Rapid Communication

Role of buffer layer in electronic structures of iron phthalocyanine molecules on Au(111)*

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We investigate the electronic structures of one and two monolayer iron phthalocyanine (FePc) molecules on Au(111) surfaces. The first monolayer FePc is lying flat on the Au(111) substrate, and the second monolayer FePc is tilted at ∼15° relative to the substrate plane along the nearest neighbour [10$\bar{1}$] direction with a lobe downward to the central hole of the unit cell in the first layer. The structural information obtained by first-principles calculations is in agreement with the experiment results. Furthermore, it is demonstrated that the electronic structures of FePc molecules in one-monolayer FePc/Au(111) system are perturbed significantly, while the electronic structures of FePc molecules in the second monolayer in two-monolayer FePc/Au(111) system remain almost unchanged due to the screening of the buffer layer on Au(111).

Keywords: iron phthalocyanine, electronic structure calculations, buffer layer
PACC: 7855K, 7115A, 7360R

1. Introduction

During the past decade great progress has been made in growing ultrathin organic conjugated aromatic molecules films and their multilayer structures due to their potential applications in future molecular electronics.[1−16] The potential applications of organic–inorganic devices further promote the study of the organic thin films on well defined substrates. The formation of organic thin film is determined by the competition between the interactions of molecule–molecule and molecule–substrate. The intrinsic electronic structures of the molecules are more or less influenced by the substrate. In order to investigate the intrinsic electronic structures of molecules, much attention has been paid to protecting the molecules from influencing by the substrate. The previous studies on this issue include the scanning tunneling microscopy (STM), as well as theoretical studies on different surfaces, for example, inert graphite and ultrathin oxide surfaces. Ho group[17,18] reported that the intrinsic fluorescence photon emission had been observed from individual porphyrin molecules adsorbed on an ultrathin alumina film epitaxially grown on a NiAl(110) surface. The other substrate also has such effects.[19] The electronic structure of pentacene could be affected by the electronic coupling between molecules and metal substrate.[20] Recently, Repp *et al.*[21] observed the unperturbed molecular orbitals of individual pentacene molecules adsorbed on ultrathin insulating sodium chloride film supported by Cu(111) substrate. These results demonstrate that it is of great importance to screen the coupling from substrates in order to obtain the intrinsic electronic and optical properties of nanostructure.

It is worthy to note that the reversible conductance transitions of Rotaxanes H_2 molecules were observed successfully on methylene dichloride (CH_2Cl_2) buffer layer grown on Au(111) surface.[22,23] It is a first choice to grow buffer layer in order to investigate the intrinsic properties of nanostructure. In this paper, the electronic structures of one- and two-monolayer FePc molecules adsorbed on Au(111) surfaces are investigated by density-functional theory (DFT) calculations. The interaction between FePc molecules in a one-monolayer FePc/Au(111) system and the metal surface changes the electronic properties of FePc molecules significantly, while the in-

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trinsic properties of second monolayer FePc molecules in a two-monolayer FePc/Au(111) system are unperturbed due to the screening of the first monolayer FePc molecules.

2. Method

First-principles calculations are carried out to study the structural and the electronic properties of one- and two-monolayers FePc molecules on Au(111) surfaces separately. Our theoretical calculations are performed within spin-polarized DFT with the generalized gradient approximation (GGA) PW91 functional.[24] The plane-wave based program, Vienna *ab-initio* simulation package (VASP),[25−28] is used. The energy cutoff of the plane-wave basis sets is 400 eV. The interaction between ions and electrons is described by the frozen-core projector augmented wave (PAW) approach.[29,30] Periodic slab models including four-layer gold substrate and one- or two-monolayer FePc molecules adsorbed asymmetrically on one side of the substrate are used to simulate the system with the potential corrections.[31,32] The bottom two substrate layers are fixed, and the other part of the substrate and the molecules are fully relaxed in geometry optimizations of the adsorption models. The force convergence criterion is 0.02 eV/Å (1 Å=0.1 nm). A single Γ point is employed for Brillouin zone matrix integrations due to the numerical limitations.

3. Results and discussion

Firstly, the electronic structures of free FePc molecule are investigated by PAW-GGA methods. The optimized structure of free FePc molecule is shown in Fig. 1(a). Our calculations reveal that the magnetic moment of free FePc molecule is 2 μ_B mainly originating from the central metal iron atom as shown in Table 1. The electronic structure of free FePc molecule is compared with the results calculated by local density approximation (LDA) method. Both methods give the same electronic structures. However, the skeleton of free FePc molecule calculated by the GGA method is expected to be slightly larger than that calculated by the LDA method.

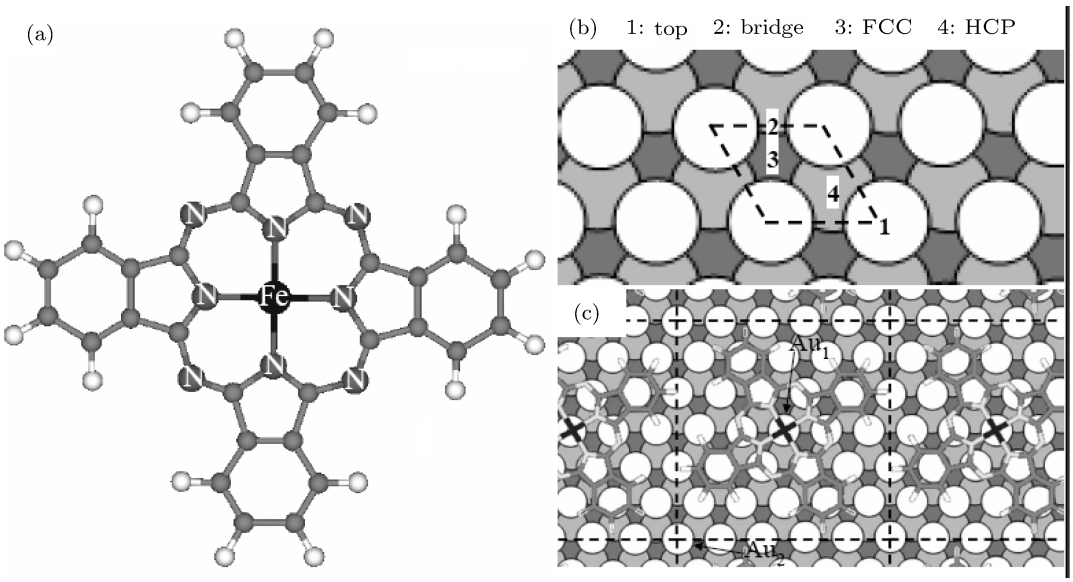


Fig. 1. (a) Ball-and-stick model of iron phthalocyanine (FePc) molecule optimized by PAW-GGA method, (b) the adsorption sites in a unit cell for FePc molecule on Au(111) surface, indicated by 1, 2, 3, 4, where the central iron atoms are located at top, bridge, FCC, HCP sites respectively, and (c) the computed most stable configuration of one-monolayer FePc molecules on Au(111) surface.

Table 1. Magnetic moment (μ_B) of central iron atom of FePc molecule for free FePc molecule, FePc in one-monolayer FePc/Au(111) system, the lower and the higher FePc in two-monolayer FePc/Au(111) system.

	magnetic moment/μ_B
free FePc molecule	1.96
FePc in one-monolayer	0.10
lower FePc in two-monolayer	1.78
higher FePc in two-monolayer	1.87

Experimentally the measurements are performed with an ultrahigh vacuum low-temperature STM system (UHV-LT-STM, Omicron GmbH) with a base pressure of 1×10^{-8} Pa. More experimental details can be found in Refs. [9], [33] and [34], and STM measurements show the real-space images of FePc molecues on Au(111) surface. A quadratic periodic structure of FePc monolayer structure is observed on Au(111) surface where the FePc molecules are lying flat on the surface as a four-lobed pattern with a bright spot in the centre. The orientation of monolayer FePc molecules are arranged along the $[1\bar{1}0]$ and the $[11\bar{2}]$ directions. In the low energy electron diffraction (LEED) experiments proposed is a square unit cell as marked by black dash lines in Fig. 1(c). For monolayer FePc molecules on Au(111), four adsorption configurations are taken into account in DFT calculations as shown in Fig. 1(b). Our PAW-GGA calculations reveal that the top site is the most favourable adsorption site (Fig. 1(c)). The relative adsorption energies of the optimized structure with respect to the most instable FCC hollow site in Fig. 1 are 330, 287, 221 meV for top, bridge, HCP hollow sites respectively. On the other hand, the nearest distance between iron atom and Au substrate in the top configuration with the lowest total energy is 2.73 Å, which is in good agreement with the previously reported results of single FePc molecule on Au(111) surface.[35] The most stable adsorption sites for isolated FePc molecules and monolayer structure FePc molecules on Au(111) surface are both associated with top sites,[9] implying that the central iron atom has important contributions to the bonding characteristics between FePc molecules and the Au(111) substrate.

In order to investigate the electronic structure of one-monolayer FePc on Au(111) surface, spin-polarized partial densities of states (SP-PDOSs) for iron atoms, gold atoms and FePc molecules are calculated. As shown in Fig. 2, the electronic structures of iron atom, gold atom and FePc molecule change significantly upon the adsorption of one-monolayer FePc on Au(111) surface. The majority spin of metal iron atom in the FePc/Au(111) system at the Fermi level has increased significantly compared with that of the zero majority spin of Fe atom in free FePc molecule. However the minority spin of Fe atom is reduced a lot due to the strong interaction with the gold atom which is situated right below the iron atom. This also leads to the reduction of the magnetic moment of central iron atom in FePc molecule as shown in Table 1. The strong coupling between gold atom and adjacent iron atom makes gold atom magnetized with a small non-vanishing magnetic moment near the Fermi level, while other gold atoms away from Fe atom carries no magnetic moments. This is very similar to the case of isolated FePc molecule on Au(111) surface.[9] The PDOS peaks near the Fermi level for free FePc molecule and adsorbed system originate from the d-orbital of central iron atom in FePc molecule. From the above analysis it follows that the electronic structures of FePc molecules are perturbed significantly. In order to obtain the intrinsic electronic properties of FePc molecules, we must screen the interaction between the molecules and the substrate.

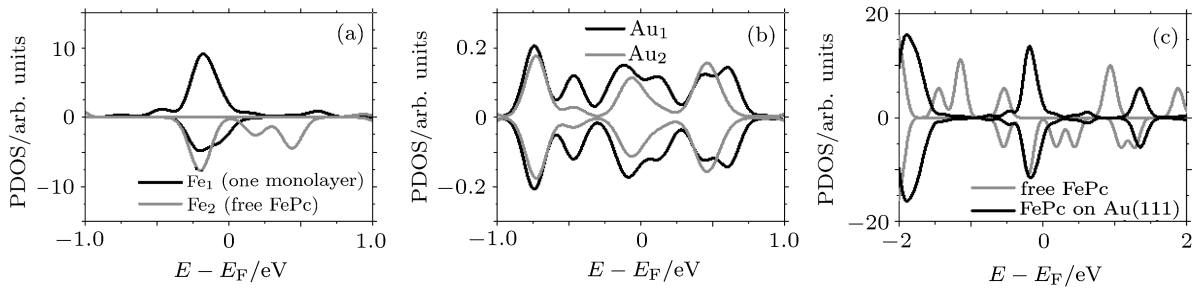


Fig. 2. SP-PDOSs of Fe atom (a), Au atom (b) and total FePc (c) for one-monolayer FePc molecules on Au(111) surface compared with that of free FePc molecule.

When FePc molecules are further deposited onto Au(111) substrate in experiment, the formed superstructure matrix of the second FePc monolayer is the same as that of the first FePc layer as shown in Fig. 3(a).[27,28] However, the FePc molecules in the second monolayer have a nonplanar adsorption configuration where the FePc molecules have a tilting angle with respect to the substrate with only three lobes and one central protrusion distinguishable (Fig. 3(c)). The tilted FePc molecules in the second monolayer might be due to the

intermolecular interaction. The observation of the tilted second FePc monolayer adsorbed on Au(111) surface is different from the case of multilayers manganese phthalocyanine on Pb(111) surface.[36]

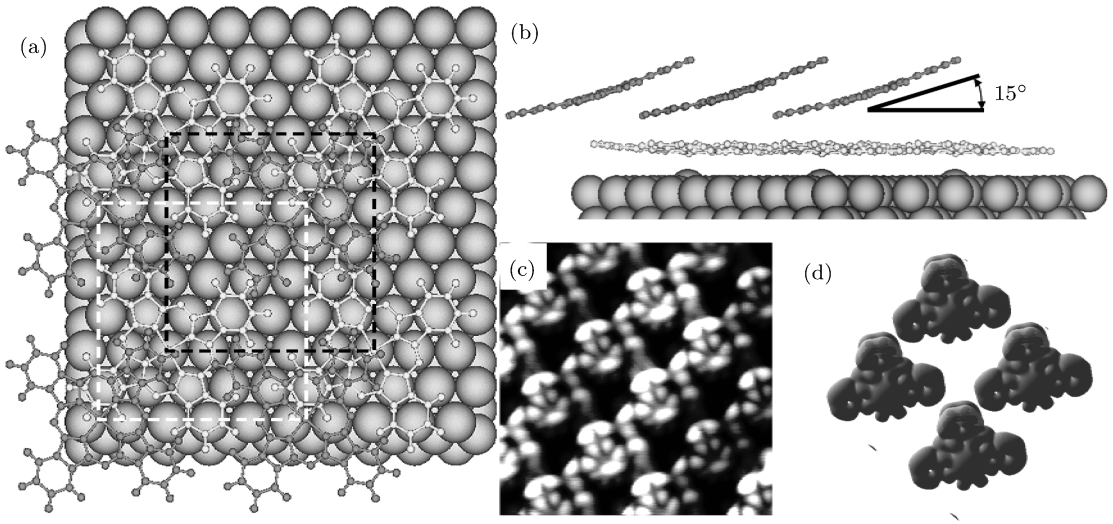


Fig. 3. Top view (a) and side view (b) of two-monolayer FePc molecules on Au(111) surface. The black and white dashed rectangles represent the computed superstructures of the first and second FePc monolayer respectively demonstrated by LEED experiments. (c) STM image of the second monolayer FePc on Au(111), with $U = -0.8$ V, and $I = 0.1$ nA. (d) The integrated electronic charge density from -0.8 eV to the Fermi level.

Based on the structures of assembly monolayer FePc on Au(111) surface (Fig. 1(c)), we build the model of the second monolayer FePc on buffer layer supported by Au(111) surface. Initially a tilted angle of 15° is supposed for the second FePc monolayer. The optimized configuration of two-monolayer FePc molecules on Au(111) surface is shown in Fig. 3(a). The central position of the second FePc monolayer is shifted away from the original position of the first FePc layer with a lobe downward to the centre of the superstructure of the first monolayer FePc. In order to verify the computational structure, the charge density of the second monolayer FePc is integrated from -0.8 eV to the Fermi level as plotted in Fig. 3(c). The integrated charge density for the second monolayer FePc is in good agreement with that obtained from the experimental STM image.

The calculated SP-PDOSs of the central iron atom in FePc molecules are shown in Fig. 4(a). The magnetic moments of central iron atoms, which originate from the asymmetric majority–minority spin distribution are 1.78 $\mu_{\rm B}$ and 1.87 $\mu_{\rm B}$ respectively for lower and higher FePc molecules in the two-monolayer FePc/Au(111) system. The PDOS of Fe atom near the Fermi level in the second monolayer of two FePc molecules on Au(111) surface is very similar to that of free FePc. The electronic properties of Fe atoms in the first monolayer of the two-monolayer FePc/Au(111) system are slightly different from those of the free FePc. Similiar to the case of a one-monolayer FePc/Au(111) system, the electronic structures of Au atoms labeled by 1 and 2 as shown in Fig. 1(c) exhibit much different features. The Au atom adjacent to the central Fe atom of the FePc molecule shows an asymmetric PDOS near the Fermi level with a non-vanishing magnetic moment. However the Au atom away from the central Fe atom of the FePc molecule does not possess any magnetic moments due to the symmetric PDOS in the vicinity of the Fermi level. The total PDOS of FePc molecule around the Fermi level as shown in Fig. 4(c), is mainly from the *d*-orbital of the central Fe atom in the FePc molecule. The negligible distinction of the partial density of states between the second monolayer FePc in the two-monolayer FePc/Au(111) system and the free FePc molecule indicates that the electronic properties of the first monolayer FePc in the two-monolayer FePc/Au(111) system are largely preserved. However the screening effect is limited since the bending behaviour of the second monolayer FePc is caused by the substrate as shown in Fig. 3(b). More importantly, the electronic properties of the first monolayer in the two-monolayer FePc/Au(111) system are also similar to that of the free FePc molecule since the distance between Au atom and the adjacent Fe atom in the one-monolayer FePc/Au(111) is 0.2 Å smaller

than the one in the two-monolayer FePc/Au(111) system. This indicates that the second monolayer FePc adsorbed on the first monolayer FePc supported by Au(111) reduces the direct coupling between the first monolayer FePc and the Au(111) substrate.

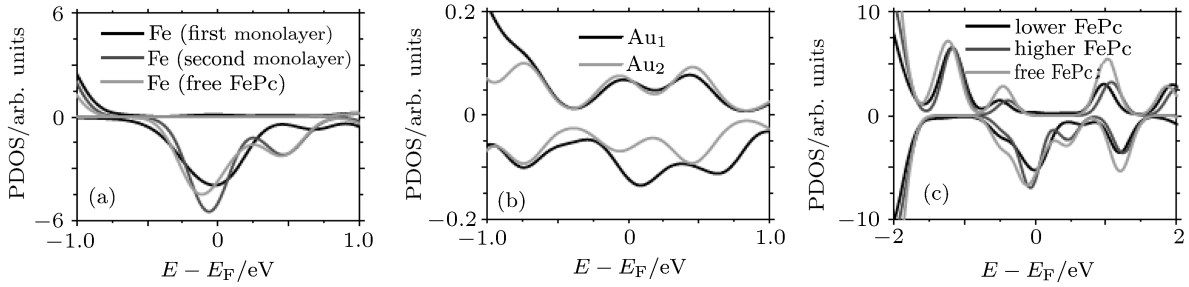


Fig. 4. (a) SP-PDOSs of Fe atoms in two-monolayer FePc/Au(111) system compared with that of Fe atoms in free FePc. (b) The SP-PDOSs of Au atoms in two-monolayer FePc/Au(111) system. The labels are the same as those in Fig. 1(c). (c) The SP-PDOSs of the total FePc molecules in two-monolayer FePc/Au(111) system compared with that of free FePc molecules.

4. Conclusions

The electronic properties of one and two FePc monolayers on Au(111) surface are studied by DFT calculations. The electronic structures of FePc molecules in one-monolayer FePc/Au(111) system is perturbed by the Au substrate substantially. The perturbation of the second monolayer FePc by the Au(111) substrate is significantly reduced by the screening of the first monolayer FePc supported by the Au(111) surface. Thus we demonstrate that the organic buffer layer can serve as an effective way to screen the interaction between organic molecules and substrates to obtain the intrinsic electronic or optical properties of organic molecules on metal substrates. These results are of great importance in designing organic electronic devices.

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