

Molecular electronics under the microscope

The field of molecular electronics has developed significantly as experimental techniques to study charge transport through single molecules have become more reliable. Three Articles in this issue highlight how chemists can now better understand and control electronic properties at the molecular level.

The improved performance of electronic devices over the past half-century has largely resulted from miniaturization of their 'top-down' manufactured components. However, making current silicon-based technology smaller will eventually reach an unavoidable limit. Where will device manufacturers turn when development stutters and our needs continue to grow? One answer is the 'bottom-up' fabrication of molecular electronic components, and using single molecules would represent the limit of miniaturization.

With this in mind, scientists have been striving to better understand the charge-transport properties of molecules. Many hurdles have been overcome since the initial proposal¹ by Arieh Aviram and Mark Ratner in 1974 that a molecule could act as a rectifier. Ratner later said² that the realization of such a proposal was "somewhere between science fiction and state-of-the-art" and indeed it took until the mid-1990s before the first significant attempts at measuring charge transport through single molecules were reported^{3,4}.

At that time, the main problem in making measurements was creating the electrode–molecule–electrode junction in a reproducible way and handling the inevitable variability in the properties of single molecules. A method to address these issues was developed by Nongjian Tao and Bingqian Xu in 2003 that involves the use of a scanning tunnelling microscope (STM) as an electrically active 'fishing rod' that picks up molecules from the surface of an electrode⁵. The STM tip is brought into contact with molecules on the surface and then gradually moved away. The molecules, which have end-groups capable of covalently bonding to both the electrode and the STM tip, can bridge the two and form electrode–molecule–electrode junctions. The conductance through a junction is measured and the procedure repeated thousands of times. This gives statistically significant results (in the form of histograms) that capture the inherent variability of single-molecule measurements, which in these systems is mostly accounted for by differences in the electrode–molecule contact geometry between experiments.

In this issue we feature three Articles that use this 'STM break junction' (STM-BJ) technique to study the electronic properties

of various conductive molecules, showing how they can be understood and controlled. The Articles are tied together not only by the technique that they use, but also by one of the basic principles of chemistry: that understanding structure–function relationships will eventually enable the design (and ultimately the synthesis) of molecules with improved properties.

The first of these Articles is from Latha Venkataraman, Luis M. Campos and colleagues (page 209). They describe how the nature of charge carriers in single-molecule junctions can be modified within a family of thiophene-1,1-dioxide oligomers simply by changing their length. They find that when the number (n) of thiophene-1,1-dioxide units is one, the molecule is a p-type conductor that transports charge by the movement of holes through its highest occupied molecular orbital (HOMO). When $n = 4$, however, the conduction is n-type, characterized by electron transport through its lowest unoccupied molecular orbital (LUMO). An intermediate regime, one that includes contributions from both the HOMO and LUMO, is seen when $n = 2$ or 3.

Venkataraman is also one of the researchers behind the second Article featured in the issue, this time in collaboration with Colin Nuckolls (page 215). This study highlights that interesting molecular electronic behaviour is not just the preserve of organic molecules and does so by demonstrating that the conductance of a family of oligosilanes can be controlled by squeezing or extending them by less than a quarter of a nanometre. Again they use the STM-BJ technique, but in this case the STM not only takes measurements, but also modifies the properties of the molecule being studied. Somewhat counterintuitively, an increase in conductance is observed as the silane-loaded STM tip is pulled away from the surface. This force-dependent switching behaviour is explained with the help of density functional theory calculations and is thought to arise from stereoelectronic effects. The strain induced by the pulling tip alters the two terminal dihedral angles ($\text{H}_3\text{C}-\text{S}-\text{CH}_2-\text{SiMe}_2$) at the end of each oligosilane molecule, resulting in a switch from one rotamer to another. In one

conformer, the bonds that attach the molecule to the electrodes are perpendicular to the plane of the Si–Si bonds, which means that the electronic coupling between these bonds and the rest of the molecule is low, reducing the overall conductivity. In the more conductive conformer, however, these bonds are better aligned with the Si–Si bonding framework.

In the third of our Articles, Nongjian Tao, Mark Ratner and co-workers explore how the base sequence of DNA can alter its charge-transport properties (page 221). Previous studies⁶ have established that short-range charge transport in DNA can be explained through coherent tunnelling, which is characterized by an exponential increase in resistance with molecular length. However, long-range transport is best explained using a 'hopping' model in which charge hops from redox-active sites that act as stepping stones and in this regime the resistance increases linearly with molecular length. Tao, Ratner and colleagues — again using the STM-BJ technique to measure conductance — observe that in DNA with stacked guanine bases, a periodic oscillation is superimposed on a standard linear length dependence, revealing a situation intermediate between hopping and coherent transport, with characteristics of both. What they see is that the hopping sites are not single bases — as explains their observations in DNA without stacked guanine bases — but rather they are made up of two or three base pairs with delocalized molecular orbitals, which bestow the system with a partially coherent transfer mechanism.

All three Articles show that molecular electronics is a fascinating playground for scientists to investigate how molecular structure affects charge transport. Step-by-step, chemists, physicists and theoreticians are continuing to write the textbook on the fundamental properties of molecules, in the hope that one day soon they can write the manual on how to use them in robust electronic devices. □

References

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