

A switch in time

By 2020 the semiconductor industry wants a memory device that can store a trillion bits of information in an area the size of a postage stamp. As companies race towards this goal, chemists are coming up with an unusual approach. **Philip Ball** reports.

It's a new year. But in the labs of Jim Heath and Fraser Stoddart in California, that year is not 2007, it's 2020. They have leapt into the future with a memory device that potentially matches the needs of the semiconductor industry 13 years from now. The array is no bigger than a single white blood cell, yet it contains 160,000 memory elements, each with an area of just 30 nanometres square — some 40 times smaller than those in existing devices.

It's not the first time someone has made a prototype ultrasmall memory that is years ahead of its time. But what distinguishes the device made by Heath, Stoddart and their colleagues is that it stores the zeroes and ones of binary information in the switchable states of organic molecules. The system, described in detail on page 414 (ref. 1), brings the idea of molecular memories a step closer to reality.

Although it may have a very high 'bit density' (the number of memory elements per square centimetre), this super-memory isn't going to appear in a laptop any time soon. The researchers are frank about its current shortcomings, not least of which is that the memory cells stop working after being switched just ten times. "It wouldn't surprise me if we really did have to wait until 2020 to see molecular devices with this bit density actually being used," admits Heath, who is based at the California Institute of Technology in Pasadena.

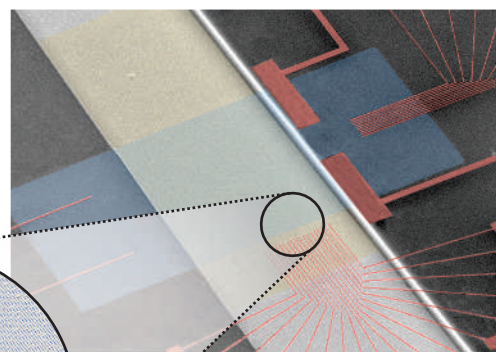
Computer memories have been reaching higher bit densities for decades — but it's becoming ever tougher to keep up with the industry's long-term trends. Today's lithographic techniques for carving silicon into circuit patterns are unlikely to deliver the 2020 target of memory cells just 30 nm or so apart. That's one reason why researchers have begun to think seriously about building memory devices from the bottom up using individual molecules.

Heath and Stoddart's work is a proof-of-concept, showing that molecular memory cells can be made with a bit density of 10^{11} per cm^2 . And it's worth taking seriously, because in terms of miniaturization, the computer companies

know that this density is what they want to achieve by 2020 — although they're still unsure of the best way to do it. There are several possible alternatives on the menu, such as storing data in magnetic or ferroelectric cells or by reversibly altering the atomic structure of thin solid films. Some of these approaches are already well advanced, and the route Heath and Stoddart are offering — a curious hybrid of silicon-based microfabrication and organic chemistry — is widely seen as an outside contender.

But Heath says that their silicon circuit has in itself been enough to catch the eye of the semiconductor industry, even though the molecular switches aren't robust, or fast. Stoddart, an organic chemist at the University of California, Los Angeles, who has been exploring switchable molecules since the 1980s, confirms that the interest from industry is real. The work has emerged from the collaborative California NanoSystems Institute, where Stoddart is the director and Heath was the founding director. The institute received four years of initial funding from many IT companies, including \$7.8 million from Hewlett-Packard, says Stoddart, and now "Intel has bought into it, to the tune of some \$30 million".

But a better memory isn't just about higher bit density. "Chemists tend to focus on one aspect of the problem: size," says Phaedon Avouris of IBM's T. J. Watson Research Center in Yorktown Heights, New York. Although he is also working on molecular devices, made from carbon nanotubes, Avouris stresses that in the end companies such as IBM want something they can make dependably and economically. "The bottom line for devices is always reliabil-



J. HEATH/ETAL

Switched on: this memory array features 160,000 junctions made by overlaying silicon and titanium wires.

ity, performance and ease of fabrication. One does not usually hear any justification for molecular electronics on those grounds. It is always just size."

Easy to forget

Today's dynamic random-access memories (DRAMs), the working memory of most electronic devices, leak charge and must be refreshed thousands of times a second, making them power-hungry and draining batteries. What's more, DRAM loses all information when the power is switched off. So power failures can cause loss of data, and a computer's operating system has to be copied afresh from the hard drive during start-up, resulting in long boot-up times.

Ideally a RAM would be non-volatile, meaning that the data don't evaporate the moment power is cut. Flash memory, used in mobile phones and digital cameras, is a form of non-volatile RAM, but it has drawbacks: writing data is very slow, its switching lifetime is limited to around 100,000 cycles, and the data do leak away eventually. That means flash memory isn't a viable option for computers.

The molecular memory made by Heath and Stoddart isn't truly non-volatile yet — the molecules begin to switch states spontaneously after an hour or so. That may be improved by tinkering with the molecular structure to make the two states more stable. But if they hope to replace DRAM or flash they have some way to go to match other non-volatile memories currently being developed.



"Chemists tend to focus on one aspect of the problem: size."

— Phaedon Avouris

Magnetic RAM (MRAM) holds data magnetically, so no power is needed to sustain it. The electrical resistance of MRAM cells changes when their magnetic orientation is switched. Last July, the company Freescale Semiconductor in Austin, Texas, released the first commercial MRAM non-volatile memory chip, with a capacity of 4 million bits and a switching time of 35 nanoseconds.

The most mature approach is ferroelectric RAM (FeRAM), where the switching involves altering the polarization state of a ferroelectric material². Commercialization of this technology is fairly advanced: Samsung markets a 64-million-bit FeRAM for low-tech applications such as smart cards. There are already prototype memory arrays with cell spacings of 45 nm — the semiconductor industry's 2010 target for DRAM. Moreover, FeRAMs switch very quickly; commercial devices take just a few nanoseconds. The barriers facing wider adoption of FeRAM are now more economic than technical, says Jim Scott, a specialist in ferroelectrics at the University of Cambridge, UK.

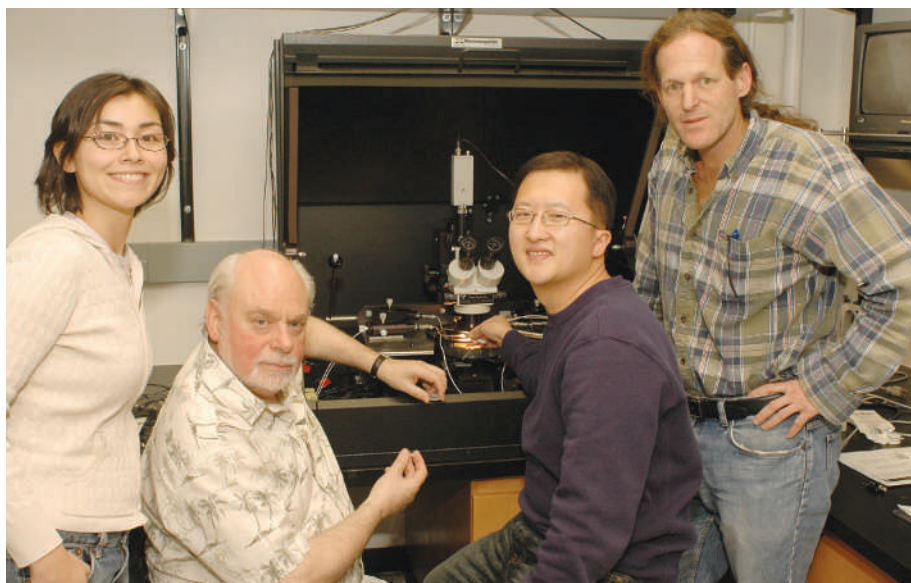
The next phase

Another option for non-volatile RAM is to record data in a 'phase-change material', whose atomic structure can be reversibly altered within a small volume. For example, heating caused by an electric current can partially melt the material, switching it between crystalline and amorphous phases with different electrical conductivity. Commercial 'PRAMs' are already being built by companies such as Samsung and Intel but the bit densities are not much higher than those of today's flash memory.

At the end of last year, IBM researchers unveiled a PRAM device³ based on a single cell measuring just 3 by 20 nanometres and switching in 2–20 nanoseconds. The team is now working on making large arrays of these elements, something that Spike Narayan, at IBM's Almaden Research Center in San Jose, calls "very feasible". He adds, however, that devices this small can't yet be made with the patterning technologies used for commercial chips.

So Heath and his colleagues face some stiff competition. What do they have to offer? Their array is made up of two sets of tiny wires — one of silicon, the other of titanium — arranged in parallel. Each of these wires is just a few tens of nanometres wide — smaller than the circuit components on today's silicon chips, which are more than 100 nm across. The researchers use a method they devised in 2003 that relies on etching ultrathin layered films rather than lithography to produce the sets of wires. To create the memory array, a set of titanium wires is placed at right angles on top of the silicon wires to form a grid with multiple junctions.

It's at these junctions that the switchable molecules, known as rotaxanes, are anchored. The rotaxanes consist of a linear chain-like molecule threaded through a molecular hoop. The hoop 'docks' at either of two sites along the rotaxane chain, and bulky groups of atoms act as



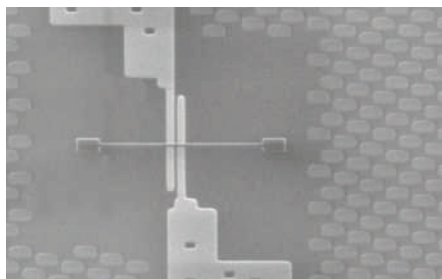
Memory gain: a team including (from left) Bonnie Sheriff, Fraser Stoddart, Jang Wook Choi and Jim Heath has created a high-density memory array that uses organic molecules to store binary data.

'stoppers' at the ends. One of these stopper groups is designed to anchor the molecules to silicon, so that they will readily attach themselves to the nanowires. A few hundred rotaxanes at the junction of two wires can be switched by applying voltages to the wires, changing the electrical conductivity of the junction as the molecules become oxidized or reduced and the hoop jumps between the docking sites.

Wired up

Heath, Stoddart and their colleagues first demonstrated that these memory cells worked in 2002, using an 8 × 8 array. Scaling this up to 400 × 400 nanowires was no easy matter, but their latest memory array has 160,000 junctions, each housing about 100 rotaxane molecules. Wiring up the whole array is challenging, so they have tested a subset of 128 junctions. They found that only half were switchable, and only about half of those gave a sufficiently reliable signal for read-out. In other words, just one in four of the memory elements actually works.

That's not great, but it's not a fatal flaw. Heath and his collaborators have shown that robust memories can be made from defective arrays by using software that finds the 'good' bits and routes around the 'bad' ones⁴. "That isn't so different from magnetic hard-disk memory," says Heath, in which bad sectors are identified so



IBM's prototype phase-change RAM is just a few nanometres big and offers very fast switching.

that those bits aren't used. Stoddart suggests the problem is not that the molecules are failing to switch, but that there are limitations to the nanofabrication — especially etching — which he anticipates will improve.

Harry Atwater of the California Institute of Technology, who is working on new types of flash memory, says that "although the rotaxane switch is a triumph for chemical synthetic technique, as a memory element it is orders of magnitude slower than a DRAM cell". Perhaps even more troubling is that ten switching cycles is enough to damage the molecules irreparably. The researchers haven't yet tried to improve the lifetimes — Heath says that automating the fabrication process is their first priority. But he argues that merely making silicon wiring at this density is impressive, and may be useful for miniaturizing standard silicon circuitry beyond memory devices.

For now, high-density PRAM or FeRAM arrays look more likely to supplant DRAMs. Narayan calls the new molecular memory a very fine piece of work, but adds that its application is likely to be different from other arrays. "Molecular memory and PRAM will ultimately cater to very different markets, and are unlikely to compete directly with each other," he says. Rather than being a replacement for conventional DRAM, rotaxane-based arrays might find applications as cheap, disposable memories — which could still be a huge market. For his part, Heath is confident that applications will be found for a device that "only a few years ago people were calling flat-out ridiculous dreams of science fiction".

Philip Ball is a consultant editor for Nature.

- Green, J. E. *et al.* *Nature* **445**, 414–417 (2007).
- Scott, J. F. & Paz de Araujo, C. A. *Science* **246**, 1400–1405 (1989).
- Chen, Y. C. *et al.* Paper 30.3 presented at IEEE International Electron Devices Meeting (San Francisco, December 2006).
- Heath, J. R., Kuekes, P. J., Snider, G. S. & Williams, R. S. *Science* **280**, 1716–1721 (1998).

REF. 3