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Engineering the magnetic properties of hybrid organic-ferromagnetic interfaces by molecular chemical functionalization

Nicolae Atodiresei,1,2 Vasile Caciuc,1 Predrag Lazić,2 and Stefan Blügel1
1Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany
2Massachusetts Institute of Technology, Cambridge, 02139 Massachusetts, USA.

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We have performed systematic first-principles calculations to tailor the magnetic properties at a hybrid organic-ferromagnetic interface by adsorbing organic molecules containing \( \pi(p_z) \) electrons onto a magnetic substrate. For such hybrid systems, magnetic properties such as molecular magnetic moments and their spatial orientation can be specifically tuned by substituting the H atoms with more electron withdrawing groups such as Cl and F. This chemical functionalization process surprisingly reveals the importance of the spin-orbit coupling present at the magnetic molecule–molecule interface. As a key result, our simulations indicate a direct connection between substituent electronegativity and these magnetic properties which can be exploited to design more efficient organic spintronic devices.

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Progress in developing cutting-edge molecular electronic devices1–3 which make use of both the electron’s spin degree of freedom and organic molecules relies on a clear theoretical understanding of the complex phenomena present at the electrode–molecule interfaces. In particular, of significant technological interest are the new functionalities of organic molecules when adsorbed on a magnetic substrate. Nowadays, a large effort is dedicated not only to understanding the molecule–magnetic surface interfaces but also to engineering and precisely controlling their spin-sensitive tunneling channels built between the molecules and the magnetic substrate.4–8

In recent combined ab initio and experimental studies, we demonstrated the universal applicability of a theory-driven concept9 that indicates the importance of interface hybrid organic-metallic states rather than the intrinsic molecular spin10 on defining the spin polarization present at hybrid organic-magnetic interfaces. Besides creating a well-defined hybrid organic-ferromagnetic interface that acts as an effective source of spin-polarized electrons, several essential issues in spintronics remain to be resolved: (1) how to induce a magnetic moment in an organic layer, (2) how to control the size of the induced magnetic moments, and (3) how to control their orientation at the molecular sites. Therefore in this Brief Report we will generalize our conceptual study10 to hybrid magnetic organic-ferromagnetic interfaces to tune their magnetic properties by using specific molecular chemical substituents. The aim of this chemical functionalization is to (1) precisely manipulate the local spin polarization present at a magnetic molecule-ferromagnetic substrate interface and more importantly to determine (2) how to induce and enhance a magnetic moment in the adsorbed organic molecules and (3) how to locally stabilize the magnetization direction of a ferromagnetic surface by the absorption of specifically functionalized organic molecules. In the later case our calculations clearly emphasize the crucial role played by the light elements building the organic molecules on the the spin-orbit coupling (SOC) occurring at the hybrid organic-ferromagnetic interface. Importantly, this SOC can be manipulated using a different electronegativity of specific substituents (Cl and F).

Our first-principles simulations9 are performed on prototypical organic molecules adsorbed on a ferromagnetic 2 monolayers (ML) Fe/W(110) surface, which is a well-established system with out-of-plane magnetization widely used in spin-polarized scanning-tunneling microscopy (SP-STM) experiments.12 Similar to our previous study,10 in a first step we selected organic molecules containing \( \pi(p_z) \)-electron systems such as benzene (C\(_6\)H\(_6\))13–15 and cyclopentadienyl radical (C\(_5\)H\(_5\))16 since they correspond to classes of organic molecules with significantly different chemical reactivities.17 In a second step, we chemically functionalized the C\(_6\)H\(_6\) and C\(_5\)H\(_5\) molecules by replacing all H atoms through electronegative atoms as F and Cl to obtain a similar \( \pi(p_z) \)-electron systems. However, owing to the significantly higher electronegativity of F and Cl atoms than that of the H atom, when F and Cl atoms form \( \sigma \) bonds with a carbon atom of the aromatic ring, they exert a strong inductive electron withdrawal effect (with charge density being displaced from C toward F or Cl) and, as a consequence, \( \pi \) conjugation is decreased.17

The spin-polarized ab initio studies are carried out in the framework of density functional theory (DFT) by employing the generalized gradient approximation (PBE)18 in a projector augmented plane-wave formulation19 as implemented in the VASP code.20,21 The molecule-Fe/W(110) system is modeled within the supercell approach [a p(5×3) in-plane surface unit cell] and contains 11 atomic layers (9 W and 2 Fe). By using a plane-wave energy cutoff of 600 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/\( \AA \).22 As depicted in Fig. 1, the C\(_6\)H\(_6\) molecule adsorsbs 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. With one fewer C than C\(_6\)H\(_6\), C\(_5\)H\(_5\) binds to the surface with a C atom and a C–C bond on top of two neighboring Fe atoms along the [001] direction. The fluorinated and chlorinated molecules [C\(_6\)X\(_5\) and C\(_5\)X\(_5\) (X = F, Cl)] adsorb in a similar geometry as the C\(_6\)H\(_6\) and C\(_5\)H\(_5\) but rotated by 90° (see Fig. 1). Note that, compared to planar molecular geometry of the isolated gas phase, after adsorption all molecules have a nonplanar
FIG. 1. (Color online) The spin-resolved projected local density of states of the C_{6}X_{6} and C_{5}X_{5} (X = H, F, Cl) molecules adsorbed on the 2ML Fe/W(110) are significantly broadened due to an effective hybridization between the molecule and the Fe surface. All adsorbed molecules present a general characteristic: energy-dependent spin polarization, i.e., in a given energy interval the number of spin-up and spin-down electrons is unbalanced and each molecule has a net magnetic moment. Note that the states with large weights crossing the Fermi level are situated in the spin-down channel at the metal site (see Fig. 2) while, at the molecular site, above the Fermi level the states with large weights are in the spin-up channel. Therefore, at the molecular site, above the Fermi level, an inversion of the spin polarization occurs with respect to the ferromagnetic surface. For the energy intervals situated just below the Fermi level, the molecules which contain less electronegative atoms such as H and Cl [C_{6}X_{6} and C_{5}X_{5} (X = H, Cl)] show also the inversion of the spin polarization while for the molecules containing very electronegative atoms such as F (C_{6}F_{6} and C_{5}F_{5}) the spin polarization is preserved like the one of the clean iron surface (see also Fig. 3).

In contrast to our previous study, from the magnetic point of view a very interesting feature is that upon adsorption on the ferromagnetic surface the molecules with F and Cl substituents [C_{6}X_{6} and C_{5}X_{5} (X = F, Cl)] have a sizable magnetic moment (see Table I) which is antiferromagnetically oriented relative to the iron substrate. In contrast, the hydrogenated molecules (C_{6}H_{6} and C_{5}H_{5}) are characterized by small magnetic moments that can practically be neglected. Even more interesting is that the magnetic moment of the adsorbed molecule correlates with the electron affinity of the substituent. The molecules containing F, a much more electronegative atom compared to Cl, have a much larger magnetic moment with respect to the chlorinated molecules while the molecules having a less electronegative atom such as H are practically nonmagnetic. Due to the molecule-substrate interaction the magnetic moments of the Fe atoms situated just below the organic molecule are decreased compared to the ones of the clean Fe surface (see Table I). The decrease of the magnetic moments of these Fe atoms can also be correlated with the increase of the electronegativity of the substituents; i.e., the table shows the magnetic moments of the adsorbed molecules and the Fe atoms below the molecule (Fe{sup 1}) and the magnetic moment of the Fe surface (Fe{sup 2}).

<table>
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<tr>
<th>Molecule</th>
<th>Magnetic moments (μB)</th>
<th>MAE (meV)</th>
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<tr>
<td>C_{6}H_{6}</td>
<td>-0.076</td>
<td>+2.515</td>
</tr>
<tr>
<td>C_{6}F_{6}</td>
<td>-0.278</td>
<td>+1.446</td>
</tr>
<tr>
<td>C_{6}Cl_{6}</td>
<td>-0.164</td>
<td>+1.755</td>
</tr>
<tr>
<td>C_{5}H_{5}</td>
<td>-0.031</td>
<td>+2.471</td>
</tr>
<tr>
<td>C_{5}F_{5}</td>
<td>-0.262</td>
<td>+1.776</td>
</tr>
<tr>
<td>C_{5}Cl_{5}</td>
<td>-0.127</td>
<td>+1.855</td>
</tr>
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<td>2ML FeW(110)</td>
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from the analysis of the spin-resolved projected local density of states (PLDOS) shown in Fig. 1, we can extract the general picture of the binding mechanism for these hybrid molecule-magnetic substrate systems. Upon adsorption a spin-dependent hybridization will occur between the $\pi$-atomic type orbitals which originally form the $\pi$-molecular orbitals and the $d$ states of the Fe atoms. This leads to the formation of new molecule-metal hybrid states with bonding and antibonding character. As a general feature of the spin-polarized PLDOS shown in Fig. 1, in the spin-up channel the hybrid bonding states are situated at low energies while the antibonding combinations of the molecule-surface orbitals appear at much higher energies, more exactly in an energy window situated around the Fermi level. As a consequence, the hybrid antibonding states with large weight are in the spin-down channel while the minority electrons are in spin-down channel.

The most stable magnetic configuration of the clean surface is obtained when the magnetization direction is pointing out of the plane (along [110]) while when aligning the magnetization direction in plane along [110] (001) the total energy of the system will increase with 0.480 (1.280) meV per Fe atom. By adsorbing organic molecules such as $\text{C}_n\text{X}_m$ ($n = 5, 6; \text{X} = \text{H}, \text{Cl}, \text{F}$) on the 2ML Fe/W(110) surface the most
stable magnetic configuration is the same as that of the clean surface; i.e., the magnetization direction is perpendicular to the surface (see Table 1). However, in the case of hydrogenated molecules (C₆H₆ and C₅H₅) adsorbed on the iron surface, the energy difference between the two most stable magnetic configurations (magnetization pointing in the [110] and [1¯10] directions) is decreased by a much larger amount with respect to the clean surface compared to the functionalized chlorinated and fluorinated molecules such as C₆Cl₆, C₅F₅, and C₅Cl₅. By analyzing the adsorption energies $E_{\text{ads}}$ [see Fig. 2 (a)] and the values of the MAE (see Table 1) we can observe that the energy difference between out-of-plane and in-plane magnetic configurations decreases much more if the molecule binds more strongly to the surface. Therefore, we conclude that the out-of-plane magnetization present in the calculated molecule-substrate systems is less stable against temperature fluctuations compared to the clean ferromagnetic surface. Consequently, this is not the case for the C₆F₆ molecule, which, after adsorption on the ferromagnetic surface, stabilizes more the out-of-plane magnetization of the system compared to the clean ferromagnetic surface. In particular, C₆F₆ has the highest magnetic moment and binds less strongly to the surface compared to all other molecules. This behavior can be correlated with a specific structure of the spin-polarized PLDOS around the Fermi level at the molecular site. More specifically, in the case of the hydrogenated molecules the antibonding hybrid molecule-surface combinations are situated below the Fermi level while for the fluorinated molecules they are shifted above the Fermi level.

To summarize, our first-principles calculations demonstrate that, by employing an appropriate chemical functionalization of organic molecules adsorbed on a ferromagnetic surface, they can become magnetic and a fine tuning of their spin-unbalanced electronic structure can be achieved. Even more important is that we have shown that there is a direct correspondence between the substituent’s electronegativity and the size of the induced molecular magnetic moment. We demonstrated that the spin-orbit coupling at the interface can be manipulated by specific organic molecules such that the adsorbed hydrogenated molecules destabilize more the out-of-plane magnetization of the ferromagnetic surface compared to molecules containing more electronegative atoms such as Cl and F, which could also enhance it. To be more specific, in the case of fluorinated molecules the magnetic contrast detected by an SP-STM tip with out-of-plane magnetization will be increased compared to that of an isolated surface. In contrast, for hydrogenated molecules the magnetic contrast detected by the SP-STM tip with out-of-plane magnetization will be decreased. Ultimately, the understanding gained in our study will allow us to precisely engineer the magnetic properties of the hybrid organic-ferromagnetic interfaces, which can be further exploited to design more efficient spintronic devices based on organic molecules.

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22We also performed relaxations including the van der Waals (vdW) forces by using the DFT-D method [S. Grimme, J. Comput. Chem. 27, 1787 (2006)] in the self-consistent cycle of our ab initio calculations and we found that the vdW interactions slightly lower the adsorption energies and do not modify the DFT relaxed geometries.
23$E_{\text{ads}} = E_{\text{system}} - (E_{\text{molecule}} + E_{\text{surface}})$, where $E_{\text{system}}$, $E_{\text{molecule}}$, and $E_{\text{surface}}$ are the total energies of the molecule-surface system, isolated gas phase molecule, and clean surface, respectively.
24Integrating the spin-resolved PLDOS up to the Fermi level yields a magnetic moment for each molecule because of a higher number of electrons in the spin-down channel($\downarrow$).
25The spin polarization is defined as $(n^\uparrow - n^\downarrow)/(n^\uparrow + n^\downarrow)$, where $n^\uparrow$ and $n^\downarrow$ are the spin-up and spin-down charge densities in a given energy interval.