VIP Spin-Crossover Multilayers

DOI: 10.1002/ange.200601885

Multilayer Sequential Assembly of Thin Films That Display Room-Temperature Spin Crossover with Hysteresis**

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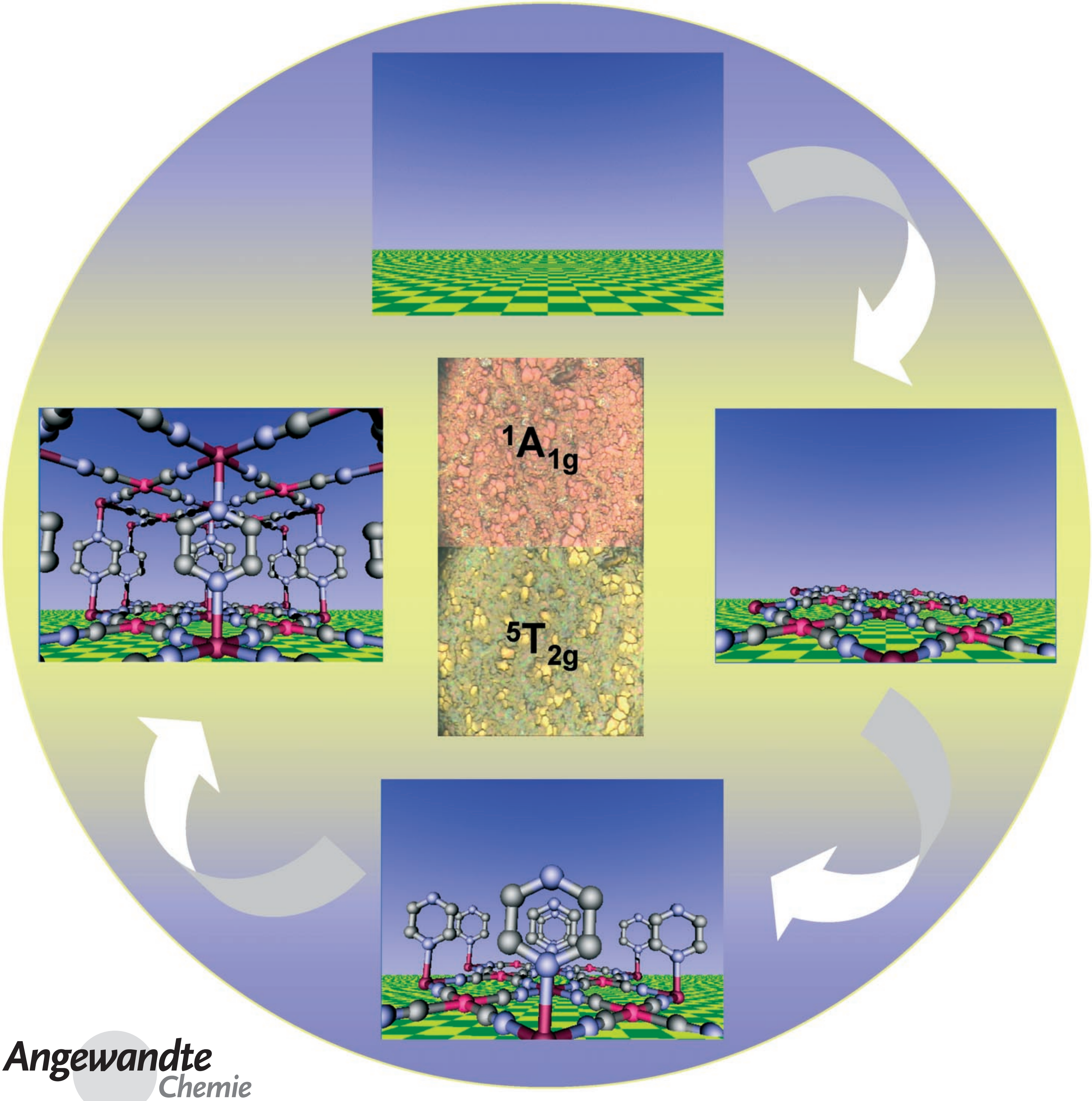
Dedicated to Professor Jean-Jacques Bonnet



The phenomenon of spin crossover between high-spin (HS) and low-spin (LS) states of $3d^4$–$3d^7$ transition-metal ions represents an important area of coordination chemistry.[1] Beside its theoretical aspects, the potential applications of this phenomenon also continue to draw attention.[2] In this context, we have recently shown that the change in spin state is accompanied also by a variation in the dielectric constant (ε) of the material and we could even observe room-temperature hysteresis of ε.[3] We suggested that this dielectric hysteresis property may be useful to build memory devices that can store information by high and low capacitance states. Further work by Freysz et al. and also by ourselves demonstrated that switching between the two spin states may be accomplished by using short (8-ns) laser pulses within the hysteresis region[4] and even at room temperature.[5]

These appealing properties cannot be exploited in bulk materials, but only if thin films of the compounds are prepared. However, up to now, very few examples for thin films of spin-crossover complexes have been reported.[6] These studies employed the Langmuir–Blodgett technique or a simple mixing of the complexes with polymers, which can be spin- or dip-coated onto surfaces. In any case, the resulting films were not purely composed of the spin-crossover complex but consisted of a mixture of the complex and a polymer or an amphiphile, which alters strongly the spin crossover as well as the dielectric and optical properties of the films.

In our quest to achieve thin layers of spin-crossover materials, our attention was drawn to an approach in which polymer multilayers were assembled on surfaces by using alternate adsorption of cations and anions.[7] This layer-by-layer assembly method has been extended to a variety of materials and allowed the deposition of dense, ultrathin films on diverse substrates, with precise control over the molecular arrangement and thicknesses on the nanometer scale. Though the assembly of films through transition-metal coordination reactions met more difficulties than the ionic route, a number of examples for successful multilayer assembly through coordination bonding have been reported.[8] Inspired by these studies, especially those of Mallouk and co-workers,[8a,b] we report herein our successful deposition of the three-dimensional (3D) spin-crossover coordination polymers, [Fe(pyrazine){$M(CN)_4$}] (M = Ni, Pd, or Pt).

The multilayer thin films consist of planar polymeric sheets formed of square-planar tetracyanometalate ions connected by six-coordinate Fe^{II} ions. Normal to these sheets, the iron ions are bridged by bidentate pyrazine ligands to form a 3D network (Figure 1). The assembly of the film involved the sequential dipping of the substrate into solutions of $Fe(BF_4)_2\cdot 6H_2O$, $(TBA)_2M(CN)_4$ (M = Ni, Pd, or Pt; TBA = tetrabutylammonium), and pyrazine in ethanol (Scheme 1). To reduce the desorption rate of the coordinated species, the reactions were conducted at low temperature (−60 °C).

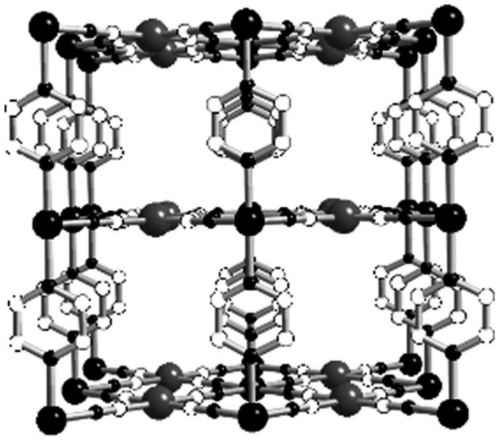
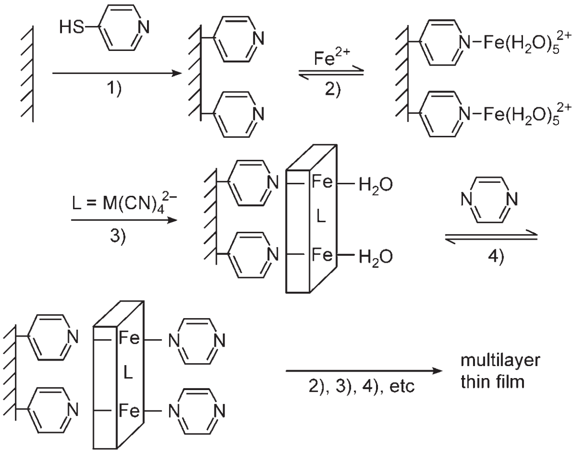


Figure 1. Schematic drawing of the 3D coordination polymers [Fe(pyrazine){$M(CN)_4$}] (M = Ni, Pd, or Pt). M gray; Fe black (large); N black (small); C white.

For the efficient adsorption of iron ions in the first adsorption cycle, the substrate surface must be modified by a monolayer of anchoring groups. We initially used mercapto-



Scheme 1. Sequential assembly of [Fe(pyrazine){$M(CN)_4$}] (M = Ni, Pd, or Pt) films.

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[**] The authors are grateful to L. Rechignat (LCC-CNRS) and G. L. Agusti (ICMol) for experimental help. This work was supported by the Plateforme Technologique du LAAS CNRS (Toulouse, France). J.A.R. is grateful to the Spanish Ministerio de Educatión y Ciencia (MEC; CTQ 2004-03456/BQU).

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pyridine or cystamine monolayers on gold, but the obtained films were rather discontinuous. Therefore, we introduced a templating film on the mercaptopyridine layer. This film was constructed on the substrate by dipping it into a solution of 4,4′-azopyridine instead of pyrazine (step 4 in Scheme 1). The 4,4′-azopyridine ligand assembles in the same way as the pyrazine analogue, but it was found to anchor more efficiently on the surface even at room temperature. The subsequent steps were performed as previously but using pyrazine in step 4. This strategy provides a surface layer whose chemistry and structure closely match that of the target compound [Fe(pyrazine){M(CN)$_4$}], allowing the "epitaxial" growth of continuous films of the latter (see Supporting Information).

To identify the compounds assembled in the thin films and to probe the spin state, we carried out Raman microscopy measurements. We have extensively employed this technique in the past to investigate the bulk form of these complexes.[9] The Raman spectra of these compounds exhibit CN stretching modes around 2200 cm^{-1} and pyrazine internal modes between 600 and 1600 cm^{-1}. The lower frequency modes can be attributed primarily to metal–ligand vibrations and lattice phonons. Several vibrational modes may be followed to probe the change in spin state, but the most useful is probably the intense pyrazine in-plane bending mode, which exhibits a shift from 645 to 675 cm^{-1} when going from the high-spin to the low-spin state.

Figure 2 shows Raman spectra of powder and film samples of [Fe(pyrazine){Pt(CN)$_4$}] recorded at 295 and 120 K. Spectra of the powder and film samples are virtually identical. Moreover, in the films we can easily recognize the frequency shifts that accompany the thermally induced spin crossover, in agreement with our previous assignments on bulk samples.[9b] The strong intensity enhancement of the pyrazine modes at 1230 and 1605 cm^{-1} in the LS state is also confirmed in the multilayers. This phenomenon is probably related to the observed color change of the sample (yellow in the HS state; red in the LS state). Note that similar spectral changes were also observed in the Ni and Pd samples (see Supporting Information).

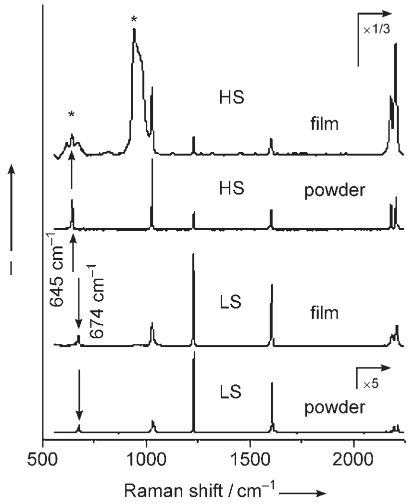

Figure 2. Raman spectra of [Fe(pyrazine){Pt(CN)$_4$}] powder and film samples recorded in high-spin (HS; 295 K) and low-spin states (LS; 120 K). Asterisks indicate Raman scattering from the Si substrate.

Figure 3 shows the temperature dependence of the Raman intensity in the cooling and heating cycles for the powder and multilayer samples. (We chose the modes at 1025 and 1230 cm^{-1} for their high intensity, but other Raman markers provided comparable results.) The powder sample reveals a hysteresis loop with a width of 25 K centered around 290 K. This hysteresis corresponds closely to the magnetic susceptibility measurements (Figure 3a). The multilayers display a hysteresis loop centered around 310 K also with a width of 25 K. The spin transition in the multilayers, however, is less abrupt and the square shape of the hysteresis is lost (Figure 3b). Similar observations were made for the Ni and Pd samples as well (see Supporting Information), which we can attribute to solvent effects. In fact, we have previously demonstrated that the spin-crossover behavior of powder samples depends in a dramatic fashion on the water content, and a heat treatment at 420 K is necessary to remove the water of crystallization.[5] Only the dehydrated powders exhibit wide, square-shaped hysteresis behavior. Annealing the film samples (which are prepared in ethanol, contrary to the powders) to 420 K influenced also the spin crossover in the multilayers, but we could not obtain abrupt spin transitions either as a result of residual solvent content or for other reasons, such as the extent of crystallinity of the films.

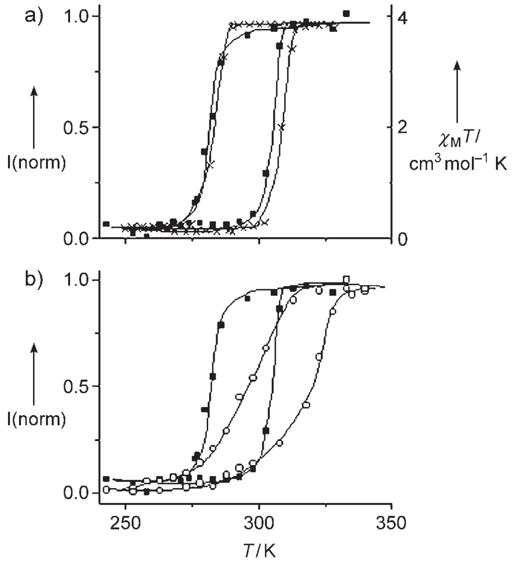

Figure 3. a) Temperature dependence of the $\chi_M T$ product (×; χ_M is the molar magnetic susceptibility) and the normalized Raman intensity ratio (■; I(norm) = I(1025 cm^{-1})/I(1230 cm^{-1})) for [Fe(pyrazine){Pt(CN)$_4$}] powder upon cooling and heating. b) Temperature dependence of the normalized Raman intensity ratio (I(norm) = I(1025 cm^{-1})/I(1230 cm^{-1})) for [Fe(pyrazine){Pt(CN)$_4$}] powder (■) and film samples (○) upon cooling and heating.

In summary, we have demonstrated a successful multilayer assembly of [Fe(pyrazine){M(CN)$_4$}] polymers through coordinate covalent bonding. To our knowledge, these samples represent the first example of unmixed, multilayer thin films that display spin-crossover phenomenon. Of additional importance is the fact that this spin crossover occurs with hysteresis and around room temperature. We believe this result provides thus not only an alternative for exploring optical and dielectric properties of spin-crossover materials but also a novel platform for the construction of devices, which is the supreme goal of our research. Studies continue to optimize the growth and physical properties of these systems and also to extend this method for other compounds.

Experimental Section

Powder samples were synthesized as described in Ref. [9a]. Thin films were assembled on 50-mm^2 gold surfaces (15-nm Au/2-nm Ti evaporated on polished Si wafers) as follows: The substrates were first functionalized by submersing them overnight into a solution of 1 mM mercaptopyridine (or cystamine) in ethanol. These wafers were soaked alternately (total of 5 cycles) in 100 mM $Fe(BF_4)_2$, 100 mM $(TBA)_2Ni(CN)_4$, and 100 mM 4,4′-azopyridine (synthesized according to Ref. [10]) in ethanol solutions (1 min) at room temperature, with rinsing in pure ethanol between steps (30 s). Then, the wafers were soaked alternately (total of 20 cycles) in 100 mM $Fe(BF_4)_2$, 100 mM $(TBA)_2M(CN)_4$ (where M = Ni, Pd, or Pt), and 100 mM pyrazine in ethanol solutions (1 min) at −60 °C, with rinsing in pure ethanol between steps (30 s). Finally, they were dried under Ar flow.

Variable-temperature magnetic susceptibility measurements were carried out at 325–225 K on the powder samples using an MPMS magnetometer (Quantum Design) operated at 1 T. Experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.

Variable-temperature Raman spectra were collected in the 150–2300 cm^{-1} frequency range. Samples were enclosed under nitrogen atmosphere on the cold finger of a THMS600 (Linkam) liquid nitrogen cryostage. Before the measurements were taken, the samples were heated to 423 K during 30 min to eliminate residues of solvents. The LabRAM-HR (Jobin Yvon) Raman spectrometer used in these experiments consists of a BXFM (Olympus) optical microscope, a single-grating spectrograph (1800 grooves mm^{-1}, $f = 800$ mm), and a DU420-OE (Andor) CCD detector. The entrance slit was kept at 100 mm, and a spectral resolution of ca. 1 cm^{-1} was obtained. The 632.8 nm line of a 17-mW He/Ne laser was used as the excitation source, and plasma lines were removed by using a narrow-band interference filter. The exciting radiation was directed through a neutral density filter (OD = 2) to avoid sample heating and was focused on the sample through a ×50, 10.6-mm working-distance objective (NA = 0.5). The scattered light was collected in a back-scattering configuration using the same microscope objective, and the Rayleigh scattering was removed by means of a holographic notch filter.

Received: May 12, 2006
Published online: July 26, 2006

Keywords: coordination polymers · multilayer assemblies · Raman microscopy · spin crossover · thin films

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