

Photo-switching spin pairs—synergy between LIESST effect and magnetic interaction in an iron(II) binuclear spin-crossover compound†

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The decrease of the magnetic response under irradiation at very low temperature was interpreted as a new evidence of synergy between magnetic interaction and spin transition in an iron(II) binuclear SC compound.

The design and the synthesis of polynuclear complexes with versatile chemical and physical properties are of current interest in the areas of molecule-based electronic, photochemistry and magnetism. The goal is to develop novel materials whose properties can be controlled by the input of external information. In this context, particular interest has been focused on iron(II) spin-crossover (SC) compounds because they can be considered among the best examples of switchable coordination molecules. A reversible transition between the paramagnetic high-spin state (HS, $S = 2$) and the diamagnetic low-spin state (LS, $S = 0$) can be induced by a change in temperature, pressure or by light irradiation.¹ This latter effect opens some interesting perspectives to design optical switches. In 1984, Decurtins *et al.* discovered that by irradiation with green light the SC compound [Fe(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole) at 20 K could be converted from the stable LS state to the metastable HS state.² Later, Hauser reported the reverse-LIESST effect, wherein red light is used to convert back the compound into the LS state.³

Up to now, most of the SC compounds exhibiting LIESST properties are assemblies of monomeric units with through-space rather than through-bond interactions. Allowing SC centers to communicate by chemical bridges, *i.e.* oligomeric or polymeric species, is an important strategy to explore and enhance cooperativity of a given system.^{4,5} Along this line, binuclear compounds of formula [Fe(L)(NCX)₂]₂(bpym) (L = bpym (2,2'-bipyrimidine), bt (2,2'-bithiazoline) and X = S, Se) represent one of the most unusual family in the SC field. These compounds are the simplest example of polynuclear SC complexes exhibiting a rich variety of magnetic regimes. Further, they are the only iron(II) example where the interplay between both spin crossover and intramolecular magnetic exchange phenomena are present in the same molecule. In [Fe(bpym)(NCS)₂]₂(bpym) the two iron(II) ions are in the HS state and couple antiferromagnetically through the bridge bpym ($J = -4.1 \text{ cm}^{-1}$ in the zero-field Hamiltonian $H = -JS_A S_B$) giving an $S = 0$ ground pair state HS–HS at low temperature.⁶ In contrast, [Fe(bpym)(NCSe)₂]₂(bpym) shows a one-step transition involving 50% of iron atoms at $T_c = 125 \text{ K}$,⁷ whereas an almost complete two-step spin transition in the range 160–210 K takes place for [Fe(bt)(NCS)₂]₂(bpym).⁸ This behavior was interpreted in terms of the occurrence of LS–LS \leftrightarrow LS–HS \leftrightarrow HS–HS pair spin states in each binuclear unit.⁸ The stabilisation of the LS–HS mixed spin pair was assigned to the synergy effect between anticooperative intramolecular and cooperative intermolecular interactions.

Recently, we have reported the unusual photomagnetic behavior stemming from the interplay between spin-crossover and magnetic coupling phenomena.⁹ At low temperature, light switches [Fe(bt)(NCS)₂]₂(bpym) from the $S = 0$ spin state of the LS–LS pair to the $S = 0$ spin state of the HS–HS pair. Warming the sample first reveals the latent magnetic coupling between the HS iron(II) ions as the $S = 1, 2, 3$ and 4 excited states are populated, then switches off this virtual pair spin state at temperatures as high as 60 K where molecules have enough energy to overcome the barrier associated with the change of molecular geometry upon spin conversion. As a continuation of this study we have investigated the LIESST effect on [Fe(bpym)(NCSe)₂]₂(bpym). As mentioned above, this compound exhibits an incomplete thermal spin transition interpreted in terms of HS–HS \leftrightarrow LS–HS conversion at 125 K (Fig. 1). The slight decrease of the magnetic response as T approaches absolute zero is due to zero-field splitting of the $S = 2$ spin state of the mixed-spin pair.

At 10 K, we observed that green light irradiation (530.9 nm, power 10 mW cm^{-2})¹⁰ induces a decrease of $\chi_M T$ from 2.6 to $1.6 \text{ cm}^3 \text{ K mol}^{-1}$. Similar behavior was recorded at 647–679, 759–799 and 830 nm. Usually, the observation of a decrease in the magnetic response under light irradiation is a signature of reverse-LIESST as the HS state is converted into the LS state. However, for [Fe(bpym)(NCSe)₂]₂(bpym) this situation is no longer valid because of the occurrence of the unusual HS–LS state and the virtual excited HS–HS state which involves a latent antiferromagnetic interaction similar in magnitude as observed for [Fe(bt)(NCS)₂]₂(bpym).⁹ Hence, a decrease of the magnetic response should be expected upon irradiation.

Fig. 1 compares $\chi_M T$ vs. T (χ_M is the molar magnetic susceptibility and T the temperature) of the photoinduced

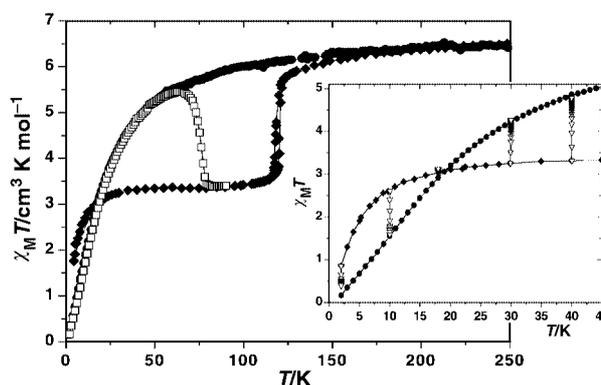


Fig. 1 $\chi_M T$ vs. T for (◆) [Fe(bpym)(NCSe)₂]₂(bpym) and (●) [Fe(bpym)(NCS)₂]₂(bpym). (□) refers to the warming mode of [Fe(bpym)(NCSe)₂]₂(bpym) after the irradiation was applied for 1 h at 10 K, then turned off. Inset: data obtained with irradiation (▽) for 1 h at 2, 10, 17, 30 and 40 K.

† Dedicated to the memory of Olivier Kahn.

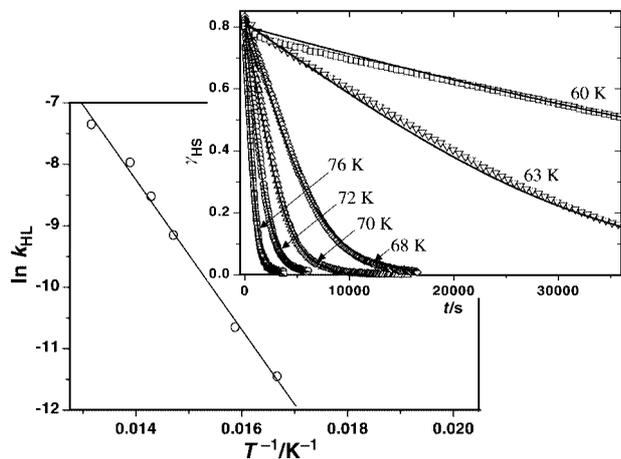


Fig. 2 $\ln k_{\text{HL}}$ vs. $1/T$ curve of $[\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})]$. Inset: time dependence at various temperatures of the HS molar fraction generated by light irradiation at 10 K.

$[\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})]$ with the binuclear $[\{\text{Fe}(\text{bpym})(\text{NCS})_2\}_2(\text{bpym})]$ compound containing two iron(II) ions in the HS–HS state in the whole temperature range.^{6–8} Both magnetic responses are similar below 40 K. It is well known that the interaction parameter, J , in a coupled binuclear compound depends essentially on the nature of the chemical bridge. As for both compounds the bridging network is similar, in case of a quasi-quantitative LS–HS \rightarrow HS–HS conversion (LIESST effect), the magnetic properties of $[\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})]$ after irradiation and $[\{\text{Fe}(\text{bpym})(\text{NCS})_2\}_2(\text{bpym})]$ should be very similar. In contrast, a LS–LS population (reverse-LIESST) should lead to a diamagnetic ground state for $[\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})]$ very different from the magnetic properties of $[\{\text{Fe}(\text{bpym})(\text{NCS})_2\}_2(\text{bpym})]$. The data displayed on Fig. 1 are in favor of the first alternative.

Fig. 1 also shows the χ_{MT} value of $[\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})]$ under light irradiation at 2, 10, 17, 30 and 40 K. In all cases, the photostationary point reached the χ_{MT} limit of $[\{\text{Fe}(\text{bpym})(\text{NCS})_2\}_2(\text{bpym})]$, confirming the HS–HS population.¹¹ What is remarkable is that at 17 K, both before and after irradiation, the compound has a similar magnetic response. This does not mean that the LIESST effect does not occur. In fact, we are faced with two totally different spin states. Before irradiation, the system acts as a HS–LS mixed-spin pair, resulting in a $S = 2$ spin state with a χ_{MT} value of $3 \text{ cm}^3 \text{ K mol}^{-1}$. After irradiation, the two iron(II) are HS and coupled antiferromagnetically with a thermal population of the low-lying spin states, $S = 1–4$, located at energies $E(S) = -JS(S+1)/2$ above the ground state $S = 0$. At 17 K, the population of the HS–HS pair, assuming a J factor of -4.1 cm^{-1} and a g value of 2.13, is 16% $S = 0$, 35% $S = 1$, 29% $S = 2$, 15% $S = 3$ and 5% $S = 4$. The resulting χ_{MT} value is then $3 \text{ cm}^3 \text{ K mol}^{-1}$ and similar to that of the HS–LS mixed-spin pair.

The kinetics of the relaxation were investigated from 2 K up to 75 K (Fig. 2). Below 55 K, the relaxation is very slow, for instance, at 10 K the magnetic response varies by ca. 0.01% in 13 h, which requires relaxation rates smaller than 10^{-6} s^{-1} . From 55 to 75 K, the dynamic of the relaxation is faster and falls within the time window of our set-up. This behavior matches the theory of HS \rightarrow LS relaxation proposed by Buhks *et al.*¹² which predicts a temperature-independent relaxation rate, *i.e.* a tunneling process, at low temperature and an activation relaxation process at higher temperatures. The decays of the HS molar fraction, γ_{HS} , vs. time, at various temperatures, are also represented in Fig. 2; γ_{HS} is deduced from $[(\chi_{\text{MT}}T)_{\text{hv}} - (\chi_{\text{MT}}T)_{\text{HS-LS}}]/[(\chi_{\text{MT}}T)_{\text{AF}} - (\chi_{\text{MT}}T)_{\text{HS-LS}}]$.¹³ An analysis of these data indicates that the relaxation curves can be satisfactorily

fitted by a sigmoidal law.¹⁴ This reflects a self-acceleration process as γ_{HS} decreases. The plot of $\ln k_{\text{HL}}$ vs. $1/T$ (Fig. 2) gives a straight line, with an activation energy $E_{\text{a}} = 850 \text{ cm}^{-1}$, a pre-exponential factor $k_{\infty} = 6.6 \times 10^3 \text{ s}^{-1}$ and an additional activation energy associated to the cooperativity $E_{\text{a}}^* = 53 \text{ cm}^{-1}$. Such parameters allow understanding of the shape of the T_{c} (LIESST) experiment¹⁴ reported in Fig. 1. In the tunneling region where the kinetic of the relaxation back to the HS–LS state is very slow, the $S = 1–4$ spin states of the local HS–HS pair are progressively populated and χ_{MT} increases. Above 55 K, the relaxation process of the local HS–HS pair becomes thermally activated and a deviation appears with the magnetic properties of $[\{\text{Fe}(\text{bpym})(\text{NCS})_2\}_2(\text{bpym})]$. The critical T_{c} (LIESST) temperature is found at 75 K.

In summary, this communication reports a new example of synergy between magnetic interaction and spin transition under light irradiation in an iron(II) binuclear SC compound. For the first time at very low temperature, the photoconversion of a LS–HS into a HS–HS pair, according to the LIESST effect, results in a decrease in the magnetic response. This behavior in the complex $[\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})]$ arises from the conversion of the $S = 2$ initial state into an $S = 0$ low-lying spin state by light irradiation.

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- In the thermally activated domain the relaxation rate is given by $\partial\gamma_{\text{LS}}/\partial t = -k_{\text{HL}}^* \gamma_{\text{LS}}$ with $k_{\text{HL}}^* = k_{\text{HL}} \exp(-(E_{\text{a}}/kT)\gamma_{\text{LS}})$ and $k_{\text{HL}} = k_{\infty} \exp(-(E_{\text{a}}/kT))$; see A. Hauser, *Chem. Phys. Lett.*, 1992, **192**, 65.
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