Anomalous Light-Induced Spin-State Switching for Iron(II) Spin-Crossover Molecules in Direct Contact with Metal Surfaces

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Abstract

The light-induced spin state switching is one of the most attractive properties of the spin-crossover materials. In bulk, low spin (LS) to high spin (HS) conversion via the light-induced excited spin state trapping (LIESST) effect may be achieved with a visible light while the HS-to-LS one (reverse-LIESST) requires an excitation in the near infrared range. Here, we show that those phenomena are strongly modified at the interface with a metal. Indeed, we report an anomalous spin conversion from HS state to LS state under blue light illumination for Fe^{II} spin-crossover molecules that are in direct contact with metallic (111) single crystal surfaces (copper, silver and gold). To interpret this anomalous spin state switching, we propose a new mechanism for the spin transition based on the light absorption by the substrate that can generate low energy valence photo-electrons promoting molecular vibrational excitations and subsequent spin state switching at the molecule-metal interface.

Introduction

Molecular switches are fascinating compounds that can lead to various applications.[1] Among them, spin-crossover (SCO) molecules[2,3] exhibiting magnetic bistability have attracted tremendous attention as both low spin (LS) and high spin (HS) states are accessibly switched by external stimuli, and this can be used for example for the conception of molecular memory devices. For Fe^{II} complexes ($3d^6$ electronic configuration) in octahedral geometry, when ligand field and spin pairing energies are of the same order of magnitude, spin-crossover may occur under external stimuli such as temperature, pressure, etc. In the last decade, research effort has focused on the investigation of the behavior of such molecules at the nanoscale, *e.g.* in nanoparticles[4–6] or even, in single-molecule junction.[7] While the switching by the use of electrical signals seems promising but yet challenging,[8–11] visible and near-infrared lights are still considered as the main switching stimuli, considering their intrinsic properties (*e.g.* wavelength, power, polarization, temporal dynamics, and easy manipulation). For

bulk compounds, the so-called Light-Induced Excited Spin State Trapping (LIESST) has been introduced, describing a visible light-induced spin state switching process between a LS ground-state and a metastable HS state.[12] Meanwhile a reverse LIESST (r-LIESST, *i.e.* switching from HS-to-LS) that can only be promoted by near infrared excitation has been discovered,[13] giving rise to applications in light driven memory devices.[14]

To develop efficient nanoscale devices,[15,16] it is mandatory to study the light-induced processes at the level of SCO molecule-substrate interfaces.[17,18] A very powerful technique to do so is X-ray absorption spectroscopy (XAS) as the measured Fe^{II} $L_{2,3}$ edges have very different shapes in the LS and HS states.[19] Scanning tunneling microscopy (STM) is also very complementary as it can probe the homogeneity of the samples and give information on the spin state transition at the molecular scale. It has already been shown on different Fe^{II} compounds that a submonolayer on graphite, bismuth or other 2D materials can undergo a complete LS to HS transition at low temperature through the LIESST effect with green light .[20–24] In this paper, we report XAS and STM experiments on Cu(111), Ag(111) and Au(111) in which we observe, for submonolayers of Fe^{II} SCO molecules ($Fe^{II}[(3,5\text{-}(CH_3)_2Pz)_3BH]_2$ Pz=pyrazolyl, called **(1)** in the following), a partial HS-to-LS (reverse-LIESST type) conversion with blue light while red light has almost no effect. This behavior is opposite to what is observed in bulk in which both blue light by a metal to ligand charge transfer (^1MLCT) excitation and red light by a *dd* excitation induce a LS to HS conversion. To account for this new anomalous effect (see below the photomagnetic response induced by LIESST and reverse-LIESST in the bulk), we propose an interpretation based on a more efficient absorption of visible light by the substrate rather than by the molecule, generating low energy valence photo-electrons that would promote indirect switching of the molecular layer from HS to LS. Moreover, we also observe a soft X-ray induced excited spin state trapping (SOX-IESST)[25] that switches molecules from LS to HS with the visible light off and under X-ray fluence. We are therefore able to switch reversibly the molecules at the interface by the subsequent use of blue (or green) light and soft X-rays.

Results and discussion

Fig. 1 shows XAS spectra around the Fe^{II} L_3 edge, recorded at 4 K for submonolayer coverage of **(1)** on a Cu(111) surface in Fig. 1a, on Ag(111) in Fig. 1b and on a Au(111) surface in Fig. 1c. The molecular coverage, around 0.5 monolayer (ML) for each sample, has been directly measured with scanning tunneling microscopy (STM) images on Cu(111) and Au(111) and by comparison of the jump at the Fe^{II} L_3 edge for Ag(111) (cf. Fig. S1, Fig. S2 and supplementary information for details). A thorough STM analysis recorded at different locations of the three samples shows that **(1)** is imaged exclusively in well-ordered two-dimensional crystals of one monolayer height with typical lateral size of hundreds of nanometers. Representative small scale images are shown in inset of Fig. 1a-c. The homogeneous lattices remarkably observed over large areas (cf. Fig. S3) of the samples strongly suggest the integrity of **(1)** on the three metallic substrates. The spectra before (red curves) and after (blue curves) blue light exposure during 20 minutes (with X-rays off) at a fluence of 0.5 $mW.cm^{-2}$ are compared.

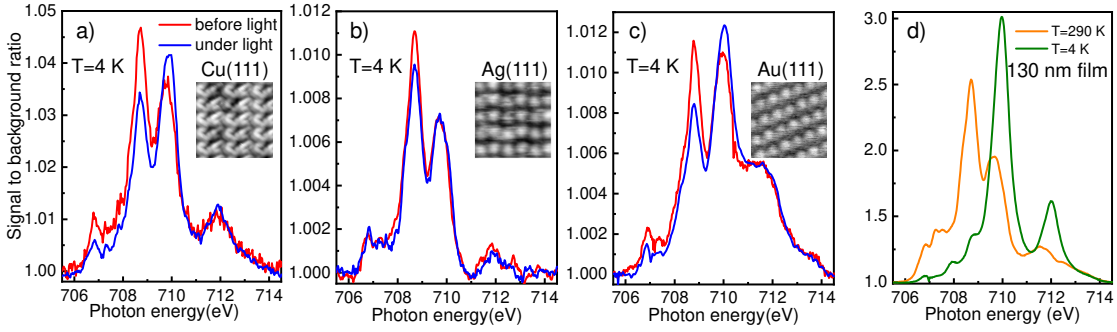

Figure 1: 4 K X-ray absorption spectra of the Fe^{II} L_3 edge before and after illumination of the sample with a blue light (405 nm) for 20 minutes for : a) 0.4±0.1 ML of **(1)** on Cu(111). b) 0.5±0.1 ML of **(1)** on Ag(111). Average over 11 spectra before light and 10 spectra under light in steady state conditions. c) 0.5±0.1 ML of **(1)** on Au(111). Average over 6 spectra before light and 13 spectra under light in steady state conditions. A linear background has been removed and the spectra have been normalized to the background value at 708.7 eV. The jump at the L_3 edge can therefore be read as a percentage of the background signal. In inset, 5x5 nm^2 STM images recorded at tunneling conditions : U=-1.3 V, I=50 pA on Cu(111), U=-1.5 V, I=10 pA on Ag(111) and U=-1.5 V, I=20 pA on Au(111). d) Reference spectra recorded at 4 K and 290 K on a 130 nm thick film of **(1)** on a SiO_2 substrate.

In such 4 K XAS spectra, the peak at 708.7 eV is characteristic of a HS state while the peak at 710 eV is characteristic of a LS state.[26] Two striking observations can be done from those spectra. Firstly, the molecular layer never shows a pure LS phase at low temperature, at the difference of what is observed in bulk by magnetometry[27–29] but a mixture of HS and LS (cf. Fig. 1d for reference spectra of pure LS at 4 K and pure HS at 290 K recorded on a thick layer of **(1)** previously annealed at 400 K[28]). Such a spin-state mixing has already been observed for other molecules on metal surfaces recently[29,30] and can be due to the epitaxial constraint imposed by the substrate on the molecular layer.[31,32] STM images (cf. Fig. S3 and related discussion) demonstrate unambiguously that this mixture of LS and HS molecules is not related to inhomogeneities and partial molecular decomposition[23,33,34] but is intrinsic to the metal-molecule interface. Secondly, the molecular layer switches partially under a blue light illumination but very differently from what is known so far for the bulk and for thin films.[27,28] Indeed, we clearly observe for the samples on Cu(111) and Au(111), that the LS feature increases after light illumination, in contradiction with the UV-visible absorption properties of both spin states[28] and the so far proposed LIESST mechanism, where blue light only switches the LS ground state into the HS state (^1MLCT excitation).[12] On the contrary, no significant evolution is observed on Ag(111).

To reach a quantitative view of the results, a linear combination analysis is performed to assign the different components in the spectra with respect to the LS and HS signals at low temperature. Because in the darkness at low temperature, we observe a mixed LS/HS phase, we have measured the HS and LS XAS references at low temperature on bulk materials (cf. Fig. S4 and related discussion for details). After a proper normalization, we fit our data by a weighted average of the two references, giving rise to the HS and LS proportions in the molecular layer.[20] More information on the fitting procedure is given in the supplementary information. With this procedure, we can give a quantitative estimation of the HS proportion in each sample. We find that on Cu(111), it is 75.0±0.7% before light and 54.9±0.6% after light. On Ag(111), it is 78.6±1.3% before light and 73.8±1.6% after light. On Au(111),

we find 65.6±1.3% before light and 49.7±1.2% after light. Therefore, beside the spin-state mixing that particularizes each pristine/as-prepared samples, it appears that the spin-state switching with blue light strongly depends on the substrate nature.

Fig. 2 shows the time evolution of the anomalous light induced HS to LS switch for the Cu(111) (Fig. 2a) and Au(111) (Fig. 2b) samples, using both blue (405 nm, ^1MLCT excitation in bulk) and red light (635 nm, $^1A_1$ to $^1T_1$ excitation in bulk) with a fluence of 0.5 mW.cm^{-2}, together with the reference experiment on the bulk compound, measured by SQUID magnetometry (Fig. 2c). In bulk, the reverse-LIESST process is triggered by near infrared light ($^5T_2$ to ^5E excitation)[13] while conversely blue and red lights induce the LIESST effect, i.e. an increase of the HS proportion (cf. Fig. 2c). In contrast, on both Cu(111) and Au(111) surfaces, we observe that a red light has a very small influence on the proportion of HS molecules and blue light switches efficiently HS molecules into LS ones. On the Ag(111) surface, no significant evolution of the HS proportion is measured, whatever the used wavelength is. From the data of Fig. 2a and 2b related to blue light irradiation, we can extract, using a single-exponential decay fit, both the amplitude in HS proportion of this light-induced effect and the typical switching time scale τ for the given fluence of 0.5 mW.cm^{-2}. On the Cu(111) surface, 20% of HS molecules are switched and τ=150 s. On the Au(111) surface, 13% of HS molecules are switched and τ=180 s. Green light (532 nm, not shown here) has an effect rather similar to blue light.

It is worth to notice that those measurements are done using X-rays that have also an influence on the spin state proportion (SOXIESST effect). However, it cannot explain the light-induced anomalous switching observed here. Indeed, firstly, we have taken great care to reduce this effect to its minimum by using a low X-rays fluence (cf. methods section for details). A comparison between the spectra on Cu(111) at 4 K (Fig. 1a) and 80 K (cf. Fig. S2a) where SOXIESST is known to be negligible[25] gives the typical small modification induced by the SOXIESST in a dark state (no visible light) and under a steady state of X-rays illumination. Secondly, the SOXIESST we have observed is a small LS-to-HS switching with

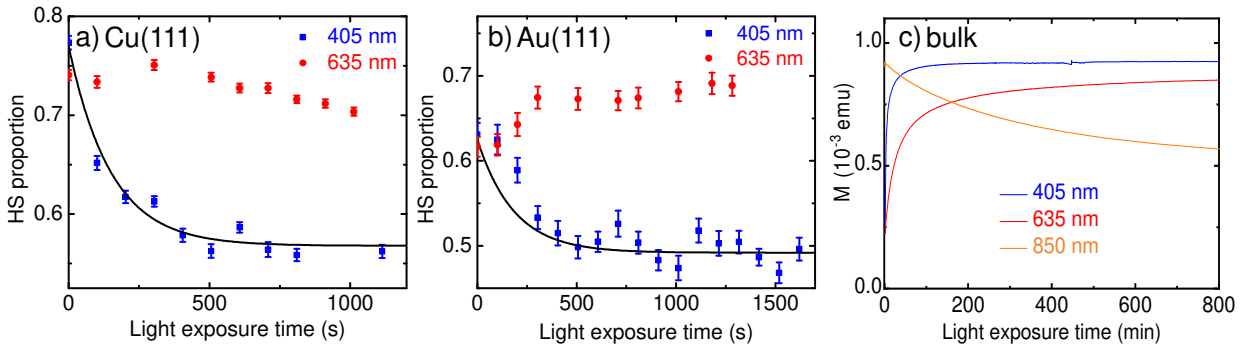

Figure 2: a) 0.6±0.2 ML of **(1)** on Cu(111). Time evolution of the HS proportion, measured at 4 K, extracted from the XAS spectra, as function of the time of illumination for a blue (405 nm) or a red (635 nm) light. The black lines are exponential decay fits. b) Same as (a) for 0.5±0.1 ML of **(1)** on Au(111). c) Magnetization (under μ_0H=0.5 T) measured by SQUID at 10 K on the bulk (powder, m=0.62 mg) of **(1)**, as function of the time of illumination for 405 (20 mW.cm^{-2}), 635 (10 mW.cm^{-2}) and 850 nm (32 mW.cm^{-2}). The usual LIESST is observed for 405 nm (^1MLCT excitation) and 635 nm ($^1A_1$ to $^1T_1$ excitation), while the reverse LIESST is observed for 850 nm ($^5T_2$ to ^5E excitation).

X-rays under time in a dark state, *i.e.* the opposite switching than the one observed with blue light on Cu(111) and Au(111). As a consequence, the amplitude of the anomalous light-induced switching is certainly slightly underestimated (few percents of the spin proportion) and the measured steady state corresponds to a dynamical equilibrium between anomalous light induced spin state switching and SOXIESST, although strongly dominated by light induced switching. Thirdly, for each samples, we have used a reference spot, virgin of X-rays but illuminated with light. In the error bar of the experimental data, we have found the same proportion of light-induced HS-to-LS switching on those spots than on spots continuously measured with X-rays. Finally, STM experiments conducted under light illumination (cf. Fig. S3) are in good agreement with the anomalous transition measured by XAS, showing once again that the X-rays can be considered only as a slight perturbation and not at the origin of this peculiar effect. Note also that for thick films of the same spin-crossover compound it has been demonstrated using the same XAS technique that illumination with a Ti:sapphs laser was inducing a LS-to-HS transition,[27] *i.e.* a normal light-induced switching behaviour as found for the bulk material with standard magnetometry techniques (cf. Fig 2c).

We therefore conclude that the observed anomalous HS-to-LS switching under blue light is specific to the metal-molecule interface.

In Fig. 3, we show on 0.6±0.2 ML of **(1)** deposited on Cu(111) that using the switching from HS to LS state with blue light and from LS to HS with X-rays (SOXIESST) we can perform almost reversible switching cycles at 4 K. The data can be nicely fitted with single-exponential decay functions. For the used fluences, the typical switching time scale are 2 min 30 s with blue light and 30 min with X-rays. Qualitatively, this behavior is rather similar to what can be obtained on bulk materials via LIESST and r-LIESST effects but using very different wavelengths and with a reduced amplitude in the HS fraction. According to the above findings, the substrate plays a decisive role in the mechanism.

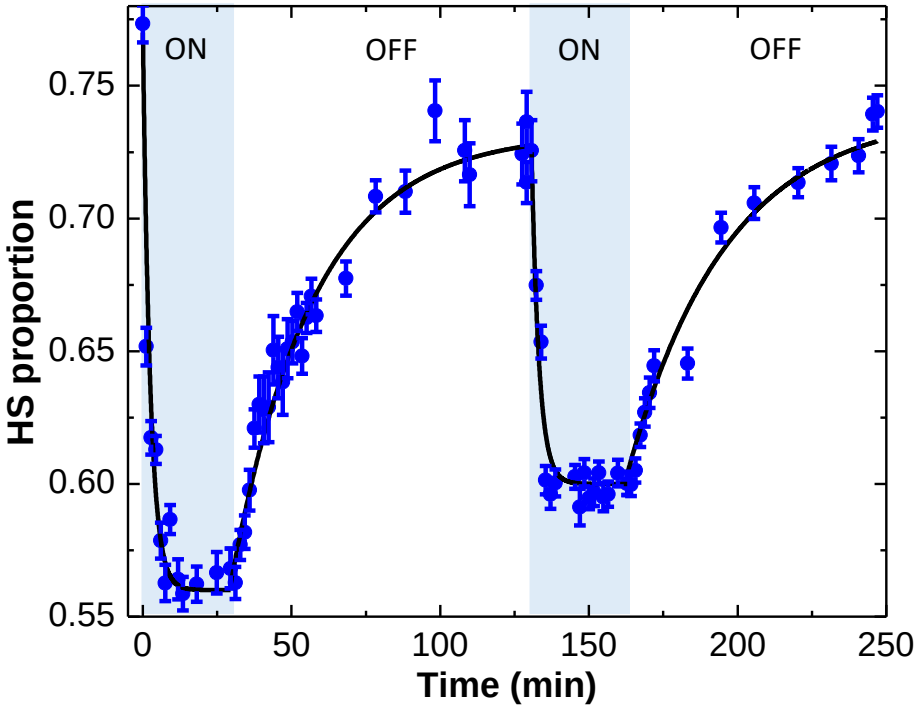

Figure 3: Reversible switching of 0.6±0.2 ML of **(1)** on the Cu(111) surface using blue light on and off irradiations series under X-rays. Blue circles are data points extracted from the XAS spectra. The black line is a fit using single-exponential decay functions.

In this section, we discuss the relationship between the nature of the substrate and the observed HS to LS switching that occurs with blue light irradiation for monolayers on surfaces

rather than with near infrared light for the bulk compound (cf. Fig. 2).

The maximum proportion of HS molecules that we have been able to switch for those molecular layers in direct interaction with Cu metal surfaces is no more than 20%. This has been already observed for similar systems[30] or in devices[35] and has been ascribed to structural changes or degraded molecules,[36] presumably modified by the X-ray beam. Although this latter explanation is likely and depends on both the molecular moities and the X-rays fluence, we believe that this partial switching is also induced by the molecule-substrate interactions.[31] Further mechano-elastic simulations considering a substrate and dynamical effects of light could confirm indeed how the elastic energy stored in the molecular layer can strongly modify the proportion of switched molecules.

Concerning the outcome of the anomalous light-induced spin state switching from HS to LS, we can rule out the direct photon absorption by the molecules in the HS state as thin films of **(1)** show no absorption in the blue or green light range.[28] Thus the usual mechanism for r-LIESST involving the transition through HS excited states is baseless. Moreover, it would not explain why the effect is more pronounced on Cu(111) and Au(111) than on Ag(111) surfaces. Therefore we propose an alternative competitive mechanism involving the absorption of light by the metallic substrate and a spin-state switching driven by low-energy valence photo-electrons. Indeed, in LIESST, r-LIESST (or SOXIESST) phenomena, it has been proposed and demonstrated that the spin-state switching occurred through transitions, driven either by direct light excitation or secondary photo-electrons excitation or injection (cf. Fig. 4), from the lowest energy states (^1A_g for LS and $^5T_{2g}$ for HS) to excited states (^1MLCT, $^1T_{2g}$ or $^1T_{1g}$ levels for LS and ^5E_g for HS), eventually decaying through intermediate states ($^3T_{2g}$ and $^3T_{1g}$).[37,38] Once again, in our case, the direct photon absorption can be ruled out, or has a relatively small efficiency, as the spin state switching is observed out of the absorption band. The absorption cross sections by the metallic substrates are well-known.[39] In the case of Ag, it is due to conduction electrons and can be well interpreted by a simple Drude model, giving rise to a very small absorption in the whole visible range (giving rise to an almost

perfect optical mirror surface). For Cu and Au, it is rather different, due to $d-sp$ interband optical transitions that occur typically for green and blue lights (giving rise to their reddish and yellowish colors). Using data from reflectance measurements, the absorption coefficients ($\alpha = \frac{2nk}{\lambda}$) can be estimated for Cu to 14 and 3 μm^{-1}, for Au to 14 and 2 μm^{-1} and for Ag to 0.8 and 0.5 μm^{-1} at 3 eV (410 nm) and 2 eV (620 nm) respectively.[39] As a consequence of this rather strong interband absorption in the blue for Cu and Au, transient low energy valence photo-electrons, typically between 0 and 1 eV with a typical lifetime of 100 fs,[40,41] are excited at the interface between the substrate and the molecular layer. We propose that those electrons, by a hopping, tunneling or energy transfer process,[42] can either populate directly the ^5E_g excited state (path labeled 1 in Fig. 4b), for the most energetic of them or, most probably, the vibrational states of the Fe^{II} ion for lower energy electrons (paths labeled 2 and 3 in Fig. 4b), allowing finally the switching from HS to LS .[43] In this second mechanism, both HS and LS molecules are *a priori* excited by the photo-electrons but it is known that the vibrational energy spacing of LS molecules is higher than for HS molecules, in a ratio close to 1.8[44] (the spacing between energy levels being typically 30 meV for HS and 50 meV for LS). The larger density of vibrational states for HS therefore induces a more efficient vibrational heating of HS molecules as compared to LS ones. Moreover, considering that the HS state is higher in energy than the LS one, the energy barrier to switch from HS to LS is smaller than the one to switch from LS to HS. Accordingly, the rate of switching from HS to LS by this mechanism is expected to be larger than the rate of switching from LS to HS, leading to an anomalous spin state switching. It is worth noting that this mechanism is in competition with the direct photon absorption by the LS molecules, that leads to the usual LIESST effect, switching from LS to HS. This can explain why for the case of red light, where a very small density of inter-band photo-electrons are excited on Au, we observe a slight increase of the HS proportion under illumination, as expected from the LIESST effect (Fig. 2b). In contrast, for blue light, the density of valence photo-electrons is much larger and their contribution to the switching, from HS to LS, dominates over the usual LIESST

mechanism. Finally, it seems that the influence of substrate induced low-energy valence photo-electrons on the switching should be inherently limited to the first molecular layers. As an example, a dominant LIESST effect is already measured for the second molecular layer on Au(111) with blue light.[45,46] It is worth noting that this whole mechanism is very close to what has been proposed recently for the photo-induced tautomerization of porphycene molecules on Cu(111).[47,48] However, future experiments on other SCO molecules stable on metal surfaces[49] will be necessary to fully confirm this model and better understand the most relevant parameters (structure of the molecule, thickness of the molecular layer, wavelengths, fluences, temperature...).

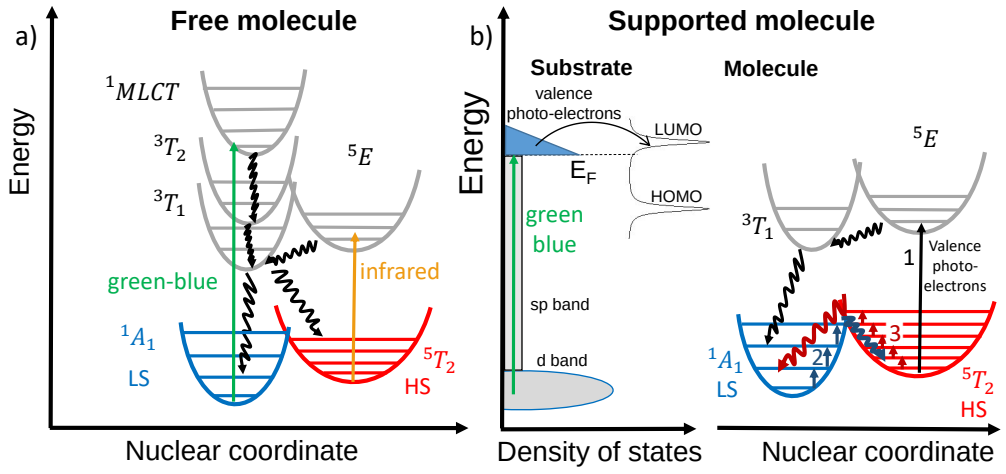

Figure 4: a) Schematic drawing of the usual LIESST (green arrow) and r-LIESST (orange arrow) mechanisms through excited states. b) Schematic drawing of the interband light absorption by the substrate and the induced low-energy valence photo-electrons HS to LS switching through the transition by excited molecular states (path labeled 1) or through vibrational heating (path labeled 2 from LS to HS and labeled 3 from HS to LS). For simplicity, we have skipped the parity index for all the irreducible representations since they are all even.

Conclusion

We have measured by XAS and STM the behavior of a single molecular layer of Fe^{II} SCO molecules adsorbed on three noble metal surfaces, namely Cu(111), Ag(111) and Au(111).

We find that the molecules keep their integrity on the three substrates, leading to well-ordered two-dimensional molecular arrays. We also find that their switching properties are strongly affected by the contact with metal surfaces. Indeed, at low temperature, only a fraction of the molecules are in a LS state. Moreover, illumination with a blue light induces a switching from HS to LS despite the absence of a HS absorption band, in contrast with the bulk behavior where the opposite is happening. By comparing the efficiency of this anomalous light induced HS to LS switching on the different substrates and at different wavelengths, we propose a possible mechanism involving the light absorption by the substrate. We believe that this specific interfacial effect between metals and spin-crossover molecules is rather general and could be observed in other systems, giving more details on the underlying mechanisms. This effect should also have important implications on the design and understanding of SCO based photo-active electronic devices.

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Supporting Information Available

The following files are available free of charge.

- Supporting Information : Anomalous light induced spin state switching for Fe^{II} spin-crossover molecules in direct contact with metal surfaces

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