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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# A new family of diamagnetic macrocyclic Fe(II) compounds exhibiting LIESST effect at high temperature

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

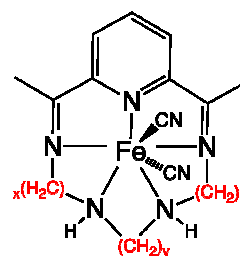
The photomagnetic properties of a new Fe(II) macrocyclic family  $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$  have been investigated with respect to the  $T(\text{LIESST})$  versus  $T_{1/2}$  relation. These compounds are diamagnetic below 400 K with  $T(\text{LIESST})$  values above 100 K, which indicates that this family presents unconventional LIESST effect that is much higher than the expected  $T_0 = 180$  K line for macrocyclic complexes.

**Introduction** Spin Crossover (SCO) phenomena continue to be an attractive area of many recent studies<sup>1</sup>. Complexes exhibiting SCO properties can change their spin state by external perturbation such as change of temperature or pressure, light irradiation or guest molecules<sup>2</sup>. These compounds are especially interesting for their potential application for data storage<sup>3</sup>. In 1984, Descurtins *et al.*<sup>4</sup> have observed a light-induced low-spin (LS)  $\rightarrow$  high spin (HS) transition during which the molecules can be quantitatively trapped in the excited HS state at sufficiently low temperatures. This so-called LIESST (Light-Induced Exited Spin-State Trapping) effect is normally observed at temperature lower than 80 K<sup>1</sup>, which prevents a direct utilization for data storage. The importance of this phenomena has lead to the introduction of the standard  $T(\text{LIESST})$  measurement, which aims to estimate the limiting temperature above which the photoinduced HS metastable state is erased<sup>5</sup>. Consequently, the increase of  $T(\text{LIESST})$  with the ultimate objective of reaching room temperature becomes one of the main topics in the field of LIESST phenomena. In order to search for key factors to increase  $T(\text{LIESST})$  value, a  $T(\text{LIESST})$  versus  $T_{1/2}$  database was established by comparing numerous SCO complexes<sup>6-8</sup>. As a result, inner coordination sphere has been identified as the effective factor to influence  $T(\text{LIESST})$  value. Following this approach, macrocyclic complexes particularly attracted the attention due to the high coordination degree of the ligand. Tremendous efforts have thus been recently contributed to interpret their fascinating SCO and high  $T(\text{LIESST})$  value behaviors<sup>9-11</sup>. However, since the LIESST effect is the transformation from LS to HS state, it means that the target system should exhibits quite high  $T(\text{LIESST})$  value and should be in LS state at room temperature. Unfortunately, such kind of system is extremely uncommon in regard to the inverse energy-gap law<sup>12</sup>. Thus the development of LS complexes with LIESST effect becomes an urgent demand.

The purpose of the present study is to fill this demand. A family of macrocyclic compounds  $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2]$  with  $x,y,z = 2,3,2; 3,2,3$  or  $2,2,3$  (Scheme 1) have been prepared and characterized based on previous work<sup>11</sup>, where the amine has been modified. Their magnetic properties have been investigated in the temperature range from 4 K to 500 K. The optical and photomagnetic properties are discussed in comparison with previously reported macrocyclic complex  $[\text{Fe}(\text{L}_{222}\text{N}_5)(\text{CN})_2] \cdot \text{H}_2\text{O}$  (compound 1).

## Results and discussion

Three compounds  $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$  with  $x,y,z = 2,3,2$   $n=2.5$  (compound 2);  $2,2,3$   $n=2.5$  (compound 3) or  $3,2,3$   $n=1.5$  (compound 4) have been obtained following a procedure described by Nelson *et al.*<sup>13</sup>. The chemical analysis and TGA measurements (see ESI<sup>†</sup>) confirm the quality of the compound and the presence of one or more water molecules per Fe(II) center. Attempts to obtain single crystals of 2, 3 and 4 using different methods and solvents for solving structure of the sample were not successful. Magnetic measurements in SQUID show that the three compounds are low spin ( $\chi_M T = 0$ ) from 300 K down to 4 K. These results are in line with the previously reported magnetic data by Nelson<sup>13</sup> for compound 2. In order to search for an eventual thermal spin conversion at higher temperature, the magnetic susceptibility has been recorded up to 500 K by a high-temperature susceptometer. The  $\chi_M T$  versus  $T$  plot is reported on the Fig. 1 for compound 3.



**Scheme 1** Representation of  $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2]$  with  $x,y,z = 2,2,2; 2,3,2; 2,2,3$  or  $3,2,3$  for compounds 1, 2, 3, and 4 respectively

Whereas the compound remains diamagnetic below 420 K, a sharp increase is observed above this value for the  $\chi_M T$  product, this product reaching the value of  $1.25 \text{ cm}^3 \text{ K mol}^{-1}$  at 475 K. If the compound is further cooled, the diamagnetic

state is never recovered ( $\chi_M T = 0.75 \text{ cm}^3 \text{ K mol}^{-1}$  at 10 K).

For compound **1**, **2** and **4**, the magnetic behaviors are similar to compound **3** with the increase of  $\chi_M T$  value at 400 K, 420 K and 450 K respectively (see Fig. S1-S3, ESI†).

Moreover, when those complexes are left at ambient atmosphere for several months after the above experiments, the  $\chi_M T$  values for all the four complexes are still around  $1 \text{ cm}^3 \text{ K mol}^{-1}$  at room temperature, which further confirms that the increases of  $\chi_M T$  values are irreversible. There are two possible reasons for this irreversible increase of  $\chi_M T$  value. The first one is that the complexes exhibit an extremely large hysteresis of more than 400 K. Nevertheless, this idea appears unrealistic, in regard to the hysteresis loop up to now encountered for SCO materials never exceed 60 K<sup>14</sup>. The second possibility is that a decomposition and/or dehydration process takes place at high temperature, which means that the chemical nature of the complexes has been irreversibly modified.

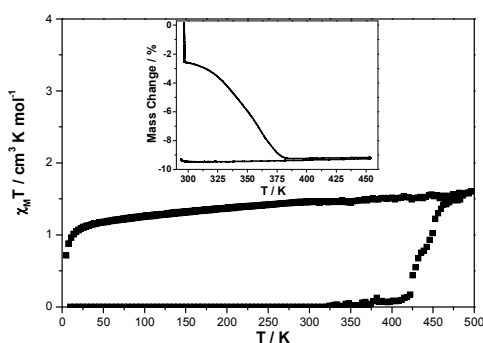


Fig. 1  $\chi_M T$  versus  $T$  plot for **3**. Inset: TGA for **3**.

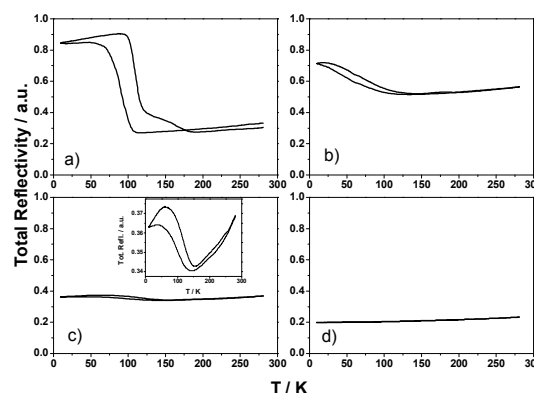
In order to identify the process that occurs at high temperature, TGA measurements have been carried out. For compound **3** (Fig. 2 inserted), a mass loss of 2.5 % is observed under nitrogen flux at 300 K. An increase of the temperature up to 380 K leads to a further mass loss of 7.0 %, the mass of the sample being stable above 380 K. The total loss observed in TGA (9.5 %) is in reasonable agreement with the 2.5 water molecules proposed in the chemical formula (calculated mass loss: 10.2%). Thus the mass loss of compound **3** can be divided into two origin: 1) the loss at room temperature can be attributed to the disadsorption of water molecule at surface; 2) the loss during the increase of temperature can be attributed to the water loss in the crystal lattice. Similar origins can be attributed in compound **1**, **2** and **4** with different percentage of mass loss (see Fig. S1-S3 insets, ESI†).

A first correlation between TGA and magnetism has been discussed in the previous paper describing compound **1**<sup>11</sup>. The mass loss occurs for the different compounds at a temperature below 400 K. On the other hand, the increases in  $\chi_M T$  for the different compounds occur above 400 K. It thus seems that the process that takes place at high temperature and that is responsible for the modification of the magnetic properties of the compound is not simply a solvent loss, but is possibly a partial decomposition of the iron complex. It is also very

likely that dehydration and some decomposition of the product occur in the same temperature range.

Since the SCO phenomenon, especially the LIESST effect can be probed by the optical properties of the material<sup>15,16</sup>, the total reflectivity as a function of the temperature has thus been recorded for the all four compounds (Fig. 2). For **1** (Fig. 2a) upon cooling, the total reflectivity shows a sharp increase at around 100 K. The maximum is found to be at ca. 60 K for the cooling branch. On further cooling, the total reflectivity signal keeps stable until 10 K. Upon warming a sharp decrease of intensity can be found at ca. 100 K. At 175 K the intensity of the warming branch reaches similar level as compared to the cooling branch. This type of behavior corresponds to Light Induced Thermal Hysteresis (LITH) introduced in 1998 for the  $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$  complex<sup>17</sup>. In this case the width of the LITH loop is 30 K. For **2** (Fig. 2b), the intensity of total reflectivity increases gradually starting at ca. 100 K upon cooling. On warming, the intensity decreases gradually from 10 K, merging with the cooling branch at ca. 120 K. In comparison with **1**, the size of the thermal hysteresis is smaller and the magnitude of the change in reflectivity at low temperature is about 4.5 times smaller. Moreover, the shape of the LITH loop is really gradual. For **3** (Fig. 2c), under irradiation the change of reflectivity signal is very small, giving a tiny LITH loop at round 100 K (Fig. 2c inset). The intensity of the LITH loop is about 10 times smaller than the one for **2**. Finally for **4** (Fig. 2d) no change of reflectivity is observed.

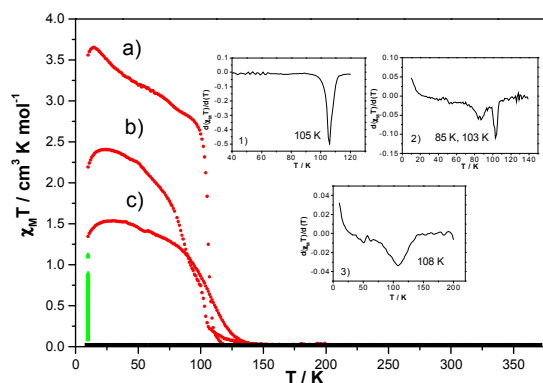
From previous investigation on **1**, the LITH loop and the LIESST effect are strongly correlated in these diamagnetic complexes. Thus the observation of LITH in **2** and **3** can be attributed to the presence of LIESST effect, which can also be confirmed by the changes in the absorption spectra as a function of wavelength at different temperature (see Fig. S4-S5, ESI†). Moreover, from the warming branch of the LITH loop, it may be anticipated a relatively long lifetime of the photo-induced HS state for **2** and **3** as the change of reflectivity occurs at around 100 K. Nevertheless, the change of intensity in reflectivity is strongly dependent on the nature of the ligands. Compound **1** shows the highest level of change. When the chain length of the ligands increases, from **2** to **4**, a decrease in the intensity is observed and a decrease of the size of LITH loop is also observed.



**Fig. 2** Total reflectivity of **1** (a), **2** (b), **3** (c) and **4** (d). Inset: Enlarged plot for total reflectivity of **3**.

Fig. 3 presents the photomagnetic experiments performed on **1**, **2** and **3**. These measurements have been carried out following the standard procedure<sup>5-8</sup>. The maximum  $\chi_M T$  value reached after irradiation depends on the nature of the compounds:  $3.5 \text{ cm}^3 \text{ K mol}^{-1}$  for **1**,  $2.5 \text{ cm}^3 \text{ K mol}^{-1}$  for **2** and  $1.5 \text{ cm}^3 \text{ K mol}^{-1}$  for **3**. The photoconversion of the compounds require long time of photo-irradiation and quite large power of irradiation: 2 hours ( $5 \text{ mWcm}^{-2}$ ) for **1**, 3 hours ( $20 \text{ mW cm}^{-2}$ ) for **2** and 10 hours ( $20 \text{ mWcm}^{-2}$ ) for **3**. As far as **4** is concerned, the irradiation during several hours ( $20 \text{ mWcm}^{-2}$ ) did not lead to any increase of magnetic susceptibility, and thus its  $T(\text{LIESST})$  value can not be measured.

$T(\text{LIESST})$  measurements are therefore performed for the compounds **1**, **2** and **3**. After reaching the photosaturation at 10 K under irradiation, the laser was switched off and the temperature increased at a defined rate of  $0.3 \text{ K min}^{-1}$ . For complex **1**, the shape and the  $T(\text{LIESST})$  value (Fig. 3a and inset 1) are in agreement with the previous work<sup>11</sup>. For complex **2**, the shape of the  $T(\text{LIESST})$  curve displays two steps at 85 K and 103 K respectively (Fig. 3b and inset 2). For **3**, the  $T(\text{LIESST})$  value is estimated at 108 K (Fig. 3c and inset 3). The two  $T(\text{LIESST})$  values are related to the domains of sample with different levels of photoconversion saturation (see Fig. S6, ESI†).



**Fig. 3**  $T(\text{LIESST})$  measurements of **1**, **2** and **3** plotted in a), b), and c) respectively. ■ = data recorded in the dark without irradiation (along line  $\chi_M T = 0$ ); ▲ = data recorded under irradiation; + = data registered by increasing the temperature after irradiation. Inset: plot of  $d\chi_M T/dT$  vs.  $T$  indicating  $T(\text{LIESST})$  values of **1**, **2** and **3** in 1), 2), and 3) respectively.

Concerning the stability of the photoinduced state, the three evaluated complexes **1**, **2** and **3** display similar  $T(\text{LIESST})$  value of about 100 K. Thus the nature of the ligand in this macrocyclic family affects the difficulty of photoexcitation (illustrated by the reached various levels of photosaturation), but not the stability of the lifetime. The three complexes display exceptional long lived lifetime for Fe(II) materials in LS state at room temperature. In fact, if we consider the inverse energy-gap law approach<sup>12</sup>, it is not expected that an Fe(II) material with a LS state at room temperature presents a photoinduced HS state with a long lifetime.

One of the reason for such atypical stability of the photoinduced HS state may be linked to role of coordination degree of macrocyclic ligands. It has been previously demonstrated that the  $T(\text{LIESST})$  versus  $T_{1/2}$  relationship depends on the nature of the ligand surrounding the metal ion (through the denticity, rigidity of the ligand<sup>7,8</sup> and/or distortion<sup>18</sup>).  $T(\text{LIESST})$  exhibits, as a first approximation, a linear relationship with the thermal spin transition  $T_{1/2}$ :  $T(\text{LIESST}) = T_0 - 0.3 T_{1/2}$ .  $T_0$  is an empirical temperature parameter that is related to the denticity of the ligands surrounding the Fe(II). For monodentates ligands  $T_0 = 100 \text{ K}$ , for bidentates ligands  $T_0 = 120 \text{ K}$ , for tridentates ligands  $T_0 = 150 \text{ K}$ . An analogous relationship has been observed in Prussian Blue analogues, with  $T_0 = 200 \text{ K}$ . For macrocyclic ligands, one point has been added on a virtual line with  $T_0 = 180 \text{ K}$ , i.e.  $[\text{Fe}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2] \cdot \text{H}_2\text{O}$  ( $\text{L}_{222}\text{N}_3\text{O}_2 = 2,13$ -dimethyl-6,9-dioxa-3,12,18-triazabicyclo [12.3.1]octadecapentaene). This compound is closely related to **1**, with the two central NH moieties of the amine being replaced by oxygen atoms<sup>9</sup>. This compound presents a high  $T(\text{LIESST})$  of 130 K, the highest to date reported for a mononuclear Fe(II) complex. Therefore one explanation of the long-lived photoinduced HS state for these diamagnetic complexes can be traced to the high denticity of the macrocyclic ligand. A  $T_{1/2}$  cannot be defined for **1**, **2** and **3**. Indeed, the thermal dehydration and/or decomposition of the compounds above 400 K prevent the observation of a genuine thermal spin conversion for the hydrated compound. If such a hypothetical spin conversion were existing for hydrated compounds, the  $T_{1/2}$  value would be higher than 400 K. Following the relationship  $T(\text{LIESST}) = T_0 - 0.3 T_{1/2}$  with  $T_0 = 180 \text{ K}$  for macrocyclic ligands, a  $T(\text{LIESST})$  value lower than 60 K should be expected. It is interesting to note that the  $T(\text{LIESST})$  values observed are notably higher.

A second reason of the high  $T(\text{LIESST})$  may be linked to a possible change in coordination of the Fe(II) metal ion. Indeed, in most of the Fe(II) spin crossover compounds, the metal center remains six coordinated, whatever the spin state. Only the mean Fe-N distance changes from around  $2.0 \text{ \AA}$  in the LS state to  $2.2 \text{ \AA}$  in the HS state. However, one exception has been found in the previous studied oxygen-contained macrocyclic compound  $[\text{Fe}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2] \cdot \text{H}_2\text{O}$ . It has been determined from the crystal structure that the iron is seven coordinated in the HS state and that it is six coordinated in the LS state<sup>9c</sup>. For the presented diamagnetic complexes, the crystal structure of **1** in the LS state has been obtained<sup>19</sup>, of which the iron is six coordinated. Since the direct observation of light-induced HS structures involves the complexity of photo-irradiation in single crystal X-ray diffractometer at liquid helium temperature, the attempts for **1** thus still need to be carried on. Nevertheless, a seven coordinated structure of **1** in HS state has been observed in a molecular magnet using **1** as building block<sup>19</sup>. These observations indicate the possibility of light-induced structural transition with a change of coordination in **1**, **2** and **3**. Definitely, in this aspect, the structures of the complexes in both LS and photoinduced HS state need to be systematically investigated. Unfortunately, up

to now such information is unavailable and our efforts to get single crystals failed. Thus our hypothesis on the 6/7 coordination change remains to be confirmed.

### Conclusion

To conclude, we have synthesized and characterized a new Fe(II) macrocyclic family with nitrogen coordination atoms on macrocyclic unit. In this family, the length of chains between the nitrogen atoms was increased and the consequence on the properties of the individual complex was investigated. From thermal analysis, it was illustrated that all the four studied complexes contained two different type of water molecule, i.e. the water of surface adsorption and the water in the crystal lattice. From magnetic studies, it was demonstrated that all the four complexes were in LS state below 420 K and presented an irreversible increase of  $\chi_M T$  product at around 420 K, which indicated that the magnetic properties of the family is independent with the chain length. Then we reported the reflectivity properties of the complexes, which demonstrated that three out of the four complexes could be photoexcited to the metastable HS state. The photomagnetic studies further confirmed the observation from reflectivity, and in addition, the three complexes which presented LIESST effect and the metastable LIESST state of this family can be observed up to 100 K. However, depending on the nature of the ligands, the level of photoexcitation is different. It can be expected, following the structures already obtained for compound **1**, that the compounds of this series are probably six coordinated in LS state and seven coordinated in metastable photoinduced HS state. In order to check this, single crystals should be obtained and studied at low temperature after irradiation. This work is in progress.

### Acknowledgements

The authors acknowledge the ANR and the Aquitaine region.

### Notes and references.

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- † Electronic Supplementary Information (ESI) available: TGA and high temperature magnetic susceptibility of compounds **2** and **4**. See DOI: 10.1039/b000000x/
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