

## Light Induced Excited Pair Spin State in an Iron(II) Binuclear Spin-Crossover Compound

Jean-François Létard,<sup>\*,†</sup> José Antonio Real,<sup>\*,‡</sup>  
Nicolás Moliner,<sup>‡</sup> Ana B. Gaspar,<sup>‡</sup> Laurence Capes,<sup>‡</sup>  
Olivier Cadot,<sup>†</sup> and Olivier Kahn<sup>\*,†</sup>

Laboratoire des Sciences Moléculaires  
Institut de Chimie de la Matière Condensée de Bordeaux  
UPR CNRS No. 9048, 33608 Pessac, France  
Departament de Química Inorgànica  
Universitat de València, Dr. Moliner 50  
46100 Burjassot, València, Spain

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The phenomenon of spin crossover (SC) between LS and HS states is one of the most spectacular examples of molecular bistability.<sup>1</sup> It was first observed in 1931,<sup>2</sup> but it was only during the 1980s that researchers realized that SC compounds could be used as active elements in memory devices.<sup>3–6</sup> SC occurs in molecular species containing an octahedrally coordinated transition metal ion with the 3d<sup>n</sup> (3 < n < 8) electronic configuration. The most extensively studied compounds of that kind are those involving the iron(II) ion, and the SC phenomenon corresponds to an intra-ionic transfer of two electrons occurring in the nanosecond scale between the e<sub>g</sub> and t<sub>2g</sub> orbitals.

The SC phenomenon may be thermally induced when the energy of the LS state in its equilibrium geometry is slightly lower than the energy of the HS state, also in its equilibrium energy. Above a certain temperature, the thermodynamically stable state may be the HS state. This is due to the fact that the entropy of the system in the HS state is much larger than that in the LS state ( $\Delta S > 0$ ), and the gain in  $T\Delta S$ ,  $T$  being the temperature, compensates the energy loss.

A very interesting facet of the SC phenomenon resides in the possibility to address either spin state through light irradiation, which opens the perspectives of optical switches. In 1984, Decurtins et al. discovered that the spin-crossover compound [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (ptz = 1-propyltetrazole) could be converted from the stable LS (<sup>1</sup>A<sub>1</sub>) state to the metastable HS (<sup>5</sup>T<sub>2</sub>) state at 10 K by irradiating the sample with a green light (LIESST effect).<sup>7,8</sup> Later, Hauser reported the reverse-LIESST effect,<sup>9</sup> wherein red light is used to convert back the compound into the LS state. Since these discoveries, several other iron(II) spin-crossover compounds have been reported to exhibit the LIESST effect. In all cases, above a certain critical temperature,  $T_c$ (LIESST),<sup>10–12</sup> the system clears the energy barrier between the two spin states, and relaxes to the LS state.  $T_c$ (LIESST) refers to the thermally activated process.

<sup>†</sup> Institut de Chimie de la Matière Condensée de Bordeaux.

<sup>‡</sup> Universitat de València.

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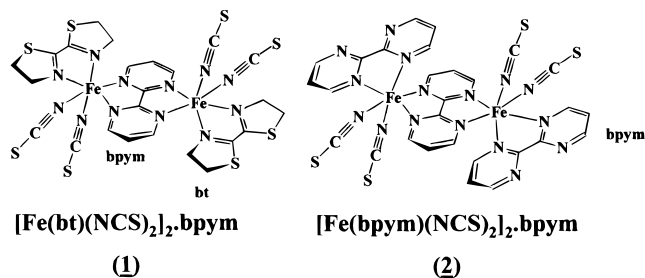
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(10) We propose to determine  $T_c$ (LIESST) as the inflexion point of the  $\gamma_{HS}$  versus  $T$  curve after light irradiation, where  $\gamma_{HS}$  is the HS molar fraction. In the case of [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>,  $T_c$ (LIESST) is found as 60 K.

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**Scheme 1.** Schematic Representation of [Fe(bt)(NCS)<sub>2</sub>]<sub>2</sub>bpyim (1) and [Fe(bpyim)(NCS)<sub>2</sub>]<sub>2</sub>bpyim (2)



So far, the LIESST effect has only been investigated on mononuclear species. In this communication, we report a new aspect of the photomagnetism of SC iron(II) compounds occurring in polynuclear species. The compound investigated was [Fe(bt)(NCS)<sub>2</sub>]<sub>2</sub>bpyim (1) (Scheme 1).

1 belongs to the family of the [Fe(L)(NCX)<sub>2</sub>]<sub>2</sub>bpyim binuclear compounds,<sup>13</sup> where bpyim = 2,2'-bipyrimidine is a bis-bidentate bridging ligand and L is a bidentate terminal ligand such as bpyim,<sup>14</sup> bzp = bromazepan,<sup>14</sup> or bt = 2,2'-bithiazoline,<sup>15</sup> and X = S or Se. In [Fe(bpyim)(NCS)<sub>2</sub>]<sub>2</sub>bpyim (2) (Scheme 1), the two iron(II) ions are HS in the whole temperature range at ambient pressure, and interact antiferromagnetically, yielding a nonmagnetic  $S = 0$  ground spin state and  $S = 1, 2, 3$ , and 4 low-lying excited spin states. The temperature dependence of  $\chi_M T$  (where  $\chi_M$  is the molar magnetic susceptibility) for 2 is displayed in Figure 1;  $\chi_M T$  tends to zero as  $T$  approaches absolute zero. These magnetic data were interpreted with an intramolecular interaction parameter  $J = -4.1 \text{ cm}^{-1}$ , the zero-field spin Hamiltonian being expressed as  $\mathbf{H} = -J\mathbf{S}_A \cdot \mathbf{S}_B$ .<sup>13</sup> On the other hand, 1 exhibits an almost complete spin conversion occurring in two steps, as shown in Figure 1. This behavior was interpreted in terms of LS-LS  $\rightarrow$  LS-HS  $\rightarrow$  HS-HS spin conversions.<sup>13,14</sup> The stabilization of the LS-HS mixed-spin isomer in the temperature range between the two steps was assigned to the synergistic effect between antiferromagnetic intramolecular and cooperative intermolecular interactions.

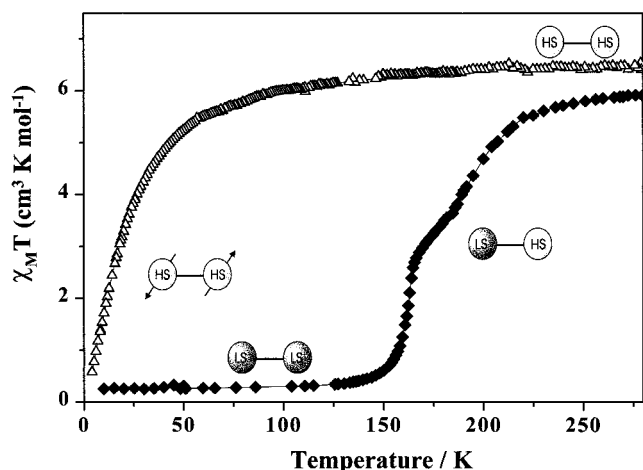
Figure 2a shows the interplay between temperature and light irradiation on the magnetic properties of 1. At 10 K,  $\chi_M T$  before irradiation is equal to  $0.30 \text{ cm}^3 \text{ K mol}^{-1}$ ; the compound is in the LS-LS form, with a weak residual amount of ca. 4% of HS ions also detected by Mössbauer spectroscopy.<sup>15</sup> When irradiating with a red light,<sup>16</sup>  $\chi_M T$  increases rapidly, and reaches  $1.6 \text{ cm}^3 \text{ K mol}^{-1}$ . Such a value seems to indicate that only ca. 24% of the iron(II) ions are converted from the ground LS state to the HS state. Without further irradiation, the temperature dependence of  $\chi_M T$  was recorded. First, the temperature was slowly lowered down to 2 K, and  $\chi_M T$  was found to decrease down to  $0.75 \text{ cm}^3 \text{ K mol}^{-1}$ , a value which corresponds to an apparent amount of 11% of HS ions. Then, the temperature was slowly increased from 2 K up to 100 K. When doing so,  $\chi_M T$  first increases dramatically up to 44

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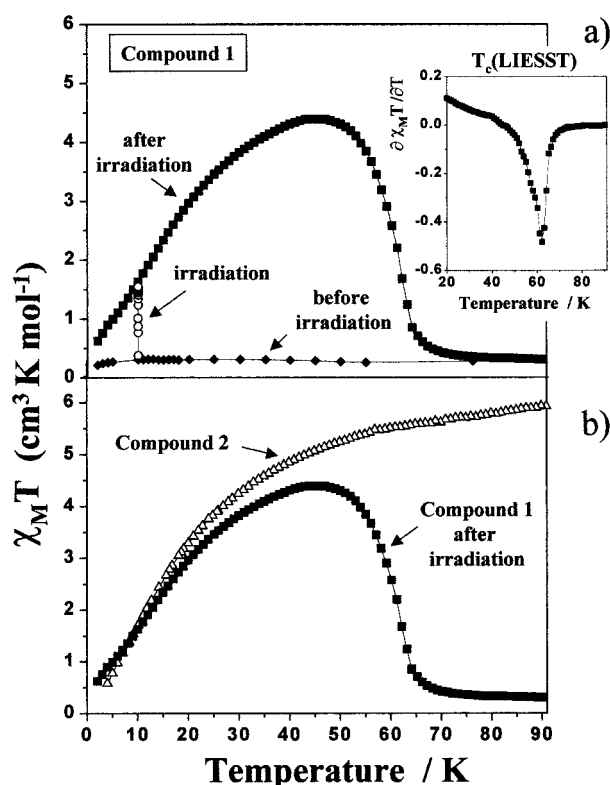
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(16) LIESST experiments were performed on a very thin layer of compound. The weight was estimated by comparing the thermal spin crossover curve with the curve recorded with a heavier and accurately weighed sample. Irradiation during 1 h was carried out by using a Kr<sup>+</sup> laser at two wavelengths, namely 647.1 and 676.4 nm. The output power on the panel meter was adjusted to 20 mW and the attenuation factor due to the optical setup was estimated to be around 50%. The local heating of the sample may be excluded due to the fact that no change was observed on magnetic response just after irradiation; a local heating of 1 would tend to decrease the  $\chi_M T$  signal.



**Figure 1.** Temperature dependences of  $\chi_M T$  for (◆)  $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$  (1) and (△)  $[\text{Fe}(\text{bpym})(\text{NCS})_2]_2\text{bpym}$  (2).



**Figure 2.** (a) Temperature dependence of  $\chi_M T$  for compound 1: (◆) data recorded in the cooling mode without irradiation; (○) data recorded with irradiation for 1 h at 10 K; (■) data recorded in the warming mode after the light irradiation was applied for 1 h, then turned off. The insert graph shows the derivative  $\partial(\chi_M T)/\partial T$  plot as a function of the temperature. (b) Comparison of the  $\chi_M T$  versus  $T$  curves for compound 2 (△) and compound 1 after irradiation (■).

K, where it reaches a value of  $4.4 \text{ cm}^3 \text{ K mol}^{-1}$ , corresponding to an apparent amount of 70% of HS ions, then drops rapidly.

The temperature dependence of  $\chi_M T$  after light irradiation is totally different from what is observed in LIESST experiments performed on mononuclear species. Normally, the HS molar fraction after irradiation remains nearly constant in the tunneling region where the kinetic of the relaxation back to the LS state is

very slow<sup>17</sup> with regard to the time window of our setup. The behavior observed for **1** is due to the synergy between the LIESST effect and intramolecular antiferromagnetic interaction. Irradiating the compound at very low temperature results in the population of the local HS states of the iron(II) ions. The antiferromagnetic interaction between these HS ions within each HS-HS pair gives rise to  $S = 0$  ground spin state. Only this nonmagnetic state is thermally populated when the temperature is close to absolute zero. What is remarkable is that both before and after irradiation, the compound has a diamagnetic  $S = 0$  ground spin state. This does not mean that the LIESST effect does not occur. In fact, we are faced with two totally different  $S = 0$  spin states. Before irradiation, the two iron(II) ions within a pair are LS, resulting in a  $S = 0$  spin state. After irradiation, the two iron(II) ions are HS, and couple antiferromagnetically, resulting in another  $S = 0$  ground spin state. As the temperature is increased, the low-lying magnetic spin states,  $S = 1-4$ , located at the energies  $E(S) = -JS(S + 1)/2$  above the ground spin state, are progressively populated, and  $\chi_M T$  increases. The temperature dependence of  $\chi_M T$  above 44 K corresponds to the relaxation of the HS local states. The critical LIESST temperature, determined as the extreme of the derivative  $\partial\chi_M T/\partial T$  (see insert of Figure 2a),<sup>12</sup> was found as 62 K.

The interaction parameter,  $J$ , in a coupled binuclear compound depends essentially on the nature of the bridging network. The bridging network in **1** (two-step spin conversion) is strictly the same as that in **2** (HS ions and antiferromagnetic interaction). It follows that in the temperature range where the iron(II) ions are trapped in the local HS states ( $T < 44 \text{ K}$ ) the magnetic properties of the former compound after irradiation should be very close to those of the latter. Figure 2b confirms that it is so, which suggests that the yield of the LIESST effect at 10 K for **1** is quasiquantitative, and not only 24% as it could be believed at first glance.

The population of the low-lying  $S = 0$  spin state of the HS-HS pair through light irradiation is further confirmed by the field dependence of the magnetization,  $M = f(H)$ , at 2 K for the photoinduced species. This curve shows an inflection point around 30 kOe corresponding to the quasicrossing of the  $S = 0$  spin state with the  $M_S = -1$  Zeeman component of the  $S = 1$  spin state.<sup>18</sup>

The binuclear nature of compound **1** also influences the kinetic of the relaxation of the photoinduced HS-HS form. For  $T < \text{ca. } 17 \text{ K}$ ,  $\chi_M T$  after light irradiation increases as a function of time, in contrast with what usually happens. This behavior arises from the fact that the relaxation occurs via the  $S = 2$  spin states of the LS-HS pair.

This communication points out a form of synergy between magnetic interaction and spin conversion in the presence of light. The  $S = 0$  ground spin state of **1** is transformed into another  $S = 0$  ground spin state under light irradiation and at very low temperature, and these two nonmagnetic molecular states store different local information.

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