

The approach by Kim and colleagues¹ is based on a completely different mechanism of the local modification of materials using ions. Rather than irradiating a metallic Co–Pd multilayer, which exhibits the required strong perpendicular anisotropy, they targeted a structure in which Co was replaced by its oxide counterpart, Co₃O₄. The as-prepared multilayer stack is thus paramagnetic as is required for the matrix material. Subsequently, they used 300-eV proton irradiation combined with a mask with nanometre-size holes. Rather than changing the order and disorder of the target regions, the irradiation reduced Co₃O₄ locally, and transformed it into metallic and ferromagnetic Co. Detailed X-ray analysis and transmission electron microscopy showed that neither proton irradiation or Co₃O₄ reduction have a

significant impact on the structural quality of the multilayer structure. This is essential for achieving a strong perpendicular anisotropy in the metallic fractions of the sample. Interestingly, the perpendicular anisotropy measured was even stronger than that observed for the as-grown Co–Pd reference sample, which according to Kim and co-workers is due to the contribution of different residual strains in the two cases.

The results from Kim and colleagues represent an important step forward in the field of nanopatterning of magnetic materials, and their method is potentially suitable for the fabrication of high-density storage structures. But the technique might have potential for applications beyond magnetic media. Any hybrid materials system consisting of nanometre-scale,

laterally confined metallic and oxidic regions could be prepared using this method. Potential applications span a broad range from plasmonics and photonic crystals to multiferroics and thermoelectrics. These will probably be the subject of further investigations in the next few years. □

Jürgen Fassbender is at the Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, PO Box 51 01 19, 01314 Dresden, Germany, and the Institute for Physics of Solids, TU Dresden, 01062 Dresden, Germany. e-mail: j.fassbender@hzdr.de

References

1. Kim, S. *et al.* *Nature Nanotech.* **7**, 567–571 (2012).
2. Chappert, C. *et al.* *Science* **280**, 1919–1922 (1998).
3. Fassbender, J. & McCord, J. *J. Magn. Magn. Mater.* **320**, 579–596 (2008).

SINGLE-MOLECULE MAGNETS

Reading a nuclear spin with electrons

A molecular spin transistor can be used to electronically measure the nuclear spin of a single atom.

H. S. J. van der Zant

Non-invasive methods can often provide valuable information about macroscopic systems. For example, plumbers do not always need to take a system of pipes apart to diagnose a problem. They can instead put an ear to a pipe and listen to the sounds produced by the water. Writing in *Nature*, Mario Ruben, Franck Balestro and colleagues show that similar strategies can also be applied on the nanoscale and used to detect the nuclear spin state of a single atom¹. Rather than using sound waves, however, the team use electrons flowing close to the atom to read-out its nuclear spin state and measure the relaxation times on spin-flip excitations. Long nuclear spin lifetimes of around ten seconds are recorded, which illustrates the non-invasive nature of the approach.

To carry out these measurements, the researchers — who are based at Institut Néel, Karlsruhe Institute of Technology, and Institut de Physique et Chimie des Matériaux de Strasbourg — used a device known as a molecular spin transistor^{2,3} (Fig. 1). This is a three-terminal device in which an individual molecule bridges the gap between two closely spaced metal electrodes (the source and drain). The third electrode (the gate) is formed from a strip of gold separated from the source/drain electrodes by an oxide layer and can

be used to change the oxidation state of the molecule.

The nanogaps between the source and drain electrodes in which a molecule is situated are obtained by electromigration, a phenomenon well known in the semiconductor industry where it is mostly seen as an annoyance. However, in nanotechnology, electromigration has become a well-proven technique for producing nanoscale gaps and three-terminal transistors, which are difficult to obtain with other methods. It works by using a high current density (approximately 10^7 A cm⁻²) to move metal atoms until a catastrophic event occurs and a void forms separating electrically continuous regions.

The nuclear spin in the experiments is provided by a single Tb³⁺ ion (a rare-earth metal) sandwiched between two organic phthalocyanine (Pc) units. The properties of these TbPc₂ double-decker molecules have been studied in the bulk and it is known that they behave as single-molecule magnets (SMMs). These are magnetic molecules that exhibit a large spin ground state and magnetic anisotropy. The anisotropy creates an energy barrier that opposes reversal of the molecular spin: at low temperatures spin flip by thermal activation over the barrier is frozen out and only slow relaxation by quantum tunnelling of the magnetization

remains^{4,5}. The molecule can therefore act as a nanoscale magnet, with the spin directed along a preferred axis.

Most SMMs are composed of several *d*-shell transition-metal ions such as Fe and Mn, whose spins are coupled by strong exchange interactions, giving rise to the large effective spin ground state with uniaxial anisotropy. More recent types of SMMs are based on only a single ion (usually a lanthanide with a partially filled *f* shell such as Tb) trapped inside an organic ligand. Quantum effects in these objects are generally more pronounced and they provide better chemical stability. This latter property is crucial in Ruben, Balestro and colleagues' experiment because the TbPc₂ molecules are deposited onto the electrodes before electromigration. The high current densities used during the electromigration process create high temperatures (up to several hundreds of Kelvins), which could disintegrate certain molecules.

To read-out the nuclear spin using an electronic current there must of course be some kind of coupling between the two. In this case, the partially filled *f* shell can provide the strong hyperfine interactions that couple the nuclear spin of the Tb³⁺ ion to the *f* electrons. Then in combination with a coupling mechanism between these *f* electrons and the electrons flowing through

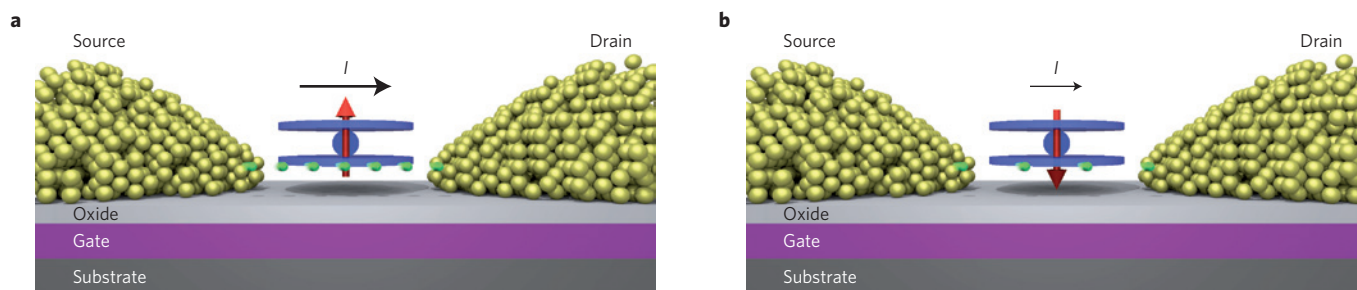


Figure 1 | A schematic of the TbPc₂ spin transistor. **a,b**, Electrons are used to probe the nuclear spin state of the single Tb³⁺ ion (blue sphere), which is sandwiched between two phthalocyanine (Pc) ligands (blue disks). In a magnetic field, quantum tunnelling induces transitions between different spin states (red arrows) and as a result of this spin flip, the current through the Pc ligand changes: the green dots represent the electrons and the size of the black arrows is a measure of the amount of current. When the giant spin reverses its direction, the number of electrons passing through the ligand is altered (smaller black arrow in **b**).

the molecule, access to the nuclear spin should be obtainable. Specifically, Tb has a nuclear spin of 3/2, which splits each of the two $J = \pm 6$ ground states into four different sub-states (with nuclear spin components $-3/2, -1/2, +1/2, +3/2$). When a magnetic field brings the energy levels of these entangled electron–nuclear spin states into resonance, quantum tunnelling between the states occurs leading to a spin flip.

The experiment consists of measuring the differential conductance as a function of the magnetic field. At dilution refrigerator temperatures (0.08 K) small conductance jumps are observed at particular magnetic field values. Using a home-built three-dimensional vector magnet and by quickly sweeping the magnetic field thousands of times, the researchers constructed histograms of the abrupt switching events. Jumps were found to occur at very specific magnetic field values corresponding to the switching fields of the Tb atom magnetic nuclear moment known from bulk TbPc₂ measurements. The proposed mechanism for this electronic read-out relies on current flow through one of the Pc ligands, which through a ferromagnetic exchange

interaction between the electron spin and the Tb³⁺ magnetic moment directly probes its nuclear spin state.

The measurements indicate that the quantum tunnelling switching behaviour of the single molecule is the same as that of a large ensemble of molecules, which have been studied by, for example, superconducting quantum interference device measurements. This result is perhaps unsurprising considering that electrons in f orbitals are usually well isolated from the outside world. On the other hand, the observation is far from trivial as the current itself should have some back-action on the spin-flip processes. Because of the challenges in building molecular spin transistors, little is still known about the properties of individual magnetic molecules wired in devices. More measurements are needed to address this issue.

Nevertheless by recording the conductance as a function of time, the dynamics of the four different nuclear spin states were determined and energy-level lifetimes in the range of tens of seconds found. This is an important result for future quantum information processing

experiments, which benefit from the long energy-level lifetimes and could take advantage of the fact that chemistry can synthesize many copies of the same molecular functional unit. The next step should be to demonstrate quantum manipulation of the single nuclear spin and to perform qubit operations on it. Furthermore, an implementation of the Grover algorithm (an algorithm for searching an unsorted database) has previously been proposed based on a nuclear 3/2 spin⁶. The TbPc₂-SMM spin transistor could be an excellent candidate for realizing this algorithm. □

H. S. J. van der Zant is at the Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628CJ Delft, the Netherlands. e-mail: H.S.J.vanderZant@tudelft.nl

References

1. Vincent, R., Klyatskaya, S., Ruben, M., Wernsdorfer, W. & Balestro, F. *Nature* **488**, 357–360 (2012).
2. Heersche, H. B. *et al. Phys. Rev. Lett.* **96**, 206801 (2006).
3. Jo, M.-H. *et al. Nano Lett.* **6**, 2014–2020 (2006).
4. Friedman, J. R., Sarachik, M. P., Tejada, J. & Ziolo, R. *Phys. Rev. Lett.* **76**, 3830–3833 (1996).
5. Thomas, L. *et al. Nature* **383**, 145–147 (1996).
6. Leuenberger, M. N. & Loss, D. *Phys. Rev. B* **68**, 165317 (2003).