Chemically uracil–functionalized carbon and silicon carbide nanotubes: Computational studies

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HIGHLIGHTS

- Single standing hybrid nanotube structures have been constructed.
- Polarizability of nanotubes has been increased in the hybrid structures.
- HOMO–LOMO gaps of nanotubes are almost the same in the gas-phase and water-solvated systems.

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ABSTRACT

Chemical additions of uracil (U) nucleobase to sidewall of each of representative (4,4) armchair carbon and silicon carbide nanotubes (CNT and SiCNT) were investigated based on density functional theory (DFT) calculations. All singular and hybrid models were optimized to obtain the minimum–energy structures. The evaluated molecular properties indicated the effects of U–attachment on properties of both of U and NT counterparts, in which additional evaluated atomic–scale chemical shifts indicated the role of atomic sites in the U–attachment processes. Both of U–CNT and U–SiCNT hybrids could be considered as achievable compounds; however, the aim of application could organize the achievement of which hybrid. There was one possibility of U–attachment for the homo–atomic system of CNT whereas there were two possibilities of U–attachment for the hetero–atomic system of SiCNT. Interestingly, the evaluated atomic and molecular properties indicated differences between the characteristics of U–SiCNT–1 and U–SiCNT–2 as an advantage of computational chemistry methodologies, in which the results were very much interesting for the water-solvated systems.

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1. Introduction

Soon after the first discovery of carbon nanostructures, several efforts have been dedicated to improve bio–compatibilities of these novel materials for possible applications in life sciences and technologies [1–3]. Up to now, several types of nanostructures including nanotube (NT), nanocone, graphene, fullerene, and nanoparticle have been very well recognized by computations and experiments [4–8]. Discoveries of non–carbon based

nanostructures have been also investigated by numerous research works to introduce materials with specific characteristics [9–11]. Moreover, physical or chemical modifications of nanostructures by additions of other atoms or molecules have become an important task to obtain specified materials for different purposes [12–14].

Additions of nucleobases to nanostructures are among proper methodologies to modify available nanostructures to have better behaviors in biological systems [15,16]. Uracil (U), RNA characteristic nucleobase, has initial active atomic positions for contributing to chemical bonds with other atoms and molecules yielding new hybrid structures [17,18]. Additions of biological structures to NTs are crucial for the purposes of NT–assisted drug design and deliveries in pharmaceutical applications [19]. The problem is that the

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carbon NTs (CNTs) are insoluble in water systems; therefore, biological hybridizations could improve bio-compatibility behavior of CNTs by better dispersion in aqueous media [20]. Heterogeneous Si–C chemical bonds of silicon carbide NTs (SiCNTs), which have been reported as stable structures by earlier works, are somehow ionic in comparison with homogeneous C–C bonds of CNTs but SiCNTs are not yet very well soluble in water [21–23]. In this case, chemical-attachments of functional groups and biological counterparts to CNTs and SiCNTs could help these materials to be better dispersed in aqueous solutions by changing the electronic properties of initial hydrophobic NTs [24,25]. Within this work, we have investigated formations of U–CNT and U–SiCNT chemical hybrids (Figs. 1 and 2) based on density functional theory (DFT) calculations. To this aim, the sidewalls of NTs have been chemically modified by the U nucleobase through its two C₅ and C₆ atomic positions, which have been earlier introduced as possible interacting atomic sites with other atoms and molecules [26]. Molecular and atomic properties including optimized geometries, types of energies and atomic chemical shifts have been evaluated for all the singular and hybrid structures of this study to investigate effects of hybridizations on the initial properties of both U and SiCNT/CNT counterparts to make the hybrid systems (Tables 1–5). It is important to note that, nanostructures are expected to play dominant roles as drug carriers and containers in life sciences; however, some of unwanted disadvantages like insolubility make them toxic materials for biology systems [27]. Therefore, further studies are still required to solve the unwanted properties of nanostructure and also to convert them to more favorite materials for the purposes in life sciences and technologies. In contrast with complicated experiments, systematic computational studies could reveal insightful information about the investigated systems in both molecular- and atomic- scale properties.

2. Computational details

The models of this work (Figs. 1 and 2) are the singular and hybrid structures including U (uracil) nucleobase and two representative (4,4) armchair CNT and SiCNT nanotubes (carbon and silicon carbide nanotubes). Because of similarity in the tubular tips of each NT and also due to molecular orbitals gap reasons, the armchair models have been considered in this work. Avoiding dangling effects [28], all atoms of tubular tips have been saturated by additional hydrogen atoms resulting Si₄₄C₄₄H₁₆ and C₈₈H₁₆ structures. Two hydrogen atoms from the C₅ and C₆ atomic positions of U nucleobase have been removed to make possible chemical attachments of U to the sidewall of NTs. The main purpose of such chemical functionalization was to construct a single standing stable hybrid structure. One possibility of attachment has been considered for CNT, U–CNT, whereas two possibilities have been considered for SiCNT due to interaction of each of C₅ and C₆ to each of Si or C atoms of SiCNT; U–SiCNT–1 and U–SiCNT–2. The atomic orbital hybridization of original NTs are sp^2 for all atoms but

converted to sp^3 only for those atoms of NTs interacting with the atoms of U nucleobase.

Avoiding the complexity of different theoretical methodologies, the DFT (density functional theory) calculations of this work have been performed based on standard levels employing the B3LYP exchange–correlation functional and the 6–31G* basis set, as implemented in the Gaussian 09 software, have been used [29]. First, geometries of all models have been allowed to relax through optimization processes to find the minimized–energy structures. Within these processes, optimized geometries (Table 1), dipole moments (D_{Moment}), total energies (E_{Total}), binding energies (E_{Binding}), energies of the highest occupied and the lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO}), and energy gaps (E_{Gap}) have been evaluated for the investigated structures (Table 2). To obtain E_{Binding} , energy differences between hybrid and singular structures have been referred. To obtain E_{Gap} , energy differences between HOMO and LUMO have been referred. To include the water medium effects, all molecular properties have been also evaluated in the water-solvated system employing the Polarized Continuum Model (PCM) [30]. Second, TD-DFT (time dependent) calculations have been performed to evaluate the HOMO and LUMO distribution patterns (Fig. 3). Third, atomic chemical shifts (δ ppm) (Tables 3–5) have been evaluated for the optimized structures based on the mentioned DFT method and the gauge-included atomic orbital approach (GIAO) [31]. Chemical shielding tensors (σ_{ij}) have been calculated and then they have been converted to isotropic chemical shielding (σ_{iso}); $\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ [32]. The equation $\delta(\text{ppm}) = \sigma_{\text{iso,Ref}} - \sigma_{\text{iso,Sample}}$ has been used to evaluate the values of chemical shifts [32]. All reference values ($\sigma_{\text{iso,Ref}}/\text{ppm}$) have been calculated based on the mentioned methodologies: $\sigma_{\text{iso,Ref}}(^1\text{H}) = 32.18$ {32.17}, $\sigma_{\text{iso,Ref}}(^{13}\text{C}) = 189.73$ {190.26} and $\sigma_{\text{iso,Ref}}(^{29}\text{Si}) = 414.48$ {414.69} in Si(CH₃)₄, $\sigma_{\text{iso,Ref}}(^{15}\text{N}) = -117.64$ {–126.98} in CH₃NO₂, and $\sigma_{\text{iso,Ref}}(^{17}\text{O}) = 316.58$ {325.62} in H₂O. It is noted that the reference values of water-solvated system are in the {braces} and the others are for the gas-phase system. Nuclear magnetic resonance (NMR) spectroscopy is among the most versatile and important techniques to recognize the properties of matters [33,34]. The chemical shielding tensors (σ_{ij}), which are arisen at the electronic sites of atoms, could very well introduce the

Fig. 1. Singular models.

Fig. 2. Different views of U-attached NTs.

Table 1
Bond lengths/Å.^a

Bond	Uracil	CNT	U–CNT	SiCNT	U–SiCNT–1	U–SiCNT–2
N ₁ –C ₂	1.396 [1.344] ^a	–	1.396 (0) ^b	–	1.397 (0.001)	1.402 (0.006)
N ₁ –C ₆	1.376 [1.341]	–	1.374 (–0.002)	–	1.368 (–0.008)	1.373 (–0.003)
N ₁ –H ₁	1.010	–	1.012 (0.002)	–	1.012 (0.002)	1.012 (0.002)
C ₂ –N ₃	1.385 [1.384]	–	1.388 (0.003)	–	1.396 (0.011)	1.385 (0)
C ₂ –O ₂	1.216 [1.230]	–	1.217 (0.001)	–	1.216 (0)	1.216 (0)
N ₃ –C ₄	1.414 [1.374]	–	1.417 (0.003)	–	1.408 (–0.006)	1.421 (0.007)
N ₃ –H ₃	1.014	–	1.014 (0)	–	1.014 (0)	1.014 (0)
C ₄ –C ₅	1.460 [1.411]	–	1.460 (0)	–	1.454 (–0.006)	1.453 (–0.007)
C ₄ –O ₄	1.219 [1.241]	–	1.219 (0)	–	1.225 (0.006)	1.219 (0)
C ₅ –C ₆	1.350 [1.408]	–	1.342 (–0.008)	–	1.360 (0.010)	1.363 (0.013)
C ₅ –X	1.081 –H ₅	–	1.481 –C ₄	–	1.518 –C ₄	1.847 –Si ₅
C ₆ –Y	1.085 –H ₆	–	1.480 –C ₅	–	1.897 –Si ₅	1.494 –C ₄
1–2	–	1.417	1.435 (0.018)	1.786	1.799 (0.013)	1.801 (0.005)
2–3	–	1.440	1.485 (0.045)	1.793	1.786 (–0.007)	1.787 (–0.006)
3–4	–	1.423	1.409 (–0.014)	1.795	1.856 (0.061)	1.837 (0.042)
4–7	–	1.423	1.409 (–0.014)	1.795	1.856 (0.061)	1.837 (0.042)
4–5	–	1.447	2.605 (1.158)	1.789	2.079 (0.290)	2.319 (0.530)
5–6	–	1.423	1.410 (–0.013)	1.797	1.818 (0.021)	1.809 (0.012)
5–10	–	1.423	1.410 (–0.013)	1.797	1.819 (0.022)	1.809 (0.012)
7–8	–	1.440	1.485 (0.045)	1.793	1.786 (–0.007)	1.787 (–0.006)
8–9	–	1.417	1.435 (0.018)	1.786	1.799 (0.013)	1.801 (0.015)
9–10	–	1.440	1.484 (0.044)	1.796	1.790 (–0.006)	1.790 (–0.006)

^a See Figs. 1 and 2 for the models and related atoms. ^a Experimental bond lengths of uracil from Refs. [40,41] are in the brackets and the other are obtained by the gas-phase optimization. ^b Differences of bond lengths between each hybrid structure and original structure are in the parentheses (Δ = Hybrid - Original).

electronic properties for atoms and also they could detect any perturbation to these regions [35]. However, due to complexity of electronic environment of NTs, it is not really easy to perform experimental NMR measurements for the nanostructures; therefore, quantum computations are very helpful to reproduce reliable NMR parameters [36].

By the advantages of computational chemistry methodologies for systematic studies of chemical structures [37], we have investigated the characteristics of our structures based on computationally evaluated molecular- and atomic-scale properties. Computational works could be represented independently; however, we have also included available experimental results for the investigated structures to compare experimental and computational results together for a better validation of the computed results of this work.

3. Results and discussion

Applications of nanostructures in biological systems are very much important because of their expected roles in several purposes from drug design to delivery and therapies [38]. Accordingly, investigating their properties is a crucial task to explore the specific

roles of nanostructures for purposes in biology-related systems. It is also important to construct single standing hybrid structures. Within this work, we have modified two types of nanotubes; CNT and SiCNT, by chemical additions of U nucleobases to their side-walls to make U–CNT and U–SiCNT hybrid structures (Figs. 1 and 2). Due to heterogeneous structure of SiCNT, two hybrid structures of U–SiCNT–1 and U–SiCNT–2 are constructed based on the conditions of atomic attachments of U to Si or C atoms of the tubular sidewalls. All evaluated molecular and atomic properties from optimizations, HOMO and LUMO distribution patterns, and NMR computations processes for the singular and hybrid structures of this work are summarized in Tables 1–5 and Figs. 1–3, which will be discussed in details among the following text.

3.1. Structural optimizations

Optimized geometries for all components of investigated model structures (Figs. 1 and 2) are presented in Table 1. First, comparisons of optimized and experimental bond lengths for U nucleobase indicate that the molecule detects crystalline effects in the real system, in which the bonds are relaxed to different lengths in the absence of these effects. Earlier works indicated that the molecular

Table 2
Molecular properties.^a

Property	Uracil	CNT	U–CNT	SiCNT	U–SiCNT–1	U–SiCNT–2
$E_{\text{Total}}/\text{kcal.mol}^{-1}$	–260301.15	–2110235.99	–2369774.39	–9051201.39	–9310754.57	–9310754.08
$E_{\text{Binding}}/\text{kcal.mol}^{-1}$	{–260309.94} ^a	{–2110239.31}	{–2369784.71}	{–9051207.27}	{–9310765.71}	{–9310766.95}
	–	–	25.12	–	10.34	10.83
			{26.86}		{13.82}	{12.57}
$E_{\text{HOMO}}/\text{eV}$	–6.87	–4.37	–4.59	–5.35	–5.40	–5.43
	{–6.72}	{–4.49}	{–4.61}	{–5.28}	{–5.29}	{–5.30}
$E_{\text{LUMO}}/\text{eV}$	–1.17	–2.50	–2.55	–2.17	–2.22	–2.25
	{–1.00}	{–2.61}	{–2.58}	{–2.06}	{–2.07}	{–2.06}
E_{Gap}/eV	5.70	1.87	2.04	3.18	3.18	3.18
	{5.72}	{1.88}	{2.03}	{3.22}	{3.22}	{3.24}
$D_{\text{Moment}}/\text{Debye}$	4.26	0	4.17	0	2.70	4.61
	{5.42}	{0}	{5.55}	{0}	{3.13}	{6.80}

^a See Figs. 1 and 2 for the models. ^a The values of water-solvated system are in the {braces} and the others are those of the isolated gas-phase system.

Table 3
Atomic chemical shifts (δ /ppm) for uracil counterpart.^a

Atom	Uracil	U-CNT	U-SiCNT-1	U-SiCNT-2
O ₂	290.36 [252.50] ^a {276.90} ^c	285.72 (−4.64) ^b {275.91 (−0.99)}	295.02 (4.66) {282.09 (5.19)}	294.64 (4.28) {283.43 (6.53)}
O ₄	386.09 [334.00] {354.31}	371.87 (−14.22) {346.56 (−7.75)}	360.27 (−25.82) {342.08 (−12.23)}	378.51 (−7.58) {349.18 (−5.13)}
N ₁	−245.85 [−248.81] {−249.47}	−241.55 (4.30) {−246.77 (2.70)}	−244.68 (1.17) {−250.20 (−0.73)}	−230.16 (15.69) {−235.87 (13.60)}
N ₃	−216.13 [−221.35] {−224.71}	−215.39 (0.74) {−223.48 (1.23)}	−216.44 (−0.31) {−224.65 (0.06)}	−218.00 (−1.87) {−226.17 (−1.46)}
C ₂	138.41 [151.39] {140.48}	138.00 (−0.41) {139.66 (−0.82)}	140.02 (1.61) {141.89 (1.41)}	139.02 (0.61) {140.91 (0.43)}
C ₄	150.69 [164.20] {153.30}	148.69 (−2.00) {150.70 (−2.60)}	151.16 (0.47) {153.52 (0.22)}	148.31 (−2.38) {150.65 (−2.65)}
C ₅	97.68 [100.11] {97.12}	110.26 (12.58) {110.63 (13.51)}	114.30 (16.62) {114.98 (17.86)}	112.29 (14.61) {111.71 (14.59)}
C ₆	130.95 [142.07] {135.62}	143.72 (12.77) {146.69 (11.07)}	152.43 (21.48) {154.93 (19.31)}	151.38 (20.43) {154.61 (18.99)}
H ₁	5.42 [10.80] {6.21}	5.60 (0.18) {6.26 (0.05)}	5.87 (0.45) {6.42 (0.21)}	5.64 (0.22) {6.32 (0.11)}
H ₃	6.04 [11.00] {6.26}	5.81 (−0.23) {6.14 (−0.12)}	6.03 (−0.01) {6.32 (0.06)}	5.82 (−0.22) {6.34 (0.08)}
H ₅	5.12 [5.45] {5.21}	—	—	—
H ₆	6.58 [7.39] {7.09}	—	—	—

^a See Figs. 1 and 2 for the models and related atoms. ^a Experimental values are in the [brackets] from Ref. [44]. ^b Differences of chemical shifts between each hybrid structure and original structure are in the parentheses (Δ = Hybrid - Original). ^c The values of water-solvated system are in the {braces} and the others are those of the isolated gas-phase system.

orientations and relaxations could be very much ordered by the crystalline effects to show the final 3D shapes [39].

The values of bond lengths with hydrogen atoms have been also calculated, which were not available in the experimental values. The computed bond lengths for U nucleobase are almost in the range of experimental measurements [40,41] and the discrepancies could be expected for the crystalline effects in real system, which are neglected in the computations. For the investigated nanotubes,

the lengths of C–C bonds and Si–C bonds are almost around the reported values of 1.43 Å and 1.80 Å for CNT and SiCNT respectively [42,43]. It is noted that different computed values of bond lengths are observed at different positions of optimized tubular structures, but the averaged values could be comparable with the already reported values. The optimized tubular diameters and lengths at the tips are 5.68 and 12.28 Å for the CNT and they are 7.11 and 15.48 Å for the SiCNT. To chemically attach the U nucleobase to the tubular sidewalls, hydrogen atoms are removed from C₅ and C₆ atoms of U and the chemical attachment is done at the tubular sidewall. For CNT, there is only one possibility of U–attachment to the sidewall whereas there are two possibilities for the SiCNT, in which each of

Table 4
Atomic chemical shifts (δ /ppm) for CNTs.^a

Atom	CNT	U-CNT
C ₁	123.17 {123.55} ^b	124.54 (1.37) ^a {127.08 (3.53)}
C ₂	123.03 {123.66}	127.11 (4.08) {125.78 (2.12)}
C ₃	121.56 {122.22}	126.43 (4.87) {124.04 (1.82)}
C ₄	120.07 {120.76}	136.55 (16.48) {130.40 (9.64)}
C ₅	112.74 {120.61}	129.37 (16.63) {135.34 (14.73)}
C ₆	120.23 {122.12}	123.58 (3.35) {127.08 (4.96)}
C ₇	121.56 {122.22}	126.43 (4.87) {124.04 (1.82)}
C ₈	123.03 {123.66}	127.11 (4.08) {125.78 (2.12)}
C ₉	123.17 {123.55}	124.54 (1.37) {127.08 (3.53)}
C ₁₀	121.66 {122.12}	123.58 (1.92) {127.07 (4.95)}
C Benzene	121.06 {128.5} ^c {121.77}	

^a See Figs. 1 and 2 for the models and related atoms. ^a Differences of chemical shifts between each hybrid structure and original structure are in the parentheses (Δ = Hybrid - Original). ^b The values of water-solvated system are in the {braces} and the others are those of the isolated gas-phase system. ^c Experimental value for benzene is in the [brackets] from Ref. [45].

Table 5
Atomic chemical shifts (δ /ppm) for SiCNTs.^a

Atom	SiCNT	U-SiCNT-1	U-SiCNT-2
Si ₁	123.22 {124.76} ^b	125.49 (2.27) ^a {126.83 (2.07)}	126.22 (3.00) {127.66 (2.90)}
Si ₃	125.82 {127.19}	149.91 (24.09) {150.62 (23.43)}	138.66 (12.84) {138.18 (10.99)}
Si ₅	125.84 {127.30}	8.30 (−117.54) {6.28 (−121.02)}	22.92 (−102.92) {20.96 (−106.34)}
Si ₇	125.82 {127.18}	150.01 (24.19) {150.76 (23.58)}	138.66 (12.84) {138.18 (11.00)}
Si ₉	123.23 {124.73}	125.50 (2.27) {126.83 (2.10)}	126.22 (2.99) {127.66 (2.93)}
C ₂	76.45 {67.80}	77.78 (1.33) {69.22 (1.42)}	77.75 (1.30) {69.21 (1.41)}
C ₄	77.69 {69.12}	58.37 (−19.32) {50.76 (−18.36)}	76.31 (−1.38) {67.90 (−1.22)}
C ₆	77.01 {68.49}	61.35 (−15.66) {53.29 (−15.20)}	66.22 (−10.79) {57.22 (−11.27)}
C ₈	76.45 {67.81}	77.73 (1.28) {69.18 (1.37)}	77.75 (1.30) {69.21 (1.41)}
C ₁₀	77.01 {68.50}	61.22 (−15.79) {53.17 (−15.33)}	66.21 (−10.80) {57.21 (−11.29)}

^a See Figs. 1 and 2 for the models and related atoms. ^a Differences of chemical shifts between each hybrid structure and original structure are in the parentheses (Δ = Hybrid - Original). ^b The values of water-solvated system are in the {braces} and the others are those of the isolated gas-phase system.

Fig. 3. HOMO and LUMO distribution patterns for the models.

C₅ and C₆ atoms of U nucleobase interacts with the Si or C atom of the SiCNT sidewall. In the U–CNT hybrid, the major effects of chemical U–attachment are observed for the C₅–C₆ bond of U and the C₄–C₅ bond of CNT whereas the effects for other bond lengths are almost negligible. It is noted that the major effects of geometries are only seen for the attachment region meaning that the overall geometrical properties of original U and CNT are almost kept unchanged in the U–CNT hybrid. Parallel results are seen for the U–SiCNT hybrids, in which the major effects of U–attachment are observed for the atomic geometries of the attachment region. Careful examinations indicate that the effects on properties of U–SiCNT–2 are more significant in comparison with the effects on properties of U–SiCNT–1. As demonstrated in Fig. 2, the C₅ and C₆ atoms of U are attached to the C and Si atoms of U–SiCNT–1 and they are attached to the Si and C atoms of U–SiCNT–2. Comparing the C₅–X and C₆–Y bond lengths, which stand for bond length of chemical attachments, reveals significant differences for the values of U–SiCNT–1 and U–SiCNT–2. However, the values of bond lengths for two attached bonds are almost identical for the U–CNT. Investigating properties of matters at the atomic scales is an advantage of computational chemistry studies revealing insightful information about the structural characteristics of matters.

The energies and dipole moments for the optimized structures are listed in Table 2. According to the magnitudes of total energies, U–SiCNT–1 is slightly more stable than U–SiCNT–2 but the binding energies show that the formation of U–SiCNT–2 could be expected more favorable than U–SiCNT–1. Comparing the results of binding energies for all three hybrids shows that the formation of U–CNT could be much more favorable than other two U–SiCNT models. Comparing the results of HOMO and LUMO indicates that the energy gap between two orbital levels of U is significantly reduced in the hybrid system. The effects of U–attachment are more obvious for U–CNT in comparison with U–SiCNT, in which the gap is wider for U–CNT versus original CNT than U–SiCNTs versus original SiCNT. The magnitudes of dipole moments for original CNT and SiCNT are zero but they are significantly modified in the U–attached models, in which the modifications are more significant for U–CNT and U–SiCNT–2 than U–SiCNT–1. As

remembered by the magnitudes of bond lengths, the changes of lengths between interacting atoms of NTs, atoms 4 and 5, were significant for the U–CNT and U–SiCNT–2 but negligible for the U–SiCNT–1, which is shown here by smaller magnitude of dipole moment for U–SiCNT–1 versus U–CNT and U–SiCNT–2. As mentioned earlier, the purpose of choosing armchair NTs was to have similar tips of nanotubes for a unique place of functionalization, in which the zero magnitudes of dipole moments for both of original CNT and SiCNT approves our idea.

Comparing the results of gas-phase and water-solvated systems indicates more stability for the structures in the water-solvated systems based on the values of total and binding energies. The levels of HOMO and LUMO are changed in the water-solvated system whereas the differences of two orbital levels are remained almost unchanged from gas-phase to water solvated system. The values of dipole moments have been increased from the gas-phase to water solvated system for the hybrid structures not for original NTs indicating the importance of constructing single-standing hybrid structures for better polarizability properties. Examining the distribution patterns (Fig. 3) also indicates that the electrons of U counterpart are all transferred to the NTs in the hybrid structures, with identical situation for both of gas-phase and water-solvated systems. As a conclusion, it could be mentioned that the properties of NTs detect the effects of U–attachments, in which the magnitudes of effects are not similar for all U–NT hybrids.

3.2. NMR properties

NMR properties including chemical shifts (δ /ppm) are presented for atoms of all optimized structures of this study in gas-phase and water-solvated systems (Tables 3–5). Earlier studies indicated that computational NMR methodology could be expected as an insightful technique to describe properties of nanostructures, avoiding the complexity of experiments [36]. Within this work, we also have employed this technique to investigate the properties of U–CNT and U–SiCNT hybrids (Figs. 1 and 2).

Table 3 presents δ parameters for original and attached U counterparts, in which the available experimental parameters

indicate the crystalline effects for the original U in comparison with the optimized one parallel to the geometries results. In the U–CNT, the major direct effects of U–attachment to CNT are observed for properties of C_5 and C_6 atoms; however, significant changes of properties are observed for some other atoms e.g., O_4 , because of indirect effects. Since the chemical environment of heterocyclic ring of U is changed during the attachment process, the effects on δ properties are observed more or less for all atoms of U. Stronger effects of attachments are observed for C_5 and C_6 atoms and also for other atoms of U in the U–SiCNT hybrids. Interestingly, depending on the attachment of each of C_5 and C_6 to Si or C atoms, strong effects are observed for their neighborhood atoms. When C_5 is attached to C atom in U–SiCNT–1, the electronic properties of O_4 detect strong effects of this attachment whereas the electronic properties of N_1 detect strong effects of the attachment because C_6 of U is attached to C atom in U–SiCNT–2. The bond length of C–C is shorter than Si–C; therefore, the effects are stronger for the neighboring atoms of C–C bond in comparison with Si–C bond. The most significant effects of U–attachment are observed for C_4 and C_5 atoms of CNT, and for C_4 and Si_5 of SiCNT, in which the indirect effects are still observed for the properties of neighboring atoms. The atomic NMR properties detect the effects of water-solvated systems; however, the magnitudes of changes from gas-phase to water-solvated system are almost similar.

Tables 4 and 5 exhibit the calculated NMR properties for NTs in singular and hybrid forms (Figs. 1 and 2). The results indicate that the original singular NTs show normal behaviors in comparison with earlier studies [42,43]. However, the normal behaviors have been perturbed by U–attachments, in which the amounts of perturbations are not similar for all atoms of NTs. For homo–atomic structure of CNT, the parameters are divided into two similar upper and lower parts with similar values of δ parameters for atoms of the two parts. However, the external field employed by the U–attachment makes significant changes to the original NMR characteristic of U–CNT hybrid. The magnitudes of effects are very much significant for the atom of attachment region but less significant for atom far from the region. For the SiCNTs, in which the atoms of original NT could be also divided into two parts based on similarities of δ parameters for atoms of two parts, the U–attachment show significant effects for the original characteristic δ parameters. Since the Si–C bonds are somehow ionic in comparison with non–ionic C–C bonds, the magnitudes of changes of δ parameters in singular and hybrid systems are much more significant than the situations of CNT and U–CNT systems. Again, the most significant effects of U–attachment are observed for the attachment region of U–SiCNT, in which the magnitudes of changes for U–SiCNT–1 are much more significant than U–SiCNT–2 hybrid. The very much significant changes of δ parameters of U–SiCNT–1 hybrid could reveal the flexibility of structure in acceptance of new attachment whereas the flexibility is lower in U–SiCNT–2 hybrid. Since the electronic systems are not localized, the effects of external perturbations could be very well detected by the computed δ parameters, which are originally electronic based elements. This trend has been better seen for the water-solvated systems, in which the magnitudes of changes of δ parameters in the water-solvated systems are significant from those of gas-phase systems. Based on the purpose of this work to construct single standing hybrid structure, the atomic scale δ parameters could very well show that the hybrid structures could play significant roles in the water-solvated systems in comparison with the original NTs. As an expectation for the NTs to be dispersed in the water media, it is very much important to have hybrid structures with better dispersion properties. In agreement with the obtained values of dipole moments, the δ parameters also indicate more polarizability for the hybrid U–NTs in comparison with the original NTs. The importance

of constructing such functionalized NTs has been also demonstrated by two important recent works [15,24]. As a concluding remark, the atomic–scale δ parameters could detect the effects of perturbations by U–attachment for both CNT and SiCNT hybrids, in which the magnitudes of effects could determine the most important atomic sites of NTs for interactions with other molecules.

4. Conclusion

DFT studies were performed to investigate the properties of U–CNT and U–SiCNT hybrids based on optimized properties and NMR parameters. The results indicated that both of evaluated molecular– and atomic–scale parameters could very well determine the effects of U–attachment on the original properties of NTs. The significant remarks of this work are based on molecular properties, which show the magnitudes of changes of original molecular properties in hybrid form, and δ atomic–scale properties, which show the roles of atomic sites in molecular hybridizations. By the obtained results, chemical attachments of U to both of CNT and SiCNT are achievable; however, the aim of attachment could be ordered by the magnitudes of changes of obtained properties in singular and hybrid structures. The tendency of U–attachment to each of CNT or SiCNT could be very well organized by binding energies. The results of water-solvated systems also demonstrated that the stabilities of hybrid structure have been increased in the solvated system based on total and binding energies. Moreover, the magnitudes of dipole moments and chemical shifts indicated that the functionalization of NTs could significantly increase the polarizability of NTs counterparts especially in the water-solvated systems.

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