



# Adsorption of perfluoropentacene on aluminum (100) surface: Structural and electronic properties from first principle study



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## ABSTRACT

The adsorption of organic molecules on the metal surfaces has received considerable attention due to their potential applications in molecular electronic devices. We have performed first principle density functional theory calculations based on the projected augmented wave (PAW) method to investigate the structural and electronic properties of perfluoropentacene/Al(100) interface. Perfluoropentacene (PFP) prefers to stay planar on Al(100) surface at bridge site, with 45° of rotation and vertical distance of 3.6 Å within LDA, 4.2 Å within GGA and 3.8 Å within DFT-D2 methods. Calculated results show that the adsorption of PFP molecule on Al(100) surface is physisorption. The change in work-function of the Al(100) surface upon the adsorption of PFP is calculated. Further, the electronic properties such as density of states (DOS), partial density of states (PDOS), Mulliken population analysis and Schottky barrier height (SBH) are studied for the stable adsorption geometry. This study shows that the charge is transferred from aluminum surface to PFP molecule and PFP/Al(100) interface is favorable for electron transport.

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## 1. Introduction

Over the past few years, organic materials have been extensively investigated for the fabrication of low-cost, flexible, lightweight and durable electronic devices. Such devices include organic light emitting diodes (OLED), organic field effect transistors (OFET), organic thin-film transistors (OTFT), organic photovoltaic cells (OPV) and solar cells [1,2]. Recently, there is also a high interest to use organic materials and their interfaces for spintronics [3–5]. Understanding the electronic structure at organic/metal interface is of great importance in developing organic electronic devices [6,7]. Different types of interaction such as chemical bonding, van der Waals (VdW) interaction and Pauli repulsion [8–11] exist at the interfaces. Hence, it is essential to understand the types of interaction at the interface and stability of the interface structure to design the efficient organic devices [12–14]. Most of the organic molecules in the literature are insulator or p-type semiconductor. Extensive efforts have been focused on the development of p-type organic semiconducting materials [15,16]. Particularly, in the study of organic field effect transistors pentacene has received much attention [11,17–20] because of its high intrinsic charge

carrier mobility up to 5.5 cm<sup>2</sup>/V s without doping [21,22]. The electronic and structural characteristics of pentacene have been extensively investigated on various model surfaces including Au(111) [23–25], Au(001) [26], Cu(110) [27], Cu(111) [17,20], Ag(111) [28], Fe(100) [29] and Al(100) [30,31]. The fabrication of complementary circuits requires n-type organic semiconductors, which have been rarely studied. Therefore, the development of n-type materials and studying their characteristics with metal surface is important for the application of organic molecules in electronics. One of the key parameters for evaluating the n-type properties of the materials is the energy of lowest unoccupied molecular orbital (LUMO). Materials with low LUMO energy have high electron affinities and it favors the electron transport. The fully fluorinated analogue of pentacene, perfluoropentacene (PFP) has been synthesized by replacing all the hydrogen atoms of pentacene with fluorine atoms [32–35]. It has been shown that the perfluorination increases the electron affinity and ionization energy and reduces the oxidation of pentacene [36–39]. It is expected that in comparison with pentacene, PFP have lesser electron injection barrier height, because the larger electron affinity makes the lowest unoccupied molecular orbital level closer to the Fermi energy of the metal electrode [40]. The electron affinity of PFP and pentacene is 4.28 and 3.36 eV, respectively, indicating that PFP is more chemically reactive than pentacene [39]. Fluorination reduces the gap between highest occupied molecular orbital and lowest

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unoccupied molecular orbital (HOMO–LUMO) from 2.21 to 2.02 eV [33]. Recently, the interaction between PFP and metal surfaces has been studied experimentally [41–49].

Duhm et al. [49] studied the structural and electronic properties of PFP on Ag(111) surface using X-ray standing wave (XSW), X-ray diffraction (XRD) and ultraviolet photoelectron spectroscopy (UPS). Götzen et al. [36] investigated the transition from 2D to 3D growth of PFP on Ag(111) surface. The above studies show that the PFP monolayer adsorb on Ag(111) surface in a flat lying orientation. Recently, Wong et al. [42] studied the molecular arrangement and the electronic structure of PFP on Ag(111) and reported that the adsorption of PFP decreases the work-function of Ag(111) surface by 0.3 eV, whereas pentacene decreases the work-function by 0.6 eV. These studies indicate the adsorption of PFP on Ag(111) surface is weaker than that of the pentacene on Ag(111) surface. Koch et al. [41,48] studied the interaction of PFP on Cu(111) and Au(111) surfaces to estimate the change in work-function and the adsorption geometry using UPS and XSW measurements. Using density functional theory (DFT), Toyoda et al. [39,46] calculated the adsorption energy of the PFP/noble metal interfaces and change in work-function of the metal surface due to the adsorption. These studies show that the fluorination on pentacene molecule increases the ionization potential and electron affinity. But, the adsorption distance between PFP and metal surface is higher than that of pentacene and metal surface.

In the present study, we have investigated the electronic structures of PFP on Al(100) surface by using first principle density functional theory calculations. Aluminum (Al) is a simple prototype *sp* metal and is technically relevant as a contact material in organic electronic devices. The work-function of aluminum is 4.20 eV [50], which is lower than the work-function of gold and palladium by ~0.84 eV [51,52]. The main aim of the work is to find the most stable adsorption geometry of the PFP molecule on Al(100) surface. For the stable adsorption geometry, the electronic properties like population analysis, density of states (DOS), partial density of states (PDOS) and Schottky barrier heights (SBH) are calculated by using density functional theory (DFT) calculations. Further, we have calculated change in work-function of the Al(100) surface due to the adsorption of PFP. The detailed computational methods are given in Section 2. The adsorption geometry, change in work-function, population analysis, DOS, PDOS and SBH are discussed in Section 3. Finally, the conclusions are summarized in Section 4.

## 2. Computational details

The Vienna Ab initio Simulated Package (VASP) code [53–55] has been used to perform all the calculations within the framework of density functional theory. In the VASP calculations, plane wave (PW) basis sets are employed to expand the electronic wave functions. The electron–ion interaction is described using the projector augmented wave (PAW) [56,57] method of Kresse, Joubert and Blöchl. The exchange and correlation functional has been parameterized according to local density approximation (LDA) [58] and the Perdew–Burke–Ernzerhof (PBE) gradient corrected exchange functional within the generalized gradient approximation (GGA) [59]. The plane wave (PW) basis sets are independent of the atomic positions. While using plane wave basis sets any region in space is treated on an equal footing. Hence the plane wave basis sets are free from “basis set superposition error” (BSSE) [60–63]. The convergence of a calculation depends only on the number of PWs included in the expansion of the electron density. The dimension of plane wave basis set is controlled by cutoff energy of 400 eV in our calculations. We used a conjugate-gradient algorithm in all calculations based on the reduction in the Hellman–Feynman forces on each constituent atom to less than 10 meV. The Brillouin-zone integration is

sampled via a  $2 \times 1 \times 1$  *k*-point mesh, which is automatically generated by using the Monkhorst–Pack method [64]. The occupation of electronic states is calculated using a Methfessel–Paxton smearing of 0.2 eV. The clean Al(100) surface is constructed by using a periodically repeated slab approach with supercell geometry of  $c(5 \times 5)$  surface unit cell. This slab consists of four layers with a vacuum region of 10 Å. A single PFP molecule is deposited on the upper surface of the slab with the aromatic rings parallel to the surface. Further, to include the van der Waals (vdW) interactions, an empirical dispersion-corrected density functional theory (DFT-D2) method proposed by Grimme et al. [65,66] has been used to study the adsorption geometry and energy. In this method, the total energy of the system is defined as a sum of the self-consistent Kohn–Sham energy ( $E_{\text{KS-DFT}}$ ) and a semiempirical dispersion correction ( $E_{\text{disp}}$ ). The general form of dispersion corrected total energy in DFT-D2 method can be expressed as,

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (1)$$

Since the vdW interaction is basically a long-range dynamical dipole–dipole interaction, the dispersion correction term ( $E_{\text{disp}}$ ) can be evaluated using semi-empirical pair potentials, i.e.,

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{i=N-1} \sum_{j=i+1}^{j=N} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}) \quad (2)$$

where  $s_6$  is a scaling factor,  $N$  is the total number of atoms,  $R_{ij}$  is the distance between the atoms  $i$  and  $j$  and the parameter  $C_6^{ij}$  describes the strength of the dispersion interaction between atoms  $i$  and  $j$ . The parameter  $C_6^{ij}$  can be evaluated as  $(C_6^i C_6^j)^{1/2}$ , where  $C_6^i$  is a semi-empirical parameter optimized for each type of atom. The damping function  $f_{\text{damp}}(R_{ij})$  eliminates the dispersion correction at short distance where the DFT energy works well.

## 3. Results and discussion

### 3.1. Aluminum surface

The structure of the Al(100) surface was optimized first. The lattice constant ( $a_{\text{Al}}$ ) of the relaxed Al(100) surface calculated at GGA-PBE method is 4.03 Å, which is in agreement with the experimental value of 4.05 Å [67]. After the full relaxation of the four layers of aluminum atoms in the slab, the work-function of the surface ( $\phi_{\text{Al}(100)}$ ) was calculated as the energy difference between the Fermi energy ( $E_{\text{F}}$ ) of the surface and the electrostatic potential energy ( $V_{\text{vac}}$ ) of an electron in the vacuum region at the distance where the potential energy has reached its asymptotic value. The calculated work-function of the Al(100) surface is 4.28 eV, which is in agreement with the previous experimental value of 4.20 eV [50].

### 3.2. Adsorption geometry

The optimized structure of isolated perfluoropentacene (PFP) is shown in Fig. 1. After the geometry optimization of the clean Al(100) surface and PFP molecule, the PFP molecule is deposited on the upper slab of the Al(100) surface. To find the most stable adsorption geometry of a PFP/Al(100) interface, one has to consider the different orientations and the position of the PFP molecule on the metal surface. In the present work, parallel (flat-lying) orientation of the PFP on Al(100) surface is considered rather than perpendicular orientation. Because, previous experimental and theoretical studies show that polycyclic aromatic molecules tend to adsorb on a metal surface in a flat lying geometry [68,69]. Recently, Glowatzki et al. [45] reported that the PFP molecules are aligned with flat-lying geometry on Cu(111) surface, which is proved through STM study. Three adsorption modes of PFP, top, hollow and bridge sites on Al(100) surface are shown in

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