

Molecular Devices

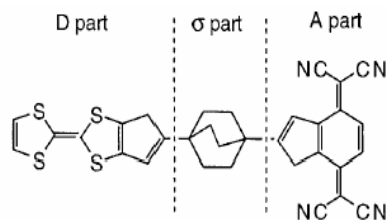
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Why Molecules?

- Molecules are small
- Molecules can be engineered
 - Many different ones!
 - Engineer band gaps, electron confinement, tunneling, pi-bonds
- Molecules can be self-assembled
- Molecules are identical

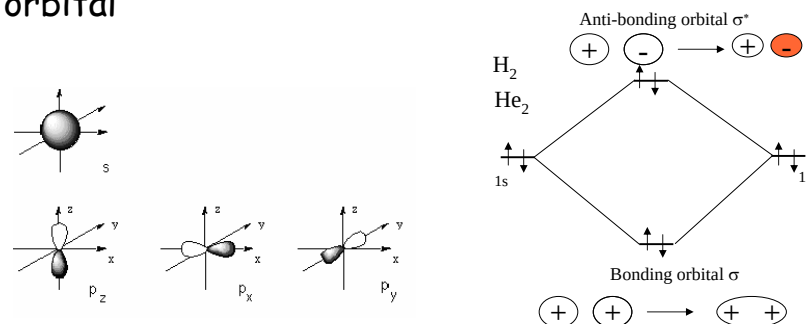
Where it all started

- Aviram & Ratner
Chem. Phys. Lett. **29**, 277 (1974)
- Donor-bridge-acceptor model for a molecular diode
- Synthesized and verified in 1997 by Metzger



Orbitals

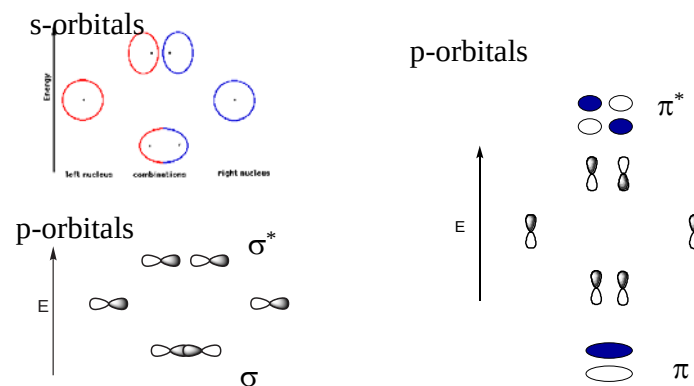
- N atomic orbitals lead to N molecular orbitals
- Most of the time, bonds are formed from combining one orbital from each atom
- We care about valence electrons - outermost orbital



Sigma vs. Pi Bonding

• Sigma bonding

Pi-Bonding

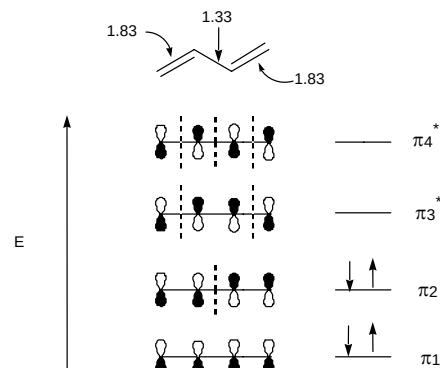


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Extended Pi Bonding

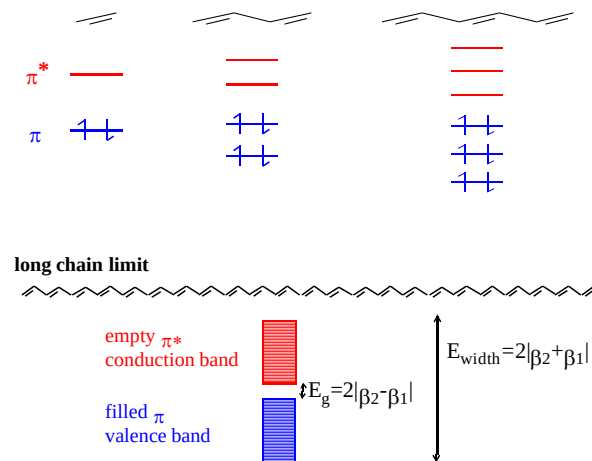


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Conjugated Polymers



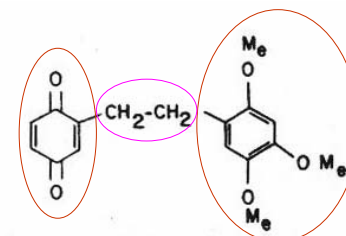
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Line diagrams

Sigma bonded segment



Pi conjugated segments

Fig. 1. An example of a hemiquinone.

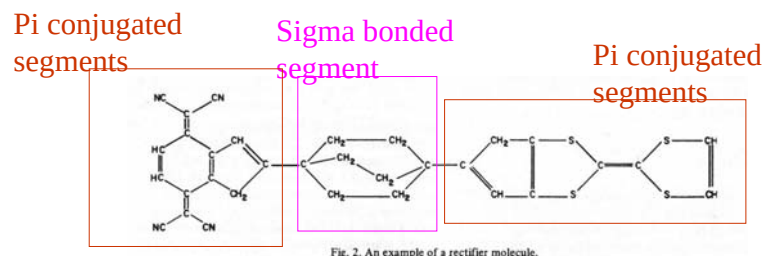
- Unlabelled vertices are carbons
- Add Hydrogens as needed to satisfy valence
 - C $\rightarrow$ 4 lines N $\rightarrow$ 3 lines O $\rightarrow$ 2 lines F $\rightarrow$ 1 line

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Another Rectifier Molecule



- Their molecules consist of two pi-conjugated segments, with sigma bonded region in between
- Pi-conjugated regions have different energies due to electron donors and acceptors

Electronegativity

- Ability of an atom to attract electrons to itself, when participating in a covalent bond
- Periodic trends
 - Increases from left to right across periodic table
 - Decreases as you move down the periodic table

H 2.1

C 2.5

N 3.0

O 3.5

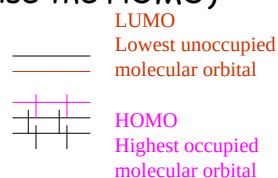
F 4.0

S 2.5

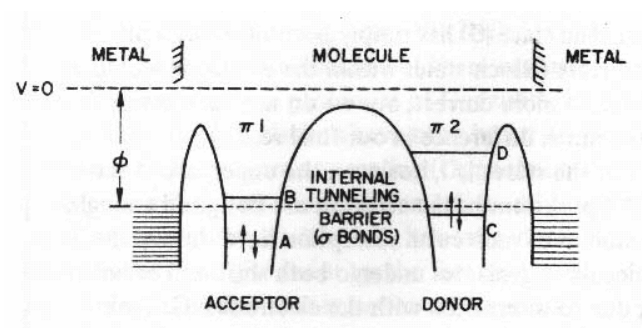
Electron Donors and Acceptors

- Electronegative elements like negative charges on themselves and so tend to withdraw (accept) electrons
 - Decrease the pi density
 - Raise electron affinity (Lower the LUMO)
- Electropositive elements like positive charges on themselves, and so tend to donate electrons
 - Increase the pi density
 - Lower ionization potential (Raise the HOMO)

For a metal, the HOMO and LUMO are degenerate, so the ionization potential = electronic affinity = work function



Energy Level Diagrams



- Acceptor will take electron into its LUMO
- Donor will lose electron from its HOMO

Mechanism for Rectification

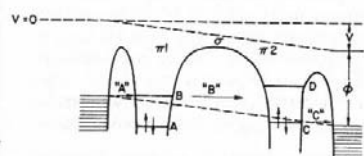
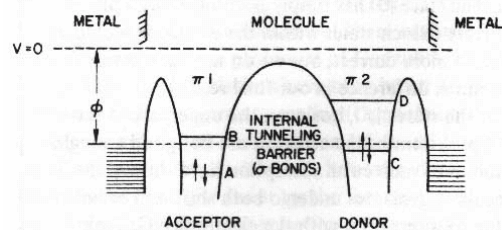


Fig. 4. Energy levels shift with applied voltage. "A", "B", and "C" are three tunneling processes.

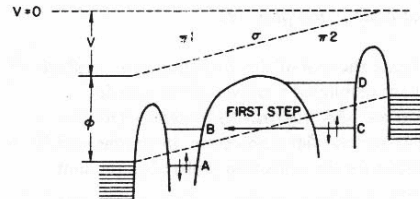


Fig. 6. Reverse applied voltage.

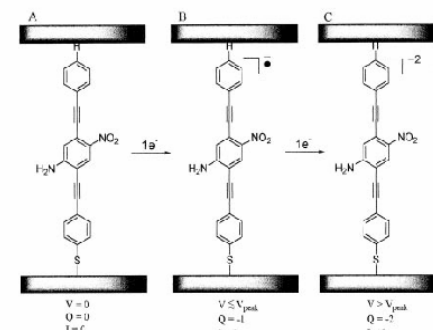
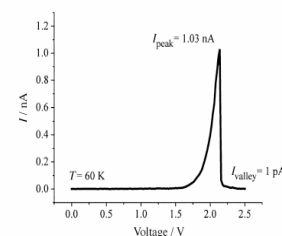
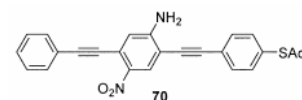
Molecular Devices

- Wires
- Rectifiers
- Tunnel Junctions
- Transistors
- Stateful Switches

Mechanisms

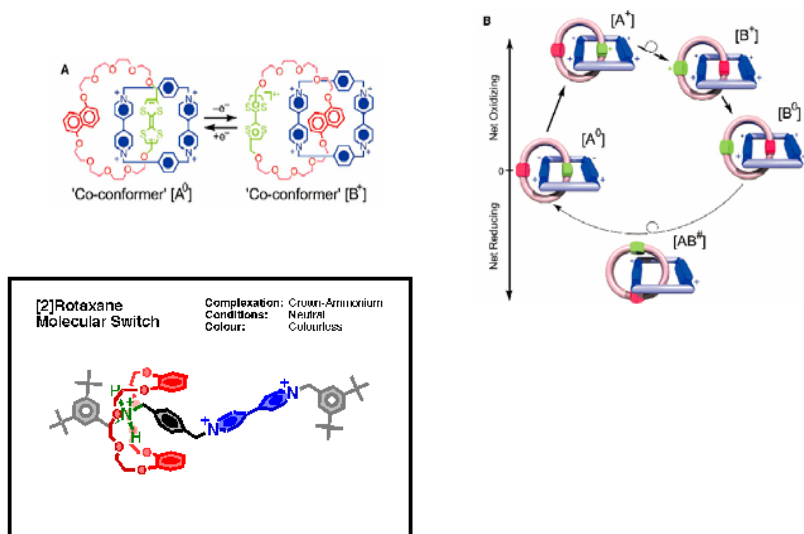
- Pi-conjugation
- Tunneling
- Diffusive charge transport
- Conformational change
- Schottky Barrier

Negative differential Resistance

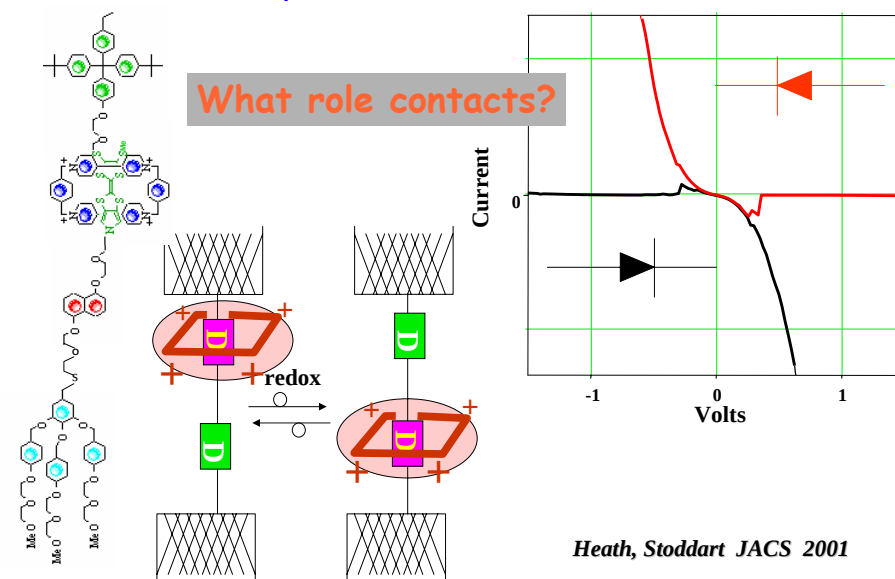


Tour&Reed 1999, Science 286(5444)

Molecular Switch

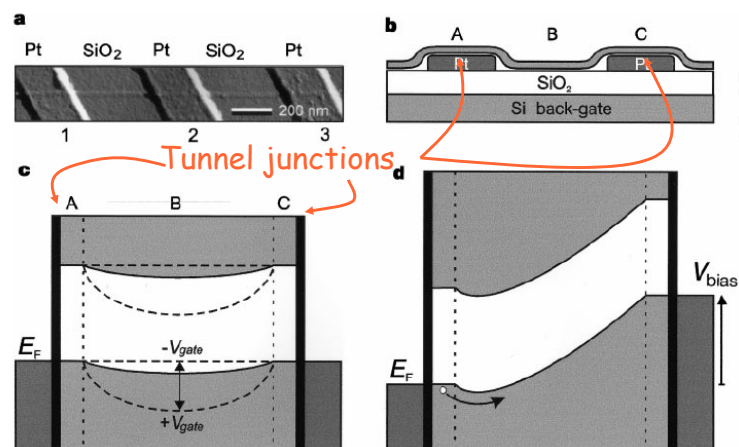


Proposed mechanism

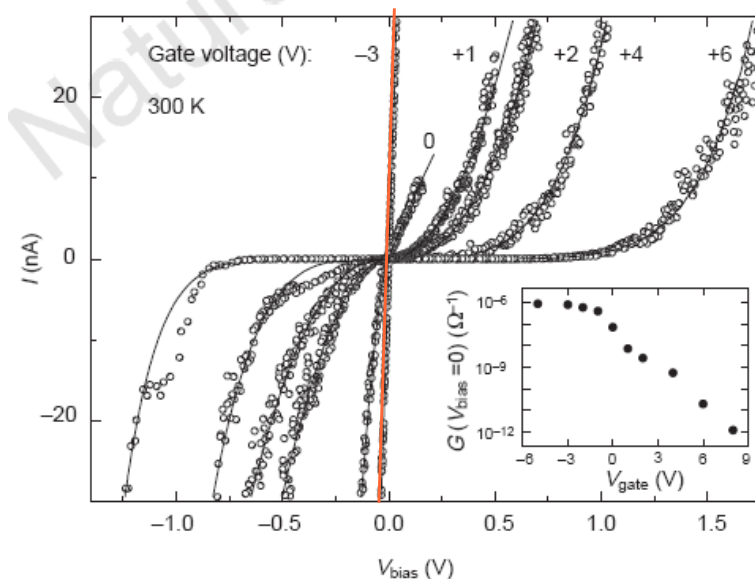


CNT FET

- Tans, et al Nature 1998
- Back-gated CNT FET

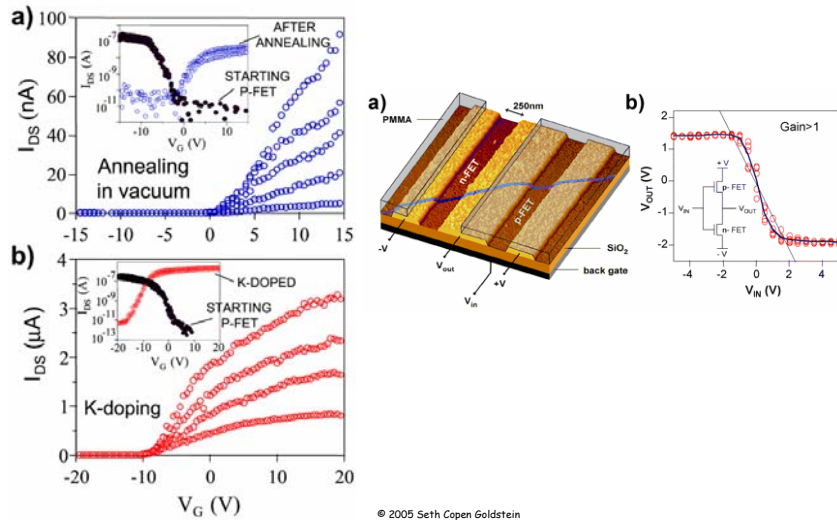


Transistor-like behavior



P and N-type CNT FETs

- Avouris, NanoLetters 2001

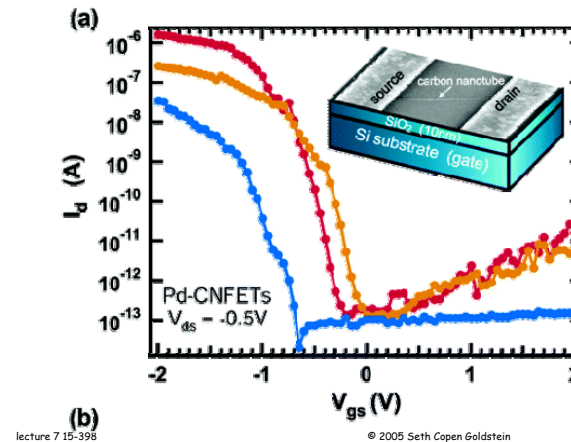


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Variance between tubes?

- $V_{th}, V_{gs}, V_{ds} = V_{gs} - V_{th} = 0.5V$



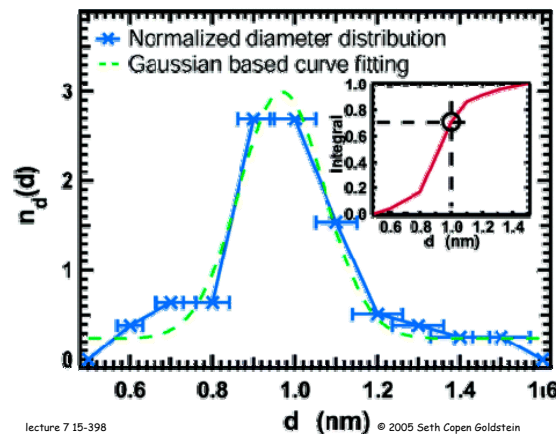
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Tube Diameter?

- Diff diameter have different energy gap. Vary from 0.6eV to 1.4eV



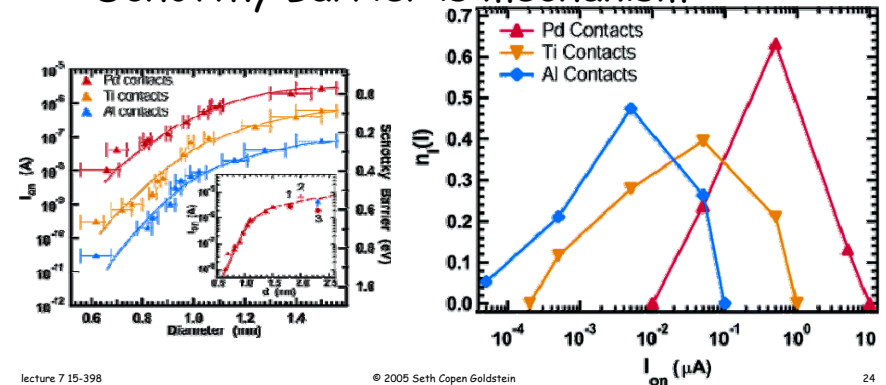
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Contacts?

- Measure I_{on} for different contact metals. Work functions increase from Pd→Ti→Al
- Schottky Barrier is mechanism



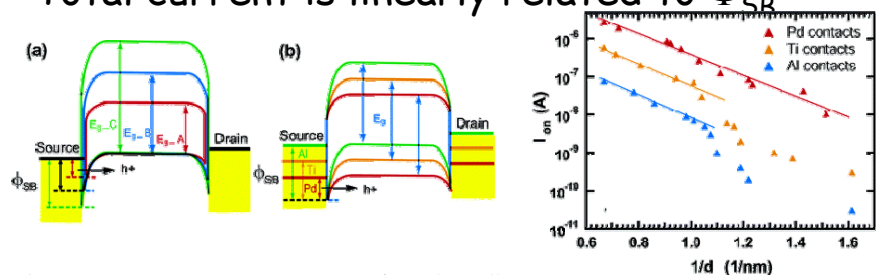
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Schottky Barrier

- Tube diameter effects E_g (larger $d \rightarrow$ smaller E_g)
- Contact metal effects Φ_{SB}
- SB height function (for p-type) of the difference between the valence band max of the tube and the fermi level of the metal
- Total current is linearly related to Φ_{SB}



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Bottom Line

- Molecular devices
 - Are diverse
 - Can produce different I-V curves
 - Have significant potential
 - Still a research area
 - Use different mechanisms
- The device-contact system is what is important
- So... back to slide 1

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Why Molecules?

- Molecules are small 
- Molecules can be engineered 
 - Many different ones!
 - Engineer band gaps, electron confinement, tunneling, pi-bonds
- Molecules can be self-assembled  
- Molecules are identical  

But contacts?

How many?

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