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Substituent effects in π-stacking of histidine on functionalized-SWNT and graphene

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ABSTRACT

Adsorptions of histidine on the functionalized (10,0) single-walled carbon nanotube (SWNT) and graphene were investigated using density function theory methods, M05-2x and DFT-D. The results show that the binding of the histidine ring to the functionalized SWNT is weaker than that to the pristine SWNT for both singlet and triplet complexes, regardless of the electron-donating (–OH, $–NH_2$) or electron-withdrawing (–COOH) character and their attached sites. The present decreased binding is opposite to the well-known enhanced binding in the substituted benzene dimers. Since the atoms of the histidine are distant from the substituent atoms by over 6 Å, there would be no *direct* interaction between histidine and the substituent, different than the case of the substituted benzene systems. The decreased binding can be mainly driven by the aromaticity of the functionalized SWNT. The nucleus-independent chemical shift (NICS) index analysis for the functionalized SWNTs in deed shows that local aromaticity of SWNT is decreased because of the electron redistribution induced by functional groups, and the π–π stacking between the histidine ring and *functionalized*-SWNT is therefore decreased as compared to the pristine SWNT. However, the above trend does not remain for the binding between the histidine and graphene. The binding of the histidine to the functionalized graphene with –OH and $–NH_2$ is just slightly weaker than that to the pristine graphene, while its binding to COOH-SWNT becomes a little bit stronger.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery in the early 1990s due to their unique physicochemical, mechanical and electrical properties as well as their broad range of potential applications [1,2]. The proposed applications of single-walled carbon nanotubes (SWNTs) in biomedical fields, such as drug or gene delivery and probes for imaging stimulated the extensive exploration for the interaction of biomoleculars with SWNTs [3,4]. Pristine CNTs are insoluble in water, greatly limiting its bio-compatibility. Chemical functionalization of CNTs by introducing molecules and groups is a conventional way to improve this issue. For example, the surface of oxidized nanotubes is mainly covered by carboxylic –COOH groups that make the oxidized nanotubes disperse better in solution than the raw material [5,6]. Moreover, chemical modification makes carbon nanotubes more amenable for other various potential applications, such as opening hollow cavities for gas storage or lithium intercalation [7], enhancing free radical scavenging [5], and mediating the desired bioconjugates for cancer therapy [8], etc. The chemical functionalized π systems also play a very important role in molecular assembly and molecular devices [9–11]. Chemical modification by functionalization was usually fulfilled via chemical decoration with organic groups (such as carboxyl and hydroxyl groups) [12], and amidination [8,13]. The recent theoretical and experimental studies demonstrated that the presence of the functional groups significantly modifies the electron structure and bioactivity of CNTs [14,5].

Despite the fact that extensive studies have been carried out on the non-covalent interaction between biomolecules and pristine SWNT [15,16], there is little detailed theoretical analysis of the substituent effects on the interactions between biomolecules and *functionalized* SWNTs, which may play major roles in understanding various biological processes. Regarding the substituent effect of the π-stacking systems, since it was defined on the benzene and x-benzene (x = OH, CH_3, F, and CN) [17], the nature and existence have been well investigated on the substituted benzene systems [18,19,20–23]. The substituents enhance the π-stacking regardless of their electron-donating or electron-withdrawing character. It is generally assumed that the major interactions between DNA bases or some amino acids and SWNTs are mediated

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by the π-electron networks. Whether the π-stacking between the biomolecules and *functionalized*-SWNTs is strengthened or weakened remains unclear. In the present work, we focused on the substituent effects on the interaction between amino acid and functionalized SWNT. Considering that the aromatic rings, nonpolar part of the amino acid, are important contributors in the specific binding to the CNTs [24,16], we have restricted our calculations using only the aromatic ring of histidine with the pristine or functionalized (10,0) zigzag SWNT. Here, the electron-donating –OH, and $–NH_2$, and withdrawing –COOH groups are used to functionalize the SWNT. Because of the importance of the interaction of biomolecules and graphene layer [25], for the sake of comparison with the functionalized SWNT the investigation was also extended to the functionalized graphene.

2. Results and discussions

Three repeat units (about 13 Å in length) of zigzag SWNT (10,0) with a diameter of 7.83 Å were used to model a finite CNT. Three different groups, –COOH, –OH and $–NH_2$, were attached directly on the sidewall as well as the open end of the SWNT to explore the substituent effects on the histidine absorption on *functionalized*-SWNT. With respect to the functionalization and adsorption sites, the complexes were noted as types of (*S*), (*L*), (*V*), and (*O*), respectively, as shown in Fig. 1. The aromatic ring of histidine was initially placed in parallel to the tangent surface of *functionalized*-SWNT at a height of approximately 4.0 Å and allowed to relax fully. Final geometries are shown in Fig. 1 for SWNT-COOH, and others in Fig. S1 of supporting materials. The optimized average distances, defined as the average from the atoms of pentagonal ring of histidine to the nearest neighbor C atom of *functionalized*-SWNT, are listed in Table 1 with binding energies.

As shown by the top views in Fig. 1, the complexes show the displaced AB type of configurations of graphite layer, benzene dimer, DNA bases-SWNT systems [17,18,26,27,15], where the pentagon ring of histidine locates above the hexagonal ring of *functionalized*-SWNT with either C or N coordinated with six carbons of *functionalized*-SWNT. Thus the present π–π stacking can be classified into the type of π–π (D) interaction [23]. As expected, the aromatic ring of histidine prefers to almost orient in parallel to the tangent plane of the SWNT with noncovalent signature of weak π–π stacking interaction. However, because of different electronegativity of C and N, the N (H) has the shortest distance to *functionalized*-SWNT at 3.15 ± 0.05 Å, resulting in a slight deviation from parallel configurations. The separation between histidine and pristine SWNT obtained with M05-2x was found to be 3.31 Å, similar to the interplanar distance 3.30 Å between histidine and (5,5) SWNT with the plane-wave GGA in the Vienna *ab initio* simulation package [16]. The separation between histidine and SWNT obtained by the PBE-D is shorter by 0.14 Å than those obtained by the M05-2x, which is attributed to the explicit van der Waals correction included in the PBE-D.

According to Fig. 1, it is obvious that functionalization has little influence on the equilibrium geometry of the histidine and *functionalized*-SWNT complexes. The aromatic ring of histidine still orients almost parallel to the *functionalized*-SWNT surface, also bearing the signature of weak π–π staking interaction. Moreover, compared with the complex of pristine SWNT, the separations between histidine ring and *functionalized*-SWNT remain the same for SWNT-COOH + His(*S*) and SWNT-OH + His(*L*), or decrease slightly by approximately 0.01–0.06 Å except for the increase of 0.1 Å in the complex SWNT-NH_2 + His(*L*). For the given functionalization groups, the separations for the end functionalized complexes (*L* and *S*) are slightly higher than those of the sidewall functionalized ones (*O* and *V*).

According to Table 1, the binding energy between aromatic ring of histidine and pristine (10,0) SWNT is approximately −5.24 kcal/mol, in between the binding energy of −3.46 and −9.22 kcal/mol for the histidine and pristine (5,5) SWNT predicted with respective GGA plane-wave and MP2 method [16]. In spite of little influence on the separation between aromatic ring of histidine and *functionalized*-SWNT, it is interesting to find that the binding energies decrease by about 0.6–1.4 kcal/mol for the π–π stacking no matter that the introduced functional groups are electron-withdrawing (–COOH) or electron-donating (–OH, and NH_2), and functional groups are attached directly on the sidewall or the open end of *functionalized*-SWNT. This phenomenon is opposite to the substituent effect in the substituted benzene systems $C_6H_5\ldots X$ [18,26], where the binding was enhanced due to the substituent groups, such as X = F, CH_3, NH_2, and OH. The current result supports the previous report that the two N atoms in the histidine ring behave very differently in π interaction from benzene [28].

Table 1 also shows that, consistent with the smaller separation between histidine ring and *functionalized*-SWNT, the PBE-D predicted binding strength is much stronger than that from the M05-2x. For the pristine SWNT, the binding energy of −10.49 kcal/mol is almost one time higher than that from the M05-2x (E_b = −5.23 kcal/mol), yet rather close to that from the MP2 for the histidine with (5,5) SWNT (−9.22 kcal/mol) [16]. Similar to the trend predicted by the M05-2x, PBE-D results again indicate that functionalization results in less binding of histidine ring to *functionalized*-SWNTs by 2.9–4.6 kcal/mol than to the pristine SWNT.

It is known that a ground state for H-saturated zigzag (n,0) SWNT cluster may be a triplet state, rather than a single state [29]. Both the M05-2x and PBE-D calculations confirmed that it is also true for the pristine (10,0) SWNT as well as *functionalized*-SWNT clusters. The triplet complexes of histidine and *functionalized*-SWNT are also more stable than the singlet ones. The binding energies and separations together with the first ionization potentials (IP) and polarizabilities (α) of *functionalized*-SWNT are summarized in Table 2. Comparing Tables 1 and 2, it can be found that separations from histidine ring and *functionalized*-SWNT for the triplet state complexes differ only by ±0.03 Å from those of the singlet complexes. For the triplet state complexes, the decrease trend between *functionalized*-SWNT and the histidine ring also remains regardless of the type and location of functional groups. Generally, the stacking *functionalized*-SWNT + His(*L*) is stronger than *functionalized*-SWNT + His(*S*). For the functionalization on the sidewall, the complex (*V*) is only slightly stronger than the complex (*O*), 0.15 kcal/mol for SWNT-COOH, 0.19 kcal/mol for SWNT-OH, and 0.45 kcal/mol for SWNT-NH_2, which may be attributed to the shorter distance between the histidine and functional groups in the case of *functionalized*-SWNT + His (*V*) than *functionalized*-SWNT + His (*O*).

Considering that π-stacking noncovalent interaction is profound importance in molecular biology and other areas, the interaction of aromatic amino acids with SWNT has been studied carefully by previous workers. An excellent correlation was observed between the polarizabilities of the aromatic moieties and their binding strength with the (5,5) SWNT [16]. To get an insight into the substituent effects on the π stacking interactions, the polarizabilities of the *functionalized*-SWNTs are also calculated. However, the correlation between the binding strength and α of *functionalized*-SWNTs was not revealed. This may be explained by the fact that *functionalized*-SWNTs have negligible deformation. It is known that the π–π stacking is stabilized mainly by dispersion effect depending on the surface area of buried as well as on the polarizability and ionization potential (IP) of the moieties. The decrease of binding strength due to the functionalization correlates well with the IP trend shown in Table 2. The primary binding also varies with the types of π interactions [23,22].