Differences in the adsorption of FePc on coinage metal surfaces*

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A study of the electronic and structural properties of iron phthalocyanine (FePc) molecules adsorbed on coinage metal surfaces Cu (100) and Cu (110) has been conducted by means of density functional theory calculations. The strength of the molecule–substrate interactions is interpreted in terms of the lateral adsorption geometry and the site specific electronic structure of the molecule. In the case of FePc on a (100)-oriented copper surface, the benzopyrrole leg is found to be oriented at an angle of 9° or 3° from the [01-1] substrate direction. Further, an upward bend in the molecular plane ranging from 7° to 10° is also observed; giving an almost buckled shape to the molecule. However, in the case of FePc on Cu (110), neither a bend nor a sizable rotation is observed. From the knowledge of the principle structural and electronic properties, it is concluded that FePc–Cu (100) interaction is relatively stronger than FePc–Cu (110) interaction, which is further evidenced by the charge transfer, work function changes, changes in the shape of the adsorbed molecular orbitals, and the orbital shifts. Furthermore, density of states analysis shows that the valence band level shift is surface- and site-dependent.

Keywords: iron phthalocyanine, copper, electronic and structural properties, density functional theory

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1. Introduction

Planar and nonplanar phthalocyanine molecules have recently gained tremendous attention due to their widespread applications (e.g., molecular electronics,[1] photodynamic cancer therapy (PDT),[2] gas-sensing devices, and fuel cells[3]). Further development of applications requires results from fundamental scientific research, raising an ever-increasing interest among scientists. Owing to their outstanding electronic and optical properties,[4] they have been recognized as promising building blocks for nanotechnology.[5] Furthermore, individual molecular layers have been proposed as active components in information storage systems.[6] However, one of the limitations of current organic technologies is the difficulty of growing a first monolayer of very high quality. Thus, precise control of the first monolayer is a prerequisite for fabricating high-quality organic thin films that would ultimately play a crucial role in the performance of metal phthalocyanine (MPc)-based organic electronic devices. On the other hand, the ordering of molecules at the organic–metal interface as well the adsorption configuration is important for charge transfer over the interface. By and large, the adsorption and ordering of molecules on solid surfaces is governed mainly by a complex balance between the substrate–molecule interaction and weak interactions among the adsorbed molecules.[7] A strong intermolecular interaction leads to the formation of three-dimensional clusters.[8] Whereas the dominant molecule–substrate interaction favors specific adsorption sites and gives rise to a highly ordered structures such as long chains.[9] Dou *et al.*[10] studied zinc phthalocyanine-Ag (100) interface with X-ray diffraction and photoemission spectroscopy techniques. They observed a strong π–d interaction between the adsorbate and the substrate in addition to the two molecular patterns which are oriented at an angle of 78° from each other.

The electronic structure of individual copper phthalocyanine (CuPc) molecules deposited on Cu (100) has been investigated by using scanning tunneling microscopy (STM).[11] In this work, the authors found that CuPc molecules adsorb in the flat-lying geometry with two different rotational orientations. However, the degree of rotation has not been measured/estimated.[11] It is well known that the adsorption configuration plays a significant role in the performance of organic molecular devices.[12,13] Therefore, to gain a better understanding of the ordering and phase transformation, a variety of other experiments have been carried out. For example, P. Palmgren *et al.* studied iron phthalocyanine (FePc) on Ag (110) surface in order to investigate self-assembly, the ordering of molecules at the interface, and the electronic and structural properties of thin films. Their study shows that the first monolayer relatively strongly binds to the substrate. Additionally, they observed two molecular patterns which are rotated $\pm$ 27° relative to the substrate.[14]

More recently, in the case of FePc–Ag (110) two simi-

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lar yet distinct ordered phases have been observed via STM; these are further evidenced by density functional theory (DFT) calculations.[15] In the monolayer case, two phases are observed wherein FePc molecular axes are rotated with respect to the [1-10] direction of Ag (110) by $(30 \pm 2)^\circ$ and $(-30 \pm 2)^\circ$ angles, respectively. In the multilayer case, STM data again shows two configurations rotated by angles of $\pm 16^\circ$ respectively, relative to the [1-10] low index direction of the Ag (110) substrate. Theoretical work regarding FePc on metal substrates has rarely been studied at the DFT level. Rather, bare FePc[16] and *M*Pcs (M = Ge, Sn, Pb)[17] have been investigated by first principles calculations. However, according to the best of our knowledge, an intermediate organic molecule tetracene on low-index copper surfaces [e.g., Cu (110) and Cu (100)] is the only system which has been studied in the framework of DFT.[18] Our recent STM study demonstrated temperature-based ordered growth behavior of FePc molecules on Cu (100) surface at mono- and multilayer coverages;[19] however, science has only begun to understand the geometry and electronic properties, and it calls for much more exploration. The focus of most work so far has been either the π–d interactions (which determine the structure and electronic properties of the adlayers) or the growth behavior of organic molecules in the first or later adsorbed layers.

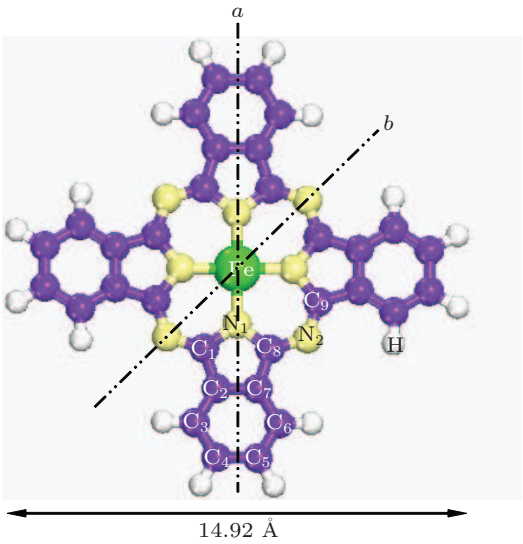


Fig. 1. (color online) Schematic perspective view of an iron phthalocyanine (FePc:$C_{32}H_{16}N_8Fe$) molecule. On the two benzopyrrole legs, special symbols identifying atoms are shown. The major and minor axes are represented by letters *a* and *b*, respectively. Iron is green, nitrogen light yellow, carbon violet, and hydrogen white.

Despite many experimental and theoretical studies, a comparison of FePc on Cu (100) and Cu (110) has not yet been accomplished, either experimentally or theoretically. As a first attempt to this end, here we present comprehensive first-principles electronic structure calculations for the monolayer adsorption of FePc on Cu (100) and Cu (110) surfaces. Our DFT study in this regard may help to: (i) truly investigate geometric and electronic structure and the most stable adsorption sites/geometries, (ii) address the strength of electronic interaction between molecule and substrate, and (iii) fill a gap in the theoretical literature and serve as a template for future MPc-based theoretical investigations. The main focus of our attention has been to find which low-index copper surface is most reactive with the organic molecule. It has also been our intention to simulate the charge transfer properties, which are at the heart of the function of any photovoltaic material. The molecular structure of FePc ($C_{32}H_{16}N_8Fe$) is schematically shown in Fig. 1 and its lateral length (diameter) is 14.92 Å (1 Å = 0.1 nm). FePc molecule is a planar molecule with fourfold symmetry (D_{4h}) which is generally broken upon adsorption on Cu (100).[11]

2. Computational method

DFT calculations of FePc on the fourfold and twofold surfaces of copper are carried out by using the DMol3 (e.g., density functional for molecules and 3D periodic solids) package integrated in the Materials Studio program of Accelrys Inc.[20] In the DMol3, the physical wave functions are expanded in terms of accurate numerical basis sets. As for the computational details, generalized gradient approximation (GGA),[21] the Perdew–Wang (PW91)[22] functional, and the DFT semi-core pseudopotential (DSPP) are used to describe electron–electron and electron–ion interactions, respectively. Concerning accuracy, the wave function and electron density are expanded by DND (double numeric plus d-function) basis sets and a real space cutoff of 4.0 Å is adopted to improve the computational performance. The sampling *k*-point set is generated automatically in the Monkhorst–Pack scheme.[23]

The convergence criteria for the geometrical optimizations are set as 2.0×10^{-5} Hartree for energy, 4.0×10^{-3} Hartree/Å for energy gradient, and 5.0×10^{-3} Å for ionic step displacement. A Fermi smearing of 0.004 Hartree (1 Hartree = 27.2114 eV) is used to minimize the errors in the Hellmann–Feynman forces, which are due to the entropic contribution to the electronic free energy.[24] For numerical integration, medium grid mesh points are employed for the matrix integration and a single point is used to calculate the total energy and charge density as a balance between time and accuracy. Under the present conditions, the lattice constant of the face centered cubic copper (Cu) crystal is $a_{Cu} = 3.615$ Å. This value agrees well with the previously determined value.[25] The next-neighbor distances in the close packed (100) and less closely packed (110) copper surfaces are 2.556 Å and 3.615 Å, respectively (drawn in the respective figures). Lippel *et al.* estimated Cu (100) atom spacing to be 2.55 Å.[11] All energies

are extrapolated to $T = 0$ K and the theoretically determined lattice constant is initially used to construct the substrate surfaces. Periodic slabs for both the fourfold (100) and twofold (110) copper surfaces are used for the larger surface unit cells. Generally, a several-layered slab (i.e., above three layers) increases the precision of the calculation but is computationally expensive in both memory and time. However, there is not a huge difference in the results between systems with three Cu layers and systems with more than three Cu layers. (To see how the quality of results depends on the size of the super cell, the interested reader is referred to Ref. [26].) In the present study, for the case of Cu (100), a (7×7)-unit cell with a four-layer slab is chosen to calculate the optimal structural. The Cu (110) surface is modeled by a four-layer slab with a (5×7)-unit cell. In both cases, the slab is repeated periodically with 20 Å (for 'flat-lying' mode) of vacuum region between the slabs. This vacuum space is wide enough to avoid any interaction between the slabs and FePc molecules in different unit cells. During the process of structural optimization, all atoms except for the bottom two Cu layers are fully relaxed.

In all our calculations, only a single molecule is adsorbed on one side of both the adopted slabs (the coverage is monolayer-ML). Our calculated work functions for (100) and (110)-oriented copper crystals are 4.136 eV and 4.05 eV, respectively. From these values, it can clearly be seen that the work function shows a (100) → (110) trend of increasing value with varying crystallographic orientation. These values and orderings are consistent with the widely accepted results (4.59 eV–4.48 eV).[27] The differences in work function are certainly relevant for an interpretation of adsorption properties of the molecules of interest on different substrates.[28,29] The ionization potential of FePc as calculated via VAMP is 7.33 eV, which is slightly larger than our experimentally determined value.[30]

3. Results and discussion

In this study, we investigate the interaction of a single iron phthalocyanine molecule with the coinage-metal Cu (100) and Cu (110) surfaces. For simplicity, plus and cross sign orientations of the molecule are chosen, which are abbreviated as "P" and "C," respectively, for each of the copper facets. Both the structural orientations are depicted in Fig. 2, with adsorption sites and configurations. The two reasons for choosing two models are: i) recent experimental findings show that FePc and other phthalocyanine molecules form two different phases or two different rotational orientations when adsorbed on copper and/or silver surfaces;[10,11,15] ii) it has been determined that adsorption configuration plays a significant role in the performance of organic molecular devices.[12,13]

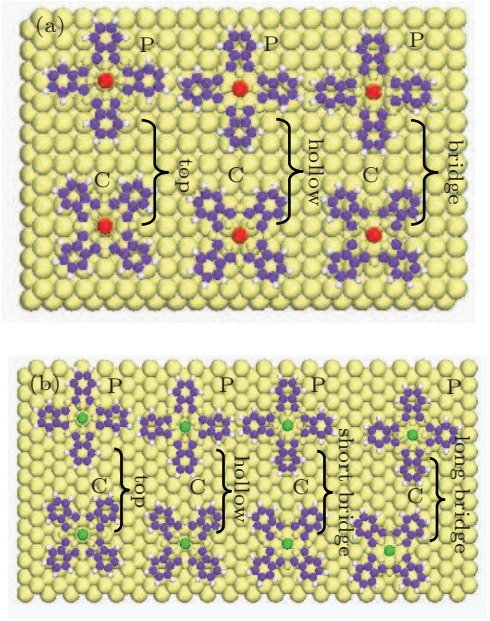


Fig. 2. (color online) All the local adsorption sites of a single FePc molecule on (a) Cu (100) and (b) Cu (110) surfaces. For simplicity, plus and cross sign orientations are chosen which are abbreviated as "P" and "C", respectively. The "P" configuration refers to any adsorption site with the major molecular axis parallel to one of the lattice directions. The "C" configuration is obtained by rotating the benzopyrrole leg by 45°. We selected top, hollow, and bridge sites for FePc on Cu (100). For FePc on Cu (110), we selected top, hollow, short bridge, and long bridge sites. Thus the series of models developed is: P–T, P–H, P–B, C–T, C–H, C–B, P–SB, C–SB, P–LB, and C–LB. The names refer to the position of the central iron atom with respect to the underlying Cu (100) and Cu (110) surfaces.

Three adsorption sites are chosen for FePc on Cu (100) and four for FePc on Cu (110), as initial structures. On each adsorption site, the calculations are carried out while considering both the P and C configurations. The adsorption geometries are considered by placing the center of mass of the molecule at, respectively, the top site (T), the hollow site (H), the bridge site (B), the short bridge site (SB), and the long bridge site (LB). Due to the fourfold symmetry of FePc molecules, the adsorption sites we investigated represent the typical adsorption configurations that maintain symmetry. The structure is optimized with the rotational angles, height of the molecule, and the maximum adsorption energy. The adsorption energy, E_{ads}, which comes from the molecule–substrate interaction, is calculated through

$$E_{\text{ads}} = (E_{\text{FePc}} + E_{\text{Cu}}) - E_{\text{FePc+Cu}}, \tag{1}$$

where $E_{\text{FePc+Cu}}$ is the energy of the adsorbed molecule interacting with the Cu slab, E_{Cu} is the total energy of the copper cluster and E_{FePc} is the energy of the gas phase adsorbed molecule. Equation (1) indicates that minimizing total energy maximizes the adsorption energy. This equation establishes a direct relationship between the energy and strength of adsorption; that is to say, the more positive the energy the stronger

the adsorption. Geometry optimizations are performed for all the fourteen models, as illustrated in Fig. 2, and the results are computed in Table 1. From Table 1 it is clear that: (I) in the case of FePc on fourfold Cu (100) surface, the top, hollow-sited configurations with orientations "P" and "C" are the most favorable structures; (II) in the case of molecule adsorbed on the twofold Cu (110) surface, top- and short-bridge-sited configurations with orientations "C" and "P" are the best adsorption geometries. For simplicity, the detailed investigations are performed only for the favorable adsorption sites, i.e. for the four models, P–T, C–H, C–T, P–SB, which are illustrated in Fig. 3. P–T and C–H geometries are for an FePc molecule on Cu (100) and C–T and P–SB are for an FePc molecule on Cu (110) surface.

Table 1. Summary of the equilibrium molecule–Cu distance $d_{\mathrm{Fe-Cu}}$, adsorption energy E_{ads}, charge transfer Q, bending angle (θ°), and rotating angle (α°) for the single FePc molecule adsorbed on the favorable adsorption sites of Cu (100) and Cu (110) surfaces. Charge transfer Q is defined as the total Mulliken charge number on the molecule (positive Q means charge transfer from the substrate to the molecule).

Surface	Model	E_{ads}/eV	$d_{\mathrm{Fe-Cu}}$/Å	$Q(e)$	θ°	α°
Cu (100)	P–T	4.101	2.70	0.864	7	9
	P–H	3.928	3.60			
	P–B	3.738	2.90			
	C–T	5.042	2.70			
	C–H	5.185	3.30	0.921	10	3
Cu (110)	P–T	4.512	2.80			
	P–H	3.967	3.20			
	P–SB	5.132	3.50	0.780	0	0
	P–LB	4.321	3.40			
	C–T	4.686	2.60	0.732	2	0
	C–H	4.120	2.90			
	C-SB	3.876	3.20			
	C–LB	4.355	3.00			

The parameters such as adsorption energy E_{ads}, charge transfer Q, distortion of the molecule due to adsorption, and its orientation relative to the substrate during the geometric optimizations of the four deeply investigated models are also shown in Table 1. Charge transfer Q is defined as the total Mulliken charge number of the molecule; where the positive Q means charge transfer from the sample substrate to the molecule. We calculated the charge transfer using the method described in our previous work.[31] Briefly, it is estimated based on the total Mulliken charge numbers of both the molecule and the sample substrate.

It is noteworthy that both the sample surfaces serve as charge donators. However, the electron charge transfer from the substrate to the molecule is greater for Cu (100) than for Cu (110). The overall charge transfer is greatest when the molecule is adsorbed on the H site of the Cu (100) surface. Such a large electron transfer indicates that the transition metal phthalocyanine is a good p-type organic semiconductor. Further, it is clear from Table 1 that the binding energy, the charge transfer, and the bending angle are largest in the case of C–H model as compared to the other models–indicating stronger interaction between the molecule and the substrate in this case. Even though the FePc molecule interacts strongly with the Cu (100) surface when placed on the H site, its fourfold symmetry does not break.

In P–T model (Fig. 3(a)), the molecular plane of FePc lies horizontally on the substrate surface. However, the plane is bent, with an angle of about 7°, at the expense of strong molecule–substrate interaction. Moreover, the major molecular axis is oriented at an angle of 9° relative to the [01-1] crystallographic direction. In C–H model (Fig. 3(b)), the molecule is horizontally adsorbed and the shorter axis is aligned 3° toward the [011] substrate direction. However, the molecular bend in this case is 10°. In the C–T and P–SB models (Figs. 3(c) and 3(d)), the molecule is again parallel to the surface but neither a swear bend nor a rotation is observed. A greater misalignment or topological phase transformation from flat to almost buckled FePc when deposited on Cu (100) (Fig. 3(b)) is at the expense of strong FePc–Cu (100) interaction. However, a smaller misalignment in the case of FePc on Cu (110) (Fig. 3(c)) can be attributed to weak FePc–Cu (110) interaction. Phase transformation or disturbed molecular form has commonly been observed for the case of FePc on copper and silver surfaces.[10,11,15]

Our DFT calculations answer the question as to why an FePc molecule is adsorbed more strongly on the fourfold copper surface as compared to the twofold. Severe changes in the molecular adsorption geometry demonstrate that molecular orientation is indeed greatly affected by the substrate's symmetric directions. Another reason is that the strength of the molecule–substrate interaction is greater in the fourfold symmetric Cu (100) surface than in the twofold symmetric Cu (110) substrate, which eventually drives the bending of the molecule. In fact, the molecular interaction with the underlying substrate, mediated by the molecular orbitals, makes the electronic structure of the adsorbed FePc significantly different from that of the gas phase molecule. The interaction between organic molecules and metal substrates is expected to be between the π-orbitals of molecules and metal d-bands, which ultimately leads to interesting features like the molecule's bending[32] and/or charge transfer.[33] From the above discussion, it is concluded that strong molecule–substrate interaction greatly affects the electronic structure of FePc.

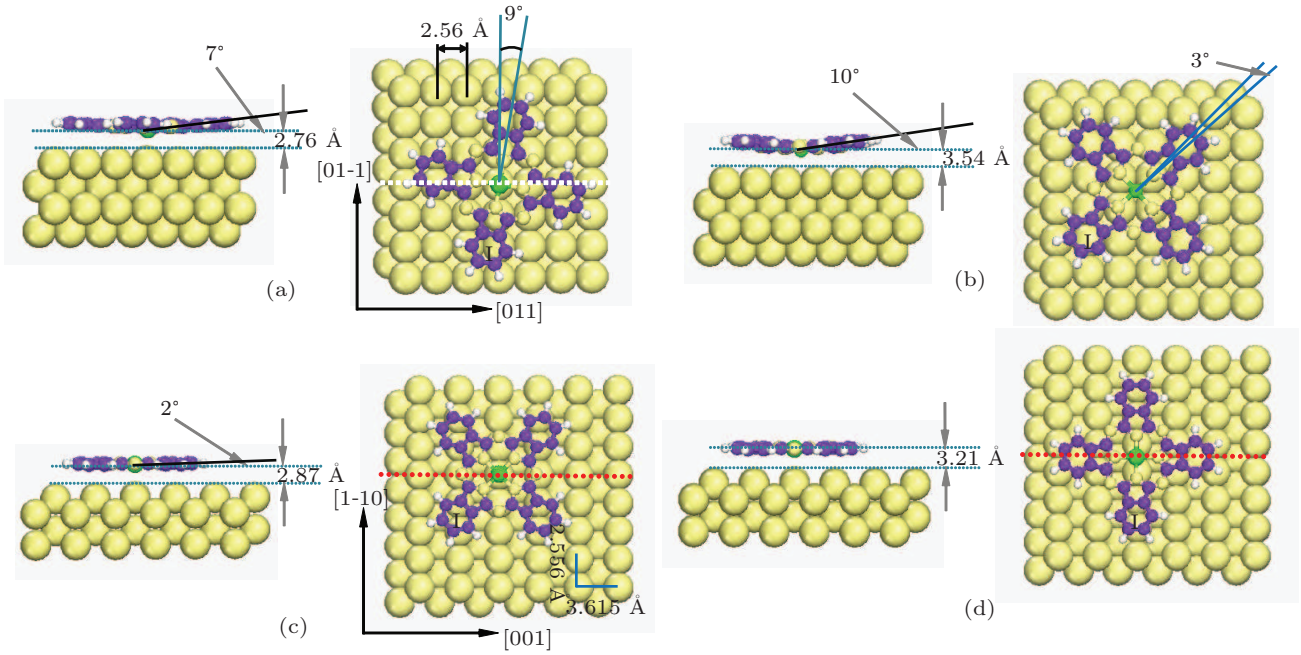


Fig. 3. (color online) Schematic illustration of the geometry changes when FePc molecule is adsorbed on the T, H sites of Cu (100) and T, SB sites of Cu (110) surfaces. Both the top and side views are shown, in the right and left sides, respectively. (a) P–T model; (b) C–H model; (c) C–T model; (d) P–SB model. The benzopyrrole unit that is used in the determination of bond lengths and bond agles is marked with the pink color I.

For further insights into the molecule–substrate interactions, we calculated structural parameters like bond lengths and bond angles for the best adsorption geometries (Figs. 3(a)–3(d)). The benzopyrrole units that are considered in the estimation of bond lengths and bond angles are labelled by the black color "I." A summary of the estimated structural parameters for the energy minimized structures is presented in Table 2. As one goes across the periodic table from bare to P–SB, there is a fluctuating trend in the bond lengths and bond angles. The bond length increases from bare to C–H, then decreases through P–T, before rising/decreasing again in the cases of C–T and P–SB. A rather similar variation can also be seen in the case of bond angles. The selection of site gradually leads to a progressive increase in the bond lengths and bond angles. Theoretical and experimental results for the structural parameters of FePc from a previous DFT calculation effort and X-ray diffraction results are also collected in Table 2. As shown in Table 2, the optimized bond lengths and bond angles for the energy-minimized structures are reasonably consistent with the previous computational and experimental findings.[34,35]

Table 2. Calculated structural parameters of the bare and adsorbed molecule (mol) of the models: P–T, C–H of Cu (100) and C–T, P–SB of Cu (110). The atomic numbering scheme used in Fig. 1 is adopted from Ref. [35]. All the bond lengths (R) are in Å and bond angles (Φ) are in degrees.

Parameters	Bare mol	P–T	C–H	C–T	P–SB	DFT[(a)]	XRD[(b)]
R_{Fe-N1}	1.916	1.917	1.920	1.911	1.914	1.918	1.927
R_{N1-C1}	1.401	1.395	1.397	1.397	1.401	1.391	1.378
R_{C1-C2}	1.437	1.445	1.446	1.442	1.439	1.450	1.449
R_{C2-C7}	1.404	1.409	1.412	1.423	1.406	1.408	1.390
R_{C2-C3}	1.389	1.399	1.400	1.409	1.407	1.399	1.395
R_{C3-C4}	1.394	1.399	1.397	1.408	1.409	1.394	1.387
R_{C4-C5}	1.405	1.409	1.410	1.417	1.419	1.412	1.394
R_{C8-N2}	1.320	1.326	1.326	1.334	1.331	1.322	1.322
$\Phi_{C1-N1-C8}$	105.777	106.895	106.810	107.256	107.188	106.7	107.2
$\Phi_{N1-C8-N2}$	126.326	126.996	127.212	126.326	126.369	127.6	129.9
$\Phi_{C8-N2-C9}$	122.966	122.386	122.533	124.425	124.448		121.3
$\Phi_{N1-C8-C7}$	110.328	109.933	109.877	109.790	109.686	110.1	110.0
$\Phi_{C2-C7-C8}$	106.773	106.590	106.701	106.629	106.712		106.4
$\Phi_{C2-C7-C6}$	121.283	120.964	120.982	120.931	121.017		121.3
$\Phi_{C5-C6-C7}$	117.579	117.845	117.897	117.820	117.760		117.0
$\Phi_{C4-C5-C6}$	121.135	121.156	121.092	121.137	121.196		121.2

[(a)] Values in this column are DFT results of FePc from Ref. [34].

[(b)] Values in this column refer to the X-ray diffraction (XRD) data of FePc from Ref. [35].

To gain better understanding and to interpret the physical nature of the molecule–Cu interaction, we further calculated the difference of charge density caused by the adsorption of FePc on all the four favorable adsorption sites. The difference of charge density before and after the adsorption can be expressed as

$$\Delta\rho = \rho_{\mathrm{FePc+Cu}} - (\rho_{\mathrm{FePc}} + \rho_{\mathrm{Cu}}), \tag{2}$$

where $\rho_{\mathrm{FePc+Cu}}$ is the electron density of the FePc + Cu system, and ρ_{FePc} and ρ_{Cu} are unperturbed electron densities of the adsorbate and substrate, respectively. The electron density difference maps of FePc–copper interfaces can be seen through Figs. 4(a)–4(d). Solely within the context of the present calculations, a distinction between the corresponding electronic density contour graphs can be observed; however, the nature of the charge redistribution in all the maps is similar. All four maps show electrons from copper substrates spilled out into the FePc molecular states. The magnitudes and direction of the electron transfer estimated in the present work are broadly consistent with the values of 0.96 eV and 0.80 eV previously calculated for FePc on Ag (110) and Ag (100) surfaces, respectively.[29,36] Obviously, the estimated magnitude of charge transfer is greatest ($0.921e$) for FePc on the H site of Cu (100), as can be seen in both Fig. 4(b) and Table 1.

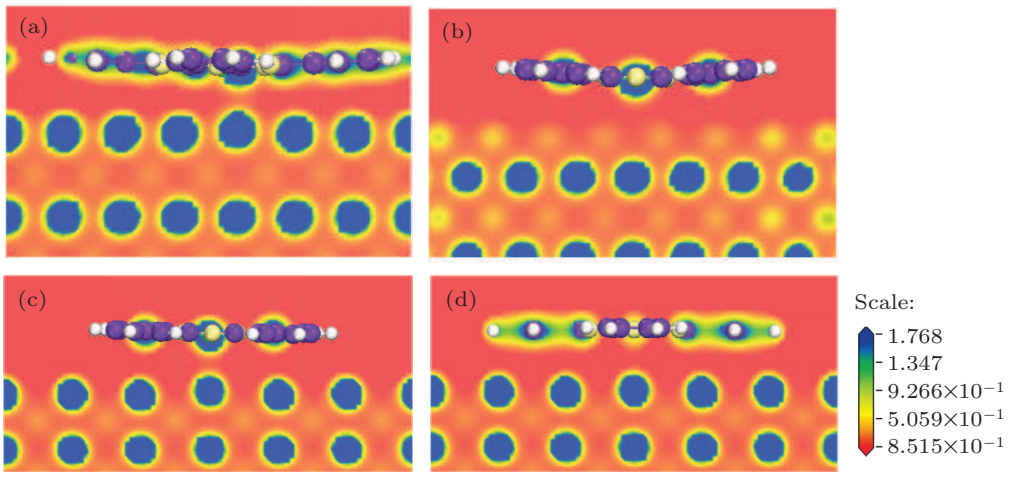


Fig. 4. (color online) Side views of the calculated electron density difference maps ($\Delta\rho$) for FePc/Cu (100) and FePc/Cu (110) interfaces, respectively. These electronic charge density contours correspond to the following adsorption geometries/models: (a) P–T; (b) C–H; (c) C–T; (d) P–SB. The maps are vertically cut along the dotted white and red lines in Fig. 3. The charge density difference is in a scale of electrons/Å^3.

In the case of FePc on Cu (110), less charge is spilled out as compared to FePc on Cu (100), indicating again the relatively weaker interaction between FePc and Cu (110). This charge transfer from the substrate to the molecule induces a charge reorganization in FePc, as is evident from the electron density difference plots shown in Figs. 4(a)–4(d). A larger charge transfer for FePc on Cu (100) makes the electron density difference highly perturbed (Figs. 4(a) and 4(b)); however, the smaller charge transfer for FePc on Cu (110) makes the electron density difference less perturbed (Figs. 4(c) and 4(d)). The variation of charge density difference is due to the dissimilar magnitudes of charge transfer and strong/weak molecule–substrate interactions.

The charge transfer is responsible for the surface dipole formation. It indicates that the greater the 'overspill' the larger the surface dipole. However, the extent of 'overspill' is a function of surface geometry. By manipulating the charge transfer values and the respective distances for the most favorable sites (C–H for FePc on Cu (100) and P–SB for FePc on Cu (110)), the interface dipoles $\mu_{\mathrm{C-H}}$ and $\mu_{\mathrm{P-SB}}$ are estimated to be 4.86×10^{-29} C·m and 4.37×10^{-29} C·m, respectively. The work function change and dipole moment are directly related through a tiny relation $\Delta\Phi = e\mu/\varepsilon_0 A$; with e being the electronic charge, μ the dipole moment, A the surface area taken up by one molecule, and ε_0 the permittivity of vacuum. Following this relation, the work function changes for the two most favorable models C–H and P–SB are estimated to be 3.7 eV and 3.3 eV, respectively. A larger surface dipole formation and greater work function change in the C–H model as compared to the P–SB model again strengthen our previous findings. However, screening effects and other related mechanisms[37] need to be taken into account in order to understand the true nature of work function change.

To obtain further insight into the interaction at the interface of FePc and Cu, we also calculated the density of states (DOS) of FePc and Cu substrates before and after the adsorption, which are shown in Figs. 5(a)–5(d). The series of DOS plots, which apparently seem similar, illustrate some of the

typical characteristics observed in the present study. Changes in the DOS features are a measure of the interaction between the adsorbate and Cu substrate. A close inspection of the lower and middle panels of Figs. 5(a)–5(d) reveals that features arising from the substrates are almost imperturbed. Features attributed to the fourfold symmetric molecule are labeled as α, β, γ, δ, and ζ, and are shown in the top panels of Figs. 5(a)–5(d). The results for the bare and adsorbed molecular structures corresponding to different adsorption sites are summarized in Table 3.

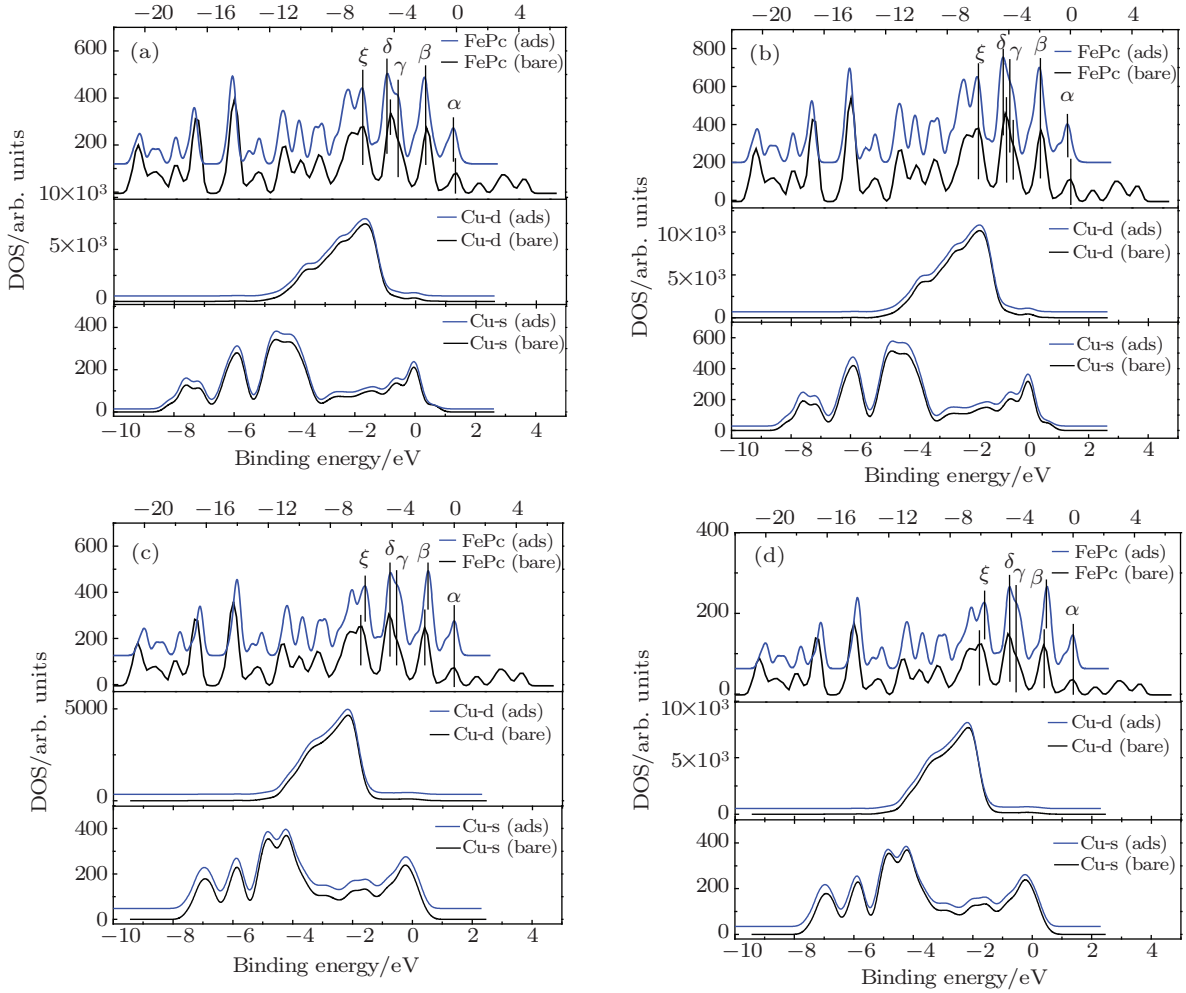


Fig. 5. (color online) Calculated density of states (DOS) for FePc/Cu (100) and FePc/Cu (110) structures: (a) molecule adsorbed on the top site of Cu (100); (b) molecule adsorbed on the hollow site of Cu (100); (c) molecule adsorbed on the top site of Cu (110); (d) molecule adsorbed on the short bridge site of Cu (110). Black solid lines: DOS of isolated molecule and bare copper surfaces. Blue solid lines: DOS in the adsorbed systems. Binding energies are referenced to the Fermi levels of copper surfaces.

Table 3. Calculated molecular structures of the free and adsorbed molecule (mol) of the models: P–T, C–H of Cu (100) and C–T, P–SB of Cu (110).

	α	β	γ	δ	ζ
Bare mol	0.013	1.961	3.714	4.156	5.974
P–T	0.175	2.014	3.714	4.440	5.974
C–H	0.208	1.961	3.935	4.377	5.974
C–T	0.013	1.668	3.714	4.109	5.710
P–SB	0.013	1.732	3.714	4.156	5.741

In the case of FePc on Cu (100) (Figs. 5(a) and 5(b), Table 3), a great difference in the line shapes and energy positions of electronic density of states can clearly be observed between the bare and adsorbed molecule; especially between the energy ranges of 0.2 eV–5 eV (Fig. 5(b)). However, only a few differences in the electronic density of states can be found when molecule is deposited on Cu (110) (Figs. 5(c) and 5(d)). Based on the DOS results it can be pointed out that the strong molecule–Cu (100) interaction provides the dominant contribution to the valence level shift; whereas, in the case of FePc–Cu (110) the valence level shift is reduced by a sizable factor (see Table 3). Probably, this finding implies that the valence band level shift is surface- and site-dependent. The molecular structures result from the π states located on the aromatic rings, benzene, and hybrid Fe–N orbitals. In the former case, the changes in the shape of the adsorbed molecular orbitals and

the orbital shifts are a clear signature of the strong molecule–substrate interaction. It should be noted that FePc molecules prefer to lie flat on the copper and silver surfaces[11,15] at the initial stage of growth, leading to maximization of the interaction between the d-band of the substrate and the π-molecular orbitals.

The changes in the electronic structure of the adsorbed molecule demonstrate that FePc interacts with the underlying substrate not only through the benzopyrrole legs but also through the singly occupied d_z^2 orbital.[38] Within the framework of our interpretation, i.e. from the knowledge of the electronic and structural properties and density of states, we conclude that the fourfold copper surface displays a stronger interaction with the molecule than the twofold copper surface. This is because the Cu (100) substrate influences the electronic structure of the molecule more heavily than the Cu (110) substrate and interacts more strongly with the adsorbate.

According to our survey, no comparative study of FePc on Cu (100) and Cu (110) surfaces has been carried out before. Therefore, in order to truly know the structural deformation and to comprehensively understand whether FePc interacts strongly with Cu (100) or Cu (110) surface, an experimental study of these two systems is much needed.

4. Conclusion

In conclusion, we have investigated the lateral adsorption geometry and electronic structure of the fourfold symmetric molecule on the fourfold and twofold copper surfaces in the framework of DFT. A greater misalignment or topological phase transformation from flat to almost buckled FePc is observed, due to the stronger FePc–Cu (100) interaction. However, a smaller misalignment in the case of FePc on Cu (110) is noted, which can be attributed to the weak FePc–Cu (110) interaction. We also simulated the charge transfer properties, which are at the heart of the function of any photovoltaic material. The optimized bond lengths and bond angles are in good correspondence with the experimental and previously calculated results. On the basis of the structural and electronic properties, it is concluded that the FePc molecule interacts more strongly with the Cu (100) surface than with the Cu (110) surface, which is further evidenced by the charge transfer and changes in the shape of the adsorbed molecular orbitals and the orbital shifts. Furthermore, a density of states analysis shows that valence band level shift is surface- and site-dependent.

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