

**Studies on Weak Interactions of Functional  
Molecules with Graphite and Carbon  
Nanotube Surfaces Using Density Functional  
Theory**

**LIN CHENSHENG**

**DOCTOR OF PHILOSOPHY  
CITY UNIVERSITY OF HONG KONG**

**December 2006**

CITY UNIVERSITY OF HONG KONG

香港城市大學

**Studies on Weak Interactions of Functional Molecules with  
Graphite and Carbon Nanotube Surfaces Using Density  
Functional Theory**

功能分子和石墨及碳納米管表面弱相互作用的密度泛  
函方法的研究

**Submitted to**

**Department of Physics and Materials Science**

物理及材料科學系

**in Partial Fulfillment of the Requirements**

**for the Degree of Doctor of Philosophy**

哲學博士學位

**by**

**Lin Chensheng**

林晨升

**December 2006**

二零零陸年拾貳月

## Abstract

Weak interactions including van der Waals force,  $\pi$ - $\pi$  electron attraction and H-bonding are important in vast systems such as solution, biology, catalytic procedure, and adsorption or desorption on surface and crystal packing. H-bonds are the source of specific properties of associated liquids, with water being the most popular among them. It relates particularly to biological systems, such as molecular recognition that could be a basis for the creation of life, formation of higher order structures of peptides and nucleic acids, and biochemical processes, in particular the enzymes catalyzed. The  $\pi$ - $\pi$  electron attraction plays an important role in the determination of geometry structures of molecules composed of aromatic groups, such as protein folding, heterocyclic molecule with high fluorescence yield applied in organic light-emitting diodes and the carbon nanotube biosensor interaction with biological molecules. In the physisorption type self assembly on metal or semiconductor surface, the weak attraction force is the main attribution to the binding energy. Theoretical studies on these systems should include the weak dispersion energy, which is hard to treat using the conventional Hartree-Fock approach or the density functional theory.

This thesis used a self-consistent charge density functional tight-binding (DFTB) approach, complemented by an empirical London dispersion correction (DFTB-D) to study several interesting weak interaction systems. First, the structures and energetics of small water clusters  $(\text{H}_2\text{O})_n$  ( $n=1-6$ ) and their adsorption behavior on graphite surface are discussed. Comparing the results predicted by the DFTB-D and MP2 methods on small water clusters  $(\text{H}_2\text{O})_n$ ,  $n=2-6$ , and fused benzene  $(\text{fbz})_m-\text{H}_2\text{O}$ , it is revealed that the DFTB-D method is reasonably reliable and efficient. The results using DFTB-D method indicates that the water dimer maintains its original structure when adsorbed on a graphite surface. The cyclic trimer, tetramer, and pentamer also maintain their cyclic geometries when they interact with a graphite surface, regardless of their assumed starting orientations. For the hexamer, it is interesting that with the influence

---

---

of a graphite sheet, the highest energy of the local minimum structure  $S_6$  will change to that of the more stable Book-like structure when its starting orientation is perpendicular to the graphite surface. With a special orientation, a Bag structure will also change to a Prism structure. However, most of the starting orientations relative to the graphite surface will keep the water clusters as their original skeleton structure but with a slight distortion. The graphite surface always keeps a perfect planar structure. The binding energy of the water cluster with a graphite surface is only dependent on the number of water molecules that are in the hydrogen bond length range, about 3.0 Å, but it is independent of the water cluster size. These physically adsorbed water clusters show little change in their IR peak position and leave an almost perfect graphite surface. For the methanol cluster adsorbed on graphite surface, its behavior is very similar to the water cluster regarding the binding energy and geometry structure, although the larger size methyl group contributes more attraction energy with graphite surface.

After having reexamined the validity and efficiency of DFTB-D method in weak interaction system, we applied the method to study the high fluorescence quantum yield materials, 1,4-bis(benzothiazole-vinyl)benzene (BT) and 2,2',2''-(1,3,5-phenylene)tris-[1-phenyl-1H-benzimidazole] (TPBI), which are of promising applications in organic light-emitting diodes devices. It is found that the isolated planar BT molecule will be distorted when it interacts with TPBI through the vdW force. The geometry distortion of BT and its interaction with TPBI are found to play an important role in the luminescence. The distortion of the BT molecule is activated by the TPBI molecule and results blue luminescence around 475 nm. The weak vdW attraction between BT and TPBI adsorbed on graphite surface is found to be slightly larger than that between each of them and the HOPG substrate. The separation of the TPBI + BT mixture on graphite surface is energetically preferred. This fact can partly explain the migration and agglomeration at elevated temperatures, which is believed to be one cause of device degradation.

---

The interaction of biosystems and carbon molecules has attracted considerable attention in recent years. This is partly associated with the practical interest in carbon nanotubes (CNTs), which have much promise in biosensor technology and other applications. The cyclic voltammetry (CV) experiment about the interaction between the CNT and the deep-embedded active group of the redox coenzyme has been reported. It is found that the peak current of the electroactive Flavin adenine dinucleotide (FAD) at single-walled carbon nanotube (SWNT)/GCE (glassy carbon electrodes) is almost 22 times as large as that found at the bare GCE. By using the DFTB-D method, it is shown that the flavin and adenine group of FAD are attracted to the CNT surface but remain at the physisorption distance when FAD interacted with CNT. The configuration with the FAD long axis perpendicular or parallel to the semiconducting (10,0) and metallic (5,5) tube axis are almost energetically degenerated. The density of states (DOS) and projected DOS (PDOS) show that in FAD/(10,0) system, FAD flavin group contributes more components in the band structure at Fermi energy, which enhances its electronic transfer as observed in the CV experiment. The calculations demonstrate that even in the cases of physisorption interaction there is a noticeable influence of the CNT electronic structure and mobility.

Self-assembly is a critical and necessary process in living organisms and plays a very important role in chemistry and material science. Now this process has been employed in the so-called “bottom-up” strategy for nanofabrication. Self-assembled monolayers (SAMs) with controlled structure and function are promising candidates in molecular electronic devices, lubrication, wetting, sensors and catalysis. Therefore, understanding the principle of two-dimensional molecular arrangement is the prerequisite for nanodevice development. The structure of SAMs is dominated by molecule-substrate interaction and intermolecular action. Based on the STM studies on the two carboxylic substituted thiophene derivatives, thiophene-2-carboxylic acid (TCA) and thiophene-2,5-dicarboxylic acid (TDA) on Au(111) surface and highly oriented pyrolytic graphite (HOPG), it was observed that the 2D supramolecular self-assemblies of TCA and TDA

---

are highly substrate dependent. Theoretical prediction indicates that the molecule-substrate interaction plays a more important role than intermolecular interaction. While the interaction between molecule and HOPG is weaker, the intermolecular action plays an equal important role as the molecule-substrate interaction for the formation and stability of assembled monolayer.

---

---

## Table of Contents

<b>Abstract</b> .....	<b>i</b>
<b>Acknowledgement</b> .....	<b>v</b>
<b>Table of contents</b> .....	<b>vi</b>
<b>List of figures</b> .....	<b>ix</b>
<b>List of tables</b> .....	<b>xiii</b>
<b>Chapter 1. Weak interaction system and theoretical methods</b> .....	<b>1</b>
1.1. Conventional theoretical approaches for studying weak interaction systems	1
1.2. Our approaches .....	3
1.3. References and notes .....	4
<b>Chapter 2. Theories and models</b> .....	<b>6</b>
2.1 DFTB method .....	6
2.1.1 Dispersion energy correction .....	11
2.1.2 Time-dependent DFTB (TD-DFTB).....	13
2.2 MP2 method.....	15
2.3 SIESTA method .....	17
2.4 References and notes.....	19
<b>Chapter 3. Water cluster and methanol cluster adsorbed on graphite</b> .....	<b>22</b>
3.1 Introduction.....	22
3.2 Method and model .....	23
3.3 Results and discussion .....	25
3.3.1 The water clusters (H <sub>2</sub> O) <sub>n</sub> .....	25
3.3.2 The adsorption of a single water molecule on a fuse-benzene surface	30

---

---

3.3.3 The adsorption of the water cluster on a fuse-benzene surface .....	32
3.4 The IR spectra of the water cluster on a fuse-benzene surface.....	43
3.5 The methanol clusters .....	44
3.6 Adsorption of the methanol clusters on a graphite surface .....	46
3.7 Conclusions.....	51
3.8 References and notes .....	52
<b>Chapter 4. Geometric and excited-state properties of BT interacting with TPBI</b> .....	<b>56</b>
4.1 Introduction.....	57
4.2 Theoretical method and molecular models .....	57
4.3 Results and discussion .....	59
4.4 Conclusions.....	70
4.5 References and notes.....	71
<b>Chapter 5. FAD coenzyme interacting with carbon nanotubes .....</b>	<b>73</b>
5.1 Introduction.....	73
5.2 Method and models.....	74
5.3 Results and discussions.....	77
5.4 Conclusions.....	87
5.5 References and notes.....	88
<b>Chapter 6. Substrate effect on the molecular architectures of thiophene derivatives.....</b>	<b>90</b>
6.1 Introduction.....	90
6.2 Model and method .....	92

---



---

6.3 Results and discussion .....	92
6.4 Conclusions.....	105
6.5 References and notes.....	105
<b>Chapter 7. Summary .....</b>	<b>108</b>
<b>List of publications .....</b>	<b>110</b>

---

---

## List of figures

**Figure 2-1.** Comparison of CPU usage for different methods including the quantum chemical INDO/S approach as well as TDDFRT with different basis sets.

**Figure 3-1.** The fuse-benzene ring model  $(fbz)_m$ ,  $m=1, 7, 19, 37$ , and  $51$ .

**Figure 3-2.** The lowest energy structures of water clusters (a) dimer, (b) trimer, (c) tetramer, and (d) pentamer.

**Figure 3-3.** Binding energies of Ring, Book-like, Cage, Prism and Bag structures of  $(H_2O)_6$ . Circles: DFTB-D; Triangles: MP2 of Ref. 36; and Crosses: MP2 result of Ref. 34, shifted 15.0 kcal/mol up).

**Figure 3-4.** Structure of (a) Benzene-water; (b)  $(fbz)_7-H_2O$ , top view, and (c)  $(fbz)_7-H_2O$ , side view.

**Figure 3-5.** Binding energy of  $(fbz)_n-H_2O$ ,  $n = 1, 7, 19, 37$ , and  $51$ .

**Figure 3-6.** Optimized  $(fbz)_{37}-(H_2O)_2$  structure, (a) side view, and (b) top view.

**Figure 3-7.** Optimized water trimer with (a) *udd* and (b) *ddd* configuration on  $(fbz)_{37}$ .

**Figure 3-8.** Optimized water tetramer, (a) *udud* and (b) *uddd* configuration.

**Figure 3-9.** Optimized water tetramer, (a) *ududd*, (b) fused 3 and 4 rings, (c) *udddd*, and (d) *uduud* configuration adsorbed on  $(fbz)_{37}$ .

**Figure 3-10.** Geometry structures of Book-like water hexamer with different orientations (a), (b) and (d) on the graphite surface, and the final adsorption structures (c), (e) and (f).

**Figure 3-11.** Optimized geometry structures of Prism water hexamer (a) and (b) and the initial Bag water hexamer(c) and its optimized structure (d) adsorbed on

---

---

the graphite surface.

**Figure 3-12.** Calculated IR spectra of free water hexamer and their adsorbed cases on a graphite surface. (a) Prism  $(\text{H}_2\text{O})_6$ , (b)  $(\text{fbz})_{37}-(\text{H}_2\text{O})_6$  Prism (a)), (c) Bag  $(\text{H}_2\text{O})_6$ , and (d)  $(\text{fbz})_{37}-(\text{H}_2\text{O})_6$  Prism (b)).

**Figure 3-13.** The optimized structures of methanol clusters.

**Figure 3-14.** Optimized geometry structures of methanol clusters adsorbed on a graphite surface. (a) monomer, (b) dimer, (c) *uuu*, (d) *upp1*, (e) *upp2*, (f) *upu*, (g) *udud*, and (h) *ududd*.

**Figure 4-1.** Schematic representation of the molecular structures of (a) TPBI and (b) BT.

**Figure 4-2.** Optimized structure of TPBI adsorbed on graphite surface.

**Figure 4-3.** Calculated (a) adsorption and emission spectrum of BT and (b) emission spectrum of TPBI. The peaks were broadened by a Lorentzian line-shape modification with 15 nm half-width.

**Figure 4-4.** Schematic representation of the four iso-energy BT molecular structures.

**Figure 4-5.** Optimized several BT molecules (a) and calculated BT molecules with net-charges surrounding the center BT molecules.

**Figure 4-6.** Calculated UV/vis spectra with isolated and solid stated BT molecules.

**Figure 4-7.** (a) Calculated absorption spectrum of BT for different  $\sigma$  bond rotation angles and (b) emission peak energy varied with the  $\sigma$  bond rotation angles.

**Figure 4-8.** Representations of the BT and TPBI mixture: (a) initial structure, and (b) equilibrium structure.

---

**Figure 4-9.** Schematic representations of the HOMO and LUMO of the BT and TPBI mixture and the isolated BT and TPBI molecules.

**Figure 4-10.** Schematic representation of one BT and one TPBI adsorbed on graphite surface, (a) initial structure; (b) optimized structure; and (c) optimized one BT molecule and five TPBI molecule adsorbed on graphite surface.

**Figure 5-1.** Chemical structure and nomenclature of FAD.

**Figure 5-2.** Schematic representation of the definition (m,n) carbon nanotube.

**Figure 5-3.** Optimized structure of the (a) perpendicular and (b) parallel configurations of FAD adsorbed on (10,0) tube.

**Figure 5-4.** Geometry of FAD/(10,0), (a) initial structure, (b) optimized structure with vdW force, (c) optimized structure without vdW force.

**Figure 5-5.** Band structure of (a) an isolated (10,0) tube, (b) FAD/(10,0) (c) an isolated FAD molecule calculated with the same periodic condition as (b).

**Figure 5-6.** The band structure corresponding to FAD HOMO in FAD/(10,0) system.

**Figure 5-7.** (a) Total density of state of (10,0) tube (dot line) and FAD/(10,0) (solid line) (b) Projected density of states of O, N and C atoms of flavin group in FAD/(10,0).

**Figure 5-8.** Isosurface of the wave functions of the (a) HOMO and (b) LUMO-derived bands at the  $\Gamma$  point for FAD adsorbed on (10,0) surface. The isovalue is 0.02 au.

**Figure 5-9.** Isosurface of the wave functions of the HOMO and LUMO-derived bands at the  $\Gamma$  point for FAD adsorbed on (10,0) surface. The isovalue is 0.02 au.

---

**Figure 5-10.** Calculated UV/vis spectra of FAD, FAD/(5,5) and FAD/(10,0).

**Figure 6-1.** Chemical structure of TCA and TDA.

**Figure 6-2.** (a) a high-resolution STM image of TDA adlayer on Au(111);  
and (b) proposed structural model for the TDA adlayer.

**Figure 6-3.** (a) a high-resolution STM image of TCA adlayer on Au(111);  
and (b) proposed structural model for the TCA adlayer.

**Figure 6-4.** (a) a high-resolution STM image of TDA domain I on HOPG;  
and (b) proposed structural model for the TDA domain I.

**Figure 6-5.** (a) A high-resolution STM image of TDA domain II on HOPG;  
and (b) proposed structural model for the TDA domain II.

**Figure 6-6.** (a) A typical STM image of TDA bilayer structure on HOPG;  
and (b) the schematic illustration of two possible molecular arrangements  
showing the relationship between the top and lower monolayers.

---

---

## List of Tables

- Table 2-1. Parameter of Slater-Kirkwood effective number of electrons  $N_\alpha$ , static atomic polarizabilities  $P_\alpha$  and the range of the overlap of two atoms  $R_0$  for atoms C, O, H, F, S, P, Al, Cu, and Au.
- Table 3-1. The geometry and binding energy ( $E_b$ ) (unit: Å and kcal/mol) of water cluster  $(H_2O)_n$ ,  $n=2$  to 5. A hexamer (Ring  $S_6$ ) is also included.
- Table 3-2. Adsorption energy (AE) and oxygen-graphite surface distance of  $(fbz)_{37}-(H_2O)_n$ ,  $n = 1 \sim 6$  (unit: Å and kcal/mol).
- Table 3-3. Adsorption energy (AE) of  $(fbz)_{37}-(H_2O)_6$  (unit: kcal/mol).
- Table 3-4. Adsorption energy ( $A_E$ , kcal/mol) and geometry ( $R_{O-O}$ , Å) of methanol clusters adsorbed on the graphite sheet.
- Table 4-1. Binding energy ( $E_b$ ) of different combinations of BT, TPBI, and graphite surface ( $G_s$ ) (unit: kcal/mol).
- Table 5-1. Band gap value of (10,0) tube predicted by SIESTA with different mesh cutoff and energy shift parameters.
- Table 5-2. Adsorption energy and equilibrium FAD/CNT distance (defined as the shortest atom-to-atom distance) of FAD/(10,0) and FAD/(5,5).
- Table 6-1. Binding energy (unit: kcal/mol) of hydrogen bond and molecules-substrates interaction obtained by theoretical calculation using the density functional theory (DFT).
-