantages lie in the fact that it is possible to create one-dimensional spin structures inside the CNT, and in the strong spin-CNT electronic interaction that can be predicted for such systems. The disadvantages mainly consist in the difficulty of inserting molecules inside CNTs without creating defects, which can severely alter the transport properties, and in the impossibility of measuring the same device before and after the addition of the spin system. This latter disadvantage might actually become mitigated as our knowledge of such spintronic systems improves, but is likely to be a severe limitation in the near future, as even the basic elements of the spin-CNT interaction need to be rationalized.

Although the chemistry of graphene shares some strong analogies with that of CNTs, the functionalization of graphene brings about some appreciable differences. First of all, if processed in solution, graphene can be functionalized on both faces, allowing the creation of chemical bonds that would be unstable if only one face were exposed. Moreover, the reactivity of graphene as a chemical substrate has been found to depend on a number of structural features[50], whose amount strongly hinge on the process used to produce the graphene. 1) *Dangling bonds* can be present both at the graphene edges and in the plane, where they are main starting anchor sites for covalent functionalization strategies. 2) Graphene exhibit strained areas and curved regions, i.e. *ripples* that undergo preferential reactivity in order to relax by re-hybridization[50]. 3) A different reactivity has been predicted for zig-zag and armchair *edges*, the former being more reactive because a complete aromatic sextet structure is not attained. However, to control the edge type remains technically challenging, so that graphene contains always a mixed combination of the two, making a targeted functionalization very difficult. 4) Graphene produced by chemical vapor deposition (CVD) shows the presence of extended line defects called *grain boundaries*,[51] constituted by a set of pentagons and heptagons whose reactivity could be altered. These peculiar features are found to influence the reactivity of graphene locally and can influence both, covalent and non-covalent functionalization. All these features have to be considered in the reactivity, and can be exploited differently depending whether covalent or non-covalent functionalization is chosen. In particular, the possible relevance of different methods to produce graphene on the reactivity is a point that still needs dedicated investigation. Another point that has been shown to be of considerable relevance is the self-assembly of SMMs on the graphene surface. As this can alter dipolar and other interactions, it has a marked effect on the dynamic magnetic properties. In addition, several studies have hinted at a possible reorganization of adsorbates on the graphene surface, following heating or light absorption. Such molecular reorganizations are of great relevance for molecular hybrids tailored for energy transfer and harvesting which can produce efficient graphene devices. SMMs could here provide an excellent testground for the fundamental reactivity of graphene surfaces.

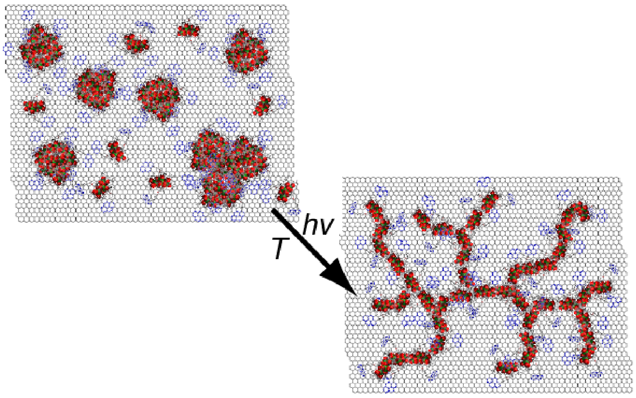

Fig.6 Possible structural reorganization of adsorbates of functionalized Fe_4 molecular magnets on graphene surfaces, creating different surface structures that can be interchanged with external stimuli. The different aggregation levels can then affect the properties of the hybrids[23].

Covalent functionalization of graphene can be of two types. One is achieved via nitrophenyl radical addition[52] and leads to the formation of sp^3 sites in place of sp^2-hybridized carbons in the honeycomb lattice. Due to the possible presence of unpaired electrons, a spin centre can be added directly with eac sp^3 bond created, making these compounds particularly relevant for the study of magnetic interactions. The second type of covalent functionalization relies on Diels-Alder chemistry[53] and leads to the creation of a pair of sp^3 carbon centres that necessarily belong to different sublattices and do not carry any free spin. The addition of covalently bonded species can be easily monitored using inelastic Raman scattering, the presence of sp^3 sites leads to the appearance of a pronounced *D* peak otherwise forbidden by momentum conservation[54]. In addition, high-resolution atomic force microscopy can be used to detect the presence of sp^3 centres since they cause an appreciable height increase.

4. Interaction with electrons

For the purposes of electron transport, molecules are perfect quantum dots built with bottom-up methods, i.e. they behave as zero-dimensional objects with quantized energy levels, and are studied using the same formalism of top-down quantum dots. The interfaces between the molecule and the metallic electrodes develop an energy barrier that the electrons experience coming in and out of the molecule. The barrier height depends on the extent of the mixing between the molecular orbitals and the wave functions of the charge reservoir. Three distinct coupling regimes can be identified[55]: 1) *strongly coupled*, in which the energy barrier is low so that the electrons are delocalized between molecule and leads. In this regime, the molecule is easily charged by the reservoir electrons. Nevertheless the molecular orbitals undergo a strong hybridization, so that the molecule loses most of its characteristic features; 2) *weakly coupled*, the molecular states are weakly hybridized with those of the leads affording a high energy barrier. The lead electrons need more energy to charge the molecule, which still maintains its characteristic features intact. 3) *intermediate coupling*, in which the molecule is perturbed effectively by the leads but still retains most of its characteristics.

These coupling regimes can be realized making use of the schemes and materials described in the previous section. The large set of possible devices can be sorted in two main categories: *single-dot* devices, in which the electrons flow through the molecule itself, and *multi-dot* devices, in which the molecule is coupled with a conducting channel of lowered dimensionality. In the following we provide a selection of illustrative examples.

For single-dot devices the molecule has to be in direct contact with macroscopic charge reservoirs. One way of achieving this is by sandwiching the molecule between two closely-spaced leads. This method creates a direct way to study the charge transport through a single magnetic centre and the cross-talking between multiple magnetic centres through different organic linkers[56]. Experimentally, the devices combine a top-down approach, where nano-sized metallic gaps are created by electro-migration or break-junction methods, and the bottom up chemistry of the SMMs, which are then inserted from solution in a purely statistical process[57]. In both cases the interaction of the molecular spins with the transferred electrons is mediated by the binding groups used to link the molecule to the source of electrons. In the case of gold break junctions both sulfonate and conjugated ligands[58] have been employed and showed to produce different regimes of coupling (see next paragraph for details). Another strategy to tune the coupling with the electrodes makes use of non-conjugated alkyl chains of different lengths[59]. An advantage of this approach is the possibility of integrating a gate that can drive the molecule in different excitation states by capacitive coupling. The first measurements on SMMs showed the presence of intriguing features, such as negative differential conductance. Later attempts allowed observing the spin multiplicity and investigating effect of charge transfers on the magnetic anisotropy. Several promising theoretical predictions have been made about this scheme, though the experimental difficulties of this approach did not allow verifying all of them, yet.

Recently the rather compelling intermediate-coupling regime, has been explored for the Fe_4 complex using the gated break junction scheme[56]. Intermediate coupling with the leads is achieved by making use of a tripodal ligand 2-hydroxymethyl-2-phenylpropane-1,3-diol carrying a phenyl ring. The molecule is seen to largely maintain its energy-level structure. By changing the gate voltage, the molecule is driven in different excited states. The molecule magnetic anisotropy is expected to differ both in magnitude and direction for different excited states and this could be nicely confirmed by measuring the angular dependence of the junction conductivity in external magnetic field.

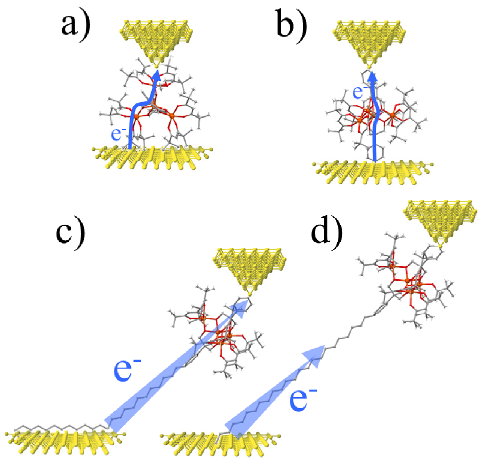

Fig.7 Probing of the electron transport with STM-tip and different peripheral sites of the molecule (here an Fe_4 SMM). a) Electron transport through non-functionalized, randomly-oriented SMMs, as for spin-coated systems. b) Electron flow pathway for functionalized SMMs anchored in a uniform way on the surface, in this case by using apical tripodal ligands on Fe_4. c) Electron flow through SMMs anchored with long alkyl chains, still partially lying on the surface. d): Electron flow with the alkyl chains fully extended, as obtainable via mechanical manipulation of the system using an STM-tip. As a result, the electron transport can be measured as a function of the linker length.

An alternative possibility to study single-dot devices is by combining the deposition on metallic surfaces with scanning tunneling microscopy (STM). In fact, by attaining submolecular resolution, STM allows probing the electron transport at different peripheral sites of the molecule. Moreover this technique allows manipulating the system mechanically, enabling the study of transport as function of the linker length (Fig. 7). Magnetic field dependent experiments would shed light on the interplay between an electric current and the molecule magnetic behaviour for different geometries[60].

The most prominent examples of multi-dot devices are SMM coupled to conductors of lowered dimensionality such as CNTs (one-dimensional) and graphene (two-dimensional). The one-dimensional structure of CNTs makes them suitable for the fabrication of carbon-based three terminal devices e.g. field effect transistors (FET). The presence of the molecular spin can influence the current flow inside the 1D conductor in different ways depending on the coupling afforded by the binding ligand. Non-covalent binding is suitable for the realization of a weak-coupling regime. In these conditions the SMM locally alters the charge density of the conducting channel via dipolar interaction, thus generating a scattering centre[61] that, in turn lowers the conductance of the device. However, the magnetic state of the molecule can also influence the charge flow in the tube, via the so-called magneto-Coulomb effect. The flip of the molecular spin induces a change in the Zeeman energy that causes a variation in the chemical potential of the molecule, which in turn induces a capacitive “gating effect” on the charge carriers of the tube[62].The magnetic moment associated with the molecular spin can also interact with the conductor charge carriers via its magnetic flux. This interaction can be probed using CNT-based superconducting quantum interference devices (SQUID)[63]. While such devices look extremely promising, their fabrication has proved very challenging, and flux detection of single molecules remains elusive. A third interaction scheme, which has led to the most appealing results, consists in using the discrete levels of the CNTs itself, and look at their variation with the magnetization of the molecule. The resulting system, which is a true double-dot device, has allowed detecting single or a few SMMs and the flipping of their magnetization, although the exact mechanism (Fig.8) of interaction remains unclear. Elucidating the functioning of the aforementioned devices is of fundamental importance, as it would open the way to true control of such spintronic devices, and to the fundamental physical mechanisms that are connected to them. Some observations also remain unclear, for example why no additional transverse anisotropy terms have been observed in the magnetic behaviour of the SMMs, while they would be expected from the alteration of the electrostatic environment. Analogously, no effect of the altered phonic environment has been observed, while they might be expected to be rather large.

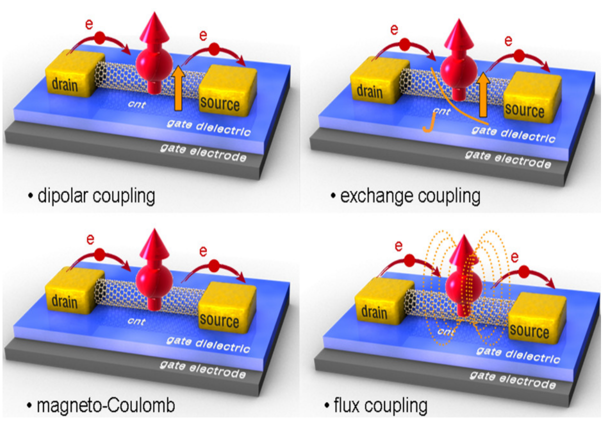

Fig.8 Different coupling schemes between a QD (here represented as a CNT) and a SMM (represented as in red) that can lead to the observation of spin effects on the electron flow of the CNT (red arrows).

The study of the interaction between molecular spins and the two-dimensional electron gas of graphene is expected to lead to an even more rich landscape of effects and device architectures. The interaction between molecular spins and the Dirac electrons in graphene is particularly appealing since, it would allow studying the effect of relativistic electrons on spins, and elucidate the fundamental physics describing relativistic particle interactions. The first results show that it leads to particularly strong perturbative effects on the SMMs. A clear signature of the graphene symmetry on the SMM properties, as shown by additional contributions described by Stevens operators with the graphene symmetry, has been found, and the perturbation could lead the SMMs into a new QT regime, as never observed in crystalline materials. For these studies, graphene flakes of several tens of micrometers can be easily produced allowing the fabrication of multi-terminal devices. This constitutes a much larger functionalization area, compared to CNTs, therefore a larger number of molecules will be grafted on the device, allowing larger statistics than for single-molecule events, but hampering single-spin detection. Only graphene nanostructuring with a weakly-coupled molecular spin may induce an appreciable polarization of the flowing charge carriers, and recent observations with multiple spins seem to indicate that this is feasible[64].

5. Controlling magnetic nanostructures with light

Photo-irradiation, as an external stimulus, is an appealing ingredient for multifunctional nanoscale-spintronic devices. Therefore finding ways to control the molecular spins by changing the properties of molecular magnets using light is a current research topic around the world. Over the past years various methods to attain photo-control over magnetic molecules have been explored and developed. These photo-induced methods span from spin-crossover systems, charge-transfer complexes and photo-chromic molecules that can change their conformation (Fig. 9). All these methods lead to changes in spin-multiplicity, redox state and induce spin transitions involving distinct changes of the magnetic properties[65,66]. In some situations, these effects can be contemporarily present and coupled one with one another.

Charge-transfer processes between molecular entities have a strong impact in photo-switchable complexes. Many examples for different electron transfer processes can be given such as an inter-metallic[67-71] or ligand-to-metal charge-transfer system, which lead in some Co based compounds to photo induced valence-tautomerism[66,72,73]. Charge transfers can be a prerequisite for spin transitions (electron-transfer coupled spin transitions, ETCSTs)[74]. Spin transitions are also achieved via spin crossover processes, which are characterized by a transition between the low spin (LS) and high spin (HS) ground states, commonly observed in octahedral transition metal complexes of d^4 to d^7 configuration. Since their first observation[75], numerous spin crossover compounds that change in colour, electric and magnetic properties using external stimuli have been reported[65,76]. A nice example of light induced spin-crossover magnetism is provided by Fe-Nb-based complexes[77], where the transition from a LS to a HS state leads the system from a paramagnetic state to a strong antiferromagnetic super-exchange interaction between the Fe^{2}_{HS} and Nb^4 magnetic centres. This results in a spontaneous magnetization triggered by light induced excited spin-state trapping (LIESST).

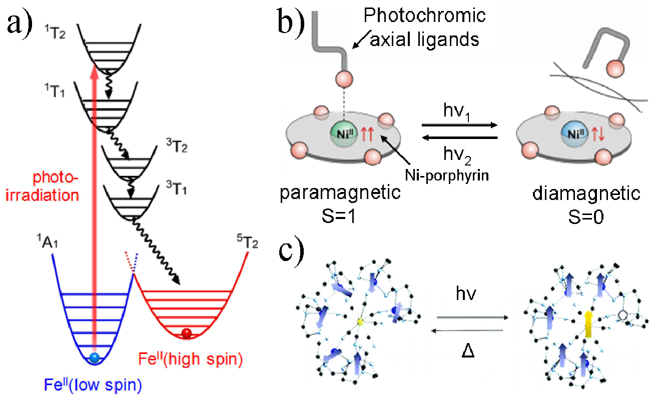

Fig.9 Overview on known photo-control processes in molecular magnets. (a) Scheme of light-induced spin crossover of Fe(II), using LIESST creating a metastable state with different magnetic properties.[77] (b) Scheme of spin state switching of Ni(II) complexes by light-induced photochromic reaction.[78] (c) Scheme of photo-induced electron transfer and of the mixed-valence photo-excited state Mo(V)Cu(I)Cu(II)$_5$.[71] Figure subpanels adapted with permission from Ref.s 71, 77 and 78.

Other tools to create different magnetic states in molecules using light are based on structural changes triggered by light[65]. These include changes in coordination number[78] and photo-isomerization[79-81]. In this way materials that show magnetic bistability with large hysteresis were also successfully switched[82]. Another appealing prospect[83] implies the photo-switching of spin-multiplicity and polarization between organic radicals, provided by the triggering of an extended π-electron system sandwiched in between. This opens new perspectives for spin systems connected by graphene, where the interaction is also mediated by delocalised π-electrons. All these processes allow switching molecular and quantum magnets, paramagnetic mononuclear complexes, heterometallic clusters and one dimensional complexes with slow dynamics[66].

In nanoscale hybrids, the implementation of molecular materials that can be switched by light is essential, since photons allow high speed and precise access to a variety of different types of materials. At nanoscale dimensions the delivery of the photons towards switchable systems can also be achieved by plasmonics transport structures. In this sense, the integration of spin systems in plasmonic devices looks particularly promising to control single nanoscaled entities. Moreover, plasmonic nano-structures constitute an alternative route to tune the intensity[84] and polarization of light[85,86], induce nonlinear effects[87] or confine irradiation spatially below the sub-wavelenght limit[88]. This opens the possibility to engineer the light emission of the molecules at the nanoscale[89] and, instead of only considering how to tailor the magnetic properties of molecules towards light, one could also tailor the properties of light to address specific molecular magnetic properties. So far not many studies have been conducted on using nanooptics in order to gain precise control over nanomagnetic systems, but plasmonics represent a promising next step towards optically tunable spintronics. Some first examples have used magnetic nanoparticles[90], in which the magnetic and optical properties could be coupled together owing to the creation of non segregated Au:Fe alloys. Nevertheless, if plasmonic structures are to be used in conjunction with metal complexes, this has to be achieved in hybrid structures, because complexes lack the delocalized electronic states necessary for plasmons to propagate.

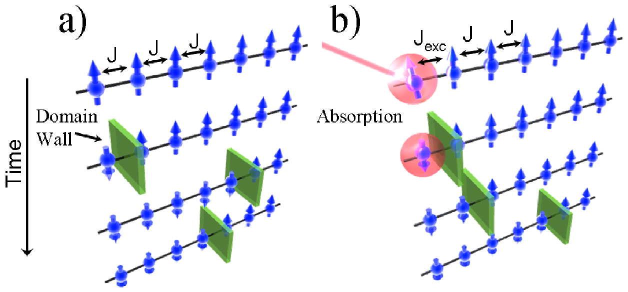

Fig.10 Scheme of the Kick-off mechanism.[91] a) Standard Glauber dynamics. The system starts out completely polarized (first row). The magnetic excitation nucleates at an energy cost (second row) and the domain wall (green) can then move by a random walk process along the chain. (third and fourth row). b) Kickoff mechanism. A photon is absorbed at one site of the chain, creating a Frenkel exciton (red ball). For the time of the excitation, the intrachain exchange coupling of the spin at the exciton site is lowered and therefore the energy cost to flip the spin is reduced (first row). The so created domain wall (second row) can propagate only after the exciton has decayed (third row). After the Kickoff, the chain follows the standard Glauber dynamics (fourth row).

Localized excitations, such as Frenkel excitons, can also be used to optically control the magnetic properties of slow-relaxing magnetic systems. A recent example on how the magnetization dynamics under light can be studied thoroughly in experiment and theory is given by the 1-dimensional ferromagnetic SCM [Co(hfac)$_2$(NIT-PhOMe)][91]. Due to its Ising-like character, the dynamics of the system can be well-described using Glauber dynamics[92]. CoPhoMe consists of Co(II) magnetic centres (effective spin s_{Co}=1/2 and Landè factor g_{Co}~7, at low T) surrounded by hfac=hexafluoroacetylacetonate molecules and bridged by the organic radical NIT-PhOMe=2-(40-p-methoxyphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (isotropic s_{R}=1/2 and g_{R}=2.0 centres)[6]. The chain crystallizes in the P3$_1$ space group and the unit cell contains three repeating units, with the chains extending along the crystallographic axis *c* in a hexagonal fashion (Fig.3b). The different magnetic centres along the chain interact via antiferromagnetic exchange interactions *(J)*, giving rise to a ferrimagnetic structure. The relaxation of the magnetization follows the Arrhenius law $\tau=\tau_0 e^{\Delta E/k_BT}$, where τ_0 is the inverse of the spin-flip attempt rate, and the energy barrier ΔE now depends only *J*. Hence, contrarily to SMMs, a faster demagnetization can be achieved in SCMs by changing the exchange interaction *J* between the magnetic centres. This can be accomplished by optically altering the electron density, for example by creating a Frenkel exciton. In [Co(hfac)$_2$(NIT-PhOMe)] a particularly suited exciton is the local perturbation of the cobalt *d* orbitals and the NO groups of the organic radicals. In the groundstate ^{3}A and ^{5}A* the HS, *S*=3/2 Co(II) and the radial, are antiferro- and ferromagnetically coupled giving a computed interaction value of *J*=163.5 cm^{-1}. Under light irradiation an excited triplet state ^{3}A* is induced, consisting of three different linear combinations of LS, *s*=1/2 Co(II) states. These are then ferromagnetically coupled to an excited doublet of the radical. Each ^{3}A* state can be coupled to a ^{1}A* state with lower energy. In such ^{1}A* states the LS, Co(II) is antiferromagnetically coupled to an excited doublet of the radical. This leads to a new interaction value J_{exc} of 126.0 cm^{-1}. The resulting Frenkel exciton is determined by the unpaired electron transfer from the localized π* NO, which interacts directly with the Co(II) ion, to the opposite localized π* NO, inducing a inner spin transition from a ground HS Co(II) to an excited LS configuration. As the electron density changes, the intrachain exchange interaction J_{exc} between the spins at the exciton site will be altered (Fig.7), compared to the interaction *J* at the other, non-excited, sites in the chain. The chain sites that absorb a photon (with a certain probability that depends on the irradiance) will then create a localized electronic excitation. For the lifetime of the exciton, τ_{lf}, the interaction at the excited site with its neighbours is reduced, leading to the possibility of nucleating an excitation at a reduced energy cost ΔE_{exc}. When τ_{lf} is longer than the inverse of the spin-flip attempt rate, the site can flip with regard to its nearest neighbours and a domain wall can be nucleated at the excited site. Once the exciton has disappeared, the new domain wall is kicked-off and can freely propagate along the chain. This means that the attempt rate will be longer than τ_{lf}, leading to a characteristic increase of τ_0. The kick-off dynamics should thus follow a new Arrhenius law: $\tau_{KO} = \tau_0^{exc} e^{\Delta E_{exc}/k_B T}$ in which the new parameter values τ_0^{exc} and ΔE_{exc}, should fulfil the boundary conditions $\tau_0^{exc} = \tau_{lf} >> \tau_0$ and $\Delta E_{exc} < \Delta E$.

In [Co(hfac)$_2$(NIT-PhOMe)], where the dynamics can be described analytically down to minute details, the experimental barrier and τ_0 under irradiation were found to match the theoretical ones, and the Kick-off model correctly predicted the dependence on the irradiation power. The implementation of such control schemes in coupled molecular systems and in hybrid devices would allow an external control of the properties without conformational chances, and is now under study together with the possibility of coherently controlling the chain system.

6. Conclusions

In conclusion we provided a unified perspective of present efforts in creating hybrid nanosystems based on molecular nanomaterials. The field holds the potential to create novel multifunctional devices, and has already allowed fabricating sensors with ultra-high sensitivity. In such hybrids the presence of an altered surrounding (e.g. flowing electrons) constitutes one of the appealing points. The control and detailed understanding of the interactions between a molecular spin and its exterior environment are of paramount importance. This constitutes a challenge at many levels, as shown here, involving the creation of novel physical instrumentation, the sapient combination of bottom-up and top-down approaches, and the development of novel theoretical tools. If all these elements are combined, a previously unthinkable control over the properties of molecular magnetic materials is within reach. Recent attempts using novel interactions with photons have shown that light-matter interaction itself can push towards new exciting breakthroughs. The combination of such systems into optical nanostructured devices, such as plasmonic structures or high-quality cavities, will likely become a promising field in the near future. The detailed study of fundamental physical mechanisms, such as the interaction of spins with relativistic particles, are also appearing right now, and might push molecular magnets at the interface between solid state sciences and fields (such as quantum optics and relativistic physics) that have remained traditionally separate.

Acknowledgments

We thank A. Hoyer, M. Burghard, J. Chin and D. Dregely for stimulating discussions. We thank the Humboldt Stiftung (Sofja Kovalevskaja Prize), German DFG (SPP-1601), the Baden-Württemberg Stiftung (Kompetenznetz Funkionelle Nanostrukturen) and the European Research Council (ERC-StG 338258 "OptoQMol") for financial support.

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[a] *1. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550, Stuttgart, Germany. Tel: +49(0)711-685-64907; Fax: +49(0)711-685-64886; E-mail: lapo.bogani@pi1.physik.uni-stuttgart.de*

† These authors contributed equally to this work.

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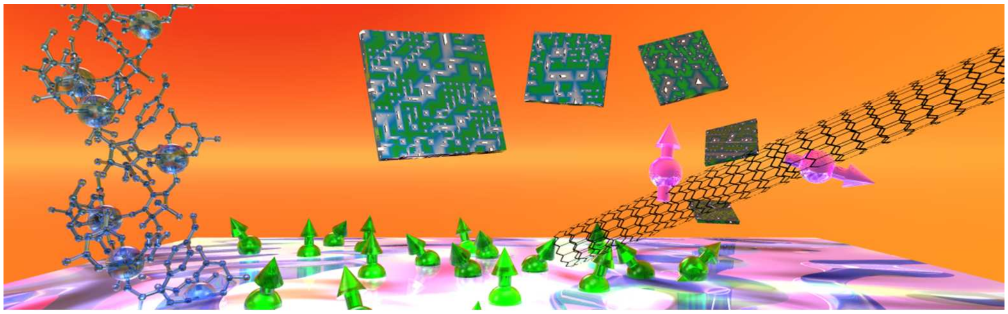

We discuss the developments in the synthesis and characterization of magnetic nanohybrids made of molecular magnets and nanostructured materials.
440x135mm (72 x 72 DPI)