Supporting Information

An azido-bridged [Fe^{II}_4] grid-like molecule showing spin crossover behaviour

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Crystallography. X-ray data for **1** and **2** were collected on a Bruker D8 VENTURE diffractometer with graphite monochromated Mo Kα (l = 0.71073 Å) and Cu Kα (l = 1.54178 Å) radiation, respectively. Lorentz/polarization corrections were applied during data reduction and the structures were solved with the SHELXT solution program using Intrinsic Phasing.[1] Refinements were performed by full-matrix least squares minimization (SHELXL) on F^2.[2] Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen atoms were added at calculated positions and refined using a riding model. Weighted R factors (wR) and the goodness-of-fit (S) values are based on F^2; conventional R factors (R) are based on F, with F set to zero for negative F^2. Since the solvent molecules in **1** could not be completely modelled due to the disorder, a part of Q peaks were subtracted by the SQUEEZE program implemented in Olex2. As a result, 272.6 electrons were found in a total solvent accessible volume of 1035.3 $Å^3$ for **1** per unit cell. Combined with the definition in the residual density map, we attribute this to the presence of four $CHCl_3$ and two CH_3OH per unit cell which account for 268 electrons that is consistent with the SQUEEZE calculations.

References

[1] Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8.

[2] Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

Table S1. Selected Crystallographic data of **1** and **2**.

Compound	**1**	**2**			
Empirical formula	$C_{168}H_{173}B_4Cl_{15}Fe_4N_{40}O_3$	$C_{156}H_{126}B_4Fe_4N_{30}$			
Formula weight	3598.85	2687.50			
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)			
Crystal size/mm^3	0.30 × 0.25 × 0.15	0.25 × 0.25 × 0.20			
Crystal system	Triclinic	Tetragonal			
Space group	P-1	$I4_1/a$			
Temp.	100 K	100 K	150 K	200 K	300 K
CCDC deposit	2015661	2015655	2078512	2015657	2015660
a/Å	18.0455(8)	17.2401(3)	17.2652(8)	17.3036(3)	17.4466(3)
b/Å	19.1164(8)	17.2401(3)	17.2652(8)	17.3036(3)	17.4466(3)
c/Å	28.9018(12)	42.898(1)	43.062(3)	43.1803(10)	43.6969(13)
α/°	89.217(2)	90	90	90	90
β/°	72.662(2)	90	90	90	90
γ/°	62.820(2)	90	90	90	90
Volume/Å^3	8377.7(6)	12750.2(5)	12836.1(15)	12928.8(5)	13300.6(6)
Z	2	4	4	4	4
ρ_{calc}g/cm^3	1.212	1.400	1.391	1.381	1.342
μ/mm^{-1}	0.449	4.124	4.097	4.067	3.954
F(000)	3192.0	5584.0	5584.0	5584.0	5584.0
2θ range /°	2.628 to 55.018	8.03 to 136.6	5.51 to 130.3	10.2 to 136.8	7.91 to 130.3
Reflections collected/unique	200308/37755	37412/5831	26305/5831	26305/5831	26215/5667
R_{int}	0.0545	0.0565	0.0794	0.0490	0.0622
R_{sigma}	0.0473	0.0307	0.0739	0.0325	0.0590
Goodness-of-fit on F^2	1.030	1.068	0.996	1.057	1.024
Final R indexes [I>2σ(I)]	R_1 = 0.0493, wR_2 = 0.1181	R_1 = 0.0369, wR_2 = 0.0965	R_1 = 0.0660, wR_2 = 0.1707	R_1 = 0.0335, wR_2 = 0.0904	R_1 = 0.0479, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0759, wR_2 = 0.1322	R_1 = 0.0459, wR_2 = 0.1011	R_1 = 0.1027, wR_2 = 0.1994	R_1 = 0.0466, wR_2 = 0.0958	R_1 = 0.0748, wR_2 = 0.1408
Largest diff. peak/hole / e Å^{-3}	0.59/-0.98	0.70/-0.23	0.54/-0.31	0.34/-0.27	0.28/-0.14

Table S2. Selected bond distance [Å] and angles [deg] of **1** at 100 K.

Fe1-N1	2.159(2)	Fe4-N16	2.183(2)	N4-Fe2-N9	175.68(7)
Fe1-N3	2.209(1)	Fe4-N18	2.179(2)	N4-Fe2-N7	109.20(7)
Fe1-N19	2.154(1)	Fe4-N22	2.196(1)	N4-Fe2-N34	93.30(7)
Fe1-N21	2.220(1)	Fe4-N24	2.160(2)	N4-Fe2-N25	84.63(7)
Fe1-N25	2.084(1)	Fe4-N28	2.103(1)	N4-Fe2-N6	72.48(7)
Fe1-N28	2.123(1)	Fe4-N31	2.121(2)	N15-Fe3-N10	172.34(7)
Fe2-N4	2.223(2)	N3-Fe1-N21	175.14(7)	N15-Fe3-N12	108.78(7)
Fe2-N6	2.151(2)	N3-Fe1-N19	111.02(7)	N15-Fe3-N34	93.04(7)
Fe2-N7	2.159(2)	N3-Fe1-N28	91.64(7)	N15-Fe3-N31	85.95(7)
Fe2-N9	2.222(1)	N3-Fe1-N25	86.10(7)	N15-Fe3-N13	72.48(7)
Fe2-N25	2.125(1)	N3-Fe1-N1	72.37(7)	Fe1-N25-Fe2	120.86(9)
Fe2-N34	2.079(2)	N16-Fe4-N22	173.87(7)	Fe1-N28-Fe4	118.79(9)
Fe3-N10	2.212(1)	N16-Fe4-N24	113.55(7)	Fe3-N34-Fe2	120.40(9)
Fe3-N12	2.157(2)	N16-Fe4-N31	86.97(7)	Fe3-N31-Fe4	118.89(9)
Fe3-N13	2.179(2)	N16-Fe4-N28	87.41(7)		
Fe3-N15	2.221(2)	N16-Fe4-N18	72.64(7)		
Fe3-N31	2.120(1)				
Fe3-N34	2.079(2)				

Table S3. Selected bond distance [Å] and angles [deg] of **2** at different temperatures.

	100 K	**150 K**	**200 K**	**300 K**
Fe1-N1	1.976(0)	1.999(4)	1.985(8)	2.150(3)
Fe1-N2	1.920(9)	1.940(4)	1.938(7)	2.141(2)
Fe1-N3C	1.930(6)	1.938(4)	1.945(8)	2.140(3)
Fe1-N4C	1.989(8)	1.986(4)	2.003(4)	2.179(3)
Fe1-N5	2.005(7)	2.002(3)	2.003(4)	2.069(3)
Fe1-N5C	2.011(8)	2.008(3)	2.017(4)	2.080(3)
N1-Fe1-N2	80.96(6)	80.60(15)	80.60(6)	74.84(10)
N1-Fe1-N3C	99.47(6)	98.04(15)	99.63(6)	103.44(9)
N1-Fe1-N4C	83.66(6)	83.35(14)	83.36(6)	81.89(10)
N1-Fe1-N5	166.43(6)	165.09(15)	165.88(7)	158.05(10)
N1-Fe1-N5C	93.42(6)	94.47(15)	93.49(6)	94.13(10)
N5-Fe1-N5C	91.80(9)	91.9(2)	92.24(9)	98.66(14)

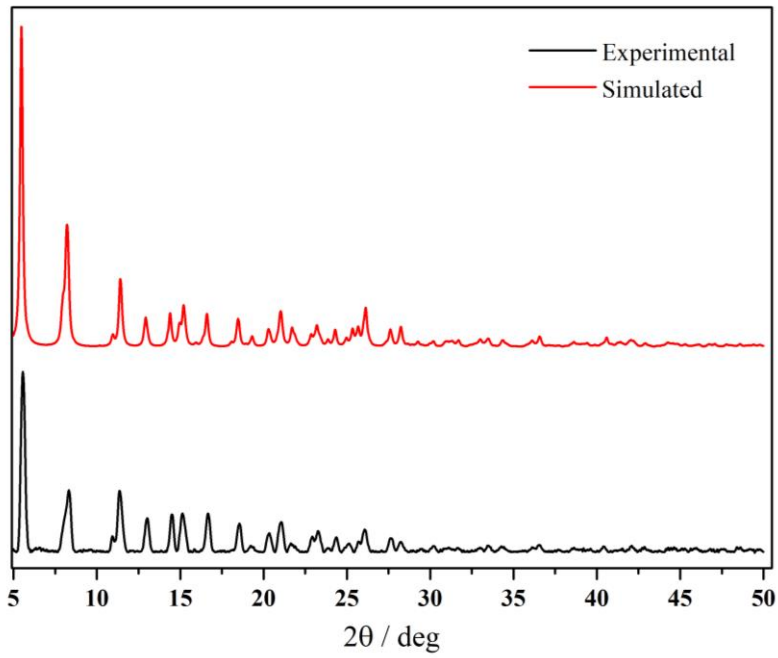

Fig. S1. The experimental and simulated PXRD patterns of **2** at 300 K.

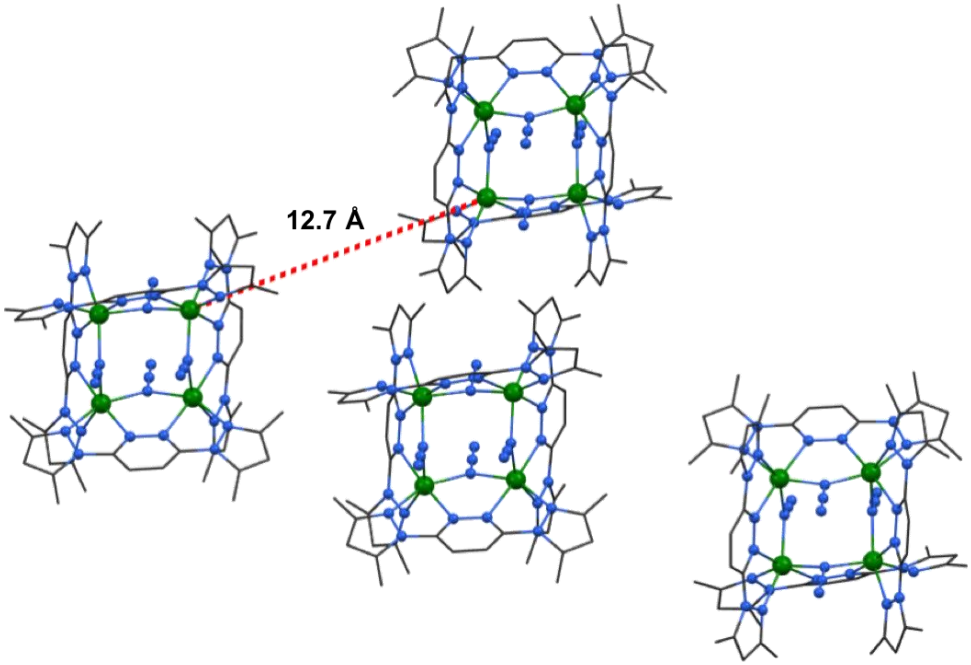

Fig. S2. The packing diagram of **1**. Hydrogen atoms, counter ions and lattice solvents are omitted for clarity.

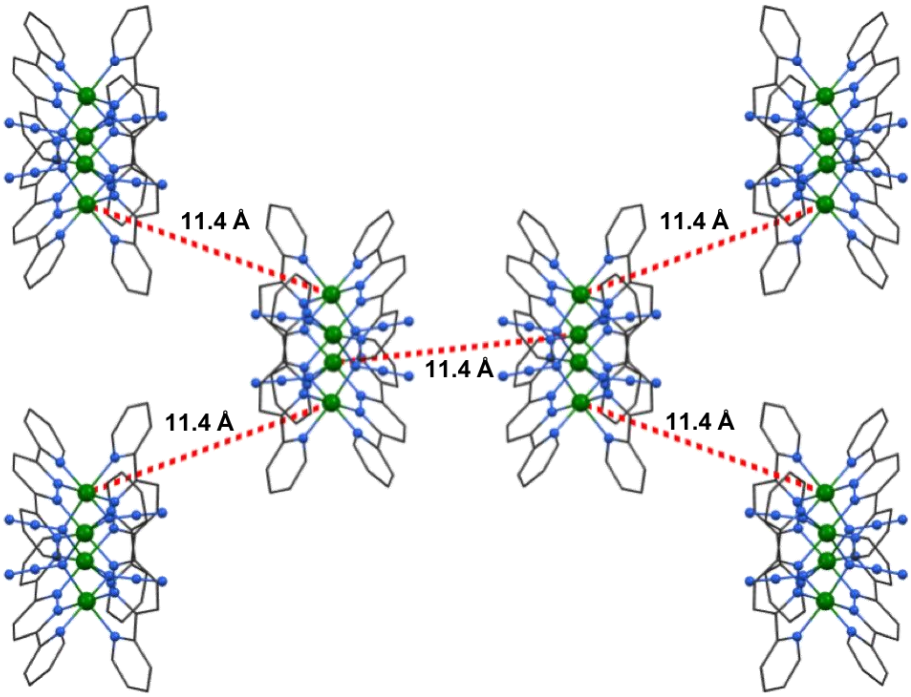

Fig. S3. The packing diagram of **2**. Hydrogen atoms, counter ions and lattice solvents are omitted for clarity.

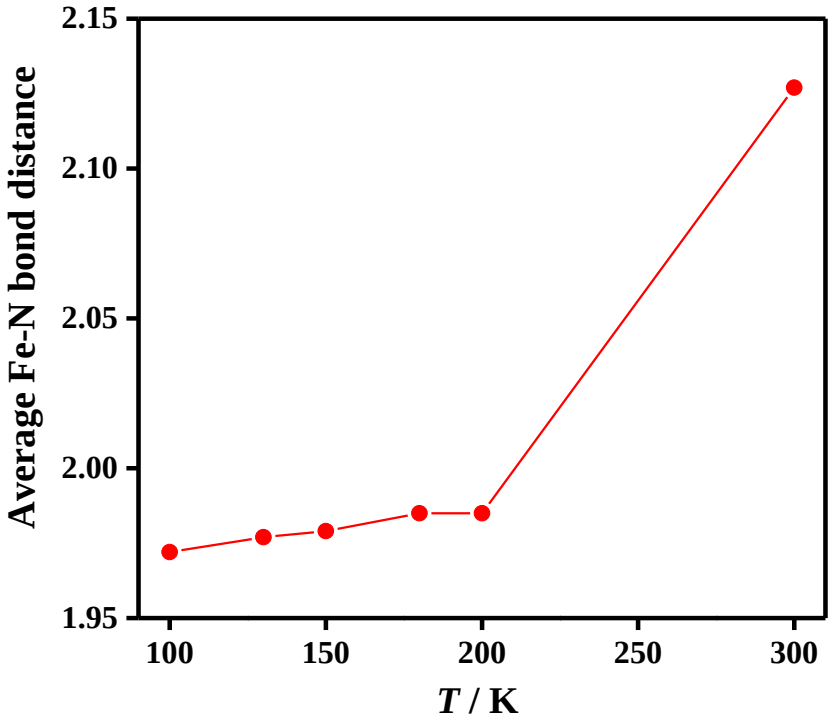

Fig. S4. Temperature dependence of average Fe-N bond distances for complex **2**. Solid lines are guided to the eye.

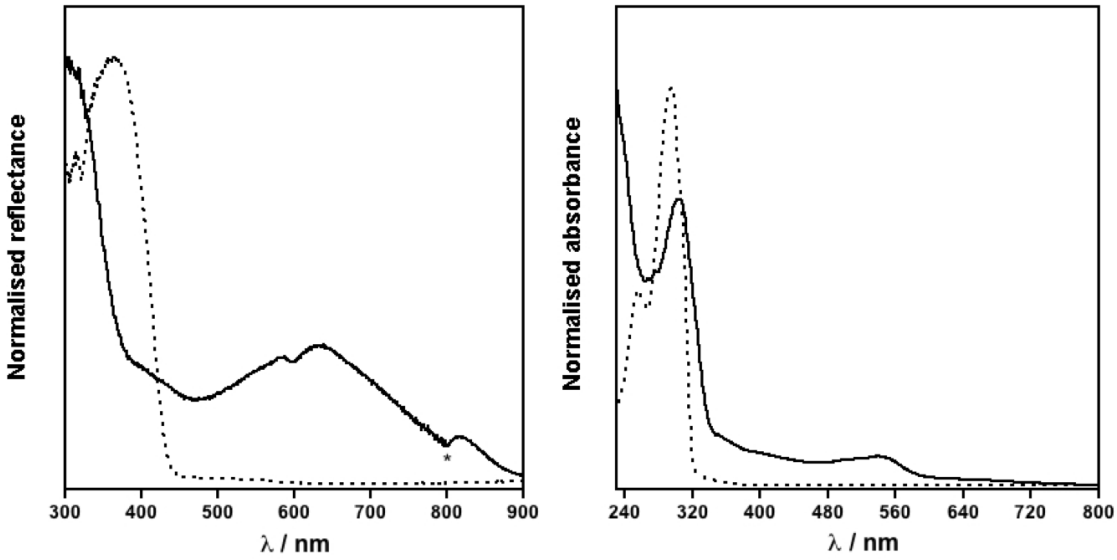

Fig. S5. Solid state (left) and acetonitrile solution (right) UV-vis spectra of **2** (solid line) and pydz ligand (dashed line) at room temperature (* is an artifact due to lamp change at 800 nm).

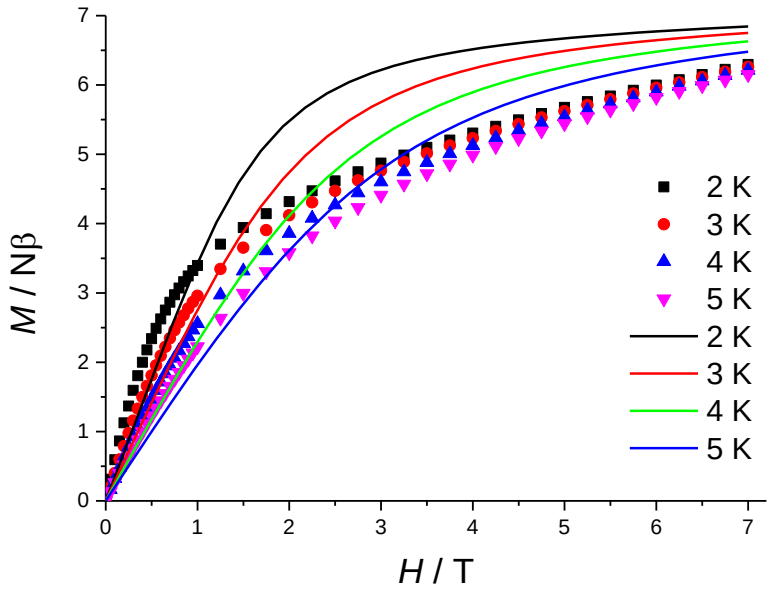

Fig. S6. *M* vs *H* data for **1** at 2-5 K. The solid lines represent the simulations using the spin Hamiltonian parameters from the *χT* fit.

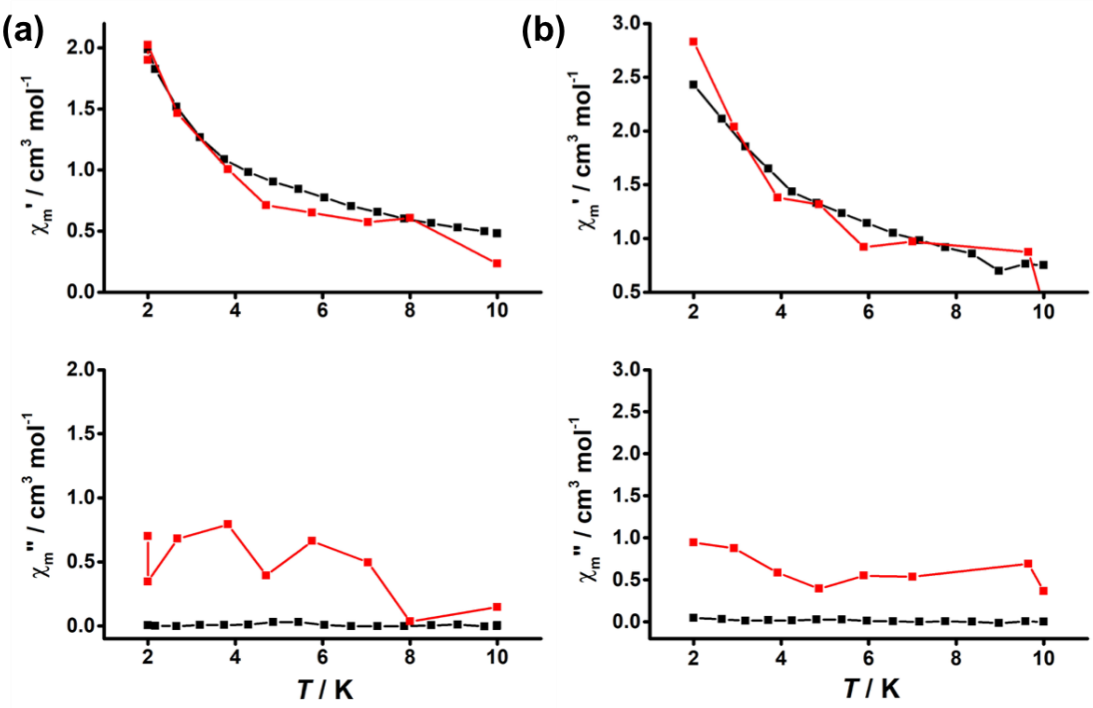

Fig. S7. AC magnetic susceptibility measurement of **1** under zero (a) and 1000 Oe (b) applied dc field.

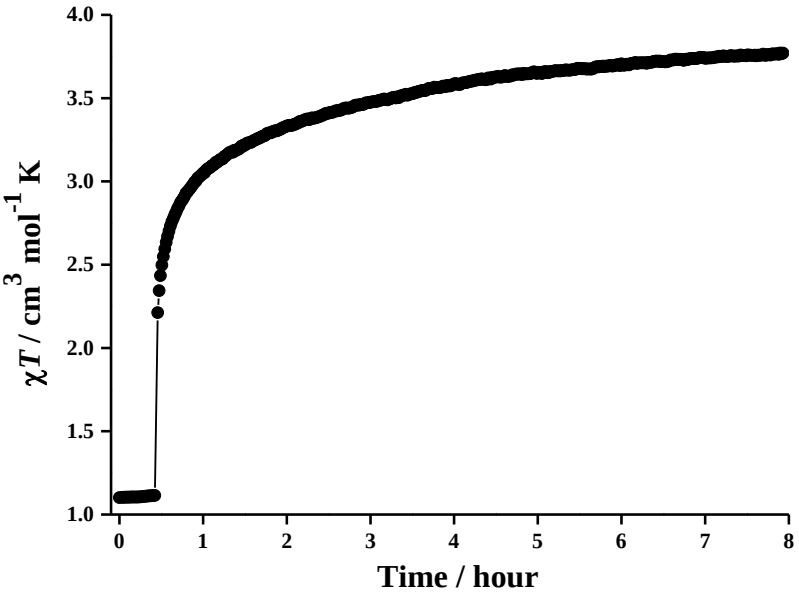

Fig. S8. Time evolution of the χT products of **2** at 10 kOe under light irradiation (808 nm, 10 mW) at 10 K.