

Charge transport in a single molecule transistor measured by scanning tunneling microscopy

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S1. Electrostatic model (Model 2)

As usual for electrostatic problems, this model is based on the minimization of the total Gibbs free energy of the system¹. From the electric field distribution in the transistor geometry, the alignment of the molecular orbitals is determined and the related charge transport properties are derived in a noninteracting single-particle picture, following the Landauer-Büttiker scattering theory^{2,3}.

Measured from the charge neutrality point, the charging shifts the electrochemical potential of the graphene by μ_D , leading to the charging energy per unit area in the drain of

$$E_d = \int_0^{|\mu_d|} \rho(E) E dE = \frac{2}{3} \frac{|\mu_D|^3}{\pi \hbar^2 v_F^2}. \quad (1)$$

Here, the density of states per unit area $\rho(E) = 2|E|/(\pi \hbar^2 v_F^2)$ of graphene was used⁴ and v_F is its Fermi velocity. Now, this energy can be expressed in terms of the surface charge density σ_d of graphene as

$$E_d = \frac{2}{3} \hbar v_F \sqrt{\pi} \sqrt{\frac{|\sigma_d|}{e}}^3, \quad (2)$$

by using that

$$\sigma_d = -\text{sgn}(\mu_d) e \int_0^{|\mu_D|} \rho(E) dE = -\text{sgn}(\mu_d) e \frac{|\mu_d|^2}{\pi \hbar^2 v_F^2} \quad (3)$$

with the sign function $\text{sgn}(x)$.

Denoting the surface charge densities of the source and the gate with σ_s and σ_g , respectively, we can express the (perpendicular component of the) electric field between the tip

and the graphene layer as

$$F_0 = \frac{1}{2\epsilon_0} (\sigma_g + \sigma_d - \sigma_s) \quad (4)$$

and the field between the graphene layer and the gate as

$$F_1 = \frac{1}{2\epsilon_1} (\sigma_g - \sigma_d - \sigma_s), \quad (5)$$

where ϵ_0 is the vacuum permittivity and ϵ_1 is the permittivity of the SiO₂ layer isolating the graphene from the gate, see Fig. 4(c) of the main text. (Electric field components parallel to the planes vanish due to the symmetry of the assumed system with infinitely extended surfaces.) The total electrostatic energy due to these fields is

$$E_{\text{Field}} = \frac{d_s}{8\epsilon_0} (\sigma_g + \sigma_d - \sigma_s)^2 + \frac{d_g}{8\epsilon_1} (\sigma_g - \sigma_d - \sigma_s)^2 \quad (6)$$

with d_s being the distance between the tip and the graphene layer and d_g that between the graphene layer and the gate.

The surface charge densities can be influenced by the power supplies, which in turn have to perform the infinitesimal work

$$dW = \left(-\frac{\Phi_s}{e} + V_b \right) d\sigma_s + \left(-\frac{\Phi_d}{e} - \text{sgn}(\sigma_d) \frac{\hbar v_F}{e} \sqrt{\frac{\pi}{e}} \sqrt{|\sigma_d|} \right) d\sigma_d + \left(-\frac{\Phi_g}{e} + V_g \right) d\sigma_g \quad (7)$$

due to any infinitesimal change in σ_s , σ_d or σ_g . The work functions of each layer are denoted by Φ_s , Φ_d and Φ_g , respectively. Since the graphene is grounded, $V_d=0$ is left out of consideration here.

Now the total Gibbs free energy of the tip/graphene/gate or source/drain/gate system at temperature $T = 0$ K is given as the sum of the charging energy of the graphene, the electrostatic field energies, and the work performed by the electrodes. This yields

$$G(\sigma_s, \sigma_d, \sigma_g) = E_d(\sigma_d) + E_{\text{Field}}(\sigma_s, \sigma_d, \sigma_g) - W(\sigma_s, \sigma_d, \sigma_g), \quad (8)$$

which depends parametrically on several parameters, particularly V_b and V_g .

To calculate the charge transport properties, we need to consider that the field $F_0(\sigma_s, \sigma_d, \sigma_g)$ shifts the molecular energy levels. We include this effect by computing the electrostatic potential at the position of the molecule for given V_b and V_g . The electrostatic problem is solved by minimizing $G(\sigma_s, \sigma_d, \sigma_g)$ with respect to all three surface charge densities under the constraint that the charge neutrality condition $\sigma_s + \sigma_d + \sigma_g = 0$ is fulfilled. The

$\partial I(V_b, V_g)/\partial V_b$ map is calculated using the Landauer formula³

$$I(V_b, V_g) = \frac{e}{\pi\hbar} \int_{-\infty}^{\infty} \mathcal{T}(E, V_b, V_g)(f(E - eV_b) - f(E)) dE. \quad (9)$$

For simplicity, we restrict ourselves to a single electronic level and employ the transmission probability

$$\mathcal{T}(E, V_b, V_g) = \frac{\Gamma_s \Gamma_d}{(E - \varepsilon(V_b, V_g))^2 + (\Gamma_s/2 + \Gamma_d/2)^2}. \quad (10)$$

In the expressions, $f(E) = \{\exp(E/k_B T) + 1\}^{-1}$ is the Fermi function, and Γ_s and Γ_d are the linewidth broadenings for source and drain. The energy of the molecular state is $\varepsilon(V_b, V_g) = \varepsilon_m + \Phi_d + \mu_d(V_b, V_g) - e d_m F_0(V_b, V_g)$, where ε_m is its energy in equilibrium at $V_b = V_g = 0$ relative to Φ_d and d_m is the molecule-graphene distance, as shown in Fig.4 (c) of the main text.

Figure 4 (a) of the main text shows the slope dV_g/dV_b of several dI/dV_b peaks extracted from measurements around $V_g = 0$ and the prediction of both models. For model 2, the results were obtained by varying ε_m and numerically determining the peak position at $V_g = 0$ and the corresponding slope dV_g/dV_b . The models show differences at $dV_g/dV_b < 0$, and model 2 describes slightly better the region in the lower right quadrant with peak positions at positive voltages and $dV_g/dV_b < 0$. Further measurements are needed to compare to the predictions of both models for the lower left quadrant at negative voltages and $dV_g/dV_b < 0$.

S2. Calculations based on density functional theory

To perform the first-principles calculations based on density functional theory (DFT), the quantum chemistry software package TURBOMOLE⁵ was used with the PBE exchange-correlation functional⁶ and the def2-TZVP basis set⁷⁻⁹. Calculations were done for a single gas-phase CoPc molecule. It was first optimized in the neutral charge state to determine the ground state geometry. Subsequently, we calculated the Kohn-Sham (KS) orbitals and their energies. To correct for the known underestimation of the gap between the HOMO and the LUMO within DFT¹⁰, we used the Delta-SCF scheme¹¹. In the procedure we determine the electron affinity, $EA = E(N) - E(N - 1) \approx 2.8$ eV, and the ionization potential, $IP = E(N - 1) - E(N) \approx 6.3$ eV, from differences of total energies. In the expressions, $E(N)$ refers to the total energy of the charge neutral ground state of the molecule with N electrons, while $E(N + 1)$ and $E(N - 1)$ are the total energies when one electron is added or

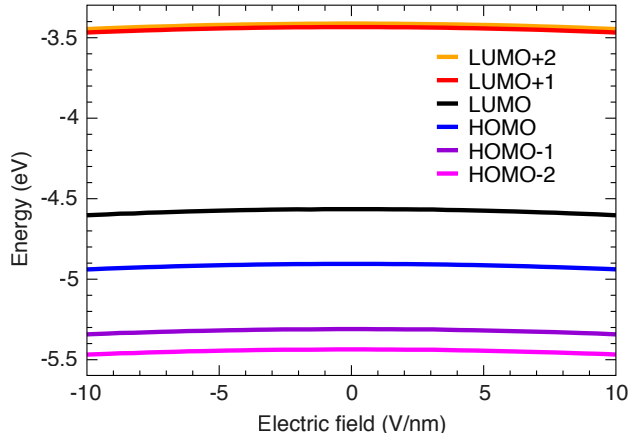


FIG. S1. Evolution of uncorrected KS molecular orbital energies under an electric field, applied perpendicular to the plane of the CoPc molecule. Orbitals around the LUMO energy are shown.

removed, respectively. In all total energy calculations the optimized ground state geometry of the neutral CoPc is used. This assumes vertical excitations without a relaxation of the nuclei, when quasiparticle energies are measured. By shifting all of the unoccupied orbitals by the same amount of $\Delta_{unocc} \approx 1.7$ eV and the occupied ones by $\Delta_{occ} \approx -1.4$ eV, we obtain the energy values displayed below the KS orbital wave functions in Fig. 2 (e) of the main text.

We wanted to analyze, whether a simple Stark shift of the molecular orbitals can explain the dependence of energy levels on the gate voltage, shown in Fig. 3 of the main text. For this reason, we studied the behavior of the KS molecular orbital energies when a homogeneous electric field is applied perpendicular to the plane of the molecule. The TURBOMOLE calculations, displayed in Fig. S1, exhibit a weak quadratic Stark effect for all orbitals.

For a field strength of 10 V/nm, at least one order of magnitude beyond what can be realized in the STM junction, molecular orbital energies are changed by less than 0.05 eV as compared to the situation with a vanishing electric field. The changes in peak positions of several 0.1 V, visible in Fig. 3, must hence be due to other electrostatic effects, explained in the main text and by the models in the previous section.

Note that CoPc is a spin-polarized molecule. Since the STM used here cannot distinguish between different spin directions, we have not discussed separately spin-up and spin-down states in Fig. S1 or Fig. 2 of the main text, but simply group them according to their energies. Using α and β to symbolize spin up and down, respectively, the states shown in Fig. S1 can

be categorized in detail as follows: HOMO-2 is a non-degenerate β state, HOMO-1 is two-fold degenerate of spin β , HOMO is spin-degenerate (i.e. $E_{\text{HOMO},\alpha} \approx E_{\text{HOMO},\beta}$), LUMO is non-degenerate of spin β , and LUMO+1 and LUMO+2 are degenerate of spin α and β , respectively.

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