

Molecular Electronics - Current Status and Future Prospects

M. A. Reed Yale University

Introduction

It is well recognized that conventional lithography-based VLSI technology is fast approaching the limits of its capabilities. The underlying issues responsible are numerous: ultra-thin gate oxides, short channel effects, doping fluctuations, and last but not least increasingly difficult and expensive lithography.[1] To surmount these problems, nanoscale quantum devices and circuits have been proposed for some time.[2,3] Over the last two decades, demonstrations of many of these technologies have been accomplished.[4] These include resonant tunneling diode (RTD) and resonant tunneling transistor (RTT) devices and circuits that promise compact multi-valued logic and memories; quantum dot and single electron devices; and others. Will these be viable technology alternatives for the post-VLSI era?

Present embodiments of these technologies demand tremendous control over the I(V) characteristics of the device, an undesirable property for downscaling. Dimensional control is a dominant obstacle, since nanodevices must operate by tunneling in some fashion. Since a barrier is needed for isolation in a 3-terminal device with gain, tunneling will be exponentially sensitive to atomic-layer fluctuations in barriers resulting in device-specific variations that may be unacceptable for large-scale integration. A related problem is that devices using discrete electron charging (single-electron transistors) only work at reduced temperatures. Robust room temperature operation with leakage requirements similar to VLSI requirements requires junctions smaller than 1 nm, which will thus suffer severe tunneling fluctuations. Last but clearly not least is that these embodiments do not critically address the major limiting factors of a 2D lithography-based technology: accessible parallel fabrication, interconnection density, and alignment. Any successful new technology must (1) solve

the interconnect problem, (2) use self-aligned fabrication, and (3) operate at room temperature and at the atomic level. The last point is because scaling any technology to the 10 nm level may not be cost-effective, as the performance increase is marginal compared to the development costs. An atomic- or molecular-scale technology may be the only approach worth the investment.

Recently, molecular electronics-based computation has attracted attention, because it addresses the ultimate in a dimensionally scaled system: ultra-dense and molecular-scale.[5,6] The significant scaling factor gained from molecular-scale devices implies eye-opening comparisons: a contemporary computer utilizes $\sim 10^{10}$ silicon-based devices, whereas one could prepare $\sim 10^{23}$ devices in a single beaker using routine chemical syntheses. An additional driving factor is the potential to utilize thermodynamically-driven directed self-assembly of components [7] such as chemically synthesized interconnects, active devices, and circuits. This is a novel technological approach for post-VLSI electronic systems, and can conceivably lead to a new era in ultra-dense electronic systems. This approach for spontaneously assembling atomic scale electronics attacks the interconnection and critical dimension control problems in one step, and is implicitly atomic scale. Concurrently the approach utilizes inherently self-aligned batch processing techniques that address the fabrication limitations of conventional VLSI.

Molecular (i.e., organic) materials for electronic and optoelectronic applications have been realized for quite some time. In addition to uses such as liquid crystal displays, devices such light emitting diodes, lasers, transistors, and sensors have been demonstrated.[5] The distinction between these (essentially "bulk") applications and molecular scale electronics is not just one of size, but of concept: the design of a molecule that itself is the active element.

Molecules were proposed as active electronic devices as early as 1973, when Aviram and Ratner[8] proposed that unimolecular rectification, or asymmetrical electrical conduction, should occur through the molecular orbitals of a single D- σ -A molecule by "through-bond tunneling". Here D is an electron donor with low ionization potential, A is an electron acceptor with high electron affinity, and σ is a covalent "bridge". The excited zwitterionic state D⁺- σ -A⁻ would be relatively accessible from the ground neutral state D- σ -A, while the opposite zwitterion D⁻- σ -A⁺ would lie several eV higher and be inaccessible. In solid state language, the system is an asymmetric resonant tunneling structure. Indeed, molecular systems have good analogies to solid state systems. Instead of the Fermi levels of the solid state, one deals with the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of molecules. Instead of metal and interconnects and degenerate contacts, one uses conjugated linear polymeric systems. Instead of "doping" to modify Fermi levels, one modifies the electron affinity and ionization potential of molecules by the chemical substitution. And by designing in the molecular orbitals, one has the equivalent of bandgap engineering.[4]

For molecular-scale electronics to come of age, fabrication and measurement techniques had to reach the atomic scale. The advent of atomic imaging techniques, such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM), have given us an atomic view of molecular placement, fabrication, and self-assembly. Nanofabrication techniques have created interconnects small enough to reliably contact molecules. A better understanding of electronic transport at the atomic level has developed over the last decade, and theoretical models of conduction through such systems are beginning to develop. All these advances have led to the first electrical measurements of molecular systems. Among these are conductivity measurements of molecules by STM [9], the first measurement of electronic conduction through a single "molecular wire" [10], and the first molecular diodes [11,12]. This paper reviews some of the initial work in this new, exciting field.

Introduction to transport in molecules

It is well-documented that bulk conjugated organic materials can be semiconducting, or conducting, when doped.[13] However, the measurements of through-

molecule long distance electron transfer are now just emerging. Candidates for molecular wires and switches include polyporphyrins, polyphenylenes, polythiophenes, and other planar organic polymers with extended π -conjugation; i.e., electron delocalization along the length of the molecule, which can be verified by optical measurements. A review of the synthesis of conjugated oligomers can be found elsewhere, [5,14] as well as a general review of candidate molecular conductors. [6,15,16,17] Examples of some of these oligomers are shown in Figure 1, which have a high degree of purity using a divergent-convergent method [18,19], a vastly more efficient and rapid process that produces monodisperse, stable, and soluble conjugated oligomers.

The study of electronic conduction in molecular systems is just now being developed, with comparison to the first experiments. The theoretical approaches to understand these mechanisms can be found elsewhere [6], but can be summarized into five different regimes:

1. Coherent electron motion: nonresonant. The most common situation for long range electron transfer reactions, and should hold for the case where the Fermi level of the contacts is in the middle of the HOMO/LUMO gap. In this case, the conductivity should exponentially decrease with length.
2. Coherent electron motion: resonant. In this case, conductance is dominated by the contact scattering, is independent of length, and increases with the number of modes. The low temperature conductance of carbon nanotubes appears to be in this regime.
3. Incoherent transfer: Ohmic behavior. If the wire is allowed to couple to other modes, such as in the environment, then the transport can become familiar with the conductivity dependent on inverse length. For long chains, this may well be more efficient than exponential nonresonant transport.
4. Quasiparticle formation & diffusion: For degenerate electronic ground states (such as polyacetylene), the carriers can be charged solitons, corresponding to a structural defect with an extra electron sitting on a free radical site (a "polaron"). In non-degenerate conductors (such as poly p-phenylene), two carriers trap near each other associated with a structural defect, giving rise to the so-called "bipolaron". Both mechanisms are postulated to be active in nonrigid polymers.
5. Gated electron transfer: Unlike solid state analogies,

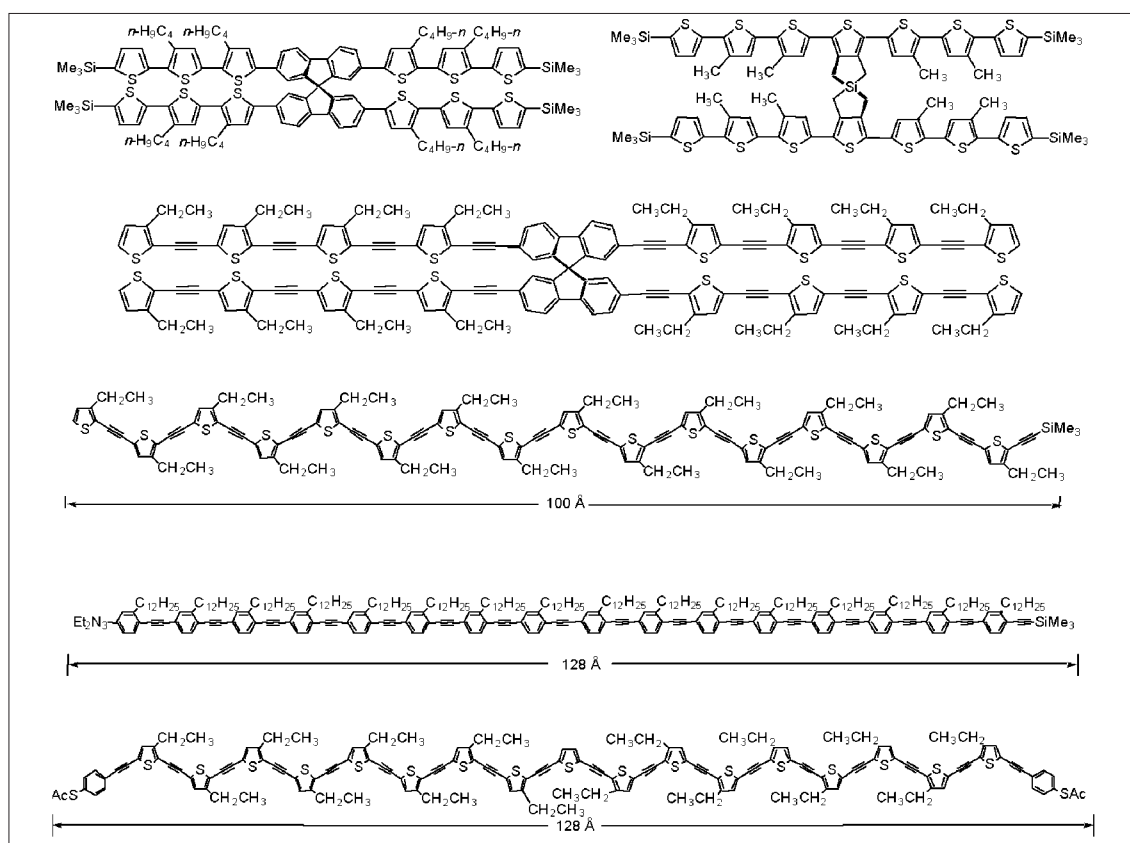


Figure 1. A variety of molecular conductors. The top three are conductive oligomers connected to an orthogonally-fused crossbar switch; the bottom two are long rigid-rod conjugated oligomers. Note the thiol termini on the bottom structure.

molecular structures show different transfer rates dependent on geometrical modification. Transfer processes through molecules capable of undergoing dynamical stereochemical change, similar to ion channels in biological systems, might be a potentially useful molecular electronic gating mechanism.

Over the last two decades, scores of candidate molecules that might selectively enhance one of the above mechanisms have been synthesized; and numerous experiments to attempt to deduce the dominant transport mechanisms have been done. Only recently has advanced nanoscale fabrication and characterization allowed the clear elucidation of these experiments.

A very interesting subfield of molecular electronics has been the use of rigid-carbon structures; i.e., C_{60} and carbon nanotubes. Although distinctly different from the types of molecules discussed previously since they do not have the desirable synthetic and functionalization properties that address the fabrication issues discussed previously, they none the less have quite interesting properties. Long coherence lengths and discrete electron states have been observed in single-wall nanotubes [20], and C_{60} [6,21] has even been

used as an electromechanical amplifier. These structures may well become the best molecular-scale wires and interconnects, and development of this field will critically depend on the development of controlled synthesis and manipulation techniques.

Self-assembled conjugated molecules

The challenge that has stymied the entire field for more than 2 decades has been the elementary task of "soldering" one of these electrically active candidate molecules between contacts. With the development of atomic imaging, one can now imagine using STM or AFM tips to maneuver, by brute force, the molecules into the correct position. A much more attractive alternative is the spontaneous self-absorption of the molecular species between the contacts. Over the last decade, the ability to form very well defined self-assembled monolayers (SAMs) of oligomers on metal has been demonstrated.[22] The most widely studied system has been the Au-SR system (R=alkyl), which forms very well ordered single monolayers with a very aggressive $\sim 2\text{eV}$ bond. In fact, the bonding strength is so large that there is indication that the SAM actually "anneals out" defects.

Functional terminal moieties such as thiols now provide the key to self-assembled structures. By synthesizing these onto the oligomer endgroups[23,24] such as the bottom oligomer example in Figure 1, we have a self-absorbing and orienting species (the thioacetyl end groups (SAC = SCOCH_3) serve as a protected self-assembled chemisorbed termini with in situ generation of the free thiol). This allows us to investigate conduction through conjugated molecules which are end-bound onto surfaces, or placed between proximal probes (e.g., for gold probes one uses thiol-end groups). In the last few years, a variety of metal (or semiconductor) surface / functional endgroup combinations have been investigated, giving design flexibility in both synthetic design and multi-terminal interconnect orientation.[7] This technique has yielded the first electrical measurements of molecular systems.

Conductivity measurements of self-assembled molecular systems

The measurement of charge transport in single organic molecules, and the determination of their conductance, has been a long sought goal. Such measurements are experimentally challenging and intriguing since one can test the validity of transport approximations at the molecular level. A conceptually simple configuration would be to connect a single molecule between metallic contacts. Such a metal-molecule-metal configuration would present the molecular embodiment of a system analogous to a quantum dot,[25-28] with the potential barriers of the semiconductor system replaced by the contact barrier of the molecule/metal interface. Although making nanofabricated planar contacts at the molecular scale is challenging, it has been done and candidate molecular conductors have been absorbed into the gaps.[29] An absence of observable conductivity in these systems may be due to inefficient electron transfer, undesirably large contact potentials, conjugation-breaking due to substrate interactions, or unfavorable absorption configurations. Thus, a number of alternative approaches have been attempted and realized.

The first obvious approach is to use STM techniques to locate and locally measure candidate oligomers absorbed on a metallic surface. However, the oligomers will not preferentially be near surface-normal in isolation. By using an alkanethiol (i.e., inert non-conductive) SAM as an inert host matrix, single conjugated molecules have been inserted randomly at defect sites and imaged[9] (Figure 2). It was

observed that the molecules had a significantly higher conductivity than the alkanethiol background; however these experiments could not give the absolute value of the conductivity due to the involvement of a tunneling gap between the STM tip and the molecule. One variant of this approach was to use Au nanoclusters onto a doubly-

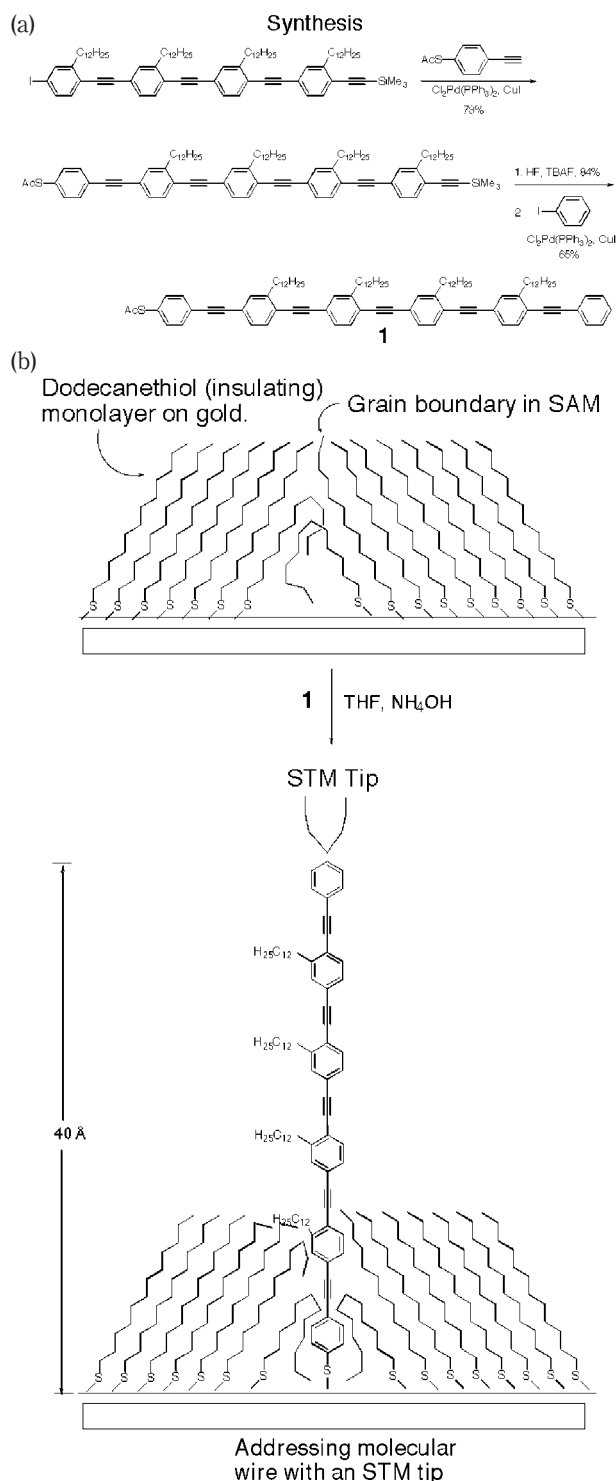


Figure 2. Schematic representation of the STM experiments to observe enhanced conductivity in π -conjugated molecular wires. The candidate wires (a) are absorbed into the grain boundaries of an alkanethiol host matrix (b)

functionalized oligomer [30,31] and by STM measurement deduce the molecule conductivity, although the uncertainty in cluster size resulted in large error bars.

The ideal embodiment is to create statically stable contacts, while concurrently restricting the number of active molecules to as few as one. This has been realized[10] (using benzene-1,4-dithiolate connected between stable proximal metallic gold contacts) using a mechanically controllable break junction (MCB) [32,33] (Figure 3). In this approach, a notched metal wire is glued onto a flexible substrate; and is fractured by bending the substrate, after which an adjustable tunneling gap can be established. A large reduction factor between the piezo elongation and the electrode separation ensures an inherently stable contact or tunnel junction. The wire contacts are atomically sharp when broken, as demonstrated in the conductance quantization. The deposition onto the contacts resulted in formation of a SAM on the gold electrodes nearly perpendicular to the surface.[34]

Current-voltage $I(V)$ and conductance $G(V)$ measurements showed reproducible characteristic features of stepped $G(V)$; the first step of $22.4 \pm 0.3 \text{ M}\Omega$. This is compared to a resistance of $\sim 9 \text{ M}\Omega$ and $18 \pm 12 \text{ M}\Omega$ deduced from the Au nanocluster experiments.[30,31] An interpretation of the observed $\sim 0.7 \text{ V}$ gap is due to the mismatch between the contact Fermi level and the LUMO (lowest unoccupied molecular orbital). Preliminary

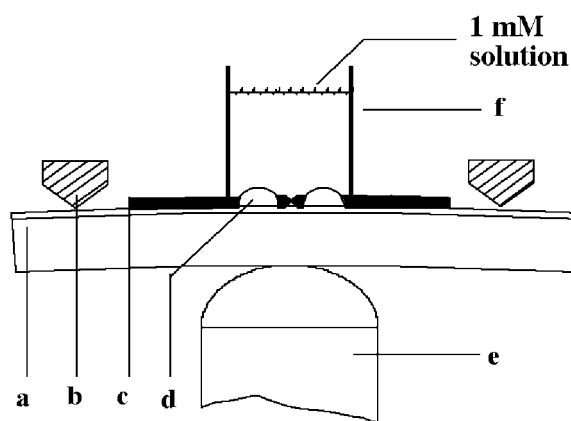


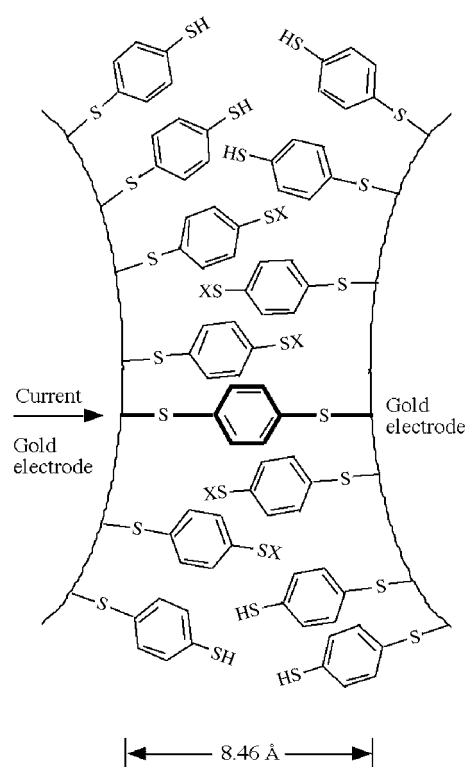
Figure 3. (above) A schematic of the MCB junction with (a) the bending beam, (b) the counter supports, (c) the notched gold wire, (d) the glue contacts, (e) the piezoelement, and (f) the glass tube containing the solution. (right) A schematic of a benzene-1,4-dithiolate SAM between proximal gold electrodes formed in a MCB. The thiolate is normally H-terminated after deposition; endgroups denoted as X can be either H or Au, with the Au potentially arising from a previous contact/retraction event.

calculations using this interpretation give similar characteristics to the experimentally observed data.[35]

Direct contacting to organic thin films has been done. However, multilayers of the molecular wires and micron scale area of the devices containing a large number of molecules have been used, which complicates the analysis of the transport mechanism of single molecules. Experiments with an evaporated-metal-top-contact/molecules/metallic-bottom-contact configuration, which has ten of thousands of parallel active molecules, have been demonstrated.[36] One experiment on an organic system [37] reported evidence for Coulomb charging. Direct contacting to and electrical measurements of a single monolayer of a small number of molecules are needed for accurate spectroscopy.

A novel fabrication technique has been reported to directly measure the conduction through a small number of organic molecules.[12] These devices, called "nanopores", consist of a self-assembled monolayer of conjugated molecular wires sandwiched between top and bottom metallic contacts. The employment of nano-scale device size insures that the adsorbed organic layer is highly ordered and defect free. A schematic of the device is shown in Figure 4. This technique gives a yield of about 80% working and stable devices.

Prominent rectifying behavior is observed: the current at 1V bias is about 500 times higher than the current at -1 V



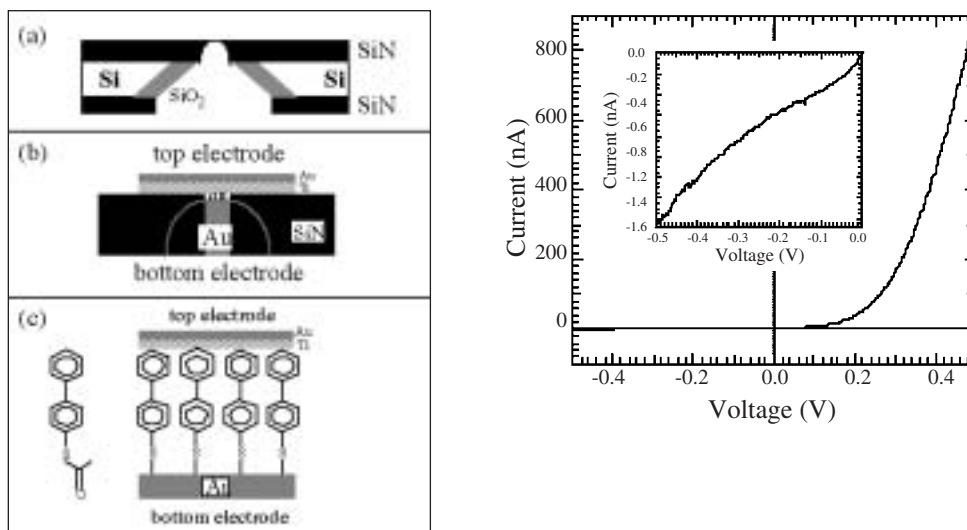


Figure 4. (left) Fabrication of nanopores. (a) Cross section of a silicon wafer showing the pore etched in a suspended SiN membrane; diameter about 300 Å. (b) Au-Ti top / SAM / Au bottom structure. (c) Specific SAM (4-thioacetylphenyl) and structure schematic. (right) Diode-like I-V characteristics at room temperature. Magnified view of the negative bias part in the inset.

bias. This is distinctly different from the Aviram-Ratner unimolecular rectifier [8] (rectification due to an asymmetric ground-state / excited state zwitterion) in which experimental results in a hexadecylquinolinium tricyanoquinodimethanide Langmuir-Blodgett film have recently been reported.[11] In the present case, the asymmetry is simply produced by the different contact barriers, loosely analogous to Schottky barriers. While the I-V curve at negative bias is rather linear [37], the I-V curve at positive bias displays exponential behavior, with $\ln(I) \propto 1/T$ and the slope is a function of the bias voltage. Using standard thermal emission theory, a value of 0.26 eV for the direct metal-molecule barrier is found. This technique lends itself to rapid synthetic and metallic variation, and is expected to be a workhorse in uncovering a wealth of metal-molecule transport characteristics previously inaccessible by other techniques.

Active Molecular Devices

One of the most intriguing aspects of this field is to reproduce the ability to "bandgap engineer" (as is commonly done in the solid state) at the molecular level. Although the field is just at the stage of understanding Ohmic contacts and Schottky barriers, the first attempts at designing active devices utilizing molecular orbital engineering have been done. Here we report the observation of large reversible switching behavior in an electronic device that utilizes molecules as the active component.

The nanostructure utilized the device structure summarized in Figure 4. The molecule used was 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate (Figure 5(a), compound **1c**). This compound was synthesized starting with 0.5 mM 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-(thioacetyl)benzene (**1a**) [39], the thioacetyl groups were selectively hydrolyzed with ammonium hydroxide (concentrated aqueous 14.8M NH_4OH , 5 μL per mg of **1a**) in tetrahydrofuran (THF) to yield the free thiol, 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiol (**1b**), which then forms the thiolate (**1c**) upon exposure to Au after 48 hours [40] under an inert atmosphere of Ar.

A series of control experiments were performed with alkanethiol-derived SAMs, silicon nitride membranes without pores, and membranes with pores but without molecules. Both the Au-alkanethiolate-Au junctions and the Au-silicon nitride membrane-Au junctions showed current levels at the noise limit of the apparatus (< 1 pA) for both bias polarities at both room and low temperatures. The Au-Au junctions gave ohmic I(V) characteristics with very low resistances. A device containing a SAM of conjugated molecules similar to **1c** but not bearing the nitroamine functionalities was fabricated and measured in nearly identical conditions [41] and did not exhibit any NDR behavior.

Typical I(V) characteristics of a Au-(**1c**)-Au device at 60 K are shown in Figure 5(b). Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact and

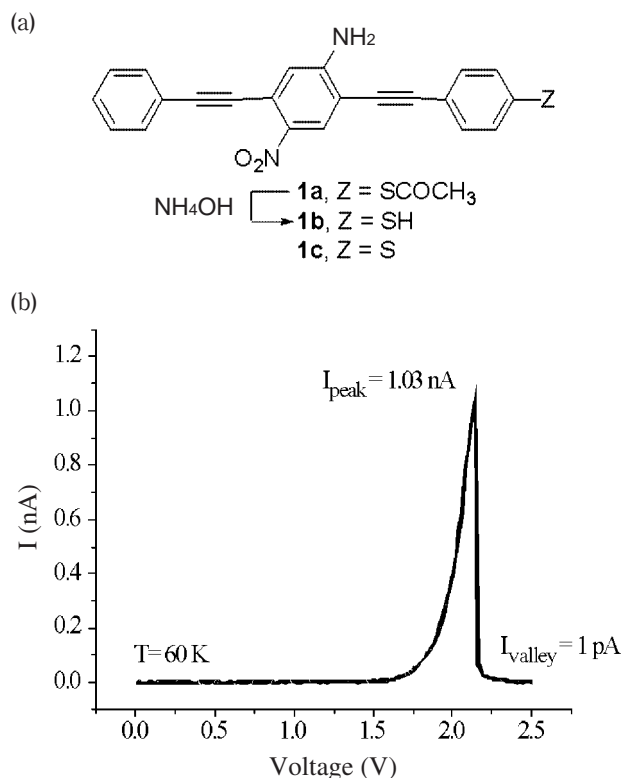


Fig. 5. (a) The active molecular compound **1c**, and its precursors, the free thiol **1b** and the thiol-protected system **1a**. (b) I(V) characteristics of a Au-(2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate)-Au device at 60 K. The peak current density is $\sim 50 \text{ A/cm}^2$, the NDR is $\sim -400 \mu\Omega\text{-cm}^2$, and the PVR is 1030:1.

electron injection from the evaporated contact. The peak current density for this device was $> 53 \text{ A/cm}^2$, the NDR is $< -380 \mu\Omega\text{cm}^2$, and the PVR is 1030:1. Unlike previous devices that also used molecules to form the active region [42], this device exhibits a robust and large NDR. The performance exceeds that observed in typical solid state quantum well resonant tunneling heterostructures [43-46]. In addition to the obvious size advantages for scaling, the intrinsic device characteristics (that is, the valley current shutoff) may be superior to that of solid state devices. The intrinsic PVR of the molecule may be considerably greater than that reported here, because the valley currents observed (on the order of picoamperes) are comparable to typical leakage currents in the silicon nitride.

A candidate mechanism for the NDR is a two-step reduction process that modifies charge transport through the molecule, as illustrated in Figure 6. As the voltage is increased, the molecule initially undergoes a one-electron reduction, thereby supplying a charge carrier for electron flow through the system (although the nitro moiety is the most electron-withdrawing group in the molecule, the charge is likely dispersed throughout the entire molecule). A further increase in voltage causes a second-electron reduction with subsequent blocking of the current. The width of the I(V) peak ($\sim 0.7 \text{ V}$) correlates well with the difference between the one-electron and two-electron peak

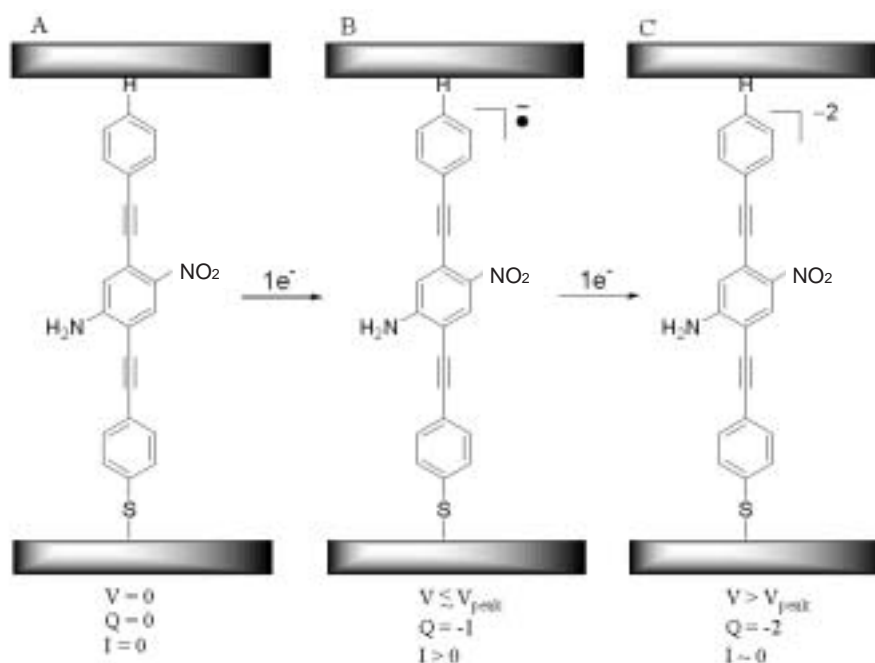


Fig. 6. Potential mechanism for the NDR effect. As voltage is applied, the molecules in the SAM (A) undergo a one-electron reduction to form the radical anion (B) that provides a conductive state. Further increase of the voltage causes another one-electron reduction to form the dianion, insulating state (C).

reduction potentials ($E_{p2}-E_{p1}=\Delta E_p = 0.63$ V and 0.68 V for 1 with $Z = \text{SCH}_3$ and $Z = \text{H}$, respectively) [47]. The NDR behavior is absent in the control molecule (no amine or nitro moieties)[41], and no electrochemical reduction peaks are observed over the corresponding voltage range. Theory to explain the temperature dependencies and future experimental work such as frequency and optical response should elucidate the transport mechanisms that would further permit engineering of device performance for room temperature operation. The NDR observation cannot be explained by the Coulomb blockade of interstitial metal particles because two-terminal localized state transport gives rise to current steps [48] and not switching behavior.

Conclusion

Discussed here are the basic concepts of self-assembled molecular-scale electronic devices. New fabrication techniques to study the transport mechanism of organic molecular wires, such as MCBs and nanoscale fabrication with special metal deposition techniques, are employed to provide metallic contacts to the self-assembled monolayer of a small number of conjugated molecular wires. We report the measurement of the conductivity of a single molecule, and the molecular equivalent of a RTD. These methods can be easily adapted to other molecular wire systems for determination of transport mechanism and band alignment. A clear and outstanding challenge is the synthesis and measurement of 3-terminal structures, and the determination of gain mechanisms in such structures.

I am indebted to the dedicated work of my students and postdocs C. Zhou, C. J. Muller, D. L. Lombardi, J. Chen, and fabrication support from J. Sleight and M. Deshpande. I am very grateful for the stimulating collaborations with J. M. Tour and D. L. Allara, and their respective research groups; and stimulating discussions with M. Ratner. I gratefully acknowledge DARPA for financial support under ONR grant N00014-95-1-1182.

References:

1. R. W. Keyes, *Science* **230**, 138 (1985); and *Sci. Amer.* June 1993, 70-78.
2. *Nanostructures and Mesoscopic Systems*, edited by W. P. Kirk and M. A. Reed (Academic Press, San Diego, 1992).
3. *Heterostructure and Quantum Devices*, volume editors N. G. Einspruch and W. R. Frensley, in the series *VLSI Electronics: Microstructure Science*, series editor N. G. Einspruch (Academic Press, San Diego, 1994).
4. *Quantum Semiconductor Structures*, C. Weisbuch and B. Vinter (Academic Press, San Diego, 1991).
5. *Molecular Electronics*, edited by J. Jortner and M. Ratner Blackwell Science, Oxford, United Kingdom, 1997).
6. *Molecular Electronics: Science and Technology*, edited by A. Aviram and M. Ratner, Annals of the New York Academy of Sciences, New York, 1998).
7. D. L. Allara et al. , in *Molecular Electronics: Science and Technology*, edited by A. Aviram and M. Ratner, Annals of the New York Academy of Sciences, New York, 1998), 349.
8. A. Aviram and M. A. Ratner, "Molecular Rectifiers", *Chem. Phys Lett.* **1974**, 29, 277.
9. L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, "Are Single Molecular Wires Conducting?", *Science* **1996**, 271, 1705-1706.
10. M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, *Science* **278**, 252 (1997).
11. R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, and G. J. Ashwell, "Unimolecular Electrical Rectification in Hexadecylquinolinium Tricyanoquinodimethanide", *J. Am. Chem. Soc.* **1997**, 119, 10455-10466.
12. C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones II and J. M. Tour, "Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures", *Appl. Phys. Lett.* **71**, 611 (1997).
13. T. A. Skotheim, Ed.; *Handbook of Conducting Polymers*, Dekker: New York, 1986.
14. Pearson, D. L.; Jones, L., II; Schumm, J. S.; Tour, J. M. "Molecular Scale Electronics. Syntheses and Testing", *Synth. Metals* **1997**, 84, 303-306.
15. For some theoretical considerations on molecular-scale wires, see: C. Joachim, and J. F. Vinuesa, *Europhys. Lett.* **1996**, 33, 635.
16. For some recent background work on the formation of molecular-based transporters and devices, see: M. D. Ward, *Chem. Ind.* 1996, 569.
17. Petty et al . (M. C. Petty, M. R. Bryce, and D. Bloor, D., Eds., *Introduction to Molecular Electronics*, Oxford Univ. Press: New York, 1995).
18. J. S. Schumm, D. L. Pearson, and J. M. Tour, "Iterative Divergent/Convergent Doubling Approach to Linear Conjugated Oligomers. A Rapid Route to a 128 Å Long Potential Molecular Wire", *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1360-1363.

19. D. L. Pearson, J. S. Schumm, and J. M. Tour, "Iterative Divergent/Convergent Approach to Conjugated Oligomers by a Doubling of Molecular Length at Each Iteration. A Rapid Route to Potential Molecular Wires", *Macromolecules* **1994**, *27*, 2348-2350.
20. Tans, S. J. et al., *Nature* **386**, 474 (1997).
21. Joachim, C. et al. 1995. Electronic transparency of a single C60 molecule. *Phys. Rev. Lett.* **74**: 2102-2105.
22. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Parikh, A.; Tao Y. T.; Nuzzo, R. G. "A Comparison of the Structures and Wetting Properties of Self-Assembled Monolayers of n-Alkanethiols on the Coinage Metal Surfaces Cu, Ag and Au," *J. Am. Chem. Soc.* 1991, *113*, 7152-7167.; Bain, C. D.; Evall, J.; Whitesides, G. M. "Formation of monolayers by the coadsorption of thiols on gold: variation in the head group, tail group, and solvent," *J. Am. Chem. Soc.* 1989, *111*, 7155-7165; Robertson, M. J.; Angelici, R. J. "Adsorption of Aryl and Alkyl Isocyanides on Powdered Gold," *Langmuir* 1994, *10*, 1488-1492; Henderson, J. I.; Feng, S.; Ferrence, G. M.; Bein, T.; Kubiak, C. P. "Self-assembled monolayers of dithiols, diisocyanides, and isocyanothiols on gold: 'Chemically sticky' surfaces for covalent attachment of metal clusters and studies of interfacial electron transfer," *Inorg. Chim. Acta* 1996, *242*, 115-124; Hickman, J. J.; Zou, C.; Offer, D.; Harvey, P. D.; Wrighton, M. S.; Laibinis, P. E.; Bain, C.D.; Whitesides, G. M. "Combining spontaneous molecular assembly with microfabrication to pattern surfaces: selective binding of isonitriles to platinum microwires and characterization by electrochemistry and surface spectroscopy," *J. Am. Chem. Soc.* 1989, *111*, 7271-7272; J. M. Tour, L. Jones II, D. L. Pearson, J. S. Lamba, T. P. Burgin, G. W. Whitesides, D. L. Allara, A. N. Parikh, and S. Atre, "Self-Assembled Monolayers and Multilayers of Conjugated Thiols, α , ω -Dithiols, and Thioacetyl-Containing Adsorbates. Understanding Attachments Between Potential Molecular Wires and Gold Surfaces", *J. Am. Chem. Soc.* **1995**, *117*, 9529-9534.
23. L. Jones II, J. S. Schumm, and J. M. Tour, "Rapid Solution and Solid Phase Syntheses of Oligo(1,4-phenylene-ethynylene)s With Thioester Termini: Molecular Scale Wires With Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support", *J. Org. Chem.* **1997**, *62*, 1388-1410.
24. D. L. Pearson and J. M. Tour, "Rapid Syntheses of Oligo(2,5-thiophene-ethynylene)s with Thioester Termini: Potential Molecular -Scale Wires With Alligator Clips", *J. Org. Chem.* **1997**, *62*, 1376-1387.
25. Reed, M.A. et al. 1988. Observation of discrete electronic states in a zero-dimensional semiconductor nanostructures. *Phys. Rev. Lett.* **60**: 535-538.
26. Kouwenhoven, L.P. et al. 1991. Single electron charging effects in semiconductor quantum dots. *Z. Phys. B* **85**: 367-373.
27. Tewordt, M. et al. 1992. Resonant tunneling in an AlGaAs/GaAs quantum dot as a function of magnetic field. *Phys. Rev. B* **46**: 3948-3952.
28. Grabert, H. et al. 1991. Single electron tunneling. Plenum, New York., and references therein.
29. D. L. Lombardi, Ph. D. thesis, Yale University, 1997.
30. Dorogi, M. et al. 1995. Room temperature Coulomb blockade from a self-assembled molecular nanostructure. *Phys. Rev. B* **52**: 9071-9077.
31. Andres, R.P. et al. 1996. Coulomb staircase at room temperature in a self-assembled molecular nanostructure. *Science* **272**: 1323-1325.
32. Muller, C.J. et al. 1992. Experimental observation of the transition from weak link to tunnel junction. *Physica C* **191**: 485-504.
33. Muller, C.J. et al. 1996. Quantization effects in the conductance of metallic contacts at room temperature. *Phys. rev. B* **53**: 1022-1025 and references therein.
34. Tour, J.M. et al. 1995. Self-assembled monolayers and multilayers of conjugated thiols, α , ω -dithiol, and thiolacetyl-containing adsorbates. understanding attachments between potential molecular wires and gold surfaces. *J. Am. Chem. Soc.* **117**: 9529.
35. Datta, S. unpublished.
36. Fischer, C.M. et al. 1995. Microstructured gold/Langmuir-Blodgett film/gold tunneling junctions. *Appl. Phys. Lett.* **66**: 3331-3333.
37. For negative bias (electrons injected from the Au bottom electrode into the conjugated molecules through the thiolates), plots of $\ln(I/V)$ vs $1/T$ fall on one line indicating hopping, and a similar analysis yields a hopping barrier of 0.19 eV. At present it is unclear whether the hopping is related to defects in the SAM or hopping between neighboring molecular wires.
38. Jones, L., II; Schumm, J. S.; Tour, J. M. "Rapid Solution and Solid Phase Syntheses of Oligo(1,4-phenylene-ethynylene)s With Thioester Termini: Molecular Scale Wires With Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support," *J. Org. Chem.* 1997, *62*, 1388-1410.
39. The starting compound (**1a**) was prepared by sequential Pd/Cu-catalyzed coupling of 2,5-dibromo-4-nitroacetanilide with phenylacetylene and 4-ethynyl(thioacetyl)benzene.
40. J. M. Tour et al., *J. Am. Chem. Soc.* **117**, 9529 (1995).

41. C. Zhou, thesis, Yale University (1999).
42. Weak room temperature NDR has been previously reported; M. A. Reed, *Proc. IEEE* **87**, 652 (1999).
43. J. H. Smet, T. P. E. Broekaert, and C. G. Fonstad, *J. Appl. Phys.* **71**, 2475 (1992)
44. J. R. Söderström, D. H. Chow, and T. C. McGill, *J. Appl. Phys.* **66**, 5106 (1989)
45. J. Day *et al.*, *J. Appl. Phys.* **73**, 1542 (1993).
46. H. H. Tsai *et al.*, *IEEE Elec. Dec. Lett.* **15**, 357 (1993).
47. The case where $Z = SH$ was avoided due to anomalies that could be caused through electrochemical disulfide formation and cleavage events.
48. M. R. Deshpande *et al.*, *Phys. Rev. Lett.* **76**, 1328 (1996).



Mark A. Reed

Mark Reed received his B.S. with Honors in Physics from Syracuse University in 1977, and continued there where he received his M.S. in Physics in 1979 and his Ph. D. degree in Solid State Physics in 1983. He then joined Texas Instruments as a Member of the Technical Staff in the Ultrasmall Electronics Branch, where he co-

founded the Nanoelectronics research program. In 1988 he was elected to Senior Member of the Technical Staff. In 1990 Mark left TI to join the faculty at Yale University where he holds a joint appointment as Professor in the Electrical Engineering and Applied Physics departments. Since 1995, he has been the Chairman of Electrical Engineering. His research activities have included the investigation of nanoscale and mesoscopic systems, tunneling and transport in heterojunction systems, artificially structured materials and devices, MEMS, nanotechnology, and molecular electronics. Mark is the author of more than 90 professional publications, has given four plenary and over 110 invited talks, and holds 15 U.S. and foreign patents on quantum effect, heterojunction, and molecular devices. His books credits include *Nanostructure Physics and Fabrication* (1989), *Nanostructures and Mesoscopic Systems* (1992), and *Nanostructured Systems* (in the series *Semiconductors and Semimetals*). He has chaired numerous international conferences and program committees, and is an associate editor for a number of technical journals (such as *Physical Review Letters* and *Physica E*). He has been elected to the Connecticut Academy of Science and Engineering, Who's Who in the World, and is a Senior Member of the IEEE. In October 1990 he was named by Fortune Magazine as one of America's most promising young scientists, and in 1994 won the Kilby Young Innovator Award. In 1997, he won the DARPA ULTRA Most Significant Achievement Award for his work in molecular electronics. In 1999, he was appointed to the Harold Hogkinson Chair of Engineering and Applied Science at Yale University.

(論文紹介)

Mark A. Reed 著

Molecular Electronics - Current Status and Future Prospects

米国DoDの将来予測では、21世紀の第一・四半期で最も目覚ましい技術革新は、情報技術、バイオテクノロジー、マイクロメカトロニクス分野で起きるであろうと考えられている。ナノテクノロジーが特に革新的とされる理由は、情報とバイオの共通領域で使用され、かつマイクロメカトロニクスの劇的な性能向上をもたらすと予測されるからである。すでに1分子の厚さを持つ素子などが発表され、この分野は急速に発展しつつある。この論文では、こうしたナノテクノロジー分野の一つの柱である分子エレクトロニクスの研究の現状と将来について述べられている。筆者は、半導体ナノ構造の分野においても優れた業績をあげた研究者であり、この論文は半導体技術者にとって分子エレクトロニクスの現状を知る格好なレビュー論文といえる。

序章では、現在の半導体ナノテクノロジーが抱える問題について、筆者の考えが述べられ、分子エレクトロニクスの魅力として、スケーリングファクタと自己組織的な形成技術といった基本概念が説明されている。また分子を能動素子に応用することが最近の研究の流れであること、半導体のアナロジーとしてドーピング技術が分子の化学的置換、バンドエンジニアリングが分子軌道デザインに置き換わることなどが述べられている。本文では、分子の電気伝導について、今まで提案されてきた幾つかのモデルが説明され、最新の実験技術が紹介されている。たとえば分子の自己組織的接合法として、チオールのような機能性末端をオリゴマーに付けて自己組織化可能な分子を作る方法などが紹介されている。さらに著者自身の研究でもある、金電極間にベンゼン1,4ジチオール分子を挟み込んだ構造やナノポーラスと呼ばれる金属電極間に挟まれた自己組織化単一分子膜(SAM)の電気伝導測定について述べられている。また最新の成果として、分子軌道エンジニアリングを施した分子による可逆スイッチを作製し、共鳴トンネルダイオードと等価な機能である負性抵抗特性(PV比1030、電流密度53A/cm²、@60K)が得られたことなどが述べられている。

(富士通株式会社 粟野祐二)