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

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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 electronegative atoms such as Cl and F. This chemical functionalization process surprisingly reveals the importance of the spin-orbit coupling present at the magnetic surface–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 devices[1–3] 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 concept[10] that indicates the importance of interface hybrid molecular-metal states rather than the intrinsic molecular spin[11] 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 study[10] 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 simulations[9] are performed on prototype 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_6H_6)[13–15] and cyclopentadienyl radical (C_5H_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_6H_6 and C_5H_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 σ 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, π 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 formulation[19] 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/Å.[22] As depicted in Fig. 1, the C_6H_6 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. With one fewer C than C_6H_6, C_5H_5 binds to the surface with a C atom and a C–C bond on top of two neighboring Fe atoms of the [001] row. The fluorinated and chlorinated molecules [C_6X_6 and C_5X_5 (X = F, Cl)] adsorb in a similar geometry as the C_6H_6 and C_5H_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

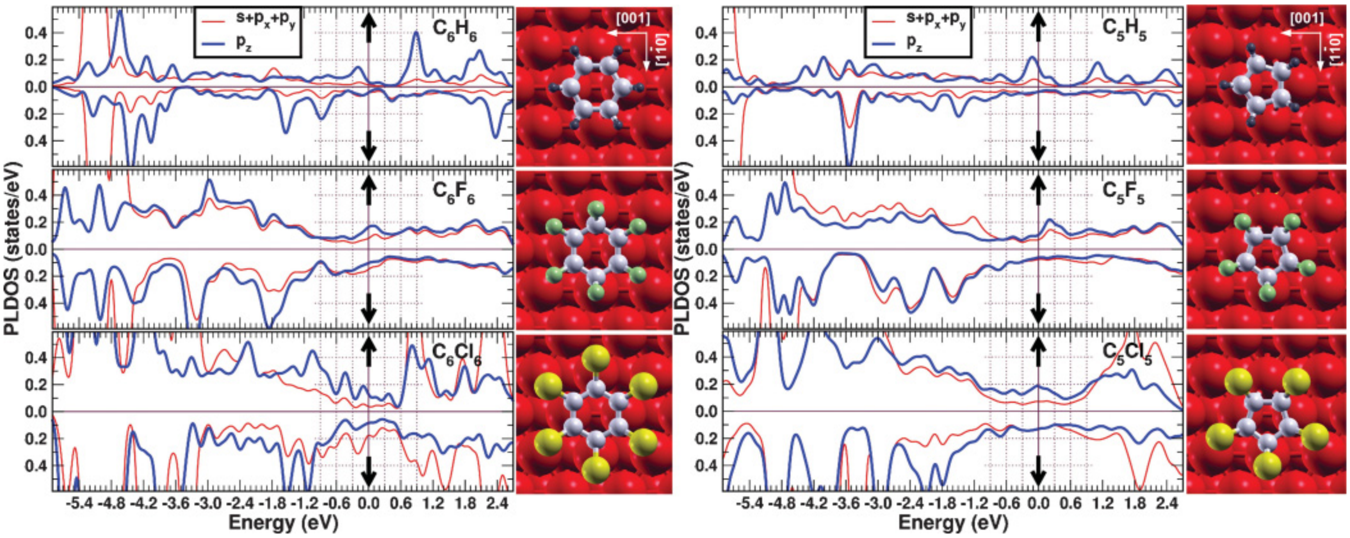


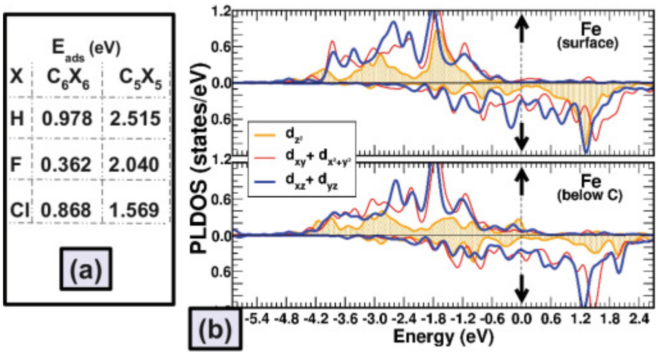
FIG. 1. (Color online) The spin-resolved projected local density of states of the C_6X_6 and C_5X_5 ($X = H$, F, Cl) molecules adsorbed on the 2ML Fe/W(110) are significantly broadened due to an effective hybridization between the molecule and the Fe surface. All adsorbed molecules present a general 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_6X_6 and C_5X_5 ($X = H$, Cl)] show also the inversion of the spin polarization while for the molecules containing very electronegative atoms such as F (C_6F_6 and C_5F_5) the spin polarization is preserved like the one of the clean iron surface (see also Fig. 3).

structure in which the H, F, and Cl atoms are situated above the C atoms.

In contrast to our previous study,[10] 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_6X_6 and C_5X_5 ($X = F$, Cl)] have a sizable magnetic moment[24] (see Table I) which is antiferromagnetically oriented relative to the iron substrate. In contrast, the hydrogenated molecules (C_6H_6 and C_5H_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,[17] 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 I. Magnetic moments (MM) of the adsorbed molecules and the Fe atoms below an C atom (Fe^1) or a C=C double bond (Fe^2) and magnetic anisotropy energies (MAE) for the adsorbed molecule-substrate systems given in meV per unit cell [corresponding to 60 Fe atoms of a double layer of 2ML Fe/W(110)]. With increasing electronegativity of the substituent from H to Cl to F the MM of the adsorbed molecule increases while the MM of the Fe atoms below the molecule decrease. For the most stable magnetic configuration the magnetization directions is out of the plane (perpendicular to the surface, i.e., aligned with the [110] direction). The positive numbers in the last two columns show with how much the total energy of the molecule-substrate system increases when the magnetization is in plane aligned along the [1$\bar{1}$0] and [001] directions.

Magnetic moments (μ_B)				MAE (meV)		
					per unit cell	
Molecule		(C) Fe^1	(C=C) Fe^2	[110]	[1$\bar{1}$0]	[001]
C_6H_6	−0.076	+2.515	+2.655	0.000	21.226	73.219
C_6F_6	−0.278	+1.446	+2.270	0.000	29.780	86.402
C_6Cl_6	−0.164	+1.755	+2.229	0.000	26.875	82.596
C_5H_5	−0.031	+2.471	+2.540	0.000	20.862	73.318
C_5F_5	−0.262	+1.776	+2.198	0.000	23.779	77.256
C_5Cl_5	−0.127	+1.855	+2.228	0.000	25.766	82.530
2ML FeW(110)		2.821		0.000	28.778	77.024



X	C_6X_6	C_5X_5
H	0.978	2.515
F	0.362	2.040
Cl	0.868	1.569

FIG. 2. (Color online) (a) The adsorption energies (E_{ads})[23] show that the C_5X_5 reactive radicals interact more strongly with the Fe substrate compared to the C_6X_6 molecules (X = H, F, Cl). (b) The spin-resolved projected local density of states of an Fe atom of the clean surface (upper panel) and an Fe atom below the C atom of C_5H_5(lower panel) indicate that the majority of electrons are in the spin-up channel while the minority electrons are in spin-down channel.

smallest magnetic moments correspond to the Fe atoms below fluorinated molecules, followed by the chlorinated, and then by the hydrogenated ones.

From the analysis of the spin-resolved projected local density of states (PLDOS) of our molecule-surface systems (Fig. 1) we can extract the general picture of the binding mechanism for these hybrid molecular-magnetic substrate systems. Upon adsorption a spin-dependent hybridization will occur between the p_z atomic type orbitals which originally form the π-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.[10,11] 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 around the Fermi level are in the spin-up channel at the molecule site (see Fig. 1) while at clean metal sites the states with large weight are in the spin-down channel [see Fig. 2(b)].

Another interesting feature is that for the hydrogenated molecules the hybrid antibonding orbitals are located mostly below the Fermi level, while for the chlorinated and fluorinated molecules these antibonding orbitals are emptied; i.e., they are pushed above the Fermi level. This feature correlates with the magnetic moment of the adsorbed molecules: the molecules containing F atoms have the largest magnetic moments, which is decreased in the case of chlorinated molecules, while the molecules containing H have negligible magnetic moments.

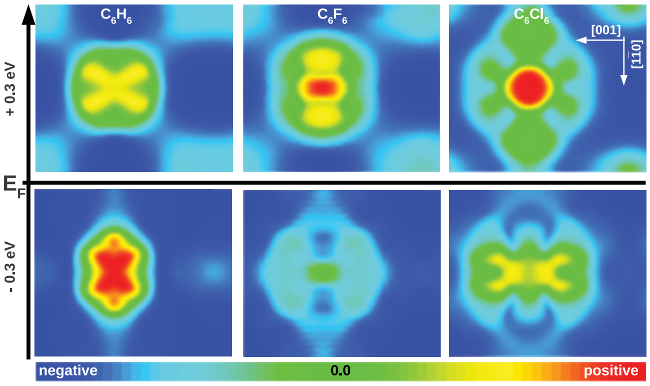


FIG. 3. (Color online) The calculated spin polarization at 3.0 Å above the C_6H_6, C_6F_6, and C_6Cl_6 molecules adsorbed on a 2ML Fe/W(110) (15.85 × 13.45 Å) surface plotted for occupied ([−0.3,0.0] eV) and unoccupied ([0.0, + 0.3] eV) energy intervals around the Fermi level. The organic molecules containing H and Cl atoms show above and below the Fermi level a high, locally varying spin polarization ranging from attenuation to inversion with respect to the ferromagnetic Fe film. In contrast, fluorinated molecules such as C_6F_6 preserve the spin polarization of the Fe surface for energy intervals just below the Fermi level and show an inversion of the spin polarization only for energy intervals above the Fermi level.

As already shown for C_5H_5 and C_6H_6,[10,11] the spin-polarized PLDOS of the chemisorbed functionalized fluorinated and chlorinated molecules also displays an energy-dependent spin polarization. This means that for a specific energy interval below or above the Fermi level, the number of spin-up and spin-down hybridized molecule-surface states is unbalanced (see Fig. 1) and in this energy interval each molecule has a net magnetic moment. As a consequence, above the Fermi level, for all studied molecules an inversion of the spin polarization[25] occurs at the molecular site with respect to the ferromagnetic surface (Fig. 2). For energy intervals below the Fermi level the same feature is present for molecules containing H and Cl substituents. In contrast, this is not the case for the molecules containing very electronegative atoms such as F. Therefore, for energy intervals below the Fermi level, the fluorinated molecules have the same spin polarization as the iron substrate and show an inversion of the spin polarization only for energy intervals above the Fermi level. These effects are clearly seen in Fig. 3, which illustrates spin-polarization maps at 3.0 Å above the molecule in the energy intervals below ([−0.3,0.0] eV) and above ([0.0, + 0.3] eV) the Fermi level. Furthermore, we have included in our simulations the effect of SOC by calculating several magnetic configurations with a given direction of magnetization. The energy difference between these magnetic configurations represents the magnetic anisotropy energy (MAE) and gives an estimate for the energy barrier necessary to stabilize the magnetic moments against quantum tunneling and thermal fluctuations.[7] We considered three possible surface-symmetry-determined directions of the magnetization in the molecule-surface systems: out of plane along the [110] direction (perpendicular to the surface) and in plane along the $[1\bar{1}0]$ and [001] directions (parallel to the surface). The clean surface and all molecule-substrate systems were relaxed by including spin-orbit coupling and without any symmetry restrictions.

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 $[1\bar{1}0]$ ([001]) the total energy of the system will increase with 0.480 (1.280) meV per Fe atom.[26] By adsorbing organic molecules such as C_nX_n ($n = 5,6$; X = H, Cl, 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 I). However, in the case of hydrogenated molecules (C_6H_6 and C_5H_5) adsorbed on the iron surface, the energy difference between the two most stable magnetic configurations (magnetization pointing in the [110] and $[1\bar{1}0]$ directions) are decreased by a much larger amount with respect to the clean surface compared to the functionalized chlorinated and fluorinated molecules such as C_6Cl_6, C_5F_5, and C_5Cl_5. By analyzing the adsorption energies E_{ads} [see Fig. 2 (a)] and the values of the MAE (see Table I) 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. Surprisingly, this is not the case for the C_6F_6 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, C_6F_6 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[5,6] based on organic molecules.

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[22] We 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] $E_{\mathrm{ads}} = E_{\mathrm{system}} - (E_{\mathrm{molecule}} + E_{\mathrm{surface}})$, where E_{system}, E_{molecule}, and E_{surface} are the total energies of the molecule-surface system, isolated gas phase molecule, and clean surface, respectively.

[24] Integrating 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*($\downarrow$).

[25] The 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.

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