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Electronic structures of CuPc on a Ag(110) surface

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Abstract

Copper phthalocyanines (CuPc) on a Ag(110) surface have been studied by ultraviolet photoemission spectroscopy (UPS). On depositing CuPc organic films, the features from the substrate 3d valence fade and four new features corresponding to the adsorbed molecules emerge at 1.68, 4.45, 6.36 and 9.20 eV below the Fermi level. These features shift in binding energy with increasing thickness of the organic films. In the case of a monolayer, angle-resolved UPS measurements suggest that the molecular plane is nearly parallel to the substrate. Further theoretical calculation indicates that the adsorption of CuPc on a hollow site is the most favourable configuration, and the separation between the adsorbate and the substrate is about 2.7 Å.

1. Introduction

Organic semiconductors have become increasingly important for applications in optical and electronic devices [1]. Nowadays, the limitation on the use of organic materials in this field is the efficiency of charge injection and the mobility of the charge carrier [2, 3]. For the fabrication of such devices as organic thin-film transistors (OTFTs), the growth of organic films on different substrates, including metals, semiconductors, glass and polymers, should be carefully controlled in order to improve the device performance. Therefore, investigation of the organic/metal and organic/semiconductor interfaces is crucial for designing and controlling functionalities at the nanometre scale in the field of molecular electronics, for example [4]. Generally speaking, the spatially periodic potential on the substrate can act as a template for the growth of organic films; commensurate and point-on-line structures of ordered organic molecules can be achieved, known as epitaxial/quasi-epitaxial growth, as has been evidenced by many previous studies [5–7].

Among the organic materials whose interactions with solid substrates have been studied, the phthalocyanine (PC) family represents one of the most interesting candidates for forming ordered organic thin films. The aromatic molecule is expected to adsorb on the metallic surface in a flat-lying geometry with maximum interaction between the extended π system and the

periodic d electron of the transition metal. The influence of the adsorption geometry on the electronic state of the organic adsorbate can significantly affect the characteristics of the organic electronic device. Recently, a long-range ordered monolayer of CuPc on the Au(110) surface has been reported by Evangelista *et al* [8]. The effects of an interface dipole layer on the energy level alignment for a monolayer of OTi-Pc under a CuPc film on a graphite surface has also been demonstrated by Kera *et al* [9]. When CuPc is deposited on a Ag(110) surface, interaction between adsorbate and substrate as well as intra-molecular interactions emerge [10]. Herein, ultraviolet photoemission spectroscopy (UPS) was used to investigate the electronic state of the CuPc molecules adsorbed on a Ag(110) surface. The occupied states as a function of surface coverage were investigated to show the interactions between the adsorbate and substrate. The interactions were somehow complex and sensitive not only to substrate geometry but also to its chemical nature. In order to establish a clear understanding of this mechanism, we then performed calculations based on the first-principles theory with optimized geometry on cluster models to determine the most stable adsorption site, electronic structure and charge transfer from substrate to molecules.

2. Experimental methods

Both sample preparation and investigation were carried out in an ultrahigh vacuum (UHV) chamber at a base pressure around 1×10^{-10} mbar. The system contains an argon-ion gun with a hot filament, low-energy electron diffraction (LEED) optics, a fixed UV source, an x-ray source and a rotatable hemispherical electron analyser (VG ADES-400 electron energy spectrometer). The sample stage can be tilted and rotated around the polar axis. Angle-resolved photoemission was measured by rotating both the hemispherical analyser and the sample in the UHV chamber. A clean Ag(110) surface was obtained by several cycles of argon-ion sputtering (1000 eV for 15 min) and then annealing at 500 °C. The surface order and cleanliness were checked by both LEED and UPS measurements. The CuPc (Sigma Aldrich) organic thin films were deposited from a resistively heated tantalum boat at an evaporation temperature of about 200 °C, with the Ag substrate at room temperature. The thickness of the organic ad-layer was monitored with a calibrated quartz crystal oscillator. The UPS measurements were performed with a common UV source; the unpolarized He I (21.2 eV) light, without satellite treatment, was neither monochomatized nor normalized. The overall resolution is 0.05 eV. A sample bias of -5.0 V was applied to obtain the correct, sample determined, secondary electron cut-off. The temperature of the sample was determined by a K-type thermocouple attached to the sample stage.

3. Results and discussion

The UPS spectra recorded from the Ag(110) surface covered with increasing amounts of organic material are shown in figure 1. The photoelectrons were collected in the surface normal direction with a photon incidence angle of 30°. The nominal thickness of the organic film (the averaged number was only determined by the micro balance) is 0.0, 0.2, 0.5, 0.7, 1.0, 2.0 and 4.0 ML respectively.

The bottom spectrum, 0.0 thickness, was collected from the clean Ag(110) surface; it distinctly shows the characteristic valence structure of Ag with the d-band states from 4 to 9 eV in binding energy [11]. With increasing thickness of the organic film, the intensity of the emission features of the Ag substrate fades gradually, and new features originating from the CuPc adsorbate appear at 4.45, 6.36 and 9.20 eV, respectively (labelled β , γ and δ in figure 1). On further increasing the coverage, the peaks originating from the organic material

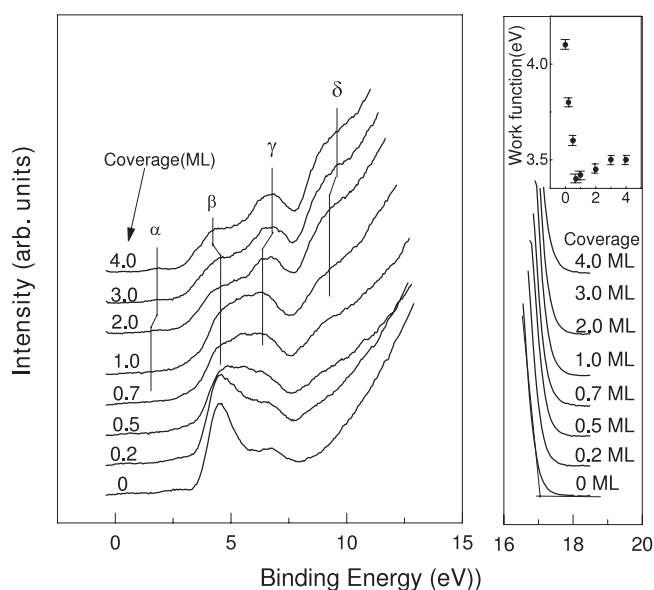


Figure 1. Left: normal emission of UPS as a function of surface coverage at room temperature. Distinct features are marked (α , β , γ and δ). Right: molecular coverage-dependent cut-off energy and the corresponding work function against the molecular coverage (inset).

are enhanced in intensity and a new peak α emerges at 1.68 eV below the Fermi level. The peaks β and γ overlap with the Ag d-band; they can be distinguished from the Ag d-band since they grow following the decrease of the Ag d-band. When the thickness is more than 2.0 ML, the valence features of the substrate almost disappear, which indicates that the Ag surface is completely covered with CuPc, and hence the present emission features represent the typical electronic structures of the organic material. Meanwhile, upon increasing the CuPc film thickness, the γ , δ peaks shift towards the higher binding energy range (the α peak shifts slightly as well), and the β peak shifts towards the lower energy range. The top spectrum in figure 1 (the coverage is about 4 ML) represents the features originating from the multilayer of the organic film, and these features are located at binding energies of 1.85, 4.34, 6.70 and 9.00 eV, respectively. The binding energy of the molecular features from the multilayer is less likely to be influenced by the substrate than that from the monolayer. The shift in binding energy can be assigned to charge redistribution [12], and indicates that the interaction occurs between the orbit of the molecule at the first layer and the d band of the Ag substrate on the interface. The clear shift in binding energy with varying coverage suggests that the growth mode of CuPc is layer-by-layer, at least in the case of the first several layers. Direct proof of this can be obtained from STM and other experiments.

Based on the variation in the secondary cut-off, we can obtain the change of the work function [13, 14], as shown in the right part of figure 1. By adding the tangents on the spectra, the cut-off energy can be determined at 17.00, 17.40, 17.60, 17.80, 17.78, 17.74, 17.70 and 17.70 eV for thicknesses of 0.0, 0.2, 0.5, 0.7, 1.0, 2.0, 3.0 and 4.0 ML, respectively; their corresponding work functions are 4.10, 3.80, 3.60, 3.40, 3.42, 3.46, 3.50 and 3.50 V, respectively. The change in work function with variation in the thickness of the organic films is shown in the inset at the top right corner of figure 1. The decrease in work function can be attributed to the formation of small polaron caused by the polarization of the organic molecule at the beginning of the deposition [15, 16]; the minimum work function of 3.40 V represents

Table 1. Theoretical and experimental results for the electronic states of a free and adsorbed CuPc molecule.

Level	Type	MO	Free molecule	Monolayer on Ag(110)	Multilayer on Ag(110)
1	π	A _u	5.10	5.08	5.35
2	π	B _{1g}	8.60	7.85	7.84
3	π	B _{2g}	11.20	9.76	10.20
4	π	B _{3u}	12.50	12.60	12.50

a coverage of 1 ML. The work function increases slightly with further deposition; the value of 3.50 V represents the work function of the organic film [16]. The change in work function with variation in the thickness of the organic films also suggests that charge redistribution and interaction occurred on the interface.

In the present work the density functional theory (DFT) calculations were performed using the program package DMol3 in the Materials Studio of Accelrys Inc [17, 18]. The physical wave functions were expanded in terms of accurate numerical basis sets. The electron–ion interaction was described by density functional semicore pseudopotentials (DSPPs) for metals. The pseudopotentials were intended for use with density functional local orbital methods such as the Dmol3 [19], and the generalized gradient-corrected (GGA) functional developed by Perdew, Burke and Ernzerhof (PBE) was used to describe the exchange–correlation function [20]. Also, a Fermi smearing of 0.004 hartree (Ha) (about 0.1 eV) was taken to minimize the errors in the Hellmann–Feynman forces due to the entropic contribution to the electronic free energy [21], and a real-space cut-off of 4 Å was used to improve computational performance. The k points were obtained from the Monkhorst–Pack scheme [22]. For the numerical integration, we adopted the MEDIUM quality mesh size of the program for a balance of time and accuracy.

All energies were extrapolated to $T = 0$ K, and the experimentally determined lattice constants were used for the production of the Ag(110) surface (4.086 Å for Ag). A 5×7 super cell with a slab of four Ag layers was used to model the adsorption mechanism. The slab was repeated periodically with a 10 Å vacuum region between the slabs. A $2 \times 2 \times 1$ k -point sampling was used. The tolerances of energy, gradient and displacement convergence were 2×10^{-5} Ha, 4×10^{-3} Ha Å⁻¹ and 5×10^{-3} Å, respectively. Under the present conditions, the Cu–N bond length for free CuPc was calculated as 1.961 Å, in good agreement with the experimental values of 1.935 Å [23].

According to the theoretical calculation for the free molecule, CuPc has photoemission peaks at 5.10, 8.60, 11.20 and 12.50 eV. Table 1 shows the calculated result for corresponding orbits with their energy, orbit type and a comparison with the photoemission from monolayers and multilayers on Ag(110). For the comparison, the data from the UPS spectra were corrected by the corresponding work function—3.40 and 3.50 V for the monolayer and multilayer, respectively.

Dependent on the data in table 1, the typical emission features from a multilayer on Ag(110) located at 1.85, 4.34, 6.70 and 9.00 eV in binding energy can be considered as coming from the same orbits of CuPc in the gas phase located at 5.10, 8.60, 11.20 and 12.50 eV, respectively. The orbit located at 1.85 eV (peak α in figure 1), corresponding to the highest occupied molecular orbit (HOMO), is well resolved, since there is no other state close to this energy. According to the DFT calculation, the HOMO orbital is dominated by π character and the electron cloud of HOMO is mainly distributed on the Pc-ring with its polarization perpendicular to the plane of CuPc molecule. A schematic diagram of the electron cloud is shown in figure 3(a).

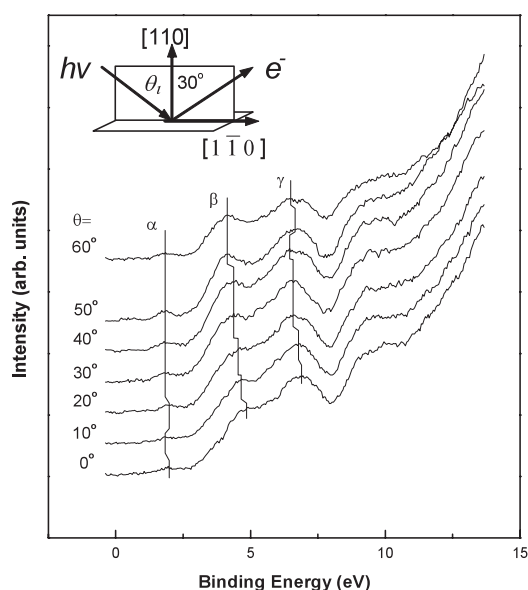


Figure 2. ARUPS measurement as a function of photon incidence angle relative to the surface normal direction from a monolayer of CuPc adsorbed on a Ag(110) surface. The top left inset shows an illustration of the experimental setting for UPS.

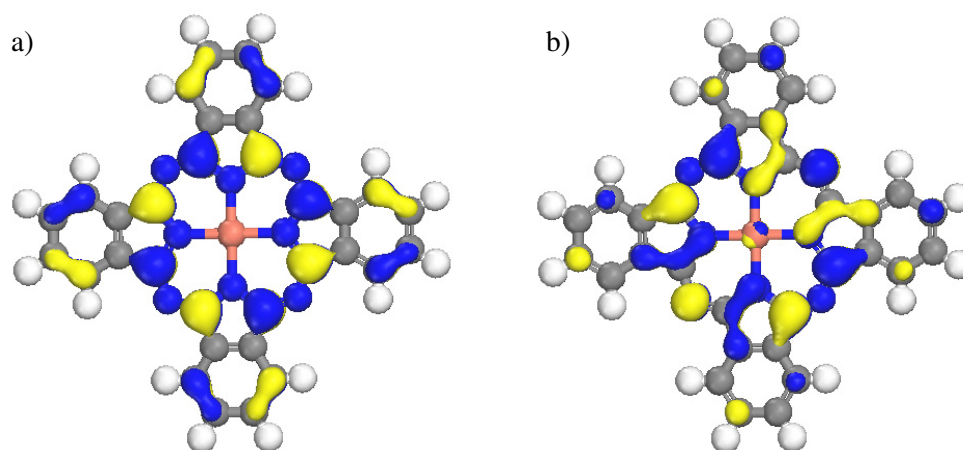


Figure 3. Schematic drawing of (a) the HOMO of CuPc and (b) the LUMO of CuPc.
(This figure is in colour only in the electronic version)

Figure 2 shows the incidence angle-dependent angle-resolved UPS (ARUPS) results from a Ag(110) surface covered with a monolayer of CuPC. The photoelectrons were collected at 30° off the surface normal direction. The incidence and emission plane is in the $[1\bar{1}0]$ azimuth. With increasing incidence angle, the intensity of the electric vector increases in the surface normal direction, but decreases in the direction parallel to the surface. An illustration of ARUPS measurements is shown in the inset at the top left corner of the figure. The ARUPS spectra show

Table 2. Theoretical calculations of adsorption energy, charge transfer and the distance between the molecule plane and the first layer atoms of the substrate for CuPc on Ag(110).

Site	SB	LB	H	T
Adsorption energy (eV)	1.45	1.50	1.95	1.30
Charge transfer (e)	0.40	0.42	0.52	0.36
Height (Å)	3.03	3.11	2.72	3.14

that the intensity of the peak α increases with increasing incidence angle. The higher intensity of the UPS signal collected at larger incidence angles suggests that the molecular plane is parallel to the substrate surface. There is no further increase in intensity of the peak α when the incidence angle is larger than 50° , possibly due to the decrease in intensity of the light in the unit area since the light intensity was not normalized.

In the ARUPS experiments, the orientation of the molecule lying flat on the substrate cannot be determined, because no difference was observed on changing the incidence plane. To further determine the adsorption structure of CuPc on Ag(110) surfaces, DFT slab calculations were carried out with an isolated CuPc molecule on one side of the Ag slab. Several adsorption configurations of the CuPc molecule on the Ag(110) surface were studied. Two top layers of the slab model together with the adsorbed molecule were allowed to be optimized, while two bottom layers of the slab were frozen in the bulk configuration. In figure 4(a), four adsorption sites of the CuPc on the Ag(110) surface were elaborated—a top site (T), long bridge site (LB), short bridge site (SB) and hollow site (H). Here the adsorption sites refer to the position of the central Cu atom of CuPc molecule. Due to the four-fold symmetry of the CuPc molecule, these investigated adsorption sites could represent the typical adsorption configuration which maintain the overall symmetry. Table 2 summarizes the calculated adsorption energies and charge transfer between the substrate and the adsorbate on different adsorption sites. The adsorption energies were calculated as follows:

$$E_{\text{ad}} = [E(\text{CuPc}) + E(\text{substrate}) - E(\text{CuPc}/\text{substrate})].$$

From the cluster DFT calculations (shown in table 2) it can be seen that the adsorption energy in the case of the hollow site is the highest, nearly 1.5 times higher than that on the top site, and the hollow site is the most favourable adsorption site. At room temperature, when the CuPc molecule is deposited on the Ag substrate, it is ready to find a favourable place to remain steadily on the substrate. Unfortunately the most favourable adsorption structure has not been confirmed by experiment. The stable structure is directly related to significant charge transfer between the substrate and molecular aromatic functional groups, more so than for other configurations. As shown in table 2, when the central Cu atom is placed on the hollow site, the separation between adsorbate and substrate is 2.72 Å, less than that on other adsorption sites, and the four nitrogen atoms around Cu, which are the main electron acceptors, are more convenient for interaction with the Ag substrate. A strong attractive interaction on the hollow site suggests a maximum overlap between four aromatic segments and the Ag atoms underneath. The molecular LUMO acts as the electron acceptor, and its distribution is shown in figure 3(b) based on molecular orbit theory. When the molecule is adsorbed on the hollow site, the LUMO of the molecule is just on top of the Ag atoms of the first layer, which suggests more overlap between the orbits of the substrate and molecule. Therefore it is not difficult to understand why more charge transfer and higher adsorption energy is achieved in this case. A similar investigation was also performed on Cu(100) by Sautet *et al* and Lippel *et al* [24, 25]; they both showed the fourfold symmetry of the molecule and the strong interaction between the orbits of the substrate and the molecule.

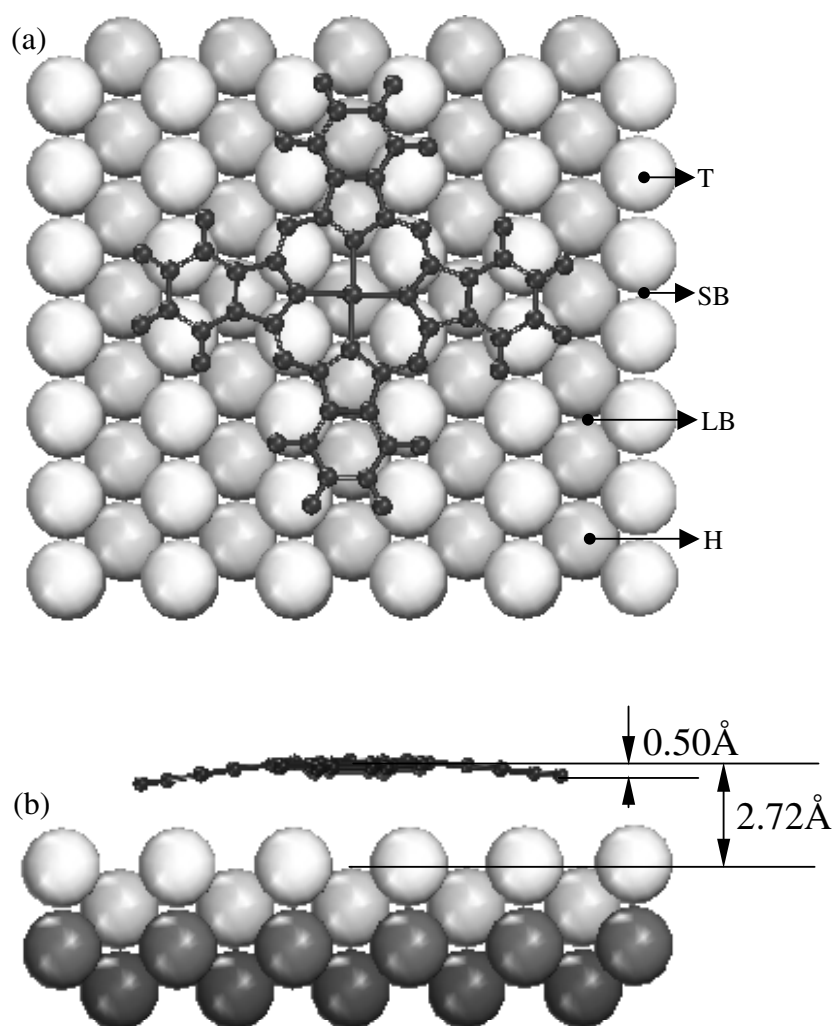


Figure 4. Schematic drawing of (a) the top view and (b) the side view of an optimized hollow adsorption structure of CuPc on Ag(110).

On the Ag(110) surface, the CuPc molecule is slightly distorted by interaction with the substrate, as seen in figure 4(b). This is partly because of the electrostatic interaction between positively charged Ag atoms and negatively charged nitrogen atoms, due to charge transfer from the substrate to the LUMO of the molecule. Based on the experimental results, in the case of a multilayer the successive layers are less influenced by the substrate, and there is less interaction between the adsorbate and the substrate.

4. Conclusion

After CuPc was deposited on a Ag(110) surface, four new features corresponding to the adsorbed molecules emerge at 1.68, 4.45, 6.36 and 9.20 eV, respectively, below the Fermi level. These features shift with increasing surface coverage, and the features originating from

the multilayer are located at binding energies of 1.85, 4.34, 6.70 and 9.00 eV, respectively. In the case of a monolayer, ARUPS measurements indicate that the molecular plane is nearly parallel to the substrate. With further theoretical calculations, the hollow site for the adsorption of CuPc on Ag(110) is the most favourable configuration; the separation between the molecular plane and the substrate is about 2.7 Å.

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