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Interactions between Organics and Metal Surfaces in the Intermediate Regime between Physisorption and Chemisorption

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**ABSTRACT:** The adsorption of pentacene, perfluoro-pentacene, other acenes and biphenyl on a Cu(111) single-crystal surface was studied by a modified version of a Van der Waals density functional. Accurate and consistent interface geometries and adsorption energies were obtained for the first time. All studied interactions between the organics and the metal are in the sensitive intermediate regime between chemisorption and physisorption, in which regime both geometric and electronic structures of the adsorbates are strongly modified by the metal surface. Adsorption induced gentle curving of flat acenes is demonstrated and explained (the ends of the acenes curving away from the metal relative to their center); in contrast, biphenyl, which is twisted when free, becomes coplanar after adsorption. More importantly, perfluoro-pentacene is “pinned” to Cu(111) by a sharp bend that creates a localized strong bond, which explains earlier puzzling experimental observations reported for perfluoro-pentacene relative to pentacene. Electronic structures of these two adsorbates are compared to further probe their different interface mechanisms.

**TOC Graphic:**

![Pentacene: gentle curve](image)

Perfluoro-pentacene: sharp bend

**Keywords:** Organic-metal interfaces, Van der Waals density functional, Perfluoro-pentacene, Acenes, Phenylene
INTRODUCTION

The structure of the contacting interface between organic molecular semiconductors and metallic substrates determines its cooperative properties in organic thin-film devices, e.g. transistors, light-emitting diodes and organic photovoltaics. Different types of interaction coexist in the complex interfacial structures, which include chemical bonding, Van der Waals (VdW) interaction, Pauli repulsion, etc. It is essential to accurately account for the different types of interaction and to predict interface structure and stability in order to design the functions and quality of these devices.

Polyacenes on surfaces, especially the archetypical organic semiconductor pentacene (PEN, C_{22}H_{14}), have received much attention in the study of organic field effect transistors because of their unusually high intrinsic charge-carrier mobility without doping. The fully fluorinated analogue to PEN, perfluoro-pentacene (PFP, C_{22}F_{14}), also received increasing attention recently, since fluorination can enhance the electron affinity and ionization energy and also reduces the prevailing susceptibility to oxidation.

PEN prefers to lie flat on metal surfaces due to its π electrons interacting with both the near-Fermi-level states and the deeper-level d electrons of transition metals. For PEN on Cu(110) and Cu(100), both experiment and theory showed a curving away from the surface of the end rings of the initially “flat” adsorbate, i.e. after adsorption the end rings are farther from the surface than the center rings (cf. Fig. 1a,c drawn for Cu(111)). The molecular corrugation of PEN calculated by density functional theory (DFT) is 0.4 Å (including H atoms) on Cu(110) and 0.16 Å (only for C atoms) on Cu(100). Although the VdW interaction is neglected in the above two simulations, the theoretical results fit experiment fairly well due to the relatively strong chemical bonding of PEN with these two less-closely packed copper surfaces.

Despite much success in recent studies for PEN and PFP on metals, understanding of the detailed interface geometries remains challenging for both experiment and theory. For PEN on the more-closely packed Cu(111), both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) measurements indicate curving geometries, similar to adsorption on Cu(100) and Cu(110). However, the chemical interaction between PEN and close-packed Cu(111) is so weak that normal DFT calculations fail to predict a correct interface geometry: an adsorption geometry without curving and larger PEN-Cu(111) separations are reported in
previous simulations. Recent work finds that the original version of the Van der Waals density functional (VdW-DF) also fails to predict the correct interface geometry for PEN on Cu(111), since the original VdW-DF tends to overestimate equilibrium adsorption distances. In the current work, accurate interface geometries and adsorption energies were obtained for PEN, PFP, heptacene ($C_{30}H_{18}$), anthracene ($C_{14}H_{10}$), naphthalene ($C_{10}H_{8}$), benzene ($C_{6}H_{6}$) and biphenyl ($C_{12}H_{10}$) on Cu(111) (Figures 1 and 2, Table 1), by adopting a modified version of VdW-DF (optB86b-VdW).

### COMPUTATIONAL DETAILS

The Vienna *ab initio* simulation package (VASP) was employed for the calculations. Inner electrons are described by the projector augmented wave (PAW) potentials, while the valence electrons were expanded in plane waves with an energy cutoff of 500 eV. The optB86b-VdW-DF was adopted, which uses an optimized B86b exchange functional to improve the accuracy of equilibrium interatomic distances and energies for both molecular and solid systems. For composite systems of molecules on metals, the optB86b-VdW functional has recently been shown to give better results compared with experiment. The surfaces are modeled by four-layer slabs with 28 or 36 atoms per metal layer with rectangular ($2\sqrt{3} \times 7$)rect or ($2\sqrt{3} \times 9$)rect cells (selected to avoid intermolecular interactions, depending on the molecule length), and the corresponding k-points mesh is (4x2). These parameters have been shown to give well converged results. Regarding the adsorption site, low-temperature STM determined that the long molecular axis is aligned with the close-packed Cu atom rows along <110>, and that the central ring is centered over hexagonal close-packed (hcp) hollow sites of the substrate. Our calculation for PEN shows that the hcp hollow site is better than the face-centered cubic (fcc) hollow site by 0.03 eV, and the hcp hollow site was therefore adopted in our simulations. Geometry optimizations were performed with a residual force threshold of 0.01 eV/Å, and all atoms in the simulation model are fully relaxed. More calculation details are included in the supporting information.

### RESULTS AND DISCUSSION
Based on our predicted adsorption geometries, which show bent or curved structures for adsorbed acenes, the current work can explain puzzling and contradictory experimental observations when comparing the adsorption behaviors of PEN and PFP on Cu(111). On one hand, X-ray standing wave (XSW) experiments appear to suggest that PEN bonds much more strongly than PFP on Cu(111): the average carbon bonding distances for PEN and PFP to Cu(111) are 2.34 Å and 2.98 Å from XSW, respectively. On the other hand, STM experiments suggest the reverse, namely that PFP bonding is more strongly bonded to the metal than PEN: PFP was seen to be immobile (“pinned”) on Cu(111) in the submonolayer regime at room temperature, while in the same experimental conditions PEN cannot be imaged due to fast molecular motion. Our VdW calculations predict a sharply bent adsorption geometry of PFP (see Figure 1c): the average height is much larger than for PEN (Table 1), while the central C-Cu bonding induces strong distortions in both C and Cu, “pinning” PFP to the surface. For PEN, the central parts remain flat (Figure 1a), allowing it to easily slide along the surface. Thus, the different interface geometries of PEN and PFP explain the contradictory experimental observations between XSW and STM, as mentioned above. More details of the calculated geometries are described below.

**Figure 1.** Adsorption geometries of PEN (a, b) and PFP (c, d) on Cu(111) in side and top views, respectively: PEN (C_{22}H_{14}) is gently curved and PFP (C_{22}F_{14}) sharply bent as shown in the side
views; numbers (in Å) denote C-Cu distances for the central and the outermost carbons. The central parts of PEN remain flat for C atoms in the dashed ellipse denoted in panel b), while PFP is strongly bent and its C-Cu bond in the dashed circle (panel d) is much stronger than at all other sites (see text). Only the top Cu layer is shown.

Figure 1 shows the relaxed geometries of PEN and PFP on Cu(111). The outermost carbons of the adsorbed PEN curve up gently by about 0.2 Å above the central carbons while the carbons in the central part remain very flat: in the dashed ellipse in Figure 1b, the vertical distortion of the PEN carbons and the Cu atoms below remains very small: the C-Cu distance changes by less than 0.02 Å across this area. So, PEN is expected to slide relatively easily on Cu(111), as reported in room temperature STM measurements.\textsuperscript{18, 21} That the central part of the 5-ring PEN remains flat is made more convincing by considering the adsorption geometry of the longer 7-ring heptacene (Figure 2b): only the outermost rings curve up while the inner rings remain quite flat. The central rings of acenes interact more strongly with copper, which is expected since the central rings are more reactive than the outermost rings due to the overlap of molecular orbitals inside the molecule.\textsuperscript{34}

The deformation of adsorbed PFP is much stronger than PEN, especially when comparing the central part, as shown in Figures 1c and 1a. For PFP, the central C-Cu bonding in the dashed circle in Figure 1d is much stronger than at other sites: the central C atom bonded with Cu is lowered by 0.26 Å below its nearest carbons, and the Cu atom below this C is higher by 0.15 Å than the average height of other atoms in the first metal layer. The strong central C-Cu bonding and the significant distortions of both C and Cu make it difficult for PFP to move on the surface, and hence PFP can be “pinned” on Cu(111) at low coverage,\textsuperscript{18, 21} even though its average C height is larger than for PEN (Table 1). More comparisons of the different PEN-Cu(111) and PFP-Cu(111) bonding are presented in the electronic structure analysis below (Figures 3 and 4). The average height of PFP is larger than for PEN due to the Pauli repulsion between F 2p electrons and the substrate states.\textsuperscript{25, 28} The molecule-metal interaction is determined by a competition of three types of interaction: the repulsive interaction due to Pauli repulsion, and the two types of attractive interactions due to hybridization (chemical interaction) and VdW force, respectively.\textsuperscript{35}
The larger average height of PFP vs. PEN on Cu(111) is ascribed in the above to the stronger repulsion between F and Cu (compared to the repulsion between H and Cu). We can prove this further by calculating the geometry of PEN on a contracted Cu(111) lattice (contracted 3% parallel to the surface, while the vertical direction is free to relax): a strongly curved adsorption of PEN, similar to PFP, is obtained, with a molecular corrugation of 0.8 Å, which is four times larger than the 0.2 Å corrugation for PEN on a normal Cu(111) lattice. See Figure 5 for this relaxed structure. The Cu(111) lattice contracted by 3% in the two parallel directions and the free relaxation in the vertical direction result in an increase by about 6% of the vertical separation between Cu layers, so as to try to keep the same volume, which means the electron repulsion in the vertical direction becomes stronger, i.e. the Pauli repulsion in the vertical direction is enhanced compared to that in the normal Cu lattice. As a result of the competition of enhanced Pauli repulsion and the attraction from chemical bonding and VdW force, PEN on contracted Cu(111) becomes strongly curved, similar to PFP on the normal Cu(111). The chemical bonding (hybridization) lowers the center of the molecule, the repulsion raises the molecule ends (the PEN center is more reactive as noted above), and the VdW interaction forces the molecule closer to the surface, thus generating the hybridization and repulsion described above.

Figure 2. Adsorption geometries of other molecules: a) and b) different curving of shorter and longer acenes (anthracene with 3 phenyl rings, heptacene with 7 phenyl rings); the central part of heptacene remains flat, which is similar to PEN; c) biphenyl, twisted between rings in the free molecule vs. coplanar geometry in the adsorbed structure. Some C-Cu distances are labeled (in Å).
Figure 2 shows the adsorption geometries of other acenes and biphenyl on Cu(111). Figures 2a and 2b display the different types of curving of the shorter 3-ring anthracene and the longer 7-ring heptacene. The two ends of all acenes are curved up, while for longer acenes the central rings remain flat, as shown in Figure 2b. Figure 2c shows that for biphenyl, whose rings are mutually twisted in the free molecule, the molecule-metal interaction forces the molecule into a coplanar structure on Cu(111) due to the VdW interaction (molecule-Cu attraction) and H-Cu repulsion. In addition to biphenyl, one can anticipate that other poly(p-phenylene) molecules will also tend to adopt a similar coplanar geometry on Cu(111).

The interface properties of PFP and PEN on Cu(111) can be probed and compared further through analysis of the electronic structure. Figures 3a and 3b display the differential charge induced by metal-molecule bonding, which shows that charge transfer occurs mainly between the Cu $d_{z^2}$ and C $p_z$ orbitals. Two notable features are observed: 1) the entire PEN molecule interacts strongly with the Cu surface, while only the central part of PFP bonds strongly to the Cu atoms underneath; 2) comparing Figures 3a and 3b, overall the PFP orbitals are less affected than PEN. These two features are in good agreement with X-ray photoelectron spectroscopy (XPS) experiments,\textsuperscript{23} which imply that for PFP, the total interaction strength is weaker and the molecular orbitals are overall less perturbed by the metal. Figure 3c shows the projected density of states (PDOS) of C $p_z$ orbitals of the molecule with its relaxed geometry in adsorption. Both the PDOS with and without the Cu(111) surface are given to exhibit the effect of surface interaction. The PDOS plots also demonstrate a stronger interaction of PEN with Cu(111) than for PFP, which is reflected in the generally increased PDOS broadening, especially below -2 eV where the interaction with Cu $d$ orbitals dominates. The PDOS of adsorbed PEN and PFP both show a metallic character, in agreement with scanning tunneling spectroscopy (STS) measurements for PEN on Cu(111).\textsuperscript{11} Note that the time-domain dynamics on the charge transfer is neglected in our simulation.\textsuperscript{36-37}
Figure 3. Electronic properties of adsorbed PEN and PFP: a) and b), differential charge induced by molecule-metal bonding mainly from the interaction of Cu $d^2$ and C $p_z$ orbitals (blue = electron accumulation, red = electron depletion; isosurface value: 0.03 electrons/Å$^3$); the PFP case is further illustrated in top view in Figure S1 of the Supplementary Information. c), density of states projected to C $p_z$ orbitals, for molecules (fixed as in their adsorbed geometries) both without and with Cu(111) to show the effect of surface interaction; the Fermi level is set to zero.

Figure 4. Density of states projected to HOMO (H, red solid lines), LUMO (L, black solid lines), and LUMO+1 (L+1, blue dashed lines) of PEN (upper panel) and PFP (lower panel). The Fermi level is set to zero.
Figure 4 compares the molecular orbital projected density of states (MO-PDOS) of PEN and PFP, i.e. projection of the full system density of states onto the orbitals of the (isolated) molecule. The resolution of the PDOS in terms of HOMO, LUMO and LUMO+1 is shown. For PEN, the HOMO and LUMO PDOS are split into two main structures (at about -1 eV and -3 eV); the lower ones in energy are from the coupling to the Cu d states. The hybridized states with the metal d bands for PEN are larger than for PFP. For PFP, the LUMO PDOS is broadened most and crosses the Fermi level, which gives a ‘peak’ at the Fermi level in the PFP total PDOS (see Figure 3c, lower panel). For PEN, the Fermi level is located in the gap between LUMO and LUMO+1, which gives a ‘dip’ at the Fermi level in the PEN total PDOS (Figure 3c, lower panel).

Figure 5. PEN (C\textsubscript{22}H\textsubscript{14}) on Cu(111) with the Cu lattice contracted by 3\% parallel to the surface: a strongly curved adsorption geometry is obtained; numbers (in Å) denote C-Cu distances at the central and the outermost carbons.
Table 1 lists the adsorption energies and average C-Cu(111) heights for different acenes and biphenyl (C_{12}H_{10}), and the comparison with some available experimental data. The calculated results are in good agreement with experiments. For PFP (C_{22}F_{14}), on average F is higher than C by 0.14 Å from our calculation, and the XSW experiment reported a height difference of 0.1 Å.\textsuperscript{18} The molecule-metal separations listed in Table 1 vary from 2.30 Å for anthracene (C_{14}H_{10}) (similar to PEN, 2.34 Å), via 2.65 Å for biphenyl (C_{12}H_{10}), to 2.93 Å for PFP. The molecule-metal separation of benzene (C_{6}H_{6}) is larger than for acenes, which can be understood from its larger H to C ratio (more H repulsion with the Cu surface). Biphenyl lies higher than benzene because the final coplanar adsorption geometry needs to overcome the twist between benzene units in free biphenyls due to H-H repulsion (see Figure 2c). All the molecule-metal interactions, judging from the average C-Cu(111) separations, are in the intermediate regime between physisorption and chemisorption, i.e. all the average heights are in between the sum of the VdW radii of Cu and C, ~3.10 Å, and the sum of the covalent radii, ~2.08 Å. The bent/curved adsorption structures result in the coexistence of chemical and VdW bonding at the interfaces.

\textsuperscript{a}Average C-Cu(111) heights are the difference between the average height of the carbons and that of the top layer Cu atoms; experimental values are derived from references\textsuperscript{7, 18, 38-41}; further calculation details are in the supporting information.
CONCLUSIONS

To summarize, the interface geometries of acenes, including PFP, PEN and biphenyl on Cu(111), are studied with a modified version of VdW-DF. All the calculated structural and electronics properties fit very well the observations from STM, XSW, and XPS experiments. Our simulated geometric and electronic structures explain the seemingly contradictory XSW and STM experimental observations when comparing PEN and PFP. The current work also demonstrates the crucial role of correctly accounting for VdW interactions in understanding the organic-metal interface mechanism at the intermediate interaction regime. The accurate adsorption geometries obtained in the current study demonstrate that it is now possible to quantitatively simulate and understand molecule-metal interface mechanisms in the regime between physisorption and chemisorption, an important factor in many devices.

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ASSOCIATED CONTENT

Supporting Information

More details of the computational methods and model, supporting figure and relaxed coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES


