

Universality in the low-voltage transport response of molecular wires physisorbed onto graphene electrodes

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We analyze the low-voltage transport response of large molecular wires bridging graphene electrodes, where the molecules are physisorbed onto the graphene sheets by planar anchor groups. In our study, the sheets are pulled away to vary the gap length and the relative atomic positions. The molecular wires are also translated in directions parallel and perpendicular to the sheets. We show that the energy position of the Breit-Wigner molecular resonances is universal for a given molecule, in the sense that it is independent of the details of the graphene edges, gaps lengths, or of the molecule positions. We discuss the need to converge carefully the k sampling to provide reasonable values of the conductance.

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Single- or few-molecule electronics is considered a plausible alternative technology to silicon, that could be deployed to enable the complementary metal-oxide semiconductor (CMOS) industry to reach the atomic limit.^{1,2} However, the few-particle nature of the contacts in single-molecule devices leads to a lack of mechanical robustness. It also leads to a large phase space of coupling configurations, each with a different conductance. The spread in experimental values of the transport response is sorted by the use of a statistically averaged conductance histogram. A large body of the research in this field has therefore concentrated on improving the robustness of the devices by searching and testing new generations of contact groups.^{3–6}

Graphene could replace noble metals as the material for the electrodes to help solve these key issues. The use of graphene brings about several clear advantages. First, its lack of atomic diffusivity makes each gap geometry stable over time. Second, graphene's planar nature allows for the visualization of the junctions, and possibly the control over the actual molecule positioning. Third, compared to the more bulky metallic electrodes, the molecular junction can be placed closer to a gate; graphene electrodes could lead to a reduced gate-field screening and therefore to an enhanced gate coupling. Furthermore, the conductance of few-layer graphene is largely gate independent so that features of the contacted molecules may not be masked by the electrodes' response to the gate. Recently it was also proven experimentally that stable and gateable molecular junctions can be formed by depositing molecules on top of a graphene nanogap fabricated by electroburning, where the molecules' anchor groups were probably contacting the edges.⁷

Graphene therefore deserves to be scrutinized as a possible material of choice for single-molecule electrodes. But graphene brings about its own series of problems that must be overcome. We mention here its complex edges morphology, passivation, and oxidation states, that are not fully characterized yet. The ability to fabricate nanogaps where gap length and edge morphology are controlled with almost atomic accuracy is yet to be developed.

A number of theoretical papers have proposed bridging graphene electrodes with molecules, whose anchor groups would be chemisorbed to the electrodes' edges.^{8–11} However, we have shown in a previous paper that the tribological nature of graphene edges leads to a large variability in the transport response of these devices.¹² An alternative approach that avoids edge anchoring was advanced in Refs. 13 and 14, where fullerene-based dumbbell wires were physisorbed onto graphene, or molecular wires were physisorbed onto carbon nanotubes. In addition, by contacting the molecules deep inside the sheets, trouble related to the size mismatch between the physical gap and the length of the molecule is avoided from the outset.¹³ Notice that this strategy cannot be implemented with bulky noble-metal electrodes.

In this paper we explore the electronic properties and the low-voltage electrical response of molecular wires physisorbed onto graphene leads. Physisorption is a gentler attachment to graphene than chemisorption. The distortion of the geometry and the electronic structure of both molecule's and graphene's contact area is expected to be only moderate and mostly related to screening effects. Specifically, charge transfer between molecule and electrodes is strongly suppressed so that the contact-induced dipoles are expected to be small. In contrast to Ref. 13, we analyze molecular wires with planar anchor groups such as porphyrine or phthalocyanine molecules. These groups are linked by polyyne chains to form dimer and trimer wires, an example of which is shown in Fig. 1. The rationale behind our choice is that increasing the contact surface area could enhance the mechanical stability of the junctions and provide an effective conductance averaging. In addition, porphyrine wires show a small conductance decay with wire length when contacted by gold electrodes.¹⁵ Porphyrine wires can also show interference and spin-filtering effects that make them promising functional units.¹⁶ As opposed to dumbbell molecules, the central region in our wires is by geometrical constraints placed always at the same height measured from the graphene layers, bringing a desirable degree of isolation to the functional central unit and, therefore, of reproducibility.

Our main result is a remarkable universality in the energy position of the Breit-Wigner (BW) molecular resonances, which is missing for junctions comprising noble-metal electrodes, or for edge-contacted graphene junctions. We find that the energy position of the BW resonances appearing in the zero-voltage transmission coefficient $T(E)$ does not shift when the molecules are displaced, or when the graphene sheets are pulled away to vary the physical gap length. We have observed this behavior not only for the junction discussed in this paper but also for monomers, dimers, or trimers made up of porphyrine or phthalocyanine planar groups physisorbed onto graphene. Our results suggest that it might be possible to attach universal energy positions to the BW resonances of a given physisorbed molecular wire. These energy positions could be controlled by a suitable gate in close proximity. We have found however a large spread in the low-voltage conductance $G = G_0 T(E = E_F)$ as a function of the molecules' and electrodes' relative positions, which we attribute to the energy shift of Fano-like resonances around the Fermi level, driven by the molecule-graphene relative motion. We comment last on the need to compute $T(E)$ using a large sampling in transverse k points. We find that $T(E \sim E_F)$ develops a cusp at the Dirac point E_F , and that it changes by orders of magnitude from the Γ point estimate, as the accuracy in the k summation is improved. This is in contrast to the results found for gold junctions, where it was shown that a few k points are more than sufficient to find accurate transport results.

We discuss our results in terms of the junction shown in Fig. 1, where a trimer molecule made up of three porphyrin units is linked by butadiynes, e.g., atomic chains made of four carbon atoms. We find that the whole of this molecule is placed roughly at the same height above the sheets (~ 3.2 Å), regardless of its position. Hence, we discuss the changes in the transmission coefficients and in the conductance when the molecule is displaced across the plane in directions parallel and perpendicular to the edges, or when the graphene sheets are pulled away or pushed towards each other. The sheets shown in Fig. 1 are terminated in an armchair configuration passivated by hydrogen atoms in a 1-1-1 sequence, which is predicted to be the most stable reconstruction and passivation on this kind of edge.¹⁷⁻¹⁹ We stress however that our strategy to reduce the conductance tribological effects brought about

by the edges relies on attaching the molecule anchor groups deep inside the graphene sheets.

We have used the density functional theory (DFT) code SIESTA,²⁰ which employs norm-conserving pseudopotentials to account for the core electrons and linear combinations of atomic orbitals to construct the valence states. In order to better describe physisorption, we have used a recent implementation²¹ of the van der Waals functional of Dion *et al.*²² We have computed the Hamiltonian and overlap matrix elements, the potential and the density using a real-space grid with fineness defined with an equivalent energy cutoff of 200 Ry. We have relaxed quickly the coordinates to forces smaller than 0.05 eV/Å using a single- ζ basis set (SZ). We have taken then these coordinates as seeds for further coordinate relaxation using a single- ζ polarized (SZP). We have repeated the procedure now with a double- ζ (DZ) and then with a double- ζ polarized (DZP). We have first relaxed an isolated porphyrin ring on top of graphene and used those coordinates as a starting point to construct the junction by joining the carbon chains and the central porphyrin ring. Tests performed with one of the junctions show that there are not very large differences in the positions calculated with different basis sets. The electronic structure is however very sensitive to the choice of the basis: we have found large differences in the transmission and the density of states when the basis set improved from SZ to SZP and to DZ. There are not however many changes in moving from DZ to DZP, which implies that the electronic structure is well converged with DZ. We have used then this basis set to perform all calculations. The junctions analyzed here are made periodic along the direction perpendicular (y) to electronic transport (z). Each electrode has ten principal layers, where each principal layer has two columns of carbon atoms. This is enough to accommodate the porphyrin molecules on top of the sheets and ensure that the electronic structure converges to the bulk electronic structure at the leftmost and rightmost layers. We have also computed the physisorption energy for chemical detachment of this and other molecules. We have found energy barriers of the order of 2 eV.

The graphene layers are pulled/pushed along the z axis opposite to each other, so that the physical gap length d increases or decreases. We have chosen a reference distance d_0 between layers equal to 9.1 Å. This corresponds to the

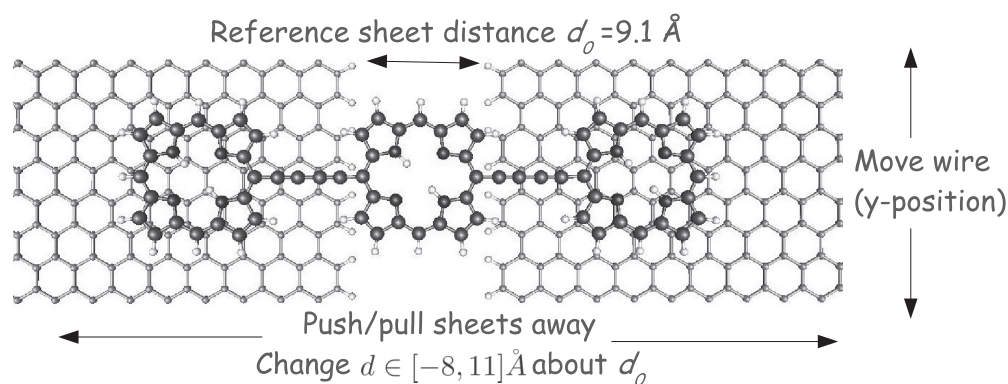


FIG. 1. Schematic plot of the single-molecule junction discussed in this paper. Small light-grey (graphene) and large dark-grey (molecule) spheres and small white spheres represent carbon and hydrogen atoms, respectively. Medium-size spheres around the center of each porphyrin ring represent nitrogen atoms. The system has a total of 446 atoms.

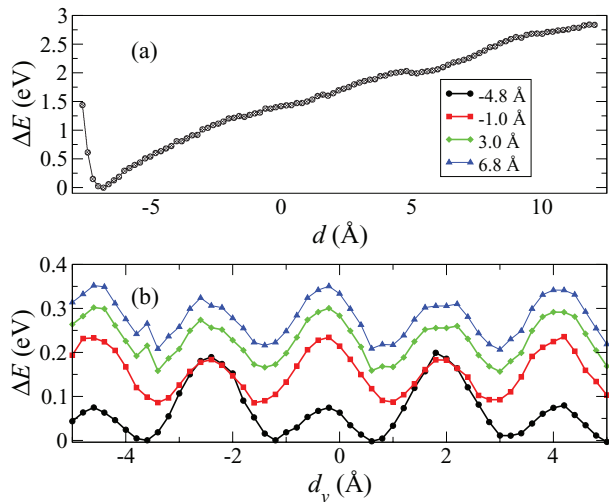


FIG. 2. (Color online) Energy analysis of the junction plotted in Fig. 1: Junction energy as a function of d_z (a) and as a function of the lateral displacement d_y for several d_z (b). In the last figure, the energy curves have been displaced in energy to fit them in the same graph.

separation in which the central porphyrin covers the gap entirely. We have varied the gap length in the range $d \in (-7.6, 11.2)$ Å in steps of 0.2 Å. We note that with our basis set, atomic orbitals at opposing electrodes cease to overlap for gap lengths $d \gtrsim -2$ Å. A plot in Fig. 2(a) of the junction energy as a function of d (e.g., when the electrodes are pulled away) shows a minimum at about $d \sim -6.8$ Å. The existence and position of the minimum reflects a tradeoff between two opposing factors: hydrogen-passivated edge repulsion versus molecule-graphene bonding.

We had computed previously the energy barriers for phthalocyanine monomers sliding on top of an infinite graphene sheet. We found values ~ 40 meV, which were consistent with a previous calculation.²³ Now, we have displaced sideways the trimer molecule in Fig. 1 for fixed d , so that it drifts parallel to the physical gap. Because the trimer has two porphyrine anchor groups bonded to the sheets as well as two polyne chains and a third anchor group interacting with the edges, we expect energy barriers two or three times bigger than the result for the monomer. The junction energy, plotted in Fig. 2(b), shows a smooth and periodic variation of the energy, whose period reflects the underlying graphene lattice. The energy barriers are of about 0.1 to 0.2 eV, consistent with our previous analysis. We can make a rough estimate of the molecule's drift length along the gap, $r \sim \sqrt{4Dt}$, using an Arrhenius equation for the diffusion constant,

$$D = D_0 e^{-E_B/k_B T}, \quad (1)$$

where we take $D_0 \sim 10^{-4}$ cm²/s and $E_B = 0.2$ eV. We find that the trimer would stay fixed at its position for temperatures up to about 100 K, but it should drift at room temperature. This quick analysis indicates that the trimer junction would be stable if energy barriers of about 0.5 eV were achieved. Achieving such high-energy barriers may be done by attaching suitable side groups, or better tailoring the anchor groups.

The junction transport properties have been computed using the newly developed multiscale multiterminal transport code

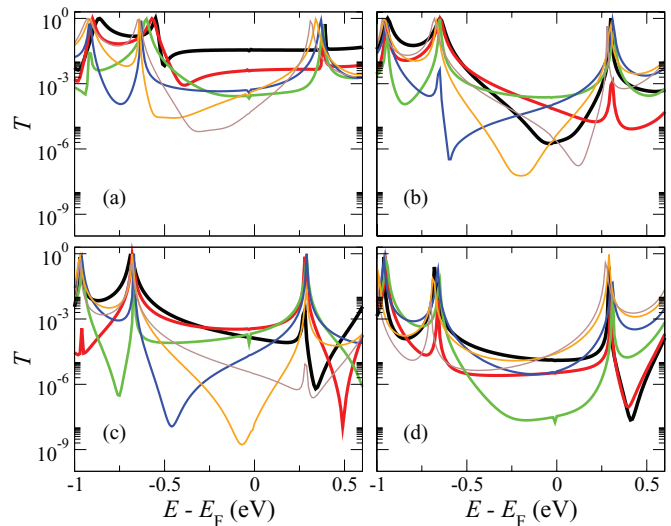


FIG. 3. (Color online) Evolution of the Γ -point transmission coefficient $T(E)$ with increasing gap length d , which varies between -7.6 Å and $+10.8$ Å relative to d_0 , in steps of 0.8 Å. Panels (a)–(d) correspond to curves in the intervals $[-7.6$ Å, -3.6 Å], $[-2.8$ Å, 1.2 Å], $[2.0$ Å, 6.0 Å], and $[6.8$ Å, 10.8 Å], respectively. Decreasing width of the lines corresponds to increasing d .

GOLLUM.²⁴ This program has a simple interface which can easily read any tight-binding model or DFT Hamiltonian, which are generically called Hamiltonian providers (HPs). The program is much faster than previous transport codes due to a new implementation of zero- and finite-voltage algorithms.²⁵ We have used in the present calculation SIESTA as the HP. We have performed Γ -point calculations to start with, and have tested the convergence of the zero-voltage transmission coefficient $T(E)$ as a function of the number of transverse k points, as discussed below.

The Γ -point estimates of $T(E)$ for different gap lengths d are plotted in Fig. 3, at intervals of 0.8 Å.²⁶ The figure shows that the position of the molecular BW resonances remains almost constant. We stress that we have found the same behavior for other junctions: the energy position of the BW resonances for a given graphene-based junction does not depend on the molecule position relative to the physical gap, provided that the bonding mechanism is by physisorption. This universality could have been anticipated: physisorption carries no charge transfer between the molecule and the sheets, nor associated dipole moments. This is so because both sides of each contact are mostly made up of the same chemical species: carbon. Also, the π - π hybridization between molecular orbitals and the electrode states is weaker than for the bonds present in most noble-metal/single-atom contacts, and does not have a large impact on the nature of the molecule orbitals.

The position of the molecular levels of a molecule is not accurately given by conventional local-density-approximation-based approaches to DFT by a number of reasons, including inherent self-interaction errors,²⁷ an improper description of quasiparticles,²⁸ and screening by the metallic electrodes.²⁹ As a consequence, the number and position of the true transmission resonances is expected to be different from those shown in Fig. 3. However, the nature and

energy position of the true strongly correlated quasiparticle states of the molecule depend only on the hybridization, the net charge of the molecule, and the screening provided by graphene. We note that these do not change as the molecule is displaced, because of the physisorbed nature of the chemical bond. We deduce that if we were able to compute the true transmission resonances accurately, then we should see that their energy position does not change with molecule position. We conclude that the universality of the energy position of the transmission resonance is robust even if strong correlations are included.

Figure 3 shows that $T(E)$ computed at the Γ point changes by orders of magnitude at energies E placed between two given BW resonances. A closer inspection indicates that this is so because Fano-like resonances tend to appear at the gaps between two BW resonances. In contrast to the BW resonances, the energy position of the Fano-like resonances shifts as the length of the physical gap increases, or if the molecule is moved around. Because this also happens at the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) gap, we expect that the Γ -point estimate of the low-voltage conductance $G = G_0 T(E_F)$ should show a wide spread. This is confirmed in Fig. 4 where G features strong oscillations as a function of the relative molecule/graphene position. Notice that these oscillations are not strictly periodic as a function of d ; see Fig. 4(a). They are however periodic as a function of d_y , as shown in Fig. 2(b), with the period of the graphene lattice along that direction (4.26 Å).

We have devised a molecule long enough to bridge the physical electrode gap, and anchor deep inside the graphene sheets via the planar porphyrine groups. This length requirement puts stringent conditions on the conjugated nature of the trimer molecule, because the conductance of a molecule decreases exponentially with its length. Butadiyne chains are an excellent choice as linking groups because they enhance the molecule's conjugated nature leading to decay exponents

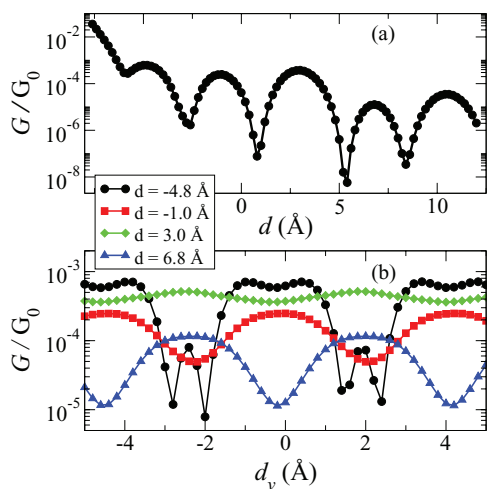


FIG. 4. (Color online) Low-voltage conductance G/G_0 as a function of changes in the junction. (a) G/G_0 as a function of the gap length d ; (b) G/G_0 as a function of the transverse coordinate d_y . G/G_0 is estimated as $T(E_F)$, using only the Γ point in the k summation.

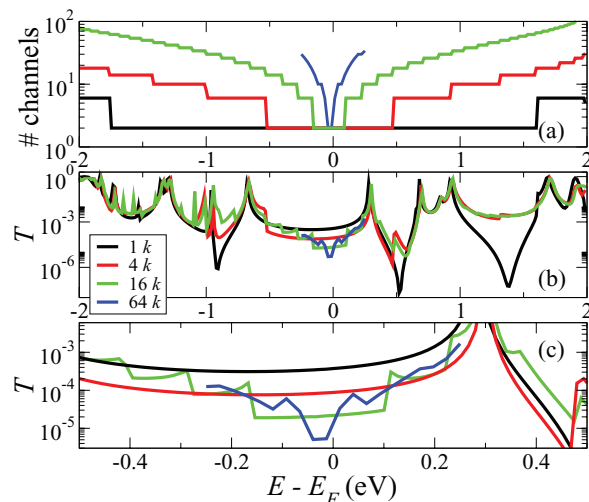


FIG. 5. (Color online) Convergence of the transport coefficients with the number of k points. (a) Number of channel as a function of energy; (b) $T(E)$ for the $d = 3.0$ Å junction; (c) Blowup of $T(E)$ to show the convergence of $T(E_F)$. Black, red, and green lines correspond to 1, 4, and 16 k points, respectively.

close to zero.¹⁵ Electrons, however, can be transferred between the graphene sheets via several paths. They may hop from the sheets to the porphyrine units or to the butadiyne molecules. The different paths lead to destructive interference effects and therefore to Fano-like resonances in $T(E)$.

We analyze now the impact of the k -point summation on $T(E)$. Figure 5(a) plots the number of channels at the graphene leads as a function of energy. As the number of k points increases, so does the number of one-dimensional subbands entering in the energy window. Because the number of channels decreases steadily as $|E - E_F|$ decreases, we expect that it is going to be far easier to converge $T(E)$ at high than at low energies relative to the Fermi level. In other words, the number of transverse k points needed to obtain accurate estimates of the low-voltage conductance will be very high. Furthermore, as the number of k points tends to be infinite, the number of channels develops a very deep cusp at the Dirac point, as can be inferred from Fig. 5(a). We expect that this will be transferred to a cusp in $T(E = E_F)$. To substantiate this reasoning, we show in Fig. 5(b) the evolution of $T(E)$ as the accuracy in the k -point summation is improved, for a given junction arrangement. Notice first that the energy position of the resonances remains the same, which supports our claim on the universality of the BW resonances. Second, the Fano-like dips are washed away. We infer that electron conduction through the new open channels does not suffer destructive interference effects. Third, the slow accumulation of open channels towards the Fermi energy implies that the largest loss of accuracy in the computation of $T(E)$ happens at low energies around E_F . This is especially so if a Fano-like resonance crosses the Fermi level, leading to a stronger kink at $T(E_F)$. For instance, the Γ -point estimates of $T(E_F)$ in Figs. 3(b) and 3(c) differ by a factor of 30. Hence, reasonably accurate estimates of $T(E \sim E_F)$ and of the low-voltage conductance in graphene-based junctions require the use of a large number of k points, so that one can infer the asymptotic behavior.

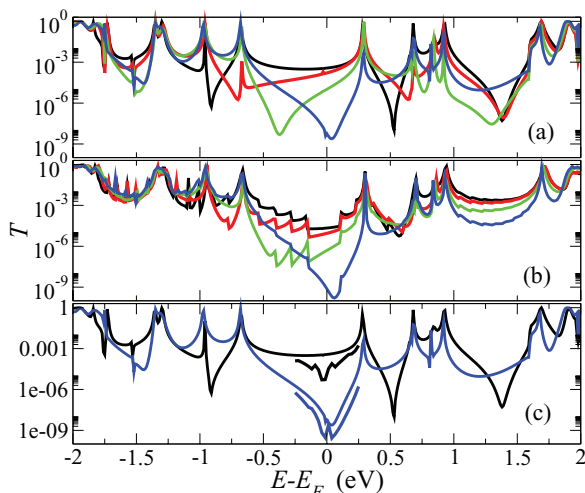


FIG. 6. (Color online) $T(E)$ for $d = 3.0, 3.8, 4.6,$ and 5.4 Å for (a) 1 and (b) 16 k points; (c) $T(E)$ for $d = 3.0$ and $d = 5.4$ Å for 1 and 64 k points are compared. This graph shows the development of a cusp at E_F .

Figures 6(a) and 6(b) show the evolution of the Fano-like resonances as the molecule moves for 1 and 16 k points, respectively. Clearly, many resonances do disappear as more channels are added. Notice in particular how for $d = 4.6$ Å a Fano-like resonance lying in the HOMO/LUMO gap is masked by the conduction through the $k \neq 0$ conduction bands available. The Fano-like resonance for $d = 5.4$ Å, however, does not disappear and remains almost unaffected even for large numbers of k points, as shown in panel (c). This indicates that only those Fano-like resonances whose dip is very close to the Dirac point survive when the number of k points increases. Computing $T(E_F)$ and therefore the low-bias conductance is complicated by the fact that strictly speaking only the $k = 0$ channel exists asymptotically at E_F even for a very large numbers of k points.

In summary, we find that physisorbing molecular wires with large-area planar anchor groups onto graphene sheets shows universality properties whereby the molecular BW resonances are placed always at the same energy position regardless of the

relative molecule/sheet position and of the physical gap length. This universality property is a consequence of the isochemical nature of the physisorbed species. Our finding is sustained by DFT simulations of several graphene junctions bridged by monomeric, dimeric, and trimeric molecular wires composed of porphyrine or phthalocyanine molecules. We have used a van der Waals functional that is suited for the problem at hand. We argue that even if the energy position of the molecular resonances is fully rearranged by strong correlations, the new spectra should follow the same universality behavior. We suggest that the above property could be used to solve the conductance variability problem inherent to noble-metal-based single-molecule junctions. This is so because the energy position of the transmission resonances may be suitably modified by the application of a gate voltage. The energy spectrum may also be tailored by synthetic chemistry methods. We stress that, contrary to the case of noble-metal electrodes, a large number of k points must be used to find accurate estimates of the low-voltage conductance, which renders theory predictions a delicate task. The transmission coefficient $T(E)$ develops a cusp at the Dirac point.

We find binding energies for molecule drift parallel to the physical gap of order 0.1–0.2 eV, which should be enough to provide mechanical stability to the junction at temperatures below 100 K. The desired room-temperature mechanical stability of this graphene junctions seems achievable by attaching side groups, or by increasing the surface area of the anchors. Furthermore, irregularities at the edges will act as anchoring points. Longer linker groups than those used in the present study could be synthesized to better avoid graphene's edges. It would be relevant to design the linker groups so as to either tailor or avoid the Fano-like resonances.

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