

**Endohedral terthiophene in zigzag carbon nanotubes: Density functional calculations**W. Orellana<sup>1</sup> and Sergio O. Vásquez<sup>2</sup><sup>1</sup>*Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile*<sup>2</sup>*Departamento de Ciencias de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Tupper 2069, Santiago, Chile*

(Received 22 May 2006; revised manuscript received 21 July 2006; published 18 September 2006)

The inclusion and encapsulation of terthiophene (T3) molecules inside zigzag single-walled carbon nanotubes (CNT's) is addressed by density functional calculations. We consider the T3 molecule inside six semiconducting CNT's with diameters ranging approximately from 8 to 13 Å. Our results show that the T3 inclusion process is exothermic for CNT's with diameters larger than 9 Å. The highest energy gain is found to be of 2 eV, decreasing as the CNT diameter increases. This notable effect of stabilization is attributed to the positively charged CNT inner space, as induced by its curvature, which is able to accommodate the neutral T3 molecule. The band structure of the T3@CNT system shows that T3 preserves its electronic identity inside the CNT's, superimposing their molecular orbitals onto the empty CNT band structure without hybridization. Our results predict that the electronic states added by the T3 molecules would give rise to optical effects and nonradiative relaxation from excited states.

DOI: [10.1103/PhysRevB.74.125419](https://doi.org/10.1103/PhysRevB.74.125419)

PACS number(s): 73.22.-f, 71.20.Tx, 31.70.-f

**I. INTRODUCTION**

Filling carbon nanotubes (CNT's) with chosen molecules which in the gas phase exhibits particular electronic properties are becoming increasingly important owing to the possibility they may modulate CNT properties. Theoretical investigations have shown that semiconducting CNT's can be amphoterically doped in a controllable way by encapsulating electrophilic and nucleophilic organometallic molecules.<sup>1</sup> Other calculations have suggested that confinement of molecules inside CNT's can induce structural phase transitions not seen in the bulk phase. For instance, encapsulated water in an 8-Å-diam CNT would exhibit a tight hydrogen-bonding network<sup>2</sup> as well as acetylene in a 7-Å-diam CNT would suffer polymerization.<sup>3</sup> In addition, recent experiments have demonstrated that template-grown large-diameter CNT's filled with fluorescent nanoparticles do emit fluorescent light, allowing the measurement of filling rates and transport of such nanoparticles inside CNT's.<sup>4</sup>

Endohedral functionalization with molecules needs a procedure to open the nanotubes at a first stage and then fill it with a particular molecule. Chemical methods are widely used, and the most simple one is using nitric acid which is very selective in attacking the carbon pentagon at the tube ends.<sup>5</sup> Recently, successful methods to fill opened multiwalled CNT's with fullerenes<sup>6</sup> and others organic molecules<sup>7</sup> have allowed endohedral inclusion in a soft low-temperature way. Organic guest molecules like oligo and polythiophenes are an interesting family of functional electron systems which have been extensively studied recently due to their use in optical devices.<sup>8-10</sup> In particular, oligothiophenes (Tn) have spectral properties dependent on the number of thiophene units ( $n$ ). They show spectral changes and efficient energy-transfer processes when included as guests in one-dimensional supramolecular architectures, as in perhydrotriphenylene crystals (PHTP).<sup>11</sup> This characteristic can be exploited for energy conversion or in detectors of short-wavelength radiation. Recently, we have reported conforma-

tional details of the PHTP:T3 inclusion compound.<sup>12</sup>

In this work, we study the energetic and electronic properties of single-walled CNT's filled with terthiophene (T3) molecules as well as the T3 incorporation mechanisms by an open-ended CNT. Single-walled CNT's, which are typically 10 Å in diameter, can be metallic or semiconducting depending on the way that a graphene sheet is rolled up, which is characterized by the chiral indices ( $n, m$ ). Metallic tubes occur if  $n-m$  is divisible by 3; otherwise, the tubes are semiconducting.<sup>13</sup> Nonchiral nanotubes with indices ( $n, 0$ ) and ( $n, n$ ) are termed *zigzag* and *armchair*, respectively, which are related to the arrangement of the C atoms around the tube. We study the T3 molecule inside six zigzag CNT's, with diameters larger than 8 Å. Our results show that the inclusion of the T3 molecule is an exothermic process for all CNT's under consideration and that the energies involved depend on the diameter of the nanotube. We also found that the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the free T3 molecule appear as sharp subbands when these molecules fill the tube, showing additional singularities in the density of states with similar energy difference than that of the free molecule. This result suggests that the T3 optical properties could be preserved when this molecule fills a semiconducting CNT.

**II. THEORETICAL METHOD**

The calculations were carried out in the framework of density functional theory (DFT),<sup>14</sup> with the generalized gradient approximation (GGA) to the exchange-correlation functional.<sup>16</sup> We use a basis set consisting of strictly localized numerical pseudoatomic orbitals, as implemented in the SIESTA code<sup>15</sup>—namely, a double- $\zeta$  singly polarized basis set. Norm-conserving pseudopotentials<sup>17</sup> in their separable form<sup>18</sup> are used to describe the electron-ion interaction. We consider zigzag ( $n, 0$ ) CNT's with  $n=10, 12, 13, 14, 15$ , and 16, which have diameters of 8.0, 9.6, 10.2, 11.1, 11.4, and 12.7 Å, respectively. Infinite CNT's are described within the

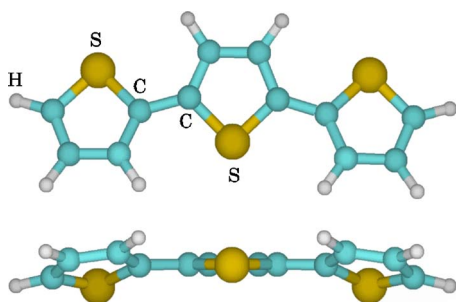


FIG. 1. (Color online) Atomic geometry of the T3 molecule ( $C_{12}H_6S_3$ ) in the gas phase. The three thiophene units adopt a non-planar configuration (lower figure) characterized by the dihedral angle S-C-C-S ( $\theta_D$ ).

supercell approach with periodic boundary conditions applied only along the nanotube axis. As the T3 molecule has a length of about  $12.4 \text{ \AA}$ , we choose a periodic CNT unit of  $17.3 \text{ \AA}$  in length. Thus, the distance between T3 molecules inside a nanotube (T3@CNT) is about  $5 \text{ \AA}$ , ensuring a negligible interaction between them. We consider a lateral distance between tubes of about  $8 \text{ \AA}$ . We also study the T3 incorporation through an open-ended CNT. This was done by taking a finite CNT segment of  $17.3 \text{ \AA}$  plus the T3 molecule which is located initially  $2 \text{ \AA}$  apart from the tube end, along its axis. Then, the molecule is gradually moved into the tube. We consider two possible scenarios for the CNT entrance, with bare C atoms and those saturated by H atoms. The other CNT end is always saturated by hydrogen. The positions of all atoms in the nanotubes and the molecule were relaxed using the conjugated gradient algorithm until the force components become smaller than  $0.05 \text{ eV/\AA}$ . Due to the large size of the supercells, we use the  $\Gamma$  point for the Brillouin zone (BZ) sampling. We check the band-structure calculations and the equilibrium geometries for the T3@(12,0) and T3@(14,0) systems considering four  $k$  points, according to the Monkhorst-Pack mesh.<sup>19</sup> Our results do not show any significant variation with respect to the  $\Gamma$ -point calculations. We also check the difference in energy between T3@(12,0) and T3@(14,0), considering one and four points. We find a very small energy difference of  $3 \text{ meV/atom}$ , showing that the  $\Gamma$  point is sufficient to ensure convergence of the BZ sampling.

### III. RESULTS AND DISCUSSION

We first discuss the structural and electronic properties of the isolated molecule and the semiconducting CNT's. Gas-phase T3 ( $C_{12}H_6S_3$ ) has been theoretically characterized by a S-C-C-S dihedral angle of  $147.2^\circ$  (Ref. 20) and experimentally by the  $S_0 \rightarrow S_1$  singlet transition of  $3.05 \text{ eV}$  (Ref. 21) Figure 1 shows our results for the equilibrium geometry; we have obtained a more planar structure with a dihedral angle of  $157.8^\circ$ , whereas the T3 HOMO-LUMO energy is found to be  $2.33 \text{ eV}$ . This discrepancy is a consequence of the DFT-GGA methodology which underestimates the gap energy. Concerning the carbon nanotubes, we find that (12,0) and (15,0) CNT's are small-gap semiconductors with a gap en-

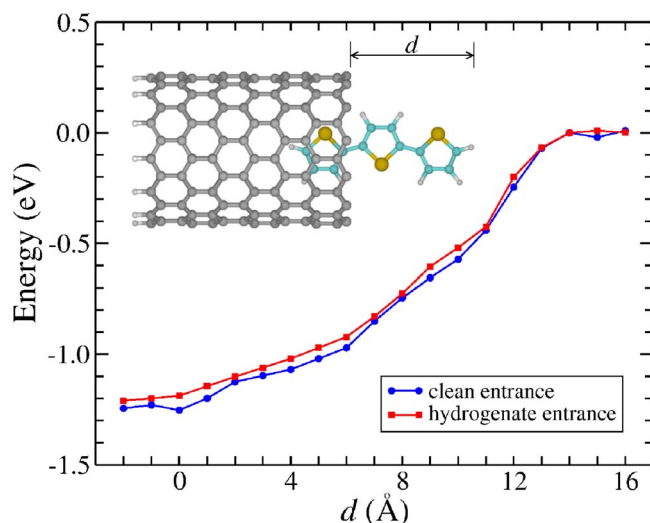


FIG. 2. (Color online) Energy profile during the axial insertion of the T3 molecule into the (13,0) CNT by both clean and hydrogenate entrances. The inset shows the T3 molecule entering inside the (13,0) CNT by the clean entrance.

ergy of  $0.04$  and  $0.05 \text{ eV}$ , respectively, in close agreement with experiments,<sup>22</sup> whereas (10,0), (13,0), (14,0) and (16,0) CNT's have larger band gap of  $0.85$ ,  $0.70$ ,  $0.60$ , and  $0.60 \text{ eV}$ , respectively.

Figure 2 shows the variation in the total energy when T3 enters into a (13,0) CNT by a clean and hydrogenated entrance. We find similar energy profiles in both cases, indicating that electrostatic forces induced by the dangling bonds at the CNT termination are not determinant for the insertion process. We observe that the incorporation reaction is exothermic by  $1.2 \text{ eV}$ . Thus, it is energetically favorable that the molecule enters into an uncapped nanotube than remains outside, exhibiting a barrierless insertion process. From the slope of the curves of Fig. 2, we can estimate the capillary forces involved in the molecule insertion, considering that  $F = \Delta E / \Delta d$ . We find that the force which pushes T3 into the tube is about  $0.15 \text{ nN}$ . In a recent work, Kim *et al.* studied the insertion of a  $C_2H_2$  molecule into the (5,5) armchair CNT which has a diameter of about  $7 \text{ \AA}$ . They found a force of  $0.22 \text{ nN}$ , very close to our results even though the  $C_2H_2$  molecule is smaller and has a linear geometry.<sup>3</sup> This suggests a general trend for the molecular insertion process in carbon nanotubes.

We investigate the energetics of zigzag CNT's of different diameters filled with T3 molecules. In our supercell approach, the molecules are aligned coaxially inside the tube with distances separating them of about  $5 \text{ \AA}$ . We find that the energy of the T3@CNT system is lower than the isolated constituents. Figure 3 shows the gain in energy of the T3@CNT systems with respect to the empty CNT plus the isolated T3 molecule. We find that T3@(12,0) has the highest energy gain of about  $2 \text{ eV}$ , whereas increasing the CNT diameters, this energy tends to decrease. This notable effect of stabilization is attributed to the difference in the relative charge between the inner and outer surfaces of the CNT. For small CNT's, the higher curvature produces a polarization normal to the tube surface which tends to dislocate the elec-

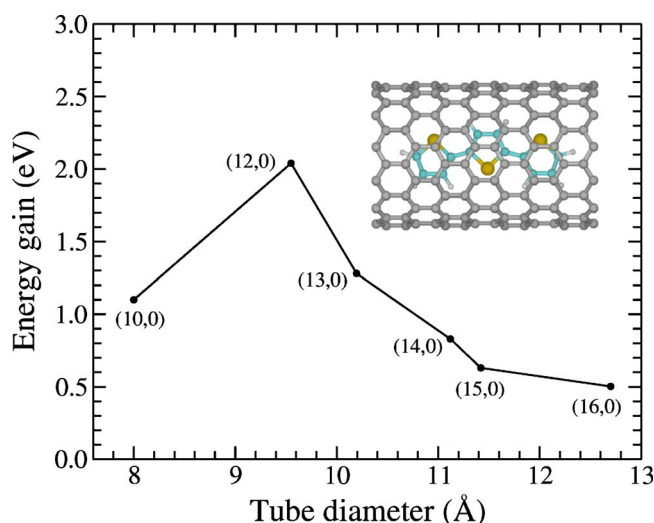


FIG. 3. (Color online) Energy gain as a function of the CNT diameters for the T3 molecule inside the  $(n,0)$  CNT's, with  $n = 10-16$ . The zero energy corresponds to T3 in the gas phase plus the empty CNT. The inset shows the unit cell of T3@(13,0).

tronic charge toward outside, as shown by Dumitrică *et al.*, based on a rehybridization model and DFT calculations.<sup>23</sup> Thus, a neutral molecule with a negative electronic cloud surrounding the positive nucleus would prefer to accommodate in the slightly positive CNT inner region than remain outside. Therefore, nanocapillarity forces acting on the T3 molecules would originate in the normal polarization between the inner and outer CNT surfaces. For larger-diameter CNT's the polarization tends to disappear because the inner and outer curvatures tend to equalize. It is worthy to note that the gain in energy for the neutral T3 molecule inside CNT's can be as high as 1.5 eV for a small diameter variation of about 3 Å, which is the difference in diameters between (12,0) and (16,0) CNT's.

Our results for the T3 molecule inside the small (10,0) CNT of 8 Å in diameter show a gain in energy of 1.1 eV with respect to the isolated components. However, the CNT shows a strong oval deformation whereas the molecule becomes completely flat, resulting in a tight encapsulation, as shown in Fig. 4(a). Although the (10,0) CNT has a stronger normal polarization owing to its enhancing curvature, the T3 inclusion process appears to be unrealistic due to steric ef-

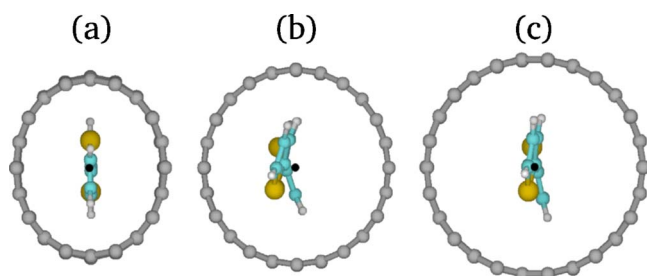


FIG. 4. (Color online) Atomic geometry of the T3 molecule inside carbon nanotubes of different diameters. (a) T3@(10,0), (b) T3@(12,0), and (c) T3@(13,0). The black dot indicates the nanotube centers.

TABLE I. Structural and electronic parameters for the T3 molecule and the T3@CNT system.  $\theta_D$  is the dihedral angle, and  $E_{HL}$  is the HOMO-LUMO energy of the molecule.  $E_G$  is the T3@CNT gap energy.

System	$\theta_D$ (deg)	$E_{HL}$ (eV)	$E_G$ (eV)
T3	157.8	2.33	
T3@(10,0)	180.0	2.24	0.73
T3@(12,0)	143.8	2.30	0.05
T3@(13,0)	157.3	2.29	0.70
T3@(14,0)	155.0	2.34	0.60
T3@(15,0)	167.8	2.34	0.05
T3@(16,0)	161.8	2.27	0.60

facts. The above result suggests that benzenelike molecules would not enter into uncapped zigzag CNT's with diameters closer to 8 Å.

Table I compares the geometry and electronic properties of T3 in the gas phase and inside the CNT's. We find a larger molecular deformation in T3@(12,0), reducing the dihedral angle in 14° with respect to the free molecules. This tendency reverses when the CNT diameter increases. Figures 4(b) and 4(c) show an axial view of the T3@(12,0) and T3@(13,0) systems. We observe that the T3 molecule inside the (12,0) CNT is shifted about 0.5 Å toward the wall from the CNT axis with the S atoms facing the wall, whereas inside the (13,0) CNT the molecule remains at the CNT axis, increasing the dihedral angle. This result somewhat confirms the positive character of the tube inner wall which in the (12,0) CNT induces a sufficiently high normal polarization that moves the molecule toward the wall, decreasing the dihedral angle. Table I also shows that both the CNT band gap and the T3 HOMO-LUMO energy remain essentially unchanged when the molecule is inside the CNT's.

Figure 5 shows the density of states (DOS) of the empty CNT's (13,0), (14,0), and (16,0) (upper panels), which are compared with the DOS of the same CNT's filled with T3 molecules (lower panels). The DOS of filled CNT's clearly shows the appearance of both HOMO and LUMO states of T3 at essentially the same energy, about  $E_F - 0.44$  eV and  $E_F + 1.86$  eV, respectively. The difference in energy between these states is found to be 2.30 eV, very close to that calculated for the free molecule, 2.33 eV. Other molecular states can be observed between  $E_F - 2.0$  eV and  $E_F - 1.5$  eV. This suggests a minor influence of the inner CNT electrostatic potential in the T3 molecular states. Therefore, we may speculate that the optical properties of the T3 molecule would be maintained inside the tube. Nevertheless, the addition of molecular states to the band structure of the CNT itself produces a system with more complex optical characteristics, where we may predict fluorescence from the T3 molecule as well as fluorescence due to transitions between the T3 HOMO band to the sharpest Van Hove singularity in the conduction band. In addition, highly probable energy transfer processes between oligothiophene molecules and the CNT may occur. In this case, a plausible mechanism would allow absorption in the near UV ( $S_0 \rightarrow S_1$  of T3), with energy transfer from T3 (acting as donor) to the CNT (acting as

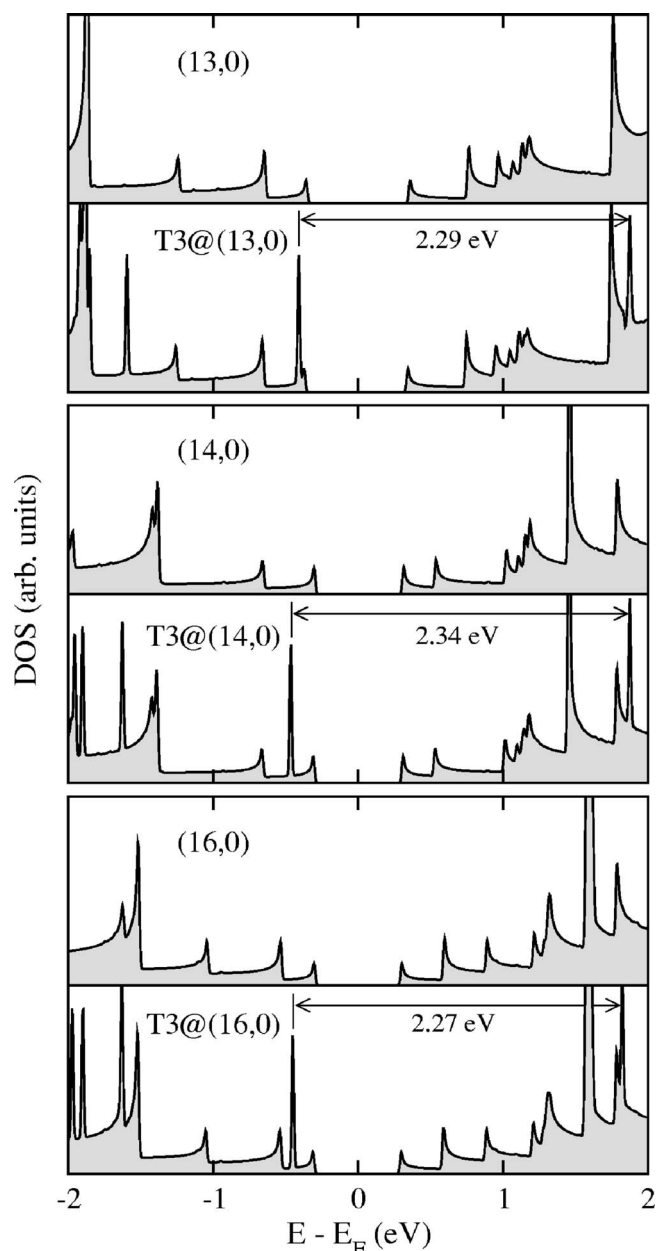


FIG. 5. Density of states (DOS) of empty CNT's (13,0), (14,0), and (16,0) (upper panels) and DOS of the same CNT's filled with T3 molecules (lower panel). The arrows indicate the HOMO-LUMO energy width of T3.

acceptor). For instance, down-conversion processes between Van Hove singularities would give fluorescent emission from  $E_{33}$  up to the  $E_{11}$  IR transition, in the case of the T3@(13,0)

system. It is important to remember that the calculated energy transitions were obtained within the DFT-GGA approach which underestimates their values. Thus, the optical properties extracted from the above results must be taken as a qualitative picture.

#### IV. SUMMARY AND CONCLUSIONS

A notable effect of stabilization is produced by the endohedral inclusion of the oligomer through open-ended zig-zag single-walled CNT's, which is the order of magnitude of a chemical bond. This effect is observed with similar magnitude in both bare and hydrogenated CNT entrances. Earlier studies of several neutral fullerenes predict that the electrostatic potential inside the cage has a positive charge character and consequently would be suitable to accommodate anionic or neutral species.<sup>26</sup> More recent calculations confirm this finding in carbon nanotubes,<sup>23</sup> showing that the curvature of the CNT walls produces a charge displacement toward the outside, leaving a positive character inside. Thus, the T3 inclusion or encapsulation in a CNT is driven in a significant extent by nanocapillarity forces induced by the interaction between the slightly positive CNT cavity and the electronic cloud of the molecule, giving an exothermic process. Thus, the drop in the energy gain for the T3 inclusion in larger-diameter CNT's can be explained in terms of their decreasing curvature.

The band structures of T3@CNT's show that the T3 molecule preserves its electronic properties, superimposing the HOMO-LUMO states onto the original CNT band structure. Semiconducting single-walled CNT's are optically active systems that are fluorescent when encased in cylindrical micelles with a striking influence on the diameter and chiral angle,<sup>24,25</sup> showing strong absorption and fluorescence due to their sharp Van Hove singularities. Our results predict that the electronic states added by the T3 molecules to the CNT band structure would give rise to optical effects in the radiative relaxation from the excited states. In addition, energy-transfer processes between T3 and the CNT suggest possible applications in optical nanodevices—for instance, in UV down-converters.

#### ACKNOWLEDGMENTS

This work was supported by the Chilean founding agencies FONDECYT under Grants Nos. 1050197 (W.O.) and 1030662 (S.O.V.) and the Millennium Nucleus of Applied Quantum Mechanics and Computational Chemistry through Project No. P02-004-F.

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