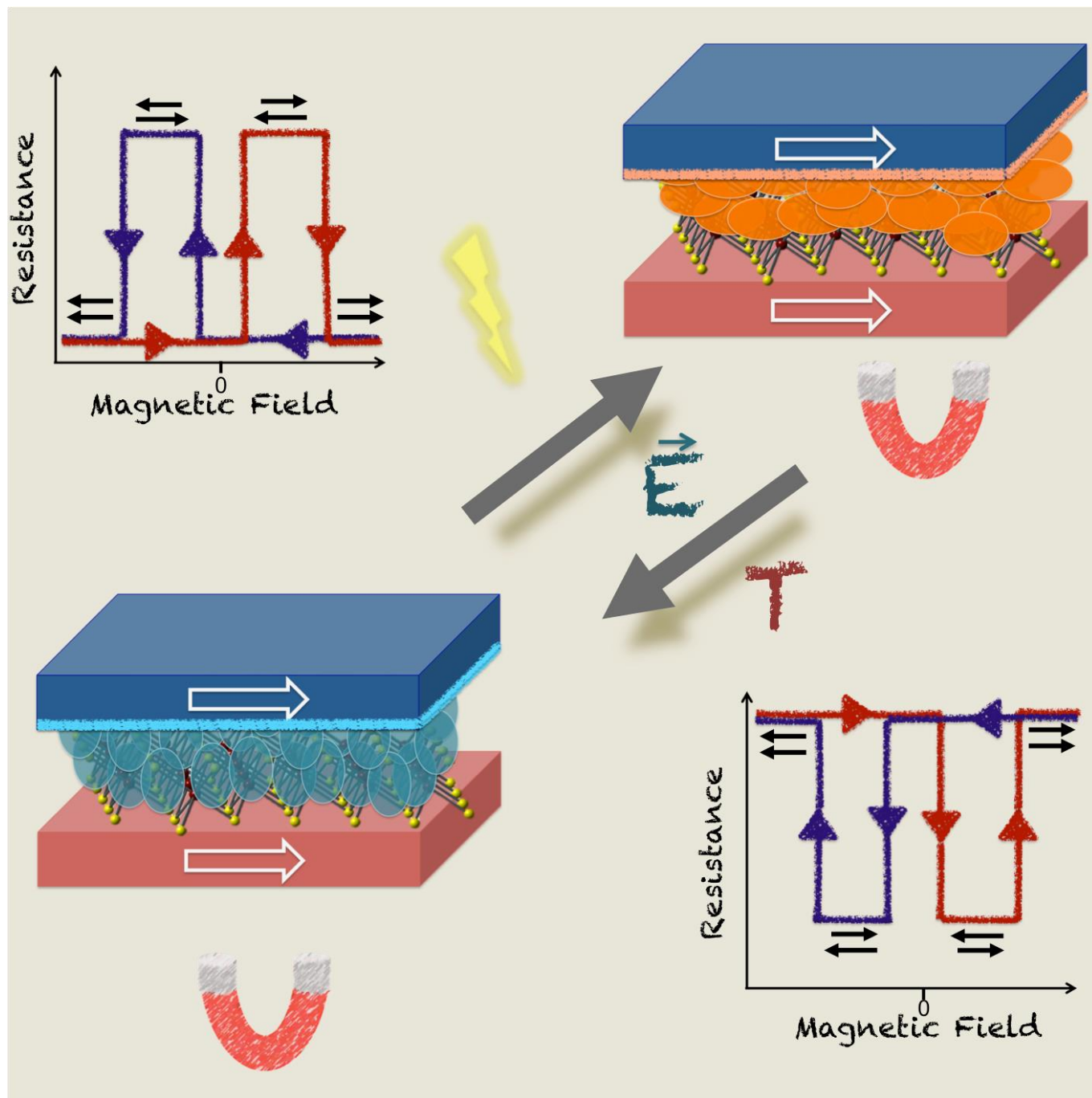


Hybrid interfaces in molecular spintronics

Alicia Forment-Aliaga,^{*[a]} and Eugenio Coronado^{*[a]}

Dedication ((optional))



PERSONAL ACCOUNT

Abstract: Molecular/inorganic multilayer heterostructures are gaining attention in molecular electronics and more recently in new generation spintronic devices. The intrinsic properties of molecular materials as low cost, tuneability, or long spin lifetimes were the original reasons behind their implementation. However, the non-innocent role played by these hybrid interfaces is a determinant factor in the device performance. In this account we will give an overview about different types of hybrid molecular system/ferromagnet interfaces, which can be of direct application in molecular spintronics. This includes the insertion of a 2D material in between the molecular system and the ferromagnet. As perspective, new hybrid interfaces able to tune the spin properties under an external stimulus, are proposed. These smart interfaces, based on switchable magnetic molecules or flexible MOFs, can open the way to new multifunctional spintronic devices able to couple the spin with a second property.

1. Introduction

The advancement of molecular-based electronic devices over the past two decades has been spectacular. Thus, organic light emitting diodes (OLED) devices based on molecules or polymers have already become available to consumers and have found applications in displays and lighting,¹ while organic photovoltaic devices are becoming competitive with respect to silicon devices in terms of low cost production and flexibility.² More recently, molecular spintronic devices have also entered in the game with the aim of fabricating a second generation of devices for hard drive information storage and magnetic sensing.³

One of the main characteristics of all these devices is their hybrid nature since they generally involve multi-layered heterostructures in which a molecular layer is sandwiched in between two inorganic electrodes. In fact, the performance of these devices is strongly controlled by the proximity effects established in these hybrid interfaces. Thus, through a suitable choice of the molecules, an interface engineering has been developed in order to improve the electron transfer between the electrodes and the active molecular layer.⁴ Still, this possibility has been little explored in the case of the spintronic devices.⁵

In this personal account we will focus on the different types of hybrid interfaces one can encounter in spintronics. In the first part we will discuss first the case of a strong hybridization between the molecular layer and the ferromagnetic substrate, and second the case of a hybrid interface formed by a self-assembled monolayer (SAM) of molecules and a ferromagnet. In

the second part the concept of hybrid interface will be extended to the 2D limit in which the inorganic component of the interface is in fact constituted by "all the substrate" i.e., by a 2D material formed by a single layer. Thus, hybrid interfaces formed by molecules in contact with a 2D material will be presented. In the context of molecular spintronics, these molecular/2D interfaces will be formed when a 2D material is inserted in between the molecular system and the ferromagnetic electrode.

In all the above systems, the hybrid interface is playing a rather passive role (protective barriers of the electrodes, modifiers of the spin polarization, spin-tunnel barriers, spin filters,...). Still, the hybrid interface can be designed in such a way that the molecular component can play a more active role being able to switch between two states under the influence of an external stimulus. This should open the possibility of preparing hybrid smart interfaces and devices. This appealing issue will be discussed in the final part of the account.

Prof. Eugenio Coronado is the Director of the Molecular Science Institute (ICMo) at the University of Valencia and the European Institute of Molecular Magnetism (EIMM). His research career has been devoted to the design, synthesis and study of new molecular materials with magnetic, electrical or optical properties. In particular, he has produced new hybrid multifunctional materials (including molecular magnetic conductors and superconductors, and stimuli responsive magnetic materials) and new molecular nanomagnets. Currently his research interest is focused on the use of these kinds of materials in molecular spintronics and quantum technologies.



Dr. A. Forment-Aliaga graduated in Chemistry and carried out her PhD on molecular magnetism at the University de Valencia (UV). Between 2004-2008 she worked as a postdoctoral researcher at Max-Planck Institute for Solid State Research (Prof. K. Kern's department) in molecular electronics. Since July 2008 she works at the Molecular Science Institute (ICMo) at the UV in Prof. E. Coronado's group. This period comprises a postdoctoral JdC contract (2008-2011) and



a tenure-track RyC contract (2011-2016), both granted by the Spanish Government. At present she has become researcher of this university and works on molecular surface engineering for spintronics, the chemical functionalization of 2D materials and their integration in hybrid devices.

[a] tDr. A. Forment-Aliaga, Prof. E. Coronado
Instituto de Ciencia Molecular
Universitat de València

2. Hybrid interfaces in molecular spintronics

2.1. Background

Spin-based electronics is one of the emerging branches in nanotechnology and the most active area within nanomagnetism. This field uses the spin of the electron besides its charge to transfer and process the information. The most common spintronic structure is formed by two ferromagnetic electrodes enclosing a semiconducting (spin valve, SV) or isolating (magnetic tunnel junction, MTJ) nanometric-thick layer. In these devices electrical conductivity is modified by switching the relative orientation of the magnetization of the two ferromagnetic electrodes to give rise to giant or tunneling magnetoresistance effects. For the most part, these devices are based on conventional materials like inorganic metals and semiconductors. However, with the unique possibilities offered by the molecular systems to perform electronic functions, a new field namely *organic spintronics* emerged fifteen years ago, which incorporated organic layers in between the ferromagnetic electrodes.⁶ This field benefits of the extremely long spin lifetimes (up to seconds) exhibited by organic compounds to construct devices featuring interesting properties. This is due to the fact that spin-orbit and hyperfine interactions, which are spin depolarization main sources, are lessened in these materials.⁷

From organic spintronics, this field has evolved towards other challenging goals such as the development of nanospintronic devices incorporating one or a few molecules (not necessarily organic) in the race towards miniaturization.⁸ Thus, nowadays the new field known as *Molecular Spintronics* integrates both organic spintronics (also known as molecular-based spintronics) and molecular nanospintronics.⁹ In this account we will focus on the first topic (organic spintronics) and, in particular in the study of hybrid interfaces affording unusual or even new properties to the device (such as spin filtering effects, unusually large working voltages, or a response to external stimuli).

2.2. Hybridization effects: The spinterface

The implementation of organic molecules in spintronic devices implies their deposition on surfaces, directly in contact with highly air sensitive ferromagnetic metals and alloys like cobalt or permalloy (NiFe alloy), on ferromagnetic oxides that are air stable such $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO), or on tunnelling insulator layers of different nature like Al_2O_3 capping the ferromagnetic metals (Figure 1).

Different molecular components can be sandwiched in between the inorganic ferromagnetic electrodes. Depending on the interaction between the molecules and the ferromagnetic substrate, different situations/degrees of mixing can be found at the molecular/inorganic interface: from strong hybridization between the orbitals of the molecules and the ferromagnetic surface to a very weak coupling, with a variety of intermediate situations where the molecules preserve their integrity. This interfacial tuning, which is essential to tailor the spin transfer

behaviour at the hybrid interface, is in general not possible for inorganic semiconductors.

Initially, the molecular layers were introduced as mere spin transport media due to their intrinsic weak spin depolarization properties. The former devices were based on well-known organic semiconductors and polymers already used in the field of OLEDs. Thus, Dediu et al. incorporated a layer of π conjugated sexithiophene (T_6) between two LSMO electrodes in a lateral spin device.¹⁰ Afterwards, Xiong et al. thermally evaporated the 8-hydroxy-quinoline aluminium complex (Alq_3) to prepare a vertical LSMO/ Alq_3 /Co structure, acting as a spin valve.¹¹ Since then, other organic semiconductors and molecules such as porphyrins, C_{60} and phthalocyanines,¹² have been integrated in spintronic devices by using standard UHV evaporation techniques.

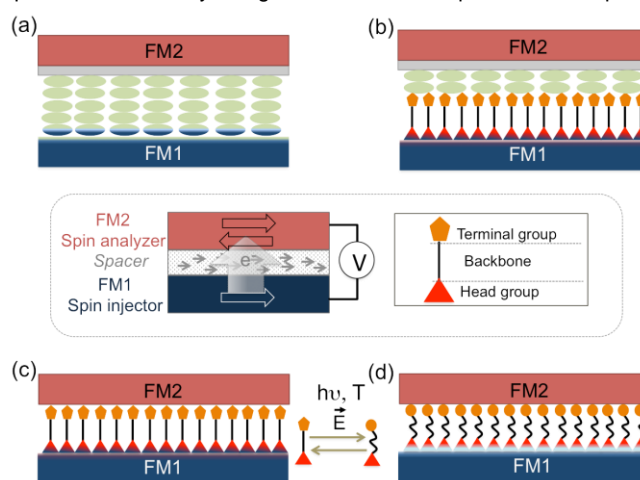


Figure 1. Sketch of multilayer molecular spin valve structures, where the spacer is a molecular compound sandwiched between two different ferromagnetic electrodes (FM1 and FM2). The direct contact of the organic molecules with the ferromagnetic material gives rise to a certain degree of hybridization. The nature and role of the molecular compound can be different: (a) an organic semiconductor deposited from solution or sublimation approach usually physisorbed on FM1; (b) a SAM attached to FM1 with specific interactions through the anchoring group (from solution or vapour phase). The SAM lays between FM1 and the organic semiconductor layer; (c) Only a SAM between both electrodes usually working as spin-tunnel barrier; (c)-(d) An active molecular system that changes its properties (volume, spin, conformation structure...) after applying and external stimulus (light, temperature, electric field, etc.), which implies a different interaction of the molecules with the electrodes. The active molecular system has been represented by a SAM but it could be also an active multilayer organic semiconductor. Inset in the middle: Left: Schematic representation of a vertical spin valve indicating the flow of the current with different resistance depending on the relative parallel or antiparallel magnetization direction of the top and bottom ferromagnetic electrodes. Right: Sketch of the molecular unit of a SAM pointing out the three main parts.

The measurement of negative magnetoresistance behaviour in some vertical spintronic devices soon made evident that molecules were playing additional role apart from the pure spin transport. In these cases, the interfacial molecules were able to tune and even to invert the spin polarization of the current extracted from ferromagnetic electrode due to a strong hybridization at the molecular/ferromagnetic interface. This effect, known as 'spinterface' effect,¹³ has become then a crucial

issue in molecular spintronics.¹⁴ An illustrative example of this effect has been recently provided by spin valves based on lanthanide quinoline molecules in which an interface-assisted sign inversion of the magnetoresistance has been measured (Figure 2). Thus, when the quinoline molecule is combined with Co and permalloy (NiFe) as spin injector and analyzer electrodes, the magnetoresistance is positive if an AlO_x barrier is inserted between NiFe and the molecule, but it changes to negative when the AlO_x layer is placed on the Co electrode. This result has been attributed to the formation of specific hybrid electronic states at the molecular/NiFe interface, which has a negative spin polarization, while at the molecular/Co interface the spin polarization stays positive.¹⁵

Notice that this kind of hybridization effect not only affects the magnetic properties of the molecular side of the interface. It can also affect the properties of the inorganic metal electrode. This was demonstrated in 2013 by Moodera et al. who observed that flat aromatic molecules of the type zinc methyl phenalenyl, deposited on a Co thin film, induced a strong magnetic hardening of this film.¹⁶ Interestingly, in that case the effect was not limited to the interfacial Co layer but extends to adjacent layers, affecting the magnetic properties of the whole metal film.

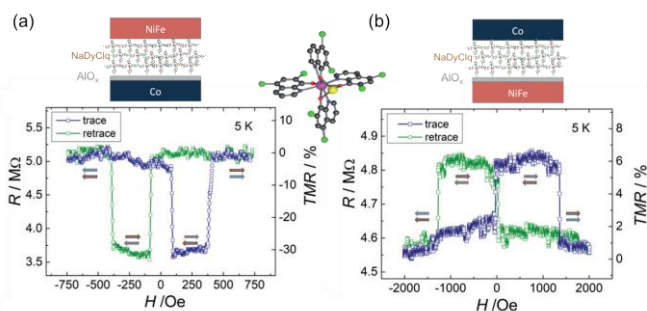


Figure 2. Sketches and magnetotransport measurements of vertical spin valves with general structure FM1(15nm)/AlO_x(1nm)NaDyClq(xnm)/FM2(15nm), where NaDyClq is the Na[Dy(5,7Cl₂q)₄] molecule (being 5,7Cl₂q = 5,7- dichloro-8-hydroxyquinolate). The role of the metal–molecule interface is studied by changing the ferromagnetic material in direct contact with the molecular layer. a) Negative tunnelling magnetoresistance (TMR) measured at 5 K and –10 mV in a Co/AlO_x/NaDyClq/NiFe spin valve. b) Positive TMR measured under the same conditions in a NiFe/AlO_x/NaDyClq/Co spin valve, highlighting the role of the top metal–molecule interface. The brown and grey arrows indicate the magnetization direction of the Co and Permalloy (NiFe) electrodes respectively. Inset: Molecular structure of the Na[Dy(5,7Cl₂q)₄] compound. Purple: Dy; yellow: Na; green Cl; red: O; black: C; blue: N. Figure adapted from ref. 15.

2.2. Self-Assembled Monolayers (SAMs) of molecules on ferromagnetic surfaces

The spontaneous organization of molecules from solution or vapour phase onto a substrate originates the growth of one molecule thick well-organized molecular layer known as SAM. The molecular unit presents three characteristic parts (see Figure 1) that play a different role in the SAM formation: 1) The terminal or anchoring group, which is the functional group with affinity for a specific substrate; it will determine the kind of surface where the molecule will be attached and the strength of

the interaction/hybridization between molecule and the surface; 2) the backbone structure of the molecule, which will define the weak intermolecular interactions needed for the self-organization process and will be relevant for the final packing and order in the layer; 3) finally, the heading functional group, which will define the new surface properties of the hybrid interface as it will be exposed to other (organic or inorganic) species deposited on this functionalized surface.¹⁷ These SAMs are extensively used in nanotechnology applications either as resistors or as building blocks in multilayer systems, as surface energy modifiers, as adhesion promoters and as protecting or isolating layers to avoid quenching of properties between two materials.¹⁸ SAMs have also found wide application in the area of molecular electronics.¹⁹ In molecular spintronics SAMs have been loosely used. Still, they can be incorporated into SV or MTJ playing two main roles:

(i) As ferromagnetic modifiers between the inorganic electrode and the molecular layer, they can improve the spin-injection efficiency by tuning the energy band alignment and the spin polarization at the hybrid interface. In addition, they can modify some chemical properties of the surface, such as morphology and wettability properties, determining the growth of the next molecular layer.²⁰

This possibility was studied by Jang and coworkers²¹ with the use of two different alkanethiols: 16-mercaptohexadecanoic acid, (MHA, HS(CH₂)₁₅CO₂H) and 1-octadecanethiol, (ODT, CH₃(CH₂)₁₇SH). The thiol provides a specific group for the covalent bonding to metals, while the alkyl chains provide high packing/good quality SAMs. The different head groups strongly define the properties of the resulting surfaces. SAMs influence the AlQ₃ growth at the interface, modulate the hybridization between this top molecular semiconductor and the bottom Co electrode, decrease the work function of the metal and influence its spin magnetic moment. In this example SAMs are formed on Co substrates from solutions containing the starting molecules and previous to the evaporation of the AlQ₃ layer, keeping all the steps of the process under inert atmosphere to avoid oxidation of the ferromagnetic metal. This unavoidable requirement has probably blocked an extensive application of SAMs as ferromagnetic surface modifiers.

(ii) As spin-tunnel barriers, they can be used as the unique molecular layer between two ferromagnetic electrodes. The SAM represents a highly organized layer one molecule thick, whose properties and strength of interaction with the ferromagnet can be modulated by chemical design of the molecule.

More than ten years ago, Petta et al. prepared the first MTJ based on a SAM. The device presented Ni/Octadecanethiol/Ni vertical structure and showed an unclear tunnel magnetoresistance (TMR) response of 16% at 4K and low bias voltages.²² Shortly afterwards Wang et al.²³ reported an equivalent structure with Co top electrode and similar responses. Both devices were prepared reducing their areas to few

nanometers in order to minimize short circuits through the narrow organic layer. SAMs were prepared in ethanolic solution and no special care was taken to protect the underlying ferromagnetic metal from oxidation, so the blurry TMR could come from spin depolarization problems at oxidized interfaces. Again, the difficulty of facing the oxidation of the ferromagnetic material probably has hidden the broad application of SAMs as tunnel barriers. The problem was solved in 2012 by using air stable ferromagnetic electrodes like LSMO. Thus, the use of alkylphosphonic acids in ethanolic solution gave rise to highly organized and compact SAMs,²⁴ with a modified work function for LSMO that could permit the tailoring of the electron and spin injection efficiencies.²⁵ This crucial step allowed Gabiati et al.²⁶ to fabricate MTJ formed by long chain alkylphosphonic acids SAMs grafted on LSMO and cobalt as top electrode. In this case, clear TMR was measured at 4K, ranging from 35% at 10 mV down to 17% at 2 V (Figure 3).²⁶ Self-assembly of phosphonic acids on LSMO has also been recently extended to the fabrication of SVs with covalently immobilized polymer brushes with an improvement in the polymer/LSMO interface in comparison with spin-coated films.²⁷ This approach has also permitted the incorporation of SAMs containing organic radicals²⁸ and single molecule magnets²⁹ onto LSMO as intermediate layer between the ferromagnetic electrode and a semiconducting Gaq₃ layer (so these devices should be included as examples of group (i)).

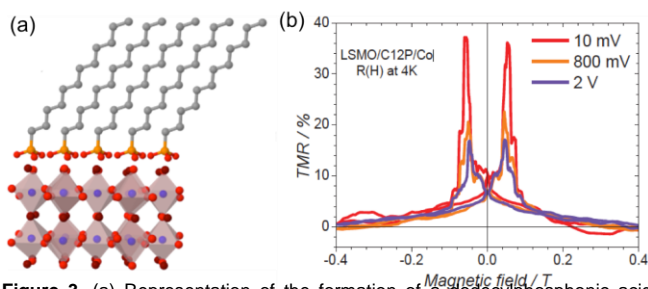


Figure 3. (a) Representation of the formation of a dodecylphosphonic acid (C12P) SAM on a LSMO substrate. SAMs were prepared in ethanolic solution in ambient conditions. Figure extracted from reference 24. (b) TMR dependence on the applied bias voltage of a vertical MTJ with structure LSMO/C12P/Co. The junction has a nanometric diameter in order to decrease short circuit probability. TMR curves recorded at 10 mV, 800 mV, and 2 V at 4K. Figure extracted from ref. 26a.

Unfortunately and despite the relevance of these results, the devices based on LSMO electrodes are limited to function at low temperatures, where LSMO maintains a 100% spin polarization. To solve this problem the substitution of LSMO by metallic highly air sensitive ferromagnets have to be faced and the growth of high quality SAMs on these surfaces is a must. Recently, we reported that passivated permalloy can be modified by the formation of a compact alkylphosphonic SAM³⁰ by means of a determinant H₂ plasma pre-activation process of the surface that increases the ratio of hydroxy groups on the passivating oxide layer. However, this oxide layer is not an ideal scenario for spin transport processes. In an ulterior paper the development of an efficient protocol to remove this oxide layer was reported.³¹ It involves a chemical treatment with glycolic acid under inert atmosphere, giving rise to an oxide free active metallic surface

that can be successfully functionalized by alkanethiol SAMs. This high quality SAM has permitted the recent successful implementation of the process to fabricate the first room temperature MTJs with a NiFe/ alkanethiol/ Cobalt configuration.³² Unfortunately, in the absence of the top electrode this compact SAM does not protect the underlying ferromagnet to air oxidation processes, so that a spontaneous reorganization of the SAM during the oxidation of the surface takes place.³³

In our opinion, due to the improvement that can be reached in the interface control and in the modulation of the spin injection by means of SAMs, research should now focus on the growth of more complex SAMs on bare ferromagnets that can work at room temperature. Some possibilities are the use of molecules having conjugated chains, which decrease the resistance of the organic layer, radical molecules that include unpaired electrons in the molecular film, or inter-linkable molecules that could permit the fabrication of air stable SAM/ferromagnet interfaces. Obviously, the increase of the complexity of the molecules will come over with the need of using solution approaches, as sublimation processes are mainly restricted to simple molecules.

3. Hybrid interfaces using 2D materials

With the discovery of graphene and other 2D materials, a new area known as 2D electronics has started to be developed. This research has been focused in the potential of graphene as flexible transparent conducting electrodes due to its unique mechanical and electronic properties with high optical transmittance,³⁴ but also, it has been triggered by the dramatic role played by the generated surface/graphene interface governing the performance for the devices³⁵ and by the possibility of making devices with channels that are extremely thin that will allow graphene field-effect transistors (FETs) to be scaled down without compromising the proper operation of the system.³⁶ Thus, the improvement in the interface quality with respect to that found in a conventional hybrid interface, thanks to the presence of a crystalline atomically-thin layer, permits avoiding short circuits due to the lack of defects in the 2D layers, reducing the device thickness and improving its properties. Graphene has been extensively used in this context.³⁷ Still, graphene is a zero-band gap semiconductor and therefore it is not a good choice for fabricating FETs with high on-off ratios, or optoelectronic devices. In this circumstances, MoS₂ and other 2D semiconductors with tuneable bandgaps have shown to be much more suitable.³⁸ For the most part, this 2D material has been integrated in purely inorganic devices, but very recently it has also been incorporated in molecular electronic devices. Thus, hybrid heterostructures formed by the combination of single layers of MoS₂ with well-known organic semiconducting layers (such as fullerene, pentacene, metal phthalocyanines, etc.) have shown to be useful to fabricate organic FETs.³⁹

The above situation is in sharp contrast with that encountered in molecular spintronics. Thus, as far as we know, no reports

describing the use of hybrid molecular/2D interfaces in the fabrication of conventional multilayer spintronic devices have been reported. The only reports are devoted to the use of 2D materials in pure spintronic devices or, when dealing with the combination of molecular systems with 2D materials, the state of the art is limited to the chemical functionalization of 2D materials with some organic molecules.

In the former aspect, the possibility of incorporating 2D materials in inorganic spintronic devices has been recently demonstrated.⁴⁰ Thus, graphene has been extensively investigated in spintronics as a source of spin-polarized currents, taking advantage of its long spin lifetimes and its large electron velocity.⁴¹ Besides graphene, h-BN⁴² was tested as a non-magnetic spacer layer in magnetic tunnel junctions proving a quite stable TMR effect. Along this direction and after some theoretical studies,⁴³ the first spin valves using MoS₂ thin layer between ferromagnetic electrodes were reported⁴⁴ and almost simultaneously, TMR was measured in a MTJ based on mechanically stacked ferromagnetic Fe_{0.25}TaS₂ thick flakes.⁴⁵ In the last two years some other experimental devices have been prepared based on other transition metal chalcogenides (TMCs),⁴⁶ but also new systems as black phosphorous (BP) are starting to be explored.⁴⁷ Therefore, given the vast number of properties exhibited by 2D materials, one can foresee that a variety of new spintronic devices based 2D layers acting as insulator spacers, semiconductors or active ferromagnetic spin injectors should be reported in the near future.

As far as the chemical functionalization of 2D materials is concerned, this aspect has started to be developed with the aim of improving the integration of 2D materials into functional devices (not necessarily spintronic devices). In fact, 2D materials present two main obstacles: (1) the chemical instability of the ultrathin sheets during their manipulation^{48,49} and (2) the lack of control over the properties of the new interfaces generated in multi-layered wickets⁵⁰ (i.e. electrode/2D material/electrode), which is a critical point for the spin and electron injection and transport.⁵¹ These facts can disrupt the original properties of the ultrathin layer and therefore should not be neglected. Hence, the surface engineering of 2D materials to solve interface issues (both with air or in between layers) is a key step toward manipulating the electronic, magnetic and optoelectronic properties of 2D material-based devices. Nowadays, 2D layers instability problem is usually tackled by working under controlled atmosphere environment (glove box), or by encapsulating the 2D material with a second 2D ultrathin layer of a different nature by means of mechanical manipulation.⁵² In spite of their efficacy, these physical approaches are limited to basic research lab studies and novel methods such as solvent-stabilization⁵³ are being evaluated. To deal with the problem about interfaces control in multi-layered devices, alternative metals, new configurations⁵⁴ or intermediate oxide layers are tested.⁵⁵ In this scenario, a great possibility is the use of molecular functionalization of the 2D layers for interface applications, and additionally, to achieve the boosting and tuning of the device properties. In order to reach the

molecular functionalization of a 2D material two main approaches have been followed namely weak- or physisorption method and strong- or chemisorption method.

Physisorption is achieved with molecules lacking of a specific functional group to react with the surface, but having a backbone that induces weak interactions with it. In spite of the lack of structural modification of the functionalized 2D layer, the charge transfer between the molecules (acting as electronic dopants) and the 2D materials is expected to induce a shift in the Fermi level, thus enabling a modulation in the optical and electrical properties of the ultrathin layers. In this group one should also include the chemical doping by adsorbed atomic species. Most of these examples can be found in the extensive literature about graphene functionalization, as for example the adsorption of metals,⁵⁶ or different organic molecules from vapour phase or by wet chemistry.^{57, 58, 59} More recently, several examples about functionalization of 2D TMCs materials by physisorption of molecules have been reported; for instance, gas adsorption of different inorganic molecules (O₂, H₂O, inert gases, etc.) has been used for the carrier doping of MoS₂, MoSe₂ or WSe₂ monolayers giving rise to very efficient molecular gating effects.⁶⁰ Sublimable organic molecules have been also deposited from vapour phase⁶¹, while more complex molecules (such as metal-phthalocyanines acting as p-type and n-type dopants) have been deposited by means of solution-based methods. In these examples a convenient control of optical and electrical properties of the atomically thin TMCs semiconductors has been achieved.⁶² Additionally, it is important to highlight that the chemical exfoliation of TMCs and other 2D materials has revealed the non-innocent role of most of the solvents during the exfoliation processes.⁶³ Thus, most solvents get adsorbed on the surfaces inducing doping effects that should be taken into consideration for the further understanding of the electronic properties of the exfoliated systems.

It is to be noted that the functionalization studies about 2D materials have been mainly devoted to graphene and to semiconducting TMC layers (specially MoS₂, WS₂ and MoSe₂). This is probably do to the larger instability exhibited by other TMCs, like the ones presenting metallic or superconducting properties, which are air sensitive systems. Despite this difficulty, very interesting effects have been achieved in these 2D materials, like the introduction of ferromagnetic interactions in a superconducting NbSe₂ layer by the adsorption of hydrazine, permitting the coexistence of both properties.⁶⁴ Special interest is the use of adsorbed molecules on the surfaces of these highly reactive TMCs and of other 2D systems to avoid the O₂ penetration and their degradation. For example, in BP it has been shown that the use of high-boiling point solvents, as for example 1-methyl-2-pyrrolidone or 1-cyclohexyl-2pyrrolidone can form compact solvation shells over the BP layers hindering the penetration of O₂ molecules.^{53,65} This stabilizing effect has also been observed by means of surfactants in water⁶⁶ or through the non-covalent functionalization with perylene diimides⁶⁷ or with an imidazolium-based ionic liquid.⁶⁸

Coming back to the use of molecules, not as protecting agents of 2D materials but as modulators of their properties, the physisorption method has a main obstacle with regards of its use in the fabrication of electronic devices: it gives rise to unstable interfaces, whose properties usually decay almost completely within a short time. This instability is due to the fact that physisorption process relies on weak van der Waals (vdW) interactions.⁶⁹

In this context, chemisorption methods can afford more robust devices. These methods require specific functional groups (anchoring groups), driving the binding to the surface through strong covalent bonds. This modification of 2D materials has been much less explored mainly due to two reasons: first, it is usually harder to control the chemical reaction process to reach specific functionalization rates, and moreover the demonstration of chemical modification of the surface is not always straightforward. In fact, sometimes the so-called physical modifications are actually chemisorption processes that have not been properly characterized; second, the disturbance of the skeleton of the 2D layer is directly associated with the modification or even collapse of its electronic structure. Still, tuning the electronic structure at will, can be very attractive for example for getting the opening of a band gap in graphene. In this context, this chemical modification (through oxidation, hydrogenation, fluorination, radical-based covalent functionalization, etc.)⁷⁰ has shown to be very useful to integrate graphene layers in FETs.^{36, 71} Moreover, it has also been observed that sometimes a chemical anchoring can maintain the peculiar band structure of graphene with its linear dispersion intact.⁶⁶

The chemical modification of other 2D materials like TMCs has been less extensive. The first evidence of covalent functionalization through thiol chemistry was made by Scanning Tunneling Microscopy (STM).⁷² Some years later Chou et al. demonstrated the thiol ligand conjugation on chemically exfoliated MoS₂ sheets.⁷³ This stimulated the nascent field of TMC covalent functionalization and new works based on the use of thiol anchoring group, specially focussing on biomedical or sensing applications, were published.⁷⁴ However, modification of the flakes with organothiols implied the anchoring of the molecule only on TMCs defects, and consequently, a low functionalization rate. Such a limitation was overcome by using diazonium salts⁷⁵ or organohalides,⁷⁶ as these organic molecules were proved to covalently modify the TMC ultrathin layers through a nucleophilic attack from the chalcogenide to the molecule.⁷⁷ Alternatively, an intermediate situation has been found by using coordination interactions between the chalcogenide of the 2D layer and a metallic salt,⁷⁸ or by using an halogen dative atom of a molecule to coordinate the metal of the TMC when a vacancy is present.⁷⁹ Several reviews can be found in literature that face detailed description of the chemical functionalization of TMCs, and the underlying interactions involved in these processes.⁸⁰

4.

Summary and outlook

In this account we have presented different types of hybrid molecular/inorganic interfaces which are of interest in spintronics. First, we have shown that the most common interface is that formed by a ferromagnetic surface in direct contact with a molecular thin film acting as spin collector. In this case, hybridization between the orbitals of the interfacial molecules and those of the ferromagnetic surface can occur, leading to interesting spin effects, as the reversal of the spin polarization, which are able to strongly affect the device properties.

Second, a more elaborated design of the interface consists in attaching a SAM of molecules on the ferromagnetic surface. This less explored possibility has afforded some appealing results as for example the observation of magnetoresistance effects at unusually high voltages. Through a wise chemical design of the molecule, this approach could afford in the future to a fine tuning of the properties of the device. Still, this is strongly limited by the quality of the SAM (as its preparation is often incompatible with UHV techniques and requires solution techniques). The insertion of other molecular monolayers having some functionality (a permanent dipolar moment or magnetism, for example) in between the inorganic ferromagnet and the molecular spin collector is also one of the future issues in this area. These functional molecules may have significant effects on the properties of the ferromagnet as they can affect its work function or its magnetic properties.

The third type of hybrid interface is that formed by a molecular layer in direct contact with a 2D material. Some efforts have been devoted to the fabrication of such heterostructures using either an electrostatic approach or a covalent one, and some reports on the influence of the molecular layer on the properties of the 2D layer have been published. Still, in the context of spintronics, the hybrid heterostructures that appear when a 2D layer is inserted in between a ferromagnet and a molecular spin collector layer have not been explored yet. This possibility is very promising since the 2D material, apart from acting as a protective layer with regards to the underneath ferromagnet,⁸¹ can generate interfaces of unprecedented high quality and low thickness. In addition, the functional properties of the 2D material (magnetism for example) can be also very useful for tuning the properties of the device (acting as spin filter, for example).

The above results can provide an idea of the state-of-the-art in this topic. In particular, they have illustrated how simple molecules can be able to tune the properties of a ferromagnetic- molecular interface and of the entire device when they are in close proximity of a ferromagnet. However, in these hybrid interfaces the capabilities of the molecules have not been fully exploited yet. In this context, an appealing possibility is that of using as molecular component stimuli-responsive molecules able to switch between two states upon the application of an external stimulus (temperature, light, pressure, electrical field,

etc.). These smart molecules can play an active role in the hybrid interface as the spin injection and transport through the device should be dependent on their electronic state. The archetypical example of this kind of molecular systems is provided by the so-called spin-crossover (SCO) complexes, which undergo a switching from low-spin to high-spin states.⁸² This spin transition is often accompanied by a thermal hysteresis at relatively high temperatures and by drastic changes in the volume of the solid (by more than a 10%), as well as in the electronic properties. In some cases the SCO can also be triggered by light at low temperatures (LIESST effect,⁸³ figure 4).

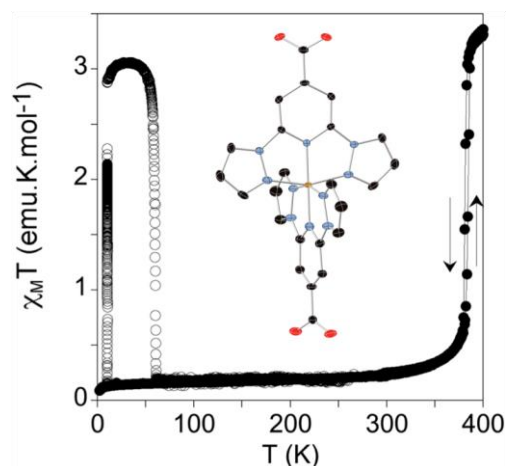


Figure 4. Magnetic behaviour of the $[\text{Fe}^{\text{II}}(\text{bppCOOH})_2](\text{ClO}_4)_2$ salt showing an abrupt spin transition with a $T_{1/2}$ of ca. 380 K and a T_{LIESST} of 60 K. Full circles: data recorded in the cooling and heating modes without irradiation; empty circles: data recorded after irradiation at 10 K. The inset graph shows the X-ray structure of the complex (C (black), N (blue), O (red) and counterions are omitted for clarity).

Figure adapted from ref.83.

The incorporation of these molecules in electronic devices has shown that the electronic transport depends on their spin state.⁸⁴ On the other hand, hybrid interfaces based on a monolayer of bistable spin-crossover nanoparticles deposited on graphene have been recently reported, in which the transport properties of graphene have shown to be dependent on the spin state of the molecular system⁸⁵ (Figure 5).

Notice that the presence of this stimuli-responsive molecular layer is not limited to spin-crossover molecules. Other molecular systems such as the so-called metal-organic frameworks (MOFs) can also be of interest in this context. Thus, hybrid interfaces formed by a thin layer of these materials deposited on a metallic (or even ferromagnetic) electrode can be prepared. Thanks to their ability to trap and release guest molecules in their pores (Figure 6), these coordination polymers have shown to be able to tune the electronic properties of the interface⁸⁶). In the future this new concept could be useful to prepare spin valves responding to a chemical stimulus; these devices should

strongly benefit of the high sensitivity provided by spintronics to be used for gas sensing.

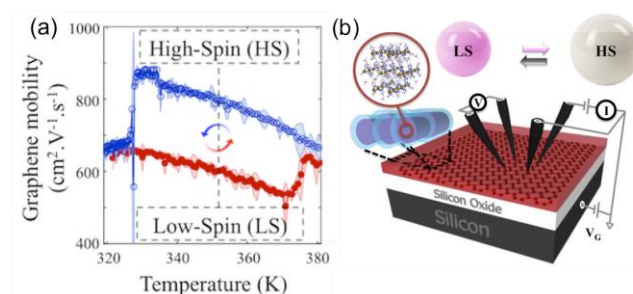


Figure 5. (a) Temperature dependence of graphene electrical properties after the ∞ -contact printing of a thin film of SCO nanoparticles using the FET device schematized in (b). Figure adapted from ref.85.

With these precedents one can envision that the fabrication of smart spintronic devices containing hybrid interfaces based on these switchable molecular systems will be soon feasible, in the same way as multifunctional molecules have already produced the first examples of multifunctional spintronic devices coupling spin with light (spin-OLEDs)⁸⁷ and spin-photovoltaic cells.⁸⁸

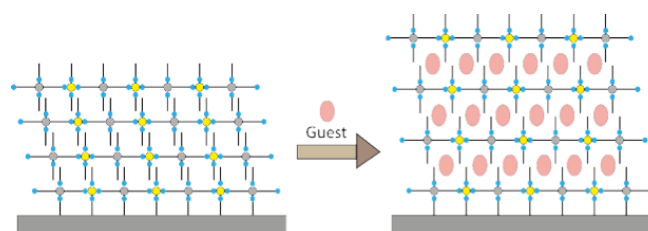


Figure 6. Scheme of the gate-opening behaviour, displayed by thin films of layered MOFs upon trapping guest molecules into the pores.

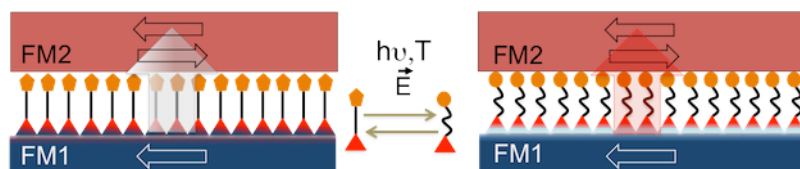
Acknowledgements ((optional))

We acknowledge the financial support from the Generalitat Valenciana (PROMETEO/2017/066), the Spanish MINECO (MAT2014-56143-R co-financed by FEDER and Excellence Unit "María de Maeztu" MDM-2015-0538) and the European Union (COSMICS (Nº 766726) and COST-Action MOLSPIN: Molecular Spintronics (CA15128)). A.F.-A. thanks Dr. M. Galbiati for scientific discussion during manuscript preparation.

Keywords: molecular spintronics • spinterface • interfaces • 2D materials • spin crossover

Entry for the Table of Contents (Please choose one layout)

PERSONAL ACCOUNT



A. Forment-Aliaga*, E. Coronado*

Page No. – Page No.

Hybrid interfaces in molecular spintronics

Next generation spintronics faces the integration of molecular-based and/or 2D materials with traditional inorganic ones. This represents the formation of new hybrid interfaces with a non-innocent role in the performance of the devices. This personal account summarises different interfaces found in the most common multilayer spintronic devices based on molecules. One step forward we consider as perspective the potential of the integration of molecular functionalized 2D materials into the devices and the formation of hybrid smart interfaces based on stimuli-responsive molecular systems.

- 1 a) S.-M. Lee, J. H. Kwon, S. Kwon, K. C. Choi, *IEEE Trans. Electron Devices* **2017**, *64*, 1922-1931; b) D. Ma, T. Tsuboi, Y. Qiu, L. Duan, *Adv Mater* **2016**, *29*, 1603253
 2 a) S. Holliday, Y. Li, C. K. Luscombe, *Progress in Polymer Science* **2017**, *70*, 34-51; b) G. Han, S. Zhang, P. P. Boix, L. H. Wong, L. Sun, S.-Y. Lien, *Progress in Materials Science* **2017**, *87*, 246-291
 3 J. Devkota, R. Geng, R. C. Subedi, T. D. Nguyen, *Adv. Funct. Mater.* **2016**, *26*, 3881-3898
 4 T.-W. Ha, Y.-B. Kim, G.-S. Heo, I. Hwang, H. G. Jeon, B. Park, *RSC Adv.* **2016**, *6*, 33063-33071.
 5 H.-J. Jang, C. A. Richter, *Adv Mater* **2017**, *29*, 1602739
 6 V. A. Dediu, L. E. Hueso, I. Bergenti, C. Taliani, *Nat Mater* **2009**, *8*, 707-716.
 7 a) S. Sanvito, *Chem. Soc. Rev.* **2011**, *40*, 3336-3355; b) P. A. Bobbert, W. Wagemans, F. W. A. van Oost, B. Koopmans, M. Wohlgenannt, *Phys. Rev. Lett.* **2009**, *102*, 156604.
 8 L. Bogani, W. Wernsdorfer *Nat. Mater.* **2008**, *7*, 179-186
 9 a) S. Schmaus, A. Bagrets, Y. Nahas, T. K. Yamada, A. Bork, M. Bowen, E. Beaupaire, F. Evers, W. Wulfhekel, *Nat Nano* **2011**, *6*, 185-189; b) R. Yamada, M. Noguchi, H. Tada, *Appl. Phys. Lett.* **2011**, *98*, 053110; c) E. Coronado, M. Yamashita, *Dalton Trans.* **2016**, *45*, 16553-16555.
 10 V. Dediu, M. Murgia, F.C. Matocotta, C. Taliani, S. Barbanera *Solid State Commun.* **2002**, *122*, 181-184
 11 Z. H. Xiong, D. Wu, Z. V. Vardeny, J. Shi, *Nature* **2004**, *427*, 821-824
 12 J. Devkota, R. Geng, R. C. Subedi, T. D. Nguyen, *Adv. Funct. Mater.* **2016**, *26*, 3881-3898.
 13 a) C. Barraud, P. Seneor, R. Mattana, S. Fusil, K. Bouzehouane, C. Deranlot, P. Graziosi, L. Hueso, I. Bergenti, V. Dediu, F. Petroff, A. Fert, *Nat Phys* **2010**, *6*, 615-620; b) S. Sanvito, *S.Nat. Phys.* **2010**, *6*, 562-564
 14 M. Cinchetti, V. A. Dediu, L. E. Hueso, *Nat Mater* **2017**, *16*, 507-511.
 15 A. Bedoya-Pinto, S. G. Miralles, S. Vélez, A. Atxabal, P. Gargiani, M. Valvidares, F. Casanova, E. Coronado, L. E. Hueso, *Adv. Funct. Mater.* **2017**, *135*, 1702099
 16 K. V. Raman, A. M. Kamerbeek, A. Mukherjee, N. Atodiresei, T. K. Sen, P. Lazić, V. Caciuc, R. Michel, D. Stalke, S. K. Mandal, S. Blügel, M. Münzenberg, J. S. Moodera, *Nature* **2013**, *493*, 509-513
 17 a) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533-1554; b) F. Schreiber *Prog. Surf. Sci.* **2000**, *65*, 151-256
 18 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103-1169.
 19 S. Casalini, C. A. Bortolotti, F. Leonardi, F. Biscarini, *Chem. Soc. Rev.* **2017**, *46*, 40-71.
 20 H.-J. Jang, C. A. Richter, *Adv Mater* **2016**, *29*, 1602739
 21 H.-J. Jang, J.-S. Lee, S. J. Pookpanratana, C. A. Hacker, I. C. Tran, C. A. Richter, *J. Phys. Chem. C* **2015**, *119*, 12949-12955
 22 J. R. Petta, S. K. Slater, D. C. Ralph, *Phys. Rev. Lett.* **2004**, *93*, 136601
 23 W. Wang, C. A. Richter, *Appl. Phys. Lett.* **2006**, *89*, 153103-153105
 24 S. Tatay, C. Barraud, M. Galbiati, P. Seneor, R. Mattana, K. Bouzehouane, C. Deranlot, E. Jacquet, A. Forment-Aliaga, P. Jegou, A. Fert, F. Petroff *ACS Nano* **2012**, *6*, 8753-8757
 25 M. Galbiati, S. Tatay, S. Delprat, C. Barraud, V. Cros, E. Jacquet, F. Coloma, F. Choueikani, E. Otero, P. Ohresser, N. Haag, M. Cinchetti, M. Aeschlimann, P. Seneor, R. Mattana, F. Petroff, *Appl Surf Sci* **2015**, *353*, 24-28.

- 26 a) M. Galbiati, C. Barraud, S. Tatay, K. Bouzehouane, C. Deranlot, E. Jacquet, A. Fert, P. Seneor, R. Mattana, F. Petroff *Adv. Mater.* **2012**, *24*, 6427-6432; b) S. Tatay, M. Galbiati, S. Delprat, C. Barraud, K. Bouzehouane, S. Collin, C. Deranlot, E. Jacquet, P. Seneor, R. Mattana, F. Petroff, *J Phys Condens Matter* **2016**, *28*, 094010.
- 27 R. Geng, A. Roy, W. Zhao, R. C. Subedi, X. Li, J. Locklin, T. D. Nguyen, *Adv. Funct. Mater.* **2016**, *26*, 3999.
- 28 L. Poggini, G. Cucinotta, A.-M. Pradipto, M. Scarrozza, P. Barone, A. Caneschi, P. Graziosi, M. Calbucci, R. Cecchini, V. A. Dediu, S. Picozzi, M. Mannini, R. Sessoli, *Adv. Mater. Interfaces* **2016**, *3*, 1500855
- 29 G. Cucinotta, L. Poggini, A. Pedrini, F. Bertani, N. Cristiani, M. Torelli, P. Graziosi, I. Cimatti, B. Cortigiani, E. Otero, P. Ohresser, P. Sainctavit, A. Dediu, E. Dalcanale, R. Sessoli, M. Mannini, *Adv. Funct. Mater.* **2017**, *50*, 1703600.
- 30 M. Mattera, R. Torres-Cavanillas, J. P. Prieto-Ruiz, H. Prima-García, S. Tatay, A. Forment-Aliaga, E. Coronado *Langmuir* **2015**, *31*, 5311-5318
- 31 M. Galbiati, S. Delprat, Michele Mattera, S. Mañas, A. Forment-Aliaga, S. Tatay, C. Deranlot, P. Seneor, R. Mattana, F. Petroff *AIP Advances* **2015**, *5*, 057131
- 32 S. Delprat PhD Thesis *Jonctions tunnel magnétiques avec des monocouches moléculaires auto-assemblées* Université Pierre et Marie Curie, **2017**
- 33 M. Mattera PhD Thesis *Molecular nanostructures on ferromagnetic metals for spintronics* University of Valencia, **2017**
- 34 T.-H. Han, H. Kim, S.-J. Kwon, T.-W. Lee, *Mater Sci Eng R Rep* **2017**, *118*, 1-43.
- 35 G. Zhao, X. Li, M. Huang, Z. Zhen, Y. Zhong, Q. Chen, X. Zhao, Y. He, R. Hu, T. Yang, R. Zhang, C. Li, J. Kong, J.-B. Xu, R. S. Ruoff, H. Zhu, *Chem. Soc. Rev.* **2017**, *46*, 4417-4449
- 36 F. Schwierz, *Nat. Nanotech.* **2010**, *5*, 487-496
- 37 M. Piquemal-Banci, R. Galceran, M.-B. Martin, F. Godel, A. Anane, F. Petroff, B. Dlubak, P. Seneor, *Journal of Physics D: Applied Physics* **2017**, *50*, 203002.
- 38 Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat Nanotech* **2012**, *7*, 699-712
- 39 a) D. Jariwala, T. J. Marks, M. C. Hersam, *Nat Mater* **2017**, *16*, 170-181; b) J. Choi, H. Zhang, J. H. Choi, *ACS Nano* **2016**, *10*, 1671-1680.
- 40 W. Han, *APL Mater.* **2016**, *4*, 032401.
- 41 a) P. Seneor, B. Dlubak, M.-B. Martin, A. Anane, H. Jaffres, A. Fert, *MRS Bulletin*, **2012**, 1245-1254; (b) E. Cobas; A. L. Friedman, O. M. J. van't Erve, J.T. Robinson, B.T. Jonker *Nano Lett.*, **2012**, *12*, 3000-3004; (c) C.-C. Lin, A. V. Penumatcha, Y. Gao, V. Q. Diep, J. Appenzeller, Z. Chen *Spin Nano Lett.*, **2013**, *13*, 5177-5181
- 42 a) A. Dankert, M. V. Kamalakar, A. Wajid, R. S. Patel, S. P. Dash *Nano Res.* **2015**, *8*, 1357-1364; b) M. Piquemal-Banci, R. Galceran, S. Caneva, M.-B. Martin, R. S. Weatherup, P. R. Kidambi, K. Bouzehouane, S. Xavier, A. Anane, F. Petroff, A. Fert, J. Robertson, S. Hofmann, B. Dlubak, P. Seneor *App. Phys. Lett.* **2016**, *108*, 102404
- 43 K. Dolui, Awadhesh Narayan, I. Rungger, S. Sanvito *Phys. Rev. B*, **2014**, *90*, 041401(R)
- 44 W. Wang, A. Narayan, L. Tang, K. Dolui, Y. Liu, X. Yuan, Y. Jin, Y. Wu, I. Rungger, S. Sanvito, F. Xiu *Nano Lett.* **2015**, *15*, 5261-5267
- 45 M. Arai, R. Moriya, N. Yabuki, S. Masubuchi, K. Ueno, T. Machida *Appl. Phys. Lett.* **2015**, *107*, 103107
- 46 a) M. Z. Iqbal, M. W. Iqbal, S. Siddique, M. F. Khan, S. M. Ramay *Sci. Rep.* **2016**, *6*, 21038 ; b)K. Zhang, Y. Xing, J. Han, J. Feng, W. Shi, B. Zhang, Z. Zeng *J. Magn. Magn. Mater.* **2017**, *432*, 10-13
- 47 L. Xu, J. Feng, K. Zhao, W. Lv, X. J. Han, Z. Liu, X. Xu, H. Huang, Z. Zeng *Adv. Condens. Matter* **2017**, *2017*, 1-7
- 48 J. O. Island, G. A. Steele, H. S. J. van der Zant, A. Castellanos-Gomez *2D Mater.*, **2015**, *2*, 011002
- 49 W. Park, J. Park, J. Jang, H. Lee, H. Jeong, K. Cho, S. Hong, T. Lee *Nanotechnology* **2013**, *24*, 095202
- 50 a) A. Allain, J. Kang, K. Banerjee, A. Kis *Nat. Mater.* **2015**, *14*, 1195-1205; b) C. Gong, D. Hinojos, W. Wang, N. Nijem, B. Shan, R. M. Wallace, K. Cho, Y. J. Chabal *ACS Nano*, **2012**, *6*, 5381-5387
- 51 I. Popov, G. Seifert, D. Tománek *Phys. Rev. Lett.* **2012**, *108*, 156802
- 52 M. Kuri, C. Kumar, B. Chakraborty, S. N. Gupta, M. H. Naik, M. Jain, A.K. Sood, A. Das *Nanotechnology* **2015**, *26*, 485704
- 53 D. Hanlon, C. Backes, E. Doherty, C. S. Cucinotta, N. C. Berner, C. Boland, K. Lee, A. Harvey, P. Lynch, Z. Gholamvand, S. Zhang, K. Wang, G. Moynihan, A. Pokle, Q. M. Ramasse, N. McEvoy, W. J. Blau, J. Wang, G. Abellán, F. Hauke, A. Hirsch, S. Sanvito, D. D. O'Regan, G. S. Duesberg, V. Nicolosi, J. N. Coleman, *Nat. Commun.* **2015**, *6*, 8563
- 54 L. Wang, I. Meric, P. Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L. M. Campos, D. A. Muller, J. Guo, P. Kim, J. Hone, K. L. Shepard, C. R. Dean *Science* **2013**, *342*, 614-617
- 55 J.-R. Chen, P.M. Odenthal, A.G. Swartz, G. C. Flod, H. Wen, K. Y. Luo, R. K. Kawakami *Nano Lett.*, **2013**, *13*, 3106-3110
- 56 I. Gierz, C. Riedl, U. Starke, C. R. Ast, K. Kern *Nano Lett.*, **2008**, *12*, 4603-4607.
- 57 (a) Z. Zhang, H. Huang, X. Yang, L. Zang, *J. Phys. Chem. Lett.* **2011**, *2*, 2897-2905; (b) Q.H. Wang, M.C. Hersam, *Nat. Chem.*, **2009**, *1*, 206-211.
- 58 T. Zhang, Z. Cheng, Y. Wang, Z. Li, C. Wang, Y. Li, Y. Fang *Nano Lett.*, **2010**, *10*, 4738-4741.
- 59 M. C. Prado, R. Nascimento, L. G. Moura, M. J. S. Matos, M. S. C. Mazzoni, L. G. Cancado, H. Chacham, B. R. A. Neves *ACS Nano*, **2011**, *1*, 394-398
- 60 S. Tongay, J. Zhou, C. Ataca, J. Liu, J. S. Kang, T. S. Matthews, L. Y., J. Li, J. C. Grossman, J. Wu Broad-range modulation of light emission in two-dimensional semiconductors by molecular physisorption gating. *Nano Lett.*, **2013**, *13*, 2831-2836
- 61 D. He, Y. Pan, H. Nan, S. Gu, Z. Yang, B. Wu, X. Luo, B. Xu, Y. Zhang, Y. Li, Z. Ni, B. Wang, J. Zhu, Y. Chai, Y. Shi, X. Wang, *Appl Phys Lett* **2015**, *107*, 183103.
- 62 (a) S. Mouri, Y. Miyauchi, K. Matsuda. *Nano Lett.*, **2013**, *13*, 5944-5948; (b) J. Choi, H. Zhang, J. H. Choi *ACS Nano*, **2016**, *10*, 1671-1680
- 63 J. Choi, H. Zhang, H. Du, J. H. Choi *ACS Appl. Mater. Interfaces* **2016**, *8*, 8864-8869
- 64 X. Zhu, Y. Guo, H. Cheng, J. Dai, X. An, J. Zhao, K. Tian, S. Wei, X. Cheng Zeng, C. Wu, Y. Xie, *Nat. Commun.* **2016**, *7*, 11210.
- 65 Kang, J.; Wood, J. D.; Wells, S. A.; Lee, J.-H.; Liu, X.; Chen, K.-S.; Hersam, M. C. *ACS Nano* **2015**, *9*, 3596-3604
- 66 J. R. Brent, A. K. Ganguli, V. Kumar, D. J. Lewis, P. D. McNaughton, P. O'Brien, P. Sabherwal, A. A. Tedstone, *RSC Adv.* **2016**, *6*, 86955-86958.
- 67 G. Abellán, V. Lloret, U. Mundloch, M. Marcía, C. Neiss, A. Göring, M. Varela, F. Hauke, A. Hirsch, *Angew. Chem., Int. Ed.* **2016**, *55*, 14557-14562.
- 68 G. Abellán, S. Wild, V. Lloret, N. Scheuschner, R. Gillen, U. Mundloch, J. Maultzsch, M. Varela, F. Hauke, A. Hirsch, *J. Am. Chem. Soc.* **2017**, *139*, 10432-10440.
- 69 H. Fang, S. Chuang, T.C. Chang, K. Takei, T. Takahashi, A. Javey *Nano Lett.*, **2012**, *12*, 3788-3792
- 70 S. Sarkar, E. Bekyarova, R. C. Haddon *Mater. Today*, **2012**, *6*, 276-285
- 71 S. Niyogi, E. Bekyarova, J. Hong, S. Khizroev, C. Berger, W. de Heer, R. C. Haddon, *J. Phys. Chem. Lett.*, **2011**, *2*, 2487-2498
- 72 (a) A. Tuxen, J. Kibsgaard, H. Gøbel, E. Lægsgaard, H. Topsøe, J. V. Lauritsen, F. Besenbacher *ACS Nano* **2010**, *4*, 4677-4682 ; (b) M. Makarova, Y. Okawa, M. Aono *J. Phys. Chem. C*, **2012**, *116*, 22411-22416
- 73 S. S. Chou, M. De, J. Kim, S. Byun, C. Dykstra, J. Yu, J. Huang, V. P. Dravid *J. Am. Chem. Soc.*, **2013**, *135*, 4584-4587
- 74 (a) L. Zhou, B. He, Y. Yang, Y. He *RSC Adv.*, **2014**, *4*, 32570-32578; (b) E. P. Nguyen, B. J. Carey, J. Zhen Ou, J. van Embden, E. Della Gaspera, A. F. Chrimes, M. J. S. Spencer, S. Zhuikov, K. Kalantar-zadeh, T. Daenke *Adv. Mater.*, **2015**, *27*, 6225-6229; (c) T. Liu S. Shi, C. Liang, S. Shen, L. Cheng, C. Wang, X. Song, S. Goel, T. E. Barnhart, W. Cai, Z. Liu *ACS Nano*, **2015**, *9*, 950-960; (d) T. Liu, C. Wang, X. Gu, H. Gong, L. Cheng, X. Shi, L. Feng, B. Sun, Z. Liu *Adv. Mater.* **2014**, *26*, 3433-3440
- 75 K. C. Knirsch, N. C. Berner, H. C. Nerl, C. S. Cucinotta, Z. Gholamvand, N. McEvoy, Z. Wang, I. Abramovic, P. Vecera, M. Halik, S. Sanvito, G. S. Duesberg, V. Nicolosi, F. Hauke, A. Hirsch, J. N. Coleman, C. Backes *ACS Nano*, **2015**, *9*, 6018-6030
- 76 D. Voiry, A. Goswami, R. Kappera, C. de Carvalho Castro e Silva, D. Kaplan, T. Fujita, M. Chen, T. Asefa, M. Chhowalla *Nat. Chem.* **2015**, *7*, 45-49
- 77 S. Presolski, M. Pumera, *Mater. Today* **2016**, *19*, 140-145
- 78 C. Backes, N. C. Berner, X. Chen, P. Lafargue, P. LaPlace, M. Freeley, G. S. Duesberg, J. N. Coleman, A. R. McDonald, *Angew. Chem. Int. Ed.* **2015**, *54*, 2638-2642
- 79 E. D. Grayfer, M. N. Kozlova, V. E. Fedorov, *Adv. Colloid. Interface Sci.* **2017**, *245*, 40-61.
- 80 X. Chen, A. R. McDonald, *Adv. Mater.* **2016**, *28*, 5738-5746
- 81 M.-B. Martin, B. Dlubak, R. Weatherup, H. Yang, C. Deranlot, K. Bouzehouane, F. Petroff, A. Anane, S. Hofmann, J. Robertson, A. Fert, P. Seneor, *ACS Nano* **2014**, *8*, 7890-7895
- 82 A. Bousseksou, G. Molnár, L. Salmon, W. Nicolazzi, *Chem. Soc. Rev.* **2011**, *40*, 3313-3324
- 83 A. Abhervé, M. Clemente-León, E. Coronado, C. J. Gómez-García, M. López-Jordà *Dalton Trans.*, **2014**, *43*, 9406-9509

PERSONAL ACCOUNT

- 84 a) F. Prins, M. Monrabal-Capilla, E. A. Osorio, E. Coronado, H. S. J. Van Der Zant, *Adv Mater* **2011**, 23, 1545-1549; b) J. Dugay, M. Giménez-Marqués, T. Kozlova, H. W. Zandbergen, E. Coronado, H. S. J. van der Zant, *Adv. Mater.* **2015**, 27, 1288-1293; c) A. Holovchenko, J. Dugay, M. Giménez-Marqués, R. Torres-Cavanillas, E. Coronado, H. S. J. van der Zant, *Adv. Mater.*, **2016**, 28, 7228–7233.
- 85 J. Dugay, M. Aarts, M. Giménez-Marqués, T. Kozlova, H. W. Zandbergen, E. Coronado, H. S. J. van der Zant, *Nano Lett.* **2017**, 17, 186-193
- 86 a) V. Rubio-Giménez, S. Tatay, F. Volatron, F. J. Martínez-Casado, C. Martí-Gastaldo, E. Coronado, *J. Am. Chem. Soc.* **2016**, 138, 2576-2584; b) V. Rubio-Giménez, M. Galbiati, J. Castells-Gil, N. Almora-Barrios, J. Navarro-Sánchez, G. Escorcia-Ariza, M. Mattera, T. Arnold, J. Rawle, S. Tatay, E. Coronado, C. Martí-Gastaldo *Adv. Mater.* In press
- 87 a) T. D. Nguyen, E. Ehrenfreund, Z. V. Vardeny, *Science* **2012**, 337, 204-209; b) J.P. Prieto-Ruiz, S.G. Miralles, H. Prima-García, A. Riminucci, P. Graziosi, M. Cinchetti, M. Aeschlimann, V. A. Dediu, E. Coronado arXiv:1612.00633[cond-mat.mes-hall]
- 88 X. Sun, S. Vélez, A. Atxabal, A. Bedoya-Pinto, S. Parui, X. Zhu, R. Llopis, F. Casanova, L. E. Hueso, *Science* **2017**, 357, 677-680
-