

Covalent hybridization of CNT by thymine and uracil: A computational study

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Abstract We have investigated the electronic and structural properties of covalent functionalization of the tip of (5,0) carbon nanotube (CNT) by di-keto and keto-enol forms of thymine (T) and uracil (U) nucleobases. Density functional theory (DFT) calculations have been performed to optimize the investigated structures and to calculate the properties such as dipole moment, bond length, band gap, total energy, binding energy and quadrupole coupling constant. The results indicated that, due to the functionalization of CNT by T and U, the hybrids exhibit new properties in which they are similar in both types of CNT-T and CNT-U hybrids.

Keywords Carbon nanotube · Hybrid · Thymine · Uracil

Introduction

Since the discovery of the carbon nanotube (CNT) by Iijima in 1991 [1], a rapidly growing number of research have been devoted to characterize the properties and applications of this novel material. Physical or chemical addition of other atoms or molecules to the CNTs is one of the interesting subjects in which the electronic structure of the CNTs could be changed during the process [2, 3]. Among them, the addition of nucleobases to the walls or

tips of the CNTs is very important in biological related technologies to construct molecular nano devices [4, 5]. The hybrids of the CNT and nucleobases could play dominant roles in biological systems such as gene therapy, drug delivery, bio-sensing, and etc. Moreover, the CNTs are initially hydrophobic materials but their hybridization with nucleobases increases their solubility in water which is important in the employing of the CNTs in the poly hydrated biological systems. Among the five nucleobases of adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U), the two latter ones are the typical nucleobases of DNA and RNA respectively. In earlier computational studies, Song et al. [6] investigated the covalent addition of nucleobases to the wall of the CNT and Das et al. [7] and Shukla et al. [8] systematically investigated the interactions between the nucleobases and the wall of the CNTs. In another interesting computational research, the physisorption of nucleobases on the wall of the CNTs was well described by Gowtham et al. [9]. The interactions between nucleic acids and CNTs have also been investigated by experimental methods; however, the non-covalent interactions have mostly been considered [10–12]. To this time, to the best of our knowledge, the functionalization of the tip of CNT by nucleobases has not been reported.

In the current research, we have investigated the covalent additions of the tautomeric forms of thymine and uracil to the tip of the small-diameter single-walled (5,0) CNT using density functional theory (DFT) calculations. It is important to note that the tautomerism of nucleobases could lead to occurring mutations in the biological systems [13, 14]. The glycosidic nitrogen atoms (N_1) of the mentioned nucleobases which originally bind to the ribose sugar were substituted by the CNT in our study. Since the atoms in the tips play the dominant roles in determining the fundamental properties of the nanotubes, additions of the nucleobases to

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the tips could be important to study. Moreover, the properties of the hybridization of the CNT by the characteristic DNA and RNA nucleobases, thymine and uracil respectively, have been investigated.

Computational aspects

In the current research, we have considered ~1-nm length the single-walled (5,0) CNT followed by the work of Gowtham et al. [9] and the tautomeric forms of the T and U nucleobases (Figs. 1 and 2). The criteria for choosing the (5,0) CNT was the balance between the diameters of the nanotube and the nucleobases and for the nucleobases was the typical nucleobase of DNA and RNA. Both T and U have di-keto forms and their tautomerization follow a similar way; therefore, comparing their properties in the functionalization of the CNT could be an interesting subject. In the first step, the geometries of the considered models have separately been optimized employing the B3LYP exchange-functional and the 6–31G* standard basis set. Subsequently, the optimized CNT has been functionalized by the optimized tautomers of T and U and the geometries of the new hybrids of CNT-T and CNT-U have been optimized at the mentioned theoretical level. In the functionalization process, one hydrogen atom was removed from the tip of CNT and the hydrogen atoms of N₁ of thymine and uracil were also removed to make possible the chemical binding of the nucleobases to the CNT. The ribose group binds with N₁ of nucleobase; therefore, this N atom plays a dominant role in the structural determination of nucleotides. The binding energies were evaluated by the calculations of the total energies for the single and hybrid systems of the nucleobases and the CNTs, $E_{Binding} = E_{CNT} + E_{Nucleobase} - E_{CNT-Nucleobase}$. It is important to note that after optimization of the CNT-nucleobase hybrid, the single point energies of the CNT and nucleobases were calculated to evaluate the binding energies. Since the covalent binding

is considered in our calculation, basis set superposition error (BSSE), which is important in the weak interacting systems, is not needed to be taken into account [15]. Band gaps and dipole moments have also been calculated for the systems of study. As a proper tool, quadrupole coupling constants (C_Q) have been calculated for the O and N atoms of the nucleobases. To this aim, electric field gradient (EFG) tensors were calculated and converted to C_Q using the equation of C_Q (MHz) = $e^2 Q q_{zz} h^{-1}$ where the Q parameters are 25.58 and 20.44 mb for the ¹⁷O and ¹⁴N atoms respectively [16]. By earlier studies, we have indicated that the properties of nucleobases and nanotubes could be well investigated by calculations of the C_Q parameters [17, 18]. The DFT calculations have been performed using the Gaussian 98 program [19].

Results and discussion

CNT-Thymine hybrid

The known most stable di-keto form of thymine and four of its possible keto-enol tautomers were added to the tip of the (5,0) CNT resulting five models of CNT-thymine (CNT-T) hybrids (Fig. 1). The geometries of these structures were optimized and the parameters consisting of dipole moment, CNT-N₁ bond length, band gap, total energy, binding energy, and quadrupole coupling constant (C_Q) were calculated (Table 1). The dipole moments are related to the polarizability of the structures and these values for five structures of CNT-T hybrids indicated that different polarizations were induced to the structures due to the functionalization of the tip of the CNT by the tautomers of T. As mentioned earlier, tautomerism could lead to mutations in biological systems and we see here that these tautomers yield different polarizations in the structures of hybrids. Moreover, polarizability is very important to solve or disperse a structure in water. The largest value of dipole

Fig. 1 The CNT-T hybrids

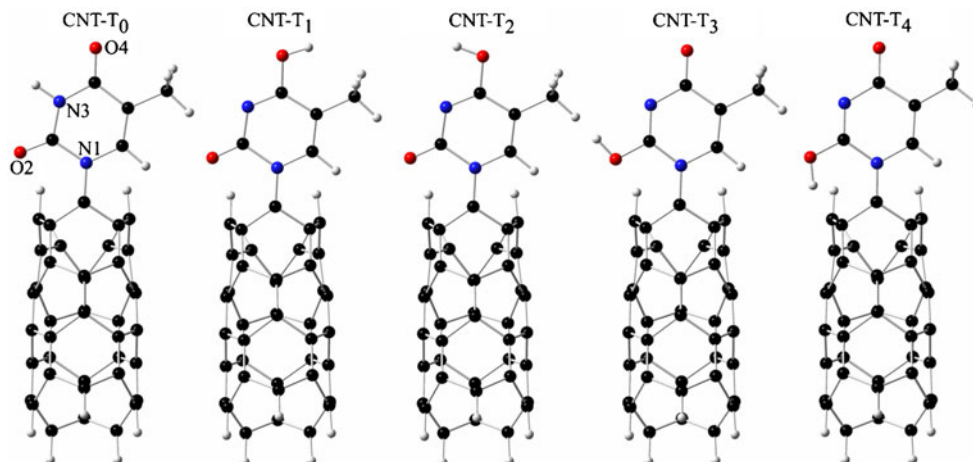


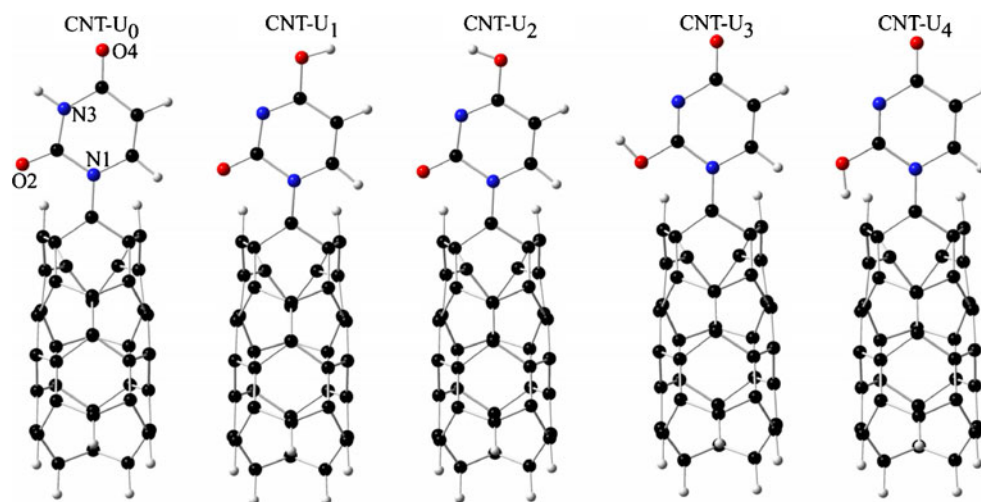
Table 1 The calculated parameters of the hybrids of CNT-Thymine *

Parameter	CNT-T ₀	CNT-T ₁	CNT-T ₂	CNT-T ₃	CNT-T ₄
Dipole moment /Debye	4.57	6.95	4.35	6.98	10.61
CNT-N ₁ Bond Length /Å	1.39	1.38	1.38	1.39	1.37
Band gap /eV	1.18	1.11	1.11	1.17	1.25
Total energy /keV	-53.95	-53.95	-53.95	-53.95	-53.95
Binding energy /eV	4.00	4.21	4.17	3.77	3.96
C _Q (¹⁴ N ₁) /MHz	2.99	2.25	2.33	2.94	2.74
C _Q (¹⁴ N ₃) /MHz	3.59	3.85	3.49	3.55	3.90
C _Q (¹⁷ O ₂) /MHz	8.60	9.18	9.16	9.41	8.80
C _Q (¹⁷ O ₄) /MHz	9.59	9.06	8.93	10.48	10.69

* See Fig. 1 for details

moment is for CNT-T₄ and the smallest one is for CNT-T₂ hybrid. Interestingly, the values of CNT-T₁ and CNT-T₃ are close to each other. The CNTs initially have low magnitudes of the dipole moment which is 1 Debye for the investigated CNT of our study. However, our calculated results indicate that the magnitude of dipole moment is increased in the hybrid of CNT-T. A larger magnitude of dipole moment is advantageous for dipole-dipole interactions; therefore, the hybrids of CNT-T could participate in these types of interactions with the surrounding system. Moreover, this ability is different for various hybrids of CNT-T based on the magnitudes of dipole moments which could emphasize the importance of tautomerism of T in determining the properties of the hybrid systems. The same values of covalent bond length of CNT-N₁, which is the distance between the C atom at the tip of CNT and N₁ atom of T, were almost calculated for all five structures. Comparing the values of band gaps indicated that the largest value is for CNT-T₄ and the smallest value is for the CNT-T₁ and CNT-T₂ hybrids. This trend again reveals that the effect of different electronic properties of the tautomers on the electronic properties of the CNT-T hybrids. Total energies did not detect any changes among the available structures whereas different values of binding energies were calculated. The binding energies indicated that CNT-T₁ has the strongest and CNT-T₃ has the weakest binding among the structures of the CNT-T hybrids. Comparing with the computational work carried out by Song et al. [6], which is the only study on the covalent nucleobase-functionalized CNTs in which the wall of CNT was functionalized by T, reveals that the functionalization of the tip of CNT by T could be more preferable due to the larger value of binding energy; the value of E_b (CNT-T) was calculated about 1.7 eV [6] and the value of E_b (CNT-T) in our study is about 4 eV. The C_Q parameters are calculated at the sites of quadrupolar nuclei such as ¹⁴N and ¹⁷O atoms and could reveal insightful trends about the electronic sites of atoms. The C_Q results indicated that the N and O atoms do not detect similar environments in the structures of CNT-T hybrids. N₁ is chemically bonded to the C atom of CNT and

as could be seen by the binding energies, different strengths were observed for these covalent bonds in the five structures. Due to this fact, the value of $C_Q(^{14}\text{N}_1)$ is very small for CNT-T₁ and very large for CNT-T₃ among the structures. N₃ has an H atom in CNT-T₁ but releases it by tautomerization process of T. In CNT-T₂ and CNT-T₃, the enol H atoms of O₄ and O₂ are toward N₃; therefore, intramolecular interactions could be expected between the H and N₃. The keto form of O₂ remains in CNT-T₀, CNT-T₁ and CNT-T₂ but it is changed into enol form in CNT-T₃ and CNT-T₄. O₂ of CNT-T₁ and CNT-T₂ detects almost equivalent electronic environment thus the value of $C_Q(^{17}\text{O}_2)$ is the same in both structures. In CNT-T₀, the EFG tensors of O₂ detect the effect of neighboring N₃-H bond; therefore, the value is different in comparison with the other two structures containing the keto form of O₂. The value of $C_Q(^{17}\text{O}_2)$ of CNT-T₃ is the largest one among other structures. As could be seen in Fig. 1, the H of O₂ is placed toward the N₃; therefore, an intramolecular interaction could be expected between them. The large value of $C_Q(^{17}\text{O}_2)$ of this structure indicated that the electronic density at the site of O₂ is more than other structures. Although, O₂ is chemically bonded to H, but it seems that this H atom shares its electronic density with N₃ thus O₂ recovers its initial electronic density which was shared by H before. O₂ of CNT-T₄ is also in enol form but the H atom is placed in the opposite of that of CNT-T₄. The small value of $C_Q(^{17}\text{O}_2)$ for this structure indicates a strong chemical bonding between O₂ and H atoms. There are also three keto forms and two enol forms for O₄ in the investigated hybrids. O₂ is a urea type whereas O₄ is an amide type of O atoms and different behaviors are expected for the electronic properties of these two O atoms in the investigated hybrids. The differences between the values of $C_Q(^{17}\text{O}_4)$ in CNT-T₁ and CNT-T₂ which are both enol forms are less significant than those of enol forms of O₂ meaning that the strength of O₄-H bond is almost equal in both hybrids. However, by changing the place of H atom from N₃ to O₂, the values of $C_Q(^{17}\text{O}_4)$ of CNT-T₃ and CNT-T₄, in which both have the keto form of O₄, are significantly increased in respect to the keto form of CNT-T₀.

Fig. 2 The CNT-U hybrids

CNT-Uracil hybrid

Figure 2 shows the known most stable di-keto form of uracil and four of its possible keto-enol tautomers which were added to the tip of the (5,0) CNT resulting five models of CNT-uracil (CNT-U) hybrids. Dipole moment, CNT-N₁ bond length, band gap, total energy, binding energy, and quadrupole coupling constant (C_Q) were calculated in the optimized structures of the investigated hybrids (Table 2). The dipole moments of five structures of CNT-U hybrids indicated different polarizations effects on the structures due to the functionalization of the tip of the CNT by U tautomers. The largest value of dipole moment is for CNT-U₄ and the smallest one is for CNT-U₂ hybrid. The larger values of dipole moments of CNT-U hybrids than the CNT and also among different hybrids indicate more ability of the hybrids for contribution to dipole-dipole interactions with surrounding system. The calculated values of covalent bond length of CNT-N₁, which is the distance between the C atom at the tip of CNT and N₁ atom of U counterpart, were almost the same for all of the five structures. Comparing the values of band gaps indicated that the largest value is for CNT-U₄ and the smallest value is for the CNT-U₁ and CNT-U₂ hybrids. Parallel to the results of

CNT-T hybrids, no changes were detected for the total energies of the CNT-U hybrids. Different values of binding energies were calculated for different hybrids of CNT-U in which CNT-U₁ has the strongest and CNT-U₃ has the weakest binding among the other structures. To this point, lots of similarities were observed for the properties of CNT-T and CNT-U hybrids. The calculated values of C_Q parameters of CNT-U hybrids are almost similar to those of the CNT-T hybrids. These results indicated that although T and U belong to two different categories of nucleic acid structures, but their electronic properties are balanced in the CNT hybrids. Moreover, the almost neutral CNT could have some point charges due to functionalization by T and U in which for both hybrids the results are almost similar. This trend is in agreement with the earlier computational work of Song et al. [6] in which the hybrids of functionalized CNTs by A, G, C and T exhibited almost similar properties.

Conclusions

DFT calculations indicated that the hybrids of CNT and T or U yield different values of dipole moments in which the

Table 2 The calculated parameters of the hybrids of CNT-Uracil *

Parameter	CNT-U ₀	CNT-U ₁	CNT-U ₂	CNT-U ₃	CNT-U ₄
Dipole moment /Debye	5.34	6.74	4.32	7.88	11.56
CNT-N ₁ bond length /Å	1.39	1.38	1.38	1.39	1.37
Band gap /eV	1.17	1.10	1.10	1.16	1.25
Total energy /keV	-52.88	-52.88	-52.88	-52.88	-52.88
Binding energy /eV	4.10	4.30	4.28	3.84	4.02
$C_Q(^{14}\text{N}_1)$ /MHz	3.00	2.22	2.30	2.98	2.78
$C_Q(^{14}\text{N}_3)$ /MHz	3.61	3.81	3.45	3.55	3.90
$C_Q(^{17}\text{O}_2)$ /MHz	8.60	9.15	9.11	9.40	8.82
$C_Q(^{17}\text{O}_4)$ /MHz	9.63	9.25	8.98	10.59	10.80

* See Fig. 2 for details

largest and the smallest values belong to the keto-enol forms of the attached nucleobase. The binding lengths of CNT and T or U were almost the same but different binding energies were calculated for the structures. The values of band gaps also detect changes among the hybrids of CNT-T and CNT-U structures. Although the di-keto forms of both T and U are known as the most stable structures, the results indicated that by attaching to the CNT, the keto-enol tautomers exhibit better properties. Total energies do not detect any changes among the hybrids but the binding energies of CNT and T or U detect some changes among the tautomers. The values of C_O parameters of N and O atoms indicate significant changes among the structures of the tautomers in which the changes are more significant for the O atoms. As an important final trend, the calculated parameters indicated that the properties of CNT and CNT-U hybrids are almost similar.

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