

Tuning the conductance of a molecular switch

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The ability to control the conductance of single molecules will have a major impact in nanoscale electronics^{1,2,3,4,5,6,7,8,9,10,11}. Azobenzene, a molecule that changes conformation as a result of a *trans/cis* transition when exposed to radiation, could form the basis of a light-driven molecular switch^{12,13,14}. It is therefore crucial to clarify the electrical transport characteristics of this molecule. Here, we investigate theoretically charge transport in a system in which a single azobenzene molecule is attached to two carbon nanotubes. In clear contrast to gold electrodes, the nanotubes can act as true nanoscale electrodes and we show that the low-energy conduction properties of the junction may be dramatically modified by changing the topology of the contacts between the nanotubes and the molecules, and/or the chirality of the nanotubes (that is, zigzag or armchair). We propose experiments to demonstrate controlled electrical switching with nanotube electrodes.

Recent theoretical studies^{13,14} have explored the use of azobenzene as an electronic switch when contacted by Au electrodes. Promising results were obtained, as a significant change in conductance was seen between the two conformations. Although a mechanism was proposed that allowed for a certain movement of the Au-leads, azobenzene and similar molecules undergoing isomerization transitions require more versatile nanocontacts that adjust appropriately to the change of length in going from one isomeric state to the other. Moreover, the coupling to Au electrodes only leads to a broadening of the molecular orbitals, without essentially perturbing the intrinsic molecular electronic structure. Although this may be a positive feature in some situations, more exciting is the possibility of having nanoscale electrodes with electronic properties that may lead, in contrast to Au electrodes, to a strong modification of the low-energy molecular electronic structure and hence to dramatic changes in conductance. The most attractive candidates are carbon nanotubes (CNTs)¹⁵, which are essentially one-dimensional systems whose conduction character (metallic or semiconducting) can be easily tuned by changing their chirality.

We focus in this paper on the transport characteristics of single *trans* and *cis* azobenzene contacted by metallic CNTs with two typical chiralities: armchair and zigzag. In order to improve the molecule-electrode coupling, the hydrogen atoms at the para-positions on the molecules are substituted by NHCO-groups, which have been used as linkers to CNT electrodes in recent transport experiments (A. Holleitner, private communication). Our main aims are to highlight the dependence of charge transport on the electronic structure of the nanotube electrodes, as well as the influence of the linker groups, which are known to play an important role¹⁶. It turns out that the oxygen atom plays a critical role in determining the conductance near the Fermi level. Finally, the sensitivity in the electrical response of the isomers may be exploited to identify them using electrical transport measurements as well as to realize a molecular

switch.

The *trans* isomer is characterized by a planar structure, but in the *cis* isomer the benzene aromatic rings are tilted with respect to each other, as seen in Fig. 1. Total energy calculations yield an energy difference between the isomers of ~ 0.2 eV, the *trans* state having the lowest energy and smallest highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) gap of ~ 1.98 eV. On addition of the linkers, the gap slightly increases to 2.03 eV. Conversely, the gap for the *cis* isomer decreases from 2.55 eV to 2.34 eV. However, the isomer geometries, when the linkers are added, are not appreciably modified after relaxation. In Fig. 1 we show the energetic position of the isomers' frontier orbitals as well as the optimized geometries.

Let us consider the CNT-azobenzene-CNT molecular junction. The complexity of the system leads to a very structured potential-energy hypersurface with many metastable states; for the sake of simplicity we only consider coaxial arrangements of the left and right CNTs. Different junction geometries varying in the way the molecule is attached to the CNT surfaces were then optimized using conjugated-gradient techniques, and the lowest-energy configurations were used for the transport calculations. We note at this point that the energy differences between the investigated metastable states are roughly of the order of a few meV per atom, so that our transport calculations can be considered as providing expected trends. Other configurations close in energy may lead to slightly different quantitative results. However, the basic conclusions of this paper should not be affected.

Concerning the CNT-molecule contact, two direct covalent bonds are formed between the azobenzene complex and the CNT leads: a $C_{CNT}-C_1$ bond and a $C_{CNT}-O$ bond. C_1 denotes the carbon atom belonging to the linker. The bond topology is, however, different

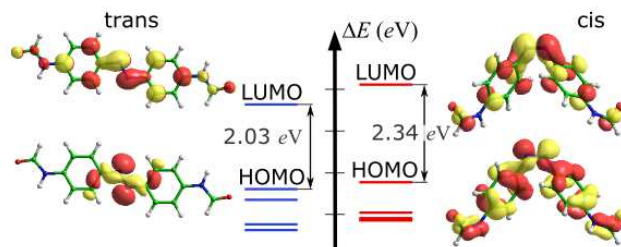


Figure 1 | Low-energy electronic states of azobenzene including the NHCO linkers. The positions of the frontier molecular orbitals of the *trans* (left) and *cis* (right) isomers are shown. The HOMO-LUMO gap is slightly smaller in the *trans* state, which is also the lowest-energy configuration. The presence of the linkers does not appreciably modify the geometric structure of the isomers. Also shown is a density isosurface plot for the HOMO and LUMO orbitals. The *trans*-HOMO is mainly localized around the N-N dimer with almost no weight on the linker groups. Notice that an extra hydrogen saturates the linker. On attaching the molecules to the CNT electrodes, this H-atom is removed and plays no further role.

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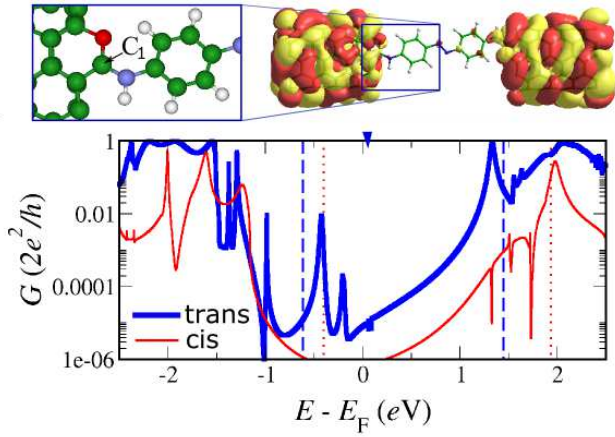


Figure 2 | Linear conductance at zero bias for a (5,5) armchair-*trans*(*cis*)-armchair junction. As a reference we indicate by vertical lines the positions of the HOMO and LUMO orbitals of the isolated *trans* (blue dashed lines) and *cis* (red dotted lines) molecules. All energies are shifted to set the Fermi energy at 0 eV, as only energy differences from the Fermi level are revealed in transport observables. Top panel: density isosurface plot of a selected molecular orbital of the extended *trans* molecule (at an energy indicated in the conductance plot by the arrow near the Fermi level). The low weight on the molecule reflects the rather low conductance at this energy. The inset is an enlargement of the CNT-molecule interface showing the formation of a carbon hexagon with an oxygen defect on relaxation. This configuration is the same for both isomers. Note that the carbon atom denoted by C₁ forms a "bottleneck" in the junction, which means that the conductance is largely determined by the spectral weight on the O-C₁ bond.

for armchair and zigzag tubes, as shown in the insets of Figs. 2 and 3. In the former case a hexagon is formed, and in the latter case a pentagon is built. This appears to be a common feature of the bonding topology, as other initial configurations led to similar connectivities upon relaxation. In the *trans* configuration attached to armchair leads, one of the benzene rings slightly rotates out of plane by about 8° so that the relaxed state deviates from the planar geometry found in the isolated molecule. This structural distortion becomes even stronger when attaching the *trans* molecule to zigzag tubes (14°). On the other hand, for the *cis* isomer, geometrical modifications on attachment to the leads do not depend so much on the chirality of the CNTs, and consist essentially of a slight reduction of the tilt angle.

Once the geometries were optimized, we first focused on the dependence of the linear conductance on the charge injection energy (Figs. 2 and 3) for armchair and zigzag junctions, respectively. It turns out that the *trans* configuration shows an overall better "transparency" (higher conductance) than the *cis* state, independently of the CNT chirality, thus suggesting that the switching behaviour may already be expected at low bias. The conductance of the armchair-*cis* junction displays a parabola-like gap around the Fermi level, indicating that transport can only take place through tunnelling, and thus very low currents are expected. However, several resonances are seen for the *trans* state around the Fermi energy, which, despite their relative low intensity, may give rise to resonant transport. These features arise from the hybridization of surface states with molecular orbitals. The resulting mixed states have a non-negligible overlap with the CNT extended bulk states and thus can contribute to transport. The fact that such states lie within a low-energy window around E_F can make conductance manipulation more feasible because these states will sensitively depend on the molecule-CNT contact topology, as can be seen from our calculations. The low transmission of

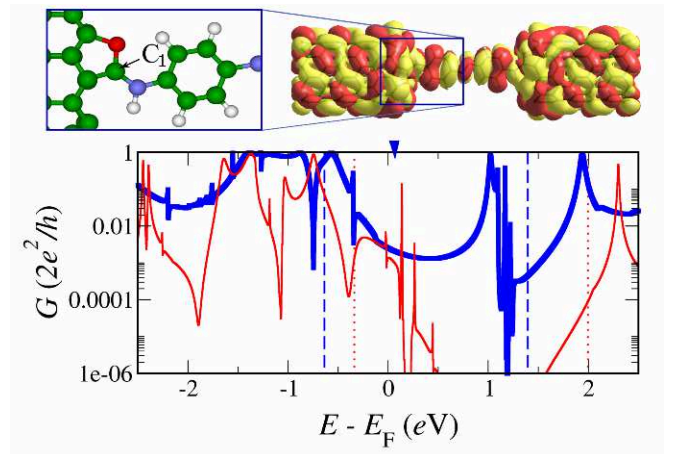


Figure 3 | Linear conductance at zero bias for a (9,0) zigzag-*trans*(*cis*)-zigzag junction. As in Fig. 2, the vertical dashed (dotted) lines indicate the positions of the frontier orbitals of the isolated *trans*(*cis*) isomers. Notice the increased conductance around the Fermi energy for both isomers as well as the more complex structure of the spectrum in this energy region. This is closely related to the strongly localized edge state at the Fermi level in zigzag tubes. Top panel: density isosurface plot of a selected orbital of the extended *trans* molecule (at an energy indicated by an arrow in the conductance plot). Note the much higher weight on the molecule when comparing with the armchair junction in Fig. 2, which explains the higher transmission at this energy. The inset shows the local atomic structure at the CNT-molecule interface, where a pentagon is formed. This local bonding topology is similar for both isomers.

the *cis*-state is related to its distorted geometry, which considerably breaks the π -conjugation along the molecular frame.

Turning now to the zigzag-azobenzene junctions, the conductance appears to be considerably larger for both isomers than for armchair junctions, as seen in Fig. 3. One should notice at this point that for both chiralities there are essentially two interfering pathways from the CNT to the azobenzene molecule, which merge in the carbon atom belonging to the linker. Our calculations show that the O-C₁ pathway completely dominates the charge transport efficiency through the junction, the oxygen atom in the NHCO linker hereby playing a crucial role. Because of its higher electroaffinity, the oxygen tends to deplete the spectral weight on the C₁ atom and thus acts as a chemical gate at the atomic scale. This mechanism is very effective for armchair junctions, but fails to have a dominant effect for zigzag junctions. Our density-functional-theory-based calculations as well as a π -orbital model hamiltonian show that, contrary to the armchair system, in zigzag junctions a much larger spectral weight on the C₁ atom persists for energies around the Fermi level. The reason for this is that the surface density of states of a zigzag tube has, as is well known, a large spectral weight close to the Fermi energy (corresponding to a localized state at the zigzag edge)¹⁷. Moreover, the strong edge resonance manifests itself in the electrode self-energies $\Sigma_{L/R}(E)$ and leads to a rather complex modification of the lower-lying molecular electronic states which is absent for armchair junctions. Thus, the conductance difference for both junctions is a result of the interplay between local (interface) chemistry and electrode surface electronic structure.

To round off our discussion, we have calculated the current-voltage (I - V) characteristics of the junctions to confirm the possible switching behaviour already suggested by the analysis of the linear conductance. To reveal in a clearer way the effects of chirality on transport, a hybrid armchair-azobenzene-zigzag system was also investigated. The results for the three cases are displayed in Fig. 4.

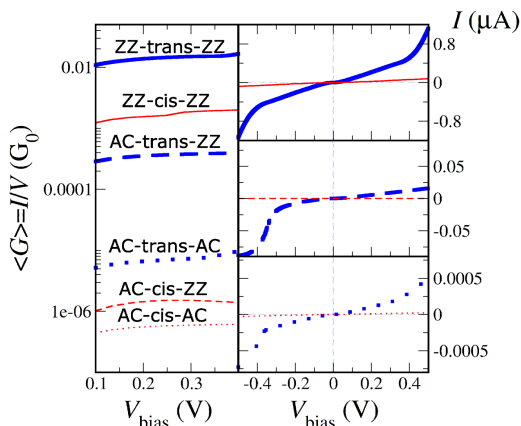


Figure 4 | Average conductance and current-voltage characteristics of the CNT-azobenzene junctions. Three possible CNT-molecule junctions are shown: zigzag(ZZ)-*trans*/cis-zigzag, armchair(AC)-*trans*/cis-zigzag, and armchair-*trans*/cis-armchair. A systematic hierarchy can be seen, showing that the *trans* state is always better conducting than the *cis* one and that armchair CNTs are always detrimental to junction conductivity.

Charge transport for the *cis* state is strongly suppressed already at low bias for all junctions, indicating a switching behaviour. Note that the zigzag-*trans*-zigzag junction shows up to three orders of magnitude larger currents than the other two junctions, where armchair tubes were used. This is even more dramatically seen in the left panel of Fig. 4 where the average conductance I/V is shown. These results further support the conclusion that the electronic structure of both molecule and electrodes is crucial in determining the low-voltage transport when nanoscale electrodes are used. Another remarkable point is the strong rectifying behaviour found in the hybrid armchair-*trans*-zigzag junction. The obvious chirality dependence of the effect suggests a different mechanism to realize diode-like functions, which would not be directly related to intrinsic electronic structure asymmetries of the molecule as in the paradigmatic case of the Aviram-Ratner molecular rectifier¹⁸. We would further like to mention that our equilibrium treatment of transport is validated by recent non-equilibrium calculations¹⁴ using Au electrodes which showed a similar qualitative behaviour for the two isomers,

that is, $I_{trans}(V) \gg I_{cis}(V)$.

Finally, we would like to comment on possible experimental realizations of the conformational switching when using CNT electrodes. One precondition to achieve it is to increase the flexibility of the junction, either by using longer linkers (which should not, however, be detrimental to conduction by inducing, for example, tunnel barriers) or by enlarging the electrode mobility. One should keep in mind that the size of the spatial gap where the molecule is placed is considerably smaller than the length of the CNTs. Thus, small lateral variations in the position of the CNTs can lead to a large change in the inter-electrode spacing. Another possibility would lie in using telescopic CNTs as electrodes and attaching the molecule to one of the inner shells¹⁹. Additionally, we might expect that for a kinematically constrained molecule such as the one studied here, the “standard” isomerization pathway would in principle be difficult to realize. Although this might be true for bulk Au electrodes, the one-dimensional nature of CNTs can considerably increase the mechanical flexibility of the junction. Alternative pathways through other metastable states compatible with the constraints can therefore become effective. Indeed, several of the relaxed junctions displayed geometric characteristics lying between those of the *trans* and *cis* states. Light irradiation or mechanical actions could trigger the transition from these metastable configurations to the final *cis* state. Another advantage of CNT electrodes lies in the fact that they may possess a negative thermal expansion factor²⁰. A combination with other metallic electrodes may thus lead to thermally more stable junctions, because normal metal electrodes would expand upon heating and hence reduce the junction flexibility.

METHODS

We have used a density-functional-tight-binding (DFTB) methodology²¹ combined with Green function techniques²² for geometry optimization and transport calculations in the frame of the Landauer approach. The linear conductance G can be obtained from the quantum mechanical transmission probability at zero voltage: $G = G_0 T(E, V = 0)$ (where $G_0 = 2e^2/h$ is the conductance quantum, e is the electron charge and h is the Planck constant). The transmission probability is related to the molecular Green function $g(E)$ and the electrodes’ self-energies $\Sigma_{L/R}(E)$ by $T(E, V) = 4\text{Tr}[g^\dagger(E)\text{Im}\Sigma_R(E)g(E)\text{Im}\Sigma_L(E)]$ (ref.23). We stress that when calculating the current $I(V)$, the full voltage-dependent $T(E, V)$ is used: $I(V) = (2e/h) \int dE [f_L(E) - f_R(E)] T(E, V)$. In the last expression $f_{L/R}(E)$ are Fermi functions of the left and right electrodes. $T(E, V)$ is calculated for the so called extended molecule, which contains the azobenzene molecule, the linkers, and the electrodes’ surface atoms. This allows the molecule-electrode coupling and the molecule electronic structure to be treated on the same footing^{22,24}.

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Competing Interests The authors declare that they have no competing financial interests.

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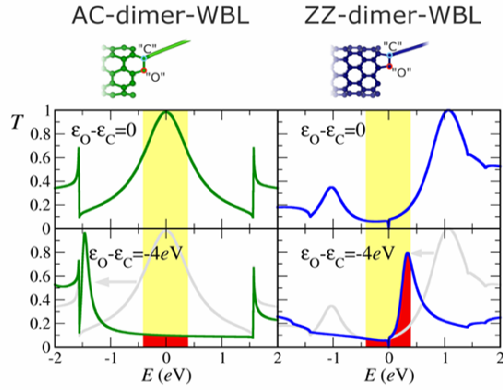


Figure S1 | **Transmission spectrum for the π -orbital model.** The left panels refer to a (5,5) armchair- C_1O dimer-wide band lead (WBL) junction and the right ones to the case in which the nanotube is a (9,0) metallic zigzag tube. The upper panels refer to a full carbon junction with equal onsite energies on the dimer. In the lower panels the onsite energy of the atom indicated as O in the sketches of the junctions has been lowered to mimic the different electronic affinities of carbon and oxygen. The shaded yellow area refers to the integration region of 0.8 Volt over which we have calculated the I - V characteristics in the main text. As it can be clearly seen in the lower panel, the zigzag junction transmission profile does result in a much higher current than for the armchair one inside this voltage window.

Supplementary Information To get further intuition on the enhanced conductance in the zigzag-azobenzene junction, we have formulated a minimal single-orbital model (see Fig. S1). The model consists of a semi-infinite armchair (zigzag) CNT, a dimer which mimics the C_1O subsystem at the CNT-molecule interface, and a semi-infinite chain connected to the C_1 site, which only fulfills the function of acting as a charge reservoir and will subsequently be treated within the wide-band approximation, *i.e.* assuming an energy-independent coupling between the dimer and the chain.

With this model, we can *qualitatively* describe the local chemistry and topology at the CNT-azobenzene interface. Our main goal is to highlight the influence of the charge state at the “oxygen” site—which can be controlled by variations of its onsite energy ε_O —as well as the role played by the nanotube surface electronic structure.

We can write an analytical expression for the transmission function in terms of the dimer Green function:

$$T(E) = 4\Gamma_R \left\{ \Gamma_L^{11}(E) \left[|G_{C_1C_1}(E)|^2 + |G_{C_1O}(E)|^2 \right] + 2\Gamma_L^{12}(E) \text{Re}(G_{C_1C_1}(E)G_{C_1O}^*(E)) \right\}.$$

In this equation, $\Gamma_L^{11}(E)$ and $\Gamma_L^{12}(E)$ describe the direct and cross coupling of the dimer to the left CNT electrode (the indices 1 and 2 refer to the C_1 and O atoms, respectively), and Γ_R the constant coupling of the C_1 atom to the wide-band lead (WBL) electrode on the right. The dimer Green function can be obtained as solution of a Dyson 2×2 matrix equation $G^{-1}(E) = E - H_{\text{dimer}} - \Sigma_L(E) - \Sigma_R(E)$.

Three contributions to the transmission function can be clearly distinguished: $G_{C_1C_1}$ is related to tunnelling pathways going from the CNT directly through the C_1 atom, G_{C_1O} describes pathways passing through the O atom and then through the C_1 atom, and the last term describes interference effects between both pathways. Our calculations show that $|G_{C_1O}(E)|^2$ is the dominant contribution to $T(E)$ for energies around the Fermi level. Additionally this Green function matrix element is the most strongly affected by a shift of the O onsite energies. Thus, we can approximately write: $T(E \approx E_F) \approx 4\Gamma_R \Gamma_L^{11} |G_{C_1O}(E)|^2$.

In Fig. S1 we show the influence of a shift in ε_O on the transmission function for both armchair and zigzag junctions (we take the C_1 onsite energy equal to that of the CNT carbon atoms). It turns out that changes in ε_O lead to a dramatic suppression of the transmission for armchair junctions at low energies (left panel of Fig. S1). For the zigzag junction, on the contrary, electronic states lying slightly above the Fermi energy are shifted down (chemical gating) towards E_F without overtaking it, and thus enter the energy window relevant for the low-bias transport (right panel of Fig. S1). The value $\varepsilon_O = -4\text{eV}$ has been extracted from our DFTB calculation. It is the difference between the $2p$ orbital energies of isolated oxygen and carbon atoms. The effect discussed here is nevertheless stable against variations around this value.

Extended calculations, which are not included here, show that this peculiar behavior of the zigzag junction should be attributed to the well-known surface state at the Fermi energy: with zigzag (ZZ) CNT leads the dimer resonances are ultimately shifted (renormalized) by the real part of the surface self-energy, which can, to a good approximation, be written near the E_F as: $\text{Re}\Sigma^{ZZ}(E) \propto (E - E_F)/(\delta^2 + (E - E_F)^2)$, inducing *de facto* a pinning of such resonances around the Fermi energy, where the surface state exists with a linewidth δ . In this way the dimer eigenstates shift into a transport sensitive energy region.