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Theoretical study on non-covalent functionalization of armchair carbon nanotube by tetrathiafulvalene molecule

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Abstract

The tetrathiafulvalene (TTF) functionalized armchair single-walled carbon nanotube (SWCNT) is investigated using self-consistent-field crystal orbital calculations based on the density functional theory. The studies focus on the structure and electronic properties upon the functionalization of the SWCNT by TTF molecule. Our calculations show that the external absorption of TTF is less stable than the encapsulated ones. It is found that the metallic character of the SWCNT remains for all the models are considered here. Additionally, we also calculated the charge carrier mobility for the one-dimensional (1D) TTF@SWCNT chain with deformational potential approach.

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Keywords: Carbon nanotubes; TTF; Electronic properties; Mobility

1. Introduction

In recent years, non-covalent functionalization of carbon nanotubes (CNTs) by using organic molecules attracted significant attention. Since there is no formation of chemical bonds between the adsorbed molecule and CNT, the chemical and mechanical properties of CNT are only weakly perturbed. Hence, non-covalent functionalization may be a suitable way to control the electronic properties of CNT without destroying the geometric structures of CNTs. Non-covalent attachments of numerous aromatic molecules to the nanotube surface and inner hole have been explored [1–3], including the tetrathiafulvalene (TTF) and tetracyano-*p*-quinodimethane (TCNQ) [4]. The combined systems exhibited the requirements of controllable doping, air stability and simplicity of synthesis that are vital in applications. Theoretical works on functionalization of CNT by TTF and TCNQ have also been carried out [5–6]. However, their studies of electronic structures are concerned mainly with the functionalization of zigzag CNTs. We would also like to know what situation is for the functionalization of armchair CNTs. It has been pointed out that charge transfer molecules interact more strongly with metallic CNTs because the polarizability of metallic CNTs is larger than that of their semiconducting counterparts [7]. In this paper, we performed self-consistent field crystal orbital (SCF-CO) calculations on an armchair single-walled carbon nanotube (SWCNT) functionalized by TTF molecules. According to our knowledge, no SCF-CO calculations on the functionalization of CNT by organic molecules have been carried out. Our aim was to probe the interactions between the SWCNT and TTF molecules, and how these interactions affect the electronic properties of the combined systems.

2. Models and methods

SWNT (8, 8) is chosen as representative of armchair nanotubes. Two models of TTF absorbed to the SWCNT are considered. TTF molecules are adsorbed to the outside wall and encapsulated inside the SWCNT, respectively, for models A and B. Here, two configurations are considered for model A: the long molecular axis is perpendicular (A-1) and parallel (A-2) to the tube axis. The unit cells for models A and B (B-1) are fourfold that of (8, 8) including one TTF and 128 carbon atoms of the SWCNT. The rate of TTF:C

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atoms are in the range of experimental estimation of 100–150 carbon atoms per TTF molecule [4]. Additionally, we also make a comparison of different concentrations of TTF encapsulated inside the SWCNT. One (B-2) contains a TTF in three unit cells of (8, 8), the other (B-3) has a unit cell fivefold as that of the tube (8, 8). Here a commensurability condition of the 1D periodicity between the tubes and absorbed TTF molecules is imposed. The geometrical structures of all models are fully optimized with cluster models composed of a TTF and six unit cells of hydrogen terminated tube (8, 8). The optimization are carried out using SCF molecular orbital method based on Perdew–Burke–Ernzerhof (PBE) [8,9] density functional theory (DFT) at the 3-21G* level with the GAUSSIAN 03 program package [10]. Then middle parts of cluster models are used to construct the combined systems as a smallest repeat unit. The band structures, energies and the electronic properties of the combined systems are calculated using the same DFT-PBE SCF-CO method with the CRYSTAL03 program [11] at the 6-21G* level, which is implemented in the program for solid-state calculations. In the SCF-CO calculations, 41 k-point sampling was employed in 0–π/a of the first Brillouin zone (BZ) and default convergence criterion was used.

3. Results and discussions

3.1. Structure and stabilities

The structure optimization can lead to energy minimum for all models. Fig. 1 shows the optimized structure of models A and B and some calculated data are listed in Table 1.

The binding energy E_b in Table 1 is defined as

$$E_b = E[\text{tube}(8,8)] + E(\text{TTF}) - E[\text{TTF} + (8,8)], \quad (1)$$

where E[tube (8, 8)], E(TTF) and E[TTF + (8, 8)] are the energy per unit cell for the SWCNT (8, 8), the isolated TTF chain and the combined systems, respectively.

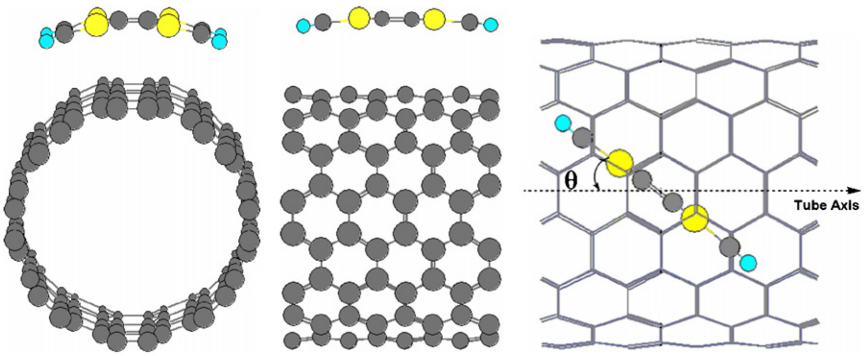
The calculated binding energies for A-1 and A-2 are 1.31 and $-0.19\,\text{kcal}\,\text{mol}^{-1}$, respectively, hence the configuration perpendicular to tube axis is more stable for the outer absorption of TTF. The nearest distances of heavy atoms between TTF molecules and wall of SWCNT are about 3.6 Å and 3.2–3.4 Å for A-1 and A-2, respectively, which are in the range of van der Waals (VDW) interaction distance. TTF molecules are all bended in A-1 and A-2, which reflects the impact on the TTF structure due to TTF–tube interaction (see Table 1).

Model B is the most stable configuration of TTF functionalized SWNT. This indicates that TTF molecules are favorable to being encapsulated inside the SWNT from a view of energy, which is consistent with the result of previous XRD analysis [4]. In the TTF@ (8, 8), TTF molecule is to lean about 36° inside the tube. These results are similar to the previous ultra-soft, pseudopotential plane–wave calculations for TTF@ (16, 0) [5]. The encapsulation of TTF inside the zigzag tube is also energetically favorable, but the TTF molecule shifts 1 Å away from the axis of tube (16, 0) which has larger diameter than tube (8, 8).

The nearest C–C and S–C distance between TTF and the SWCNT for TTF@ (8, 8) is close to that for model A. Although the corresponding H–C distance is smaller in TTF@ (8, 8) than in model A, the distance is still bigger than VDW space of H–C, i.e., no covalent bonding exists between TTF and the SWCNT. Therefore, the tube–TTF interaction should be VDW-like. The smaller binding energies also exhibit the weak tube–TTF interaction and the doping of TTF molecules can be characterized as physisorption.

Table 1
Calculated binding energy E_b (kcal/mol), charge transfer from per TTF molecule (Q, $|e|$), and the nearest distance of atoms between TTF and the SWCNT (Å)

Models	E_b	Q	H–C	S–C	C–C
A-1	1.31	0.024	3.701	3.612	3.608
A-2	−0.19	0.025	3.124	3.464	3.246
B-1	7.72	0.176	2.757	3.620	3.476
B-2	4.82	0.166	2.757	3.620	3.476
B-3	5.46	0.167	2.757	3.620	3.476



A-1 A-2 B-1

Fig. 1. Structure of models A and B.