

Supplementary Material for:

Abrupt spin crossover in an iron(III) quinolyisalicylaldimine complex: Structural insights and solvent effects

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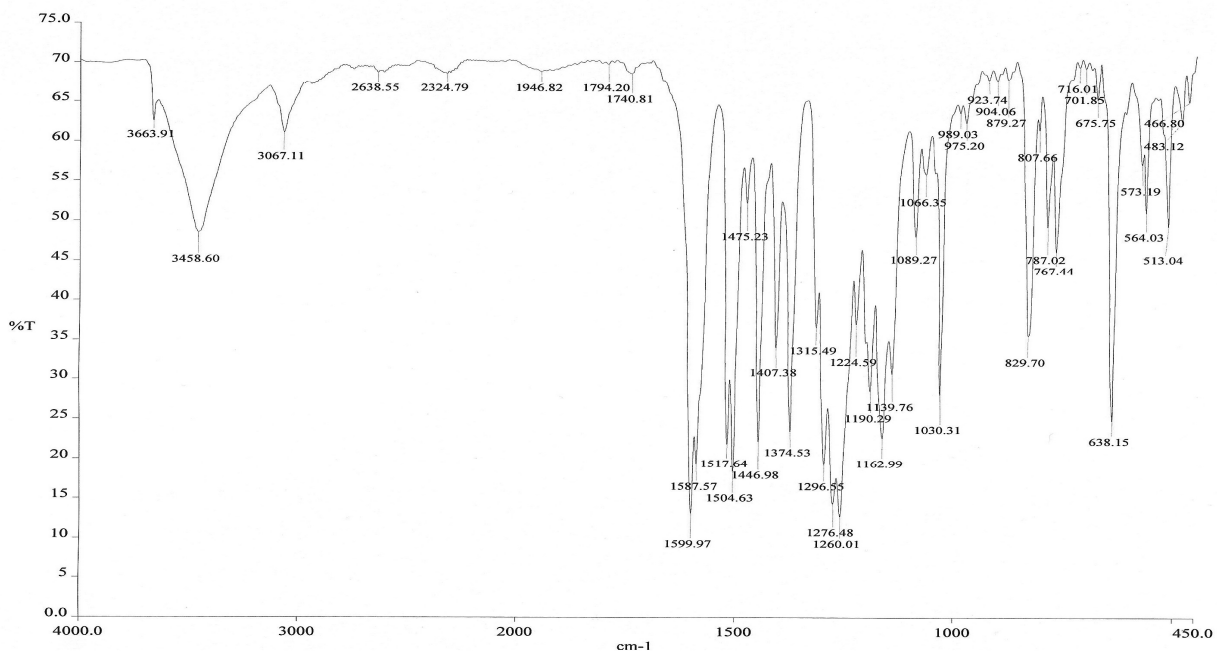
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1. General Remarks

All reactions were carried out at room temperature in air. With the exception of Hqsal-I,¹ all chemicals were purchased from Aldrich Chemical Company and used as received. Infrared spectra (as KBr discs) were recorded on a Perkin-Elmer Spectrum One infrared spectrophotometer in the range 400-4000 cm⁻¹. Elemental analyses were carried out by using a Eurovector EA3000 analyser. ESI-MS were recorded by using a Bruker Daltonics 7.0T Apex 4 FTICR Mass Spectrometer at the National University of Singapore.

Synthesis of [Fe(qsal-I)₂]OTf·MeOH: Hqsal-I (154 mg, 0.4 mmol) was dissolved in CH₂Cl₂ (2 ml) giving an orange solution. NEt₃ (56 μl, 0.4 mmol) was added resulting in a change to dark orange. CH₃OH (3 ml) was layered on top of the Hqsal-I solution. In a separate flask, FeCl₃ (34 mg, 0.2 mmol) was dissolved in CH₃OH (5 ml) giving a yellow solution and AgCF₃SO₃ (155 mg, 0.6 mmol) added resulting in formation of a white powder (AgCl) which was filtered off. The yellow solution of Fe(CF₃SO₃)₃ was then layered on top of the blank CH₃OH and left for 4 days. The black crystals formed were washed with hexane (2 x 1 ml) and air dried (90 mg, 47%). IR (KBr): $\tilde{\nu}_{\max}$ = 3067 ($\nu_{\text{Ar-H}}$), 1600 ($\nu_{\text{C=N}}$), 1276 ($\nu_{\text{S-O}}$), 1139 ($\nu_{\text{C-F}}$), 1030 ($\nu_{\text{S-O}}$) cm⁻¹. (ESI): m/z = 802.0 [Fe(qsal-I)₂]⁺, 149.2 [CF₃SO₃]⁻. *Anal. Calc.* for C₃₄H₂₄F₃FeI₂N₄O₆S: C, 41.51; H, 2.46; N, 5.70. Found: C, 41.76; H, 2.39; N, 5.84%.



IR spectrum of [Fe(qsal-I)₂]OTf·MeOH

2. X-ray crystallography

X-ray crystallographic data were collected at 163, 230 and 293 K on a Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator (Cu α radiation, 1.54178 Å), high-flux Osmic multilayer mirror optics, and a curved image-plate detector. The data were integrated and scaled and averaged with FS Process.² The structures were then solved by direct methods and refined on all F^2 data using the SHELX suite of programs.³ In all

cases non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters which were *ca.* $1.2 \times$ (aromatic CH) or $1.5 \times$ (CH₃, OH) the equivalent isotropic thermal parameters of their parent carbon or oxygen atoms. All pictures were generated using the POV-Ray interface in X-SEED.⁴

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

	163 K	230 K	293 K
Formula	C ₃₄ H ₂₄ F ₃ FeI ₂ N ₄ O ₆ S	C ₃₄ H ₂₄ F ₃ FeI ₂ N ₄ O ₆ S	C ₃₄ H ₂₄ F ₃ FeI ₂ N ₄ O ₆ S
Molecular weight / gmol ⁻¹	982.79	982.79	982.79
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
<i>a</i> / Å	12.2488(5)	12.2189(5)	11.7726(4)
<i>b</i> / Å	12.3956(4)	12.4526(7)	12.6918(4)
<i>c</i> / Å	12.8192(9)	12.8877(9)	13.3179(9)
α / °	70.108(5)	70.115(5)	69.437(5)
β / °	87.581(6)	87.282(6)	85.020(6)
γ / °	68.745(5)	68.604(5)	67.526(5)
Cell volume / Å ³	1698.40(15)	1710.35(17)	1719.03(14)
<i>Z</i>	2	2	2
Absorption coefficient / mm ⁻¹	19.012	18.879	18.784
Reflections collected	19123	22723	21734
Independent reflections, <i>R</i> _{int}	6290, 0.0875	6316, 0.0792	4843, 0.0681
Max. and min. transmission	1.0 and 057	1.0 and 0.36	1.0 and 0.34
Restraints/parameters	6/462	0/462	12/462
Final R indices [<i>I</i> > 2σ(<i>I</i>)]: <i>R</i> ₁ , <i>wR</i> ₂	0.0969, 0.3147	0.0681, 0.2060	0.0715, 0.2346

Table S2 Fe-N/O bond lengths and octahedral distortion parameters for **1-MeOH**.

	163 K/LS1	230 K/LS2	293 K/HS	Δ Fe-L (LS2-LS1)	Δ Fe-L (HS-LS1)
Fe-N1	1.965(9)	1.948(8)	2.096(7)	-0.017	0.131
Fe-N2	1.939(10)	1.997(6)	2.145(7)	0.058	0.206
Fe-N20	2.010(10)	2.005(6)	2.157(8)	-0.005	0.147
Fe-N21	1.948(9)	1.966(7)	2.098(7)	0.018	0.15
Fe-N_{ave}	1.966(10)	1.979(8)	2.124(8)	0.014	0.158
Fe-O1	1.874(8)	1.890(5)	1.906(6)	0.016	0.032
Fe-O20	1.878(8)	1.878(5)	1.907(7)	0.000	0.029
Fe-O_{ave}	1.876(8)	1.884(5)	1.906(7)	0.008	0.031
Σ	43	39	65	-4 ($\Delta\Sigma$)	22 ($\Delta\Sigma$)
Θ	61	60	189	-1 ($\Delta\Theta$)	128 ($\Delta\Theta$)

Table S3 Interactions in [Fe(qsal-l)₂]OTf.MeOH.

	163 K	230 K	293 K
π-π			
Type A	3.36	3.37	3.46
Type B	3.39	3.44	3.48
P4AE			
Cent...Cent	3.65(1)	3.65(1)	3.67(1)
C-H... π	2.47(1)	2.51(1)	2.57(1)
H-bond			
O101...H200	2.087(9)	2.014(6)	2.089(10)
O101...O200	2.765(13)	2.781(10)	2.741(15)
\angle O200-H200...O101	137.5(8)	153.5(7)	136.3(11)
C-H...X Interactions			
O100...H11	2.55(1)	2.58(1)	2.47(1)
F2...H15	2.49(1)	2.49(1)	2.63(1)
Triflate embraces			
O100...H22	2.52(1)	2.53(1)	2.82(1)
O101...H34	2.49(1)	2.55(1)	2.59(2)
O102...H21	2.64(1)	2.64(1)	2.70(1)
O102...H35	2.50(1)	2.52(1)	2.61(1)
MeOH embraces			
O200...H2	2.61(1)	2.63(1)	2.70(2)
O200...H16	2.41(1)	2.44(1)	2.59(2)

I... π interactions

I1... π (C20-C25)	3.717(1)	3.751(1)	3.740(1)
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3. Magnetic susceptibility, Mössbauer spectroscopic and DSC studies

Data were collected using a Quantum Design MPMS 5 SQUID magnetometer under an applied field of 1 T over the temperature range 350–4 K. The powdered or polycrystalline samples were placed in gel capsules and care was taken to allow long thermal equilibration times at each temperature point. The scanning rate was 90 sec/°C. The Mössbauer samples were treated similarly using only the microcrystalline product. Spectra were then recorded using a conventional constant acceleration spectrometer, calibrated with α -Fe and with isomer shifts quoted relative to α -Fe at room temperature. Fitting was carried out with the Recoil[®] software. DSC measurements were performed on the non-solvated crystals [Fe(qsal-I)₂]OTf **1**.

4. Supporting Figures

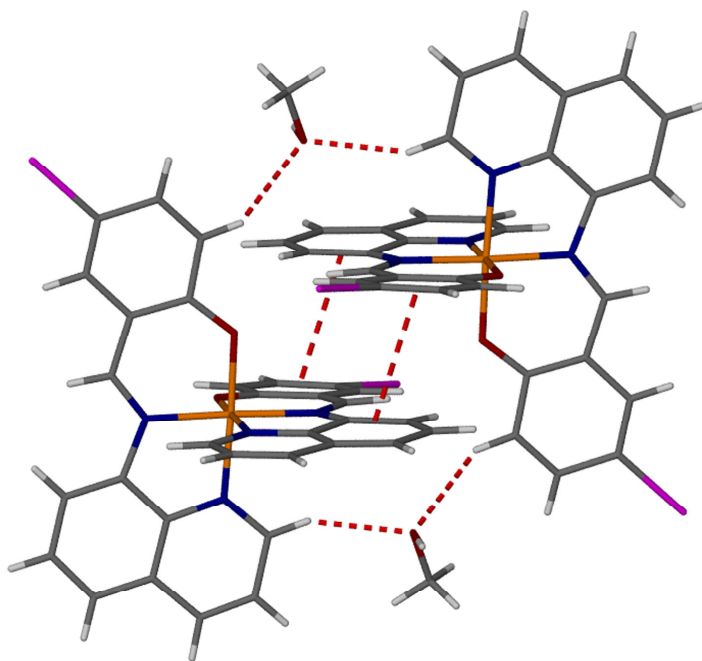


Figure S1 Type A π - π interactions showing the supporting MeOH interactions at 163 K.

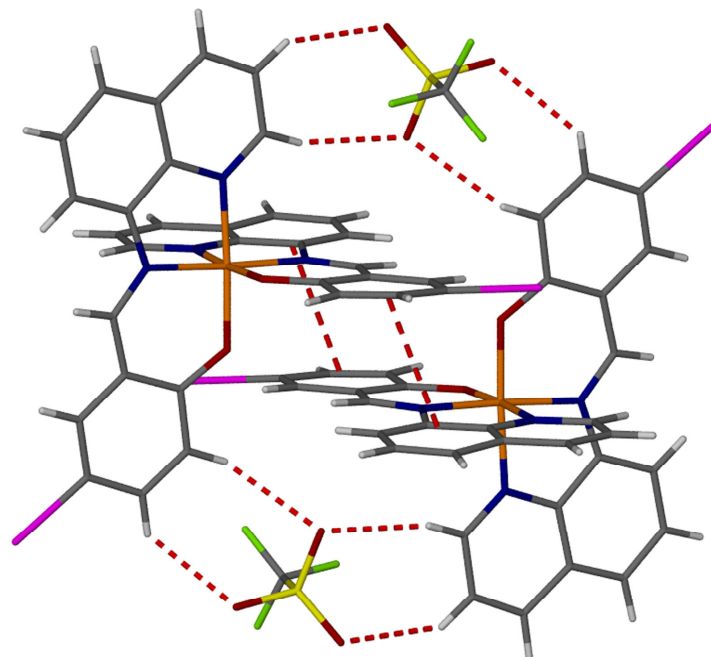


Figure S2 Type B π - π interactions showing the supporting triflate embraces at 163 K.

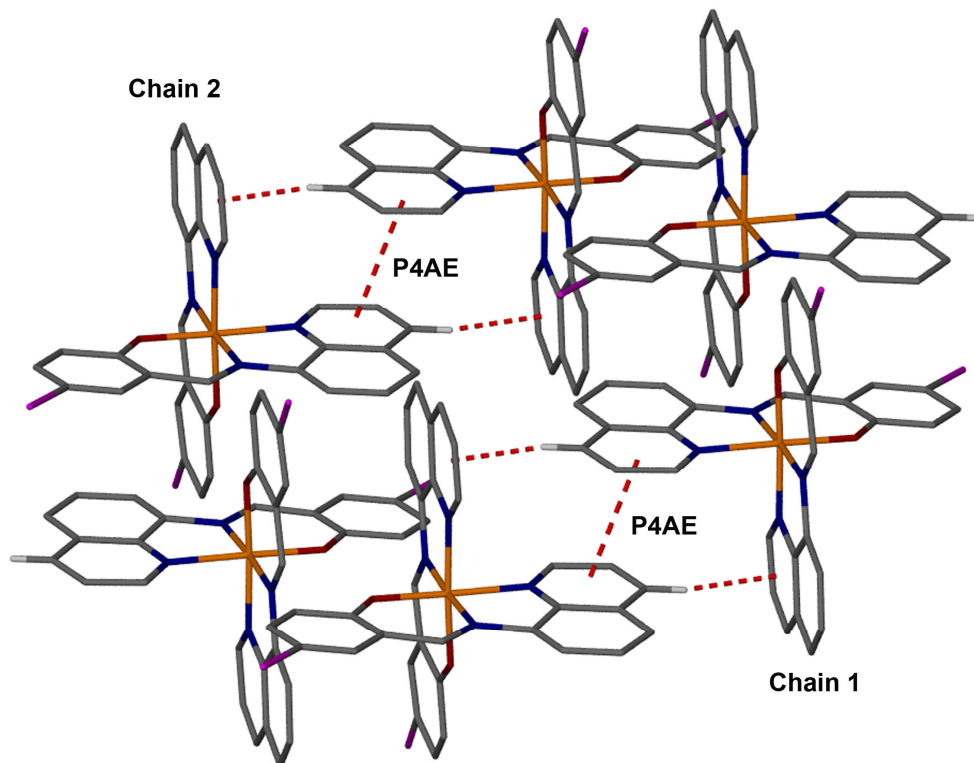


Figure S3 P4AE interactions in 1-MeOH showing the π - π and C-H... π interactions at 163 K.

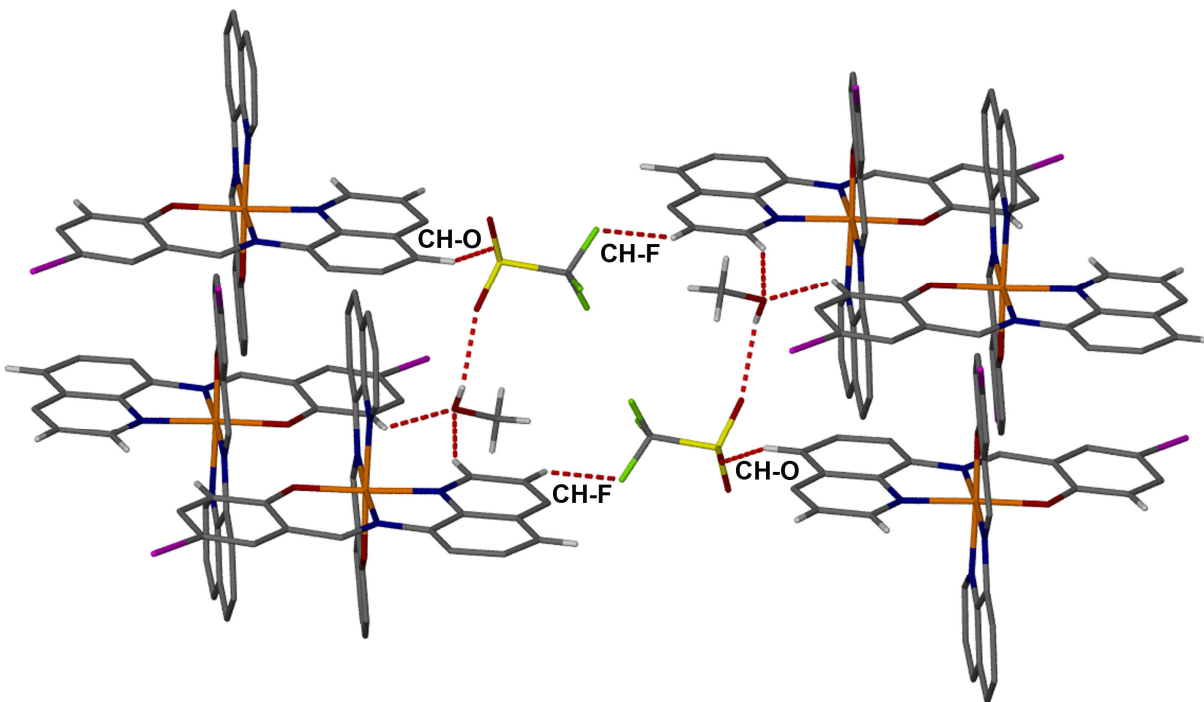


Figure S4 C-H...F and C-H...O interactions in 1-MeOH at 163 K.

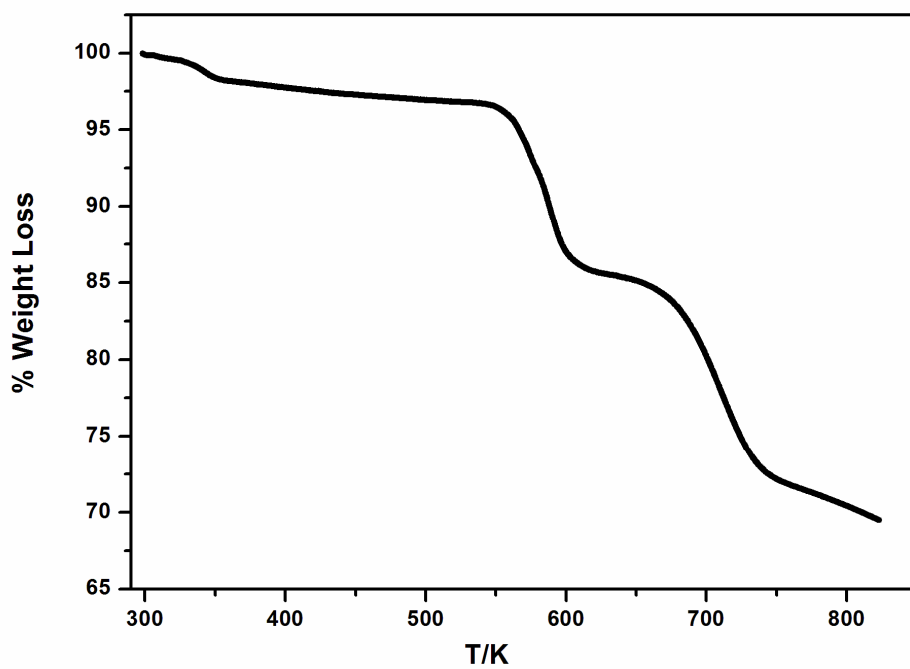


Figure S5 Thermogravimetric analysis of 1-MeOH.

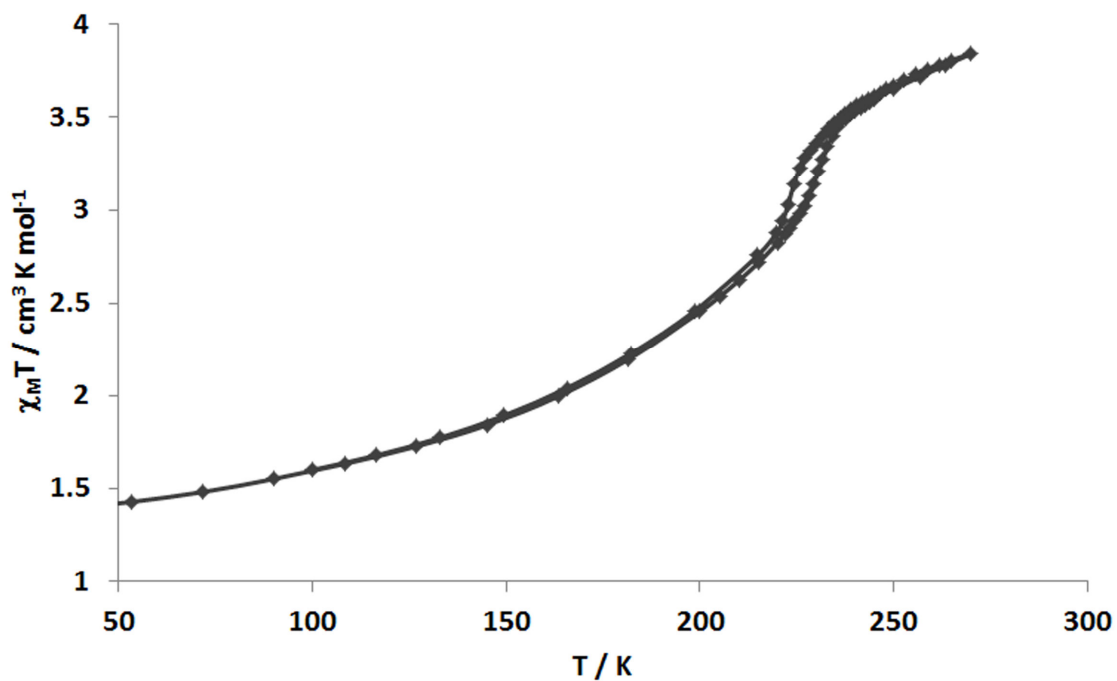


Figure S6 Thermal variation of $\chi_{\text{M}}T$ versus T plot for powdered **1**.

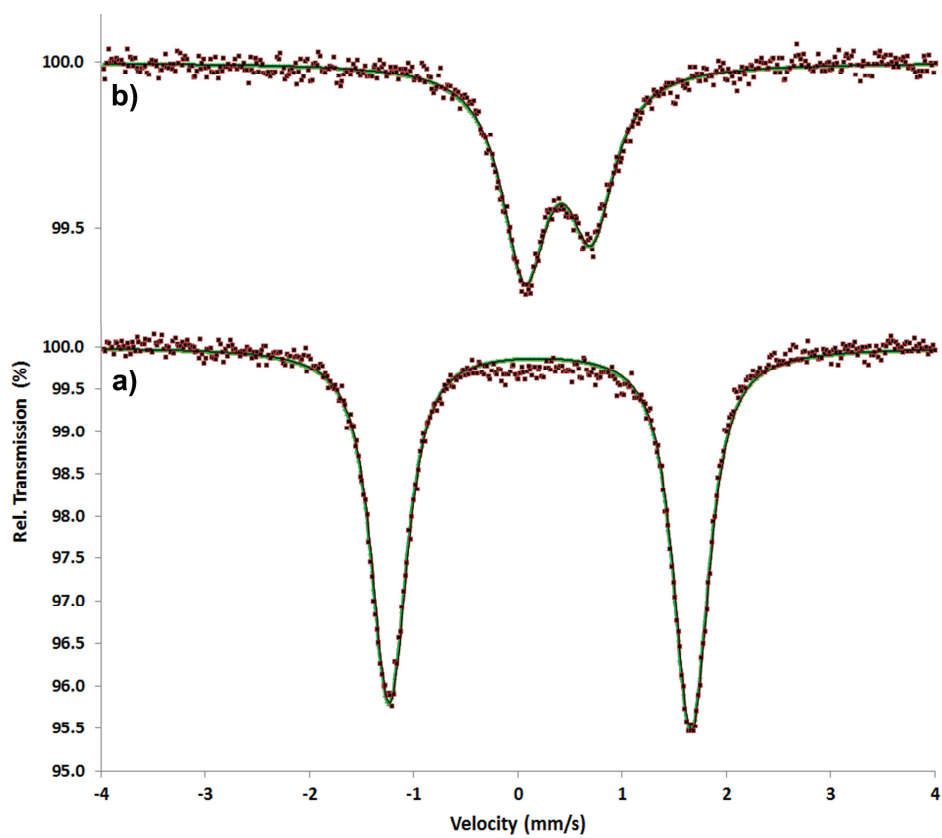


Figure S7 ^{57}Fe Mössbauer spectra of **1** at a) 77 K and b) 298 K.

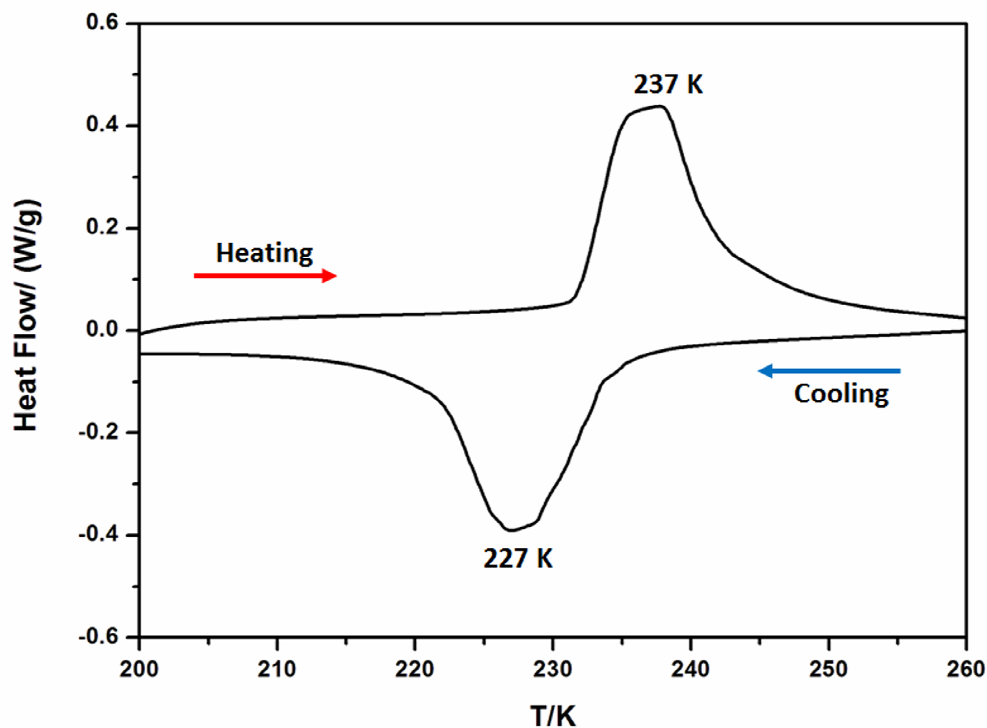


Figure S8 DSC measurements of 1.

5. References

1. J. Sirirak, W. Phonsri, D. J. Harding, P. Harding, P. Phommon, W. Chaoprasa, R. M. Hendry, T. M. Roseveare and H. Adams, *J. Mol. Struct.*, 2013, **1036**, 439-446.
2. Rigaku, Rigaku Corporation, Tokyo, Japan, 1996.
3. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.
4. a) L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189-191; b) J. L. Atwood and L. J. Barbour, *Cryst. Growth & Des.*, 2003, **3**, 3-8.