

## ORGANIC SPINTRONICS

# Filtering spins with molecules

Conventional magnetoresistive devices are composed of magnetic and non-magnetic films. It is now shown that, at low temperature, a carbon nanotube decorated with single-molecule magnets can function as an all-organic spin valve.

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Any modern technology, regardless of its complexity, fundamentally relies on a single device concept. The transistor, for instance, underpins information processing, whereas the most recent advances in magnetic data storage have been enabled by the spin valve. The spin valve is essentially a resistor whose resistance can be modified by an external magnetic field. So far, spin valves have been constructed mainly by using magnetic transition-metal alloys and insulators. Now, writing in *Nature Materials*, Urdampilleta and co-workers<sup>1</sup> report that a single-walled carbon nanotube decorated with magnetic molecules can act in just the same way as a conventional spin valve, albeit only at low temperature.

The idea of magnetism affecting the flow of electrons in a material goes back to Mott, who, 75 years ago, proposed that the current in a metal is carried by two spin fluids<sup>2</sup>. These 'fluids' are formed by

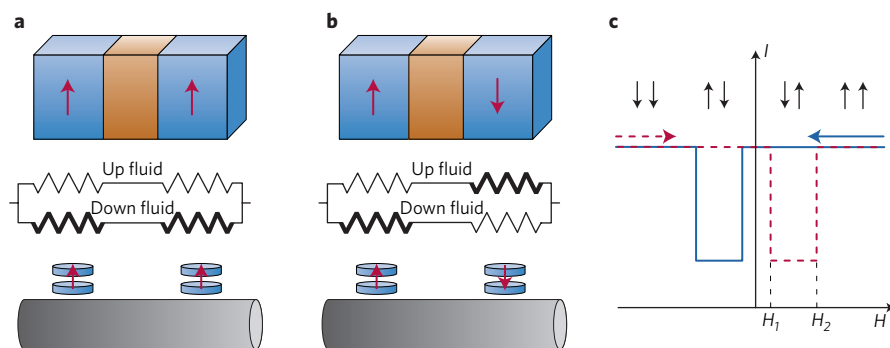
electrons of opposite spins, which flow identically in a normal metal. In a magnet, each of the two fluids experiences a different resistance which depends on the orientation of the electrons' spins with respect to the magnetization. This idea inspired the discovery of the giant magnetoresistance (GMR) effect<sup>3,4</sup> and underpins the functioning mechanism of the spin valve.

In a spin valve two magnets are arranged around a non-magnetic spacer in a sandwich architecture. When the magnetizations of the two magnets are parallel to each other the device resistance is low, but when their alignment is antiparallel the resistance is high. Figure 1 helps in understanding this phenomenon. Let us suppose that the resistance of each of the magnets is low for the fluid in which the electrons' spins point in the direction of the magnetization (the 'up' fluid) and high for the other one (the 'down' fluid). In the parallel configuration the up fluid experiences low resistance

in both magnets, but in the antiparallel case neither of the two fluids encounters a low-resistance path. Accordingly, when an external magnetic field switches the alignment of the magnetizations from parallel to antiparallel the overall device resistance increases. The typical fingerprint of such a mechanism is a 'butterfly' shape in a plot of the device current ( $I$ ) as a function of magnetic field ( $H$ ). In this  $I$ - $H$  plot, abrupt changes in the current coincide with the magnetic field strengths at which the magnetization of one of the two magnets rotates with respect to the other.

In general it takes only a thickness of a few nanometres to create two uneven spin fluids in a magnetic metal, that is, to spin-polarize the electron current. Surprisingly, as the experiment of Urdampilleta and co-workers shows, even a single magnetic molecule can be an efficient spin polarizer when it is gently attached to a carbon nanotube. The molecule of choice is *bis*-phthalocyaninato-terbium(III), a member of the single-molecule-magnets family. The magnetization of these miniature magnets originates from a single ion (in this case  $Tb^{3+}$ ), but their response to an external magnetic field is similar to that of a macroscopic magnet. As such the device constructed by Urdampilleta and co-workers is essentially a spin valve in which molecules replace the metallic magnets. Also in this case, the fingerprint of the spin-valve operation is a butterfly-like shape in the  $I$ - $H$  plot. However, this signature exists only below 1 K, as the magnetization direction of the molecules fluctuates at higher temperatures.

How is it possible for a single molecule to perform as efficiently as 10 nm of iron? The key is the ability of a chemical bond to modify the magnetic properties of a surface, which has been studied under the suggestive name of 'spininterface science'<sup>5</sup>. It has already been shown that an attached molecule can alter the spin-polarization of the electrons emerging from a magnetic surface<sup>6,7</sup>; the experiments of Urdampilleta and co-workers now prove the opposite effect — namely that a magnetic molecule can alter the spin polarization of the current flowing in



**Figure 1** | Working principle of a spin valve. **a,b**, A conventional spin valve is made of two layers of magnetic material that are separated by a non-magnetic spacer (top panels). Depending on the mutual orientation of the magnetizations of the magnetic layers, the device can be in **a**, a low-resistance state (parallel orientation) or **b**, a high-resistance state (antiparallel orientation). In the two-spin-fluids model, the resistance of a magnet depends on whether the electrons' spins point in the same (up fluid) or in the opposite (down fluid) direction to the local magnetization (red arrows). Accordingly, a spin valve can be represented by two resistor circuits (middle panels). The device resistance is small in the parallel orientation (because the up fluid forms a low-resistance state), whereas in the antiparallel configuration both spin fluids encounter high resistance (bold resistor symbols) and the overall resistance is large. In the experiments of Urdampilleta *et al.*<sup>1</sup> two single-molecule magnets take the role of the magnetic layers (lower panels). **c**, The corresponding typical butterfly-shaped plot of the current as a function of applied magnetic field. The low current (high resistance) state corresponds to the antiparallel configuration. Blue and dashed-red arrows indicate the swiping direction of the magnetic field.  $H_1$  and  $H_2$  are the coercive fields of the two magnets in the spin valve.

a non-magnetic material. Two particular features make this possible. First, the magnetic centre must be sufficiently close to the conduction channel. In this respect, the case of *bis*-phthalocyaninato-terbium(III) is rather peculiar, because the  $Tb^{3+}$  ion ( $Tb^{3+}$  carries a total angular momentum,  $J = 6$ ) is sandwiched between two phthalocyanine ligands, and it is at least 1 nm away from the nanotube — too far to transfer any magnetic information. However, there is a second source of spin in this molecule, namely a  $S = 1/2$  radical delocalized over the two phthalocyanine ligands. These are likely to participate in the bond and help to spin-polarize the electron current. Second, the conduction channel must be sufficiently sensitive to the local magnetic moment. All the atoms in a single-walled carbon

nanotube reside on the surface, so that a surface modification results in an alteration of the entire electronic structure. It is an extreme surface sensitivity that makes this spin valve work.

The experiments by Urdampilleta and co-workers are the first demonstration of a fully functional spin device that is entirely made of organic materials at the single-molecule level. Their architecture adds to a number of other devices aiming at exploring spin transport in organics<sup>8</sup>. Indeed, the system is still not ideal for applications. The low operating temperature, the fact that the entire structure is rather fragile and that it cannot be manufactured with high yield, and the difficulties of performing any magnetic characterization beyond a transport measurement, are all obstacles to overcome

in the future. Yet, the demonstrated possibility of manipulating spins with single molecules opens a completely new world to spintronics, where memory, logic and possibly quantum logic may be integrated. □

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## SINK OR SWIM

Some of the best technology is the oldest. Sandbags have been used by armies to stop bullets since the Napoleonic Wars, because the granular medium is very efficient at absorbing the energy of the projectile and dissipating it as friction between grains.

Experiments on the shock-absorbing capabilities of granular materials generally show that a projectile penetrates only to a shallow depth before coming to rest. Military researchers hope to exploit this property in armour that might be considered a sort of ‘advanced sandbag’, with grains tailored for maximal stopping power — for example, arranged as tapered chains of gradually increasing or decreasing grain size, sandwiched between confining plates<sup>1</sup>.

But anyone who studies granular media knows well to take nothing for granted. For instance, they can switch between solid-like and fluid-like behaviour in response to vibration or shearing — a dangerous capability in the case of seismic hazard. Some lizards exploit that duality to actually swim through sand, using an undulatory motion to control the solid–fluid transition<sup>2</sup>.

Even bearing such subtleties in mind, a new observation of projectile motion in a granular medium by Pacheco-Vázquez and colleagues<sup>3</sup> is remarkable. They find that an object penetrating into grains under

gravity can, in some circumstances, acquire a finite terminal velocity — in other words, it never comes to rest, but penetrates to (in theory) an infinite depth.

The researchers demonstrated this experimentally by dropping heavy balls (ping-pong balls filled with small steel spheres) into a deep silo of expanded polystyrene beads a few millimetres in diameter. The beads are packed loosely by first blowing air through them: the packing fraction of 0.637 sounds rather close to the random close-packed fraction of 0.64, but in fact the bed is rather less than close-packed because of the polydispersity of bead sizes.

Balls of lighter mass come to rest within the column of grains, but above a certain mass threshold they sink all the way to the bottom. In the latter case the balls appear to reach a constant speed as they descend. This, Pacheco-Vázquez and colleagues argue, is a genuine terminal velocity.

As counter-intuitive as it might seem, the behaviour is not hard to rationalize. One of the striking properties of granular media is that, below a certain depth, the pressure reaches a constant value — in contrast to the case for ordinary liquids, where pressure continues to increase with depth. This pressure determines the friction experienced by a descending particle, and so it is possible for the drag to balance the downward force



PHILIP BALL

due to gravity, just as with an object falling at terminal velocity in a normal viscous fluid.

However, these situations are not identical. Resistance to the projectile’s motion is caused by the temporary formation of chains of grains in contact. This means that the force of resistance fluctuates, so that descent proceeds in a jerky, stick–slip fashion — as the researchers’ simulations confirm. They end with what sounds like a warning for military sandbag engineers: in certain circumstances, they say, “we believe that self-propelled intruders in static sand may also reach terminal speeds.” □

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