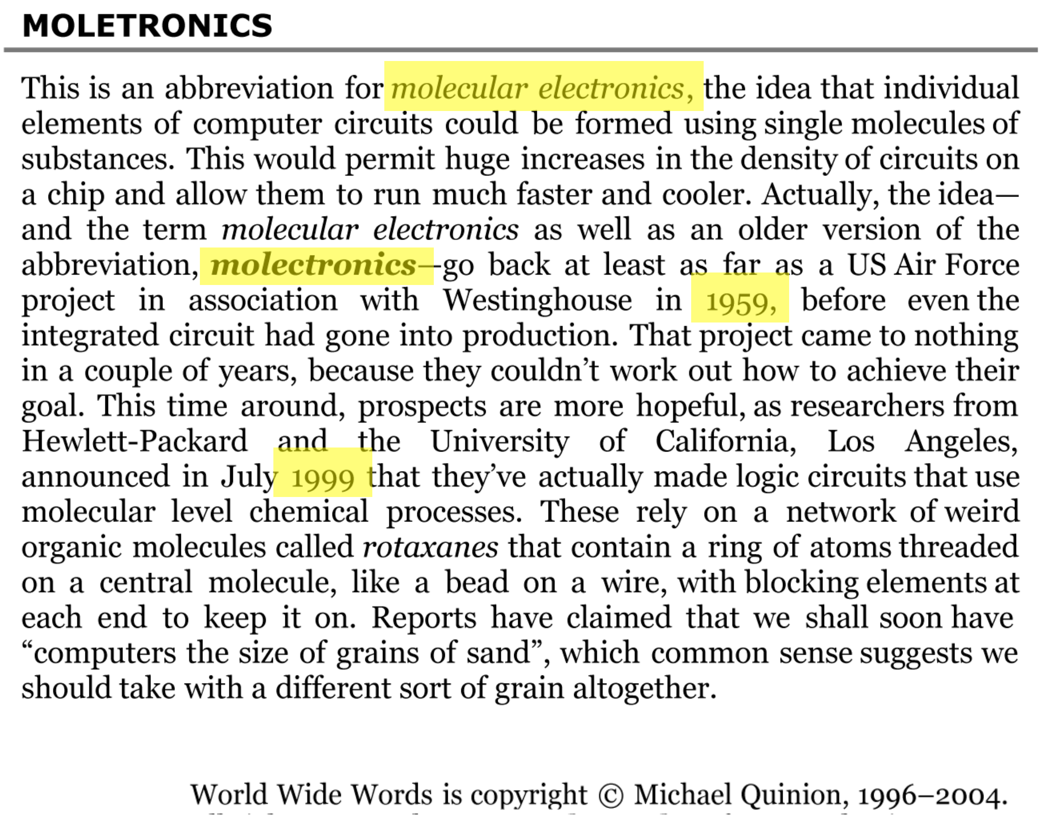
Moletronics



MOLETRONICS

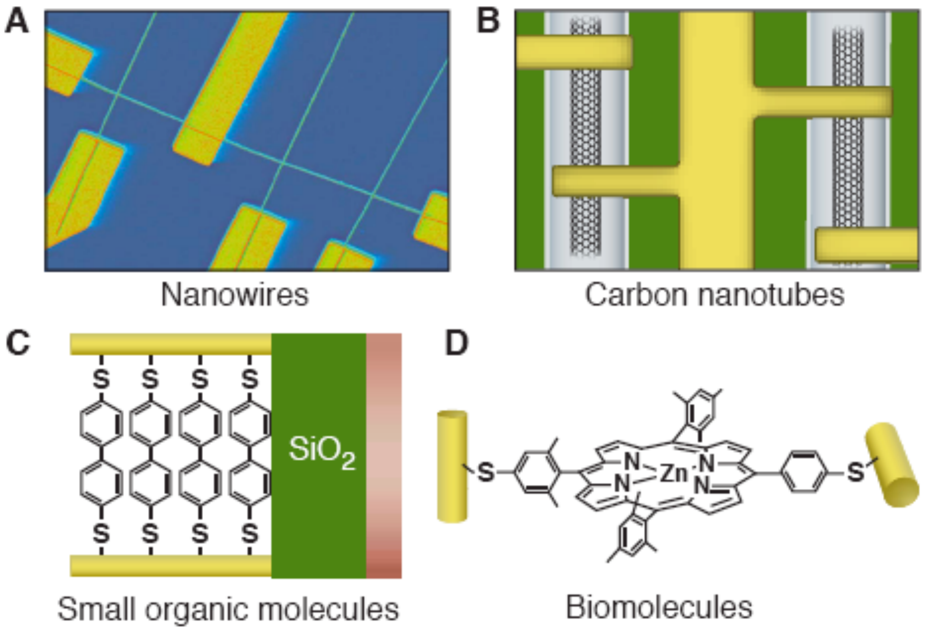
This is an abbreviation for *molecular electronics*, the idea that individual elements of computer circuits could be formed using single molecules of substances. This would permit huge increases in the density of circuits on a chip and allow them to run much faster and cooler. Actually, the idea—and the term *molecular electronics* as well as an older version of the abbreviation, ***molectronics***—go back at least as far as a US Air Force project in association with Westinghouse in 1959, before even the integrated circuit had gone into production. That project came to nothing in a couple of years, because they couldn't work out how to achieve their goal. This time around, prospects are more hopeful, as researchers from Hewlett-Packard and the University of California, Los Angeles, announced in July 1999 that they've actually made logic circuits that use molecular level chemical processes. These rely on a network of weird organic molecules called *rotaxanes* that contain a ring of atoms threaded on a central molecule, like a bead on a wire, with blocking elements at each end to keep it on. Reports have claimed that we shall soon have "computers the size of grains of sand", which common sense suggests we should take with a different sort of grain altogether.

- Late 1940s -Mulliken & Szent-Gyorgi's theory of molecular conduction.
- 1959 - Feynman
- 1974 - Ratner & Aviram proposed molecular rectifiers.
- 1999 - first single molecule measurements demonstrated.

http://www.quinion.com/words/turnsofphrase/tp-mol1.htm

Toward Nanocomputers

Greg Y. Tseng and James C. Ellenbogen



Nanowires

Carbon nanotubes

Small organic molecules

Biomolecules

Approaches to molecular-scale electronics.

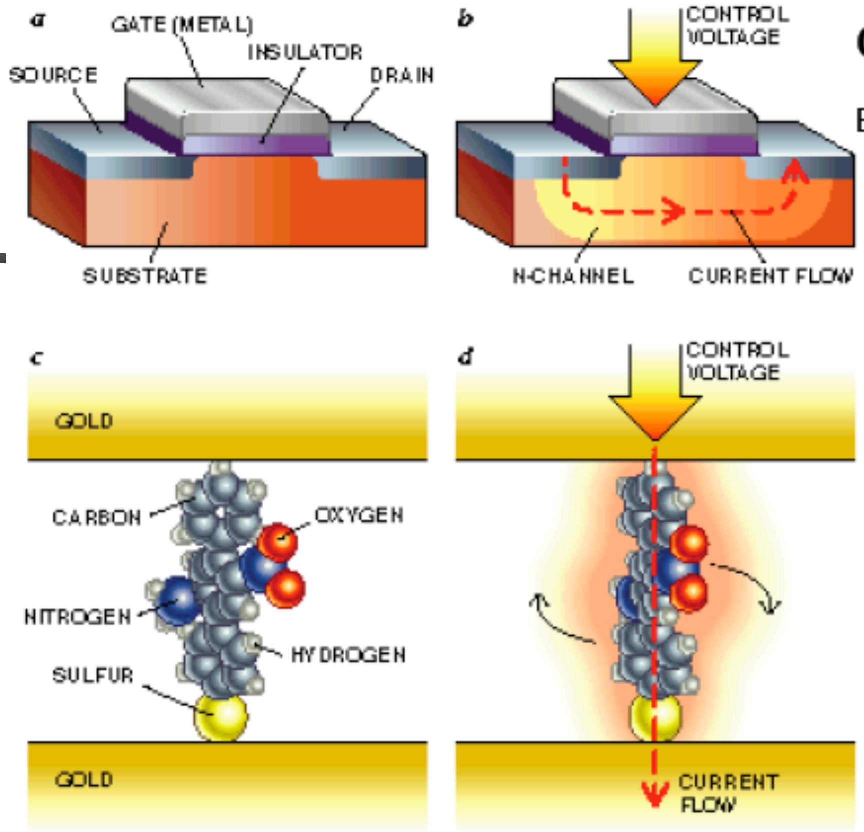
- Single crystal nanowires (Si, Ge, etc.)
- Carbon nanotubes
- Quantum dots
- Organic molecules
- Biomolecules

SCIENCE VOL 294 9 NOVEMBER 2001 1293

June 20, 2000 Scientific American

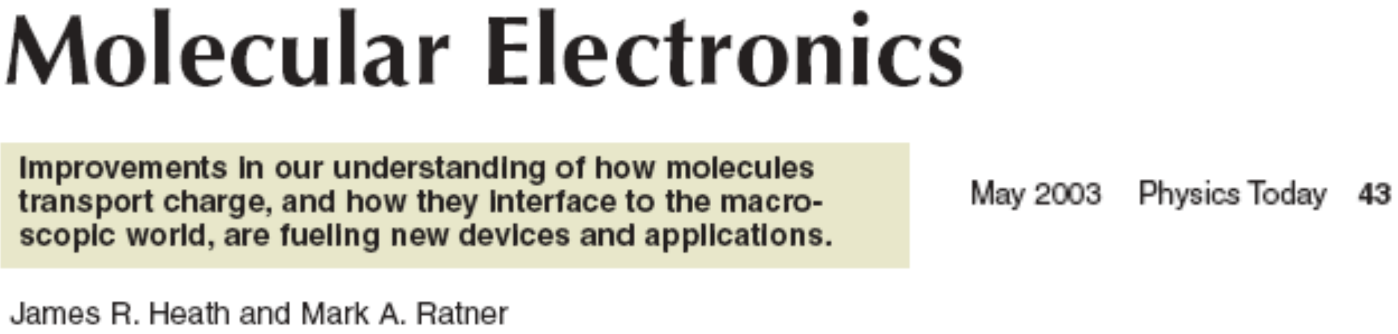
Computing With Molecules

By Mark A. Reed and James M. Tour



CONVENTIONAL MICROTRANSISTOR (a) has three terminals, known as the source, gate and drain. A positive voltage applied to the gate draws electrons to the insulator (b), enabling current to flow from the source to the drain. A molecule based on three benzene rings (c) was also used to switch an electric current. The center ring had asymmetric fragments, enabling it to be twisted by an electrical field (d). With a specific voltage applied, the electrical field twisted the molecule and permitted current to flow.

- Break junctions.
- Electric cut junctions.
- SAM on curved electrodes.
- SPM, STM.



Molecular Electronics

Improvements in our understanding of how molecules transport charge, and how they interface to the macroscopic world, are fueling new devices and applications.

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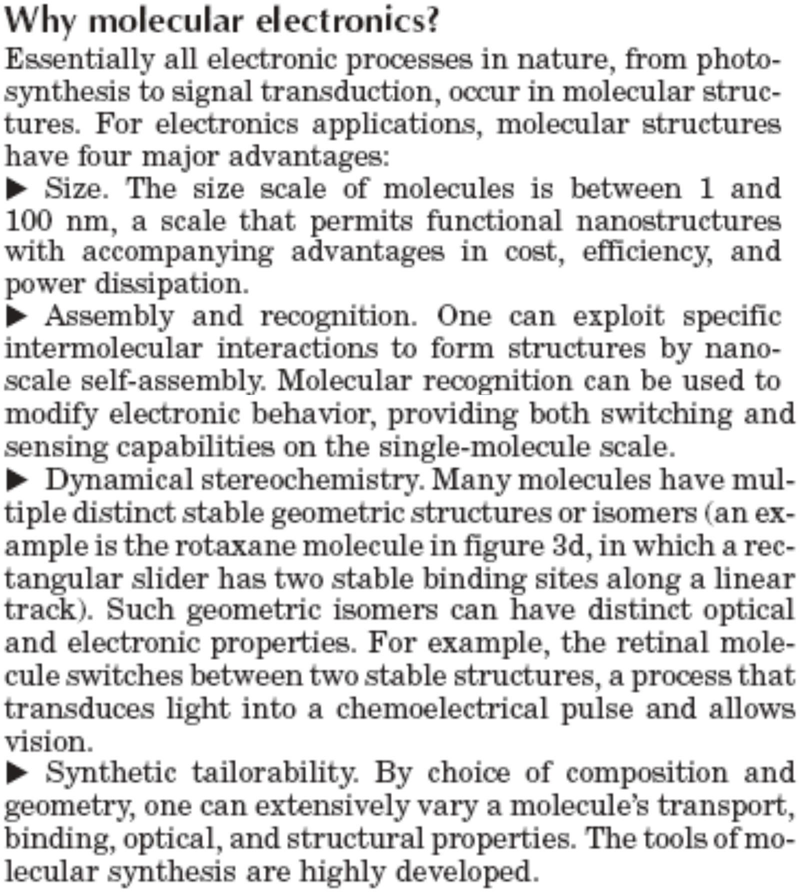
James R. Heath and Mark A. Ratner

- Single electron devices.
- Single atom switching.
- Switching by biomolecular recognition.
- Spintronics.



Why molecular electronics?

Essentially all electronic processes in nature, from photosynthesis to signal transduction, occur in molecular structures. For electronics applications, molecular structures have four major advantages:

▶ Size. The size scale of molecules is between 1 and 100 nm, a scale that permits functional nanostructures with accompanying advantages in cost, efficiency, and power dissipation.

▶ Assembly and recognition. One can exploit specific intermolecular interactions to form structures by nanoscale self-assembly. Molecular recognition can be used to modify electronic behavior, providing both switching and sensing capabilities on the single-molecule scale.

▶ Dynamical stereochemistry. Many molecules have multiple distinct stable geometric structures or isomers (an example is the rotaxane molecule in figure 3d, in which a rectangular slider has two stable binding sites along a linear track). Such geometric isomers can have distinct optical and electronic properties. For example, the retinal molecule switches between two stable structures, a process that transduces light into a chemoelectrical pulse and allows vision.

▶ Synthetic tailorability. By choice of composition and geometry, one can extensively vary a molecule's transport, binding, optical, and structural properties. The tools of molecular synthesis are highly developed.

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Crossbar architectures

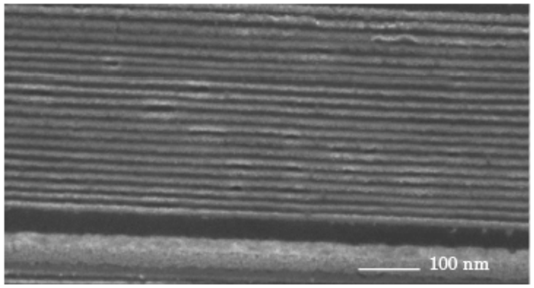

Figure 2. Array of nanowires, each approximately 5 nm in diameter. The lattice constant is 15 nm. Certain materials parameters important to solid-state devices, such as the average density of dopant atoms, no longer hold meaning at these nanoscale dimensions. At this size scale, however, chemical control over molecular properties is highly developed.

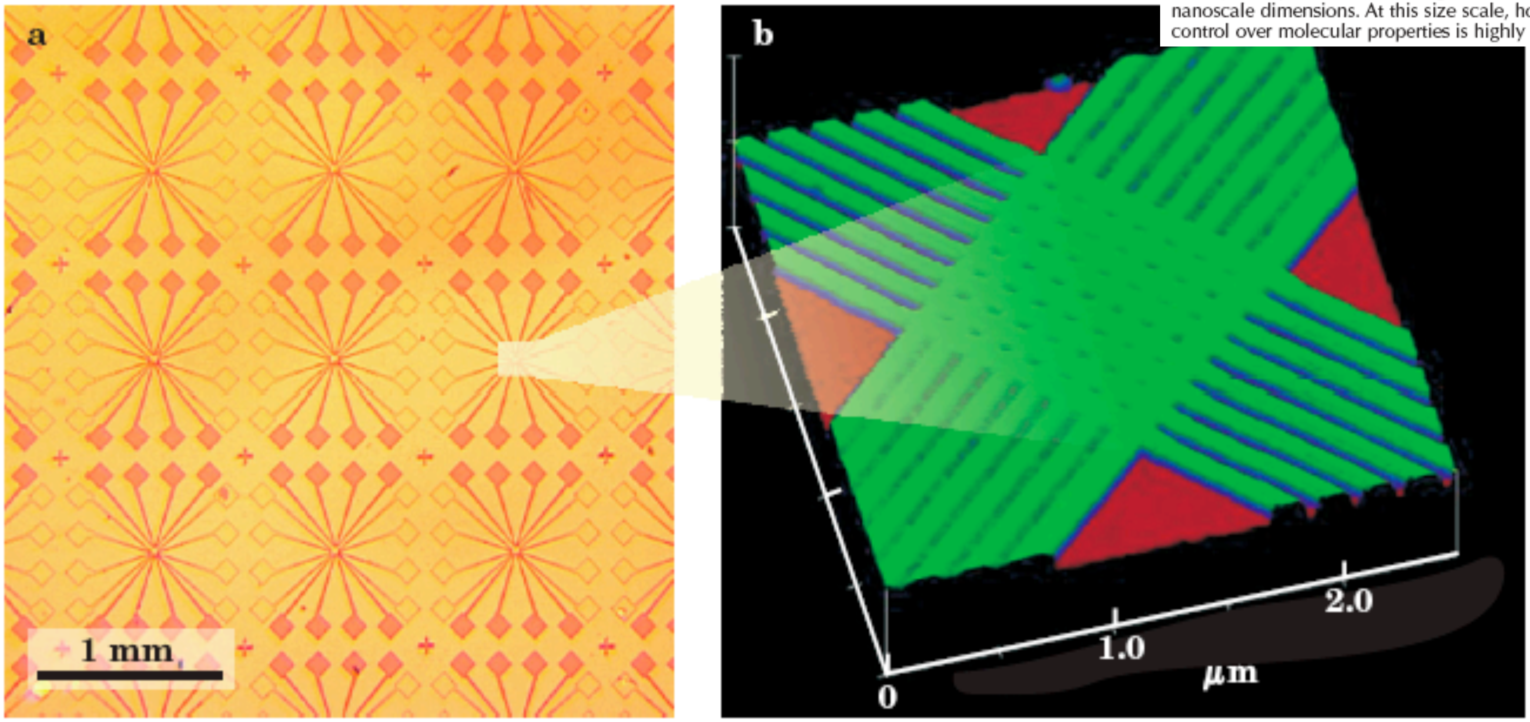

Figure 1. Molecular electronics devices. (a) This optical micrograph shows a collection of 64-junction molecular circuits, fabricated by a combination of soft-imprinting techniques for the wires and chemical assembly for the molecules at the wire intersections. (b) An atomic force micrograph of one of the circuits, which could be used either as a random access memory or as a combination logic and memory circuit. The molecules used in this circuit are bistable [2]rotaxanes. (After Y. Chen et al., ref. 13. Courtesy of Stan Williams, Hewlett–Packard Co.)

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Molecular devices

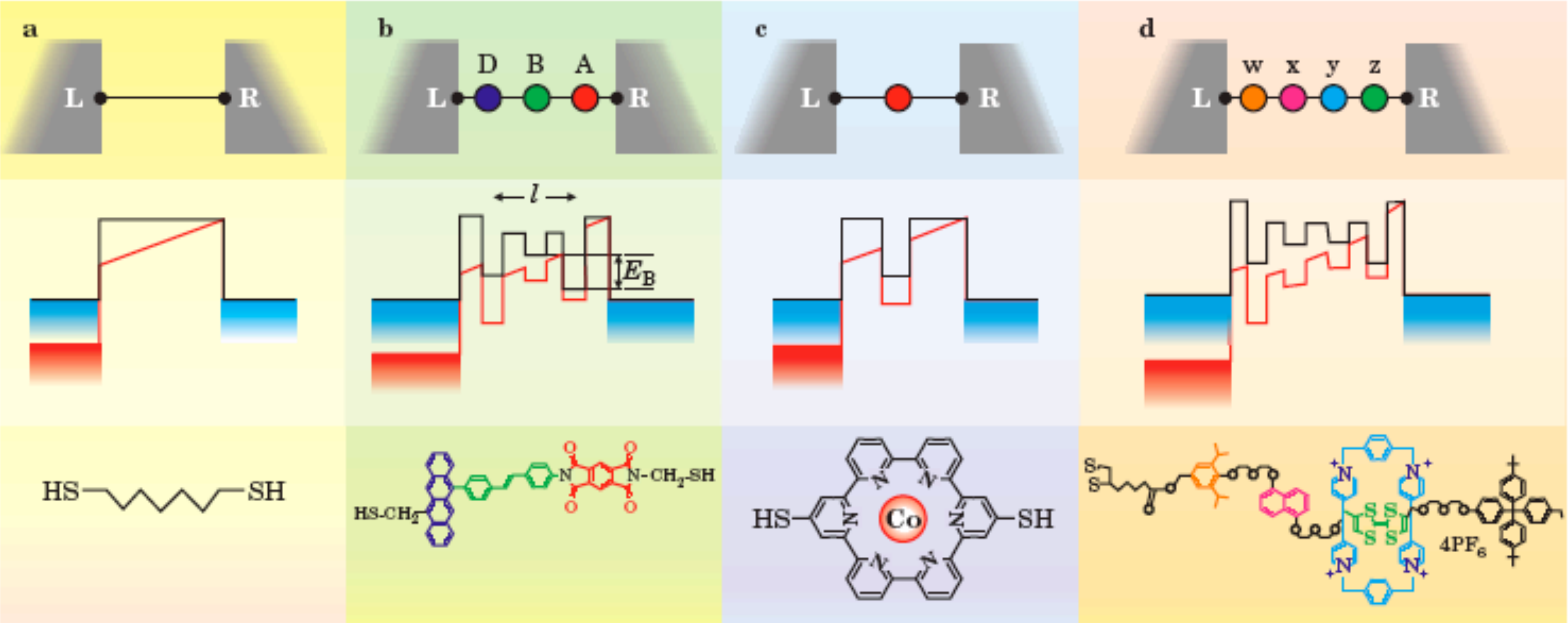

Figure 3. Examples of molecular transport junctions. The top panels depict molecules with various localized, low-energy molecular orbitals (colored dots) bridging two electrodes L (left) and R (right). In the middle panels, the black lines are unperturbed electronic energy levels; the red lines indicate energy levels under an applied field. The bottom panels depict representative molecular structures. **(a)** A linear chain, or alkane. **(b)** A donor-bridge-acceptor (DBA) molecule, with a distance l between the donor and acceptor and an energy difference E_B between the acceptor and the bridge. **(c)** A molecular quantum dot system. The transport is dominated by the single metal atom contained in the molecule. (Adapted from ref. 3.) **(d)** An organic molecule with several different functional groups (distinct subunits) bridging the electrode gap. The molecule shown is a [2]rotaxane, which displays a diverse set of localized molecular sites along the extended chain. Two of those sites (red and green) provide positions on which the sliding rectangular unit (blue) can stably sit. A second example of a complex molecule bridging the electrodes might be a short DNA chain.

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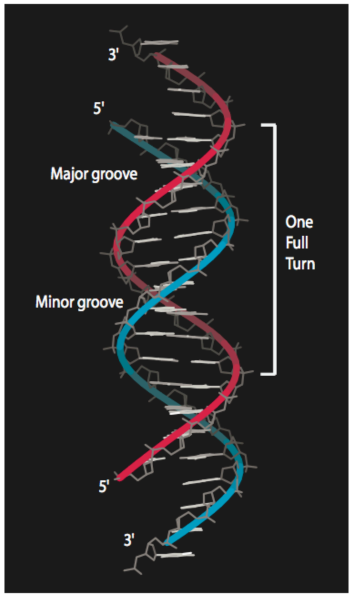
Some difficulties in data interpretation

- Contact resistance.
- Multiple conduction mechanisms.
- Molecular distortions.
- Specific example: DNA conductivity
  - Insulator, semiconductor, conductor, superconductor.



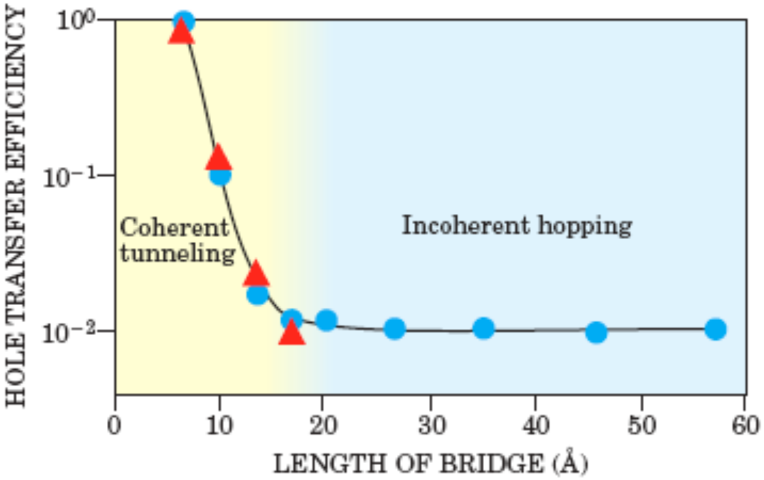


Figure 5. DNA shows a competition between different charge transport mechanisms. Plotted here are the experimental (triangles and circles) and theoretical (solid line) results for the relative rate of hole transfer between guanine–cytosine (GC) base pairs on DNA oligomers. The theoretical model incorporates both tunneling for nearest neighbor GC pairs and hopping between GC pairs separated by a bridge of several adenosine–thymine pairs, which have higher energy. Coherent tunneling dominates for short distances, and shows a characteristic exponential decay. Incoherent hopping dominates over long distances. (Adapted from ref. 10.)

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Key difficulties to be overcome for molecular circuit design

- Scalability to near molecular dimensions.
- Tolerance of manufacturing defects.
- Introduction of non-traditional fabrication methods (e.g. chemically directed self-assembly).
- Bridging between device densities potentially achievable at molecular scale with those at for standard lithography.
- Simplicity of fabrication.

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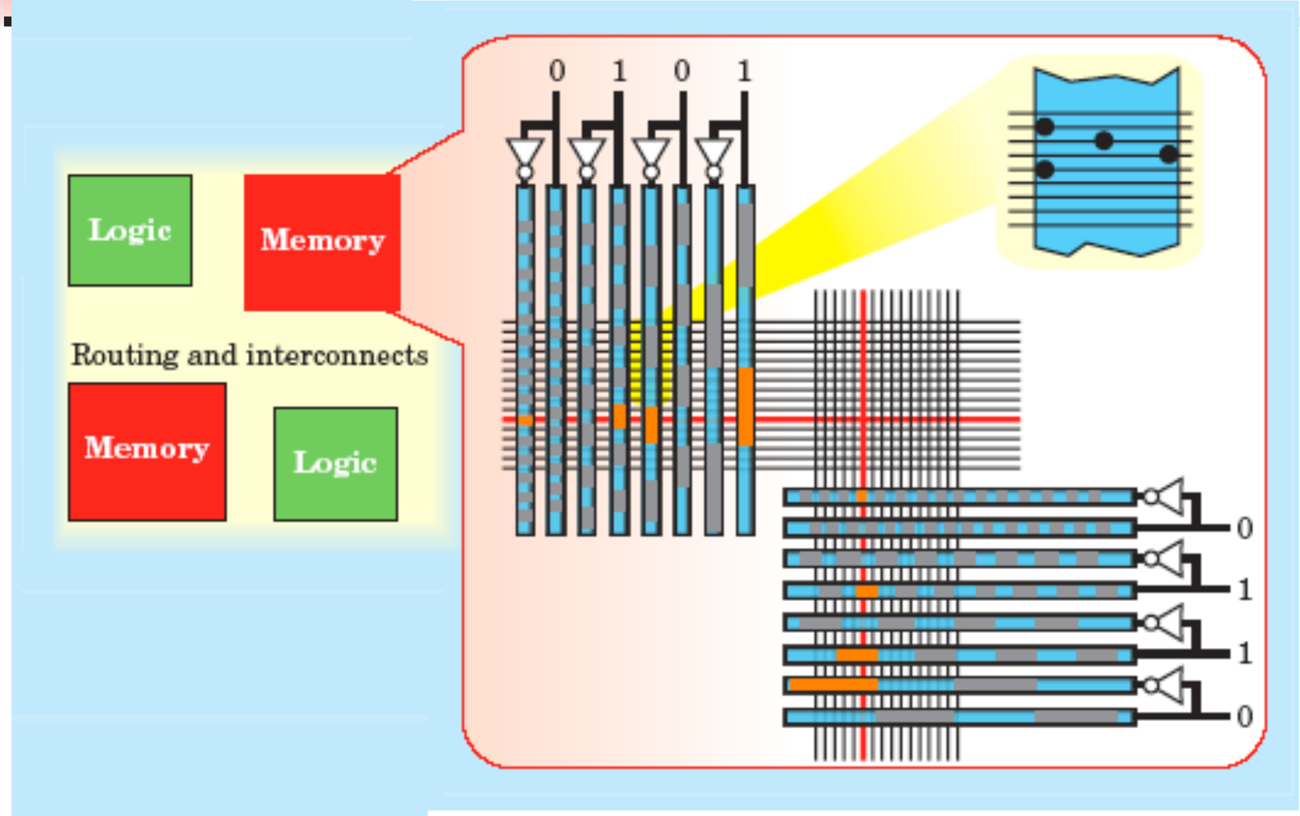
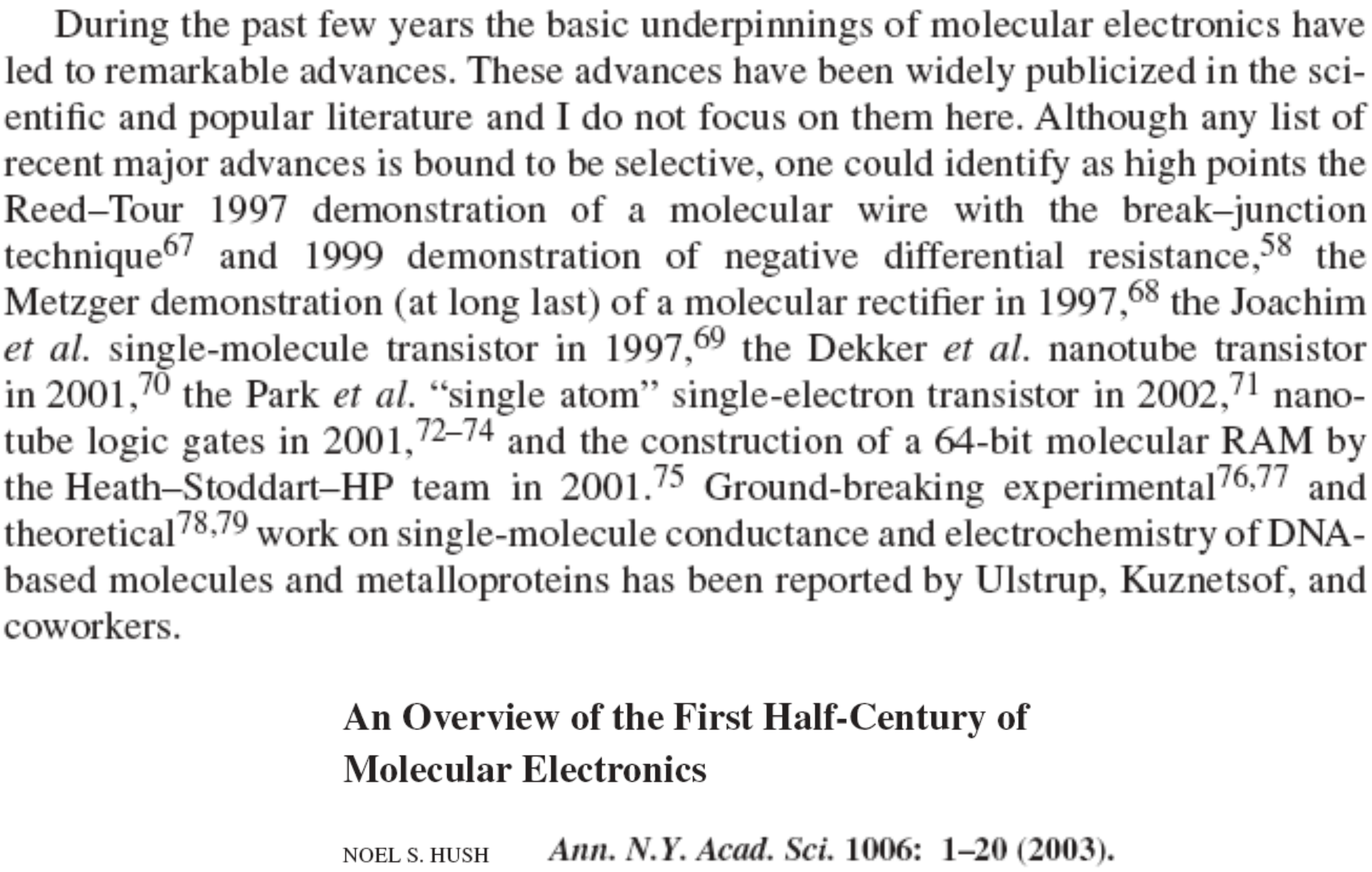
Crossbars and demultiplexers



Binary tree multiplexer

- Memory circuit details shown.
- 2^n memory bits (black nanowire crossings) can be addressed by n pairs of micro wires (blue).
- ME components located at nanowires crossings.

Summary of ME advances in recent years:



During the past few years the basic underpinnings of molecular electronics have led to remarkable advances. These advances have been widely publicized in the scientific and popular literature and I do not focus on them here. Although any list of recent major advances is bound to be selective, one could identify as high points the Reed–Tour 1997 demonstration of a molecular wire with the break–junction technique[67] and 1999 demonstration of negative differential resistance,[58] the Metzger demonstration (at long last) of a molecular rectifier in 1997,[68] the Joachim *et al.* single-molecule transistor in 1997,[69] the Dekker *et al.* nanotube transistor in 2001,[70] the Park *et al.* "single atom" single-electron transistor in 2002,[71] nanotube logic gates in 2001,[72–74] and the construction of a 64-bit molecular RAM by the Heath–Stoddart–HP team in 2001.[75] Ground-breaking experimental[76,77] and theoretical[78,79] work on single-molecule conductance and electrochemistry of DNA-based molecules and metalloproteins has been reported by Ulstrup, Kuznetsof, and coworkers.

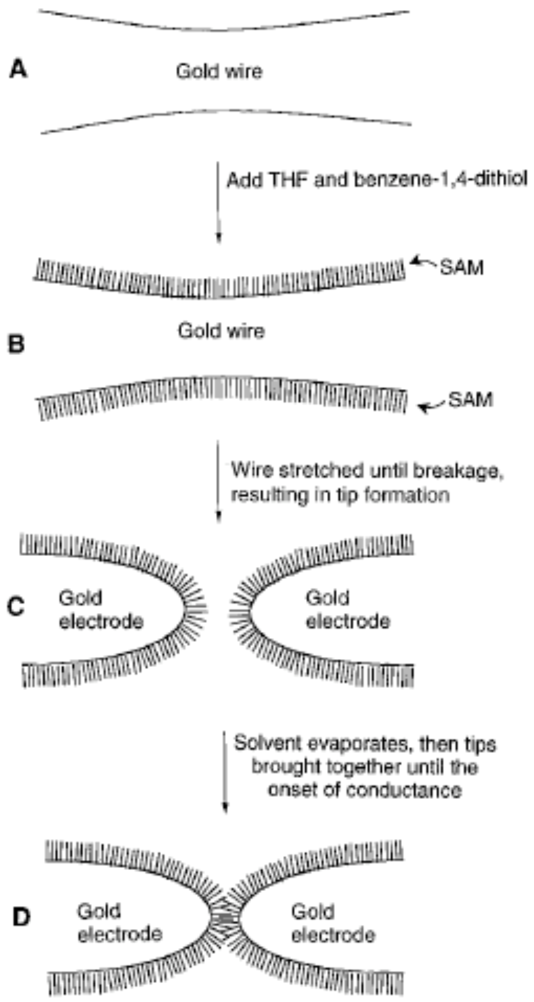
An Overview of the First Half-Century of Molecular Electronics

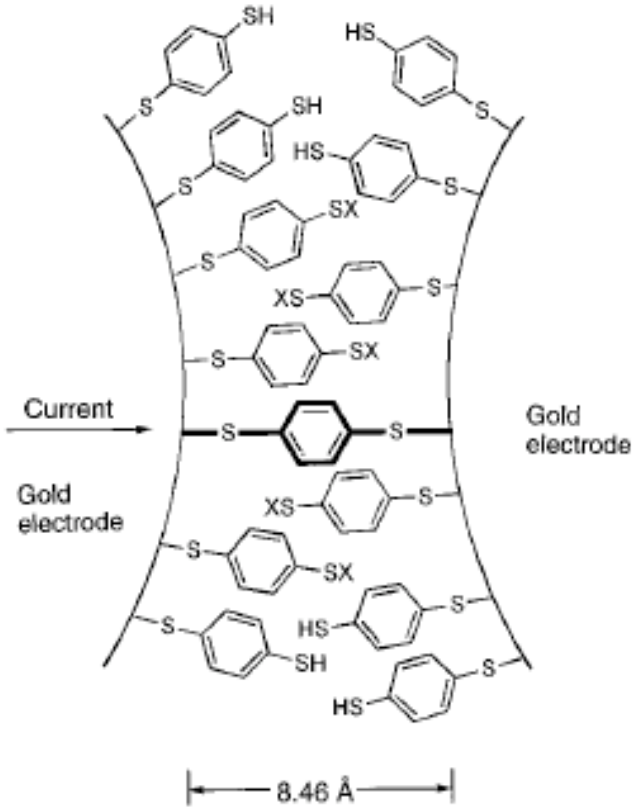
NOEL S. HUSH *Ann. N.Y. Acad. Sci.* **1006: 1–20 (2003).**

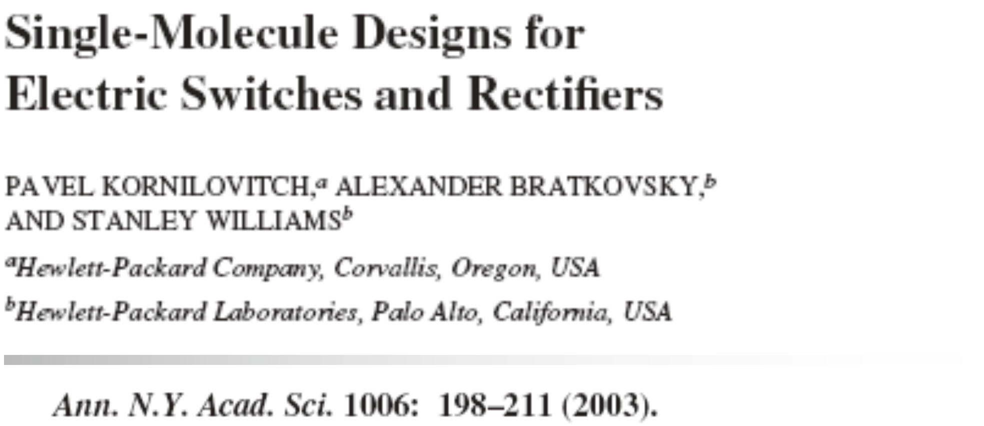
Conductance of a Molecular Junction

M. A. Reed,* C. Zhou, C. J. Muller, T. P. Burgin,
J. M. Tour*

SCIENCE • VOL. 278 • 10 OCTOBER 1997







Single-Molecule Designs for Electric Switches and Rectifiers

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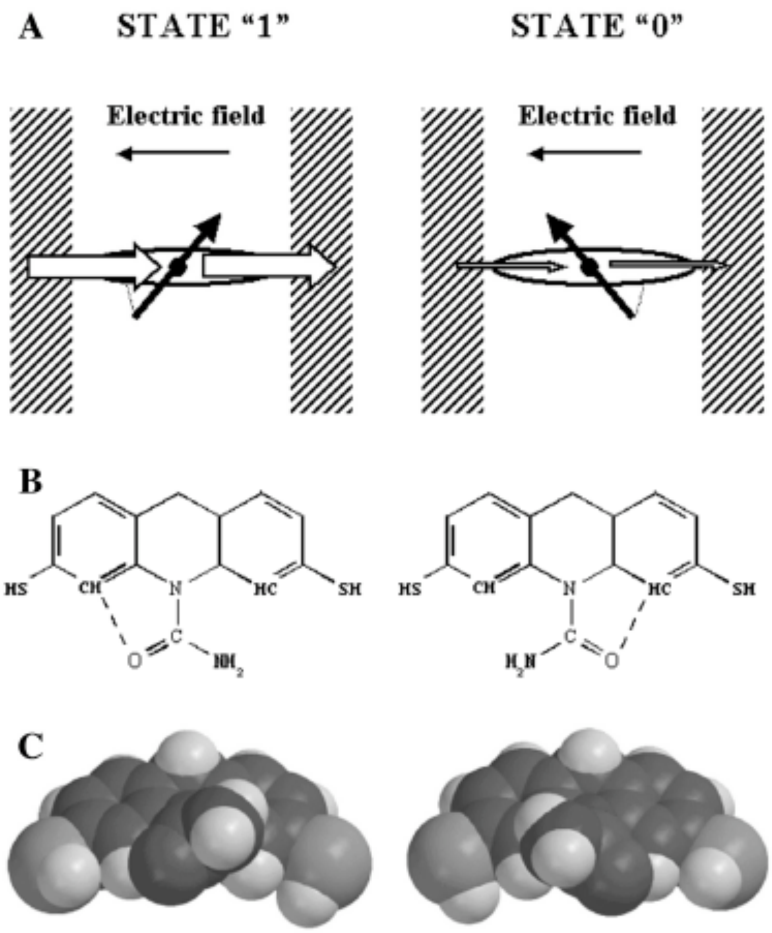
AND STANLEY WILLIAMS[b]

[a]*Hewlett-Packard Company, Corvallis, Oregon, USA*
[b]*Hewlett-Packard Laboratories, Palo Alto, California, USA*

Ann. N.Y. Acad. Sci. 1006: 198–211 (2003).



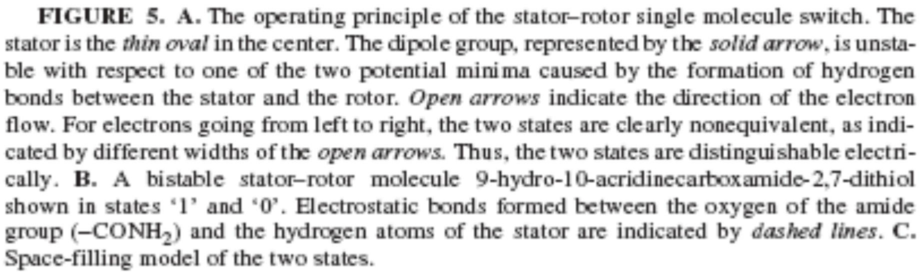


FIGURE 5. A. The operating principle of the stator–rotor single molecule switch. The stator is the *thin oval* in the center. The dipole group, represented by the *solid arrow*, is unstable with respect to one of the two potential minima caused by the formation of hydrogen bonds between the stator and the rotor. *Open arrows* indicate the direction of the electron flow. For electrons going from left to right, the two states are clearly nonequivalent, as indicated by different widths of the *open arrows*. Thus, the two states are distinguishable electrically. **B.** A bistable stator–rotor molecule 9-hydro-10-acridinecarboxamide-2,7-dithiol shown in states '1' and '0'. Electrostatic bonds formed between the oxygen of the amide group (–CONH$_2$) and the hydrogen atoms of the stator are indicated by *dashed lines*. **C.** Space-filling model of the two states.

Electronically Configurable Molecular-Based Logic Gates

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J. F. Stoddart,[1] P. J. Kuekes,[2] R. S. Williams,[2] J. R. Heath[1†]

SCIENCE VOL 285 16 JULY 1999

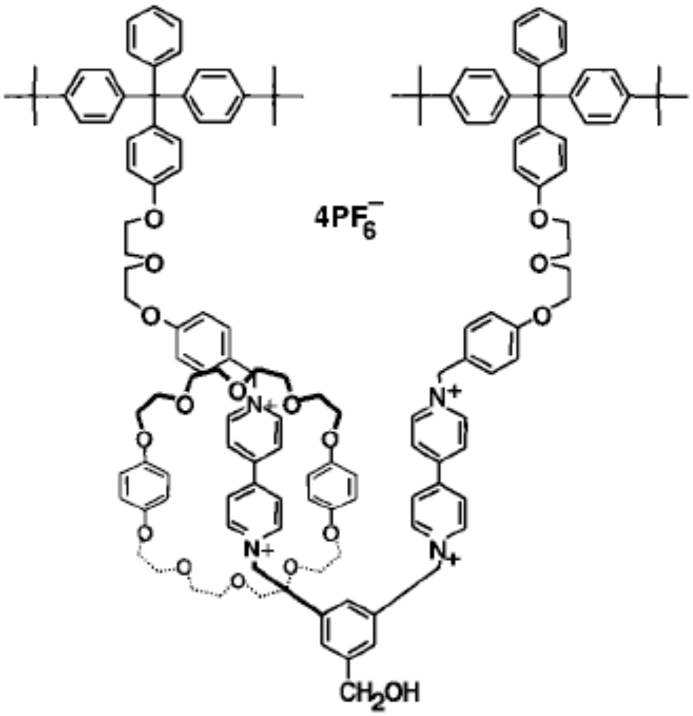
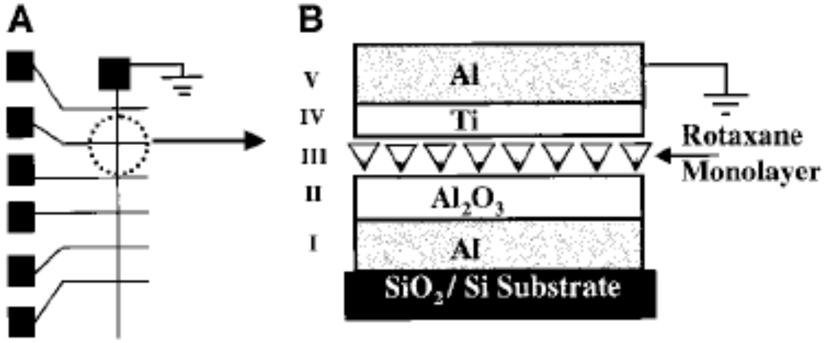


Fig. 2. A drawing of the R(1) rotaxane molecule used here.



Each junction contained several million molecules.

Bio•Nano•Technology

- Biomolecules in artificial nanosystems.
- Biological inspiration or principles.
- Engineering and *in vitro* evolution of biomolecules.
- Chemical self-assembly.
- Molecular electronics.