

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Molecular electronics, one of the major fields of current efforts in nanoscience, involves the exploration of the electronic level structure, response and transport, together with the development of electronic devices and applications that depend on the properties of matter at the molecular scale. This includes single molecules, molecular arrays and molecular networks connected to other electronic components. Its major application areas include sensors, displays, smart materials, molecular motors, logic and memory devices, molecular scale transistors and energy transduction devices. Often molecular electronics is envisioned as the next step in device miniaturization. The importance of molecules in device applications stems not only from their electronic properties, but also from their ability to bind to one another, recognize each other, assemble into larger structures, and exhibit dynamical stereochemistry.

Molecular electronics (sometimes called *moletronics*) is a branch of applied physics which aims at using molecules as passive (e.g. resistive wires) or active (e.g. transistors) electronic components. The concept of molecular electronics has aroused much excitement both in science fiction and among scientists due to the prospect of size reduction in electronics offered by such minute components. It is an enticing alternative to extend Moore's Law beyond the foreseen limits of small-scale conventional silicon integrated circuits. As a result, molecular electronics is currently a very active research field.

1.2 HISTORY

Study of charge transfer in molecules was advanced in the 1940s by Robert Mulliken and Albert Szent-Gyorgi in discussion of so-called "donor-acceptor" systems and developed the study of charge transfer and energy transfer in molecules. Likewise, a 1974 paper from Mark Ratner and Avi Aviram¹ illustrated a theoretical molecular rectifier. Later, Aviram detailed a single-molecule field-effect transistor in 1988.

Further concepts were proposed by Forrest Carter of the Naval Research Laboratory, including single-molecule logic gates.

Apart from the Aviram and Ratner proposal, molecular electronics received an initial boost from the experimental discovery of conducting polymers in the mid-seventies. Before this date, organic molecules (which form crystals or polymers) were considered insulating or at best weakly conducting semi-conductors. In 1974, McGinness, Corry, and Proctor reported the first molecular electronic device in the journal *Science*. As its active element, this voltage-controlled switch used melanin, an oxidized mixed polymer of polyacetylene, polypyrrole, and polyaniline. The "ON" state of this switch exhibited extremely high conductivity. This device is now in the Smithsonian's collection of historic electronic devices. As Hush notes, their material also showed negative differential resistance, "a hallmark of modern advances in molecular electronics". Melanin is also the first example of a "self-doped" organic semiconductor, though McGinness *et al* also looked at dopants such as diethylamine.

A few years later, in 1977, Shirakawa, Heeger and MacDiarmid rediscovered the potential high conductivity of oxidized ("doped") polyacetylene, producing a passive highly-conductive form of polyacetylene. For this discovery and its subsequent development, they received the 2000 Nobel prize in physics. Subsequently, chemists greatly improved the conductance of conjugated polymers. These findings opened the door to plastic electronics and optoelectronics, which are beginning to find extensive commercial application.

1.3 ABOUT MOLECULAR ELECTRONICS

The guiding principle of this research is that biological systems can provide useful paradigms for developing electronic and computational devices at the molecular level. For example, natural photosynthetic reaction centers are photovoltaic devices of molecular dimensions, and the principles dictating the operation of reaction centers may be useful in the design of synthetic optoelectronic switches. In this project, several classes of molecular photovoltaic species are being synthesized and studied. These include porphyrin-fullerene dyads, carotenoid-fullerene dyads, a carotenoid-porphyrin-fullerene triad, carotene-porphyrin-imide triads, and molecular dyads and triads containing two porphyrin moieties.

The approach involves the design and synthesis of dyads, triads and other super molecular species using the techniques of organic chemistry. The newly-prepared molecules are then studied by a variety of physical methods, including time-resolved laser spectroscopy, NMR spectroscopy, and cyclic voltammetry in order to determine how and how well they functioned as molecular electronic elements. The information gained can then be used to design new generations of these molecules.

Once functional molecular photovoltaics, logic gates, or other elements have been prepared, ways must be developed for interfacing these with electronic circuits. Possibilities are being investigated in a collaborative project with Professor Michael Kozicki, in the Department of Electrical Engineering.

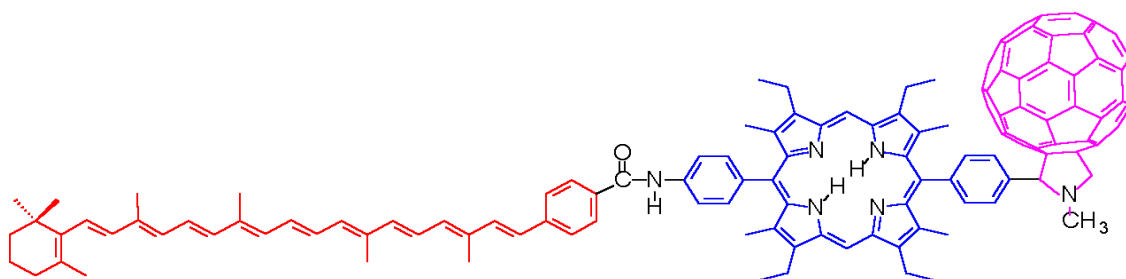


Figure 1.1 Molecular Triad

The triad shown above is an example of a molecule that may be useful in molecular electronic applications. Buckminsterfullerene (C_{60}) and its relatives have generated considerable excitement in recent years due to their status as new and unusual forms of carbon which are completely unrelated to the many carbon compounds synthesized by living organisms. In spite of their non-biological origin, it turns out that fullerenes are nearly ideal as components of molecules that mimic natural photosynthetic energy and electron transfer.

This molecular "triad" consists of a synthetic porphyrin (P) covalently linked to both a fullerene (C_{60}) and a carotenoid polyene (C) (*J. Am. Chem. Soc.* 1997, 119, 1400-1405). When the porphyrin absorbs light, it donates an electron to the fullerene, yielding $C-P^{\square\square}-C_{60}^{\square\square}$. The carotenoid then transfers an electron to the porphyrin to give a final $C^{\square\square}-P-C_{60}^{\square\square}$ charge-separated state. This state has a relatively long lifetime, and stores a considerable fraction of the light energy as electrochemical

potential energy. This conversion of light energy to electrochemical potential is analogous to the way plants carry out solar energy harvesting during photosynthesis.

The charge-separated state is formed even at 8 degrees Kelvin in a frozen environment, and ultimately decays by charge recombination to yield the carotenoid triplet excited state, rather than the original ground-state molecule.

The generation in the triad of a long-lived charge separated state by photo induced electron transfer, the low-temperature electron transfer behavior, and the formation of a triplet state by charge recombination are phenomena heretofore observed mostly in photosynthetic reaction centers.

The triads are molecular-scale photovoltaic cells. Their nanometer size and their ability to generate an electrical response to light may help point the way to the development of molecular-scale optoelectronic devices for communications, data processing, and sensor applications. In fact, the triad shown above functions as a molecular-scale AND logic gate. Two inputs (light and a weak magnetic field) are required to switch on the output of the gate, which may be detected optically or electrically. ("Magnetic Switching of Charge Separation Lifetimes in Artificial Photosynthetic Reaction Centers," D.Kuciaukas, P. a.Liddell, A.L.Moore, T.A.Moore and D.Gust, J.Am.Chem. Soc., **120**, 10880-10886 (1998).

1.4 ORGANISATION OF THE THESIS

The rest of the thesis is organized as follows

Chapter 2: This chapter discusses about technology used in these electronics

Chapter 3: This chapter discusses about molecular electronic devices and characteristics

Chapter 4: This chapter discusses about future scope of molecular electronics

Chapter 5: This chapter discusses about advantages and applications of this technology

Chapter 6: This chapter provides concluding comment

CHAPTER 2

2. MOLECULARELECTRONICS TECHNOLOGY

2.1 TECHNOLOGY USED

The field of molecular electronics seeks to use individual molecules to perform functions in electronic circuitry now performed by semiconductor devices. Individual molecules are hundreds of times smaller than the smallest features conceivably attainable by semiconductor technology. Because it is the area taken up by each electronic element that matters, electronic devices constructed from molecules will be hundreds of times smaller than their semiconductor-based counterparts. Moreover, individual molecules are easily made exactly the same by the billions and trillions. The dramatic reduction in size, and the sheer enormity of numbers in manufacture, is the principle benefits offered by the field of molecular electronics.

The field of molecular electronics seeks to use individual molecules to perform functions in electronic circuitry now performed by semiconductor devices. Individual molecules are hundreds of times smaller than the smallest features conceivably attainable by semiconductor technology. Because it is the area taken up by each electronic element that matters, electronic devices constructed from molecules will be hundreds of times smaller than their semiconductor-based counterparts. Moreover, individual molecules are easily made exactly the same by the billions and trillions. The dramatic reduction in size, and the sheer enormity of numbers in manufacture, is the principle benefits offered by the field of molecular electronics.

At the heart of the semiconductor industry is the semiconductor switch. Because semiconductor switches can be manufactured at very small scales and in combination can be made to perform all desired computational functions, the semiconductor switch has become the fundamental device in all of modern electronics. California Molecular Electronics Corporation's Chiropticene® Switch is a switchable device that goes beyond the semiconductor switch in size reduction. This switch is a single molecule that exhibits classical switching properties.

The material listed herein provides insight into important technology areas of molecular electronics. The documents are a "collection of works" on various topics in the field of molecular electronics assembled by California Molecular Electronics Corporation (CALMEC®) for the purposes of informing the non-scientific community on the exciting technology of molecular electronics. At present, the topics include an introduction to CALMEC's Chiropticene Molecular Switch Design, the principles behind the Chiropticene Switch technology, its molecular engineering, and the patents that protect the Chiropticene Switch technology.

2.2 WHY MOLECULAR ELECTRONICS ?

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

1. 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.
2. 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.
3. Many molecules have multiple distinct stable geometric structures or isomers (an example is the relaxant 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 chemical electrical pulse and allows vision.

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.

2.3 TRANSCENDING MOORE'S LAW WITH MOLECULAR ELECTRONICS

The future of Moore's Law is not CMOS transistors on silicon. Within 25 years, they will be as obsolete as the vacuum tube. While this will be a massive disruption to the semiconductor industry, a larger set of industries depends on continued exponential cost declines in computational power and storage density. Moore's Law drives electronics, communications and computers and has become a primary driver in drug discovery and bioinformatics, medical imaging and diagnostics. Over time, the lab sciences become information sciences, and then the speed of iterative simulations accelerates the pace of progress.

There are several reasons why molecular electronics is the next paradigm for Moore's Law:

1. Size: Molecular electronics has the potential to dramatically extend the miniaturization that has driven the density and speed advantages of the integrated circuit (IC) phase of Moore's Law. For a memorable sense of the massive difference in scale, consider a single drop of water. There are more molecules in a single drop of water than all transistors ever built. Think of the transistors in every memory chip and every processor ever built, worldwide. Sure, water molecules are small, but an important part of the comparison depends on the 3D volume of a drop. Every IC, in contrast, is a thin veneer of computation on a thick and inert substrate.
2. Power: One of the reasons that transistors are not stacked into 3D volumes today is that the silicon would melt. Power per calculation will dominate clock speed as the metric of merit for the future of computation. The inefficiency of the modern transistor is staggering. The human brain is ~100 million times more power efficient than our modern.
3. microprocessors. Sure the brain is slow (under a kHz) but it is massively parallel (with 100 trillion synapses between 60 billion neurons), and interconnected in a 3D volume. Stan Williams, the director of HP's quantum science research labs, concludes: "it should be physically possible to do the work of all the computers on Earth today using a single watt of power."

4. **Manufacturing Cost:** Many of the molecular electronics designs use simple spin coating or molecular self-assembly of organic compounds. The process complexity is embodied in the inexpensive synthesized molecular structures, and so they can literally be splashed on to a prepared silicon wafer. The complexity is not in the deposition or the manufacturing process or the systems engineering. Biology does not tend to assemble complexity at 1000 degrees in a high vacuum. It tends to be room temperature or body temperature. In a manufacturing domain, this opens the possibility of cheap plastic substrates instead of expensive silicon ingots.
5. **Elegance:** In addition to these advantages, some of the molecular electronics approaches offer elegant solutions to non-volatile and inherently digital storage. We go through unnatural acts with CMOS silicon to get an inherently analog and leaky medium to approximate a digital and non-volatile abstraction that we depend on for our design methodology. Many of the molecular electronic approaches are inherently digital and immune to soft errors, and some are inherently non-volatile.

2.4 MECHANISMS OF MOLECULAR CHARGE TRANSPORT

The synthesis and characterization of molecules are endeavors typically conducted in solution. Decades of research have given chemist's intuitive models that serve as a guide for using synthetic control to design physical properties into a molecule. A key challenge in molecular electronics is to translate that solution-phase intuition into solid-state device setting. Certain molecular structures have emerged as models for relating intermolecular electron transfer rates in solution to solid-state molecular junction conductance. A picture of electron transport through molecular devices is emerging, and it couldn't be more different from what is observed for more traditional conductors. Disregard, for the moment, the details of the electrical contact. In a semiconductor or metal wire, charge transport is ohmic: For a given wire diameter, longer wires have proportionately higher resistance. Such a picture is usually wrong for molecules because of the localized nature of most molecular electronic states.

Consider the energy diagrams of figure 3, in which four types of molecular-electronic junctions are represented, with examples of molecular structures. In figure 3a, one electrode functions as an electron donor and the other as an electron acceptor. The electrodes are bridged by a linear chain (an alkane). In 1961, Harden McConnell wrote

down the rate constant for electron transfer across molecular bridge: $k_{ET} \propto e^{-bl}$, where l is the bridge length and b is an energy-dependent parameter characterizing the molecule. For alkenes up to a certain length and for small applied voltages, this approximation works well: Current through a junction decreases exponentially with increasing chain length, and the alkane effectively serves as a simple energy barrier separating the two electrodes. The possible mechanisms for electron transport are much richer for the electron donor-bridge-electron acceptor (DBA) molecular junction of figure 3b. DBA complexes serve as models for understanding how charge transport mechanisms in solution translate into the conductivity of solid-state molecular junctions. In DBA complexes, the donor and acceptor sites are part of the molecule, and the lowest unoccupied sites on the donor and acceptor components are separated from one another by a bridging component that has molecular orbital of differing energy. In a process called electron-type super exchange; electrons that tunnel from the right electrode into the acceptor state when a bias is applied may coherently transfer to the donor state before tunneling to the left electrode. Alternatively, in hole-type super exchange, the tunneling from the molecule into the left electrode might occur first, followed by refilling of the molecular level from the right. In fact, both processes will occur, and it is their relative rates that determine the nature of coherent conductance through a DBA junction.⁷ A third possibility is that an electron from the donor can jump to the acceptor due to either thermal or electrical excitation. Those incoherent, diffusive processes quite closely related to ohmic charge flow. DBA junctions illustrate some of the beauty and richness of molecular electronics. From a chemist's perspective, The diversity of conduction mechanisms represents an opportunity to manipulate the electrical properties of junctions through synthetic modification. The observed conduction in DBA molecular junctions usually differs radically from that in traditional ohmic wires and can more closely resemble coherent transport in mesoscopic structures. Key factors include a dependence on the rates of intermolecular electron transfer between the donor and acceptor sites. This dependence can be exploited: The donor and acceptor components could be designed to differ energetically from one another (as in figure 3b), so that even with no applied bias voltage, the energy landscape is asymmetric. Under some conditions, the conductance of a DBA junction can vary with the sign of the applied voltage; such junctions represent a molecular approach toward controlling current rectification.⁸ The competition between charge

transport mechanisms through a DBA molecule can also be affected by the bridge. Shorter bridges produce larger amounts of wave function overlap between the donor and acceptor molecular orbitals. For a short bridge (5–10 Å), the super exchange mechanism will almost always dominate. For sufficiently long bridges, the hopping mechanism will almost always dominate. The molecular structure of the bridge can be synthetically varied to control the relative importance of the two mechanisms. For example, in a bridge containing conjugated double bonds, low-lying unoccupied electronic states within the bridge will decrease in energy with increasing bridge length (DEB of figure 3b is lowered) and will thereby decrease the activation barrier to hopping. Because double bonds, both in chains and in rings, facilitate charge delocalization, they are very common in molecular electronics. Certain molecules will isomerism—that is, change shape—upon receiving a charge or being placed in a strong field, and in many cases, such transformations can be tightly controlled. Different molecular isomers are characterized by different energies and possibly by different relative rates for the hopping and super exchange transport mechanisms. Driven molecular isomerization therefore presents opportunities for designing switches and other active device elements.¹ Molecular quantum dots (figure 3c) represent a simpler energy level system than DBA junctions, and have become the model systems for investigating basic phenomena such as molecule–electrode interactions and quantum effects in charge transport through molecular junctions. Representative molecules contain a principal functional group that bridges two electrodes. Early versions of these devices utilized mechanical break junctions—essentially fractured gold wire that forms a pair of electrodes—in a two-terminal device configuration.⁹ Although those experiments were a tour de force in terms of device preparation, small structural variations from device to device, which translate into large conductance changes, make quantitative interpretation of the data very difficult. More recent experiments have employed an electrical break junction together with a gate electrode. The gate can be used to tune the molecular energy levels with respect to the Fermi levels of the electrodes and thus somewhat normalize the device-to-device fluctuations that often characterize two electrode measurements. An equally important advantage is that the gated measurements, when carried out at low temperatures, can resolve the molecular energy levels to a few meV. Such resolution allows, for example, measurements of the signatures of electron-vibration coupling. Two recent papers reported on a unique

quantum effect known as a Kondo resonance (see figure 4) in organic molecules containing paramagnetic metal atoms.³ That this resonance was designed by chemical synthesis into two different molecules, and was observed in single-molecule transport measurements, represents a spectacular success for molecular electronics.

CHAPTER 3

MOLETRONIC DEVICES

3.1 ELECTRODE EFFECT

The molecule–electrode interface is a critically important component of a molecular junction: It may limit current flow or completely modify the measured electrical response of the junction. Most experimental platforms for constructing molecular-electronic devices are based on practical considerations. This pragmatic approach is, in many ways, the boon and the bane of the field. For example, the sulfur–gold bond is a terrific chemical handle for forming self-assembled, robust organic monolayer on metal surfaces. Other methods, such as using a scanning probe tiptop contact the molecule, are frequently employed; in part because they avoid processing steps that can damage or unpredictably modify the molecular component.

Ideally, the choice of electrode materials would be based not on the ease of fabrication or measurement, but rather on first principles considerations of molecule–electrode interactions. However, the current state of the art for the theory of molecule–electrode interfaces is primitive. Poor covalent bonding usually exists between the molecule and electrode. Consequently, at zero applied bias some charge must flow between molecule and electrodes to equilibrate the chemical potential across the junction. That flow can cause partial charging of the molecule, and local charge buildup gives Scotty-like barriers to charge flow across the interface. Such barriers, which can partially or fully mask the molecule’s electronic signature, increase for larger electro negativity differences. For this reason—and others, including stability, reproducibility, and generality—chemical bonds such as carbon–carbon or carbon–silicon will likely be preferred over gold–sulfur linkage at the interfaces. Very little theory exists that can adequately predict how the molecular orbital’ energy levels will align with the Fermi energy of the electrode. Small changes in the energy levels can dramatically affect junction conductance, so understanding how the interface energy levels correlate is critical and demands both theoretical and experimental study. A related consideration involves how the chemical nature of the molecule–electrode interface affects the rest of the Molecule. The zero-bias coherent conductance of a molecular junction may be

described as a product of functions that describe the molecule's electronic structure and the molecule–electrode interfaces (see box 1 on page 46). However, the chemical interaction between the molecule and the electrode will likely modify the molecule's electron density in the vicinity of the contacting atoms and, in turn, modify the molecular energy levels or the barriers within the junction. The clear implication (and formal result) is that the molecular and interface functions are inseparable and thus must be considered as a single system.

3.2 CONDUCTANCE THROUGH DNA

Consider a protein that spans cell membrane and shuttles information across that membrane. The protein self-assembles and self-orientates in the membrane; it recognizes and binds to other very specific proteins; it also might switch between two forms, only one of which will transmit the chemical signal. Proteins are large molecules, and, indeed, a certain molecular size is required to achieve such a rich combination of properties. The rotaxane molecule shown in figure 3d might appear large and complex, but it is actually small and efficiently designed, given the set of mechanical, chemical, and electronic properties that have been built into it. DNA oligomers represent perhaps the best-studied experimental example of this category. In addition to its biological importance and its use as a synthetic component of molecular nanostructures, the DNA molecule is of interest as a charge transfer species.⁴ Here the relationship between intermolecular electron transfer rates in solution and solid-state molecular junction transport becomes crucial to our understanding of transport processes. Connections to electrodes are also of great importance. Intramolecular electron transfer rates in DNA have been extensively investigated in solution⁴, and it is now becoming clear that the underlying processes exhibit large mechanistic diversity. In general, for very short distance motion (over a few base pairs), coherent tunneling can occur. For transfer over more than six or seven base pairs, inelastic hopping has been strongly suggested. The fundamental motion of electrons or holes from one site to another very broadly follows the standard model developed by Rudy Marcus, Noel Hush, and Joshua Jortner for charge transfer rates. The model assumes that for a charge tunneling from a donor to an acceptor site, the tunneling parameters—the height and width of the tunnel barrier—are modulated by interactions with a bath of harmonic oscillators that account for the chemical environment.

Exponential decay in the conductance with increasing distance has been seen directly in DNA molecules folded into hairpin shapes, and the transition to incoherent hopping has been seen in measurements of the efficiency with which holes are transferred along the molecule. The rich mechanistic palette observed for DNA charge transfer is becoming well understood due to elegant experiments and theory (see, for instance, figure 5).^{4,10} Indeed, the early suggestions that, because of its broad range of mechanistic possibilities, DNA might act as a paradigm for electron transfer generally seem to be correct.

Electrical transport in DNA molecular junctions is much messier—as should be true for any molecular junction of the type represented in figure 3d. If the measurements and systems were well defined, the junction conductance through functionally diverse **OK?** molecular systems would still be complex. Electrode mixing, structural dynamics and disorder, geometric reorganization, and sample preparation all add to the intricacies. As a result, the measurements are difficult to interpret, and appropriate extensions to theory are not really available. For example, in the past two years, reports in reputable journals have stated that DNA acts as an insulator, a semiconductor, a metal, and a superconductor. Most probably, transport in DNA junctions will show that the molecule (or at least naturally occurring DNA) is essentially a wide-band gap semiconductor characterized by localized hole hopping between the low-energy guanine–cytosine (CG) pairs (G yields the most stable positive ion). Because the band gap is large, DNA appears uncolored and long-range coherent charge motion is improbable. Significant effects should arise from various other processes, such as polar on-type hopping, in which charge motion is accompanied by molecular distortion; Anderson type charge localization, caused by the difference in energy between electrons localized on GC and adenosine–thymine (AT) pairs; structural reorganization; counter-ion motion; and solvent dynamics. The available data are, more or less, consistent with the suggestion by Cees Dekker and his collaborators that DNA is a wide-band gap semiconductor¹¹ that can exhibit activated transport for relatively short distances (less than 10 nm or so) but effectively behaves as an insulator at distances exceeding 20 nm. The complexity and richness of DNA junction behavior typify the challenge that the molecular electronics community faces in predicting and understanding transport in molecular junctions.

3.3 MOLECULAR ELECTRONICS CIRCUITS

The power of chemical synthesis to design specific and perhaps even useful device behaviors is rapidly being realized. The ensuing question, what sorts of circuit architectures can best take advantage of molecular electronics, is now receiving quite a bit of attention both from computer scientists (who have published largely in the patent literature) and from experimentalists; progress toward identifying and constructing working molecular electronics circuitry has advanced quickly. The proposed circuit architectures have attempted to deal with five key issues: scalability to near molecular dimensions; tolerance of manufacturing defects; introduction of non-traditional fabrication methods, such as chemically directed assembly; bridging between device densities potentially achievable at the molecular scale and those associated with standard lithography; and fabrication simplicity. The dominant circuit structure that has arisen from those considerations is the crossbar, 12, which is essentially an expanded ticktacktoe board, formed from wires and having individual molecular or molecular-scale devices sandwiched within the junctions. The crossbar is an intrinsically versatile circuit and is tolerant of manufacturing defects. Both memory and logic circuits have been demonstrated from molecular electronics and Nan wire crossbars.^{1, 13} A rapidly developing area of architectural research involves stitching together a patchwork quilt of different types of crossbars with the goal of configuring an efficient computational platform.¹⁴ Box 2 (above) illustrates how such a patchwork integrated-circuit architecture might be laid out and presents some detail on the simplest of the circuit components—a molecular-electronic random access memory. This particular circuit satisfies all five of the key.

3.4 CROSSBARS AND DEMULTIPLEXERS

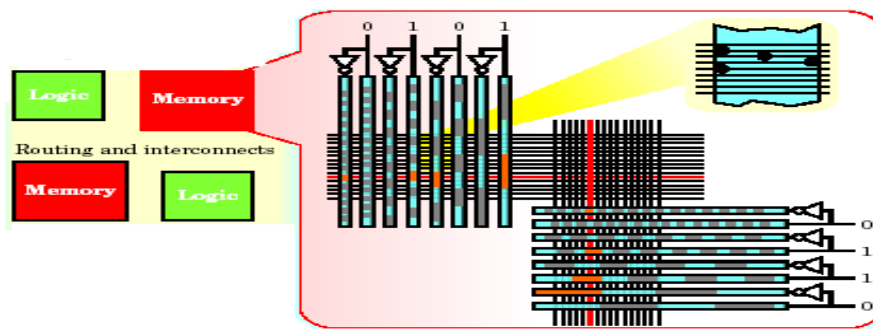


Figure 3.1 Molecular Memory

One of the most attractive architectures for designing molecular-electronics circuits for computational applications and interfacing them to the macroscopic world is the crossbar. The general concept is shown on the left, where a sort of patchwork quilt of logic, memory, and signal routing circuits is laid out. The simplest of these circuits—and one that has been experimentally demonstrated—is a memory circuit.

The memory, shown on the right, consists of two major components. The central crossbar—the crossing of 16 vertical and 16 horizontal black wires—constitutes a 256-bit memory circuit. Bitable molecular switches are sandwiched at the crossings of the densely patterned Nan wires, and each junction can store a single bit. Each set of the larger blue wires is arranged into what is called a binary tree multiplexer. The multiplexers here adopt some interesting architectural variations that allow them to bridge from the micron or sub micron scale of the blue wires to the nanometer scale of the black wires. Each multiplexer consists of four sets of complementary wire pairs, designed to address 24 nano wires. The scaling is logarithmic: 210 nanowires, for example, would require only 10 wirehairs for each multiplexer. One wire within each pair has an inverted input; a “0” input, for example, sends one wire low and its complement high. Along each blue wire is a series of rectifying connections (gray bars) to the Nan wires; each pair of wires has a complementary arrangement of connections. When a given address (0110, for example) is applied, the multiplexer acts as a four-input AND gate so that only when all four inputs are “high” does a given Nan wire go high. The orange bars indicate how one wire (red) is selected by each multiplexer. At

the upper right is shown more detail for a multiplexer wire that selects a pattern of four connects followed by four opens. Note that the separation between the individual contacts is much larger than the pitch of the nano wires; that larger separation greatly reduces the fabrication demands. Note also that the frequencies of the patterns of connections are important, but not the absolute registry: Each nano wire is uniquely addressable, but the mapping of addresses to nanowires is not important. Those two characteristics allow the architecture to bridge the micron or submicron length scales of lithography to the nanometer length scales of molecular electronics and chemical assembly.

3.5 MOLECULAR ELECTRONICS DEVICES

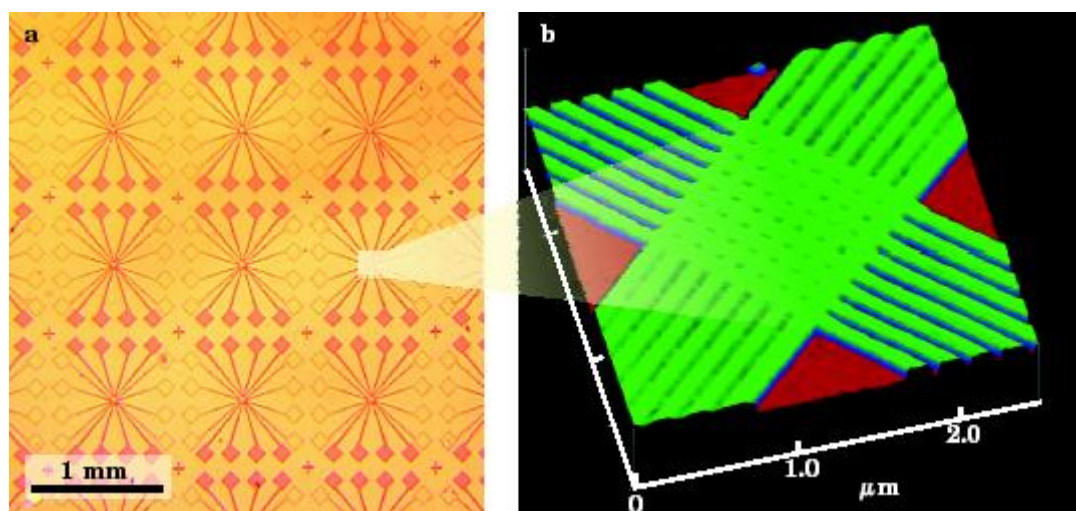


Figure 3.2 Molecular Electronic Circuits

<p>(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.</p>	<p>(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 bitable relaxants.</p>
---	--

CHAPTER 4

THE FUTURE OF MOLECULAR ELECTRONICS

4.1 FUTURE OF MOLECULAR ELECTRONICS

The fundamental challenges of realizing a true molecular electronics technology are daunting. Controlled fabrication to within specified tolerances—and its experimental verification—is a particular problem. Self-assembly schemes based on molecular recognition will be crucial for that task. Fully reproducible measurements of junction conductance are just beginning in labs at Cornell, Harvard, Delft, Purdue, and Karlsruhe Universities and at the Naval Research Laboratory and other centers. There is a real need for robust modeling methods to bridge the gap between the synthesis and understanding of molecules in solution and the performance of solid-state molecular devices. Additional challenges involve finding fabrication approaches that can couple the densities achievable through lithography with those achievable through molecular assembly. Controlling the properties of molecule–electrode interfaces and constructing molecular electronic devices that can exhibit signal gain are also problems.

Rapid progress is being made to address these challenges. Voltage-gated, single-molecule devices may emerge as the high-resolution spectroscopy tool that will eventually link experiment and theory. Binary tree multiplexers, such as the one presented in box 2, have the potential to *bridge* sub micron to nanometer length scales.¹⁵ Nanowire field-effect transistors have demonstrated gain, and so the challenge may be one of integration of multiple device types rather than discovery of new devices. But no molecular electronics logic or memory device has been tested against any of the “abilities”: reliability, temperature stability, and the like. Many of the technology goals of molecular electronics, such as the computational applications discussed in this article, should probably be viewed as drivers for steering the field forward and for defining the critical and rate limiting challenges that must be overcome. If, for example, someone does demonstrate a robust, energy-efficient computational platform based on molecular electronics, interfaced to the outside world, and fabricated at a device density between 10^{11} and 10^{12} cm^{−2}, we will have made so many fundamental advances that it would be surprising if some computational application is

even the most useful result of such work. Interfaces to bios stems, ultra dense single-molecule sensor arrays, and pathways toward molecular mechanical and Nan mechanical devices are among the likely beneficiaries of the successful development of molecular-electronic integrated circuitry.

4.2 NEW WAY OF MAKING MOLECULAR TRANSISTORS

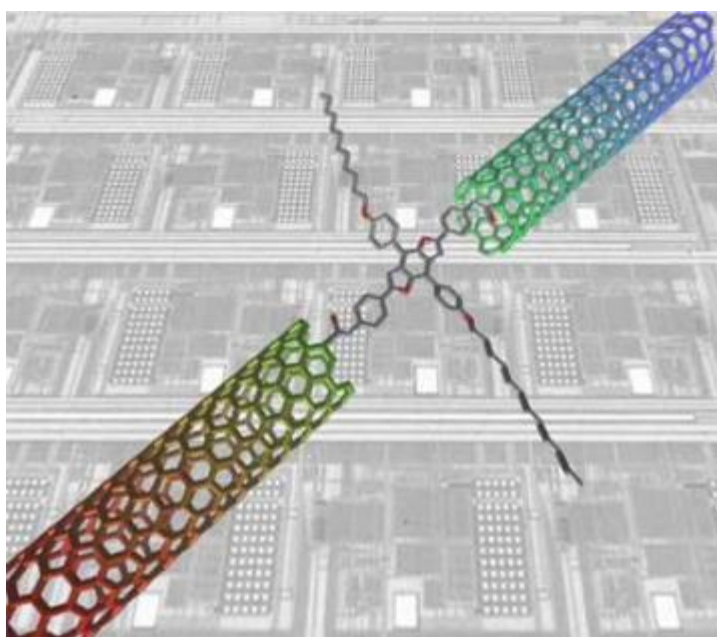


Figure 4.1 carbon nanotube

Scientists have long been intrigued by carbon nanotubes, tiny straws of pure carbon measuring less than a hair's width across. Successfully linking them in stable arrangements would allow for an impressive increase in both the speed and power of a variety of electronics. This new research at Columbia sets the stage for advances in real-time diagnosis and disease treatment, surgical robotics, and information storage and retrieval, potentially rendering room-sized supercomputers obsolete.

In the Jan. 20, 2006, issue of *Science*, Columbia scientists explain how they have developed a unique way to connect the ends of carbon nanotubes by forming robust molecular bridges between them. The Columbia team was able to combine the best qualities of carbon nanotubes and organic molecules in a single electronic switch,

the journal reported. Previously, researchers working in this area of nanotechnology have made transistors out of carbon nanotubes with switches connecting molecules to metal wire leads. This Columbia research illustrates a more elegant way of making molecular transistors, since the nanotube leads are already the same size as the molecules, and they are made of carbon, making it easier to connect them chemically.

This new method of wiring molecules into the gaps of single-walled carbon nanotubes employs oxidative cutting -- a lithographic technique that makes each cut-end of the nanotube more prone to molecular bonding. These new methods of constructing molecular bridges could one day revolutionize the size and scale of computer hardware " Molecular electronics has real-world relevance," says Colin Nuckolls, an associate professor of chemistry, and a co-author of the Science paper. "It opens the door to new types of ultrasmall switches and sensors. We are able to form a bridge, both literally and figuratively, by combining reaction chemistry with ultrafine lithography. "

The nanotubes themselves are long, thin cylinders of carbon unique for their size, shape and physical structure. They can be thought of as a sheet of graphite forming a hexagonal lattice of carbon, (see image) rolled into a tube, explains Columbia senior research scientist Shalom Wind, another co-author of the paper. They have been shown to possess remarkable mechanical and electronic properties, he added. Attaching molecular wires to single-walled nanotubes involves cutting a tube using nanolithography combined with a localized oxidation process that leaves a nanotube with two ends that are capped with carbon-based acid groups and separated by a molecule-sized gap. The nature of this work is also expected to keep alive "Moore's Law," the prediction made in 1965 by Intel co-founder Gordon Moore who predicted the number of transistors per square inch on integrated circuits would double every year. Moore said the trend would continue for the foreseeable future; but without an order-of-magnitude shift in the scale of computer circuitry -- a promise represented in Columbia's latest work--that prediction could hit a wall in the next decade, experts say.

CHAPTER 5

5. IMPORTANCE OF MOLECULAR ELECTONICS

5.1 ADVANTAGES

- Tiny
- Low power consumption
- Able to integrate large circuit
- Re-configurable

5.2DISADVANTAGES

- Controlled fabrication within specified tolerances.
- Hard experimental verification.

5.3 APPLICATIONS

- Sensors
- Displays, Energy transduction devices
- Smart Material, Molecular scale transistors
- Molecular Motors, Logic and memory devices

CHAPTER 6

CONCLUSION

Molecular electronics clearly has the advantage of **size**. The components of these circuits are molecules, so the circuit size would inherently range between 1 to 100 NM. Molecular systems, or systems based on small organic molecules, possess interesting and useful electronic properties. The rapidly developing area of organic -or plastic- electronics is based on these materials. The investigations of molecular systems that have been performed in the past have been strongly influenced.

Molecular electronics is reaching a stage of trustable and reproducible experiments. This has lead to a variety of physical and chemical phenomena recently observed for charge currents owing through molecular junctions, posing new challenges to theory. The potential application of molecular electronics has already attracted the interest of some large corporate.

REFERENCE

1. <http://technews.acm.org/articles/2002-4/0805m.html>
2. www.ieee.org
3. "An Overview of the First Half-Century of Molecular Electronics" by Noel S. Hush, *Ann. N.Y. Acad. Sci.* 1006: 1–20 (2003).
4. Reed, M. A. *et al. Proc. IEEE* (1999) **87**, p. 652, and references therein
5. https://books.google.co.in/books?hl=en&lr=&id=jjbjmvjCWHYC&oi=fnd&pg=PA41&dq=molecular+electronics&ots=pn1E_4jjm7&sig=kY5zTFsIAdBJQr_yaZ7Ihb r-BGQ#v=onepage&q=molecular%20electronics&f=false
6. <http://www.nature.com/nchem/focus/molecular-electronics/index.html>
7. <https://www.techopedia.com/definition/30814/molecular-electronics>
8. <https://www.britannica.com/topic/molecular-electronics>