SUPPORTING INFORMATION FOR "Conduction Properties of Bipyridinium Functionalized Molecular Wires"

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Supplementary information on electron transport properties of alkanedithiol wires is presented.

Figure 1S illustrates electron tunneling through alkanedithiols. Since the Fermi energy (E_F) is placed inside the HOMO-LUMO gap, the transmission $T(E)$ through a Au-alkanedithiol-Au junction drops rapidly around -2.2 eV below E_F (alkane HOMO, $E_{\rm HOMO}$) and a nearly insulating gap spreads up all the way until 5.3 eV (alkane LUMO). Expected with tunneling mechanism, the conductance through n-alkanedithiols decays exponentially (Fig.1Sb): $G(n) = G_c \exp(-\beta_n n)$ with $\beta_n \propto \sqrt{\Phi_A}\, d_0$, where $\Phi_A = E_F - E_{\rm HOMO}$ is the potential barrier height, $d_0 = 1.28$ Å is a unit length of alkane chain, and G_c is a contact conductance. Using the standard BP86 GGA-functional [1], we obtained $\beta_n = 0.83$ per CH_2 group.

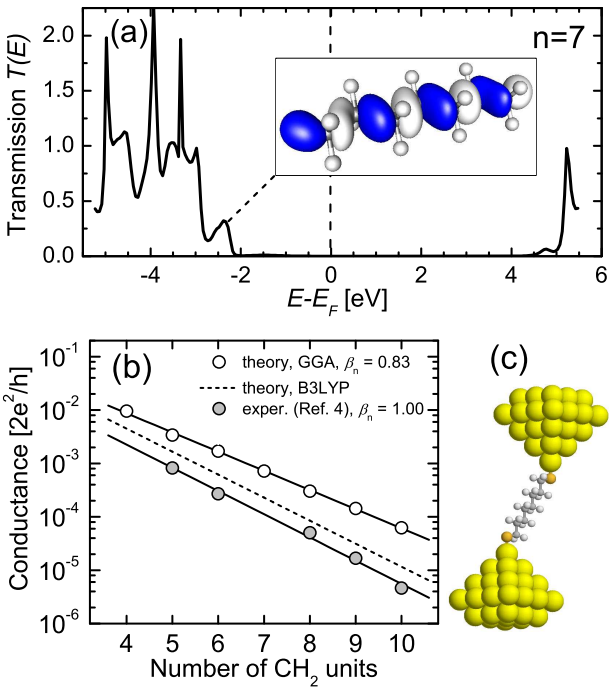

FIG. 1S: (a) Energy dependent transmission through the alkanedithiol wire with $n = 7$ units (inset shows alkane's HOMO); (b) Chain length dependence of the single molecule conductance — experimental (gray circles, Ref. 4) *vs* calculated points (open circles, GGA functional) are shown; the dashed line with a slope $\beta_n = 1.0$ is an extrapolation of calculated values accounting for the higher tunneling barrier obtained within the hybrid B3LYP functional; (c) Junction geometry used in calculations with both S atoms in "atop" position.

In order to estimate the uncertainty related to a local GGA functional, we have tested hybrid methods, based on the DFT and Hartree-Fock approaches. Calculation within the B3LYP functional [2] leads to a downward shift of the alkane-HOMO with respect to E_F that implies a higher tunneling barrier $\Phi_A^* = 3.1$eV. Such a behavior is due to a partially recovered $(-1/r)$ asymptotic of the exact Kohn-Sham potential. Assuming the contact conductance G_c to be unchanged, and scaling the tunneling exponent as $\beta_n^* \simeq \beta_n \sqrt{\Phi_A^*/\Phi_A}$, we find a slightly higher value $\beta_n^* \simeq 1.0$ (dashed line in Fig.1Sb) [3] even closer to the experimental data of Ref. 4.

The transport properties of alkanethiols and -dithiols were explored intensively: in particular, the data of Ref. 4 (Fig. 1Sb) are consistent with *low* values reported by Tao *et al.* [5]. However, different experimental groups observed different exponents. While most of researches found $\beta_n \approx 1.0$ [5–7], absolute values of conductances attributed to single molecules are not unique, as well as sometimes smaller values for β_n ranging from ~ 0.8 down to ~ 0.5 have been observed [8]. We mention, that this puzzling controversy has been addressed in our recent study [9], where we proposed the different sulfur-gold couplings and trans/gauche conformations as a plausible explanation for several conductance traces $G(n)$.

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