Charge-State Assignment of Nanoscale Single-Electron Transistors from their Current-Voltage Characteristics

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1. Charge Assignment at 77 K

1.1. Device A

Figure S1. a) Full charge stability diagram of device A at 77 K. b) and c) corresponding current-gate voltage traces at ± 0.4 V (b) or ± 0.2 V (c). The resonances below -2 V were unstable and not suited to high-resolution low-temperature measurements. However, from our method, the assignment of the transition at approximately -3 V is a 1-2 transition, which indicates that the GQD follows the Aufbau principle on a ladder of spin-degenerate orbitals with significant level spacing. The reason for the large differences in current between the different orbitals is the fact that the electronic coupling between the electrodes / molecule is significantly different for different molecular orbitals.

Figure S2. a) Zoomed charge stability diagram of device A at 77 K showing the two resonance regions described in the main text. The areas where the current is highest are indicated with yellow and purple on the positive and negative side, respectively. These areas are on the side of the doublet state, as proven in the main text. b) Current vs. gate voltage traces at a bias voltage of 0.4 V (red) and -0.4 V (blue). At this voltage the two SET regions overlap in the center (around $V_g = 0.5$ V), but the differences between positive and negative peak voltages (for the left resonance 0.3 nA and -0.14 nA, for the right resonance 0.15 and -0.25 nA) are larger than the contribution of the overlapping resonance (approximately 0.07 nA and -0.06 nA, respectively). c) Current vs. gate voltage traces at a bias voltage of 0.2 V (red) and -0.2 V (blue). At these voltages the SET regions do not overlap and the current asymmetry is clearly visible.

1.2. Porphyrin Monomer Devices

Figure S3. Stability diagrams and current-gate voltage traces ($V_b \pm 0.2$ V) of single porphyrin transistors with various anchor groups.¹ The anchor groups are indicated in the figures: HBC: hexabenzocoronene, TDP: 1,3,6-tri(dodecoxy)pyrene, TBF: tetrabenzofluorene, 2py: 2-pyrene. For the device in Figure S3b, the transition described is at 60 V_g . The charge state of each SMT at $V_g = 0$ was assigned using the method described in the main text, and indicated in each figure. Out of 12 devices, 7 were 0-1 (singlets), 4 were doublets (1-2) and 1 had a charge degeneracy point at $V_g = 0$ (device in Figure S3l).

2. Explaining the current asymmetry

To describe the current through a molecular transistor in the weakly coupled regime (*i.e.*, $E_c > k_B T > \Gamma$), we use a rate-equation model:²

$$I = |e| \frac{\gamma_{ox}^S \gamma_{red}^D - \gamma_{ox}^D \gamma_{red}^S}{\gamma_{ox}^S + \gamma_{red}^D + \gamma_{ox}^D + \gamma_{red}^S}$$

Here, γ_r^l is the rate of the oxidation or reduction reaction for $r = ox, red$, occurring at the source or drain electrodes for $l = S, D$, respectively. The reduction (oxidation) rates are calculated from the overlap of the occupied (unoccupied) levels in the electrodes (given by the Fermi-Dirac distribution function: $f(\epsilon)$) with the rate constant $k_r(\epsilon)$. The rate constant can be further deconstructed into a **density of states** function which we will call $\hat{k}_r(\epsilon)$ (**it has units of eV^{-1}**), as well as the electronic coupling with electrode l (Γ_l) and a statistical factor (σ_r) originating from the Pauli exclusion and Aufbau principles (see below). This leads to the following description for the rates:³

$$\gamma_{red}^l = \frac{\Gamma_l \sigma_{red}}{\pi} \int f_l(\epsilon) \hat{k}_{red}(\epsilon) d\epsilon$$

$$\gamma_{ox}^l = \frac{\Gamma_l \sigma_{ox}}{\pi} \int [1 - f_l(\epsilon)] \hat{k}_{ox}(\epsilon) d\epsilon$$

We first note that on resonance (*i.e.*, when the position of the molecular level coincides with the Fermi levels of the unbiased leads, $\epsilon_M = 0$), and for a symmetrically applied bias voltage (which is experimentally approximated due to fairly equal capacitance between the molecular species and each electrode):²

$$\hat{k}(\epsilon) = \hat{k}_{red}(\epsilon) = \hat{k}_{ox}(-\epsilon)$$

$$f_S(\epsilon) = 1 - f_D(-\epsilon)$$

$$1 - f_S(\epsilon) = f_D(-\epsilon)$$

which allows us to rewrite rates in terms of each other as follows:

$$\gamma_{ox}^S = \frac{\Gamma_S \sigma_{ox}}{\pi} \int f_D(-\epsilon) \hat{k}(-\epsilon) d\epsilon = \frac{\Gamma_S \sigma_{ox}}{\Gamma_D \sigma_{red}} \gamma_{red}^D$$

and we define the ratios:

$$\alpha = \frac{\Gamma_S}{\Gamma_D}, \beta = \frac{\sigma_{ox}}{\sigma_{red}}$$

This approach allows us to write the oxidation rate at the drain electrode in terms of the reduction rate at the source electrode. Inserting the resulting expressions into the rate equation gives us:

$$I = \beta \frac{\alpha \gamma_{red}^D{}^2 - \alpha^{-1} \gamma_{red}^S{}^2}{(1 + \alpha \beta) \gamma_{red}^D + (1 + \alpha^{-1} \beta) \gamma_{red}^S} = \frac{\alpha \beta}{1 + \alpha \beta} \frac{(\gamma_{red}^D + \alpha^{-1} \gamma_{red}^S)(\gamma_{red}^D - \alpha^{-1} \gamma_{red}^S)}{\left(\gamma_{red}^D + \frac{1 + \alpha^{-1} \beta}{1 + \alpha \beta} \gamma_{red}^S \right)}$$

In situations where $|V_b| \gg k_B T$, either γ_{red}^D or γ_{red}^S will be approximately zero, so we can neglect terms including $\gamma_{red}^D \gamma_{red}^S$, thus we can write:

$$I = \frac{\alpha\beta}{1 + \alpha\beta} \frac{\left(\gamma_{red}^D + \frac{1 + \alpha^{-1}\beta}{1 + \alpha\beta} \gamma_{red}^S\right) \left(\gamma_{red}^D - \alpha^{-1} \frac{\alpha^{-1} + \beta}{1 + \alpha^{-1}\beta} \gamma_{red}^S\right)}{\left(\gamma_{red}^D + \frac{1 + \alpha^{-1}\beta}{1 + \alpha\beta} \gamma_{red}^S\right)}$$

This can be simplified to:

$$I = \frac{\alpha\beta}{1 + \alpha\beta} \gamma_{red}^D - \frac{\beta}{\alpha + \beta} \gamma_{red}^S$$

Now, inserting the definitions of α and β , we obtain:

$$I = \frac{\Gamma_D \sigma_{red} \Gamma_S \sigma_{ox}}{\Gamma_D \sigma_{red} + \Gamma_S \sigma_{ox}} \frac{1}{\pi} \int f_D(\epsilon) \hat{k}(\epsilon) d\epsilon - \frac{\Gamma_S \sigma_{red} \Gamma_D \sigma_{ox}}{\Gamma_S \sigma_{red} + \Gamma_D \sigma_{ox}} \frac{1}{\pi} \int f_S(\epsilon) \hat{k}(\epsilon) d\epsilon$$

and finally:

$$I = \frac{1}{\pi} \int [\xi_D f_D(\epsilon) - \xi_S f_S(\epsilon)] \hat{k}(\epsilon) d\epsilon$$

where:

$$\xi_D = \frac{\Gamma_D \sigma_{red} \Gamma_S \sigma_{ox}}{\Gamma_D \sigma_{red} + \Gamma_S \sigma_{ox}} \quad , \quad \xi_S = \frac{\Gamma_S \sigma_{red} \Gamma_D \sigma_{ox}}{\Gamma_S \sigma_{red} + \Gamma_D \sigma_{ox}}$$

Together ξ_D and ξ_S determine the asymmetry in the current at positive/negative voltage. Under conditions of strongly asymmetric electrode coupling these simplify further. For example, if $\Gamma_S \gg \Gamma_D$:

$$\xi_D = \Gamma_D \sigma_{red} \quad , \quad \xi_S = \Gamma_D \sigma_{ox}$$

$$I = \frac{\Gamma_D}{\pi} \int [\sigma_{red} f_D(\epsilon) - \sigma_{ox} f_S(\epsilon)] \hat{k}(\epsilon) d\epsilon$$

Conversely if $\Gamma_D \gg \Gamma_S$:

$$\xi_D = \Gamma_S \sigma_{ox} \quad , \quad \xi_S = \Gamma_S \sigma_{red}$$

$$I = \frac{\Gamma_S}{\pi} \int [\sigma_{ox} f_D(\epsilon) - \sigma_{red} f_S(\epsilon)] \hat{k}(\epsilon) d\epsilon$$

For a solely spin-degenerate frontier orbital, $\sigma_{ox} / \sigma_{red}$ is either 1/2 or 2/1 depending on the transition involved. Therefore, a ratio of 2 is observed between the magnitudes of current at different polarities of V_b in the case of strongly asymmetric coupling.

3. Extracting the rate constants from the conductance trace at mK temperatures.

Using the expression for electric current from the previous section, the differential conductance is given by

$$G = \frac{dI}{dV_b} = \frac{1}{\pi} \int \frac{d}{dV_b} [\xi_D f_D(\epsilon) - \xi_S f_S(\epsilon)] \hat{k}(\epsilon) d\epsilon$$

At $T = 0$ K, the Fermi-Dirac functions become step functions, and therefore their derivatives become delta function (remembering a symmetrically applied bias):

$$G = \frac{1}{\pi} \int \left[\xi_D \delta\left(\epsilon + \frac{V_b}{2}\right) + \xi_S \delta\left(\epsilon - \frac{V_b}{2}\right) \right] \hat{k}(\epsilon) d\epsilon$$

Evaluating the above integral yields the following:

$$G = \frac{1}{\pi} \left[\xi_D \hat{k}\left(-\frac{V_b}{2}\right) + \xi_S \hat{k}\left(\frac{V_b}{2}\right) \right]$$

We can then calculate the value of $k'(x)$ by subtraction of the following equations:

$$\pi G(2x) = \xi_D \hat{k}(-x) + \xi_S \hat{k}(x)$$

$$\pi G(-2x) = \xi_D \hat{k}(x) + \xi_S \hat{k}(-x)$$

$$\frac{\pi G(2x)}{\xi_D} - \frac{\pi G(-2x)}{\xi_S} = \frac{\xi_S}{\xi_D} \hat{k}(x) + \frac{\xi_D}{\xi_S} \hat{k}(x) = \left(\frac{\xi_S}{\xi_D} + \frac{\xi_D}{\xi_S} \right) \hat{k}(x) = \left(\frac{\xi_D^2 + \xi_S^2}{\xi_S \xi_D} \right) \hat{k}(x)$$

and therefore

$$\hat{k}(x) = \pi \frac{\xi_S G(2x) + \xi_D G(-2x)}{\xi_D^2 + \xi_S^2}$$

The values of ξ_S and ξ_D can be obtained from the asymmetry in the current at high bias. However, since small changes in the current can lead to large changes in ξ_l , especially when α is very large or very small, it is advised to fit their values to the current instead using the master equation.

From **the DOS**, $\hat{k}(x)$, we can obtain the rate constants for both reactions at both electrodes $k_r^l(x)$. However, as ξ_l contain cross-terms in Γ_l and σ_r , they cannot be independently determined on resonance. Instead, we must make an assumption regarding either the electronic coupling or the statistical factor. In most cases, it is easier to assume a certain orbital degeneracy, and set σ_{red} and σ_{ox} to the corresponding values. The simplest case for molecular transistors is a spin-degenerate level, where, depending on the transition involved, either: $\sigma_{red} = 2$ and $\sigma_{ox} = 1$, or $\sigma_{red} = 1$ and $\sigma_{ox} = 2$. For each case we extract Γ_S and Γ_D by fitting to the resonant IV trace. Thereby from each case we can generate a combination of the four rate constants $k_r^l(x)$ which describe the current based on which of the statistical factors we set to 2.

4. Statistical factors for spin and orbital degeneracy.

For a single spin-degenerate level with no orbital degeneracy, two situations exist for transport of electrons. Either the transition occurs from a unoccupied to a singly occupied orbital (**0-1** transition), or from a singly occupied to a doubly occupied orbital (**1-2** transition). For the former case, electrons of either

spin can hop onto the molecule, therefore $\sigma_{red} = 2$, but only that specific electron can tunnel off, therefore $\sigma_{ox} = 1$. For the 1-2 transition, only an electron with spin opposite of the electron already residing in the SOMO of the molecule can hop onto the molecule, therefore $\sigma_{red} = 1$, but either electron in what is now the HOMO of the molecule can hop off, therefore $\sigma_{ox} = 2$. This is the simplest case that is used in the main body of this work, shown in Figure 1c. Less trivial situations which involve molecular structures with doubly or triply degenerate frontier orbitals are depicted in Figure S4a and b. The corresponding values for σ_{red} and σ_{ox} are shown next to the electrodes in Figure S4. We assume the validity of the Aufbau principle, *i.e.*, degenerate orbitals are filled by single electrons before pairing opposite spin electrons into the same orbital. In such systems, it is also assumed that the electronic structure remains unchanged upon charging the molecule. In reality it is likely that charging changes the degeneracy of the orbitals and that therefore different statistical factor arise based on the molecule than the ones predicted herein. This should be taken into account when considering systems with higher degeneracy.

Figure S4. Schematic representation of the statistical factors for electron transport through molecules with either doubly degenerate (a) or triply degenerate (b) orbitals. The reactive electrons / holes are indicated in red, and the arrow indicates the electron spin (up or down). S = Source electrode, D = Drain electrode.

5. Molecular orbital structure of the porphyrin molecule

Figure S5. Four frontier orbitals of a model of the molecule (TDP₂-zinc porphyrin) used in the SMT in Figure 5, calculated using DFT (B3LYP/6-31G(d)) in Gaussian09. For simplicity, and to help converging, the long alkyl tails on the Si atoms, as well as the pyrene anchor groups have been replaced by methyl groups. The energies of the levels show the lack of orbital degeneracy in the orbitals involved in electron transfer. The spacing between subsequent charge transitions is the energy level spacing plus a charging energy, and therefore we expect the spin state of the molecule to oscillate between singlet and doublet as the charge on the molecule changes by one.

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