

Figure 2.1: Bridge mediated ET in a system where the donor given by a metal complex of Ruthenium (left terminal site) and the acceptor by a Cobalt complex (right terminal site). The bridge is formed by an oligomer of the amino acid proline (upper panel, the chemical structure is $[(\text{bpy})_2\text{Ru(II)}\text{L}(\text{Pro})_n\text{Co(III)}(\text{NH}_3)_5]^{3+}$, carbon atoms are shown in grey, nitrogen in weak grey, oxygen as well as the Ruthenium and Cobalt atoms in black). Lower panel: Length-dependence of the overall ET rate at room temperature. Comparison of experimental data (open circles, after S. S. Isied, M.Y. Ogawa, J. F. Wishart, Chem. Rev., **92**, 381 (1992)) and theoretical computations from E. G. Petrov and V. May, J. Phys. Chem. A **105**, 10176 (2001) (full squares). The thin lines show an estimate of the bridge number dependence of the rate if it is dominated by the superexchange mechanisms or the sequential one (reprinted from E. G. Petrov and V. May, J. Phys. Chem. A **105**, 10176 (2001)).

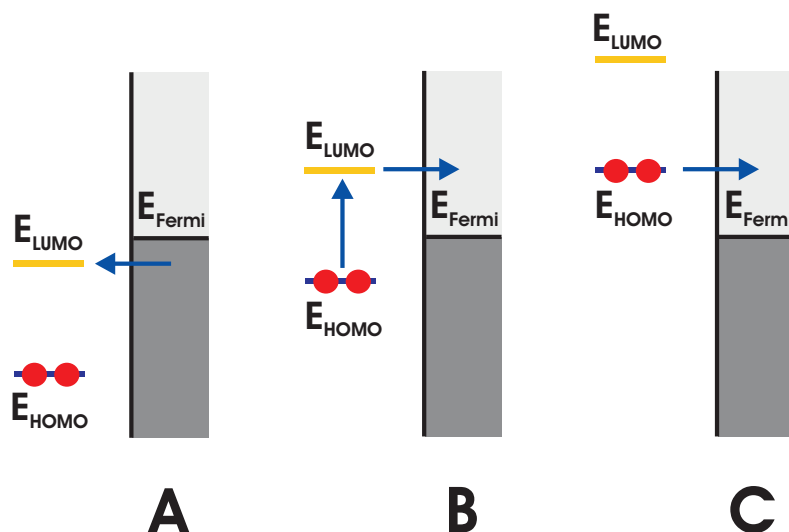


Figure 2.2: Possible HET reactions between a molecule represented in a HOMO LUMO scheme and a metal with a single band filled by electrons up to the Fermi level E_F (dark gray). (A) $E_{LUMO} < E_F$: charge injection proceeds from the Fermi sea into the LUMO level, (B) $E_{LUMO} > E_F$ but $E_{HOMO} < E_F$: charge injection into empty band state above the Fermi edge (light gray) becomes possible after photo excitation of an electron from the HOMO to the LUMO, (C) $E_{HOMO} > E_F$: an electron can be transferred from the LUMO into empty band state.

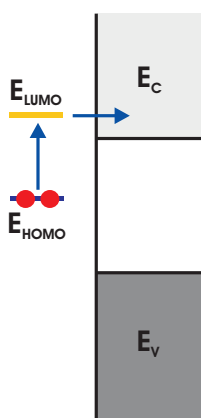


Figure 2.3: HET reactions between a molecule represented in a HOMO LUMO scheme and a semiconductor with a filled valence band with energies E_V (dark gray) and an empty conduction band with energies (E_C , light gray). Both band edges are separated by the band gap (white).

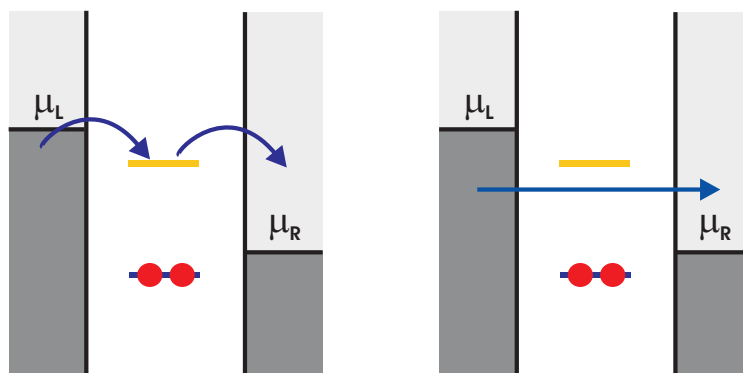


Figure 2.4: Charge transmission through a single molecule represented in a HOMO LUMO scheme. The charge comes from the left electrode (with chemical potential μ_L) and moves to the right electrode (with chemical potential μ_R). Sequential (inelastic) transmission is drawn in the left panel (an electron hops into the molecule, relaxation follows and afterwards it hops to the right electrode). Direct (elastic) transmission is presented in the right panel (the electron moving from the left to the right undergoes an elastic scattering process at the molecular levels).

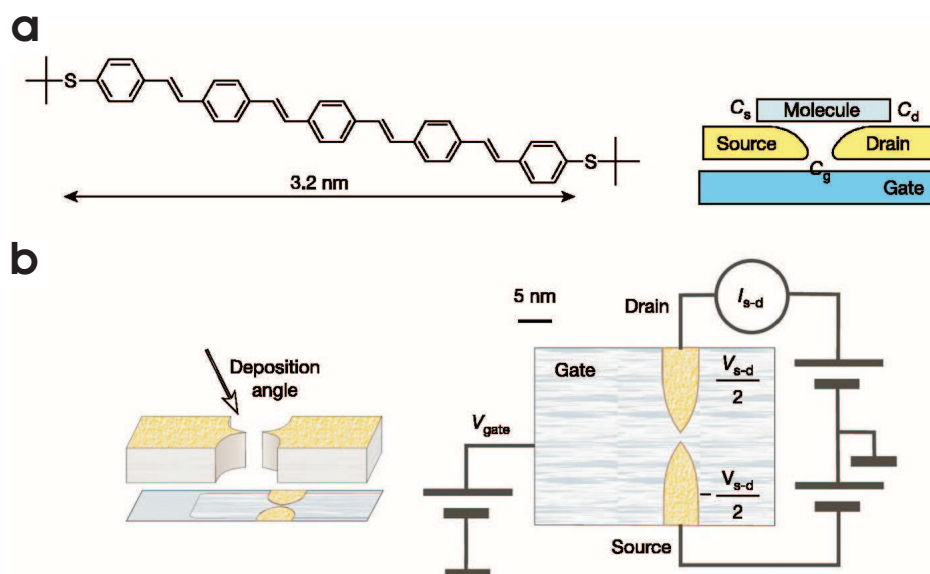


Figure 2.5: Single molecule transistor including different charging states of the molecule OPV5 ((E,E)-1,4-bis4-(E)-4-(tert-butylthio)styrylbenzene, see left upper panel). Also shown is the field-effect transistor arrangement with source, drain, and gate electrode as well as the device preparation procedure (first and second row, reprinted from S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J.-L. Bredas, N. Stühr-Hansen, P. Hedegard, and Th, Bjornholm, *Nature* **425**, 698 (2003)).

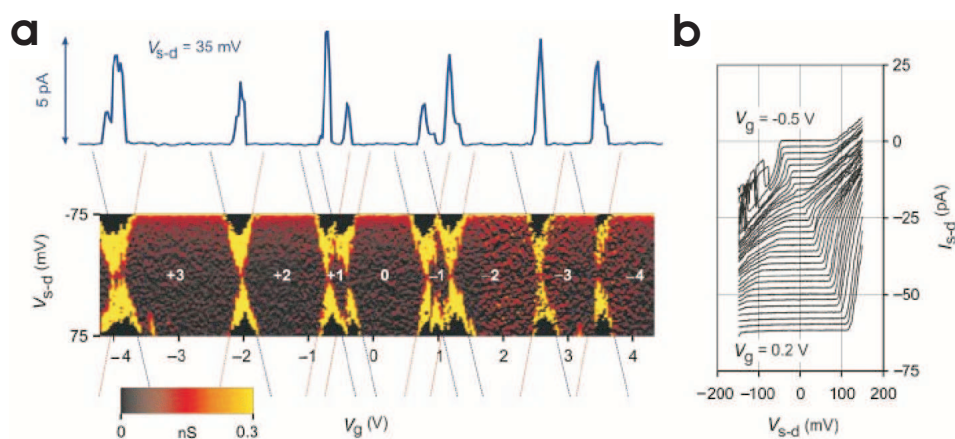


Figure 2.6: IV-characteristics of the single molecule transistor of Fig. 2.5. Shown are measurements (at $T = 4.2$ K) of the differential conductance dI_{s-d}/dV_{s-d} (derivative of the the source drain current I_{s-d} with respect to the source–drain voltage V_{s-d}) as a function of V_{s-d} as well as of the gate potential V_g (the various numbers indicate the different charging states; the full line at the top of the figure shows a typical $I_{s-d} - V_g$ trace). Current–voltage characteristics ($I_{s-d} - V_{s-d}$ curves) at different V_g are drawn in the bottom right panel (curves are shifted vertically for clarity, reprinted from S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J.-L. Bredas, N. Stuhr–Hansen, P. Hedegard, and Th. Bjornholm, *Nature* **425**, 698 (2003)).

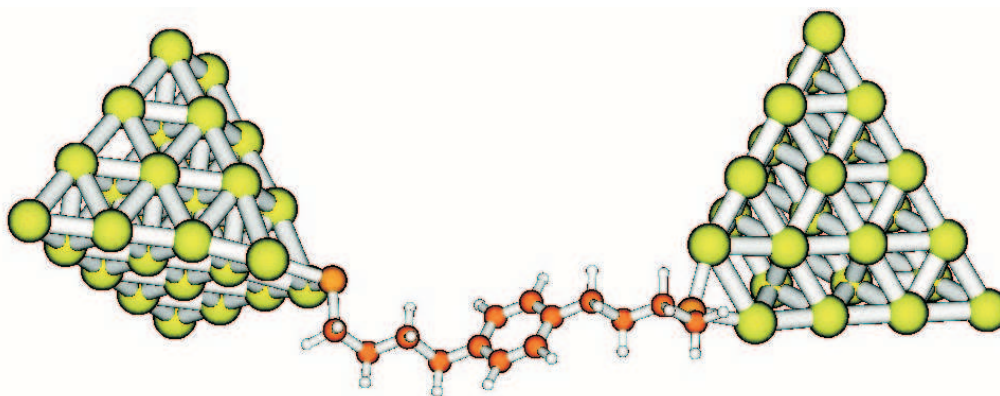


Figure 2.7: A single benzene-di(butanethiolate) molecule between two pyramidal gold nanocontacts (reprinted from C. Benesch, M. Cizek, J. Klimes, M. Thoss, and W. Domcke, *J. Phys. Chem.* **112**, 9880 (2008)).

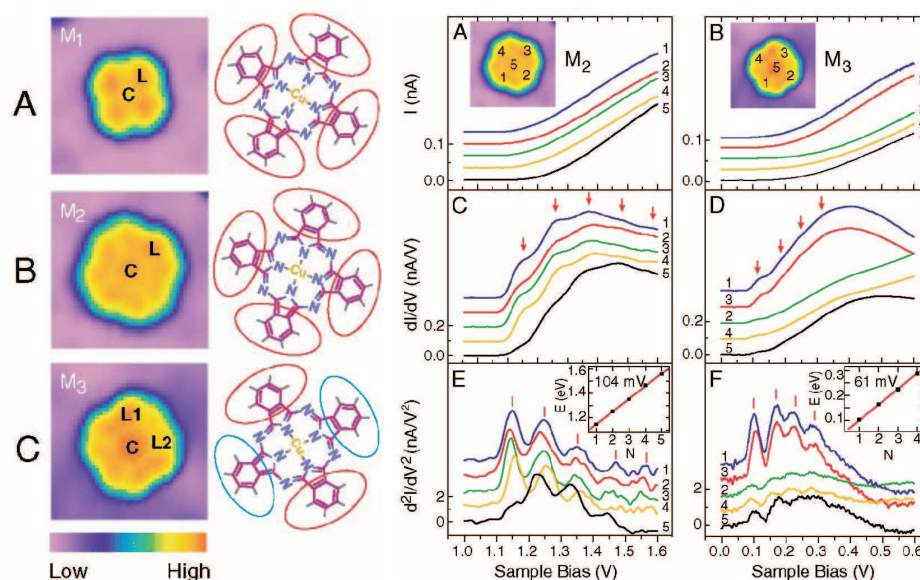


Figure 2.8: Vibrational contributions in the IV-characteristics of a single copper phthalocyanine molecule contacted by the tip of a scanning tunneling microscope (STM) and a NiAl(110) surface with an ultrathin Al_2O_3 film separating the molecule from the metal surface. First (left) row: STM scans of different arrangements of the molecule at the NiAl(110) surface (the different contact points of the STM tip are indicated, scan size 37 \AA times 37 \AA), second row: related molecular structure in the respective positions, third row: measured differential conductance versus applied voltage taken at the different contact points, fourth and fifth row: examples of measured differential conductance as well as their first (C and D) and second (E and F) derivative with respect to the applied voltage. The distinct equidistant peaks in the latter are related to vibrations associated with the deformations of the inner ring of the phthalocyanine macrocycle (E) and vibrations involving the out-of-plane motions of the isoindole atoms (F, reprinted from X. H. Qiu, G.V. Nazin, and W. Ho, *Phys. Rev. Lett.* **92**, 206102 (2004)).