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Density-functional theoretical study of fluorination effect on organic/metal interfaces

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ABSTRACT

Density-functional theory with a semi-empirical dispersion correction was used to systematically examine how the number of fluorine (F) atoms affects atomic and electronic structures of fluorinated pentacene ($C_{22}F_nH_{14-n}$) adsorbed on Cu(1 1 1) surfaces. The fluorination effect on the carrier injection efficiency at organic/metal interfaces was investigated. We found that as the number of F atoms decreases, the electron affinity of isolated molecules decreases, suggesting that the molecule becomes less reactive. However, for adsorbed systems, as the number of F atoms decreases, molecular orbitals of $C_{22}F_nH_{14-n}$ strongly hybridize with the substrate states while retaining the n-type energy level alignment, resulting in lowering the barrier height of the carrier injection. Based on the calculation results, we propose using $C_{22}F_nH_{14-n}$ ($n \leqslant 8$) with Cu electrodes for efficient electron injection.

1. Introduction

Understanding the electronic structure at organic/metal interfaces is of great importance in developing organic devices [1,2]. The interface dipole at organic/metal interfaces induces vacuum level shift that modifies the barrier height of the carrier injection, which plays a decisive role in organic devices [1,2]. Therefore, accurate prediction and control of the interface dipole is crucial to designing the electrodes of organic devices.

Pentacene ($C_{22}H_{14}$, Pen) and perfluoropentacene ($C_{22}F_{14}$, PFP) are prototypical p-type [3] and n-type [4] organic semiconductors, respectively. Accordingly, the interactions of Pen and PFP with metal substrate have been studied extensively both experimentally and theoretically [5–20]. In particular, elucidation of the electronic properties of PFP on metal is crucial, because n-type organic/metal interfaces are not as well understood as p-type organic/metal interfaces [21,22]. Efficient n-type interfaces must be designed to fabricate complementary integrated circuits.

PFP is expected to lower the electron injection barrier height, because larger electron affinity makes the lowest unoccupied molecular orbital (LUMO) level closer to the Fermi energy of the electrode than that of Pen [23]. However, experimental reports have shown that the highest occupied molecular orbital (HOMO) state relative to the Fermi energy for PFP/Cu(1 1 1) is almost the same as that for Pen/Cu(1 1 1) [11], and moreover, that the PFP–substrate distance is larger than that for Pen/Cu(1 1 1) [16]. These indicate that the electron injection for PFP/Cu(1 1 1) is less efficient than that for Pen/Cu(1 1 1), because the overlap between the molecular orbitals and the substrate for PFP/Cu(1 1 1) becomes smaller than that for Pen/Cu(1 1 1). Our previous paper pointed out that the large PFP–Cu(1 1 1) distance originates from repulsion of F atoms by the substrate [10]. Therefore, it might be possible to modify the adsorption distance and electron injection barrier, by changing the number of F atoms in PFP.

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In this work, we have examined systematically how the number of F atoms affects the atomic and electronic structures of fluorinated pentacene ($C_{22}H_nF_{14-n}$) adsorbed on Cu(1 1 1) using density-functional theory (DFT) within the generalized gradient approximation (GGA) with a semi-empirical dispersion correction. We show that adsorption distance and hybridization of molecular orbitals of $C_{22}H_nF_{14-n}$ on Cu(1 1 1) are tunable by changing the number of F atoms, and we propose an optimal organic/metal interface for efficient electron injection.

2. Calculation method

Calculations were carried out using STATE [24], which implements a plane wave basis set and pseudopotentials [25,26]. The plane-wave kinetic-energy cutoff for the wave functions and augmented charge density were set to 25 and 225 Ry, respectively. The Perdew–Burke–Ernzerhof (PBE)-GGA [27] was adopted to describe the exchange–correlation functional. Because a semilocal GGA functional cannot correctly describe van der Waals (vdW) forces, which dominate the interaction between π conjugated molecules and metal surfaces [5,7–10,18,19,28–31], we used a semi-empirical dispersion correction proposed by Grimme [32] (DFT-D) for adsorption systems. DFT-D was shown to yield accurate adsorption distances of organic molecules on metal surfaces as well as the work-function changes [7,9,10].

In this work, we examined the following three $C_{22}F_nH_{14-n}$ molecules as shown in Fig. 1: 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 14-dodecanefluoropentacene (F12), 1, 2, 3, 4, 8, 9, 10, 11-octafluoropentacene (F8), and 2, 3, 9, 10-tetrafluoropentance (F4). The numbers of F atoms in F12, F8, and F4 were 12, 8, and 4, respectively.

Isolated molecules were calculated in a $2 \times 1 \times 1$ nm^3 rectangular unit cell using the Γ point.

The Cu(1 1 1) surface was represented by a repeated slab model, in which one slab consisted of four Cu atomic layers. A vacuum region of ~2 nm was inserted in between slabs. A $C_{22}F_nH_{14-n}$ molecule was adsorbed on only one surface of the slab with its molecular plane parallel to the surface in a $\sqrt{43} \times 2\sqrt{3}$ surface unit cell, which is the same as that used in our previous calculation of PFP/metal systems [10]. A 2×4 **k**-point mesh was used to sample the surface Brillouin zone. The center of $C_{22}F_nH_{14-n}$ was assumed to be located at an hcp-hollow site on the Cu(1 1 1) surface with the long molecular axis aligned with close-packed metal atom rows as shown in Fig. 2. In the geometry optimization, we fixed the bottom layer of the substrate slabs at their respective bulk positions. The remaining degrees of freedom were optimized with the DFT-D method until the maximum force dropped below a threshold value of 0.2 nN. The work-function difference between the two surfaces of a slab was compensated for by using a dipole correction [33]. Work-functions were calculated from the difference between the Fermi energy of the system and the average electrostatic potential at the center of the vacuum region, and the vacuum level shifts were calculated from the work-function changes induced by the adsorption of $C_{22}F_nH_{14-n}$.

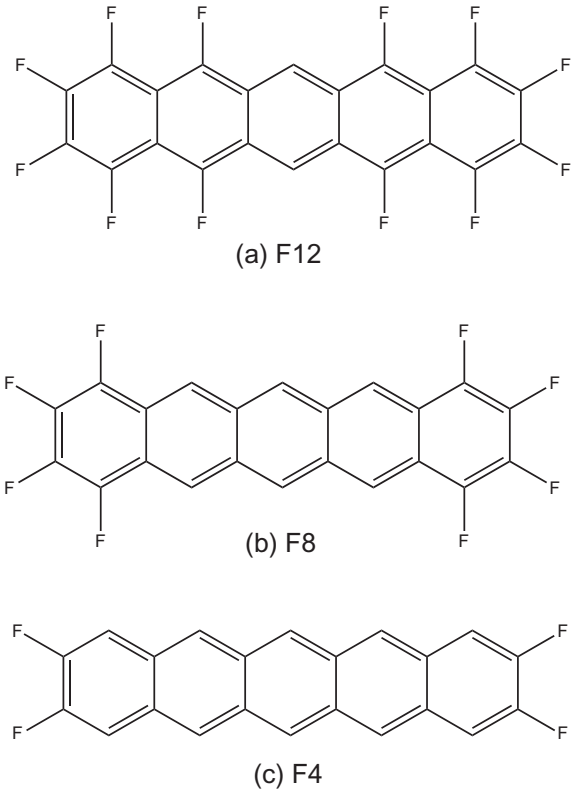

Fig. 1. The structural formula of (a) F12, (b) F8, and (c) F4.

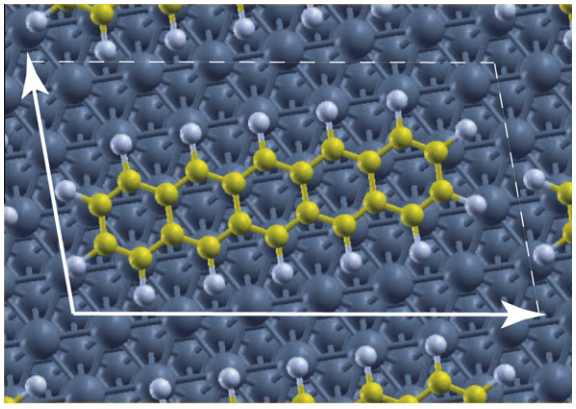

Fig. 2. Plan view of a $C_{22}F_nH_{14-n}$ molecule on Cu(1 1 1).

3. Results and discussion

3.1. Isolated molecules

First, we calculated the atomic and the electronic structures of isolated PFP, F12, F8, F4, and Pen molecules. The optimized molecular structures of F12, F8, and F4 are planar, similar to Pen and PFP. The ionization potential (IP) and electron affinity (EA) of PFP, F12, F8, F4, and Pen are summarized in Table 1. The IP and EA were estimated from