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Title: Spin-transition of Fe(II)-complexes noninvasively attached to HOPG

Experimenters

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Experimental report

Abstract

We proposed to study the electronic as well as the magnetic properties of the pyrene-decorated Fe(phen)₂(NCS)₂ (phen=1,10-phenanthroline) (**1**) spin crossover complex (SCO) at submonolayer-regime at the vicinity of the spin crossover temperature. Due to the noninvasive interaction between HOPG and the pyrene-anchoring groups, the spin transition (ST) behavior of the molecules is supposed to be retained on a surface with low coverage.

Scientific background

Switchable molecules as parts of spintronic devices in the information storage technology are of high technological interest. To develop molecular based devices utilizing spin-crossover building blocks, the study of the behavior of surface-assisted ST complexes at submonolayer-regime is necessary. Fe(phen)₂(NCS)₂ (phen=1,10-phenanthroline) (**2**) is one of the most thoroughly investigated ST compounds; in bulk it exhibits a LS \leftrightarrow HS ($S=0 \leftrightarrow S=2$) transition at 176 K [1a]. Moreover, complex **2** (see figure 1) presents a very rare case of neutral and sublimable ST compounds. High-quality films of about 300 nm thickness of complex **2** were deposited on silicon and glass substrates by evaporation under high vacuum conditions. The ST compound **2** maintains the expected electronic structure on thick film [1b], as well as in the micro- and nanopatterning regime [1c] similar to the bulk situation. The processing of ST compounds into switchable nanostructures was achieved so far only by soft-lithography or nanopatterning techniques [1b, 3] leading to multi layered structures. We propose to arrange ST molecules **1** (see figure 1) in a monolayer/submonolayer-regime at HOPG and investigate their spin transition behavior. The critical part of this configuration is the interaction between the molecules and the surface. Implementation of electron rich metal surface can invalidate the ST due to efficient coupling. Therefore we propose to use HOPG as substrate instead of a metallic surface and decorate the ST complex with pyrene-anchoring groups suitable for noninvasive interaction with sp²-carbon materials yielding complex **1**. This procedure will avoid strong interaction of the Fe ion with the substrate leading to the conservation of the ST behavior. The integration of metal complexes via pyrene groups to graphene and carbon nanotubes has been shown to lead to confined magnetic systems of high interest for supramolecular spintronic applications [2].

Results

We studied the Spin transition compound $[\text{Fe}(\text{phen})_2(\text{SCN})_2]$ as a powder sample and as in situ sublimated submonolayer on HOPG.

The spectra of the powder sample (figure 2 and figure 3) give a reference concerning the spectral features and the transition temperature. The compound shows a very clear transition for both cases, cooling down and warming up.

For high temperatures, the Fe is in the high spin state, has the largest peak at lower energy. For low temperatures, it is in the low spin state and the largest peak is at higher energy.

The spectra of the submonolayer sample are shown in figures 4 and 5. The coverage is about 10% of a monolayer and to avoid radiation damage we reduced the X-Ray intensity. So the signal to noise ratio is not too good.

A transition is visible, but with a complete different behavior compare to the powder sample. The pictures show only the maximum of the L3 edge. The low energy peak is normalized to 1.

Between 300 K and 100 K it seems to switch continuously. At 100 K the maximum of the second peak is reached and for lower temperatures it decreases again. This characteristic seems very strange. But if you have a look on the “warm up” graph, it reproduces almost 100%. That indicates that we can exclude artifacts in the measurement or radiation damage of the sample.

It is definitively not a 100% HS-LS transition. We estimate the high spin-low spin amount by simulating with the powder spectra:

Figure 6 shows simulated mixings of HS and LS spectra for different amounts of the two states.

Comparing the peak intensities in the simulated spectra with those of the submonolayer tells you the amount of each spin state. So it seems that in the submonolayer the high spin state is between 60% and 90%. So most of the molecules are pinned in a high spin state, but some of them can be switched with temperature.

References:

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Figures:

Figure 1

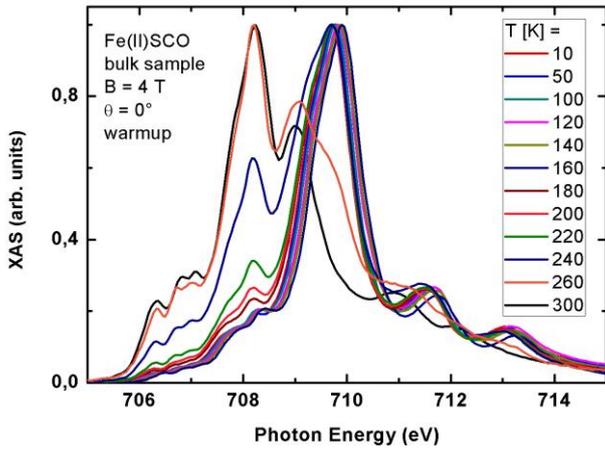
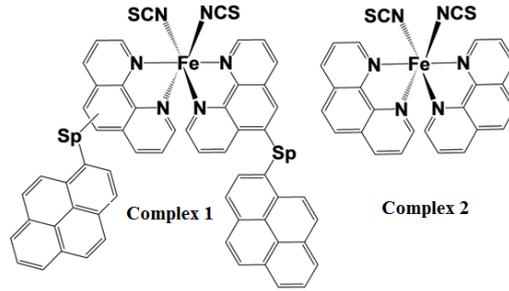


Figure 2

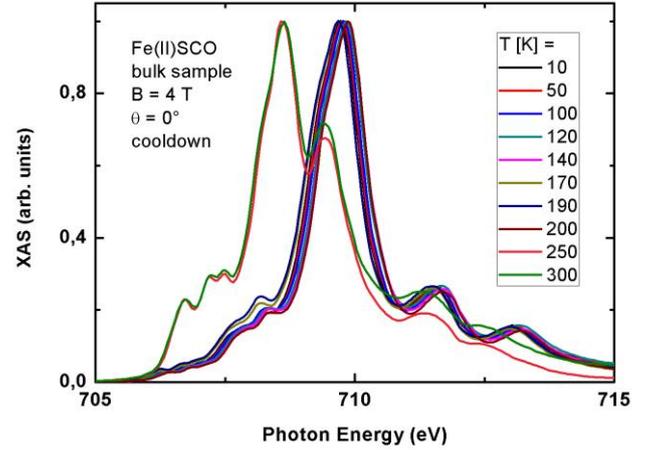


Figure 3

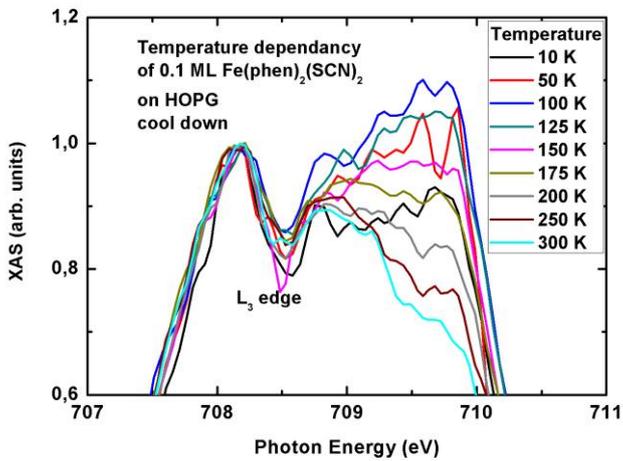


Figure 4

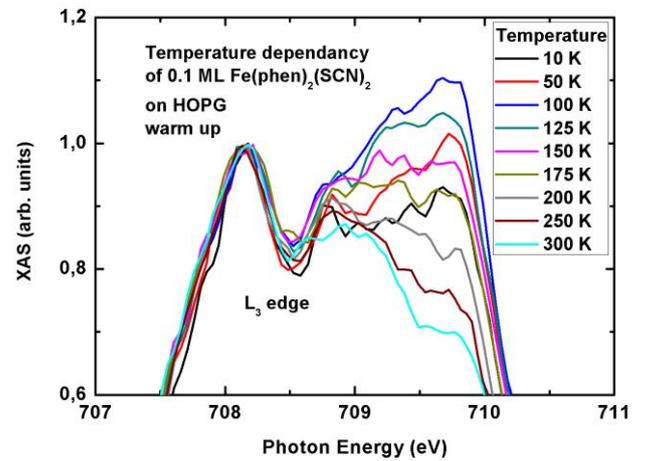


Figure 5

Figure 6

