

Supporting Information for

## Cooperative spin transition in a lipid layer like system

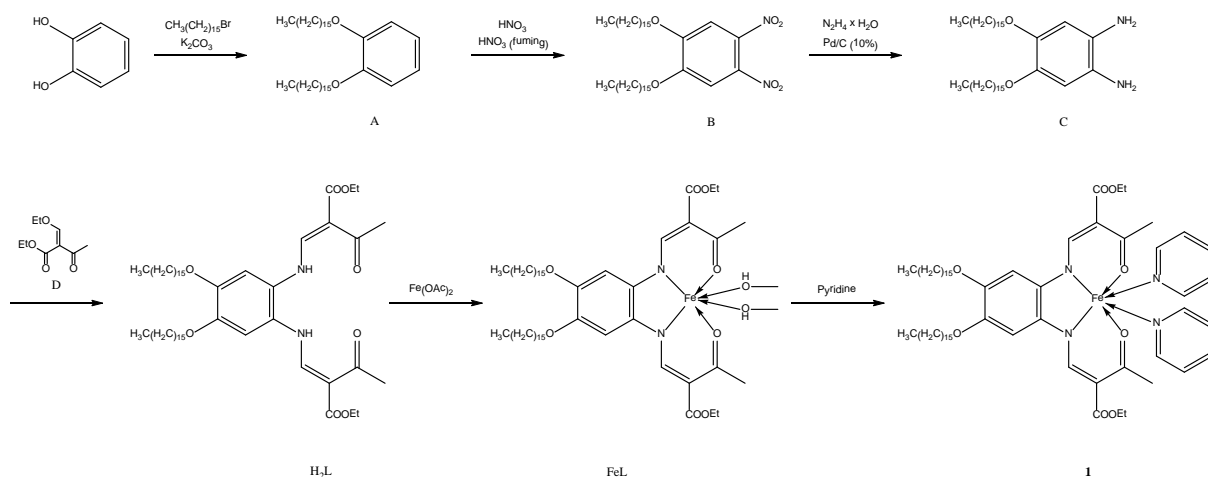
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### Synthesis of H<sub>2</sub>L and the iron complex [FeL(py)<sub>2</sub>] (**1**)

The free ligand H<sub>2</sub>L was synthesised according to [1] and [2] with slight modifications. In a first step, catechol and 2 equivalents of 1-bromohexadecane were converted with K<sub>2</sub>CO<sub>3</sub> in DMF to give, after filtration and washing with plenty of water and methanol, 1,2-dihexadecyloxybenzene (**A**) in good yields. This white precipitate was nitrated according to [3] and [4]. It was suspended in acetic acid and a mixture of HNO<sub>3</sub> and fuming HNO<sub>3</sub> were added dropwise. The dinitro product (**B**) appears bright yellow coloured. Reducing of the functional groups with Palladium on activated charcoal and hydrazine-mono-hydrate similar to [4] gives the white diamino product (**C**) which is air sensitive. Further reaction with Ethoxymethyleneethylacetoacetate (**D**) [5] in an approximate ratio of 1:2 gives the yellow ligand H<sub>2</sub>L which is not any more air sensitive and reaction with iron(II) acetate [6] in methanol the corresponding brown microcrystalline iron(II) complex [FeL(MeOH)<sub>2</sub>]. To obtain the pyridine complex **1**, [FeL(MeOH)<sub>2</sub>] was converted in pyridine under reflux conditions and a crystallisation approach was made with water diffusing into the black solution. Several reproductions with different concentrations of possible product in the solution turned out that it takes at least 40-50 days of formation until greenish-black thin platelet-like crystals can be isolated.



## Experimental Section

**1,2-dihexadecyloxybenzene (A).** In a two neck round-bottom flask (1 L) fitted with a condenser and a dropping funnel 8 g (72.65 mmol, 1 eq.) catechol and 20.08 g (145.3 mmol, 2 eq.)  $K_2CO_3$  were stirred at room temperature in 500 mL DMF for 45 min under nitrogen atmosphere. 44.4 g (145.4 mmol, 2 eq.) 1-Bromododecane were added dropwise to the turquoise suspension and the mixture was heated to 90 °C for 8 h. After cooling overnight the white solid was filtered off, washed with water and methanol and dried under reduced pressure. Yield: 22.15 g (87%).  $C_{38}H_{70}O_2$  (558.96); MS (DEI+) [ $m/z$  (%)] 559 (100)  $[M]^+$ , 334 (7), 110 (33); Anal. calcd. C 81.65, H 12.62; found C 81.50, H 11.47.  $\delta$   $^1H$ -NMR ( $CDCl_3$ , 399.81 MHz, 296 K): 0.87 (6H, t, 7.0 Hz,  $CH_3$ ), 1.07-1.39 (48H, m,  $CH_2$ ), 1.39-1.51 (4H, m,  $CH_2$ ), 1.74-1.85 (4H, m,  $CH_2$ ), 3.97 (4H, t, 6.7 Hz,  $CH_2$ -O), 6.87 ppm (4H, s,  $H_{Arom.}$ ).  $\delta$   $^{13}C$  ( $CDCl_3$ , 399.81 MHz, 296 K): 14.1 ( $CH_3$ ), 22.7 ( $CH_2$ ), 26.1 ( $CH_2$ ), 29.3 ( $CH_2$ ), 29.4 (2  $CH_2$ ), 29.6 ( $CH_2$ ), 29.7 (7  $CH_2$ ), 31.9 ( $CH_2$ ), 69.2 ( $CH_2$ ,  $CH_2$ -O), 114.1 ( $CH$ ,  $C_{Arom.}$ ), 121.0 ( $CH$ ,  $C_{Arom.}$ ), 149.2 ppm ( $C_q$ ,  $C_{Arom.}$ -O).

**4,5-dihexadecyloxy-1,2-dinitrobenzene (B).** 22 g (39.36 mmol) **A** were suspended in 150 mL acetic acid for 1 h. Under stirring, a mixture of 20 mL nitric acid and 150 mL fuming nitric acid were added dropwise over 1.5 h. The yellow suspension was stirred at room temperature for 20 h and poured into 1.5 L ice-water. The yellow precipitate was filtered off and washed with water until neutrality. It was recrystallised from 500 mL Ethanol, washed with methanol and dried overnight. Yield: 23.90 g (94 %).  $C_{38}H_{68}N_2O_6$  (648.96); MS (DEI+)

[*m/z* (%) ] 649 (100) [*M*]<sup>+</sup>, 584 (97), 377 (24), 359 (26); Anal. calcd. C 70.33, H 10.56, N 4.32; found C 70.40, H 10.33, N 4.26.  $\delta$  <sup>1</sup>H (CDCl<sub>3</sub>, 399.81 MHz, 296 K): 0.86 (6H, t, 7.0 Hz, CH<sub>3</sub>), 1.15-1.38 (48H, m, CH<sub>2</sub>), 1.40-1.50 (4H, m, CH<sub>2</sub>), 1.79-1.90 (4H, m, CH<sub>2</sub>), 4.08 (4H, t, 6.5 Hz, CH<sub>2</sub>-O), 7.27 ppm (2H, s, H<sub>Arom.</sub>).  $\delta$  <sup>13</sup>C (CDCl<sub>3</sub>, 399.81 MHz, 296 K): 14.1 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.7 (6 CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 70.2 (CH<sub>2</sub>, CH<sub>2</sub>-O), 107.8 (CH, C<sub>Arom.</sub>), 136.4 (C<sub>q</sub>, C<sub>Arom.</sub>-NO<sub>2</sub>), 151.8 ppm (C<sub>q</sub>, C<sub>Arom.</sub>O).

**1,2-diamino-4,5-dihexadecyloxybenzene (C)**. Under nitrogen atmosphere, 23.65 g (36.44 mmol) **B** and 2.46 g palladium on activated charcoal (10 % Pd) were suspended in 800 mL ethanol and 67.50 g (1.35 mol, 37 eq.) hydrazine-monohydrate were added dropwise under stirring. The mixture was heated to reflux for 6 h till the yellow suspension turned into white. It was filtered off hot through Celite<sup>®</sup> 545 coarse. After cooling, the white precipitate was filtered off, washed twice with 20 mL ethanol and dried under reduced pressure. Yield: 10.70 g (50 %). C<sub>38</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub> (588.99); MS (DEI+) [*m/z* (%) ] 588 (100) [*M*-H]<sup>+</sup>, 139 (37); Anal. calcd. C 77.49, H 12.32, N 4.76; found C 77.30, H 11.32, N 4.78.

**Ethoxymethyleneethylacetoacetate (D)** was synthesised according to literature [5].

**(E,E)-[diethyl-2,2'-[4,5-dihexadecyloxy-1,2-phenylenebis(iminomethylidene)]bis-3-oxobutanato] H<sub>2</sub>L**. Under nitrogen atmosphere, 2 g (3.40 mmol) **C** was dissolved in 200 mL ethanol. A slight excess of **D** (1.40 g, 7.47 mmol, 2.2 eq.) was added and the yellow solution was heated to reflux for 70 min. After cooling to room temperature, the yellow precipitate was filtered off, washed with ethanol and methanol and dried in presence of air. Yield: 2.5 g (85 %). C<sub>52</sub>H<sub>88</sub>N<sub>2</sub>O<sub>8</sub> (869.26); MS (EI) 869 (23) [*M*]<sup>+</sup>, 823 (100), 777 (33), 614 (45); Anal. calcd. C 71.85, H 10.20, N 3.22; found C 71.44, H 10.06, N 3.28.  $\delta$  <sup>1</sup>H (CDCl<sub>3</sub>, 399.81 MHz, 296 K): 0.85 (6H, t, 7.1 Hz, CH<sub>3</sub>), 1.14-1.38 (48H, m, CH<sub>2</sub>), 1.30 (6H, t, 6.5 Hz, CH<sub>3</sub>(Et)), 1.39-1.50 (4H, m, CH<sub>2</sub>), 1.75-1.85 (4H, m, CH<sub>2</sub>), 2.52 (6H, s, CH<sub>3</sub>), 3.98 (4H, t, 6.5 Hz, CH<sub>2</sub>-O), 4.22 (4H, q, 7.1 Hz, CH<sub>2</sub>(Et)), 6.72 (2H, s, H<sub>Arom.</sub>), 8.24 (2H, d, 12.5 Hz, CH=), 12.84 ppm (2H, d, 12.5 Hz, NH).  $\delta$  <sup>13</sup>C (CDCl<sub>3</sub>, 399.81 MHz, 296 K): 14.1 (CH<sub>3</sub>), 14.5 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.6 (3 CH<sub>2</sub>), 29.7 (7 CH<sub>2</sub>), 31.2 (CH<sub>3</sub>), 31.9 (CH<sub>2</sub>), 60.0 (CH<sub>2</sub>, CH<sub>2</sub>(Et)), 70.0 (CH<sub>2</sub>, CH<sub>2</sub>-O), 103.7 (C<sub>q</sub>), 106.5 (CH, C<sub>Arom.</sub>),

124.9 (C<sub>q</sub>, C<sub>Arom.-N</sub>), 148.5 (C<sub>q</sub>, C<sub>Arom.-O</sub>), 154.1 (CH), 166.9 (C<sub>q</sub>, O-C=O), 201.0 ppm (C<sub>q</sub>, C=O).

**(E,E)-[diethyl-2,2'-[4,5-dihexadecyloxy-1,2-phenylenebis(iminomethylidyne)]bis-3-oxobutanato]}(2-)iron(II) × 2 MeOH [FeL1(MeOH)<sub>2</sub>] (6).** Under nitrogen atmosphere, 2 g (2.30 mmol) **5** and 0.85 g (4.89 mmol, 2.13 eq.) Fe(OAc)<sub>2</sub> (synthesis see lit. [6]) were dissolved in 95 mL methanol and heated to reflux for 2 h 15 min. Already while boiling, a brown solid precipitated from the black solution that was filtered off after cooling to room temperature. It was washed twice with 15 mL methanol and dried under reduced pressure so one obtained a brown, microcrystalline powder. Yield: 2.05 g (90 %). C<sub>54</sub>H<sub>94</sub>FeN<sub>2</sub>O<sub>10</sub> (987.18); Anal. calcd. C 65.70, H 9.60, N 2.84; found C 65.96, H 9.44, N 2.90.

**[FeL1(Py)<sub>2</sub>] (1).** 0.20 g (0.20 mmol) **6** was dissolved in 20 mL pyridine and the black solution was heated to reflux for 5 h. The solution was allowed to cool slowly to room temperature, and a crystallisation approach was made with water diffusing into the solution. After 50 days, the product was formed as greenish-black thin crystals. The overlaying solution was decanted and the remaining H<sub>2</sub>O/pyridine was removed in vacuo. Yield: 0.18 g (83 %). C<sub>62</sub>H<sub>96</sub>FeN<sub>4</sub>O<sub>8</sub> (1081.29); Anal. calcd. C 68.87, H 8.95, N 5.18; found C 68.49, H 8.67, N 4.78.

**Magnetic susceptibility** data of 1·0.25 H<sub>2</sub>O were collected using a Quantum Design MPMSR2 SQUID magnetometer under an applied field of 0.5 T over the temperature range 50–400 K in the settle mode. All samples were placed in gelatine capsules held within plastic straws. The data were corrected for the diamagnetic magnetization of the ligands, which were estimated using tabulated Pascal's constants and of the sample holder. **Differential scanning calorimetry** data were recorded on a Perkin–Elmer DSC Pyris 1 instrument equipped with a cryostat operating down to 98 K following a described procedure.<sup>[7]</sup>

The intensity data of 1·0.25 H<sub>2</sub>O were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated MoK<sub>α</sub> radiation. The data were corrected for Lorentz and polarisation effects. The structure was solved by Direct Methods (SIR 97)<sup>[8]</sup> and refined by full-matrix least-square techniques against F<sub>o</sub><sup>2</sup> (SHELXL-97)<sup>[9]</sup>. The hydrogen atoms were included at calculated positions with fixed displacement parameters. All non-hydrogen atoms

were refined anisotropically. ORTEP-III<sup>[10]</sup> was used for the structure representation, SCHAKAL-99<sup>[11]</sup> and MERCURY for the representation of the molecule packing. Cell parameters and refinement results are summarised in Table S1. CCDC 821515 (1·0.25 H<sub>2</sub>O, HS) and CCDC 821516 (1·0.25 H<sub>2</sub>O, LS) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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**Table S1.** Parameters for crystal structure determination.

	[FeL1(Py) <sub>2</sub> ] <sup>h</sup>	[FeL1(Py) <sub>2</sub> ] <sup>l</sup>
sum formula	C <sub>62</sub> H <sub>94</sub> FeN <sub>4</sub> O <sub>8</sub>	C <sub>62</sub> H <sub>96</sub> FeN <sub>4</sub> O <sub>8</sub>
formula weight	1081.28	1081.28
crystal System	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> [Å]	9.9758(2), 10.0579(2), 31.5743(7)	9.0910(3), 9.9180(3), 34.3520(11)
$\alpha$ , $\beta$ , $\gamma$ [°]	90.3395(11), 97.4097(11), 97.2664(12)	90.0897(19), 93.550(2), 101.8404(15)
<i>V</i> [Å <sup>3</sup> ]	3115.54(11)	3025.29(17)
<i>Z</i>	2	2
$\rho_{\text{calcd.}}$ [g cm <sup>-3</sup> ]	1.153	1.187
$\mu$ [mm <sup>-1</sup> ]	0.295	0.304
F(000)	1172	1172
crystal size [mm]	0.23×0.09×0.03	0.23×0.09×0.03
temperature [K]	250	125
radiation [Å]	Mo-K $\alpha$ , 0.71073	Mo-K $\alpha$ , 0.71073
$\theta$ -min, $\theta$ -max [°]	3.2, 27.5	3.2, 27.4
<i>hkl</i>	-12: 12; -13: 12; -40: 40	-11: 11; -12: 12; -44: 44
measured reflections	24716	40712
independent reflections	14173	13662
<i>R</i> <sub>int</sub>	0.089	0.064
reflections with <i>I</i> ≥ 2σ( <i>I</i> )	5818	8937
reflections	14173	13662
parameters	727	682
<i>R</i>	0.0703	0.0594
<i>wR</i> <sup>2</sup>	0.2016	0.1485
<i>S</i>	0.99	1.03
<i>shift/error</i> <sub>max</sub>	0.00	0.00
$\Delta\rho_{\text{max}}$	0.84	0.96
$\Delta\rho_{\text{min}}$	-0.36	-0.38

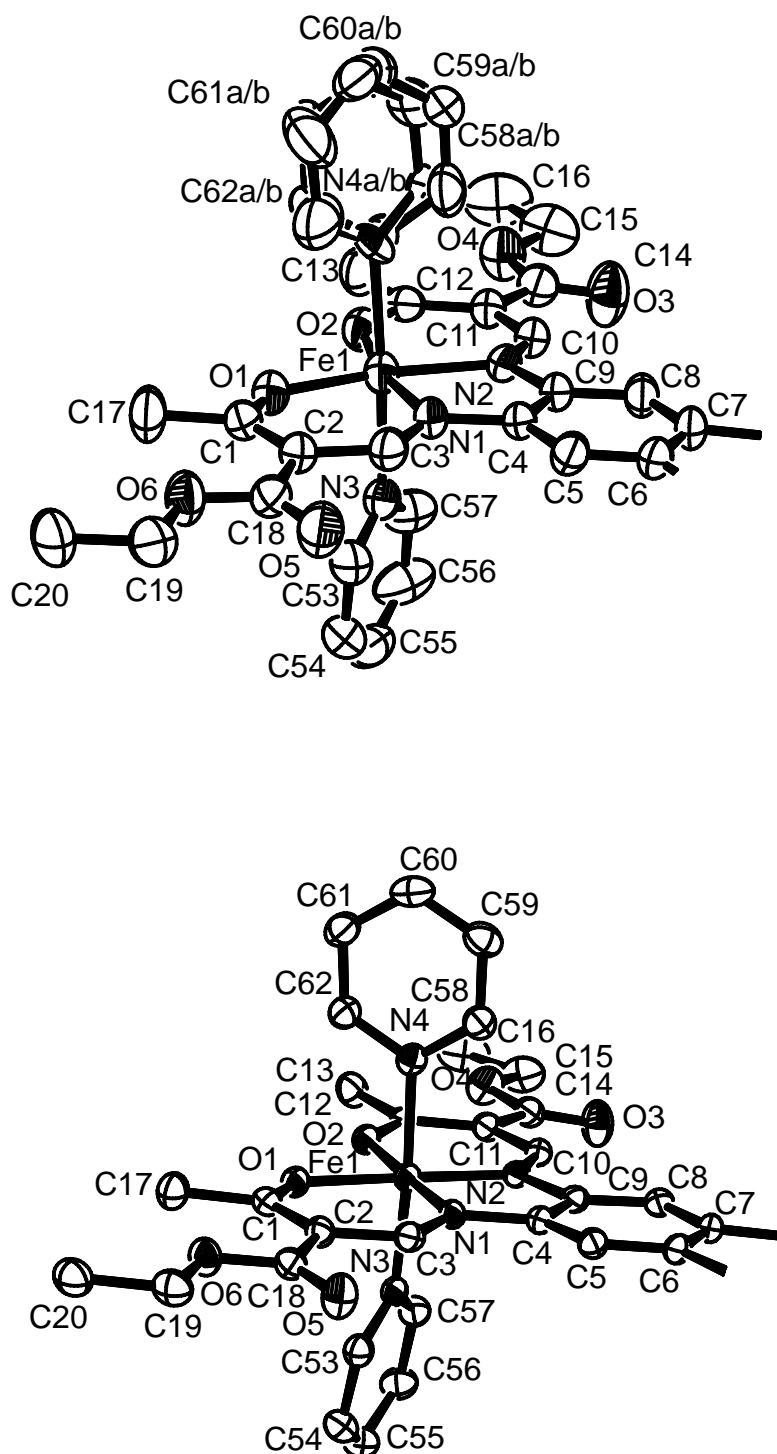
**Table S2.** Geometric parameters and symmetry codes of short contacts and non-classic hydrogen bonds in **1**·0.25H<sub>2</sub>O in the LS and HS state (Å, °).

	D—H···A	D—H	H···A	D···A	D—H···A	
<b>LS</b>	C62—H62···O99	0.95	2.31	3.19	153.6	-1+x,1+y,z
	C16—H16C···O99	0.98	2.33	3.12	137.4	1-x,-y,1-z
	C13—H13A···O99	0.98	2.36	2.24	148.8	
	O2···O99			2.80		
	O3···O99			2.87		
	C61—H61···O3	0.95	2.44	3.15	130.9	1+x,y,z
<b>HS</b>	C62A—H62A···O99	0.94	2.52	2.28	99.3	-1+x,1+y,z
	C15—H15A···O99	0.98	2.19	3.13	158.8	x,1+y,z
	O2···O99			2.97		
	O3···O99			3.31		
	C61A—H61A···O3	0.94	2.57	3.12	118.2	1+x,y,z
	C62A—H62A···O3	0.94	2.42	3.05	124.5	1+x,y,z
	H61B···H36F		1.67			

**Table S3.** Thermodynamic parameters of **1** derived from DSC.

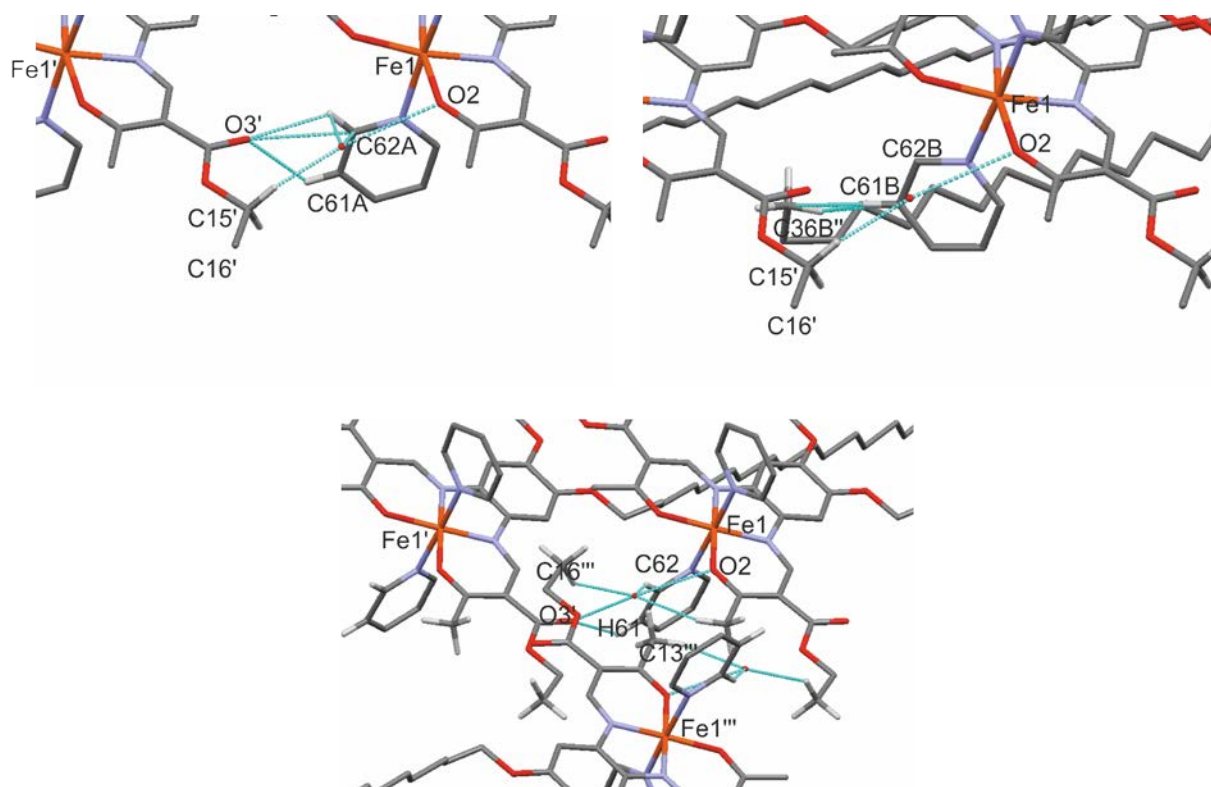
Mode	Peak	$T_{\max}$ (K)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)
Cooling	2	226(1)	6(1)	27.6(1)
300K to 98 K	1	207(1)	4(1)	23.3(1)
Warming	1	235(1)	4(1)	17.1(1)
98 K to 300 K	2	250(1)	9(1)	36.6(1)

**Fig. S1** Excerpt of the coordination environment of the ORTEP drawing of the asymmetric unit of **1** in the HS (top) and LS (bottom) states. Hydrogen atoms and the water molecule have been omitted for clarity. Displacement ellipsoids are shown at the 50 % probability level.





**Fig. S2** Excerpt of the packing of the molecules of  $1 \cdot 0.25\text{H}_2\text{O}$  in the crystal projected along  $c$ -axis for a better illustration of the changes in the H-bond network upon spin transition. Top: HS state with the disorder resolved in two separate pictures, bottom: LS state. Short intermolecular contacts are illustrated as dashed lines. Hydrogen atoms and molecules not involved in the H-bond network were omitted for clarity.



**Fig. S3** Packing of the molecules of  $1 \cdot 0.25\text{H}_2\text{O}$  in the crystal projected along  $[0\ 1\ 0]$ . Top: HS state, bottom: LS state, short intermolecular contacts are illustrated as dashed lines.

