Does cooperativity influence the lifetime of the photo-induced HS state?

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Abstract. We have first recalled the T(LIESST) procedure which consists to determine the temperature above which the photo-magnetic effect is erased. In addition we have selected to series of iron(II) spin crossover complexes, the \([\text{Fe(PM-L)}_2(\text{NCS})_2]\) and \([\text{Fe(bpp)}_2\text{X}_2\cdot n\text{H}_2\text{O}]\) families, to analyse the influence of the cooperativity on the stability of the photo-induced HS state. Some of these complexes exhibit gradual thermal spin crossover behaviours while some others undergo an abrupt thermal transition, with and without hysteresis. Interestingly, whatever the cooperativity effect on the thermal spin crossover transition, the lifetime of the metastable state of all these derivates remains governed by the \(T(\text{LIESST}) = T_\sigma - 0.31 T_{1/2}\) relation. Finally, we have investigated the magnetic and the photomagnetic properties of a \([\text{Fe(bpp)}_2\text{-Nafion}]\) film. Once more the role of the cooperativity on the stability of the photo-induced HS state appears minor. Conversely, the influence of the nature and the geometry of the inner coordination sphere appears preponderant.

1. Introduction.

In the last thirty years, the interest in "molecular materials" possessing a property or a set of properties relevant for practical applications has considerably increased. The molecular scale is, in fact, more and more considered as the answer of the miniaturization of the components used in the construction of working devices. In this context, coordination complexes are especially promising since a judicious choice of metal ions and ligands allows one to modulate the final physical properties of the complexes, and even in some cases, to combine in a synergistic way different physical properties.
In the present article, we focus our attention on the spin crossover (SCO) property encountered in some coordination complexes having a d^n (n = 4-7) electronic configuration. In some specific cases, iron(II) molecular materials may exhibit a change of spin state under external perturbations (change of temperature, application of pressure, by light irradiation or by pulsed magnetic field) combined with (i) room-temperature working range, (ii) stability over successive cycles (iii) low addressing power (about 5 x 10^2 mW/µm²), (iv) short addressing time since the transition is purely electronic in nature (nanosecond scale) and (v) an hysteresis effect when the transition between the two states is accompanied by cooperative effects [1,2].

In the view of photonic molecular device, the first evidence of the Light-Induced Excited Spin-State Trapping (abbreviated as LIESST) in an iron(II) SCO material was reported by J. McGarvey et al. [3] in solution and then by S. Decurtins et al. [4] in solid state. The major drawback of this phenomenon is the relaxation process; i.e. the lifetime of the photoinduced HS state is, in fact, long at very low temperature (weeks at 20 K for [Fe(ptz)₆](BF₄)₂ [5]) but above 50 K usually the phenomenon becomes thermally activated and in few seconds the stored light-induced information is vanished. In some rare cases, however, long-lived lifetimes have been described up to 100 K [6-10], showing by the way that some factors are able to stabilise the photoinduced HS state. In the present paper we would like to discuss the peculiar role of the cooperativity on the stabilisation of the photo-induced HS state. For that we have selected the [Fe(PM-L)₂(NCX)₂] series and the [Fe(bpp)₂]X₂•nH₂O family, both well-known to exhibit thermal and photo-induced spin transition [11-15].

2. Experimental

The three members of the [Fe(PM-L)₂(NCX)₂] family investigated in this study are the [Fe(PM-AzA)₂(NCS)₂] (PM-AzA = N-2'-pyridyl-methylene)-4-(phenylazo)aniline), the [Fe(PM-FIA)₂(NCS)₂] (PM-FIA = N-2'-pyridylmethylene-4-(2-amino) fluorene) and the phase I of the [Fe(PM-BiA)₂(NCS)₂] (PM-BiA = N-2'-pyridylmethylene)-4-(amino-biphenyl). These complexes were obtained by using the procedure described in Ref. [12]. The synthesis of hydrated and anhydrous complex salts [Fe(bpp)₂]X₂, with bpp = 2,6-bis(pyrazol-3-yl)pyridine and X = PF₆, NCS, NCSe, BF₄, Br and I, have been obtained from Ref. [14]. The elemental analyses (C,H,N and Fe) of all these derivatives were consistent with the expected composition. Concerning now the preparation of the [Fe(bpp)₂]-Nafion film, the method was as recently reported for the [Fe(H-trz)₃]-Nafion (trz = 1,2,4-triazole) [16]. The Nafion film, originally developed by DuPont Company, is composed of a polytetrafluoroethylene backbone with perfluorinated ether side chains terminated by sulfonic acid groups.

The thermal spin crossover properties have been followed by measuring the magnetic susceptibility and the study of the photomagnetism was performed by using a Krypton Laser coupled through an optical fiber to the cavity of a SQUID magnetometer. The technique used was as previously published [17]. Basically, each sample own the shape of a very thin layer of compound to avoid any problem of light penetration for which the weight was calculated from the thermal spin crossover curve recorded with a heavier and accurately weighed sample.

3. Results

3.1. T(LIESST) Database

In order to understand the factors which predispose a SCO system to exhibit a photomagnetic effect at relatively high temperatures, we have recently proposed to create a database of critical LIESST temperature, T(LIESST), defined as the temperature for which the light-induced HS information is erased [11, 18]. Briefly, the procedure consists to cool a sample at 10 K, to irradiate until photo-saturation, and then to slowly warm at 0.3 K/min in the dark. The minimum of the derivative is used to define the T(LIESST) value.

This procedure was initially criticized, as strictly speaking the T(LIESST) values are somewhat dependent on the detection method. Nevertheless with a constant procedure, irradiation at 10 K and warming mode of 0.3 K.min⁻¹, this method appears rapidly useful. The first work based on a
A comparison of T(LIESST) temperatures was made in 1999 [17]. In this study, the magnetic and the photomagnetic properties of twenty two SCO compounds were determined (Figure 1, samples 1-22); i.e. the thermal spin transition T_{1/2} as well as the T(LIESST) temperatures. It was suggested that the T(LIESST) versus T_{1/2} experimental points could be represented by two parallel lines following the relationship T(LIESST) = T_0 - 0.31 T_{1/2} with T_0 estimated at T→0 [17].

Three years later, a systematical investigation of hydrated and dehydrated [Fe(bpp)_2][X_n]•nH_2O complexes (with X = PF_6, NCS, NCSe, BF_4, Br and I) showed a T(LIESST)-T_{1/2} plot distributed in a such way that the T_0 - 0.3 T_{1/2} relation established earlier remained valid and a third line with a T_0 value of 150 K was proposed (samples 23-30) [15]. In the same year, Hashimoto et al. [19] provided a new evidence for the validity of the T(LIESST) = T_0 - 0.3 T_{1/2} relation. The selected family was the Co-Fe Prussian Blue analogues, [Na_xCo_yFe(CN)_6]•zH_2O with a atomic Co/Fe composition ratio of 1.37, 1.32 and 1.26. These authors determined for each Co/Fe composition the T_{1/2} and T(LIESST) temperatures and observed a new line (Figure 1, samples 31-33) parallel to the third previous ones with a T_0 value of 200 K.

![Figure 1. Variation of T(LIESST) versus T_{1/2} for fifty spin crossover compounds [18] and thermal spin crossover properties of [Fe(PM-AzA)_2(NCS)_2], [Fe(PM-FlA)_2(NCS)_2] and the phase I of the [Fe(PM-BiA)_2(NCS)_2].](image)

A first general tendency, noticeable for all these “T_0 lines”, is a decrease of T(LIESST) value with the increase of T_{1/2} (Figure 1). This behavior is, in fact, in perfect agreement with the inverse-energy gap law already introduced by Hauser [20]. The HS → LS relaxation (and then the T(LIESST) value) is a direct dependence of ΔE_{HL} energy gap (i.e. the enthalpy factor, ΔH, at T → 0), and consequently of T_{1/2}, if we assume that the entropy factor (ΔS) is almost constant for all SCO
compounds. But what is more interesting to elucidate is the nature of the parameters affecting the \( T_0 \) value. In a few years, the \( T_0 \) lines have been progressively shifted from 100 K to 200 K [18]. In the literature, it is sometime proposed that the cooperativity factor is able to stabilize the photoinduced HS state [21,22]. Let us check now the validity of such assumption.

3.2. Cooperativity factor: The \([\text{Fe}(\text{PM-L})_2(\text{NCX})_2]\) family

In the context of the mononuclear SCO complexes, it is known that the \([\text{Fe}(\text{PM-L})_2(\text{NCX})_2]\) members despite a close chemical similarity are able to cover the whole spectrum of SCO regimes due to a subtle balance of the intermolecular hydrogen and \( \pi-\pi \) interactions into the lattice [12,13]. For instance, the \([\text{Fe}(\text{PM-AzA})(\text{NCS})_2]\) displays a gradual SCO at around 189 K [12] while the \([\text{Fe}(\text{PM-FlA})_2(\text{NCS})_2]\) is characterized by an intermediate cooperativity [16] and the phase I of the \([\text{Fe}(\text{PM-BiA})(\text{NCS})_2]\) by an exceptionally abrupt spin transition at \( T_{1/2}^\downarrow = 168 \) K and \( T_{1/2}^\uparrow = 173 \) K with a narrow hysteresis [11]. Concerning the photomagnetic properties, these three complexes exhibit some LIESST effect at low temperature and we have determined the \( T(\text{LIESST}) \) values (Figure 1). For an almost constant \( T_{1/2} \) temperature of about 170 K, the \( T(\text{LIESST}) \) value increased from 31 K for the gradual SCO \([\text{Fe}(\text{PM-AzA})(\text{NCS})_2]\) compound (11), to 64 K for the moderate cooperative \([\text{Fe}(\text{PM-FlA})_2(\text{NCS})_2]\) sample (13) and to 78 K for the abrupt SCO \([\text{Fe}(\text{PM-BiA})(\text{NCS})_2]\) compound (20).

Based on this, combined with others results found in the \([\text{Fe}(\text{PM-L})_2(\text{NCX})_2]\) family (Table 1), we have proposed in 2002 a general relation between the \( T(\text{LIESST}) \) temperature and the cooperativity \( C \) factor [21].

### Table 1. Inversion temperature \( T_{1/2} \) [K], enthalpy variation \( \Delta H_{\text{HL}} \) [kJ mol\(^{-1}\)], entropy variation \( \Delta S_{\text{HL}} \) [J K\(^{-1}\) mol\(^{-1}\)], and least-squares fitted cooperativity coefficient \( C \) (see Ref. [21]).

| Compounds                                | \( T_{1/2} \) | \( \Delta H_{\text{HL}} \) | \( \Delta S_{\text{HL}} \) | \( T(\text{LIESST}) \) | \( C \) |
|------------------------------------------|---------------|-----------------|-----------------|------------------|------|
| \([\text{Fe}(\text{PM-AzA})(\text{NCS})_2]\) | 189           | 6.68            | 35.34           | 31               | 0.48 |
| \([\text{Fe}(\text{PM-FlA})_2(\text{NCS})_2]\) | 165           | 5.19            | 31.45           | 64               | 1.00 |
| \([\text{Fe}(\text{PM-FlA})_2(\text{NCSe})_2]\) | 236           | 6.68            | 28.31           | 40               | 0.76 |
| \([\text{Fe}(\text{PM-BiA})(\text{NCS})_2]\) | 168 / 173     | 10.06 / 10.05   | 59.88 / 58.09   | 78               | 1.16 |
| \([\text{Fe}(\text{PM-FlA})(\text{NCSe})_2]\) | 194 / 231     | 8.86            | 59.65 / 23.02   | 40               | 1.60 |
| \([\text{Fe}(\text{Ptz})_6(\text{BF}_4)_2]\) | 128.0 / 134.2 | 60              |                 |                  |      |
| \([\text{Fe}(\text{phen})(\text{NCS})_2]\) | 176.29 / 176.00 | 8.60 / 7.90 | 48.78 / 45.40 | 62 | 1.18 |
| \([\text{Fe}(\text{phen})(\text{NCSe})_2]\) | 231.26        | 11.60           | 51.22           | 47               | 0.83 |
| \([\text{Fe}(\text{abpt})(\text{NCS})_2]\) | 180           | 5.80            | 33              | 40               | 0.80 |
| \([\text{Fe}(\text{abpt})(\text{NCSe})_2]\) | 224           | 8.60            | 38              | 32               |      |
| \([\text{Fe}(\text{bt})(\text{NCS})_2]_2(\text{bypm})\) | 171.7 / 180.9 | 9.54            | 54.4            | 62               |      |
| \([\text{Fe}(\text{bt})(\text{NCSe})_2]_2(\text{bypm})\) | 217.5 / 221.4 | 9.11            | 41.5            | 46               |      |
| \([\text{Fe}(\text{py})(\text{phen})(\text{NCS})_2]_2(\text{py})\) | 106           | 3.70            | 37              | 47               | 0.86 |

Nevertheless, by carefully investigating the X-ray structures of the \([\text{Fe}(\text{PM-L})_2(\text{NCX})_2]\) family, we have now realized that the difference in the \( T(\text{LIESST}) \) values is mainly originated in intramolecular structural features and particularly in the distortion of the metal coordination sphere. Indeed, on the basis of a large structural data base [13], we show that within the \([\text{Fe}(\text{L})_2(\text{NCS})_2]\) SCO complexes, the \( T(\text{LIESST}) \) linearly depends on the octahedricity of the Fe(II) polyhedron. The higher the trigonal distortion in the HS state, the higher \( T(\text{LIESST}) \) [24]. In particular, the differences between the photomagnetic behaviors of the \([\text{Fe}(\text{PM-BiA})(\text{NCS})_2]\) and \([\text{Fe}(\text{PM-AzA})(\text{NCS})_2]\)
complexes are perfectly explained by the comparison of the octahedricity of the metal environment. Consequently, the distortion of the coordination sphere plays a paramount role on T(LIESST). One can argue that the polyhedron distortion may be influenced by the crystal packing but such effects of cooperativity can be considered as indirect and weak.

Elsewhere, if we consider the influence of the cooperativity on the HS → LS relaxations, it is well-known from the work of Hauser et al. [20] that the activation energy barrier is a function of the HS (or LS) fraction in reason of an internal pressure created by the large modification of the volume of the metal polyhedron occurring between the HS and the LS states. As a consequence, the activation energy barrier for a given HS fraction is reduced when the cooperativity increases, and thus, as recently demonstrated by doing some theoretical simulations, the T(LIESST) temperature is slightly reduced [25].

Figure 2 reports the calculated T(LIESST) curves by using the kinetic parameters of the phase I of the [Fe(PM-BiA)2(NCS)2] as a function of the additional activation energy associated to the cooperativity, Eₐ*. Clearly, the shape of the T(LIESST) curve becomes more gradual as the cooperativity decreases. This behaviour agrees with the experimental data recorded for the phases I and II of the [Fe(PM-BiA)₂(NCS)₂]; i.e. The T(LIESST) curve was found to be gradual for the weakly cooperative phase II and abrupt in the case of phase I [25,26]. From the Figure 2, it can be also noticed that the calculated T(LIESST) value is predicted to slightly increase when the cooperativity is reduced. This effect is linked to the increase of the height of the activation energy for a given HS fraction when Eₐ* is reduced.

Figure 2. Influence of the kinetics parameters on the T(LIESST) curve. (a) Variation of Eₐ* ; 0, 120 and 300 cm⁻¹.

In conclusion, the influence of the cooperativity on the T(LIESST) temperature appears to be very weak. This idea is also supported by the experimental work performed on the [Fe(bpp)₂]X₂•nH₂O family (Figures 1 and 3, samples 23-30) [15].

3.3. Cooperativity factor: The [Fe(bpp)₂]X₂•nH₂O family
In first let us recall that Goodwin et al. [14] have shown that the thermal SCO properties of the [Fe(bpp)₂]X₂•nH₂O series are strongly affected by the hydration degree, because the hydrated salts participated to an extended hydrogen-bonded network involving the uncoordinated NH groups of the pyrazole moieties, the anion and the water molecules. Consequently, any change of the hydration degree affects the electronic of the ligand and modifies the thermal spin crossover behaviour. But interestingly the photomagnetic properties of the hydrate and of the dehydrated compounds follow the same T₀ line, suggesting that the influence of the electronic factor on the T₀ factor is negligible [15]. This also suggests that the T₀ parameter is relatively insensitive to any change occurring beyond the inner coordination sphere. In this peculiar context, the influence of the long range, as well as of the short range, interactions on the T₀ factor seems to be negligible. For instance, a gradual spin transition has been observed for [Fe(bpp)₂](BF₄)₂•3H₂O and an abrupt spin transition with a broad hysteresis occurs for [Fe(bpp)₂](BF₄)₂ (Figure 3). But independently of the cooperativity of these thermal spin transitions, all the [Fe(bpp)₂]X₂•nH₂O series follow the same 150 T₀ line.
Figure 3. Temperature dependence of $\chi_{MT}$ for four members of the $[\text{Fe}(\text{bpp})_2](X)_2 \cdot n\text{H}_2\text{O}$, in the cooling mode without irradiation (■), with irradiation at 10 K (○) and T(LIESST) experiment (◇).

In addition to that let us present here the data obtained on $[\text{Fe}(\text{bpp})_2] \cdot \text{Nafion}$ film. The Figure 4a reports the thermal and the light-induced spin crossover properties. As we can see, the transition of the $[\text{Fe}(\text{bpp})_2]$ complex at the surface of the Nafion film is gradual. This absence of cooperativity is also reflected by the investigation of the kinetics of the photoinduced HS state (Figure 4b). The various kinetics recorded in the 10-70 K range can be all satisfactorily analyzed by using a stretched exponential model as usually recorded for a non-cooperative system. The decrease of the cooperativity on the surface of a Nafion Film is, in fact, in perfect agreement with the data reported on $[\text{Fe}(\text{H-trz})_3] \cdot \text{Nafion}$ films, where a gradual spin transition was recorded instead of a hysteresis loop for the powder form [16]. These authors attribute this effect to the preparation in Nafion Film of an one-dimensional iron(II) network. But interestingly, the couple T(LIESST)/T$_{1/2}$ of our $[\text{Fe}(\text{bpp})_2] \cdot \text{Nafion}$ film remains once more in the vicinity of the $T_0 = 150$ K line. This provides a new evidence that the cooperativity factor does not governed the stabilization of the photo-induced HS state.

Figure 4. Magnetic and photomagnetic properties of $[\text{Fe}(\text{bpp})_2] \cdot \text{Nafion}$ film (a) and HS $\rightarrow$ LS relaxation as function of the temperature after a LIESST experiment (b).
4. Conclusion

In the present work, we have discussed the influence of the cooperativity on the stabilization of the photo-induced HS state. For that we have selected two iron(II) SCO family displaying different SCO regime, i.e. from gradual to abrupt with and without thermal hysteresis. Whatever this change of cooperativity, the $T_{(LIESST)} = T_0 - 0.3 T_{1/2}$ lay remains valid. Even the preparation of a $[\text{Fe(bpp)}_2]$ complex in a Nafion film, which exhibits as expected a gradual spin conversion, obeys to this relation. Consequently, it is clear that the cooperativity can only have a weak influence on the $T_{(LIESST)}$ values; i.e. on the lifetime of the photo-induced HS state.

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