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Design of the Local Spin Polarization at the Organic-Ferromagnetic Interface

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By means of *ab initio* calculations and spin-polarized scanning tunneling microscopy experiments the creation of a complex energy dependent magnetic structure with a tailored spin-polarized interface is demonstrated. We show this novel effect by adsorbing organic molecules containing $\pi(p_z)$ electrons onto a magnetic surface. The hybridization of the out-of-plane p_z atomic-type orbitals with the d states of the metal leads to the *inversion* of the spin polarization at the organic site due to a p_z - d Zener exchange-type mechanism. As a key result, we demonstrate the possibility to selectively and efficiently inject spin-up and spin-down electrons from a ferromagnetic-organic interface, an effect which can be exploited in future spintronic devices.

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Combining molecular electronics with spintronics represents one of the most exciting avenues in building future nanoelectronic devices [1–3]. For example, widely used in spintronic applications, the spin valve [4] is a layered structure of two ferromagnetic electrodes separated by a nonmagnetic spacer to decouple the two electrodes and allows spin-polarized electrons to travel through it. The efficiency of a spin valve depends on the spin transport throughout and the spin injection into the nonmagnetic spacer. Organic molecules are made of light elements (as C and H) with weak spin-orbit coupling. Therefore, spin transport properties (spin coherence with time and distance) are improved compared to conventional semiconductors present in today's devices [5–7]. A crucial issue that remains is the spin injection efficiency at the ferromagnetic-organic interface [8–10]. Understanding the relevance of interface hybrid states for the transmission of spin information to tailor the electronic and magnetic structure of such interfaces will help to overcome the significant spin loss observed in spintronic devices [11]. In this Letter, we will present a conceptual study to understand the local spin polarization present at the interface for single organic, even diamagnetic molecules adsorbed on a ferromagnetic surface. The experimental observation of the local spin polarization above an industrially relevant diamagnetic macromolecule supports our interpretation.

In a first step, we performed *ab initio* calculations of prototype conjugated organic molecules adsorbed on a ferromagnetic 2 ML Fe/W(110) surface, a well-established system in spin-polarized scanning tunneling microscopy (SP-STM) experiments [12]. We selected organic molecules containing $\pi(p_z)$ -electron systems like benzene (Bz), cyclopentadienyl radical (Cp), and cyclooctatetraene (Cot) because they are representative of classes of organic molecules with significantly different reactivities [13]. More precisely, the choice of the calcu-

lated molecule-ferromagnetic surface systems can be understood by the following: (i) although having a low reactivity, Bz (C_6H_6) is an aromatic 6π -electron system [13] that can form sandwich-type compounds with d metals [14] and chemisorbs on reactive surfaces [15,16]. (ii) a highly reactive 5π -electron system, Cp (C_5H_5) strongly interacts with d metals and forms an aromatic 6π -electron system in sandwich type molecules like ferrocene [13] and strongly interacts with metallic surfaces [17]. (iii) an 8π -electron system, Cot (C_8H_8) binds strongly the metal atoms by forming an aromatic 10π -electron system [13] and is well known to react even with f electrons of rare earth metals [18,19] forming sandwich type molecules and long nanowires [20].

Our spin-polarized first-principles calculations are carried out in the framework of density functional theory (DFT) by employing the generalized gradient approximation (PBE) [21] in a projector augmented plane-wave formulation [22] as implemented in the VASP code [23,24]. The molecule-Fe/W(110) system is modeled within the supercell approach [$p(5 \times 3)$ in-plane surface unit cell] and contains five atomic layers (3 W and 2 Fe) with the adsorbed molecule on one side of the slab [25]. Using a plane-wave energy cutoff of 500 eV in our *ab initio* calculations, the uppermost two Fe layers and the molecule atoms are allowed to relax until the atomic forces are lower than 0.001 eV/Å. The Bz molecule adsorbs with two C atoms on top of two neighboring Fe atoms along the [001] direction while the other four C atoms sit in bridge positions between Fe atoms of adjacent [001] rows. The Cp molecule adsorbs in a similar geometry. With one C atom less than the Bz, Cp binds to the surface with a C atom and a C-C bond on top two neighboring Fe atoms of the [001] row. The Cot molecule binds to the surface with two C atoms and a C-C bond on top of Fe atoms, while the other C atoms sit in bridge sites between Fe atoms of

adjacent [001] rows. As a general characteristic of the adsorption geometry, we note that all adsorbed molecules have a nonplanar structure in which the H atoms are situated above C atoms (0.35 up to 0.45 Å). The shortest C-Fe bond is about 2.1 Å and corresponds to the C atoms sitting directly on top of Fe while the C atoms situated in bridge positions are 2.3 up to 2.5 Å away from Fe atoms. Furthermore, each of the molecules is nonmagnetic [26] upon adsorption on the ferromagnetic surface.

A general picture of the binding mechanism between Bz, Cp, and Cot molecules and the ferromagnetic surface can be extracted from the analysis of the spin-resolved local density-of-states (LDOS) of the calculated molecule-surface systems shown in Fig. 1. In the spin-up channel, the p_z atomic type orbitals which originally form the π -molecular orbitals hybridize with the majority d states of the Fe atoms forming molecule-metal hybrid states with bonding and antibonding character. The bonding states are situated at low energies while the antibonding states appear at much higher energies, more precisely in an energy window situated around the Fermi level. Because of the p_z - d interaction in the spin-up channel, the spin-down p_z atomic type orbitals are lowered in energy and slightly hybridize with the minority d states of Fe. As a consequence, the states with large weight around the Fermi level are in the spin-up channel at the molecule site and in the spin-down channel at clean metal sites. To be more specific, in Fig. 1(a) we plot the LDOS of a clean surface Fe atom (upper panel) and an Fe below a C atom (lower panel). As compared to the clean surface Fe atom, for the Fe below C, the shape of the out-of-plane spin-up d states (d_{z^2} , d_{xz} , d_{yz}) is strongly changed due to the hybridization with the out-of-plane spin-up p_z atomic orbitals of the C. However, the spin-down d states of iron and p_z orbitals of carbon as well as the in-plane states in both spin channels $d_{x^2+y^2}$, d_{xy} of the metal and s , p_x , p_y of the molecule are less affected by the molecule-surface interaction. Characteristic for the strongly interacting molecules as Cp and Cot [Fig. 1(b)] are the spin-up p_z - d bonding states in the $[-5.0, -3.0]$ eV energy interval and the spin-up antibonding states around the Fermi level in the $[-1.0, +1.0]$ eV energy interval. In the spin-down channel the states having large weight at the molecular site are situated at low energies, i.e., $[-3.0, -2.0]$ eV energy interval for the Cot molecule and around $[-3.5, -1.5]$ eV energy interval for the Cp molecule. Since the Bz-surface interaction is weaker as compared to Cp and Cot molecules [see adsorption energies (E_{ads}) given in Fig. 1(c)], the spin-up antibonding molecule-surface hybrid states have smaller weight around the Fermi level while the spin-down states at the molecule site are not shifted as low in energy (i.e., $[-2.0, -0.8]$ eV energy interval).

The mechanism explaining the hybridization occurring at the molecule-metal interface resembles the well known p_z - d Zener exchange mechanism [27] present in diluted magnetic semiconductors. A magnetic impurity in a semi-

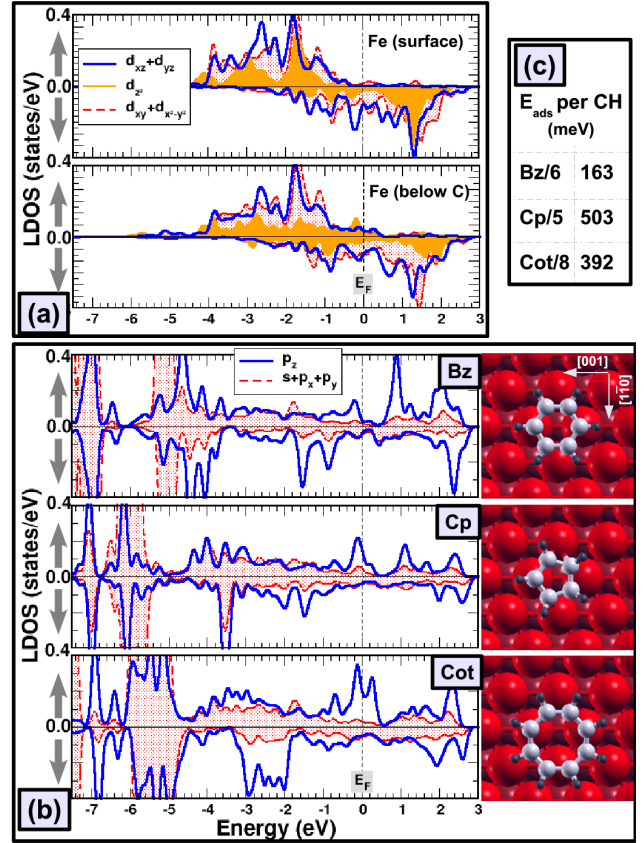


FIG. 1 (color online). (a) Spin-resolved local density of states of an Fe atom of the clean surface (upper panel) and an Fe atom below the C atom of the Cot molecule (lower panel); (b) adsorption geometries and the spin-resolved local density of states of the Bz, Cp and Cot molecules adsorbed on the 2ML Fe/W(110); (c) the adsorption energies of the Bz (C_6H_6), Cp (C_5H_5) and Cot (C_8H_8) are given in meV per CH group of atoms. Compared to Bz, Cp and Cot molecules interact strongly with the surface due to an effective hybridization between out-of-plane orbitals (p_z of C and d_{z^2} , d_{xz} , d_{yz} of Fe), while the in-plane orbitals are weakly interacting (s , p_x , p_y of C and/or $d_{x^2+y^2}$, d_{xy} of Fe). All adsorbed molecules show a general characteristic: the energy dependent spin polarization, i.e., in a given energy interval the number of spin-up and spin-down electrons is unbalanced. For this specific interval the molecule has a net magnetic moment delocalized over the molecular plane, although the total magnetic moment of the molecule is $0.0 \mu_B$. Note also the increased weight of the states crossing the Fermi level situated in the spin-down channel at metal site and in the spin-up channel at molecular site. Therefore, at the molecular site, an inversion of the spin polarization occurs with respect to the ferromagnetic surface.

conductor host remains magnetic [28] where, due to the p - d mixing, the p band of the semiconductor is broadened and part of it is pushed above the Fermi level. In our specific case, the nonmagnetic molecule represents the impurity while the magnetism is carried by the ferromagnetic surface [29].

The spin-polarized LDOS of the adsorbed Bz, Cp, and Cot molecules show a very intriguing feature: the energy

dependent spin polarization. As clearly visible in Fig. 1(b) for a given energy interval the number of spin-up and spin-down states is unbalanced. For that specific interval the molecule has a net magnetic moment delocalized over the molecular plane since it is carried mostly by the p_z states. Even more interesting, as depicted in the LDOS, around the Fermi level the states with large weight are in the spin-up channel at the molecular site, while on the clean Fe surface these states are in the spin-down channel. As a consequence, at the molecular site an inversion of the spin polarization [30] occurs with respect to the ferromagnetic surface.

This effect is clearly seen in Fig. 2 which illustrates the spin polarization at 2.5 Å above the molecule in the energy intervals below $[-0.4, 0.0]$ eV and above $[0.0, +0.4]$ eV the Fermi level. A common characteristic for all the molecule-ferromagnetic surface systems is the high and locally varying spin polarization ranging from attenuation to inversion with respect to the ferromagnetic surface. Since the carbon's p_z atomic orbitals of the Cp and Cot molecules are strongly interacting with the d states of the iron atoms, as compared to Bz molecule, an amplification of the molecule's local spin polarization below Fermi level occurs. Besides this, the presence of a large number of p_z electrons in the Cot molecule causes an amplification also above the Fermi level because a larger number of anti-bonding p_z - d hybrid states are generated.

So far, our first-principles calculations suggest that the spin injection efficiency ranging from inversion to amplification can be tailored by an appropriate selection of organic molecules adsorbed. Even when the molecule is

nonmagnetic [26], the spin-unbalanced electronic structure implies the presence of a voltage-driven and voltage-dependent spin current generated at the interface accessible by any kind of experimental approach with energy selectivity.

In a recent study [31], we addressed the spin current through a paramagnetic molecular system. Thereby, our observations in that study suggested the importance of interface hybrid states rather than the molecular spin on the spin polarization. To demonstrate here the universal applicability of the theory driven concept, we apply in a second step SP-STM [32,33] to directly observe with site-sensitivity the spin polarization above a fully diamagnetic, metal free phthalocyanine molecule (H_2Pc), adsorbed on out-of-plane magnetized 2 ML Fe/W(110). In a simplified view H_2Pc consists of four benzene rings and two hydrogens attached to a $(C-N)_9$ cycle forming a conjugated 40π -electron system. Compared to previously discussed fundamental units of organic chemistry (e.g., Bz, Cp, and Cot), H_2Pc can be experimentally easily adsorbed as a single molecule and is accessible with submolecular precision without the occurrence of lateral displacements during experiments.

Surfaces are prepared and experiments performed in an ultrahigh vacuum environment with minimized rate of contaminations. H_2Pc which is very reactive toward metals [34], is dosed at ≈ 100 K onto the surfaces to prevent an element exchange at the central position. Then, the sample is directly cooled to the operation temperature of the STM at 6 K. The molecule-substrate system is structurally well defined and molecules which are identically oriented are easily identified in STM images even among different domains of the Fe layer. To map the local spin polarization, oppositely magnetized Fe domains with H_2Pc adsorbed onto it are probed by a magnetic, Cr-coated tip in constant-current mode. This is demonstrated in the overview image of Fig. 3. The appearance of H_2Pc on the different domains varies significantly as demonstrated in Figures 3(a) and 3(b), which presents color encoded height maps at an applied bias voltage of 0.05 V. Therefore, a positive bias voltage reflects probing of unoccupied interface states and, in the given case, only interface states in the energy interval $[0.0, 0.05]$ eV contribute to the observed spin-dependent contrast. From the spin-dependent height maps, we can directly deduce the spin polarization above the investigated H_2Pc molecules in respect to the spin polarization above the ferromagnetic Fe layer in the same energy interval. Following the established routine to extract the local spin polarization as introduced in Ref. [35], the experimentally determined local spin polarization is depicted in Fig. 3(c). Whereas at the sites of the hydrogens an insignificant spin polarization remains, an inversion of the spin polarization can be observed above all four benzene rings. With the tip-molecule distance certainly larger than 2.5 Å as calculated, we can deduce the presence of a significant and device-relevant spin polarization even far above the interface localized at the benzene

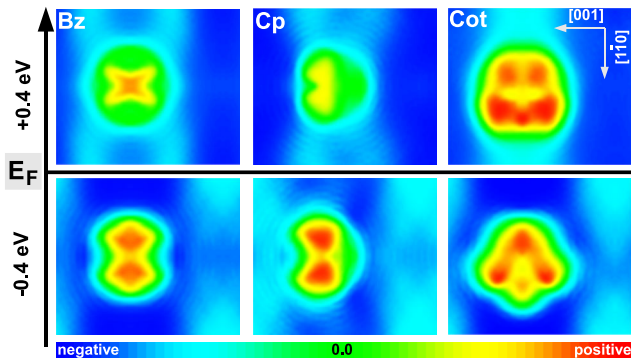


FIG. 2 (color online). The spin polarization at 2.5 Å above the Bz, Cp and Cot molecules adsorbed on the 2ML Fe/W(110) ($15.85 \text{ \AA} \times 13.45 \text{ \AA}$) surface plotted for occupied ($[-0.4, 0.0]$ eV) and unoccupied ($[0.0, +0.4]$ eV) energy intervals around the Fermi level. All the organic molecules show a high, locally varying spin polarization ranging from attenuation to inversion with respect to the ferromagnetic Fe film. As compared to Bz, the strongly interacting Cp molecule shows an amplification of the inversion of the spin polarization below Fermi level, while the Cot molecule shows a strong amplification of the inversion of the spin polarization for both occupied and unoccupied states around the Fermi level due to a higher number of p_z interacting electrons.

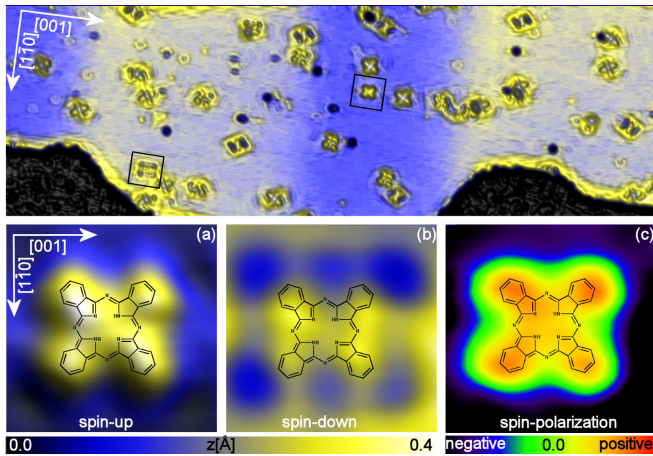


FIG. 3 (color online). Overview SP-STM image of a multi-domain (blue/yellow) 2 ML Fe stripe on W(110) with intact and few metalized H_2Pc present in three distinct orientations. Experimental ($22 \text{ \AA} \times 22 \text{ \AA}$) SP-STM images for H_2Pc adsorbed on 2 ML Fe/W(110) at $U = +0.05 \text{ V}$ for both spin channels [i.e., up (\uparrow) and down (\downarrow)] and local spin polarization. H_2Pc molecules show a high, locally varying spin polarization ranging from attenuation to inversion with respect to the ferromagnetic Fe film.

rings. The same behavior is observed for H_2Pc in all orientations.

To summarize, the spin polarization of a ferromagnetic surface can be locally tailored by flat adsorbing organic molecules containing $\pi(p_z)$ electrons onto it. The complex energy dependent magnetic structure created at the organic molecule-surface interface resembles the p_z - d exchange type mechanism. Although adsorbed molecules are non-magnetic, due to an energy dependent spin polarization, in a given energy interval the molecules have a net magnetic moment delocalized over the molecular plane. Highly electronegative molecules as Cp and Cot strongly interact with the ferromagnetic surface which yields to an amplification of the inversion of the spin polarization as compared to less reactive molecules as Bz. Moreover, the generality of the concept predicted by the theoretical calculations on model systems is supported by our SP-STM experiments on H_2Pcs adsorbed on the 2ML Fe/W(110) surface which clearly show the inversion of the local spin polarization near the Fermi level even at larger distances. Our combined first-principles and experimental study demonstrates that electrons of different spin [i.e., up (\uparrow) and down (\downarrow)] can selectively be injected from the same ferromagnetic surface by locally controlling the inversion of the spin polarization close to the Fermi level, an effect which can be exploited to increase the efficiency of future molecular spintronic devices.

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