



50 YEARS AGO

The Way Things Are. By Prof. P. W. Bridgman — In this remarkable compilation the author gives us his views, frequently unorthodox, on Marxism, death, integrity, psycho-analysis, taxation, freewill, Red Indian languages, martyrdom, sovereignty, faith, military service, McCarthy, the economic status of the teaching profession, and the illogicality of women. Income tax provokes Prof. Bridgman's indignation as much as anything. "To me the thing that is hardest to bear is the obvious inequity of it all. I do not expect my neighbour to give to me of his goods because I need them more than he does—why should society compel me to give of my goods to society because society needs them more than I do, society being only all my neighbours together? Every time I pay my income tax I smart under a sense of unfairness as keen as that of the old militant suffragette, denied the right to vote merely because of her sex. I feel exploited and discriminated against on the basis of superior ability and industry. It is hard to keep away the bitterness."

From *Nature* 26 December 1959.

100 YEARS AGO

The Revue générale des Sciences of November 30 contains a lengthy and important article by Dr. Louis Wickham on the therapeutic action of radium on cancer ...

The illustrations ... are even more startling than those which have appeared in the English journals cited. The appearances presented before and after treatment are such as will, almost surely, carry conviction to all laymen, whether healthy or suffering from cancer, that radium can cure the disease. But Dr. Wickham does not write in a corresponding spirit of optimism. Indeed, the only note of triumph is the phrase "It is delightful to think that the whole evolution of radiotherapy (the marvellous discovery of radium by P. Curie and Mme. Curie, the construction of perfected apparatus, therapeutical applications) is almost entirely French."

From *Nature* 23 December 1909.

among the core subunits of T4S systems, and it is not evident how multisubunit substrates could gain access to the core's chamber for translocation.

Finally, the diameter of the α -helical pore in the new crystal structure¹ is only 32 Å, a size that could accommodate DNA and unfolded protein substrates, but not a multisubunit protein substrate or, for that matter, the conjugative pilus (80–120 Å in diameter)¹⁴ without inducing gross structural rearrangements.

These and other issues await further study, but in the meantime Waksman and colleagues are to be credited for a quantum leap in our understanding of macromolecular translocation in bacteria. On the structural front, the next task is to resolve even larger subassemblies of T4S systems and, ultimately, the entire translocation machine. Defining how the core complex physically associates with the conjugative pilus will also be a formidable technical challenge, but this is an essential goal if we are to understand the role, if any, of the pilus in substrate transfer. Equally necessary are functional studies to establish that the structures solved *in vitro* exist and have biological activity *in vivo*. Besides stimulating these and other avenues of research, Waksman and colleagues' findings¹ move us a step closer to developing

drugs that target T4S systems, for controlling the spread of antibiotic resistance and mitigating the proliferation of medically important pathogens. ■

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NANOTECHNOLOGY

Molecular transistors scrutinized

James Kushmerick

Transistors have been made from single molecules, where the flow of electrons is controlled by modulating the energy of the molecular orbitals. Insight from such systems could aid the development of future electronic devices.

Transistors, the fundamental elements of integrated circuits, control the flow of current between two electrodes (the source and drain electrodes) by modifying the voltage applied at a third electrode (the gate electrode). As manufacturers compete to produce ever smaller devices, one logical limit to circuit miniaturization is transistors whose channels are defined by a single molecule. The construction and characterization of such a device has been a long-standing goal of nanoelectronics.

In fact, solid-state molecular transistors have already been made, and are based on two mechanisms: Coulomb blockade, in which the flow of electrons is controlled by the sequential charging of a molecule; and the Kondo effect, in which conducting electrons interact with local spin (intrinsic angular momentum) in a molecular junction^{1–4}. A third approach has been predicted⁵, based purely on electrostatic modulation of the molecular-orbital energy of a single molecule. On page 1039 of this issue, Song *et al.*⁶ describe the first practical realization of this approach, and characterize the

resulting devices in unprecedented detail.

Despite various reports^{1–4,7} of single molecules being electrically connected to two electrodes, achieving this feat is a daunting task. Song *et al.*⁶ fabricated their devices by coating gold wires with the molecules of interest, then breaking the wires using a technique called electromigration and thus producing nanometre-scale gaps in the wires (Fig. 1). On occasion, the molecules coating the wire fortuitously become trapped in the gaps. This results in systems of source/drain electrodes — two broken ends of the wire — spanned by the molecules, forming a junction through which electrons can 'tunnel'. One of the benefits of this fabrication method is that the junction can be formed directly over an oxidized-aluminium gate electrode, thus providing the necessary three-terminal geometry of a transistor.

Where Song and colleagues' study excels is in the detailed examination of their molecular junctions. The field of molecular electronics has long been plagued by concerns that the observed current–voltage characteristics

of reported devices are caused by impurities or defects in the systems, rather than by the molecular species under study. Song *et al.*⁶ have avoided such uncertainties by thoroughly characterizing the charge-transport properties of their devices using a combination of spectroscopy techniques *in situ*. In this way, they provide unprecedented insight into the underlying physics of charge transport in their molecular transistors.

The authors used inelastic electron tunnelling (IET) spectroscopy to measure the interactions between the tunnelling electrons and the vibrational modes of the molecules in their devices. This technique provides definitive proof that the measured currents actually pass through the molecules in single-molecule transistors, and yields some information about the pathways taken by electrons as they cross the junctions⁸. The authors tested two types of transistor, each with a different molecule in the junction — either an alkane dithiol (which contains two SH groups connected by a saturated hydrocarbon chain) or an aromatic dithiol (which contains two SH groups connected by a benzene ring). Because each dithiol has its own vibrational ‘fingerprint’, the IET spectra of the devices provide unambiguous evidence of the molecules in the junctions.

The second technique used by Song *et al.* was transition-voltage spectroscopy. Electrons crossing a molecular junction do so using one of two tunnelling mechanisms that depend on the magnitude of the source–drain voltage; the transition voltage (V_{trans}) is the voltage at which tunnelling switches from one mechanism to the other. It has previously been shown⁹ that V_{trans} is proportional to the difference in energy between the gating orbital of the molecular junction (the orbital that modulates electron tunnelling) and the Fermi levels of the source and drain electrodes, where the Fermi level is the highest possible energy for a conducting electron in an electrode. By measuring V_{trans} using transition-voltage spectroscopy at different applied gate voltages, Song *et al.* demonstrated that a linear relationship exists between gate voltage and molecular-orbital energy in their devices, as expected for single-molecule transistors.

The nature of the molecular orbital that couples to the tunnelling electrons (that is, whether or not the orbital is occupied by electrons from the molecule in the junction) can be determined from the change in conductance of the transistor with respect to the applied gate voltage. Song *et al.* found that both of their transistor types become more conducting when a negative gate voltage is applied. Because negative gate voltages lower the energy difference between the highest occupied molecular orbital (HOMO) of the molecular junction and the electrode’s Fermi level, this indicates that, in their device, tunnelling electrons couple to the HOMOs of the molecules.

The authors found further evidence that the current through their device was gated by the HOMO energy of the molecular junction by

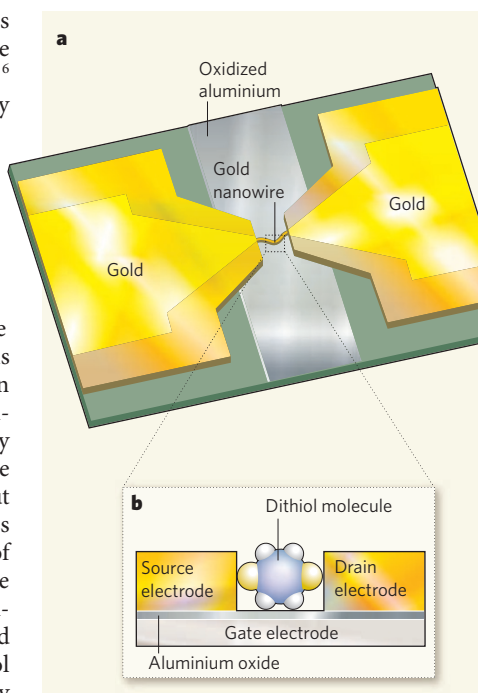


Figure 1 | Single-molecule transistors. Song *et al.*⁶ have made and characterized single-molecule transistors in which current flow is controlled by electrostatically modulating the energy of the molecular orbitals of a single molecule. **a**, Each device consists of a fractured gold nanowire overlaid on a strip of oxidized aluminium. **b**, Side-on, close-up view of a device. The broken ends of the nanowire form the source and drain electrodes of the transistor, and the oxidized aluminium forms the gate electrode. Aluminium oxide on the surface of the gate electrode provides a necessary layer of insulating material known as the gate dielectric. A single molecule (here, an aromatic dithiol) connects the source and drain electrodes. The electric field created by the gate electrode modulates the energies of molecular orbitals in the dithiol, which in turn control the amount of current that flows through the source and drain electrodes. The components of the device are not drawn to scale.

examining the dependence of the IET spectra on the applied gate voltage. The IET spectra of the transistors that incorporate alkane dithiols were essentially unaffected by the gate voltage. This indicates that electron tunnelling through the device is always ‘non-resonant’, that is, there is a large energy difference between the dithiol’s HOMO and the electrode’s Fermi level.

Conversely, Song *et al.* observed that the applied gate voltage strongly modulates the IET spectra of transistors that incorporate an aromatic dithiol. Specifically, when a negative gate voltage is applied (which brings the energy of the molecular junction’s HOMO closer to that of the electrode’s Fermi level), the signal intensities of the spectra increase greatly and the shapes of the vibrational peaks change. The change in peak shape is a clear indication of increased coupling between the tunnelling charge carrier and the molecular vibrations, owing to a resonance between the HOMO and the Fermi

level¹⁰. The authors have thus provided the first experimental demonstration that resonant and non-resonant vibrational coupling can be tuned in single-molecule transistors.

One of the most surprising features of Song and co-workers’ study⁶ is the strong effect of the gate voltage on the molecular-orbital energy of their device. For both dithiols studied, the molecular orbitals shifted in energy by 0.25 electronvolts when 1 volt was applied to the gate electrode, a remarkably strong coupling. It is unclear why the gate coupling should be so strong, but the most likely explanation is that the molecules are extremely close to, or in intimate contact with, the gate dielectric (the oxidized aluminium of the gate electrode). The need for such precise alignment may in part explain why so few of the devices prepared by the authors functioned properly as transistors — only 35 out of 418 were found to have the desired current–voltage characteristics.

Through their multi-spectroscopy approach, Song *et al.*⁶ have provided the first conclusive evidence that a solid-state molecular transistor can function through the relative alignment of its orbital energies with the electrode’s Fermi level, and that this alignment can be efficiently tuned by the applied gate voltage. Their work sets a benchmark for the validation of future studies of charge transport in molecular systems. But much work remains to be done before molecular electronic devices can effectively compete with their larger silicon-based brethren. For example, a fabrication method that provides high yields of densely packed single-molecule devices has yet to be developed. In the meantime, Song and colleagues’ work provides an excellent foundation for further development of well-characterized molecular devices. ■

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Word of the Year

The News & Views WoTY for 2009 is ‘critical’. But this is not an accolade. This devilish little word has an honourable place in the scientific lexicon when bound together with such terms as ‘mass’, ‘angle’ and ‘temperature’. But in an evolutionary battle to convey the sense of ‘having a decisive importance’, it has all but killed off such alternatives as ‘crucial’, ‘vital’, ‘essential’ and ‘necessary’. We can but hope that its spread is halted in 2010.