

Nonmechanical Conductance Switching in a Molecular Tunnel Junction

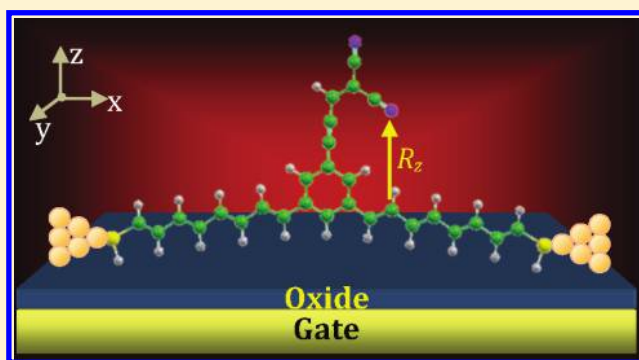
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S Supporting Information

ABSTRACT: We present a molecular junction composed of a donor (polyacetylene strands) and an acceptor (malononitrile) connected together via a benzene ring and coupled weakly to source and drain electrodes on each side, for which a gate electrode induces intramolecular charge transfer, switching reversibly the character of conductance. Using a new brand of density functional theory, for which orbital energies are similar to the quasiparticle energies, we show that the junction displays a *single*, gate-tunable differential conductance channel in a wide energy range. The gate field must align parallel to the displacement vector between donors and acceptor to affect their potential difference; for strong enough fields, spontaneous intramolecular electron transfer occurs. This event radically affects conductance, reversing the charge of carriers, enabling a spin-polarized current channel. We discuss the physical principles controlling the operation of the junction and find interplay of quantum interference, charging, Coulomb blockade, and electron–hole binding energy effects. We expect that this switching behavior is a generic property for similar donor–acceptor systems of sufficient stability.

SECTION: Electron Transport, Optical and Electronic Devices, Hard Matter



In recent years, gated molecular junctions, weakly coupled to source-drain (SD) electrodes, were studied experimentally and analyzed theoretically. The gate shifts differential conductance channels with respect to the chemical potential (Fermi level) of the metallic leads,^{1–15} and also affects nuclear configuration by inducing electron transfer from metal electrode to the molecule.^{16–18} A key question is how to increase junction polarizability and its response to the gate field. Several works have addressed this by using a junction composed of a relatively large number of conjugated phenyl rings.^{19–24} However, this has significant side effects, such as a high density of electron-conducting states, delocalized electron orbitals, and loss of Coulomb blockade effects, all of which reduce the sharp switching behavior of the junction. It is the purpose of this Letter to present a new, different conceptual idea toward junctions, where sensitivity to the gate is obtained along with sharp switching mechanism. We use a specific molecular junction and explain its electronic behavior showing the variety of physical processes affecting its transport properties (e.g., interference, charging energies, electron–hole binding energy, polarizability, and Coulomb blocking). The resulting system displays a single, narrow, highly tunable, resonance state supporting a differential conductance channel capable of switching spin-polarized currents.

Our analysis is theoretical and makes use of density functional theory (DFT) based on the first-principles-tuned Baer–Neuhauser–Livshits (BNL*)^{25,26} range-separated

hybrid.^{27,28} This functional allows for good molecular structure prediction while being especially suitable for conductance calculations because its orbital energies were found to approximate quasiparticle energies closely, a property not available in the more common density functionals. (See the Supporting Information for a comparison of BNL* and B3LYP gaps.)^{29,30} The functional also allows calculation of accurate charge transfer³¹ as well as valence³² excitation energies with linear response time-dependent density functional theory (TDDFT). All electronic structure calculations were performed using this BNL* functional^{25,26,33} within the 6-31G/6-31+G* basis set and Q-CHEM v3.1 package.³⁴ See the Supporting Information for details of basis sets, tuning, and a comparison with B3LYP.

The active part of the molecular junction is composed of the 2-(3-phenylprop-2-ynylidene) malononitrile molecule, where the malononitrile group (MN) acts as an electron acceptor and the two thiol-terminated short *trans*-polyacetylene (PA) segments connect in meta position to the benzene ring, acting as electron donors (Figure 1). Configurational stability of the junction, hindering bending and rotary distortions, even under strong gate fields and charge shifts, is achieved by using conjugated PA segments as donors and CC triple bond

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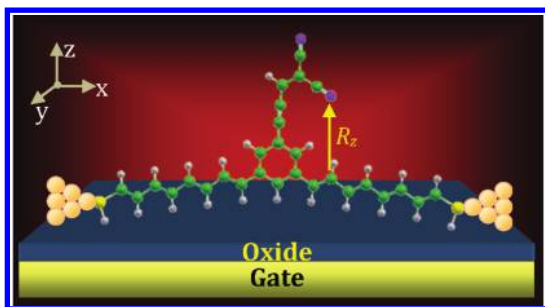


Figure 1. Schematic depiction of the molecular junction explored in this Letter: two thiol-terminated short *trans*-polyacetylene (PA) segments (SH-(HC=CH)₄-) acting as meta substituents on the aromatic ring of a 2-(3-phenylprop-2-ynylidene) malononitrile molecule. The thiol group facilitates bonding to gold metallic source drain electrodes. The PAs are electron donors determining the ionization potential ($I \approx 7$ eV) of the molecule, whereas the MN is an electron acceptor, endowing the electron affinity $A \approx 1$ eV. The molecular plane is parallel to x - z and lies above a planar gate electrode parallel to the x - y plane. The latter creates an electric field E_z in the vertical direction. The smallest vertical distance between MN and PA is large ($R_z \approx 5.9$ Å), facilitating the high tunability of the fundamental gap $I-A$ by E_z . A sufficiently strong E_z induces spontaneous electron transfer from PA to MN. Because of interference effects, electric current cannot flow through the aromatic ring from left to right PAs but must go instead through the MN. Therefore, E_z also controls the differential conductance channel of the junction.

connecting the acceptor to the aromatic ring. (See the Supporting Information for a description of stability under gate fields.)

We now study charge carriers in the molecule. Consider first the creation of a hole by removing an electron, a process involving investment of energy, the ionization potential I . In the quasiparticle picture, the hole has a single-particle wave function, described as a frontier DFT orbital on one of the donors (orbital 1 or 3 of Figure 2). The energy of the hole, $-I$,

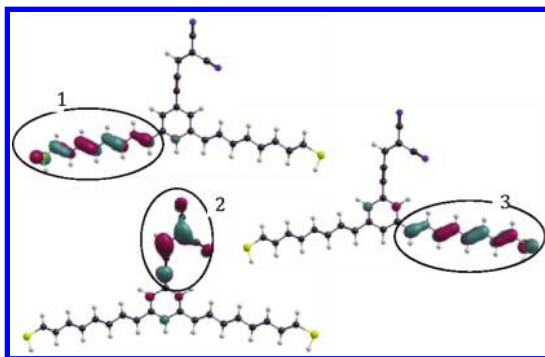


Figure 2. Graphical depiction of three frontier orbitals dominating the electronic properties of the junction. The occupied orbitals 1 and 3 (localized on the left and right donors) and the unoccupied orbital 2 (localized on the acceptor). The energy of orbital 1 is slightly higher than that of 3.

is closely approximated by the DFT highest occupied molecular orbital (HOMO) energy ϵ_H .^{26,29,30} Similarly, we can add an electron to the molecule; this releases energy of the amount equal to the electron affinity, A . In the DFT calculation, the electron quasiparticle wave function is orbital 2 in Figure 2, localized primarily on the MN acceptor. The energy of the

electron, $-A$, is closely approximated by the lowest unoccupied molecular orbital (LUMO) energy, ϵ_L .

Now consider how a negatively charged gate electrode in the x - y plane below the molecule affects its electronic structure. The electrode creates an electric field in the z direction, E_z , or a potential difference, $e\bar{z}E_z$, between the electron on MN and the hole on PA, displaced by a distance \bar{z} and where ϵ is the molecular dielectric constant. Therefore, the gate-field affects the electron-hole energy gap as

$$\epsilon_g(E_z) = \epsilon_g(0) - \frac{e}{\epsilon}\bar{z}E_z \quad (1)$$

In Figure 3 (left), we plot the DFT-calculated orbital gap, ϵ_g , versus the gate field, E_z , showing linear dependence, from

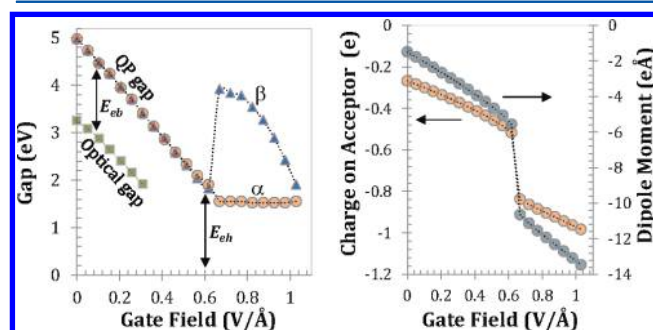


Figure 3. BNL*-DFT spin-polarized LUMO-HOMO (quasi-particle) gap and TDDFT optical gap (left), z -component dipole moment, and Mulliken charge on malononitrile (MN) group (right) versus gate field.

which

$$-\frac{d\epsilon_g}{dE_z} = 5.1e\text{Å} \equiv \frac{e}{\epsilon}\bar{z} \quad (2)$$

An abrupt change in the gap occurs at a certain critical value of the field $E_z^* = 0.63$ V/Å. This critical behavior is due to a spontaneous charge transfer induced by the gate, clearly seen in Figure 3 (right), where the dipole moment and charge on the MN acceptor jump discontinuously at E_z^* . We have carefully checked that if the sulfur atoms are held in place (as happens when the molecule is connected to the metallic leads) then the geometry of the molecule is only slightly distorted by this internal electron transfer.

In Mulliken's theory,³⁵ the energy of electron transfer from donor to acceptor is $E_{CT}(E_z) = I(E_z) - A(E_z) - E_{eh} \approx \epsilon_g(E_z) - E_{eh}$, where $E_{eh} = e^2/(4\pi\epsilon_0\epsilon\bar{z})$ is the energy of Coulomb attraction between the electron and hole. Charge spontaneously transfers from donor to acceptor once $E_{CT}(E_z) \leq E_{CT}(E_z^*) = 0$, so from Figure 3 (left)

$$E_{eh} = \frac{e^2}{4\pi\epsilon_0\epsilon\bar{z}} = \epsilon_g(E_z^*) = 1.9 \text{ eV} \quad (3)$$

Using eqs 2 and 3, we can estimate the internal dielectric constant $\epsilon = 1.2$ and the electron-hole effective z -displacement $\bar{z} = 6.2$ Å; the latter is in agreement with the minimal donor-acceptor z -displacement $R_z = 5.9$ Å.

In Figure 3 (left), we also plot the optical gap, ϵ_{opt} , calculated from linear response TDDFT using the same functional. ϵ_{opt} is the first excitation energy corresponding to a transition dipole moment pointing in the z direction. Note that ϵ_{opt} depends

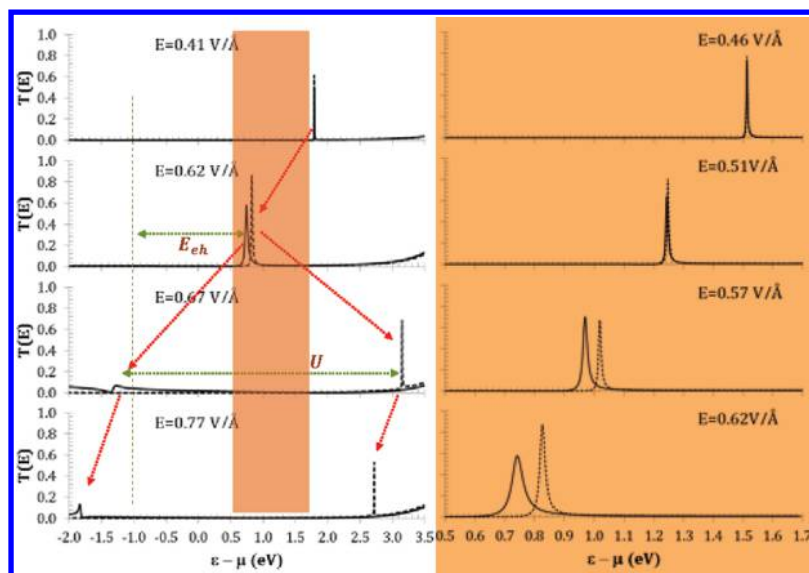


Figure 4. Calculated transmittance function $T(E)$ through the junction, assuming clamped nuclei, from the zero bias BNL* Hamiltonians (eq 4) at different gate fields. On the left, a broad energy view of the transmission channels, from $\epsilon - \mu = -2$ to 3.5 eV at several gate fields, and on the right, a zoom into the energy range of 0.5 to 1.7 eV for gate fields before the charge-transfer event. The full (dotted) line is the transmission of the α (β) spin states. The vertical line at -1.1 eV is the position of the HOMO energy.

linearly on E_z , predicting strong electro-absorption effects for z -polarized light in this junction. It is readily visible in Figure 3 (left) that the exciton binding energy, namely, the difference $E_{eb} = \epsilon_g - \epsilon_{opt} \approx 1.7$ eV, is nearly constant. The fact that the value of E_{eb} is close to that of E_{eh} of eq 3 is no coincidence because both describe electron–hole attraction energy.

Once $E_z > E_z^*$, that is, the field is strong enough to induce charge transfer, a spin α (say) electron moves from one of the donors (orbital 1 or 3) into the orbital localized on the acceptor (orbital 2). Orbital 2, the previous LUMO, now has its energy spin-dependent: the α orbital energy drops abruptly slightly below the HOMO level (due to the electron–hole binding energy E_{eh} discussed above), and it becomes occupied by an electron, whereas the β -orbital energy shoots up in energy above some of the other unoccupied levels of the PAs. This latter effect is due to Coulomb repulsion: the energy to add a second electron to the acceptor is much higher now due to the presence of the first transferred electron. Therefore, immediately after the charge transfer, orbital 2 is no longer a frontier orbital: both the α and β LUMOs are now donor orbitals, and as a result the α and β gaps become independent of E_z . Further increase in the field lowers the energies of both spin components of orbital 2. The α component digs deeper into the occupied levels, but the β component energy reduces until it resumes its role as the LUMO at $E_z > 0.8$ V/Å, making the β gap once again field-dependent.

Thus far, we discussed this donor–acceptor system as a molecule and not as part of a molecular junction. The junction we consider is formed by attaching the molecule to left and right metallic leads of chemical potential μ . (Additional effects of the metallic electrodes are discussed below.) The thiol-terminated PA segments provide for very weak coupling, and the molecule preserves much of its chemical and electronic properties: its orbitals and its orbital energies slightly shift to sharp differential conductance resonance channels. We imagine an experimental setup where the energy needed to transfer an electron from the molecule to the metal; that is, $\mu - \epsilon_H$ is controlled and kept fixed for all values of the gate field (in our

case, $\mu - \epsilon_H = 1.1$ eV). We assume a symmetric application of the bias potential V_{SD} across the leads, where the chemical potential of the left (right) lead is $\mu + eV_{SD}/2$ ($\mu - eV_{SD}/2$). In this setup, experimental realization of current through a resonance at energy $\epsilon = E + \mu$ requires a bias of $V_{SD} > 2|E|$.

We study the differential conductance of the junction using Landauer's theory, based on the ground-state DFT Hamiltonian where the peaks of the transmittance $T(E)$ (the probability for an electron of energy $\epsilon = E + \mu$ to cross the junction from left to right) are directly associated with the differential conductance channels. In weakly bound junctions, the positions of these peaks are close to the quasiparticle energies, which are close to the orbital energies of our DFT Hamiltonian.^{21,22} The transmittance $T(E)$ is thus calculated by³⁶

$$T(E) = 4\text{tr}\{G^\dagger(\epsilon)\Gamma_L G(\epsilon)\Gamma_R\} \quad (4)$$

where Γ_i ($i = L, R$) are absorbing potentials³⁷ laid on the left and right PA segments and $G(\epsilon)$ is the Green's function corresponding to the DFT Hamiltonian. (See ref 38 for further details and explanations of this method.)

The calculated $T(E)$ is plotted in Figure 4 for several values of the gate field E_z . Remarkably, at a very broad energy interval ($-4 < E < 3$ eV), the system displays only a single transmittance peak (which, under sufficiently large gate field, may split into two spin-polarized components, as discussed below). Whereas there are many occupied and some unoccupied orbitals associated with the PA strands in this energy range (e.g., orbitals 1 and 3 in Figure 2), none of them seem to conduct current. This is due to the strong destructive interference effect associated with the connection of the PA strands in a meta position on the benzene ring.^{38–42} The position of the conductance peak, with respect to the HOMO energy (the vertical line in Figure 4 (left)), is almost exactly equal to the gap ϵ_g (Figure 3 (left)), indicating that transmission occurs through the LUMO orbital, that is, orbital 2 of Figure 2, mainly localized on MN, the electron acceptor part of the molecule. Therefore, the $T(E)$ peak at low fields corresponds to tunneling

transmission of electrons through orbital 2. As a result, the SD voltage needed for reaching this conducting state is tunable by E_z . This can be seen in the right panel of Figure 4 zooming into the orange strip region of Figure 4 (left). As the gate field E_z increases (by steps of ~ 0.03 to 0.05 V/Å), the V_{SD} position of the conductance peak drops by steps of ~ 0.3 eV. This high tunability of differential conductance facilitates a transistor-like operation mode for the junction, as current is reversibly switched on/off by the gate field.

As the gate field E_z approaches the critical value E_z^* , the differential conductance resonance splits into two resonances at slightly different energies (Figure 4 (right)), each corresponding to a different value of the z -component of spin. As often happens in DFT calculations, the breaking of spin symmetry signals strong correlation effects in the electronic system. At the critical gate field E_z^* , a catastrophic spin-split occurs: one spin resonance (say, spin α) shoots down in energy below the HOMO level (vertical line in Figure 4 (left)), gets occupied by an α electron, and becomes a hole-conducting channel, whereas the other resonance shoots up in energy and becomes an electron-conducting channel. The energy splitting between these two spin resonances for gate fields slightly above E_z^* is $U = 4.3$ eV. As explained above, the drastic change of electronic structure happens because of the intramolecular charge transfer: an α electron transfers from one of the frontier orbitals (orbital 1 or 3 of Figure 2) of the donors to orbital 2 of the acceptor. Because the acceptor now populates an electron, conductance of β electrons is blocked due to Coulomb repulsion (unless V_{SD} is considerably increased). As the field E_z is further increased beyond E_z^* , the hole differential conductance peak still responds to the field and can be further lowered, resulting in highly controllable spin-polarized differential conductance channel.

Thus far, we treated the gold electrodes as particle reservoirs of chemical potential, μ . We now briefly comment on their effect on the electronic structure of the junction. In the Supporting Information, we describe the electronic behavior of the junction, where both hydrogen atoms, connected to the left and right sulfur atoms, are replaced with two gold clusters, each composed of three atoms. We find that the relevant electronic energy levels change with the donor–acceptor energy gap reduced by 0.6 eV. This is in accordance with recent findings on the renormalization of molecular gaps near metal surfaces.⁴³ Furthermore, because of delocalization of the HOMO, the electron–hole binding energy is reduced from 1.9 to 1 eV, causing the critical field required for charging the LUMO to grow from 0.6 to 0.7 V/Å. Despite these changes in numerical values, the essential electronic operation of the junction remains intact: the sensitivity to the critical gate voltage, causing charging of the highly localized LUMO (orbital 2), its dependence on the electron–hole binding energy, and the spin-polarized Coulomb blockade effect.

In summary, we have presented a molecular junction (Figure 1) with well-separated donor–acceptor sites for which proper orientation with respect to a gate field allows exceptional control of the conductance and optical properties. The junction is structurally stable under the strong gate fields. It displays a single conductance peak at a broad energy range, allowing its meticulous control over a large SD voltage and gate field intervals. The strong electronic response should render the system less sensitive to stray fields and temperature effects. We summarize the conductance properties of the junction in Figure 5, exhibiting gate control of the differential conductance level,

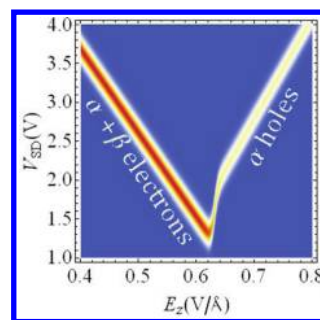


Figure 5. Expected differential conductance of the molecular junction in Figure 1 as a function of gate field and source-drain voltage.

allowing a transistor-like operation and the switch into a *spin-polarizable* regime (due to the Coulomb blockade effect) when $E_z > E_z^*$. Although we here treat a specific system, the principle of operation is generic because it is based on sound physical principles; therefore, other junctions containing similar design elements should exhibit similar conductance behavior.

■ ASSOCIATED CONTENT

Supporting Information

Tuning procedure, comparison of BNL* and B3LYP, effects of gold electrodes on the junction, and optimization of the ground state geometry. This material is available free of charge via the Internet <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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