Interaction of Pyrimidine Nucleobases with Silicon Carbide Nanotube: Effect of Functionalization on Stability and Solvation

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ABSTRACT

This study is about Complexes of Li doped silicon carbide nanotube with Thymine and Cytosine in gas phase and aqueous solutions. Li doped silicon carbide nanotube and its pyrimidine nucleobase compounds were first modeled by Quantum mechanical calculations in gas phase and in water. Calculated binding energies indicated the stronger ability of thymine to functionalize silicon carbide nanotube than Cytosine. After that, Monte Carlo simulation and Free Energy Perturbation method was utilized to calculate solvation free energies and complexation free energies to evaluate solvation behavior and stability of the related structures. The results indicated that Li doped silicon carbide nanotube-thymine has more stability in water.

Keywords: Silicon carbide nanotube; Cytosine; Thymine; Solvation free energy; Simulation

INTRODUCTION

Carbon nanotubes (CNTs) due to their unique onedimensional nanostructure and remarkable mechanical, thermal, optical, and electronic properties, may find many applications in both materials and life sciences [1]. CNTs have come under intense multidisciplinary studies because of their unique physical and chemical properties [2, 3]. The well-defined shape and size of NTs make them attractive candidates for theoretical and experimental studies of various nanoscopic phenomena such as protection and confinement of molecular species as well as transport of molecules through their interior pores [4].

Applications of CNTs into biotechnology have recently emerged, raising a great potential in such a few areas as biosensors, DNA and protein transporters for therapy Purpose[5,6].

Although the interfacing CNTs with biological systems can lead to significant applications in various disease diagnoses, the toxicity of CNTs interacting with living cells is an issue of strong concern [7-9].However, it has been found that silicon carbide nanotubes(SiCNTs) have less toxic effect than CNTs[10].

CNTs themselves have a very low solubility in aqueous solutions, which had

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been a major barrier for a variety of potential applications. In contrast to the hydrophobic surface of CNTs, the SiCNT surface is hydrophilic [11]. The existence of a specific charge arrangement in SiCNTs makes them attractive alternative materials for solution phase. Therefore it seems that SiCNT are better candidates for application in biological systems because of their higher solubility [12] and less toxicity.

Theoretical studies [13, 14–16] performed on the structure and stability of SiCNTs have shown that the most stable structures contain Si and C atoms at a ratio of 1:1. In fact, among energetically stable forms of SiCNTs, the one in which the Si and C atoms have alternating positions in the tube wall is full of point charges.

Furthermore, Strategic approaches toward solubilization of nanotubes(NTs) have been developed mainly through their surface functionalization of either covalent or noncovalent attachments to the sidewalls of NTs[17,18]. Noncovalent functionalization could not only enhance solubility of NTs but also maintain their attractive geometric, electronic and mechanical properties. Several recent review papers deal with the functionalization of single-walled CNTs (SWCNT) with biomolecules and their biomedical applications [19-21]. Nucleic acids have been explored to noncovalently functionalize CNTs toward various biomedical applications ranging from nanodevices, gene therapy, and drug delivery to membrane separation [22, 23].

Nucleobases are the fundamental constituents of nucleic acids. Interaction strengths of nucleobases with single-walled carbon nanotubes (SWNTs) and graphene have been estimated theoretically [24–27]. The experimental binding energies of nucleobases with SWNTs decrease in the order T>A>C, in agreement with calculations showing a trend of

G>T>A>C[24]. This trend is obtained from theory only when solvation effects are included. These heterocyclic molecules also have an ability to coordinate a variety of metal ions, which could be used for the stabilization of superstructures as well as to support metal-aided catalytic transformations. Therefore, new hybrid materials comprising both nucleobases and CNTs would be extremely interesting in view of the remarkable properties of CNTs and recognition properties of nucleobases. Therefore, study of the interaction of nucleo bases and metal doped NTs in gas phase and aqueous solution were the purposes of this study.

The binding energies of the interaction of Li-doped SiCNT (SiCNT-Li) with cytosine(C) and thymine(T) were studied in order to investigate the stability of related structures . In this research, the effect of functioalization with nucleobases on the properties of nanotubes is also evaluated.

Quantum mechanical calculations were used for estimating of binding energies in gas phase and aqueous solution. Monte Carlo simulation and perturbation methods were used to calculate complexation free energies and compare stability of these compounds. Our results provide fundamental knowledge of new biological compounds using in nanobiotechnology.

COMPUTATIONAL METHOD

In this study, the interaction of SiCNT-Li with cytosine and thymine nucleobases was studied in the gas phase and in the presence of water. The research comprised two sections: quantum mechanics (QM) and Monte Carlo (MC) simulation. In the quantum mechanical part, isolated molecules were optimized. Binding energies and the stability of the structures in gas phase and solution was then studied by quantum mechanical calculations. Then it has been applied Monte Carlo simulation

for dilute solutions of nanotubes in water. Solvation free energies and complexation free energies of the related structure were computed in this section.

QM part

Quantum mechanical calculations were used for isolated solute molecules (cytosine, thymine, SiCNT-Li , SiCNT-Li-C and SiCNT-Li- T). The armchair nanotube structures [a (6, 6) SiCNT] were considered as solute samples. Pyrimidine nucleobases were coordinated with Li atom in SiCNT-Li. Binding of cytosine and thymine with SiCNT was done via the active sites. The most favorable sites for binding are the N3site in cytosine and N1 and N3 in thymine [28, 29].

These sites have lone pairs available for participating in coordination. Therefore, these sites of nucleobases are seen to interact with SiCNT-Li. Each species (SiCNT-Li, SiCNT-Li-C, and SiCNT-Li-T) was optimized by the DFT/B3LYP method using the 6– 31 G*[30] basis set. In all calculations, nanotubes were capped with hydrogen atoms. Natural bond orbital (NBO) theory was applied to optimized geometries to determine natural atomic charges. In aqueous solution properties of these complexes are different. To evaluate the stability of the structures in water solution, conductor-like polarizable continuum model (CPCM) was used.

The calculations were performed by using the GAUSSIAN 2003 suite of programs [31].

MC part

It has been applied Monte Carlo simulation for dilute solutions of nanotubes in water.

The monomers were represented by interaction sites usually located on nuclei. The interaction energy between two molecules, a and b, were expressed by pair wise sum of interaction contributions:

$$E_{ab} = \sum_{i}^{ona} \sum_{j}^{onb} E_{ij}^{AB} \qquad (1)$$

The Transferable Intermolecular Potential function (TIP3) [32, 33] was applied for modeling water molecules. The TIP3 parameters for water have been included in Table 1.

The pair potential function was represented by Coulombic and Lennard-Jones terms between sites centered on nuclei.

$$E_{ij}^{AB} = \frac{q_i q_j e^2}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \qquad (2)$$

A_{ij} and C_{ij} are the repulsion and attraction coefficients for the non bonded interactions; r_{ij}, q_i, and q_j are the interatomic distance between atoms i and j and the atomic charges on atoms i and j. The Lennard–Jones parameters between pairs of different atoms are obtained from the Lorentz–Berthelodt combination rules. Appropriate Lennard-Jones parameters for Carbon [34], Silicon [35], Li [36] and nucleo base [37] have been used in calculations.

The free energy difference between two states A and B, of a system may be derived from classical statistical mechanics allowing us to express this difference as:

$$\Delta G = G_B - G_A = -RT \ln \langle \exp - (E_B - E_A)/RT \rangle$$
$$= \langle E_B - E_A \rangle \qquad (3)$$

Table 1. TIP3 parameters for water molecule

Site	q	$10^{-3}A$ kcalÅ^{12}/mol	C kcalÅ^6/mol
O	-0,834	582	595
H	0,417	0	0

*Charges (q) are in electron

Equation 3 is the Free Energy Perturbation (FEP) master equation. $E_B - E_A$ is the potential energy difference between states A and B of the system, and the symbol $\langle \ \rangle$ indicates an ensemble average of $E_B - E_A$.

In practice, one introduces a coupling parameter (λ) into the potential function which allows us to calculate the free energy difference over a series of more closely related states. Using this parameter, the free energy difference between states A and B becomes the following:

$$\Delta G = \sum_{i=1}^{N} \Delta G_i =$$
$$\sum_{i=1}^{N} - RT \ln \left\langle \exp - \left[E_{\lambda(i+1)} - E_{\lambda(i)} \right] / RT \right\rangle_{\lambda i}$$
$$(4)$$

In fact the relationship between the initial, final and intermediate states is usefully described in terms of a coupling parameter (λ). As λ is changed from 0 to 1, the potential energy varies from E_A to E_B.

In all separate MC simulations performed here, throughout a standard manner the Metropolis sampling technique [38] in canonical (T, V, N) ensemble was used. Each setup includes two sections: a solute fragment and water molecules. All calculations were performed in a cubic box at the experimental density of water, 1 g/cm^3. The optimum edges of the box were 50×50×50 Å, which corresponds to almost 4000 H$_2$O molecules of pure solvent. The symmetry center of the NT was in the geometrical center of the cell. An acceptance rate of 50% for new configurations was achieved by using suitable ranges for translations and rotation about a randomly chosen axis. Periodic boundary conditions were employed in computation. The system was thoroughly equilibrated using several hundred thousand configurations. Every calculation was extended to include as many configurations as were necessary to reduce the statistical error to the level at which calculated energy differences have quantitative significance.

RESULTS AND DISCUSSION
1. Gas phase
At first we studied the interaction of SiCNT-Li with cytosine and thymine nucleobases in gas phase individually. The radius of the SiCNT after full optimization of the geometry is 5.16 Å, with the average Si-C bond lengths of 1.82 Å. The optimized structures of two SiCNT-Li-pyrimidine nucleobase compounds are shown in Figure 1. In the subsequent simulation step, these geometries and quantum mechanical natural charges were applied.

The results of density functional calculations on SiCNT-Li, complex of SiCNT-Li With cytosine and thymine are given in table 2. Comparison of total energies of SiCNT-Li, SiCNT-Li-C and SiCNT-Li-T indicated that cytosine and thymine can create the stable complexes with SiCNT-Li in gas phase.

The binding energies of the interaction of SiCNT-Li with pyrimidine nucleobases were calculated using the total energies of each isolated species. The binding energy, E_b, is defined as follows:

E_b = E (SiCNT-Li -nucleobase) - E (SiCNT-Li) – E (nucleobase)

$$(5)$$

By definition, $E_b < 0$ in Eq. (5) corresponds to stable complexes of SiCNT-Li with bases. The binding energies were calculated for optimized structures shown in figure 1.
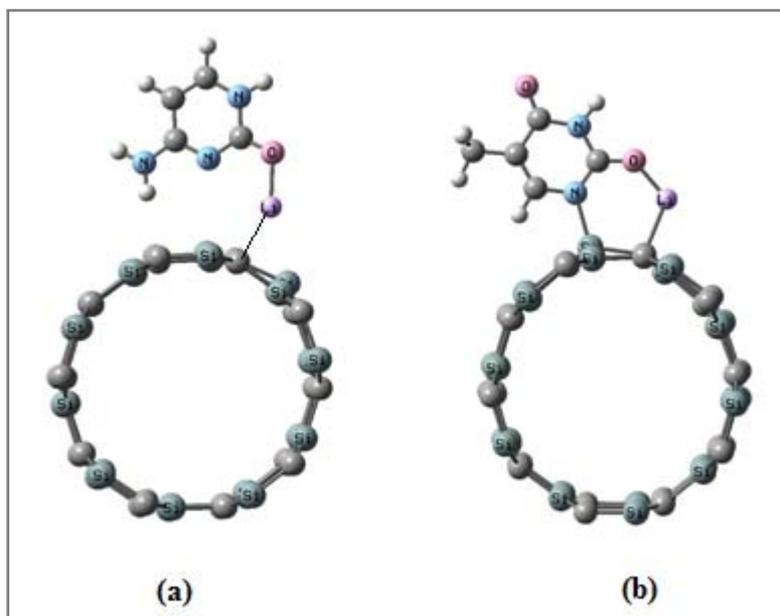
Fig. 1. Optimized structures of (a) SiCNT-Li-C (b) SiCNT-Li-T.

Table 2. Total energies in gas phase and aqueous solution

species	E(kcal mol^{-1})	
	gas phase	**water medium**
Cytosine	-247821.18	-247834.40
thymine	-284973.89	-284982.73
SiCNT-Li	-9263056.94	-9263103.75
SiCNT-Li-C	-9510919.76	-9510956.54
SiCNT-Li-T	-9547729.31	-9547729.30

Table 3. Binding Energy (E_b) and some vertical separations of Nucleobase complexes with SiCNT-Li in gas phase

species	E_b (kcal mol^{-1})	Li- base(Å)	Li-C(Å)	Li charge
SiC-Li-C(g)	-41.67	1.86	2.17	0.40
SiC-Li-T(g)	-301.52	1.75	2.07	0.84

*Charges are in electron

As can be seen from table 3, thymine with the binding energy of -301.52 kcal mol^{-1} has more powerful interaction with SiCNT-Li than cytosine. Binding energy is dependent upon a number of factors, e.g., the reactivity of the NTs, the reactivity of the base, steric factors, etc. Thymine has the greatest binding strength with SiCNT-Li due to the formation of a six-membered

ring between thymine and SiCNT-Li. As can be seen in Fig. 1, thymine interacts with SiCNTLi via two sites: one from nitrogen to the Si atom of the nanotube and the other through oxygen to Li.

In the case of cytosine, the existence of the NH2 group prevents the formation of the six-membered-ring and so the stability of SiCNT-Li-C is less than that of SiCNT-

Li-T. In SiCNT-Li-C, the base interacts with SiCNT-Li only at one site. Thus, it is expected that SiCNT-Li- T is more stable complex. The results are comparable with other experimental and theoretical studies[39,40]. Quantum mechanical calculations have indicated that thymine more efficiently functionalizes CNT than does cytosine [40].

Table 3 also contains of vertical separation of base from SiCNT-Li. the distance between Li and the base in SiCNT-Li- T and SiCNT-Li-C complexes is 1.75 and 1.86 Å respectively. This evidence confirms that thymine must make more stable complex and also has more binding energy.

2. Water medium
2.1 QM part
The results of CPCM calculations for all species of the system in water are also given in table 2.

Comparison of total energies of SiCNT-Li, SiCNT-Li-C and SiCNT-Li-T indicated that cytosine and thymine can also create the stable complexes with SiCNT-Li in water medium too.

The CPCM predicted binding energies for the complexes are tabulated in table4. As can be seen, thymine with the binding energy of -159.24 kcal/mol comparison with -18.39 for cytosine made more stable complex in water medium. Binding energies change with nucleobase because of geometries of the related structures and

the sequence of binding energies after taking into account solvent effects is compatible with gas phase. However, the bindings of each species in water medium are significantly weakened by 23 kcal/mol (for cytosine complex) and 140 kcal/mol (for thymine complex) approximately. In fact the solvation of nucleobases will decrease their binding energies with SiCNT-Li. The solvation of nucleobases, hinder their interaction with SiCNT-Li so that binding strength of cytosine and thymine with SiCNT-Li in solution are weaker than gas phase. This is the reason of increasing of the vertical separation of base from SiCNT-Li in water. As can be seen in table 4, the distance between Li and the base in SiCNT-Li- T and SiCNT-Li-C complexes in water is 1.83 and 1.90 Å respectively(comparable with 1.75 and 1.86 Å for cytosine and thymine complexes in gas phase).

2.2 Monte Carlo Simulation
In the Monte Carlo simulations, a very dilute solution of SiCNT-Li and its complexes with cytosine and thymine were used. So one molecule of solute has merged in water and the average energies were then calculated from Monte Carlo simulations. As an example, the resultant configuration of the MC simulation of SiCNT–Li–T in water is shown in Fig. 2. This gives a qualitative idea of the formation of the solvation shell around the solute.

Table 4. Binding Energy (E_b)and some vertical separations of Nucleobases complexes with SiCNT-Li in water medium

species	E_b (kcal mol^{-1})	Li- base(Å)	Li-C(Å)
SiC-Li-C(g)	-18.39	1.90	2.34
SiC-Li-T(g)	-159.24	1.83	2.39
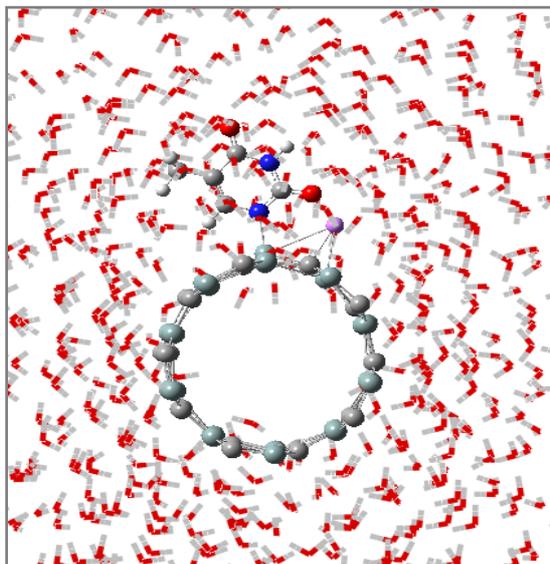
Fig. 2. Simulation of SiCNT-Li-T in water.

Table 5. Monte Carlo simulation results

NT	N_{H2O}	$< E >$ (kcal mol^{-1})	inside local density	outside local density
SiCNT-Li	4009	-140.30	0.155	0.032
Cytosine	4071	-9.25	-	-
Thymine	4069	-9.21	-	-
SiC-Li-Cytosine	4004	-139.78	0.115	0.032
SiC-Li-Thymine	4006	-144.98	0.162	0.032

*local densities are in molecule/Å^3

The total energy of the compounds in water was calculated. E_{tot} can be explained as the sum of the energy contributions from solute-solvent (E_{soln}), solvent-solvent (E_{solv}), and intramolecular (E_{int}) interactions. The average energy ($< E_{tot} >$) calculated from Monte Carlo simulations is given in Table 5. This table also includes the number of solvent molecules (N_{H2O}) in the cubic box and local density of water inside and outside of the nanotube.

The results indicate that the absolute total energies of these SiCNT-Li compounds in water appear in the following order:

E_{total}(SiCNT - Li - T) > E_{total}(SiCNT - Li) > E_{total}(SiCNT - Li - C)

In the polar solvent (water), the electrostatic terms play an important role in the total energy. Point charges on the material's surface can improve total energy because they increase the interaction energy of H2O molecules and the solute. The atomic charges in the solutes affect the electrostatic terms of intermolecular energies directly. As mentioned above, the charges were given from quantum mechanical calculations for all of these NTs. Calculations indicated that the atoms in the nanotube around Li have larger charges when we used thymine. This is due to the larger natural atomic charge in Li. The charges of carbon and silicon atoms near the Li decreased in SiCNT-Li-C. Therefore, the absolute total energy of SiCNT-Li-C in water is less than that of SiCNT-Li.

The amount of water molecules in the NTs have represented as local densities. Calculated values for SiCNT-Li, SiCNT-Li-C and SiCNT-Li-T samples are given in Table 5. As can be seen, local density of water inside SiCNT-Li-T is larger than SiCNT-Li-C and SiCNT-Li that is correspond to the larger atomic charges on the tube wall and less hydrophobic effect of SiCNT-Li-T sample. So it appears that SiCNT-Li-T prefers to adsorb water molecules rather than pass them through the NT. The outside local densities for all three NTs are equals to 0.032 that correspond to the limit of bulk water in all samples.

Absolute free energies of the reaction of cytosine and thymine with SiCNT-Li have been calculated using thermodynamic cycle. The complexation free energy in solution has been given by:

$$\Delta G_r = \Delta G_{sol}(L \rightarrow 0) + \Delta G_{sol}(NT \rightarrow 0) - \Delta G_{sol}(LNT \rightarrow 0) \quad (6)$$

$\Delta G_{sol}(L \rightarrow 0)$, $\Delta G_{sol}(NT \rightarrow 0)$ and $\Delta G_{sol}(LNT \rightarrow 0)$ are solvation free energies of ligand(pyrimidine nucleobase), SiCNT-Li and SiCNT-L- nucleobase complex respectively.

The solvation free energy of the species A (SiCNT-Li and nucleobase complexes of SiCNT-Li) can be written in terms of perturbations where the species disappear to nothing in the gas phase and in solution:

$$\Delta G_{sol}(A) = \Delta G_{gas}(A \rightarrow 0) - \Delta G_{sol}(A \rightarrow 0) \quad (7)$$

Thermodynamic perturbation has wide applicability not only in studies of absolute solvation free energies but also in studies of binding free energies.

Equation 6 was used to calculate each complexation free energy. For this purpose, we need three solvation free energies: solvation free energies of nucleobases, SiCNT-Li and, SiCNT-Li-nucleobases. Solvation free energies were calculated using equation 7. The results are tabulated in Table 6.

Between two types of SiCNT-Li-pyrimidine nucleobase, complex of thymine with SiCNT-Li has the larger absolute solvation free energy than cytosine. In SiCNT-Li- T charges accumulated strongly around Li atom, making the nanotube walls highly reactive to external molecules like H2O. Thus thymine complex of SiCNT-Li had the most negative solvation free energy.

The complexation free energy (ΔG_r) of the SiCNT-Li-T species is more negative than that of the SiCNT-Li- C(table 6). In fact, between the two pyrimidine nucleobases, only thymine makes a stable compound with SiCNT-Li.

As mentioned above in SiCNT-Li-C, cytosine interacts with Li-doped SiCNT only at one site. But in SiCNT-Li- T, thymine interact with nanotube via two sites (figure 1). In fact, in the thymine complex, we have a sixmembered- ring between the base and the NT that stabilizes the complex. Thus, it is expected that SiCNT-Li- T is the most stable complex.

Furthermore, the computed intermolecular distance from quantum mechanical calculations in solution indicated that the distance between Li in SiCNT and O in thymine, is 1.83 Å, and that between Li and O in cytosine is 1.90 Å(table 4). Comparison of the distance between Li and the base indicates that thymine must make the most stable complex with SiCNT Li. Thus it is predicted that cytosine complex has less complexation free energy than thymine.

Moreover, greater charge separation in SiCNT-Li-T enhances the stability of this complex in water compared with SiCNT-Li-C.

Table 6. Computed solvation free energies and complexation free energies (in kcal mol^{-1})

species	ΔG_{sol}	ΔG_r
SiC-Li	-393.43	---
Cytosine	-20.10	---
Thymine	-13.10	---
SiC-Li-C	-395.17	4.46
SiC-Li-T	-403.40	-4.12

CONCLUSION

The interaction of biomolecules with nanotubes is a topic of current research interest. In this research binding of cytosine and thymine with SiCNT-Li was studied. The research included two parts. In QM part, binding energies of SiCNT-Li-C and SiCNT-Li-T were calculated in gas phase and aqueous solution. Calculations indicated that thymine has more powerful interaction with SiCNT-Li than cytosine. Thus, in the interaction with pyrimidine nucleobase, thymine is preferred.

In MC part, solvation free energies of SiCNT-Li and SiCNT-Li- nucleobases were estimated. These energies are unattainable experimentally because of the lack of volatility of these compounds. The computations showed that the solvation of SiCNT-Li- thymine complex in water is more than cytosine complex. Computed complexation free energies of these two complexes, indicated that SiCNT-Li-T is more stable species in the water. Therefore, it is concluded that, between pyrimidine nucleobases, thymine is preferred to functionalize SiCNT.

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