CO adsorption effects on the electronic properties of Fe tape-porphyrin

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Abstract
We investigated the electronic properties of Fe tape-porphyrin and the effect of CO adsorption on it within the framework of density functional theory. As for the numerical results, we found that the Fe tape-porphyrin is metallic, and that the CO-adsorbed Fe tape-porphyrin is an insulator. Comparing the electronic structures of the Fe porphyrin molecule and the CO-adsorbed one, we found that the metal–insulator transition is caused by the hybridization of the d_{xz} and d_{yz} orbitals of Fe with the π_g^* orbital of CO.

1. Introduction

Since the proposal of molecular electronic devices [1], many kinds of organic functional molecules have been studied both theoretically and experimentally. As a result of this, recent advances in the fabrication techniques of substrates, including metal nanoelectrodes, have made it possible to realize molecular electronic devices. Compared to the conventional Si-based electronics, molecular electronic devices have mainly two advantages [2]. One is size reducibility. It is well known that the integration degree per chip of molecular electronic devices is hundreds of times higher than that of conventional Si-based electronics due to their smaller size. The other advantage is that we do not need to apply doping procedures for molecular electronic devices. In the case of Si-based electronics, as the devices become smaller, the statistical variation due to doping procedures will be so critical that we won't be able to maintain their properties. On the other hand, we can manage the electronic properties of the molecules used in molecular electronics at the early stage of synthesis. In addition, the functions of molecular electronics can be realized by varying the molecular interactions. For example, if the conductive property of a molecular wire changes drastically via the adsorption of a certain molecule on the wire, the molecular wire may be used as a molecular sensor. Therefore, in order to discuss the functions brought about by the modification in the molecular electronics, it is necessary to investigate the interaction between molecules involved in the process.
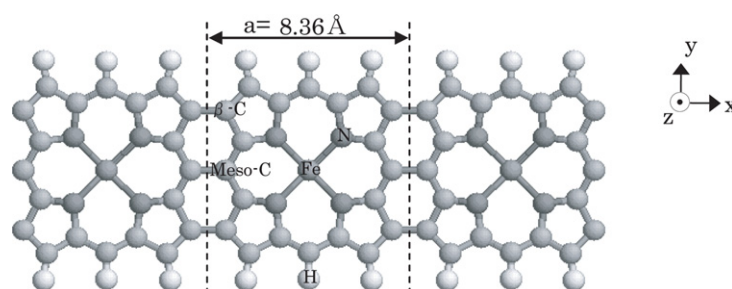
Figure 1. Top view of the model system for Fe tape-porphyrin. The x-axis is along the tape-porphyrin's growth direction. The macrocycle unit is indicated between the broken lines.

Among the various types of functional molecules, molecular wires have been extensively investigated. In most cases, these wires are oligomers of some building blocks such as thiophene and so on [3]. Porphyrin is one of the building blocks from which several types of differently conjugated molecular wires have been prepared [4]. In particular, tape-porphyrins, where the porphyrin macrocycles are linked by three conjugating C–C bonds aligned in parallel (i.e., meso–meso, β–β bonds (see figure 1)), have attracted much attention [5–7]. Because of their extremely small HOMO–LUMO energy gaps, tape-porphyrins are expected to be good conducting molecular wires. Experimentally, only Zn tape-porphyrins have been synthesized so far. But it is well known that the porphyrin molecule can coordinate with most metal atoms [8–12]. For example, the Fe porphyrin molecule is a haem of haemoglobin in human blood, which is famous for its role in carrying O_2 to our body. But the Fe porphyrin molecule binds with CO more strongly than with O_2; therefore, in the presence of CO, O_2-carrying Fe porphyrin is disturbed [13].

As a first step in discussing the possibility of tape-porphyrin being applied to molecular electronics devices, we investigated theoretically the electronic properties of Fe tape-porphyrin and the adsorption effects of CO on Fe tape-porphyrin using density functional calculations. In order to investigate the origin of the electronic property of these tapes and the adsorption effects on them, we compared with the calculated results in the case of the corresponding Fe porphyrin molecule, whose meso- and β-carbons are terminated by hydrogen atoms, and its complex with CO. In the following discussions, we give a detailed report based on the calculated electronic band structures, molecular energy levels, the local density of states (LDOS), and the charge density distributions.

2. Calculation method

The calculations for Fe tape-porphyrin, Fe porphyrin molecule, and their complexes with CO are based on the spin-polarized density functional theory, using the generalized gradient approximation (GGA) for the exchange–correlation energy [14]. We performed calculations with plane waves and the PAW method [15]. We set the cutoff energy of 500 eV to limit the plane-wave basis set. In the calculations, the tape-porphyrins are represented in the supercell shown in figure 1. The one-dimensional Brillouin zone for the calculation of Fe tape-porphyrin was sampled using 30 k-points along the tape-porphyrin's growth direction (the x-axis in figure 1). In the calculations performed here, we terminated the side chain groups with hydrogen atoms. We used a cell length of 'a' along the x-axis. In order to avoid interactions between the tape in the cell and its nearest periodic image tapes, we separated them with a vacuum region of about 8.0 Å for the y-axis and z-axis directions shown in figure 1. We
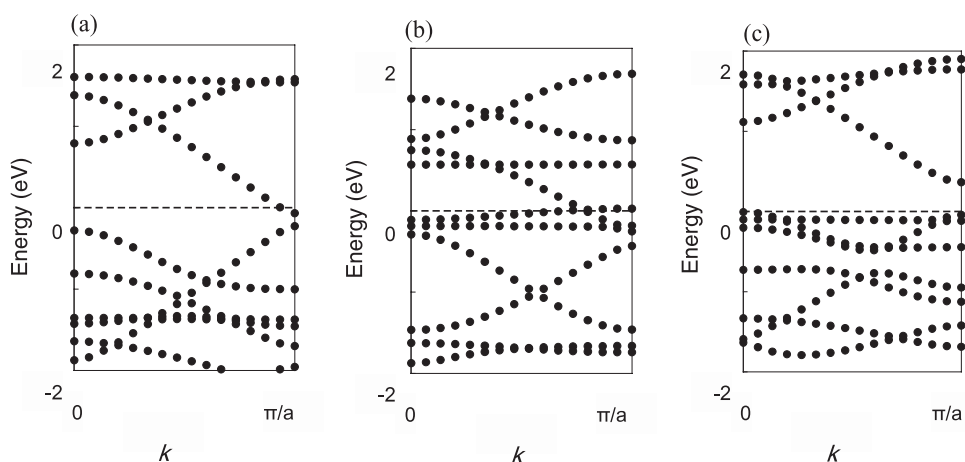
Figure 2. (a) Majority-spin and (b) minority-spin electron band structures for Fe tape-porphyrin. (c) The electron band structure for CO-adsorbed Fe tape-porphyrin.
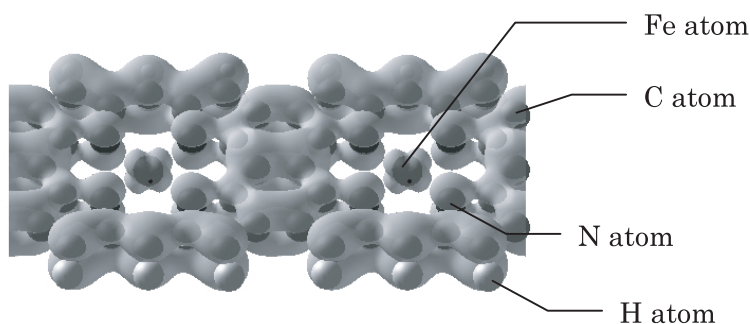

Figure 3. Contour plots of the space distribution of the conduction state of the majority-spin electron of Fe tape-porphyrin near the Fermi level.

also placed a vacuum region of 8.0 Å for the *x*-axis, *y*-axis, and *z*-axis directions between the molecules in the calculations of the molecules considered here. We performed structural optimizations by minimizing the total energy until the residual forces became smaller than 0.05 eV Å^{-1}. As a result, we got a 8.36 Å as the cell length along the *x*-axis for the most stable structure. We made sure that we obtained converged calculations results using these settings. All the calculations were performed using the Vienna *ab initio* simulation package (VASP) [16].

3. Results and discussion

3.1. Fe tape-porphyrin and CO-adsorbed Fe tape-porphyrin

The electronic band structures for the Fe tape-porphyrin are shown in figures 2(a) and (b), representing the majority-spin and minority-spin electrons, respectively. We found that Fe tape-porphyrin is metallic. For the majority-spin electron state, it can be observed that there is a high dispersion on the energy band crossing the Fermi level. This is due to the high charge density distribution on the meso- and β-carbon atoms which construct the bonds between porphyrin
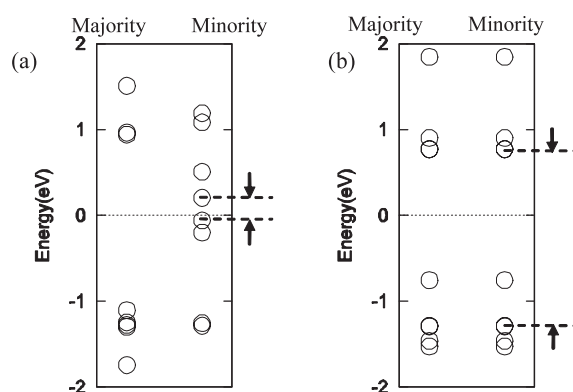
Figure 4. Molecular orbital energy levels of the majority-spin electron (left) and of the minority-spin electron (right) for (a) the Fe porphyrin molecule and (b) its complex with CO. Arrows indicate the energy levels of the wave function distributed near the meso- and β-carbons. The origin pertains to the Fermi level.
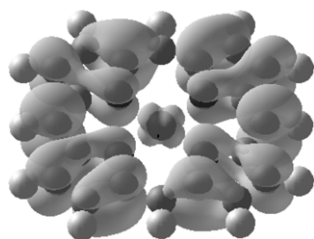

Figure 5. Contour plots of the space distribution of the LUMO of the majority-spin electron of Fe porphyrin molecule.

macrocycles as shown in figure 3. We also found that this band contains the d_{xz} orbital of the Fe atom. We tried another calculation, initially setting two porphyrin macrocycles into a supercell with ferromagnetic and antiferromagnetic configurations of Fe spins. As a result, we found that both resulted in a ferromagnetic state. The total magnetic moment is 2.123 μ_B per porphyrin macrocycle.

The electronic band structure for CO-adsorbed Fe tape-porphyrin is shown in figure 2(c). The total magnetic moment disappears and band structures of the majority-spin and minority-spin electrons are the same. For the first time, we found that the CO adsorption on Fe tape-porphyrin induced a metal–insulator transition. The Fe tape-porphyrin has the potential to be used as a 'molecular sensor' and/or 'molecular switch'.

3.2. Understanding the conductive property of Fe tape-porphyrin through the electronic structure of the Fe porphyrin molecule

To understand the reason why Fe tape-porphyrin is metallic, we will discuss here the electronic structures of the corresponding Fe porphyrin molecule, whose meso- and β-carbons are terminated by hydrogen atoms. The molecular energy levels for this molecule are shown in figures 4(a). Comparing the electronic structures of the Fe porphyrin molecule and Fe tape-porphyrin, we obtained the following typical observations. First, we found that all the bands near the Fermi level of Fe tape-porphyrin have the corresponding molecular orbitals of the
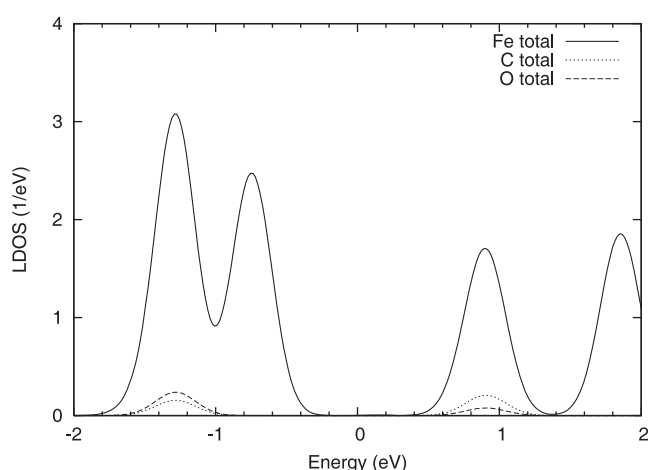
Figure 6. Local density of states (LDOS) of the Fe atom (solid line) and C (dotted line), O (broken line) atoms of adsorbed CO. Bonding and antibonding orbital composed by the d_{xz}, d_{yz} of Fe and π_g^* of CO appear as the peaks at -1.25 eV and at 0.90 eV, respectively. The origin pertains to the Fermi level.

Fe porphyrin molecule in terms of the charge density distribution. For example, the electron charge density distribution of the LUMO of the majority-spin state of the Fe porphyrin molecule is shown in figure 5. It is clear that the charge density distribution shown in figure 5 is quite similar to that in figure 3. Second, we confirmed that if there is high charge density near the meso- or β-carbon atoms in the case of the Fe porphyrin molecule, the corresponding band of Fe tape-porphyrin has large dispersion. This is easily understood in terms of the magnitude of the overlap integral between the electron states of the adjacent porphyrin macrocycles. And third, we also found that, near the Fermi level in the case of the Fe porphyrin molecule, the molecular orbitals which contain the wave function distributed near the meso- or β-carbon also contain the wave functions of d_{xz} or d_{yz} states of the Fe atom, which is shown in figure 5. Based on these observations, we can conclude that since the energy difference between the Fermi level and the levels of the molecular orbitals, which contain the d_{xz} or (d_{yz}) orbital of the Fe atom near the Fermi level is small, compared with the overlap integral between the electron states of the adjacent macrocycles, the corresponding Fe tape-porphyrin is metallic.

3.3. Understanding the physical origin of the metal–insulator transition of Fe tape-porphyrin through the electronic structure of the CO-adsorbed Fe porphyrin molecule

To understand the reason why CO-adsorbed Fe tape-porphyrin becomes an insulator, we will discuss here the electronic structures of the corresponding CO-adsorbed Fe porphyrin molecule. The energy difference between the molecular orbitals described above for the CO-adsorbed Fe porphyrin molecule is 2.065 eV. This value is bigger than that for the Fe porphyrin molecule, 0.262 eV. In addition, we investigated the molecular orbitals of CO which contributed greatly to the metal–insulator transition of Fe tape-porphyrin. The local density of states shown in figure 6 gives us the molecular interaction effects on Fe, C and O atoms. The CO molecule is adsorbed on the Fe porphyrin molecule with the hybridization between the d_{z^2} orbital of Fe and the $3\sigma_g$ orbital of CO, as well as a more effective π back-bonding (i.e., the hybridization between the d_{xz} (or d_{yz}) orbitals and the π_g^* orbitals of CO) [9]. The molecular orbitals containing d_{xz} or d_{yz} orbital of the Fe atom, which correspond to the bands that cross the Fermi level in the

case of Fe tape-porphyrin, split into bonding and antibonding orbitals due to the adsorption of CO. Thus the energy difference described above becomes larger. This is the main origin of the metal–insulator transition induced by the CO adsorption.

4. Conclusions

We investigated the electronic properties of Fe tape-porphyrin, the Fe porphyrin molecule, and their complexes with CO within the framework of density functional theory. We found that Fe tape-porphyrin is metallic, and that CO adsorption causes a metal–insulator transition. The Fe tape-porphyrin has the potential to be used as a 'molecular sensor' and/or a 'molecular switch'. From the analysis of the electronic structures, we clarified that such a metal–insulator transition is caused by the hybridization of the d_{xz} and d_{yz} orbitals of Fe with the π_g^* orbitals of CO.

Acknowledgments

References

 [1] Aviram A and Rantner M A 1974 *Chem. Phys. Lett.* **29** 277
 [2] Ogawa T, Kobayashi K, Masuda G, Takase T, Shimizu Y and Maeda S 2001 *Trans. Mater. Res. Soc. Japan* **26** 733
 [3] Farajian A A, Belosludov R V, Mizuseki H and Kawazoe Y 2006 *Thin Solid Films* **499** 269
 [4] Tsuda A and Osuka A 2001 *Science* **293** 79
 [5] Yamaguchi Y 2002 *J. Chem. Phys.* **117** 9688
 [6] Tagami K and Tsukada M 2003 *Curr. Appl. Phys.* **3** 439
 [7] Kang B K, Aratani N, Lim J K, Kim D, Osuka A and Yoo K-H 2006 *Mater. Sci. Eng.* C **26** 1023
 [8] Tsuda M, Dy E S and Kasai H 2005 *J. Chem. Phys.* **122** 244719
 [9] Tsuda M, Dy E S and Kasai H 2006 *Eur. Phys. J.* D **38** 139
[10] Tsuda M, Diño W A and Kasai H 2005 *Japan. J. Appl. Phys.* **44** L57
[11] Tsuda M, Diño W A, Nakanishi H and Kasai H 2005 *Chem. Phys. Lett.* **402** 71
[12] Liao M-S and Scheiner S 2002 *J. Chem. Phys.* **117** 205
[13] Rovira C, Kunc K, Hutter J, Ballone P and Parrinello M 1997 *J. Phys. Chem.* A **101** 8914
[14] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[15] Blöchl P E 1994 *Phys. Rev.* B **50** 17953
[16] Kresse G and Joubert J 1999 *Phys. Rev.* B **59** 1759