PHYSICAL REVIEW B **79**, 115413 (2009)

Organic molecule assembled between carbon nanotubes: A highly efficient switch device

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(Received 13 January 2009; published 12 March 2009)

We report a highly efficient switch built from an organic molecule assembled between single-wall carbon nanotube electrodes. We theoretically show that changes in the distance between the electrodes alter the molecular conformation within the gap, affecting in a dramatic way the electronic and charge transport properties, with an on/off ratio larger than 300. This opens up the perspective of combining molecular electronics with carbon nanotubes, bringing great possibilities for the design of nanodevices.

DOI: 10.1103/PhysRevB.79.115413 PACS number(s): 73.63.Fg, 73.63.Rt, 85.65.+h

One of the pursuits of researchers in nanotechnology is the search for devices at this scale that are equivalent to their "larger" counterparts, such as transistors and switches. This usually requires new concepts and designs. Moreover, one of the challenges is to find a single type of material that can perform a variety of functions, thus opening up the perspective of integration. One of the possible candidates are carbon nanotubes (CNTs) (Ref. 1) due to their wide variety of superb properties.[2,3] This has stimulated their functionalization as different types of nanodevices, such as chemical sensors,[4,5] field-effect transistors (FETs),[6,7] and polymer nanocomposites[8,9] to name a few. The amazing development of experimental techniques to handle materials at the nanoscale is undoubtedly the engine behind these advances. Recently, it has been possible to manufacture a spatial gap in a single-wall CNT (SWCNT) and assemble organic molecules in it.[10–13] Another impressive example of nanomanipulation is provided by the experimental work where it was possible to have a controllable and reversible telescopical extension of multiwall CNT (MWCNT).[14]

The perspective of combining those two experimental achievements brings up the possibility of having assembled molecules between carbon nanotube electrodes (CNTes) with a controllable spatial gap. This kind of device has great potential to nanoelectronics since the transport properties of the whole system are highly dependent on the changes in the molecular conformation[15] being useful to build nanoswitches by suitable molecular engineering.[16] However, for this it is necessary to understand the relationship between the mechanical and structural properties of such systems and how they can cause geometrical changes that can affect the transport properties. This may allow the integration of two important fields in nanotechnology, viz., molecular electronics and carbon nanotubes, opening up different vistas for the design of complex devices. Even though there have been some previous theoretical studies on the transport properties of molecular bridges linking SWCNTs,[17–19] there still exists lack of knowledge about: (i) the mechanism behind the molecular structural stability; (ii) how it is possible to controllably change its conformation; and (iii) how these changes are correlated with the charge transport.

In this paper, we theoretically investigate all these issues using as a prototype a benzene covalently assembled between metallic single-wall carbon nanotube electrodes (SWCNTes). We study in great detail the correlation between geometry and transport properties. Varying the spatial gap between SWCNTes, we obtained an insight about how to control the molecular angular orientation. We show that relatively small changes in the size of the spatial gap between electrodes cause a rotation of the benzene molecule, resulting in a change of coupling character between molecular and SWCNT orbitals. As a consequence the transmittance can suffer enhancements by a factor greater than 300, thus indicating that organic molecules assembled between SWCNTs can be used as very sensitive nanoswitches.

Our calculations were performed in the framework of *ab initio* density-functional theory (DFT),[20] within the generalized gradient approximation for the exchange-correlation functional,[21] as implemented in the SIESTA code.[22–24] The structural geometries and the total energies were obtained using a supercell approximation, where a (5,5) SWCNT was "cut" and the two sides were separated, generating in this way a spatial gap. The dangling bonds were passivated with hydrogen atoms, except one on each side, where a benzene molecule was attached (Fig. 1). The supercell had a total number of 136 (22) carbon (hydrogen) atoms with a 20 Å lateral separation between images. We used a mesh cutoff of 200 Ry and two special **k** points for the Brillouin-zone integration. All atoms were fully relaxed within a force convergence criteria of 30 meV/Å. The transport properties were also investigated through *ab initio* methods, where the electronic structure of contacts and the atomic relaxations of the whole system are taken into account.[25–28] This simulates a benzene assembled into semi-infinite SWCNTes. In this way open boundary conditions were used to describe the electronic and the transport properties. We used the TRANSAMPA code, which is based on a nonequilibrium Green's function formalism coupled with DFT (NEGF-DFT), see details in Ref. 25. The scattering region was described by a total number of 278 atoms, as shown in Fig. 1.

A (5,5) SWCNT is an armchair, metallic CNT,[3] with elec-

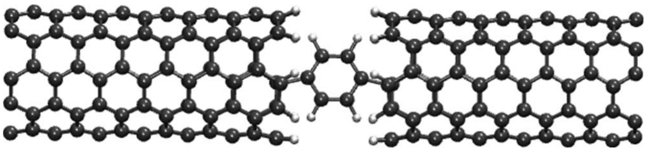

FIG. 1. Structural model of a (5,5) SWCNTes with passivated edges attached to a benzene molecule.

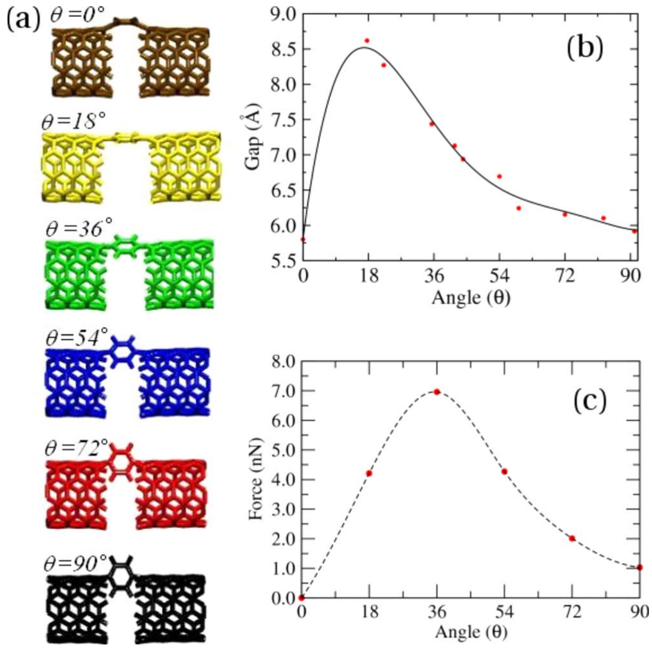

FIG. 2. (Color online) (a) Relaxed geometries for the representative torsion angles $\theta=0$, 18, 36, 54, 72, and 90°. (b) Dependence of the torsion angle θ with the spatial gap. (c) External force needed to cause a transition from a previous configuration to the next one as a function of the torsion angle θ.

tronic properties close to the Fermi level dominated by π/π^* states. Considering the growth axis of the CNT, those states are formed by linear combinations of perpendicular atomic p orbitals. Considering now the cut SWCNT with the assembled benzene, the passivation of SWCNTe edges occurs by σ bonds between hydrogen and carbon orbitals. The assembled benzene is bonded to the carbon atoms of the SWCNT edges and can present different angular orientations relative to the nanotube walls. As will be described below, these geometric conformations are fully correlated with the spatial gap width.

To understand the molecular rotation mechanism, we defined a CNT tangent plane (TP) which contains the carbon edge atoms involved in the bonding to the benzene molecule. The angle between this TP and the molecular plane is considered as the torsion angle. Performing total-energy calculations, by varying the spatial gap it was possible to correlate it with the molecular conformation for each torsion angle. Allowing full geometric relaxation for a fixed torsion angle, we found the corresponding spatial gaps for the following representative torsion angles: $\theta=0$, 18, 36, 54, 72, and 90°, as shown in Fig. 2(a).

Total-energy calculations revealed the presence of a large repulsion between the SWCNTes passivating hydrogen atoms and the benzene H atoms. This is a consequence of the short linking between the benzene molecule and the SWCNT. For instance, the maximum repulsion occurs when $\theta\sim 18°$ due to the high alignment between those hydrogen atoms. Once this extreme configuration is crossed, the molecular torsion tends to reduce the hydrogen repulsion. Consequently, the perpendicular conformation ($\theta=90°$) represents the global minimum configuration, whereas the $\theta\sim 18°$ is the maximum energy one. Figure 2(b) elucidates the correlation between the spatial gap and the torsion angle θ of the benzene molecule. As a rule, the larger the torsion angle, the smaller the spatial gap, which is a consequence of the competition between an increase in the molecule-SWCNTes bond strength and the minimization of the repulsion between the hydrogen atoms. The only exception is the parallel case ($\theta=0°$), which exhibits a spatial gap width of 5.8 Å. This proximity occurs because in the parallel case the benzene molecule is dislocated upward, out of the tangent plane, due to the hydrogen repulsive interaction.

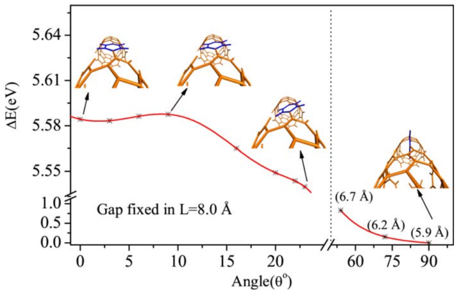

FIG. 3. (Color online) Proposed path to go from $\theta\cong 0°$ to $\theta=90°$ configuration. The left part of the figure has a spatial gap fixed at 8 Å, whereas the right part presents a gradual decrease in the spatial gap (shown in parenthesis). The insets show the geometrical conformations for each corresponding points along the path. The energy reference is the global energy minimum with $\theta=90°$ at a spatial gap of 5.9 Å.

Although there is a high hydrogen repulsion at the $\theta=18°$ configuration, it can be easily reached via the application of an external force [see Fig. 2(b)]. In fact, starting from an initial molecular conformation θ, all other configurations are accessible by applying an external force that produces an elongation/reduction in the spatial gap, which then alters the molecular conformation [Fig. 2(b)]. Moreover, the magnitudes of these forces are in complete agreement with applied forces in the mechanical manipulation experiments of CNTs.[14,29,30]

Increasing the spatial gap, the hydrogen repulsion is reduced and the benzene molecule rotation becomes thermally accessible. Thus, the transition between the $\theta=0°$ and other configurations can be generated by a two-step reversible process—one that involves an applied external force followed by a thermal relaxation. In Fig. 3 we illustrate one of these possible pathways for the transition from the parallel to the perpendicular configuration. Starting from the $\theta=0°$ configuration with a spatial gap around 5.5 Å, the nanotubes are separated up to a spatial gap of 8 Å, which can be reached by an external force of $\simeq 3.6$ nN. During this stretching process the molecule becomes trapped at a local energy minimum that exists for all spatial gaps and always has $\theta\cong 0°$. The basic difference between these minima and the global minima is the upward displacement of the molecule from the tangent plane. It is possible to see that there is a very small energy barrier ($\simeq 3$ meV) from local minimum with $\theta\cong 0°$ to configurations with larger torsion angles (the system relaxes toward $\theta=23°$ for such a gap). Thus, thermal activation can easily overcome this barrier and causes the rotation of

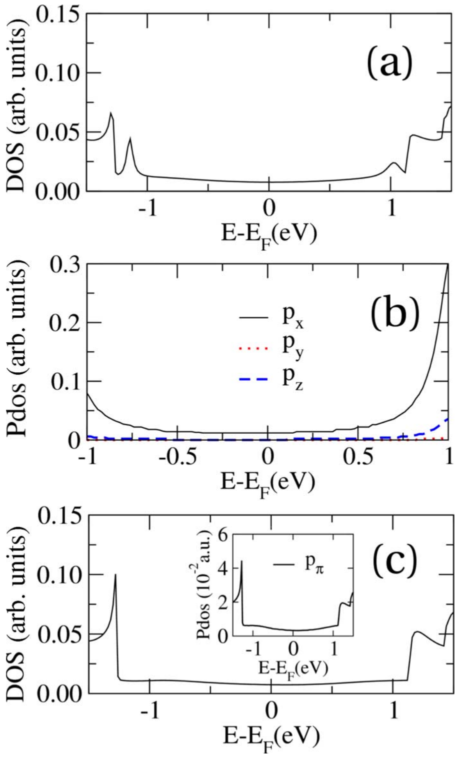

FIG. 4. (Color online) Electronic properties as a function of energy. (a) Total DOS for the $\theta=0°$ configuration. (b) PDOS for the benzene molecule p orbitals for the $\theta=0°$ configuration (the x direction is perpendicular to the benzene molecular plane, whereas the y and z directions are in the plane of the molecule). It shows the presence of molecular π states close to E_F. (c) Total DOS for the $\theta=90°$ configuration. The inset shows the PDOS for the SWCNTe carbon atoms.

the molecule. By further compressing the SWCNTes the global energy minimum conformation for $\theta=90°$ can easily be reached via a barrierless transition. It is important to stress that (i) after thermal activation process, it is possible to obtain any desired final configuration just by controlling the spatial gap according to Fig. 2(b) and (ii) the pathway is completely reversible.

The geometrical differences of the benzene angular orientation between parallel and perpendicular cases affect dramatically the electronic properties, which, as a consequence, will cause significative differences in the charge transport properties. For $\theta=0°$, the π-like molecular orbitals couple to the π-SWCNTe orbitals. This matching between π states of benzene and SWCNTes results in a nonzero contribution of molecular states to the density of states (DOS) (Ref. 31) close to E_F [Fig. 4(b)]. In Fig. 4(a) we present the total DOS for the $\theta=0°$ configuration, whereas in Fig. 4(b) the projected density of states (PDOS) for the benzene molecule p orbitals is shown. The metallic character of the SWCNTes is clearly seen in the nonzero and almost constant density of states around the Fermi energy. From the PDOS, it is possible to see the contribution from the π states of the benzene molecule around E_F (the x direction is perpendicular to the benzene molecular plane, whereas the y and z directions are in the plane of the molecule for the $\theta=0°$ configuration). The other p states, oriented in the plane of the molecule, contribute mostly to σ orbitals and basically do not contribute to the DOS around the Fermi energy.

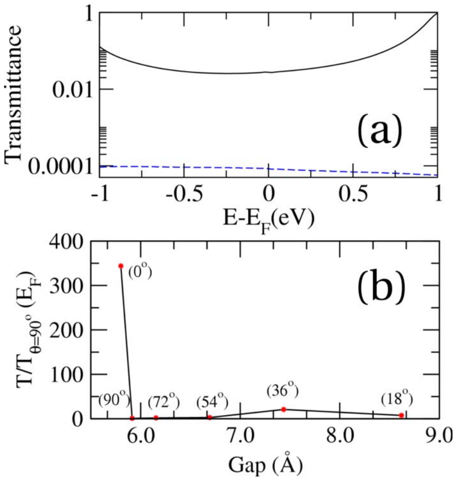

FIG. 5. (Color online) (a) Black solid (blue dashed) line shows the transmittance curve, in logarithmic scale, for the $\theta=0°$ ($\theta=90°$) configuration. (b) Ratio between the transmittances (at E_F) for the configurations shown in Fig. 2(a) and the transmittance for the $\theta=90°$ configuration. The results are presented as a function of the spatial gaps corresponding to each torsion angle shown in parenthesis [see Fig. 2(b)].

For the perpendicular case, on the other hand, the mismatch between the molecule and SWCNTe π orbitals results in an absence of molecular states close to E_F. In fact, for $\theta=90°$, the calculated PDOS for the benzene carbon atoms gave a null contribution inside an energy range of ±1.0 eV around E_F (the overall DOS in this energy range is very similar for both the perpendicular and parallel cases since it is dominated by the SWCNTe states; see Fig. 4). Since there are no molecular states to contribute to the transport in this energy range, we expect that the transmittance close to E_F will be basically due to the direct tunneling between the SWCNTe states shown in Fig. 4(c). Thus, it is expected that there will be a large difference in the transmittance between the two orientations. Figure 5(a) shows the transmittance curves for the $\theta=0°(T_{0°})$ and the $\theta=90°(T_{90°})$ cases, in logarithmic scale, within an energy range of ±1.0 eV around E_F. For $\theta=90°$, the transmittance is almost constant inside this energy window and presents the very low value of 8.0×10^{-5} at the Fermi energy. Due to the π-orbital matching that occurs exclusively for the parallel case, at the Fermi energy, $T_{0°}$ is 325 larger than $T_{90°}$.

Connecting now the mechanical and transport properties, Fig. 5(b) presents the transmittances (normalized by $T_{90°}$), at E_F, for each representative configuration shown in Fig. 2(a). The results have shown that a contraction/elongation of the spatial gap around 5.8 Å results in a huge change in current. Those results indicate that by controlling the structural transitions it is possible to use SWCNTes assembled with organic molecules as highly efficient switch devices.

One possible scheme to build such a device involves a mechanism based on two already available nanomanipulation techniques, the telescopic movement of CNTs,[14] coupled with the manufacturing of a spatial gap in a SWCNT assembled with an organic molecule.[10,11] Then, with torsion angle transitions induced by the spatial gap control, it is possible to obtain a switch with an on/off ratio larger than 2 orders of magnitude.

In conclusion, based on *ab initio* theoretical calculations we showed that a benzene molecule assembled between SWCNTes works similar to a highly efficient switch mediated by mechanical stretching. By reducing/elongating the SWCNTe spatial gap, it is possible to induce changes in the molecular conformation, thus altering the coupling between the molecule and the SWCNTes. As a consequence, there are large transmittance variations with an on/off ratio larger than 300. Moreover, we also present a possible energetic pathway for the transition between the parallel and perpendicular molecular conformations. Even though we demonstrated the switch functionality with a benzene molecule directly connected to the nanotubes, most likely it will be better to use larger molecular links to establish this connection in order to reduce the hydrogen repulsion, making it easier to develop a reversible torsion mechanism. Moreover, usage of a larger molecule will make the transmittance of the perpendicular case even smaller, since it is mostly due to direct tunneling between the electrodes. This will cause an even larger on/off ratio. In this way, our results strongly indicate that by a suitable molecular engineering and nanofabrication, it is possible to build highly efficient switches based on organic molecules assembled between SWCNTes. Finally, the perspective of interlinking the fields of molecular electronics and carbon nanotubes, as well as the coupling of mechanical control and transport, brings up great possibilities for the design of nanodevices.

The authors acknowledge financial support from the Brazilian agencies FAPESP and CNPq.

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