

Tin-phthalocyanine adsorption and diffusion on Cu and Au (111) surfaces: A density functional theory study

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ABSTRACT

Through density functional theory based calculations, we study the adsorption and diffusion of tin phthalocyanine (SnPc) molecule on Au(111) and Cu(111) surfaces. SnPc has two conformers with Sn pointing to the vacuum (Sn-up) and substrate (Sn-down), respectively. The binding energies of the two conformers with different adsorption sites on the two surfaces, including top, bridge, fcc, hcp, are calculated and compared. It is found that the SnPc molecule binds stronger on Cu(111) surface, with binding energy about 1 eV larger than that on Au(111). Only the bridge and top adsorption sites are stable on Cu(111), while all the four adsorption sites are stable on Au(111), with small diffusion barriers between them. Moreover, the flipping barrier from Sn-up to Sn-down conformer is of the same magnitude on the two metal surfaces. These results are consistent with a recent experiment [Zhang, *et al.*, *Angew. Chem.*, 56, 11769 (2017)], which shows that conformation change from Sn-up to Sn-down on Cu(111) surface can be induced by a C₆₀-functionalized STM tip, while similar change is difficult to realize on Au(111), due to smaller diffusion barrier on Au(111).

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1. Introduction

Metal phthalocyanine (MPc, with M representing metal and Pc representing the phthalocyanine ligand) is one of the most important class of molecules that have received intensive study in surface science and molecular electronics [1–21]. Its mechanical, electrical, optical and magnetic properties on different surfaces have been explored by the use of a scanning tunneling microscope (STM) [12–16]. Its nearly flat geometrical structure reduces the structural uncertainty, and increases the thermal stability when adsorbed on surfaces. Meanwhile, introducing different kinds of metal atom in the center gives the versatile possibility of engineering their chemical and physical properties.

Most of the MPc molecules have a planar structure with D_{4h} symmetry. When adsorbed on metal surfaces, the symmetry reduces to D_{4v} [22]. But if the central metal atom is large, the molecule changes to a shuttlecock shape, with the metal atom going out of the phthalocyanine frame [23]. Tin phthalocyanine (SnPc) is one example of this kind of molecule. When adsorbed on metal surfaces, the SnPc molecule has two possible conformations. One conformation corresponds to the Sn atom pointing to the vacuum, the other corresponds to the Sn atom pointing to the substrate [24,25]. The electrical properties may be sensitive to the conformations, thus enabling the possibility of realizing single molecular switch. Different kinds of stimuli have been used to induce

transition between these two conformers on different metal surfaces. Through electron or hole injection from a STM tip, Wang *et al.* achieved one-by-one reversible switch between Sn-up and Sn-down conformers in self-assembled layers of SnPc on Ag(111) surface [26]. Similar attempt fails for SnPc adsorbed on Cu(111) and Au(111) surfaces. But, using a robust functionalized C₆₀ tip, switching from Sn-up to Sn-down is achieved by applying mechanical force to SnPc on Cu(111) [27]. On Au(111), the pushing of C₆₀ tip leads to diffusion of the SnPc molecule away from the tip, presumably due to the weaker binding between SnPc and Au(111) surface.

Inspired by this experimental work, here we study theoretically the adsorption of SnPc molecule on Au(111) and Cu(111) surfaces. On each metal surface, we compare the binding energies of different adsorption sites, and the diffusion barrier between them, considering both the Sn-up and Sn-down conformers. We also compare similar adsorption site on the two metals surfaces. Our calculation shows that, while the flipping barrier from Sn-up to Sn-down conformer is similar, the binding energies and diffusion barriers on Au(111) are smaller than those on Cu(111). This means that mechanical pushing of Sn atom through the Pc frame is difficult to realize on Au(111) surface, since the force may be compensated by lateral motion of the molecule. Our calculations are consistent with the experimental results [27].

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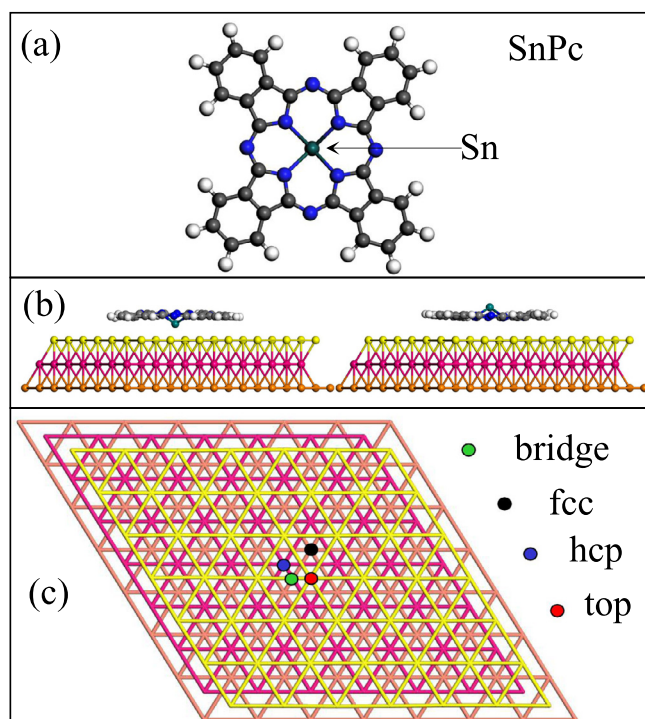


Fig. 1. (a) Top view of a free SnPc molecule. (b) Side view of SnPc on metal surface with the Sn-up (left) and Sn-down (right) conformation. (c) Top view of the Au(Cu)111 substrate, where the different points indicate the possible adsorption sites on the substrate. Different colors of the substrate represent atoms in different layers.

2. Methods

Density functional theory (DFT) calculations are performed with the Perdew–Burke–Ernzerhof (PBE) [28] version of generalized gradient approximation (GGA) and projector augmented wave (PAW) [29,30] pseudopotentials, as implemented in Vienna *Ab-initio* simulation package (VASP) [31]. For the geometry relaxation, the SnPc molecule and metal atoms in the topmost layer are allowed to fully relax while the remain-

ing atoms are kept fixed. The electronic wave functions are expanded in plane wave basis with an energy cutoff of 600 eV, and Γ -point k sampling is used due to the large number of atoms in the system. The atoms are relaxed until the forces acting on them are smaller than 0.01 eV/Å and the convergence criteria for the electronic self-consistent loops is set to 1×10^{-6} eV. The van der Waals (VDW) interaction is taken into account using DFT-D3 [32,33] method of Grimme. A vacuum region of 15 Å is added to avoid interactions between atoms in neighbor cells. The diffusion and flipping barriers are calculated using the nudged elastic band (NEB) [34] method with the VTST code [35].

3. Results and discussions

The structures considered in the simulation are shown in Fig. 1. Top view of the SnPc molecule is shown in Fig. 1 (a). The central Sn atom does not belong to the Pc molecular plane due to its large radius, thus, SnPc molecule shows a shuttlecock shape. When adsorbed on metal surface, it has two stable conformations. In one conformation the Sn atom points toward the vacuum, while in the other conformation the Sn atom points toward the substrate, which are denoted as Sn-up and Sn-down, respectively, as depicted in Fig. 1 (b). In the calculation, the substrate is simulated with a 7×7 periodic slab including three metal layers which are drawn with different colors in Fig. 1. Four different adsorption sites are considered as shown in Fig. 1 (c). They are bridge, fcc and top sites, respectively.

The relaxed structures of SnPc on Au(111) and Cu(111) are shown in Figs. 2 and 3, respectively. The corresponding energies are summarized in Table 1. The binding energy E_b is calculated as: $E_b = E_{\text{sub}} + E_{\text{mol}} - E_{\text{tot}}$, where E_{tot} is the total energy of the SnPc/Au(111) or SnPc/Cu(111) system, E_{sub} and E_{mol} are the energies of the isolated metal slab and SnPc molecule with the relaxed structures. It can be seen that, the binding energies on Cu(111) are ~ 1 eV larger than those on Au(111). For the same adsorption site, the Sn-down configurations have larger binding energies than the Sn-up counterparts. This is easy to understand, since the Sn atom binds strongly to the metal surfaces in the Sn-down structures. Through the NEB barrier calculation, we find that the top site for Sn-down on Au(111), the fcc and hcp sites for SnPc on Cu(111) are not stable, i.e., there is no barrier separating them with other adsorption sites. Thus, we mark them as unstable with slashes in the table.

The difference in the binding energy can be understood from the charge transfer between the SnPc molecule and the metal substrate.

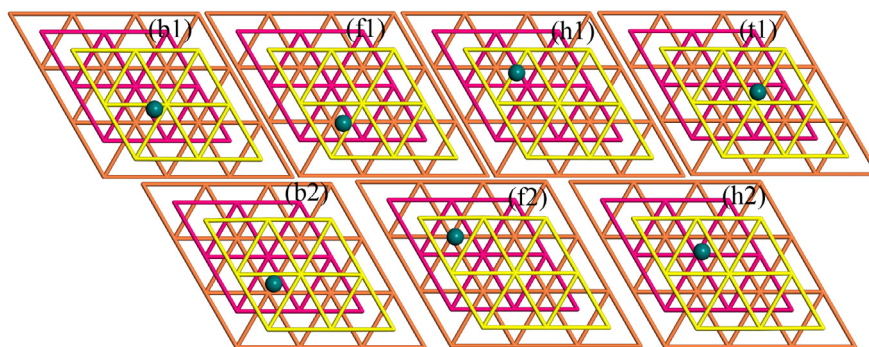


Fig. 2. Top view of the relaxed structures of SnPc on Au(111). The letters b, f, h and t represent bridge, fcc, hcp and top sites, respectively, while the numbers 1 and 2 indicate Sn-up and Sn-down configurations.

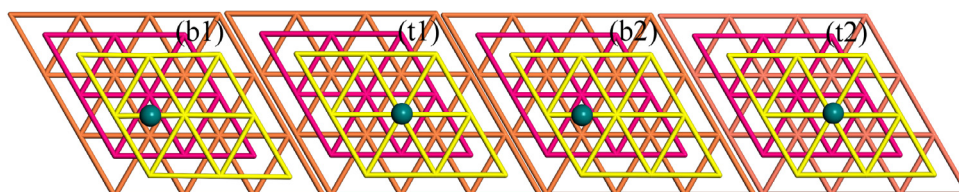


Fig. 3. Similar plot to Fig. 2 but on Cu(111). Only the bridge (b) and top (t) configurations are stable. The fcc and hcp configuration transform to the bridge configuration during the structure relaxation.

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