

## Supplementary Information

### Features of optoelectronic processes in a molecular junction based on a fluorophore with optically active frontier $\pi$ -orbitals: electrofluorochromism in a ZnPc-based junction

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#### Appendix A: Theoretic approach in the Fock space

When electrons are transferred through the molecular junction "electrode1-molecule-electrode2" (1M2), which is a many-body system, electrons occupy and release single-particle states in both the electrodes and the molecule. Therefore, it is quite appropriate to describe this process in the Fock space, where the states of a multi-electronic system are characterized by sets of occupation numbers. For the 1M2 system, these numbers are [1–3]  $N_{r\mathbf{k}\sigma} = 0, 1$  and  $n_{\lambda\sigma} = 0, 1$ . Symbol  $\sigma = \pm 1/2 (\equiv \uparrow, \downarrow)$  indicates the projection of the electron spin, which can occupy, respectively, a state with the wave vector  $\mathbf{k}$  in the conduction band of the  $r$ th electrode or fill  $\lambda$ th MO. Hence, the many-electron state for the  $r$ th electrode and the corresponding electronic energy are given by the forms  $|\{\mathcal{N}\}_r\rangle = |N_{r\mathbf{k}_1\sigma_1}, N_{r\mathbf{k}_2\sigma_2}, \dots\rangle = \prod_{\mathbf{k}\sigma} |N_{r\mathbf{k}\sigma}\rangle$  and  $E(\{\mathcal{N}\}_r) = \sum_{\mathbf{k}\sigma} E_{r\mathbf{k}} N_{r\mathbf{k}\sigma}$ , respectively. (In the non-magnetic electrodes under consideration and in the absence of a magnetic field, the electron energy  $E_{r\mathbf{k}}$  does not depend on  $\sigma$ ). Since the interaction of electrodes with a molecule manifests itself as a perturbation, in the Fock space, the basic states of the 1M2 system and the corresponding energies can be represented as [3, 4]

$$\begin{aligned} |\{\mathcal{N}\}\rangle &= |\{\mathcal{N}\}_1, M(N), \{\mathcal{N}\}_2\rangle, \\ E(\{\mathcal{N}\}) &= \sum_{r=1,2} E(\{\mathcal{N}\}_r) + E_{M(N)}, \end{aligned} \quad (\text{A1})$$

where the abbreviation of the electronic state of system 1M2  $|\{\mathcal{N}\}_1, M(N), \{\mathcal{N}\}_2\rangle$  is identical to  $\prod_{\mathbf{k}\sigma} |N_{1\mathbf{k}\sigma}\rangle \times |M(N)\rangle \times \prod_{\mathbf{k}'\sigma'} |N_{2\mathbf{k}'\sigma'}\rangle$ . The Eq. (A1) shows that in the Hamiltonian of the 1M2 system

$$H = H_0 + V_{em} \quad (\text{A2})$$

the main interactions are concentrated in the term

$$H_0 = \sum_{\{\mathcal{N}\}} E(\{\mathcal{N}\}) |\{\mathcal{N}\}\rangle \langle \{\mathcal{N}\}| \quad (\text{A3})$$

related to the non-interacting electrodes and the molecule, whereas the interaction between them,

$$V_{em} = \sum_{r\mathbf{k}\sigma, \lambda} (\beta_{rk, \lambda} a_{r\mathbf{k}\sigma}^+ c_{\lambda\sigma} + \beta_{rk, \lambda}^* c_{\lambda\sigma}^+ a_{r\mathbf{k}\sigma}), \quad (\text{A4})$$

acts as a perturbation [1, 5]. It is responsible for single-electron transitions between many-electron states  $|\{\mathcal{N}\}_r\rangle$  and  $|M(N)\rangle$ . Transitions are generated by electron creation (annihilation) operators  $a_{r\mathbf{k}\sigma}^+$  ( $a_{r\mathbf{k}\sigma}$ ) and  $c_{\lambda\sigma}^+$  ( $c_{\lambda\sigma}$ ) acting on

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single-electron states belonging to the conduction band and  $\lambda$ th MO, respectively. The spin-independent coupling between these states is  $\beta_{rk,\lambda}$ .

In low-temperature experiments (4.5 K) with STM-induced EL, the current does not exceed 1 nA, which indicates a single-electron charge transmission through a 1M2 junction. This means that the elementary hopping process

$$|N_{r\mathbf{k}\sigma}, M(N)\rangle \rightarrow |N'_{r\mathbf{k}\sigma}, M'(N')\rangle \quad (\text{A5})$$

responsible for recharging the molecule occurs under conditions

$$E_{r\mathbf{k}}N'_{r\mathbf{k}\sigma} + E_{M'(N')} = E_{r\mathbf{k}}N_{r\mathbf{k}\sigma} + E_{M(N)} \quad (\text{A6})$$

and

$$N'_{r\mathbf{k}\sigma} + N' = N_{r\mathbf{k}\sigma} + N \quad (\text{A7})$$

indicating the conservation of energy and charge, respectively. Since at 4.5 K the overwhelming number of electrons in the conduction band fill the energy levels below the Fermi level, then, following the Eqs. (A6) and (A7), we can see that  $M(N) \rightarrow M'(N')$  recharge of the molecule becomes possible if

$$\begin{aligned} \Delta E_{M(N)M'(N')}^{(r)} &= E_{M(N)} - E_{M'(N')} \\ -\mu_r(\delta_{N',N-1} - \delta_{N',N+1}) &> 0, \end{aligned} \quad (\text{A8})$$

where  $\mu_r$  is the chemical potential of the  $r$ th electrode. As follows from the Eq. (A8), due to the interaction of the molecule with the electrode  $r$  the direction of recharging of the molecule changes at  $\Delta E_{M(N)M'(N')}^{(r)} = 0$ . This happens at certain critical voltages

$$V_b = V_{M(N),M'(N')}^{(r)} = -V_{M'(N'),M(N)}^{(r)}. \quad (\text{A9})$$

In addition to recharging the molecule, Eq. (A5), the processes

$$|N_{r\mathbf{k}}, M(N), N_{r'\mathbf{k}'\sigma'}\rangle \rightarrow |N'_{r\mathbf{k}}, M'(N), N'_{r'\mathbf{k}'\sigma'}\rangle \quad (\text{A10})$$

are also possible. They reflect direct elastic and inelastic tunneling of electrons between different electrodes  $r$  and  $r'$ , when the molecule, respectively, does not change ( $M'(N) = M(N)$ ) or changes ( $M'(N) \neq M(N)$ ) its electronic state. Such single-step electron tunneling is generated by the operator  $V_{e-e} = V_{em}G(E)V_{em}$ , where  $G(E) = [E - H + i0^+]^{-1}$  is the Green operator. Given that the interaction  $V_{em}$  is a weak perturbation, then in the Green operator the Hamiltonian of the 1M2 system  $H$  can be replaced by  $H_0^{(eff)}$  [3, 4, 6]. The difference from  $H_0$  that in it the energy of the molecule is replaced by  $E_{M(N)} - (i/2)\Gamma_{M(N)}$ , where  $\Gamma_{M(N)}$  is the broadening of the energy level caused by interaction  $V_{em}$ .

When tunneling electrons, Eq. (A10), the conservation of energy and charge is determined by the conditions

$$\begin{aligned} E &= E_{r\mathbf{k}}N_{r\mathbf{k}\sigma} + E_{M(N)} + E_{r'\mathbf{k}'}N_{r'\mathbf{k}'\sigma'} \\ &= E_{r\mathbf{k}}N'_{r\mathbf{k}\sigma} + E_{M'(N)} + E_{r'\mathbf{k}'}N'_{r'\mathbf{k}'\sigma'} \end{aligned} \quad (\text{A11})$$

and

$$N'_{r\mathbf{k}\sigma} + N'_{r'\mathbf{k}'\sigma'} = N_{r\mathbf{k}\sigma} + N_{r'\mathbf{k}'\sigma'}, \quad (\text{A12})$$

respectively.

Taking into account the structure of the Fock states  $|\{\mathcal{N}\}\rangle$  and using the method of nonequilibrium density matrix [7], it becomes possible to find both the temporal behavior of the occupancies  $P(M(N), t)$  of molecular terms and the electronic current  $I_r(t)$  outgoing from the  $r$ th electrode. The corresponding equations have the form

$$\dot{P}(M(N), t) = \frac{\partial}{\partial t} \text{tr}' \left( \rho(t) |M(N)\rangle \langle M(N)| \right) \quad (\text{A13})$$

and

$$I_r(t) = -|e| \frac{\partial}{\partial t} \sum_{\mathbf{k}\sigma} \text{tr}' \left( \rho(t) a_{r\mathbf{k}\sigma}^+ a_{r\mathbf{k}\sigma} \right). \quad (\text{A14})$$

Here  $|e|$  is the absolute value of the electron charge and  $\rho(t)$  is the density matrix of the 1M2 system. The symbol  $tr'$  means that when calculating the trace, summation covers all quantum numbers  $\{\mathcal{N}\}$  with the exception of  $M(N)$  (in the Eq. (A13)) and  $N_{rk\sigma}$  (in the Eq. (A14)). The operator  $\rho(t)$  evolves over time  $t$  in accordance with the equation

$$\partial\rho(t)/\partial t = (i/\hbar)[H, \rho(t)] - \hat{D}\rho(t), \quad (\text{A15})$$

where  $H$  is the Hamiltonian of the 1M2 system (given by the Eqs. (A2) - (A4)), whereas  $\hat{D}$  is a superoperator characterizing fast relaxation processes caused by the interaction of the electronic system with a bath or/and a stochastic field.

### Appendix B: States and energies of a molecule in a two-orbital $\pi - \pi^*$ basis

In adiabatic approximation under consideration, the state of molecular term can be represented as  $|M(N)\rangle = |m, s_z; v\rangle \simeq |m, s_z\rangle|v\rangle$ , where the symbols  $m$  and  $v$  are associated with the corresponding electronic and vibrational characteristics of the molecule. The spin projection  $s_z$  is 0 and 0,  $\pm 1$  (for the singlet and triplet states of the molecule in its charge-neutral form, respectively) and  $\pm 1/2$  (for the doublet states of both the anionic and cationic forms of the molecule). Accordingly, in the absence of a magnetic field, the energy of the term can be represented in the form

$$E_{M(N)} = E_{mv} = E_m + E_v^{(m)}, \quad (\text{B1})$$

where  $E_m$  is the electronic energy depending on the filling of the MOs with electrons at a fixed spin value, and  $E_v^{(m)}$  is the contribution associated with nuclear oscillations. Below we will use the symbols  $m = (j = 0, S, T)$  to denote the ground singlet ( $S_0$ ), excited singlet ( $S_1$ ) and excited triplet ( $T_1$ ) electronic states of a charge-neutral molecule, as well as symbols  $m = (\alpha = +, *, -)$  for the ground cation, excited cation and the ground anion states of a charged molecule. During the optoelectronic process, a change in the electronic energy of the molecule occurs, associated almost exclusively with the filling of the frontier  $\pi$  electrons of the ring. Therefore, omitting the contribution to the total electronic energy of that part that does not change, the Hamiltonian of the fluorophore molecule can be represented as

$$H_{mol} = \sum_{\lambda} \left[ \sum_{\sigma} (\varepsilon_{\lambda\sigma} + U_{\lambda} c_{\lambda-\sigma}^+ c_{\lambda-\sigma}) c_{\lambda\sigma}^+ c_{\lambda\sigma} + \frac{1}{2} \sum_{\lambda' \neq \lambda} \left( U_{\lambda\lambda'} \sum_{\sigma} c_{\lambda\sigma}^+ c_{\lambda\sigma} \sum_{\sigma'} c_{\lambda'\sigma'}^+ c_{\lambda'\sigma'} - J_{\lambda\lambda'} \hat{s}_{\lambda} \hat{s}_{\lambda'} \right) \right], \quad (\text{B2})$$

where  $\lambda, \lambda' = \pi, \pi^*$ . The parameters of Coulomb and exchange interactions between electrons located on different MOs are denoted by  $U_{\pi\pi^*}$  and  $J_{\pi\pi^*}$ , respectively, while on-site interaction is characterized by the parameter  $U_{\pi\pi}$ . The spin operator  $\hat{s}_{\lambda}$  refers to the electron on the  $\lambda$ th MO. In Fock space, the state of an electron occupying the  $\lambda$ th MO with spin projection  $\sigma = \uparrow, \downarrow$  can be represented as  $|1_{\lambda\sigma}\rangle = |c_{\lambda\sigma}^+\rangle$ , where  $c_{\lambda\sigma}^+$  is the operator of electron creation in a given one-electron state. Therefore, using the symbols  $j = 0, S, T$ , we present the corresponding ground singlet, excited singlet and excited triplet electronic states of the molecule in the forms  $|0\rangle \equiv |S_0\rangle = |c_{\pi\uparrow}^+ c_{\pi\downarrow}^+\rangle$ ,  $|S\rangle \equiv |S_1\rangle = (1/\sqrt{2})|(c_{\pi\uparrow}^+ c_{\pi^*\downarrow}^+ - c_{\pi\downarrow}^+ c_{\pi^*\uparrow}^+)\rangle$ , and  $|T_0\rangle = 1/\sqrt{2} |(c_{\pi\uparrow}^+ c_{\pi^*\downarrow}^+ + c_{\pi\downarrow}^+ c_{\pi^*\uparrow}^+)\rangle$ ,  $|T_{\pm 1}\rangle = |c_{\pi\uparrow(\downarrow)}^+ c_{\pi^*\uparrow(\downarrow)}^+\rangle$ . Similarly, denoting the doubly degenerate states of a charged molecule by  $\alpha = +, *, -$ , for the ground and excited states of the cation, as well as the ground state of the anion, we have, respectively  $|+, \sigma\rangle = |c_{\pi\sigma}^+\rangle$ ,  $|*, \sigma\rangle = |c_{\pi^*\sigma}^+\rangle$  and  $|-, \sigma\rangle = |c_{\pi\uparrow}^+ c_{\pi\downarrow}^+ c_{\pi^*\sigma}^+\rangle$ . Using these expressions, for the proper energies of the Hamiltonian (B2) we get

$$E_m = \varepsilon_{\pi} n_{\pi} + \varepsilon_{\pi^*} n_{\pi^*} + U_{\pi\pi} n_{\pi\uparrow} n_{\pi\downarrow} + U_{\pi\pi^*} n_{\pi} n_{\pi^*} - J_{\pi\pi^*} \langle m | \hat{s}_{\pi} \hat{s}_{\pi^*} | m \rangle. \quad (\text{B3})$$

Therefore, counting the electronic energy of a molecule from its value in the ground state  $|0\rangle$ , which is equal to  $2\varepsilon_{\pi} + U_{\pi\pi}$ , it becomes possible to represent the electronic energies of the molecule as

$$\begin{aligned} E_0 &= 0, \\ E_+ &= -(\varepsilon_{\pi} + U_{\pi\pi}), \\ E_- &= \varepsilon_{\pi^*} + 2U_{\pi\pi^*}, \\ E_* &= \varepsilon_{\pi^*} - \varepsilon_{\pi} - (\varepsilon_{\pi} + U_{\pi\pi}), \\ E_S &= \varepsilon_{\pi^*} - (\varepsilon_{\pi} + U_{\pi\pi}) + U_{\pi\pi^*} + \frac{3}{4} J_{\pi\pi^*}, \\ E_T &= \varepsilon_{\pi^*} - (\varepsilon_{\pi} + U_{\pi\pi}) + U_{\pi\pi^*} - \frac{1}{4} J_{\pi\pi^*}. \end{aligned} \quad (\text{B4})$$

These expressions correspond to electronic configurations reflecting the filling of the  $\pi$  and  $\pi^*$  orbitals with electrons in accordance with scheme (a) Fig. 2 If we use the electronic configuration, as in scheme (b) of Fig. 2, then the

expression for the same electronic energies can be presented in the form given by the Eq. (2) (main text). In the case of the cationic form of the molecule, the electronic gap  $\Delta E_{el}^{(+)}$  and optical gap  $E_{opt}^{(+)} = E_* - E_+$  completely coincides, i.e.

$$\Delta E_{el}^{(+)} = E_{opt}^{(+)} = \varepsilon_{\pi^*} - \varepsilon_{\pi}. \quad (\text{B5})$$

### Appendix C: Critical transmission gaps

Taking into account the Eqs. (A8) and (B1) we arrive at the following expression for the electron-vibrational transmission gap:

$$\Delta E_{\alpha v, j v'}^{(r)} = \Delta E_{\alpha j}^{(r)} + E_{\alpha}^{(v)} - E_j^{(v')}. \quad (\text{C1})$$

Here, the value

$$\Delta E_{\alpha j}^{(r)} = \Delta E_{\alpha j}(0) - \kappa_{\alpha} |e| V_b (\delta_{r,2} - \eta) \quad (\text{C2})$$

coincides with the recharge energy of the molecule during the 0-0 vibrational transition. The unbiased part of this energy,

$$\Delta E_{\alpha j}(0) = \begin{cases} (E_{+(* )} + E_F) - E_j, \\ (E_- - E_F) - E_j, \end{cases} \quad (\text{C3})$$

can be attributed to the basic transmission gap. As follows from the Eqs. (C1) and (C2), the general expression for critical voltages has the form

$$V_{\alpha v, j v'}^{(r)} = \kappa_{\alpha} \frac{\Delta E_{\alpha v, j v'}(0)}{|e|(\delta_{r,2} - \eta)}, \quad (\text{C4})$$

where  $\Delta E_{\alpha v, j v'}(0)$  is the unbiased electron-vibrational transmission gap.

### Appendix D: Kinetic equations and transfer rates.

The characteristic times  $\tau_{vib}$  and  $\tau_{met}$  of establishing, respectively, the equilibrium Boltzmann distribution  $W(m, v) = \exp(-E_v^{(m)}/k_B T) / \sum_v \exp(-E_v^{(m)}/k_B T)$  (for the probability of occupation of vibration levels in the molecular term) and the Fermi distribution  $f_r(E) = \{\exp[(E - \mu_r)/k_B T] + 1\}^{-1}$  (for electrons in the conduction band of the metal) is much less than  $\tau_{tr}$ . [In the above distributions,  $k_B$  and  $T$  are the Boltzmann constant and the absolute temperature, respectively.] The appearance of equilibrium distributions on the time scale  $\Delta t \gg \tau_{vib}, \tau_{met}$  allows us to carry out a coarse-grained description of the kinetic process by studying the temporal behavior of integral occupancies  $P(m, t) = \sum_{v, s_z} P(M(N), t)$  of molecular terms on the time scale  $\Delta t \sim \tau_{tr}$ . Therefore, using the approach presented in the refs. [6, 8] and based on the Eqs. (A13) and (A15), we arrive at a set of coarse-grained kinetic equations

$$\dot{P}(m, t) = - \sum_{m'} [q_{mm'} P(m, t) - q_{m'm} P(m', t)] \quad (\text{D1})$$

associated with the normalization condition

$$\sum_m P(m, t) = 1, (m = 0, S, T, +, *, -). \quad (\text{D2})$$

Obtaining the Eq. (D1) assumes that the broadening  $\Gamma_r$  of the orbital energy level caused by the interaction (A4) of the molecule with the  $r$ th electrode is so small that the inequality

$$\Gamma_r \ll k_B T \quad (\text{D3})$$

holds for both frontier MOs coupled to the band states of  $r$ th electrode. The transfer rates between the six molecular states involved in the optoelectronic process are determined by three contributions:

$$q_{mm'} = q_{mm'}^{(mol)} + q_{mm'}^{(chrg)} + q_{mm'}^{(ine)}. \quad (\text{D4})$$

The first one,  $q_{mm'}^{(mol)}$  characterizes the conventional type of intramolecular transitions associated with the intersystem crossing, light emission/absorption and the spontaneous emission. The rates  $q_{mm'}^{(chrg)}$  and  $q_{mm'}^{(ine)}$  characterize, respectively, the charging of the molecule and non-radiative processes caused by inelastic interelectrode tunneling of electrons.

The kinetic equations for the occupancies  $P_m$  are determined in terms of the transfer rates  $q_{mm'}$  (Eqs. (D1) and (D2)). There are three types of transfer rates. The first one,

$$q_{mm'}^{(mol)} = (k_m^{(isc)} + k_m^{(d)})(\delta_{m,S}\delta_{m',0} + \delta_{m,*}\delta_{m',+}) + k_m^{(isc)}(\delta_{m,S}\delta_{m',T} + \delta_{m,T}\delta_{m',0}) + k_{m'}^{(f)}(\delta_{m,0}\delta_{m',S} + \delta_{m,+}\delta_{m',*}), \quad (D5)$$

characterizes the non-radiative intersystem conversional transitions, the light emission, light absorption and the spontaneous transitions (elementary rates  $k_m^{(isc)}$ ,  $k_m^{(d)} = k_m^{(f)} + k_m^{(spont)}$ ,  $k_m^{(f)}$  and  $k_m^{(spont)}$ , respectively). The second type of rates,

$$q_{mm'}^{(chrg)} = A_{mm'}^{(chrg)} \sum_{r=1,2} K_{mm'}^{(r)} (\delta_{m,\alpha}\delta_{m',j} + \delta_{m,j}\delta_{m',\alpha}) \quad (D6)$$

is associated with the recharging of the molecule, carried out under the action of interaction  $V_{em}$  (Eq. (A4)). Here,

$$A_{\alpha j}^{(chrg)} = \delta_{j,0}(\delta_{\alpha,+} + \delta_{\alpha,-}) + \frac{1}{2}(\delta_{j,S} + 3\delta_{j,T})(\delta_{\alpha,+} + \delta_{\alpha,-} + \delta_{\alpha,*}), \quad (D7)$$

$$A_{j\alpha}^{(chrg)} = 2[\delta_{j,0}(\delta_{\alpha,+} + \delta_{\alpha,-}) + \frac{1}{2}(\delta_{j,S} + \delta_{j,T})(\delta_{\alpha,+} + \delta_{\alpha,-} + \delta_{\alpha,*})]$$

are the factors reflecting the spin characteristics of the  $j$ th and  $\alpha$ th states of the molecule. The elementary hopping process (charging) is determined by the rates

$$K_{\alpha j}^{(r)} = (\Gamma_r/\hbar) \sum_{vv'} W(\alpha, v) \langle v'|v \rangle^2 N(\Delta E_{\alpha v, j v'}^{(r)}). \quad (D8)$$

The forms are obtained under the assumption that, in the wide-band approximation, the broadening of the orbital energy levels,  $\Gamma_{1(2)}$ , associated with the interaction of the molecule with the electrode 1(2), is the same for both frontier MOs. The function

$$N(\Delta E) = [\exp(\Delta E/k_B T) + 1]^{-1} \quad (D9)$$

controls the recharge of the molecule through the transmission gap  $\Delta E = \Delta E_{\alpha v, j v'}^{(r)}$ , Eq. (C1).

The experiment shows [9, 10] that in a ZnPc-based junction at a low temperature, the intensity of the 0-0 transitions greatly exceeds the phonon-accompanying transitions. Therefore, instead of the form (D8) we can employ the simplified expression

$$K_{j\alpha}^{(r)} \simeq \gamma_r N(\Delta E_{\alpha j}^{(r)}), \quad (D10)$$

$$K_{\alpha j}^{(r)} \simeq \gamma_r N(-\Delta E_{\alpha j}^{(r)}),$$

where the rate  $\gamma_r = (1/\hbar)\Gamma_r$  characterizes the electron hopping between the molecule and the  $r$ th electrode. The third type of transfer rates,

$$q_{mm'}^{(ine)} = A_{mm'}^{(ine)} K_{mm'}^{(ine)} (\delta_{m,j}\delta_{m',j'} + \delta_{m,*}\delta_{m',+} + \delta_{m,+}\delta_{m',*}), \quad (D11)$$

refers to the rate of inelastic electron tunneling that accompanies an intramolecular nonradiative transition. In the Eq. (D11) the factors

$$A_{jj'}^{(ine)} = \delta_{j,0}(\delta_{j',S} + 3\delta_{j',T}) + \delta_{j,S}(\delta_{j',0} + \frac{3}{2}\delta_{j',T}) + \delta_{j,T}(\delta_{j',0} + \frac{1}{2}\delta_{j',S}) \quad (D12)$$

and

$$A_{\alpha\alpha'}^{(ine)} = 2(\delta_{\alpha,+}\delta_{\alpha',*} + \delta_{\alpha,*}\delta_{\alpha',+}) \quad (D13)$$

reflect the role of the spin states of the molecule, while

$$K_{mm'}^{(ine)} = \frac{1}{\hbar} \sum_{rr'} F_{mm'}^{(rr')} \quad (D14)$$

is the elementary tunneling rate. Using the same assumptions that were employed to obtain the expressions (D10) and taking into account the fact that at low temperature the Heavyside unit function  $\Theta(\mu_r - E)$  simulates the Fermi distribution function  $f_r(E)$ , we get

$$\begin{aligned} F_{jj'}^{(rr')} &= \Gamma_r \Gamma_{r'} \Theta(E_j + \mu_r - E_{j'} - \mu_{r'}) \\ &\times \left[ \frac{1}{\Gamma_+} (\varphi_{+j'}^{(r)} - \varphi_{+j}^{(r')}) + \frac{1}{\Gamma_-} (\varphi_{-j'}^{(r')} - \varphi_{-j}^{(r)}) \right. \\ &\left. + \frac{1}{\Gamma_*} (\varphi_{*j'}^{(r)} - \varphi_{*j}^{(r')}) (\delta_{j,S} \delta_{j',T} + \delta_{j,T} \delta_{j',S}) \right] \end{aligned} \quad (D15)$$

for  $j, j' (= 0, S, T)$ , and

$$\begin{aligned} F_{\alpha\alpha'}^{(rr')} &= \Gamma_r \Gamma_{r'} \Theta(E_\alpha + \mu_r - E_{\alpha'} - \mu_{r'}) \\ &\times \sum_j \frac{1}{4\Gamma_j} (\delta_{j,S} + 3\delta_{j,T}) (\phi_{\alpha j}^{(r)} - \phi_{\alpha' j}^{(r')}). \end{aligned} \quad (D16)$$

for  $\alpha, \alpha' (= +, *)$ . The dependence of the values (D15) and (D16) on the bias voltage is concentrated in the transmission gaps (C2) through factors

$$\begin{aligned} \varphi_{\alpha j}^{(r)} &= \arctan \left( 2\Delta E_{\alpha j}^{(r)} / \Gamma_\alpha \right), \\ \phi_{\alpha j}^{(r)} &= \arctan \left( 2\Delta E_{\alpha j}^{(r)} / \Gamma_j \right), \end{aligned} \quad (D17)$$

as well as by means of broadenings of the energy levels of the charge-neutral molecule and its charged forms,

$$\Gamma_j = \sum_\alpha A_{j\alpha}^{(chrg)} \sum_r \Gamma_r \Theta(-\Delta E_{\alpha j}^{(r)}) \quad (D18)$$

and

$$\Gamma_\alpha = \sum_{j \neq 0} A_{\alpha j}^{(chrg)} \sum_r \Gamma_r \Theta(\Delta E_{\alpha j}^{(r)}), \quad (D19)$$

respectively.

### Appendix E: Sequential and direct (tunneling) components of an electronic current

To obtain an expression for the electron current, we use the Eqs. (A14) and (A15). By introducing the current unit  $I_0 = (|e|/\pi\hbar) \times 1 \text{ eV} \approx 77.8 \mu\text{A}$ , the partial sequential component of the current can be represented as

$$\begin{aligned} I_m^{(r,seq)} &= (-1)^{r+1} 2\pi\hbar I_0 \\ &\times \left[ \delta_{m,j} \sum_\alpha A_{j\alpha}^{(seq)} K_{j\alpha}^{(r)} + \delta_{m,\alpha} \sum_j A_{\alpha j}^{(seq)} K_{\alpha j}^{(r)} \right] \end{aligned} \quad (E1)$$

where  $K_{j\alpha}^{(r)}$  and  $K_{\alpha j}^{(r)}$  are the elementary hopping (charging) rates, Eq. (D10), while

$$\begin{aligned} A_{j\alpha}^{(seq)} &= \delta_{j,0} (\delta_{\alpha,-} - \delta_{\alpha,+}) \\ &+ \frac{1}{2} (\delta_{j,S} + \delta_{j,T}) (\delta_{\alpha,-} - \delta_{\alpha,+} - \delta_{\alpha,*}), \\ A_{\alpha j}^{(seq)} &= \frac{1}{2} [\delta_{j,0} (\delta_{\alpha,-} - \delta_{\alpha,+}) \\ &+ \frac{1}{2} (\delta_{j,S} + 3\delta_{j,T}) (\delta_{\alpha,-} - \delta_{\alpha,+} - \delta_{\alpha,*})] \end{aligned} \quad (E2)$$

are the spin factors. [Multiplier  $(-1)^{r+1}$  fixes the direction of sequential electron transfer from the electrode  $r = 1$  at  $\mu_1 > \mu_2$ .]

The partial component of the elastic current,

$$I_m^{(ela)} = I_0 \hbar (\delta_{m,j} A_j^{(ela)} + \delta_{m,\alpha} A_\alpha^{(ela)}) K_m^{(ela)} \quad (\text{E3})$$

is expressed through the elementary tunneling rate

$$K_m^{(ela)} = \frac{1}{\hbar} (F_{mm}^{(12)} - F_{mm}^{(21)}) \quad (\text{E4})$$

and the corresponding spin factors

$$\begin{aligned} A_j^{(ela)} &= 2\delta_{j,0} + \frac{1}{2}\delta_{j,S} + \frac{3}{2}\delta_{j,T}, \\ A_\alpha^{(ela)} &= 2(\delta_{\alpha,+} + \delta_{\alpha,-} + \delta_{\alpha,*}). \end{aligned} \quad (\text{E5})$$

As for the partial component of the inelastic current,

$$I_m^{(ine)} = I_0 \hbar \sum_{m' (\neq m)} A_{mm'}^{(ine)} K_{mm'}^{(ine)}, \quad (\text{E6})$$

it is determined by the elementary tunneling rate  $K_{mm'}^{(ine)}$ , Eq. (D14) and the spin factor  $A_{mm'}^{(ine)}$ , Eqs. (D12) - (D13).

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