

Contact Transparency of Nanotube-Molecule-Nanotube Junctions

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The transparency of contacts between conjugated molecules and metallic single-walled carbon nanotubes is investigated using a single-particle Green's function method which combines a Landauer approach with *ab initio* density functional theory. We find that the overall conjugation required for good contact transparency is broken by connecting through a six-member ring on the tube. Full conjugation achieved by an all-carbon contact through a five-member ring leads to near perfect contact transparency for different conjugated molecular bridges.

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To create a well-defined molecule-electrode contact with good transparency is one of the greatest challenges in molecular electronics [1]. Control of the contact structure between an organic molecule (like benzenedithiol) and a metal electrode (like gold) is difficult because bonding to metal atoms, although potentially strong, is not strongly directional. This leads to poor reproducibility of most metal-molecule-metal junctions [2–4]. A natural path to improvement is to use semiconductors as electrodes [5] as they can provide a well-defined contact structure through directional covalent bonds. Alternatively, carbon nanotubes (CNTs) have become a very promising material for nanoelectronics because of their robust structure and rich electronic properties [6]. Using metallic CNTs, which still have directional covalent bonds, for connecting to molecules combines the best features of both approaches. In particular, one expects conduction from the π -bonded network of the CNT through the π -bonded molecular orbital of the conjugated molecule to be good. Recently, there was an experimental report [7] on attaching cut single-walled CNTs to molecules through amide linkages. The measured conductance for various molecules showed, however, poor contact transparency, which was unexplained.

Here we use quantum conductance calculations to uncover the source of the poor transparency in the experiment and point to a way around it. Our calculations adopt an *ab initio* single-particle Green's function method [8,9]. We first study the experimentally proposed connection through an amide anchoring group [7] by linking a benzene molecule across a gap in a (5,5) CNT [10,11]. We find that the contact transparency is poor because the structure mismatch destroys the overall conjugation. This is consistent with the experimental report of very small conductance for various conducting molecules [7].

We then study possible junctions with an all-carbon connection, looking for better contacts. This is motivated by recent experimental progress in synthesizing all-carbon CNT-molecule connections by reliable organic and organometallic methods [12,13]; indeed, conducting polymers can be grown from the end of a cut CNT [14]. We study junctions involving various conjugated molecules: simple

benzene as well as units of the conducting polymers polypyrrole (PPR), polythiophene (PTP), and oligo-phenyleneethynylene (OPE). We find, first, that a direct connection to a 6-member ring of the open end of the CNT leads to the tube wall and the molecular plane being nearly *perpendicular* because of the large repulsion between the saturant side groups on both the CNT end and the molecule. This configuration destroys the overall conjugation and leads to poor contact transparency. In contrast, a connection through a 5-member ring on the CNT decreases significantly the twisting force and yields a nearly *parallel* and *in-plane* configuration. This preserves the overall conjugation and leads to a contact transparency which is nearly perfect.

To investigate electron transport through the molecular junctions, we adopt a standard single-particle Green function method [8,9] which combines a Landauer approach with *ab initio* density functional theory (DFT) [15]. In practice, the infinitely long system is divided into three parts: left lead, right lead, and device region; the latter contains the molecule plus large parts of the CNT to accommodate the molecule-CNT interaction (Fig. 1). The self-consistent Kohn-Sham Hamiltonian of the device region and the self-energies of the two semi-infinite CNT leads are used to construct a single-particle Green function from which the transmission coefficient at any energy is calculated. The conductance G then follows from a Landauer-type relation.

This standard approach has recently been criticized [16], particularly in the case of weakly coupled molecules or bonding between very unlike materials. Since in our case all the components are organic and the coupling should be strong, we expect the approach to be adequate for the qualitative issues on which we concentrate.

The computational techniques have been described in detail previously [8]. Briefly, for the DFT electronic structure calculation, we use a numerical basis set to expand the wave functions [17]. A double zeta plus polarization basis set is adopted for all atomic species. We make use of optimized Troullier-Martins pseudopotentials [18] for the atomic cores. The Perdew-Burke-Ernzerhof (PBE) version

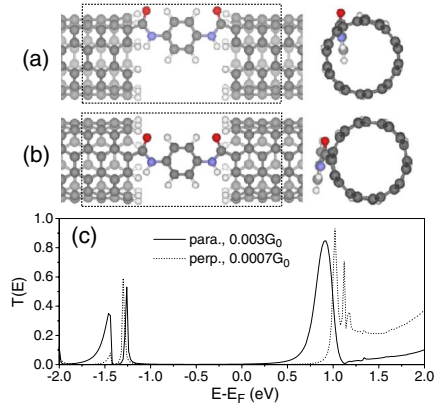


FIG. 1 (color online). Optimized structures of the (5,5)CNT-benzenediamide-CNT junction in (a) perpendicular and (b) parallel configurations, along with (c) their transmission functions. The two configurations have almost the same energy. The device region is indicated by the dashed frames; the equilibrium conductance is in the legend in units of $G_0 = 2e^2/h$. Note the poor transmission over a wide window around E_F .

of the generalized gradient approximation (GGA) [19] is used for the electron exchange and correlation. The atomic structure of the junctions (including the molecule-CNT separation) are fully optimized by minimizing the atomic forces on the atoms to be smaller than $0.02 \text{ eV}/\text{\AA}$.

Let us start with the amide anchoring group (CONH) used in the experiment [7]. There, a gap in a single-walled CNT was created by oxidative cutting which produces a carboxylic acid terminated end, leading to amide linkages upon reaction with molecules. Here we consider the simple case of a benzene molecule bridging the gap (Fig. 1) [10,11]. We find two optimized structures with almost the same binding energy (difference $< 0.01 \text{ eV}$), one in which the plane of the molecule and the surface of the CNT are nearly *parallel* and one in which they are nearly *perpendicular*. Both configurations yield a very small conductance, consistent with the experiments on several molecules. The conductance in the perpendicular configuration is smaller because the networks of π bonds in the CNT and benzene do not match. The parallel configuration, while it gives a larger conductance, also cannot provide a good match because the molecular plane is considerably above the surface of the CNT (i.e., *off-plane*).

To keep the overall conjugation, next we consider all-carbon connections. These can be created using reliable organic and organometallic methods [12,13]. For example, starting with the carboxylic acid terminated CNT, the acid groups can be converted to bromide groups via treatment with PPh_3Br_2 followed by rhodium-catalyzed decarboxylation. Finally, palladium-catalyzed cross-coupling with 2-tributylstannyl-3,4-thiophene will form the 3,4-thiophene-terminated CNT.

First we consider a connection directly through a 6-member ring of the CNT end. Calculations for three bridging molecules— C_6H_4 , two units of PPR, and two units of PTP—are shown in Fig. 2. Because of the strong repulsion

between the H atoms on the molecule and on the CNT end, the binding energy of the parallel configuration is much higher than that of the perpendicular one (by several eV). Therefore, we only consider the latter case. The transmission functions in Fig. 2(d) show, as expected, that the contacts are not transparent.

A natural way to reduce the twisting force causing the perpendicular geometry is to increase the distance between the edge of the CNT and the molecule. Here we propose a simple route to achieve this: make the connection through a 5-member ring on the CNT, or in other words, through an apex C atom. The fully optimized structures of three junctions in Fig. 3 show that all of the junctions are in the *in-plane* parallel configuration, confirming the intuitive idea that increased separation reduces the twisting force. The parallel configuration preserves the overall conjugation and therefore should lead to very good CNT-molecule coupling. However, there are two points which need to be carefully considered before turning to $T(E)$.

First, for connections through a charge neutral 5-member ring, our calculations yield local spin polarization connected to the nominally unpaired p_z electron on the apex C atom. For benzene, this polarization lowers the energy by 0.07 eV . The two configurations of the local spins, parallel and antiparallel, are degenerate in energy because of the very weak interaction through the molecular bridge. Figures 3(d) and 3(e) show the corresponding transmission functions; note the large broad resonant peak near the Fermi energy for both spin components in both spin

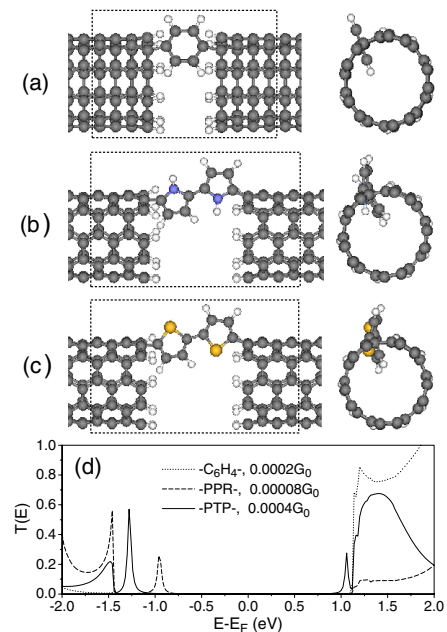


FIG. 2 (color online). Structures with all-carbon connections from 6-member rings of (5,5) CNTs to (a) C_6H_4 , (b) two units of polypyrrole (PPR), and (c) polythiophene (PTP), as well as (d) their transmission functions. Only the perpendicular configuration is shown as it is much more stable. The transparency is poor in all three cases.

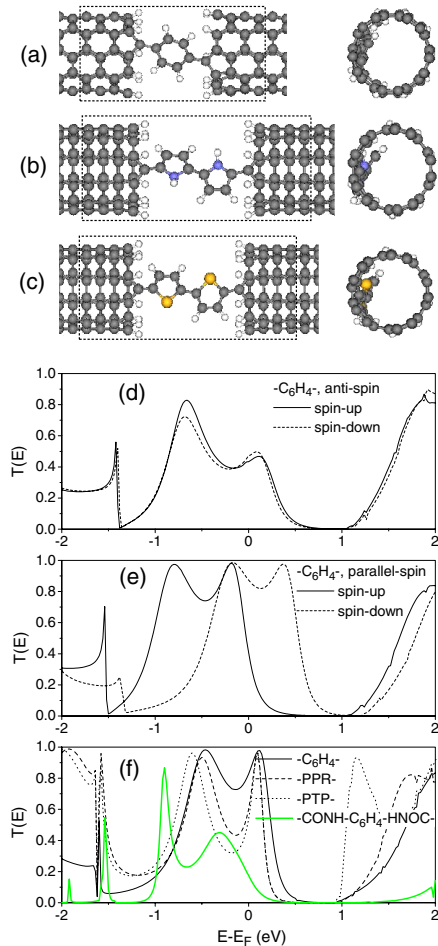


FIG. 3 (color online). Structures with all-carbon connections from 5-member rings of (5,5) CNTs to (a) C_6H_4 , (b) polypyrrole (PPR), and (c) polythiophene (PTP). Only the much more stable parallel configuration is shown. (d), (e) Transmission function of charge neutral benzene for the two spin configurations. (f) Transmission functions of the three systems under doping. Note the excellent transparency near E_F . $T(E)$ for an amide-linked benzene system is also shown in (f).

configurations. This broad resonant peak also exists for the PPR and PTP systems (not shown); it is the signature of strong coupling totally changing the electronic structure of the molecule (see also discussion about longer molecules below). In contrast, for weak coupling, E_F should be in the HOMO-LUMO gap [see Fig. 2(d)] because the molecule-lead charge transfer is small.

Second, we show that the local spin polarization can be compensated by doping the CNTs. Experimentally, doping could be achieved either chemically with alkali atoms or by applying a back-gate voltage. To simulate this, we dope the junction with two electrons which are then compensated by an equivalent background charge spread uniformly over the whole extended molecule. We find that doping indeed leads to additional charge around the two apex C atoms which compensates the local spin. The transmission functions for junctions with doping are shown in Fig. 3(f). For benzene, the broad resonance around the Fermi energy

remains. When two units of PPR or PTP form the molecular bridge, the resonance peaks are similar to those of benzene. We find, then, that the simple idea of connecting through a 5-member ring works extremely well: the contact transparency is nearly perfect.

An interesting thing here is to go back and see if the 5-member-ring connection also helps for the amide linkage. Our calculation for benzene shows that this leads to, indeed, a near parallel in-plane configuration similar to those shown in Figs. 3(b) and 3(c). The transmission function given in Fig. 3(f) [the thick green (or gray) line] shows that the contact transparency is significantly improved (compared to Fig. 1) though it is not as good as for the all-carbon connection.

The generality of the above conclusions is further supported by results on (1) miscut tubes and (2) longer molecules. On the first point, while the results above involve a metallic armchair CNT with a regular (flat) end, in the experiments the CNT may not be metallic or have a regular end. We investigate these two possibilities by considering (Fig. 4) a benzene molecule bridging a diagonally cut gap of a (5,5) CNT and a flat gap of a semiconducting (9,0) CNT. In both cases, the CNT terminates in a zigzag edge with 6-member rings. The optimized structures show that in both cases the twisting force is quite strong (although not as strong as for an armchair termination, Fig. 2), and the contact atomic configuration is of the perpendicular type. As a result, there is a large gap in $T(E)$ around E_F [much larger than the small intrinsic gap of the (9,0) tube]. Notice that $T(E)$ of the two junctions are very similar although the two tubes are quite different, indicating that the transport is dominated by the connection at the contact.

With regard to longer molecules, the large conductance obtained for short conjugated molecules using a 5-member ring connection should not necessarily hold for long molecules: their HOMO-LUMO gap may give rise to a long tunneling barrier which the strong coupling to the leads does not overcome. In order to separate clearly the effects

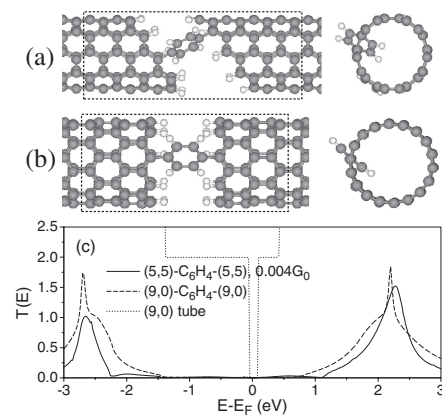


FIG. 4. Connections to zigzag CNT ends. Benzene connected to (a) diagonally cut (5,5) tubes, and (b) (9,0) tubes. Their transmission functions are given in (c) together with that of a perfect (9,0) tube (dotted line).

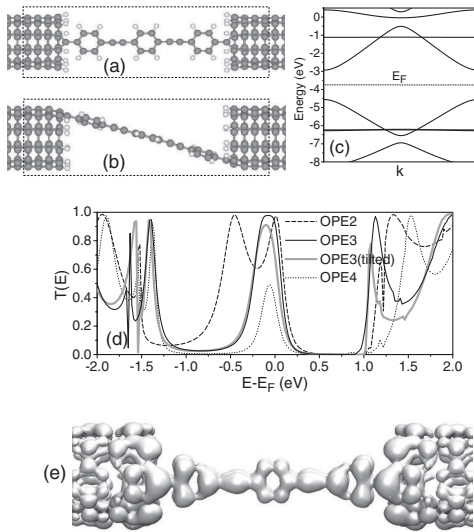


FIG. 5. Optimized structures for (a) straight and (b) tilted junctions of (5,5)-C-OPE3-C-(5,5). (c) Band structure of the uniform OPE chain. (d) Transmission functions of the doped junctions. (e) Local density of states in the energy window $[-0.5 \text{ eV}, 0.5 \text{ eV}]$ for the junction in (a). Note that the peak around $T(E_F)$ decays when the molecule gets longer.

of the contact from those of the molecule, we consider a conjugated OPE molecule of varying length—OPE $_n$ with $n = 2, 3$, or 4—connected to the CNT through a 5-member ring. An optimized structure is shown in Fig. 5(a). The HOMO-LUMO gap of an OPE decreases as its length increases; an infinitely long OPE chain has a band gap of $\sim 1.5 \text{ eV}$ (DFT-GGA), as shown in Fig. 5(c). Figure 5(d) shows that the resonance in $T(E)$ around the Fermi energy shrinks when the molecule gets longer. When the molecule is short (OPE2 and OPE3), strong coupling allows lead states tunneling into the molecule to meet in the middle (sometimes called metal-induced gap states), causing a resonance near E_F despite the gap of the isolated molecule. As the molecule gets longer, such tunneling is suppressed, and the molecular HOMO-LUMO gap will gradually dominate: The peak is indeed significantly narrowed for the longer OPE4 shown in Fig. 5(d). The local density of states (LDOS) in Fig. 5(e) further confirms this picture: the LDOS around the contacts is significantly modified while on the middle ring it is closer to that of the isolated molecule.

When the molecule becomes long enough, the molecular bridge may not be straight but rather become tilted, as in Fig. 5(b). The calculated $T(E)$ in Fig. 5(d) shows that this change in geometry does not affect conductance significantly, at least for thin CNTs.

Finally, although we have presented results for thin CNTs and narrow conjugated molecules, we mention that the conclusion also holds for CNTs with a large diameter and for some wide molecular bridges [20]. Experimentally,

once two CNT-molecule contacts with good transparency are created, other functional molecules can be inserted or grown in between. We also note that the carriers in conducting polymers are usually solitons or bipolarons rather than electrons or holes; the contact transparency studied here is related to the carrier conversion that would occur near the contacts in a CNT-conducting polymer-CNT system.

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