Giant magnetoresistance through a single molecule

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Magnetoresistance is a change in the resistance of a material system caused by an applied magnetic field. Giant magnetoresistance occurs in structures containing ferromagnetic contacts separated by a metallic non-magnetic spacer, and is now the basis of read heads for hard drives and for new forms of random access memory. Using an insulator (for example, a molecular thin film) rather than a metal as the spacer gives rise to tunnelling magnetoresistance, which typically produces a larger change in resistance for a given magnetic field strength, but also yields higher resistances, which are a disadvantage for real device operation. Here, we demonstrate giant magnetoresistance across a single, non-magnetic hydrogen phthalocyanine molecule contacted by the ferromagnetic tip of a scanning tunnelling microscope. We measure the magnetoresistance to be 60% and the conductance to be 0.26 G0, where G0 is the quantum of conductance. Theoretical analysis identifies spin-dependent hybridization of molecular and electrode orbitals as the cause of the large magnetoresistance.

Spin-polarized transport through a single molecule has attracted interest, because it combines the goals of downward size scaling of electronic components (to lower power consumption while increasing speed and density) and increasing computational bandwidth by manipulating spin in addition to charge. The concept of spin electronics5–7 was pioneered with the discovery that the resistance of two ferromagnetic layers separated by a thin non-magnetic spacer may be driven by an external magnetic field or the flow of charge. In the case of a thin metallic spacer, this effect is termed giant magnetoresistance (GMR)3,4, and for ultrathin insulating layers it is called tunnelling magnetoresistance (TMR)5–6. Across thin organic semiconducting layers, transport may occur via tunneling or sequential tunneling, that is, diffusive hopping7,8, demonstrating a magnetoresistance thanks to the low values of spin–orbit coupling, despite the presence of defects in these imperfectly mastered semiconductors9,10.

Spin electronics has led to new generations of read heads in hard disk drives and random access memory, but further progress in downsizing spintronic devices has been challenging. Indeed, although TMR values may dwarf those of their GMR counterparts through a judicious selection of ferromagnets11 and inorganic12,13 or organic13,14 tunnel barriers, downsizing such devices can lead to high resistances9 and shot noise, which are incompatible with high-frequency applications15. Separately, as the device size is reduced, the GMR bias output shrinks below the bias drop of the leads, which in turn requires one to artificially lower the current densities to achieve a high magnetic sensitivity16.

A promising approach to extreme downsizing has been to study electronic single-molecule devices such as diodes17 and transistors18–20. Turning now to molecular spintronics, recent studies have described the spintronic impact of chemisorption of molecules21 onto ferromagnets. This highly conductive interface22 can drive spintronic properties23,24, due in part to ferromagnetic coupling between the transition metal site of the molecule and the ferromagnetic surface21,23,24.

Here, we present a combined experimental and theoretical study on spin-polarized charge transport across a single molecule in the GMR regime that takes advantage of these novel molecular spintronic properties. The junction, built with the help of a scanning tunnelling microscope (STM), consists of two ferromagnetic electrodes bridged by a hydrogen phthalocyanine (H2Pc = C32H30N8) molecule. Our study shows that, due to charge transfer towards the molecule and the hybridization of molecular orbitals near the Fermi level with bulk electronic states of the electrodes, transport across the molecule is nearly resonant in the minority channel with an ultralow areal resistance product. Surprisingly, the molecule can sustain a large current density with substantial spin-polarization, thus validating the concept of nanoscale spintronic devices. Indeed, despite the absence of transition metal sites on the molecule that could contribute to spin filtering, we observe a high differential GMR value of ~60% across the molecular junction, with an areal resistance product of only 70 µΩ µm2. Our ab initio theoretical analysis explicitly identifies this effect as a strong, generic, spin-dependent hybridization mechanism that can also dominate the magnetoresistance in the TMR regime, as was reported phenomenologically8.

Sample characterization

STM25–27 and break-junction28,29 techniques have generally proven to be powerful and versatile tools with which to study the transport properties of single-molecule junctions. In this work, we use magnetic electrodes to measure the magnetoresistance of single molecules using spin-polarized STM (Sp-STM). Experiments were carried out in a home-built STM instrument working in ultra-high vacuum at 4 K (ref. 30) on individual H2Pc molecules sandwiched between cobalt-coated tungsten tips and ferromagnetic cobalt nano-islands on Cu(111) single crystals (see Supplementary Information).

Figure 1a presents the STM topography of the sample. The cobalt nano-islands exhibit a spontaneous out-of-plane magnetization due to a strong interfacial anisotropy31,32. With cobalt-coated tips...
(10 monolayers) showing an out-of-plane magnetization, we can use the sensitivity of the Sp-STM technique to the spin-polarized density of states\(^{25}\) to determine the orientation (parallel or antiparallel) of the magnetization of individual islands relative to that of the tip. Figure 1b shows typical differential conductance (\(dI/dV\)) curves measured on top of cobalt islands of parallel and antiparallel orientation. Particularly large differences in the spectra are found at \(\pm 350\) meV, which corresponds to the surface state of cobalt\(^{34}\). By recording maps of the differential conductance at this bias voltage (Fig. 1a), we can thus identify the spin orientation of the cobalt islands and determine the differential TMR. The latter is defined as the difference in differential conductance (\(dI/dV\)) divided by the smaller differential conductance of the tunnel junction formed by the tip and cobalt island for ensembles of junctions with parallel and antiparallel oriented cobalt islands. As can be seen in Fig. 1c, the differential TMR for such cobalt/vacuum/cobalt junctions is strongly energy-dependent, as reported previously\(^{32}\). Remarkably, the differential TMR reaches only \(\sim 5\%\) at low bias voltage.

**Spin-dependent conductance across a single molecule**

The H\(_2\)Pc molecules that were also deposited adsorb lying flat on the cobalt surface\(^{24}\), and are therefore easily recognized in Fig. 1 by their four aromatic isoindole (BzPy) side groups\(^{35}\). Although the local spin-polarization in the tunnelling regime has been imaged with Sp-STM for phthalocyanine molecules with 3\(d\) metal centres\(^{24,36}\), we here focus on GMR transport measurements across non-magnetic H\(_2\)Pc molecules in the contact regime. To observe the spin-polarization in the tunnelling regime has been imaged with Sp-STM for H\(_2\)Pc molecules, the transition between the flat adsorption and the contact geometry has been ascribed to the 20 meV vibrational bending mode of the aromatic side groups of the H\(_2\)Pc molecule. Note that when voltages higher than this vibrational mode are applied in the contact geometry, the vibration can be excited by the current and the molecular contact becomes unstable (see Supplementary Information).

The conductance after the jump-to-contact encompasses two contributions: the current across the molecule \(G_{\text{mol}}\) and a leakage current \(G_{\text{tun}}\) due to direct tunnelling between the tip and sample\(^{26}\) (Fig. 2c). To obtain a reasonable estimate of the molecular conductance \(G_{\text{mol}}\), we therefore subtract the conductance \(G_{\text{tun}}\) measured before the jump from the conductance \(G_{\text{cont}}\) measured after the jump, that is, \(G_{\text{mol}} = G_{\text{cont}} - G_{\text{tun}}\). Because measurements on two parallel and antiparallel oriented cobalt islands are required, using identical tip conditions, to extract the GMR correctly, we record the traces from two such islands in the same topographic scan. This method notably eliminates possible magnetostriction effects between the two ferromagnetic electrodes, because neither the tip nor the island magnetization need be switched by an external magnetic field.

In the particular measurement at 10 mV in Fig. 2a, we find a conductance of \(G_{\perp} = 0.26G_{\parallel}\) for the parallel and \(G_{\text{AP}} = 0.19G_{\parallel}\) for the antiparallel magnetic configuration in units of \(G_0 = 2e^2/h\). These rather large conductance values underscore a strong hybridization between the electronic levels of the metallic electrodes and those of the molecule\(^{21}\). This is in sharp contrast to the orders of magnitude lower values reported for almost insulating molecular TMR devices\(^{8,33}\) and single-molecule devices based on \(G_0\) (ref. 39).

Each such measurement was repeated several hundred times on the four side groups of about 10 molecules adsorbed onto the two parallel and antiparallel oriented islands, leading to a distribution of the conductances across these parallel-type and antiparallel-type junctions as depicted in Fig. 2d. Compared to previous results\(^{26}\), the width of the resulting conductance distribution is relatively narrow. The broadening and possible structural elements of these distributions could reflect variation in the contact and binding geometries, but also fluctuations in the spin-polarized density of states.
bars indicate statistical errors in the conductance distribution. A Gaussian fit is used to determine the statistical conductance upon further reducing the distance. Transport across the contacted molecule increases as the molecule jumps into contact, and then varies only slightly between the tip and the cobalt surface. This GMR ratio is one order of magnitude larger than the differential TMR ratio found for direct tunnelling across single H$_2$Pc molecules. Surprisingly, this GMR ratio is one order of magnitude larger than the differential TMR ratio found for direct tunnelling on the islands. Gaussian fits were used to determine the average conductances and the GMR from the measurement statistics. We find $G_0 = (0.253 \pm 0.005)G_0$ and $G_{AP} = (0.158 \pm 0.005)G_0$. These values result in an optimistic GMR ratio at $V = 10$ mV of

$$\text{GMR} = \frac{G_0 - G_{AP}}{G_{AP}} = (61 \pm 9)\%$$

Surprisingly, this GMR ratio is one order of magnitude larger than the differential TMR ratio found for direct tunnelling between the tip and the cobalt surface.

Transport calculations
To understand what causes this large value of GMR, we performed transport calculations based on density functional theory (DFT) using the non-equilibrium Green’s function (NEGF) formalism and the TURBOMOLE package (see Supplementary Information). The atomic structure of the molecular junction was found by optimizing the H$_2$Pc geometry on a Co(111) surface that was modelled using a 65-atom cluster. Our analysis suggests that H$_2$Pc adsorbs preferentially in the bridge position onto Co(111) (Fig. 3a), due to a binding energy $\approx 18.7$ eV that is larger than the one found in either the hollow site position ($\approx 8.06$ eV) or the atop site position ($\approx -7.45$ eV), which is consistent with earlier findings.

We have calculated spin-polarized transport in the linear response at low bias voltage for two junction geometries, schematically shown in Fig. 3a,b, corresponding to the TMR and GMR transport regimes (see Supplementary Information). Qualitatively, these calculations (Fig. 3c) reproduce very well our experimental findings (Fig. 2a). We confirm the exponentially increasing conductance in the tunnelling regime, $G_{tun}(d) \propto e^{-d/\beta}$, for which the distance $d$ between the two electrodes is still large. The slope is independent of the relative alignment of electrode magnetizations, and the computational values of $W_{\text{tho}} = 1.87$ Å$^{-1}$ (and the work function $W_{\text{tho}} = 3.24$ eV) are in agreement with experiment ($\beta = 1.9 \pm 0.3$ Å$^{-1}$; $W = 3.2$ eV).

Once contact between the tip and the molecule has been established, the variation of $G_{tun}(d)$ with the contact distance $d$ is very weak, just as observed in the experiment. It is, however, still sensitive to the relative orientation of the magnetization of the electrodes. We find that $G_{tun}(d)$ is always much lower than $G_0(d)$. To quantitatively compare with experiment, we consider the theoretical GMR ratio at the distance $d$ at which the ratio $r = G_{tun}/G_{cont}$ matches the value $r \approx 4$ found experimentally. We thus find that GMR $\approx 65\%$ and is only weakly dependent on $d$.

We now discuss the basic conduction mechanism that underlies the large GMR measured. Pc molecules are characterized by the energetically isolated highest occupied molecular orbital (HOMO) and the nearly doubly degenerate lowest unoccupied molecular orbital (LUMO). We note that the HOMO* levels corresponding to the aromatic group hybridize only very weakly, with almost no amplitude on the bridging nitrogen (N$_b$)$_x$. In contrast, the LUMO states are located on two of the four aromatic groups, with a strong hybridization to all nitrogen atoms forming the inner macrocycle (see Supplementary Information). Because the nitrogen bond to cobalt includes states at the Fermi energy $E_F$, transport should occur via the (quasi-degenerate) LUMO level. We confirm this fact by examining in Fig. 4a the transmission probability per spin direction $T_{\uparrow, \downarrow}(E)$ near the Fermi energy across a parallel oriented junction. We find that, for both spin directions, the transmission probability per spin is exponentially increasing as the tip approaches the molecule, the tunnel barrier width decreases, so the conductance increases exponentially. Below a certain tip-to-surface separation (typically 3–4 Å), the conductance abruptly increases as the molecule jumps into contact, and then varies only slightly upon further reducing the distance. Transport across the contacted molecule reflects both tip-to-surface tunnelling and conductance across the molecule. Histogram of corrected molecular conductances (381 parallel and 366 antiparallel). A Gaussian fit is used to determine the statistical conductance in the parallel and antiparallel configurations, and thus the GMR ratio. Error bars indicate statistical errors in the conductance distribution.

Figure 2 | Current-distance traces and magnetoresistance measured across single H$_2$Pc molecules. a, Typical set of conductance-distance curves measured on top of a H$_2$Pc molecule adsorbed onto parallel and antiparallel magnetized islands with a constant tunnelling voltage of 10 mV ($G_0 = (2\pi e^2/h)$). b, As the tip approaches the molecule, the tunnel barrier width decreases, so the conductance increases exponentially. Below a certain tip-to-surface separation (typically 3–4 Å) the conductance abruptly increases as the molecule jumps into contact, and then varies only slightly upon further reducing the distance. Transport across the contacted molecule reflects both tip-to-surface tunnelling and conductance across the molecule. c, Conductance of H$_2$Pc sandwiched between two parallel or antiparallel aligned Co(111) surfaces in the tunnelling (before contact) and ballistic (after contact) junction geometries.

Figure 3 | Ab initio simulations of current-distance traces and the magnetoresistance effect across a H$_2$Pc molecule. a,b, Contact geometry used in the transport calculation: for a H$_2$Pc molecule adsorbed on the Cobalt island (a), and in simultaneous contact with the tip and the cobalt surface through a lifting of the aromatic group (b). Cobalt sites, grey; hydrogen, white; carbon, green; nitrogen, cyan. c, Conductance of H$_2$Pc sandwiched between two parallel or antiparallel aligned Co(111) surfaces in the tunnelling (before contact) and ballistic (after contact) junction geometries.
The peak width is determined by the amount of hybridization of the molecular LUMO orbital (through N–Co binding) with the states of the cobalt electrodes. Because the surface density of states of the cobalt electrodes at $E_F$ is enhanced for minority spin electrons as compared to majority spin electrons, the LUMO broadening found for a parallel oriented junction is stronger in the minority transport channel than in the majority channel (Fig. 4a). This broadening asymmetry is, of course, less pronounced for an antiparallel oriented junction (Fig. 4b). Note that our experiments operate at low voltage, 10 meV, in the regime where the current response to the bias voltage is still linear. In this regime, the conductance resembles transmission at the Fermi energy.

The dependence of LUMO broadening on a given spin channel and the relative alignment of electrode magnetizations both, in turn, have a direct impact on the GMR obtained across the molecular junction. Indeed, the conductance across a single level of the quasi-degenerate LUMO generically takes on the Breit–Wigner form,

$$G \approx 2 \Gamma_{\text{substrate}}^{\text{tip}}/((E_{\text{LUMO}} - E_F)^2 + (\Gamma_{\text{substrate}} + \Gamma_{\text{tip}})^2)/4.$$  

This expression considers the energy separation between the LUMO and $E_F$, as well as the LUMO broadenings (inverse lifetimes) $\Gamma_{\text{substrate}}$ and $\Gamma_{\text{tip}}$ due to hybridization to the substrate and tip, respectively. Each is, in turn, split into $\Gamma_{\text{min}}$ and $\Gamma_{\text{maj}}$ depending on the spin channel considered. Because transport is off-resonant, that is, $|E_{\text{LUMO}} - E_F| \gg \Gamma_{\text{min}}$, we have $G \approx 2 \Gamma_{\text{min}}/(E_{\text{LUMO}} - E_F)^2$, where $G \approx 4 \Gamma_{\text{min}}/(E_{\text{LUMO}} - E_F)^2$. Introducing the ratio $\rho \approx \Gamma_{\text{min}}/\Gamma_{\text{maj}}$, we thus find

$$\text{GMR} \approx \frac{(\Gamma_{\text{min}} - \Gamma_{\text{maj}})^2}{2 \Gamma_{\text{min}} \Gamma_{\text{maj}}} \approx \frac{(1 - \rho^2)}{2 \rho}.$$  

This simple formula implies two important rules of thumb for spin-polarized transport off-resonance across a molecule. First, the GMR is insensitive to the precise location of the resonance energy provided that $E_F$ lies reasonably within the level broadening. Second, the GMR is mainly indicative of the ratio $\rho$ of minority and majority molecular orbital broadenings due to hybridization. As such, the GMR may reach larger (here order-of-magnitude) values than its TMR counterpart without molecules.

Several papers have recently described means of tuning this spin-polarized broadening of molecular orbitals near $E_F$, and the resulting amplitude/sign of interfacial spin polarization useful for spin injection into organic materials. For instance, Barraud and co-workers invoke disorder to explain, within a phenomenological model, the presence at $E_F$ of a localized molecular state that promotes spin-polarized resonant transport in the tunnelling regime.

Other reports have considered the impact of intrinsic molecular states near $E_F$ on spin polarization. Relative to these reports, our results explicitly reveal the fundamental and applied interest in the direct coupling of two such ferromagnet–molecule interfaces. In this case, the spin selective broadening of the LUMO leads to a highly conductive situation in the parallel configuration with electronic states delocalized across the whole molecule, much like the classical and metallic GMR junctions.

The resulting single-molecule spintronic junction, operating in the contact regime, combines a low resistance (52 kΩ) for high-frequency applications, a low resistance–area product (70 μΩµm²) for increased density, and a large spintronic response (60%) for enhanced data-processing capabilities. This effect should also be present in nanoscale solid-state devices consisting of two ferromagnetic electrodes separated by a monolayer of organic molecules useful for applications.

**Methods**

The Cu(111) crystal was cleaned by several cycles of Ar⁺ sputtering and annealing. The molecules were evaporated in situ from a Knudsen cell heated to ~508 K.
During the deposition process the sample was maintained at 270 K to reduce thermal diffusion of the deposited molecules. dV/dI curves were measured on the bare islands with a lock-in technique. DFT-based transport calculations were carried out with a homemade code building upon the NEGF formalism and the TURBOMOLE package. Our implementation enabled us to perform transport simulations with free boundary conditions, which for the present case were extended to account for the spin-polarized electronic structure of the magnetic electrodes (for further details, see Supplementary Information). The gradient-corrected approximation (GGA) DFT energy was amended by empirical corrections to account for dispersive van der Waals interactions between the molecule and the surface.

Received 22 November 2010; accepted 14 January 2011; published online 20 February 2011

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