Spin Crossover

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Electron-Induced Spin Crossover of Single Molecules in a Bilayer on Gold**

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Molecules with switchable magnetic properties are promising building blocks for spintronics. Such systems can be realized on the basis of the spin crossover (SCO) effect. This phenomenon is observed in first-row transition-metal complexes of d^4–d^7 configuration, the largest number of examples being available for iron(II). Depending on the nature and field strength of the surrounding ligands, the central iron ion may exist in two different electronic configurations, low spin (LS, $S=0$) and high spin (HS, $S=2$). External stimuli, such as temperature, light, or pressure, may be used to switch between these states.[1–3] To date, such spin-state switching has been reported from bulk materials and films.[4–9] Alternatively, the spin of a transition-metal ion may be switched by coordination/decoordination of a ligand. This coordination-induced spin-state switching (CISSS) has been demonstrated at room temperature in solution.[10,11] Similar effects have been evidenced in thin films.[12,13] Conformational changes have also been reported to influence magnetic properties of molecules on surfaces.[14,15] Ultrathin layers of SCO molecules have been prepared from solution on highly oriented pyrolytic graphite.[16,17] While single-molecule resolution was not available, spectroscopic differences between clusters have been attributed to high- and low-spin states.[16] The observation of a Kondo effect from an iron(II)-containing complex in electron transport experiments has been interpreted in terms of spin crossover.[18]

To achieve spin-state switching on the level of single SCO molecules, it is desirable to grow well-defined ultrathin molecular layers on single-crystal surfaces by molecular-beam epitaxy. Unfortunately, the thermal stability of most SCO complexes is low for this approach. Recently, however, successful vacuum deposition of two SCO systems, [Fe(phen)$_2$(NCS)$_2$] and [Fe(bpz)$_2$phen] (**1**; Figure 1 a), have been reported (phen = 1,10-phenanthroline, bpz = dihydrobis(pyrazolyl)borate).[19,20]

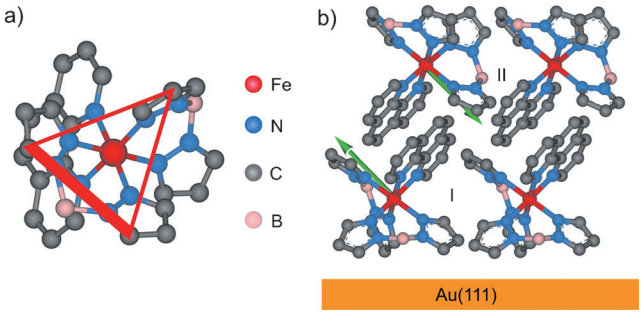

Figure 1. a) View of [Fe(bpz)$_2$(phen)] (**1**) along a pseudo-trigonal molecular axis. A triangle connecting three pyrazole groups is used to represent the orientation of the molecule. The thicker and shorter side indicates the two pyrazole groups of a single bpz ligand. b) Proposed adsorption geometry of **1** on Au(111). Side view of the first two molecular layers. Arrows depict the orientations of the dipoles of two molecules.

Herein, we show reversible and selective spin-state switching of single molecules of compound **1** in a densely packed layer. The experiments were performed with a low-temperature scanning tunneling microscope (STM) on double layers of **1** on Au(111). Sublimation of this SCO molecule under retention of the LIESST effect (light-induced excited spin-state trapping)[2] has recently been demonstrated.[20] Our STM images and spectroscopic data show switching of second-layer molecules between two distinct electronic states. The observed change of the electronic structure indicates that the switching is due to transitions between low- and high-spin states of the SCO complex. The experimental data are consistent with the calculated orbital structure of the different spin states. Moreover, we observe a Kondo resonance from molecules in the high-spin state, which is absent for low-spin molecules. The many-body Kondo effect signals the interaction of localized unpaired spins with delocalized electronic states and has been used to probe single atoms, molecules and nanostructures.[18,21–28] In our experiments, its presence or absence reflects the different spin states of the SCO molecule. Switching of molecules in the first layer was not observed.

Coverages close to two monolayers of **1** were produced in an ultrahigh vacuum system by sublimation onto Au(111) surfaces at room temperature. STM images (see the Supporting Information) recorded after cooling the sample to 5 K suggest that **1** in the first monolayer orients with three pyrazole groups towards and the phenanthroline group away from the substrate. Second-layer molecules exhibit an opposite orientation (Figure 1 b). This geometry enables a favor-

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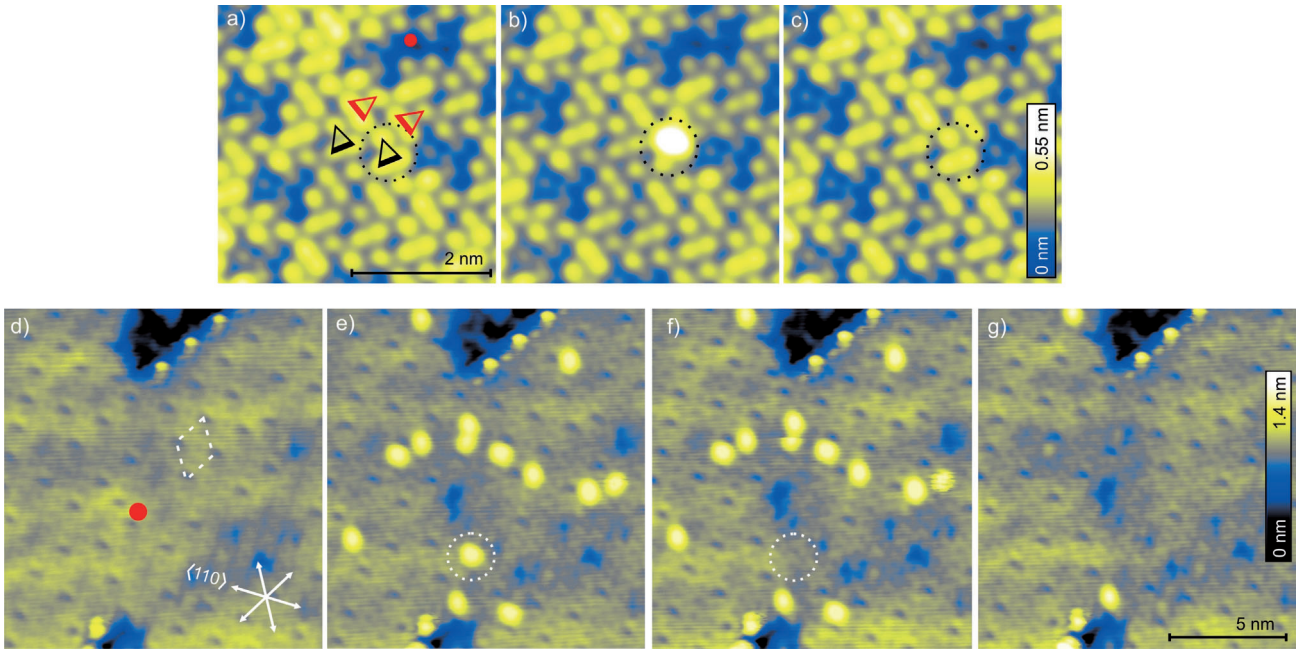

Figure 2. Constant-current STM topographs of a double layer of [Fe(bpz)$_2$(phen)] on Au(111). a)–c) Submolecular resolution ($V=-1.6$ V, $I=50$ pA). Triangles in (a) indicate selected molecules (see Figure 1a). Dotted circles in (a)–(c) indicate a molecule which is switched from LS (a) to HS (b) and back to LS (c). To switch from LS to HS, a 3 V pulse was applied with the tip positioned above the red dot in (a). HS–LS switching was obtained by pulsing directly above the HS molecule in (b). d) Overview of a larger area ($V=1.6$ V, $I=50$ pA). LS molecules in the second layer appear yellowish. No HS molecules are observed in ordered areas. A small first layer area is discernible at the upper edge of the image. Some molecules at the edge of the second layer appear higher, which may reflect a different spin state. Compact directions of the Au(111) surface are indicated by arrows. A dashed parallelogram shows a unit cell of the superstructure of the layer. e) Image recorded after applying a pulse at the position indicated by a red dot in (d). Several molecules have switched to HS and appear higher (brighter). f) Upon applying 1.8 V at 500 pA for about 0.5 s to the HS molecule circled in (e), switching to LS took place. g) After applying pulses to all HS molecules in (f), most molecules have returned to the LS state.

able π–π interaction of the phenanthroline groups as known from bulk crystals of similar molecules.[29]

Figure 2 displays images of the ordered bilayer. Three-lobed features (marked with triangles in Figure 2a) are attributed to three pyrazole groups of the pyrazolylborate ligands. The slightly smaller distance between two of these lobes (bold edges of the triangles in Figure 2a) are assigned to the pyrazole groups of a single bpz ligand (compare with the triangle in Figure 1a). Molecules in alternate rows (Figure 2a, red and black triangles) are rotated by about 70° with respect to each other. The unit cell of the molecular pattern comprises 2×2 molecules (dashed parallelogram in Figure 2d).

Compound **1** is in a HS state at ambient temperature in the bulk as well as in thin films, and it converts into LS at a transition temperature of about 160 K.[20,30,31] Therefore, in the present experiments at 5 K, **1** in the second layer is expected to be in a LS state. Switching of these LS molecules is achieved by placing the STM tip over an arbitrary position over the bilayer (red dot in Figure 2a) and increasing the sample voltage V from conditions under which LS molecules can stably be imaged ($V=\pm1.6$ V, current $I=50$ pA) to $V=3$ V for a sub-second time interval while maintaining the tip-sample distance constant. A subsequent STM image (Figure 2b) reveals a molecule at a remote location with an apparent height that has increased by 2–4 Å depending on the polarity of V. This drastic change reflects a corresponding modification of the electronic structure and signals a HS state, as will be discussed below. While switching from LS to HS occurs for molecules in a nanometer distance from the position of the STM tip, the reverse process may be selectively induced on a given HS molecule. To this end, the STM tip is placed above it (circle in Figure 2b) and a strongly increased current ($I=0.5$ nA) is used at a slightly elevated voltage ($V=1.8$ V).[32] On a timescale of seconds, the current suddenly drops, which signals the transition to LS, as confirmed by a subsequent STM image (Figure 2c). A similar switching sequence is displayed in Figures 2d–g. These STM images of a larger area indicate that the LS–HS transition occurs on several molecules that are located at nanometer distances from the tip position (d to e). Moreover, selective HS–LS switching is demonstrated again (e to f) and its reproducibility is evidenced (g).

From repeated measurements we observed that the number of switching events and the maximum distance over which switching from LS to HS occurs increase with sample voltage. Occasionally we also observed HS–LS switching of remote molecules. No switching was found at negative sample voltages. Voltages exceeding 3.1 V usually destroyed the bilayer. Below this critical voltage bidirectional switching was repeatedly performed.

The spin state of **1** has an influence on the molecular volume;[30,31] nevertheless, this effect cannot explain the

drastic change of the apparent molecular height reported above. Furthermore, the energies of the frontier orbitals are known to depend strongly on the spin state. Density functional theory calculations (see the Supporting Information) indicate that the gap between the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO) is significantly larger in the LS state (ca. 2.1 eV) than in the HS state (ca. 0.4 eV). The modified gap is consistent with the observed change of the image contrast. Direct information on the gap was obtained by recording spectra of the differential conductance dI/dV as a function of sample voltage. LS molecules (Figure 3a, blue) exhibit an occupied state close to −1.2 V and an onset of a strong unoccupied feature near 0.5 V. The spectrum of HS molecules (Figure 3a, black) exhibits intense features close to the Fermi energy. These clear differences of the electronic structure match the expectations for LS and HS states. They also exhibit similarities with the calculated transmission spectra of iron(II) complexes, which are attached by S–Au bonds to Au leads.[33] Furthermore, data from HS molecules at higher resolution (Figure 3b) reveal a narrow antiresonance at the Fermi level, which is not observed from LS molecules. The feature is consistent with the typical Fano line shape that is due to the Kondo effect and indicates the presence of unpaired spins. The HS state of similar molecules was previously addressed using Kondo resonances.[18,21] A Fano fit (Figure 3b, green line) yields a Kondo temperature $T_K \approx 150$ K.[34]

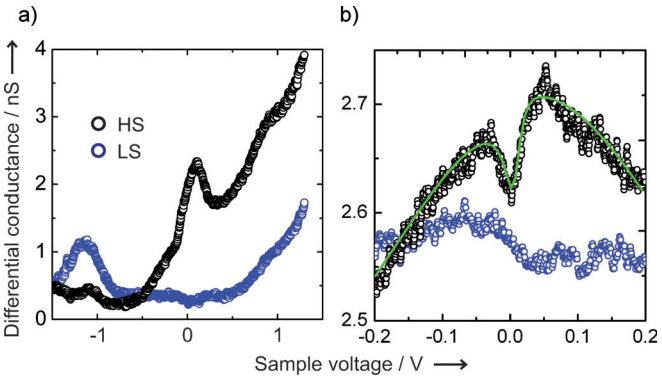

Figure 3. Spectra of the differential conductance (dI/dV) of [Fe(bpz)$_2$(phen)] (**1**) in its LS (blue circles) and HS states (black circles). a) Overview of a wide bias range reveals differences between the molecular resonances of LS and HS molecules. b) Spectra around the Fermi level ($V = 0$) at increased resolution. The LS data has been vertically offset for clarity. The HS data exhibits a sharp antiresonance. It may be described by a Fano line shape, which is typical of a Kondo resonance. For a fit (green line), the background owing to molecular resonance at about 50 mV is modeled with a Gaussian curve.

The high selectivity of the HS–LS transition enabled further experiments, which provide some insight into the switching mechanism. Time series of the current from HS molecules recorded at constant tip–sample distance show a sudden change of the conductance. From series of measurements on different molecules, it was found that the time required to switch a molecule from HS to LS at a fixed bias is approximately proportional to the inverse of the current I. In other words, the switching rate is proportional to the first power of I, which is indicative of a one-electron process. The observed threshold voltage for switching (approximately 1.5 V at elevated currents) and the absence of switching at reversed polarity are consistent with a process which is mediated by electron injection into an unoccupied orbital. This mechanism is also consistent with the absence of switching for molecules in the first layer. The lifetime of an electronically excited state is expected to be significantly shorter for a molecule in direct contact with the metal substrate. As a result, energy transfer to the substrate is too rapid to enable the rearrangement of the atomic positions that accompanies the spin transition.

Unfortunately, we did not succeed in obtaining a similarly reproducible result for LS–HS switching. Nevertheless, we may state that LS–HS switching was only observed at positive voltages exceeding approximately 2.5 V, which suggests an electron-induced process. Moreover, LS–HS switching was found for molecules which were located at distances as large as about 13 nm from the tip position. This striking observation is analogous to the case of non-local dissociation of dimethyldisulfide on Au(111). In that case, hot electrons injected from the tip are laterally transported via surface resonances at the Au(111) surface and induce dissociation over distances up to 100 nm from the point of injection.[35] This mechanism is consistent with the present data. As an alternative mechanism for remote switching, a field-induced process has to be considered.[36,37] A characteristic property of field-induced processes in STM is switching at large tip–sample distances in the limit of vanishing current.[38,39] In the present case, no switching was observed at increased tip–sample distances for bias voltages as large as ±10 V. Moreover, as the dipole moment of **1** is oriented at about 45° with respect to the surface normal in the proposed adsorption geometry (compare with Figure 1b), field-induced switching would be expected at both bias polarities, which is in contrast to the experimental observations.

LIESST in bulk crystals is well understood.[1–3] A SCO molecule in its LS ground state absorbs light to make a vertical transition to an electronically excited state. This transition is followed by intersystem crossing to an intermediate spin state from where the molecule stochastically relaxes to its HS or LS state. At temperatures well below the spin transition, the HS state is long-lived. Through the reverse-LIESST effect, a HS molecule can be transformed to LS via the same excited electronic states.[40] We tentatively propose similar pathways of excitation and relaxation for the switching reported herein, which may be termed electron-induced excited spin-state trapping (ELIESST). Without considering the intricacies of spin coupling between the incoming electron and the six d electrons of the iron(II) center,[41] it can be assumed that injection of an electron to an unoccupied orbital of a LS molecule excites it to LS^-, followed by relaxation to an intermediate state I^-, from which the molecule further statistically relaxes to its HS or LS states. The excess electron may tunnel to the substrate. As the temperature of the experiment is well below the spin transition temperature, a molecule excited to the HS state is trapped there. The HS state is stable on a time scale of hours.

The suggested pathway is consistent with a previous report of electron-induced excitation of LS molecules to charged HS states.[18] The reverse switching from HS to LS is mechanistically less-demanding, as it corresponds to the de-excitation of a metastable state. Thus it can selectively be applied on a given single molecule in the high-spin state. In analogy to the LS–HS transition, it may proceed via a charged intermediate.

To conclude, electron-induced reversible switching of single SCO complexes has been demonstrated. The change of the electronic structure along with a switchable Kondo resonance indicate a transition between low- and high-spin states of the complex $[Fe(bpz)_2(phen)]$. The switching does not induce any instability of the ordered layer, which would limit the number of switching cycles of a given molecule.[44] Controlling the spin state of an assembly of single molecules with atomic resolution is an important ingredient to spintronics,[42] thus paving the way to novel applications in molecular electronics and data storage.[43]

Experimental Section

Experiments were performed with a home-built STM operated at 5 K and in ultrahigh vacuum with a base pressure of 10^{-9} Pa. The synthesized molecules[27,28] were purified by gradient sublimation and evaporated from a tantalum crucible at about 200 °C. The deposition rate was monitored using a quartz microbalance and calibrated by STM images. All depositions were carried out at room temperature. Electrochemically etched tungsten tips and sample surfaces were prepared in vacuo by argon ion bombardment and annealing.

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