

NANOTUBE LIGHT-CONTROLLED ELECTRONIC SWITCH

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A novel carbon nanotube electronic device is proposed: a light-controlled electronic switch. A charged molecule has been designed for a noncovalent modification of the nanotube. Photon absorption by the molecule results in nanomechanical switching of the charge position which controls the electron/hole transport through the nanotube.

Keywords: Nanotube; light-controlled switch; theory; electronic structure.

1. Introduction

The use of carbon nanotubes for field effect nanoelectronic devices, which has been recently demonstrated,^{1,2} motivates further studies of electrochemical and chemical analogues of nanotube molecular transistors.^{3,4} However, chemical gating is not applicable for modern electronics due to its slow response.

Herein we propose a novel molecular electronic device: Nanotube Light-Controlled Switch (NLCS). The device consists of a carbon nanotube and a switching molecule attached to its surface. The switching molecule consists of two parts: an “anchor” connected to the nanotube sidewall and a charged “tail”. A fast nanomechanical motion of the charged “tail” of the molecule, which is caused by a photon absorption, produces an electrostatic potential modulation, i.e., results in a local electrostatic gating. The variation of the potential of this molecular gate is predicted to lock/unlock the current through the nanotube. The switching molecule charge creates an electrostatic barrier for the nanotube charge carrier motion that causes their scattering and decreases the conductance. We show that the current modulation for a single switching molecule is 40–50%.

In order to demonstrate the efficiency of the proposed device we have simulated the modulation of the ballistic conductance of a p-doped zigzag single-wall carbon nanotube (SWNT) by applying a local electric field of a single charge placed near the surface of the nanotube. The nanotube valence band bends due to an external electrical potential of the charge. The external potential creates a barrier for holes

and by this controls the current. The hole transmission coefficient is calculated quantum mechanically taking into account the semiclassical tunneling. Unlike previous studies, our work utilized a *full selfconsistent* electrostatics calculation for the SWNT electronic structure, which allows to obtain a precise band bending picture at the equilibrium in a continuum approximation.

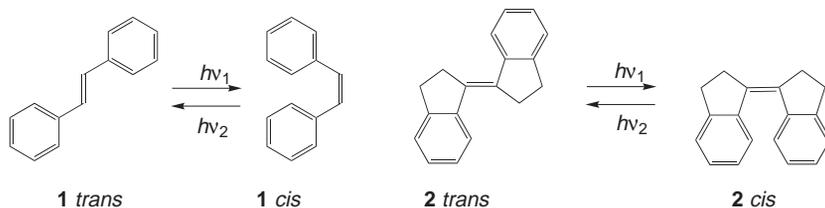
A multiscale approach is implemented through the paper because the problem as a whole cannot be treated with the same level of accuracy. Therefore, (i) the geometry of the charged molecule-SWNT complex, its electronic structure and charge transfer are studied using *ab initio* methods, (ii) the electronic structure of the SWNT is calculated within a tight-binding approximation (TBA), (iii) the tunneling and transmission coefficients are computed within semiclassical WKB approximation and (iv) the response function of the nanotube is calculated selfconsistently within a continuum statistical model.

2. Molecular Switch Design

Local gating in the proposed NLCS device will be controlled by moving a charge closer or away from the nanotube surface. This requires the ability to attach a charged molecule to the surface, and the ability to change the geometry of its charged portion. A switching molecule has to satisfy the following requirements: (i) It has to be attached to the sidewall of the nanotube, which can be considered as a large aromatic molecule, by van der Waals (or π - π) interactions. Such an attachment would greatly reduce modification of the electronic structure of the nanotube. Hence, the ideal anchor does not change the conductance of the device at all. (ii) The charged part of the molecule has to be able to move between two mechanically stable positions: far and near the nanotube surface. (iii) The choice of a mechanism of switching is dictated by the balance between the speed of device switching ON and OFF, and the stability of the ON/OFF states. The charged part of the molecule cannot be too flexible to prevent random ON/OFF switching due to the thermal motion, but it cannot be too rigid because then the energy required for switching will be too large and large-scale device integration will meet the problem of energy dissipation.

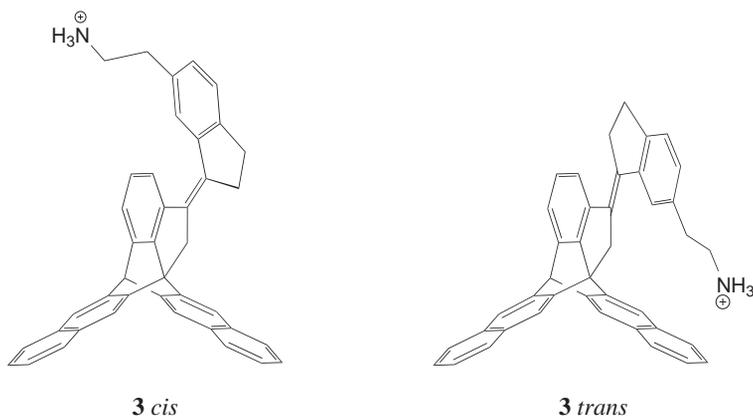
Recently, a number of reports describing a noncovalent modification of SWNT surface based on π - π interactions of electron-rich aromatic molecules with the nanotube have appeared.³ For the proposed NLCS device, in addition to providing the desired π - π interaction, the aromatic “anchor” of the molecule should provide a geometry suitable for the attachment of a charged moiety (such as a substituted ammonium cation) in a way that places it in the near proximity of the SWNT surface. A bicyclic aromatic system (see below) has been selected to function as an “anchor” in a NLCS device.

Several classes of molecular switches based on photochromic behavior, optical control of chirality, fluorescence, intersystem crossing, electrochemically and photochemically induced changes in liquid crystals, thin films, membranes, and



photoinduced electron and energy transfer have been reported.^{5,6} The fastest of the molecular switching processes are intramolecular and intermolecular electron and energy transfer, and *cis/trans* isomerization of stilbenes **1**⁶ and similar molecules appeared a suitable switching mechanism for a NLCS device. Additional rotation around single bonds of stilbenes makes their use in a NLCS device questionable, therefore, rigid 1,1'-biindanylidene **2** ("stiff stilbene")⁷ was selected for the switching part of the charged molecule.

After combining the components described above, we propose structure **3** as a prototype switching molecule. It incorporates the bicyclic aromatic "anchor" suitable for noncovalent attachment to the nanotube surface, with the photoswitchable 1,1'-biindanylidene unit carrying a charged ethylammonium moiety. The ON (*cis*) and OFF (*trans*) states in **3** can be interconverted by irradiation with UV light of 352 nm and 340 nm wavelength,^{7,8} respectively, and switching time will be on the order of 1–60 ps.⁹ The "tail" of the molecular switch has been chosen to bear a positive charge because we propose its use for modulating the transport in the p-doped nanotubes.



2.1. Geometry and charge calculation

To obtain an accurate geometrical and electronic description of a charged molecule interacting with SWNT surface we considered a zigzag [17,0] nanotube 1.3 nm in diameter interacting with the ammonium (NH₄⁺) ion. *Ab initio* and DFT methods

are presently too expensive to allow calculations of such large molecular systems. Therefore, we used the ONIOM approach,^{10,11} which consists of dividing a large molecular system into two or three levels, where a relatively small section essential for a SWNT property of interest is treated at higher level of theory, while the remaining one or two serve mostly to constrain the general geometry and are described by a computationally less demanding method (molecular mechanics or semiempirical methods).^{10,11} Recently, the ONIOM approach was used to study the addition of hydrogen and fluorine atoms to zigzag [10,0] and armchair [4,4] SWNT sidewalls^{12–14} and the amidation of terminal carboxylic groups of SWNTs.¹⁵

In the present work we used a two-level ONIOM approach^{10,11} implemented in the Gaussian 98 suite of programs.¹⁶ UFF force field¹⁷ was used for the low-level treatment, and the Becke's three-parameter hybrid method¹⁸ with the exchange functional of Lee, Yang, and Parr¹⁹ (B3LYP) was used for the high-level description, in conjunction with the 6-31G(d) basis set. The nanotube fragment we used contained 272 carbon atoms and was capped by 34 hydrogen atoms. Thirty carbon atoms were used for the high level treatment together with the ammonium (NH_4^+) ion. The minimized structure consisted of the ammonium situated 0.32 nm from the surface of the tube. The tube geometry was not significantly distorted, the average C–C bond length in the tube was 0.141 nm and its diameter was 1.33 nm. Both Mulliken and NBO²⁰ charges of the ammonium ion (+0.85 e and +0.91 e, respectively) show some degree of charge transfer from the tube to the cation. Based on the quantum mechanical calculations we concluded that the SWNT lattice will be left unperturbed by a sufficiently large charged molecule placed near the SWNT surface.

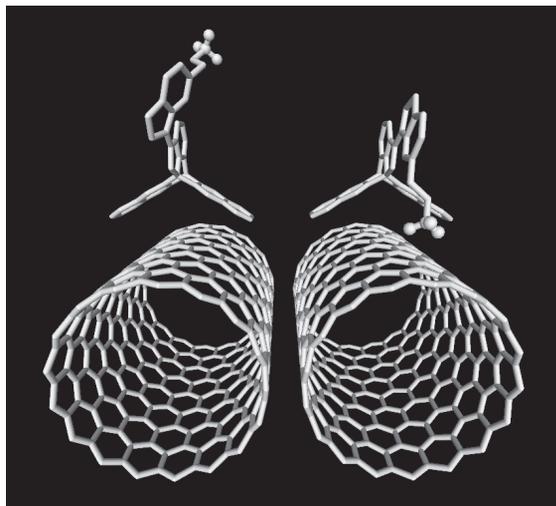


Fig. 1. Switching molecule for the local gating at the nanotube surface. Left: the ON state of the NLCS, right: the OFF state of the NLCS, the charged ammonium terminus is shown as balls.

The structures of *cis* and *trans* isomers of **3** were optimized at B3LYP/6-31G* level of theory.¹⁶ These structures were used in the optimization of the distance between the isomers of **3** and the surface of a short fragment of [17,0] nanotube described above, at HF/3-21G* level of theory.²¹ The distance from the bicyclic aromatic “anchor” of the molecule to the surface of the nanotube was found to be 0.38 nm. In the *trans* (OFF) isomer, the distance from the charged ammonium moiety to the nanotubes surface was 0.38 nm, similar to that calculated for the charged ammonium complex described above. In the *cis* (ON) isomer this distance increased to 1.58 nm. Complexes of *cis* and *trans* isomers of **3** with a SWNT fragment are shown in Fig. 1.

3. Calculation of the Valence Band Bending

The electrostatic potential of the charge near the nanotube surface depends on its position relative to the tube axis and the substrate surface. Neither the longitudinal nor the angular coordinate of the charged molecule in the complex is fixed, while the radial distance to the axis of the SWNT, ρ , was calculated in the previous section. We have demonstrated earlier²² that the potential created by a charged molecule has a short longitudinal length of several nanometers, and long weak tails, which decay as $1/z^3$. As long as the charge is at the distance of tens of nanometers from the side contacts, the influence of leads on the gating is negligible. Thus, we ignore all the contact phenomena which may appear at the leads and focus in this paper only on the change of the SWNT conductance due to the reflection of the electrons by the electrostatic potential created by the charged molecule and its image charge in a substrate:

$$q^* = q \frac{1 - \varepsilon}{\varepsilon + 1}, \quad (1)$$

where ε is the dielectric function of the substrate. For typical values of $\varepsilon \sim 12$ for Si, we can neglect the difference between the absolute value of the image charge and the original charge.

Next we consider the local band bending which is due to the subbands of the SWNT electronic structure being shifted by the electrical potential. The full quantum mechanical description of this mechanism is presented elsewhere.²³ In neglecting the mixing between subbands, which means that the angular momentum, m , is conserved, only the component of the electric potential with the full cylindrical symmetry is considered. In cylindrical coordinates, the effective potential of the charge is obtained as follows:

$$\phi^{xt}(z, R, \varphi, \rho) = \frac{q}{\sqrt{R^2 + \rho^2 + z^2}} + \frac{q^*}{\sqrt{R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2 + z^2}}, \quad (2)$$

where ρ and φ are the cylindrical coordinates of the charge, R is the nanotube radius and h is the distance between the tube axis and the substrate. The one-dimensional potential $\phi^{xt}(z)$ has a weak dependence on φ which varies in the range

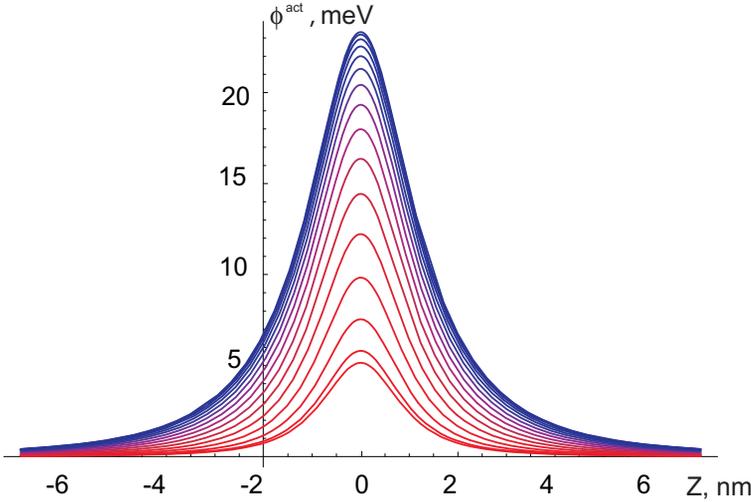


Fig. 2. Selfconsistent solution for the one-dimensional electric potential (created by a charged impurity) along the SWNT axis, z . The color of each curve (from red to blue) corresponds to the angular position of the charge (from $-\pi/3$ to $\pi/2$).

$-\pi/3 < \varphi \leq \pi/2$ (where the left inequality is restricted because the molecule is not assumed to penetrate *under* the SWNT laying on the substrate). For the charged tail of the switching molecule, as has been shown in the previous section, $\rho = R + 3.8 \text{ \AA}$ in the OFF state and $\rho = R + 15.8 \text{ \AA}$ in the ON state.

As has been demonstrated earlier,²⁴ the induced charge density in the SWNT is linearly related to the local external potential ϕ^{xt} . A similar expression was found for the full electrostatic potential ϕ^{act} , which we will call “an acting potential” hereafter. The relationship between the external and acting potentials was obtained in the selfconsistent way for the SWNT in Ref. 24:

$$\phi^{\text{act}} = \frac{C_Q^{-1}}{C_g^{-1} + C_Q^{-1}} \phi^{xt} \simeq \phi^{xt} \frac{C_Q^{-1}}{C_g^{-1}} \quad (3)$$

here we used notations $C_g = 1/(2 \log(L/R))$ and $C_Q \sim 3.2$ for the capacitance of a metal cylinder and the quantum capacitance,²⁴ respectively. The characteristic length L is given by the working length of the SWNT device, estimated as the distance between the side electrodes. Because this length is placed under the logarithm sign, the resulting depolarization factor changes only slightly and is in the range of 0.02–0.04 for almost any typical SWNT device.

Finally, the band bending as a function of the coordinate along the nanotube is given by the equation:

$$U(z) = \frac{C_Q^{-1}}{C_g^{-1}} \left(\frac{q}{\sqrt{R^2 + \rho^2 + z^2}} + \frac{q^*}{\sqrt{R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2 + z^2}} \right), \quad (4)$$

and is drawn in Fig. 2 as a function of the distance from the charged tail for different angular positions of the switching molecule. As the charge approaches the surface of the substrate, the potential decreases because the image charge potential cancels it.

4. Transmission Probability

We model now the ballistic transport of holes through the potential barrier induced by the positively charged molecule assuming that the nanotube is moderately p-doped. By expanding the acting potential near the maximum we obtain the harmonic potential barrier as follows:

$$U(z) \simeq U_0 - \frac{z^2}{2} \frac{C_Q^{-1}}{C_g^{-1}} \frac{eq}{(R^2 + \rho^2)^{3/2}} \left(1 + \frac{q^*}{q} \frac{(R^2 + \rho^2)^{3/2}}{(R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2)^{3/2}} \right), \quad (5)$$

where U_0 is the maximum value of the selfconsistent potential at $z = 0$ which reads as follows:

$$U_0 = \frac{eq}{\sqrt{R^2 + \rho^2}} \left(1 + \frac{q^*}{q} \frac{\sqrt{R^2 + \rho^2}}{\sqrt{R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2}} \right). \quad (6)$$

Using semiclassical probability for the reflection from the harmonic potential barrier²⁵ we obtain the transmission coefficient for a single molecular gate as follows:

$$\mathcal{T}_i(E) = \frac{1}{1 + \exp \left[-2\pi((E - U_0)/\hbar) \sqrt{\frac{m^*}{(\partial^2 U / \partial z^2)}} \right]}, \quad (7)$$

where m^* is an effective mass which is about 0.06 of the free electron mass.

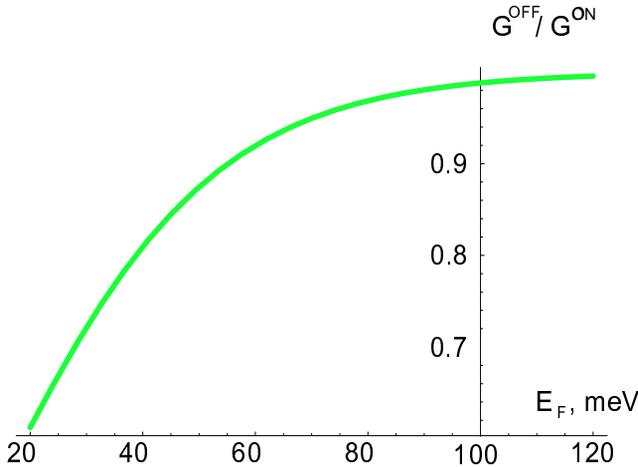


Fig. 3. Ratio of conductances of the NLCS for the switching molecule in ON and OFF states as a function of the electron energy (Fermi level).

In a ballistic regime, the conductance of the modified zigzag SWNT is given by a simple relationship:

$$G = 2G_0\mathcal{T}(E_F), \quad (8)$$

here $G_0 = e^2/h$ is the quantum of conductance. We note that the transmission probability \mathcal{T} is an exponential function of the charge-nanotube distance, ρ .

Considering the low voltage (linear) regime, the current modulation is given by the modulation of the conductance as in Eq. (8). We plot in Fig. 3 the ratio of the conductance in the ON state ($\rho = 22.3 \text{ \AA}$) and the conductance in the OFF state ($\rho = 10.3 \text{ \AA}$) as a function of the Fermi energy. This ratio is equal to 0.57 for the fixed Fermi energy $E_F = 16 \text{ meV}$, which is lower than the band edge at the maximum of the electrostatic potential in the OFF state ($U_0^{\text{OFF}} \simeq 18.2 \text{ meV}$) but higher than the band edge at the maximum of the electrostatic potential in the ON state ($U_0^{\text{ON}} \simeq 7.5 \text{ meV}$). Thus, the conductance modulation at one switching molecule can be as high as 43% for a reasonable value of the hole doping of the nanotube and other device parameters.²⁶

5. Conclusions

We propose a novel electronic device based on a carbon nanotube noncovalently modified at its surface, a Nanotube Light-Controlled Electronic Switch. We designed a molecule that operates as a nanophotomechanical switch and moves a charge closer or away from the nanotube surface under the UV irradiation. Based on the previously developed continuum theory for the local gating effect of an external charge and its influence on the ballistic transport in a single-wall carbon nanotube,²² we obtained an analytical expression for the conductance of the nanotube with a single charge scatterer. In order to calculate the nanotube valence band profile in a selfconsistent way we employed a new model of nanotube electrostatics.²⁴ *Ab initio* and DFT calculations were used to obtain the charge and optimized geometry of the switching molecule. This molecule is attached to the nanotube surface by van der Waals interactions, which do not perturb the nanotube electronic structure and do not affect its conductance. The switching molecule carries an ethylamino group that can be charged by protonation. The charged “tail” and the van der Waals anchor of the switching molecule are connected by an 1,1'-biindanylidene unit that can be *cis/trans* isomerized by UV irradiation, and thus can move the charge between two stable positions: near and far from the nanotube surface. For a single switching molecule we demonstrate that the modulation of the current through the nanotube can be ca. 40%. An experimental realization of the NLCS is attractive and will be attempted in the near future, which might require the use of a partially charged molecule, or of a molecule containing a strong π -donor, and the use of either a stilbene or an azobenzene as the *cis/trans* isomerizable unit.

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