Electronic and Magnetic Properties of Metal Phthalocyanines on Au(111) Surface: A First-Principles Study

Zhenpeng Hu, Bin Li, Aidi Zhao, Jinlong Yang,* and J. G. Hou*

Hefei National Laboratory for Physical Sciences at Microscale, University of Science & Technology of China, Hefei, Anhui 230026, People’s Republic of China

Received: May 15, 2008; Revised Manuscript Received: June 24, 2008

A first-principles study is performed to explore the electronic and magnetic properties of several 3d transition metal phthalocyanines (including MnPc, FePc, NiPc, and CuPc) adsorbed on a Au(111) surface. Our results show that the most favorite adsorption site is the top site for MnPc molecule whereas it is the hcp site for other molecules. The electronic structures of MnPc and FePc change obviously when they are adsorbed onto the Au(111) surface, while those of NiPc and CuPc change slightly near the Fermi level due to the weak molecule–surface interactions. By analyzing the properties of d orbitals at the spatial and energy scales, we have discussed the possible Kondo effect related to these metal phthalocyanines adsorbed on the Au(111) surface.

Introduction

Metal phthalocyanine (M-Pc, Figure 1) molecules are man-made macrocycles conventionally used as dyes and pigments. Recently, these molecules have been found to be of much potential in nanotechnology applications such as light-emitting diodes,1,2 field-effect transistors,3,4 photovoltaic cells,5,6 and single-molecule devices.7 Various experimental techniques, such as photoemission spectroscopy,8,9 electronic paramagnetic resonance,10 nuclear magnetic resonance,11 and gas-phase electron diffraction12 have been used to explore the unique properties and functions of M-Pc molecules at the nanoscale. Especially, in the past two decades, scanning tunneling microscopy (STM) and spectroscopy experiments have been focused on the M-Pc molecules.13–19 Recently, study on the Kondo effect of single M-Pc molecules adsorbed on the metal surfaces20–22 has attracted much academic interest of the researchers. This effect is a result of the exchange interaction between the local magnetic moment in the molecule and the conducting electrons.

For actual applications, such as nanodevices, the configurations of the M-Pc molecules adsorbed on a certain substrate or electrode and the interactions between the M-Pc molecules and the substrate/electrode are very important, since they determine the physical and chemical properties of the M-Pc molecular systems. For example, our recent STM experimental and theoretical studies show that the magnetic moment of the central ion in a CoPc molecule will disappear when the molecule is adsorbed onto an Au(111) surface, but it will be restored if eight hydrogen atoms are cut by the voltage pulse of STM tip.22 Therefore, the first step toward a meaningful interpretation of these complex systems and developing its further applications is an accurate theoretical determination of configuration and electronic structure of the single molecule adsorbed on the metal surface. However, previous theoretical studies either are focused on the electronic structure of free molecules23–30 or only give a few simple results of adsorbed molecules without any detail of their calculation and further analysis,20 so far there is no systematic work about these complex nanosystems.

In this paper, we employ the first-principles calculations based on density functional theory to study the effect of Au(111) surface on the electronic structures of various 3d transition metal M-Pc (M = Mn, Fe, Ni, and Cu) adsorbates and to explore how different metal ions influence the adsorption configuration, the electronic structure, and especially the magnetic properties, of these M-Pc molecules. The most favorite site of these M-Pc molecules on the Au(111) surface, the changes of the electronic structures and magnetic moments before and after adsorption, their adsorption energies, and the electronic transfers between molecules and surface are calculated and analyzed. Based on the electronic structures, we discuss the Kondo effect related to the local magnetic moment of these adsorbed M-Pc molecules.

Computational Method

Using the DMol3 package,31 we have performed the calculations in local spin density approximation (LSDA) with the
Vosko–Wilk–Nusair local correlation functional. The basis sets are double numerical atomic orbital augmented by polarization functions, which are comparable to 6–31G** sets. The density functional semicore pseudopotentials are used to take the relativistic effect into account and reduce the time of calculations.

In all calculations, we have employed a periodic slab model to describe the M-Pc molecule–surface adsorption system. The same method has been used in our previous work of CoPc adsorbed on an Au(111) surface. A supercell contains total 225 atoms: one M-Pc molecule with 57 atoms, as well as a three layers metal slab with 56 Au atoms per rectangular layer. The M-Pc molecule is on one side of the metal slab, and this slab is separated from its periodic image by a vacuum space of 17.0 Å, which is wide enough to avoid the interactions between the slabs and the M-Pc molecules in different unit cells. Although the crystal structure of M-Pc indicates the molecule is not perfectly square planar, in the gas phase, its symmetry is generally D4h. Considering in the experiments the molecules are usually dispersed by evaporation, we use a planar structure shown in Figure 1 to describe a free molecule. All gold atoms are fixed, but the molecule is fully relaxed in geometry shown in Figure 1 to describe a free molecule. All gold atoms in the free molecules are spin-polarized, which indicate the existence of local magnetic moments in these metal ions in the free molecules and in the adsorbed molecules with the lowest energy configurations are presented in Figure 3a–d to identify the influences of Au surface on electronic structures of the adsorbates. Except for the case of NiPc, projected densities of states (PDOS) of the metal ions in the free molecules are spin-polarized, which indicate the existence of local magnetic moments in these molecules. But after the molecules have been adsorbed onto the Au surface, the PDOS of metal ions change variably. In the case of MnPc molecule (Figure 3a), peaks at about +0.8 eV disappear, and other peaks have been shifted about 0.1–0.2 eV. In the case of FePc (Figure 3b), the main differences in PDOS of the Fe ion exist near the Fermi level: in the spin down component, the peak at +0.2 eV is absent, and the peak at +0.7 eV has been shifted to +1.0 eV; in the spin up component, all peaks are shifted nearer to the Fermi level. These changes make the ratio of different spins near the Fermi level smaller than that of the free molecule. In the case of NiPc, there also exist peak shifting and intensity changes in PDOS of the Ni ion (Figure 3c), but its electronic structure remains non-spin-polarized. In the case of CuPc (Figure 3d), there is almost no difference between the PDOS of the free molecule and the adsorbed one near the Fermi level, and the changes of electronic structure can only be found within the energy range lower than −1.4 eV relative to $E_F$. From the

Results and Discussion

Adsorption Configurations. Table 1 lists our calculated total energies of the optimized structures for four M-Pc molecules adsorbed on Au(111) layers with four adsorption sites, in which the total energy values for the most favorite adsorption site are set to zero. From Table 1, we can find that for the MnPc molecule the top site is the most favorite adsorption site (Figure 2c), which is the same as the previously reported result of MnPc on a Pb surface. However, for other M-Pc (M = Fe, Ni, Cu) molecules, the configurations of the molecules adsorbed at the hcp site on the Au(111) surface (Figure 2b) have the lowest total energy. It can be also noticed that, for the cases of MnPc and FePc, the energy difference between two configurations with the top and hcp adsorption sites is ~20–30 meV, which suggests that these two configurations may exist simultaneously at room temperature. Although the same geometric configurations are used, our results for the case of FePc are at variance with a previous work, which suggests the configurations with bridge and top adsorption sites should have much lower energy. This difference will be discussed in the next subsection. It may be noted that our previous experimental and calculation results show that the CoPc molecule is also adsorbed at the hcp site on the Au(111) surface. The distances between metal ions and Au surface in the configurations with the lowest total energy are 2.81, 2.73, 3.06, and 3.04 Å for the cases of MnPc, FePc, NiPc, and CuPc molecules, respectively. These data suggest that the interactions between molecules and Au surface may be stronger for the cases of MnPc and FePc.

Electronic Structures. Since we are interested in the magnetic properties of the systems, spin-polarized density of states projected on the metal ions in the free molecules and in the adsorbed molecules with the lowest energy configurations are presented in Figure 3a–d to identify the influences of Au surface on electronic structures of the adsorbates. Except for the case of NiPc, projected densities of states (PDOS) of the metal ions in the free molecules are spin-polarized, which indicate the existence of local magnetic moments in these molecules. But after the molecules have been adsorbed onto the Au surface, the PDOS of metal ions change variably. In the case of MnPc molecule (Figure 3a), peaks at about +0.8 eV disappear, and other peaks have been shifted about 0.1–0.2 eV. In the case of FePc (Figure 3b), the main differences in PDOS of the Fe ion exist near the Fermi level: in the spin down component, the peak at +0.2 eV is absent, and the peak at +0.7 eV has been shifted to +1.0 eV; in the spin up component, all peaks are shifted nearer to the Fermi level. These changes make the ratio of different spins near the Fermi level smaller than that of the free molecule. In the case of NiPc, there also exist peak shifting and intensity changes in PDOS of the Ni ion (Figure 3c), but its electronic structure remains non-spin-polarized. In the case of CuPc (Figure 3d), there is almost no difference between the PDOS of the free molecule and the adsorbed one near the Fermi level, and the changes of electronic structure can only be found within the energy range lower than −1.4 eV relative to $E_F$. From the

Table 1: Calculated Relative Energies (meV) of Selected Configurations

<table>
<thead>
<tr>
<th>Configurations</th>
<th>MnPc</th>
<th>FePc</th>
<th>NiPc</th>
<th>CuPc</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp</td>
<td>22.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>fcc</td>
<td>66.4</td>
<td>47.0</td>
<td>37.8</td>
<td>53.3</td>
</tr>
<tr>
<td>bridge</td>
<td>104</td>
<td>41.6</td>
<td>87.6</td>
<td>90.3</td>
</tr>
<tr>
<td>top</td>
<td>0</td>
<td>25.3</td>
<td>55.4</td>
<td>194</td>
</tr>
</tbody>
</table>

Figure 2. (a) Four high-symmetry sites of Au(111) surface in a 1 × 1 unit cell. (b) and (c) Two configurations with the lowest total energy for different M-Pc molecules.
above descriptions, we can deduce that the adsorptions do not change the polarization properties of the four M-Pc molecules we studied, which is different from the case of the CoPc molecule where PDOS of the Co ion changes from being polarized to being nonpolarized with the magnetic moment of the Co ion turning to zero when CoPc is adsorbed onto the Au(111) surface. Our results also indicate the adsorbed molecules, including MnPc, FePc, NiPc, and CuPc, should still have the local magnetic moments.

It is noticed that our results for the case of FePc are quite distinct from a previous report in ref 21, especially the PDOS of the Fe ion in the free molecule. In Figure 4c of ref, for a free FePc molecule, there is almost zero for the spin down component in PDOS of Fe ion, but there exist some clear peaks in our results. By performing additional calculations on the free FePc molecule using the VASP package with PBE functional and PAW-PBE pseudopotential, which is the same as that used in ref 21, we have obtained the electronic structure consistent with our results from the LSDA calculation presented in this paper. On the other hand, previous theoretical works also support our results of obvious electronic states with a spin down component of the Fe ion existing between -1.0 and +1.0 eV in the free molecule. We have also performed additional calculations for FePc adsorbed on the Au(111) surface by using the same VASP-PBE method as that in ref 21, and the obtained result of the relative energy of molecule at a different adsorption site is not consistent with that in ref 21, but in agreement with the DMol-LSDA result presented in this paper.
Adsorption Energy and Charge Transfer. In order to describe the strength of molecule—surface interaction, we have calculated the adsorption energies ($E_{ad}$) and charge transfers when different M-Pc molecules are adsorbed onto the Au(111) surface. The adsorption energy is defined by the terms of the energies of the various species as follows:

$$E_{ad} = E(\text{sub}/\text{mol}) - \{E(\text{sub}) + E(\text{mol})\}$$

where $E(\text{sub}/\text{mol})$ is the total energy of the molecule—surface adsorption system and $E(\text{sub})$ and $E(\text{mol})$ are energies of the surface and a free molecule, respectively. Our calculations obtained the adsorption energies of $-3.58$, $-3.67$, $-3.25$, and $-3.27$ eV for the cases of MnPc, FePc, NiPc, and CuPc, respectively. Here, negative values mean the adsorptions of these molecules are exothermic processes. More interestingly, these data are nearly linear with the distances between metal ions and Au surface, suggesting a trend that the molecule—surface interaction will be stronger with M-Pc molecule closer to Au surface.

To get the quantity of charge transfer, we adopt a method described in a theoretical study about the C60 molecule on metallic surfaces, in which an $xy$-integrated differential electron density curve against the $z$ coordinate is plotted to determine the boundary between the C60 molecule and the surface. Here the differential electron density can show the change in electron density that occurs in the molecule and the surface when the molecule is adsorbed onto the surface. Our calculation results of the differential electron densities of different molecules are presented in Figure 4. Figure 4a is a sketch map showing the spatial positions of the surface and M-Pc molecule. The $z$ axis is along [111] direction of Au surface while $y$ axis is along [112] direction. Panels b—e in Figure 4 show the differential electron densities integrated over the $y$ direction for the cases of four M-Pc molecules. For all four adsorption cases of M-Pc molecules, there are obvious charge transfers between metal ions and surface at the molecule—surface interface, and the most significant differences between them are seen to occur at the central part of the M-Pc molecule, where the metal ion resides. There exist some regions of increase in the electron density around the metal ions for the cases of MnPc and FePc (Figure 4b and c). However, for the cases of NiPc and CuPc molecules (Figure 4d and e), there are only regions of decrease in the electron density around the metal ions. This phenomenon is consistent with the argument that MnPc and FePc having a unoccupied low-lying bonding orbital are much easier to get an electron to form anions than NiPc and CuPc having a high-lying antibonding orbital. It may be also suggested that, for the cases of MnPc and FePc, there is a complex redistribution of electrons around the metal ions because of the stronger molecule—surface interaction. According to our calculations, the total amounts of electron transfer from M-Pc molecules to Au surfaces are 0.68, 0.56, 0.73, and 0.70 $e$ for the cases of MnPc, FePc, NiPc, and CuPc, respectively. We find that the electron transfer from FePc to the Au surface is obviously lower than those from other three M-Pc molecules, which may be related to the greatest changes of PDOS of metal ion in the FePc molecule after its adsorption as discussed before.

Magnetic Property and Kondo Effect. Spin-polarized electronic structures of the metal ions can lead to a local magnetic moment in the M-Pc molecules. Our calculated results of electronic magnetic moment from Mulliken analysis have been presented in Table 2. Whether being adsorbed on the Au surface or not, MnPc, FePc, and CuPc molecules have the local magnetic moments, with variance only in the changes of quantity after the adsorption. The magnetic moment of the MnPc molecule changes in a small amount of 0.22 $\mu_B$ after its adsorption onto the Au(111) surface, but for FePc, the value is 0.98 $\mu_B$, which is almost half of the magnetic moment in a free FePc molecule, while the magnetic moment of CuPc keeps a value of 0.54 $\mu_B$. All these changes are consistent with the changes of PDOS and charge transfers discussed above. The magnetic moment of the NiPc molecule is always zero before and after being adsorbed onto the Au surface due to the nonpolarized electronic structure. Specially, a free CoPc molecule has a magnetic moment of 1.10 $\mu_B$, but the magnetic moment has been quenched when the CoPc molecule is adsorbed onto the Au surface, and after cutting eight hydrogen atoms by STM tip CoPc molecule recovers its magnetic moment, as shown by our previous research.

Generally, the existence of a local magnetic moment is an important precondition of the Kondo effect observed in the STM experiments. The Kondo effect has been observed when the MnPc molecule is adsorbed on the Pb surface, and a similar result has also been reported for the case of FePc adsorbed on the Au surface. Although the CuPc molecule has a magnetic moment, there is no report on the observation of the Kondo effect until now. To understand these experimental results, we present the density of states projected on different symmetries of d orbital in the metal ions for the cases of MnPc, FePc, and CuPc (Figure 5). The $d_x$, $d_y$, and $d_z$ orbitals dominate the PDOS of adsorbed MnPc and FePc molecules (Figure 5a and b) near the Fermi level, and the $d_z$ orbital has only a very small component, which is different from the calculation results in ref 21. But for the case of CuPc molecule (Figure 5c), the $d_{x2-y2}$ orbital dominates the PDOS of CuPc near the Fermi level, which is consistent with the result from a recent study combining experiment and simulation. Although the $d_x$ and $d_z$ orbitals have stronger $z$-direction component which is perpendicular to Au surface, while the $d_{x2-y2}$ orbital has more components in the molecular plane parallel to the surface. Thus, the electrons of $d_x$ and $d_z$ orbitals can couple much more with the electron in two electrodes (such as STM tip and Au substrate in an STM experiment) than those of $d_{x2-y2}$ orbital (see Figure 5d). As a result, the Kondo temperature of CuPc molecule may be too small to be observed under current experimental conditions. In our previous report for the case of CoPc, the PDOS of the $d$-CoPc molecule (with eight hydrogen atoms being cut) near the Fermi level is dominated by the $d_z$ orbital, and the pairing of these states of STM tip and Au substrate (such as STM tip and Au substrate in an STM experiment) give a similar result (see Figure 5d). As a result, the Kondo temperature of CuPc molecule may be too small to be observed under current experimental conditions. Furthermore, we predict that the Kondo effect could be also observed due to the spin-polarized electronic structure near the Fermi level when a MnPc molecule is adsorbed on the Au(111) surface, and there could be no Kondo effect for the NiPc molecule adsorbed on the Au surface due to its nonpolarized electronic structure.

### Summary

The calculated results presented in this work demonstrate that M-Pc (M = Fe, Ni, Cu) molecules would like to be adsorbed on the hcp site of the Au(111) surface, whereas the top site is most favored for the MnPc molecule. The interactions between M-Pc molecules and the Au surface are different and may be related to various d orbital occupations of those metal ions. These discrepancies result in different changes in PDOS of metal ions when

### Table 2: Electronic Magnetic Moment ( $\mu_B$ ) of Molecules

<table>
<thead>
<tr>
<th>M-Pc</th>
<th>free</th>
<th>adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = Mn</td>
<td>3.17</td>
<td>2.95</td>
</tr>
<tr>
<td>M = Fe</td>
<td>2.03</td>
<td>1.05</td>
</tr>
<tr>
<td>M = Ni</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>M = Cu</td>
<td>0.54</td>
<td>0.54</td>
</tr>
</tbody>
</table>
these molecules are adsorbed onto the Au surface, different molecular adsorption energy, and different quantities of electron transfers from M-Pc molecules to Au surface. Because of the magnetic moments remaining, the Kondo effect can be observed in the related experiments of MnPc and FePc adsorbed on the Au(111) surface. And we predict the adsorbed NiPc molecule has no Kondo effect due to its nonpolarized electronic structure. As a special case, we believe a magnetic moment existing in the adsorbed M-Pc molecules to Au surface. Because of the weak coupling between the electron of the d$_{z^2}$ orbital in the Cu ion and the electrons in the electrodes. Above all, our results on the basis of electronic structures can give reasonable explanations and predictions on the coupling between the orbital of electrode and d orbitals.

Acknowledgment. This work is partially supported by the National Natural Science Foundation of China (50721091, 20532030, 10704069), by National Key Basic Research Program under Grant 2006CB922000, by the Shanghai Supercomputer Center, the USTC-HP HPC project, and the SCCAS.

References and Notes

(33) We also perform some calculations using the Perdew-Burke-Ernzerhof (PBE) GGA functional, but it may fail in correctly describing the electronic structures of some molecules, such as CuPc, which is also reported in ref 25. So we just take the LSDA results.


