Electronic transport in oligo-*para*-phenylene junctions attached to carbon nanotube electrodes: Transition-voltage spectroscopy and chirality

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We have investigated, by means of a nonequilibrium Green's function method coupled to density functional theory, the electronic transport properties of molecular junctions composed of oligo-*para*-phenylene (with two, three, four, and five phenyl rings) covalently bridging the gap between metallic carbon nanotubes electrodes. We have found that the current is strongly correlated to a purely geometrical chiral parameter, both on-resonance and off-resonance. The Fowler-Nordheim plot exhibits minima, V_{min} , that occur whenever the tail of a resonant transmission peak enters in the bias window. This result corroborates the scenario in which the coherent transport model gives the correct interpretation to transition voltage spectroscopy (TVS). We have shown that V_{min} corresponds to voltages where a negative differential resistance (NDR) occurs. The finding that V_{min} corresponds to voltages that exhibit NDR, which can be explained only in single-molecule junctions within the coherent transport model, further confirms the applicability of such models to adequately interpret TVS. The fact that the electrodes are organic is at the origin of differences in the behavior of V_{min} if compared to the case of molecular junctions with nonorganic contacts treated so far.

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I. INTRODUCTION

Advances in molecular electronics necessarily require a thorough understanding of electronic transport properties in single-molecule devices.¹⁻³ This generally constitutes a challenging task, since the current through single-molecule junctions depend on several factors such as the molecular conformation and length, the nature details of the electrodes, environmental aspects (e.g., UHV, temperature, stress), and the electronic structure of the molecule itself. In particular, the energy difference between the frontier molecular orbitals to the electrodes Fermi level plays a crucial role in electronic transport in molecular junctions and may be determined from the resonant peaks in the conductance curve. A major hurdle in extracting this spectroscopic information from transport measurements is that the bias voltage required to induce resonant tunneling through typical single-molecule junctions is of the order of several volts, resulting in large electric fields and hence leading to the breakdown of the junction. An important progress toward circumventing this difficulty has been achieved by the development of transition voltage spectroscopy (TVS).^{4,5} The purpose of TVS is to extract the position of the frontier molecular orbital from the currentvoltage (I-V) characteristics, even though the bias voltage necessary to resonance tunneling has not been achieved. In single-molecule junctions with gold contacts, the plot of $\ln(I/V^2)$ versus 1/V, the so-called Fowler-Nordheim (FN) graph, exhibits a minimum V_{\min} that has been shown to be linearly proportional to the difference between the Fermi energy of the electrodes and the highest occupied molecular orbital (HOMO) level, where the gap was measured by ultraviolet photoelectron spectroscopy.⁵ Since FN graphs allows one to determine V_{\min} at not so large voltages,

i.e., before the breakdown of the junction, TVS has been employed as a versatile spectroscopic technique in molecular electronics. $^{4,6-10}$

Despite the large applicability of TVS in single-molecule electronics, the underlying physical mechanism of TVS is still under debate.^{11–13} The original interpretation of TVS is based on Simmons model,^{4,5} where the electronic transport through molecular junctions is treated as a tunneling process. Within this model, the TVS minimum V_{\min} characterizes a transition in the transport mechanism, induced by the application of an external bias voltage, from tunneling to field emission. As a result, the shape of the tunneling barrier changes from trapezoidal to triangular. However, the interpretation of TVS based on Simmons model has been criticized by Huisman et al., who have argued that it does not agree with experimental data; they have showed that experimental results are better explained by the coherent molecular transport model instead.¹¹ Within this model, electronic transport occurs by the occupation of molecular levels and it is described by the energy-dependent transmission function. Theoretical calculations have revealed that the coherent molecular transport model indeed captures the physics necessary to correctly interpret TVS.¹¹⁻¹³ According to the coherent transport model $V_{\rm min} \propto E_F - E_{\rm HOMO}$, the energy gap between the Fermi level of electrodes E_F and the HOMO energy level of the molecule, provided $|E_F - E_{HOMO}| \gg \Gamma$, where Γ is associated with the coupling between the molecule and the electrodes.¹⁴ This condition is usually satisfied for nonorganic electrodes (e.g., gold) that are typically employed in single-molecule junctions. The validity of the relation $|E_F - E_{HOMO}| \gg \Gamma$ hence guarantees the applicability of TVS as an spectroscopic tool.¹¹

So far, all experimental and theoretical efforts to interpret TVS have dealt with nonorganic electrodes. However, many theoretical calculations on this topic suffer the welldocumented limitation of DFT in correctly describing the alignment of the Fermi level of nonorganic electrodes and the frontier molecular orbitals [see for instance Ref. 15 and references therein], inducing errors in the description of charge transfer between the molecule and nonorganic contacts. This difficulty can be circumvented by considering molecular junctions with organic electrodes, where the molecule-leads electronic coupling naturally occurs via the carbon-carbon covalent bond. Examples are a carbon chain¹⁶ or a biphenyl molecule attached to carbon nanotubes (CNTs).¹⁷ Considering organic electrodes thus facilitates the mismatch between the Fermi level of the leads and the frontier molecular orbitals of the central molecule, dispensing the use of a "clip-alligator" molecule to mediate the coupling.

With this motivation in mind, we present an analysis of TVS in systems of oligo-*para*-phenylene attached to metallic CNT electrodes. In view of the previous arguments, this system could be regarded as an ideal testbed to investigate TVS. In addition, the employment of CNT electrodes¹⁸⁻²⁰ offers many advantages if compared with usual organic electrodes since they exhibit many advantages in comparison to ordinary metallic contacts: they show higher conductivity,²¹ permit better contact to organic molecules,²⁰ and reduce the screening of the gate electric fields due their smaller size.¹⁹ Furthermore, recent advances in nanofabrication techniques permit a precise control of the gap size in between the CNT leads,²² which is crucial in the development of single-molecule junctions. Previously, we have shown that the current-voltage characteristics of a molecular junction composed of a biphenyl molecule attached to metallic carbon nanotubes is strongly correlated to the behavior of $\cos^2 \theta$ (θ being the twist angle between neighboring aromatic rings),¹⁷ in agreement with measurements of a series of biphenyl junctions.²³ Also, we have demonstrated that $\cos^2 \theta$ is proportional to a purely geometrical chiral parameter, revealing the importance of molecular conformation in the transport properties of these systems.¹⁷ In the present paper we demonstrate that the connection between the chiral parameter also holds for larger molecular junctions, composed of more than two phenyl rings. By means of a nonequilibrium Green's functions (NEGF) method coupled to density functional theory, we demonstrate that the FN plot exhibits a minima, V_{\min} , that occurs whenever a resonance in the (I-V) characteristics is reached, a result that agrees with the coherent transport model to interpret the transition voltage spectroscopy. We find that V_{\min} also corresponds to the positions where negative differential resistance (NDR) occurs. The fact that the electrodes are organic is at the origin of differences in the behavior of V_{\min} if compared to case of molecular junctions with nonorganic contacts treated so far.

This paper is organized as follows. In Sec. II we describe the electronic transport calculations and detail the methodology used. Section III is devoted to the discussion of TVS, whereas Sec. IV deals with results concerning the geometrical degree of chirality of the system. Finally, Sec. V is reserved for the conclusions.

II. TRANSPORT CALCULATIONS AND METHODOLOGY

We investigate the electronic transport properties of singlemolecule junctions composed of n-phenyl rings (up to five) as a finite central bridge and resistive region and two CNTs as semi-infinite leads with different chemical potentials. The model geometry of the system under study is depicted in Fig. 1.

The DFT²⁴ coupled to the NEGF formalism has been demonstrated to be highly reliable in describing electronic transport properties of single-molecule devices.^{17,25–27} As other methodologies,²⁷ our calculation procedure is developed to determine the electronic properties of molecular junctions attached to very large electrodes (reservoirs). To calculate the *I-V* characteristics of CNT-*n*-phenyl-CNT, we utilize first-principles calculations based on DFT coupled to an NEGF methodology implemented in FORTRAN code as previously presented,²⁶ as well as the SIESTA package.²⁷

The calculations employ the local density approximation (LDA) and with norm-conserving pseudopotentials. Single- ζ pseudoatomic orbital basis set were employed as it is recommended for CNTs. Also, larger basis set were tested but no qualitative results were found. The Hamiltonian matrices are constructed for the left and right leads from standard first-principles calculations on bulk periodic device for a semi-infinite region. To reach the self-consistency, the charge density is determined by integrating the contributions from scattering states between the lead's chemical potentials given by the Fermi-Dirac distribution. This procedure will lead to a different charge density until the self-consistency is achieved.

Before performing the transport calculations in the junctions, we have investigated the transport properties of individual capped CNTs separately. We have verified that the CNTs are metallic, exhibiting ohmic and nonresonant behavior. This results confirms that the CNTs can be considered bulklike and hence adequate to be employed as electrodes in a Landauer transport calculation.

The current calculation is composed of two procedures, with molecular relaxation of the organic structure done by quantum mechanical methodologies with specific functional and basis set, both the LDA and the generalized gradient approximation (GGA), as presented in previous works.¹⁷ Similar results for the total energy calculations have been obtained using the first-principles methodology in the framework of DFT using SIESTA,²⁸ within the generalized grad-



FIG. 1. (Color online) Model geometry for DFT + NEGF calculations consisting of a oligo-*para*-phenylene (with three phenyl rings) bridging the gap between single-wall metallic carbon nanotubes. In this work we have considered systems with up to five phenyl rings.

dient approximation for the exchange-correlation potential due to Perdew, Burke, and Ernzerhof.²⁹ The electron-ion interactions are described using ab initio norm-conserving fully separable Troullier-Martins pseudopotentials³⁰ in the Kleinman-Bylander form.³¹ The Kohn-Sham wave functions are expanded in combinations of pseudoatomic numerical orbitals. Double- ζ basis sets including polarization functions (DZP) are employed to describe the valence electrons.³² To guarantee a good description of the charge density, a cutoff up to 200 Ryd for the grid integration was utilized to project the charge density in real space and to calculate the self-consistent Hamiltonian matrix elements. All geometries were optimized until the remaining forces were less than 0.01 eV/Å in conjugate gradient coordinate optimization. Eight special k points were used for Brillouin zone sampling. To simulate the molecular junction, each optimized molecule, including the carbon atoms of the leads, were translated into a semi-infinite junction with several carbons and the supercell consists of two metallic zigzag carbon nanotubes as the left and right layers (with hundreds of atoms) and the *n*-phenyls bridging them. In the beginning of the calculation, the molecule is allowed to freely relax with the application of external bias and a structural rearrangement of the whole junction occurs as a result of the optimization procedure of the *ab initio* calculation. Therefore, there is an optimized molecular configuration and a torsional angle θ for each value of the applied bias. All atoms are relaxed, including a very tight optimization process, resulting in a force field less than 0.11 eV/Å. For the NEGF formalism, the electronic current is calculated after molecular relaxation by applying an external voltage V_e ranging from 0.0 V up to 1.1 V between the leads. The current is given by the Landauer-Büttiker formula³³:

$$I(V_e,\theta) = \frac{2e}{h} \int_{U_L(V_e)}^{U_R(V_e)} T(E, V_e, \theta) dE, \qquad (1)$$

where $T(E, V_e, \theta)$ is the transmission coefficient at energy E, $U_R(V_e)$ and $U_L(V_e)$ are the energies corresponding to the right and left leads, respectively.

III. ELECTRONIC TRANSPORT AND TRANSITION VOLTAGE SPECTROSCOPY

In Fig. 2 we exhibit the FN graph, $\ln(I/V^2)$ versus V^{-1} for oligo-para-phenylene molecules, composed of two, three, four, and five phenyl rings, attached to metallic CNTs. We have found from this figure that the calculated FN graphs exhibit a similar behavior as the experimental curves obtained for molecular junctions with nonorganic (Au) electrodes.⁵ The FN graphs shows a voltage minimum V_{\min} , after which the behavior is almost linear. The TVS minimum V_{\min} is found from the minimum of the FN graph. The inset of Fig. 2 shows the current-voltage (I-V) characteristics for the system composed of three phenyl rings. From the inset one identifies three voltages (indicated by circles at applied bias around 0.77, 0.90, and 1.03 V) where NDR occurs, i.e., a nonohmic behavior in which the current decreases with increasing bias voltage. Figure 2 reveals that V_{\min} in the FN graph correspond to voltages where NDR occur. We have verified that the correspondence between V_{\min} and the voltages where NDR occurs also holds for all other junctions we have considered.



FIG. 2. (Color online) Fowler-Nordheim (FN) graph for oligopara-phenylene composed of two (blue circles), three (dark blue lozenges), four (red triangles), and five (green stars) phenyl rings. The inset exhibits the current-voltage characteristics for system composed of three phenyl rings. The points labeled by circles correspond to voltages where negative differential conductance occurs, which coincide with the minima in the FN graph.

In general, the number of minima in the FN graph corresponds to the number of NDR in the I-V characteristics. In particular, for the system with three phenyl rings, there are three voltages where NDR occurs and, correspondingly, three minima in the FN graph (indicated by circles in Fig. 2). It is important to mention that NDR has been recently demonstrated, by means of *ab initio* calculations, to arise from the formation of monatomic carbon chains in molecular junctions with CNTs electrodes¹⁶ and also show up here in junctions composed of oligo-*para*-phenylene molecules attached to CNTs.

In order to understand the physical origin of NDR and its connection to V_{min} , in Fig. 3 the transmission coefficient as a



FIG. 3. (Color online) Transmission coefficients for the junctions composed of three rings of oligo-*para*-phenylene attached in CNTs as a function of energy for several different values of the external applied voltage V_e .

function of energy is exhibited for several values of the applied bias for the system composed of three phenyl rings. The NDR can be explained by noting that the effect of varying the bias voltage around V_{\min} is twofold. On the one hand, as the bias voltage increases before reaching the value V_{\min} , more resonant peaks enter in the bias window, contributing to an initial increase of the current. On the other hand, the increase of the bias voltage around V_{\min} also leads to a simultaneous decrease in the height of the transmission peak near the Fermi energy, which gives the largest contribution to the current. This can be seen by comparing the height of the transmission peaks near the Fermi energy at 0.32 V (well below $V_{\min} = 0.77$ V), 0.83 V (around V_{\min}), and 0.96 V (above V_{\min}): the height is large at low voltage, minimum around V_{\min} , and increases again above V_{\min} . As a result, this reduces the contribution, around the V_{\min} , of the resonant peak near the Fermi to the current in Eq. (1). Hence the net effect is an overall drop in the current and the onset of NDR around V_{\min} . A similar explanation for NDR also applies to linear chains of carbon atoms attached to CNTs leads.¹⁶ Furthermore, it is important to note in Fig. 3 that V_{\min} corresponds to vicinities of resonances below the HOMO level. More precisely, we have verified that V_{\min} occurs whenever the tail of a transmission peak enters in the bias window, as one can see by the position of the peak at $V_{\min} = 0.77$ V relative to lower limit of the bias window at this voltage. This result agrees with recent theoretical predictions based on the coherent transport model¹² and therefore corroborates with the scenario in which this model offers the correct interpretation to TVS.

The behavior of V_{min} as function of $E_F - E_{\text{HOMO}}$ and the molecular length is shown in Fig. 4. The energy of the HOMO level is determined by the position of the first maximum of the transmission coefficient below the Fermi level of the electrodes. In the *ab initio* calculation, the variation of the external bias voltage was conducted by use of discrete steps. The error bars in Fig. 4 correspond to these variations,



FIG. 4. (Color online) Fowler-Nordheim minimum voltage, V_{\min} , as function of (a) $E_F - E_{\text{HOMO}}$ (solid black triangles) and (b) length of the system (solid blue squares). The numbers on each point correspond to the number of phenyl rings in the molecule. (b) The energy gap (open red circles) between the Fermi level of the CNTs electrodes and the position of the HOMO level of the molecule as a function of the molecular length.

which are not homogenous. As a result, the error bars have different sizes. From the analysis of Fig. 4, one can see that V_{\min} is independent of length for molecules longer than 1.3 nm, i.e., for molecules composed of more than three phenyl rings. The fact that V_{\min} does not depend on the molecular length after a critical length qualitatively agrees with recent experiments.⁴ Figure 4 also reveals that the behavior of V_{\min} as a function of the energy difference between the Fermi energy of the CNTs electrodes and the HOMO energy of the central molecules, $E_F - E_{HOMO}$, is not strictly linear. The coherent transport model predicts that $V_{\min} \propto E_F - E_{HOMO}$ provided that $|E_F - E_{HOMO}| \gg \Gamma$, where Γ is associated with the electronic coupling between the molecule and the electrodes.¹⁴ This condition is not fulfilled in the system under study since, being organic, the electrodes permit a better electronic coupling to the molecular bridge, in contrast to what usually occurs for typical nonorganic (e.g., gold) electrodes. As a result, here the value of Γ is larger than it would be for typical molecular junctions composed of nonorganic electrodes, so the condition $|E_F - E_{HOMO}| \gg \Gamma$ for the occurrence of a linear relation between V_{\min} and $E_F - E_{HOMO}$ is not satisfied. On the other hand, the better coupling between the molecular bridge and the electrodes would permit a higher stability of the junction,²⁰ allowing for the application of higher values of the external voltage before a mechanical breakdown of the junction. Finally, it is important to mention that, as the coupling between the central molecules and the electrodes is strong, the *ab initio* calculations are less sensitive to the specific DFT exchange-correlation model used.³⁴ As a result, our results would not be significantly modified by the use of other functional instead of LDA.

IV. GEOMETRICAL DEGREE OF CHIRALITY AND MOLECULAR TRANSPORT

The aim of this section is to investigate if there exists a connection between the geometrical degree of chirality ψ and the transport properties of the oligo-*para*-phenylene attached to CNTs. The strong correlation between ψ and the *I-V* characteristics of single-molecule junctions composed of PPV²⁵ and biphenyl derivatives¹⁷ was recently unveiled, suggesting that it constitutes a more general trend in molecular electronics. In order to test this hypothesis we employ the chiral index ψ , introduced to determine the degree of chirality of molecules composed of a single atomic species, defined in Ref. 35 according to

$$\psi = Q^{il} B^{jm} \epsilon_{ijk} S^{klm}, \qquad (2)$$

with ϵ_{ijk} the Levi-Civita tensor. In Eq. (2) the tensors *S*, *B*, and *Q* are given by

$$S^{klm} = \sum_{\alpha} \left[r_{\alpha}^{k} r_{\alpha}^{k} r_{\alpha}^{l} - \frac{1}{5} (r_{\alpha})^{2} \left(r_{\alpha}^{k} \delta^{lm} + r_{\alpha}^{l} \delta^{km} + r_{\alpha}^{m} \delta^{kl} \right) \right],$$

$$B^{ij} = \psi_{B} \left(e_{1}^{i} e_{1}^{j} - e_{2}^{i} e_{2}^{j} \right) \equiv \psi_{B} \widetilde{B}^{ij},$$

$$Q^{ij} = \psi_{Q} \left(e_{3}^{i} e_{3}^{j} - \frac{1}{3} \delta^{ij} \right) \equiv \psi_{Q} \widetilde{Q}^{ij}.$$

(3)

In Eqs. (3) δ^{ij} is the Kronecker delta, \mathbf{r}_{α} is position vector of the atom α relative to the molecular center of mass, and ψ_B and



FIG. 5. (Color online) Current (left vertical axis) calculated by the DFT coupled with NEGF (solid symbols) and chiral index ψ (right vertical axis, open symbols) as a function of the external bias voltage for systems composed of *n* phenyl rings attached to carbon nanotube electrodes with (a) n = 2 (lozenges), n = 4 (circles) and (b) n = 3 (stars), n = 5 (pentagons).

 ψ_O are the eigenvalues corresponding to the matrices \widetilde{B} and \widetilde{Q} , respectively. The orthonormal basis of vectors $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ specifies the directions of the principal axis of the molecule. ψ , which depends only on the atomic positions, mathematically provides a measure of how much chiral an arbitrary molecule is. As a chiral measure, ψ is a pseudoscalar invariant under rotations, which guarantees that no rotation of the molecule exists that maps the mirror image of such molecule onto itself. Also, ψ must vanish for achiral configurations, such as bidimensional structures and molecules composed of less than four atoms.³⁵ The definition of chiral indexes for molecules composed of different atomic species exists and takes into account different weight functions that reflect the atomic weight.³⁵ However, for the oligo-para-phenylene attached to CNTs, the difference between the values of these indexes and ψ [Eq. (2)], is negligible due to the small atomic weight of the hydrogen relative to the carbon atoms.

In Fig. 5 the geometrical degree of chirality is calculated using the atomic positions and Eq. (2) and compared with the I-V characteristics of molecular junctions containing two to six phenyl rings. It is important to mention that the calculation of ψ probes the geometrical degree of chirality of the whole junction, including the CNTs, which are chiral molecules themselves. However, since CNTs are semi-infinite electrodes, their contribution to ψ remains constant as the applied bias voltage varies. The application of an external voltage V_{e} induces structural changes in the junction geometry, resulting in a different value of ψ for each value of V_e . From Fig. 5, one can see that the geometrical degree of chirality of the junction increases as the bias voltage is switched on. For molecules composed two phenyl rings, it was demonstrated that the angle between the rings θ is the relevant parameter in determining the value of ψ .¹⁷ For $\theta \approx 0$ the molecule is quasiplanar so ψ reaches its minimal value. As V_e varies, the molecules acquires a large out-of-plane component, the angle between the phenyl rings increases, and hence ψ also

tends to increase. For larger systems, composed of more than two phenyl rings, the dependence of the chiral index on molecular conformation is more complex, as ψ depends on the relative angles between all neighboring phenyl rings. As a result of the variation of the angle between the phenyl rings, the overlap between the π orbitals also varies, affecting the electronic conductance through the junction.²³ Other examples of the interplay between molecular conformation and electronic transport in biphenyl junctions, including the influence of temperature, have been discussed in Ref. 36. Figure 5 reveals that there exists a strong correlation between the current flowing through the molecular junctions and the purely geometrical chiral index ψ , showing that this result applies not only to some specific molecular junctions but also to a broader range of systems. This result confirms our suspicion that the connection between the geometrical degree of chirality and electronic transport properties of single-molecule junctions is a more general trend in molecular electronics, suggesting that transport measurements could be explored to determine the chirality and handedness of molecules, as optical activity measurements. Finally, from Fig. 5, one can see that ψ captures structural modifications in the molecular junction as the external voltage varies that show up in the I-V characteristics. As a result, it is interesting to remark how resonances in transport induces a significant structural and geometrical rearranging of the molecular junction.

V. CONCLUSIONS

In conclusion, we have investigated, by means of a nonequilibrium Green's function method coupled to density functional theory, electronic transport in molecular junctions composed of oligo-para-phenylene (with two, three, four, and five phenyl rings) attached to metallic carbon nanotubes electrodes. The FN plot exhibits minima, Vmin, that correspond to voltages where an NDR occurs in the current-voltage characteristics. We have found that V_{\min} occurs whenever the tail of a resonant transmission peak enters in the bias window. This result agrees with recent calculations performed within the coherent transport model,¹² hence corroborating the scenario in which this model gives the correct interpretation to TVS. It is important to emphasize that our finding that V_{\min} corresponds to voltages that exhibit NDR, which can be explained only in single-molecule junctions within the coherent transport model, further confirms the applicability of such model to adequately interpret TVS. Furthermore, the fact that the electrodes are organic is at the origin of important differences in the behavior of V_{\min} if compared to the case of molecular junctions composed of nonorganic (e.g., gold) treated so far. In particular, the expected linear behavior between V_{\min} and the energy gap between the electrodes Fermi levels and the HOMO level, observed for junctions with nonorganic contacts,^{4,5} does not occur as a result of a stronger coupling between the molecular bridge and the carbon nanotube electrodes. Finally, we have demonstrated that the strong correlation between a purely geometrical chiral index and the electronic transport properties in single-molecule junctions, recently unveiled in Refs. 17 and 25, also applies for more complex molecular bridges, composed of up to five phenyl rings.

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