

The geometrical and electronic structures of open-end fully functionalized single-walled carbon nanotubes

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Abstract

We have investigated the geometrical and electronic structures of open-end single-walled carbon nanotubes (SWNTs) having chemically modified tips, using semi-empirical AM1 and density functional theory methods. The hydroxyl (–OH), carboxyl (–COOH) and amide (–CONH₂) functional groups were used to saturate the open-ends of nanotubes. The effects of functional groups were studied by comparison with the pristine tubes, of which the tubular lengths vary from two to ten unit-cells (40 Å). The results show that the C–C bond lengths of all model tubes are only slightly different, and the behavior of converging bond lengths in COOH– and CONH₂–SWNTs is very similar to the pristine tube. Tip functionalization alters the frontier orbitals of the pristine tube, but these effects seem to rapidly decrease as the tubule becomes longer. In general, it can be concluded that the geometrical and electronic structures of pristine tubes after tube-end “full” functionalization will be preserved, hence supporting that more real-world “partially” functionalized SWNTs can be used in the same way as the pristine version in most application areas.

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1. Introduction

In recent years, the unique properties of single-walled carbon nanotubes (SWNT) have become widely known, e.g., chemical and thermal stability, extremely high tensile strength and elasticity, and high conductivity [1–3]. Because of its remarkable electronic and mechanical properties, SWNT is one of the best candidate materials to use in various industrial applications [4]. However, there are some intrinsic properties that limit its use in many applications. For instances, the pristine carbon nanotube is not

soluble in water or common solvents [5,6], which hinders chemical approaches, manipulation and preparation of nanocomposite materials. To overcome this problem, functionalization is one effective means for modifying properties of the pristine tubes so as to be appropriate for solution processing [7,8]. Unfortunately, functionalization of SWNTs may also lead to unwanted modification of the physical and chemical properties of SWNTs that are essential for intended applications. The ability to solubilize carbon nanotubes with intact physico-chemical properties would aid in their purification, followed by easier solution processing that will eventually lead to the most efficient uses of such materials. The first chemical synthesis of soluble SWNTs was reported in 1998 [9,10]. The open-ends of soluble SWNTs were terminated by carboxylic acid groups (–COOH). Such groups were

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converted into acylchloride groups by treatment with thionylchloride [9,10]. The long-chain amine, e.g., octadecylamine, was subsequently added to form amide functionalities [10]. The resulting SWNTs can be soluble in common organic solvents, such as chloroform, dichloromethane, aromatic solvents (e.g., benzene, toluene, chlorobenzene, 1,2-dichlorobenzene), CS_2 and water [9–14]. In spite of many successful experiments on the soluble SWNTs, effects of functional groups on the geometrical and electronic structure of pristine SWNTs are not yet clearly understood due to absence of a reliable theoretical model. Therefore, studying the geometrical and electronic structures of individual nanotubes before and after functionalization is necessary in order to ascertain whether these properties have been affected. So far, most papers report the effects of only one functional group, i.e., COOH, at the end [15] and at the sidewall of nanotubes [16]. In the real situation, it is possible that there are several functional groups concurrently attached to the nanotube end and sidewall. In this research, we have explored an extreme case, where all open bonds at the tips are saturated with functional groups, or so-called “fully functionalized” SWNT. Three functional groups: hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$) and amide ($-\text{CONH}_2$) are chosen in order to study their effects on the geometrical and electronic properties of nanotubes.

2. Model and methods

The OH -, COOH - and CONH_2 -terminated SWNTs (Fig. 1) were investigated by semi-empirical and first-principles calculations. The zigzag (9,0) tube was chosen because its edges are more reactive than those of the armchair tube [17], thereby supportive to our model where the tube edges are saturated by functional groups. Effects of the functional end groups were studied by comparing with

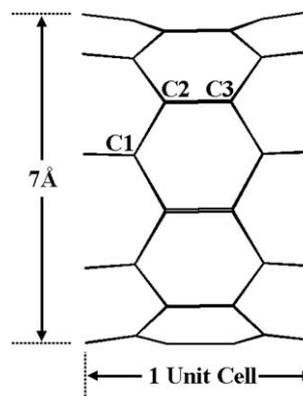


Fig. 2. Definition of C1–C2 and C2–C3 bonds of a 1 unit-cell (IUC) SWNT.

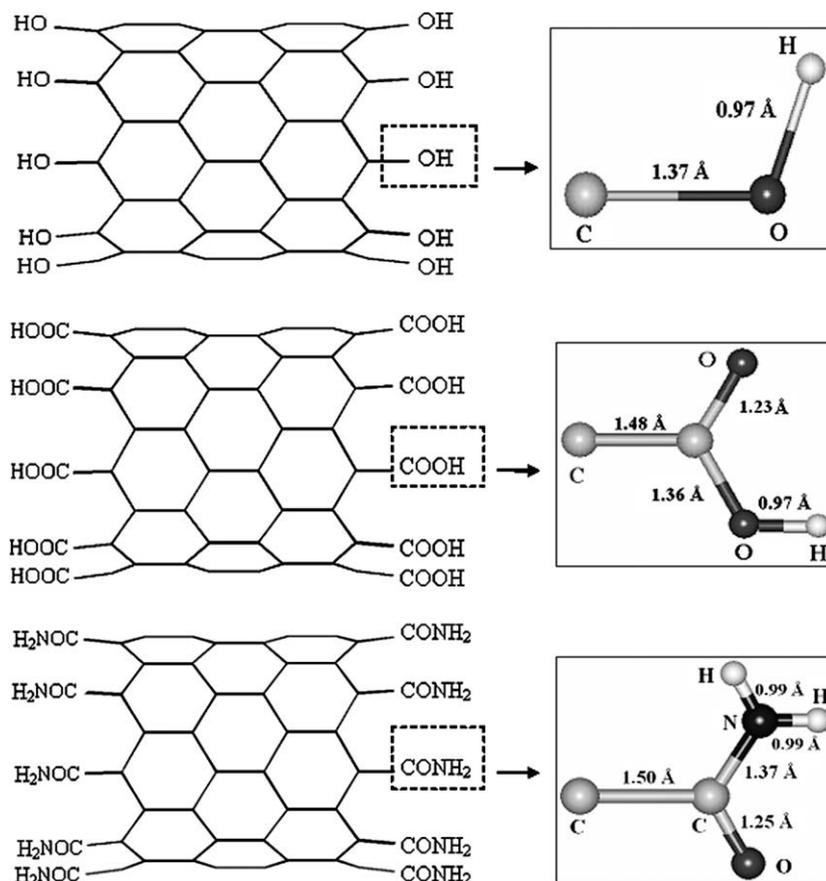


Fig. 1. Model geometries of the (a) OH - (b) COOH - and (c) CONH_2 -terminated (9,0) SWNTs. The insets show average bond lengths.

Table 1
Comparison of some geometrical and electronic properties of one unit-cell OH-SWNT calculated at different levels of theory (see definition of C1–C2, C2–C3 in Fig. 2)

	MM	AM1	HF/3-21G*	HF/6-31G*	B3LYP/3-21G*	B3LYP/6-31G*
C1–C2 (Å)	1.356	1.418	1.404	1.409	1.415	1.418
C2–C3 (Å)	1.346	1.449	1.464	1.474	1.460	1.465
HOMO (eV)	–	–6.305	–4.790	–4.471	–3.692	–3.394
LUMO (eV)	–	–1.589	0.355	0.867	–2.609	–2.417
δE (eV)	–	4.716	5.145	5.338	1.082	0.977

Table 2
Dependence of C₁–C₂ (in { }) and C₂–C₃ (in []) bond lengths on the tubular length of H, OH, COOH and CONH₂-terminated (9,0) SWNT as obtained from geometry optimization using AM1 Method (see definition of C1–C2, C2–C3 in Fig. 2)

Number of unit-cells	H-terminated		OH-terminated		COOH-terminated		CONH ₂ -terminated	
	Terminal	Middle	Terminal	Middle	Terminal	Middle	Terminal	Middle
2	{1.411}	{1.420}	{1.422}	{1.420}	{1.423}	{1.418}	{1.423}	{1.418}
	[1.440]	[1.431]	[1.434]	[1.429]	[1.440]	[1.429]	[1.439]	[1.429]
3	{1.411}	{1.424}	{1.423}	{1.424}	{1.423}	{1.426}	{1.423}	{1.425}
	[1.439]	[1.428]	[1.434]	[1.427]	[1.439]	[1.427]	[1.439]	[1.427]
4	{1.411}	{1.425}	{1.423}	{1.425}	{1.424}	{1.425}	{1.423}	{1.425}
	[1.439]	[1.426]	[1.433]	[1.426]	[1.439]	[1.426]	[1.439]	[1.426]
6	{1.411}	{1.425}	{1.423}	{1.426}	{1.423}	{1.426}	{1.424}	{1.426}
	[1.439]	[1.425]	[1.433]	[1.426]	[1.439]	[1.426]	[1.439]	[1.426]
8	{1.411}	{1.425}	{1.426}	{1.431}	{1.423}	{1.426}	{1.425}	{1.426}
	[1.439]	[1.425]	[1.427]	[1.415]	[1.439]	[1.425]	[1.439]	[1.425]
10	{1.412}	{1.425}	{1.425}	{1.431}	{1.423}	{1.426}	{1.425}	{1.426}
	[1.439]	[1.425]	[1.427]	[1.415]	[1.439]	[1.425]	[1.440]	[1.425]

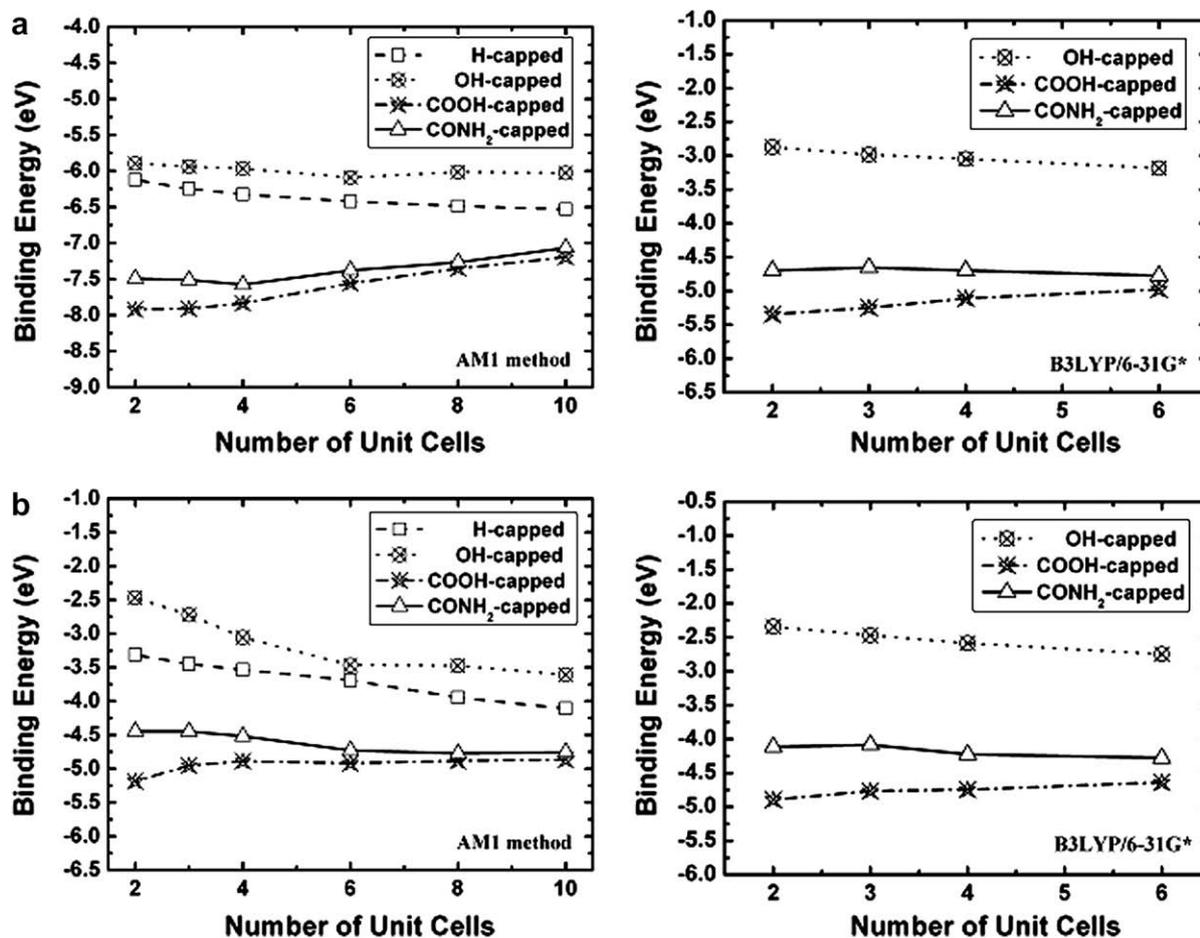


Fig. 3. (a) HOMO (b) LUMO energies based on AM1 (left) and B3LYP/6-31G* (right).

the pristine tube (whose edges are saturated by hydrogen atoms). The tubular lengths of all models vary from two to ten unit-cells (~ 8 – 40 Å, 72 – 360 carbon atoms). Definition of a one unit-cell is exhibited in Fig. 2. A semi-empirical method based on the Austin Model 1 (AM1) Hamiltonian [18] at the Restricted Hartree Fock level [19] within GAMESS04 package [20] was used to prepare fully optimized structures of all types and lengths. In AM1 method, it is an assumption that orbitals from two neighboring atoms are orthogonal and only valence electrons are considered. The AM1 valence (val) Hamiltonian based on the Born–Oppenheimer approximation can be written in the following form:

$$H_{\text{val}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} \quad (1)$$

where M is the number of nuclei. i and j denote each of the N electrons in the system.

The basis sets employed in the semi-empirical method are specially optimized minimal basis sets composed of the Slater-type orbitals (STO),

$$\Phi_{\text{STO}}(\zeta, n, l, m; r, \theta, \phi) = N r^{\zeta} e^{-\zeta r} Y_{lm}(\theta, \phi) \quad (2)$$

where N is a normalization constant. ζ is the Slater exponent. r , θ , and ϕ are spherical coordinates, and Y_{lm} represents the angular momentum.

The results from other methods, such as molecular mechanics calculation using MM3 [21] force field, *ab initio* Hartree–Fock and density functional theory (DFT) calculations [22] on one unit-cell of OH-terminated SWNT were compared in order to verify the quality of the AM1 method. The all-electron Gaussian-type basis sets, 3-21G* and 6-31G*, in which the valence shell is described by splitting functions, including the polarization functions for hydrogen atoms, were employed for quantum mechanical calculations. The C–C bond lengths of all tubes were measured and reported. The electronic structures, such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), energy gap, and orbital shape were investigated using the AM1 method. Becke3 and Lee–Young–Parr composite exchange–correlation function (B3LYP) and the 6-31G* basis set were employed to investigate the electronic structure of nanotubes with lengths up to six unit-cells. Extended Hückel molecular orbital (EHMO) method [23] was also performed for comparison.

3. Results and discussion

The geometrical and electronic properties of one unit-cell OH-terminated SWNT after energy optimization at different levels of theory are given in Table 1. For the purposes of discussing the geometry of nanotubes, C–C bond lengths including C1–C2 and C2–C3 (see Fig. 2) that lie on the circumference and parallel with the tube axis, respectively, were reported. From the average bond lengths in

Table 1, we have observed that the AM1 optimized structure is in agreement with B3LYP/3-21G* within a resolution of 0.01 Å. On the other hand, the optimized structure obtained by AM1 is also close to the result calculated by B3LYP/6-31G*, despite B3LYP/6-31G* level having usually been found to be much more reliable on the average bond lengths [24]. Therefore, in accordance with a previous study by Stobinski et al. [25], we can assume that the AM1 method is good enough for approximation of the carbon nanotube's geometry. From Table 1, the differences in C–C bond lengths obtained from all methods, except for MM3, are within the range of 0.01–0.04 Å. Hence, the molecular mechanics is not an appropriate method to predict the geometry of this system, corresponding to our previous results on the pristine SWNT [26]. For electronic properties, it was shown that the AM1 and HF methods are rather poor in describing LUMO, leading to overestimation of the HOMO–LUMO energy gap in comparison with the B3LYP values. Therefore, HOMO and LUMO from AM1 method will be used only for qualitative purposes, for example, comparing between the OH-, COOH- and CONH₂-terminated SWNTs with the pristine nanotubes, as also suggested by the previous study [26].

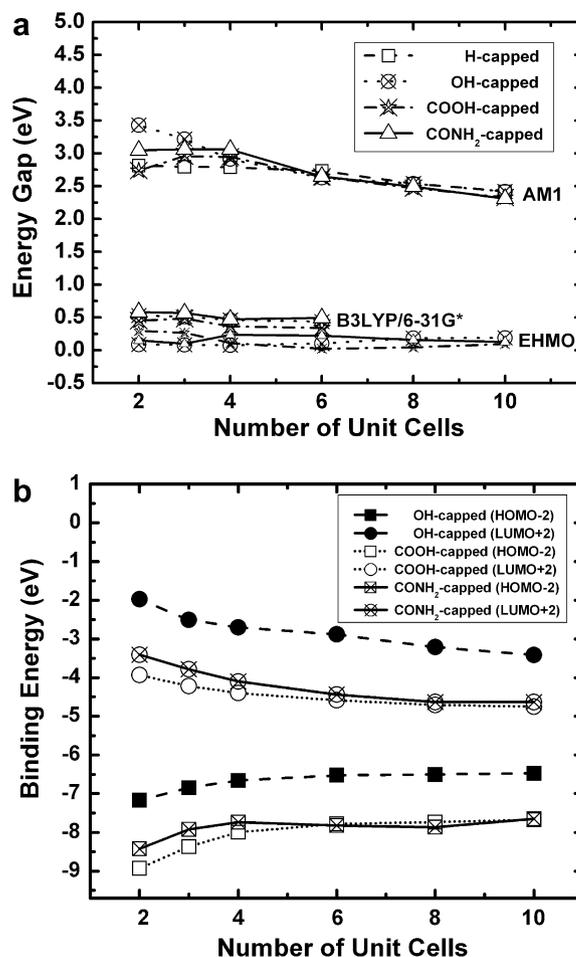


Fig. 4. (a) Energy gap based on AM1, B3LYP/6-31G* and EHMO of H-, OH-, COOH- and CONH₂-terminated SWNTs. (b) Comparison of the delocalized frontier orbitals of the functionalized structures.

Effects of the functional groups and tubule lengths on the geometrical properties are given in Table 2. Such groups cause differences in the C–C bonds located at the terminal ends and at the middle cylinder. For the pristine tubes at all lengths, the C1–C2 and C2–C3 bond lengths located at the terminal ends are around 1.411 and 1.440 Å, respectively. In other words, the local geometry at the terminal ends does not depend on the tubule length. In contrast, the C–C bond lengths located at the middle cylinder are affected by tubule lengthening from 1 up to 4 unit-cells. Beyond such tubular length, a converging value of 1.425 Å for the C–C bonds is finally established. The above-mentioned behavior and tendency are also applicable to the functionalized SWNTs. In particular for the

COOH- and CONH₂-SWNTs, the middle cylinder of such tubes has the same converging C–C bond length as the pristine tube (1.425–1.426 Å), albeit the carbon bonds at the immediate vicinity of the functional groups become slightly elongated (from 1.411 to 1.424 Å). It can be said that functionalization does not introduce noticeable structural deformation to SWNT. It is noteworthy that the average C–C bond length of a perfect SWNT with sp² hybridization is 1.42 Å, and full functionalization causes bond length distortion within a 0.02 Å limit.

Fig. 3a and b shows that functionalization alters HOMO and LUMO energies. In comparison with the H-terminated tube, the hydroxyl group destabilizes HOMO and LUMO, while the carboxylic and amide groups

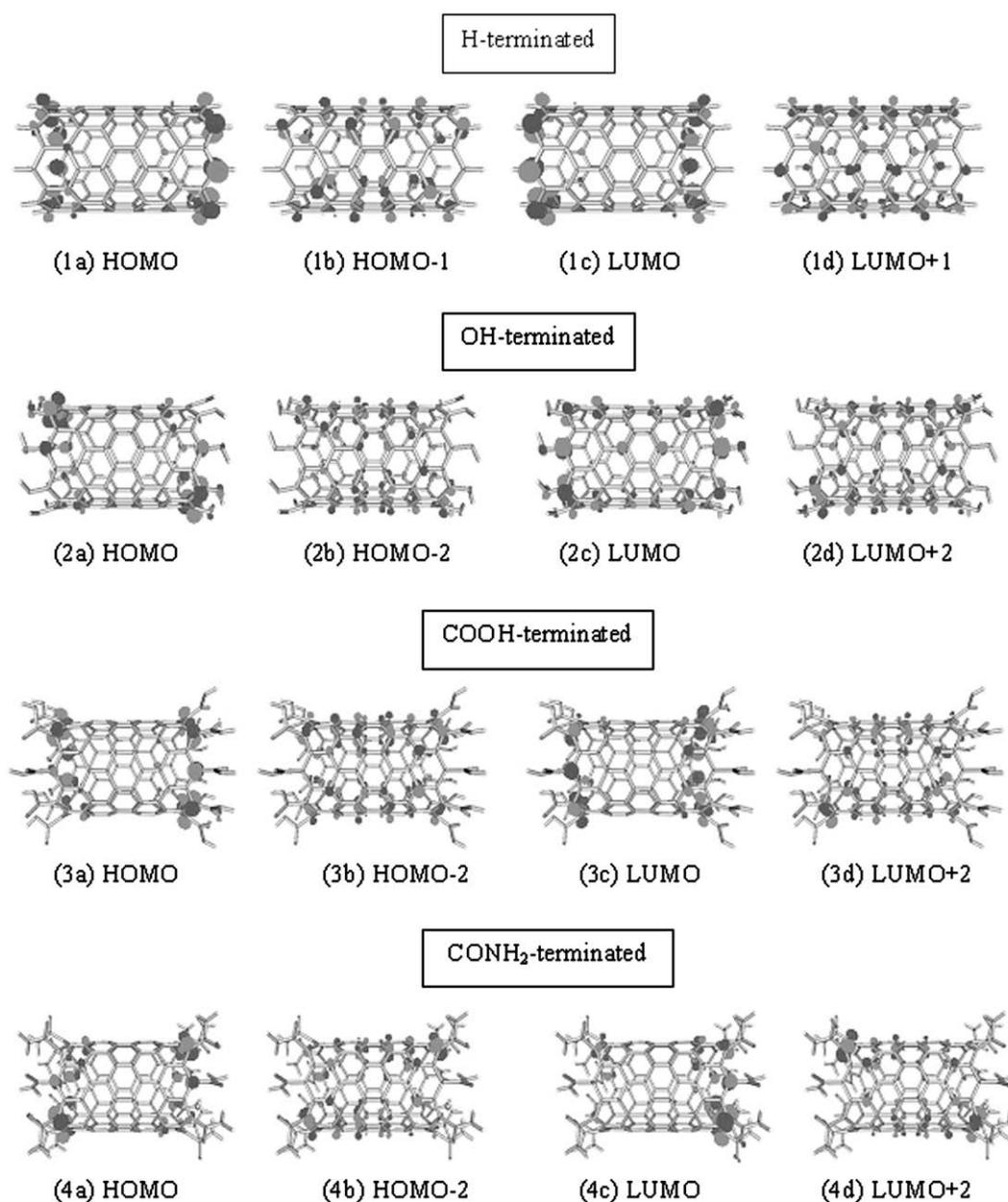


Fig. 5. Side views of 3D-isosurface plots of selective occupied molecular orbital and unoccupied molecular orbital calculated using AM1 method.

stabilize them. Because the carboxylic and amide groups share a similar carbonyl group, their respective energy levels are more correlated. Interestingly, although AM1 overestimates the HOMO energy, it can reproduce LUMO and the same ordering of energy levels obtained from different functional groups, comparative to those of DFT. Such results confirm that AM1 is an effective tool for qualitative study of functionalized nanotubes. Fig. 4a plots the HOMO–LUMO energy gap versus tubule length based on the AM1, DFT and EHMO methods. All levels of theory predict a decreasing energy gap. For sufficiently long tubes, the energy gaps become converged to an approximately similar value (2.3–2.4 eV at AM1 level) regardless of how the tube-ends are functionalized. It can be said that the functional groups do not disturb the sp^2 hybridization of a nanotube, so that eventually the energy gap is still preserved [27]. In general, the realistic energy gap should locate between the extreme values obtained from AM1 (overestimated) and EHMO (underestimated), making DFT a better choice for obtaining such a value. Since DFT is more time-consuming and resource-intensive, it was however used as a complementary method to AM1 in this study. Based on this concept, the finite-length open-end functionalized (9,0) SWNTs are small-gap semiconducting, for which they will become metallic when the length is great enough [28–30].

The energy gap shown in Fig. 4a is rather illusive since a previous study reported that HOMO and LUMO in an open-end H-terminated SWNT are defected states caused by the capping hydrogen atoms [26]. This study also proposed a more sensible way to represent the energy gap in terms of the delocalized states. Fig. 5 visualized the molecular orbitals of selective frontier states, using Facio version 10.3.1 package [31]. In all model tubes, HOMO and LUMO are localized at the terminal ends of the tubes. To compute the energy gap, the most frontier delocalized states should be considered. For the pristine tube, HOMO-1 and LUMO+1 (Fig. 5-1b and 5-1d) are relevant, whereas functionalization shifts the frontier delocalized states downward/upward to HOMO-2 (Fig. 5-2b, 5-3b and 5-4b) and LUMO+2 (Fig. 5-2d, 5-3d and 5-4d), respectively. The new plot of energy gap versus tubule length as shown in Fig. 4b, reveals a converging value of 2.9 eV for all functionalized nanotubes. Although the new energy gaps are higher than the original HOMO–LUMO gap, they are independent of the chemical groups and can represent the real electronic characteristics of the functionalized SWNTs.

4. Conclusion

So far, most previous studies report the effects of only one functional group, i.e., –COOH, at the end and at the sidewall of carbon nanotubes. In the present work, we have explored an extreme case, where all hydrogen caps are replaced with functional groups (–OH, –COOH and –CONH₂) or so-called “fully functionalized” SWNTs. The

results suggest that the low-cost AM1 method in conjunction with DFT can be an effective tool for studying functionalized carbon nanotubes. In conclusion, the “full” functionalization at the open-ends of finite-length SWNTs do not significantly change the geometrical and electronic properties of the original pristine nanotubes, supporting a notion that more real-world “partially” functionalized SWNTs can be used in the same way as the pristine version in most application areas.

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