MOLECULAR ELECTRONICS

Charges feel the heat

The thermoelectric properties of molecular junctions can now be investigated with scanning tunnelling microscopy. Such experiments provide insights into charge transport in single molecules, which is inaccessible to more standard transport techniques.

Hongkun Park
is in the Department of Chemistry and Chemical Biology and the Department of Physics, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, USA.
e-mail: Hongkun_Park@harvard.edu

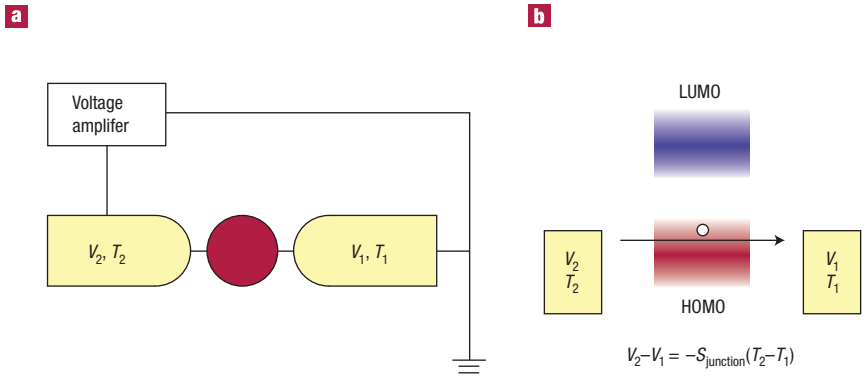

Figure 1 Thermoelectric measurements in a metal–molecule–metal junction. **a**, When the temperature gradient ($\Delta T = T_2 - T_1$) is applied to a metal–molecule–metal junction, heat is carried by the majority charge carrier, giving rise to a thermoelectric voltage ($\Delta V = V_2 - V_1$) that can be detected by a voltage preamplifier. **b**, When the metal Fermi level lies closer to the highest occupied molecular orbital (HOMO) of the molecule as shown in the figure, the heat conduction occurs predominantly by holes (p-type conduction), and the junction Seebeck coefficient ($S_{junction}$) is positive. When the heat conduction is n-type, that is, by electrons moving through the lowest unoccupied molecular orbital (LUMO), $S_{junction}$ is negative. Both the HOMO and LUMO of the molecule are broadened by the molecule–metal coupling.

Molecular charge transport has long been a central problem in chemistry and biology because it underlies every process involving oxidation and reduction of molecular species[1,2]. It is also becoming increasingly important in numerous technological applications, including organic light-emitting diodes, plastic electronics, and energy-conversion devices. Most of our knowledge about charge motion through molecules has been obtained through ensemble measurements such as electrochemistry, bulk transport studies, and spectroscopic investigations. However, ensemble averaging hides many phenomena that occur at the single-molecule level.

Considerable recent work has been devoted to developing techniques for probing charge transport through single molecules[3,4], mirroring earlier efforts in the field of single-molecule optical imaging and spectroscopy[5]. Pramod Reddy and his co-workers have recently reported in *Science* an experimental method that provides new insight into single-molecule charge transport[6]. They used a scanning tunnelling microscope (STM) to investigate thermoelectricity — the voltage generated by a temperature gradient — across a molecular junction.

In principle, studying charge transport through individual molecules should be simple: a single molecule is trapped between two electrodes, and the current (I)–voltage (V) characteristics are measured as a function of various external variables, such as temperature and electric/magnetic fields. Unfortunately, the extremely small size of molecules (typically 0.5–5 nm) makes this conceptually simple task difficult to realize experimentally because the reliable trapping of a single molecule with a reproducible contact geometry is not feasible. STM and micro- and nanolithography techniques have introduced the possibility of experiments on single molecules[3,4]. The great advantage of STM is that the molecule under investigation can be imaged, and I–V measurements can be repeated for many different molecules. There are limitations with this as the experimental geometry does not allow for more sophisticated measurements in which the number of charges in the molecule is varied[4], but such measurements can be performed using planar junctions fabricated by nanolithography[4,7–9]. Reliable trapping of single molecules into planar junctions remains a significant challenge, however, and although the identity of the molecule can be inferred through vibrational 'fingerprinting' in some cases[7,9,10], doubts remain about the reproducibility of measurements on single-molecule charge transport.

Overall, STM and planar junction experiments have provided complementary information. STM measurements have yielded resistance information for various molecules, and planar junction measurements at low temperatures have illustrated the importance of Coulomb interactions in molecular charge transport. However, the two types of measurements cannot be directly compared with each other or synthesized into a coherent understanding. Recent theoretical studies have offered important insights into some of these problems[3,4], but even such simple questions as whether the charge transport occurs via the highest occupied or the lowest unoccupied molecular orbital (HOMO or LUMO) have not been resolved conclusively.

The report by Reddy *et al.* demonstrates that thermoelectric measurements by STM provide a solution to this problem

and enable the determination of the charge-carrier type responsible for molecular conduction (see Fig. 1). Thermoelectricity refers to the appearance of a voltage difference between the opposite sides of a material or a junction when they are at different temperatures. This effect arises because the electrons and holes not only carry electrical charge but also heat, and it is the physical basis behind thermocouple and heat-power conversion devices (such as solid-state heat engines and refrigerators). Inspired by the theoretical work of Paulsson and Datta[11], Reddy and co-workers used STM to measure the voltage drop induced by a temperature gradient across a metal–molecule–metal junction and deduced the junction Seebeck coefficient, $S_{junction}$ (the ratio between the voltage difference and temperature difference across the junction). Their work beautifully demonstrates that $S_{junction}$ can be measured reproducibly all the way down to the single-molecule level. Significantly, the sign of $S_{junction}$ enables the unambiguous determination of the dominant charge-carrier type (holes passing through the HOMO in the case of the benzenedithiol family sandwiched between two gold electrodes), and the magnitude of $S_{junction}$ provides information on the relative position of the HOMO with respect to the metal Fermi level. These insights can be obtained because $S_{junction}$ is an intrinsic property of the metal–molecule–metal junction, yet is often insensitive to the exact details of the molecule–metal coupling. The report by Reddy *et al.* is the first example in which the carrier type and the HOMO position are measured experimentally in a molecular junction. As such, it represents an important development in the study of molecular charge transport. Moreover, the report suggests that a molecular junction could be the basis, not only for molecule-based electronics, but also for thermoelectric energy conversion devices.

Most importantly, the report by Reddy *et al.* demonstrates the need for new experimental techniques to address long-standing problems in molecular charge transport. Indeed, many questions pertinent to this important topic have yet to be tackled. These include the coupling between charge transport and molecular degrees of freedom, the effect of that coupling and of chemical functionality on I–V characteristics, and the understanding of the metal–molecule junction. The thermoelectric measurements reported by Reddy *et al.* add an important new tool for addressing these problems, but more experimental innovations in both fabrication and characterization of molecule-based devices will undoubtedly be required for the field to advance further.

References

1. Bard, A. J. & Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York, 2001).
2. Stryer, L. *Biochemistry* (W. H. Freeman, New York, 1995).
3. Joachim, C. & Ratner, M. A. *Proc. Natl Acad. Sci. USA* **102,** 8801–8808 (2005).
4. Tao, N. J. *Nature Nanotech.* **1,** 173–181 (2006).
5. Moerner, W. E. & Orrit, M. *Science* **283,** 1670–1676 (1999).
6. Reddy, P., Jang, S.-Y., Segalman, R. & Majumdar, A. *Science* **315,** 1568–1571 (2007).
7. Park, H. *et al. Nature* **407,** 57–60 (2000).
8. Kubatkin, S. *et al. Nature* **425,** 698–701 (2003).
9. Dadosh, T. *et al. Nature* **436,** 677–680 (2005).
10. Yu, L. H. *et al. Phys. Rev. Lett.* **93,** 266802 (2004).
11. Paulsson, M. & Datta, S. *Phys. Rev. B* **67,** 241403R (2003).

MATERIAL WITNESS

Proof by construction

It's seldom noted that buildings are one of the most important items on the climate agenda. In 1990, the construction and use of residential, commercial and institutional buildings was responsible for about one-third of global energy use and its associated carbon emissions. In developed nations, buildings account for 40 per cent of total energy consumption and 60 per cent of electricity use. Some projections of energy use in the buildings sector show a doubling between 1990 and 2020; aggressive adoption of energy-efficient technologies could reduce this growth to just 36 per cent.

Much of the focus on making buildings greener has been on energy-efficiency: better insulation, low-energy lighting and so forth. That makes sense, although it is disheartening to see traditional low-energy methods such as wind-catchers and ice cooling in the Middle East being replaced by energy-hungry air-conditioning.

But it is sobering to discover the costs of construction alone in terms of energy and materials. As John Fernández of the Massachusetts Institute of Technology points out in a recent review (*Science* **315,** 1807; 2007), 70 per cent by weight of materials use in developed nations is accounted for by the built environment, and 60 per cent of non-industrial waste comes from construction and demolition of buildings. And get this: 8 per cent of global CO_2 emissions come from concrete production alone.

So there are lots of good reasons to use new materials in buildings: potentially this could cut their energy consumption, reduce waste and increase their lifetimes. Fernández lists many of the attractive solutions that now exist, but he points out that historically materials innovation has been slow in building technology. It took six decades for commercialized PVC to become a construction material, and adoption of the glass-substitute ethylene tetrafluoroethylene has also been slow. Neither of these is perhaps the 'greenest' of materials, but this reticence in the building trade is general.

Why is that? Sometimes advanced materials are just not economical. 'Active' glazing, with electro-, photo- and thermochromic properties, offers low-energy solutions but at often prohibitive cost. The same remains true for organic light-emitting diodes. But one of the main obstacles is that designers and engineers fear the legal liability they face from using materials of unknown lifetime and performance. And neither the client nor the builder wants to pay for testing of unproven materials.

But where there are substantial potential benefits from the introduction of new materials, this seems a most unsatisfactory situation. Is it time for the construction industry to follow the lead of some energy companies in supporting blue-sky innovations that might help the environment?

Of course, sound materials use doesn't need to be high-tech. Large civic buildings are typically expected to last for 120–150 years today, but medieval churches made from stone, wood, metal and glass are still functional centuries later. True, they often need extensive restoration and maintenance; but they show that there is no reason, technical or aesthetic, why we should not sometimes aim to build for eternity.

Philip Ball