Molecular Electronics. Synthesis and Testing of Components

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Received April 13, 2000

ABSTRACT
Molecular electronics involves the use of single or small packets of molecules as the fundamental units for computing. While initial targets are the substitution of solid-state wires and devices with molecules, long-range goals involve the development of novel addressable electronic properties from molecules. A comparison of traditional solid-state devices to molecular systems is described. Issues of cost and ease of manufacture are outlined, along with the syntheses and testing of molecular wires and devices.

Introduction

In the past few years, a small interdisciplinary group of chemists, physicists, and engineers has performed a series of demonstrations showing that individual or small packets of molecules, mounted within addressable scaffolds, can conduct and switch electrical currents, and can retain electrical bits of information. Molecular electronics involves the replacement of a wire, transistor (the basic electronic device for both electronic logic and memory), or other basic solid-state (usually silicon) electronic element with one or a few molecules.[1] Each molecule is approximately one million times smaller in area than their present-day microelectronic counterparts. Although the strict terminology remains problematically dynamic, we maintain here that molecular electronics is not the use of films or crystals that contain many trillions of molecules per device; in such a large molecular embodiment, we prefer the previously suggested terminology of molecular materials for electronics.[1d] Nor is molecular electronics, in ultimate application, the use of molecules in solution where configuration to realistic electronic platforms is impossible. Molecular electronics is also distinctly different from DNA computing, which encodes and retrieves information based on the formation and cleavage of chemical bonds, a relatively slow process which requires

solution-based conditions.[2] Further, molecular electronics is quite different than the recently heralded quantum computing, which depends on quantum coherence states for computation.[3] Ultimately, molecular electronics could capitalize on the unique properties offered by molecules in order to generate novel, heretofore unrealized electronic devices, thereby making molecules the fundamental computational components by the end of the decade.

Comparison of Solid-State to Molecular Devices

How small and how dense can the circuits in electronic digital computers become? For the most part, the industry has even exceeded "Moore's law" predictions, wherein there is a doubling of devices per chip every 18–24 months. However, due to the inevitable roadblocks ensuing through traditional downsizing of silicon devices, alternate technologies must be considered. This is not simply an isolated view from a silicon industry outsider. The limits that will be realized in the next 5–10 years have recently been outlined by the silicon industry's ivory tower itself, Intel Corporation.[4] The roadblocks arise from fundamental physical constraints as well as monetary restrictions. The fundamental scientific barriers include oxide layers at the three-atom-thick level that are inadequately insulating, thereby resulting in charge leakage. Moreover, silicon no longer possesses its fundamental band structure when it is restricted to very small sizes. Molecules, on the other hand, have comparatively large energy level separations at room temperature and at the nanometer-size level due to their discrete orbital levels, making them independent of broad band properties. From the monetary standpoint, a current fabrication line costs $2.5 billion to construct, and that cost is projected to rise to $15 billion by the year 2010, and over $100 billion by 2015.[1a] These costs will exceed the means of even large industrial consortia. In essence, the cost arises because silicon device fabrication is a top-down approach: etching away at a silicon crystal to form micrometer-sized devices and circuitry, which are forced to become smaller and denser each year. Furthermore, maintaining the chip manufacturing process often requires the construction of new fabrication lines for each generation of chips. By contrast, molecular construction is a bottom-up technology that uses atoms to build nanometer-sized molecules[5] that could further self-assemble into a desired computational circuitry. This bottom-up approach gives rise to the prospect of manufacturing electronic circuits in rapid, cost-efficient, flow-through processes. These processes could be analogous to the production of photographic film, with overall enormous cost savings over traditional microchip fabrication.

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As a further comparison, in the past 40 years of device manufacturing, there have been nearly 10^{20} transistors fabricated from silicon. However, consider this: there are 10^{21} water molecules in just one drop of water. As a direct density comparison, the 10^7-10^8 devices on a Pentium chip occupy approximately 1 cm² of chip real estate. Using typical-sized organic molecules that have three branches, much like the source, drain, and gate of a transistor, spanning 1–3 nm, one could fit approximately 10^{14} molecules in 1 cm².

There are, of course, numerous significant problems to be solved before a molecular computer could be realized. Each one of those 10^8 transistors in the Pentium is addressable and connected to a power supply. Molecules, though easier to synthesize in large quantities, can be more difficult to arrange on a surface or in a three-dimensional array. It is equally difficult to ensure that the molecules stay in place. If one must sacrifice the density advantages of molecules in order to individually address each one with a micrometer-sized lithographically formed address line or other macroscopic tip, then there is no size advantage to be gained from molecular-based systems. Equally important is the consideration of heat dissipation. A Pentium chip, with 10^7-10^8 transistors operating at the present nanosecond rate, can emit 40 W of heat (100 W in extreme cases)—similar in radiant heat to a home range-top cooking surface. Since molecular computing could take advantage of a million-fold increase in circuit density, an enormous cooling fan would be needed to prevent the ensuing meltdown! Hence, the heat dissipation concerns and the ball-and-chain of lithographically addressing molecular devices remains a major obstacle that provides real challenges for molecular electronic computing research. New design and operating paradigms are likely to be needed for molecular electronic computers. Stepping out of the silicon box, or off the silicon chip, is required to grapple with the fundamental challenges of molecular electronic computer design.

Chemistry alone is not the answer. While we concede that logic fundamentals predate electronic wiring and circuitry, insertion of molecular electronics into viable and competitive computation or memory architectures is difficult to envision without first interfacing them to present silicon input/output (I/O) platforms.[6] Traditionally, chemists have proposed using "soups" of molecules moving randomly in beakers for "computing systems" without regard to realistic interface strategies. More specifically, designs in molecular computing should even have I/O signal homogeneity (e.g., voltage in and voltage out) and magnitudes within devices so that the second device can be driven with the same signal type and relative signal size that operated the first device; these are requirements in almost any architecture that can be envisioned. Putting an electron into the system and getting a photon out may provide a fine laboratory experiment; however, construction of a device array based upon this typical chemical experiment is wholly impractical.
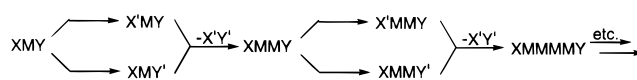

FIGURE 1. Schematic outline of the iterative divergent/convergent approach to molecular length doubling.

Though none of the current molecular electronic computer design challenges have been tackled with any degree of satisfaction, presented here are a few of the achievements and architectural scenarios being considered in order to construct molecular wires and devices, arrange large arrays of molecules, deal with the potential heat dissipation problems, and take advantage of the number of devices available from synthetic chemistry.

Syntheses of Molecular Wires

Solution-Phase Syntheses of Molecular Wires. There has been considerable recent effort to prepare large conjugated molecules of precise length and constitution.[5] The iterative divergent/convergent approach that we followed is outlined in Figure 1.[7] The advantages of this approach are that the molecular length grows rapidly, at a rate of 2^n, where n is the number of iterations, and incomplete reactions yield unreacted material that is half the size of the desired compound. Thus, purification at each step is far simpler since separation involves, for example, an octamer from a 16-mer. This iterative divergent/convergent approach is therefore particularly attractive.

Specific illustrations of this approach are outlined in Figures 2 and 3.[7,8] More recently, we developed an approach to grow the molecular systems from both ends after each iteration (Figure 4).[9] This proved to be a very simple route for the rapid construction of these oligomers in solution using an in situ deprotection and coupling. In this way, the isolation of oxidatively unstable α,ω-bis-(terminal alkyne) intermediates could be avoided.

Attachment of molecular alligator clips to one or both sides of related molecules has been demonstrated (Figure 5).[7,8] We have utilized several types of molecular alligator clips in a quest to minimize the contact resistance with metallic probes.[10] These include sulfur, selenium, tellurium, and isonitrile end groups. We have studied these both experimentally and theoretically.[10,11] There remains a need to develop molecular alligator clips that minimize the impedance mismatches between molecular structures and metal surfaces, thereby affording a better energy match between the lowest unoccupied molecular orbital (LUMO) of the molecule and the Fermi level of the metallic contact.

Solid-Supported Syntheses of Molecular Wires. We have extended these synthetic molecular doubling approaches to solid-phase methods for streamlining the syntheses and making them suitable for automation. For example, the 16-mer oligo(phenylene ethynylene) has been prepared starting from Merrifield's resin as the solid support phase (Figure 6).[8] More recently, we used the solid support methodology to grow the oligomers from both ends, a process that could not be carried out in solution
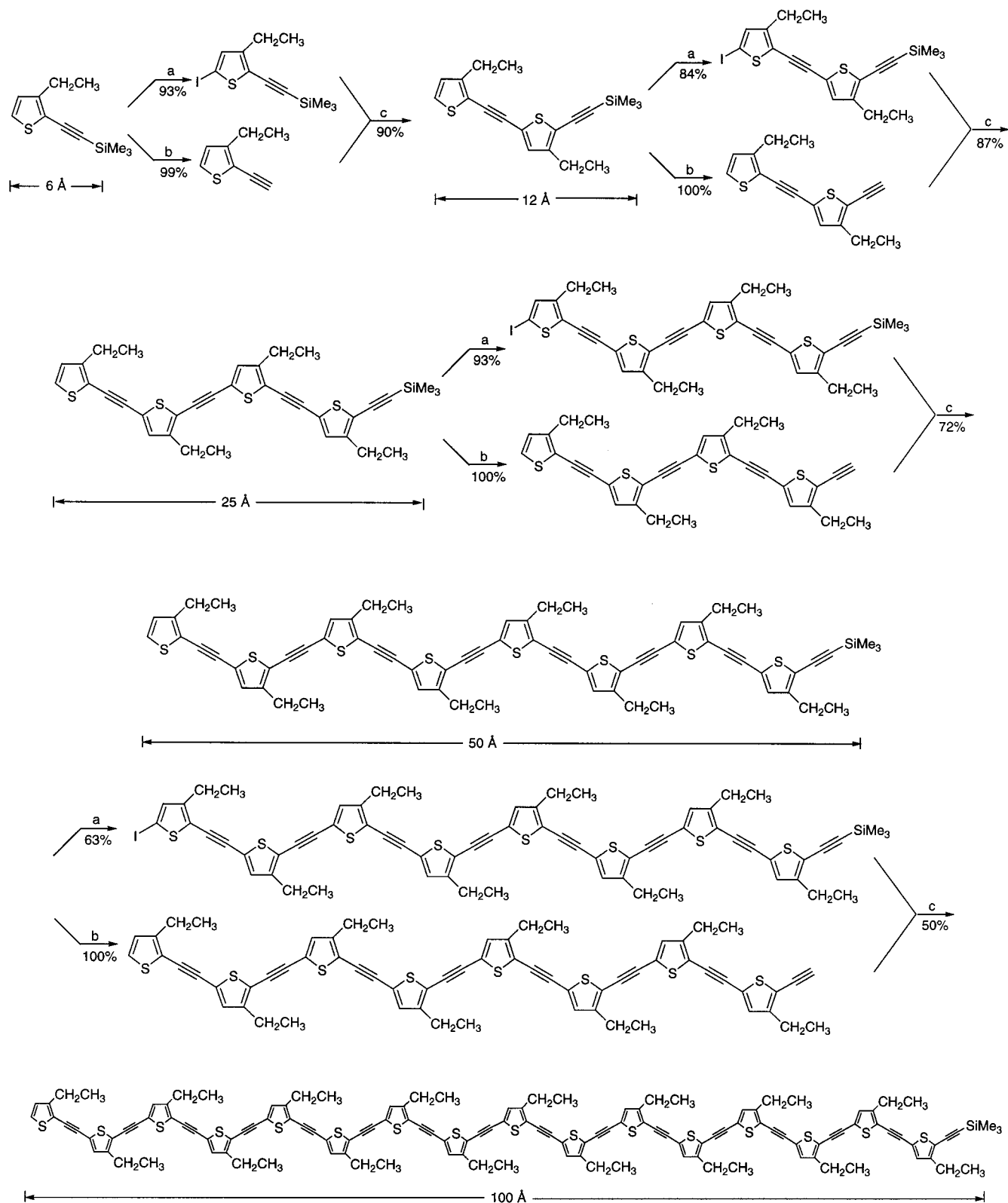
FIGURE 2. Solution-phase synthesis of the oligo(thiophene ethynylene)s by the divergent/convergent doubling approach. Reagents: (a) LDA, Et₂O, −78 °C to 0 °C then I₂, −78 °C; (b) K₂CO₃, MeOH, 23 °C; (c) Cl₂Pd(PPh₃)₂ (2 mol %), CuI (1.5 mol %), THF, *i*-Pr₂NH, 23 °C.

due to polymerization of the compounds (Figure 7). This gave a route to molecular length tripling at each iteration, and the homooligomers proved an easy target for the process (Figure 8).[12] Additionally, alternating block co-oligomers could be rapidly prepared using this methodol-

ogy (Figure 9).[13] This block cooligomer route could be particularly attractive for preparing devices based upon linear systems since all device structures must have some element of heterogeneity to be useful in computational applications.
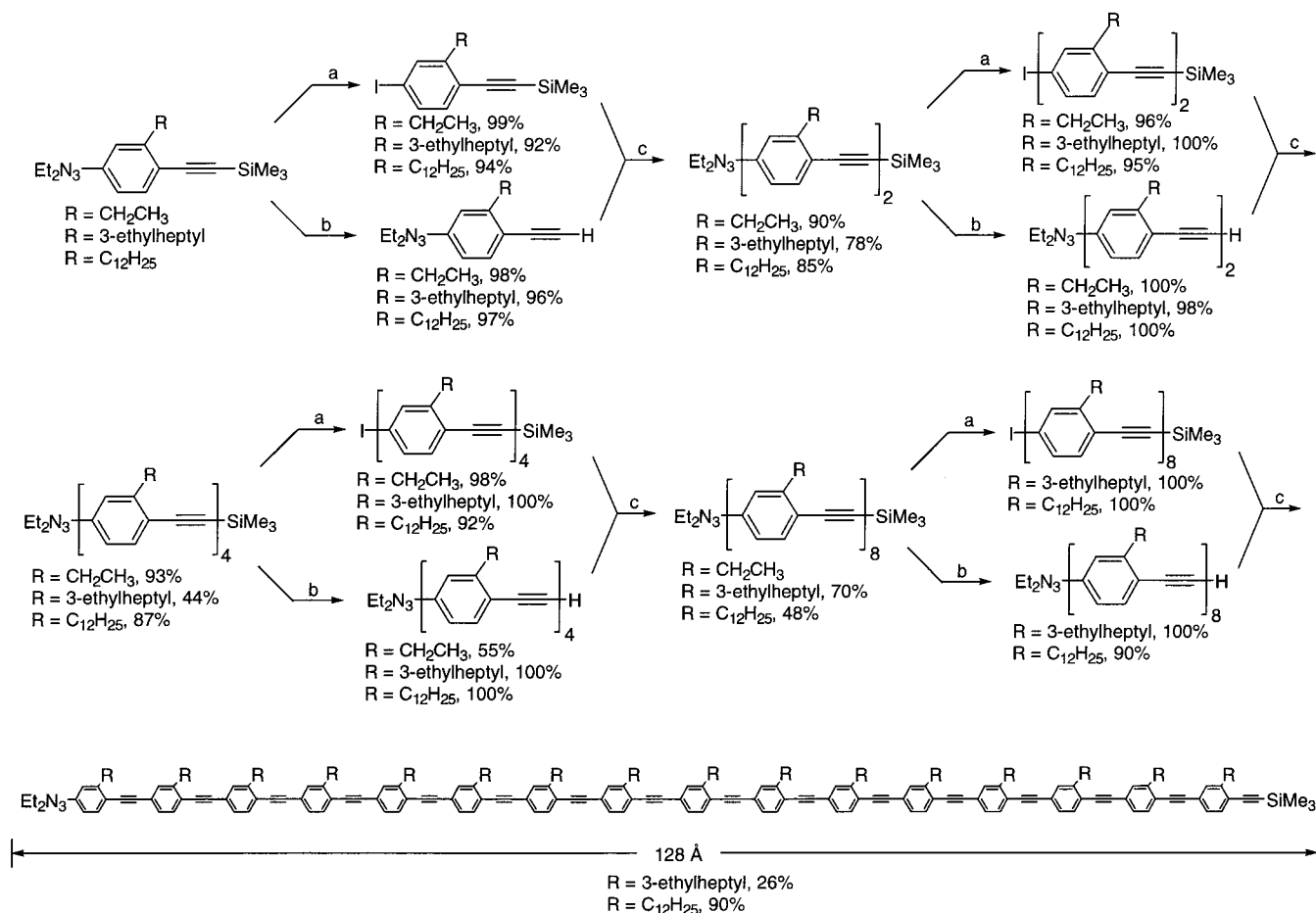
FIGURE 3. Solution-phase synthesis of the oligo(phenylene ethynylene)s by the divergent/convergent doubling approach. Reagents: (a) MeI as solvent, 120 °C in a screw-cap tube; (b) K_2CO_3, MeOH, 23 °C or n-Bu$_4$NF, THF, 23 °C; (c) Pd(dba)$_2$ (5 mol %), CuI (10 mol %), PPh$_3$ (20 mol %), i-Pr$_2$NH/THF (1:5), 23 °C.

## Syntheses of Molecular Devices

Two-Terminal Molecular Devices. The molecular devices discussed here are of precise length and constitution, and they bear molecular alligator clips on, at least, one terminus. Molecular devices could be systems having two or more termini with current–voltage responses that would be expected to be nonlinear due to intermediate barriers or heterofunctionalities in the molecular framework. For example, we began our molecular device syntheses by inserting tunnel barrier methylene fragments into the conjugated systems, as shown in Figure 10.[14] Notice that both one- and two-barrier systems have been prepared. A number of porphyrin-based molecular devices have also been prepared (Figure 11) with and without central metal atom (Zn, Co, Mn) incorporation.[15] We have recently prepared molecular systems that have hetero-functionality along the backbone of the molecule (Figure 12).[16] These have proven particularly useful in generating nonlinear device properties from conjugated molecules (vide infra).

Three- and Four-Terminal Molecular Devices. We have prepared several three-terminal molecules for po-tential device applications, although they have not been successfully addressed to date. Using Pd/Cu coupling methodologies, we have prepared molecular analogues of simple junctions, switches, and logic gates (Figure 13).[14a] Notice that in the two device cases (**22** and **23**), at least one tunnel barrier is needed for the device functionality. Additionally, we have prepared orthogonally fused systems that have been targeted for switchlike applications (Figure 14).[17] However, we have not yet affixed molecular alligator clips to these structures, as these compounds will require a six-probe testing array, a platform unlikely to be constructed soon.

Ordering Molecular Wires and Devices

So, how could one orient 10^{14} molecules in a predefined array on a 1-cm^2 chip? The atomic order of a surface coupled with molecular packing requirements can give rise to thermodynamically driven self-assembly over large surfaces.[18] The gold thiolate (R–S–Au) system is the most commonly studied self-assembled monolayer (SAM). The assembly takes place within seconds, minutes, or days, depending on concentration and molecular structure, and crystalline ordering of the system can occur in domains ranging to hundreds of square nanometers. The gold thiolate bond has a strength of ~2 eV or ~50 kcal/mol; hence, it is quite robust relative to typical bonds that can be formed at ambient temperature. Moreover, a SAM also
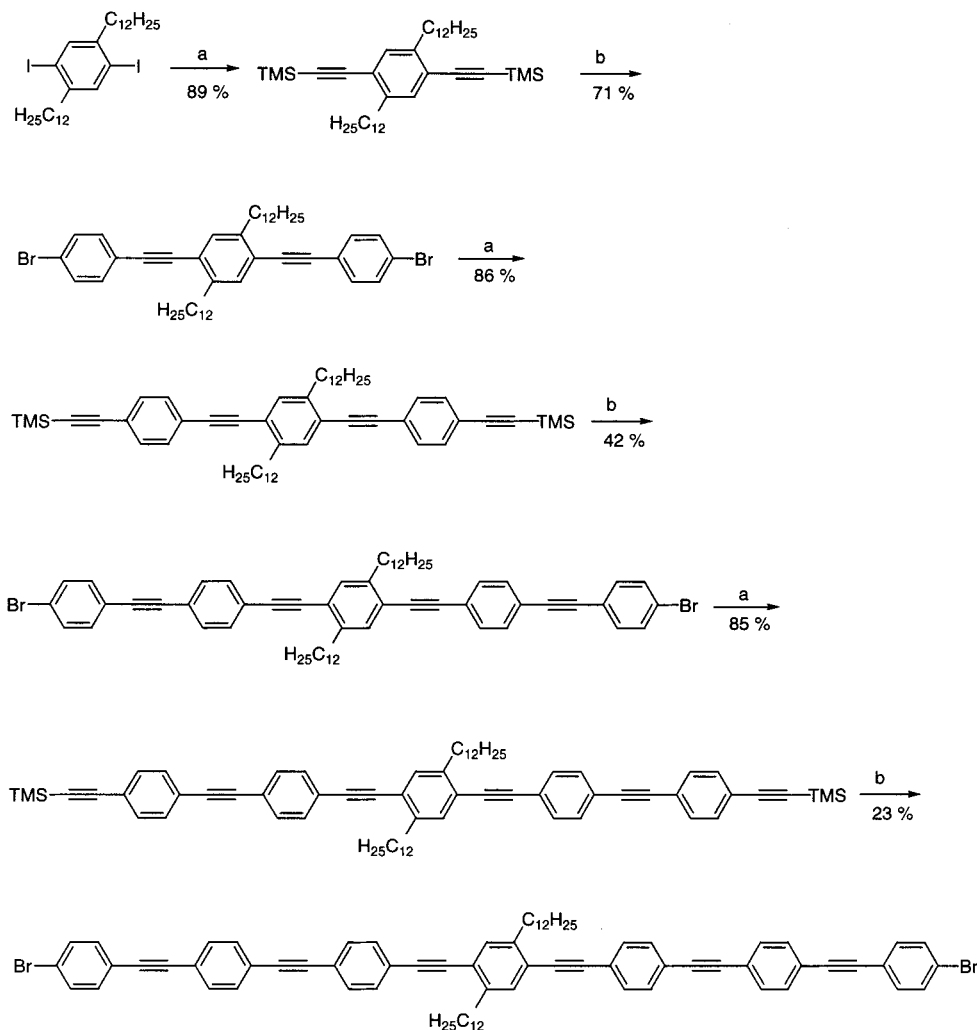
FIGURE 4. (Phenylene ethynylene)-based conjugated oligomers prepared in solution using a bidirectional growth approach with in situ deprotection and coupling. Conditions: (a) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, PPh₃, Et₃N, THF; (b) 1-bromo-4-iodobenzene, Pd(dba)₂, CuI, PPh₃, K₂CO₃, MeOH, THF.
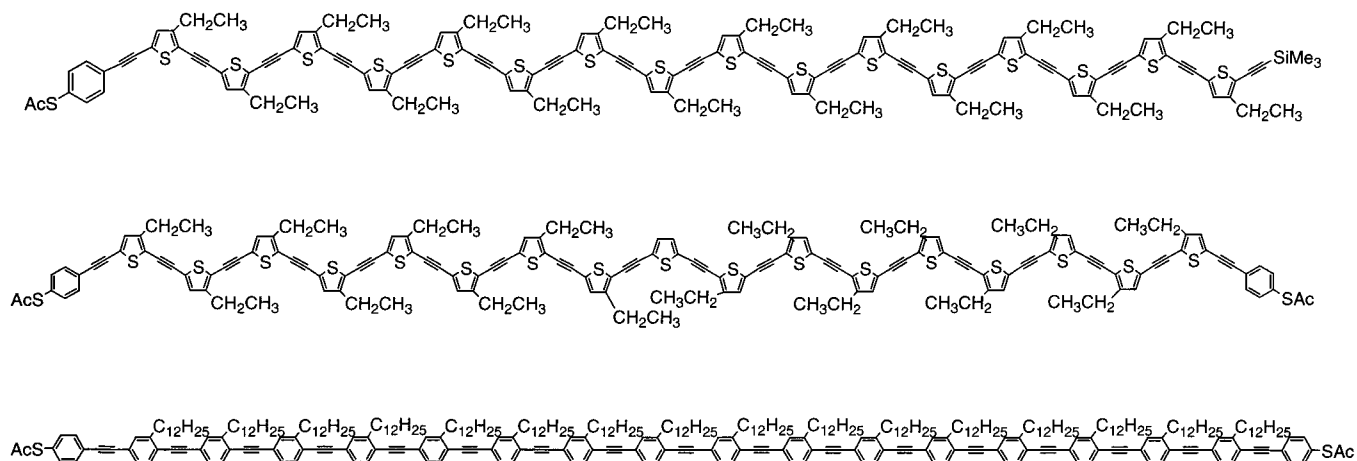
FIGURE 5. Precise molecular wires bearing protected alligator clips (SAc) at one and two ends.

retards surface reconstruction, a phenomenon that often causes rapid randomization of surface atoms.[11,19] There are numerous other surfaces that have been employed in SAM construction.[18] Despite some problems associated with using self-assembly, it promises to be far superior to tedious single-molecule manipulations using, for example, a scanning probe microscopy (SPM) tip.

Present silicon chips are amazingly reliable. For instance, on the Pentium chip with $10^7 - 10^8$ transistors, virtually all of the devices will function properly. Although
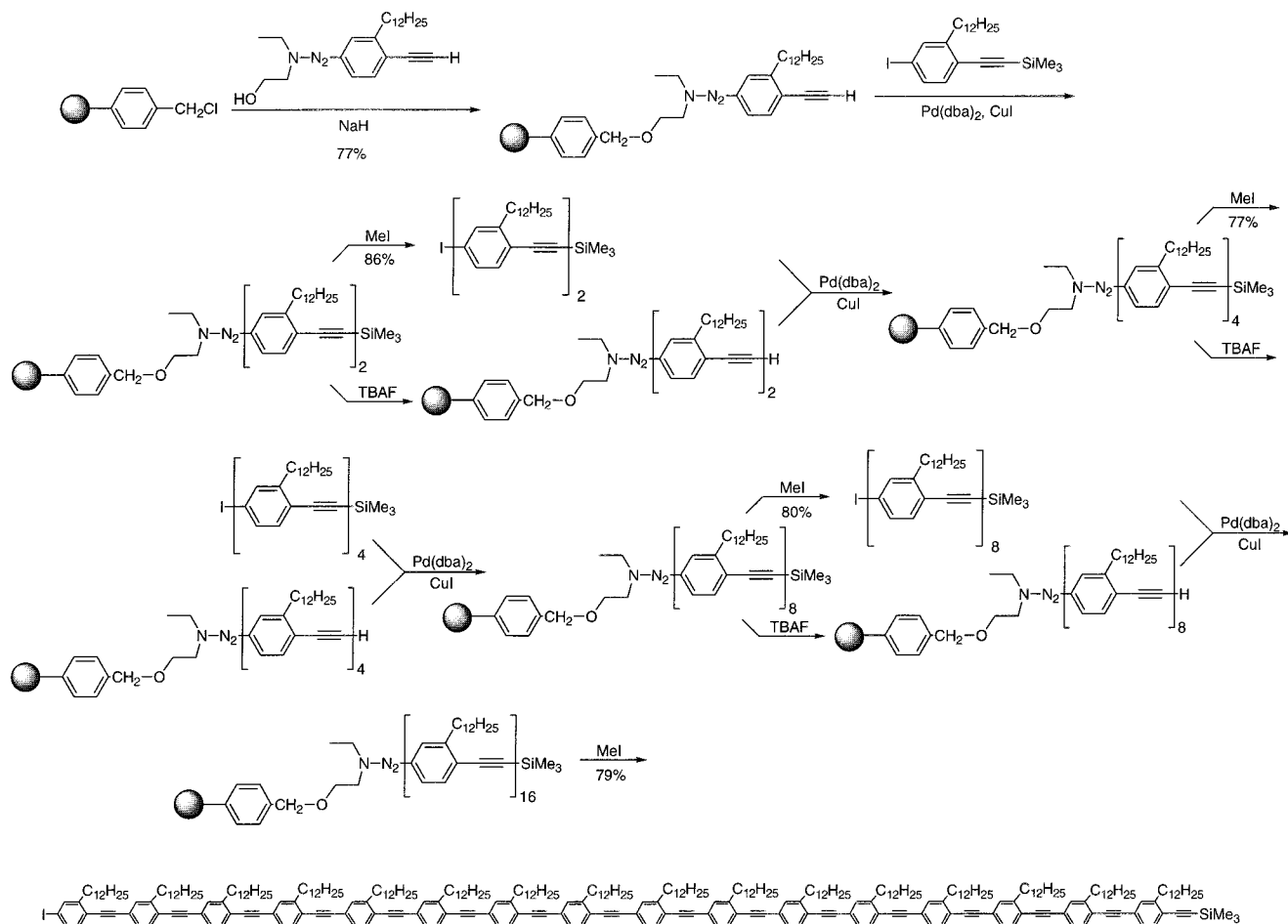
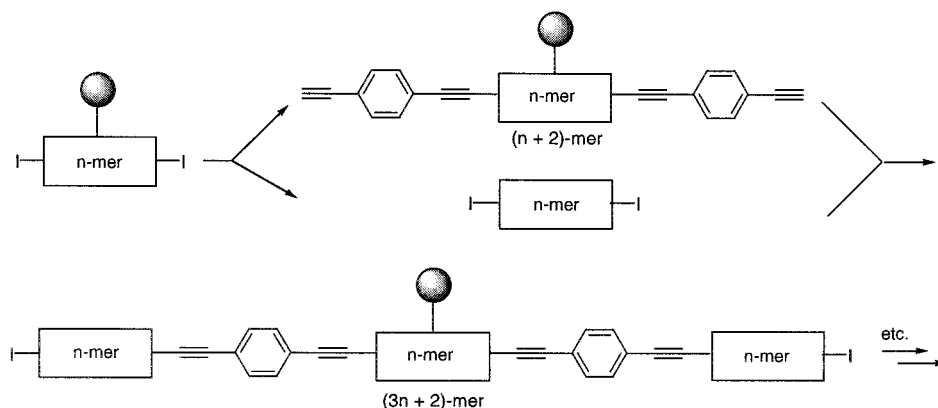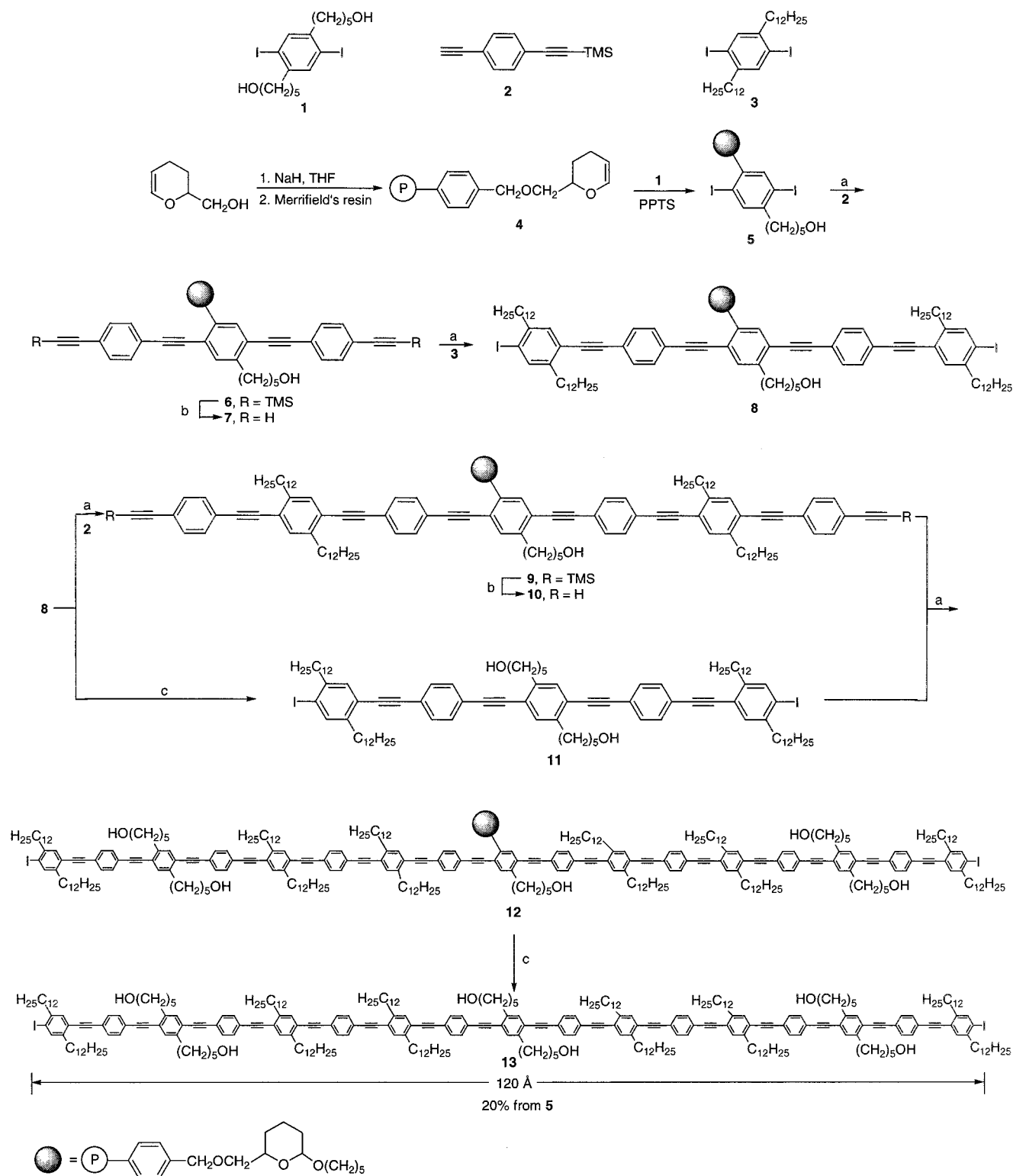**FIGURE 6.** Iterative divergent/convergent molecular doubling growth on a polymer support.

FIGURE 7. General scheme for the iterative divergent/convergent molecular tripling growth approach on a polymer support.

SAMs are remarkable for their ability to extract order from randomness, the arrays thus formed are laden with defects arising from mismatches in long-range registry due to underlying surface defects, step edges, growth patterns during the thermodynamic process, contaminants, etc. Therefore, will the self-assembly processes, which can only afford defect-ridden arrays, ever be useful for assembling viable electronic systems? Certainly, the defect density will depend on the surface, the alligator clips, and the molecules used. So this very question brings us to our second consideration for molecular computing: the construction of systems with high defect tolerance.[20] In a well-ordered self-assembled molecular array, the defect density may be 1–5%. Since device regions are often coupled due to the need for signal transfer throughout the system, a 1–5% defect density could result in 50–90% of the chip being unusable. But with 10^{14} devices per square centimeter and only a 10% usable region, there still exist 10^{13} usable devices per square centimeter and a 100 000-fold advantage over present systems. Likewise, high levels of redundancy, i.e., dependence on 10 molecular devices for a "yes" average output to afford high assurance levels, would be a simple strategy to employ in the molecular electronic computer. In this way, an occasional molecular degrada-
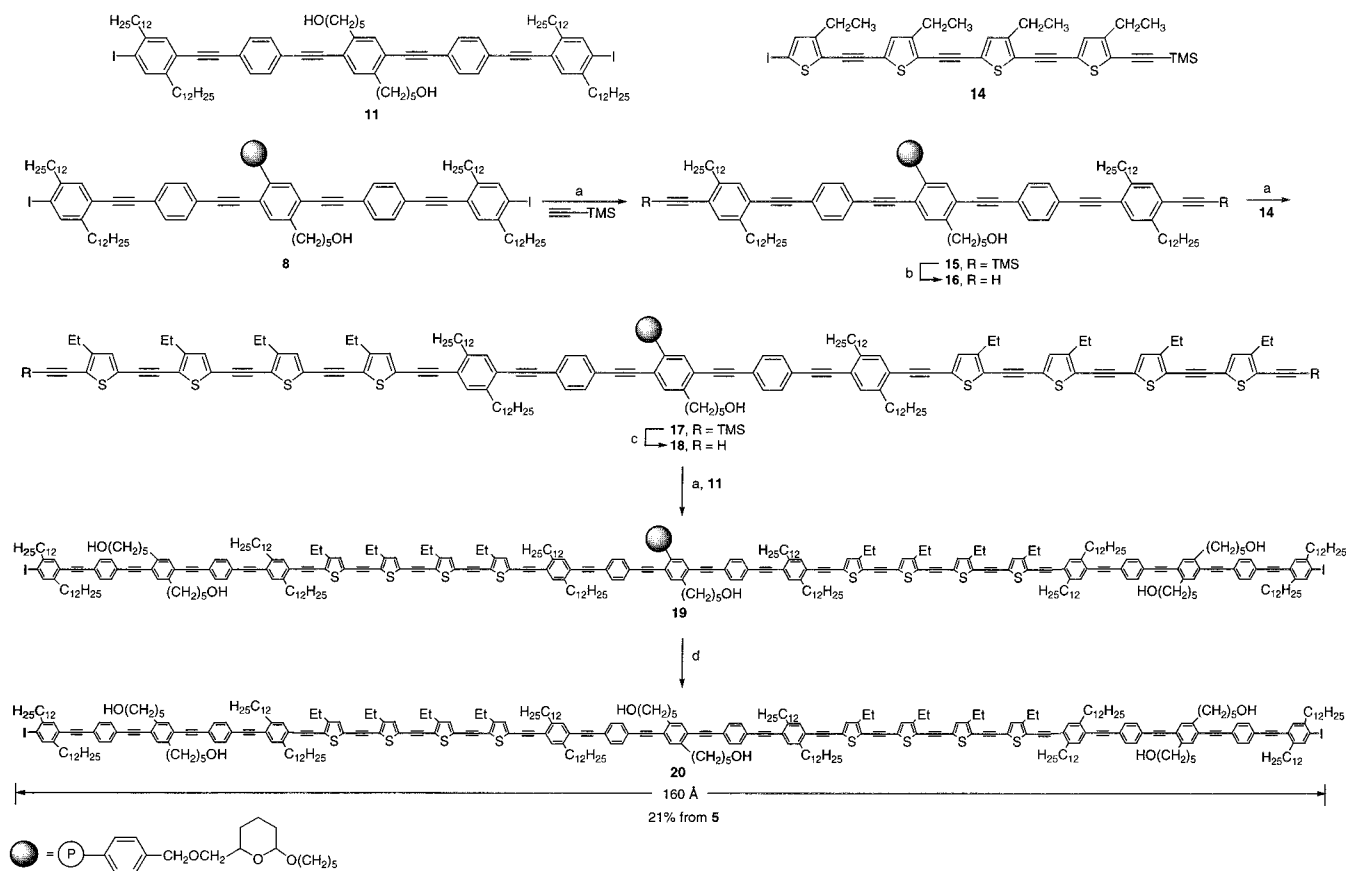
FIGURE 8. Tripling iterative divergent/convergent molecular growth approach on a polymer support to prepare homooligomers. Reagents: (a) Pd(dba)$_2$, PPh$_3$, and CuI (5 mol %, 10 mol %, and 5 mol %, respectively, per iodide atom), Et$_2$NH/THF (1:4); (b) TBAF, THF; (c) PPTS, n-C$_4$H$_9$OH, ClCH$_2$CH$_2$Cl.

tion by, for example, oxidative decomposition of a molecule would cause little problem to the overall system. But even considering defect-tolerant systems, the addressing difficulties (vide supra) remain.

Since any potential molecular wire must bridge two electrodes, the question arises as to how these rigid rod difunctional oligomers will order themselves on metallic surfaces. For example, will the oligomers bridge the gold— gold gap as in Figure 15a, or will they reside nearly parallel to the surface of the gold by either dithiol or aromatic adsorption to the gold surfaces as in Figure 15b and c, respectively?[5] By making SAMs on gold surfaces, we have
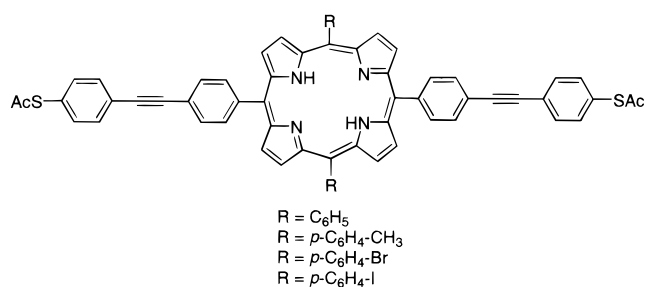
FIGURE 9. Tripling iterative divergent/convergent molecular growth approach on a polymer support to prepare [AB] block cooligomers. Reagents: (a) Pd(dba)$_2$, PPh$_3$, and CuI (5 mol %, 10 mol %, and 5 mol %, respectively, per iodide atom), Et$_2$NH/THF (1:4); (b) TBAF, THF; (c) K$_2$CO$_3$, CH$_3$OH, CH$_2$Cl$_2$; (d) PPTS, n-C$_4$H$_9$OH, ClCH$_2$CH$_2$Cl.
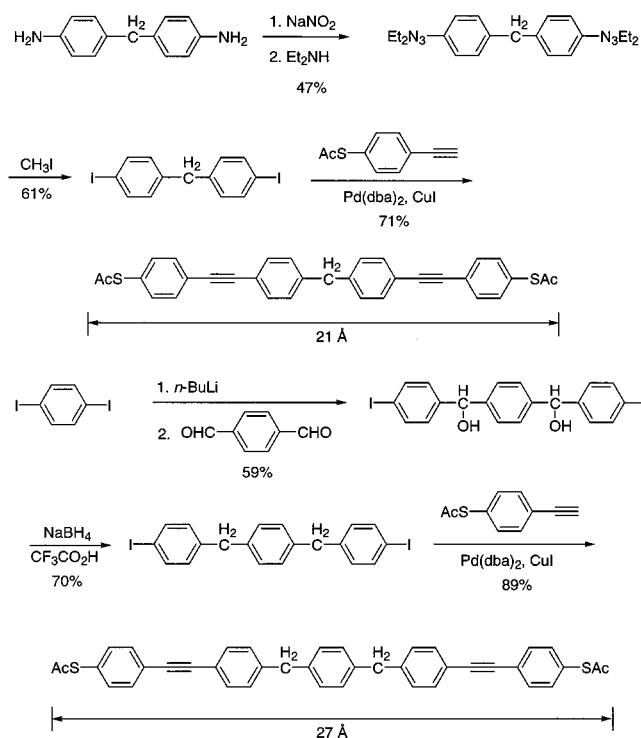
FIGURE 10. Two-ended molecular devices with methylene tunnel barriers.

R = C$_6$H$_5$
R = p-C$_6$H$_4$-CH$_3$
R = p-C$_6$H$_4$-Br
R = p-C$_6$H$_4$-I

FIGURE 11. Porphyrin-based molecular devices with alligator clips.

demonstrated, using ellipsometry, XPS, and grazing angle IR measurements, that the rigid rod systems stand nearly perpendicular to the surface, the thiol groups dominating the adsorption sites on the gold. Even when the oligomers were α,ω-dithiol-substituted, the rigid molecules tended to stand on end as judged from the ellipsometric thickness of the adsorbate layer.[11,19,21] This trend holds true for oligo-(phenylene ethynylene)s up to ∼50 Å in length; however, beyond that length, it became difficult to obtain densely packed well-ordered monolayers. Note that we used thioacetate end groups since these could be selectively deprotected in THF to afford the free thiol, using ammonium hydroxide during the deposition process.[21] Alkali metal salts were avoided since they tend to disrupt electronics measurements. Use of the free thiols, rather than the thioacetates, proved to be problematic since these were prone to very rapid oxidative disulfide formation. Although disulfides can self-assemble on gold, the assembly is ∼1000 times slower than that with the thiols.
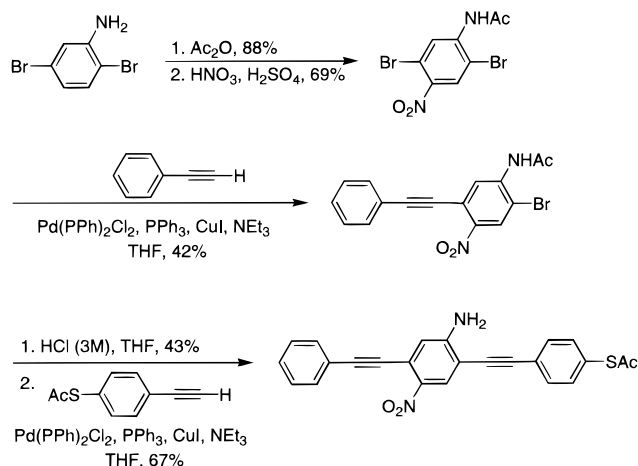
FIGURE 12. Synthetic route to a molecular device that bears functionality for electron capture. This nitroaniline exhibits negative differential resistance and molecular random access memory effects.

Moreover, when using the α,ω-dithiols, oxidative polymerization ensues which rapidly results in insoluble material. Hence, in situ removal of the acetates has proven to be quite effective.

Testing of Molecular Wires

In testing our molecular systems, a wire is defined as a two-terminal entity that possesses a reasonably linear $I(V)$ curve prior to the breakdown limit. If recorded currents, over a few volts, are in the nanoampere region, our instruments can record them, although we far prefer working in the tenths of microamps region, the region in which much of present-day microelectronics operates.

Our initial efforts were directed toward straddling longer molecular wires across lithographically patterned proximal gold-coated probes separated by approximately 100 Å, but these studies were unreliable.[11] Our long-time collaborator, Mark Reed, has developed a technique for determining the conductances of our molecular systems using a nanopore arrangement. In this embodiment, electronic measurements are performed in a nanostructure that has a metal top contact, a SAM active region of ~1000 molecules in a 30-nm-diameter region, and a metal bottom contact.[22] Using this small area, we eliminated pinhole and other defect mechanisms that could hamper through-monolayer electronic transport measurements. Using this procedure, $I(V)$ could be recorded on a series of molecular wire systems as well as two-terminal devices (vide infra). Controlled-temperature variations during $I(V)$ recording on the molecular wires in the nanopore demonstrated that the current could be modulated via temperature-induced variations in the molecular conformations. Additionally, the contact barrier between molecule and metallic probe, via the alligator clips, could be determined.[22,23] Recently, along similar lines, Metzger[24] and the team of Heath, Stoddart, and Williams[25] were able to use micrometer-sized regions of Langmuir–Blodgett (LB) films for evaporation of top contacts without forming overwhelming electrical shorts due to defects in the LB structure. In the latter case, LB formation occurred on an aluminum oxide surface; therefore, if metal leakage through the SAM occurred, the shorts would be passivated at the surface.[25]

In collaboration with Paul Weiss and David Allara, we have been able to address single molecular wires that had been inserted at grain boundaries within a self-assembled monolayer of dodecanethiolate on gold (Figure 16). This technique has permitted the isolation of single molecular wires from their neighbors, and it has also allowed the addressing of the vertically arranged systems. Using scanning tunneling microscopy (STM), the molecules could then be individually imaged and addressed. Qualitative results of the conductance levels showed that the molecular wires, although topographically higher above the gold surface, were more highly conducting than the surrounding alkanethiolate structures.[19,26] Such a result is intuitive; however, it had never before been demonstrated in a single conjugated molecule, projecting on end, that was isolated from all its neighbors. We further developed methods to insert the molecular wires at controlled rather than at random locations. By applying controlled voltage pulses to an alkanethiolate SAM under a solution of molecular wires (Figure 17), we were able to achieve the precise placement of molecular wire bundles (<10 molecules/bundle) at programmed positions (Figure 18).[27] To

21 **22** **23**
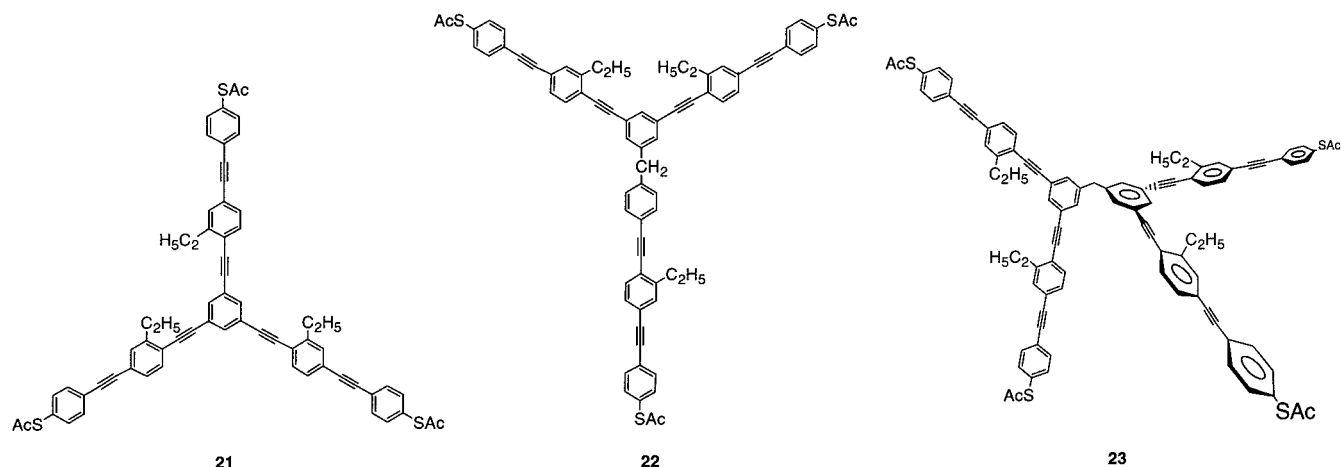
FIGURE 13. Three-terminal molecular junction (**21**), molecular switch (**22**), and four-terminal molecular logic gate (**23**).
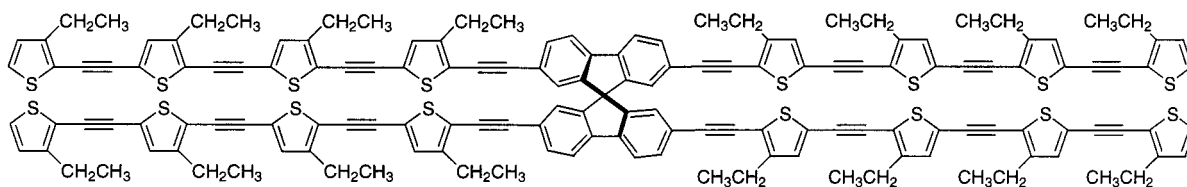
FIGURE 14. Orthogonally fused system that could act as a molecular switching device.
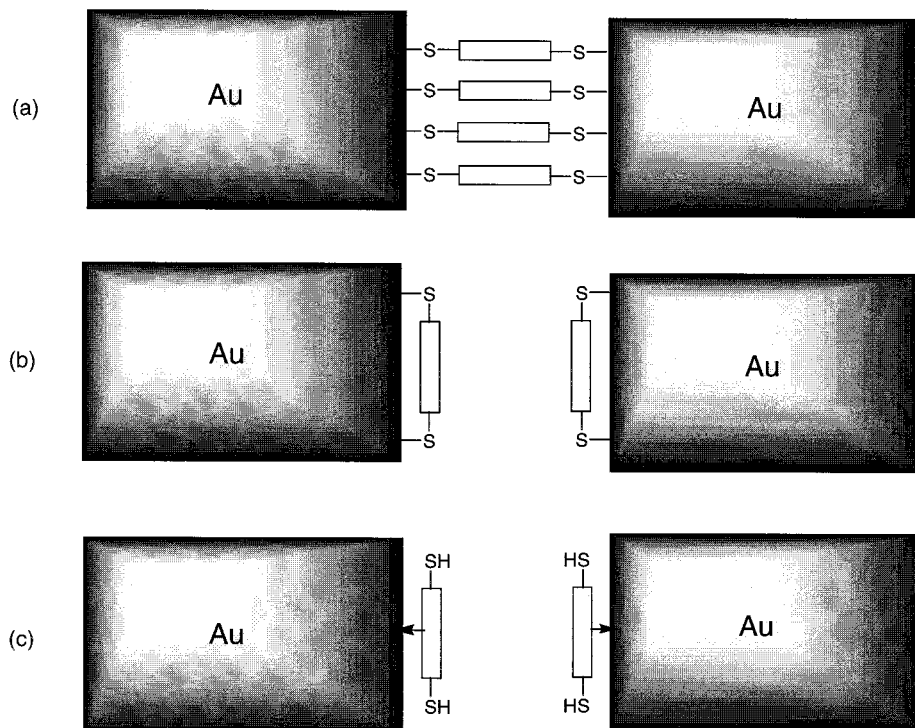

FIGURE 15. Modes for molecular wire assembly (a) as desired between proximal gold probes, (b) adsorbed via the thiols without bridging the probes, or (c) having the adsorption sites dominated by the aromatic units.
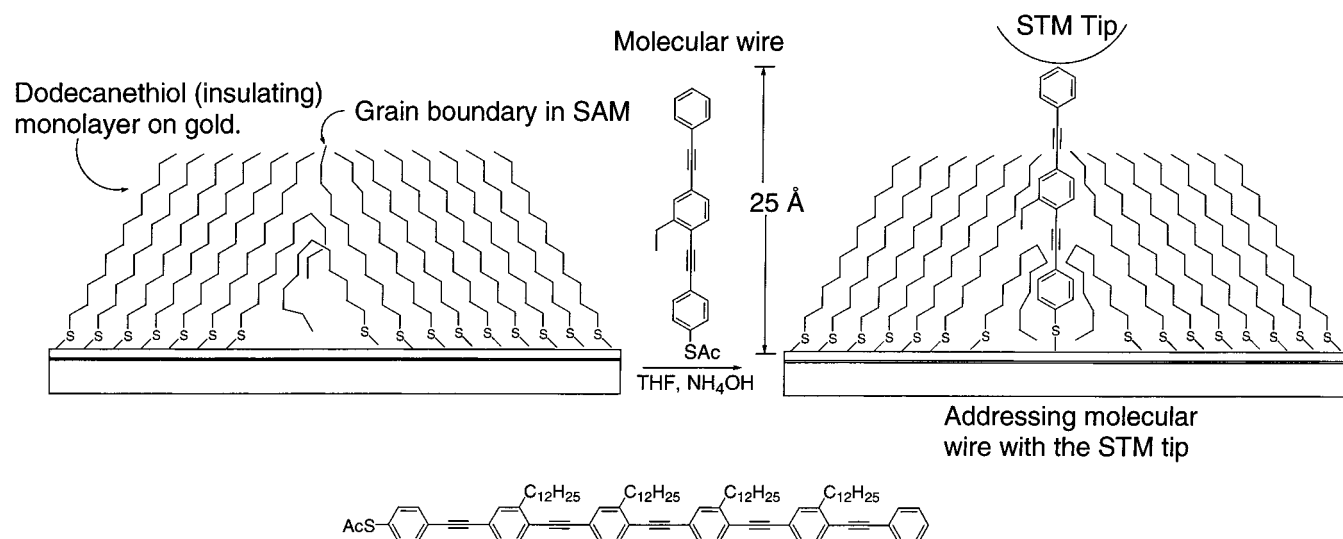

FIGURE 16. Protocol for inserting molecular wires into dodecanethiolate SAMs at grain boundaries. Relative conductance recording was done with an STM tip. The molecule shown at the bottom has also been used in this study.

quantify the degree of current that could be passed through a single molecule, we again worked with Reed's group to utilize a mechanically controllable break junction method for addressing single molecules. Using this device, two gold tips could be generated and moved in picometer increments with respect to each other by use of an underlying piezo element (Figure 19).[28] Conductance quantization (changes in the conductance in discrete steps of $2e^2/h$) observed in the probe system ensured that the movements of the tips were controllable in subatomic-
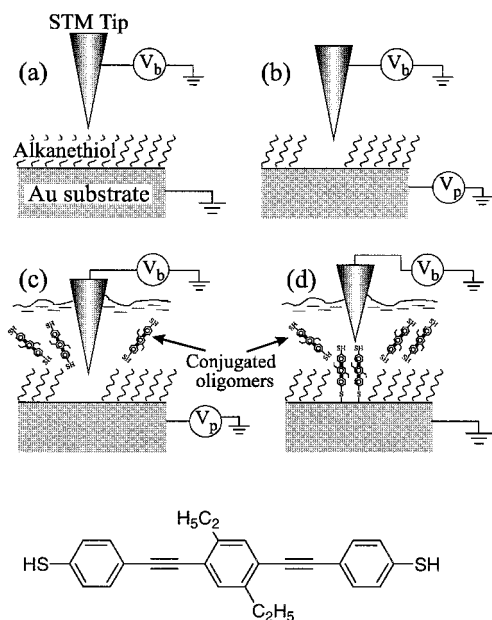
FIGURE 17. Schematic of the lithographic patterning and replacement of conjugated molecules in an alkanethiolate matrix. (a) Normal STM imaging of an alkanethiolate SAM with tip bias V_b. (b) SAM removal by applying a voltage pulse V_p to the substrate. (c) Carrying out the same voltage pulse as in (b), but under a solution of molecular wires (expanded structure at bottom) causes (d) insertion of the wires into the newly vacated site.

length increments. Benzene-1,4-dithiol (generated in situ from the dithioacetate) was permitted to self-assemble on the two tips that were, initially, widely separated. The two tips were then moved together, in picometer steps during the close contact point, until one molecule bridged the gap (Figure 20).[28] Current/voltage responses were recorded for a single molecule bridging the gap. Remarkably, 0.1 mA current could be recorded through a single molecule. However, few or none of those 10^{12} electrons per second were colliding with the nuclei of the molecule; hence, all the heat was dissipated in the contact. Note that the mean free path of an electron in metal is hundreds of angstroms; hence, it is not surprising that collisions did not take place within the small molecule. Most importantly, since most computing instruments operate on microamps of current, the viability of molecular electronics became all the more tangible.

Testing of Molecular Devices

While wires exhibit reasonably linear $I(V)$ curves, a device should show nonlinear $I(V)$ characteristics. Two terminal devices have been fashioned from many types of molecular systems. In 1997, Metzger and co-workers used a multilayer structure of **24** to observe electrical rectification.[24] Similarly, the groups of Heath, Williams, and


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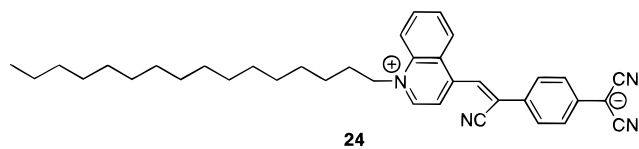
Stoddart used a monolayer film of a rotaxane to generate a switchable device structure, albeit irreversible, when sandwiched between aluminum and titanium electrodes.[25] While an alligator clip-terminated oligo(phenylene ethynylene) acted as a wire (nearly linear $I(V)$ curve),[22] we recently showed that functionalization of the oligo-(phenylene ethynylene) permitted the formation of several device structures. For example, using the nanopore setup as described above, the nitroaniline (Figure 12) showed an intense negative differential resistance (NDR) effect with a peak-to-valley (PVR) ratio of >1000:1 (Figure 21).[16] NDR is an inflection in the current/voltage curve where there is a sudden spike in the current as the voltage is scanned. While silicon devices do not show this effect, gallium arsenide exhibits this property at levels typically on the order of <100:1. Hence, that the molecular system showed a response of >1000:1 was, indeed, remarkable. Theoretical studies suggest that the switching is based upon dramatic changes in the LUMO upon charging.[29] Modifications of the structure have also permitted the storage of current in these systems, and this can be used as a molecular memory.[30] This current storage persisted for as long as 10 min and is reminiscent of a random access memory cell. While most silicon-based DRAMs are refreshed every 10^4-10^5 s^{-1}, these were extraordinary long hold times from the molecular systems where the electronic charging of the molecules affects the conductance of the system.

In exciting complementary work, Joachim, Gimzewski, and co-workers were able to record the electronic transport of a single molecule of C_{60} sandwiched between a metallic surface and an STM tip. By mechanically compressing the C_{60} molecule with the STM tip against the metallic surface, the internal electronic structure of the molecule was continuously modified. By compressing the molecule with tip, there was a measured voltage gain of 5, making this the first demonstration of a single-molecule amplifier.[31]

We have not yet addressed any of our three- and four-terminal systems either as single molecules or as nanometer-sized bundles. This stems from the fact that it is far easier to bring two probes into close proximity than to bring three probes into near contact. Macroscopic leads are akin to basketballs: touching two basketballs together at the same junction point is simple; however, trying to touch three together at a common contact point is impossible. It is the same when addressing single molecules. However, in a very clever experiment by Klein and co-workers, a single 5.5-nm CdSe nanocrystal was permitted to contact two leads, and the third lead was an underlying doped silicon substrate separated from the nanocrystal by an SiO_2 layer for a field-effect third terminal. In this manner, the authors formed a single-nanocrystal-based single-electron transistor.[32] Amazingly, some of the same team recently conducted a similar experiment using a single molecule of C_{60} to produce a single-molecule transistor.[33]
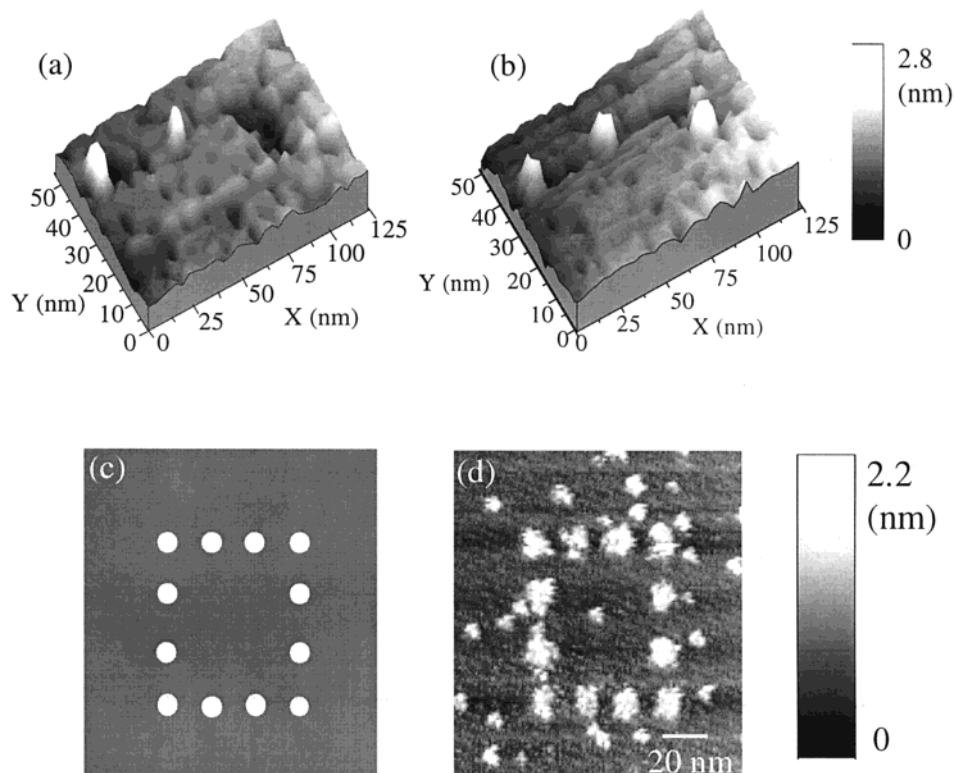
FIGURE 18. (a) Dodecanethiolate SAM surface after three consecutive voltage pulsing events. The first two pulsed locations have molecular wires inserted, while the third location remains to be filled. (b) The image taken a few minutes later shows that wire insertion at the third pulse location is now complete. (c) A programmed rectangular pattern for controlled voltage pulses. (d) The image of the patterned SAM after pulsing and molecular wire insertion. Some random insertions at grain boundaries or other defect sites are also evident.
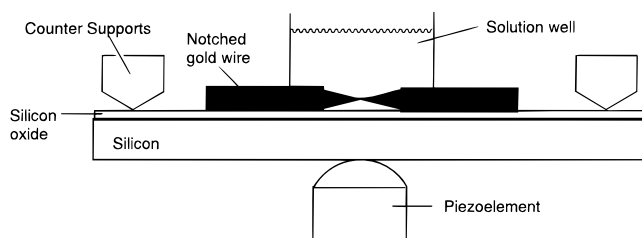
FIGURE 19. Schematic of the mechanically controllable break junction showing the bending beam formed from a silicon wafer, the counter supports, the notched gold wire which is glued to the surface, the piezo element for controlling the tip-to-tip distance through bending of the silicon platform, and the glass capillary tube containing the solution of molecular wires.

Electrostatics Method of Computation

As mentioned previously, heat dissipation remains a significant obstacle for densely arrayed molecular devices. It is here that some of the most radical departures from traditional system designs may need to be invoked if one is to exploit the inherent advantageous qualities available to molecules. As initially described by Lent, Porod, Tougaw, and co-workers[34] in what they termed a quantum cellular automata (QCA) model, and later by our own group and J. Seminario,[14a] nanometer-sized devices could function by electric field repulsions. In particular, molecular devices could function by electrostatic interactions (electric fields) produced by small reshapes of the electron density due to the input signals. In turn, electrostatic potential interactions between molecules would then transport the information throughout the CPU. In solid-state devices, one bit of information requires 16 000–18 000 electrons; however, perturbations of the electrostatic potential impart fractions of an electron. A charge or field on one side of the molecule would reshape the electron density, providing a different potential at the output that could then be detected. This would reduce the heat dissipation by several orders of magnitude.[14a]

Alternate Methods for Computational Architectures

Thus, major operational changes have been suggested in an effort to deal with the heat dissipation concerns in dense molecular arrays. However, there are alternate yet equally valid designs that could be followed for a molecular electronic computer architecture. For example, consider relaxing the design proposals for 10^{14} molecular devices/cm^2 and fractions of an electron per bit of information to 10^{12} molecular devices/cm^2 and 100 electrons/bit. This still represents a 10^4 increase in packing density and about a 10^2 decrease in the number of electrons per bit compared to the present Pentium chip. However, consider operation at 10^4 s^{-1} rather than the 10^9 s^{-1} rate presently used. That would result in a power dissipation of only $\sim 10^{-2}$ W. Therefore, as demonstrated by the ubiquitous biological computers, namely brains, for applications where massive information transfer rates are not critical, one need not invoke grossly different
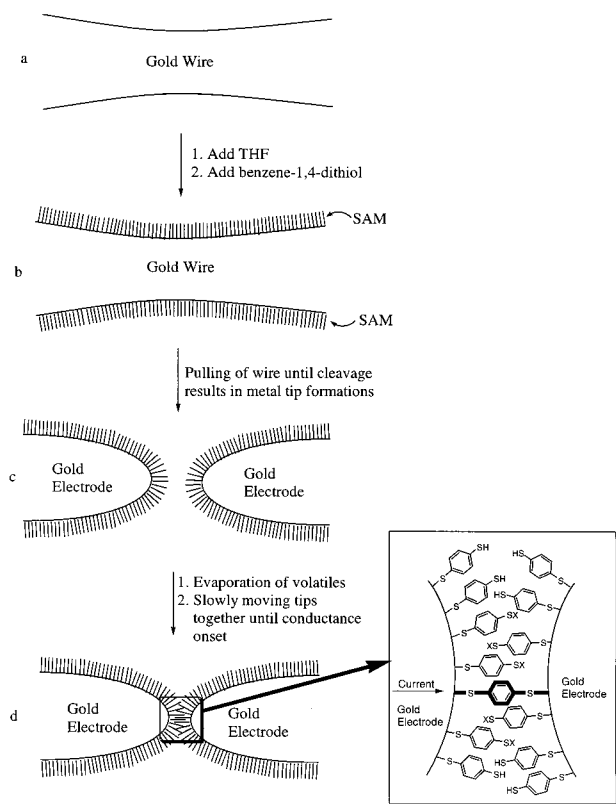
FIGURE 20. Representation of the technique used in the mechanically controllable break junction for recording the current through a single molecule. (a) The gold wire was coated with a SAM of the molecular wires (b) and then broken, under solution (c), via extension of the piezo element under the silicon surface (see Figure 19). Evaporation of the volatile components and slow movement of the piezo downward (see Figure 19) permits one molecule to bridge the gap (d) that is shown, in expanded view, in the inset. The inset shows a benzene-1,4-dithiolate molecule between proximal gold electrodes. The thiolate is normally H-terminated after deposition; end groups denoted as X can be either H or Au, the Au potentially arising from a previous contact/retraction event.
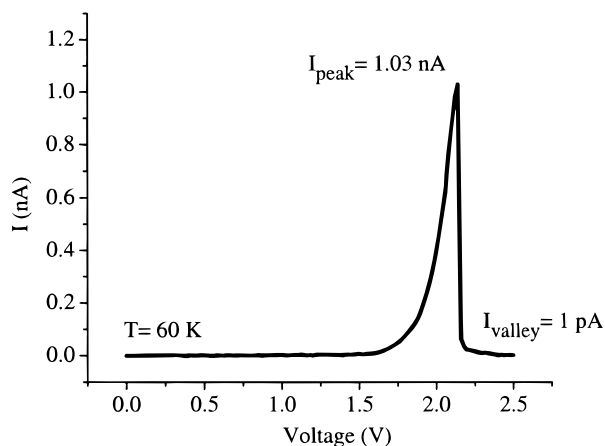
FIGURE 21. $I(V)$ characteristics of a Au−(2′-amino-4,4′-di(ethynylphenyl)-5′-nitro-1-benzenethiolate)−Au device at 60 K. The peak current density is ∼50 A/cm^2, the NDR is ∼ −400 $\mu\Omega\cdot$cm^2, and the PVR is 1030:1.

functional designs for molecular computing. This might well be the initial design route that is followed for molecular-based systems.

Summary

As a result of the rising cost and physical limits involved in the continual downsizing of microelectronics, maintaining a course along Moore's law will require a transition away from traditional solid-state devices. Molecular electronics, involving chemically designed components, could permit the continued scaling into the nanosized regime, even though several formidable challenges remain to be solved. Although dramatic departures from present computing design paradigms may eventually be needed in order to realize the full potential of molecular computing systems, it is probable that substantial gains could even be achieved with more subtle present-day architectures. Hence, molecular systems are not likely to supplant solid-state technologies in the near term; rather they will be complements to traditional electronic devices, specifically hybrid systems where molecules work in concert with silicon. For example, one solid-state transistor may provide the gain for 10 000 molecular devices. However, in light of the physical and monetary roadblocks, molecules could become the primary devices of future computer hardware. Not only will they be considerably smaller and less expensive to produce than their solid-state counterparts, but they may also possess unforeseen behavior that is either superior to or unattainable from solid-state systems. Indeed, molecules are the most probable electronic components for the ultradense and ultrafast computational demands of the new millennium.

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AR0000612