

**Figure 2** Signalling events in chemotaxis. On binding chemoattractant, the chemoattractant receptor signals through the G-protein  $\beta\gamma$  subunit to activate PI(3)K $\gamma$ . Activated PI(3)K $\gamma$  generates lipid signals such as PtdIns(3,4,5)P<sub>3</sub>. Proteins with pleckstrin-homology (PH) domains bind the lipid-signalling elements (perhaps under the influence of small GTPases), and activate cellular responses. Such responses include reorganization of the cytoskeleton for lamellipodial extension and cell motion.

lial cells towards platelet-derived growth factor<sup>6</sup> or that of macrophage-like cells towards colony-stimulating factor-1 (ref. 7). Thus it is possible that the PI(3)K signalling pathway is generically involved in directed cell movements.

How might the PI(3)K-derived lipid signals work? Chemotaxis involves an array of responses including cytoskeletal reorganization, modulation of integrin adhesive properties and membrane trafficking. From studies of two model systems, *Dictyostelium* amoebas and neutrophil-like HL-60 cells<sup>4,5,8</sup>, it seems that proteins with phosphoinositide-binding pleckstrin homology (PH) domains are selectively recruited to the leading edge of chemotaxing cells. This polarization is much sharper than the causative chemotactic gradient, and occurs despite the uniform distribution of receptors around the cell periphery. It is not clear how the steep signalling gradient is generated, but it seems likely to involve the production and degradation of phosphoinositides; in this context it is interesting that mice deficient in SHIP (SH2-containing inositol-5-phosphatase), an enzyme that hydrolyses PtdIns(3,4,5)P<sub>3</sub>, suffer from lethal infiltration of the lungs by macrophages and neutrophils<sup>9</sup>. So abnormal persistence of the PtdIns(3,4,5)P<sub>3</sub> signal might lead to excessive inflammation.

Another of the new papers<sup>5</sup> suggests that members of the Rho family of small GTPases, GTP-regulated molecular switches, are involved in the differential recruitment of PH-domain-containing proteins to the cell's leading edge. The Rho GTPases have been implicated in other cell-signalling systems both upstream and downstream of PI(3)Ks,

and mediate the polymerization of actin (the main component of the cytoskeleton). So they might well have a key part in the cooperative signalling events leading to chemotaxis. This possibility is supported by the attenuated chemotactic behaviour of cells derived

from mice in which Rac-2, a member of the Rho family, was knocked out<sup>10</sup>.

Clearly, there is still a long way to go before we have a comprehensive description of chemotaxis. The precise means by which asymmetrical signalling is generated remain unclear. The identity of the lipid signals and indeed their cellular targets have not been convincingly defined, although preliminary evidence implicates protein kinase B (ref. 10) and Bruton's tyrosine kinase<sup>11</sup>, both of which have PH domains. Finally, there is the need to unravel the relationship between this signalling system and others involved in coordinating chemotactic responses, such as those using cyclic adenosine monophosphate and intracellular calcium.

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Molecular electronics

# Pushing electrons around

Mark Ratner

Most of the designs and prototypes for 'molecular electronics' circuits and devices<sup>1</sup> involve an interface between a molecule and a conductive (metal or semiconductor) bulk material. At this interface the discrete electronic structure of the molecule confronts the continuous electronic band structure of the bulk material, or electrode. The interaction between these structures results in a number of striking phenomena, including charge transfer. But building these devices is not easy; there are problems with the energy threshold and stability of currents through the molecules.

On page 166 of this issue Vilan *et al.*<sup>2</sup> show how molecular layers (rather than individual molecules) can control the electrical behaviour of a 'classical' metal–semiconductor device. This work represents a new approach to the use of molecular layers in electronics because the control is achieved without any electron transport through the molecules themselves.

The device that Vilan *et al.*<sup>2</sup> modify is a

tunnel diode — this is a type of diode that relies on electron tunnelling, whereby electrons make use of quantum mechanics to tunnel through a potential barrier that they can't cross classically. (A typical semiconductor diode is a junction through which electrons can only flow in one direction.) In a tunnel diode the electrons can tunnel or pass across the junction only when the voltage is positive. Vilan *et al.* modified their metal–semiconductor diode by adsorbing tartaric acid molecules on to the semiconductor crystal (gallium arsenide, GaAs). The molecules bind very strongly to the crystal surface, producing a single layer on which the metal contact (in this case gold) was gently deposited. A benzene group was also attached to the tartaric acid molecules to which groups with various dipole moments could be added. The authors found that by switching these groups, and therefore changing the dipole moment, they could alter the current flowing through the diode (Fig. 1, overleaf).

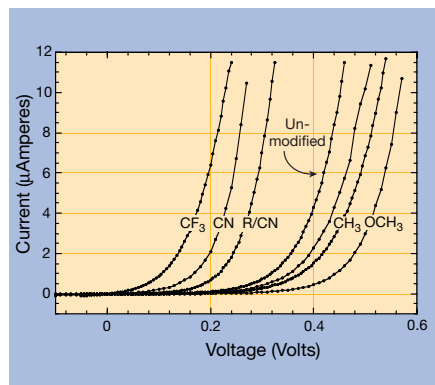


Figure 1 Current–voltage plot for the ‘molecular electronics’ device built by Vilan *et al.*<sup>2</sup>. A characteristic diode junction allows current to flow only when positive voltage is applied. The curves shown here are recorded from metal–semiconductor junctions that are identical except for the group attached to a molecular layer on the semiconductor surface. The groups have either increased or decreased dipole moments compared with the unmodified junction, and the change in current flow through the modified junctions is due to this dipole control.

Interfaces between electrodes and individual molecules are required in ‘molecular wire’ circuits, whose preparation, measurement and modelling are being intensely studied<sup>1,3–11</sup>. The energy properties that dominate such circuits are the effective work function,  $q\phi$ , of the metal and the electron affinity,  $\chi_{sc}$ , of the semiconductor, both of which characterize the transport of charges in these materials. A molecular layer can produce a substantial shift in the values of these parameters from  $q\phi^0$  or  $\chi_{sc}^0$  of the bare electrode. This modification can be understood in several ways, ranging from simple electrostatics to reasonable electronic structure calculations<sup>12</sup>. Qualitatively, much of the change from  $q\phi^0$  or  $\chi_{sc}^0$  to  $q\phi$  or  $\chi_{sc}$  arises from the way in which the molecular dipole distribution at the interface perturbs the potential felt by the electrons in the bulk phase. This perturbation will substantially shift the current–voltage characteristics of a molecular wire circuit<sup>1,3,4</sup> or the voltage dependence of the charge injection in organic light-emitting diodes.

Because the molecular layers can so dramatically alter the surface work function, they can provide a substantial level of control over the electrode properties. Vilan *et al.*<sup>2</sup> show that the tunnelling barrier height for a pure metal–semiconductor junction can be controlled by the molecular dipole layer, so that the net barrier height  $q\phi^b$  for the junction is given by  $q\phi^b = q\phi_{metal}^0 - \chi_{sc} + q\phi_{dipole}$ . The unmodified junction height (without the molecular layer) is given by just the metal and semiconductor terms, as defined previously. The extra term,  $q\phi_{dipole}$ , is the change in barrier height due to the molecular layer. By

changing the molecular dipole moment value and sign, the barrier height can be altered.

Vilan *et al.* demonstrate this control by changing the polarity of the group attached to the molecular layer — from dipoles, such as  $CF_3$  and  $CN$ , that increase  $q\phi_{dipole}$ , to others ( $CH_3$  and  $OCH_3$ ) that reduce it. As the dipole effect changes, so does the net barrier height  $q\phi^b$ . The actual barrier heights were calculated from the current–voltage characteristics of the junctions (Fig. 1), and the value increases linearly by 90 millielectron volts on changing from  $CN$  to  $OCH_3$  (see their Fig. 2 on page 167). What is so striking is that electron transport through the molecules seems to contribute little or nothing to the change in junction properties — the effect is due entirely to the molecular dipoles.

Several recent contributions have shown that molecular layers can modify the surface properties of semiconductors in a significant way<sup>13–15</sup>. The demonstration by Vilan *et al.* that changes in the molecular dipole moment are linearly reflected in changes in the junction barrier is an important advance in the engineering of charge transport at molecular electronics interfaces. In cases where the current is actually carried through the molecule, the change in charge injection properties can alter the conductance by changing the effective state density. This means that states into

which the electrons tunnel become available at altered energies. If the charge is transported through the films by gaps, shorts or direct tunnelling (that is, if the monolayer is not perfect), tuning the molecular dipole layer can, as Vilan *et al.* show, lower or raise the threshold for tunnelling conductivity. Both molecular wire circuits and charge injection in organic devices vary strongly with effective barrier heights; the adsorption of molecular dipole layers apparently offers a general and practical approach to customizing these barriers.

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Entomology

Love is not puffed up

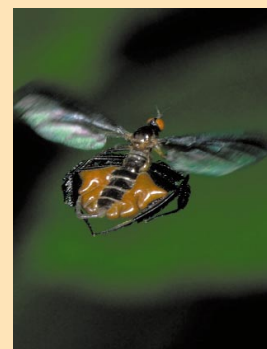
When it comes to picking a mating partner, the females of most species usually get to do the choosing. Sometimes, as in the case of the long-tailed dance fly *Rhamphomyia longicauda*, the roles are reversed. David Funk and Douglas Tallamy show in *Animal Behaviour* (**59**, 411–421; 2000), however, that even here the females seem to be holding all the cards.

Female dance flies cannot hunt for prey for themselves, and instead rely on nuptial gifts presented to them by the males in exchange for mating. This trade-off takes place in female leks, where females gather and wait for the males to bring them food. In contrast to many species, this means that it is the males that get to do the picking. But Funk and Tallamy reveal that the females have evolved a clever way to increase their odds of being chosen.

The males prefer to mate

with females with swollen abdomens. The likely reason is that abdomen size is perceived to be a good indicator of egg maturity — for a related species, *R. sociabilis*, multiple regression analysis revealed a significant relationship between these two variables. Funk and Tallamy propose that, given that males want their sperm to be the ones that fertilize the egg, waiting until the eggs are mature is a good way to ensure that this happens.

But female *R. longicauda* cheat. The females puff up their abdomens (pictured) — probably by ‘swallowing’ air — so creating the impression that their eggs are more mature than they really are. (Multiple regression analysis showed no significant relationship between egg maturity and the size of the inflated abdomen.) But it seems that the males of this species are still fooled. The



males hover beneath the females, and all that they see is the expanded shape of the abdomen. They have no further clues to the actual state of the females’ eggs.

All of this means that females whose eggs are not yet mature can gain the sustenance needed to complete egg development at least once. It seems that, contrary to appearances, it is the females who still retain the upper hand in this mating game.

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