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Spinn Crossover

Spin-State Patterns in Surface-Grafted Beads of Iron(II) Complexes**

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In memory of Dieter Sellmann

Novel strategies for the design of functional materials are in increasing demand, as the down-scaling of lithographic processes (the top-down approach) will soon encounter the fundamental physical limits of miniaturization.[1] One of the fascinating perspectives of molecular electronics[2,3] is information storage at the single-molecule level, on the basis of arrays of molecular switches.[4] Spin-crossover (SCO) compounds hold considerable potential in this context.[5,6] SCO can occur in octahedral transition-metal complexes in which the metal ion has a d^4 to d^7 electron configuration.[7,8] The transition may be stimulated externally, by a change in temperature or pressure, or by irradiation.[7,8] SCO is entropy-driven and, in the solid state, is influenced strongly by intermolecular interactions, such as hydrogen bonding or π–π stacking. Such interactions give rise to cooperativity between SCO complexes within the ensemble. High cooperativity can cause the change in spin state to be accompanied by hysteresis, which confers bistability on the system and thus a memory effect.[5,7] A viable reading/writing procedure, that is, a means of reproducible actuation on the single-molecule level, is a formidable challenge that has yet to be met, but in this way SCO compounds could serve in devices of unsurpassable storage density. In principle, reliable information storage could be achieved even in the absence of hysteresis, provided the energy difference between low-spin state and high-spin state of the complexes within the SCO ensemble is sufficiently large (on the order of several kT). A large number of spin-crossover systems are known,[7] with complexes of iron(II) the most numerous, both in solution and in the solid state. Usually, ferrous iron is in a quasi-octahedral N_6 coordination environment, and switching occurs between a low-spin (LS, $^1A_{1g}/t_{2g}^6$, $S=0$) and a high-spin state (HS, $^5T_{2g}/t_{2g}^4e_g^2$, $S=2$).

SCO systems have been characterized by physical techniques including Mössbauer and UV/Vis spectroscopy, magnetic susceptibility measurements, and diffraction methods, applied to the bulk solids.[5,8] Many attempts have been made to obtain SCO materials in the form of thin films, multilayers, or nanocrystals.[9] Recent strategies include the sequential assembly of coordination polymers on metal or biopolymer supports (such as gold or chitosan) and the preparation in polymeric matrices, in surface-grown multilayer thin films incorporating iron(II) coordination polymers, and in nanoparticulate iron(II) complexes.[9–15]

Our approach is to use spin-switchable iron(II) complexes of bis(pyrazolyl)pyridine ligands, with a variety of substituents that can serve as surface anchors depending on the kind of substrate. We studied the spin state of adsorbates at the single-molecule level with scanning tunneling microscopy (STM) techniques at room temperature (298 K). For the present study, we chose $[Fe^{II}(L)_2](BF_4)_2$ (**1**; L = ligand), whose synthesis, solid-state structure, and spin behavior have been reported in detail.[16] The solid-state structure of the dication in **1** is shown in Figure 1 a. The magnetic susceptibility of **1**

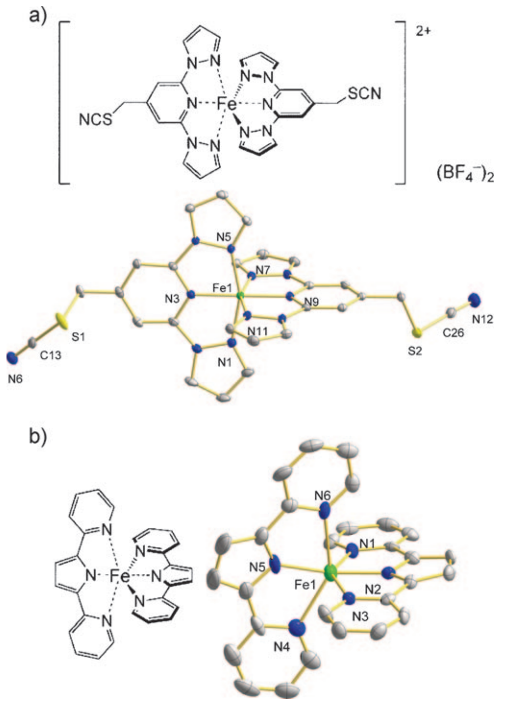

Figure 1. Structural formulas and X-ray crystal structures of the iron(II) complexes **1** and **2** (thermal ellipsoids at the 50% probability level). a) The dicationic complex **1** (tetrafluoroborate salt, low-spin form); structure determined at 100 K; mean Fe–N distance: 1.951(1) Å. b) The neutral complex **2** (high-spin form); structure determined at 150 K; mean Fe–N distance: 2.213(3) Å.

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changes abruptly at 272 K in the crystalline solid (Figure 2 a), and this change is caused by a transition between the diamagnetic low-spin and the paramagnetic high-spin state.[16] For comparison, we also investigated an analogue of **1** which is high-spin independent of temperature (complex **2**, Figures 1 b and 2 b).[17] The spectroscopy possibilities of STM, such as current-imaging tunneling spectroscopy (CITS),[18] allow us to probe electronic states of the molecules as a function of energy within a few electronvolts (eV) around the Fermi level.[19–23] Generally, CITS measurements provide direct information about the local conductance at these energies. We have successfully applied the CITS technique to a range of metal complexes.[20–23] As we show in the following, we have succeeded in high-resolution topography mapping and simultaneous measurement of the current–voltage characteristics of single complexes of **1** and **2**, and clusters of complexes, deposited on highly oriented pyrolytic graphite (HOPG) surfaces.

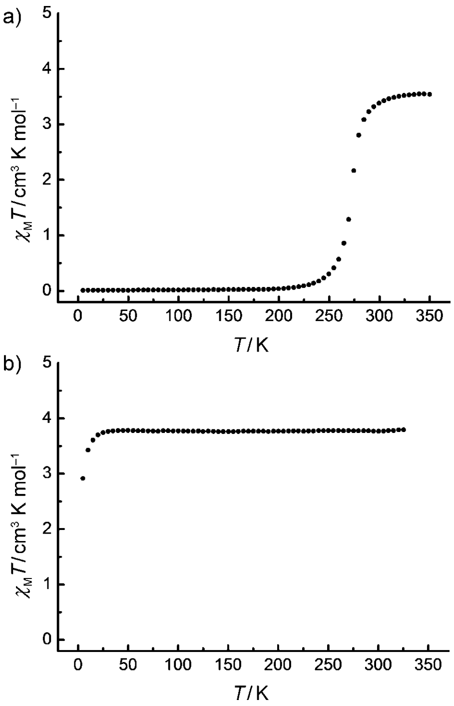

Figure 2. $\chi_M T$ vs. T plots for complexes **1** and **2** determined in the solid state. a) Complex **1**, spin transition at 272 K.[16] b) Complex **2**, no spin transition.

Typical STM topography images of complex **1** on HOPG are shown in Figure 3. We observe chainlike arrangements of clusters containing two or three molecules of **1** (Figure 3 a,b). Some aggregates mirror substrate contours, while others extend across substrate steps (Figure 3 b). The high-resolution STM image in Figure 3 c shows two coordination entities arranged side by side on the surface. The underlying HOPG lattices are visible in the topography. Our coordination entities may assemble through face-to-face and edge-to-face aromatic interactions, producing a pattern known as the "terpyridine embrace motif".[24,25] We suggest that, in the case of **1**, such π–π interdigitation results in the formation of oligonuclear clusters of complexes, which then aggregate in linear fashion, guided by and in register with the HOPG substrate. The exact positioning of the counteranions is as yet unclear, but seems to have little, if any, effect on the overall growth pattern, as complex **2**, which is neutral, shows the same aggregation behavior on HOPG (Figure 5).

Figure 3 d depicts a constant-current topography of a single-molecule arrangement of **1**, with simultaneous CITS measurements (Figure 3 e, current map at 0.8 V). In the topography image, the diameter of a single spot is around 2 nm, which is in good agreement with the diameter of a single molecule as obtained from X-ray structure data.[16] The current map has two distinct features at these positions. At the third and fifth spots in the line of complexes (counted from the top), the tunneling current is suppressed even below the value of the HOPG surface at all bias voltages (Figure 3 f). The change in tunneling conductivity is spread over the whole spot. All other spot positions show a strong increase in tunneling current (Figure 3 f).

The reasonable conclusion is that this behavior is associated with one of the spin states, either high-spin or low-spin. As the diameter of complex **1** is considerably greater in the HS state than in the LS state, we expect the conductance of the molecule in the HS state to be lower than in the LS state, because hybridization should be significantly decreased. This conclusion is supported also by macroscopic conductance measurements of a similar material.[26] As the current maps shown are recorded at constant bias voltage, a smaller conductance should translate into a "darker" feature. This means, in the spectroscopy images, that molecules in the HS state are "dark", and molecules in the LS state are "bright". In this sense, the spin-state information within the arrangement formed by complex **1** can be read out directly by current imaging tunneling spectroscopy, in other words, conductance measurements of a single molecule. Repeated scans of the same position did not show any change in spectroscopic contrast. We therefore conclude that the spin states of single, isolated molecules are either pinned by the substrate, or by a more elaborate mechanism like adsorption of a guest or desorption,[27] and are thus stable at least within the time frame of our measurement cycle. Only statistically distributed sequences of "bright" and "dark" spots, corresponding to the respective iron(II) LS or HS states, can be observed along single molecular chains,[28] indicating that there is no cooperativity of the spin states in a one-dimensional molecular arrangement.

In some cases, we detected state changes during our CITS measurements at the same position. Figure 4 shows a set of two successive CITS measurements of a line of clusters of complex **1**. Each cluster consists of two or three molecules. Resolution of single molecules within the clusters was not achieved. The second measurement was made 5 min after the first. In Figure 4 b, we observed the end of a line of clusters, which provided a unique position tag. In comparing Figure 4 b and Figure 4 d, we see that the first and second cluster from below have changed their respective spin state, that is, from LS to HS (first cluster) and from HS to LS (second cluster). This observation rules out oxidation ($\mathrm{Fe^{II}} \rightarrow \mathrm{Fe^{III}}$) during the

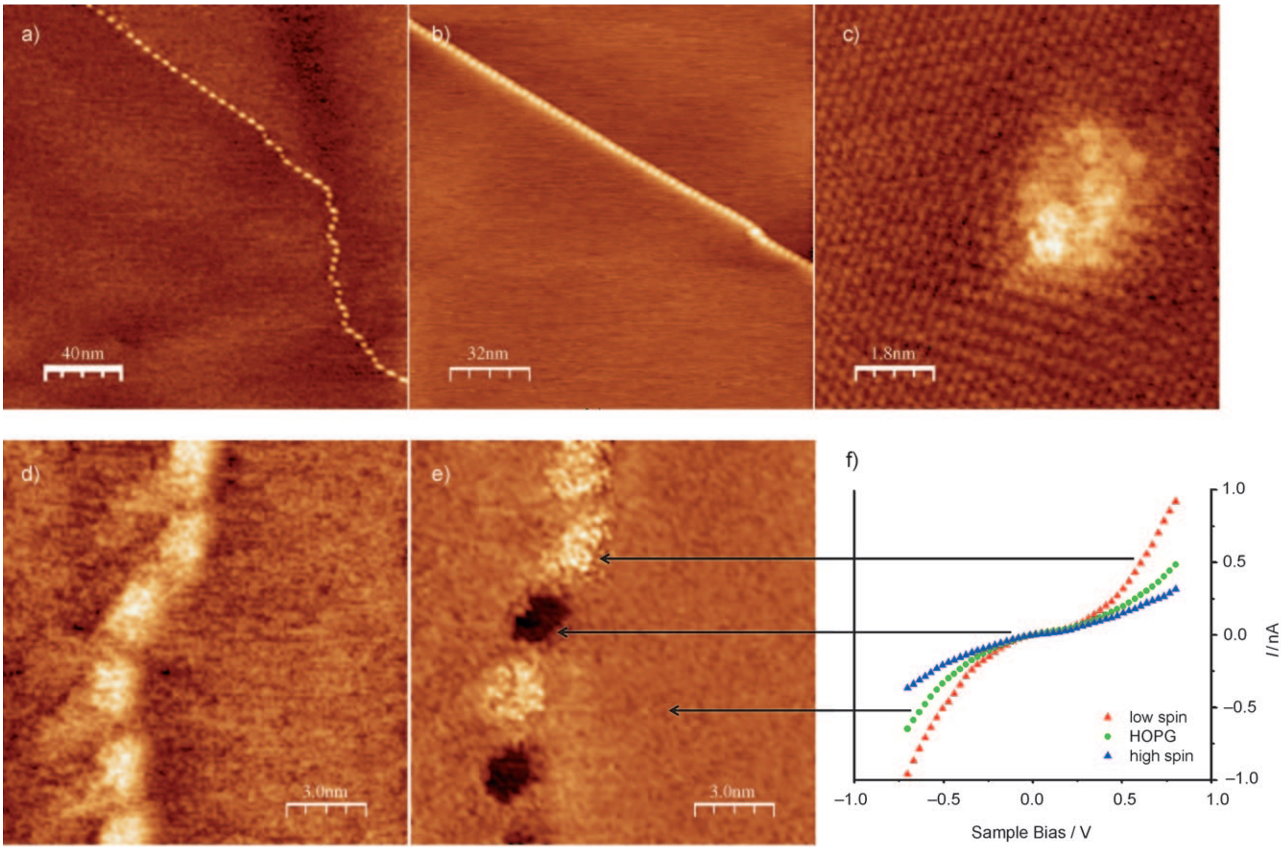

Figure 3. STM images of complex **1** deposited on an HOPG surface. a, b) Regular chains of clusters of complex **1**. c) Dimeric combination of iron complexes (bias: −100 mV; 100 pA), mapped with molecular resolution. The background shows the underlying graphite lattice. d, e) Simultaneously recorded topography (d) and CITS current images (e) of a line of single molecules of **1**. The topographic parameters are −100 mV and 28 pA (CITS: bias voltage +0.8 V). Note the significant contrast in the spectroscopy images. At the same time, the topography image does not show any variance of brightness. f) *I*/*V* characteristics recorded at three different positions (marked by black arrows) of the CITS current image (in e).

spectroscopic measurements. On the other hand, the spectroscopic features are remarkably stable with respect to an increase in temperature. Local heating with an infrared laser (808 nm, $P < 300$ mW) resulted in a temperature increase of at least 40 K but we never observed any accompanying abrupt changes.

We should emphasize two important findings at this point: Firstly, we have always found clusters of more than two molecules to have a uniform spin state. Secondly, during repeated CITS measurements, the state of small clusters can change from LS to HS and back. The optimistic conclusion is that even clusters of a few molecules show some degree of cooperativity,[29] which suggests that the spin state has sufficient thermal stability. This conclusion will have to be tested by careful temperature-dependent measurements. In any case, practicable writing approaches are needed,[28] which may be based on photomagnetic,[30] electrical,[31] or mechanical effects.

Our observation of switching during repeated scanning is intriguing, as it could be an indication that a moderate current flow already suffices to trigger the transition from LS to HS. It emerges that, within the limits discussed above, small clusters of spin-crossover molecules are realistic candidates for nanometer-sized, room-temperature-stable magnetic storage devices, well beyond the superparamagnetic limit.

As a reference material, we also investigated the non-SCO complex **2** (Figure 1 b).[17] The temperature-dependent bulk susceptibility measurement of **2** is shown in Figure 2 b. $\chi_M T$ reaches a value of 3.8 cm^{3}mol^{-1}K at around 40 K and remains nearly constant over the complete temperature range. This value is typical for iron(II) complexes in the high-spin state. There is no evidence for a spin transition.

Using the same approach as for complex **1**, we conducted STM/CITS measurements with samples of complex **2**. Figure 5 a shows a chain of clusters of **2**, similar to the clusters of complex **1** (Figure 3 a and Figure 3 b). Figure 5 b shows a small cluster with molecular resolution. The diameter of the spot is around 2.2 nm. This size corresponds to a cluster of two or three molecules. Figure 5 c and d show simultaneously recorded topography and CITS current-image maps, respectively. The dimension of a single spot in the constant current topography map is approximately 4 nm. Each spot therefore corresponds to a cluster of four molecules. Apparently, the conductance of all clusters is significantly smaller than that of the HOPG substrate, which correlates well with all complexes being in the high-spin state. “Bright” spots were never found.

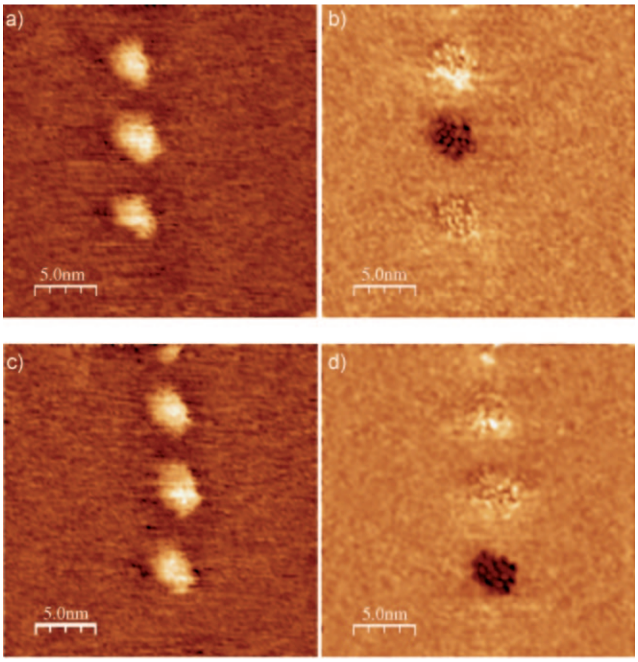

Figure 4. Sets of simultaneously recorded STM topographies (a, c) and CITS current images (b, d) from two different scans at the same position of an isolated linear aggregate. The images in (c) and (d) were recorded 5 min after the images in (a) and (b). Clusters in positions 1 and 2 (counted from below) interchange their spin state. See text for details.

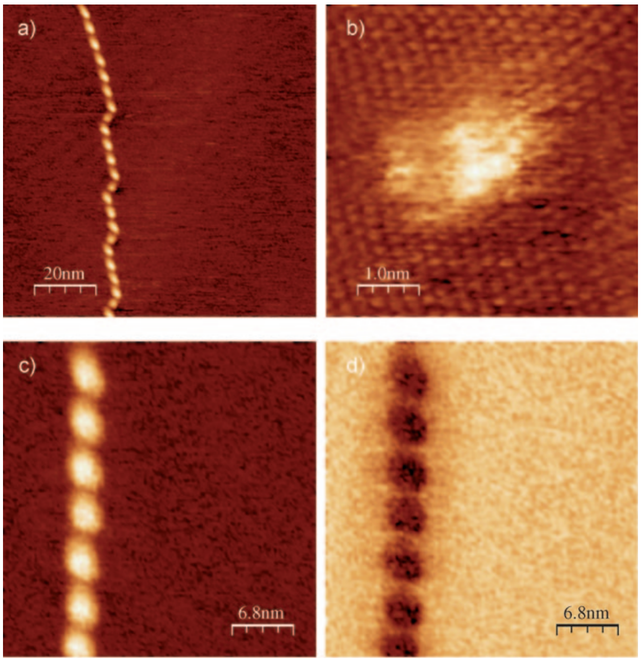

Figure 5. Constant-current STM topographies of complex **2** on an HOPG surface. a) A chain of clusters of molecules. b) A cluster of two molecules mapped with molecular resolution (sample bias: −100 mV, set point current: 100 pA). The background shows the underlying graphite lattice. c, d) Simultaneously recorded topography (c) and CITS current images (d) of complex **2** (bias voltage: +0.8 V). See text for details.

In conclusion, we have shown that complexes **1** and **2** self-assemble on HOPG at room temperature, predominantly like beads on strings several microns in length, which even extend across the step edges of the substrate. Single-molecule entities were detected and imaged with molecular resolution. The iron(II) HS and LS states of **1** show a drastic contrast: The local tunneling conductance of the LS state is at least three times higher than that of the HS state. A certain amount of cooperativity is conserved even in very small assemblies of complex **1** on the surface. In the case of complex **2**, we detected only HS behavior in our conductivity measurements. This nicely conforms to our bulk magnetic measurements, which show the molecules to be in the HS state independent of temperature. The significant difference in molecular conductivity between the spin states of iron(II) holds considerable promise for new concepts in high-density data storage, provided that there is sufficient thermal stability. In current work we are addressing the fine-tuning of SCO complex assemblies on the basis of iron(II), and their controlled self-organization and addressability on surfaces.

Experimental Section

The STM investigations were performed using a home-built, low-drift STM head interfaced with a home-developed controller and software. For all measurements, prior to imaging, a droplet of a solution of complex **1** (10^{-8} M) in acetonitrile or of complex **2** (10^{-8} M) in tetrahydrofuran was applied to a freshly cleaved HOPG surface. Distances in the STM images were calibrated based on the observed atomic spacing of HOPG. All topography images were recorded in constant-current mode. Typically, for the STM measurements, tunneling currents between 5 and 100 pA were employed. The bias voltage was ±50 mV to ±100 mV for topography measurements. The scan frequency was varied between 2 and 5 Hz. Resolution was 256 × 256 points for topography, and 128 × 128 in the CITS measurements. CITS measurements were performed simultaneously with topographic imaging, using the interrupted feedback loop technique. This was achieved by opening the feedback loop at a fixed separation of tip and sample, and ramping the bias voltage over the range of interest. I/V curves were acquired at every pixel of the topography image. This produced a four-dimensional map of the current as a function of position and voltage. The data set was then usually decomposed into a set of current maps, that is, current I vs. position, for any measured value of the bias voltage. The scan range of voltages was typically from −0.8 V to 0.8 V relative to the tip potential for approximately 100 discrete voltage steps. Typically, tunneling resistances of the order of 2 GΩ were set. We used Pt/Ir (90:10) tips mechanically cut from wires with a diameter of 0.25 mm. Figures 3–5 were produced using the program WSxM.[32]

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