Supporting Information

Bi-stable spin-crossover characteristics of a highly-distorted [Fe(1-BPP-$COOC_2H_5)_2$]$(ClO_4)_2.CH_3CN$ complex

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Experimental

Materials and methods: Anhydrous solvents and $Fe(ClO_4)_2.6H_2O$ were purchased from commercial sources and used as received. Glassware are dried in a vacuum oven at 150°C prior to the experiments. The complexation reactions were performed under argon (Ar) atmosphere.

Instrumentation

X-ray crystallography

X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N2 device, using Cu-Kα radiation (λ = 1.54178 Å). The crystal-detector distance was 40mm. The cell parameters were determined (APEX2 software) [1] from reflections taken from three sets of 20 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-2014 [2]. The refinement and all further calculations were carried out using SHELXL-2014 [2]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. A semi-empirical absorption correction was applied using SADABS in APEX2 [1]; transmission factors: Tmin/Tmax = 0.5220/0.7528. The atoms O4, C28 and the hydrogens of C27 are disordered over two positions. The oxygen atoms O9, O10, O11, O12 from one counter-anion are disordered over two positions.

Magnetic measurements

All herein reported magnetic measurements were performed on a MPMS-XL5 SQUID magnetometers (Quantum Design). For the standard magnetic measurement in the dark, the temperature dependent magnetization was recorded at B_{DC} = 0.1 T external magnetic field. The temperature sweeping rate was 1 K min^{-1} and it was the same for the cooling and heating modes. Gelatine capsules were used as sample holders in the temperature range 5 ↔ 300 K. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants.

DSC and SAXS measurements

DSC measurements were performed with a TA Instruments DSCQ2000 instrument operated at a scanning rate of 2 and 8 K min^{-1} with Liquid Nitrogen Cooling System (LNCS) on heating and on cooling. SAXS patterns were obtained with a linear monochromatic Cu $K_{\alpha 1}$ beam (λ= 1.5405 Å) obtained using a sealed-tube generator equipped with a bent quartz monochromator and a curved Inel CPS 120 counter gas filled detector; periodicities up to 70 Å can be measured, and the sample temperature controlled to within ±0.01 °C from 20 to 200 °C. The sample was filled home-made sealed cells with aluminium windows and exposure times were of 6 hours.

Synthesis of the complex 1: Ligand, 1-bpp-COOEt, (0.058g, 0.2 mmol) was solubilized in 10 ml of ACN. To this $[Fe(ClO_4)_2].6H_2O$ (0.1 mmol) was added and the mixture was stirred at RT for 2 hrs under Ar atmosphere. The reaction mixture was filtered and portioned into test tubes followed by diffusion of ether over a period of 2-3 weeks yielded good quality crystals suitable for X-ray analysis.

Characterization: Yield of the complex: 40 mg (46%). Elemental analysis: calc for $C_{28}H_{26}Cl_2FeN_{10}O_{12}.CH_3CN$: C, 41.78; H, 3.39; N; 17.87. Found: C, 41.47, H, 3.38, N, 17.66. ESI-MS: calculated for $C_{28}H_{26}ClFeN_{10}O_8$ $[M+ClO_4]^+$: 721.0968, found: 721.1034.

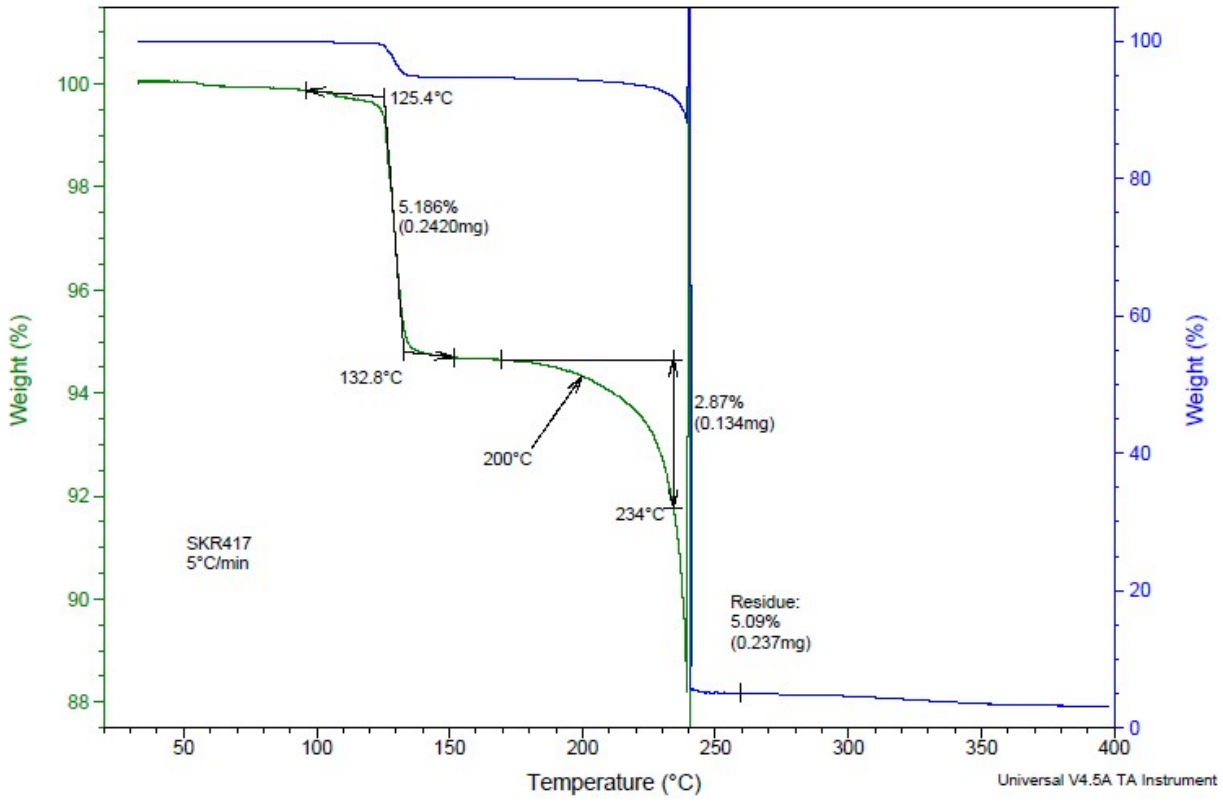

Figure S1. Thermogravimetric analysis (TGA) of the complex [Fe(1-BPP $COOC_2H_5)_2](ClO_4)_2.CH_3CN$ (**1**) indicating loss of acetonitrile solvent molecule around 125°C. A 5.2% weight loss in the temperature range of 125°C -133°C corresponds well with the 4.8% expected weight loss due to the loss of the acetonitrile solvent.

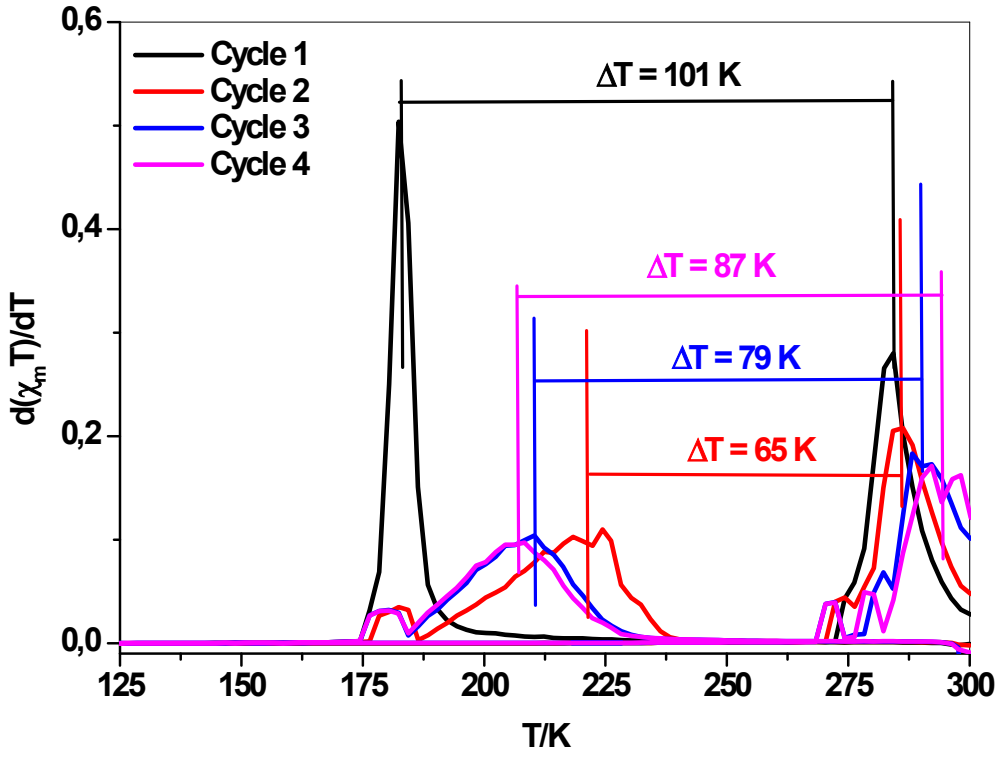

Figure S2. First derivative of the χT vs. T plots used to calculate the thermal hysteresis widths (ΔT).

Table S1. Parameters associated with the SCO transition of the complex [Fe(1-BPP - $COOC_2H_5)_2$]$(ClO_4)_2$.CH_3CN (**1**).

Cycle	χ_mT (HS)/ cm^3Kmol^{-1}	$T_{1/2}$/K	ΔT/K
1	3.38	233	101
2	3.24	254	65
3	3.01	250	79
4	2.87	251	87

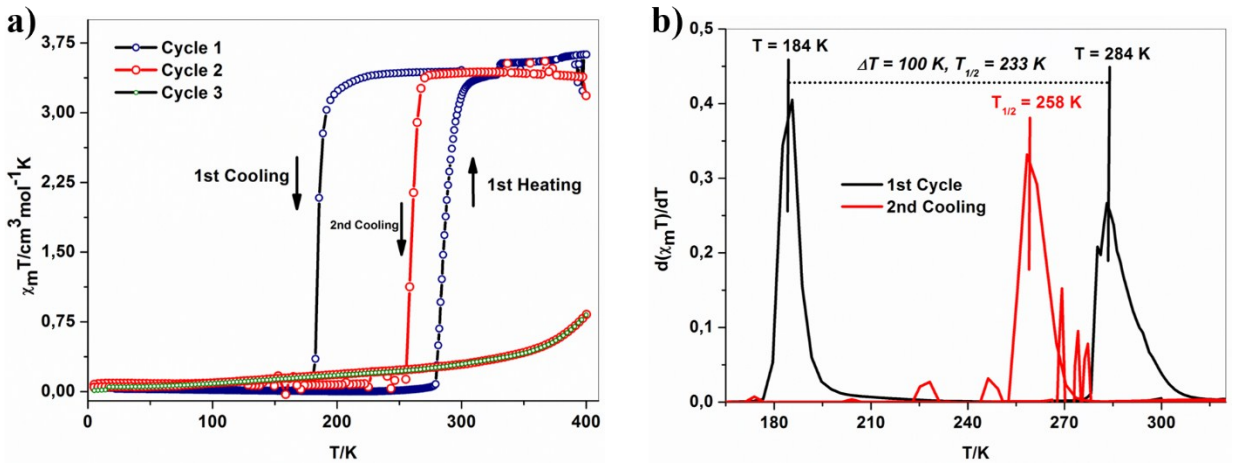

Figure S3. (a) $\chi_m T$ vs. T plot of the freshly prepared complex **1**, first cooling of the sample was started at 300 K and (b) First derivative of the χ_mT vs. T plots showing the measured thermal hysteresis width (ΔT) and $T_{1/2}$ values.

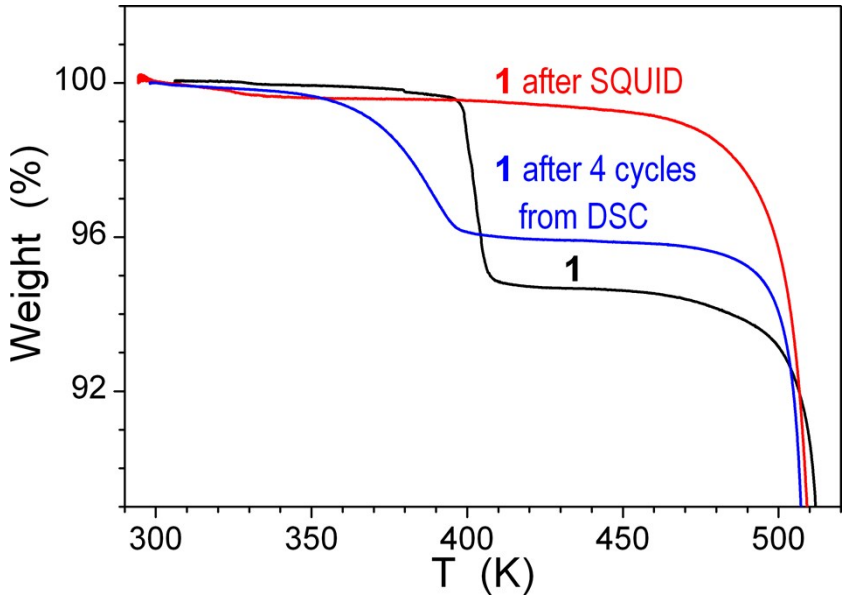

Figure S4. Comparison between the TGA of complex **1** before), after four cool-heat DSC cycles at 2K/min (blue) performed in the 143-323 K range, and after SQUID measurements (red) performed in the 5-400 K range. The two co-crystallized solvent molecules of the pristine complex are released at 398 K, while solvent gradually evaporates from 350 K after DSC cycles and is not present in the sample cycled up to 400 K with SQUID.

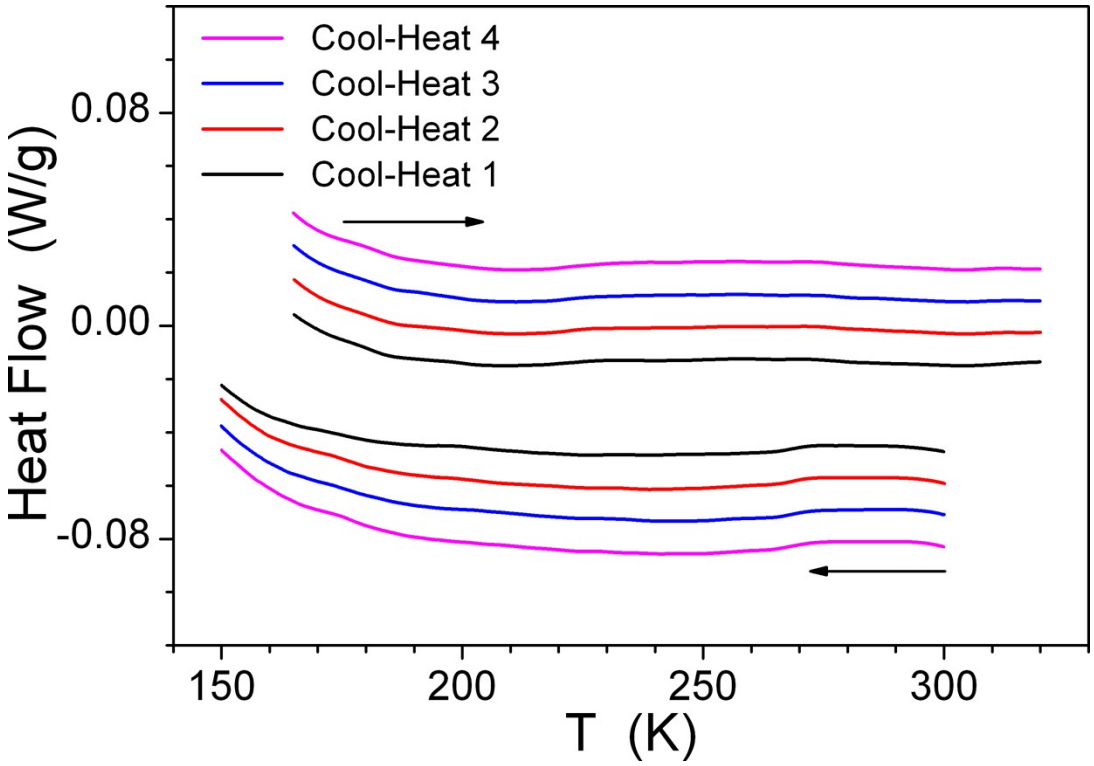

Figure S5. DSC analysis at 8 K/min of the complex **1** after SQUID measurements performed in the 5-400 K range (endotherm up).

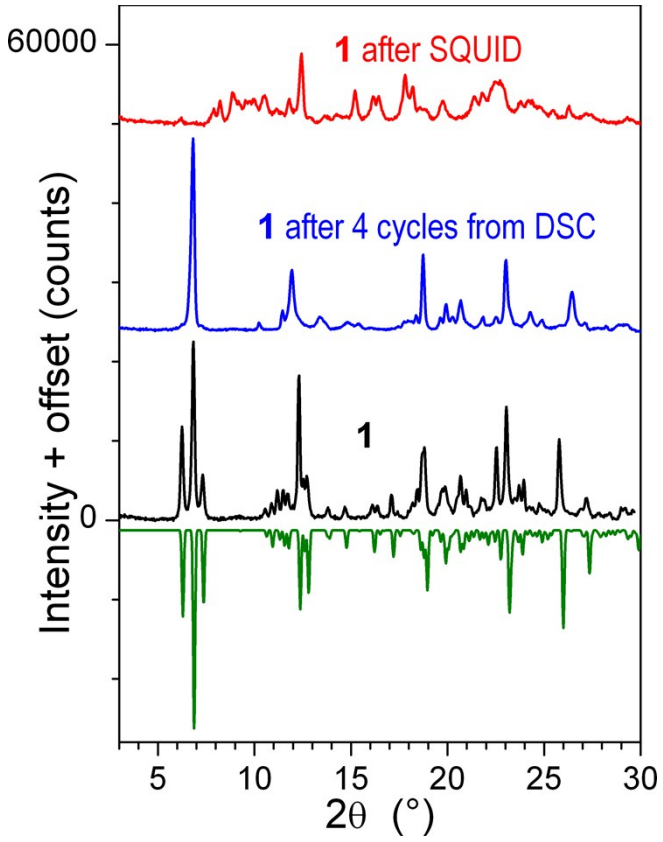

Figure S6. Powder X-ray diffraction patterns of complex **1** before (black), after four cool-heat DSC cycles at 2K/min (blue) performed in the 143-323 K range, and after SQUID measurements (red) performed by cycling the sample in the 5-400 K range. Note the excellent match between the crystalline sample used to perform SQUID measurements and the pattern simulated from the single crystal X-ray diffraction studies (green), and the change of structure after DSC and SQUID cool-heat cycles.

Table S2. Parameters obtained from DSC measurements. Average values obtained from the cool-heat cycles are reported for each cycle.

Cycle	Scan rate = 2 K/min				Scan rate = 8 K/min			
	$T_{1/2}$[a]	ΔT[a]	ΔH[b]	ΔS[c]	$T_{1/2}$[a]	ΔT[a]	ΔH[b]	ΔS[c]
1	231	104	7.15	32.35	230	113	6.3	28.9
2	243	86	7.2	30.58	244.5	89	6.25	26.32
3	241	98	7.15	30.9	242	98	6.1	26.19
4	240.5	103	7.15	31.11	239.5	103	6.1	26.68

[a] in K; [b] in kJ/mol; [c] in J/Kmol

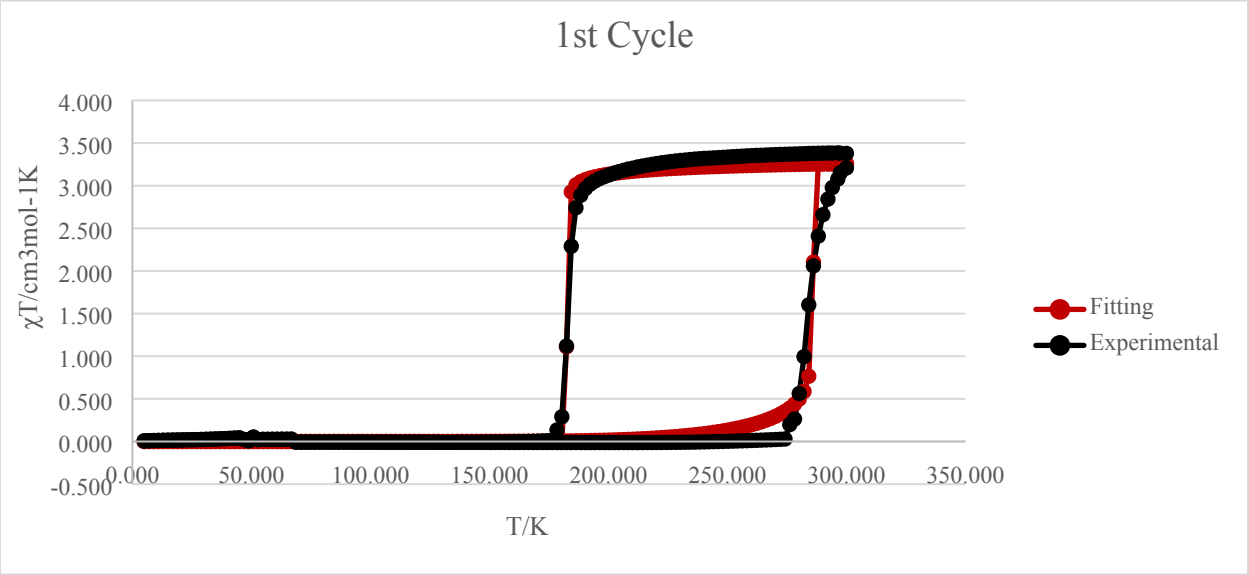

Figure S7. A fitting of the χT curve obtained in the first cycle, using the Slichter-Drickamer (SD) model. Black and red curves represent experimental and fitted curves, respectively.

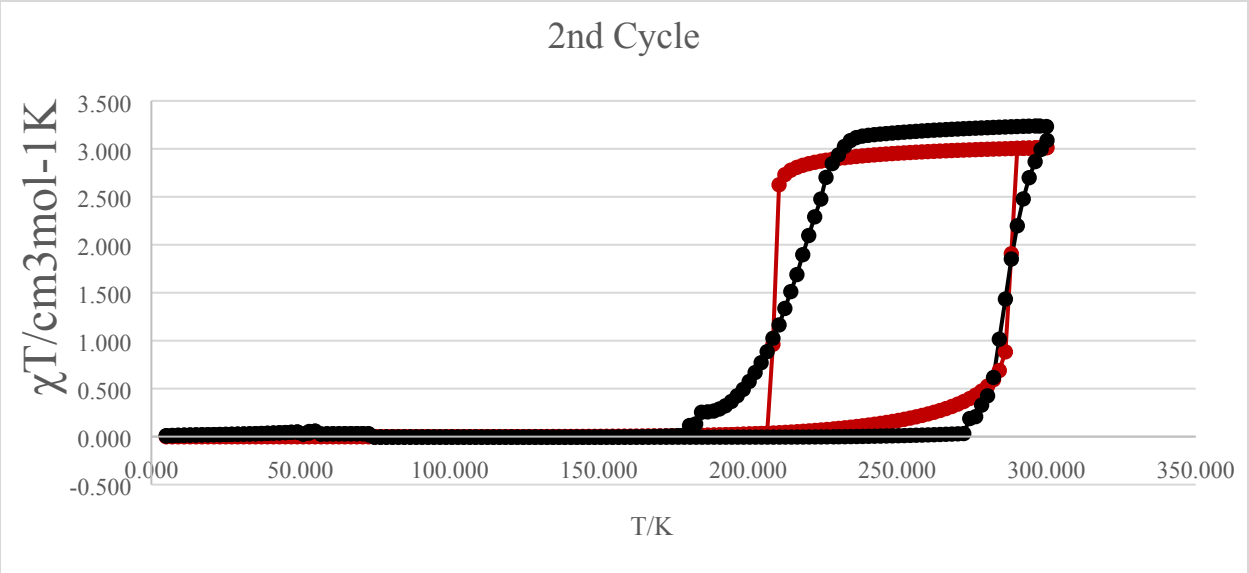

Figure S8. A fitting of the χT curve obtained in the second cycle, using the Slichter-Drickamer (SD) model. Black and red curves represent experimental and fitted curves, respectively.

Table S3 Crystallographic data of the complex[a]

Formula	$C_{30}H_{29}Cl_2FeN_{11}O_{12}$	V/Å^3	1864.2 (4)
FW/g.mol^{-1}	862.39	Z	2
T/K	253	ρ/g.cm^{-3}	1.536
Crystal System	Triclinic	μ/mm^{-1}	5.230
Space group	*P -1*	θ min-max/°	3.150 – 67.035
a/Å	9.5859(13)	Reflns collected	27020
b/Å	13.8752(17)	Indep Reflns	6492
c/Å	15.248(2)	Parameters	515
α/°	67.744 (7)	GOF on F^2	1.068
β/°	83.316(8)	R1	0.0763
γ/°	87.620(8)	wR2	0.2390

[a] ccdc 1589139

References

1. “M86-E01078 APEX2 User Manual”, Bruker AXS Inc., Madison, USA, 2006.

2. G. M. Sheldrick, *Acta Cryst.* 2008, **A64,** 112-122.