Spintronics with single molecules

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Abstract—**We demonstrate that with the help of Scanning Tunneling Microscopy (STM), spintronic functions can be realized with single molecules.**

First, spin transport across single organic molecules was investigated and a molecular giant magnetoresistance (GMR) junction was realized. For this, single phthalocyanine molecules (Pc) were contacted by two ferromagnetic electrodes or by an antiferromagnetic and a ferromagnetic electrode. As substrates, ferromagnetic Co nano-islands grown Cu(111) or anti-ferromagnetic Mn films on Fe(100) were used, onto which the Pc molecules were deposited. The magnetic state of the substrate was determined by spin-polarized STM with Co or Fe tips. Then, the tip of the STM was approached in a controlled way to contact the molecule. Below 0.4 nm distance, an attractive interaction between the tip and the molecule leads to a jump to contact of one of the side groups of the molecule and to a well defined molecular junction. Through the contacted molecule, a GMR of 60% was observed in case of Co substrates and Co tips. In case of Mn surfaces and Fe tips, a negative GMR of -50% was seen. These results are explained on basis of ab initio calculations showing a selective hybridization of the molecular states with states of the electrodes.

Second, we demonstrate that single spin-crossover molecules can be switched between a non-magnetic and a magnetic state reversibly and deterministically by the application of local tunneling currents and that the lifetimes of both states exceed practical measuring times of STM. Thus, we demonstrate a magnetic memory device containing a single magnetic molecule and which can be read and written entirely by electric currents.

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I. INTRODUCTION

Spin electronics is used today mainly in read heads in hard disk drives and random access memory. To increase the information density, the devices need to be scaled down in size which has become challenging in the recent past. Although tunneling magnetoresistance (TMR) devices offer large values of magnetoresistance, the large areal resistance puts a limit to downsizing the devices, as in these the current through the devices becomes too small and a fast read out is hampered [1]. In contrary to that, current perpendicular to the plane GMR junction show a very low areal resistance, such that devices using this principle suffer from comparably large lead resistances reducing the overall magnetoresistance of the complete device [2]. A promising approach to extreme downsizing is to form a single molecular contact between the two magnetic electrodes of a GMR junction.

An even more promising molecular class are spin-crossover (SCO) complexes containing a transition metal ion that can be switched between a low-spin (LS) and a high-spin (HS) state by external stimulus as temperature, light, pressure, magnetic or electric fields or charge flow [3-5]. The two configurations may lead to different conductances but, more importantly, their switchable spin of the metal ion has a high potential for magnetic storage within individual molecules [6].

In this work, we will address all these functions using low temperature scanning tunneling microscopy (STM) [7] to realize and characterize molecular functions down to the individual molecule.

II. GIANT MAGNETORESISTANCE ACROSS SINGLE MOLECULES

A. Contacting single phthalocyanine molecules with an STM

Recently phthalocyanine molecules attracted interest with regard to their electronic properties on different metal substrates [8]. The behavior of this group of molecules on magnetic (Co) and non-magnetic (Cu) surfaces were investigated. Figure 1a displays the chemical structure of a phthalocyanine molecule. These molecules are used to bind metal cations in the center, and by incorporation of different metals their properties can be changed. In our experiments hydrogen (H_2Pc) and cobalt phthalocyanine (CoPc) were studied. As substrate we use the (111) surface of a copper single crystal, which was cleaned by cycles of Ar-sputtering and annealing. The molecules were sublimed from a

Knudsen cell at 550 K. Additional experiments were carried out on substrates, where a sub-monolayer amount of Co was deposited on Cu(111) leading to the formation of double layer islands of Co [9].

Topographic measurements show that both H_2Pc and CoPc are adsorbed flat and as single molecules when only a small amount is deposited (see Fig. 1b). In both cases a non-magnetic tungsten tip was used for imaging.
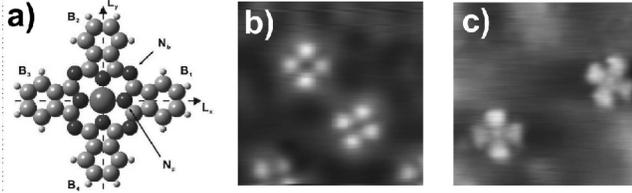
Fig. 1. a) Model of cobalt phthalocyanine. The molecule consists of four benzopyrrol units (B_1-B_4), which are connected by nitrogen bonds (N_b). In its center the cobalt cation is surrounded by the nitrogen atoms of the pyrrol (N_p) and a metal organic complex is formed. Topographic image of b) H_2Pc on Cu (8 nm x 8 nm) , c) CoPc on Cu (6 nm x 6 nm). In all cases one can see the single molecules and four lobes from the benzol rings. H_2Pc shows an empty space in the middle while CoPc displays a protrusion.

To study the transport properties of the molecules distance curves were recorded, in which the tunneling current I was measured as function of the distance between tip and sample at constant sample bias V. The distance curves are measured in the following way. After detecting a molecule, the STM tip was moved atop of it at a low voltage (typically 10 mV). Then the feedback loop of the STM was switched off. By ramping the voltage on the z-piezo, the tip was approached towards the surface in a controlled way. Afterwards, the tip was retracted back to the initial position and another approach was begun. The tunneling current was recorded during the approach phase.

In Fig. 2 we present the results for H_2Pc on copper. On the bare Cu(111) an exponential increase of the tunneling current with approaching of the tip is found. This reflects the
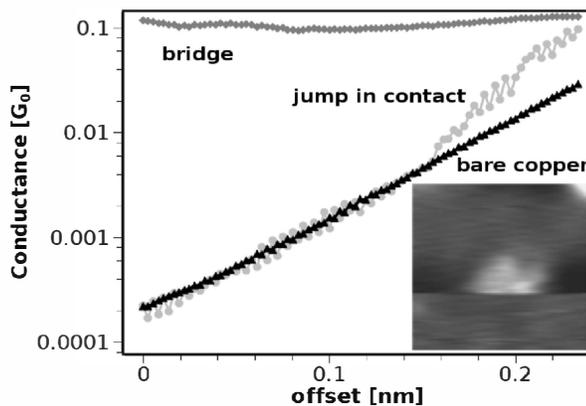
Fig. 2. Distance curves for H_2Pc on bare copper. The black triangles show the measurements on bare copper. One can see the perfect exponential behavior, which is expected for tunneling currents. The light gray circles are measured during the first approach, where an super-exponential increase to a saturation current is observable. The dark grey diamonds show a nearly constant current. In the inset one can see in the topographic image (5 nm x 5 nm) that the molecule has disappeared after the distance curves were recorded. $G_0=2e/h$.

reduction of the tunneling barrier width. The current recorded upon approaching the molecule, however, rises faster. The super-exponential behavior can be explained by a partial lifting of the molecule due to the close proximity of the tip. Ultimately, the molecule jumps into contact with the tip and bridges the tunneling junction [10]. The bond which is formed remains intact after retracting the tip. This can be observed in the nearly constant current for the following distance curves. In this bridge position of the molecule, a relatively high conductance of 0.1 G_0 was observed, which most likely reflects the conductance via the delocalized π-orbitals of the molecule. When the topographic scan is continued (see insert of Fig. 2), the molecule disappears. The molecule was transferred to the tip. This can be explained by the phthalocyanine forming a more stable bond to the W tip than to the copper surface. Similar results with identical conductances have been achieved for CoPc on Cu.

Measurements of H_2Pc and CoPc on the Co islands show a similar jump into contact behavior like on Cu. In contrast to the experiments on Cu the subsequent distance curves measured on Co start at the original current set point. This means that the molecule-tip bond that establishes during the jump to contact is broken again when retracting the tip. In agreement to that, the molecule is also seen in the following topographic scan. We conclude that the bond of the molecule to cobalt island is stronger than to the W tip. Interestingly, also the conduction in the bridged position is with about 0.3 G_0 higher than that in the Cu case. This holds for both CoPc and H_2Pc. This finding can be explained by the different adsorption mechanism. While on Cu(111) the molecules are only physisorbed, on Co(111) they are chemisorbed. The charge transfer in the latter case leads to a shift of the lowest occupied molecular orbital (LUMO) to the Fermi energy thus leading to resonance transport. This mechanism also explains the stronger binding of the molecule to Co in respect to Cu [10,11].

B. Spin transport across H_2Pc molecules

By using Co coated tips STM becomes sensitive to the spin. To detect the direction of magnetization of individual Co islands on Cu(111), dI/dV curves were measured on the bare islands with the lock-in technique. The differential conductivity is proportional to the local density of states (LDOS) within the Tersoff-Hamann model. Especially at surface states or bulk band edges appearing as peaks in the dI/dV spectrum the LDOS is highly spin-polarized. As a result the dI/dV recorded with spin-polarized tips shows a dependence of the peak intensities on the relative orientation of the sample and tip magnetization. Figure 3b shows the dI/dV curves for two different islands, one magnetized parallel the other antiparallel to the tip. Particularly large differences in the spectra are found at -350 meV stemming from the surface state of Co [9]. This difference is used to detect the local magnetization direction of Co islands by

recording maps of the local differential conductivity at this voltage. The brightness of Figure 3a represents this local differential conductivity, indicating areas magnetized parallel in bright and antiparallel to the tip in dark. The tunneling magneto resistance (TMR) defined as the difference of conductivity over the smaller conductivity of the tunneling junction formed by the tip and sample is strongly energy dependent as depicted in Fig. 3c. Note that at small bias the TMR is only of the order of 5%.
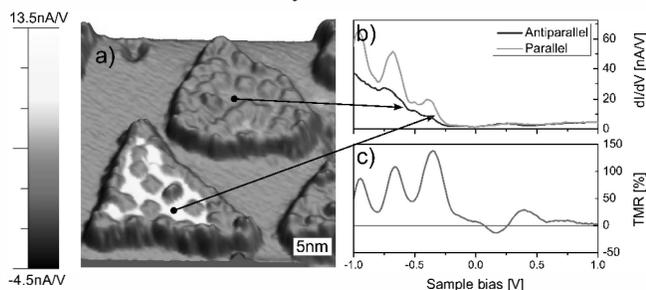
Fig. 3. a) Topographic image of two Co islands on the Cu(111) surface. The brightness indicates the measured *dI/dV* signal at -310 mV. On can distinguish between parallel (bright) and antiparallel (dark) magnetization of the islands with respect to the tip. b) shows the *dI/dV* spectra taken on two oppositely magnetized islands. In c) the TMR ratio calculated from the *dI/dV* spectra is plotted. The highest value is measured at around -350 meV. This is used to distinguish between the two differently magnetized islands.

To perform spin transport measurements across single molecules, we positioned the magnetic tip above a molecule at the aromatic side groups, opened the feed-back loop, and approached the tip towards the molecule as before. The current after the jump only depends slightly on the distance and represents the conductance of the molecule. This conductance in contact depends on the relative orientation of the magnetization of tip and sample (see Fig. 4). For the parallel case the conductance is found to be around 0.30 G_0 while in the antiparallel case it is smaller (0.17 G_0).
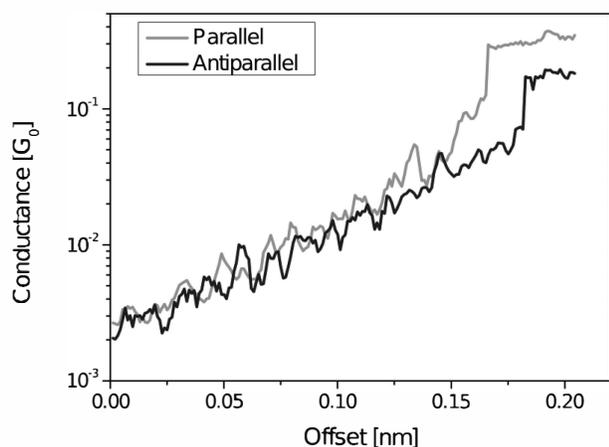
Fig. 4. Two typical single conductance distance curves measured at two contrariwise magnetized islands with a constant tunneling voltage of 10 mV. Below a certain tip-surface separation the curves shows a jump of the conductance to higher values. This can be identified by a jump of the molecules into contact. After the jump there are two contributions to the transport.

To ensure measurements with the same tip, the data on

two Co islands with opposite perpendicular magnetization were recorded in the same scan. This measurement has been repeated several hundred times and the distribution of the observed molecular conductance is depicted in Figure 5a. The observed scatter of the conductance, be it due to noise of the current measurement or to slightly different binding geometries of the molecule to the tip, is not negligible. Nevertheless, one can clearly see the difference between the two magnetization directions. A lower tendency is observed for the anti parallel measurement. To determine the GMR from the statistical measurements Gaussian fits were used. In the parallel case we measured an averaged conductance value of $G_p=(0.253\pm0.005)\ G_0$ and in the anti parallel case $G_{ap}=(0.148\pm0.005)\ G_0$. These values result in an optimistic GMR ratio of 61%. This is one order of magnitude larger than the TMR for direct tunneling. This can be explained by the fact that the molecular states couple to specific highly spin polarized Co minority states. In the parallel case, the electron wave function in the minority channel extends over the whole junction causing a high conductance (see Fig. 5b). In the antiparallel case, the wave functions of both spin channels only extend over the molecule and one of the electrodes leading to a low conductance [11].
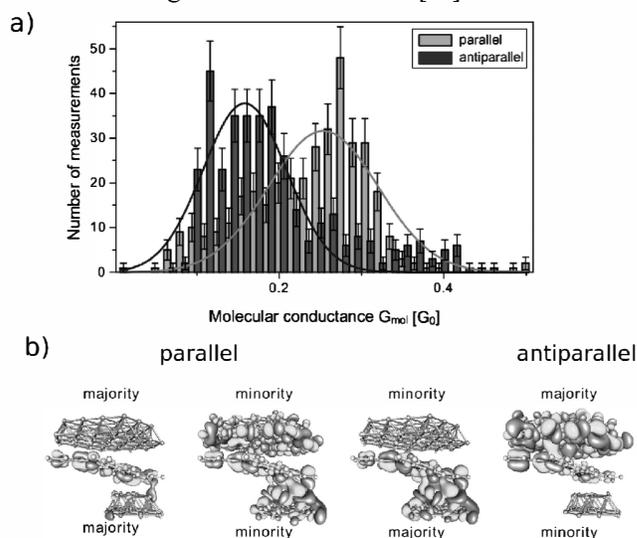
Fig. 5. a) Histogram of the molecular conductances (381 times parallel and 366 times antiparallel). A Gaussian fit is used to determine the conductance and calculate the GMR ratio. b) Calculated electron wave functions for parallel and antiparallel oriented magnetizations for the two spin channels.

Similar GMR experiments have been carried out for H_2Pc on Mn films grown on Fe(100) contacted with Fe-coated tips. In this case, the bottom electrode is antiferromagnetic. As the hybridization of the molecular states with the substrate is only local, this configuration still leads to well defined spin of the bottom electrode and as a consequence to a GMR. As will be shown elsewhere [12], the GMR is negative in this case but of large size (50%). The use of antiferromagnets as one of the electrodes has the advantage, that the antiferromagnet is the ideal hard magnetic layer thus simplifying the structure of a GMR sensor.

III. SWITCHING INDIVIDUAL SPIN-CROSSOVER MOLECULES

Molecular spintronic devices may also be based on spins located within the molecule. As the directions of these spins are usually unstable even at cryogenic temperatures, information cannot be stored in the direction of the spin. Spin-crossover (SCO) molecules show relatively stable spin configurations which differ in the size of the magnetic moment. These are much more promising for storing magnetic information in individual molecules.
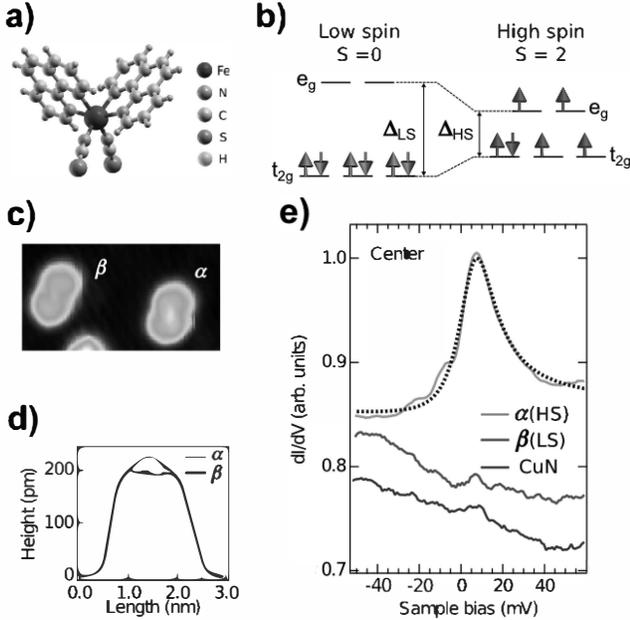
Fig. 6. a) Three dimensional model of an Fe-phen molecule. b) Simplified electronic configuration of the Fe(II)-3d states in the ligand field. c) STM image of isolated Fe-phen molecules on the CuN/Cu(100) surface and d) line scans across the long axis of the molecules. e) dI/dV spectra taken on the center of the Fe-phen molecules.

As a prototypical SCO complex, Fe(1,10-phenanthroline)$_2$(NCS)$_2$ (Fe-phen) molecules (see Fig. 6a) exhibit a low spin (LS) to high spin (HS) transition when heated above 175 K that is accompanied by a change in the Fe-N bond distances and angles [3], leading to a reduction in the ligand fields around the Fe site. At low temperatures, the splitting Δ between the t_{2g} and the e_g states is so large that Hund's rules are broken and a LS state with $S=0$ is formed. At high temperatures, the ligand field is reduced and Hund's rules yield a state with $S=2$ (see Fig. 6b).

Here we demonstrate how to electrically switch the spin state of, and the conductance across, individual Fe-phen molecules on CuN/Cu(100) surface using STM.

Figure 6c shows an STM image of isolated Fe-phen molecules on CuN/Cu(100). Due to the strong affinity of S to the CuN surface, the STM image suggests that the molecules adsorb with the SCN groups onto the CuN surface, and two types of molecular conformations denoted as type α and type β are observed. The two types reveal slight differences in the height profiles (cf. Fig. 6d): the central region of type α is higher than that of type β. The differential conductance (dI/dV) spectra near the Fermi

energy recorded on the center of both types show a clear Kondo resonance only on type α and a weak spectroscopic feature on type β (see Fig. 6e). A Kondo resonance is a signature of unpaired spins and is caused by a many-body state including the substrate electrons. Thus, these spectroscopic experiments ascribe a type α molecular conformation as the HS and type β as the LS state. A Fano fit to the spectrum reveals a Kondo temperature of about 105 K.

Fe-phen molecules on CuN/Cu(100) can be electrically switched between the HS and LS states reproducibly, leading to a single-molecule device whose state can be deterministically selected. When performing cyclic I(V) curves atop the molecule's center with the STM feedback loop opened, conformational switching can be seen as an abrupt jump in the I(V) curve. Figure 7a displays a cyclic I(V) sweep with arrows indicating the sweep direction. An abrupt current increase (decrease) is seen on the forward (reverse) sweep at about +1.2 V (about -0.8 V). The cyclic I(V) curves depict a hysteretic behavior at intermediate voltages indicated by two branches of the I(V) curve. Repeated forward and reverse I(V) sweeps reveal the switching between the two states to be fully reversible.
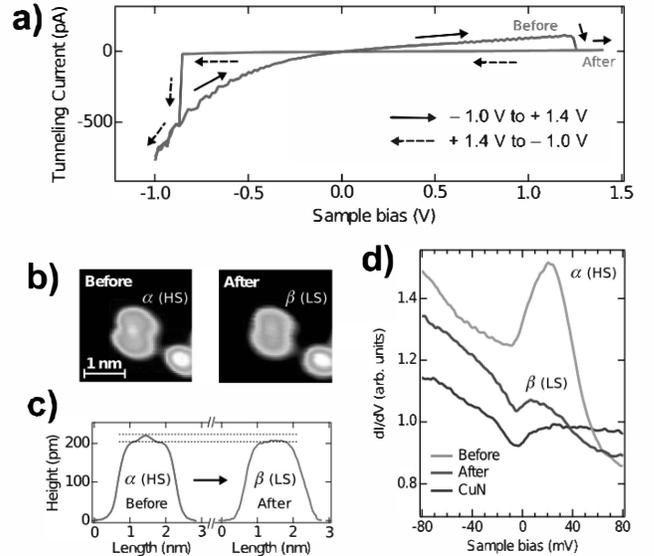
Fig. 7. a) I(V)-curves of isolated Fe-phen molecules recorded on the center of the molecule. b) STM images c) and corresponding height profiles acquired before and after the switching event. d) dI/dV spectra recorded on the center of the molecule before and after a switching event.

This switching behavior falls into the general category of memristive effects, which generically describe how it is electrically possible to reversibly alter a device's conductance. In our case, the two branches of the I(V) curve are related to the HS and LS state of the Fe-phen molecule as seen by comparing STM images and dI/dV spectra of the molecule in each of the two branches.

When ramping the sample bias up, the molecule in the HS-state (type α) is found to change its conformation after the abrupt drop in the tunneling current to the LS-state (type β) as shown in Figs. 7b and 7c. This observation is

reinforced by the corresponding changes in the *dI/dV* spectra (cf. Fig. 7d). Equally, switching from the LS to the HS state has been verified.

This unambiguously ascribes the intrinsic SCO property of Fe-phen as the origin of this nanoscale memristive behavior [13]. We emphasize that it is not only the amplitude of the sample voltage but also its polarity that determines the state of the molecule. After the molecule has been switched from the HS to the LS state by a positive voltage, it is not switched back by high positive voltage to the HS state. Only applying a negative voltage switches the molecule back to the HS state. The same holds for the opposite switching process. This proves that addressing the memory device is fully deterministic.

CONCLUSION

In conclusion, we have shown that single molecules adsorbed onto surfaces can be addressed individually by the tip of an STM to show a large molecular GMR effect. Using SCO molecules, individual molecules can be switched deterministically between a HS and a LS state that not only differ in their magnetic moment but also in their conductance. These functions are the elementary functions for molecular spintronic devices, i.e., sensing a magnetic configuration of the metallic leads and storing digital information in the spin state of single molecules. While these are only demonstrations of the working principles, real devices need to be assembled as solid state circuits. For these, a single molecule or few molecules can be integrated in thin film devices probed by local currents and voltages.

ACKNOWLEDGMENT

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