Electronic Supporting Information for

Inducing Hysteretic Spin Crossover in Solution

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Supporting Information

1. Electronic Absorption Spectra

Electronic absorption spectra of a 5 mM dichloromethane solution of $[Fe^{III}L]BF_4$, **1**, were recorded on a Perkin Elmer Lambda instrument at 171 K and 298 K.

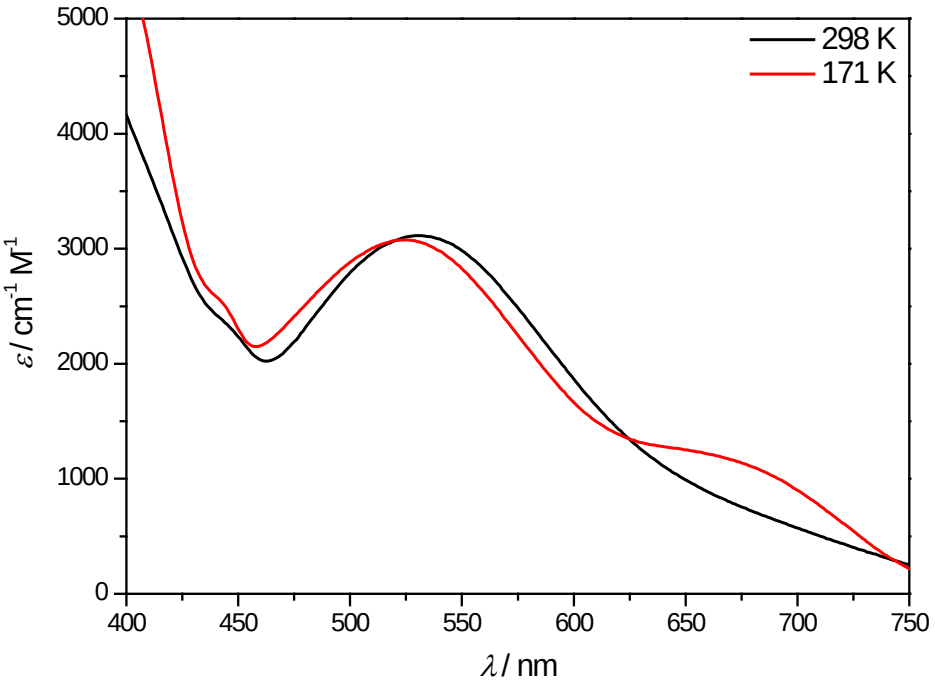

Figure S1. Electronic absorption spectra of $[Fe^{III}L]BF_4$, **1**, at 298 and 171 K.

2. EPR Spectra

ESR spectra of a 5 mM dichloromethane solution of $[Fe^{III}L]BF_4$, **1**, were recorded on a Magnettech Miniscope MS200 spectrometer operating at *ca.* 9.5 GHz (X-band).

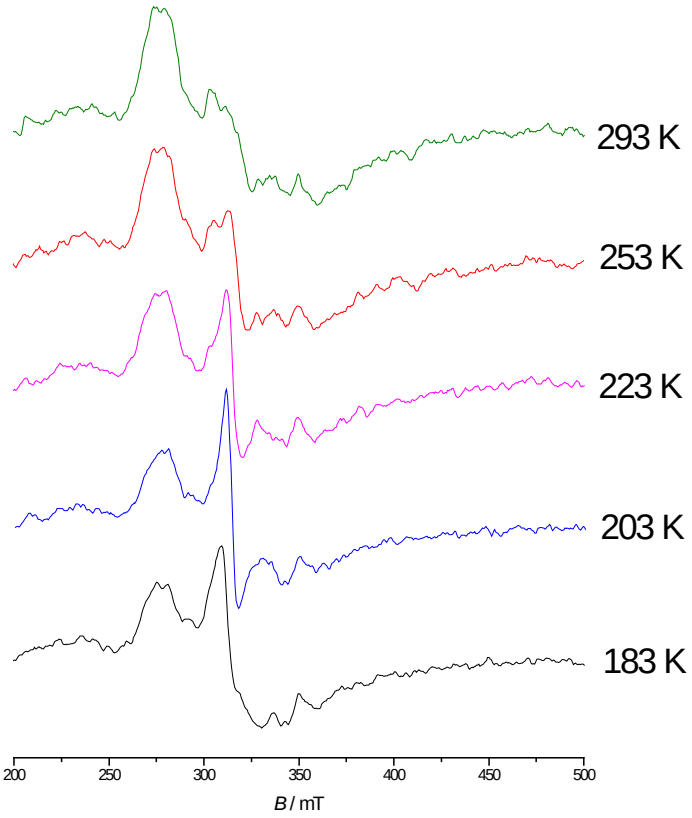

Figure S2. Variable temperature EPR spectra of 5 mM dichloromethane solution and glass of $[Fe^{III}L]BF_4$, **1**.

3. Magnetic Data – Solid State

Variable temperature magnetic susceptibility measurements were performed on a MPMS®XL-SQUID magnetometer in the temperature range of 10K- 300K in cooling mode only at 10 K min^{-1} with 5 K intervals in an applied field of 5000 Oe.

Table S1. Magnetic Data of solid sample of $[Fe^{III}L]BF_4$, **1**, recovered from initial synthesis.

T / K	$\chi_m T$ / $cm^3\,mol^{-1}\,K$	T / K	$\chi_m T$ / $cm^3\,mol^{-1}\,K$	T / K	$\chi_m T$ / $cm^3\,mol^{-1}\,K$
300.0594	2.73441	200.0695	2.22954	100.0499	1.49878
295.055	2.72186	195.0668	2.19153	95.05149	1.45889
290.0656	2.70826	190.0656	2.15234	90.04505	1.42016
285.0663	2.69443	185.0651	2.11545	85.04023	1.37915
280.0725	2.67815	180.0628	2.07758	80.03788	1.3448
275.061	2.66603	175.0654	2.03996	75.02465	1.322
270.061	2.63866	170.0668	2.00243	70.02917	1.30432
265.0637	2.6167	165.0638	1.9651	65.02229	1.28666
260.0619	2.594	160.0702	1.92971	60.02061	1.26924
255.0671	2.56478	155.0664	1.89421	55.02072	1.25277
250.0602	2.54078	150.0697	1.85913	50.01107	1.23746
245.0725	2.52299	145.0637	1.82449	45.00137	1.2232
240.0605	2.49246	140.0598	1.78971	40.00616	1.20985
235.0636	2.46431	135.0707	1.75494	35.00421	1.19692
230.0636	2.43499	130.0581	1.72014	30.00319	1.18391
225.064	2.40403	125.0585	1.68483	25.00302	1.17219
220.0638	2.37139	120.067	1.65026	19.9976	1.16139
215.0664	2.3379	115.0557	1.61437	14.99784	1.15204
210.0677	2.30231	110.0594	1.57591	9.99837	1.13047
205.063	2.26609	105.0542	1.53784		

Table S2. Magnetic Data of solid sample of $[Fe^{III}L]BF_4$, **1**, recovered after lyophilisation.

T / K	$\chi_m T$ / cm^3 mol^{-1} K	T / K	$\chi_m T$ / cm^3 mol^{-1} K	T / K	$\chi_m T$ / cm^3 mol^{-1} K
299.9977	2.578	199.9036	2.23448	99.9986	1.6264
294.9279	2.57232	194.9038	2.21463	95.00762	1.59249
290.032	2.56166	189.9109	2.18855	90.0107	1.55952
284.8571	2.54164	184.912	2.16379	85.0124	1.52862
280.022	2.52941	179.9272	2.1397	80.01948	1.5004
274.8702	2.49787	174.9194	2.10168	75.01434	1.47787
270.0431	2.49756	169.9424	2.08124	70.01917	1.45611
264.8742	2.47839	164.9381	2.05847	65.00835	1.43673
259.9393	2.46291	159.9527	2.02861	60.01941	1.42152
254.865	2.44597	154.9523	1.99871	55.01651	1.42254
249.8936	2.42797	149.9579	1.95202	50.01471	1.39607
244.8963	2.40912	144.9545	1.94014	45.01507	1.38432
239.8677	2.39409	139.9679	1.90606	40.00911	1.37366
234.896	2.37379	134.9764	1.87246	34.99763	1.36321
229.8805	2.35556	129.9813	1.83907	29.99894	1.3534
224.8785	2.34002	124.9797	1.78721	24.9956	1.33092
219.9153	2.32096	119.9877	1.76958	20.00878	1.33421
214.8887	2.29677	114.9907	1.73986	15.0058	1.3225
209.9019	2.2811	109.9993	1.69976	10.00154	1.29601
204.8987	2.25616	104.995	1.6634		

4. Magnetic Data – Solution

^{1}H NMR spectra of 5 and 11 mM solutions of [Fe^{III}L]BF_4, **1**, in CD_2Cl_2 with 0.03% tetramethylsilane (TMS) were recorded in warming and cooling modes between 188-303 K against a reference of CD_2Cl_2 with 0.03% TMS on a Varian Inova 500 MHz instrument. The measurements were performed using an NMR tube fitted with an insert for the reference solvent and carefully sealed to minimize the possibility of solvent evaporation.[1] The molar magnetic susceptibility, χ_m, for a long cylindrical sample oriented parallel to the magnetic field (*B*) was calculated using:[2]

$$\chi_m = \chi_0 \frac{MW(Solute)}{MW(Solvent)} + \frac{3000\Delta\nu}{4\pi\nu_0 CM}$$

where χ_0 is the molar susceptibility of the solvent (-46.6×10^{-6} cm^3 mol^{-1}), $\Delta\nu$ is the paramagnetic shift difference of the reference in Hz, ν_0 (= 499.796*10^6), is the operating RF frequency of the spectrometer in Hz, *C* is the concentration of the sample in moles per litre and *M* is the molecular weight of the paramagnetic molecule.

References

[1] L. A. Yatsunyk, F. A. Walker, *Inorg. Chem.*, **2003**, *43*, 757.

[2] S. K. Sur, *J. Magn. Reson.*, **1989**, *82*, 169.

4.1 Magnetic Plots from Evans method for 5 and 11 mM solutions of $[Fe^{III}L]BF_4$, **1**.

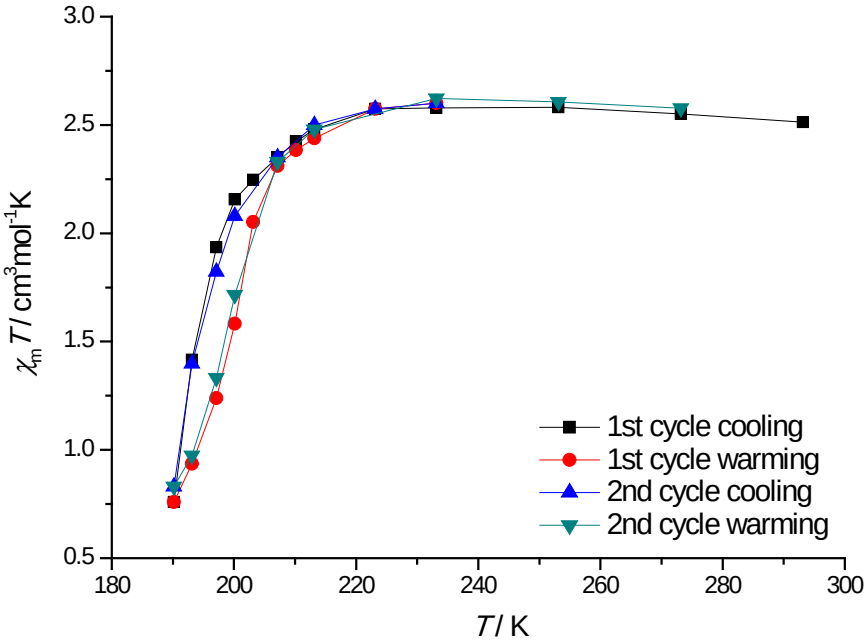

Figure S3. Plot of $\chi_m T$ vs T for a 5 mM CD_2Cl_2 solution of **1** over two cooling/heating cycles.

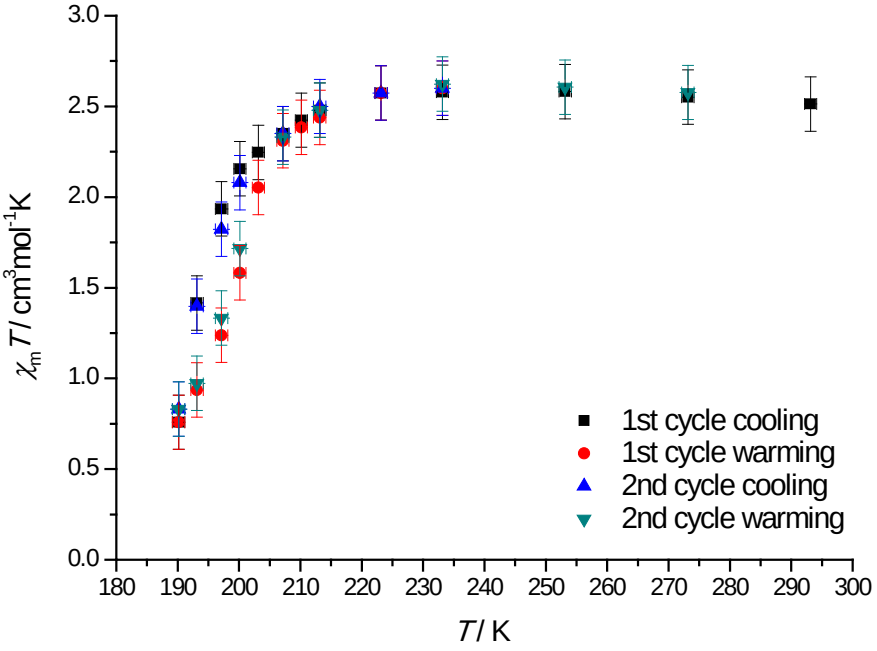

Figure S4. Plot of $\chi_m T$ *vs* T for a 5 mM CD_2Cl_2 solution of **1** over two cooling/heating cycles with error bars assuming 30% error for concentration.

Table S3. Variable temperature magnetic data of 5 mM CD_2Cl_2 solution sample of $[Fe^{III}L]BF_4$, **1**.

T (K)	Δν (Hz)	χ_p	χ_m^{para}	$\chi_m T$
293.15	85	8.07E-03	8.57E-03	2.51
273.15	93	8.84E-03	9.34E-03	2.55
253.15	102	9.70E-03	1.02E-02	2.58
233.15	111	1.06E-02	1.11E-02	2.58
223.15	116	1.10E-02	1.15E-02	2.57
213.15	117	1.11E-02	1.16E-02	2.48
210.15	116	1.10E-02	1.15E-02	2.42
207.15	114	1.08E-02	1.13E-02	2.35
203.15	111	1.06E-02	1.11E-02	2.25
200.15	108	1.03E-02	1.08E-02	2.16
197.15	98	9.32E-03	9.82E-03	1.94
193.15	72	6.83E-03	7.33E-03	1.42
190.15	37	3.49E-03	3.99E-03	0.76
193.15	46	4.35E-03	4.85E-03	0.94
197.15	61	5.78E-03	6.28E-03	1.24
200.15	78	7.41E-03	7.91E-03	1.58
203.15	101	9.60E-03	1.01E-02	2.05
207.15	112	1.07E-02	1.12E-02	2.31
210.15	114	1.08E-02	1.13E-02	2.38
213.15	115	1.09E-02	1.14E-02	2.44
223.15	116	1.10E-02	1.15E-02	2.57
233.15	112	1.07E-02	1.12E-02	2.60
223.15	116	1.10E-02	1.15E-02	2.57
213.15	118	1.12E-02	1.17E-02	2.50
207.15	114	1.08E-02	1.13E-02	2.35
200.15	104	9.89E-03	1.04E-02	2.08
197.15	92	8.74E-03	9.24E-03	1.82
193.15	71	6.74E-03	7.24E-03	1.40
190.15	41	3.87E-03	4.37E-03	0.83
193.15	48	4.54E-03	5.04E-03	0.97
197.15	66	6.26E-03	6.76E-03	1.33
200.15	85	8.07E-03	8.57E-03	1.72
207.15	113	1.07E-02	1.12E-02	2.33
213.15	117	1.11E-02	1.16E-02	2.48
233.15	113	1.07E-02	1.12E-02	2.62
253.15	103	9.79E-03	1.03E-02	2.61
273.15	94	8.93E-03	9.43E-03	2.58

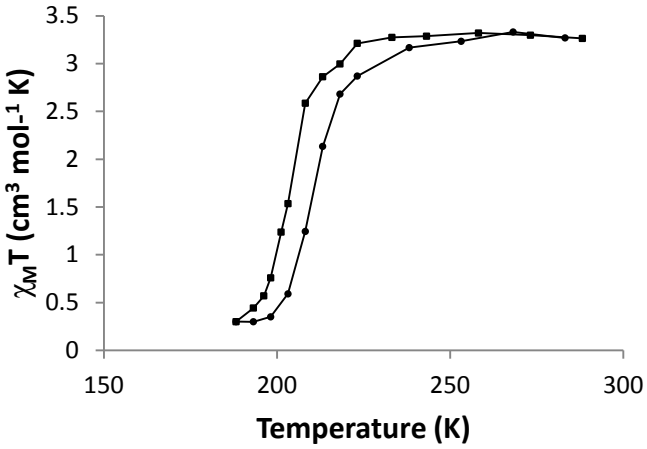

Figure S5. Plot of $\chi_m T$ vs T for an 11 mM CD_2Cl_2 solution of **1** over one cooling/heating cycle.

Table S4. Variable temperature magnetic data of 11 mM CD_2Cl_2 solution sample of $[Fe^{III}L]BF_4$, **1**.

T (K)	Δν (Hz)	χ_p	χ_m^{para}	$\chi_m T$
303.15	232	1.01E-02	1.06E-02	3.22
288.15	248	1.08E-02	1.13E-02	3.26
273.15	265	1.16E-02	1.21E-02	3.30
258.15	283	1.24E-02	1.29E-02	3.32
243.15	298	1.30E-02	1.35E-02	3.29
233.15	310	1.35E-02	1.40E-02	3.27
223.15	318	1.39E-02	1.44E-02	3.21
218.15	303	1.32E-02	1.37E-02	3.00
213.15	296	1.29E-02	1.34E-02	2.86
208.15	273	1.19E-02	1.24E-02	2.59
203.15	162	7.06E-03	7.56E-03	1.53
201.15	130	5.65E-03	6.15E-03	1.24
198.15	77	3.33E-03	3.83E-03	0.76
196.15	56	2.41E-03	2.91E-03	0.57
193.15	42	1.79E-03	2.29E-03	0.44
188.15	26	1.09E-03	1.59E-03	0.30
193.15	25	1.05E-03	1.55E-03	0.30
198.15	30	1.27E-03	1.77E-03	0.35
203.15	56	2.41E-03	2.91E-03	0.59
208.15	126	5.48E-03	5.98E-03	1.24
213.15	218	9.51E-03	1.00E-02	2.13
218.15	270	1.18E-02	1.23E-02	2.68
223.15	283	1.24E-02	1.29E-02	2.87
238.15	293	1.28E-02	1.33E-02	3.17
253.15	281	1.23E-02	1.28E-02	3.23
268.15	273	1.19E-02	1.24E-02	3.33
283.15	253	1.10E-02	1.15E-02	3.27
298.15	241	1.05E-02	1.10E-02	3.29

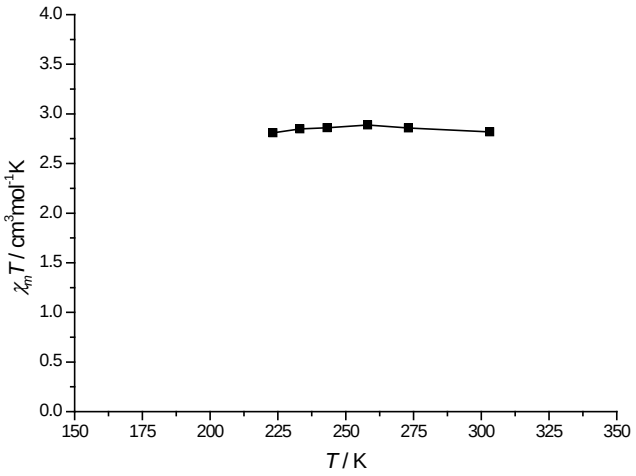

Figure S6. Plot of $\chi_m T$ vs T for a 21 mM CD_2Cl_2 solution of **1** in cooling mode only to 223 K. Further cooling in this case was precluded due to freezing of the NMR probe.

4.2 NMR spectra for 5 mM CD_2Cl_2 solution of $[Fe^{III}L]BF_4$, **1** in region to measure Δν (Hz).

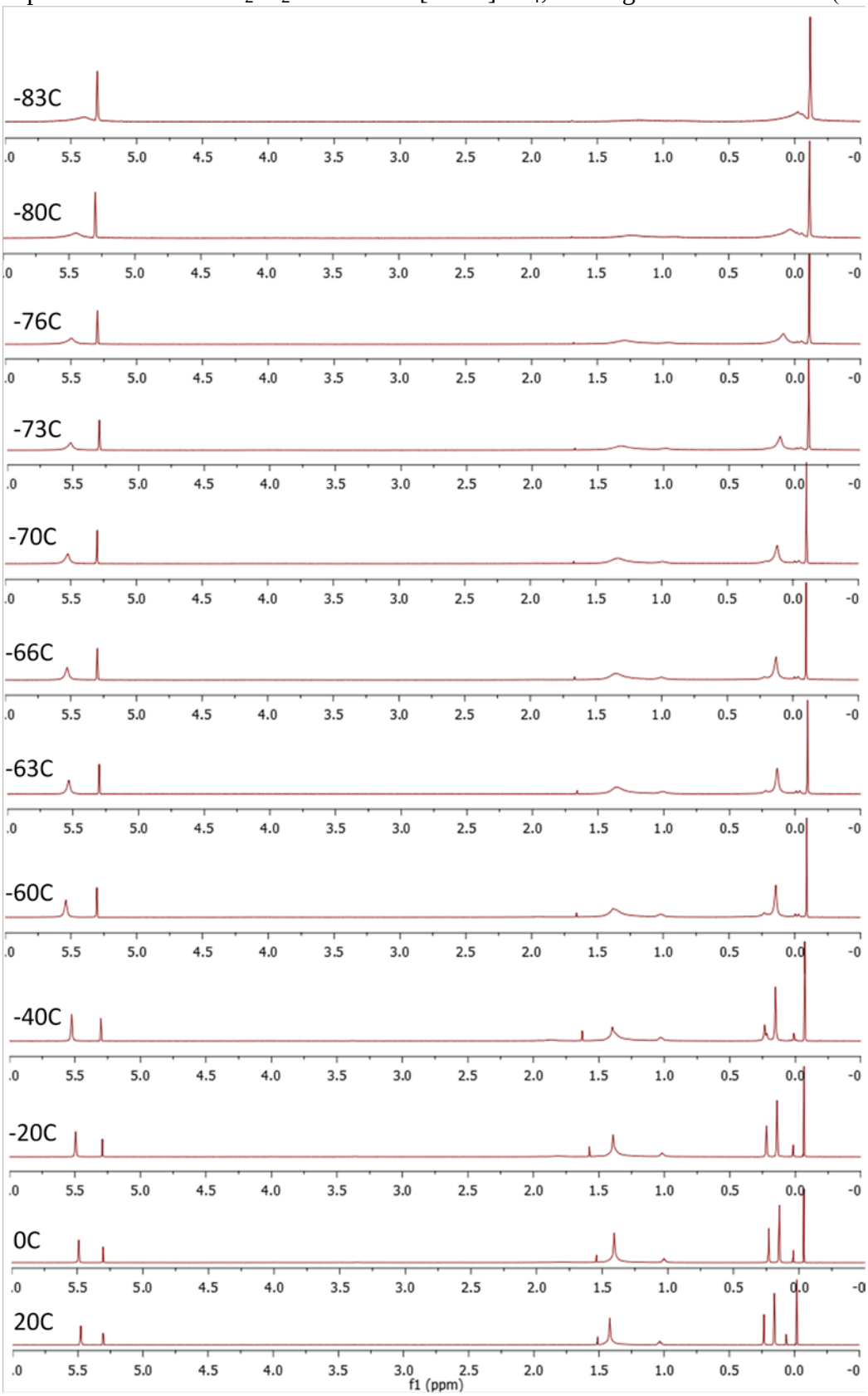

Figure S7. Variable temperature ^1H NMR spectra of 5 mM solution of **1** on cooling.

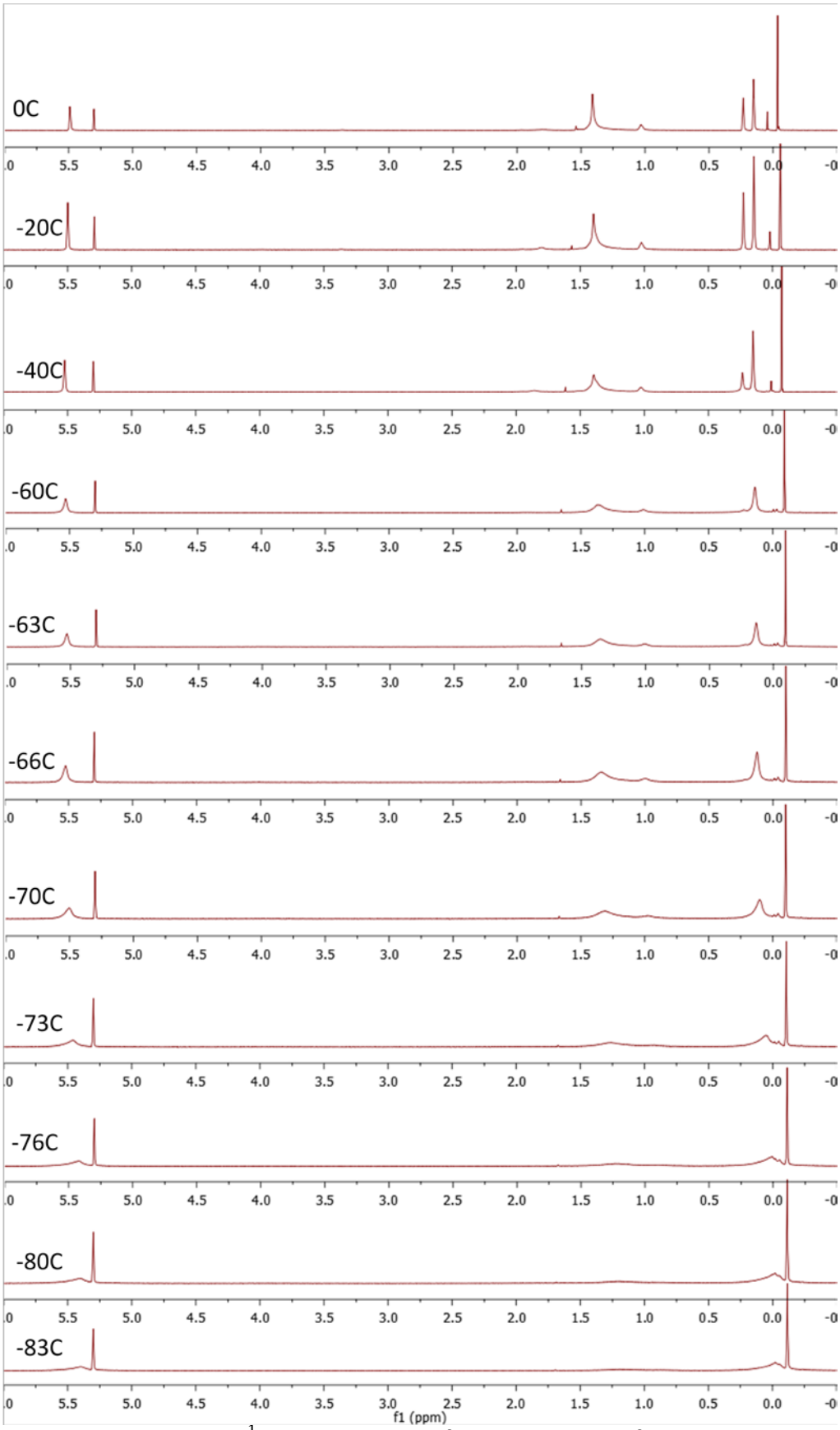

Figure S8. Variable temperature ^{1}H NMR spectra of 5 mM solution of **1** on warming.

5. Cryo-SEM

A 5 mM dichloromethane solution of 1 was rapidly frozen by plunging into sub-cooled liquid nitrogen slush and transferred to a quorum cryo-prep chamber attached to a FEI Nova200 Cryo-FEGSEM/FIB microscope. The sample then underwent sublimation at -90 ^{o}C for 5 minutes before being cooled and sputter-coated with platinum/palladium. It was then transferred to the cryo-stage of the microscope and imaged at -140^{o}C at 2-5kV using an ETD secondary electron detector.

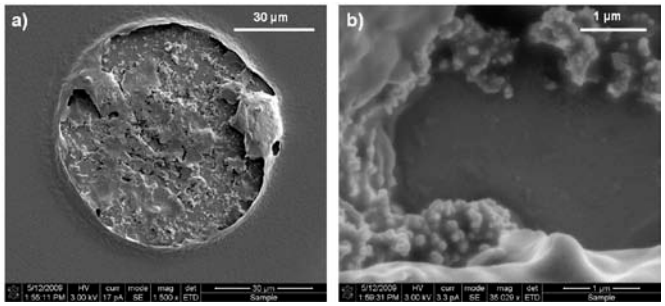

Figure S9. Cryo-SEM images of a 5 mM solution of **1** at a) x 1500 and b) x 35000 magnification.

6. Lyophilisation.

A 5mM solution of **1** in dichloromethane was flash frozen in liquid nitrogen and the solvent removed under high-vacuum. Complete lyophilisation of the sample was not achieved because the solvent was not able to be sublimed. The magnetic profile of the dried product was recorded via SQUID between 10-300 K in cooling and warming modes Figure S10 main paper and Table S2.

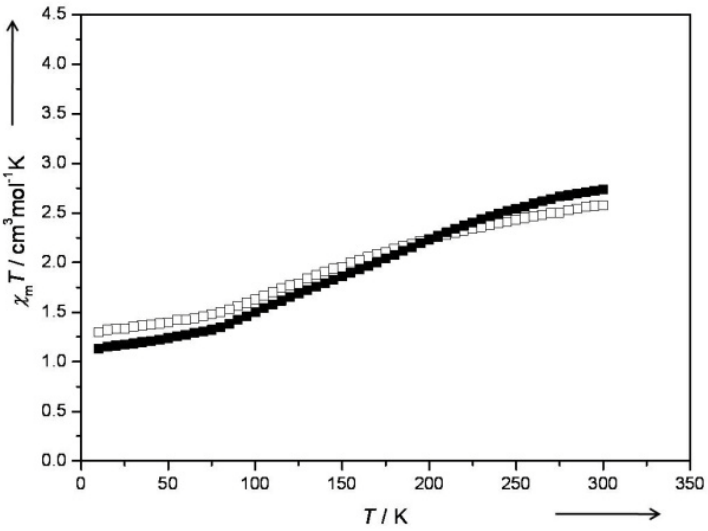

Figure S10. Plot of $\chi_m T$ vs T of [Fe^{III}L]BF$_4$, **1**, in cooling and heating modes between 10-300 K for bulk solid (black squares) and for solid obtained after lyophilisation of 5 mM dichloromethane solution (white circles).