Stable single helical C- and I-chains inside single-walled carbon nanotubes*

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(Received 4 January 2016; revised manuscript received 11 May 2016; published online 20 July 2016)

The helicity of stable single helical carbon chains and iodine chains inside single-walled carbon nanotubes (SWCNTs) is studied by calculating the systematic van der Waals interaction energy. The results show that the optimal helical radius increases linearly with increasing tube radius, which produces a constant separation between the chain structure and the tube wall. The helical angle exhibits a ladder-like decrease with increasing tube radius, indicating that a large tube can produce a small helicity in the helical structures.

Keywords: nanotube, peapod, carbon chain, iodine chain

PACS: 61.46.–w, 61.46.Fg, 61.46.Km, 62.23.Hj **DOI:** 10.1088/1674-1056/25/9/096105

1. Introduction

The unique one-dimensional space of single-walled carbon nanotubes (SWCNTs) not only provides structural stability, but also induces a novel nanowire effect that is absent in the bulk structure.[1–10] The analysis of encapsulated guest molecule structures inside SWCNTs has attracted much attention, because the physical and chemical properties are sensitive to their formed structures. Studies of the optimal configuration of hard spheres in cylindrically confined spaces show that spherical molecules exhibit different chiral structures within different tubular diameters.[2] For example, ordered phases, such as one- (chain), two- (zigzag), or three-dimensional stacking structures of encapsulated C_{20}, C_{28}, C_{60}, and C_{70}, have been theoretically predicted inside SWCNTs.[3–12] Some of these ordered structures have been confirmed experimentally in double-walled carbon nanotubes.[8] Additionally, encapsulated non-fullerene molecules (e.g., $H_8Si_8O_{12}$ and diamondoids) exhibit dynamics behaviors in SWCNTs similar to that of encapsulated fullerene molecules.[13,14] Perhaps more interesting, scientists have analyzed the atomic-scale structures that form in SWCNTs due to their more exotic structural and electronic properties. For instance, quasi-one-dimensional atomic nanowires (Ag) and one-dimensional crystal structures have been identified experimentally in the nanotubes.[15–24] These hybrid materials, so-called peapods, provide enormous possibilities for both the advancement of nanotechnology and materials science in general, but also for basic research, such as the interaction mechanism and its role in a confined space.

Recently, quasi-one-dimensional carbon (C-) and iodine (I-) chains have been successfully synthesized in MWCNTs and SWCNTs, respectively.[25,26,29] The novel structure of these nanowires makes them ideal candidates for the design of nanometer-sized devices for applications in nanoelectronics, nanomechanics, and nanomaterials. The cohesive energy calculation shows that a carbon nanowire is more energetically stable than the fullerene C_{60} molecule. However, it is less stable than a carbon nanotube.[27,28] The high-resolution transmission electron microscope (HRTEM) analysis suggests that the helical structure consists of C-chains, which is similar to reports of helical gold and iodine nanowires formed in SWCNTs.[25,29] Similarly, in a study by Fan *et al.*, it was found that stable double helical I-chains can be prepared in SWCNTs.[29] Different chain periodicities are analyzed using theoretical simulations. However, only a few tubes have been used to study encapsulated C- and I-chains. No detailed theoretical or experimental work has been reported regarding stable structures of helical C- and I-chains encapsulated in different SWCNTs. Thus, it is interesting to give a comprehensive analysis of the stable structures of encapsulated helical C- and I-chains in different diameter SWCNTs.

In this work, a one-dimensional (1-D) continuous model is constructed to study stable structures of single helical C- and

*Project supported by the National Basic Research Program of China (Grant No. 2011CB808200), the National Natural Science Foundation of China (Grant Nos. 11504150 and 51320105007), and the Cheung Kong Scholars Program of China.

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I-chain in SWCNTs. We focus on helicity analysis, including helical radius (r) and helical angle (φ), of optimal single helical structure for a given tube radius ($R_{\rm T}$). The results show that the optimal helical radius of a C- or I-chain increases linearly as $R_{\rm T}$ increases. The separation between the tube wall and the C-chain or the I-chain range from 3.4 Å to 3.5 Å and 3.7 Å to 3.8 Å, respectively. The C-chain or I-chain optimal helical angle decreases in a ladder-like shape as $R_{\rm T}$ increases, indicating that a large tube can induce a chain structure with a small helicity. Compared to the encapsulated double helical I-chains, a larger helicity (i.e., a larger φ) has been obtained for single helical I-chains when both are introduced into the identical tubes. This study gives a more comprehensive understanding of the tube confinement effect on the filled single helical C- (or I-) chain and provides a guideline for experimental studies.

2. Model and simulation method

To identify the minimum energy configuration of single helical chains inside SWCNTs in detail, we construct a continuous cylindrical model to represent a real tube. This continuous approximation, which ignores the discrete atomic positions, provides a good estimate of the packing geometry and has been successfully used to analyze the C_n@SWCNTs peapod system.[4,5] As shown in Fig. 1, we place the tube and chain structure in a vacuum crystal cell with lattices $OA = OB$ and OC of 40 Å and 500 Å, respectively. The center of mass of the tube and chain is located at the center of crystal cell, with the long axis of the tube aligned along the direction of the OC lattice. In the (x,y,z) Cartesian coordinate system, the crystal cell is centered at the origin o. The OA, OB, and OC coincide with ox, oy, and oz, respectively. The tube length is equal to OC (500 Å). The C-chain or I-chain growth begins on the positive x axis with a helical radius $r \geq 0.1$ Å. The growth direction is along the positive and negative directions of the z axis, respectively. The bonding lengths (d) of the C- and I-chains are set as 1.266 Å and 2.9 Å, based on Refs. [25]–[29]. For a given bond length, d, the spatial positions of arbitrary carbon or iodine atoms are defined as the coordinates $(r\cos n\varphi, r\sin n\varphi, n(d^2-(2r\sin(\varphi/2))^2)^{1/2})$ with the number of atoms being $n = 0,1,2,3,\ldots N$ $(N = 2\Pi/\varphi)$, where r and φ correspond to the helical radius and helical angle, respectively. According to the z coordinates, the square root $d^2-(2r\sin(\varphi/2))^2$ should be equal to or larger than zero. Thus, the range of φ is restricted by

$$r\begin{cases} \leq d/2, & 0 \leq \varphi \leq 2\pi, \\ > d/2, & 0 \leq \varphi \leq 2\arcsin(d/2r). \end{cases} \tag{1}$$

The periodic unit is the non-repeating part that symmetrically cuts the helical chain about the origin o. The periodic unit length, $(L_{\rm unit} = N(d^2-(2r\sin(\varphi/2))^2)^{1/2})$, is determined by r and φ. In this work, we set the minimum helical angle to $\varphi = 5^\circ$, because the $L_{\rm unit}$ of the chain structure becomes too long to calculate when $\varphi < 5^\circ$ and also deviates from reality. For the minimum helical angle, φ (5°), $L_{\rm unit}$ of the C- and I-chains have maximum values equal to 91.5 Å and 208.8 Å, respectively. In this case, the systematic edge effect can be ignored because the tube length is long compared to the C- or I-chain lengths considered in this work. The simulation presented implements the surface-continuum approximation with a smooth surface density of $\sigma = 0.38$ Å^{-2} and a continuous tube radius.[30] Similar to the fullerene peapod system, the interaction between the C- or I-chains and the tube is not due to chemical bonds, but to the van der Waals interaction given by the Lennard–Jones 12-6 potential. The total interaction potential for a given tube radius, $R_{\rm T}$, can be obtained by use of the nanotube field potential given by

$$V(R_{\rm T},r,\varphi) = \sigma R_{\rm T}\sum_i^n \int_0^{2\pi} {\rm d}\varphi \int_0^c v(|\boldsymbol{r}_i - \boldsymbol{\rho}|)\,{\rm d}z, \tag{2}$$

where r_i and ρ are the coordinates of C (or I) in the helical chain and the tube, respectively. The $L_{\rm unit}$ of the helical chain is different for different r and φ values, so the monatomic interaction energy, $V(R_{\rm T})_{\rm atom}$, that gives the average interaction energy for a single carbon (or iodine) atom, is calculated by

$$V(R_{\rm T})_{\rm atom} = V(R_{\rm T})/N. \tag{3}$$

The Lennard–Jones 12-6 potential is applied to describe the van der Waals interaction between atoms separated by a distance r

$$v(r) = D_0(-2(R_0/r)^6 + (R_0/r)^{12}), \tag{4}$$

where D_0 is 0.105 and 0.1886 for C–C and C–I, respectively, and R_0 is 3.851 and 4.1755 for C–C and C–I, respectively.[31] Such an interaction potential has been previously used to describe the C_n-peapod system.[32–44]

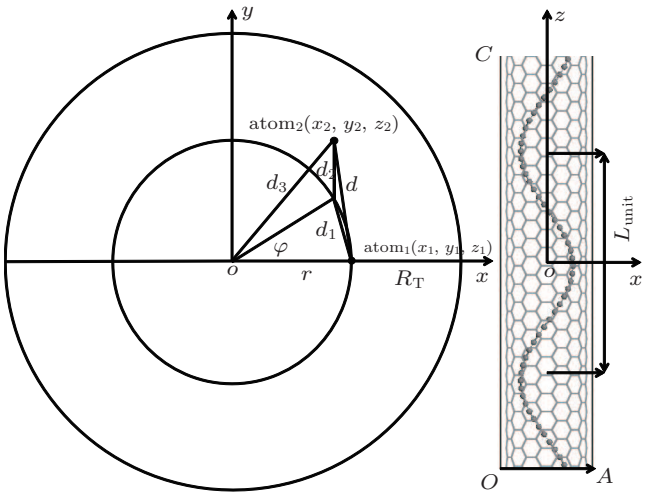


Fig. 1. Schematic of the simulated model in the Cartesian coordinate system. Parameters r, φ, and $L_{\rm unit}$ correspond to the helical radius, helical angle, and periodic unit length of the C- or I-chain with a given tube radius, $R_{\rm T}$, respectively.

The calculation is described in the following steps. First, we take R_T as a variable that ranges from 5.5 Å to 10 Å for C-chains (or 6.0 Å to 10 Å for I-chains) with a step size of $\Delta R_T = 0.1$ Å. With the fixed R_T, r of the C- or I-chain increases from 0.1 Å to R_T with a step size of $\Delta r = 0.1$ Å. For each r value, φ increases from 5° with a step size of $\Delta\varphi = 1°$ to the maximum defined in Eq. (1). Thus, a complete helical chain can be determined with r and φ value. Next, a systematic interaction energy $V(R_T, r, \varphi)_{atom}$ can be obtained by use of Eqs. (2)–(4). Thus, the optimal helical radius opt(r) and helical angle opt(φ) of a single chain structure can be determined such that the configuration has a minimized interaction energy $V(R_T)_{atom}$.

3. Results and discussion

In the following sections, we first analyze the structure of the encapsulated single helical C-chains in SWCNTs. As shown in Fig. 2, we present the systematic interaction energy of the minimum tube radius ($R_T = 5.5$ Å) to identify the opt(r) and opt(φ) of a C-chain. Moreover, several helical C-chains will be presented for an intuitive analysis later. It can been seen that opt(r) and opt(φ), which correspond to the minimum interaction energy $V(R_T)_{atom} = -3.165$ kcal/mol, are 2.0 Å and 33°, respectively. For the more comprehensive analysis, as shown in Fig. 3, we can see that opt(r) increases linearly from 2.0 Å to 6.5 Å as the tube radius, R_T, increases from 5.5 Å to 10 Å. The separation between the C-chain and the tube wall is kept at 3.4 Å–3.5 Å, which is close to the interwall spacing of C_n@SWCNTs peapod systems (3.4 ± 0.2 Å),[45] the interlayer distance of graphite (3.3 Å),[10] and the interlayer distance of multiwall carbon nanotubes (3.4 Å).[41] Note that the separation fluctuations (3.4 Å or 3.5 Å) may be due to the radius step size, $\Delta r = 0.1$ Å. Namely, a smaller value of Δr (e.g., 0.01 Å or 0.001 Å) should produce a more uniform separation, but is not considered due to the computational expense. Since the intermolecular separation can be used to probe the interaction mechanism between molecules, the similarity between the separation obtained here and in the C_n@SWCNT and the graphite system indicates that the same interaction mechanism, such as the primary repulsion and attractive interaction for the small and large tubes, also works in this system.

The opt(φ) and L_{unit} of the optimal C-chain configurations are presented in Fig. 4. It can be seen that the opt(φ) for the C-chain decreases in a ladder-like shape from 33° to 11° as the tube radius, R_T, increases linearly. As is well known, the periodic unit ($L_{unit} = N(d^2 - (2r\sin(\varphi/2))^2)^{1/2}$) decreases for a given φ in a platform as r increases for a constant bonding length, d, and the total number of atoms, N. This can be directly tested by the structures presented ($R_T = 6.3$, 6.4, 6.6 Å, $\varphi = 19°$ and $R_T = 9.1$, 10 Å, $\varphi = 11°$) in Fig. 5. On the other hand, a decreasing opt(φ) will produce an abrupt L_{unit} increase due to the increase in the total number of atoms, N. This is shown in the structures presented ($R_T = 6.2$ Å, $\varphi = 26°$; $R_T = 6.3$ Å, $\varphi = 19°$ and $R_T = 8.5$ Å, $\varphi = 14°$; $R_T = 8.6$ Å, $\varphi = 13°$) in Fig. 5. Thus, we note that the L_{unit} exhibits an inverse relationship with the variable φ.

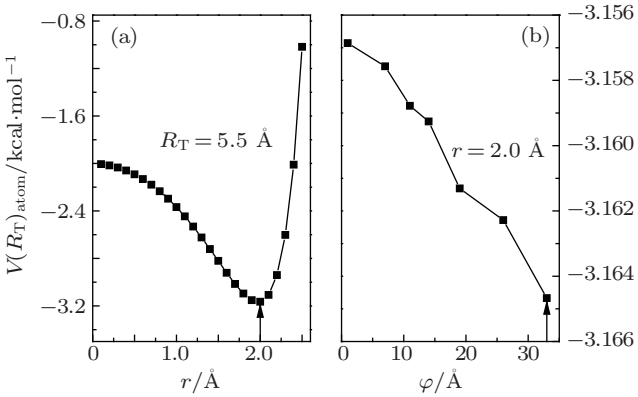


Fig. 2. Systematic interaction energies with the variable helical radius r (a) and helical angle φ (b) of C-chain with a tube radius R_T of 5.5 Å.

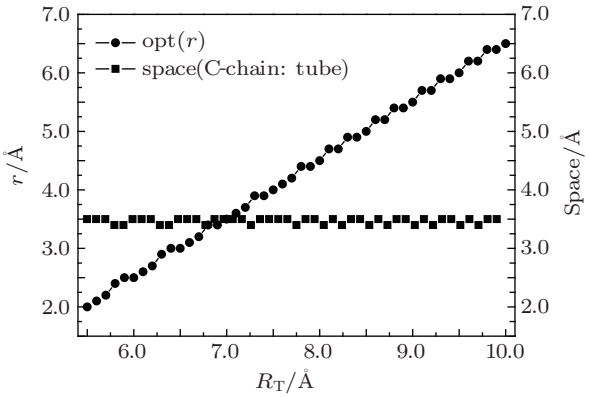


Fig. 3. The dot line and the square line correspond to the optimal helical radius, r, and the space between the C-chain and the tube for a given tube radius R_T, respectively.

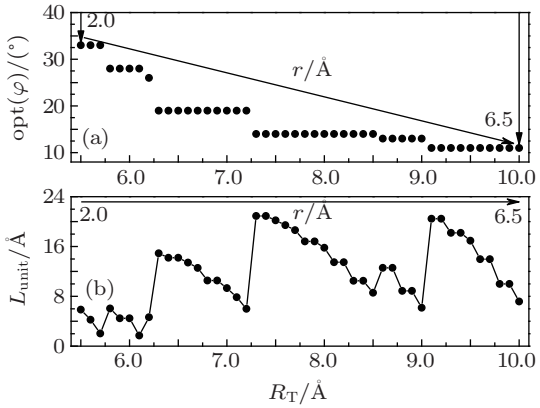


Fig. 4. The helical angles φ (a) and the periodic unit lengths L_{unit} (b) of optimal configurations of C-chains with a variable tube radius R_T.

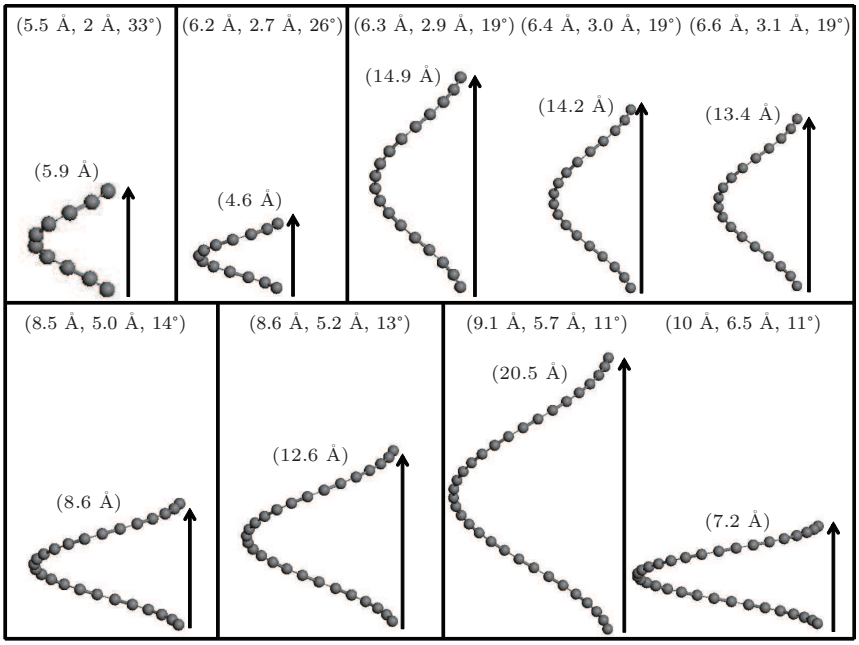


Fig. 5. (color online) Illustrations of optimal helical C-chains for a variable tube radius R_T.

The structure analysis of the encapsulated single helical I-chain in SWCNTs is shown in Fig. 6. It can be seen that opt(r) increases from 2.2 Å to 6.2 Å as tube radius, R_T, increases from 6.0 Å to 10 Å. The separation between the tube wall and the I-chain is held at 3.7 Å or 3.8 Å, which is consistent with the reported separation ($\sim$ 3.75 Å) of the tube wall and the double helical I-chain in experimental analysis.[29] The larger separation value obtained in the I-chain compared to the C-chain is due to its larger van der Waals interaction parameter. As shown in Fig. 7, opt(φ) decreases from 73° to 26° in a ladder-like shape with R_T increasing from 6 Å to 10 Å. The periodic unit length, L_{unit}, also exhibits an inverse relationship with tube radius, R_T, as it increases from 6 Å to 10 Å. In Ref. [29], the 15 Å periodicity of the double helical I-chain is identified in the (10, 10) SWCNT with a tube radius, R_T, of 6.8 Å. For the same tube, we obtain an L_{unit} of 6.1 Å when the encapsulated I-chain constitutes the single helical structure (see Fig. 8). This different periodicity obtained in the same tube may be the result of the extra I–I interaction in the double helical structure. This repulsive/attractive interaction between the two I-chains may induce a smaller helical angle in the double helical chain than in the single helical chain. Thus, I–I interaction between the I-chains can induce a larger L_{unit} as the total number of atoms in a periodic structure increases. Moreover, the single helical structures for tube radius, R_T, of 7.2 Å, 7.6 Å, 8.0 Å, and 8.1 Å have also been presented in Fig. 8. It can be seen that the L_{unit} = 14.7 Å (close to 15 Å of double helical I-chains) of single helical I-chains need a larger tube radius (R_T = 8.1 Å). Thus, for the single helical structure to obtain the same periodicity of the double helical structure, the former requires a larger tube radius. This comparative analysis tells us that the single helical structure possesses a larger helicity (namely, a larger opt(φ) and a smaller L_{unit}) than the double helical structure when confined within identical tubes due to the absence of the I–I interaction between the I-chains.

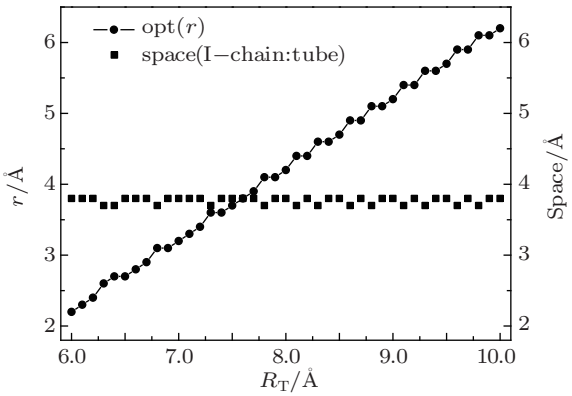


Fig. 6. The dot line and the square line correspond to the optimal helical radius r and the space between the I-chain and the tube with a given tube radius, R_T.

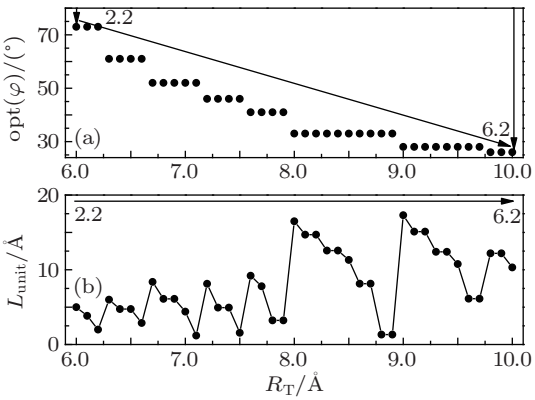


Fig. 7. (color online) The helical angles φ (a) and the periodic unit lengths L_{unit} (b) of the optimal configuration of I-chains with a variable tube radius R_T.

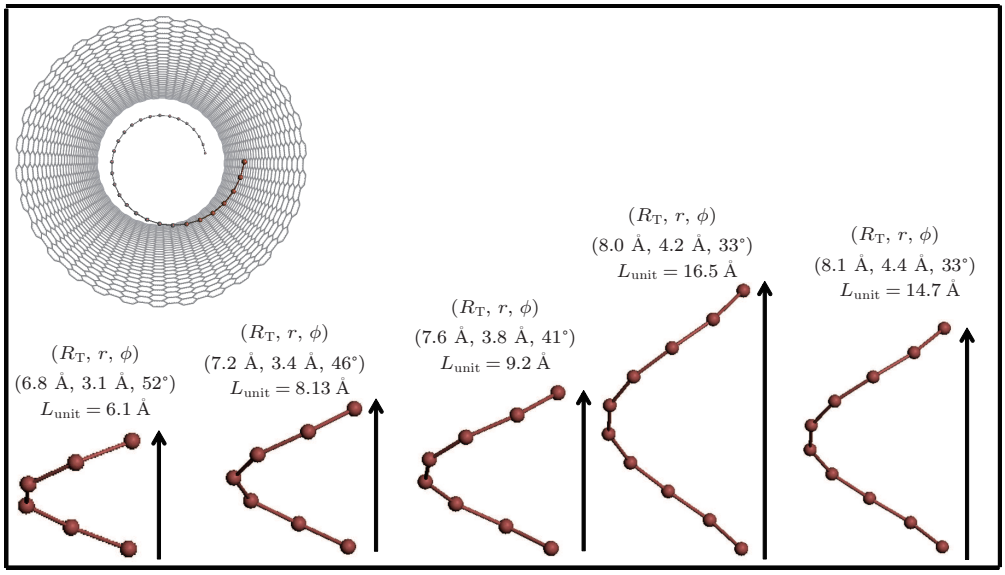


Fig. 8. (color online) Illustrations of the optimal helical I-chains with a variable tube radius R_T.

4. Conclusion

In summary, we presented a detailed study of the stable single helical C- and I-chain inside SWCNTs using a 1-D periodic continuous model. Our aim is to identify the helicity, including opt(r) and opt(φ), of encapsulated C- and I-chains in SWCNTs with different tube radii, R_T. The results show that these two structural parameters of C- and I-chains exhibit the same tendency for the variable R_T. Namely, opt(r) increases linearly with increasing R_T, which produces a constant separation of 3.4 Å–3.5 Å and 3.7 Å–3.8 Å for the encapsulated C- and I-chains, respectively. The optimal helical angle, opt(φ), of C-chain decreases in a ladder-like shape from 33° to 11° as the tube radius, R_T, increases from 5.5 Å to 10 Å. The obtained opt(φ) for the I-chain also decreases in a ladder-like shape from 73° to 26° as the tube radius, R_T, increases from 6.0 Å to 11.0 Å. The L_{unit} of both the C- and the I-chains exhibits an inverse relationship with R_T. A further comparative analysis shows that the single helical I-chain possesses a larger helicity than the double helical I-chain in identical tubes, due to the lack of the I–I interaction among the I-chains. These results not only present visual structural images of the encapsulated single helical C- and I-chains inside SWCNTs, but also demonstrate the usefulness of computational approaches for the design of new materials.

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