

Functionalization of $(n, 0)$ CNTs ($n = 3-16$) by uracil: DFT studies^{*}

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Abstract. Density functional theory (DFT) calculations were performed to investigate stabilities and properties for uracil (U)-functionalized carbon nanotubes (CNTs). To this aim, the optimized molecular properties were evaluated for $(n, 0)$ models of CNTs ($n = 3-16$) in the original and U-functionalized forms. The results indicated that the dipole moments and energy gaps were independent of tubular diameters whereas the binding energies showed that the U-functionalization could be better achieved for $n = 8-11$ curvatures of $(n, 0)$ CNTs. Further studies based on the evaluated atomic-scale properties, including quadrupole coupling constants (C_Q), indicated that the electronic properties of atoms could detect the effects of diameters variations of $(n, 0)$ CNTs, in which the effects were very much significant for the atoms around the U-functionalization regions. Finally, the achieved results of singular U, original CNTs, and CNT-U hybrids were compared to each other to demonstrate the stabilities and properties for the U-functionalized $(n, 0)$ CNTs.

1 Introduction

Since the early days of carbon nanotubes (CNTs) discovery by Iijima [1], so many researchers have shown their interests to explore advantages of this novel material for possible applications in life sciences and technologies [2,3]. However, some significant disadvantages such as hydrophobicity, led the researchers to first evaluate modified CNTs for the specific purposes in biological systems [4]. In this case, considerable efforts have been dedicated to examine the structural modifications of CNTs through functionalization processes by other atomic and molecular groups [5–8]. Specifically, formations of biomolecular functionalized CNTs and their properties have been investigated by either computations or experiments to construct suitable compounds for biological applications [9–11]. Proteins, peptides, nucleic acids, and so many other biomolecules have been examined as proper functional groups to convert pristine CNTs into hybrid compounds [12,13]. The possibility of covalent functionalization of CNTs by nucleobases has been earlier approved based on experiments [14]. Moreover,

experimental adsorption of uracil on the surface a CNT-based electrode has been earlier investigated [15]. Cytosine and uracil, which are pyrimidine nucleobases, could contribute to covalent bonds formations to other structures through their atomic sites to make combined structures e.g., combinations of two CNTs by nucleobase molecular bridge [16,17]. The hybridizations of carbon atoms of tubular sidewalls are in sp^2 form, in which they could be converted to sp hybridizations with more reactivity especially at the tubular tips [16–18]. Hence, the valance shells of atoms of tubular tips are usually saturated by hydrogen atoms to avoid dangling effects in the computational research works [19]. Earlier studies on chemical and physical properties of CNTs demonstrated that the electronic properties of CNTs are mainly dependent on their geometries; therefore, investigating properties for functionalized CNTs with different geometries could be an interesting task of research for the tubular systems [20,21]. Avoiding the complicated experiments, computational studies could very well generate the optimized structures and their corresponding electronic properties for the exact models of NTs at the molecular and atomic scales [22–24].

Within this work, quantum chemical computations have been performed to explore stabilities and properties for the uracil (U)-functionalized $(n, 0)$ CNTs with different curvatures ($n = 3-16$) (Figs. 1 and 2). Possibilities of formations of U-modified CNTs have been approved

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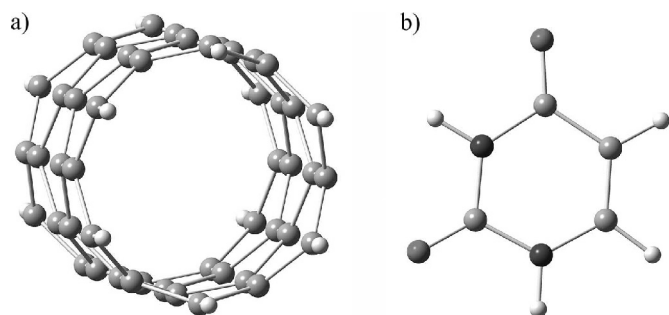


Fig. 1. (a) The (6,0) CNT representing $(n, 0)$ CNTs; $n = 3$ –16, and (b) the singular U counterpart.

by earlier works to show the capability of employing U nucleobase, RNA characteristic nucleobase, for structural modifications of CNTs [16,25–28]. Chemical modifications of tubular tips by the U nucleobases have been done to make stable single-standing hybrid structures in this work. Molecular and atomic scales properties (Tabs. 1–4) have been evaluated based on quantum chemical computations for all singular and hybrid models of this work to examine the effects of tubular geometries on the characteristic properties of U-functionalized $(n, 0)$ CNTs.

2 Computational details

2.1 Models

Stabilities and properties for 14 models of ten-angstrom length of $(n, 0)$ CNTs ($n = 3$ –16) (Fig. 1) were investigated in the forms of original and U-functionalized systems (Fig. 2). The original CNTs were all hydrogen-terminated to avoid dangling effects at the tubular tips [19]. Therefore, one hydrogen atom of the tip was removed to make *sp* hybridization ready for contributing to covalent bond with U nucleobase. Moreover, the hydrogen atom of nitrogen number one of U was also removed to provide possibility of formation of N_1 – C_1 covalent bond with the CNT. Models of this study include one singular U, 14 original CNTs, and 14 CNT-U hybrids. It is worth noting that the chemical U-modifications of CNTs were done to have single-standing structures of CNT-U hybrids for investigations in this work.

2.2 Computations

First, the structures were fully optimized to obtain the minimum-energy structures and molecular properties including dipole moments (D_m), energy gaps (E_g), connection distances ($d_{[C1-UN1]}$), and binding energies (E_b) (Tab. 1). Energy differences between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) were used to obtain E_g . Energy differences between the singular and hybrid compounds were used to obtain E_b . Second, the atomic-scale quadrupole coupling constants (C_Q) were evaluated for deep investigations of properties of the optimized models. Electric field gradient (EFG) tensors were calculated at the atomic sites and they were converted to C_Q ; $C_Q(\text{MHz}) = e^2 Q q_{zz} h^{-1}$

[29]. e , Q , q_{zz} , and h stand for electronic charge, nuclear electric quadrupole moment, main EFG eigenvalue, and Planck's constant, respectively [29]. Nuclear quadrupole resonance (NQR) spectroscopy is among the most versatile techniques to characterize materials in solid phases [30,31]. Earlier works indicated the efficiencies of EFG tensors, represented by C_Q , to detect any perturbations to the electronic sites of atoms in chemical structures [32–34]. Indeed, it is a benefit of computational chemistry to reproduce C_Q properties for nanostructures avoiding the complexity of electronic systems in experiments [32–34]. All computations of this work were done based on density functional theory (DFT) employing the B3LYP exchange-correlation functional and the 6-31G* and 6-311G* standard basis sets as implemented in the Gaussian 09 program [35]. It is noted that only 6-31G* basis set has been used for the optimization processes but both of 6-31G* and 6-311G* basis sets have been used for single point calculations to evaluate the properties. Since the tendencies of obtained values from both basis sets were the same to each other, the discussion have been carried out on the achievements of 6-31G* basis set and the results of 6-311G* basis set have been included in Supplementary Tables S5–S8 of supporting information file for attracting attentions of potential readers. The basis set superposition error (BSSE) and the effects of dispersion forces corrections are very much important mainly for the non-covalent interacting systems [36–39]. However, we examined these corrections for the covalently bonded hybrids of this work for further confidence, in which the magnitudes of differences were almost meaningless.

3 Results and discussion

3.1 Optimized properties

The evaluated molecular properties including D_m (dipole moments), E_g (energy gaps), $d_{[C1-UN1]}$ (connection distances), and E_b (binding energies) for U, CNT, and CNT-U models (Figs. 1 and 2) have been summarized in Table 1. The zero-magnitudes of D_m parameters show non-polarity property for the original CNTs independent of tubular diameters of $n = 3$ –16 geometries. It could be expected that the non-polarity, a disadvantage of CNTs to be dispersed in water media, could be overcome for the molecular functionalized models to show better dispersion behaviors [40]. Conditions of polarities are changed for CNT-U models due to existence of U heads in each of the hybrid structures which change electronic orientations of the structures. The CNT-U hybrids show similar properties with the order of 5–6 for magnitudes of D_m in tubular diameters $n = 5$ –16, and with the order of 2–3 in $n = 3$ and 4 models. The current achievements reveal that the polarities of CNTs are dependent on the chemical structures but independent of tubular sizes as could be seen by the magnitudes of D_m in the original CNTs and CNT-U hybrids. The ultra small NTs show different properties regarding the larger NTs, in which the current results show their differences arising from $n = 5$. Moreover, the small size of NT does not allow the electronic

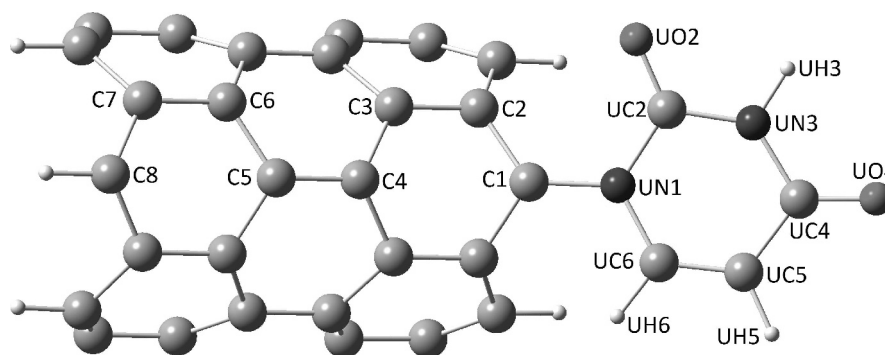


Fig. 2. Two-dimensional schematic representation of CNT-U hybrids.

Table 1. Optimized structural properties for U, CNT, and CNT-U models.

| Model | Stoichiometry | d_{C1-UN1} (Å) | BSSE (eV) | D_m (Debye) | E_b (eV) | E_g (eV) |
|-----------|-----------------------|------------------|-----------|---------------|------------|------------|
| U | $C_4H_4N_2O_2$ | — | — | 4.30 | — | 5.68 |
| (3, 0) | $C_{24}H_6$ | — | — | 0.01 | — | 2.05 |
| (3, 0)-U | $C_{28}H_8N_2O_2$ | 1.38 | 0.24 | 2.07 | 0.46 | 2.01 |
| (4, 0) | $C_{32}H_8$ | — | — | 0 | — | 2.11 |
| (4, 0)-U | $C_{36}H_{10}N_2O_2$ | 1.40 | 0.23 | 2.89 | 0.61 | 1.90 |
| (5, 0) | $C_{40}H_{10}$ | — | — | 1.07 | — | 0.78 |
| (5, 0)-U | $C_{44}H_{12}N_2O_2$ | 1.39 | 0.25 | 5.36 | 0.43 | 1.17 |
| (6, 0) | $C_{48}H_{12}$ | — | — | 0 | — | 0.44 |
| (6, 0)-U | $C_{52}H_{14}N_2O_2$ | 1.41 | 0.27 | 5.44 | 0.95 | 0.43 |
| (7, 0) | $C_{56}H_{14}$ | — | — | 0 | — | 0.50 |
| (7, 0)-U | $C_{60}H_{16}N_2O_2$ | 1.45 | 0.25 | 5.06 | 0.57 | 0.51 |
| (8, 0) | $C_{64}H_{16}$ | — | — | 0 | — | 0.42 |
| (8, 0)-U | $C_{68}H_{18}N_2O_2$ | 1.41 | 0.24 | 5.06 | 1.21 | 0.41 |
| (9, 0) | $C_{72}H_{18}$ | — | — | 0 | — | 0.40 |
| (9, 0)-U | $C_{76}H_{20}N_2O_2$ | 1.42 | 0.25 | 5.04 | 1.25 | 0.36 |
| (10, 0) | $C_{80}H_{20}$ | — | — | 0 | — | 0.41 |
| (10, 0)-U | $C_{84}H_{22}N_2O_2$ | 1.42 | 0.24 | 5.06 | 1.35 | 0.40 |
| (11, 0) | $C_{88}H_{22}$ | — | — | 0 | — | 0.38 |
| (11, 0)-U | $C_{92}H_{24}N_2O_2$ | 1.42 | 0.23 | 5.03 | 1.39 | 0.34 |
| (12, 0) | $C_{96}H_{24}$ | — | — | 0 | — | 0.41 |
| (12, 0)-U | $C_{100}H_{26}N_2O_2$ | 1.42 | 0.27 | 5.45 | 0.82 | 0.36 |
| (13, 0) | $C_{104}H_{26}$ | — | — | 0 | — | 0.35 |
| (13, 0)-U | $C_{108}H_{28}N_2O_2$ | 1.42 | 0.26 | 5.72 | 0.80 | 0.30 |
| (14, 0) | $C_{112}H_{28}$ | — | — | 0 | — | 0.28 |
| (14, 0)-U | $C_{116}H_{30}N_2O_2$ | 1.42 | 0.26 | 5.47 | 0.86 | 0.33 |
| (15, 0) | $C_{120}H_{30}$ | — | — | 0 | — | 0.31 |
| (15, 0)-U | $C_{124}H_{32}N_2O_2$ | 1.43 | 0.25 | 5.64 | 0.87 | 0.24 |
| (16, 0) | $C_{128}H_{32}$ | — | — | 0 | — | 0.22 |
| (16, 0)-U | $C_{132}H_{34}N_2O_2$ | 1.42 | 0.26 | 5.76 | 0.81 | 0.26 |

Models of CNTs are designated by $(n, 0)$, see Figures 1 and 2. The values are obtained by the 6-31G* basis set.

system to be very well polarized; therefore, smaller values of D_m have been observed for $n = 2$ and 3 in comparison with $n > 5$ NTs. Examining the magnitudes of E_g , which are energy differences of HOMO and LUMO levels, shows that the HOMO–LUMO gaps of CNTs are independent of tubular diameters in $n = 5$ –16 and $n = 3$ and 4 models. Moreover, effects of U-functionalizations on the E_g properties are not significant for the CNT-U hybrids. Based on current achievements by the obtained magnitudes of D_m and E_g for the investigated systems, it could be mentioned that the initial molecular electronic

properties of CNTs are independent of tubular diameters in both original and hybrid models. In contrast, the atomic electronic properties of connection distances ($d_{[C1-UN1]}$) indicate effects of tubular diameters on the C–N bond distances of CNT-U hybrids. Accordingly, the magnitudes of E_b , which are released energies of functionalization processes, indicate favorable chemisorptions of $n = 8$ –11 CNT-U models. Remembering the observations about D_m values, it could be mentioned here that the size of NTs is very much important in U-functionalization process, in which in lower effects could be seen for the

Table 2. Quadrupole coupling constants for CNTs (C_Q/MHz).

| Model | C_1 | C_2 | C_3 | C_4 | C_5 | C_6 | C_7 | C_8 |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|
| (3, 0) | 3.92 | 1.79 | 2.99 | 1.88 | 1.88 | 2.99 | 1.79 | 3.92 |
| (4, 0) | 2.71 | 1.13 | 1.09 | 1.22 | 1.22 | 1.09 | 1.13 | 2.71 |
| (5, 0) | 2.90 | 1.31 | 0.98 | 1.45 | 1.45 | 0.98 | 1.31 | 2.90 |
| (6, 0) | 1.36 | 1.76 | 1.41 | 1.53 | 1.53 | 1.41 | 1.76 | 1.36 |
| (7, 0) | 1.38 | 1.86 | 1.51 | 1.64 | 1.64 | 1.51 | 1.86 | 1.38 |
| (8, 0) | 1.51 | 1.93 | 1.59 | 1.71 | 1.71 | 1.59 | 1.93 | 1.51 |
| (9, 0) | 1.59 | 1.98 | 1.66 | 1.77 | 1.77 | 1.66 | 1.98 | 1.59 |
| (10, 0) | 1.59 | 2.02 | 1.69 | 1.80 | 1.80 | 1.69 | 2.02 | 1.59 |
| (11, 0) | 1.64 | 2.04 | 1.73 | 1.84 | 1.84 | 1.73 | 2.04 | 1.64 |
| (12, 0) | 1.64 | 2.07 | 1.75 | 1.86 | 1.86 | 1.75 | 2.07 | 1.64 |
| (13, 0) | 1.67 | 2.08 | 1.78 | 1.88 | 1.88 | 1.78 | 2.08 | 1.67 |
| (14, 0) | 1.66 | 2.02 | 1.81 | 1.89 | 1.89 | 1.78 | 2.10 | 1.66 |
| (15, 0) | 1.69 | 2.11 | 1.80 | 1.91 | 1.91 | 1.80 | 2.11 | 1.69 |
| (16, 0) | 1.60 | 2.12 | 1.81 | 1.84 | 1.84 | 1.81 | 2.12 | 1.60 |

See Figure 2 for details. Models of CNTs are designated by $(n, 0)$. The values are obtained by the 6-31G* basis set.

Table 3. Quadrupole coupling constants for CNT-Us (C_Q/MHz).

| Model | C_1 | C_2 | C_3 | C_4 | C_5 | C_6 | C_7 | C_8 |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|
| (3, 0)-U | 3.48 | 1.97 | 2.46 | 1.88 | 1.89 | 3.02 | 1.75 | 3.91 |
| (4, 0)-U | 2.18 | 1.26 | 1.07 | 1.18 | 1.26 | 1.05 | 1.14 | 2.71 |
| (5, 0)-U | 2.41 | 1.34 | 1.32 | 1.33 | 1.57 | 1.72 | 1.24 | 1.66 |
| (6, 0)-U | 1.73 | 1.22 | 1.53 | 1.23 | 1.64 | 1.26 | 1.76 | 1.60 |
| (7, 0)-U | 2.84 | 1.95 | 2.24 | 1.60 | 1.72 | 1.60 | 1.73 | 2.94 |
| (8, 0)-U | 1.67 | 1.35 | 1.65 | 1.50 | 1.76 | 1.48 | 1.94 | 1.60 |
| (9, 0)-U | 1.73 | 1.42 | 1.74 | 1.58 | 1.81 | 1.59 | 1.96 | 1.86 |
| (10, 0)-U | 1.66 | 1.41 | 1.73 | 1.61 | 1.85 | 1.59 | 2.02 | 1.66 |
| (11, 0)-U | 1.67 | 1.46 | 1.77 | 1.66 | 1.87 | 1.66 | 2.03 | 1.79 |
| (12, 0)-U | 2.05 | 1.98 | 1.80 | 1.88 | 1.85 | 1.62 | 2.03 | 2.07 |
| (13, 0)-U | 2.08 | 2.02 | 1.81 | 1.90 | 1.87 | 1.73 | 2.09 | 1.71 |
| (14, 0)-U | 2.07 | 2.02 | 1.85 | 1.91 | 1.89 | 1.65 | 2.06 | 2.12 |
| (15, 0)-U | 2.02 | 2.03 | 1.85 | 1.90 | 1.91 | 1.68 | 2.07 | 2.08 |
| (16, 0)-U | 2.25 | 2.08 | 2.08 | 1.90 | 1.86 | 1.96 | 2.12 | 1.57 |

See Figure 2 for details. Models of CNTs are designated by $(n, 0)$. The values are obtained by the 6-31G* basis set.

Table 4. Quadrupole coupling constants for uracil counterparts (C_Q/MHz).

| Model | UN ₁ | UC ₂ | UO ₂ | UN ₃ | UH ₃ | UC ₄ | UO ₄ | UC ₅ | UH ₅ | UC ₆ | UH ₆ |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| U | 3.91 | 1.77 | 8.37 | 3.67 | 0.25 | 2.42 | 9.51 | 0.73 | 0.21 | 2.38 | 0.20 |
| (3, 0)-U | 3.01 | 1.69 | 8.61 | 3.61 | 0.25 | 2.43 | 9.75 | 1.18 | 0.20 | 2.81 | 0.19 |
| (4, 0)-U | 3.24 | 1.64 | 8.61 | 3.60 | 0.25 | 2.42 | 9.63 | 1.10 | 0.20 | 2.71 | 0.19 |
| (5, 0)-U | 3 | 1.66 | 8.61 | 3.61 | 0.25 | 2.42 | 9.64 | 1.11 | 0.20 | 2.68 | 0.19 |
| (6, 0)-U | 3.07 | 1.57 | 8.55 | 3.56 | 0.25 | 2.38 | 9.45 | 0.98 | 0.20 | 2.52 | 0.20 |
| (7, 0)-U | 3.74 | 1.79 | 8.41 | 3.59 | 0.25 | 2.49 | 9.34 | 0.69 | 0.21 | 2.56 | 0.20 |
| (8, 0)-U | 3.25 | 1.58 | 8.61 | 3.62 | 0.25 | 2.40 | 9.49 | 0.97 | 0.20 | 2.59 | 0.20 |
| (9, 0)-U | 3.24 | 1.58 | 8.59 | 3.61 | 0.25 | 2.40 | 9.46 | 0.94 | 0.20 | 2.59 | 0.20 |
| (10, 0)-U | 3.33 | 1.59 | 8.62 | 3.62 | 0.25 | 2.40 | 9.46 | 0.96 | 0.20 | 2.60 | 0.20 |
| (11, 0)-U | 3.34 | 1.59 | 8.61 | 3.62 | 0.25 | 2.40 | 9.48 | 0.94 | 0.20 | 2.61 | 0.20 |
| (12, 0)-U | 4.01 | 1.72 | 8.42 | 3.63 | 0.25 | 2.46 | 9.38 | 0.70 | 0.21 | 2.51 | 0.20 |
| (13, 0)-U | 3.99 | 1.72 | 8.43 | 3.64 | 0.25 | 2.46 | 9.37 | 0.69 | 0.21 | 2.51 | 0.20 |
| (14, 0)-U | 4 | 1.72 | 8.44 | 3.634 | 0.25 | 2.46 | 9.38 | 0.69 | 0.21 | 2.50 | 0.20 |
| (15, 0)-U | 4.02 | 1.72 | 8.44 | 3.63 | 0.25 | 2.46 | 9.38 | 0.70 | 0.21 | 2.50 | 0.20 |
| (16, 0)-U | 3.95 | 1.73 | 8.46 | 3.64 | 0.25 | 2.47 | 9.35 | 0.66 | 0.21 | 2.50 | 0.20 |

See Figure 2 for details. Models of CNTs are designated by $(n, 0)$. The values are obtained by the 6-31G* basis set.

electronic and structural properties of specific sizes NTs. Based on geometries, the magnitudes of E_b are dependent on connection distances and structural characters, in which both of them could put significant influences on formations of CNT-U hybrids. In this case, the investigated NTs could be divided into three sets by the obtained magnitudes of E_b , $n = 3-7$, $n = 8-11$ and $n = 12-16$. However, further investigations of formations of CNT-U hybrids of this work would be done by analyzing the atomic-scale C_Q properties in the following text. Thus, only some trends could be mentioned here as quick concluding remarks of the optimized molecular properties. First, the magnitudes of D_m and E_g are independent of tubular sizes. Second, the magnitudes of E_b are dependent on tubular sizes. Third, favorable chemisorptions of $n = 8-11$ CNT-U hybrids could be expected. Finally, different behaviors of properties of too-small sizes (3, 0) and (4, 0) models in comparison with $n = 5-16$ models indicate that the electronic environments of small sizes are not flexible enough to be re-oriented in different structural conditions for both of CNT and CNT-U hybrid systems.

3.2 Quadrupole coupling constants

The atomic-scale C_Q (quadrupole coupling constants) parameters have been evaluated for all atoms of the optimized singular and hybrid structures (Tabs. 2-4, Figs. 1 and 2) to further investigate the nature of CNT-U hybrids. Examining the magnitudes of C_Q from Table 2 indicates that the atoms of tubular sidewalls could be divided into equivalent atomic layers based on similarities of atomic properties as indicated by C_1 to C_8 symbols. This trend is in agreement with earlier achievements on layer-like similarities of atomic properties of nanotubes sidewalls [41]. In this case, similar properties could be observed for the atoms of layer pairs of C_1-C_8 , C_2-C_7 , C_3-C_6 , and C_4-C_5 ones. However, the layer-like similarities of atoms are perturbed in the CNT-U hybrids because of U-functionalization processes. Comparing the magnitudes of C_Q for the C_1 atoms the tubular connection site, of original CNTs and CNT-U hybrids indicates the significant effects of U-functionalization on the properties of this atom. However, magnitudes of changes are less significant for wider nanotubes, $n = 8-11$. This trend reveals that the atomic-scale properties are kept almost unchanged from the singular CNT to the CNT-U hybrids for wider nanotubes, $n = 8-11$. Remembering here the achievement of most favorability of U-functionalizations for $n = 8-11$ ($n, 0$) CNTs regarding the magnitudes of E_b . Further analysis indicates that the properties for inner atomic layers do not detect significant changes of atoms at the tip or closer regions. The C_Q properties are very much sensitive to the electronic environments of matters; therefore, different properties have been obtained for the atoms of different tubular diameters. The similarities of atomic properties between layer-like pairs of tubular sidewalls of original CNTs are now perturbed in the CNT-U hybrids. Important to note that similarities of properties for atoms of one layer are still remained; however, there is not much similarity between the pair layers, which was

seen for the original CNTs. Comparing obtained properties at the atomic and molecular scales indicates that the changes at lower atomic scale are much more obvious than the changes at higher molecular scale, revealing the importance of obtaining detailed information for the chemical structures by the helps of computational chemistry.

The atomic-scale C_Q properties for U counterparts in both original and hybrid models (Figs. 1 and 2) are listed in Table 4. Possibilities of combinations of U, the characteristic RNA nucleobase, with nanostructures have been studied by earlier works [26-28]. The UN_1 , the atom of connection site, makes direct C_1-N_1 bond with the CNT to make the CNT-U hybrids. Remembering here the achievements by connection distances and binding energies (Tab. 1) reveals that the C_1-N_1 bond could be further analyzed here based on atomic-scale C_Q properties. The electron-sharing nature of covalent bond is very well known and the magnitudes of electronic changes at the contributing atoms could be directly related to the strength of constructed chemical bond. Approving this trend could be done by careful examinations of C_Q properties for the C_1 and N_1 atoms of CNT-U hybrids and singular counterparts. Moreover, the magnitudes of C_Q properties for the UN_1 atoms of $n = 8-11$ ($n, 0$) CNT-U hybrids are almost similar approving the favorability of chemisorptions of $n = 8-11$ models based on molecular properties and the C_Q properties of CNTs. In contrast with UN_1 , the effects of hybridizations are not so much significant for the properties of other nitrogen atom, UN_3 . Existences of nitrogen and oxygen atoms are always important because of their lone pairs of electrons, which could be contributed to other atomic environments in the chemical structures. There are two oxygen atoms in the U counterpart, which are initially located in two different chemical environments; UO_2 is a urea type and UO_4 is an amide type oxygen [42]. The initial properties for UO_2 and UO_4 atoms in the singular U are different, in which the same difference could be also observed for the properties of UN_1 and UN_2 atoms. The oxygen atoms are located outside the pyrimidine ring, but the slight effects of U-functionalizations could be still very well detected by the C_Q properties. The changes of properties could be also seen for the carbon atoms of U counterparts in the CNT-U hybrids in comparison with the singular U. The properties for UC_5 atom, which is the typical atom of U to be functionalized for pharmaceutical applications [43], detect significant effects of functionalizations in the too-small $n = 3-5$ sizes nanotubes whereas the effects are less significant for larger models. The low electronic densities at the sites of hydrogen atoms could be represented by the small magnitudes of C_Q and their very slight changes in different models could be also detected. In addition to detections of stabilities for hybrid materials, detections of the atomic-scale properties are also very much important to define their specific applications.

The achievements of C_Q results could reveal that the atoms of chemical structures have different roles regarding their electronic characteristics. The atomic-scale properties could approve the obtained molecular properties as indicated by favorability of chemisorptions for $n = 8-11$ CNT-U hybrids by both scales of parameters. Moreover,

distinct effects of structural changes could be also very well analyzed by the atomic-scale properties in addition to general achievements of molecular properties. Finally, the changes of atomic properties because of functionalization processes could be divided into direct and indirect effects, in which the direct effects are observed for the atoms of connections sites and surrounding atoms whereas the indirect effects are observed for the atoms farther from the connection regions.

4 Conclusions

DFT calculations have been performed to explore stabilities and properties of the U-functionalized CNTs through optimized molecular and atomic-scale C_Q properties. The concluding remarks of this work could be mentioned among some trends. First, the D_m and E_g molecular properties of the original and U-functionalized CNTs are independent of tubular diameter. Second, the most favorable chemisorptions of U-functionalized CNTs are seen for the $n = 8$ –11 models of $(n, 0)$ CNT-U hybrids according to their binding energies. The most unfavorable chemisorptions are seen for the too-small sizes $n = 3$ –5 $(n, 0)$ -U hybrids. Third, the C_Q properties indicate similarities of properties for atoms of tubular sidewalls dividing into atomic layers for the original CNTs. The atoms at opposite tubular sides are similar to each other according to the magnitudes of their C_Q parameters. Fourth, the properties of connecting atoms in the CNT-U hybrids could approve the validities of energetically observed favorability of chemisorptions for $n = 8$ –11 of $(n, 0)$ CNT-U hybrids. Fifth, the magnitudes of C_Q parameters for UC_5 atoms show that the properties of this atom could detect significant changes in the too-small sizes $n = 3$ –5 $(n, 0)$ CNT-U hybrids in comparison with larger models. And finally, the obtained results indicated that the properties of U-functionalized CNTs could be very well analyzed by the combinations of molecular and atomic scales properties in the singular and hybrid systems.

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Author contribution statement

M.M., K.H., E.J. and O.G. initiated the subject of this work and they prepared the first draft of manuscript. A.S.R. helped for discussing the materials of manuscript especially preparing and analyzing Table 1 and the corresponding Table S5. Further preparing and analyzing the manuscript was done by contributions of all authors to produce the final draft of manuscript.

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Functionalization of (n,0) CNTs (n=3–16) by uracil: DFT studies

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Supporting Information

Tables S5–S8

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Table S5: Optimized structural properties for U, CNT, and CNT-U models*

| Model | BSSE (eV) | D_m (Debye) | E_b (eV) | E_g (eV) |
|-----------|-----------|---------------|------------|------------|
| U | — | 4.37 | — | 5.65 |
| (3, 0) | — | 0.01 | — | 2.05 |
| (3, 0)–U | 0.17 | 2.04 | 0.57 | 2.01 |
| (4, 0) | — | 0 | — | 2.12 |
| (4, 0)–U | 0.17 | 2.76 | 0.92 | 1.90 |
| (5, 0) | — | 1.09 | — | 0.77 |
| (5, 0)–U | 0.18 | 5.21 | 0.54 | 1.18 |
| (6, 0) | — | 0 | — | 0.45 |
| (6, 0)–U | 0.17 | 5.03 | 1.09 | 0.44 |
| (7, 0) | — | 0 | — | 0.46 |
| (7, 0)–U | 0.17 | 4.77 | 0.60 | 0.51 |
| (8, 0) | — | 0 | — | 0.43 |
| (8, 0)–U | 0.16 | 4.72 | 1.34 | 0.42 |
| (9, 0) | — | 0 | — | 0.42 |
| (9, 0)–U | 0.16 | 4.67 | 1.38 | 0.38 |
| (10, 0) | — | 0 | — | 0.42 |
| (10, 0)–U | 0.16 | 4.75 | 1.48 | 0.41 |
| (11, 0) | — | 0 | — | 0.39 |
| (11, 0)–U | 0.16 | 4.71 | 1.51 | 0.35 |
| (12, 0) | — | 0 | — | 0.42 |
| (12, 0)–U | 0.17 | 5.43 | 0.90 | 0.36 |
| (13, 0) | — | 0 | — | 0.35 |
| (13, 0)–U | 0.17 | 5.72 | 0.89 | 0.31 |
| (14, 0) | — | 0 | — | 0.31 |
| (14, 0)–U | 0.16 | 5.46 | 0.87 | 0.30 |
| (15, 0) | — | 0 | — | 0.31 |
| (15, 0)–U | 0.17 | 5.65 | 0.87 | 0.24 |
| (16, 0) | — | 0 | — | 0.22 |
| (16, 0)–U | 0.17 | 5.75 | 0.82 | 0.26 |

* Models of CNTs are designated by (n, 0), see Figs. 1 and 2. The values are obtained by the 6-311G* basis set.

Table S6: Quadrupole coupling constants for CNTs (C_Q /MHz)^{*}

| Model | C ₁ | C ₂ | C ₃ | C ₄ | C ₅ | C ₆ | C ₇ | C ₈ |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| (3, 0) | 4.37 | 2.02 | 3.27 | 2.13 | 2.13 | 3.27 | 2.02 | 4.37 |
| (4, 0) | 3.06 | 1.25 | 1.22 | 1.38 | 1.38 | 1.22 | 1.25 | 3.06 |
| (5, 0) | 2.48 | 1.47 | 1.12 | 1.51 | 1.51 | 1.12 | 1.47 | 2.48 |
| (6, 0) | 1.52 | 1.98 | 1.59 | 1.72 | 1.72 | 1.59 | 1.98 | 1.52 |
| (7, 0) | 1.53 | 2.09 | 1.70 | 1.84 | 1.84 | 1.70 | 2.09 | 1.53 |
| (8, 0) | 1.68 | 2.16 | 1.79 | 1.91 | 1.91 | 1.79 | 2.16 | 1.68 |
| (9, 0) | 1.75 | 2.22 | 1.86 | 1.98 | 1.98 | 1.86 | 2.22 | 1.75 |
| (10, 0) | 1.75 | 2.25 | 1.89 | 2.01 | 2.01 | 1.89 | 2.25 | 1.75 |
| (11, 0) | 1.80 | 2.28 | 1.93 | 2.04 | 2.04 | 1.93 | 2.28 | 1.80 |
| (12, 0) | 1.80 | 2.30 | 1.94 | 2.06 | 2.06 | 1.94 | 2.30 | 1.80 |
| (13, 0) | 1.83 | 2.32 | 1.96 | 2.08 | 2.08 | 1.96 | 2.32 | 1.83 |
| (14, 0) | 1.83 | 2.32 | 2.09 | 2.05 | 2.05 | 2.09 | 2.32 | 1.83 |
| (15, 0) | 1.84 | 2.34 | 1.99 | 2.10 | 2.10 | 1.99 | 2.34 | 1.84 |
| (16, 0) | 1.83 | 2.31 | 1.94 | 2.13 | 2.13 | 1.94 | 2.31 | 1.83 |

^{*} See Fig. 2 for details. Models of CNTs are designated by (n, 0). The values are obtained by the 6-311G* basis set.

Table S7: Quadrupole coupling constants for CNT-Us (C_Q /MHz)^{*}

| Model | C ₁ | C ₂ | C ₃ | C ₄ | C ₅ | C ₆ | C ₇ | C ₈ |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| (3, 0)–U | 3.84 | 2.18 | 2.67 | 2.12 | 2.13 | 3.30 | 1.98 | 4.36 |
| (4, 0)–U | 2.42 | 1.37 | 1.18 | 1.32 | 1.43 | 1.18 | 1.26 | 3.02 |
| (5, 0)–U | 2.48 | 1.47 | 1.12 | 1.51 | 1.51 | 1.12 | 1.47 | 2.47 |
| (6, 0)–U | 1.89 | 1.39 | 1.72 | 1.39 | 1.83 | 1.44 | 1.98 | 1.73 |
| (7, 0)–U | 3.21 | 2.19 | 2.52 | 1.78 | 1.94 | 0.89 | 1.95 | 3.28 |
| (8, 0)–U | 1.84 | 1.53 | 1.86 | 1.69 | 1.98 | 1.68 | 2.17 | 1.75 |
| (9, 0)–U | 1.91 | 1.61 | 1.94 | 1.78 | 2.03 | 1.78 | 2.20 | 2.04 |
| (10, 0)–U | 1.83 | 1.60 | 1.93 | 1.81 | 2.06 | 1.78 | 2.26 | 1.82 |
| (11, 0)–U | 1.85 | 1.65 | 1.97 | 1.85 | 2.08 | 1.84 | 2.27 | 1.96 |
| (12, 0)–U | 2.35 | 2.20 | 2.01 | 2.08 | 2.06 | 1.80 | 2.26 | 2.29 |
| (13, 0)–U | 2.38 | 2.23 | 2.00 | 2.10 | 2.08 | 1.92 | 2.32 | 1.87 |
| (14, 0)–U | 2.38 | 2.24 | 2.07 | 2.10 | 2.10 | 1.82 | 2.29 | 2.35 |
| (15, 0)–U | 2.32 | 2.24 | 2.06 | 2.09 | 2.11 | 2.14 | 2.30 | 2.29 |
| (16, 0)–U | 2.42 | 2.31 | 2.31 | 2.10 | 2.10 | 2.15 | 2.33 | 1.92 |

^{*} See Fig. 2 for details. Models of CNTs are designated by (n, 0). The values are obtained by the 6-311G* basis set.

Table S8: Quadrupole coupling constants for uracil counterparts (C_Q /MHz)^{*}

| Model | UN ₁ | UC ₂ | UO ₂ | UN ₃ | UH ₃ | UC ₄ | UO ₄ | UC ₅ | UH ₅ | UC ₆ | UH ₆ |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| U | 4.29 | 2.03 | 8.77 | 4.03 | 0.25 | 2.75 | 10.06 | 0.84 | 0.21 | 2.71 | 0.20 |
| (3, 0)-U | 3.25 | 2.05 | 9.06 | 3.95 | 0.24 | 2.77 | 10.33 | 1.34 | 0.20 | 3.14 | 0.19 |
| (4, 0)-U | 3.52 | 1.99 | 9.09 | 3.94 | 0.24 | 2.76 | 10.21 | 1.26 | 0.20 | 3.05 | 0.19 |
| (5, 0)-U | 3.25 | 2.20 | 9.08 | 3.95 | 0.25 | 2.76 | 10.22 | 1.27 | 0.20 | 3.02 | 0.19 |
| (6, 0)-U | 3.37 | 1.92 | 9.03 | 3.94 | 0.25 | 2.72 | 10.04 | 1.14 | 0.21 | 2.86 | 0.20 |
| (7, 0)-U | 4.09 | 2.05 | 8.84 | 3.94 | 0.25 | 2.84 | 9.89 | 0.82 | 0.21 | 2.91 | 0.20 |
| (8, 0)-U | 3.56 | 1.94 | 9.09 | 3.96 | 0.25 | 2.74 | 10.07 | 1.12 | 0.21 | 2.93 | 0.20 |
| (9, 0)-U | 3.56 | 1.93 | 9.07 | 3.96 | 0.25 | 2.74 | 10.04 | 1.09 | 0.21 | 2.93 | 0.20 |
| (10, 0)-U | 3.65 | 1.94 | 9.10 | 3.97 | 0.25 | 2.74 | 10.07 | 1.10 | 0.21 | 2.94 | 0.20 |
| (11, 0)-U | 3.66 | 1.94 | 9.09 | 3.97 | 0.25 | 2.74 | 10.05 | 1.09 | 0.21 | 2.94 | 0.20 |
| (12, 0)-U | 4.38 | 1.98 | 8.86 | 3.99 | 0.25 | 2.80 | 9.93 | 0.82 | 0.21 | 2.85 | 0.20 |
| (13, 0)-U | 4.37 | 1.98 | 8.87 | 3.99 | 0.25 | 2.80 | 9.92 | 0.81 | 0.21 | 2.85 | 0.20 |
| (14, 0)-U | 4.37 | 1.98 | 8.87 | 3.99 | 0.25 | 2.80 | 9.92 | 0.81 | 0.21 | 2.84 | 0.20 |
| (15, 0)-U | 4.39 | 1.99 | 8.87 | 3.99 | 0.25 | 2.80 | 9.93 | 0.81 | 0.21 | 2.84 | 0.20 |
| (16, 0)-U | 4.31 | 1.99 | 8.89 | 3.99 | 0.25 | 2.80 | 9.91 | 0.79 | 0.21 | 2.85 | 0.20 |

^{*} See Fig. 2 for details. Models of CNTs are designated by (n,0). The values are obtained by the 6-311G* basis set.