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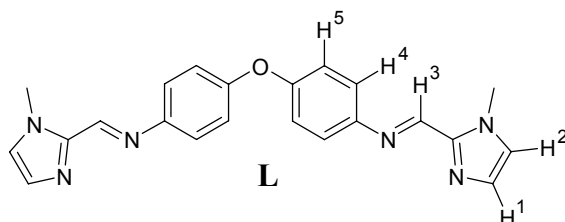
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Asymmetric spin-crossover behaviour and evidence of light-induced excited spin-state trapping in a dinuclear iron(II) helicate

Diane Pelleteret,^a Rodolphe Clérac^{*c,d} Corine Mathonière,^{ef} Etienne Harte,^{c,d} Wolfgang Schmitt^{*g} and Paul E. Kruger^{*a,b}

Supporting information

Synthetic methods: All reagents and solvents were purchased from commercial sources (Aldrich) or local solvent suppliers and used without further purification. Chemical analyses were performed at the Microanalytical Laboratories, University College Dublin, Ireland.



Synthesis of L: 1-Methyl-2-imidazolecarboxaldehyde (220 mg, 1.96 mmol) and 4,4'-oxydianiline (200 mg, 0.97 mmol) were stirred in methanol (10 ml) for 18 hrs. The clear solution was evaporated to dryness; the oil obtained was dissolved in dichloromethane. The organic solution was dried over MgSO₄, filtered and the solvent was removed. The residue obtained was recrystallised from acetonitrile. The off-white compound formed was collected by filtration. Yield: 215 mg, 58 %; mp: 154 °C; elemental analysis calcd (%) for C₂₂H₂₀N₆O: C 68.72, H 5.25, N 21.87; found: C 68.47, H 5.44, N 21.53; HR TOF MS: m/z for M+1: calc. mass. 385.1777 found 385.1765; ¹H NMR [(CD₃)₂SO, 400 MHz, 293K]: δ = 8.52 (s, 1H, H³), 7.43 (s, 1H, H¹), 7.37 (d, 2H, J = 8.8 Hz, H⁵), 7.16 (s, 1H, H²), 7.08 (d, 2H, J = 8.8 Hz, H⁴), 4.05 (s, 3H, Me); ¹³C NMR [(CD₃)₂SO, 100 MHz, 293K]: δ = 155.3 (Q), 150.5, 146.3 (Q), 142.8 (Q), 129.7, 126.5, 122.8, 119.4, 35.2.

Synthesis of [Fe₂(L)₃][ClO₄]₄ (1): Ligand L (0.1 g, 0.26 mmol) was dissolved in methanol (10 ml) and a methanolic (5 ml) solution of iron perchlorate hydrate (60 mg, 0.20 mmol) was added dropwise. A red/orange precipitate formed instantly. The reaction mixture was stirred for 30 min and the product collected by filtration. Yield:

130 mg, 91 %; elemental analysis calcd (%) for $[\text{Fe}_2(\text{C}_{22}\text{H}_{20}\text{N}_6\text{O})_3][\text{ClO}_4]_4 \cdot 2\text{H}_2\text{O}$: C 46.69, H 3.80, N 14.86; found: C 46.32, H 3.67, N 14.31; ^1H NMR (CD_3CN , 400 MHz, 293K): δ = 126.3 (br s, 1H), 75.7 (br s, 1H), 69.7 (s, 1H), 17.6 (br s, 2H), 2.8 (s, 3H), 0.7 (br s, 2H). Crystals suitable for single crystal X-ray diffraction studies were obtained from a solution of **1** in acetonitrile following the slow diffusion of methanol.

CAUTION! No problems were encountered during the preparation and the study of the perchlorate derivate described above. However, suitable care must be taken when handling such potentially explosive materials.

Physical characterizations: ^1H NMR spectra were acquired on a Bruker DPX400 machine and referenced to the residual proton shifts in the internal deuterated solvent.

Mass spectra were recorded on a Micromass LCT electrospray instrument.

The magnetic susceptibility measurements were obtained with a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal. The magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on a 5.42 mg polycrystalline sample. The magnetic data were corrected for the sample holder and the diamagnetic contributions. Due to the sensitivity of the crystals to solvent loss and in order to avoid structural heterogeneity of the sample, the measurements have been performed on a polycrystalline compound dried for a few hours at 60°C (at this temperature all the solvent molecules are lost based on the TGA data). It is worth noting that the integrity of the helicate after the drying process was verified by NMR.

The photomagnetic experiments were performed with a 150 W halogen lamp (LEICA CLS 150X) coupled through an optical fibre directed into the magnetometer cavity. 2 to 3 mg of powdered samples were packed in a thermoformed SQUID straw maintained at about 4 mm from the optical fibre. Data in the dark have been systematically subtracted at each temperature from the data after irradiation without any type of correction. The obtained difference was simply added to the dc measurements obtained with the standard SQUID set-up in order to plot the final data after irradiation (blue or red dots). The effective power of the lamp received by the

sample was measured at 200(40) mW/cm² under white light irradiation and about 30(5) mW/cm² under 650 nm light irradiation. Note that the temperatures have been corrected to take into account the light irradiation heating. Systematic calibration of the temperatures has been done taking as reference the data without irradiation. De-excitation of the photo-excited state has been tested without success.

The surface reflectivity set up has been performed under a white-light irradiation (90 mW cm⁻²) using a home-built reflectivity system housed at the Institut de Chimie de la Matière Condensée de Bordeaux. It is composed of a CVI spectrometer and three optical fibres: two for incoming lights for white light irradiation and spectral analysis and one for out coming light for spectral analysis. The reflectivity signal was compared with two standard references: barium sulphate for the white colour (R = 1, Abs. = 0) and activated charcoal for the black colour (R = 0, Abs. = 1). This experimental set-up allows us to collect absorption spectra, within the range of 430-800 nm, between 10 and 280 K (3 K/min), and then, simultaneously, to observe the temperature dependence of the reflectivity signal at two different wavelengths (\pm 2.5 nm) at different temperatures.

The thermogravimetric analysis were carried out using a Perkin Elmer pyris 1 TGA under air flow using platinum crucibles (c.a. 5 mg sample; heating rate of 10 °C min⁻¹; range 25-800 °C).

Single crystal data and experimental details for **1** are summarised in Table S1. The single crystal analysis was performed at 150(2) K with a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-K α radiation (λ = 0.71073 Å). Data were collected, processed, and corrected for Lorentz and polarization effects using SMART¹ and SAINT-NT² software. The structure was solved using direct methods and refined by full matrix least squares against F² using the SHELXTL³ programme package. Selected bond lengths [Å] and angles [°] for **1** are in Table S2.

1. Bruker SMART, Version 5.629, 1997-2003, Bruker-AXS Inc.
2. Bruker SAINT-NT, Version 6.45, 1997-2003, Bruker-AXS Inc.
3. G.M. Sheldrick, SHELXTL, Version 5.1, 1998, Bruker-AXS Inc.

Table S1. Crystal data and structure refinement for **1**.

Identification code	1	
Empirical formula	C70 H66 Cl4 Fe2 N20 O19	
Formula weight	1744.93	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 21.250(4) Å	$\alpha = 90^\circ$.
	b = 10.756(2) Å	$\beta = 90.32(3)^\circ$.
	c = 33.469(7) Å	$\gamma = 90^\circ$.
Volume	7650(3) Å ³	
Z	4	
Density (calculated)	1.515 Mg/m ³	
Absorption coefficient	0.604 mm ⁻¹	
F(000)	3592	
Crystal size	0.25 x 0.25 x 0.15 mm ³	
Theta range for data collection	1.13 to 25.50°.	
Index ranges	-25 ≤ h ≤ 25, -13 ≤ k ≤ 13, -40 ≤ l ≤ 40	
Reflections collected	82388	
Independent reflections	14219 [R(int) = 0.0513]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14219 / 0 / 1052	
Goodness-of-fit on F ²	1.088	
Final R indices [I > 2σ(I)]	R1 = 0.0572, wR2 = 0.1509	
R indices (all data)	R1 = 0.0749, wR2 = 0.1637	
Largest diff. peak and hole	0.726 and -0.488 e.Å ⁻³	

Table S2. Selected bond lengths [\AA] and angles [$^\circ$] for **1**.

Fe(1)-N(7)	1.959(3)
Fe(1)-N(13)	1.967(3)
Fe(1)-N(1)	1.976(3)
Fe(1)-N(9)	2.004(3)
Fe(1)-N(3)	2.028(3)
Fe(1)-N(15)	2.042(3)
Fe(2)-N(11)	1.960(3)
Fe(2)-N(5)	1.965(3)
Fe(2)-N(17)	1.975(3)
Fe(2)-N(16)	2.009(3)
Fe(2)-N(10)	2.026(3)
Fe(2)-N(4)	2.027(3)
O(1)-C(13)	1.387(4)
O(1)-C(10)	1.396(4)
O(2)-C(32)	1.387(4)
O(2)-C(35)	1.396(4)
O(3)-C(57)	1.393(4)
O(3)-C(54)	1.397(4)
N(7)-Fe(1)-N(13)	88.28(12)
N(7)-Fe(1)-N(1)	90.38(12)
N(13)-Fe(1)-N(1)	88.93(11)
N(7)-Fe(1)-N(9)	80.41(11)
N(13)-Fe(1)-N(9)	93.86(11)
N(1)-Fe(1)-N(9)	170.28(11)
N(7)-Fe(1)-N(3)	89.91(11)
N(13)-Fe(1)-N(3)	168.96(11)
N(1)-Fe(1)-N(3)	80.19(11)
N(9)-Fe(1)-N(3)	96.57(11)
N(7)-Fe(1)-N(15)	167.50(12)
N(13)-Fe(1)-N(15)	80.02(11)
N(1)-Fe(1)-N(15)	93.76(11)
N(9)-Fe(1)-N(15)	95.90(11)
N(3)-Fe(1)-N(15)	102.41(11)
N(11)-Fe(2)-N(5)	88.96(12)

N(11)-Fe(2)-N(17)	90.91(13)
N(5)-Fe(2)-N(17)	94.99(13)
N(11)-Fe(2)-N(16)	93.87(12)
N(5)-Fe(2)-N(16)	174.57(12)
N(17)-Fe(2)-N(16)	80.35(12)
N(11)-Fe(2)-N(10)	79.90(12)
N(5)-Fe(2)-N(10)	90.54(12)
N(17)-Fe(2)-N(10)	169.20(12)
N(16)-Fe(2)-N(10)	94.51(11)
N(11)-Fe(2)-N(4)	168.49(12)
N(5)-Fe(2)-N(4)	79.53(11)
N(17)-Fe(2)-N(4)	89.86(12)
N(16)-Fe(2)-N(4)	97.58(11)
N(10)-Fe(2)-N(4)	100.29(11)
C(13)-O(1)-C(10)	117.9(3)
C(32)-O(2)-C(35)	117.2(3)
C(57)-O(3)-C(54)	116.8(2)

¹H NMR data:

¹H NMR spectroscopy was used to attribute the symmetry of compound **1**. As revealed by the spectra (Fig. S1 and S2), compound **1** adopts a C₃ symmetry characteristic of the triple-stranded helicate. The low field values observed are due to the paramagnetic contribution due to the high spin state of the Fe(II) centres in compound **1**.

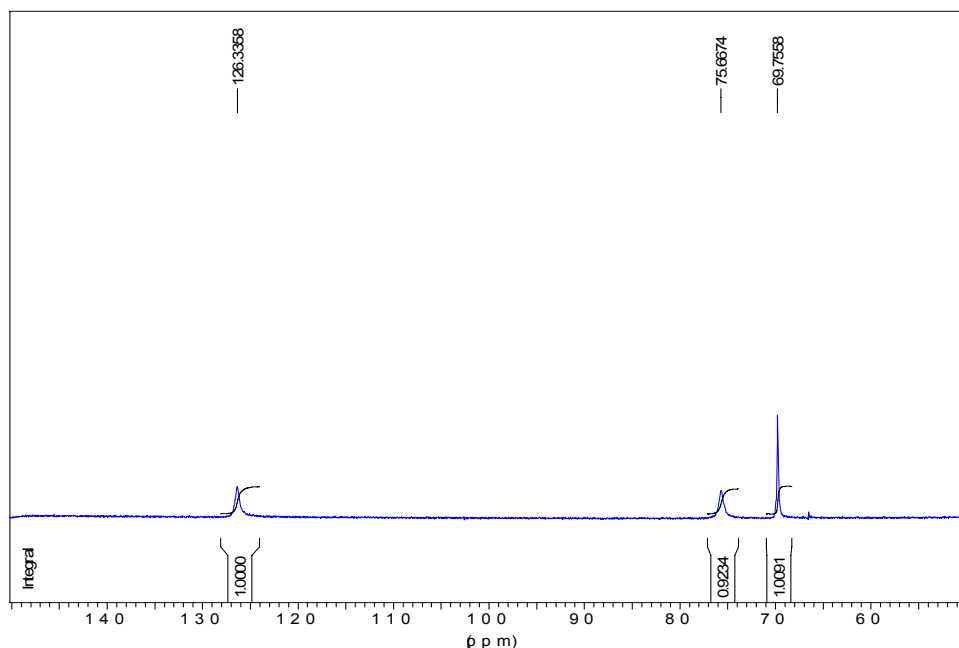


Fig. S1 ¹H NMR spectrum of **1**, window from 150 to 50 ppm (400 MHz, CD₃CN, 298K)

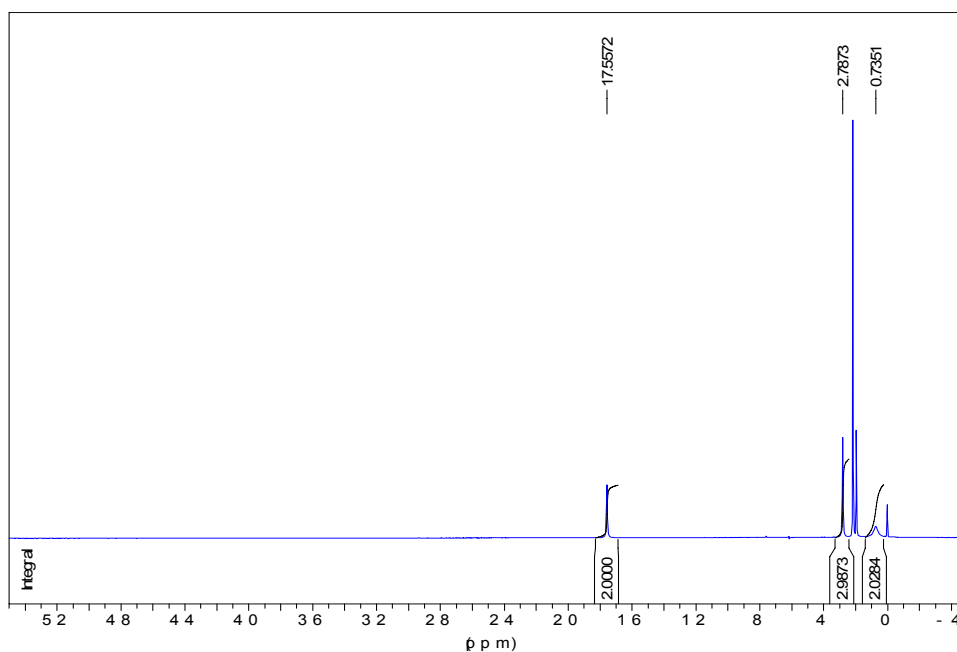


Fig. S2 ¹H NMR spectrum of **1**, window from 55 to -5 ppm (400 MHz, CD₃CN, 298K)

The integrity of the dried polycrystalline compound **1** used for magnetic susceptibility measurements was checked by ^1H NMR (**Fig. S3-5**). No significant changes are visible compared to the ^1H NMR spectra recorded before the drying process, confirming that the integrity of compound **1** was preserved through the drying process.

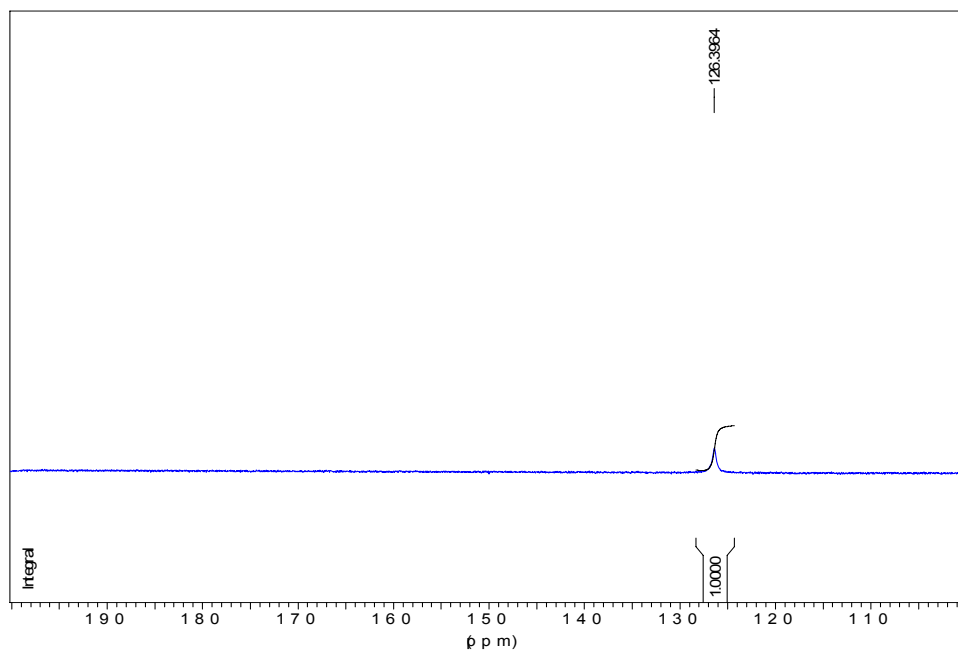


Fig. S3 ^1H NMR spectrum of **1** dried at 60°C, window from 200 to 100 ppm (400 MHz, CD_3CN , 298K)

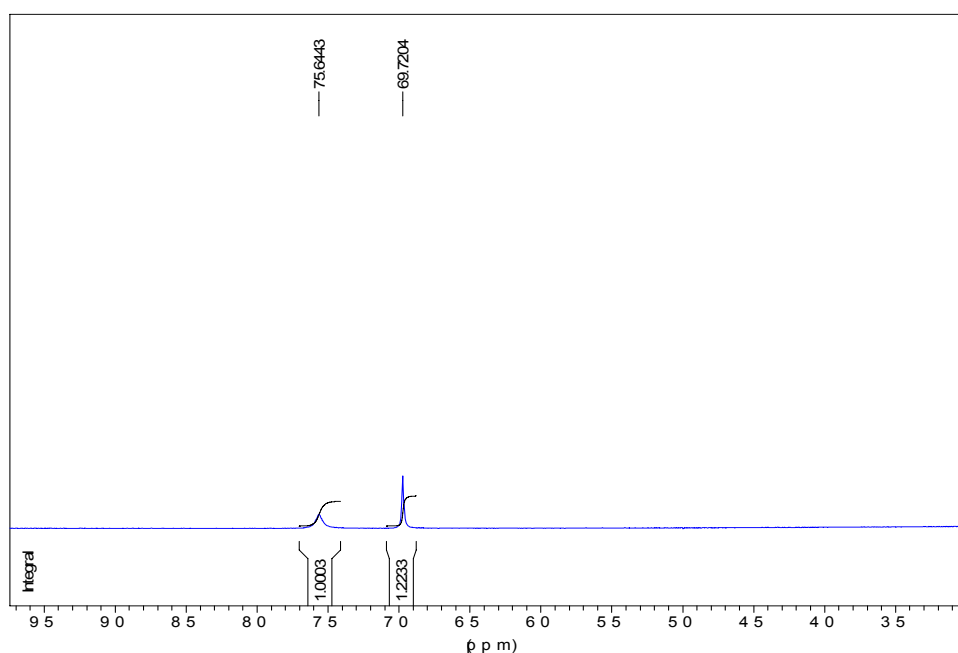


Fig. S4 ^1H NMR spectrum of **1** dried at 60°C, window from 95 to 30 ppm (400 MHz, CD_3CN , 298K)

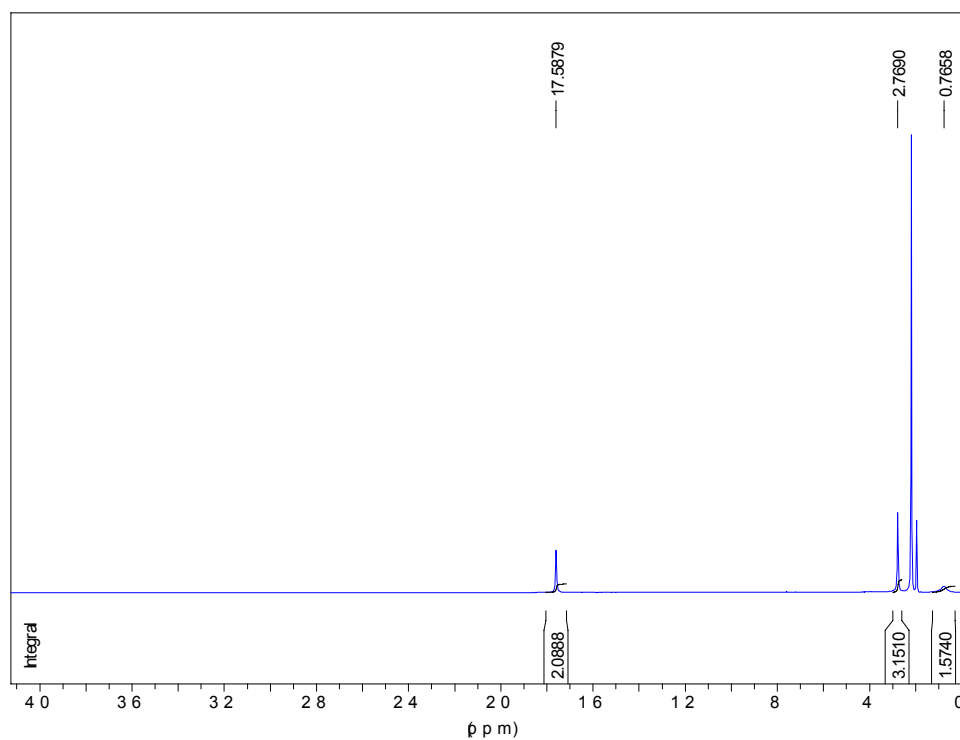


Fig. S5 ^1H NMR spectrum of **1** dried at 60°C , window from 40 to 0 ppm (400 MHz, CD_3CN , 298K)

Thermogravimetric Analysis: The TGA carried out for compound **1**·2H₂O dried at room temperature (**Fig. S6**) confirms the presence of two molecules of water with a *ca.* 2.25% weight loss (calc. 2.12%). The compound **1** dried at 60 °C (**Fig. S7**) is fully dehydrated. It is worth noting that the discontinuity observed *ca.* 260 °C in both TGA curves is due to the fact that at this temperature both compounds are subject to an explosive decomposition typical for perchlorate salts.

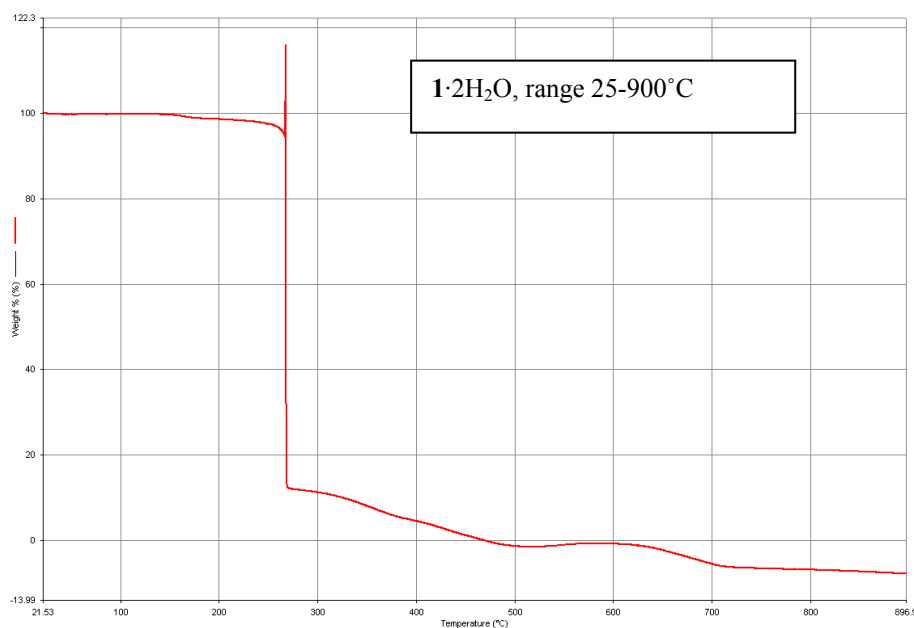


Fig. S6: TGA for **1**·2H₂O dried at room temperature

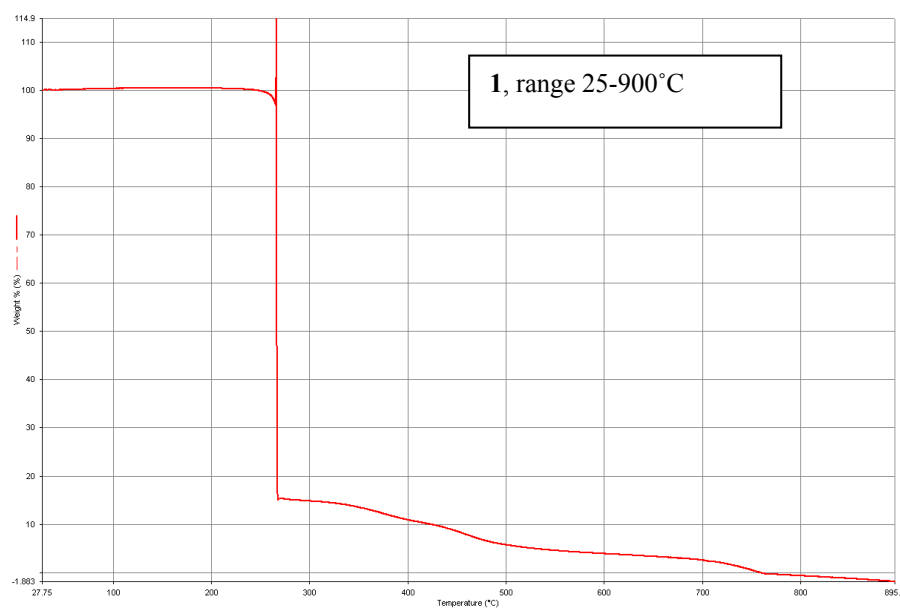


Fig. S7: TGA for compound **1** dried at 60 °C

Optical density spectrum: The solid-state spectrum of complex **1** was collected by a diffuse reflectance sphere at room temperature (Fig S8) with a Cary 5E spectrometer. Above 400 nm, the spectrum is formed by two main broad components: one in the near IR region (maximum around 820 nm) and one in the visible region with a maximum position at 510 nm. An additional absorption is clearly present in the UV region below 400 nm. By comparison with other Fe(II) complexes in similar environment (N-donor ligands), the NIR absorption band is assigned to the d-d transition of the Fe(II) ion in a high-spin state $^5T_2 \rightarrow ^5E$, and the visible region may be assigned to a MLCT.

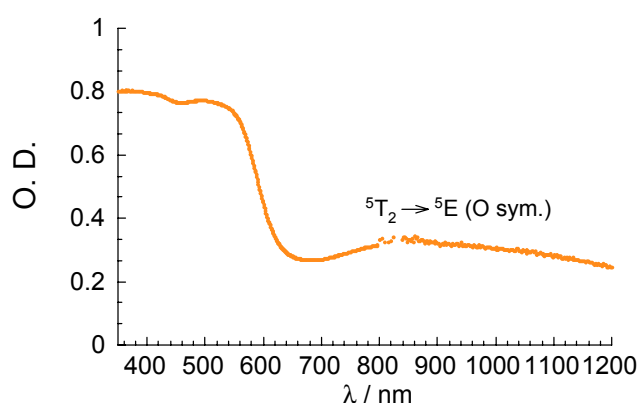


Fig. S8: Absorption spectra for **1** at room temperature obtained with a diffuse reflectance sphere plotted as O.D. vs wavelength. O.D. is Optical Density, and is calculated as $O.D. = -\log I/I_0$ where I is the intensity of the reflected beam and I_0 is the intensity of the incident beam.

We provide below (**Fig. S9**) the full data set of spectra collected, for compound **1**, under white light irradiation between 280 and 10 K in cooling mode during the solid-state reflectivity study.

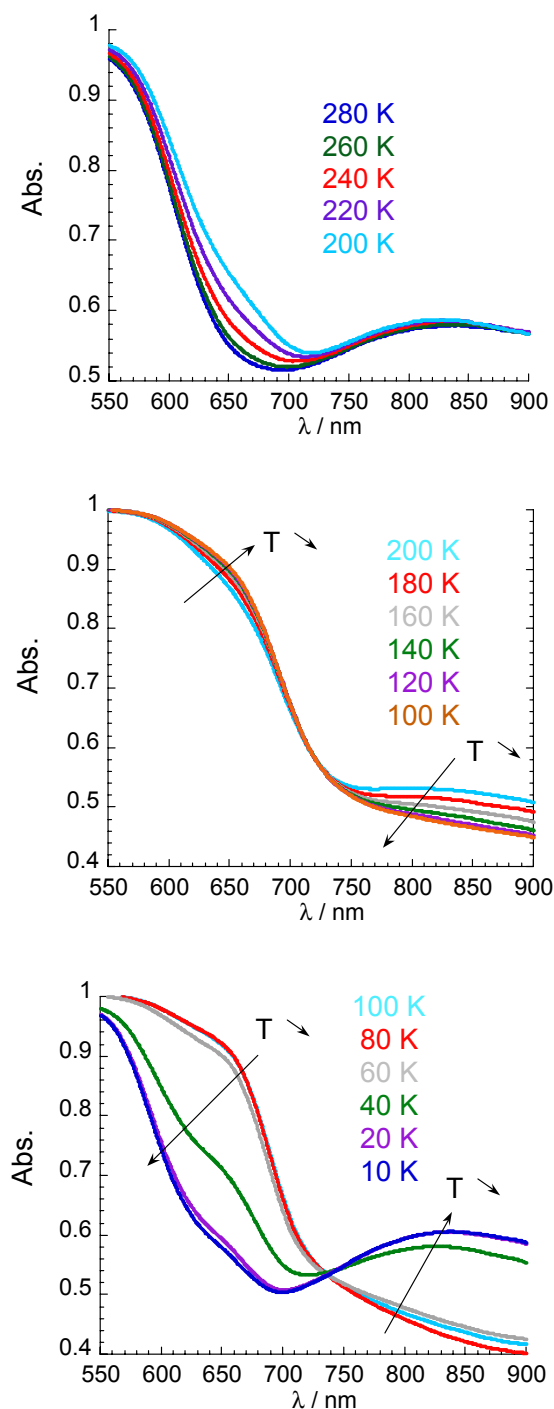


Fig. S9 Surface reflectivity spectra for **1** at variable temperature under white light irradiation. Top: 280-200 K range. Middle: 200-100 K range. Bottom: 100-10 K range. The absorption (note Abs. calculated as $\text{Abs.} = 1 - R$, R being the measured reflectivity) is plotted versus the wavelength.