

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

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Electronic Supplementary Information

Experimental details

Fig. S1 $\chi_M T$ versus T plot and TGA for **1**.

Fig. S2 $\chi_M T$ versus T plot and TGA for **2**.

Fig. S3 $\chi_M T$ versus T plot and TGA for **4**.

Fig. S4 Changes in the diffuse absorption spectra of **2** and **3**.

Fig. S5 Changes in the diffuse absorption spectra of **4**.

Fig. S6 Magnetic and photomagnetic behaviors of **2** with irradiation for 10 hours (15 mW cm⁻²).

References

Experimental

The synthesis of $[\text{Fe}(\text{L}_{232}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$ (**2**, $\text{L}_{232}\text{N}_5=2,14\text{-dimethyl-}3,6,10,12,19\text{-penta-azabicyclo [13.3.1]-nonadeca-1(19),2,13,15,17-pentaene}$) was performed as described by Nelson et al.^[1] i.e. a mixture of 2,6-diacetylpyridine, N,N'-Bis(2-aminoethyl)-1,3-propanediamine and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was firstly prepared in a deoxygenated methanol/aqueous solution, and then after partial concentration, the solution was filtrated into an aqueous solution of NaCN. The product was washed with distilled water and obtained by drying under vacuum. The synthesis of compound $[\text{Fe}(\text{L}_{223}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$ (**3**, $\text{L}_{223}\text{N}_5=2,14\text{-dimethyl-}3,7,10,13,19\text{-pentaazabicyclo [13.3.1]-nonadeca-1(19),2,13,15,17-pentaene}$), and $[\text{Fe}(\text{L}_{323}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$ (**4**, $\text{L}_{323}\text{N}_5=2,15\text{-dimethyl-}3,7,10,14,20\text{-pentaazabicyclo [14.3.1]-icosan-1(20),2,14,16,18-pentaene}$) were performed in the same method as above^[1], except that the amine parts were changed to N-(2-Aminoethyl)-N'-(3-aminopropyl)ethylenediamine tetrahydrochloride, and 1,2-Bis(3-aminopropylamino)ethane for **3** and **4** respectively. For **3**, the amine was dissolved aqueous solution containing NaOH for deprotonation. Attempts to obtain single crystals of **2**, **3** and **4** using different methods and solvents for solving structure of the sample were not successful.

Characterization and Measurements

Elemental analyzes C, H, N and S were performed on an automatic elemental analyzer FlashEATM 1112. Anal. Calc. for compound 2: C, 49.10; H, 6.87; N, 22.27; Fe, 12.68%; Found: C, 49.31; H, 6.19; N, 23.16; Fe, 12.75 %. Anal. Calc. for compound 3: C, 49.10; H, 6.87; N, 22.27; Fe, 12.68%; Found: C, 48.59; H, 6.87; N, 22.08; Fe, 13.64%. Anal. Calc. for compound 4: C, 52.30; H, 6.93; N, 22.47; Fe, 12.80%; Found: C, 53.01; H, 7.14; N, 22.28; Fe, 13.38%.

TGA has been recorded on a Setaram MTB10-8 TGA apparatus. The sample was first left in nitrogen flux for 3 hours at room temperature, and then the temperature was increased up to 450 K with a rate of 1 K min⁻¹. Later on, the temperature was decreased back to room temperature slowly. The mass of the sample was continuously measured during the whole process.

The apparatus of reflectivity, developed at ICMCB, consists of a halogen lamp (Fiber Optic Illuminator Model 77501) equipped with a filter centered at 530 nm. The sample, placed in a quartz sample holder, is continuously measured on the surface by the white light emitted by the halogen lamp. The device is equipped with a SM240 spectrometer (Opton Laser International) and coupled to cryogenic helium.

The magnetic properties were recorded using a SQUID magnetometer (Superconducting Quantum Interference Device) Quantum Design MPMS-5S. Photomagnetic Experiments are performed using the SQUID apparatus coupled to a LASER (Krypton, Kr +). The high temperature susceptometer, operating in the range 300-800 K, is equipped with a 2 T electromagnet and a Eurotherm temperature controller.

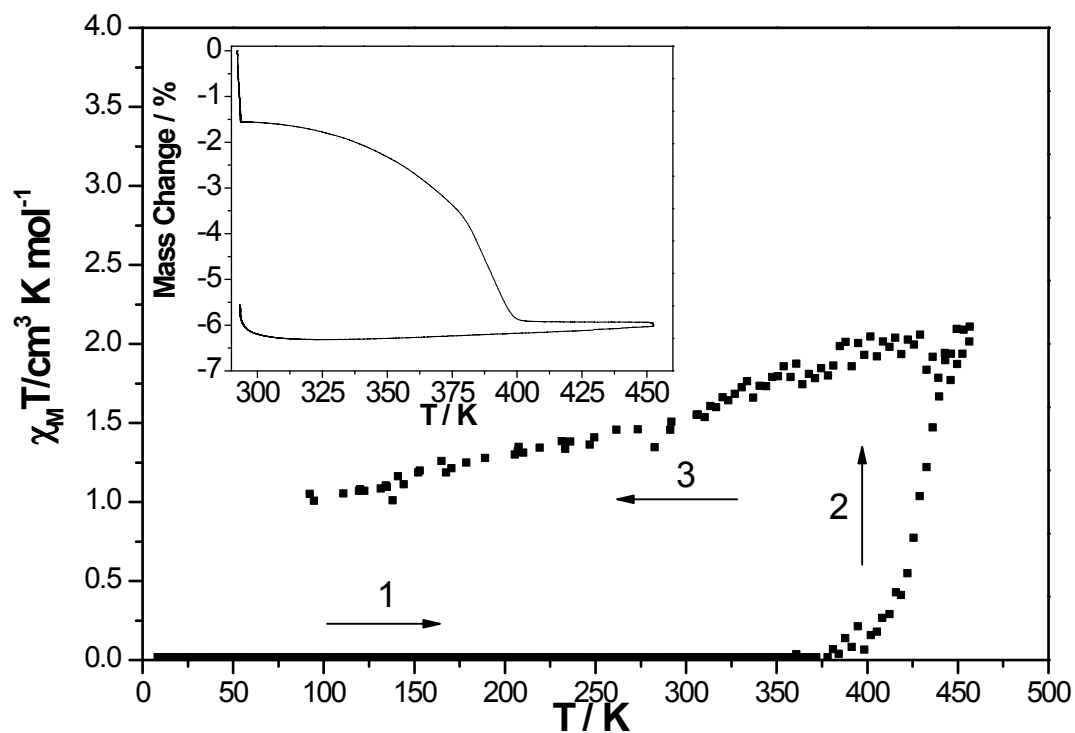


Fig. S1 $\chi_M T$ versus T plot for **1**. Inset: TGA for **1**. Step 1 and 2: heating. Step 3: cooling.

Compound **1** is diamagnetic from 10 K to 370 K in perfect agreement with previously reported measurements [2]. In higher temperature region, it shows an increase of $\chi_M T$ value starting at 400 K. When the temperature increases above 425 K, $\chi_M T$ increases sharply to reach about $2.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 450 K. When the temperature is then decreased, the $\chi_M T$ value decreases very slowly to reach about $1.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 80 K. In conclusion, after an initial thermal treatment up to 400 K, the magnetic properties of **1** never come back to the initial diamagnetic state.

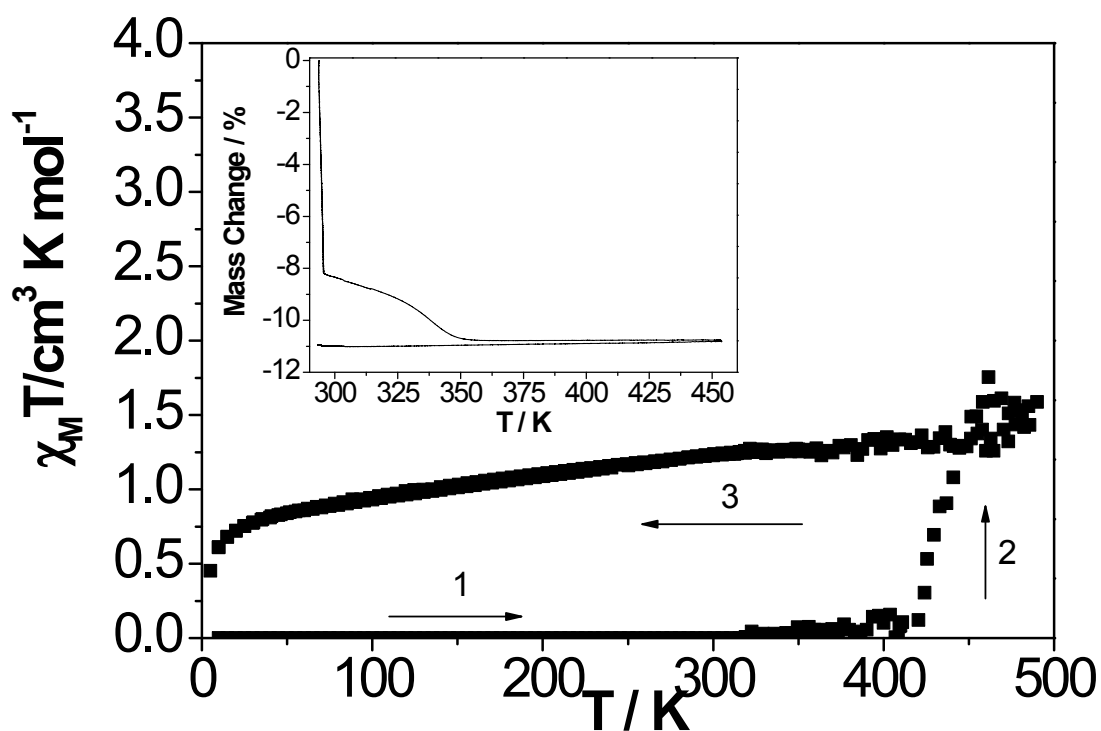


Fig. S2 $\chi_M T$ versus T plot for **2**. Inset: TGA for **2**. Step 1 and 2: heating. Step 3: cooling.

Magnetic behaviors of **2** (Fig. S2) and **4** (Fig. S3) are similar to **1** (Fig. S1). They are diamagnetic from 10 K to 370 K. On warming to higher temperature region, an increase of $\chi_M T$ value can be found at 420 K and 450 K respectively for **2** and **4**. The maximum $\chi_M T$ value is $1.5 \text{ cm}^3 \text{ K mol}^{-1}$ for all the three complexes at ca. 500 K. On cooling, the $\chi_M T$ value decreases very slowly. At 50 K, $\chi_M T$ value reaches $0.8 \text{ cm}^3 \text{ K mol}^{-1}$ for both **2** and **4**. Thus the increases of $\chi_M T$ are irreversible for these three complexes.

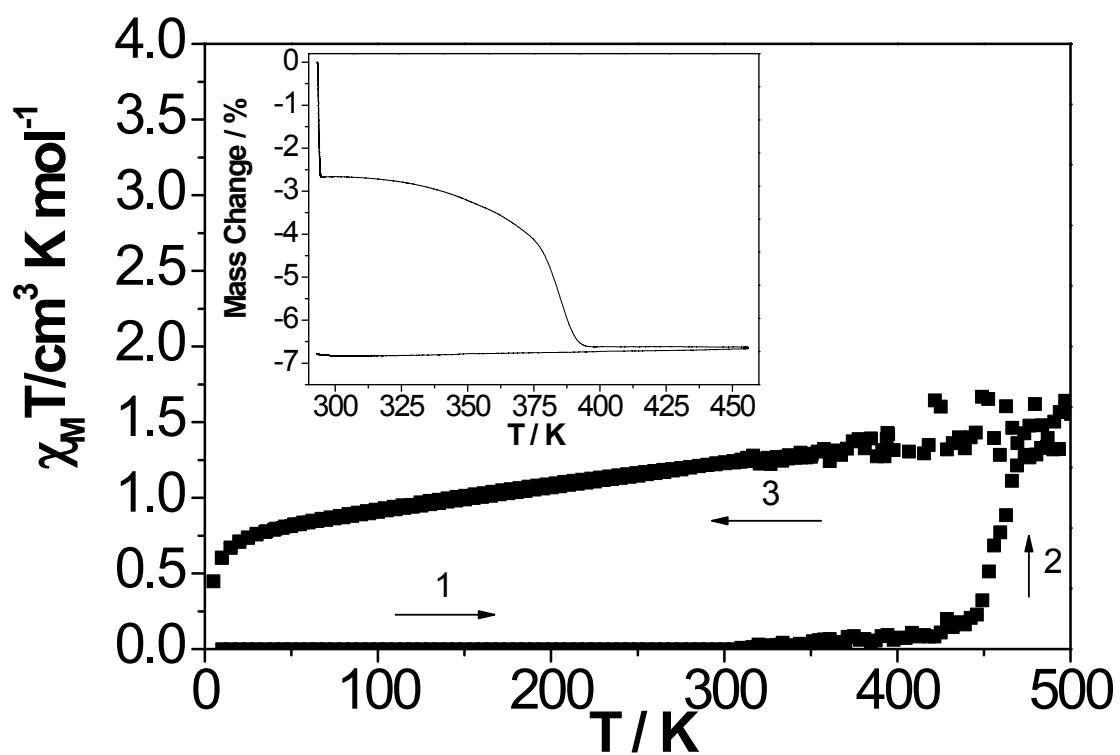


Fig. S3 $\chi_M T$ versus T plot for 4. Inset: TGA for 4. Step 1 and 2: heating. Step 3: cooling.

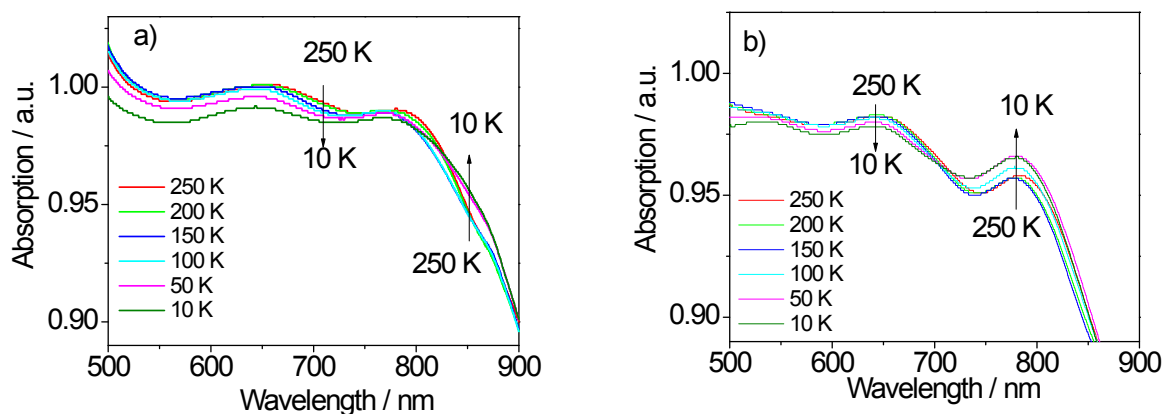


Fig. S4 Changes in the diffuse absorption spectra of **2** and **3** in a) and b) respectively upon cooling under light irradiation.

For both **2** and **3**, a decrease of the temperature between 250 and 10 K leads to a slight increase of absorption between 800 and 850 nm and a decrease of absorption between 500 and 650 nm. The increase of the 800–850 nm bands characterizes the appearance of the d–d transition associated to the HS state. The decrease of the 500–650 nm transition is assigned to the decrease of both d–d and MLCT (metal-to-ligand charge transfer) bands of the LS iron metal center^[3]. Such an increase of d–d HS transition at 800–850 nm band from room temperature to 10 K under irradiation suggests that at the surface of the samples a photoconversion process may occur according to the well-known LIESST effect^[4-7].

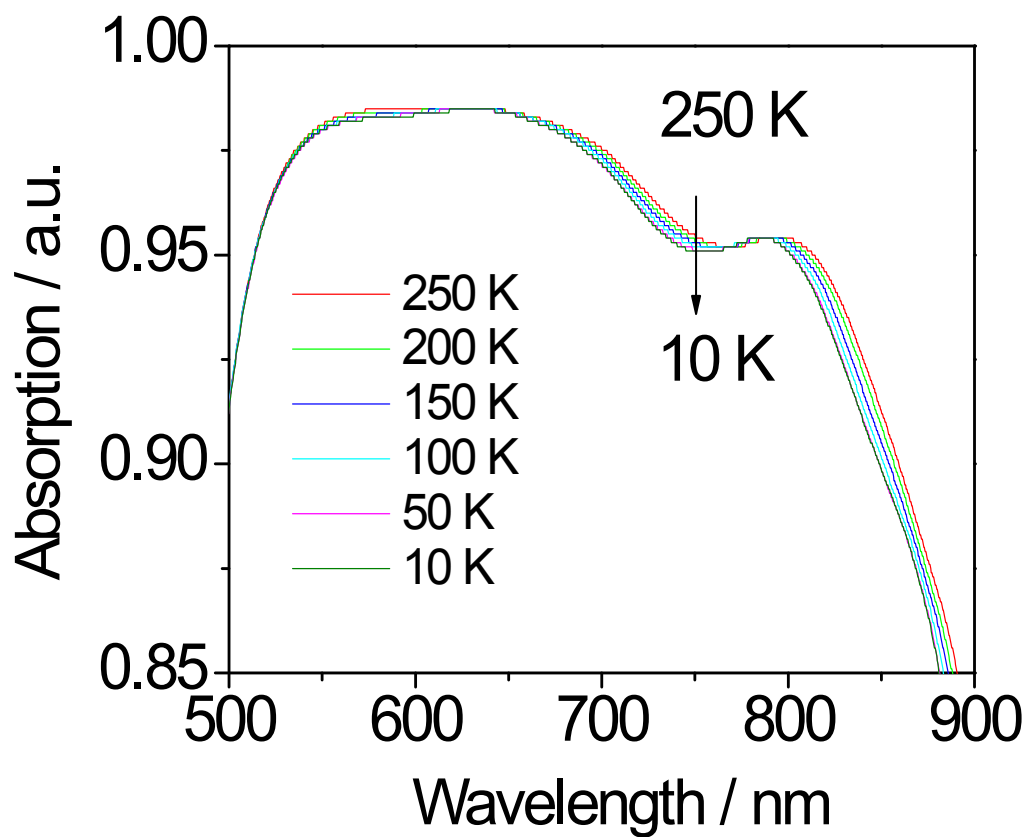


Fig. S5 Changes in the diffuse absorption spectra of **4** upon cooling under light irradiation.

Fig. S5 presents the absorption spectra of **4** between 500 nm and 900 nm. From 250 K to 10 K, a continuous decrease can be observed in a broad range from 500 to 900 nm. In contrast to the two above complexes, the complex **4** does not exhibit an increase of d-d HS transition band (800-850 nm) at low temperature under irradiation. This complex may not present some LIESST properties at low temperatures.

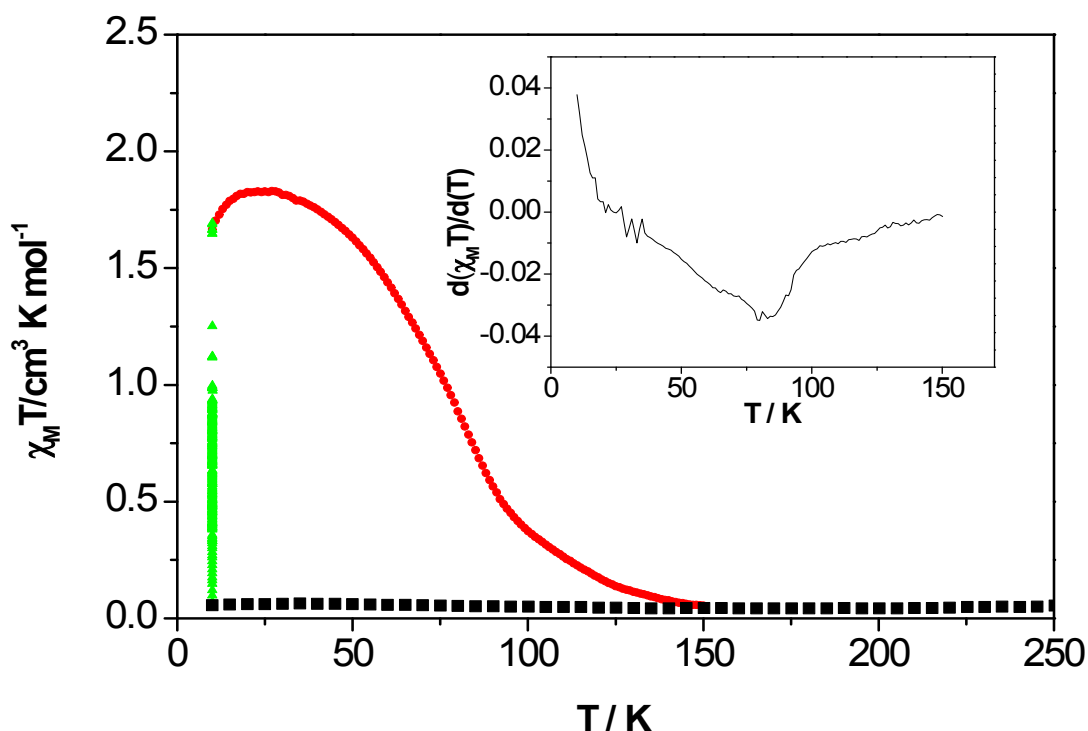


Fig. S6 Magnetic and photomagnetic behaviors of **2** with irradiation for 10 hours (15 mW cm^{-2}). The minimum of the derivative of $\chi_M T$ vs. T curve is found to be at 80 K.

Concerning the presence of two $T(LIESST)$ values for **2**, the following experiment was performed. Instead of using an irradiation power of 20 mW cm^{-2} , the experiment with an intensity of 15 mW cm^{-2} is reproduced. The recorded $\chi_M T$ vs. T curve is presented in Fig. S6. The photostationary limit found at 10 K under this condition provides a $\chi_M T$ value of $1.7 \text{ cm}^3 \text{K mol}^{-1}$, which is lower than the one obtained by irradiation with 15 mW cm^{-2} light. What is more important is that in such condition, the $T(LIESST)$ curve presents only one minimum at 80 K, that is at lower value of the two minima recorded by applying 20 mW cm^{-2} of irradiation. Therefore with a lower power, only one $T(LIESST)$ value is recorded at 80 K; while when higher power is applied, the $T(LIESST)$ value shifts to higher temperature, reaching 103 K (Fig. 3b). Consequently, the two $T(LIESST)$ values observed on Fig. 3b can be attributed respectively on domains of the sample with different level of saturation of photoconversion. Of course it would be interesting to apply higher power for irradiation. Unfortunately in SQUID cavity, the use of higher power destabilize of the temperature.

References

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