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# Computing With Molecules

By Mark A. Reed and James M. Tour

How fast and powerful can computers become? Will it be possible someday to create artificial "brains" that have intellectual capabilities comparable--or even superior--to those of human beings? The answers to these questions depend to a very great extent on a single factor: we can make computer circuits.

Few if any researchers believe that our present technology--semiconductor-based solid-state microelectronics--will lead to circuitry dense and complex enough to give rise to true cognitive abilities. And until recently, none of the technologies proposed as successors to solid-state microelectronics had shown enough promise to rise above the pack. Within the past year, however, scientists have achieved revolutionary advances that may very well radically change the future of computing. And although the road from here to intelligent machines is still rather long and might turn out to have unbridgeable gaps, the fact that there is a potential path at all is something of a triumph.

The recent advances were in molecular-scale electronics, a field emerging around the premise that it is possible to build individual molecules that can perform functions identical or analogous to those of the transistors, diodes, conductors and other key components of today's microcircuits. After a period of high hopes but few tangible results, several developments over the past few years have raised expectations that this technology may one day provide the building blocks for future generations of ultrasmall, ultradense electronic computer logic. In a remarkable series of demonstrations, chemists, physicists and engineers have shown that individual molecules can conduct and switch electric current and store information.

Last July, in an achievement widely reported in the popular press, researchers from Hewlett-Packard and the University of California at Los Angeles announced that they had built an electronic switch consisting of a layer of several million molecules of an organic substance called rotaxane. By linking a number of switches, the researchers produced a rudimentary version of an AND gate, a device that performs a basic logic operation. With well over a million molecules apiece, the switches are far larger than would be desirable. And they could be switched only one time before becoming inoperable. Nevertheless, their assembly into a logic gate was of fundamental significance.

Within months of that announcement, our groups at Yale and Rice universities published results on a different class of molecules that acted as a reversible switch. And one month later we described a molecule we had created that could change its electrical conductivity by storing electrons on demand, acting as a memory device.

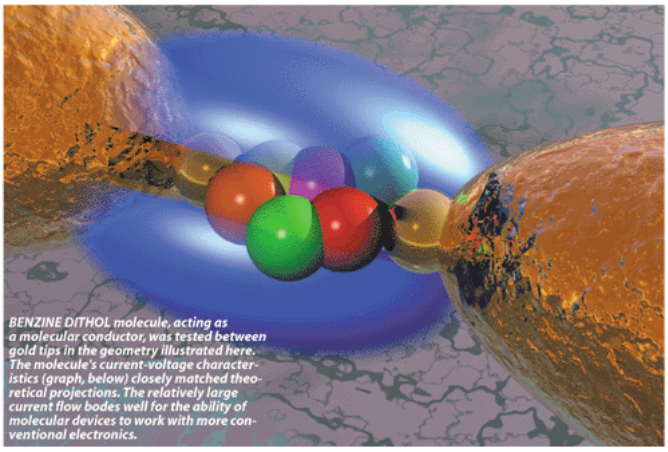



Illustration: MARK A. REED

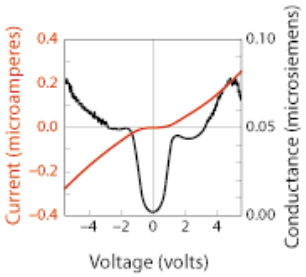
To produce our switch, we inserted regions into the molecules that trapped electrons, but only when the molecules were subjected to certain voltages. Thus, the degree to which the molecules resisted a flow of electrons depended on the voltage applied to them. In fact, by varying the voltage, we could repeatedly change the molecules at will from a conducting to a nonconducting state--which is the basic requirement for an electrical switch. The tiny device actually consisted of a layer of about 1,000 molecules of nitroamine benzenethiol sandwiched between metal contacts.

After creating the switch, we realized that if we could redesign the molecule so that it could retain electrons rather than trapping them briefly, we would have something that could work as a memory element. We went to work on the trapping region of the molecule, modifying it so that its conductivity could be changed repeatedly. The resulting "electron sucker" could retain electrons for nearly 10 minutes--compared with a few milliseconds for conventional silicon-based dynamic random-access memory.

Although the advances were encouraging, the challenges remaining are enormous. Creating individual devices is an essential first step. But before we can build complete, useful circuits we must find a way to secure many millions, if not billions, of molecular devices of various types against some kind of immobile surface and to link them in any manner and into whatever patterns our circuit diagrams dictate. The technology is still too young to say for sure whether this monumental challenge will ever be surmounted.

**The End of the Road Map**

Given the magnitude of the challenges ahead, why did researchers and even the mainstream media pay so much attention to the recent advances? The answer has to do with industrial society's dependence on microelectronics--and the limits of the form of the technology we have today.




That form--solid-state and silicon-based--follows one of the most famous axioms in technology: Moore's Law. It relates that the number of transistors that can be fabricated on a silicon integrated circuit--and therefore the computing speed of such a circuit--is doubling every 18 to 24 months. After following this remarkable curve for four decades, solid-state microelectronics has advanced to the point at which engineers can now put on a sliver of silicon of just a few square centimeters some 100 million transistors, with key features measuring 0.18 micron.

These transistors are still far larger than molecular-scale devices. To put the size differential in perspective, if the conventional transistor were scaled up so that it occupied the printed page you are reading, a molecular device would be the period at the end of this sentence. Even in a dozen years, when industry projections suggest that silicon transistors will have shrunk to about 120 nanometers in length, they will still be more than 60,000 times larger in area than molecular electronic devices.

Moreover, no one expects conventional silicon-based microelectronics to continue following Moore's Law forever. At some point, chip-fabrication specialists will find it economically infeasible to continue scaling down microelectronics. As they pack more transistors onto a chip, phenomena such as stray signals on the chip, the need to dissipate the heat from so many closely packed devices, and the difficulty of creating the devices in the first place will halt or severely slow progress.

Indeed, various nagging (though not yet fundamental) problems in the fabrication of efficient smaller silicon transistors and their interconnections are becoming increasingly bothersome. Many experts expect these challenges to intensify dramatically as the transistors approach the 0.1-micron level. Because of these and other difficulties, the exponential increase in transistor densities and processing rates of integrated circuits is being sustained only by a similar exponential rise in the financial outlays necessary to build the facilities that produce these chips. Eventually the drive to downscale will run headlong into these extreme facility costs, and the market will reach equilibrium. Many experts project that this will happen around or before 2015, when a fabrication facility is projected to cost nearly $200 billion. When that happens, the long period of breathtaking advances in the processing power of computer chips will have run its course. Further increases in the power of the chips will be prohibitively costly.

Unfortunately, this impasse will almost certainly occur long before computer chips have reached the power to fulfill some of the most sought-after goals in computer science, such as the creation of extremely sophisticated electronic "brains" that will enable robots to perform on a par with humans in intellectual and cognitive tasks.

**Billions and Billions**

The extraordinarily small size of molecular devices brings advantages beyond the simple ability to pack more of them into a small area. To grasp these important benefits requires an understanding of how the devices work--which in turn demands some knowledge of how electrons behave when confined to regions as small as atoms and molecules.

Free electrons can take on energy levels from a continuous range of possibilities. But in atoms or molecules, electrons have energy levels that are quantized: they can only be any one of a number of discrete values, like rungs on a ladder. This series of discrete energy values is a consequence of quantum theory and is true for any system in which the electrons are confined to an infinitesimal space. In molecules, electrons arrange themselves as bonds among atoms that resemble dispersed "clouds," called orbitals. The shape of the orbital is determined by the type and geometry of the constituent atoms. Each orbital is a single, discrete energy level for the electrons.

Even the smallest conventional microtransistors in an integrated circuit are still far too large to quantize the electrons within them. In these devices the movement of electrons is governed by physical characteristics--known as band structures--of their constituent silicon atoms. What that means is that the electrons are moving in the material within a band of allowable energy levels that is quite large relative to the energy levels permitted in a single atom or molecule. This large range of allowable energy levels permits electrons to gain enough energy to leak from one device to the next. And when these conventional devices approach the scale of a few hundred nanometers, it becomes extremely difficult to prevent the minute electric currents that represent information from leaking from one device to an adjacent one. In effect, the transistors leak the electrons that represent information, making it difficult for them to stay in the "off" state.

**Building from the Bottom Up**

Besides enabling molecular devices to contain their electrons more securely, quantum mechanical phenomena can also be exploited in specially designed molecules to perform other functions. For example, to construct a "wire" we need an elongated molecule through which electrons can flow easily from one end to the other. Electrons in any quantized structure such as a molecule tend to move from higher- to lower-energy levels, so in order to channel electrons we need a molecule that has an empty, low-energy orbital that is dispersed throughout the molecule from one end to the other. A typical empty, low-energy electron orbital is known as a pi orbital. And the configuration in which electron clouds overlap from one molecular component to the next is called conjugated, so our molecular wire is known as a "pi-conjugated system."

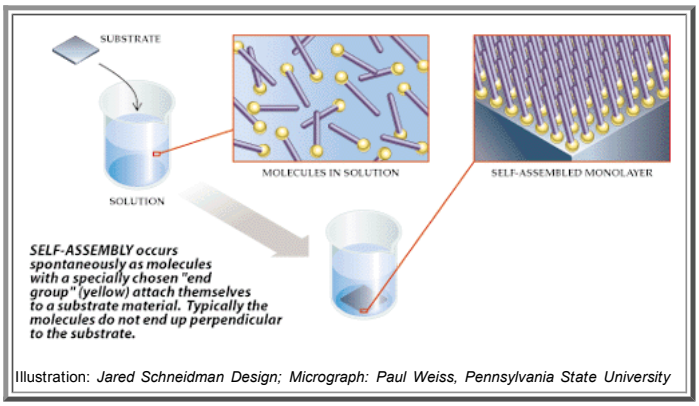


Illustration: *Jared Schneidman Design; Micrograph: Paul Weiss, Pennsylvania State University*

An active device such as a transistor, however, has to do more than merely allow electrons to flow--it has to somehow control that flow. Thus, the task of the molecular device engineer is to exploit the quantum world's discrete energy levels--specifically, by designing molecules whose orbital characteristics achieve the desired kind of electronic control. For example, with the right overlap of orbitals in the molecule, electrons flow. But when the overlap is disturbed--because the molecule has been twisted or its geometry has been otherwise affected--the flow is blocked. In other words, the key to control on the molecular scale is manipulating the number of electrons that are allowed to flow at low orbital energy by perturbing the orbital overlap through the molecule

Already the standard methods of chemical synthesis allow researchers to design and produce molecules with specific atoms, geometries and orbital arrangements. Moreover, enormous quantities of these molecules are created at the same time, all of them absolutely identical and flawless. Such uniformity is extremely difficult and expensive to achieve in other batch-fabrication processes, such as the lithography-based process used to produce the millions of transistors on an integrated circuit.

The methods used to produce molecular devices are the same as those of the pharmaceutical industry. Chemists start with a compound and then gradually transform it by adding prescribed reagents whose molecules are known to bond to others at specific sites. The procedure may take many steps, but gradually the pieces come together to form a new potential molecular device with a desired orbital structure. After the molecules are made, we use analytical technologies such as infrared spectroscopy, nuclear magnetic resonance and mass spectrometry to determine or confirm the structure of the molecules. The various technologies contribute different pieces of information about the molecule, including its molecular weight and the connection point or angle of a certain fragment. By combining the information, we determine the structure after each step as the new molecule is synthesized.

One of our simplest active devices was a molecule based on a string of three benzene rings, in which the orbitals overlapped (were conjugated) throughout. We made the connections between the benzene rings structurally weak, so that slight twists or kinks weakened or strengthened the conjugation of the orbitals. All we needed was a way to control this twisting and we would have a molecular device in which we could control current flow--a switch, in other words.

To the center benzene ring in the molecule, we added $NO_2$ and $NH_2$ groups, projecting outward from the string on opposite sides of the center ring. This asymmetrical configuration left the molecule with a strongly perturbed electron cloud. That asymmetric, perturbed cloud in turn made the molecule very susceptible to distortion by an electric field: applying an electric field to the molecule twisted it. We now had an active device: every time we applied a voltage to the molecule, an electric field was set up that twisted the molecule and blocked current flow. With the voltage removed, the molecule sprang back to its original shape, and the current flowed again. In follow-up experiments, we found that for our infinitesimal device the abruptness of the switching from one state to the other was superior to that of any comparable solid-state device.

Of course, a lot of advanced technology and years of research were necessary before we could even test one of these devices. The basic challenge is reaching into an unfathomably Lilliputian domain in order to contact and interact with a single molecule and bring information about the behavior of that molecule into our macroscopic world.

The task was all but impossible before the invention, in the 1980s, of the scanning tunneling microscope (STM) at IBM's research laboratories in Zurich. The STM gives scientists a window on the atomic world, letting them visualize and manipulate single atoms or molecules. With an atomically sharp tip of metal held precisely over a surface, the topography of the surface is sensed by the minute current of tunneling electrons that flows between the surface and the tip. Rastering the tip back and forth creates a picture of the hills and valleys on the surface.

Although scanning tunneling microscopy is crucial for testing and constructing individual devices, any useful molecular circuit will consist of vast numbers of devices, orderly arranged and securely affixed to a solid structure to keep them from interacting randomly with one another. Progress toward solving this huge challenge has emerged from studies of self-assembly, a phenomenon in which atoms, molecules or groups of molecules arrange themselves spontaneously into regular patterns and even relatively complex systems without intervention from outside.

**Molecular Glue**

Once the assembly process has been set in motion, it proceeds on its own to some desired end [see "Self-Assembling Materials," by George M. Whitesides; Scientific American, September 1995]. In our research we use self-assembly to attach extremely large numbers of molecules to a surface, typically a metal one [see illustration on self-assembly]. When attached, the molecules, which are often elongated in shape, protrude up from the surface, like a vast forest with identical trees spaced out in a perfect array.

Researchers have studied a variety of self-assembly systems. Our work often requires us to attach molecular devices to a metal (usually gold) surface. So we frequently work with a molecular fragment that we attach to one or both ends of our device and that has a high affinity for gold atoms. The specific fragment we commonly use, called a "sticky" end group for obvious reasons, is based on an atom of sulfur and is known in chemical terminology as thiol.

To initiate the self-assembly, we need only dip a gold surface into a beaker. In solution in this container are our molecular devices, each with thiol end groups on both ends. Spontaneously and in unimaginably large numbers, the devices attach themselves to the gold surface.

Handy though it is, self-assembly alone will not suffice to produce useful molecular-computing systems, at least not initially. For some time, we will have to combine self-assembly with fabrication methods, such as photolithography, borrowed from conventional semiconductor manufacturing. In photolithography, light or some other form of electromagnetic radiation is projected through a stencil-like mask to create patterns of metal and semiconductor on the surface of a semiconducting wafer. In our research we use photolithography to generate layers of metal interconnections and also holes in deposited insulating material. In the holes, we create the electrical contacts and selected spots where molecules are constrained to self-assemble. Thus, the final system consists of regions of self-assembled molecules attached by a mazelike network of metal interconnections.

The first successful demonstration of self-assembly in molecular electronics occurred just four years ago, in 1996, when Paul S. Weiss's group at Pennsylvania State University tested self-assembled molecules. One of us (Tour), then at the University of South Carolina, synthesized the devices. Weiss and his colleagues found that by mixing a small amount of a solution of molecules that were designed to have conducting properties with another containing a known inert insulating molecule, they could get a self-assembled layer in which conductive molecules were very sparsely interspersed among nonconductive ones. By positioning the tip of an STM directly over one of the isolated conducting molecules, they could qualitatively measure the conductivity. As expected, it was significantly greater than that of the surrounding molecules. Similar results were also obtained by a group at Purdue University, which tagged the top of the conductive molecules with minute gold particles

At the same time at Yale, one of us (Reed) performed the first quantitative electrical measurements of a single molecule, which was also fabricated by self-assembly. Specifically, Reed and his group measured how much current could flow across a single molecule. The heart of the experimental setup was an STM modified to enable it to position two tips opposite each other with sufficient precision and mechanical stability to contain a single molecule in between [see illustration]. A very simple molecule was used to convey mobile electrons: a single benzene ring with sticky thiol end groups on both ends to contact the metal leads of the STM tips. It turned out that the resistance of the molecule was in the range of tens of millions of ohms.

The Yale researchers also found that the molecule could sustain a current of about 0.2 microampere at five

## The Basics

The inexorable drive to produce smaller devices may leave technologists no choice but to migrate to a new form of electronics in which specially designed individual molecules replace the transistors of today's circuits. That forced migration could come about within the next decade, some researchers believe.

The bare requirements for a general-purpose computer are a switching device (like a transistor), memory and a way of connecting arbitrarily large numbers of the devices and memory elements. So far scientists have managed to produce single-molecule switches and memory elements. The switch, however, had only two terminals. Realistically, to construct complex logic circuits requires a device with more than two terminals, in which, for example, current flow between two is controlled by a third (that is the way transistors work).

Even more imposing, scientists lack a method of connecting huge numbers of the devices. Although no potential solutions to this problem are apparent yet, researchers suspect that radically new architectures and

volts--which meant that the molecule could channel through itself roughly a million million (1012) electrons per second. The number is impressive--all the more so in light of the fact that the electrons can pass through the molecule only in single file (one at a time). The magnitude of the current was far larger than would be expected from simple calculations of the power dissipated in a molecule, leading to the conclusion that the electrons traveled through the molecule without generating heat by interacting or colliding.

needed to exploit molecular devices fully.

These initial observations of conduction in molecules were followed quickly by demonstrations of basic devices. The simplest electronic device is a diode, which can be thought of as a one-way valve for electrons. In 1997, only a year after the first measurements of conduction in molecules, two separate research groups built diodes. At the University of Alabama, Robert M. Metzger's group synthesized a molecule that had an internal energetic lineup of orbitals, which varied depending on the polarity of the voltage applied to it. The lineup of orbitals was analogous to the rungs on a ladder. With the voltage applied in one direction, the lineup corresponded to a ladder propped against a house. In this orientation, it takes considerable effort to climb the ladder. With the opposite voltage polarity, the orbital lineup was analogous to the rungs of a ladder lying flat on the ground, where it can be traversed with little effort.

In the other group at Yale, Chong-Wu Zhou took a slightly different tack. With this molecular diode, the differences in the lineup of the energy levels occurred externally to the molecule, where it contacted the metal. This scheme also worked well and helped to set the stage for the design of more useful and interesting molecular devices and circuits.

**Connecting from the Top Down**

As they began constructing such devices, the Yale group adapted a structure first made by Kristin Ralls and Robert A. Buhrman of Cornell University. The structure contained an extremely minute hole, called a nanopore, in which an "active region" was created by self-assembling a relatively small number of molecular devices in a single layer, or monolayer. In a hole just 30 nanometers wide, approximately 1,000 of the molecular devices were allowed to self-assemble. Evaporating a metal contact onto the top of the self-assembled monolayer ("SAM") completed the device.

After using this configuration to produce and test molecular diodes, the Yale group quickly moved on to more complex devices, namely, switches. A controllable switch of some kind is a minimum requirement for a general-purpose computer. Even more desirable is a switch that can amplify a current, besides merely turning it on and off. Such amplification is necessary to connect vast numbers of the switches, as is required to build complex logic circuits. The silicon transistor fulfills both those requirements, which is why it is one of the great success stories of the 20th century

The molecular equivalent of a transistor that can both switch and amplify current is yet to be discovered. But researchers have taken the first steps along the path by constructing switches, such as the twisting switch described earlier. In fact, Jia Chen, a graduate student in Reed's Yale group, observed impressive switching characteristics, such as an on/off ratio greater than 1,000, as measured by the current flow in the two different states. For comparison, the analogous device in the solid-state world, called a resonant tunneling diode, has an on/off ratio of around 100.

Similar behavior was observed in the U.C.L.A./HP experiments. In their demonstration, they showed that the conductivity of a molecular layer of rotaxanes, molecules that resemble a core with a surrounding barbell, could be predictably interrupted when a high voltage was applied to a junction containing the molecules. At this voltage, the molecules reacted and changed configuration, altering the lineup of orbitals and interrupting the flow of current through the molecule. Combining a series of these junctions, they built a device that performed a simple logic function.

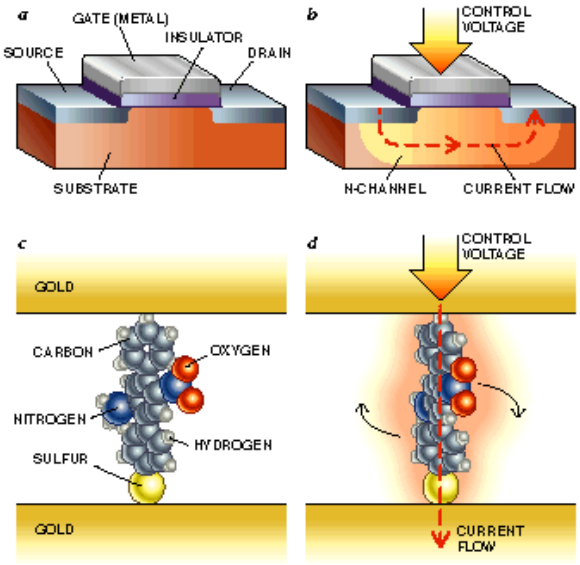
Perhaps most encouragingly, molecular devices have already proved themselves as memory elements. Besides active, transistorlike devices, memory is the other main requirement for a useful, general-purpose computer. Recall our twisting switch. We altered the internal electrically active unit (the lopsided center benzene ring with opposing NO2 and NH2 groups) by keeping just the "electron-sucking" nitro group, NO2. The change made the molecular orbitals susceptible to becoming modified--either spread out or localized depending on the charge state of the internal group. Absence or presence of charge in the internal node would modify the conduction of electrons through the molecule. By storing charge on the nitro group, we blocked the conduction, which represents a binary "0." Conversely, with no charge stored on the group, the conduction was high, representing a binary "1." Significantly, the molecular memory cell retained (or "remembered," if you will) the stored bit for nearly 10 minutes--an astounding amount of time in comparison with an ordinary silicon dynamic random-access memory (DRAM) element, which can hang on to a bit for only a few milliseconds (silicon DRAMs must be frequently refreshed by an external circuit to retain their data). The construction of the memory element, which involved a relatively straightforward modification to the twisting switch, also demonstrated the ease and flexibility in which molecular-scale devices can be redesigned.

Given the enormous potential advantages of molecular devices, why don't we scrap silicon research and proceed wholeheartedly to molecular-based systems? Because despite the recent auspicious advances, a number of significant obstacles, some fundamental, still stand in the way of fabulously complex and powerful circuits.

**Needed: The Next Transistor**

Foremost among them is the challenge of making a molecular device that operates analogously to a transistor. A transistor has three terminals, one of which controls the current flow between the

other two. Effective though it was, our twisting switch had only two terminals, with the current flow controlled by an electrical field. In a field-effect transistor, the type in an integrated circuit, the current is also controlled by an electrical field. But the field is set up when a voltage is applied to the third terminal.




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

Illustration: *Jared Schneidman Design*

A three-terminal molecular device will make possible the chemical synthesis of tremendously efficient and complex circuits. Even before then, combinations of molecular systems with conventional electronics will probably be used in places where the advantages of self-assembly are natural. But interfacing between the molecular and microelectronic worlds will present its own challenges. Computer chips today have two levels of size scale. From the macroscopic level of the chip we can see and hold in our hand, there is a factor of 1,000 in size reduction to get to the gross wiring level, encompassing the largest connections on the chip, which are smaller than a human hair. Then another factor-of-1,000 reduction is necessary to get to the level of the smallest connections and components of the transistors. If molecular devices are to be added to a chip, they will represent yet another factor-of-1,000 reduction in scale down from the smallest microelectronic device components.

Thermal challenges are also staggering, especially if engineers wind up with no alternatives to using molecular devices in modes and configurations similar to those used now with transistors in conventional chips. At present, a state-of-the-art microprocessor with 10 million transistors and a clock cycle of half a gigahertz (half a billion cycles per second) emits almost 100 watts--greater in radiant heat than a range-top cooking surface in the home. Such a unit is close to the thermal limitation of semiconductor technology. Knowing the minimum amount of heat that a single molecular device emits would help put a limit on the number of devices we could put on a chip or substrate of some kind.

This fundamental limit of a molecule, operating at room temperature and at today's speeds, is about 50 picowatts (50 millionths of a millionth of a watt). That figure suggests an upper limit to the number of molecular devices we can closely aggregate: it is roughly 100,000 times more that what we can now do with silicon microtransistors on a chip. Although that may seem like a vast improvement, it is still far below the density that would be possible if we did not have to worry about heat.

For these calculations, we followed the convention in silicon microelectronics that every device is addressable--or, put another way, that any device can be picked out from among the countless millions through the interconnections, like a house with a unique street address. This kind of addressing (which is called random access) would be required, for example, to retrieve the contents of a particular memory location.

Right now no one knows how to create such an interconnect structure on the molecular level. Straightforward extensions of the present techniques we employ to fabricate complex microelectronics are not practical for molecular-scale electronics, because the lithography needed for creating the interconnections to single molecules is far beyond the capability of known technologies. Is the ability to address ever y device, the common architecture we use today, necessary or efficient at molecular-scale densities? What will large-scale circuits of this technology look like? Can we use nanotubes, single-walled structures of carbon with diameters of one or two nanometers and lengths of less than a micron, as the next generation of interconnects between molecular-scale devices?

Decades from now, radical departures from present computing design will probably be needed to exploit molecular computing systems fully if we are to extend electronics significantly beyond Moore's Law. We have only very limited ideas about what these departures might be. The ability

to construct complex molecular devices, with new paradigms and lists of rules about connecting the various devices, will open up an entirely different way to think about computer design.

Although such departures are fraught with problems, we have no alternative but to solve them if electronics is to continue advancing at something like its current pace well into the next century. And difficult though the challenges may be, the rewards for those who solve the problems could be staggering. By pushing Moore's Law past the limits of the tremendously powerful technology we already have, these researchers will take electronics into vast, uncharted terrain. If we can get to that region, we will almost certainly find some wondrous things--maybe even the circuitry that will give rise to our intellectual successor.

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Further Information:

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