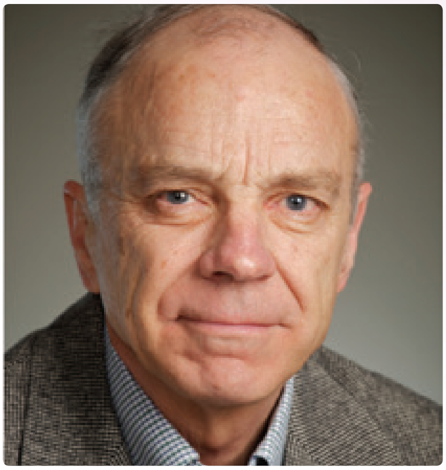
Manufacturing molecular devices

In his study of molecular electronics, **Professor Richard McCreery** collaborates with physicists, chemists and engineers. Here, he describes how molecules can be used to create novel electronic functions, the resultant practical applications, and the first-rate facilities available to his group



Could you describe your professional and academic backgrounds, and how they led you to become Senior Research Officer at the National Institute of Nanotechnology (NINT)?

I earned a PhD in chemistry from the University of Kansas, then took a faculty position at Ohio State University where I conducted research in electrochemistry and spectroscopy until 2006. Our research in 2000-06 involved solid state electronic devices of interest to NINT, so I moved to Canada in 2006 to become a Senior Research Officer at NINT and Professor of Chemistry at the University of Alberta. NINT offered facilities and collaborations that matched our research objectives, and provided an excellent opportunity to further develop our research area.

What are NINT's and your group's objectives?

First, we seek to understand how molecules behave as elements in electronic circuits, and exploit the wide range of molecular structures to achieve novel electronic functions. Second, we wish to demonstrate molecular circuit components in useful electronic devices that are not feasible with conventional semiconductor technology, with potentially lower cost and power consumption.

Could you provide a brief introduction to molecular electronics and the research you are conducting in this field?

Molecular electronics investigates single molecules and collections of molecules inserted into electronic circuits, particularly to enable novel electronic functions that are difficult or impossible with silicon. Molecular electronics is distinguished from the much older field of organic electronics by the distances charge carriers (such as electrons) travel, with molecular electronics involving very short distances of <20 nm, and organic electronics usually having transport distances of >50 nm. For the 'nanoscale' dimensions in molecular electronics, the transport mechanisms are fundamentally different, and may have major advantages in the areas of speed, power consumption, electronic function and cost.

What advantages are afforded by replacing silicon-based technologies with molecular electronics devices? Which sectors in particular could benefit from such advancements?

It is unlikely that molecular electronics will replace silicon, as silicon technology is highly developed and continues to improve. However, areas where molecular electronics might augment silicon, probably in hybrid silicon/molecular circuits, include new functions such as chemical sensing, fast operation in molecular tunnel junctions, and possibly lower power and/or cheaper applications. Our molecular tunnel junction is currently being commercialised as a component in analogue overdrive pedals for electric guitars. The sound resulting from a molecular junction differs fundamentally from that currently derived from silicon diodes, with a richer, more pleasing sound. The same junctions should be capable of very high speed operation, with ballistic transport much faster than the diffusive transport currently operative in silicon microelectronics. In addition, diffusive transport in silicon devices generates heat and consumes power, and these issues could be mitigated by molecular devices based on tunnelling or resonant transport. While 'pure' molecular circuits may be a long way off, hybrid circuits combining silicon and molecular components are possible today.

Does your group provide teaching or educational opportunities?

Our group has the attraction of a large chemistry department with the major additional asset of a national laboratory. NINT has many professional scientists and support staff plus excellent facilities, and students and postdocs work together with this staff to perform experiments that are rare in a traditional chemistry department. NINT is organised more like a corporate research lab than an academic department, so students are exposed to a realistic research environment. The University of Alberta also offers excellent microfabrication, microscopy and surface science facilities to NINT staff and students. Our work is interdisciplinary and problem orientated, with a focus on practical applications.

Enhanced electronics

An interdisciplinary group of researchers at the University of Alberta is developing hybrid electronic devices that incorporate molecules. With a commercially available product due in early 2015, these devices could soon enhance silicon microelectronics on a large scale

AT PRESENT, THE world of electronics is dominated by silicon, used widely in the semiconductor and microelectronics industries. In fact, today silicon is the most popular material used to build both high power semiconductors and integrated circuits. However, these products require the use of high-purity crystalline silicon, and their functions are approaching physical limits in size and heat dissipation. Molecular electronics has the potential to enhance silicon electronics, introducing a variety of novel functions at low cost.

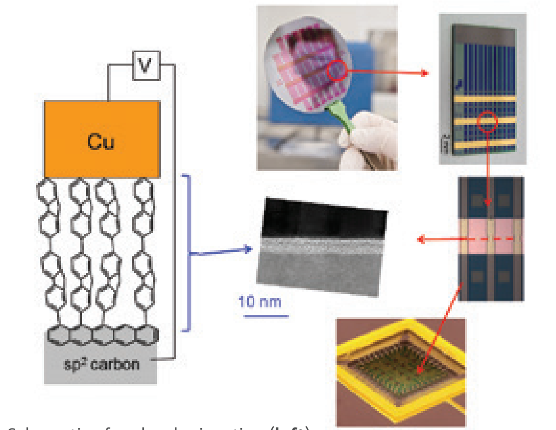
Richard McCreery, Professor of Chemistry at the University of Alberta, is a proponent of this approach and fabricates solid state electronic devices that contain molecules as active components. He has a joint appointment as Senior Research Officer at the National Institute for Nanotechnology (NINT), and leads a research effort at both institutions to investigate molecular electronics devices. By combining conventional semiconductors with novel molecular electronics elements, he plans to bring a new class of hybrid electronics to the market; with new functions, lower power consumption and at affordable prices.

MAKING PROGRESS

For over 40 years, scientists have considered using individual molecules as building blocks in electronic circuits, but experimental roadblocks have prevented practical application. With recent advances in the study of single molecule junctions and methods for bonding molecules to surfaces, this could all be about to change.

Augmenting silicon-based microelectronics with molecular electronics devices has huge potential. It could reduce cost and power consumption and introduce pioneering functions such as chemical sensing, non-volatile memory (computer memory that can retrieve stored information even when not powered) and new interactions with light.

In order to manufacture such devices, McCreery studies the relationship between molecular structure and electronic behaviour. At the heart of this issue is the fundamental process of molecular electronics: the transport of electrons through molecular components. McCreery's group seeks to understand how molecular structure controls transport, and ultimately how molecules behave as circuit elements when connected to metals or semiconductors.



Schematic of molecular junction (**left**), and images obtained with increasingly higher magnification (**right**).

SPECTROSCOPIC STEPS

This work is the product of years of research, based both on carbon electrode surface modification and advances in Raman spectroscopy. McCreery's lab was the first to combine fibre optics, diode lasers and light detectors called charge-coupled devices (CCDs) into a Raman spectrometer, leading to many of the commercial systems we use today. Using this technique, the team was able to obtain spectra of ultrathin molecular layers on carbon surfaces – for the first time without relying on electromagnetic field enhancement from metal nanoparticles. Their vibrational spectroscopy techniques were more sensitive than anything seen before, finding application in solid state electronics, corrosion, and the detection of cancer.

Importantly, their work also facilitated observations of the structural changes taking place in molecular junctions during fabrication and while in operation. Their experience in Raman spectroscopy thus enabled the group to confront one of the major challenges of molecular electronics – characterising the structure of devices containing very thin layers (<20 nanometres) of molecular components, and they produced the only known examples of *in situ* Raman spectroscopy of functioning molecular devices. Combined with novel methods for forming contacts between molecular and conducting carbon substrates, Raman spectroscopy permitted fabrication of the world's first robust, reproducible, large area molecular junctions.

PRACTICAL APPLICATION

In order for molecular electronics to be commercially viable, it must show genuine advantages over silicon. There are many potential benefits, and many applications that would not be possible using silicon, from printable electronics to chemical sensing and affordable diagnostic devices. With a view to bringing these products to market, the McCreery group's approach to device design is to assure the molecular components are 'manufacturable' and tolerant of conditions and temperatures encountered in real-world processing and applications. The primary objective underlying the entire research programme is creating practical molecular electronic devices which are difficult or impossible to replicate with conventional semiconductors.

Although some fabrication techniques used by the team are traditional, their experimental paradigms and device materials are entirely unique. "We use a carbon substrate made by heat treatment of a patterned photoresist polymer layer, to which we bond organic molecules by reducing diazonium reagents," McCreery explains. The carbon-carbon bond that is subsequently formed between the bottom contact and the molecular component is remarkably stable, enabling the team to create devices that have both a wide temperature tolerance and long lifetime. These properties are not only highly desirable for practical applications, but also enable high yield and reproducibility during fabrication. Carbon-based molecular junctions made at NINT with high yield (90-100 per cent) are capable of billions of current voltage cycles, tolerant of wide temperature excursions (-250 °C to +350 °C), compatible with many conventional

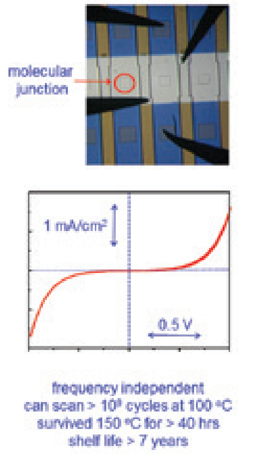
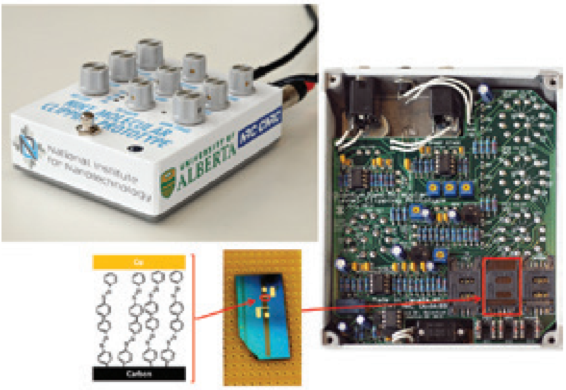


Image of a molecular junction, with its current/voltage response and characteristics.



Prototype analogue distortion circuit containing a molecular junction (**left**) with a photograph of its circuit board, showing the position of a molecular junction on a standard 'SIM' card.

semiconductor processing techniques, and have a >seven-year shelf life.

AUDIO PROCESSING AND MOLECULAR MEMORY

Given the reliable, robust and high yield carbon-based molecular devices, the group is pursuing two commercial applications with attractive performance compared to their silicon counterparts. Analogue distortion circuits are widely used in electronic music to change the harmonic distribution to yield more pleasing or unusual 'sounds'. At least 200 manufacturers worldwide produce a variety of commercial devices, most of which are based on silicon diodes and their nonlinear characteristics. Carbon-based molecular junctions are tunnelling devices rather than pn-junctions, resulting in a fundamentally different physical mechanism and a unique sound in molecular circuits. A prototype system is currently being evaluated by musicians and accessory manufacturers, and commercial release is anticipated in early 2015. A second application on nonvolatile memory devices based on molecular components is also under development; this has a potentially much lower power demand and better life cycle than today's silicon-based 'flash' memory.

PROMISING FUTURE

Capitalising on the success with experimental paradigm, the main goal of McCreery's current research is to investigate electron transport through molecular orbitals in advanced versions of the junction design. Specifically, the team will investigate resonance electron transport, a phenomenon that allows extensive molecular circuits while providing the means to rationally design novel electronic components. Transport in molecular junctions is fundamentally different from the diffusive transport seen in silicon, and in principle is very fast, with a frequency response greatly exceeding today's ubiquitous field effect transistors.

Applying established electrochemical and physical concepts in an innovative environment of an extremely thin solid state molecular layer, McCreery's group is establishing the design rules for the nascent field of molecular electronics. "The audio distortion circuit based on molecular junctions is a niche application, but is important because it uses fundamentally different physics than the silicon alternatives," he adds. "Whatever the commercial success of the analogue distortion circuit, it will establish that molecular electronic devices can be used in practical circuits to perform functions not currently possible with silicon." The tunnelling mechanism which results in the unique sound of a molecular junction is a simple concept in molecular electronics, but is really the tip of the iceberg in terms of what is possible. Given the wide variety of molecules available and a stable, reliable molecular junction paradigm, there should be many more applications of molecular electronics not possible with silicon.

NINT

The National Institute for Nanotechnology (NINT) is a partnership between the National Research Council of Canada (NRC), the University of Alberta and the province of Alberta. It houses around 60 full-time researchers and 150 students, postdocs and fellows, all working together in a 50,000 square foot facility within the University of Alberta. The University has excellent clean room and surface analysis facilities, and NINT has its own clean room with specialised techniques such as atomic layer deposition, nano-imprint lithography, and carbon nanotube synthesis. NINT is a national centre for electron microscopy and surface characterisation, all located in a specialised, low vibration, controlled atmosphere facility.

INTELLIGENCE

MOLECULES IN CIRCUITS: A NEW BREED OF MICROELECTRONICS?

OBJECTIVES

- To understand the relationship between molecular structure and electronic behaviour of solid state molecular electronic devices
- To design and test 'manufacturable' molecular electronics devices with sufficient lifetime and temperature tolerance for practical applications at affordable cost

KEY COLLABORATORS

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FUNDING

Natural Sciences and Engineering Research Council of Canada (NSERC)

Alberta Innovates Technology Futures

National Research Council of Canada

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RICHARD MCCREERY is currently Professor of Chemistry at the University of Alberta, with a joint appointment as a Senior Research Officer at the National Institute for Nanotechnology. Until 2006, he was Dow Professor of Chemistry at The Ohio State University. He received his BS in Chemistry from the University of California, Riverside, in 1970, and PhD under Ralph Adams at the University of Kansas in 1974. His research involves molecular electronics, charge transport in electronic materials, and spectroscopic probes of electrochemical and solid state processes.

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