Impact on Interface Spin Polarization of Molecular Bonding to Metallic Surfaces

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We have studied the repercussion of the molecular adsorption mechanism on the electronic properties
of the interface between model nonmagnetic or magnetic metallic surfaces and metallo-organic phtha-
locyanines molecules (Pcs). Our intertwined x-ray absorption spectroscopy experiments and computa-
tional studies reveal that manganese Pc (MnPc) is physisorbed onto a Cu(001) surface and retains the
electronic properties of a free molecule. On the other hand, MnPc is chemisorbed onto Co(001), leading to
a dominant direct exchange interaction between the Mn molecular site and the Co substrate. By promoting
an interfacial spin-polarized conduction state on the molecule, these interactions reveal an important lever
to tailor the spintronic properties of hybrid organic-metallic interfaces.

The injection of electron spin across and away from the
interface between a ferromagnetic metal and an inorganic
semiconductor is driven by wave function transmission
across the spacer [1,2], as well as by the electronic prop-
erties of the interface. In the latter case, the appearance of
magnetic moments, induced on the atomic sites of the
semiconductor due to bonding-induced exchange interac-
tions with the ferromagnet, determine in turn which wave
functions will most efficiently hybridize into evanescent
states for tunneling transmission [3].

To this date, this pillar of our understanding of spin
electronics has yet to be verified experimentally [4].
Meanwhile, a rapid and accelerating convergence is occur-
ring between the fields of spin electronics and organic
electronics through incremental successes at spin-
polarized transport across ultrathin [5,6] or thin [7] organic
layers. A number of experimental reports have also drawn
attention to the peculiar electronic properties present at the
interface between the metals used as spin injectors and the
molecules that constitute the organic spacer layer. These
reports range from ferromagnetic (FM) coupling [8] be-
tween the metal site in metallo-organic molecules [see
Fig. 1(a)] and a ferromagnetic substrate, predicted to
underscore an indirect exchange interaction, to the inferred
presence of an electronic state within the organic layer's
forbidden gap [9] that appears to drive the device's spin-
tronic response [10]. These results are likely to reflect the
impact on transport of the chemical bonds between the
molecule and the ferromagnet [11].

We have studied the interface between model, metallic,
fcc(001)-oriented surfaces—either nonmagnetic Cu or fer-
romagnetic Co, and the metallo-organic molecule manga-
nese phthalocyanine (MnPc) [see Fig. 1(a)]. Experimental
samples were grown within the preparation chamber (base
pressure of $P = 5 \times 10^{-10}$ mbar) of the 7 T cryomagnet
setup maintained by the IPCMS and installed on the SIM

beamline at the Swiss Light Source. MnPc was sublimated
($P = 2$–3×10^{-9} mbar) so as to form ultrathin films (1–
5 ML; 1 ML = 4 Å) on Co(5 ML)/Cu(001) and Cu(001)
substrates. X-ray absorption spectroscopy (XAS) spectra
were acquired in total electron yield mode at $P < 2 \times
10^{-10}$ mbar by reversing both the circular polarity of the
photons and the sign of the external magnetic field. All
density functional theory calculations were carried out
using the PWSCF package [12] and the generalized gradient
approximation as an exchange-correlation functional with
the Perdew, Burke, and Ernzerhof parametrization [13].
We used the *ab initio* pseudopotential method with
Vanderbilt ultrasoft pseudopotentials [14]. A plane-wave
basis set was used with kinetic-energy cutoffs of 30 Ry at
the Γ point of the first Brillouin zone. Fcc Co(001) and fcc
Cu(001) surfaces were modeled by using periodic super-
cells, each made of 3 atomic layers of 8×8 atoms and
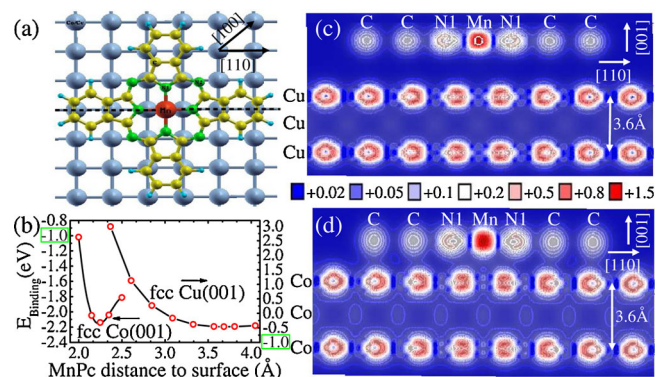vacuum. The supercell lattice parameter perpendicular to

FIG. 1 (color online). (a) Adsorption geometry of MnPc on an
fcc (001) surface. (b) Binding energy vs MnPc distance to the
Co(001) and Cu(001) surfaces. Charge density profiles [cut in a
(110) plane, along the line shown in panel (a)] for (c) MnPc/Cu
and (d) MnPc/Co in the plane perpendicular to the substrate.

the layers was 1.4 nm. Each supercell consisted of 249 atoms, including the 57 atoms of MnPc. Since Co was epitaxially grown on Cu, we used the fcc lattice parameter of 3.6 Å for both Co and Cu. The adsorption geometry of the Pc molecule on the (001) fcc surface is shown in Fig. 1(a). Increasing the vacuum spacing did not significantly alter the electronic structure or the total energy.

Both our experimental data and theory indicate that MnPc molecules lie flat onto the substrate, in agreement with a report on a similar system [9]. According to our *ab initio* calculations, the molecule adsorbs in the bridge position for both Cu(001) and Co(001). We found that other positions, like top and hollow, are less favorable. Figure 1(b) shows how the binding energy of the system is minimized when the MnPc molecule lies ~2.25 Å away from the Co surface and ~3.60 Å away from the Cu surface. The distance between the Mn and the first Co neighbors is 2.58 Å, close to the 2.51 Å separating two Co first neighbors. We find binding energies of 2.2 eV for MnPc/Co and 0.5 eV for MnPc/Cu. This shows that MnPc is more strongly bonded to Co than to Cu, which can be visualized in Fig. 1(c) and 1(d) through the charge density contours across the two interfaces along the direction indicated in Fig. 1(a). Indeed, while MnPc does not share much charge density with the surface Cu atoms, contours that propagate from Co atoms to the C, N and Mn molecular sites indicate the formation of covalent bonding and antibonding states. Thus, despite the same adsorption geometry, the molecular distance to the surface and the nature of the ensuing bond strongly depend on the couple molecule or surface that is considered [15]: MnPc is physisorbed onto Cu(001), while it is chemisorbed onto Co(001). Including van der Waals (vdW) interactions could shrink the MnPc-Cu distance to ~3.2 Å [16], but this still remains too large for chemisorption, in agreement with our experimental observation of a mostly unperturbed molecule (see hereafter). The already low MnPc-Co distance should be mostly unaffected by vdW interactions.

We present in Fig. 2 XAS spectra acquired at the N K edge with the photon's electric field out of the molecular plane [Fig. 2(a), N $1s \rightarrow \pi^*$] [17]; and in the plane [Fig. 2(b), N $1s \rightarrow \sigma^*$]. For both experimental geometries,
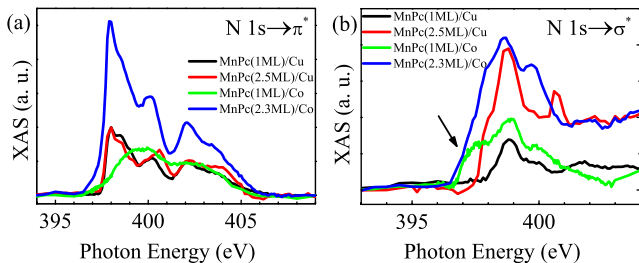
the spectra acquired for 1 ML and 2.5 ML MnPc thicknesses on Cu(001) are essentially the same. This shows that the electronic properties on the N site are the same whether at, or away from, the MnPc/Cu interface, in agreement with the aforementioned low impact on the molecule's electronic properties of physisorption onto Cu(001). For the MnPc/Co system, the XAS spectra acquired for 2.3 ML MnPc on Co(001) share some of the essential features of the XAS spectra found on Cu(001). However, referring to the N $1s \rightarrow \sigma^*$ transitions of Fig. 2(b), the edge is also weighed to lower energies by a vanishing contribution. When the MnPc thickness is decreased to 1 ML, this contribution now dominates the N pre-edge region, such that the onset of the N edge is effectively shifted by ~1 eV to lower energies. This is the manifestation on the XAS spectra of the formation of bonding states between N and Co, and their impact on the σ-dominated intramolecular electronic structure. Similarly, spectra acquired for MnPc(1 ML)/Co that probe the N $1s \rightarrow \pi^*$ transitions are strongly modified with a spectral weight to the center of the transition.

We present in Fig. 3 the σ and π N site-resolved partial density of states (PDOS) for the MnPc free molecule and MnPc/Cu(001) and MnPc/Co(001) interfaces. To identify what part of the electronic properties reflects the Mn-N bonds within the molecular plane, we have also plotted the σ- and π-resolved N PDOS for the metal-free H$_2$Pc molecule. The spectral tightening of the N π PDOS for MnPc/Co compared to MnPc/Cu is in line with experimental results [see Fig. 2(a)], underscoring the impact of the molecular chemisorption to Co through out-of-plane N bonds, and in contrast to physisorption onto Cu. However, the complexity of the spectra complicates any further analysis. We now turn in Fig. 3(b), to σ-resolved PDOS, to explain the presence of the XAS edge onset shift for MnPc(1 ML)/Co. Indeed, the N PDOS for the MnPc free molecule reveals the presence of molecular orbitals (MOs) starting precisely just above the Fermi level E_F. Since these MOs are absent from the H$_2$Pc N PDOS, we conclude that these MOs describe the Mn-N bond in the plane of the MnPc molecule. Yet, while these MOs remain essentially unchanged when the MnPc molecule is physisorbed onto Cu(001), an additional feature in the σ PDOS appears at
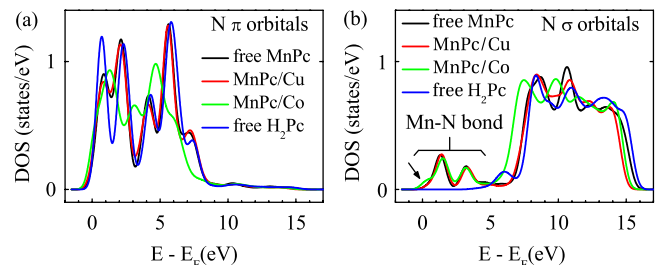
FIG. 2 (color online). XAS spectra at the N K edge acquired at $T = 300$ K and $H = 0$ for MnPc(1; 2.5 ML)/Cu and MnPc(1; 2.3 ML)/Co so as to probe (a) N $1s \rightarrow \pi^*$ and (b) N $1s \rightarrow \sigma^*$ transitions.

FIG. 3 (color online). Unoccupied N PDOS for (a) π and (b) σ orbitals of free MnPc and H$_2$Pc molecules, MnPc/Cu and MnPc/Co.
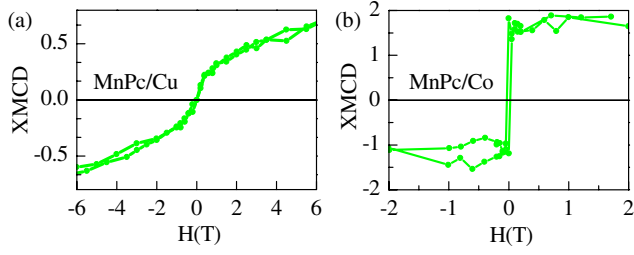
FIG. 4 (color online).   XMCD H dependence at the Mn L_3 edge   ($E = 640$ eV)   for   (a)   MnPc(2.5 ML)/Cu   and (b) MnPc(1 ML)/Co.

lower energies when the MnPc molecule is deposited onto Co(001) [see arrow on Fig. 3(b)], in agreement with experiment (see Fig. 2). These two bonding scenari also have consequences on the electronic and magnetic properties of the central Mn molecular site (see the supplementary information [19]).

We now discuss the magnetic field dependence of the x-ray magnetic circular dichroism (XMCD) amplitude at the Mn L_3 edge. For MnPc/Co [Fig. 4(b)], we observe a square loop that coincides with that found for Co, implying a FM coupling between the Mn molecular site and the Co substrate as reported in similar cases [8,20]. On the other hand, for MnPc/Cu, the unsaturated loop resembles the Brillouin dependence of a paramagnetic ion [see Fig. 4(a)].

To explain these stark differences in the XAS spectra for MnPc on Cu(001) and Co(001) surfaces, we present in Fig. 5 the calculated spin-polarized partial densities of states (PDOS) for the two systems, and compare them to the Mn PDOS found for a free MnPc molecule. Regarding MnPc on Cu, we find little hybridization near E_F between the Mn 3d and Cu 3d states: the DOS of MnPc on Cu(001) is close to that of a free molecule, implying that the MnPc/Cu interface is magnetically inactive in agreement with the XMCD field dependence. On the other hand, due to the exchange splitting, the Co 3d band exhibits a substantial energy overlap with the Mn 3d PDOS. Because of the resulting hybridization between Mn 3d and Co 3d states, the majority spin Mn PDOS is smeared to resemble that of Co, while the multiplet features in the minority spin Mn PDOS are broadened. While the calculated magnetic

moment of the Mn site for the MnPc molecule on Cu is the same as that for a free molecule (3.47 μ_B), it is reduced for a MnPc molecule on Co (2.90 μ_B). A similar reduction in magnetic moment was observed by Hu *et al.* for MnPc or FePc on Au(111) surface, while a slight increase of the magnetization of Fe octaethylporphyrin chloride (OEP) was obtained by Wende *et al.* [8,15]. These results imply that the MnPc/Co interface is magnetically active, in agreement with the experimentally observed FM coupling. Our experiment and theory thus depict the MnPc molecule as physisorbed onto Cu(001) with the electronic properties of a free molecule, thus leading to a magnetically inactive interface. On the other hand, the chemisorption of MnPc onto Co(001) at a 2.25 Å distance leads to out-of-plane bonds between the Mn, N and C molecular sites and Co surface sites as underscored in the data of Figs. 2–5. The small change in the in-plane Mn-N MO, which would take part in an indirect FM interaction between Mn and Co, is overshadowed by the large changes to out-of-plane MOs. As explained in [19], chemisorption could explain the alteration of the multiplet structure at the Mn L_3 edge. We therefore attribute the observed FM coupling between Co and Mn to a direct coupling, as suspected by Scheybal *et al.* regarding similar molecules [20]. This is in contradiction to Wende *et al.* who reported for a similar molecule, namely OEP, a distance [8] that was too large [21] and put forward an indirect coupling mechanism mediated by the N surrounding the central element [8].

To assess the spintronic impact of this magnetically active MnPc/Co interface, we now discuss spin-polarized transport channels at E_F. We present in Fig. 6 spin-polarized spatial maps, taken along the direction shown in Fig. 1(a), of the DOS, integrated over $E_F < E < E_F + 0.15$ eV so as to realistically reflect the effects of broadening. Generally, the molecule's spin ↓ DOS is one order of magnitude larger than the spin ↑ DOS, in line with the Co DOS. In particular, the spin ↓ DOS on the Mn site is parallel with the Co spin ↓ DOS, in agreement with the observation of FM coupling discussed above. We find that a small spin ↑ DOS bridges the Mn, N and C sites to the Co sites, in
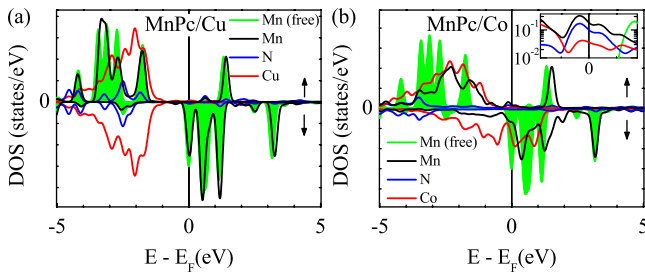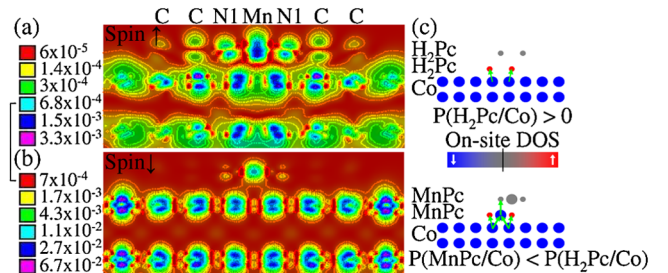

FIG. 5 (color online).   The spin-polarized PDOS of Mn within the free MnPc molecule is compared with the Mn, N and Cu(Co) spin-polarized PDOS for MnPc on (a) Cu(001) and (b) Co(001). Inset to panel (b): spin ↑ PDOS of MnPc/Co near E_F.

FIG. 6 (color online).   Charge density profiles over the energy range $E_F < E < E_F + 0.15$ eV of MnPc/Co(001) for spin (a) ↑ and (b) ↓ charge carriers. (c) On-site DOS at the H$_2$Pc/Co and MnPc/Co interfaces. Green arrows indicate wave function hybridization toward decay into the hypothetical Pc film. Only the central and N1 molecular sites are represented for clarity.

agreement with data from the inset to Fig. 5(b). The spin ↓ channel is, however, driven by a strong metallic bridge between Mn and Co. Referring to Fig. 6(c), if the Mn-Co bridge is absent, i.e., in the case of a metal-free H_2Pc/Co interface, then weak metallic conduction in the spin ↑ channel will occur from the Co sites to the C and N sites at the interface. In analogy to wave function hybridization arguments made for inorganic spintronics [3], this should lead to a positive interfacial spin polarizarion $P_{int} > 0$. Relative to this case, if the bridge is present, e.g., for the MnPc/Co interface, the many weak spin ↑ channels mediated by the N and C sites [Fig. 6(a)] will compete with a strong Co-Mn spin ↓ conduction channel [Fig. 6(b)] [22] to define the amplitude and sign of P_{int}, whether through metallic or localized interface states [24]. See [19] for a more rigorous demonstration of this spintronics control over a molecular magnetic junction (e.g., in a scanning tunneling microscopy experiment; STM).

We now qualitatively discuss the impact of our results on real devices with a finite semiconductor thickness. As discussed previously (see Fig. 2), the properties of additional layers away from the interface should resemble those of bulk MnPc. As we argue in [19], both the highest occupied molecular orbital and lowest unoccupied molecular orbital of bulk MnPc should be weighed with Mn character. This means that wave functions with Mn character shall efficiently transmit (see e.g., [1,2]) across bulk MnPc. This implies that the control over P_{int} through the presence of Mn in MnPc relative to H_2Pc shall carry over to an effective spin polarization for elastic tunneling (See [19] for more information). These results thus explicitly demonstrate how an interface state can drive the spin-polarized tunneling properties of a device, as was recently argued to account for large values of magnetoresistance across an organic magnetic tunnel junction [10]. In addition, our results also show how to control the spintronic response of this interface state. To extend this argument to the diffusive transport regime, one should also take into account the organic semiconductor resistivity and spin diffusion length [25], which depends on the nature of transport [10].

In conclusion, we have experimentally and theoretically examined the consequences for molecular spintronics of the adsorption mechanisms that bind MnPc to model surfaces. While MnPc is physisorbed onto Cu(001) and retains the electronic structure of a free molecule, chemisorption onto Co(001) leads to covalent bonding and direct ferromagnetic coupling between the molecule's Mn site and the Co surface sites. The ensuing metallic bridge across the two sites effectively shifts the onset of tunneling onto the molecule, which is thus part of the electrode. We find that removing the Mn site from the Pc molecule will change the interfacial tunneling spin polarization to be observed in a STM experiment, and also in principle the effective spin polarization of a tunnel junction interface. This research underscores the tremendous potential to craft the interfacial electronic properties for molecu-

lar spintronic devices with novel responses, and, in particular, to achieve control over the sign of the interfacial tunneling spin polarization through only a subtle modification of the interface structure. This ease of spintronics control is unparalleled in inorganic spintronics [26].

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