Electronic Supplementary Information

Abrupt spin transition around room temperature and light induced properties in Fe^{II} complexes with N_4O_2 coordination sphere

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Synthesis of the ligand

The ligand 4-hydroxy-N'-((pyridin-2-yl)-methylene)benzohydrazide (**HL**) was prepared using similar method described in the literature.[1] Yeild: 80 %. FT-IR (cm^{-1}): 3219(b), 3060(b), 2683(b), 1650(s), 1608(m), 1589(m), 1563(m), 1514(s), 1471(m), 1438(w), 1356(w), 1278(s), 1247(m), 1179(m), 1150(m), 843(m), 765(m). Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.34; H, 4.45; N, 17.21 %.

Synthesis of the compound $Fe(L\text{-}OEt)_2ClO_4\cdot EtOH\cdot H_2O$ ($2\cdot EtOH\cdot H_2O$):

An equimolar amount of solid NaOH (7 mg, 0.2 mmol) was added to a suspension of ligand (47 mg, 0.2 mmol) in EtOH. The resulting deprotonated ligand solution was stirred and then enthanolic solution of iron(III) perchlorate (46 mg, 0.1 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and filtered, green block crystals were obtained by slow diffusion of ether into the clear filtrate for two weeks. Yeild: 50 %. FT-IR (cm^{-1}): 3346(b), 3105(b), 2982(b), 1614(s), 1595(s), 1570(m), 1500(s), 1469(m), 1444(w), 1427(m), 1361(s), 1325(s), 1263(m), 1247(m), 1189(m), 1166(m), 1100(m), 846(w), 754(m). Anal. Calcd for $C_{32}H_{36}ClFeN_6O_{12}$: C, 48.78; H, 4.60; N, 10.67. Found: C,48.90; H, 4.45; N, 10.31 %.

X-ray Crystallography

Crystallographic data for single crystal of the compounds were collected on a Nonius Kappa CCD diffractometer with a 2.0-kW sealed-tube source using graphite monochromated Mo Kα radiation of λ = 0.71073 Å. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct method, and refined by full-matrix least-squares on F^2 using SHELX program.[2] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added by calculated geometry. Some constraints were used to model the disorder in solvent molecules.

Crystal and structure refinement parameters for **2**·EtOH·H$_2$O: $C_{32}H_{36}ClFeN_6O_{12}$, M_r = 787.97. Monoclinic, $P2_1/n$, a = 12.716(3), b = 23.544(5), c = 12.907(3) Å, β = 108.41°, V = 3666.6(13) Å^3, Z = 4, μ(Mo-Kα) = 0.553 mm^{-1}, 45225 measured reflections, 6408 independent, R_{int} = 0.1194; final $R1$ = 0.0586 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.1490. CCDC 756167.

Magnetic measurements

The variable temperature magnetic susceptibility measurements were carried out on sample constituted of monocrystals (~ 10 mg) using a Quantum Design MPMS-XL5 SQUID-Magnetometer at two field strengths (2 kOe and 5 kOe) in the heating an cooling mode within a temperature range from 2 to 390 K. Gelatine capsules were used as sample containers for measurements. The data were corrected for the magnetization of the sample holder, and diamagnetic corrections were estimated using Pascal's constants.[3]

The photomagnetic measurements were performed using a LD Pumped All-Solid-State Laser with 532 nm or 660 nm wavelength coupled *via* an optical fiber to the cavity of a Quantum Design MPMS-XL5 SQUID-Magnetometer operating with an external magnetic field of 10 kOe. The sample was located at the center of the standard sample holder produced by Quantum Design Company. The weight was estimated by comparing the thermal SCO curve with that for an accurately weighted sample. It was noted that there was no change in the data due to irradiative heating of the sample. Standardized method for determining LIESST properties was followed.[4] After being cooled slowly to 10 K, the sample was irradiated and the change in magnetism followed. When the saturation point had been reached, the irradiation was ceased and the temperature increased at a rate of 0.3 K min^{-1} while the magnetization was measured every 1 K. T(LIESST) was determined from the minimum of the $d\chi_M T/dT$ vs. T curve. For the LITH experiments, the sample was first slowly cooled from 200 K down to 10 K, and then heated slowly to room temperature and finally cooled down to the initial temperature 200 K with continuous green light irradiation. The data were corrected for the magnetization of the sample holder and the diamagnetic contributions, estimated from the Pascal's constants.

Thermal analysis

Thermal analyses were performed on SDT Q600 thermal analyzer (thermogravimetric analysis/differential thermal analysis, TGA/DTA) and a Q100 differential scanning calorimeter (DSC), under a nitrogen gas flow (50 mL min^{-1}) with a constant heating or cooling rate of 5 K min^{-1}. Temperature and enthalpy were calibrated using the melting point of indium.

References

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4 J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcen, G. Chastanet, M. Marchivie and L. Goux-Capes, *Chem.-Eur. J.*, 2005, **11**, 4582; J.-F. Létard, *J. Mater. Chem.*, 2006, **16**, 2550; J.-F. Létard, C. Carbonera, E. Courcot and J. S. Costa, *Bull. Mater. Sci.*, 2006, **29**, 567.

Table S1. Selected bond lengths and angles for **1·CH$_3$OH** and **1** at 290 K.

1·CH$_3$OH			
Fe1-N1	1.951(2)	Fe1-N2	1.866(1)
Fe1-O1	1.982(1)		
N2#1-Fe1-N2	179.07(8)	N2-Fe1-O1	79.80(6)
N2#1-Fe1-N1	97.73(6)	N1-Fe1-O1	161.38(5)
N2-Fe1-N1	81.62(6)	N1#1-Fe1-O1	92.89(6)
N2#1-Fe1-N1#1	81.62(6)	N2#1-Fe1-O1#1	79.80(6)
N2-Fe1-N1#1	97.73(6)	N2-Fe1-O1#1	100.87(5)
N1-Fe1-N1#1	90.80(9)	N1-Fe1-O1#1	92.89(6)
N2#1-Fe1-O1	100.87(5)	N1#1-Fe1-O1#1	161.38(5)
O1-Fe1-O1#1	89.42(7)		
1			
Fe1-N1	2.221(2)	Fe1-O1	2.079(2)
Fe1-N2	2.101(2)		
N2-Fe1-N2#2	162.48(8)	O1-Fe1-N2#2	119.26(8)
O1-Fe1-N1	147.22(8)	N1-Fe1-N2	73.85(8)
O1-Fe1-N2	73.38(8)	N1-Fe1-N1#2	83.20(8)
O1-Fe1-O1#2	96.56(7)	N1-Fe1-N2#2	92.89(8)
O1-Fe1-N1#2	98.89(8)		

Symmetry transformations used to generate equivalent atoms: #1: -x, y, -z+1/2; #2 -x, y, 3/2-z.

Table S2. Selected bond lengths and angles for **2·EtOH·H$_2$O** at 290 K.

Fe1-O1	1.943(3)	Fe1-O4	1.952(3)
Fe1-N4	2.175(4)	Fe1-N5	2.087(3)
Fe1-N1	2.147(4)	Fe1-N2	2.079(3)
O1-Fe1-O4	97.04(14)	N2-Fe1-N1	75.11(15)
O1-Fe1-N2	75.71(13)	N5-Fe1-N1	97.32(14)
O4-Fe1-N2	114.99(13)	O1-Fe1-N4	93.29(14)
O1-Fe1-N5	111.92(13)	O4-Fe1-N4	149.57(13)
O4-Fe1-N5	74.88(13)	N2-Fe1-N4	95.28(14)
N2-Fe1-N5	167.40(15)	N5-Fe1-N4	74.70(14)
O1-Fe1-N1	150.67(13)	N1-Fe1-N4	92.25(14)
O4-Fe1-N1	92.56(15)		

Table S3. Main hydrogen-like interactions in for **1·CH_3OH** and **1** at 290 K.

	D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (^{o})
1·CH_3OH	O2-H2A···N3[a]	0.82	1.950	2.756(2)	169.00
1	O2-H2A···N3[b]	0.82	1.910	2.723(3)	171.00
	C6-H6···O1[c]	0.93	2.560	3.215(3)	128.00
	C9-H9···O2[d]	0.93	2.570	3.436(3)	155.00

Symmetry codes: [a] -1/2-x,-1/2+y,1/2-z ; [b] 1/2-x, 1/2+y, 3/2-z; [c] x, -y, 1/2+z; [d] 1/2-x, -1/2+y, 3/2-z.

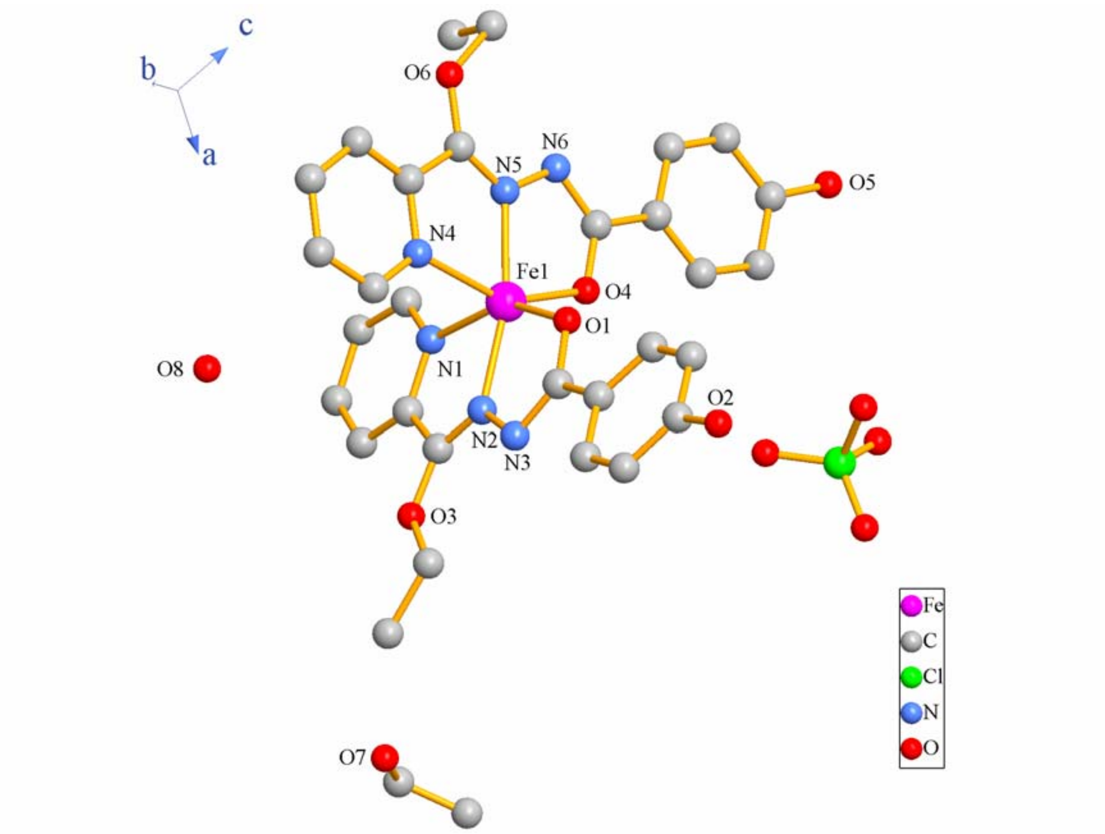

Figure S1. Molecular structure of **2·EtOH·H$_2$O** at 290 K.

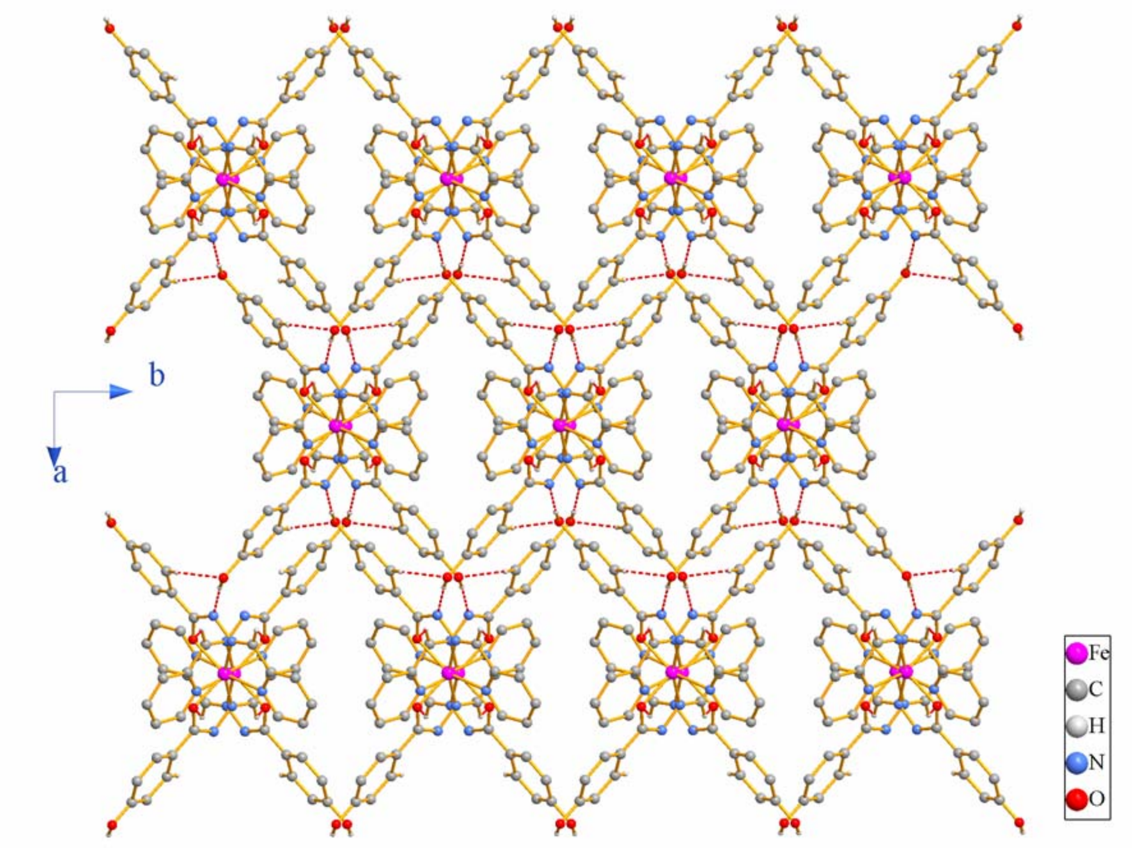

Figure S2. Crystal packing view of **1** at 290 K.

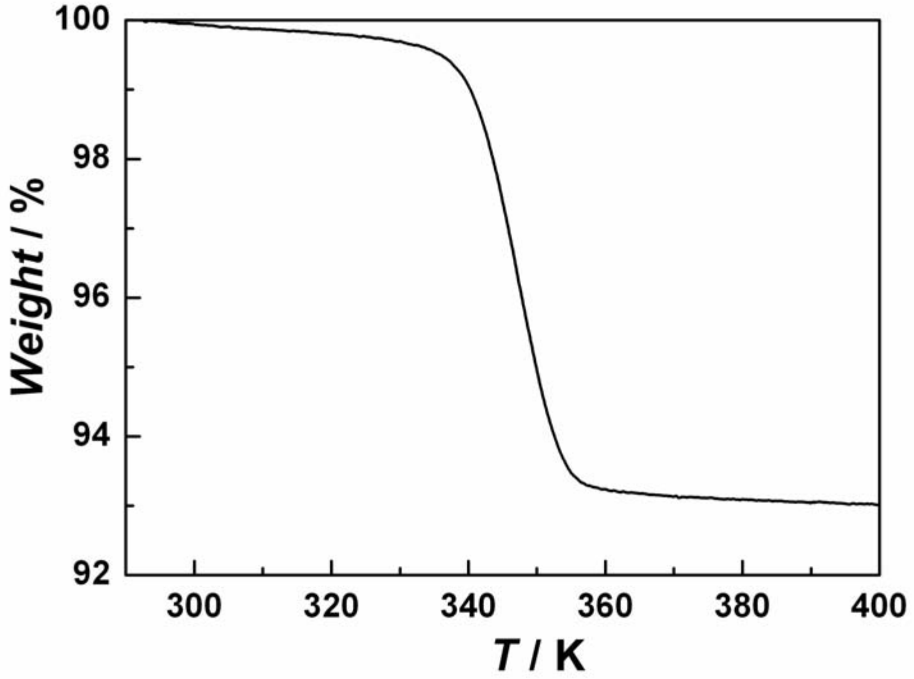

Figure S3. Thermal analysis of **1·CH_3OH**.

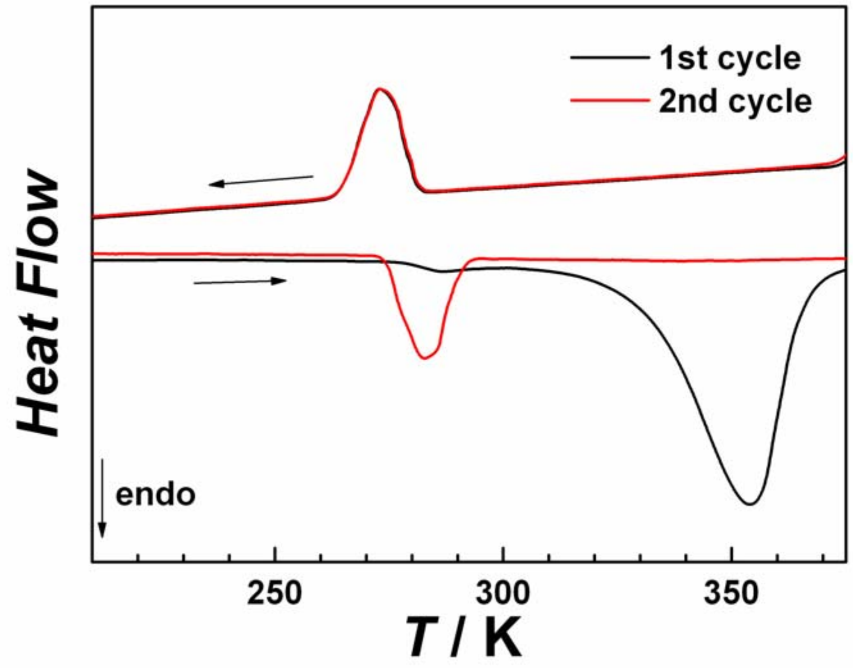

Figure S4. DSC analysis for **1·CH_3OH** in the heating and cooling modes.

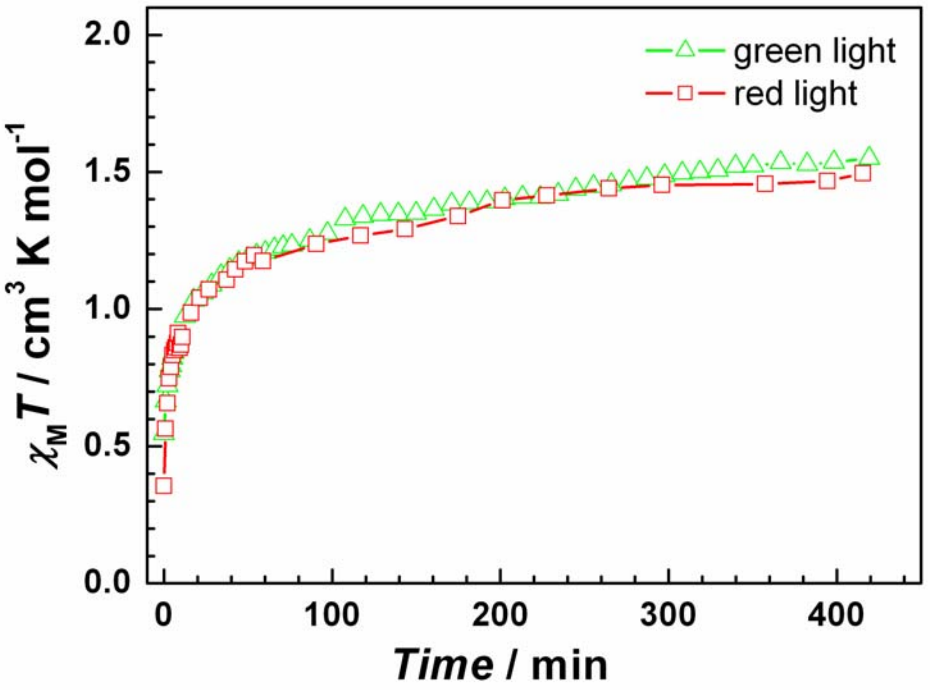

Figure S5. $\chi_M T$ versus time plot for **1** at 10 K under green light and red light irradiations at 10 K.