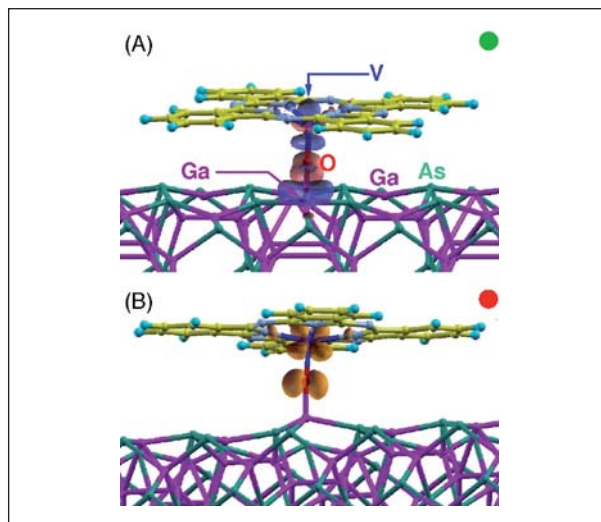


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## Controlling the Magnetic Properties of a Single Phthalocyanine Molecule through its Strong Coupling with the GaAs Surface

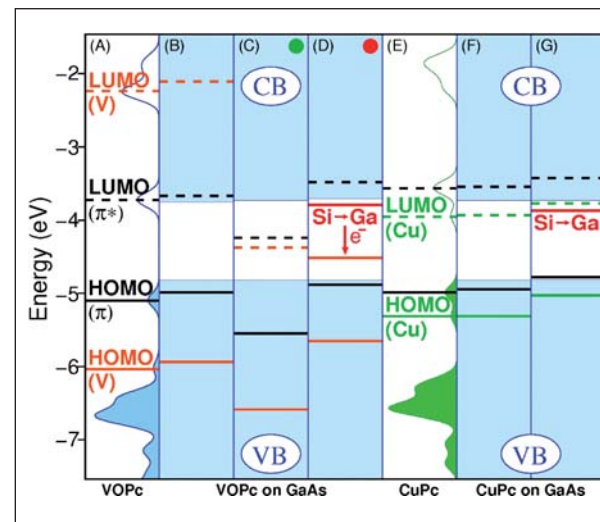
In the discipline of spintronics, the spin degree of freedom of mobile charge carriers is exploited, in addition to their charge, to carry information as well as to realize different interactions with magnetic materials (1). Recent research efforts in this field have been directed toward organic materials, in particular, toward the properties of single metallo-organic molecules (MOMs), like phthalocyanines (Pcs), which can be seen as single magnetic atoms, e.g., a central transition metal (TM), dressed with an organic macrocycle (2,3). In this regard, several studies have investigated electron and spin injection as well as magnetic coupling and switching in MOMs adsorbed on magnetic or nonmagnetic metals and semiconductors (see, e.g., Refs. 4-6). A major goal of all of these investigations is to control and manipulate individual spins in a single molecule by exploiting their coupling to the environment. In this context, we focus here on the paramagnetic vanadyl-phthalocyanine (VOPc), where the central metal is replaced by a metal-non metal (V-O) group, and propose a TM-substrate coupling mediated by the central O atom. Moreover, we consider the Ga-rich GaAs (001)  $z(4 \times 2)/c(8 \times 2)$  surface as a semiconductor substrate. The properties of the VOPc/GaAs system have been investigated by using first-principles DFT methods in the U-corrected local spin density generalized gradient approximation (LSD-GGA+U) and a supercell approach (7,8). The CuPc/GaAs system has been also considered for comparison. Further details on the methods are given in Ref. 9. The electronic structure of the first component of the VOPc/GaAs system, the magnetic VOPc, is characterized by a HOMO(p) (highest occupied molecular orbital) and a doubly degenerate LUMO(p\*) (lowest unoccupied molecular orbital) highly delocalized on the organic macrocycle. Moreover, the VOPc presents two frontier orbitals involving the central V atom and responsible for its magnetic properties: a single-occupied MO composed of a V 3d atomic orbital, HOMO(V), and an unoccupied MO composed of a different V 3d atomic orbital and an O 2p atomic orbital, referred to as LUMO(V).

The interaction of the VOPc molecule with the GaAs surface leads to the formation of a molecule-surface O-Ga bond (Figure 1A), as indicated by an O-Ga distance of 1.77 Å, an adsorption energy  $E[\text{ads}]$  of 2.41 eV, and by the difference density map  $r_{\text{diff}}$  [VOPc/GaAs], shown in the same Figure. At the onset of the molecule-surface interactions, this difference density indicates indeed a charge displacement toward the O atom and the O-Ga bond region, both from the V and surface Ga atoms, thus settling a V-O-Ga bridging bond. To clarify the effects of the V-O-Ga bond on the electronic and magnetic properties of the VOPc molecule, let us consider the electronic levels of the isolated molecule, of the molecule adsorbed on the GaAs surface with the O atom upward, and of the molecule bonded to the surface (shown in Figure 1A), schematically represented in Figure 2A-C, respectively, together with the valence band (VB) and conduction band (CB) edges of GaAs. The comparison of Figure 2A with Figure 2B shows that without a bridging bond with the substrate, the VOPc electronic structure is unchanged. On the contrary, Figure 2C shows that the formation of the V-O-Ga bond has impressive effects on the LUMO(V), which decreases about 2 eV



**Fig. 1.** – VOPc molecule interacting with the Ga-rich GaAs (001) surface. (A) Equilibrium geometry of the VOPc/GaAs system and isosurface of the difference electron density ( $r_{\text{diff}}$ ). The  $r_{\text{diff}}$  map shows the displacements of electronic charge at the molecule-surface interaction. Red surfaces cover areas where the difference is positive, and blue surfaces cover areas where it is negative. (B) Equilibrium geometry of the VOPc/(n-doped)GaAs system and  $|y|^2$  plot of the LUMO(V†) (see the text). The  $|y|^2$  isosurfaces correspond to the value of  $0.005e/(\text{a.u.})^3$ . The green and red full circles indicate a correspondence between the equilibrium configurations of the present Figure and the electronic levels of Figure 2.

in energy, locates in the GaAs energy gap and, most interestingly, reverses its position with respect to the LUMO(p\*). Such changes of the VOPc electronic structure can have important effects on the magnetic behavior of this molecule. First, because carrier injection involves the frontier orbitals, let us note that in isolated molecules such orbitals are the macrocycle spin-insensitive HOMO (p) and LUMO (p\*), whereas in the bonded molecule the carrier injection involves the new LUMO(V) which has a majority spin character and is strongly localized on the VO central group carrying the VOPc magnetic moment. Then, we probed this new LUMO(V) by investigating a charge transfer from a GaAs donor impurity to this orbital. We have simulated an n-doped GaAs (n-GaAs) by substituting a Ga(III) with a Si(IV) atom, which induces a donor level (represented by a red line in Figure 2D) near the minimum of the GaAs CB. The donor level, higher in energy than the LUMO(V) (now the proper lowest unoccupied energy level of the VOPc/GaAs system), induces a charge-transfer process from the semiconductor to the molecule, as indicated by the red arrow in Figure 2D, which fills the LUMO(V) with one electron. The filled LUMO(V), hereafter referred to



**Fig. 2.** – Total (spin up+spin down) DOS and electronic levels of the VOPc and CuPc molecules, isolated or interacting with the GaAs (001) surface. All of the levels are aligned to a common reference. The HOMO(p) and LUMO(p\*), related to the macrocyclic ligand, are represented by full and dashed black lines, respectively. The HOMO(V) and LUMO(V), (HOMO(Cu) and LUMO(Cu)) related to the central V (Cu) atom, are represented by full and dashed orange (green) lines, respectively. The blue color background delimits the valence band (VB) and conduction band (CB) regions relative to the GaAs band structure. A dopant donor level is indicated by a red line. (A) Isolated VOPc molecule; (B) VOPc molecule interacting with the GaAs surface (the O atom points upward); (C) VOPc molecule bonded to the GaAs surface (the O atom points downward); (D) VOPc molecule bonded to an n-type, Si-doped GaAs surface (i.e., the case of surface to molecule charge transfer inducing a high-spin configuration); (E) Isolated CuPc molecule; (F) CuPc molecule interacting with the GaAs surface; (G) CuPc molecule interacting with an n-doped GaAs surface. The green and red full circles indicate a correspondence between electronic levels of the present Figure and the equilibrium configurations of Figure 1.

as LUMO(V†), maintains its location in the GaAs energy gap. These results indicate that the new LUMO(V) is potentially available for electron injection in the bonded VOPc molecule. A further remarkable consequence of the VOPc-GaAs bonding is that the filled LUMO(V†) is highly spin selective; the triplet configuration (total magnetic moment 2 mB), involving the LUMO(V†), is 1.0 eV lower in total energy than the singlet one. Finally, it has to be taken into account that in the bonded VOPc the LUMO(V) orbital as well as the LUMO(V†) are partially overlapped with the LUMO(p\*) orbital. This suggests the possibility of coupling of electrons injected in the LUMO(p\*) orbital with the electron occupying the LUMO(V†). It is worth stressing that none of the above effects have been found with the nonbonded VOPc (O in the upward direction) because

no substrate-to-molecule charge transfer is induced by a Si donor in the GaAs substrate. In this case, the LUMO(V) and the LUMO(p\*) are higher in energy than the Si donor level, which rests occupied by its exceeding electron. A similar result is found for the CuPc/GaAs system. The electronic levels of the CuPc molecule when isolated, adsorbed on the surface, and adsorbed on the n-type surface, are shown in Figure 2E-G, respectively. These panels show that such levels are almost unperturbed by the interaction with the surface and that no surface-to-molecule charge transfer occurs in presence of a Si donor.

As for the non bonded VOPc, the exceeding donor electron occupies its shallow level close to the CB and located below both the LUMO(Cu) and the LUMO(p\*). It may be noted that the systems considered in the panels A-F of Figure 2 are all characterized by a total magnetic moment of 1 mB, except for the system of panel D, which presents a total magnetic moment of 2 mB. The resulting theoretical picture suggests that the effects of the VOPc-GaAs strong coupling on the magnetic behavior of the VOPc molecule could be observed in scanning tunneling microscopy (STM) experiments involving a single molecule adsorbed on an n-GaAs surface or in electron transport experiments performed in single-molecule transistors (10,11), where a GaAs substrate is used as a back gate. In the former case, an electron injected in the LUMO(p\*) orbital is expected to give rise to an appreciable spin coupling to the

LUMO(V†) electron because of the LUMO(p\*)-LUMO(V†) overlap, the high spin localization of the latter orbital, and the high stability of the triplet spin configuration discussed above. Altogether, these conditions should favor the appearance of Kondo-like resonances. Similarly, Kondo effects should be observed in single-molecule transistors where, in addition, the Kondo resonances could be tuned reversibly using the gate voltage to change the spin configuration of the V atom. Such a kind of experiment should evidently be the key property of the proposed VOPc/GaAs system; that is, the injection of holes in the GaAs VB can neutralize the effects of the n-type doping by removing the electron transferred to the LUMO(V†), thus changing the VOPc triplet state to a doublet one. In other words, the VOPc triplet state can be switched on/off by injecting carriers in the semiconductor. In conclusion, present results show that the equipment of a paramagnetic Pc with a central metal-nonmetal pair permits us to realize a strong molecule-semiconductor coupling that directly involves the central metal and can be exploited to manipulate its magnetic properties.

#### Acknowledgment

We acknowledge the CINECA award under the ISCRA initiative, for the availability of high performance computing resources and support.

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