# Control of electron transport through Fano resonances in molecular wires

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Using a first principles approach, we study the electron transport properties of two molecules of length 2.5 nm, which are the building blocks for a new class of molecular wires containing fluorenone units. We show that the presence of side groups attached to these units leads to Fano resonances close to the Fermi energy. As a consequence electron transport through the molecule can be controlled either by chemically modifying the side group, or by changing the conformation of the side group. This sensitivity, which is not present in Breit-Wigner resonances, opens up new possibilities for novel single-molecule sensors.

The ability to position single molecules in electrical junctions[1–6] and demonstrations that molecular and nanoscale structures are capable of basic electronic functions such as current rectification, negative differential resistance, and single electron transistor behavior[7–12] suggest that single-molecule electronics may play a key role in the design of future nanoelectronic circuits. However, the goal of developing a reliable molecular-electronics technology is still over the horizon and many key problems, such as device stability, reproducibility, and the control of single-molecule transport need to be solved. In addition, since contacting molecules via break junction and SPMs is not a scalable technology, the question of wiring large numbers of molecules on a single chip still needs to be addressed.

One approach to developing a scalable technology involves placing molecules between arrays of preformed lithographically grown contacts. Such an approach requires the length of the molecules to match the spacing between the contacts and since in practice, the spacing between such contacts can only be reliably controlled on the scale of 1–10 nm, it is desirable to synthesize families of molecular wires with this range of lengths.

Recently[13–15] a family of rigid molecules has been synthesized with lengths up to 10 nm. These are $\pi$-conjugated oligomers based on rigid-rod-like aryleneethynylene backbones, containing fluorenone units. The presence of terminal thiol groups allow assembly onto gold surfaces and therefore make them ideal for use in single-molecule device fabrication. In this paper we investigate the properties of the smallest of these molecular wires, of length 2.5 nm, since these form the building blocks of the longer wires. The central part consists of a single fluorene unit, which could be chemically modified, e.g., by replacing the oxygen with pyridine or bipyridine rings, as shown in Fig. 1.

In many molecular devices, electron transport is dominated by conduction through broadened highest occupied molecular orbital or lowest unoccupied molecular orbital states, leading to Breit-Wigner resonances.[16] In contrast, for this family of molecules, we find that transport is dominated by Fano resonances[17] associated with the presence of side groups, such as the oxygen atom or bipyridine. Generic properties of Fano resonances, have been discussed in several contexts recently. Reference 18 deals with Fano resonances in one-dimensional (1D) waveguides, applied to GaAS heterojunctions. Reference 19 analyzes a generic model of a

double quantum dot. References 20 and 21 address inelastic scattering, which can be an issue at finite bias, but is not the focus of attention in our paper. Reference 22 is concerned with low temperature transport below the Kondo temperature. "Conductance cancellation" in 1D tight-binding chains has also been noted[23] and a Hückel model of resonant transport recently considered.[24]

None of the above papers contain *ab initio*, material-specific calculations, which treat the metallic electrodes in a realistic manner. Recently, this limitation has been removed by state-of-the-art calculations on dithiol benzene,[25] which contain many examples of Fano resonances. Depending on specific conditions, these can take on a wide variety of shapes, ranging from Breit-Wigner type line shapes to strongly asymmetric profiles. However, the Fano resonances are neither controlled nor engineered into the molecule. They arise from a complicated interaction between the molecule and contacts and cannot be identified with a particular section of the molecule.

The aim of this paper is to demonstrate that there are advantages in engineering molecules to possess Fano resonances associated with specific parts of the molecule, which can be modified externally to achieve control over transport. Through an *ab initio* simulation of the molecules in Fig. 1, we demonstrate that Fano resonances near the Fermi energy can be controlled by altering the properties of the attached
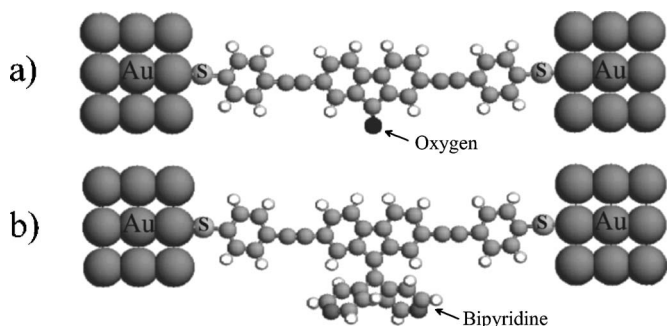


FIG. 1. The ground state geometry of the 2.5 nm molecules extended to self-consistently include eight layers of gold on the (111) surface, each containing nine Au atoms. Color codes: C (grey), H (light grey), N (dark grey), and O (black). (a) The top molecule contains a single oxygen atom attached to the central fluorene unit and (b) the oxygen has been replaced by a bipyridine unit.
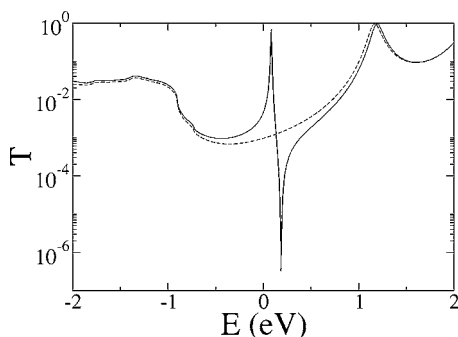
FIG. 2. Solid line: Electron transmission coefficient versus energy for the molecule having attached an oxygen atom as a side group. Dashed line: Oxygen bonds removed from the Hamiltonian.



FIG. 3. Transmission against energy for the bipyridine attached molecule for rotation angles of 0° to 90°.

side group. This is in marked contrast with the behavior of Breit-Wigner resonances, which are relatively insensitive to the state of the side group. These results suggest that the control of Fano resonances opens intriguing possibilities for single-molecule sensing.

To compute electron transport properties, we use a combination of the DFT code SIESTA[26] and a Green's function scattering approach, as encapsulated in the molecular electronics code SMEAGOL.[27] Initially the isolated molecule is relaxed to find the optimum geometry and the molecule is then extended to include surface layers of the gold leads, so that charge transfer at the gold-molecule interface is included self-consistently. The number $N_g$ of incorporated gold layers is increased until computed transport properties no longer change with increasing $N_g$. We find that this occurs for $N_g$ =8 layers of gold, each consisting of nine atoms on the (111) plain. Using a double-$\zeta$ basis plus polarization orbitals, Troullier-Martins pseudopotentials,[28] and the Ceperley-Alder LDA method to describe the exchange correlation,[29] an effective tight-binding Hamiltonian of the extended molecule is obtained, from which a scattering matrix and electron transmission coefficient $T(E)$ are computed. The zero-bias electrical conductance is then given by the Landauer formula $G=(2e^2/h)T(E_F)$, where $E_F$ is the Fermi energy.[30]

For the molecule shown in Fig. 1(a), which has an oxygen atom attached to the fluorene unit, the transmission coefficient $T(E)$ is shown in Fig. 2 (black line). For $E \approx 1.2$ eV, this exhibits a typical Breit-Wigner resonance. As expected, since the molecule and contacts are symmetric, the maximum value of this peak is unity. However, in the vicinity of the Fermi energy ($E_F=0$) transport is dominated by the presence of an asymmetric Fano resonance,[17] comprising a resonant peak followed by an antiresonance.

We now demonstrate that antiresonances arise from quasibound states associated with the side groups of the molecules in Fig. 1. For the molecule of Fig. 1(a), this is demonstrated by the simple theoretical trick of artificially setting the hopping matrix elements connecting the oxygen atom to the fluorene unit to zero. This yields the transmission coefficient shown by the dashed line in Fig. 2, which shows that artificial removal of the chemical bonds to the oxygen destroys the Fano resonance, whereas the remainder of the transmission spectrum remains largely unaltered.
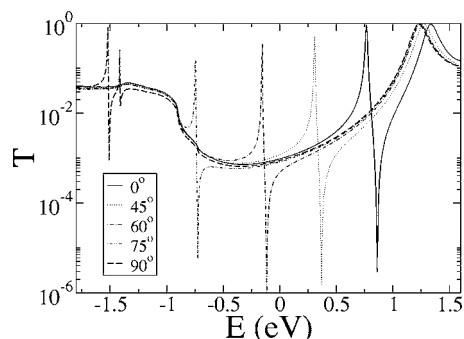
The ability to manipulate Fano resonances, by chemical

means or otherwise, opens up new possibilities for controlling single-molecule transport. To explore this possibility in greater detail and to demonstrate that Fano resonances are a generic feature of molecular wires with attached side groups, we examine the molecule shown in Fig. 1(b), in which the oxygen has been replaced by a bipyridine unit. Recent STM experiments on related wires have shown that it is possible to change the rotational conformation of attached side groups[31] and therefore we examine transport properties as a function of the angle of rotation $\theta$ of the bipyridine side group. (We define the angle $\theta=0°$ when the two rings lie parallel to the molecule axis and $\theta=90°$ when they lie perpendicular to it.) The computed transmission through this molecule is shown in Fig. 3 for five values of $\theta$. This demonstrates that Fano resonances persist when one side group (namely, the oxygen atom) is replaced by another and furthermore, the position of the Fano resonance is sensitive to the conformation of the side group. In contrast, the Breit-Wigner peak at 1.25 eV is almost unaffected by such changes.

To demonstrate that the Fano resonance is associated with localized states on the side group, we examine the energy spectrum of the isolated molecule. Figure 4 shows how the energy levels of the isolated molecule depend on the rotation angle $\theta$. This shows that while most of the levels remain unaffected, one of them is sensitive to changes in $\theta$, varying from 1.57 eV at $\theta=0°$ to 0.0 eV at $\theta=90°$. To demonstrate that this level belongs to the fluorene unit and bipyridine, Fig. 5 shows the local density of states (LDOS) for two
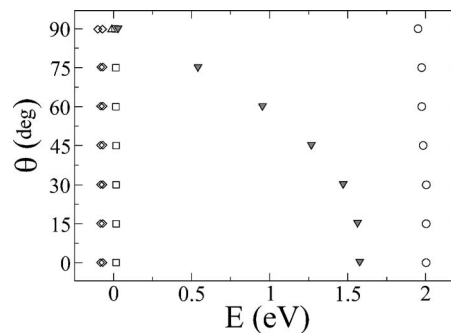


FIG. 4. Rotation angle $\theta$ dependence of the energy levels of the isolated molecule. The eigenstates corresponding to Fano resonances are represented by triangles while the circles represent those corresponding to Breit-Wigner resonances.
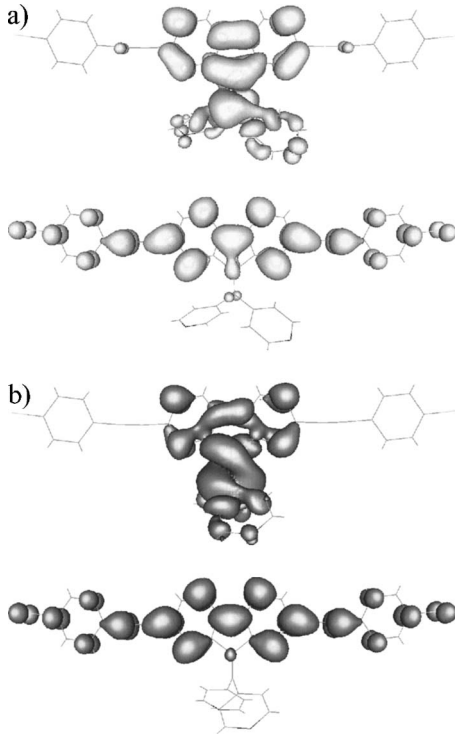
FIG. 5. Constant LDOS surface for (a) 30° rotation and energy values of 1.46 and 2.00 eV. (b) 75° rotation and energy values of 0.54 and 2.00 eV.



FIG. 7. (a) A plot of Eq. (1) for two sets of parameters, chosen to fit the *ab initio* results for $\theta=0°$ and $\theta=75°$. Solid line: The values used are $\varepsilon_+=1.34$ eV, $\varepsilon=0.86$ eV, and $\varepsilon_-=0.77$ eV. Dashed line: $\varepsilon_+=1.23$ eV, $\varepsilon=-0.72$ eV, and $\varepsilon_-=-0.74$ eV. For both curves $\Gamma=0.05$ eV. (b) For comparison, the lower figure shows the corresponding *ab initio* results.

different energy values when $\theta=30°$ (ground state of the molecule) and $\theta=75°$. Energies $E=2.0$ eV clearly correspond to states delocalized along the backbone, with almost no weight on the bipyridine. This state is responsible for the Breit-Wigner resonances in Figs. 2 and 3. On the other hand, for $E=1.46$ and 0.54 eV the orbitals are found to be localized on the central unit.

To capture the generic features of this combination of a Fano resonance and nearby Breit-Wigner resonance, we now develop a model of the system sketched in Fig. 6, which consists of a backbone $A$ composed of atomic orbitals numbered $i=1,2,\ldots,N$, coupled to a side group $B$ by matrix elements $H_1$. (The geometric arrangement of the sites is irrelevant, provided $A$ sites are weakly coupled to $B$ sites.) Sites $i\leq0$ belong to the left lead and sites $i\geq N+1$ to the right lead. These are coupled to the ends of the backbone via weak hopping elements $V, W$.

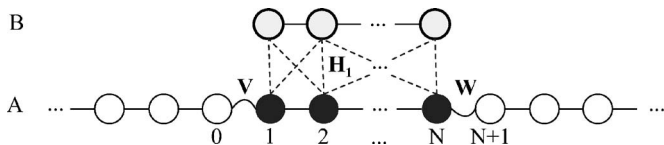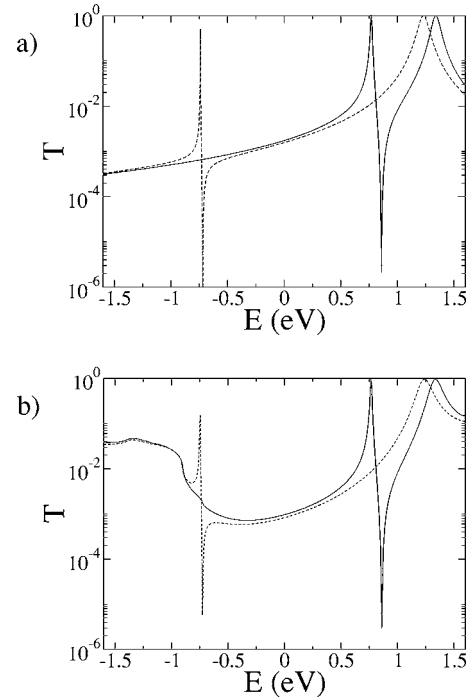In the absence of coupling to the side chain, we assume that transmission through the backbone takes place through a single backbone state $\Phi_m(k)$, with a resonant energy $\varepsilon_0$. In this case, the relevant self-energy $\Sigma$ is

$$\Sigma = \frac{\omega\omega^*}{E - \varepsilon_0 + i\Gamma},$$

where $\omega=\langle\Psi|H_1|\Phi\rangle$. In this expression, $\Gamma=\Gamma_1+\Gamma_2$ is the broadening due to coupling of the backbone to the leads, with $\Gamma_1=|V\Phi_m(1)|^2 N_0(E)$, $\Gamma_2=|W\Phi_m(N)|^2 N_{N+1}(E)$, and $N_0(E)$ $[N_{N+1}(E)]$ the local density of states for the left (right) contacts. This yields for the transmission coefficient

$$T = \frac{4\Gamma_1\Gamma_2}{\left(E - \varepsilon_0 - \frac{\omega\omega^*}{E - \varepsilon}\right)^2 + \Gamma^2}. \tag{1}$$

Equation (1) shows that when $\omega=0$, no antiresonance occurs and the transmission coefficient exhibits a simple Breit-Wigner peak. More generally, Eq. (1) shows that transmission is a maximum at energies $E=\varepsilon_\pm$, where $\varepsilon_\pm$ are the roots of equation $(E-\varepsilon_0)(E-\varepsilon)-\omega\omega^*=0$ and vanishes when $E=\varepsilon$. For small $\omega$, a Breit-Wigner peak of width $\Gamma$ occurs in the vicinity of $\varepsilon_+\approx\varepsilon_0$. In addition a Fano peak occurs in the vicinity of $\varepsilon_-\approx\varepsilon$ with width $\frac{\Gamma\omega\omega^*}{(\varepsilon_0-\varepsilon)^2}$. A comparison between Eq. (1) and the *ab initio* results of Fig. 3 is shown in Fig. 7. This demonstrates that with an appropriate choice of parameters, Eq. (1) captures the essential features of Fano resonances in aryleneethynylene molecular wires.



FIG. 6. A backbone of sites labeled 1 to $N$ coupled to left and right leads by matrix elements $V, W$ and to a side group of sites by $H_1$.

In summary we have shown that transport through a class of molecular wires composed of fluorene subunits with side groups is dominated by Fano resonances rather than Breit-Wigner resonances. As a consequence electron transport through the molecule can be controlled either by chemically modifying the side group, or by changing the conformation of the side group. This sensitivity, which is not present in Breit-Wigner resonances, opens up the possibility of novel single-molecule sensors.

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