Electronic Supplementary Material (ESI) for Dalton Transactions.

Selecting the spin crossover profile with controlled crystallization of mononuclear Fe(III) polymorphs

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1. X-ray Data

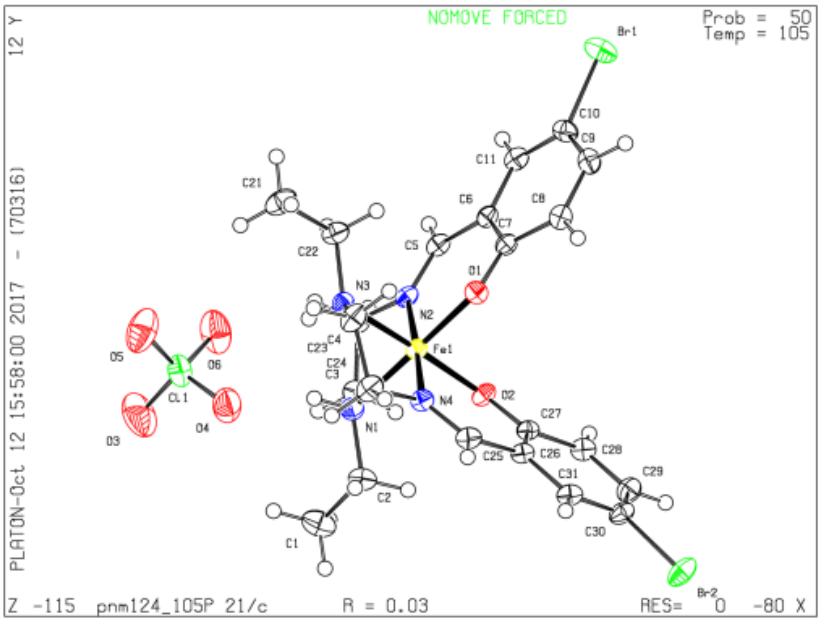

Figure S1. ORTEP diagram of **1a** at 105 K. Thermal ellipsoids are drawn at the 50% probability level.

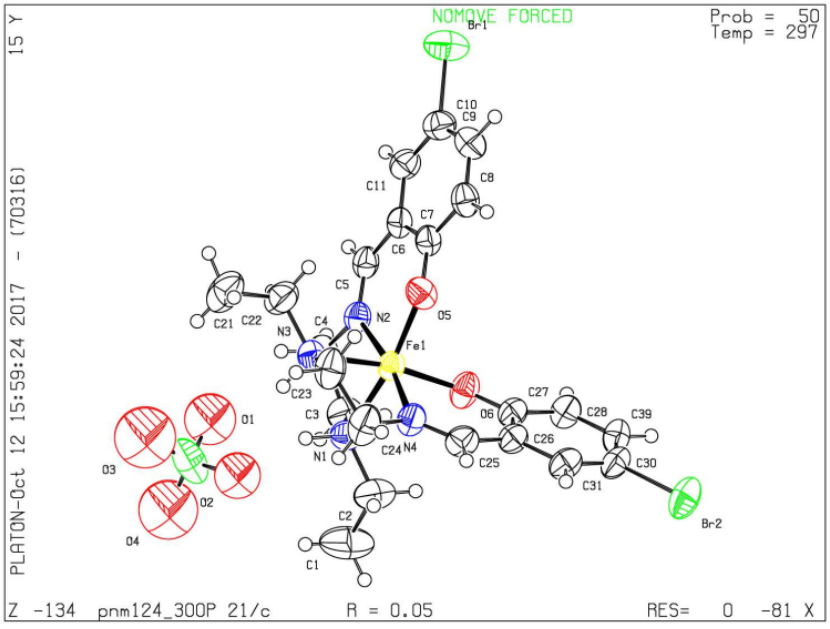

Figure S2. ORTEP diagram of **1a** at 297 K. Thermal ellipsoids are drawn at the 50% probability level.

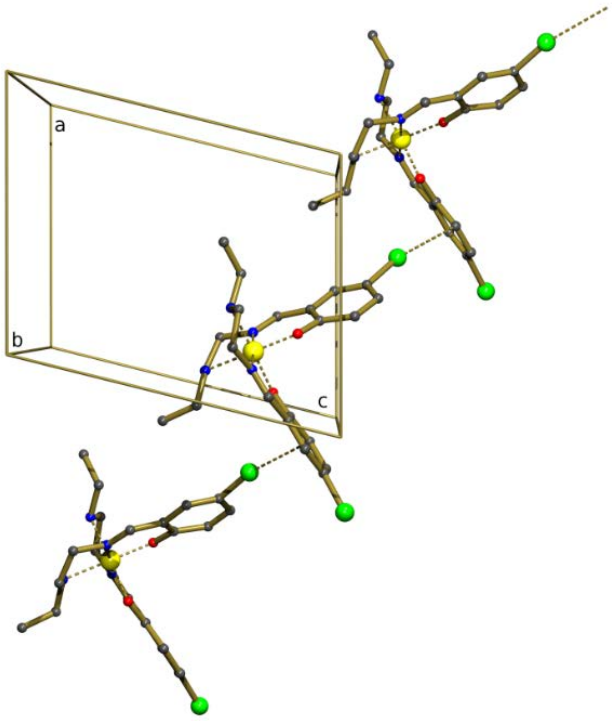

Figure S3. Short C-Br...π halogen bonds between Br and C atoms of neighbour rings, giving rise to infinite chains running along [201].

Table S1. Selected distances and angles in polymorph **1a** at 297 K.

	1a (T=297K)
a (Å)	9.9692
b (Å)	23.6219(6)
c (Å)	12.0380(3)
β (°)	103.3972(13)
Vol ($Å^3$)	2757.7
Fe…O(Å)	1.905/1.912
Fe…N_{im} (Å)	2.095/2.100
Fe…N_{am} (Å)	2.209/2.225
N_{am}…Cl (Å)	3.806/3.830
N_{am}-H…O (Å)	3.206/3.405 3.133/3.362
N_{am}-H…O (°)	145/159 / 147/157
C2-N1-C3-C4 (°)	-175.13 / -173.59
C3-C4-N2-C5 (°)	-140.80 / -149.09
C5-C6-C7-O (°)	-96.68 / -2.04
α (°)	79.5

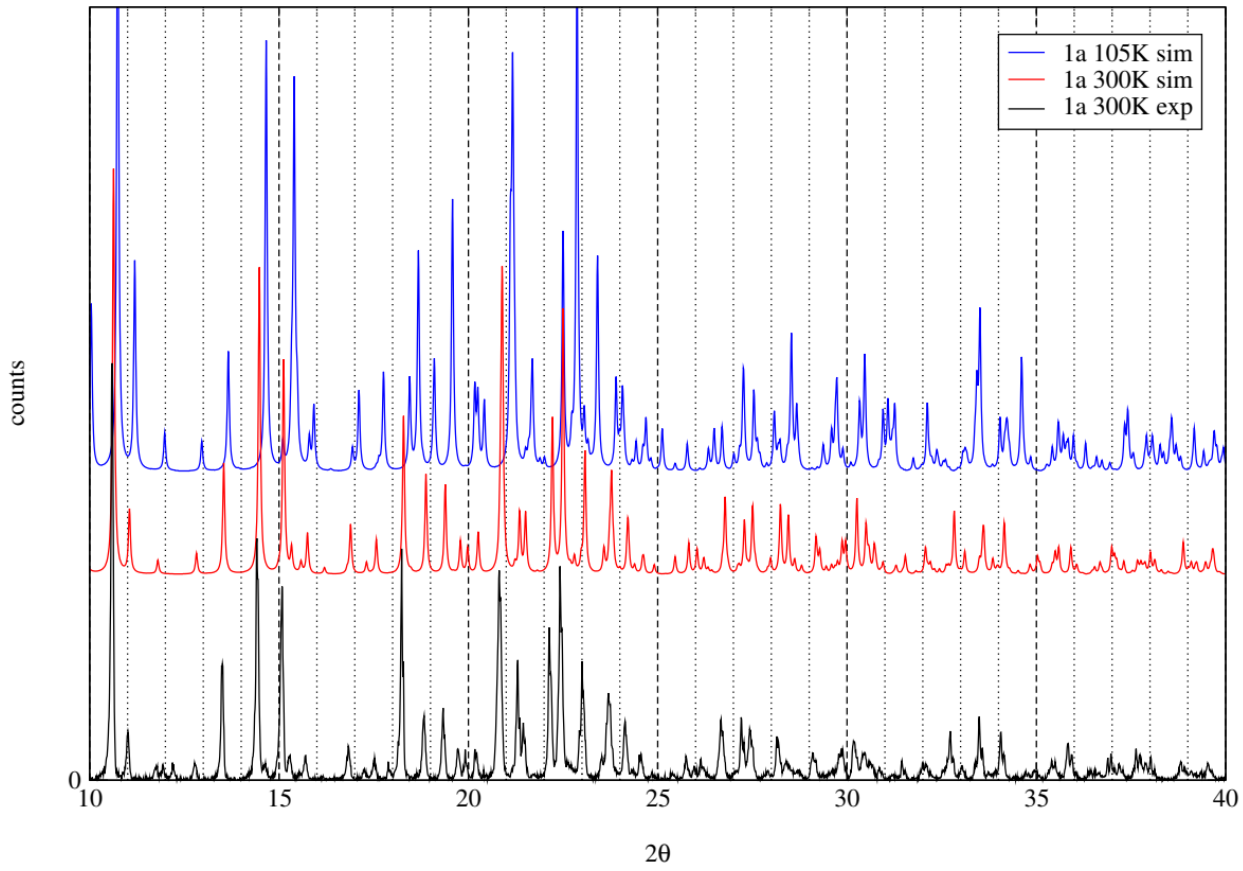

Figure S4. Simulated X-ray powder diffractograms from corresponding crystal structures; the latter crystal structures were calculated from single crystal X-ray data using direct methods and non-linear least-squares fitting.

2. DSC Data

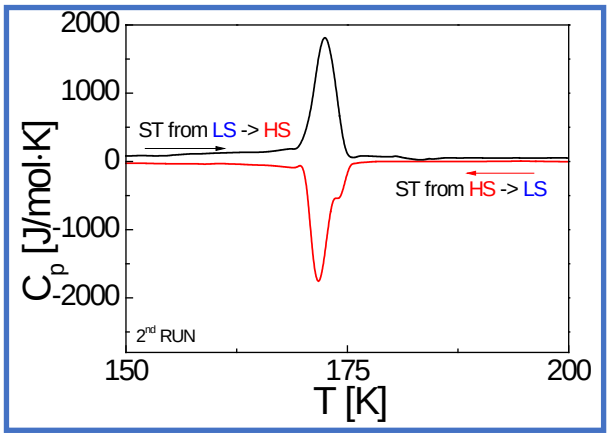

Figure S5. Plot of heat capacity vs. T for sample **1a**, on warming and cooling at 10 K/min, over the range 150 K and 200 K, 2nd RUN.

3. SQUID Data

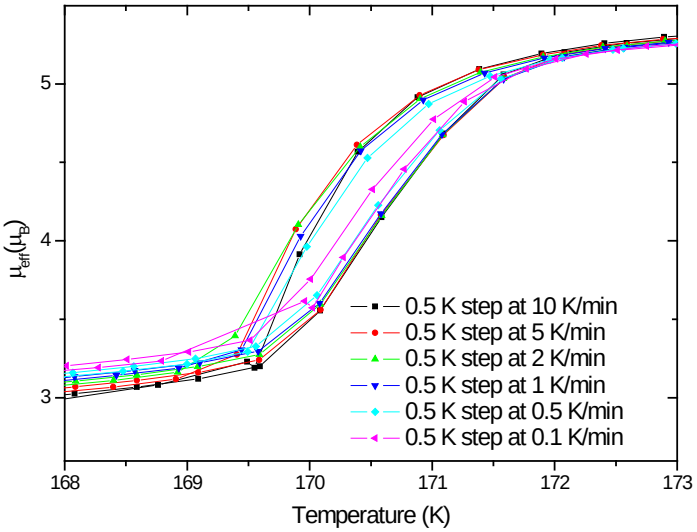

Figure S6. Temperature dependent magnetic measurements for polymorph **1a** using different scan rates (10 K/min to 0.1 K/min) with 0.5 K steps.

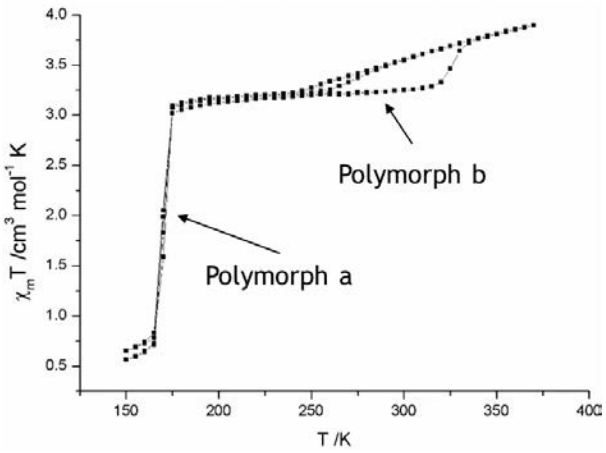

Figure S7. Temperature dependent magnetic measurements for $[Fe(5\text{-Br-salEen})_2]ClO_4$ showing a mixture of the two polymorphs (**1a** and **1b**).