Part 7: Molecular Electronics at the Nanoscale

- Polymers - Structure:
  - Unconjugated
  - Conjugated – Semiconductor

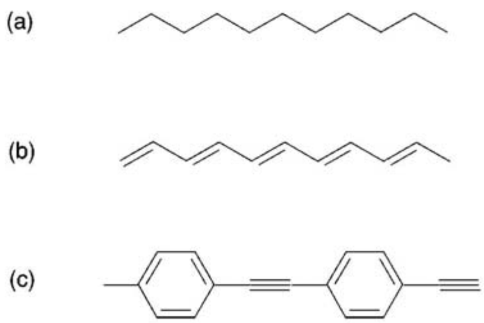

FIG. 1. Three organic periodic molecules.

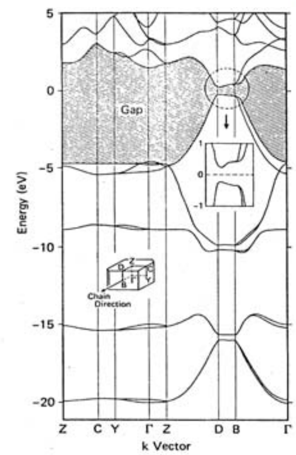

FIG. 11. Calculated band structure of *trans*-$(CH)_x$ from Grant and Batra (1979).

E-k diagram: Electron energy dispersion showing a semiconductor

 Tomfohr & Sankey, Physical Review B, 65 (2002) 245105 Heeger, Kevilson, Schrieffer, & Su, Review of Modern Physics 60 (1988) 781

Molecular Electronics at the Nanoscale

- Nanowires and Devices

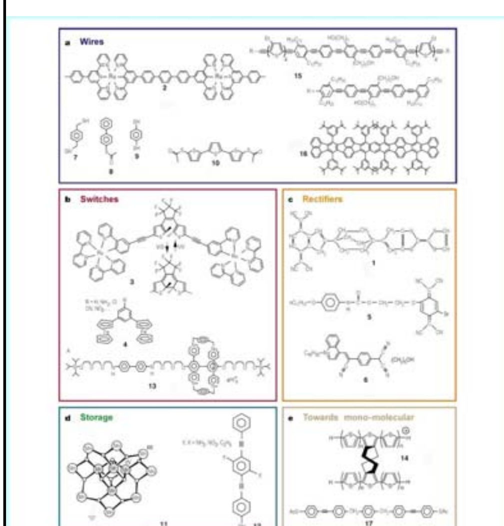

Figure 1 The molecules described in the text. **a**, Wires, **b**, hybrid molecular electronic (HME) switches, **c**, HME rectifiers, **d**, storage, and **e**, two molecules that show promise for mono-molecular electronics. Only the manganese acetate molecule **11** of formula $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ is not completely represented, for clarity. All these molecules have been synthesized apart from the historical design **1** of a d–s–a molecular rectifier. Molecules **14** and **15** have not yet been characterized. **14** is the first proposal of an intramolecular transistor and **17** is an intramolecular quantum well.

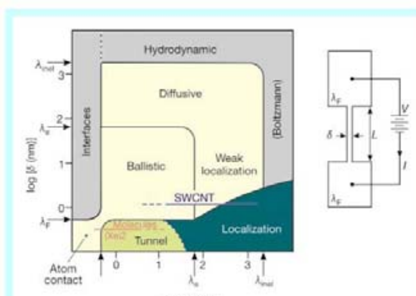

Figure 3 Regimes of electronic transport as a function of the wire width δ and length L. λ_F is the de Broglie carrier wavelength in the contact electrodes (away from the constriction), λ_e the elastic mean free path in the wire and λ_{inel} the inelastic mean free path in the wire. Characteristic orders of magnitude for λ_F, λ_e and λ_{inel} are taken for noble metals at low temperature. Hydrodynamic (Boltzmann), diffusive (weak localization) and ballistic regimes have been well studied in the past for metals and semiconductors. Ballistic and weak localization regimes are now being studied on SWNTs[25], atomic metallic wires[23] and the tunnel regime on single molecules[14,18,19,76] and short atomic wires[96].

Joachim, Gimzewski & Aviram, Nature (Nov. 2000) 541-548

Molecular Electronics at the Nanoscale

- Nanowires and Devices

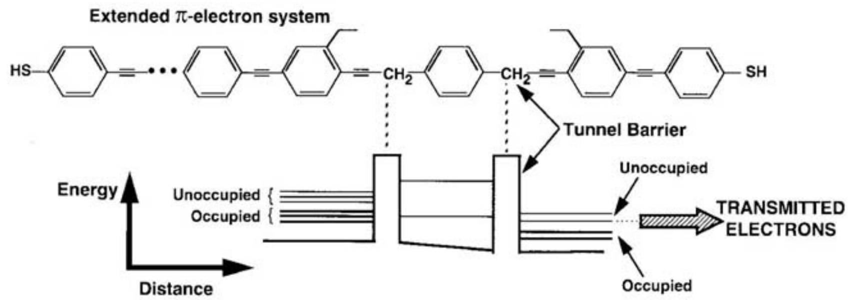

Fig. 8. Structure and mechanism for possible molecular RTD proposed by tour [94]. (a) Conducting chain molecule, like that shown in Fig. 7, but with insulating barrier groups that may generate (b) potential well for quantum confinement that could (c) create a resonant tunneling effect when the molecule is subjected to a voltage bias, permitting a current of electrons to be transmitted through the device. Compare this schematic with that in Fig. 3 for an analogous, but much larger, solid-state device.

Proceedings of the IEEE, Goldhaber-Gordon, *Overview of Nanoelectronic Devices, 85* (1997) 521

Molecular Electronics at the Nanoscale

- Defect Particles:
  - Plasmon:
    - electrons vibrating in unison creating a wave packet of vibrating electrons.
    - Collective oscillations of free carriers.
  - Exciton:
    - An *electron-hole* pair spatially near so that they interact and create an electron-hole particle
    - But energetically apart so that they do not recombine instantaneously
  - Polarons & Bipolarons – *electron-phonon* or lattice interaction that creates
  - Polariton – *plasmon-photon* interaction or *exciton-photon* interaction
  - Solitons – mid-gap electronic state in which conjugation is interrupted

Heeger, Kevilson, Schrieffer, & Su, Review of Modern Physics 60 (1988) 781

Molecular Electronics at the Nanoscale

- Defects:
  - Solitons – mid-gap electronic state in which conjugation is interrupted
  - Polarons & Bipolarons – carrier-phonon or lattice interaction

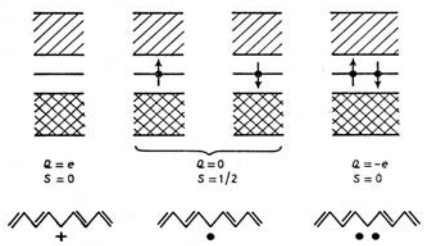

FIG. 22. Electronic structure leading to various charge and spin states of a soliton. The localized chemical shorthand for these delocalized structures is sketched.

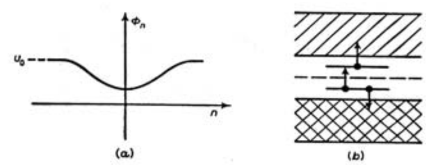

FIG. 23. Order parameter and band diagram for a polaron: the staggered order parameter ϕ_n as a function of n for a polaron; (b) two states symmetrically split off from the band edges for a polaron. An electron is missing from the upper state for an electron polaron, and only a single electron occupies the lower state for a hole polaron.

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