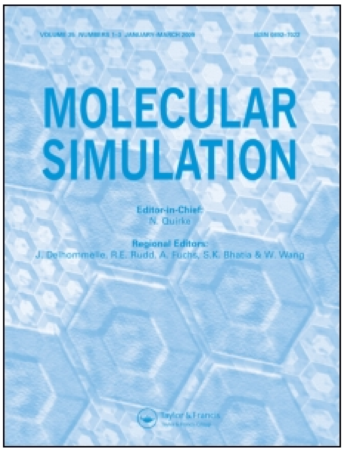

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β-Carotene encapsulation into single-walled carbon nanotubes: a theoretical study

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β-Carotene encapsulation into single-walled carbon nanotubes: a theoretical study

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Recently, the encapsulation of β-carotene molecules into carbon nanotubes has been achieved. In this work, we report molecular dynamics simulations and tight-binding density functional-based results for a theoretical study of the encapsulation processes. Our results show that the molecules undergo geometrical deformations when encapsulated with significant changes in their electronic structure. Based on these results, we propose a new interpretation to the changes associated with the β-carotene absorption bands experimentally observed.

Keywords: β-carotene; encapsulation; nanotube; molecular dynamics; DFTB

1. Introduction

Since their discovery [1], carbon nanotubes (CNTs) have been seen as remarkable materials for a variety of technological applications. It is possible to alter their mechanical or electronic properties, for example, through functionalisation. Functionalisation is a process involving chemical reactions (creating/breaking chemical bonds) [2] between CNTs and atoms or molecules. Another possibility of obtaining similar results without chemical reactions is through encapsulation of atoms or molecules into CNTs [3].

Recently, Yanagi et al. [4,5] have reported experimental studies of the encapsulation of β-carotenes into CNTs with the possibility of light harvesting. This opens new and interesting perspectives to the use of molecular encapsulation for optical applications. Carotene is a general term used to describe several structures presenting a $C_{40}H_{56}$ molecular formula. The carotenes can be found in many different configurations: (α, β, γ, ζ and ε) [4,5]. β-Carotene (Figure 1) is the most abundant one and we have investigated its structure in this work.

In this work, we have theoretically investigated the encapsulation processes of β-carotene into different diameter CNTs using molecular dynamics (MD) simulations and tight-binding (TB) density functional-based methods. In particular, we have investigated how the encapsulations affect conformational and electronic aspects for different CNTs. Based on these results, we propose a new interpretation to the changes associated with the β-carotene absorption bands experimentally observed.

2. Methodology

In order to address the dynamical aspects of the β-carotene encapsulation, we have carried out MD simulations using the well-known molecular universal force field (UFF) [6,7] as implemented in the CERIUS2 package.[1]

UFF is a force field that includes bond stretch, bond angle bending, inversion, torsion, rotations and van der Waals terms. Electrostatic and solvent effects can also be easily incorporated [6,7].[1] UFF particularly describes well the van der Waals interactions, which are of fundamental importance to the encapsulation problem of guest molecule into CNTs. UFF has been successfully used in the structural and dynamical investigations of nanostructures [8–10] similar to the ones we are investigating here. However, as the UFF is not a reactive force field, in order to validate the methodology, it is necessary to determine whether significant charge transfer can occur between the molecule and the tube. This can be done with the use of a quantum method. In order to do this, we have chosen the DFTB+ method by the advantages discussed below. It is well known that density functional theory (DFT) methods do not well describe the van der Waals interactions, and they are very important in our present problem. In order to circumvent these problems, we used the geometries obtained from the classical method (believed to be reliable) as input to DFTB+ calculations. Combining these two methodologies, we believe that we can properly address the main physical aspects of the problem. From the DFTB+ results, we did not observe significant charge transfer, thus validating the classical results that van der Waals interactions play the major role in our problem.

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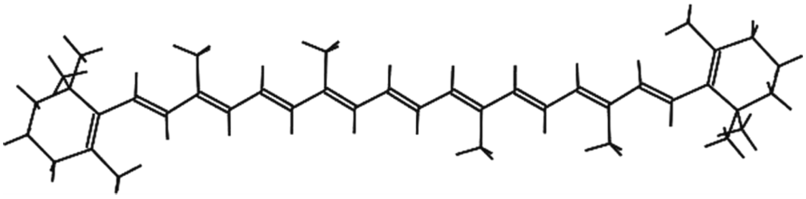

Figure 1. β-Carotene structure ($C_{40}H_{56}$).

As mentioned above, we obtained the electronic structure of our systems using the DFTB + package [11,12]. DFTB + is a tight-binding (TB) method based on DFT. TB methodologies can produce accurate results for many classes of materials, from crystals to clusters [13–19]. The DFTB + represents a tentative to obtain more precise results using parameters adjusted from *ab initio* DFT calculations. There are two major DFTB families with relation to how charges are calculated; a self-consistent procedure or a static one. For the DFTB we used here [11,12], the charges are calculated self-consistently.

3. Results and discussions

Initially, we carried out a molecular mechanics geometric optimisation for the isolated tubes and β-carotene. We have considered the (11,9), (12,7) and (13,5) single-walled CNTs because these are the structures related to the experimental work [4]. We have considered tubes long enough to prevent border effects. We considered tubes with both ends opened and with hydrogen atoms added to passivate the dangling bonds (see Table 1 and Figure 2).

Once the optimised geometries were obtained from molecular mechanics calculations, we carried out the MD simulations. We used a canonical ensemble (NVT) and considered room temperatures (298 K) to mimic the experimental conditions. The initial configurations for the MD calculations were the β-carotene located at about 3.5 Å from the nanotube ends and aligned with the main axis of the nanotube. The simulation time was of 25 ps with an integration step of 1 fs. For the time considered in the simulations and for all the CNTs considered here, we observed that β-carotene was easily encapsulated (see videos in the Supplementary Materials, available online).

Table 1. Lengths, diameters, energy stabilisation and total energy values for the CNTs considered here.

UFF total energy (kcal/mol)			
Nanotube	Energy stabilisation	Length (Å)	Diameter (Å)
(11,9)	− 8.69	72.14	13.56
(12,7)	− 12.63	69.32	13.12
(13,5)	− 11.02	66.83	12.52

Note: For reference, the β-carotene UFF energy is also presented.

Starting from the final configurations obtained from the MD simulations, we reoptimised the geometries (the used criterion convergence was of 10^{-4} kcal/mol in energy and 5×10^{-3} kcal Å/mol for maximum force among atoms). The optimised configurations are displayed in Figure 2, where in order to facilitate the visualisations of the molecular conformations, the CNT front part was made transparent.

As can be seen from the Figure 2, the β-carotene conformations into the different tubes are almost parallel (but a little off) to the main axis tube, in agreement with the available experimental data [4].

As the encapsulations occur spontaneously, we can expect that their final energy configuration should be lower than that of the non-encapsulated configurations. Due mainly to the van der Waals interactions between the molecule and the tube walls, there is an energy stabilisation gain (the energy difference between the sum of the energies of the isolated molecule and tubes subtracted from the energy of the tubes with the encapsulated molecule). However, this gain is not proportional to the tube diameter (Table 1). This could be due in part to molecular distortions

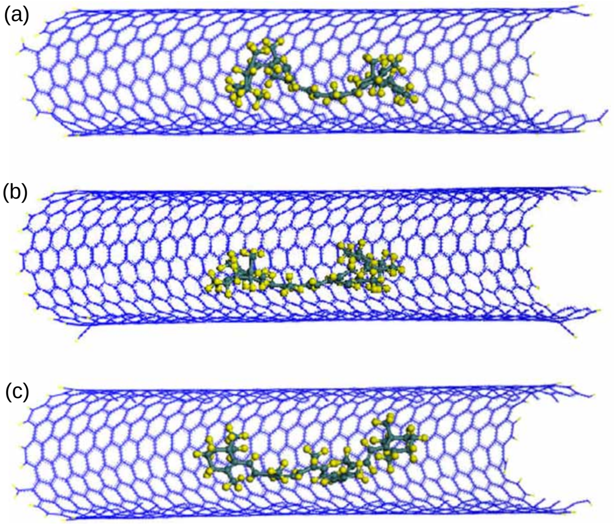

Figure 2. UFF molecular mechanics optimised geometries: (a) β-carotene@cnt(11,9), (b) β-carotene@cnt(12,7) and (c) β-carotene@cnt(13,5), respectively. Frontal parts of the CNTs were made transparent for a better visualization of the β-carotene conformations.

Table 2. Energy values (kcal/mol) for the molecules calculated from the geometries inside the CNTs and the associated estimated elastic energy values (difference in relation to the values of the isolated molecule).

	Elastic energy
(11,9)	0.75
(12,7)	3.00
(13,5)	3.19

Note: See text for discussions.

Table 3. Mulliken charge values before and after encapsulation.

	Mulliken charges	
Nanotube	Isolated	After encapsulation
(11,9)	4858.00	4857.98
(12,7)	4472.00	4472.01
(13,5)	4186.00	4185.98

Note: The β-carotene number of electrons is 216.0.

as a result of the interactions with the tube walls and the fact that the molecule is highly flexible. In order to verify whether this in fact happens, we carried out additional calculations. We compared the energies of the isolated molecules against the energies of the geometries obtained with the molecules inside the nanotubes.

The summary of these results is displayed in Table 2. As we can see from the table values, the molecular distortions are different for the different tubes. For the tubes considered here, the elastic distortions are inversely proportional to the tube diameter. Thus, we have a competitive process for the molecular encapsulation; although there is a net gain (mainly due to van der Waals interactions) with the encapsulation, this gain is reduced as a consequence of the molecular distortions. These aspects will have important consequences to the optical and electronic behaviour, as we will discuss later.

We then proceeded to investigate how the electronic structure is affected as a result of the encapsulation process.

Due to the large number of atoms in our investigated structures (~1200), the use of full *ab initio* methods is cost prohibitive and, as we mentioned Section 2, we have opted to use the DFTB+ [11,12], which represents a good compromise between quality results and computational costs. For the electronic structure calculations, we used as geometries the ones obtained from the MM geometric optimisations properly hydrogen terminated to passivate the dangling bonds.

Two major aspects can affect the light-harvesting yield [4,5], charge transfer and electronic changes induced by the encapsulation processes. In Table 3, we present the results for the calculated Mulliken charges. As we can see from the table values, there is no significant charge transfer between the molecule and the tubes for all the cases considered here.

In Table 4 and Figures 3 and 4, we present the electronic structure DFTB+ results. As we can see from the results, there is a significant electronic coupling between encapsulated β-carotene and nanotubes.

Yanagi et al. [4] have reported that in their photoluminescence excitation (PLE) data, the absorption band was clearly observed for the (11,9) and (12,7) tubes but not for the (13,5) encapsulated tube. Based on that, they interpreted that the CNT with small diameters could not incorporate the β-carotene molecules.

Our results from the MD simulations show, however, that the β-carotene can be easily encapsulated into the (13,5) tube. Based on the following data obtained from the combined use of MD simulations and DFTB+ calculations, we would like to propose an alternative explanation to the changes associated with the β-carotene absorption bands.

- Molecular simulations show that the encapsulation is possible for the (13,5) tube.
- The encapsulated molecules experience significant geometrical distortions that are nanotube diameter dependent (Table 2).
- DFTB+ shows no significant charge transfer between the molecules and the tube.
- Significant electronic coupling between the molecules and the tube, with relevant frontier orbital energy level values (Figures 3 and 4).

Although the luminescence of β-carotene was observed to be quenched by encapsulation into the (13,5) tube, its explanation remains open to interpretation. Previous experimental results [4] were interpreted as that CNTs with small diameters could not incorporate

Table 4. DFTB+ frontier orbital energy values.

	β-carotene	(13,5)	(11,9)	β@(13,5)	β@(11,9)
LUMO + 1	−2.620	−4.216	−4.261	−4.184	−4.283
LUMO	−3.726	−4.234	−4.288	−4.213	−4.295
HOMO	−4.617	−4.839	−4.775	−4.569	−4.522
HOMO − 1	−5.155	−4.852	−4.798	−4.847	−4.788

Notes: HOMO and LUMO refer to highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. All values are in electron volts (eV).

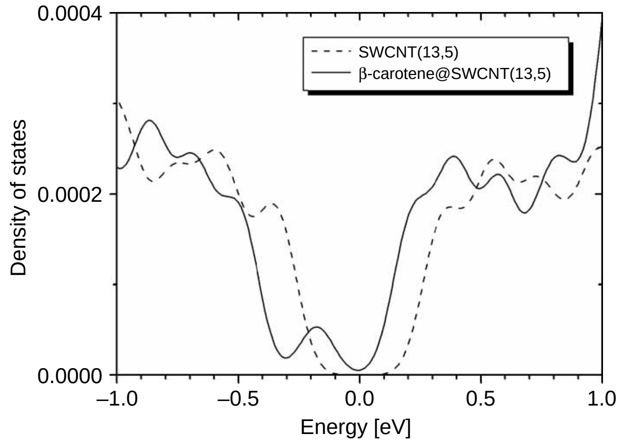

Figure 3. DFTB+ density of states (DOS) for the isolated and β-encapsulated (13,5) CNT. The Fermi level was shifted to the zero value as reference.

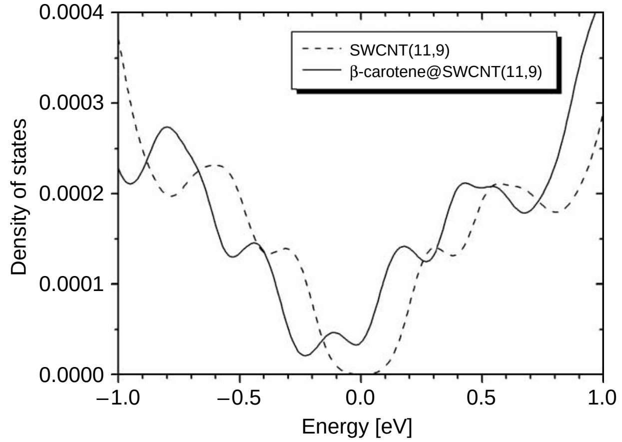

Figure 4. DFTB+ DOS for the isolated and β-encapsulated (11,9) CNT. The Fermi level was shifted to the zero value as reference.

β-carotenes. However, our MD results showed that the encapsulation is possible for the (13,5) tube. As the deformations are larger to smaller diameter tubes, larger deformations should be expected for the (13,5) tube than for the (11,9) and (12,7) tubes. Considering that structural deformations could affect the whole process of absorption by β-carotene followed by energy transfer to the CNT bands, a large deformation could affect the PLE spectrum mainly in the case of β-carotene encapsulation into the (13,5) tube producing a luminescence quenching. In this light, the data presented in figure 5 of Ref. [4] seem to be consistent with this interpretation.

In summary, our results from MD simulations and DFTB+ calculations suggest that the experimentally observed quenched PLE of β-carotene and (13,5) CNT can be the direct result of electronic changes caused by elastic molecular deformations after its encapsulation into the CNT, and not that its incorporation does not occur, as previously proposed in the literature. Further experimental and theoretical investigations are necessary in order to clarify which interpretation is correct.

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Note

1. Cerius2 is a suite of simulation programs available from Accelrys at http://www.accelrys.com.

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