

## Interface-assisted molecular spintronics

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# APPLIED PHYSICS REVIEWS—FOCUSED REVIEW

## Interface-assisted molecular spintronics

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Molecular spintronics, a field that utilizes the spin state of organic molecules to develop magneto-electronic devices, has shown an enormous scientific activity for more than a decade. But, in the last couple of years, new insights in understanding the fundamental phenomena of molecular interaction on magnetic surfaces, forming a hybrid interface, are presenting a new pathway for developing the subfield of interface-assisted molecular spintronics. The recent exploration of such hybrid interfaces involving carbon based aromatic molecules shows a significant excitement and promise over the previously studied single molecular magnets. In the above new scenario, hybridization of the molecular orbitals with the spin-polarized bands of the surface creates new interface states with unique electronic and magnetic character. This study opens up a molecular-genome initiative in designing new handles to functionalize the spin dependent electronic properties of the hybrid interface to construct spin-functional tailor-made devices. Through this article, we review this subject by presenting a fundamental understanding of the interface spin-chemistry and spin-physics by taking support of advanced computational and spectroscopy tools to investigate molecular spin responses with demonstration of new interface phenomena. Spin-polarized scanning tunneling spectroscopy is favorably considered to be an important tool to investigate these hybrid interfaces with intra-molecular spatial resolution. Finally, by addressing some of the recent findings, we propose novel device schemes towards building interface tailored molecular spintronic devices for applications in sensor, memory, and quantum computing. [<http://dx.doi.org/10.1063/1.4890496>]

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### I. INTRODUCTION

The quest for magnetism in organic molecules has generated a strong research interest in the scientific community.<sup>1,2</sup> The search began more than four decades ago when McConnell proposed a theoretical framework for the design of ferromagnetic (FM) molecular solids.<sup>3</sup> Although an intuitive model, extension of his work later led to the development of charge-transfer-complexes with donor-acceptor radical chains that exhibit a *cooperative* magnetic

phenomenon.<sup>4,5</sup> As a result, today, molecular solids showing ferromagnetism at room temperature are observed.<sup>6</sup> However, achieving magnetism at a single molecular level is still a challenging activity. In the recent years, there is a strong need to design magnetic molecules, which are stable up to room temperature, due to its technological relevance in data storage,<sup>7,8</sup> sensor,<sup>8,9</sup> quantum computing,<sup>10</sup> and other single molecular spintronic applications.<sup>11</sup> In this regard, spin bearing transition metal (TM) centers with localized d- and/or f- states in metal-organic frameworks are considered to be a promising class of material for the above exploration. In certain molecules, *viz.*, single molecular magnets (SMMs), these localized TM spin centers are stabilized by the single ion anisotropy of the molecular framework,<sup>12–14</sup> demonstrating magnetization hysteresis response.<sup>14–16</sup> However, the strength of magnetic anisotropy in such molecules is observed to be relatively weak, making them paramagnetic at higher temperatures ( $\sim 30$  K for the case of Terbium(III) bis-phthalocyaninato (TbPc<sub>2</sub>) molecule with a record height of the anisotropy barrier<sup>17</sup>). Hence, the search for room temperature SMMs is an ongoing activity.

Various approaches to develop pseudo-SMMs that show magnetic stability at higher temperatures are also experimented in literature; these include growing molecules on inert<sup>7,16,18,19</sup> as well as magnetic surfaces,<sup>20–22</sup> by taking assistance of surface induced magnetic anisotropy and/or surface induced magnetic exchange coupling (Fig. 1(a)). In this effort, investigations using planar coordinated spin bearing

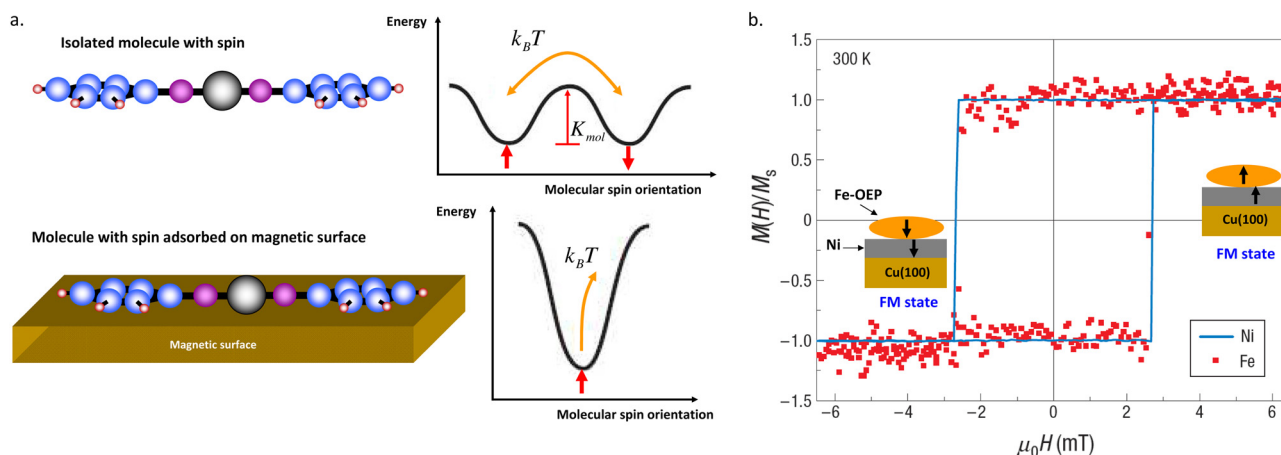


FIG. 1. (a) (Top) The magnetic moment of an isolated SMM with low magnetic anisotropy energy ( $K_{Mol}$ ) can be flipped easily by thermal excitations ( $k_B T$ ). This process can be circumvented by growing the molecule on a magnetic surface (bottom), which enhances the thermal stability of the molecule by surface induced magnetic exchange coupling and/or magnetic anisotropy. (b) Element-specific magnetic hysteresis curves of the Fe (filled squares) and Ni (full line) atoms, obtained by the L3 edge XMCD maxima of octaethylporphyrin Fe(III) chloride molecule on Ni/Cu(100) at 300 K. The plot shows a stable molecular moment which follows the magnetization of the underlying Ni surface, suggesting a strong FM coupling at the interface. Here, an independent switching response of molecular magnetization is not observed which has led to our research efforts in developing pseudo-SMMs. Reprinted with permission from Wende *et al.*, Nat. Mater. 6, 516–520 (2007). Copyright 2007 Macmillan Publishers Ltd.

TM centers in porphyrins<sup>20–22</sup> and phthalocyanines<sup>23,24</sup> have shown promise in tailoring the surface induced spin stability and spin anisotropy of the TM centers. For example, in a study involving adsorption of Fe porphyrin molecules on Ni surface, a magnetic hysteresis response of the molecules coupled with the bottom Ni surface was observed up to room-temperature<sup>21</sup> (Fig. 1(b)). However, an independent switching of the spin state of TM center relative to magnetization of the magnetic surface to demonstrate a pseudo SMM response was not feasible. Following these observations, extensive studies using X-ray magnetic circular dichroism (XMCD) have been performed to understand the origin of magnetic interaction between the localized TM spin centers and the bottom magnetic surface.<sup>25–27</sup> These reports have shown the possibility to engineer and tune the spin states of these TM centers using *in-situ* magnetochemistry (controlled adsorption/desorption of ligands to the molecule causing a change in spin moment of the TM center).<sup>28</sup> However, such mechanisms provide limited scope in selectively addressing single molecule switching, continuing our research efforts to develop pseudo-SMMs.

In this review article, we focus our attention in exploring the adsorption of carbon-based aromatic structures having delocalized electron density on magnetic surfaces to construct pseudo-SMMs, a study that so far has received very little or no attention. In recent years, a number of promising results using such investigations have opened up exciting new avenues to tailor adsorbed molecular properties by engineering the free-molecule and surface chemistry.<sup>8,29,30</sup> Furthermore, these reports provide new insights in understanding the magnetic interactions between metal-porphyrins or -phthalocyanines and magnetic surfaces.<sup>29,31</sup> Therefore, understanding the fundamental mechanism contributing to such interface interactions is becoming an important topic of research. We begin this article by giving a brief overview of the mechanisms affecting the magnetic surface-molecule interactions (Sec. II). Subsequently, in Sec. III, we provide

details of the interface spin-chemistry by taking help of state-of-the-art *ab initio* computational modeling and spin-polarized scanning tunneling spectroscopy (SP-STs) studies. In Sec. IV, we give considerable attention to the recent observations of interface magnetic phenomena, such as induced molecular magnetism, magnetic exchange coupling, and magnetic hardening of surfaces. Finally, in Sec. V, we provide a brief overview on the recent advances and future prospects of this promising field towards tailoring molecular spin functionalities for potential device applications.

## II. INTERACTIONS AT MAGNETIC SURFACE/MOLECULE INTERFACE

When a molecule is brought closer to the surface, a range of bonding interactions may occur starting from a weak physisorption to a strong chemisorption. The strength of these interactions can greatly modify the electronic structure of the molecules.<sup>32</sup> In the case of physisorption, the discrete molecular electronic levels, observed in gas phase, are weakly broadened due to its proximity with the spatially extended metallic states<sup>33,34</sup> (Fig. 2(a)). In addition, the surface-molecule interaction causes rearrangement of the electron density, polarizing the interface. Such surface-adsorbate physical effects cause renormalization of the electronic levels and modify the alignment of the frontier orbital energies, namely, the highest occupied molecular orbital level and the lowest un-occupied molecular orbital level, in comparison to the value in gas phase.<sup>34–36</sup> The presence of these weak interactions has been confirmed experimentally using spectroscopy studies<sup>37</sup> and could be described using perturbation analysis within the linear combination of atomic orbital model.<sup>32</sup> A physical charge transfer may also happen on account of alignment of the Fermi level across the interface.

On the contrary, in the case of chemisorption, the interface is characterized by a strong charge transfer and possible hybridization (i.e., mixing of charge and energy) forming a

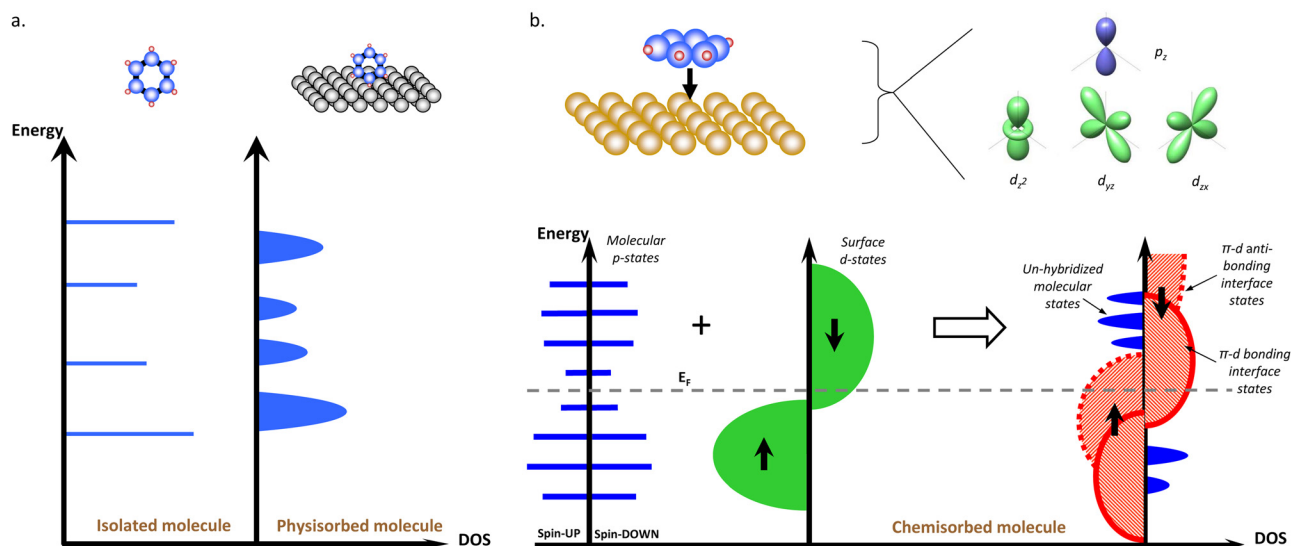


FIG. 2. Molecular adsorption on surfaces: (a) Physisorption: Schematics show the discrete electronic energy levels of a gas-phase molecule to softly broaden, realign, and renormalize upon adsorption. (b) Chemisorption: Schematics show a planar adsorption of an aromatic organic molecule on magnetic surface (top left). The strong overlap of specific orbitals (top right), *viz.*,  $p_z$  orbital of the molecule with the out-of-plane  $d$  orbitals of the surface ( $d_{x^2-y^2}$ ,  $d_{xy}$ , and  $d_{z^2}$ ) creates  $\pi$ - $d$  hybridized interface states with spin-asymmetry in interface DOS (bottom). Certain molecular states that weakly interact with the surface, labeled as un-hybridized molecular states, may only softly broaden. Also notice, morphology of the molecule at the interface strongly influences the electronic property of the interface.

chemical bond (Fig. 2(b)). Due to a strong overlap of the atomic orbitals in energy and space across the interface, new hybridized interface states with bonding and anti-bonding molecular orbital combinations of the participating atomic orbitals are formed.<sup>32</sup> In such a scenario, the resulting properties (i.e., chemical, structural, electronic, and magnetic) of the interface can turn out to be very different, without any resemblance to the properties of either the clean surface or the molecule. Of particular interest is to understand the interface interaction between TM containing surfaces and aromatic organic molecules. TMs contain spin-polarized exchange-split  $d$ -bands and/or  $f$ -bands that are often responsible for inducing magnetism in the bulk material. At the interface, these orbitals interact with the extended molecular  $\pi$ -orbitals leading to formation of hybridized  $\pi$ - $d$  or  $\pi$ - $f$  interface states which gives it a unique spin and magnetic character. Figure 2(b) shows a simplified picture describing a strong overlap of specific orbitals between the adsorbed planar molecule and the TM surface. Orbital symmetry and overlap at the interface lead to a stronger interaction of the out-of-plane  $d$ - and  $p$ -orbitals creating spin-resolved hybridized  $\pi$ - $d$  interface electronic states. Understanding these interactions is a complicated study and its origin depends on a number of parameters such as, not limiting to, molecular structure and morphology,<sup>38</sup> chemical sensitivity of the molecule,<sup>39</sup> surface property, image-potential,<sup>36</sup> and van der Waals (vdW) interaction<sup>39</sup> at the interface. As a general rule, one may assume that due to steric hindrance, non-planar molecules would bind less strongly with the magnetic surface than planar molecules.<sup>40</sup> However, in the case of chemically active elements (for example, sulphur, nitrogen, oxygen, etc.) attached to either the surface or the molecule, the local chemistry might dominate the interface interaction irrespective of the structural form of the molecule.

The interface chemistry also plays a strong role in influencing magnetism, both in the magnetic surface and the

molecule. At the surface, the extent and the shape of the wave-functions of the atoms and the associated coordination chemistry differ from the bulk.<sup>41,42</sup> The crystal symmetry is broken which can produce un-quenched spin-orbit interactions. All the above effects can modify the magnetic moment of the surface atoms, the magnetic exchange interaction, and the magnetic anisotropy of the surface.<sup>43</sup> Not to mention, the adsorption of a molecule on the surface, which gives a very different chemical environment to the surface, may further weaken the surface symmetry and show surprising results with severely affecting the spin-resolved surface density of states (DOS).<sup>30</sup> Importantly, one can observe many exciting effects such as an enhancement or weakening of the surface magnetic anisotropy ( $K_{\text{sur}}$ ), an enhancement or weakening of the inter-planar magnetic exchange coupling between the surface and the bulk ( $J_{S\perp}$ ), an enhancement or weakening of the in-plane surface magnetic exchange coupling ( $J_{S\parallel}$ ) (Fig. 3), or even cause a non-magnetic TM surface to become weakly magnetic. Study in these directions has only begun<sup>8</sup> and many of such effects are actively being explored.

Furthermore, it is apparent that the magnetic surface can transfer magnetic interactions across the interface to an adsorbed molecule. This transfer involves inducing a moment, magnetic anisotropy ( $K_{\text{mol}}$ ), and magnetic exchange coupling to the molecule ( $J_{S\text{-Mol}}$ ) (Fig. 3). An induced magnetic anisotropy, by alone, may not be possible to stabilize the molecular magnetism to much higher temperatures, since the adsorption chemistry only marginally affects the molecular anisotropy.<sup>44</sup> This is due to the small single ion anisotropy energy of the TM spin centers in the case of metal-organic molecules and the small spin-orbit coupling strength in the case of aromatic organic molecules made up of low atomic number elements. On the other hand, controlling the induced magnetic exchange interactions across the interface due to the  $\pi$ - $d$  magnetism shows a

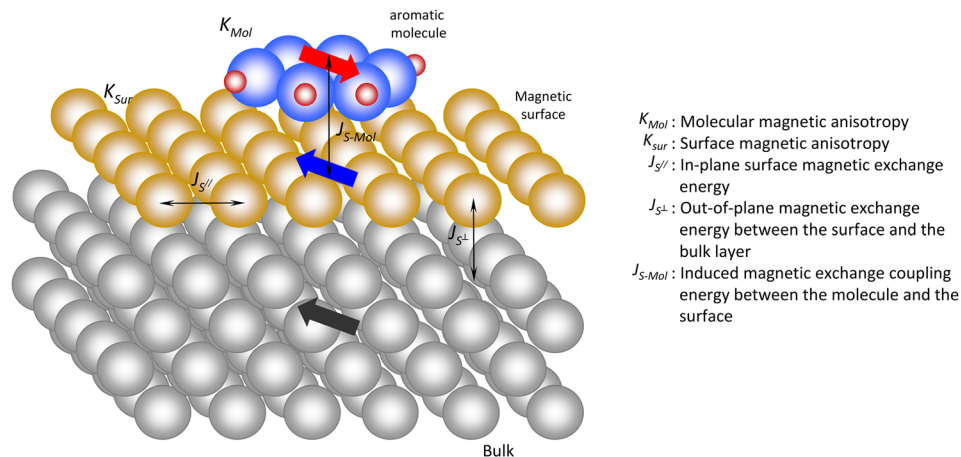


FIG. 3. Schematics of an aromatic molecule surface interface highlighting the important interface magnetic parameters modified by the interface spin-chemistry. The absorption process affects the induced molecular moment, its magnetic anisotropy ( $K_{Mol}$ ), and the induced interface magnetic exchange coupling ( $J_{S-Mol}$ ). Additionally, the above process can affect the atomic magnetic moment, surface magnetic anisotropy energy ( $K_{Sur}$ ), strength of intra-plane ( $J_{S//}$ ), and inter-plane magnetic exchange coupling ( $J_{S\perp}$ ) of the magnetic surface. The possibility to controllably tune these processes open up a new subfield of interface-assisted molecular spintronics.

potential path forward to stabilize molecular magnetism for room temperature demonstrations<sup>8,45</sup> (Fig. 3). Therefore, the interface magneto-electronic properties that originate from the chemistry of its constituent elements, *viz.*, the surface and the molecule, require fundamental exploration with help from advanced computational and experimental tools.

### III. UNDERSTANDING HYBRID INTERFACE STATES

#### A. *Ab initio* interface modeling

The use of computational *ab initio* materials' modeling using density functional theory (DFT) provides a new perspective to understand, predict, and suggest materials trend and properties. Not to mention, its use to simulate the complex molecule-substrate interactions<sup>32,34</sup> opens up a molecular-genome initiative in providing insights on our fundamental understanding of interface spin-chemistry and, secondly, to design molecules and engineer the interface spin responses for exploring new phenomena driving next-generation of functional molecular spintronic devices.

The calculation of absorption energy, a macroscopic quantity which refers to the energy needed to separate the adsorbed molecule from the surface in its minimum energy configuration, provides us with the measure to predict the bonding chemistry at the interface. This value depends on the interface factors such as the molecule morphology, orientation, molecular spacing above the surface, and surface crystal orientation; all of which strongly influence the signature of electronic interface states. Apart from the standard limitations of DFT<sup>46</sup> in determining the appropriate electron exchange-correlation functional,<sup>47,48</sup> such calculations do not take into account certain important physical effects in simulating a metal-organic interface. These include the image potential experienced by the molecule when close to a metallic surface<sup>36</sup> and the long range vdW force,<sup>39,49</sup> both of which modify the equilibrium molecular spacing above the surface. Semi-empirical approach in DFT has been extensively developed in literature to include the above effects. For example, the work of Atodiresi and co-authors<sup>32</sup> shows the importance of vdW forces in determining the right chemistry of the interface. In one such computational study,<sup>45</sup> involving an interaction between a fluorinated benzene

molecule and two monolayers (MLs) of iron (Fe) on tungsten (W(110)), they show that the molecule develops an induced moment ( $\sim 0.3\mu_B$ ), which is aligned anti-ferromagnetically to the bottom Fe surface. Such results were also supported by the first direct experimental evidence of molecular magnetism using adsorbed graphene fragment molecules.<sup>8,40</sup>

The above study is also expected to have a pronounced effect on the properties of the adsorbed planar metal -porphorin or -phthalocyanine molecules, a possibility that was not explored in the earlier analysis.<sup>20</sup> For example, we take the specific study of cobalt phthalocyanine (CoPc) molecule with a net spin moment ( $\sim 0.9\mu_B$ ) on the Co site, adsorbed on W(110)/2 ML Fe.<sup>29</sup> Here, the inclusion of vdW force causes a significant reduction in the average spacing between the molecular plane and the surface (by 0.5 Å), changing the interface chemistry from a physisorbed to a chemisorbed surface (Fig. 4). This is also noted by the considerable increase in the adsorption energy caused by the stronger interaction of the Fe surface with the aromatic phthalocyanine structures of the molecule forming  $\pi$ -*d* interface states. Figure 4(a) shows the simulated spin-resolved electronic projected DOS of the adsorbed molecule with and without the vdW's correction. The contribution of the  $\pi$ -*d* states to the total electronic interface states is evident in these studies. Furthermore, as a result of the strong  $\pi$ -*d* hybridization, the molecule is observed to become non-magnetic with the Co center in the molecule losing its spin moment.

#### B. SP-STTS

In the recent years, SP-STTS has provided a significant thrust in probing the spin-resolved electronic states of adsorbed surfaces with intra-molecular spatial resolution.<sup>29,30</sup> In this technique, a conducting magnetic tip is used to measure the spin-dependent tunneling current from the surface as a function of applied voltage bias giving information of the spin-dependent electronic DOS over a wide electron-energy spectrum.<sup>50</sup> The two spin-channels of the interface states that are formed due to the  $\pi$ -*d* hybridization extend in space away from the surface towards the magnetic tip with different decay rates. One can draw analogy with symmetry driven spin-filtering in epitaxial Fe/MgO/Fe tunnel structures,<sup>51</sup> where the spin-dependent evanescent states

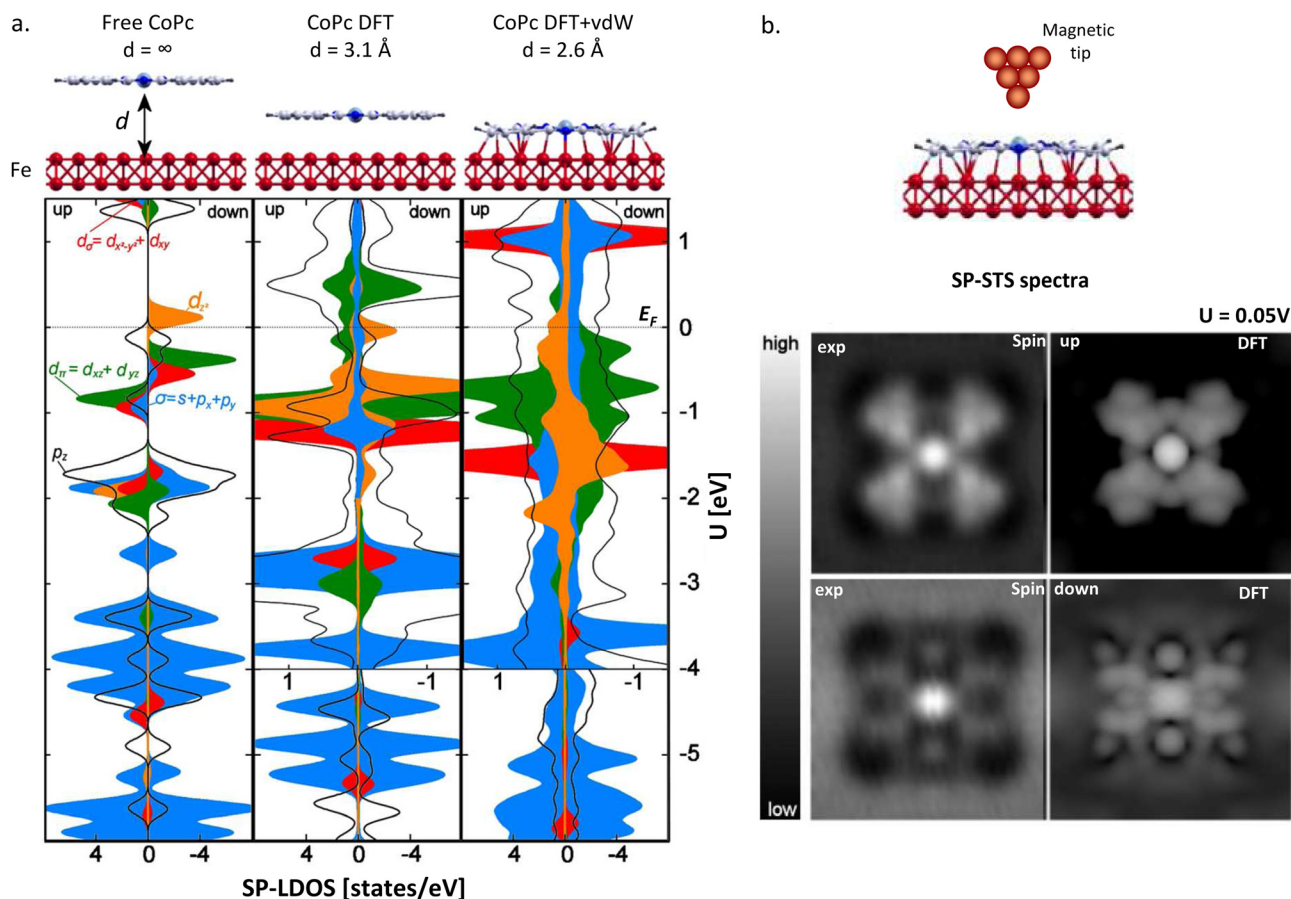


FIG. 4. Formation of hybridized interface states: (a) DFT calculations show spin-resolved local DOS of free CoPc molecule (left), and CoPc adsorbed on a Fe surface without (middle) and with (right) vdW forces. The reduction in the molecular spacing with vdW correction shows strong chemisorption with broadened hybridized interface states. (b) Experimental and simulated SP-STs images at applied bias of  $U = 0.05$  V for both spin directions show a very good match. The simulation was performed by including corrections to vdW force and spin-orbit coupling effects. Reprinted with permission from Brede *et al.* Phys. Rev. Lett. **105**, 047204 (2010). Copyright 2010 American Physical Society.

of different symmetries show different decay rates within the barrier. In the present case, the decay rates for the hybridized  $\pi$ - $d$  interface states of the two spin channels show a strong variation in energy leading to an energy-dependent interface spin-polarization,<sup>29</sup> which can be measured using an SP-STs setup. The interface spin-polarization ( $P$ ) represents the normalized difference in the DOS of the two electron spin channels at a given energy and can be expressed as (a detailed analysis of  $P$  may be found in Refs. 52 and 53)

$$P(E) \approx \frac{DOS_{\uparrow}(E) - DOS_{\downarrow}(E)}{DOS_{\uparrow}(E) + DOS_{\downarrow}(E)}.$$

The value of  $P$  plays an important role in the study of tunneling magnetoresistance effect (TMR),<sup>54</sup> defined as the change in tunnel-resistance of the device with applied magnetic field. The variations in  $P$  (or TMR) can also be quantitatively predicted using first principle calculations to simulate an SP-STs setup and are shown in Fig. 4(b) for the previously discussed case of CoPc adsorption on Fe surface by calculating the energy-distributed spectrum of the spin polarization. These spectrums of  $P$  were found to match very well with the spectrums measured using SP-STs by Wiesendanger's group<sup>29</sup> (Fig. 4(b)). These above findings confirm the formation of broadened hybridized  $\pi$ - $d$  states at the interface with

strong spin asymmetry. More importantly, they highlight the sensitivity involved in the computational work to accurately simulate the equilibrium configuration of the interface system. Similar SP-STs studies on other interface systems have revealed an amplification and/or inversion of interface spin-polarization,<sup>30</sup> which may explain the inconsistency in the previously reported TMR values of macroscopic organic tunneling devices.<sup>55</sup>

#### IV. INTERFACE MAGNETISM STUDY

Advanced spectroscopy techniques such as photoemission spectroscopy,<sup>24,56,57</sup> XMCD,<sup>20,27</sup> and others<sup>58</sup> serve as powerful tools to analyze the magnetic contrast of the molecule-surface interface. They can probe the spin-selective chemical and the electronic property of the surface and of the molecule to study the effect of interface coordination chemistry.<sup>26</sup> Such studies are instrumental in the investigation of surface magnetic anisotropy,<sup>58</sup> nature of the magnetic exchange coupling at the interface,<sup>20</sup> and chemical activity of the interface responsible for the magnetic hysteresis response.

In the study of metal-porphyrins and phthalocyanines, XMCD measurements were extensively used with a focus to understand the magnetic coupling between the TM center

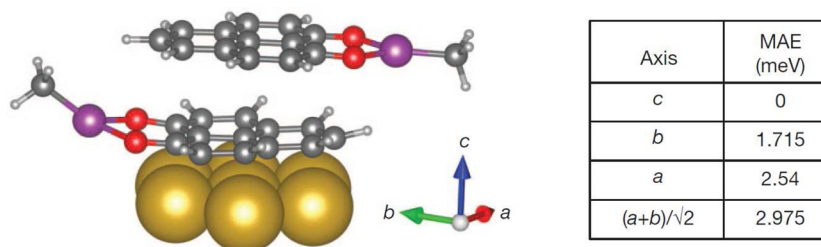


FIG. 5. DFT calculation of MAE due to surface magneto-crystalline anisotropy of model organometallic supramolecule interface system comprising of seven hybridized Co atoms (gold) with a dimer of zinc methyl phenalenyl molecule on top. The MAE of the supramolecule is calculated (table) for three different in-plane magnetization orientations with *c*-axis as a reference. The in-plane MAE is calculated to be  $180 \mu\text{eV}/\text{Co}$  atom, an enhancement by a factor of 10 compared to the value of MAE in bulk Co (*fcc*) ( $\sim 19 \mu\text{eV}/\text{Co}$  atom). Reprinted with permission from Raman *et al.*, Nature **493**, 509–513 (2013). Copyright 2013 Nature Publishing Group.

and the magnetic surface.<sup>27</sup> These studies suggested the coupling to be of significant strength, causing the molecular moment to follow the magnetization of the surface even at room temperature<sup>21</sup> (Fig. 1(b)). The mechanism for such a strong coupling was credited<sup>20</sup> to either or both of the following effects: (a) direct coupling between the TM spin center and the underneath magnetic atoms of the surface and (b) indirect super-exchange coupling between the TM center and the magnetic surface via oxygen or nitrogen atoms that are either within the molecule<sup>31</sup> or forming a monolayer above the magnetic surface.<sup>59,60</sup> However, in addition to the above, one important mechanism that has received inadequate attention is the interaction of delocalized electron cloud of the aromatic ligands in these molecules with the magnetic surface that may strongly stabilize and influence the magnetic exchange coupling strength between the TM spin center and the surface. In fact, the recent realization of inclusion of vdW forces (that reduces the molecule-surface distance), leading to strong  $\pi$ -*d* hybridization in chemisorbed aromatic molecules,<sup>29,31</sup> suggests the need to explore the above magnetic interactions from a new perspective (discussed below) to controllably tune molecular magnetism.

The recent adsorption studies using delocalized electron systems, such as zinc methyl phenalenyl (ZMP),<sup>8</sup> graphene,<sup>61</sup> or even chemically functionalized benzene,<sup>45</sup> offer a new lead in tuning molecular magnetism. The reports of an induced delocalized spin density and molecular moment with stability up to room temperature<sup>8</sup> strongly hint at probing the origin of  $J_{S-\text{Mol}}$  (see Fig. 3) by exploring alternate exchange mechanism paths that may contribute to the magnetic and thermal stability of the chemisorbed molecule. The possibility to enhance  $J_{S-\text{Mol}}$  is of important technological relevance in using such molecules for information storage. In addressing the origin of  $J_{S-\text{Mol}}$ , one can find phenomenological similarity with the earlier reports<sup>62,63</sup> of magnetic exchange coupling in linear magnetic molecules composed of atomic chains of carbon capped with TM atoms, i.e.,  $\text{TM-C}_n\text{-TM}$  (where *n* is number of carbon atoms linked between the two TM centers). In the above study, using DFT and atomic orbital theory under tight binding approach, it was shown that the carbon atoms develop a small induced magnetic moment which influences the strength and sign of the magnetic coupling between the two TM centers. Although a different level of complexity, in the case of a planar adsorption of the molecule on a TM surface, the formation of a

large set of non-collinear  $\text{TM}_i\text{-C}_n\text{-TM}_j$  ( $[i \neq j]$ , where *n* can vary for each pair of  $\{i, j\}$  TM atoms below the molecule) mediated magnetic exchange interactions may determine the stable magnetic coupling state of the hybrid interface. Further, a change in molecular configuration on the surface may lead to a change in sign and magnitude of  $J_{S-\text{Mol}}$ . Such processes are rich in physics and require further theoretical and experimental exploration to qualitatively predict and engineer the strength and sign of  $J_{S-\text{Mol}}$  for the controlled manipulation of molecular spin responses.

Spin-dependent spectroscopic investigations using such aromatic structures on magnetic surface have only recently begun.<sup>58</sup> However, most of these investigation tools require a large probing area leading to a macroscopically averaged response of the interface.<sup>55</sup> Therefore, they lack the sensitivity to investigate the interface magnetism at the single molecular level. In this regard, SP-STs provides intramolecular spatial sensitivity, making it a supreme tool to investigate spin interface science.<sup>50</sup> Additionally, non-collinear magnetic studies using spin-polarized DFT, with corrections due to spin-orbit coupling effect, corroborate well with the experimental evidences and provide new fundamental insights. They are extremely useful in predicting the changes in the atomic moment, the magnetic anisotropy energy (MAE), and the magnetic exchange coupling. For example, recent experimental reports of a higher switching field of a surface layer of Co caused by the adsorption of a graphene fragment molecule, with signs of magnetic decoupling from the Co bulk, were understood to arise due to weakening of  $J_{S\perp}$  by 83% and enhancement in  $K_{\text{sur}}$  by a factor of 10 compared to the values in the bulk<sup>8</sup> (see Fig. 5). Here, a Heisenberg spin model was used to determine the values of *J*. Recently, similar results of magnetic hardening of the Co surface were experimentally observed in Co/F4-TCNQ<sup>58</sup> and Ir(111)/1 ML Co/graphene<sup>61</sup> interface systems. In addition, studies on other interface systems highlight interesting trends.<sup>64</sup> In lieu of these recent advances, scientific interest in understanding the origin of magnetic hardening/softening at the magnetic surface, caused by changes in  $J_{S\parallel}$ ,  $J_{S\perp}$ , and  $K_{\text{sur}}$ , is gaining considerable attention. Such studies are very useful in tuning the magnetic switching response of a device.

## V. RECENT ADVANCES AND FUTURE PROSPECTS

The last few years have witnessed significant advances in our understanding of the spin-chemistry and spin-physics

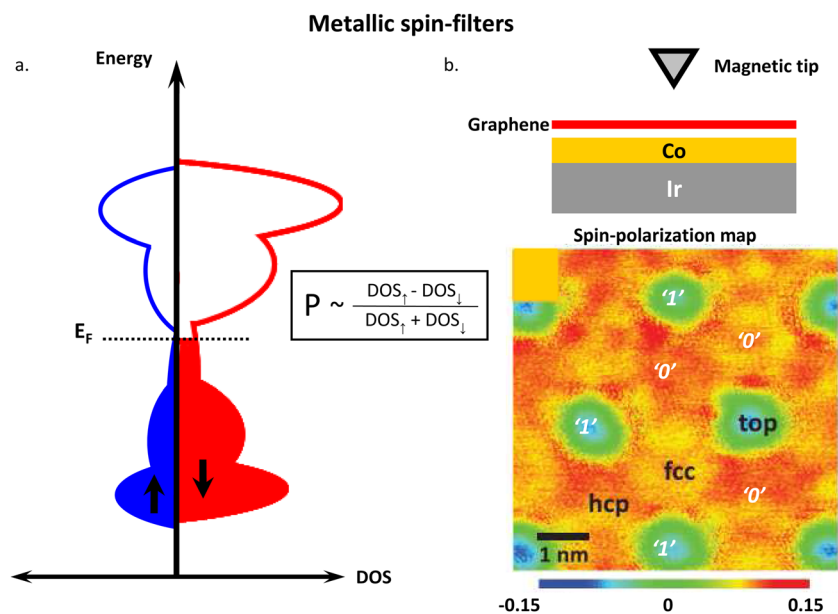


FIG. 6. Metallic spin-filters: (a) Schematics show the spin-resolved local DOS of the broadened interface molecular states for the two spin channels with states at Fermi level ( $E_F$ ). The spin asymmetry in the DOS at  $E_F$  leads to spin polarization of the interface. (b) Interface spin-polarization is measured using SP-STs for the case of graphene sheet adsorbed on Ir(111)/1 ML Co surface showing regions of positive (“0” state) and negative (“1” state) polarization at different fragments on the graphene sheet with its induced moment aligned parallel and anti-parallel to the bottom Co layer, respectively. The work suggests a method to store memory-bits on an adsorbed sheet of graphene. Reprinted with permission from Decker *et al.*, Phys. Rev. B **87**, 041403(R) (2013). Copyright 2013 American Physical Society. Note, the figure is modified and reanalyzed to show a prototype of a molecular storage device.

of the interface. New phenomena have been observed and theoretically developed which allows exploring novel methods to control, tune, and engineer these interactions for potential applications. In this section, we focus our attention towards identifying new molecular functionalities, which can serve as building blocks for the construction of molecular spintronic devices.

### A. Molecular storage medium

The process of inducing magnetism in otherwise non-magnetic organic molecules on surfaces is showing interesting physics.<sup>8,61</sup> The delocalized spin density within the molecule causes the constituent atoms (which are mostly carbon, oxygen, and nitrogen) to develop a small atomic moment. As a result, these molecular nano-magnets exhibit weak magnetization density (or magnetic dipolar fields). Even though the molecule is weakly magnetic, experimental reports have suggested a large value of  $J_{S-Mol}$ , which aids in stabilizing the molecular magnetism up to higher temperatures<sup>8</sup> (see Sec. IV). Such characteristics are very promising for application in magnetic data storage with high storage densities (>500 Terabit per square inch, also see Fig. 6) beyond the single particle super-paramagnetic limit of  $\sim 50$  Terabit per square inch.<sup>65</sup>

### B. Molecular sensor for read and write operation

Accessing and writing information in the molecular magnetic bit are also an important task in realizing molecular data storage. For reading information, the use of interface modified molecular spin-filters is potentially exciting. They may be broadly classified into two kinds: metallic spin-filters

and resistive spin-filters; each associated with a fundamentally different role.

In metallic spin filters, the spin-polarized hybridized interface states are broadened in energy with significant states at  $E_F$ <sup>29,30</sup> (Fig. 6(a)). This makes the molecule magnetic and metallic with a finite DOS of either one or both the spin channels at  $E_F$ . The DOS mismatch for the two spin channels at  $E_F$  leads to interface spin-polarization. By using a magnetic tip, the spin filtering response can be measured presenting a direct way to read the spin state of the molecule. Recent study on Ir(111)/1 ML Co/graphene interface system<sup>61</sup> reveals that the chemisorbed graphene becomes weakly magnetic with local variations in the spin-density over the graphene sheet (Fig. 6(b)). Such observations present an archetype for storing and reading binary information of “0” and “1” states at the different fragments of graphene sheet, defined by changes in the sign of  $J_{S-Mol}$  (ferromagnetic or anti-ferromagnetic (AFM) coupling).

Alternatively, in the case of resistive spin-filters, the unavailability of states at the Fermi level creates a barrier height for charge injection into or tunneling through the spin-filter molecule.<sup>8,40,66</sup> However, the spin-dependent hybridization gives rise to a spin-splitting of the interface states above and/or below the Fermi level (Fig. 7(a)). Since the injection current depends exponentially on the barrier height, a spin-dependent barrier height<sup>67</sup> causes only one spin channel to efficiently filter through the molecule giving a large spin polarization of the current. The formation of such molecules on magnetic surfaces has been demonstrated using SP-STs.<sup>68,69</sup> Resistive spin-filters can give rise to magnetoresistance signals using only one magnetic electrode, coined as interface magnetoresistance (IMR) effect,<sup>8</sup> which suggests the possible use of a non-magnetic conducting tip



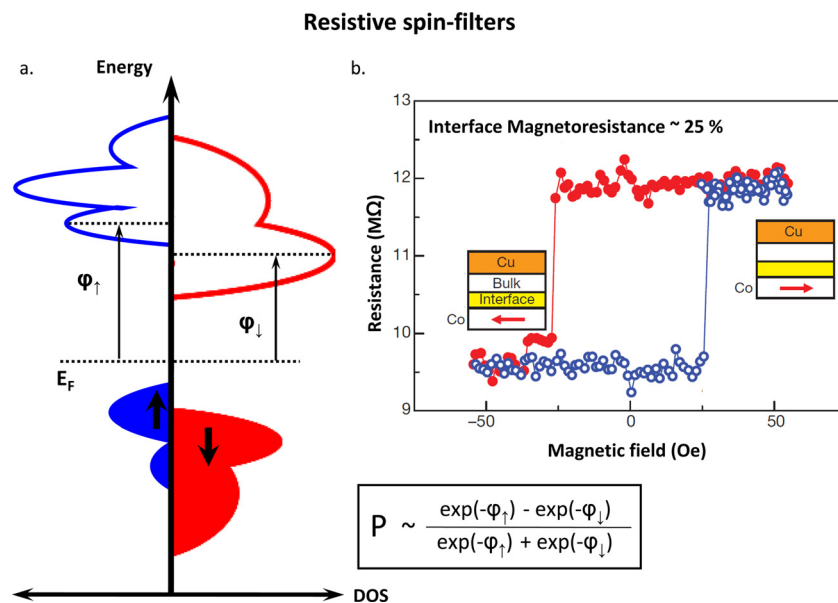


FIG. 7. Resistive spin-filters: (a) Schematics show the spin-resolved local DOS of a less broadened molecular interface states formed due to a weaker interface interaction. Here, no electronic states are available for conduction in the adsorbed molecule at Fermi level ( $E_F$ ). The spin-splitting in the DOS causes the spin-dependent injection/tunneling current to depend exponentially on the barrier heights ( $\varphi$ ) of the two spin-channels, resulting in a fundamentally larger value of spin-polarization. (b) Experimental plot shows an IMR effect in the device-Co (8 nm)/zinc-methyl-phenalenyl (40 nm)/Cu (12 nm) arising due to an independent switching of the bottom Co electrode with respect to a magnetically hardened resistive spin-filter supramolecular layer at the interface as described in Figure 5. Reprinted with permission from Raman *et al.*, Nature **493**, 509–513 (2013). Copyright 2013 Nature Publishing Group.

for the detection of magnetic state of the molecule (Fig. 7(b)).<sup>65</sup> Such mechanisms that can greatly simplify fabrication challenges in designing molecular spintronic devices are yet to be explored at the molecular level.

The possibility to reversibly control and switch the molecular spin state shows a path forward in writing molecular information. In this regard, different methods to modulate the spin-chemistry of the adsorbed molecules are actively experimented. Some of these methods include a controlled adsorption and thermal desorption of axial ligands in switching the spin state of the TM center in adsorbed metal-porphyrins or-phthalocyanines,<sup>28,59,60</sup> strain induced switching in molecular magnets,<sup>70</sup> electrically induced switching in spin-crossover molecules,<sup>9</sup> photo-switching,<sup>71</sup> or electromagnetic switching<sup>8</sup> of molecular magnetism in adsorbed aromatic molecules. In the case of latter, such excitations modify molecular configuration on the surface<sup>71</sup> that weaken or switch sign of  $J_{S-Mol}$ . Such studies are promising and open up new channels to develop an all-electrical or electro-optical stimulus to individually modulate the magnetic state of organic molecules. For example, resistive spin-filters show interesting prospects in developing an integrated all-electrical design of a molecular memory device.<sup>65</sup> Reports of an exchange biased IMR in junction devices using a phenalenyl derivative molecule have suggested the possibility to independent switch the molecular magnetization<sup>8</sup> with respect to the bottom magnetic surface (Fig. 8(a)), a trait that so far has not been observed in the study of SMMs or other metal-organic molecules adsorbed on magnetic surfaces. Figure 8(b) shows the design of a memory bit that consists of a supramolecular bi-layer with a bottom magnetic molecule and a top access molecule serving as a resistive spin-filter.<sup>65</sup> The purpose of access molecule is to provide a conduit for reading and switching the spin

information in the magnetic molecule by utilizing the spin-filtering action of IMR effect (Fig. 7(b)).

### C. Molecules in quantum computing

Interface assisted molecular nanomagnets also find significant potential in quantum computing applications. Previous studies using spin-cluster molecular magnets,<sup>72</sup> which consist of few TM spin centers linked together by super-exchange bridges in organic ligand frameworks, have demonstrated multi-level qubit systems with sufficiently long electron spin decoherence time.<sup>73</sup> Also, the nuclear spins in these TM centers have proven to be promising for qubit encoding.<sup>74</sup> However, due to the weak spin stability limited to low-temperature range and the structural complexity of these molecules, controlling inter-molecular spin coupling for realizing quantum entanglement of the qubits is a challenging activity. But, with the recent advances in spinterface science, the study offers new avenues in quantum computing to develop dense quantum memories by incorporating multiple coupled molecular nanomagnets that can be chemically engineered to self assemble on surfaces<sup>75,76</sup> for controlled entanglement over precise molecular-length scales; a basic requirement for quantum phase coherence. This research work involves developing novel molecular design schemes to engineer the interactions with magnetic surfaces to build molecular qubits and, second, to propose device schemes for the construction of quantum devices. One such example is the use of double-decker supramolecule consisting of a TM center, serving as the qubit, between two planar aromatic ligand structures (Fig. 9).<sup>17,68,77</sup> When adsorbed on the magnetic surface, the bottom aromatic structure develops an induced magnetism which magnetically stabilizes the

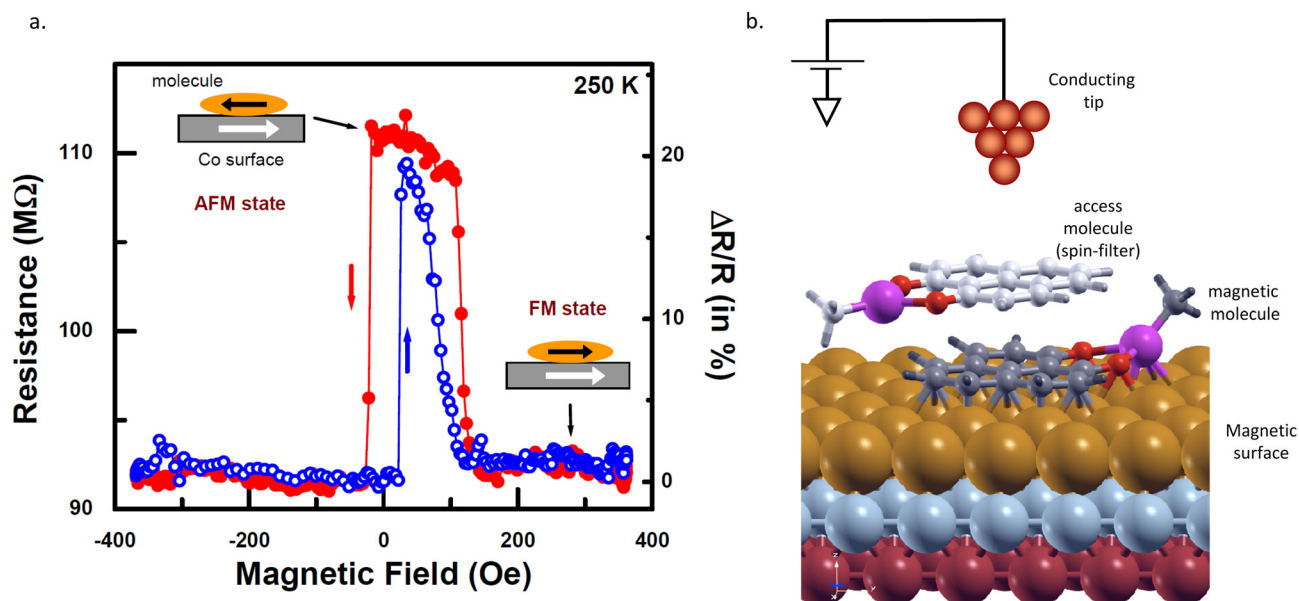


FIG. 8. (a) Asymmetric IMR response from the bottom Co/ZMP interface in the device-Co (8 nm)/ZMP (35 nm)/Py (12 nm) showing an exchange-biased effect which confirms the switching of the interface magnetic coupling ( $J_{S-Mol}$ ) between FM and AFM state (see inset) [data adapted from Ref. 8]. (b) Molecular memory design: Supra-molecule composed of two weakly interacting planar aromatic molecules on a magnetic surface forming a molecular storage device. The bottom molecule develops an induced magnetic moment, serving as a storage bit, while the top access molecule serves as a resistive spin-filter molecule. Using a non-magnetic conducting probing tip, the spin-filter molecule generates spin-polarized current to read or switch the information in the storage element. Reprinted with permission from Raman *et al.*, Nature **493**, 509–513 (2013). Copyright 2013 Nature Publishing Group.

qubit through the ligand-mediated exchange interaction, while the top aromatic structure serves as the access spin-filter molecule.<sup>68</sup> Using a conducting tip under resonant electrical biasing conditions, the access molecule can indirectly couple and gain access to the qubit states, subsequently read or modify the qubit, and finally, be brought out-of-resonance to isolate the qubit from its environment for information processing. Recent experimental study on these molecules presents interesting trends.<sup>78</sup> Further, the possibility to use linker ligands<sup>73</sup> to controllably turn on or off the intermolecular coupling allows selective entanglement of the qubits. Apart from the above, the possibility to controllably

intercalate TM atoms<sup>61</sup> between sheets of graphene in multi-layer structure offers new ways to build scalable quantum computing devices. These above and similarly other novel molecular designs<sup>79</sup> and device schemes<sup>80</sup> show a promising future in developing interface-assisted molecular spintronics.<sup>81</sup> However, the study does face significant challenges due to the sensitivity involved in molecular templating on surfaces and in achieving molecular device integration. Channeling our research efforts in the above with a strong inter-disciplinary support would offer exciting opportunities for scientists to develop this field for potential technological advancement.

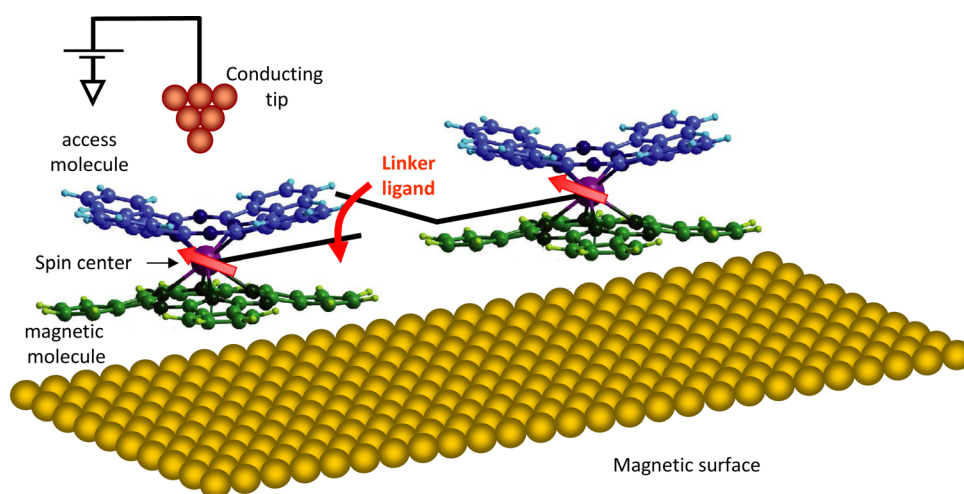


FIG. 9. Molecular design for quantum computing: Double-decker supramolecular design composed of a TM center between two planar aromatic structures adsorbed on a magnetic surface. Similar to the molecular design in Fig. 8(b), the bottom molecule forms a magnetic layer, while the top structure serves as the access spin-filter molecule. The electron spin and/or the nuclear spin state of the TM center constitute the qubit. Using a conducting probing tip, the access molecule allows to access, modify, and isolate the qubit from the environment for performing computing operations. Introducing linker ligands can allow selective and controlled entanglement of the qubits. Various modifications to the above molecular design may be envisioned.

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