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Functional Patterning

Micro- and Nanopatterning of Spin-Transition Compounds into Logical Structures**

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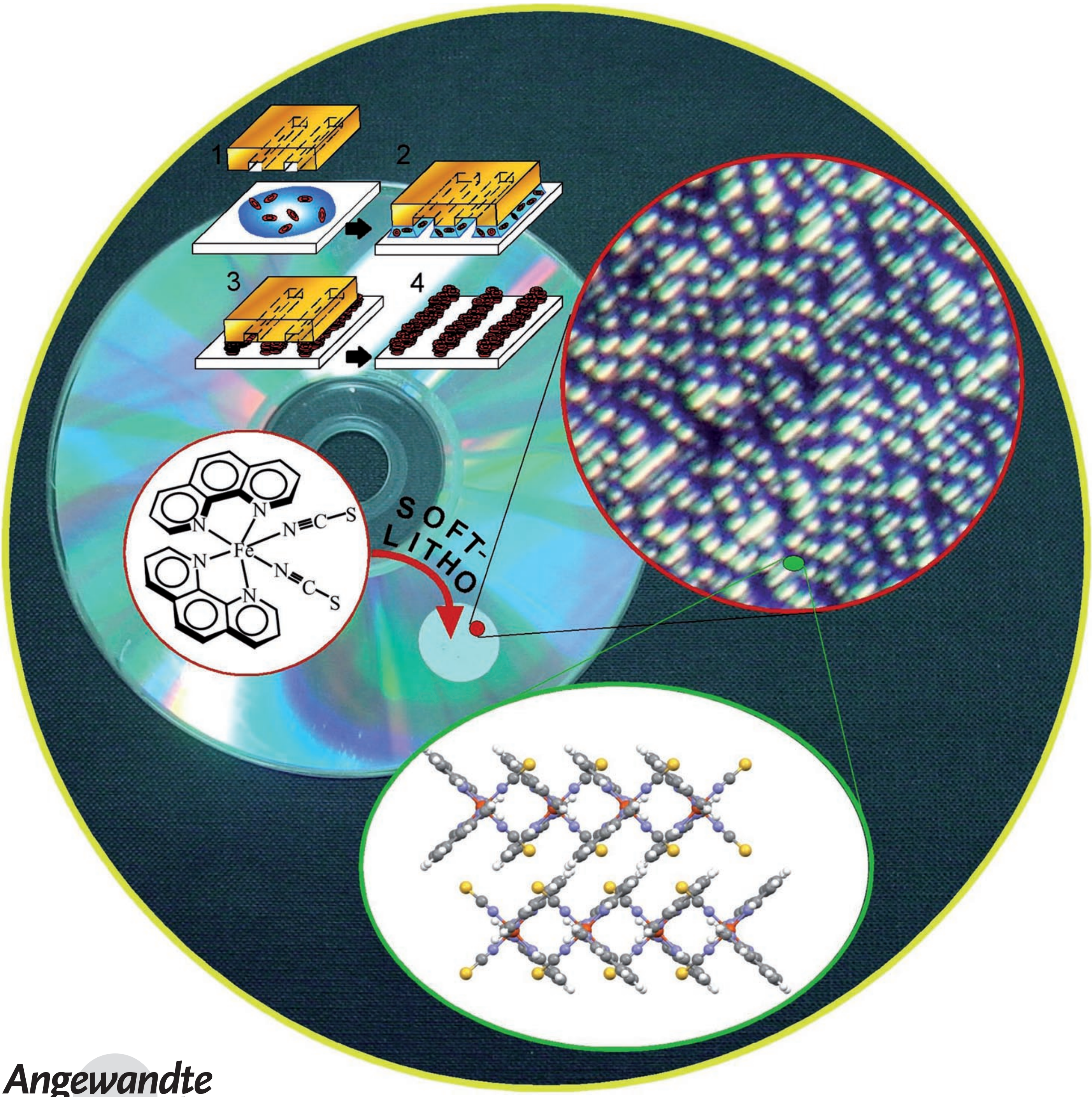


The demand for more efficient information storage is one of the pivotal requirements of knowledge-based development and a prime challenge for current scientific and technological research.[1] Currently, computer hard disks store data by defining the magnetic anisotropy orientation of small regions of a spinning disk. In one of the most successful technological developments of the last decades, scientists and engineers have boosted the capacities of storage devices by shrinking the size of the effective magnetic storage regions.[2] This trend is predicted to continue until the so-called superparamagnetic limit is reached.[3] Close to that frontier, ambient heat can trigger de-orientation of magnetic domains as a result of their reduced size. Among the proposals to overcome this obstacle (e.g. perpendicular recording,[4] antiferromagnetic coupled media,[5] added heaters[6]), nanopatterning of the storage domains seems to be very promising.[7]

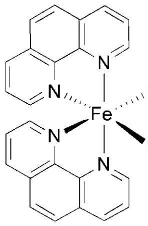
In this context, a series of different molecular switching units have been tested based on, for example, change in conformation,[8] redox states,[9] spin states,[10] and shape,[11] which can be influenced by external stimuli, such as pressure,[12] temperature,[13] magnetic fields,[14] irradiation,[15] and mechanical perturbation.[11] Among the investigated materials, molecular spin-transition (ST) compounds of $3d^4$ to $3d^7$ transition-metal ions have been proven to be excellent candidates for application in information technology.[16]

Particular interest, both from a fundamental and applicative point of view, was attracted by the ST of Fe^{II} ions in an octahedral ligand field, since, by populating the respective t_{2g} and e_g sets of d orbitals, the $3d^6$ valence shell may exist in either the diamagnetic ($S=0$) low-spin (LS) or the paramagnetic ($S=2$) high-spin (HS) state. The LS↔HS transition can be triggered by external stimuli (temperature, pressure, electromagnetic radiation) giving rise to variations in color, spin state, metal–ligand distance, and dielectric constant.[17] Furthermore, it was shown that steep switching and hysteretic behavior could be realized at ambient conditions.[18] Based on these properties, ST compounds have been proposed to act as active switching units in molecular devices for applications in molecular memory, sensors, and displays.[19–21]

Since the information generated in a ST switching event occurs within the nanometric regime, the interfacing of the molecular switching units with the microscaled device environment is of crucial importance. In this respect, micro- and nanopatterning of switchable functional materials with the ultimate goal of storing information or sensing at the single-molecule level has attracted considerable interest.[22] Only recently, a breakthrough in this direction has been achieved as a result of the skillful combination of thin-film and patterning techniques. The first fabrication of ST thin films was reported in 1998 using Langmuir–Blodgett techniques; however, the physical properties of the obtained films, in particular the dielectric constant, had been altered.[23] Films of ST coordination polymers can also be grown by layer-by-layer assembly,[24] and the same material patterned using electron beam lithography.[19] Moreover, molecular layers of ST compounds can processed by spin coating.[25]

A further alternative for the preparation of nanopatterned ST structures relies on the self-organization of molecular ST units into hierarchically organized domains across different length scales.[16] In this context, the fabrication of ST units in ordered nanopatterns by a method able to exploit self-organizing properties of the molecular materials would be highly desirable. Since it is known that ST properties depend critically on the local molecular environment (e.g. packing, solvent molecules, anions, etc.),[26] the development of methods giving access to nanostructures that preserve internal ordering is technologically of utmost importance for the application of ST compounds.

Herein we report on the successful patterning of crystalline aggregates of the neutral ST complex cis-bis(thiocyanato)bis(1,10-phenanthroline)iron(II) (**1**),[27] with controlled size at the frontier of micrometric- (thus optically accessible) and nanometric-scaled structures. Compound **1** is one of the most thoroughly investigated ST compounds; it exhibits a LS↔HS transition at 176 K and we consider it to be a representative for this class of switchable metal complexes.



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For structuring, we use two stamp-assisted deposition techniques: micro-inject molding in capillaries (MIMIC)[28] (Figure 1 a) to fabricate micrometric stripes and lithographically controlled wetting (LCW)[29] (Figure 1 b) to pattern submicrometric and nanostructures. A detailed description of MIMIC and LCW is provided in the Supporting Information. Noticeably both methods[30] exploit the self-organization properties of

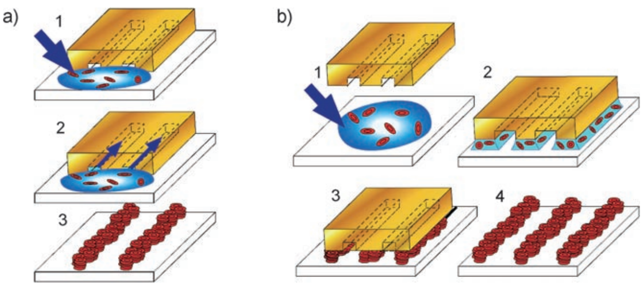

Figure 1. Representations of the processes occurring during a) micro-inject molding in capillaries and b) lithographically controlled wetting. For details see the Supporting Information.

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molecules at the later stages of shrinking (Figure 1 b). By MIMIC and LCW ST compound **1** crystallizes into micro- and nanowires or dots. The obtained patterns were characterized by atomic force microscopy (AFM), polarized optical microscopy, grazing incidence X-ray diffraction (GIXD), and Raman spectroscopy.

AFM studies of structures of **1** printed by MIMIC on silicon reveals the formation of striplike structures (micrometric stripes) 1 µm in width, similar to the features of a stamp (Figure 2 a). Optical images obtained by polarized microscopy (Figure 2 b,c) indicate behavior typical for optically anisotropic materials exhibiting birefringence. In particular, the microstripes appear homogeneously colored; this indicates that their thickness is almost constant over the entire stripe but that it changes between different stripes. The microstripes extinguish in four positions at intervals of 90°. The occurrence of light extinction at the same orientations in the all places of microstripes suggests that the crystalline domains are grown with the same orientation. Thus, we can deduce that the confined deposition by MIMIC has induced a coherent, long-range order along the length of the stripes. The resolution limit of patterned stripes was further pushed down into the nanometer regime by using the LCW technique. Structures with a resolution of approximately 160 nm could be achieved by estimation of the full width at half-maximum; below this limit the stamp features were not perfectly replicated. Figure 2 d shows an AFM image of the nanostripes obtained by LCW.

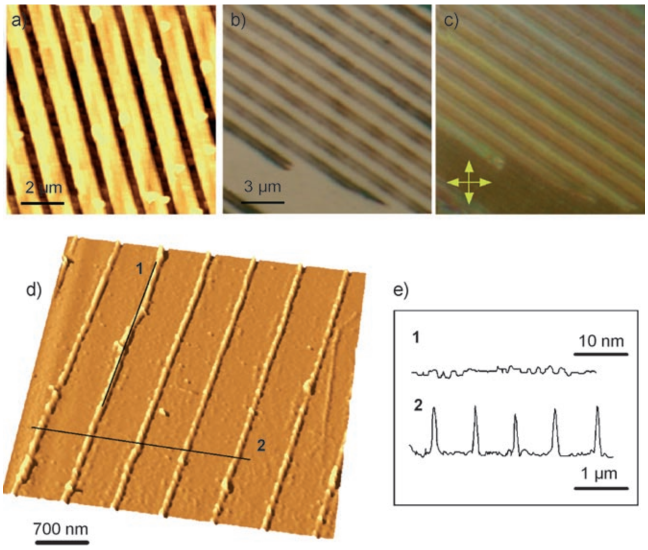

Figure 2. Microstripes of **1** fabricated by MIMIC on a silicon surface. a) AFM topography (z scale is 50 nm). b) Optical micrographs recorded with unpolarized light. c) Micrographs recorded with crossed polars oriented along the axes of the image. d) AFM topography of nanostripes fabricated by LCW. e) Line profile (1) and cross section (2) of the nanostripes corresponding to the features labeled in (d).

The structure of the nanopatterned films was investigated by means of GIXD. Inside the patterned region probed by the X-ray beam ($23 \times 0.5\,\text{mm}^2$), the molecules assemble in crystalline domains able to produce strong diffracted peaks. Moreover, the existence of a preferential orientation of the crystallites with respect to the stripes direction could be verified by means of azimuthal scans: the detector was placed at the scattering positions for different (*hkl*) planes and the diffraction patterns were recorded by turning the sample around the surface normal (azimuthal scan, or θ scan, where $\theta = 0°$ corresponds to the sample position with the stripes lying parallel to the beam direction).

Interestingly, in the azimuthal scan for the 010 reflection diffracted signals were recorded in two angular regions centered at $\theta = 68.57°$ (see Figure 3 a) and at 106.72° (not shown). In each region, two peaks, few hundredths of a degree apart, are associated with a double population of crystallites, that is, a high amount of small crystallites (the strong and broad peak) and a smaller amount of larger crystallites (the weak and sharp peak). The (010) planes are oriented perpendicular to the surface and at almost 70.4° to the direction of the stripes. Since the same angular displacement of around 38° was observed between the sharper (wider) peaks of the two angular regions, it can be concluded that the crystallites align along two directions almost symmetrically centered with respect to the stripes and 38° apart. Similar results have been obtained for the 001 reflection, which confirms unambiguously that the stripes of **1** are formed by crystallites highly oriented with respect to the stripes. The fact that azimuthal scans for both 010 and 001 reflections could be measured, which are forbidden for the original structure, indicates that the molecular arrangement (with loss of symmetry elements) is slightly different from that in the bulk. This is confirmed by a slight difference in the scattering angles, which is not unusual for thin-film structures.

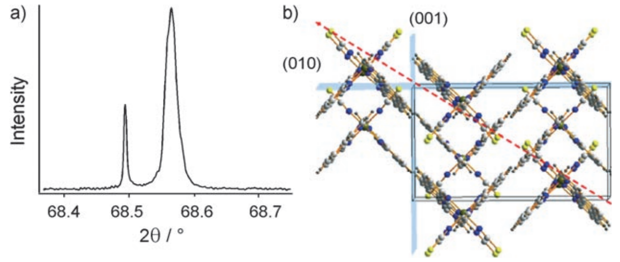

Figure 3. a) GIXD azimuthal scan for the (010) of microstripes printed by MIMIC. b) top view of the 3D structure of **1** in the microstripes, as oriented in one domain. The red arrow indicates the orientation of the microstripes.

After we had obtained these encouraging results we sought to further advance this approach by focusing on patterning **1** into domains with controlled shapes and positions. Since our final aim of ST patterning represents information storage, we molded films of **1** by LCW into a logic pattern, which had been transferred from a replica of a recorded compact disk. The imaging of the patterned film by dark-field optical microscopy and AFM reveals that an ordered array of crystallites of **1** was also generated under these conditions (Figure 4). This result proves for the first

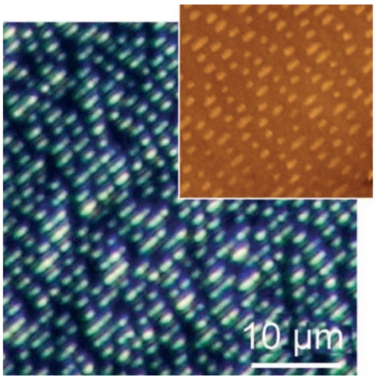

Figure 4. Optical micrograph of logic pattern of **1** printed on silicon surface. The micrograph is taken under dark field optical microscopy (scale bar 10 µm). The inset shows the corresponding AFM image (*z* scale 0–80 nm).

time that it is possible to write with ST compounds structurally to give readable logic patterns.

µ-Raman spectroscopy is a useful technique to probe the spin-state information and confirm that **1** still exhibits the spin-crossover phenomenon after processing.[32] This is particularly important for the logic structures shown in Figure 4, since the laser spot size (< 1.5 µm) in the µ-Raman experiment allows the spin-state detection with the resolution of a single dot. With this aim we performed Raman characterization as a function of temperature on freshly prepared films. Figure 5 shows the Raman spectra recorded at 77 K and 300 K, using laser excitation at $\lambda = 632.8$ nm. The films exhibit Raman spectra very similar to those of the powder. Furthermore, in agreement with the literature[32] the Raman spectra at different temperatures show the typical behavior observed in spin transition, which for **1** occurs at 176 K (see in details the diagnostic peaks at 1449, 1420, and 2070 cm^{-1}).

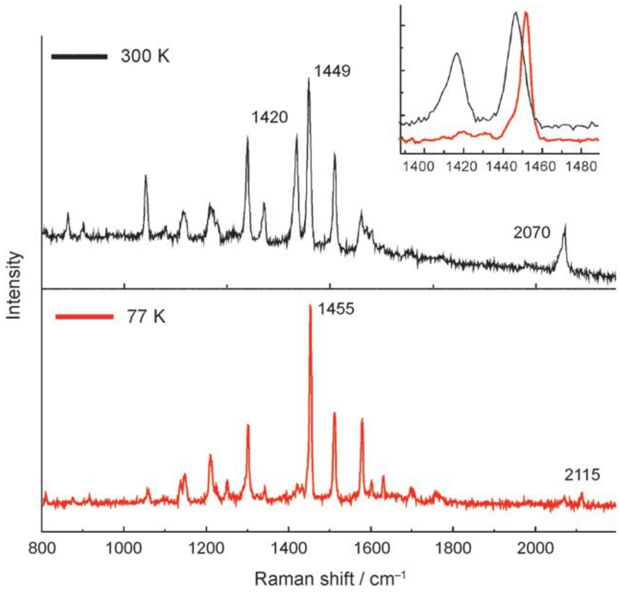

Figure 5. Raman spectra of a freshly prepared film of **1** in the high-spin state at 300 K and low-spin state at 77 K. The inset shows the diagnostic peaks.

It must be noted that occasionally the spectra at low temperature (i.e. LS state) still exhibit some peaks characteristic of the spectra at high temperature (i.e. HS state). This is probably a consequence of partial decomposition of **1** during the process. The presence of aging effects that are enhanced in thin films and patterned samples confirm this hypothesis. In fact when **1** is exposed to air and/or to relatively high-power laser light it tends to decompose and lose its switching properties (we observed that it remains in the HS state also at low temperature).

In conclusion, unconventional and soft lithography techniques have been used to fabricate reliably nanopatterns of ST compounds. The ST compound **1** could be lithographically processed into crystalline micro- and nanostripes as well as into logic patterns on a technologically relevant surface. The appearance of crystallinity in well-oriented nanostructures is a breakthrough, since molecular ST properties critically depend on the uniformity of the local environment around the ST switching units. In this respect, our work represents an important advance in view of the application of ST compounds in molecular devices. In forthcoming work, the resolution of the nanopatterning process can still be scaled down to smaller length scales. In addition, further technological developments such as encapsulation of ST compounds (to overcome the stability problem), the realization of processable room temperature ST, or the introduction of new triggers (e.g. electrical fields) for device integration is under progress. This ongoing work will lead to the development of new generation storage media based on a variety of molecular responses, for instance spin flip, conformational, optical anisotropy changes and changes of the dielectric constant.

Experimental Section

Synthesis: Compound 1 was synthesized followed reported literature methods. The magnetic properties of the bulk sample were checked by SQUID (MPMS-5T) measurements.[27]

Lithography: The elastomeric polydimethylsiloxane (Sylgard 184 Down Corning) stamps were prepared by replica molding of a blank or written Compact Disk support that acts as a structured master. The curing process was carried for 6 h at 60 °C. Once cured, the replica is peeled off from the master and washed in pure ethanol for one hour. The stamp motif consists of parallel lines with a periodicity of 1.5 µm, width at half height 500 nm and 220 nm deep. The stamps for LCW were coated with 100 nm of Au. Substrates: The substrates consist in a piece 10 × 10 mm^2 of silicon covered by native oxides. It was cleaned by: sonication for 2 min. in electronic-grade water (milli-pure quality), 2 min. in acetone (Aldridch chromatography quality) then 2 min. in 2-propanol (Aldridch spectroscopic grade quality). The solutions were prepared using *N*,*N*-Dimethylformamide (Aldrich $\geq$ 99 % quality).

Characterization: Raman scattering measurements were recorded in backscattering geometry using a 50 × objective with 632.8 nm excitation wavelength with laser power in the range of 10–20 µW. Low temperature were achieved by means of an open cycle liquid N_2 flow cryostat mounted on an micro xyz stage. Optical micrographs were recorded with a Nikon i-80 microscope equipped with epi-illuminator, dark-field and cross polars using 50X objective. AFM images were recorded with a commercial AFM (NT-MDT) operating in air, in contact mode (25° with relative humidity 55 %). Si_3N_4 cantilevers, with typical curvature radius of a tip 10 nm were used. GIXD measurements have been performed at the ID32 beamline of the European Synchrotron Radiation (ESRF, Grenoble, France). A double-bounce silicon (111) monochromator was used to select the energy of 18.06 keV from the emission spectrum of the undulators source. During the different scans, the incident angle of the X-ray beam on the sample surface was kept constant to 0.1°.

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