

## *UCLAís J. Fraser Stoddart on Switching to Molecular Electronics*



It is not just the world that seems to be getting smaller with each passing year, but also the gadgetry that goes with it. This curve of ever-smaller devices has always had a roadblock sitting at the end of it, at least in the world of computing, which has been delineated by the quasi-law of nature known as Moore's Law. If the number of transistors that can be packed on a computer chip doubles every 18 to 24 months, as Intel co-founder Gordon Moore suggested it did, then the physical limits of how many devices can be packed on a silicon chip will be reached within a decade. This has inevitably raised the question, what is next?

For the past two decades, one promising answer has been the technology known as molecular computing or molecular electronics, in which molecules play the role of silicon semiconductors and the proponents dream of building artificial electronic machines on nanometer scales. The technology has always held enormous potential, although it has also evoked its fair share of skeptics who have inevitably suggested that, so far, the promise and imagination have managed to considerably outdistance the actual accomplishments.

In the 20 years since the concept of molecular electronics was born, the single most influential figure in the field has been the British chemist Fraser Stoddart. In the 1980s, Stoddart identified one of the first highly modular ranges of synthetic molecules that could function as switches, the critical role required by any binary computing scheme. Since then, his influence has been striking. At this writing, Stoddart is ranked <sup>SM</sup> at #3 in the latest *Essential Science Indicators* Web product listing of the [most-cited chemists of the last decade](#), with over 11,000 total citations and an average of almost 40 citations per paper. His 1995 *Chemical Reviews* article, "Interlocked and intertwined structures and superstructures," has racked up almost 700 citations itself (see table below). More recently, a bimonthly update of the Hot Papers database earlier this year featured seven notably cited papers by Stoddart and colleagues published in the last two years.



*"We're now able to proceed from switches to actuators and show how we can produce mechanical motion from chemical reagentsómechanical energy from chemical energy,"* says J. Fraser Stoddart of UCLA.

Photo: Manuello Paganelli

Stoddart, now 63, was born in Edinburgh, Scotland, and undertook his higher education in chemistry at the University of Edinburgh, where he earned a bachelor's degree in 1964, a Ph.D. in 1966, and a Doctor of Science degree in 1980. After a spell as a postdoctoral researcher at Queen's University in Ontario, Canada, he moved back to England in 1970 to start his independent academic career as a lecturer in chemistry at the

University of Sheffield, where he stayed until 1978. He then spent three years working at the Imperial Chemical Industries Corporate Laboratory in Runcorn, before returning to Sheffield. In 1990, Stoddart moved to the University of Birmingham, where he was professor of organic chemistry, until America beckoned. Since 1997, Stoddart has been at the University of California, Los Angeles, where he has held chairs in organic chemistry and, currently, NanoSystems Sciences and where he is director of the California NanoSystems Institute (CNSI).

Professor Stoddart spoke to *Science Watch* from his office at UCLA.



**The story is that the invention of your first molecular switches somehow emerged out of pesticide research. Does that have any truth in it?**

Actually, yes. Back in 1978-81, I was working at Imperial Chemical Industries (ICI). They have a commodity chemical that is sold worldwide as a weed killer, a mixture of two herbicides, Diquat and Paraquat. These herbicides are toxic—they are not only bad news to plants but will also kill people if ingested inadvertently or intentionally. Finding an antidote to this poisoning in people was the rationalization for the work in the beginning. It happens that one of these herbicides, Paraquat, is a somewhat rectangular-shaped molecule. When we saw from solid-state structures its way of nesting inside large ring molecules called crown ethers, it looked like a rod passing through a loop. Once we had that picture in our minds it didn't take much imagination to think that, if we could feed one molecule through another, like a rod through a ring, we could then put big stoppers on both ends of the rod, giving us a mechanically interlocked structure. I knew that although this exotic structure had been much talked about in the chemical literature, it had hardly been studied at all. This abacus-like molecule, composed of a dumbbell-shaped component and a trapped ring component, is called a rotaxane. The other near-relative of it is called a catenane. The simplest catenane is composed of two mechanically interlocked rings, and these molecules enter into the story as well.

We were incredibly lucky, since the herbicidal properties of Diquat and Paraquat are a direct consequence of the fact that they have a rich *redox* chemistry. In essence, they are compounds that you can visit with electrons and then get these electrons back out of them again. First of all, the two compounds both carry two positive charges. So they are amenable to being reduced with electrons. You can put one electron in at one potential, and another one at a higher potential, changing their properties quite considerably. In fact, you can switch off their molecular recognition for crown ethers. By the mid-1980s we knew that we had all the know-how to make mechanically interlocked compounds. We not only had the ability to bring bits and pieces together in a mechanical sense—these rods and rings—but once we'd done that, we had a way of controlling how the pieces move with respect to each other.



**How do you take these molecules and turn them into a switch that can be used in some kind of molecular electronic system?**

The first catenane we made in a staggering 70% yield contained four recognition sites—a pair in each of the rings. With this level of cross-talk between two mechanically interlocked rings we were justified in starting to think about molecular switches. The problem with the first generation of these catenanes and rotaxanes was that, although their components move round and round, and back and forth, between two states, the states are indistinguishable. This situation pertained because we were using simple systems in which the pairs of states are identical. So the challenge then was to tweak these two mechanically interlocked molecules, so that in either one of the two components you have two different states rather

than two identical ones. We first accomplished this goal in the early 1990s. In an article in *Nature* (see table, paper #4) in 1994 we describe a rotaxane where the ring occupies one state 80% of the time at equilibrium, and the other state 20% of the time. At last, we had a switch. It wasn't a perfect switch, but it was a switch nonetheless.



### What was your vision for these molecules, and how has that changed with time?

As we made the move from Sheffield to Birmingham, I realized we were standing at the entrance to a gold mine. It was an incredible time. It was one when it seemed almost like a child could come up with the next idea of what to do for it was almost like playing with toys. Regarding the big picture, however, my vision was already that these molecules could form a basis for molecular computing. I may have overstated the possibilities in terms of time-scale, simply because we were so excited about what we had discovered. Certainly, from around 1991 onward, we felt these two-state catenanes and rotaxanes could become the basis for a new form of switch that would be miniscule in size, and by 1998 we had a switchable catenane that was one cubic nanometer. It is difficult to believe that you could ever go a lot smaller than this with molecules. I'm not saying you can't, but to this day, it remains difficult for me to visualize how it would be done.

We now had a switch that is close to perfect, and we could demonstrate switching in solution. The critics, however, would say, "Okay, you can show that these compounds can switch in solution, but this technology is not going anywhere until you can put the molecules onto surfaces or into interfaces, into bilayers." This is one reason why I've been working with Jim Heath since I came to UCLA (see [Science Watch, 12\[1\]: 3-4, January/February 2001](#)). We'd already perfected the art of self-assembling these two-state molecules at air-water interfaces. Jim showed he was able to take these molecular monolayers and spread them between two electrodes. It is far from being an absolutely defect-free process and never will be, but it works. It certainly doesn't approach anything like the same precision the semiconductor industry relies upon when silicon-based chips are being fabricated. Jim, however, by introducing me to the concept of defect-tolerant computing, put my mind at rest. We very quickly had a wide range of two-state catenanes and rotaxanes that switched very nicely indeed in solid-state devices. The rest has, more or less, been history.



### How does this idea of defect-tolerant computing make up for the presence of the defects?

The point of defect-tolerant computing is that it was opening the door for molecules to come into the game. If you're going to spread molecules onto electrodes, you're going to do so with something less than perfect precision. If you put the molecules down

#### Highly Cited Papers by J. Fraser Stoddart *et al.*, Published Since 1992 (Ranked by total citations)

Rank	Paper	Citations
1	D.B. Amabilino, J.F. Stoddart, " <b>Interlocked and intertwined structures and superstructures</b> ," <i>Chem. Rev.</i> , 95(8): 2725-2828, 1995.	709
2	P.L. Anelli, <i>et al.</i> , " <b>Molecular meccano. 1. [2]rotaxanes and a [2]catenane made to order</b> ," <i>J. Am. Chem. Soc.</i> , 114(1): 193-218, 1992. [ <a href="#">see also</a> ]	497
3	C.P. Collier, <i>et al.</i> , " <b>Electronically configurable molecular-based logic gates</b> ," <i>Science</i> , 285(5426): 391-4, 1999.	466
4	R.A. Bissell, <i>et al.</i> , " <b>A chemically and electrochemically switchable molecular shuttle</b> ," <i>Nature</i> , 369(6476): 133-7,	379

in a monolayer, at best you're going to have some imperfections. If you have 30 molecules in a device, in a little cell, you can compare this to a group of high-school kids. At any one time, there will be two or three who are misbehaving. At the same time, you have to have worthwhile educational activity going on and of course you do, because you can suffer this little bit of misbehaving going on in the background.



**In your papers, you use the term "molecular meccano." What does that mean?**

Molecular meccano simply broadens the whole scope of work from just involving the two-state molecules as switches to using them as assemblies in order to create other types of devices where actuation become the primary goal. Just toward the end of last year, for example, we described a particular variant of our switchable molecules tethered to the surface of micron-sized cantilevers. We then showed that in a purpose-built fluidic cell, we could get the cantilever beams to bend, depending on the redox properties of the chemicals present in the solution. So we're now able to proceed from switches to actuators and show how we can produce mechanical motion from chemical reagents—mechanical energy from chemical energy. What we can do with chemical potential, we can do more cleanly in an electrochemical cell by taking electrical energy and re-expressing it as mechanical motion. We've also made some progress using light to bring about mechanical motion. This opens up a world of very, very small nanoelectromechanical systems or NEMs—that is, artificially made molecular machines that can drive whatever particular actions you might be seeking to bring about.



**Can you give us an example of an application?**

We have just announced in the July 19<sup>th</sup> issue of the *Proceedings of the National Academy of Sciences* the creation of a nanovalve that can be opened and closed at will to trap and release molecules (see T.D. Nguyen, *et al.*, *PNAS*, 102[29], 10029-43, 2005). The nanovalve consists of moving parts in the form of switchable rotaxane molecules attached to a tiny piece of porous glass around 500 nanometers in diameter. The channels in the porous glass are long but only a few nanometers in diameter, just big enough to allow small molecules to enter. These nanovalves which are very much smaller than living cells could be adapted to cross cell membranes and so could potentially be used as highly targeted drug-delivery systems to, for example, cancerous cells in someone's body.



**What will it take to turn all this into a working technology, and one that might be as ubiquitous as silicon chips?**

The rate of technological change in the past half-century has been awesome. Personally, I can reflect how my own life has progressed from one that began on a farm in the lowlands of Scotland in the 1940s and 1950s with horses and carts and without electricity to one where in 2005 we are surrounded by technology in every shape and form that works rather well for the most part. The dramatic growth in information technology, in the wake of the hardware that sustains it, has had a huge impact on our daily lives over the past 25 years. As far as computing is concerned, the silicon-based technology will surely continue on track, according to Moore's Law, for about another decade. Thereafter, what happens is anyone's guess. Of the different options on the horizon, molecular electronics could start to make inroads into the commercial marketplace in conjunction with silicon in a hybrid fashion, possibly in the form of

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- 5 C.P. Collier, *et al.*, "[A \[2\]catenane-based solid state electronically reconfigurable switch](#)," *Science*, 289(5482): 1172-5, 2000. [[see also](#)] [[see also](#)] [[see also](#)] [[see also](#)] [[see also](#)]

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inexpensive memory chips that could be embedded in plastic supports, for example. The economics of the semiconductor industry dictate that the massive investment that has been made in fabrication plants worldwide will continue to dominate the technological arena in the short term. At present, those of us researching in the area of molecular electronics must recognize the need for a lot of fundamental investigations to be carried out well into the future. In the universities, this effort will have the virtue also of producing a new generation of scientists and engineers who will bring a fresh perspective to the field of molecular electronics.

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