Tuning the Magnetic Interaction between Manganese Porphyrins and Ferromagnetic Co Substrate through Dedicated Control of the Adsorption

3 AUTHORS:

Md. Ehesan Ali
Institute of Nano Science and Technology
26 PUBLICATIONS 515 CITATIONS

SEE PROFILE

Biplab Sanyal
Uppsala University
239 PUBLICATIONS 3,286 CITATIONS

SEE PROFILE

Peter M. Oppeneer
Uppsala University
315 PUBLICATIONS 4,801 CITATIONS

SEE PROFILE

Tuning the Magnetic Interaction between Manganese Porphyrins and Ferromagnetic Co Substrate through Dedicated Control of the Adsorption

Md. Ehesan Ali,* Biplab Sanyal, and Peter M. Oppeneer

Department of Physics and Materials Science, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

Received: March 24, 2009; Revised Manuscript Received: June 17, 2009

We report, on the basis of density-functional theory+U (DFT+U) calculations that metalloporphyrins can adsorb on ferromagnetic metal surfaces in two distinct configurations. Two separate adsorption minima are obtained for manganese porphyrin (MnP) on Co from our DFT+U total energy calculations, which correspond to strong and weak adsorption strengths, respectively. By steering the nature of adsorption, we find that distinct chemical interactions as well as magnetic exchange interactions between the metalloporphyrin and the metal surface can be realized. We furthermore show that a switching of the MnP molecule's spin state can occur even for the weakly adsorbed case. This new discovery opens up prospects for engineering the chemical and magnetic exchange interaction in new functionalized spintronic materials.

Magnetic molecules deposited on metal surfaces are currently of great interest due to their expected use as molecular spintronic materials in nanodevices.[1,2] It has already been shown recently that metallorganic molecules, such as metalloporphyrins and -phthalocyanines, can be assembled on substrates, positioned, and moved to desired positions.[3,4] A second important feature for the application of metallorganics in molecular spintronic devices is related to the spin of the open-shell 3d ion, which gives rise to magnetic interactions with magnetic surface atoms. Induced magnetic ordering and switching of metalloporphyrins on magnetic surfaces through the molecule−surface interaction was recently shown,[5,6] as well as tuning of this interaction through preadsorbed oxygen.[7]

A fundamental understanding of the interaction between the metalloporphyrin and metal substrate is far from being achieved. Varying molecule−surface interaction strengths have been observed with scanning tunneling microscopy.[8] A weak and indirect interaction between the 3d ion and the surface was concluded from recent X-ray magnetic circular dichroism experiments.[5,6] X-ray and ultraviolet photoemission spectroscopy on Co metalloporphyrins on Ag showed conversely a more pronounced Co−Ag interaction.[9] The reasons for these differences have not yet been solved.

Here we demonstrate, using density-functional theory (DFT) based calculations, that metalloporphyrins can be adsorbed on metal surfaces in two *distinct* stable configurations that correspond to a strong and a weak molecule−surface interaction, respectively. Using manganese porphyrin (MnP) on Co as a prototypical case, we obtain for the case of strong chemical interaction a relatively short molecule−surface distance of 2.1 Å, while in the other case we compute a large separation of 3.5 Å and a much weaker chemical interaction. The former case corresponds evidently to chemisorption, whereas the later is, as will be discussed below, close to physisorption. Our investigation reveals that through control of the adsorption process, distinct molecule−surface interactions can be realized,

and also, that depending on the type of metalloporphyrin, a transition of the metallorganic spin state can occur upon adsorption.

To investigate the adsorption process of a manganese porphyrin (MnP) molecule on a ferromagnetic Co surface, we performed DFT+U calculations. Our calculations have been performed by the VASP full-potential plane-wave code, in which pseudopotentials together within the projector augmented wave method are used.[10] A kinetic energy cutoff of 400 eV was employed for the plane waves. For the DFT exchange-correlation functional, we used the generalized gradient approximation (GGA) in the Perdew−Wang parametrization.[11] Recently, it has been shown that the commonly used DFT-GGA approach fails in describing adequately the high-spin state of metalloporphyrins.[12] A correct description of the molecular spin state can be achieved when strong Coulomb correlations within the open 3d-shell are taken into account. The latter can appropriately be done through the DFT+U approach, in which an additional Coulomb interaction in 3d-shell is supplemented, defined through the Coulomb and exchange parameters U and J. In our calculations, the U and J were taken to be 4 and 1 eV, respectively; earlier, these values were shown to provide the correct spin state for metalloporphyrins.[12,13] The metallic surface was modeled through three atomic layers Co (adopting the fcc Co lattice parameter of 3.61 Å). We performed full geometric optimizations of the porphyrin molecule and its distance to and position on the surface. To reduce the computational effort, we kept the Co atoms fixed in most simulations. Through test calculations we verified that this is indeed a good approximation; complete relaxation of all atomic distances revealed that the molecule−surface distances (and consequently, interactions) did not change, but a small relaxation of the top to second Co layer occurred. The whole simulation cell consisted of 187 atoms; for the reciprocal space sampling we used $2 \times 2 \times 2$ Monkhorst-Pack *k*-points.

First, we performed full geometric relaxation of the MnP molecule on the surface. Depending on the initial molecule−surface separation, we observe convergence to two distinct, stable optimized geometries. In one of these, the obtained short equilibrium distance reflects strong chemical interaction between the molecule and the surface Co atoms, typical of chemisorption.

---

* To whom correspondence should be addressed. E-mail: ehesan.ali@fysik.uu.se.
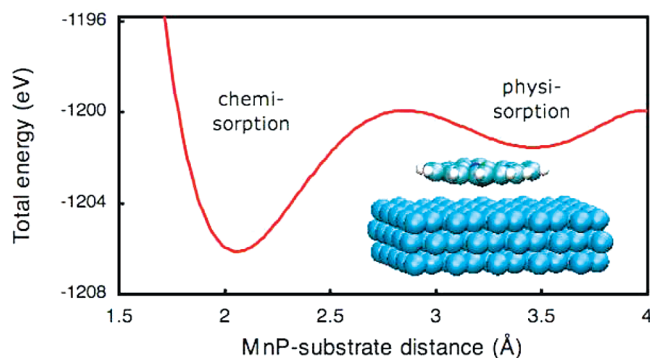
Figure 1. Calculated DFT+U total energy vs the MnP molecule−surface layer distance. The two energy minima correspond to the strongly and weakly adsorbed state, respectively.

In the other geometry, we also optimized the system by placing the MnP at the three different possible locations on the surface, which are the "on top", "bridge", and "hollow" positions as described by Leung et al.[13] We find that the total energies of these three positions are very similar, signifying a very weak site preference of the molecule on the surface. This is typical for physisorption, which is driven mainly by higher-order electrostatic interactions. Conversely, for the chemisorption case, we find that the Mn atom *strongly prefers* the top position of the second layer.

We emphasize that the weakly interacting case is its appearance similar to physisorption. Generally, for physical adsorption, the long-range van der Waals forces that are due to dipole−dipole interaction are important but present implementations of DFT do not properly describe the van der Waals forces.[14] In itself, long-range electrostatic interactions are incorporated in DFT calculations employing nonlocal GGA functionals, but the correct asymptotics of these approximate functionals is an issue.[14] Hence, the weakly adsorbed situation described here cannot be exclusively due to a pure van der Waals type attraction, but electrostatic forces are nonetheless present, even if there is no direct overlap between the orbitals of the substrate and the molecule. Consequently, in the absence of a chemical bonding, the weakly adsorbed state can be considered as being close to physisorption.

We have computed the total energies of the system as a function of the distance between the MnP and Co surface top layer; the obtained total energy is shown in Figure 1. The total energy curve clearly exhibits two minima, one at 2.1 Å and a shallow one at around 3.5 Å. The difference of the total energies of these two adsorption types is not small (5.6 eV).

To explain the two different chemical interactions occurring between MnP and the Co surface, we have investigated the electronic properties of these adsorbed MnPs in addition to comparing to those of a free MnP molecule. Figure 2 shows the computed electron localization function (ELF) of weakly and strongly adsorption of MnP as well as the spin-resolved partial density of states (DOS) of weakly adsorbed MnP. The ELF given in Figure 2A does not show a noticeable chemical bonding arising from direct overlap between orbitals of the molecule and substrate for the weakly adsorbed state. Conversely, Figure 2B clearly reveals a considerable amount of hybridization between the N and C p-orbitals and the d-orbitals of Co surface atoms in the case of chemisorption. The DOS plot for chemisorbed MnP, given in Figure 3, shows that hybridization has occurred in both bonding and antibonding regions. Hence, the chemisorption is driven by significant pπ−dπ and dπ−pπ* chemical bonding between the substrate
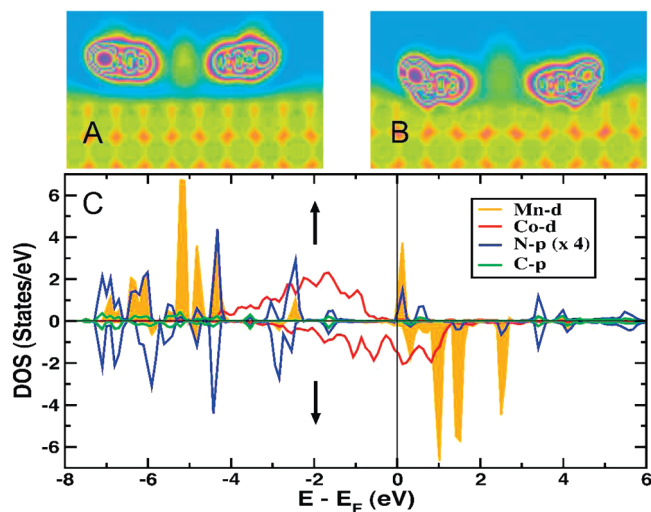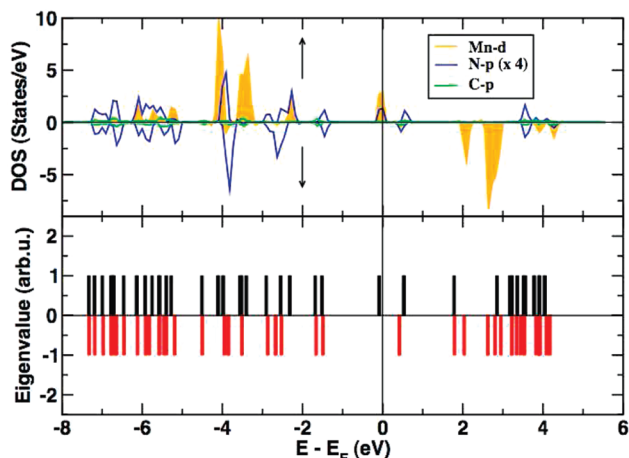

Figure 2. Electron localization function (ELF) computed for weakly adsorbed (A) and chemisorbed (B) MnP on Co (blue color represents low (i.e., 0) ELF and red color high (i.e., 1) ELF). (C) Spin-resolved partial DOS of weakly adsorbed MnP on Co.
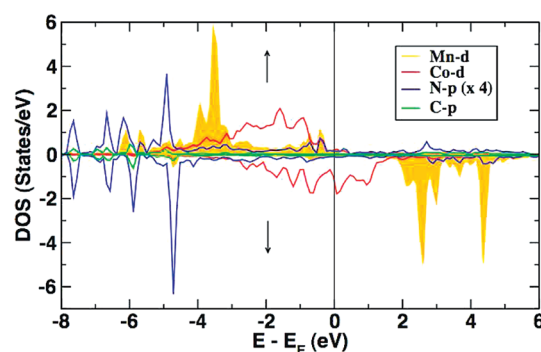
Figure 3. Spin-resolved partial density of states (DOS) of a MnP molecule chemisorbed on a ferromagnetic Co surface.

and porphyrin ring. This bonding brings the MnP, especially C, N, but also Mn, atoms closer to the Co surface. As a result, a modest direct hybridization of Mn and Co appears (see Figure 2B). Because of the absence of such chemical interaction for the terminal H atoms, the H atoms move up from the porphyrin plane to minimize their overlap with the surface atoms.

In the weakly adsorbed case, MnP has definitely a weaker interaction with the surface (cf. Figure 2A). A detailed comparison with the free MnP molecule reveals nonetheless some intriguing differences. A table with optimized geometries of the free MnP and the weakly and strongly adsorbed MnP molecules is provided in the Supporting Information. The free molecule is computed to have a planar geometry (D_{4h} symmetry) with a Mn−N bond length of 2.10 Å. The free molecule's spin state, furthermore, is computed to be S = 5/2, which is the high-spin value that is expected for a half-filled 3d shell with strong Hund's rule coupling (cf. ref 13). In contrast to our DFT+U result, earlier DFT calculations[15] predicted an intermediate S = 3/2 spin for MnP. Upon weak adsorption, we find that the molecule's symmetry on the substrate is lowered (to C_{4v}) and that, due to a weak electrostatic interaction, the Mn atom deviates out of the macrocyclic plane by 0.14 Å toward the substrate. Simultaneously, the Mn−N bond-length is reduced by 0.09 Å and the molecule slightly bends with its metal center toward the surface. The computed DOS (Figure 2C) reveal the common, pronounced hybridization of Mn-d and N-p orbitals. It is noteworthy that when compared to the DOS of free MnP

Interaction between Mn Porphyrins and Ferromagnetic Co

J. Phys. Chem. C, Vol. 113, No. 32, 2009 **14383**

Figure 4. Top: spin-resolved partial DOS of the free MnP molecule. Bottom: spin-projected molecular energy levels of the MnP molecule (black bars represent spin-up, red bars spin-down energy levels).

(Figure 4) one observes that one Mn-d, N-p hybridized level has shifted to above the Fermi energy E_F for the weakly adsorbed MnP. Consequently, the magnetic moment on Mn is reduced: the MnP spin state changes from S = 5/2 for the free molecule to S = 2 for weakly adsorbed MnP. The reduction of the moment occurs as the spin-up (spin-down) channel loses (gains) 0.5 (0.25) electron, giving rise to less charge imbalance in two spin channels for the weakly adsorbed MnP. An electrostatic redistribution hence plays a role in the spin-crossover to the S = 2 spin state. A calculation for the bend molecule without substrate additionally reveals that the deviation from planarity supports a transition to a lower spin state, S = 3/2; through the weak charge redistribution, this value increases to S = 2 for the weakly adsorbed state. Chemisorption leads to an elongation of all bonds in the macrocyclic porphyrin ring without losing the planarity. The planarity in the macrocycle arises from the $sp^2 - sp^2$ σ-bonded framework. The remaining p-orbital in each sp^2-hybridized atom provides extra stability through participating in double bond formation and aromaticity, which shortens the bond distances. Upon chemisorption, the atomic hybridization of the macrocycle does not change, hence the planarity persists, but now the p-orbitals of the macrocyclic atoms interact with the surface atoms, leading to the increase of bond distances. Because of the molecule−surface hybridization, we also obtain for chemisorbed MnP a moment of 4.26 μ_B, between the S = 2 and 5/2 values. In the weakly adsorbed state we find, in addition to the rather weak direct Mn−Co interaction, a weak interaction between Co-d orbitals and N-p orbitals, leading to a spin-polarization of 0.06 μ_B on each N. The spin-polarization of the N atoms in the free and the chemisorbed molecules is, conversely, negligible. A previous investigation[6] of Fe-porphyrin (FeP) on Co also indicated a spin-polarization occurring on the N's, but the FeP was not found to suffer a change in its (S = 1) spin state upon physisorption. The situation is subtly different for MnP, where the high-spin free molecule has a hybridized Mn-d level just below E_F, giving rise to a spin state switching already for a weak interaction.

We further studied the magnetic exchange interaction between the surface atoms and the metalloporphyrin for the two adsorption geometries by carrying out DFT+U total energy calculations for ferromagnetic (FM) and antiferromagnetic (AFM) alignments of the Mn and Co spins. We always obtain the ferromagnetic alignment to be most favorable. The magnetic

exchange interaction ($E^{AFM} - E^{FM}$) is, with 34 meV, weak for weakly adsorbed MnP and with 123 meV considerably stronger for chemisorbed MnP. Thus, next to stronger chemical bonding, the magnetic interaction is enhanced, too, for the chemisorbed molecule.

In conclusion, using MnP on Co as a prototypical case, we have shown that the chemical and magnetic interactions between metalloporphyrins and metallic substrates can be modified through the different adsorption processes. Depending on the type of porphyrin and metallic surface, a spin state switching of the molecule may occur. These findings offer new prospects for tuning the properties of molecular spintronic devices through dedicated control of the molecule−surface interaction.

Supporting Information Available: Optimized geometry of gas-phase manganese porphyrin (MnP), comparison of bond lengths, out-of-plane displacement of the Mn atom (Δz), and the dihedral angle in MnP for three difference cases. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rocha, A. R.; Garcia-Suarez, V. M.; Bailey, S. W.; Lambert, C. J.; Ferrer, J.; Sanvito, S. *Nat. Mater.* **2005**, *4*, 335–339.

(2) Mannini, M.; Pineider, F.; Sainctavit, P.; Danieli, C.; Otero, E.; Sciancalepore, C.; Talarico, A. M.; Arrio, M.-A.; Cornia, A.; Gatteschi, D.; Sessoli, R. *Nat. Mater.* **2009**, *8*, 194–197.

(3) Jung, T. A.; Schlitter, R. R.; Gimzewski, J. K.; Tang, H.; Joachim, C. *Science* **1996**, *271*, 181–184.

(4) Barth, J. V. *Annu. Rev. Phys. Chem.* **2007**, *5*, 375–407.

(5) (a) Scheybal, A.; Ramsvik, T.; Bertschinger, R.; Putero, M.; Nolting, F.; Jung, T. A. *Chem. Phys. Lett.* **2005**, *411*, 214–220. (b) Wang, Y.; Kröger, J.; Berndt, R.; Hofer, W. A. *J. Am. Chem. Soc.* **2009**, *131*, 3639–3643.

(6) Wende, H.; Bernien, M.; Luo, J.; Sorg, C.; Ponpandian, N.; Kurde, J.; Miguel, J.; Piantek, M.; Xu, X.; Eckhold, Ph.; Kuch, W.; Baberschke, K.; Panchmatia, P. M.; Sanyal, B.; Oppeneer, P. M.; Eriksson, O. *Nat. Mater.* **2007**, *6*, 516–520.

(7) Bernien, M.; Miguel, J.; Weis, C.; Ali, M. E.; Kurde, J.; Krumme, B.; Panchmatia, P. M.; Sanyal, B.; Piantek, M.; Srivastava, P.; Baberschke, K.; Oppeneer, P. M.; Eriksson, O.; Kuch, W.; Wende, H. *Phys. Rev. Lett.* **2009**, *102*, 047202.

(8) (a) Barlow, D. E.; Scuderiero, L.; Hipps, K. W. *Langmuir* **2004**, *20*, 4413–4421. (b) Iancu, V.; Deshpande, A.; Hla, S.-W. *Nano Lett.* **2006**, *6*, 820–823. (c) Gao, L.; Ji, W.; Hu, Y. B.; Cheng, Z. H.; Deng, Z. T.; Liu, Q.; Jiang, N.; Lin, X.; Guo, W.; Du, S. X.; Hofer, W. A.; Xie, X. C.; Gao, H.-J. *Phys. Rev. Lett.* **2007**, *99*, 106402. (d) Zhao, A.; Hu, Z.; Wang, B.; Xiao, X.; Yang, J.; Hou, J. G. *J. Chem. Phys.* **2008**, *128*, 234705.

(9) Lukasczyk, T.; Flechtner, K.; Merte, L. R.; Jux, N.; Maier, F.; Gottfried, J. M.; Steinrück, H.-P. *J. Phys. Chem. C* **2007**, *111*, 3090–3098.

(10) (a) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561. (b) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186. (c) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979. (d) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(11) Perdew, J. P.; Wang, J. *Phys. Rev. B* **1992**, *45*, 13244–13249.

(12) (a) Panchmatia, P. M.; Sanyal, B.; Oppeneer, P. M. *Chem. Phys.* **2008**, *343*, 47–60. (b) Oppeneer, P. M.; Panchmatia, P. M.; Sanyal, B.; Eriksson, O.; Ali, Md. E. *Prog. Surf. Sci.* **2009**, *84*, 18–29. (c) Scherlis, D. A.; Cococcioni, M.; Sit, P.; Marzari, N. *J. Phys. Chem. B* **2008**, *111*, 7384.

(13) Leung, K.; Rempe, S. B.; Schultz, P. A.; Sproviero, E. M.; Batista, V. S.; Chandross, M. E.; Medforth, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 3659–3668.

(14) (a) Andersson, Y.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **1996**, *76*, 102–105. (b) Kohn, W.; Meir, Y.; Makarov, D. E. *Phys. Rev. Lett.* **1998**, *80*, 4153–4156.

(15) Liao, M.-S.; Watts, J. D.; Huang, M.-J. *Inorg. Chem.* **2005**, *44*, 1941–1949.

JP902644Q