Supporting information for the manuscript
"Donor-acceptor systems as molecular diodes:
a self-consistent description of the intramolecular electron flow",
submitted by Celso P. de Melo and Augusto C. L. Moreira to ACS Nano

Here, we will consider in more details three important steps in the calculation described in the accompanying manuscript:

I - **Tunnel Current Probabilities:**

In this part of the manuscript, we have followed closely the discussion of "Tunneling in Metal-Insulator-Metal Structures", presented in Chapter 4 of A.T. Fromhold, "Quantum mechanics for applied physics and engineering. Dover Publications: New York, 1991; p xvi, 430 p."(our Ref. 5). In this manner, the probability P_{in1} of charge transport from the cathode (region 1) to the molecule (region 2), for instance, can be constructed by considering the electronic flux incident at the interfaces and the quantum mechanical transmission coefficient.

To calculate the incident flux we have considered initially the density of states $D(E)$ resolved into a spectrum $D(E,p_x)$ characterized by the value of the x-component of the momentum (i.e., in the direction of the applied electric field), such that

$$D(E) = \int_{-\infty}^{\infty} D(E, p_x) dp_x \ .$$

Then, $2D(E,p_x).dp_x.dE$ represents the number of electronic states with total energy in the range E to $E+dE$ but restricted to have x-component of momentum in the range p_x+dp_x. Since the occupation probability is given by the Fermi-Dirac function $f(E)$, the corresponding number of occupied states is $2f(E)D(E, p_x)dp_xdE$. The product of this number by the x-component of the velocity $v_x=p_x/m$ gives the flux of electrons incident on the barrier,

$$Flux = \iint 2.(p_x / m).D_{(E,\, p_x).} f_{(E).} dp_x.dE \ .$$

If there is a barrier between the metal and the molecule, the maximum number of electrons that could cross this barrier corresponds to the product of the incident flux by a transmission coefficient (T) given by (in our case, chosen to be) a trapezoidal barrier.

$$T_{(E).}(Flux) = \iint T_{(E).} 2.(p_x / m).D_{(E,\, p_x).} f_{(E).} dp_x.dE \ .$$

But an electron will effectively cross the barrier only if there is a corresponding unfilled allowed state on the other side. So we can proceed in the same way and define the probability of finding unoccupied states as $A(E)D(E)dE$, where $A(E)=1-f(E)$ is the un-occupation probability and $D(E)$

the density of states in the device region. For the case of discrete levels, *D(E)* is given by a Dirac-Delta function $D(E_S) = \sum_{\sigma} \delta(E - E_{\sigma,S})$, with $E_{\sigma,S}$ representing the σ^{th} energy level of the *S*-charge sate. Once we concatenate all this information together, we obtain:

$$J^{S}_{1\to 2} = \iiint T(E).2.(p_x / m).D_1(E, p_x).D_2(E).f_1(E).A_2(E).dp_x.dE_1.dE_2 ,$$

where the subscripts 1 and 2 represent the different sides of the barrier (region 1 for cathode and region 2 for the molecule for example). Hence, the probability of transport through the cathode to molecule (in a S-charge state) can be written as: $P^{S}_{in1} = \sum_{\sigma} P^{\sigma_S}_{in1} = \frac{J^{S}_{1\to 2}}{Flux}$. The other probabilities can be derived by adopting a similar reasoning.

II - T-matrix:

A very common approach to study excited states of molecular systems is the Configuration Interaction with Single excitations (CIS) approximation. Within this formalism, the CIS molecular wavefunction Ψ^R includes the one corresponding to the (Hartree-Fock) ground state of the system plus a linear combination of the determinants $\psi^{\sigma\lambda}$ corresponding to all configurations resulting from a single (i.e., one electron) excitation out of the HF ground state, in the form

$$\Psi^R = c_0\psi_0 + \sum_{\sigma=occ}\sum_{\lambda=un} c_R^{\sigma\lambda}\psi^{\sigma\lambda} \qquad ,$$

where the ***c***´s are linear coefficients to be determined (in a variational manner) and $\psi^{\sigma\lambda}$ is the determinant form of the wavefunction associated to the configuration where an electron is excited from an occupied orbital σ to a virtual one λ. A set of CIS wave functions with their correspondent energies could be (variationally) determined by solving the matrix eigenvalues equation resulting from differentiating the standard Hamiltonian energy expression with respect to the elements of the CI coefficient vector ***c*.** The corresponding eigenstates are called the CI eigenstates and once they have been determined, the dipole moment μ and the oscillator strength f_R could be calculated as $\mu^R = \left\langle \Psi^R \middle| \mu \middle| \Psi^R \right\rangle$ and $f_R \square \left|\mu^R\right|^2$.

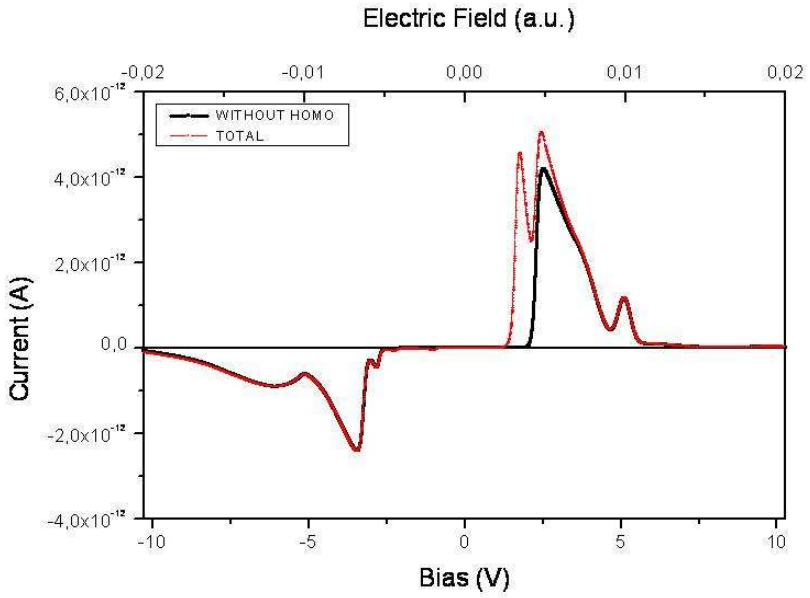
In quantum mechanics, an oscillator strength is usually interpreted as a measure of the relative probability that a transition occurs between the two molecular states involved and, with this in mind, the elements of the T-matrix can be written as $T_{\sigma\lambda} = \sum_{R} \left|c_R^{\sigma\lambda}\right|^2 f_R$, where indicates that all transitions are between the ground state and the *S*-excited state.

III – Identification of the role played by individual occupied molecular orbitals in the charge transport of the AMNB molecule:

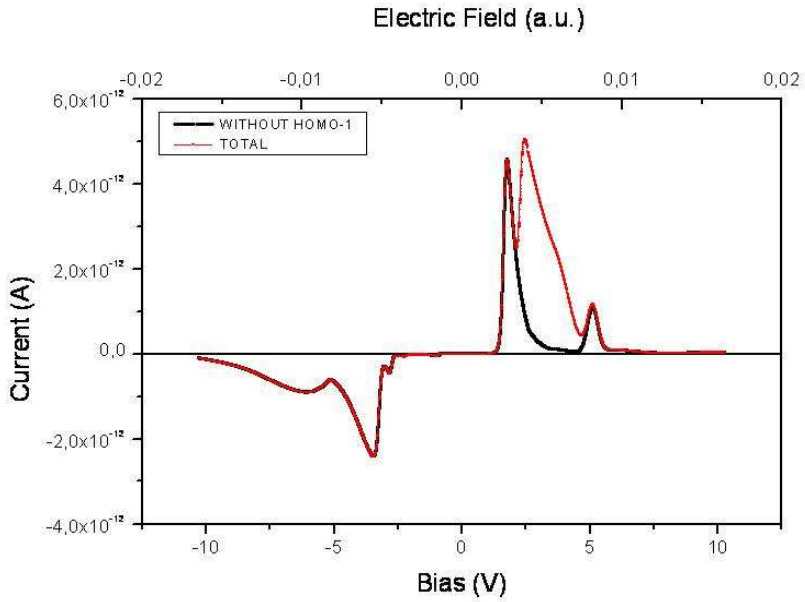
To assess the relative contribution of some of the FMOs to the intramolecular charge transport in the AMNB molecule, we have implemented calculations where the HOMO, HOMO-1 and HOMO-2 were artificially suppressed from the molecule.

In the figures below, the total current as a function of the value of the externally applied electric field ξ (superior horizontal axis) [bias V (inferior horizontal axis)] is represented by the red curve.

a) Suppression of the HOMO: The corresponding current as a function of the value of the externally applied electric field ξ (superior horizontal axis) [the bias V (inferior horizontal axis)] is represented by the black curve. Note that, for instance for positive bias, the first peak and part of the second one seen in the full calculation are suppressed.



b) Suppression of the (HOMO-1): The corresponding current as a function of the value of the externally applied electric field ξ (superior horizontal axis) [the bias V (inferior horizontal axis)] is represented by the black curve. Note that, for instance for positive bias, the second peak seen in the full calculation is almost entirely suppressed.



a.

c) Suppression of the (HOMO-2): The corresponding current as a function of the value of the externally applied electric field ξ (superior horizontal axis) [the bias V (inferior horizontal axis)] is represented by the black curve. Note that, for instance for positive bias, the third peak seen in the full calculation is almost entirely suppressed.