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RAPID COMMUNICATION

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Ab initio study of transport properties of an all-carbon molecular switch based on C_{20} molecule

Abstract Choosing closed-ended armchair (5, 5) single-wall carbon nanotubes (CCNTs) as electrodes, we have investigated the electron transport properties across a carbon molecular junction consisting of a C_{20} molecule sandwiched between two semi-infinite carbon nanotubes. It is shown that the Landauer conductance of this carbon hybrid system can be tuned within several orders of magnitude not only by varying the tube-C_{20} distance, but more importantly by changing the orientation of the C_{20} molecule and rotating the C_{20} molecule or one of the tubes around the symmetry axis of the system at fixed distances. This fact could make this all-carbon molecular system a possible candidate for a nano-electronic switching device. Moreover, our study also reveals that molecular configuration selection and structural relaxation would play an important role in the design of such devices.

Keywords transport properties, C_{20} molecule, molecular junction, density-functional theory

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1 Introduction

As new techniques for the atomic-scale manipulation and modification of materials progressed, such as chemical synthesis, scanning probe microscopy and break junction techniques, the seminal idea of using molecular scale conductors as active components of electronic devices [1] has received a new impetus in recent years [2–6]. To date, special attention has been focused on atomic and molecular systems, such as organic molecules and fullerenes, because they are expected to be the ultimate size limit of functional devices and show unique behaviors that are different from those of macroscopic systems. Fullerenes are considered promising candidates for basic elements in nanoscale devices, and several examples of fullerene-based devices have been investigated both experimentally [7−10] and theoretically [11−15].

One of the most intensively studied fullerene molecules is the C_{20} molecule, which is the ground-state structure of the C_{20} clusters, within density-functional theory [16–21]. It has a relatively small gap of 0.96 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Recently, a C_{20} cage solely with pentagons has been produced from $C_{20}H_{20}$ [22], which is the smallest fullerene and one of the candidates of much smaller electronic devices. Although, the electronic transport of the C_{20}-based devices have been studied by several authors [23–26], there remains much to be learned about their electronic characteristics.

Owing to their exceptional electronic and structural properties, single- and multiple-wall carbon nanotubes (CNTs) are one of the prime targets as possible building blocks for nanoscale electronics devices, which have been extensively studied over the decade following their discovery. Recently, the resolution of the STM tips have been enhanced by attaching to them carbon nanotube (CNTs) segments [27, 28]. It has also been shown that if the CNTs are placed on a graphite substrate, the interface resistance can be tuned by changing the tube orientation on the graphite plane in- or out-of-registry, with an atomic force microscope tip [29]. This gives support to the idea that CNTs can indeed be employed as wiring elements and active device elements in molecular circuits [30–34].

In this paper, we present the *Ab initio* quantum transport

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calculations of electron transport properties across a carbon molecular junction consisting of a C_{20} molecule sandwiched between two carbon nanotubes. To the best of our knowledge, this is the first report focusing on the study of an pure-carbon molecular junction based on C_{20} cage. This choice is motivated by the recent fabrication of fullerene-based NEMS devices such as the C_{60}-amplifier and the single $C_{59}N$ molecular rectifier [10]. As the smallest fullerene, the C_{20} cage represents a useful model for typical fullerene-based devices that are at the same time numerically tractable. Our main results are the following. Surprisingly, we find that the Landauer conductance of this carbon hybrid system can be tuned within several orders of magnitude not only by varying the tube-C_{20} distance, but more importantly by changing the orientation of the C_{20} molecule and rotating the C_{20} molecule or one of the tubes around the symmetry axis of the system at fixed distances. This fact could make this all-carbon molecular system a possible candidate for a nano-electronic switching device. Furthermore, our study also reveals molecular configuration selection and structural relaxation would play an important role in the design of such devices.

2 Methods and results

First, we use closed-ended armchair (5, 5) single-wall carbon nanotubes (CCNTs) as electrodes to form the CCNT-C_{20}-CCNT hybrid system (a sketch of the device is illustrated in Fig.1). The tubes act as donor and acceptor electron reservoirs. The closed-ended CCNT is obtained by connecting the C_{60} semi-sphere to the armchair (5,5) CNT, because their diameters are almost equivalent. *S* is the axial distance between the electrodes (the axis is along the direction of the carbon nanotube wall in units of nm).

We carry out the quantum transport calculation of this all-carbon hybrid system by using an *ab initio* code package, Atomistix ToolKit (ATK) [11, 12, 35], which is based on real-space, nonequilibrium Green's function (NEGF) formalism and the density-functional theory (DFT) as implemented in the SIESTA approach [36, 37]. The main feature of the *ab initio* code package, ATK, is to model a transport nanostructure coupled to external electrodes with different electrochemical potential (corresponding to different gate voltage and bias voltage) and to realize the transport simulation of the whole two-probe system. The calculation of the complete system can be obtained from two independent calculations of the electrode regions, and a two probe calculation of the central scattering region. The electrode calculations are performed under periodical boundary conditions, with the unit cell being four atomic layers along the tube axis and the *k*-point grid being 1×1×50. The selfconsistent calculations are performed with a mixing rate set to be around 0.05, and the mesh cutoff of carbon atom is 100 Ry to achieve a balance between the calculation efficiency and the accuracy. The structural optimization is performed by using conjugate-gradient techniques and taking into account a cluster consisting of the C_{20} cage and two unit cells of the CCNTs on either side of it. To simulate the effect of the semi-infinite leads we allowed only the fullerene and the cap atoms of the tubes (nearest to C_{20}) to relax, thus defining the scattering region of Fig. 1.

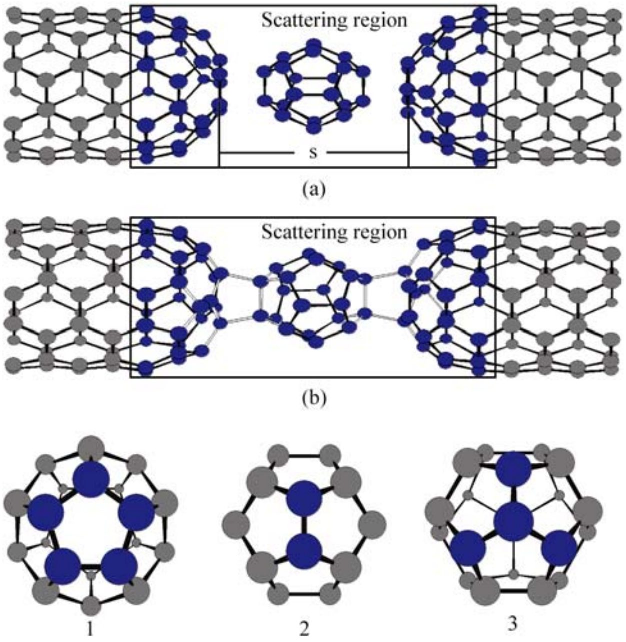

Fig. 1 Geometric configuration [**(a)** Unrelaxed; **(b)** Relaxed] of the molecular junction discussed in this paper: a C_{20} molecule bridges two closed-ended armchair (5, 5) single-wall carbon nanotubes (CCNTs). The real-line frame encloses the scattering region. The lower panel represents schematically three typical different orientations of C_{20} with respect to the surface cross sections of the nanotubes [e.g., the upper panel geometry corresponds to orientation 2].

In the following, we explore the sensitivity of the electron transport to the topology of the molecule/electrode interface in the proposed system by changing the orientation of C_{20} at a fixed tube-tube distance. Three typical orientations of the C_{20} [depicted by the polygon (s) facing the tube symmetry axis in the lower panel of Fig. 1] have been considered. Figure 2 shows their transmission spectra for both the relaxed [see Fig. 2 (b)] and the unrelaxed [see Fig. 2 (a)] structures at the zero-bias voltage. As can be seen in Fig. 2 (b), the results for the relaxed molecular junction reveal that, at the Fermi energy, configuration 2 has a transmission lower by about 3 orders of magnitude than configuration 3. Comparing what can be seen in Fig. 2 (a) and (b), it is shown that neglecting relaxation decisively influences the transmission properties of the molecular junction. Such is consistent with the previous report of C_{60} molecular junction [14]. The differences in the transmission among the different models are mostly caused by the number of atoms facing the electrodes.

Next, we find, unexpectedly, that a large variation of the conductance over 2−3 orders of magnitude can be achieved not only by rotating the C_{20} molecule but also by rotating one of the tubes around the symmetry axis at a fixed

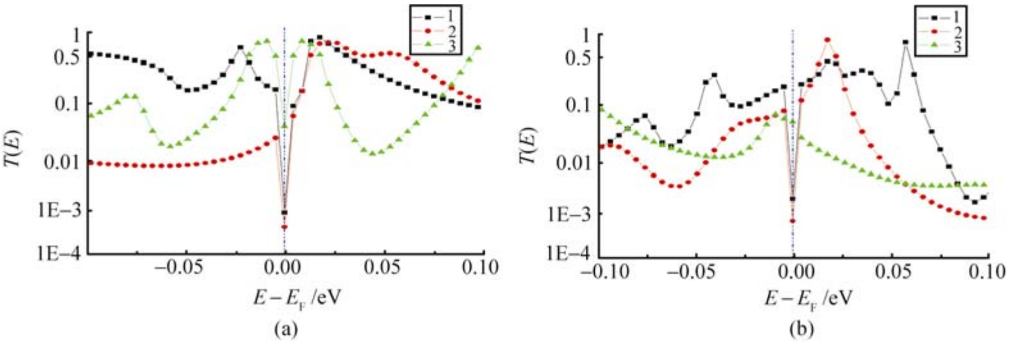

Fig. 2 Transmission spectra for both unrelaxed (*upper panel*) and relaxed (*lower panel*) configurations. *S* is fixed at 0.592 nm. Numbers indicate different molecular orientations as depicted in the lower panel of Fig. 1.

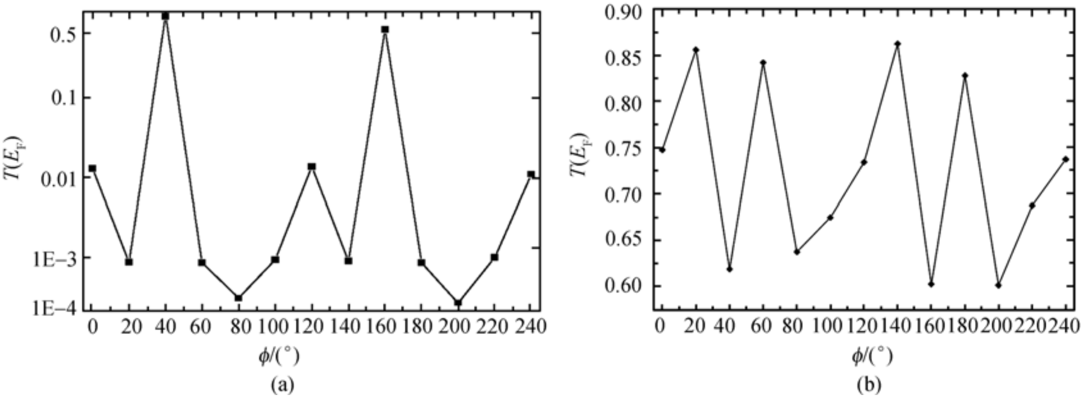

Fig. 3 **(a)** Transmission at the Fermi energy as a function of the rotation angle Φ of the C_{20} around the symmetry axis of the system. The two electrodes distance *S* is 0.592 nm and C_{20} has orientation 3 of Fig. 1. **(b)** Current (uA) at bias voltage 0.02 V as a function of the rotation angle Φ of the C_{20} around the symmetry axis of the system. The two electrodes distance *s* is 0.592 nm and C_{20} has orientation 3 of Fig. 1.

tube-C_{20} distance. Figure 3 shows the results of the dependence of the conductance upon the rotation of the C_{20} molecule and one of the tubes around the symmetry axis. As shown in Fig. 3 (a), the conductance at the Fermi energy can be tuned down by three orders of magnitude by rotating the C_{20} molecule by 20°. Simultaneously, the periodic features in the conductance are found. The rotation angle $\Phi = 0^\circ$ case corresponds to the Fermi level value of the transmission function for orientation 3 in Fig. 1. The period of oscillation of the conductivity is 120°, reflecting the symmetry of the molecule with orientation 3. When rotating one of the electrodes around the symmetry axis. It also can be found that the transmission can be tuned by three orders of magnitude(not shown). Moreover, as Fig. 3 (b) shows, we give the results of Current at bias voltage 0.02 V as a function of the rotation angle Φ of the C_{20} around the symmetry axis of the system.

A large variation of the conductance of this all-carbon hybrid system over several orders of magnitude can be achieved not only by changing the orientation of the C_{20} molecule, but by rotating the C_{20} molecule or one of the tubes respectively around the symmetry axis of the system at fixed distances. This effect could be exploited in a molecular switching device on the nanoscale, since as manipulation of fullerenes by using STM or atomic force microscope tips is becoming a standard technique in the field [7–38].

To investigate the distance dependence of the conductance for a given configuration, we collected the results of the conductances and the transmissions at the Fermi level of three different distances between the two CCNTs in Tables 1 and 2 (Table 1 for the case of the relaxed configuration 2 in Fig. 1 and Table 2 for the unrelaxed one).

Table 1 Conductances and transmissions at the Fermi level for the case of the relaxed configuration 2 with different distances between two CCNTs in Fig. 1.

S/nm	0.592	0.698	0.804
Conductances/uS	0.995 035	0.254 075	0.020 702 8
Transmissions	0.012 842 3	0.003 279 2	0.000 267 198

Table 2 Conductances and transmissions at the Fermi level for the case of the unrelaxed configuration 2 with different distances between two CCNTs in Fig. 1.

S/nm	0.592	0.698	0.804
Conductances/uS	10.698 4	3.044 01	0.166 602
Transmissions	0.138 078	0.039 29	0.002 150 23

As can be seen in Table 1, large variations in the transmission of up to 2 orders of magnitude are found for different distances. The physical origin may lay in that a reduction of *S* increases the molecule-lead coupling and leads to a strong broadening and shifting of the resonances. It also can explicitly be seen that the presented results for the distance dependence are very sensitive to the inclusion of structural relaxation and strongly differ from results for unrelaxed structures.

Different from other investigations that assume semi-infinite aluminum or Au jellium electrodes [24, 25], the absolute values of the transmission found here are small. In the former case, the high conduction property (the conductances are near $1G_0$ [25]) is attributed to a significant amount of the charge transfer from the electrodes to the molecules, which is localized at the interface between the electrodes and the molecules. In our all-carbon molecular device, however, charge transfer effects are much weaker. Thus, rather than a ballistic-like transport, tunneling through the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) Gap is the main mechanism of electronic conductance [39]. The latter is determined by the superposition of the resonance tails and for molecules with highly degenerate HOMO and LUMO manifolds such as the isolated C_{20}, an increase of this overlap can be achieved by lifting the degeneracy [40]. In our investigations, coupling to the leads changes the electronic structure of the fullerene molecule in a similar fashion. The differences in the transmission among the different models are mostly caused by the number of atoms facing the nanoelectrodes and the strength of coupling to the leads. The wave function overlap between the components at a molecular junction, which includes nanoelectrodes, sensitively depends on the exact atomic configuration [41] and, hence, the shape and the position of the molecular resonances.

3 Conclusions

In conclusion, we have investigated an all-carbon molecular nanobridge based on a C_{20} cage sandwiched between two semi-infinite closed-ended carbon nanotubes. The electronic transport in this pure-carbon electronics setup is studied in the Landauer formalism utilizing nonequilibrium Green's function (NEGF) techniques combined with a density functional theory (DFT) based approach. The transmission can be efficiently tuned not only by the rotations of the C_{20} molecule or one of the tubes but also by varying the tube-C_{20} distance. This fact would make this all-carbon hybrid system a possible candidate for a nano-electronic switching device. In addition, it is demonstrated that the conductance of such molecular devices strongly depends on the structural relaxation of the junction, and the molecular configuration selection and structural relaxation may not be neglected in the design of such molecular switching devices. We hope that our observations may stimulate corresponding experimental analysis.

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