

# Etude par spectroscopie Raman des complexes à transition de spin $[\text{Fe}(\text{L})(\text{NCX})_2]_2(\text{bpym})$

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## Résumé :

Différentes perturbations extérieures telles que la température (processus thermo-induits), la pression (processus piézo-induits), le champ magnétique (processus magnéto-induits) ou la lumière (processus photo-induits) peuvent changer (commuter) l'état de spin d'un certain nombre de matériaux moléculaires dits à transition de spin. L'enjeu actuel des processus photo-induits est de taille dans le domaine de l'adressage optique. Notre objectif sera d'explorer la commutation optique de 4 composés binucléaires à transition de spin,  $[\text{Fe}(\text{L})(\text{NCX})_2]_2(\text{bpym})$  où L est le ligand bpym = 2,2, -bipyrimidine ou bt = 2,2, -bithiazoline et X = S ou Se. La transition de spin induite par la lumière est connue sous le nom de l'effet LIESST (Light-Induced Excited Spin-State Trapping). Dans un premier temps, nous avons étudié le complexe binucléaire  $[\text{Fe}(\text{bt})(\text{NCS})_2]_2(\text{bpym})$  qui présente une transition de spin thermo-induite en deux étapes. L'origine de ce « double-step » est au centre des débats dans la communauté "transition de spin" mondiale depuis plusieurs années. Récemment, nous avons montré que la transition photo-induite de ce complexe peut être également réalisée en deux étapes à l'aide d'applications successives de deux longueurs d'onde infrarouge et rouge. Nous venons aussi de montrer qu'il était possible de réaliser un phénomène de LIESST inverse: sous l'effet d'une irradiation dans l'infrarouge le système peut rebrousser son chemin. Il s'agit de 2 résultats extrêmement excitants et originaux. Notre but sera d'étudier ce complexe mais aussi notre intérêt se porte sur l'étude complète de toute la famille des binucléaires. Elle se fera principalement par spectroscopie Raman et spectroscopies optiques résolues dans le temps aux longueurs d'onde infrarouges. Ces techniques devront nous permettre d'approfondir les études antérieures et de mieux comprendre les mécanismes physiques mis en jeu. Ainsi le caractère sélectif de la photo conversion de ce complexe pourra être clairement interprété.

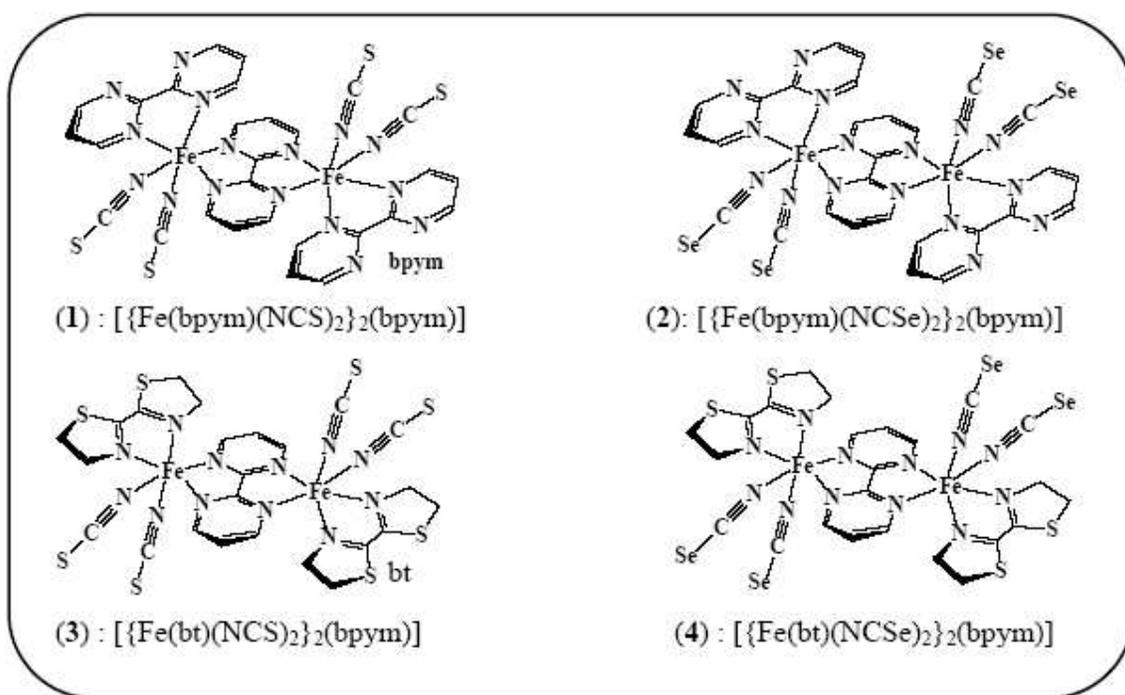
## Abstract :

It is well known that different external perturbations such as temperature (thermo-induced process), pressure (piezo-induced process), magnetic field (magneto-induced process), light (photo-induced process) can switch the spin state of certain molecular materials called spin crossover compounds. Recently a class of solid compounds presenting an interesting photo-excited state dynamics called "photo-induced phase transitions" became considerably attractive because they are potentially good candidates for optical data storage. We wish to study the series of binuclear iron (II) complexes  $[\{\text{Fe}(\text{L})(\text{NCX})_2\}_2\text{bpym}]$  where L is bpym = 2,2, -bipyrimidine or bt = 2,2, -bithiazoline and

X = S or Se. The spin transition induced by light irradiation is called LIESST effect (Light-Induced Excited Spin-State Trapping). First we studied the binuclear compound  $[\text{Fe}(\text{bt})(\text{NCS})_2]_2(\text{bpym})$ , presenting a thermal spin transition in two steps. The origin of the double step has been a main issue for the spin crossover community, for several years. We have found recently that the photo excitation of this compound can also occur in two steps using two different wavenumbers (infrared and red lights). We obtained also the reverse-LIESST process. These results are originals and very exciting. Our study will focus on this compound as well as on the whole the binuclear family using Raman spectroscopy and times resolved optical spectroscopy, in the infrared region. These techniques could give us a better understanding of physical mechanisms and the origin of the selective character of the different photo-switching process in binuclear compounds.

## Introduction

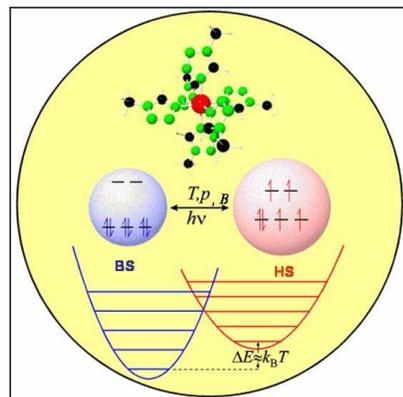
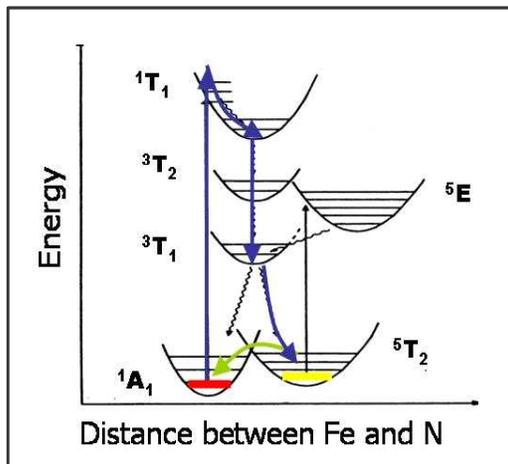
Current developments in advanced electronic and photonic technologies require new functional materials exhibiting bistability behavior at the molecular scale. The series of binuclear iron (II) complexes  $[\{\text{Fe L}(\text{NCX})_2\}_2(\text{bpym})]$  is one of the most unusual family of spin crossover compounds. They are the simplest example of polynuclear SC complexes exhibiting a rich variety of magnetic behaviours. Furthermore, they are the only examples of compound where the interplay between intra-molecular magnetic exchange and spin crossover are present in the same molecule. As a result of this propriety the photo-magnetic behaviour of the binuclear family is also quite unusual and very interesting; this offers interesting prospects in an area where the molecular level is increasingly being considered as the answer to miniaturization of electronic components.



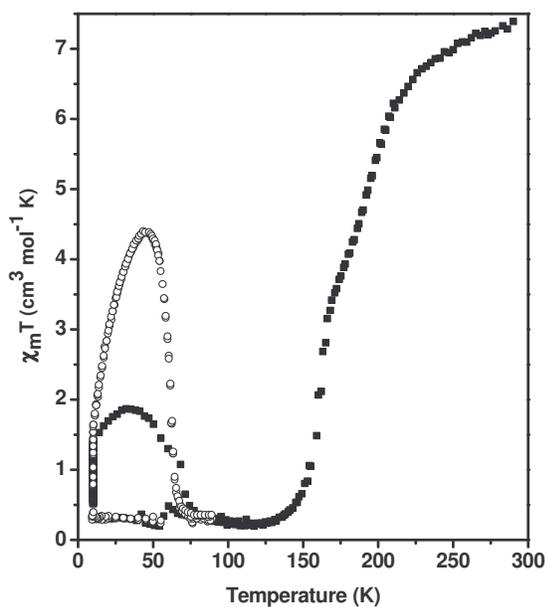
*Figure 1* Molecular structures of  $\{\{\text{Fe}(\text{L})(\text{NCX})_2\}_2(\text{bpm})\}$  at room temperature

## LIESST Effect

The light irradiation of certain SCO samples induces different metastable states having a virtually infinite lifetime provided the temperature is maintained sufficiently low.



## SQUID measurement

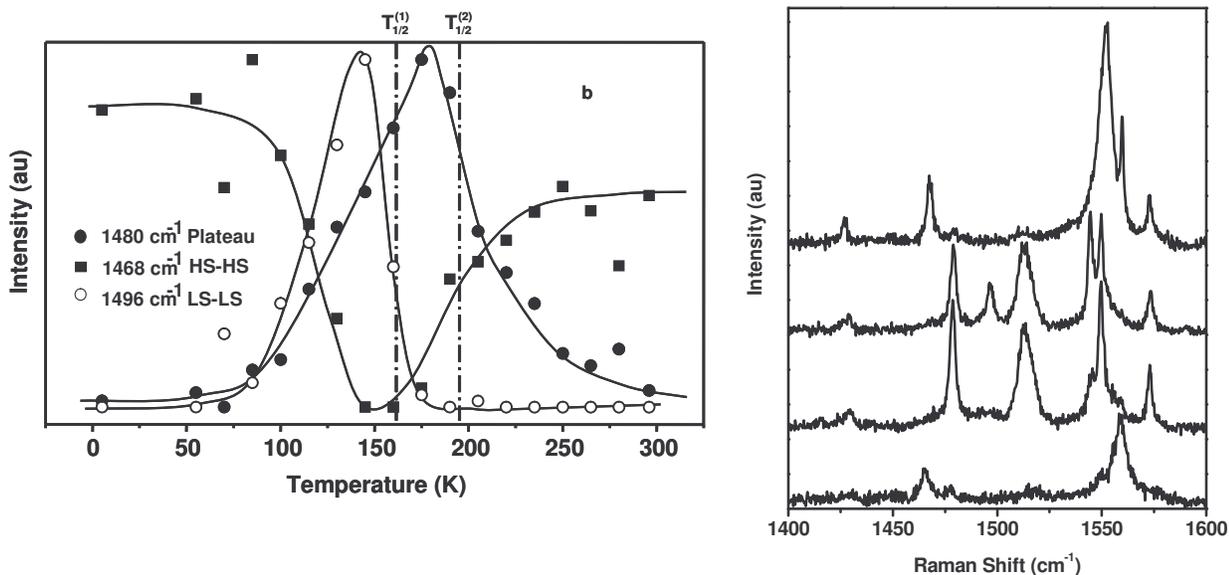


The  $[\text{Fe}(\text{bt})(\text{NCS})_2]_2(\text{bpym})$  compound exhibits a thermal spin state change in two steps centered at  $T_{1/2}^{(1)} = 163 \text{ K}$  and  $T_{1/2}^{(2)} = 197 \text{ K}$  (Figure 2). The plateau between the steps corresponds to ca. 50 % spin conversion. The occurrence of the plateau was associated with the intermediate LS-HS pairs of  $\text{Fe}^{\text{II}}$  ions and the transformations LS-LS  $\leftrightarrow$  LS-HS  $\leftrightarrow$  HS-HS.

Red light switches the LS-LS pair to the HS-HS state. The antiferromagnetic interaction between the two HS  $\text{Fe}(\text{II})$  ions within each binuclear unit gives rise to an  $S = 0$  ground state and  $S = 1-4$  low-level excited states, therefore  $\chi_m T$  increases upon heating. The temperature dependence of  $\chi_m T$  above 44 K corresponds to the relaxation of the metastable HS-HS state. For 1342 nm irradiation we observe only a very small increase of  $\chi_m T$  with increasing temperature. It means that light switches the LS-LS state to the paramagnetic ( $S = 2$ ) HS-LS state.

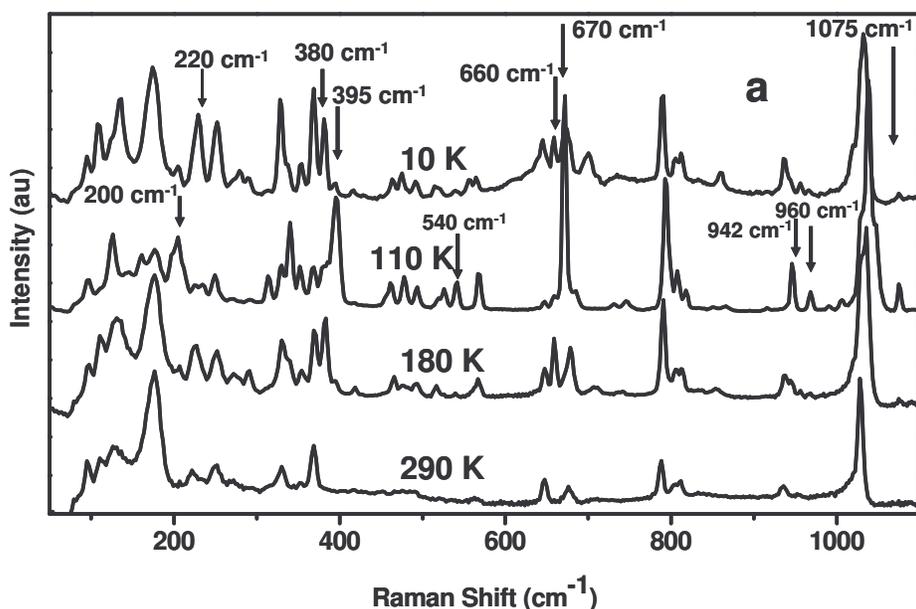
## Visible Raman spectroscopy

Selected Raman spectra obtained at different temperatures using red laser:



Interring stretching frequencies at 1468, 1496 and 1480 cm<sup>-1</sup> can be assigned to the HS-HS, LS-LS and the plateau region, respectively. To better illustrate these assignments, the normalized intensity of selected Raman modes is plotted as a function of temperature in the last Figure revealing a clear correspondence with the two-step magnetic susceptibility curve. The Raman spectrum of the photo-excited state is clearly different from the HS-LS and LS-LS spectra and corresponds well to that of the high temperature phase (HS-HS).

## IR Raman spectroscopy



The HS-LS form, which constitutes the plateau, appears at 10 K under 1342 nm excitation and shows a paramagnetic behavior.

## Perspectives

We wish to complete this study with a structural (X-ray diffraction) and quantum chemical (DFT) investigation and also to extend it to the whole family of compounds [ $\{\text{FeL}(\text{NCX})_2\}_2\text{bpym}$ ]. A correlation between the binuclearity and the two-step character (thermal and light induced) of the binuclear systems is expected that we propose to describe theoretically in the framework of an Ising-like model adapted for binuclear compounds

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