

## Review

### Chemical and van der Waals Interactions at Hybrid Organic-Metal Interfaces

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#### Abstract

In this highlight we briefly review several of our recent theoretical studies focused on how the interplay between the chemical and the van der Waals interactions determines the bonding mechanism of several chemically functionalized  $\pi$ -conjugated organic molecules on non-magnetic and magnetic surfaces. In particular, we focus on the issue how to tailor the strength of the interaction between such  $\pi$ -conjugated organic molecules with a substrate of choice such that the nature of the molecular bonding has the specific features of the physisorption or chemisorption processes. Furthermore, we show how the precise control of these binding mechanisms allows us to design specific electronic and magnetic properties of hybrid organic-metallic interfaces.

## 1 Introduction

The intense research effort witnessed in the last decade to employ organic molecules as basic components in electronic devices triggered the development of the molecular electronics field [1] with the hope to become a viable alternative to the complementary metal-oxide-semiconductor (CMOS) technology to construct integrated circuits. Indeed, up to now the organic molecules clearly demonstrated their ability to be used as elementary functional units in devices as diodes [2], molecular switches [3], organic field-effect transistors [4, 5] or ultra-high-density memory circuits [6]. Despite of these impressive achievements, basic theoretical and experimental research is still required to close the technological gap between the CMOS and the molecular electronics.

Additionally, the use the spin degree of freedom in molecular-based devices extended the realm of molecular electronics to molecular spintronics [7]. For instance, single molecule magnets [8] were incorporated in supramolecular spin-valve devices [9] or magnetic molecules exhibit a spin-filter functionality of a magnetic surface [10]. Interestingly, the latter effect can be present even if the organic molecule is non-magnetic [11]. Overall, the field of molecular spintronics opens new exciting technological opportunities that are still to be explored [12].

## 2 Physisorption vs. Chemisorption Bonding Mechanism

### 2.1 Overview

The adsorption of an adsorbate (i.e., an atom, a cluster of atoms or a molecule) on a substrate implies two complementary aspects: (1) the change of the adsorbate’s and substrate’s electronic structure due to their mutual interaction in a degree determined by (2) the strength of the adsorbate–surface interaction which is quantitatively described by the adsorption energy  $E_{\text{ads}}$ <sup>1</sup>. In this respect, there are two main bonding mechanisms, namely *physisorption* and *chemisorption*. A schematic representation of the basic features displayed by the physisorption and chemisorption bonding mechanisms is depicted in Fig. 1.

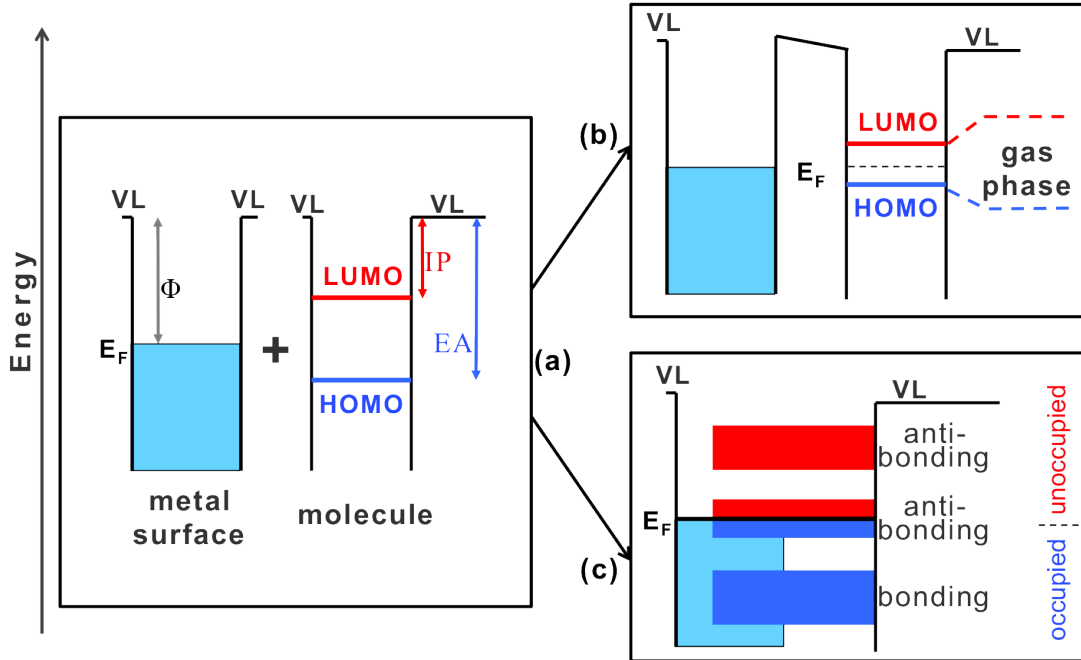


Figure 1: (a) Schematic illustration of the energy level alignment between a molecule and a surface of choice. Depending on the strength of the molecule–surface interaction, the adsorption process can be labelled as (b) physisorption or (c) chemisorption.

Initially, as shown in Fig. 1(a), the adsorbate (i.e., in our case a molecule) and the surface under consideration are well separated such that their electronic structure are aligned with respect to the vacuum level at infinity [13]. Then in the case of physisorption [see Fig. 1(b)], the gas-phase electronic structure of the adsorbate as well that of the surface are not significantly changed upon adsorption. In consequence, for a physisorbed molecule the concept of the molecular orbitals (MOs) obtained as a linear combination of the atomic orbitals of its atomic constituents is still a meaningful theoretical instrument that can be used to describe the molecular electronic structure. In this context, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) known also as frontier orbitals [14] are of a particular

<sup>1</sup>The adsorption energy is defined as  $E_{\text{ads}} = E_{\text{sys}} - E_{\text{surf}} - E_{\text{molec}}$ , where  $E_{\text{sys}}$  is the total energy of the molecule–surface system while  $E_{\text{surf}}$  and  $E_{\text{molec}}$  denote the total energy of the clean surface and that of the molecule in the gas phase, respectively.

importance to rationalize the molecule–substrate interaction [15]. Additionally, it is important to note that a renormalization of the HOMO-LUMO gap can occur if a molecule is physisorbed on a polarizable surface due to the additional adsorbate–substrate image potential interaction [16, 17, 18]. From the energetic point of view, the molecule–surface interaction is relatively weak with an upper value of the adsorption energy of  $\sim 0.1$  eV while the adsorbate–substrate equilibrium distance is typically  $\geq 3$  Å. Importantly, the physisorption bonding mechanism is driven by the long-range dispersion-induced van der Waals (vdW) forces [19].

In contrast to physisorption, in the case of chemisorption the molecule and the substrate merge to form a new quantum mechanical system. As a consequence, for a chemisorbed system hybrid adsorbate–surface states are formed which can contain mixed electronic states without any resemblance to the states of the separated molecule and substrate [20, 21]. From a methodological point of view, the formation of the new hybrid molecule–surface states can be seen as the result of the hybridization (i.e., mixing) process between the adsorbate and the surface electronic states. Historically, one of the first quantitative model used to describe this process is that proposed by Newns [22] on the basis of the Anderson impurity Hamiltonian [23], model referred to as Newns-Anderson (for a review see, for instance, Ref. [24]). In the Newns-Anderson model one can distinguish between the weak and strong chemisorption. A weak chemisorption process takes place when the adsorbate’s electronic state of interest becomes a broad resonance due to its interaction with an extended and featureless *sp* band of the surface. On the contrary, the interaction between the molecule’s energy level with a sharp *d(f)* band induces the creation of the bonding and anti-bonding hybrid molecule–surface electronic states as depicted in Fig. 1(c).

From this perspective, the strong chemisorption in the Newns-Anderson model is very similar to the formation of bonding and antibonding combinations of the atomic orbitals to form MOs as described by the frontier molecular orbital theory [14]. In both weak and strong chemisorption bonding mechanisms, the hybridization of the molecular electronic states with those of the substrate are instrumental to obtain hybrid molecule–surface electronic states. It is worth to mention that for an optimal hybridization process two basic conditions must be fulfilled: (1) the molecule and substrate wavefunctions must have the appropriate symmetry to maximize the spatial overlap and (2) the overlapping electronic states must be close in energy to ensure a large energetic splitting between the bonding and antibonding hybrid states which in turn increases the stability of the molecule–surface system.

## 2.2 Theoretical Description

Nowadays the density functional theory (DFT) [25] is the theoretical tool of choice to investigate the structural and electronic properties of physical systems ranging from free atoms to complex systems such as single molecules or molecular layers on surfaces. While in principle exact for the ground-state properties, in practice DFT relies on the use of approximate exchange-correlation functionals such as the local density approximation (LDA) [26, 27] or the generalized gradient approximation (GGA) in various flavours (see, for instance, Refs. [28, 29, 30, 31]). In particular, for the chemisorbed molecular systems the use of an approximate exchange-correlation functional leads to adsorption energies that are not chemically accurate [32].

As regarding the physisorbed molecular systems, a major shortcoming of the currently used semi-

local GGA exchange-correlation functionals is the fact that they do not describe the long-range attractive van der Waals (London dispersion) interactions while LDA leads to binding in such physisorbed systems due to the exchange and not as a result of the correlation effects [33]. This failure is related to the intrinsic non-local character of the correlation effects responsible for the vdW forces, feature that is not captured in the commonly used local or semi-local approximations for the exchange-correlation energy functional. Nevertheless, these dispersion interaction can be included in DFT in a semi-empirical way as proposed, for example, by Grimme [34], Grimme *et al.* [35], Ortmann *et al.* [36], Tkatchenko and Scheffler [37] or Tkatchenko *et al.* [38]. This approach relies on the summing of atomic pairwise contributions of the form  $-C_6^{ij}/R_{ij}^6$ , containing the  $C_6^{ij}$  coefficient for the atomic pair  $ij$  in question separated by the distance  $R_{ij}$ . Additionally, a damping function is required to avoid near singularities at small inter-atomic distances (for more details see the previously mentioned references). On the other hand, starting from the adiabatic connection fluctuation dissipation (ACFD) theorem [39, 40], the non-local correlation effects have been included in the first-principles vdW-DF functional [41] and subsequent effort was devoted to improve its predictive power [42, 43]. So far, vdW-enhanced DFT calculations have been performed for various organic molecule–surface systems [44, 45, 46, 47] or for the graphene (an extended  $\pi$  system) on several metal surfaces [48, 49, 50, 51], to cite just few examples. Further details regarding the incorporation of the London dispersion interactions in DFT can be found in two recent  $\Psi_k$  highlights [52, 53].

### 3 Application to Molecular Electronics

An important goal in molecular electronics is to gain the ability to rationally tune the strength of the molecule–surface interaction to specifically modify the functionality of a molecule-based electronic device. In this respect, two different strategies can be adopted to systematically investigate this problem: (1) for a given substrate to modify the chemical structure of the molecule of interest through a chemical functionalization process (see, for instance, [21, 54, 55]) and (2) for the same molecule to vary the chemical nature of the substrate (see, for example, [56, 57, 58]).

The chemical functionalization process at the heart of the path (1) consists in the replacement of an atom or a group of atoms in a molecule through other atoms or group of atoms with a specific functionality (i.e., a functional group). A schematic illustration of this process viewed from the electronic structure point of view is shown in Fig. 2. More precisely, starting from benzene ( $C_6H_6$ ) the replacement of a CH functional group by one N atom leads to pyridine ( $C_5H_5N$ ) and through a further substitution one obtains pyrazine ( $C_4H_4N_2$ ). The effect of this chemical functionalization of benzene is twofold: (a) by including a N atom in the aromatic ring the  $\pi$  character of HOMO is changed to  $\sigma$  and (b) the occupied  $\pi$  MOs such as  $\pi_1$  are shifted to lower energies. Importantly, this energy shift increases with the number of N atoms, i.e., HOMO-1 and HOMO-2 of pyrazine are at lower energies as the similar MOs for pyridine.

We explored how the chemical functionalization of benzene with N atoms specifically determines the nature of the molecule–substrate interaction by investigating the bonding mechanism and the electronic structure of single benzene, pyridine and pyrazine molecules adsorbed flat on the

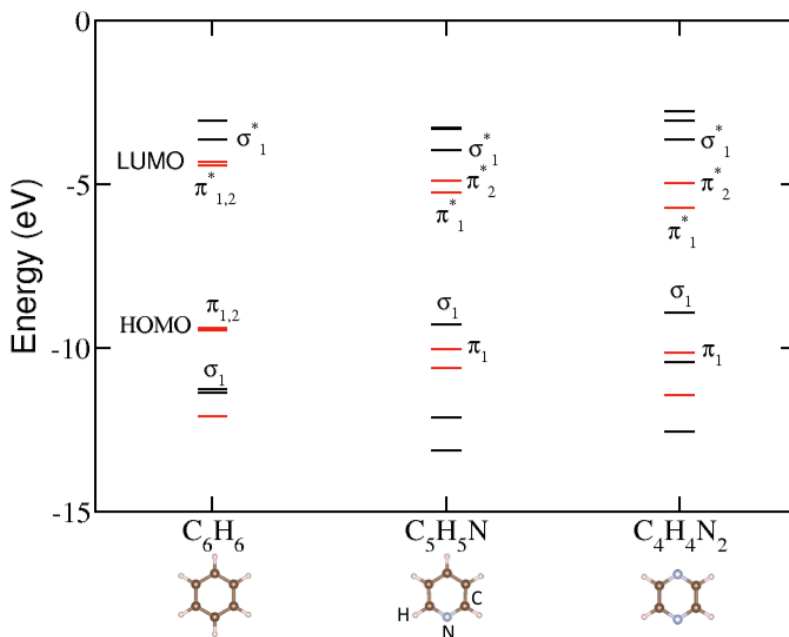


Figure 2: Energy level diagram for the planar  $\pi$ -conjugated benzene ( $C_6H_6$ ), pyridine ( $C_5H_5N$ ) and pyrazine ( $C_4H_4N_2$ ) molecules in the gas phase. With respect to benzene, the presence of N in the aromatic ring (a) changes the character of the HOMO from  $\pi$  to  $\sigma$  and (b) gradually lowers in energy the HOMO-1 level with a  $\pi$  character by increasing the number of N atoms. Note that the HOMOs are aligned using the  $\delta$ SCF recipe in all three cases, i.e.,  $E_{\text{HOMO}} = E(N) - E(N-1)$ , where  $E(N)$  is the total energy of the neutral molecule while  $E(N-1)$  represents the energy of the corresponding cation.

Cu(110) surface [59]. On this substrate, the benzene is chemisorbed with its molecular plane parallel to Cu(110) [60, 61]. As regarding the pyridine, in a previous study [62] we have shown that this molecule is also chemisorbed on Cu(110) such that in the ground state it adsorbs with the aromatic ring via the N atom perpendicularly to surface. Nevertheless, when starting from a flat adsorption geometry like that in the case of benzene, the pyridine can preserve this flat geometry or it turns in an upright configuration, depending on its specific position on the Cu(110) surface [62].

This observation clearly emphasizes the importance of such flat adsorption geometries for a flat aromatic molecule like pyridine on a metal surface since they can be intermediate configurations on the adsorption path from the gas-phase to a metal surface. Therefore a similar flat adsorption configuration was considered also for the pyrazine molecule. The corresponding *ab initio* DFT simulations were carried out using the PBE exchange-correlation functional [28] and the London dispersion interactions were considered within the framework of the semi-empirical DFT-D2 [34] and the first-principles vdW-DF [41] methods.

Table 1 summarizes the average equilibrium distances  $d_{\text{eq}}$  and the adsorption energies  $E_{\text{ads}}$  evaluated for these three  $\pi$ -conjugated molecules using the DFT and the DFT-D2 relaxed geometries. The main outcome of the DFT calculations is that the benzene is chemisorbed on Cu(110) while in a flat adsorption geometry the pyridine and pyrazine molecules are physisorbed with an av-

	DFT		DFT-D2	
	$d_{\text{eq}}$ (Å)	$E_{\text{ads}}$ (meV)	$d_{\text{eq}}$ (Å)	$E_{\text{ads}}$ (meV)
Bz	2.43	-253	2.35	-492
Py	2.98	-108	2.43	-417
Pz	2.99	-36	2.59	-371

Table 1: The average equilibrium distances  $d_{\text{eq}}$  and the adsorption energies  $E_{\text{ads}}$  obtained for the benzene, pyridine and pyrazine molecules for a flat adsorption configuration on the Cu(110) substrate using the DFT and DFT-D2 relaxed geometries.

average adsorption distance of  $\sim 3$  Å. In this regard, this picture changes significantly when the dispersion interactions are considered in the DFT calculations. More specifically, as expected, the inclusion of the vdW interactions leads to a significantly smaller molecule–surface distance in the case of pyridine and pyrazine while it remains almost the same for the benzene molecule. A smaller DFT-D2 separation distance due to the inclusion of the long-range attractive dispersion interactions has a significant impact on the electronic structure of the adsorbed molecules.

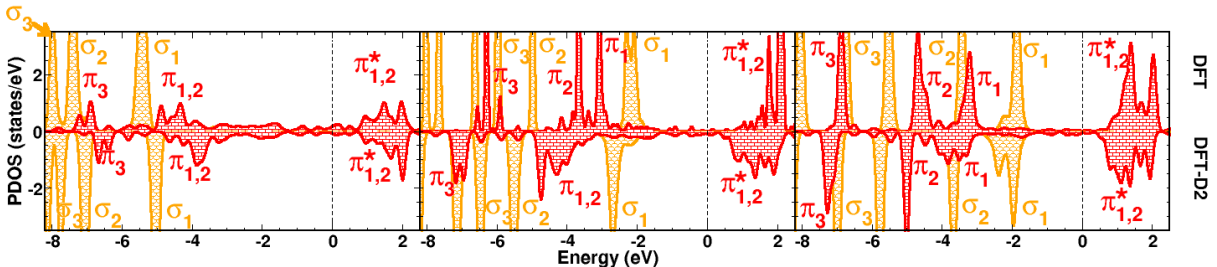


Figure 3: The DFT (upper figures) and DFT-D2 (lower figures) projected density of states (PDOS) of the benzene, pyridine and pyrazine molecules adsorbed flat on the Cu(110) surface. On this substrate the benzene is chemisorbed at the DFT level of the *ab initio* simulations such that the inclusion of the vdW interactions by means of the semi-empirical DFT-D2 method does not significantly change the electronic structure evaluated with DFT. On the contrary, in the case of pyridine and pyrazine, the inclusion of the dispersion interactions bring them closer to the Cu(110) substrate that leads to a stronger hybridization between the molecules  $p_z$ -orbitals and the Cu  $d$ -bands. (adapted after [59])

As shown in Fig. 3, the benzene electronic structure is not sensibly modified when the vdW interactions are taken into account. On the contrary, in the case of pyrazine the  $\pi_1$  and  $\pi_{1,2}^*$  PDOS features at the molecular site are significantly broader for the DFT-D2 relaxed geometry than for the DFT one. This implies that in a flat adsorption geometry pyridine becomes chemisorbed due to the London dispersion forces. Indeed, also the calculated adsorption energy  $E_{\text{ads}}^{\text{DFT-D2}}$  is lower than  $E_{\text{ads}}^{\text{DFT}}$ . A similar conclusion can be drawn for pyrazine where the vdW interactions significantly lowers its small DFT adsorption energy that implies that pyrazine binds to Cu(110) mainly via the dispersion interactions.

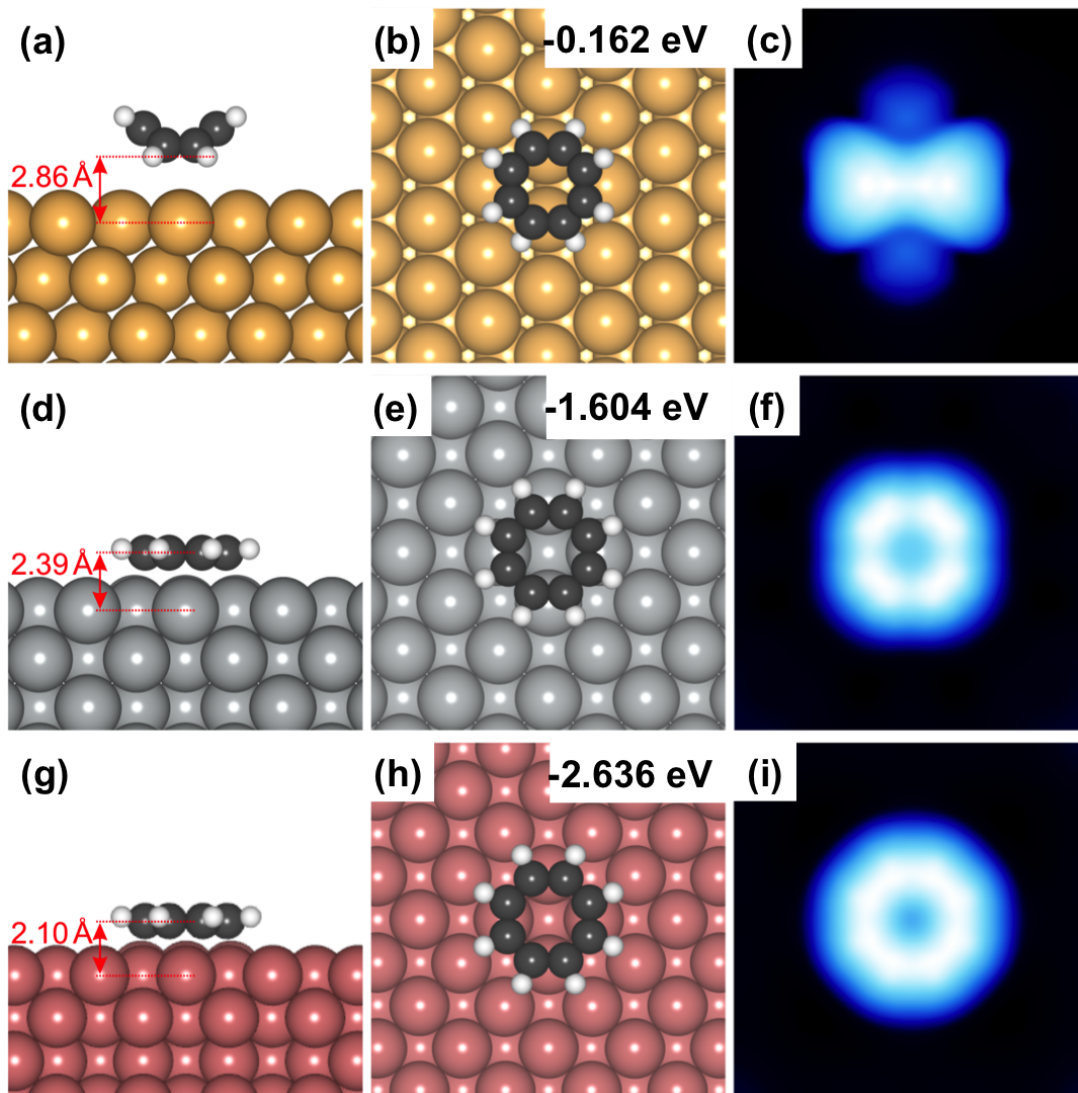


Figure 4: (left panel) Side views and (middle panel) top views of the adsorption geometries and (right panel) the theoretical STM maps obtained for the  $C_8H_8$  (COT) molecule adsorbed on the Au(111) (top row), the Ag(100) (middle row) and the Cu(100) (bottom row) surfaces. On Au(111), COT exhibits a tub conformation as in the gas phase and thus the molecule is physisorbed on this surface. On the contrary, on the Ag(100) and Cu(100) substrates COT is chemisorbed and therefore it adopts a flat adsorption geometry. It is also worth to mention that the COT–surface adsorption distance significantly decreases starting from the Au(111) to Ag(100) and Cu(100) surfaces. Note also that the simulated STM images are in excellent agreement with the experimental STM maps shown in Ref. [58])

As already mentioned, a second modality to engineer the nature of the molecule–surface bonding mechanism is to modify the chemical reactivity of the substrate by studying the same molecule. Recently, we illustrated this possibility for annulene 1,3,5,7-cyclooctatetraene ( $C_8H_8$ , hereafter denoted as COT) [58]. This molecule is interesting since in the gas phase it has a non-aromatic tub conformation since it does not fulfil the Hückel’s  $4n+2$  rule for the  $\pi$  electrons of a planar aromatic molecule. However, when doubly charged it becomes planar and aromatic.

An interesting alternative route to induce aromaticity in COT is to make use of the hybridization process between its molecular electronic states and those of a surface of choice. This possibility is illustrated in detail in Fig. 4. Our *ab initio* simulations indicate that on the Au(111) surface the COT molecule preserves its tub geometry as in the gas phase and therefore on this substrate COT is physisorbed (a similar conclusion can be drawn from the analysis of the PDOS [58]). Indeed, the experimental and the simulated STM images are remarkably similar which emphasizes the validity of the previous conclusion. However, on the Ag(100) and the Cu(100) surfaces the COT molecule is chemisorbed and becomes flat. Also for these substrate the simulated STM images agree well with the experimental ones. Note that the adsorption energy is significantly stronger for COT on Cu(100) than on Au(111) that denotes a stronger molecule–substrate interaction in the former case. Therefore depending on reactivity of the underlying surface, one can tune the strength of the molecule–substrate interaction from physisorption to chemisorption.

## 4 Application to Molecular Spintronics

As in detail discussed in the previous section the physisorption is a weak interaction with no hybridization between molecular orbitals and the electronic states of the surface. On the contrary, characteristic for the chemisorption process is the strong molecule-surface interaction that leads to the creation of a new hybrid organic-metallic material due to a strong hybridization between atomic type orbitals that originally form the molecular orbitals and the electronic states of the surface. As a consequence, the electronic and magnetic properties of both molecule and metallic surface are drastically modified and in the most cases do not resemble the properties of the separated systems. In practice both physisorption and chemisorption processes can coexist within the same system as in the case of graphene on Ir(111) and Co/Ir(111) surfaces [49, 63]. However, for certain molecule-metal systems the binding is dominated by physisorption [64, 49, 58] while for other hybrid systems the binding is driven by chemisorption [11, 65, 58]. Furthermore, in addition to physisorption and chemisorption processes a charge transfer between organic material and surface might occur that can specifically modulate the molecule-surface interaction [63, 66].

A basic goal of the molecular electronics is to further take advantage of the electron spin degree of freedom by (i) incorporating specific spintronic functions within single molecular building blocks and (ii) using organics to modify the magnetic properties of magnetic substrates. For example, the most important factors that determine the functionality of a spintronic device are (1) the spin-polarized current injected from the hybrid interface and (2) the substrate magnetic properties like magnetic exchange couplings, stability and direction of the magnetic moments of the metal atoms interacting with the organic material. More precisely, the spin-polarized current above the organic layer injected from the hybrid interface is one of the key factors that determine



the efficiency of a spin-valve electronic device. Large efforts, see for instance [11, 66, 67, 65], are dedicated to understand how to manipulate the interface hybrid states in order to control the transmission of the spin information, i.e. to create an effective source of spin-polarized electrons at the interface.

In several recent studies performed in our group, we clearly demonstrated that the hybrid organic-metallic states rather than the intrinsic molecular spins are decisive in defining the spin-polarization across the hybrid interface [11, 65]. Moreover, the generality of our *ab initio* driven concept studies were clearly proven by spin-polarized scanning tunneling microscopy (SP-STM) experiments performed on  $\pi$ -conjugated organic materials like molecules [11, 66] and graphene [63] adsorbed on ferromagnetic surfaces.

In the following, we will remind how by adsorbing prototype  $\pi$ -conjugated organic molecules like cyclopentadienyl-type radicals onto a ferromagnetic substrate such as 2ML Fe/W(110), the magnetic properties of the hybrid system can be tailored by controlling the molecule-surface interaction, i.e. by chemically functionalizing the adsorbed organic molecules. As a result, the interface spin-polarization, the molecular magnetic moments and their spatial orientation can be finely tuned by using substituents with different electronegativities to the organic molecules which in turn lead to a different reactivity of the molecule towards the ferromagnetic surface.

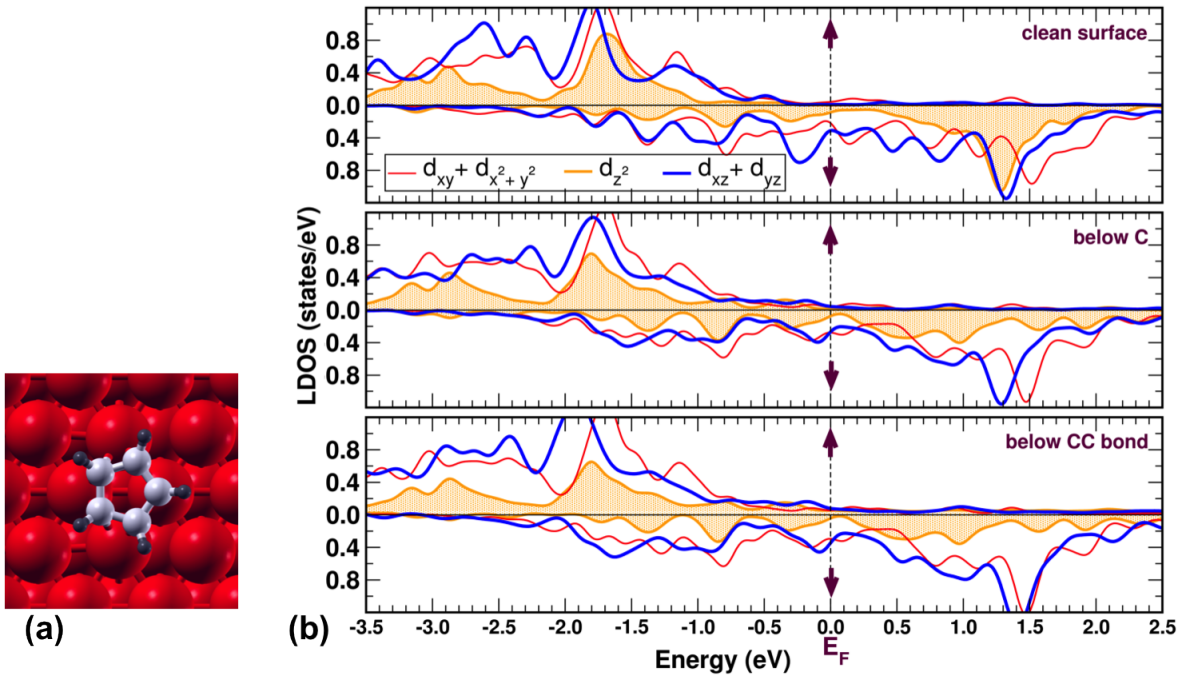


Figure 5: (a) Geometry (top view) of the  $C_5H_5$  molecule adsorbed on the Fe/W(110) substrate. (b) The spin-resolved local density of states of an Fe atom of the clean surface (upper panel), an Fe atom below a C atom (middle panel) and an Fe atom below a CC bond (lower panel) of the  $C_5H_5$  molecule show that the majority of electrons are in spin-up channel while the minority electrons are in spin-down channel. The strong molecule-metal hybridization leads to a change of the magnetic moments of the Fe atoms (e.g.  $2.47 \mu_B$ ) binding to the C atoms as compared to the Fe atoms (e.g.  $2.82 \mu_B$ ) of the clean surface [11, 65].

As an instructive example, we can consider the adsorption of the hydrogenated and fluorinated

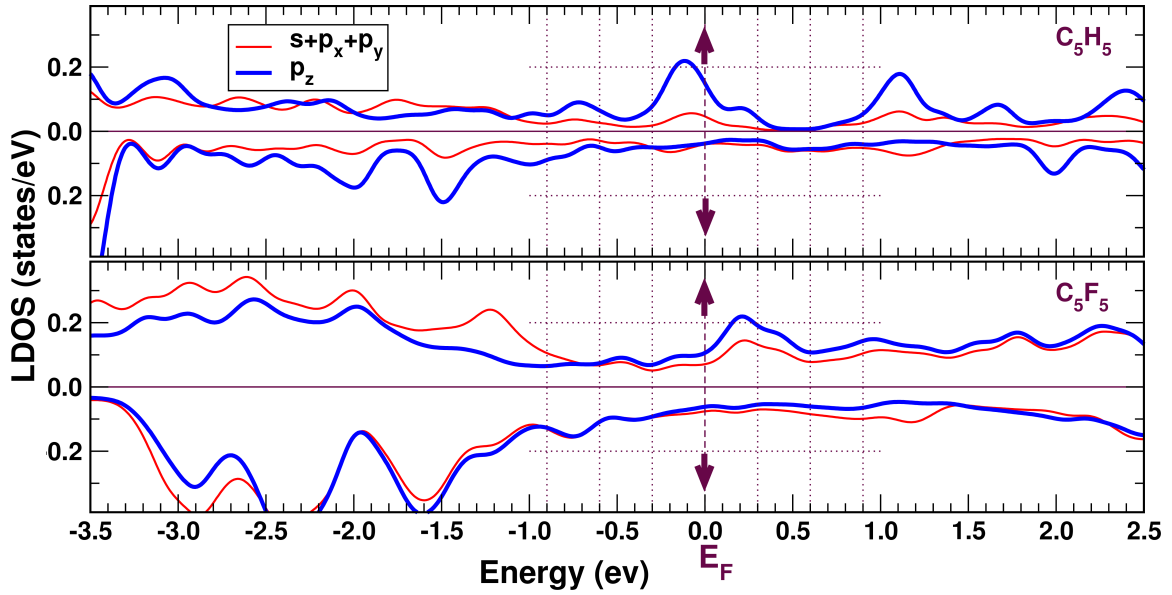


Figure 6: The spin-resolved local density of states of the  $C_5H_5$  and  $C_5F_5$  molecules adsorbed on the 2ML Fe/W(110) surface show broadened states as a result of an effective interaction with Fe atoms. In particular, a strong hybridization occurs only between out-of-plane orbitals (i.e.,  $p_z$  of C and Fe  $d$ -orbitals with a  $z$ -component as  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$ ) while the in-plane orbitals slightly interact (i.e.,  $s$ ,  $p_x$   $p_y$  of C and Fe  $d$ -orbitals as  $d_{x^2-y^2}$  and  $d_{xy}$ ). Interestingly, both adsorbed molecules show an energy-dependent spin-polarization. This implies that in a specific energy interval the number of spin-up and spin-down states is different and, as a consequence, the molecule has a net magnetization density that can be measured as a spin-contrast in SP-STM experiments [11, 66].

cyclopentadienyl radicals ( $C_5H_5$  and  $C_5F_5$ ) onto the ferromagnetic 2ML Fe/W(110) surface. Compared to H atom, the F atoms have a significant higher electronegativity that leads to the formation of polar C-F bonds. Therefore, in the  $C_5F_5$  radical the F atoms have a strong inductive electron withdrawal effect (i.e. the charge density is displaced from C towards F) and the  $\pi$ -conjugation is decreased as compared to  $C_5H_5$  radical. Similar to the adsorption of pyridine and pyrazine on the Cu(110) substrate, the binding of  $C_5F_5$  to the magnetic substrate is much weaker than the  $C_5H_5$  molecule although both molecules  $C_5H_5$  and  $C_5F_5$  chemisorb on the 2ML Fe/W(110) surface, i.e. the adsorption energies are 2.040 eV for  $C_5F_5$  and 2.515 eV for  $C_5H_5$  [65].

The binding mechanism between the molecules (i.e.,  $C_5H_5$  and  $C_5F_5$ ) and the 2ML Fe/W(110) substrate can be explained by using the spin-resolved local density-of-states (LDOS) of the molecule-surface systems shown in Fig. 5 and Fig. 6. As a general feature, the strong interaction between the organic molecules with the ferromagnetic surface leads to a spin-dependent hybridization. In particular, the spin-up  $p_z$ -atomic orbitals which originally form the  $\pi$ -molecular orbitals strongly hybridize with the majority  $d$ -states of Fe atoms creating hybrid organic-metal states with bonding and antibonding character. Interestingly, the hybrid antibonding states are situated around the Fermi energy while the hybrid bonding states are located at much lower energies (see also Fig. 7). On the contrary, in the spin-down channel, the  $p_z$ -atomic orbitals

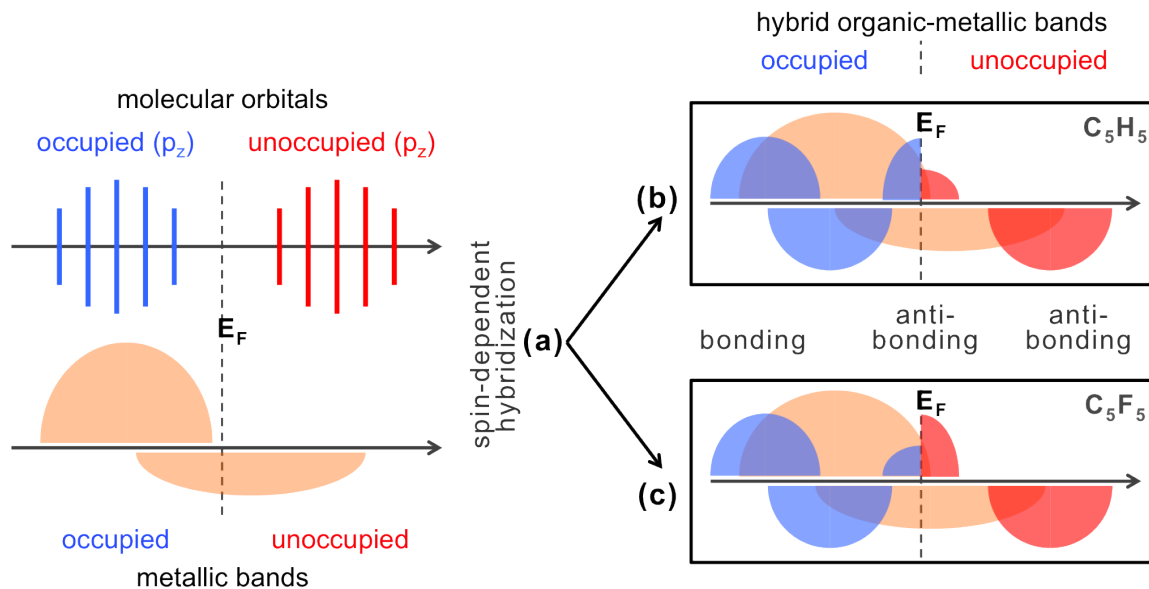


Figure 7: The general scheme used to explain the interaction between non-magnetic organic molecules and ferromagnetic surfaces. (a) Schematic drawings of the molecular orbitals (upper panel) and  $d$ -states of the ferromagnetic substrate (lower panel). (b, c) Due to a spin-dependent hybridization, the bonding states in both spin-up and spin-down channel appear at low energies well below Fermi level. The spin-up antibonding states are located in an energy window around the Fermi energy while the spin-down states appear at higher energies above Fermi energy. As an interesting characteristic, for the  $C_5H_5$  molecule most of the hybrid antibonding states are situated below Fermi energy (see also upper panel in Fig. 6) while for the  $C_5F_5$  most of these antibonding states are shifted just above Fermi energy (see also lower panel in Fig. 6) and lead to an induced magnetic moment at fluorinated molecular site.

hybridize with the minority  $d$ -states of Fe atoms such that the hybrid bonding states appear well below Fermi energy while the hybrid antibonding states are located at high energies above Fermi energy (see Fig. 6). Therefore, characteristic for the complex organic-ferromagnetic systems, the electronic states with large weight around the Fermi energy are in the spin-up channel at the molecular site and the spin-down channel at the clean surface site (Fig. 5 and Fig. 6).

Conceptually, the electronic structure formed at the organic molecule–ferromagnetic interface due to the spin-dependent hybridization resembles the  $p_z - d$  Zener exchange mechanism [68] and is schematically depicted in Fig. 7. Furthermore, this exchange mechanism explains the spin-dependent electronic structure of other  $\pi$ -conjugated organic materials adsorbed on a ferromagnetic substrate, i.e., the adsorption of CoPc molecules on 2ML Fe/W(110) [66] or graphene on ferromagnetic Co/Ir(111) surface [63]. We note in passing that the Zener-type exchange mechanism [68] also describes the interaction of  $\pi$ -conjugated organic materials with ferromagnetic atoms as lanthanides for which a  $\pi - f$  exchange mechanism occurs [69, 70].

Integrating the spin-resolved LDOS for the  $C_5H_5$  molecule yields a very small magnetic moment of  $0.003 \mu_B$  which can be neglected and the molecule can be considered practically nonmagnetic. A very interesting feature is that upon adsorption, the fluorinated cyclopentadienyl radical

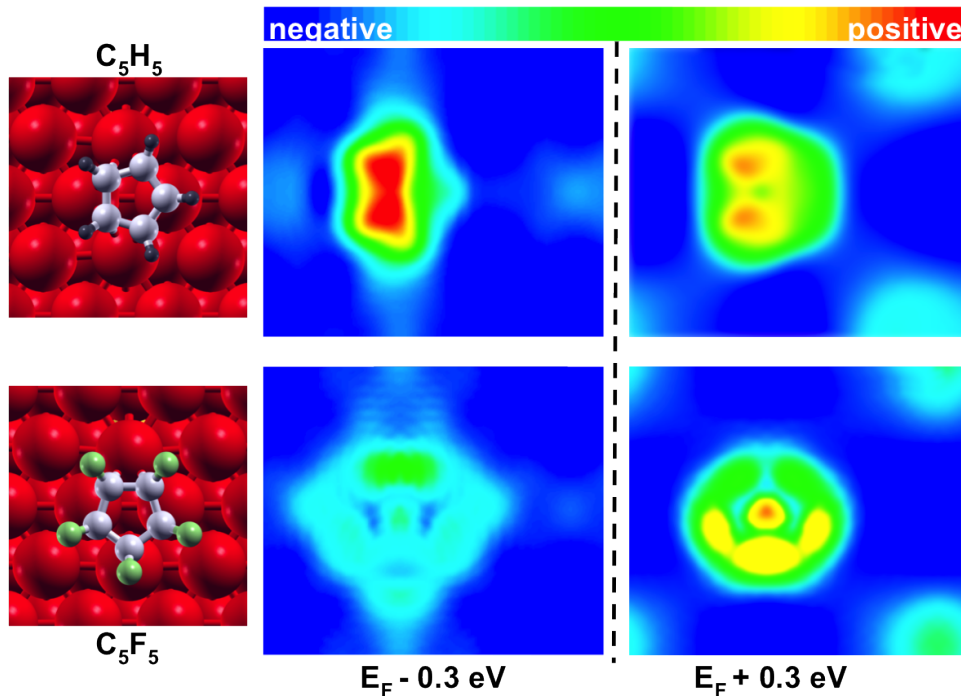


Figure 8: The simulated spin-polarization above the  $C_5H_5$  and  $C_5F_5$  molecules adsorbed on the 2ML Fe/W(110) surface for occupied ( $[E_f - 0.3]$  eV) and unoccupied ( $[E_F + 0.3]$  eV) energy intervals. The adsorbed  $C_5H_5$  molecule shows an inversion of the spin-polarization with respect to the ferromagnetic substrate for energy intervals below and above Fermi level. On the contrary, the adsorbed  $C_5F_5$  molecule shows an inversion of the spin-polarization with respect to the ferromagnetic substrate only for energy intervals above Fermi level and preserves the spin-polarization of the iron surface for energy intervals below Fermi level.

$C_5F_5$  acquires a large magnetic moment ( $0.262 \mu_B$ ) oriented antiferromagnetically relative to the underlying magnetic substrate. As shown in Fig. 6 and schematically depicted in Fig. 7, the molecular magnetic moment in the  $C_5F_5$  originates from the shift of the hybrid antibonding interface states above Fermi energy. It is important to note that the induced molecular magnetic moment is located mostly in the hybrid organic-metallic orbitals with  $\pi(p_z)$ -character at the molecular site. Furthermore, as compared to the Fe atoms of the clean surface, the molecule-ferromagnetic metal interaction leads to a decrease of the magnetic moments of the Fe atoms directly binding to the C atoms. Interestingly, the decrease of the magnetic moments of these Fe atoms correlates with the increase of the substituent electronegativity, i.e., largest magnetic moment corresponds to the  $C_5H_5$  while the smallest correspond to the  $C_5F_5$  [65].

As already mentioned above, the spin-resolved LDOS of the adsorbed  $C_5H_5$  and  $C_5F_5$  molecules show an energy dependent spin-polarization which implies an unbalanced number of spin-up and spin-down hybrid interface states for a given energy interval below or above Fermi energy. In practice, this means that in a specific energy window the molecule has a net magnetization density that can be visualized as a magnetic contrast in SP-STM experiments [11, 66]. Fig. 8 shows that for an energetic window above Fermi energy ( $[E_F + 0.3]$  eV) an inversion of the spin-polarization with respect to the ferromagnetic substrate occurs for both  $C_5H_5$  and  $C_5F_5$

molecules. This is also the case for the hydrogenated molecule ( $C_5H_5$ ) for an energy interval below the Fermi level ( $[E_F - 0.3]$  eV). In contrast, in the energy window  $[E_F - 0.3]$  eV, the fluorinated molecule ( $C_5F_5$ ) has the same spin-polarization as the ferromagnetic iron surface. To conclude, our results demonstrate that by a carefully choose of the molecular substituent and the bias voltage we can precisely control the spin-polarization above the molecular site, i.e., the spin orientation of the injected electrons above the hybrid interface.

In addition, by including the spin-orbit coupling (SOC) in our *ab initio* calculations we demonstrated that the magnetization direction of the hybrid organo-metallic interface can be manipulated by the adsorption of specific organic molecules. More precisely, the adsorbed hydrogenated molecules destabilize more the out-of-plane magnetization direction of the 2ML FeW(110) substrate as compared to fluorinated molecules which can enhance it [65]. The important message of these results is that in a spin-dependent STM experimental measurement, the magnetic contrast detected by a SP-STM tip with out-of-plane magnetization for the fluorinated molecules will be much larger as compared to that of a hydrogenated molecule.

To conclude this section, we have shown how the spin-polarization above an organic material adsorbed on a ferromagnetic substrate (i.e., the spin-polarized current injected from a hybrid interface) can be understood by performing *ab initio* simulations. Furthermore, by employing an appropriate chemical functionalization of the adsorbed organic molecule and by applying specific bias voltages we can precisely control the spin-polarization of the hybrid organic-ferromagnetic interface. As challenging theoretical outlook, a very important question which remain to be answered is how the magnetic properties like magnetic exchange couplings and spin-orbit interactions of the underlying magnetic substrate are modified due to the interaction with non-magnetic organic materials. Very recently, we demonstrated that the adsorption of  $\pi$ -conjugated molecules on ferromagnetic surfaces mediates the creation of new local molecular magnetic units. More precisely, the organic-ferromagnetic interaction leads to a magnetic hardening effect, i.e., locally it increases the strengths of the magnetic exchange interactions of the magnetic atoms binding directly the molecule, stabilizes the magnetization direction and enhances the barrier for the magnetization switching with respect to the clean surface [71]. Even more interestingly, depending on the specific molecular structure and ferromagnetic substrate, a strong decoupling of the molecular mediated magnetic unit with respect to the magnetic electrode occurs (magnetic softening) and can be successfully used in building spintronic devices that work close to room temperature [12]. A detailed understanding and the precise control of the electronic effects responsible for the magnetic hardening and the magnetic softening effects induced by the adsorption of non-magnetic organic molecules on ferromagnetic substrates is the subject of future theoretical studies.

## 5 Acknowledgments

The computations were performed under the auspices of the VSR at the computer JUROPA and the GCS at the high-performance computer JUQUEEN operated by the JSC at the Forschungszentrum Jülich. We thank to Professor P. H. Dederichs for his guidance and fruitful discussions.

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