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Report:

The aim of our experiment was to study by Synchrotron Mößbauer Spectroscopy (SMS)[1] the SCO transition down to the nanoscale of two different kinds of complexes based on ^{57}Fe. Spin Crossover (SCO) metal complexes are molecular systems able to swap spin states under thermal and light irradiation stimuli and, thanks to these properties, they constitute promising building blocks for spintronics, data storage and sensing devices. [2,3] These systems can be assembled intact onto different substrates, with controlled thicknesses from micrometers down to sub-monolayer coverage even if several details on the behavior of these molecules at the nanoscale are still missing, being strongly debated if a monolayer of these molecule can maintain the reversible switching between the two spin states. Among this class of complexes, many iron based complexes were investigated with synchrotron based technique, following the SCO transition by x-ray absorption spectroscopies.[4–7] Previously, SCO metal complexes were deeply studied by standard in house Mößbauer Spectroscopy in the massive phase. This is the first experiment based on SMS of successful measurement of the SCO effect at the nanoscale in these model samples opening the possibility for the whole communities of molecular magnetism and molecular spintronics of studying Fe-based SCO in different environments. SMS is an alternative and more specific technique to evaluate the spin state of very thin deposits of SCO and to study the influence of physisorption on the SCO effect. We studied two different SCO complexes, named Fe(phen) and Fe(qnal).[8,9] Both molecules have a Fe(II) ion as the metallic center, that is however connected to different ligands. The molecules were enriched in ^{57}Fe and deposited on a gold substrate by thermal sublimation in UHV or by drop casting. Different sublimated samples were realized with thicknesses between 50 nm and

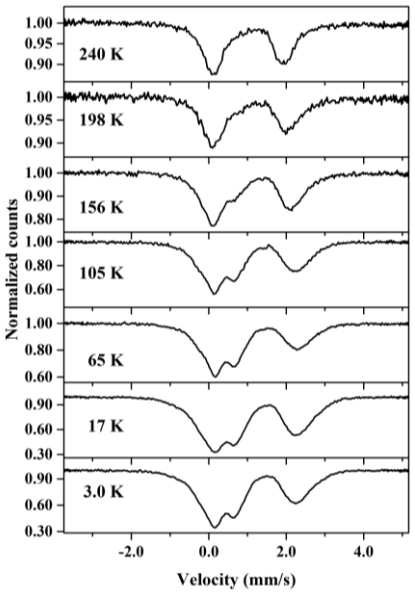

Figure 1 Mößbauer spectra of the 50 nm thick sublimated sample of Fe(phen) molecules on gold as a function of the temperature

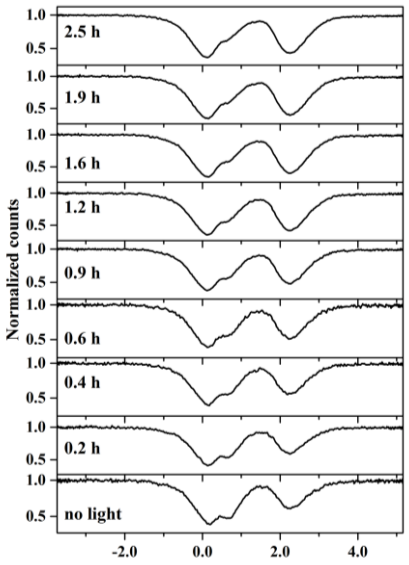

Figure 2. Mößbauer spectra of the 50 nm thick sublimated sample of Fe(phen) molecules on gold for different irradiation times (LIESST effect).

5 nm. Thicker samples were realized by drop casting, that were prepared freshly at the ESRF chemistry lab. The first study considered the thermal SCO efficiency of the Fe(phen) complex. Mößbauer spectra of the samples were realized from 240 K to 3.0 K in the grazing incidence geometry of the SMS setup. [1] All spectra show a clear conversion from the high spin (HS) state to the low spin (LS) state passing from high to low temperature (see Figure 1). However, the SCO transition is not complete, *i.e.* at 3.0 K a significant percentage of the molecules seems to remain in the HS state. This behavior differs from that reported for bulk samples, where a complete SCO transition takes place.[8,10] This feature points out to a possible effect of the interaction of the molecules with the substrate, that affects their SCO transition efficiency. A second series of Mößbauer measurements were realized to assess the LIESST effect, *i.e.* the SCO transition induced by illumination of the molecules with an appropriate wavelength.[11,12] To this aim, we supplied modified sample holders suitable to accommodate a couple of LEDs for each sample and the corresponding electrical cables. Mößbauer spectra were realized at low temperature for different irradiation lengths up to about 3 hours (see Figure 2). The spectra show that the 990 nm wavelength radiation effectively promotes the transition of the Fe(phen) molecules from the LS state to the HS state. Similar thermal and light characterizations were carried out on Fe(qnal) complex (the LIESST effect was induced by 545 nm wavelength radiation). The results are qualitatively similar to those obtained for the Fe(phen) molecule (see Figure 3). As already demonstrated by a study of Fe_4 single molecule magnets deposited on gold, performed by some of us at ID18,[13] the SMS is perfectly suited to study thin sublimated samples. Moreover, our measurements show that, once deposited on gold, the SCO efficiency of the molecules is modified with respect to the bulk phase. The analysis of the collected data will quantify this behavior, enabling to compare the thermal and light induced SCO efficiency and to assess their dependence on the thickness of the samples.

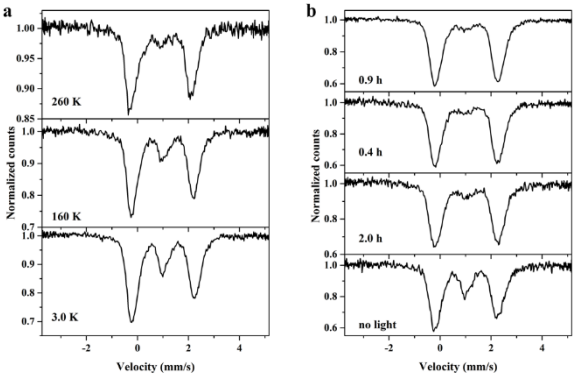

Figure 3. Mößbauer spectra of the 50 nm thick sublimated sample of Fe(qnal) molecules on gold as a function of the temperature (a) and for

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