Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Material for:

Abrupt two-step and symmetry breaking spin crossover in an iron(III) complex: an exceptionally wide [LS-HS] plateau

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1. General Remarks

All reactions were carried out at room temperature in air. With the exception of Hqsal-Br,[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 $[Fe(qsal\text{-}Br)_2]NO_3 \cdot 2MeOH$: Hqsal-Br (131 mg, 0.4 mmol) was dissolved in CH_2Cl_2 (2 ml) giving an orange solution. NEt_3 (56 µl, 0.4 mmol) was added resulting in a change to dark orange. CH_3OH (3 ml) was layered on top of the Hqsal-Br solution. In a separate flask, $Fe(NO_3)_3 \cdot 9H_2O$ (83 mg, 0.2 mmol) was dissolved in CH_3OH (5 ml) giving a yellow solution. The yellow solution was then layered on top of the blank CH_3OH and left for 4 days. The black crystals formed were washed with hexane (2 x 1 ml) and air dried (41 mg, 24%). IR (KBr): ν_{max} = 3052 ($\upsilon_{Ar\text{-}H}$), 1597 ($\upsilon_{C=N}$), 1365 ($\upsilon_{N\text{-}O}$), cm^{-1}. (ESI): m/z = 707.8 $[Fe(qsal\text{-}Br)_2]^+$. Anal. Calc. for $C_{34}H_{28}Br_2FeN_5O_7$: C, 48.95; H, 3.38; N, 8.39. Found: C, 48.31; H, 2.68; N, 8.66%.

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 300–4 K. The polycrystalline samples were placed in gel capsules and care was taken to allow long thermal equilibration times at each temperature point.

The Mössbauer spectroscopic sample was enclosed in Vaseline and rapidly frozen in liquid nitrogen. The sample was then placed in the spectrometer running at 5.1 K. This rapidly quenched sample was then warmed slowly to 100 K, 170K and 294 K. A small magnetic field of 47 mT was applied parallel to the γ-ray. Spectra were calibrated with α-Fe and isomer shifts are quoted relative to α-Fe at room temperature.

DSC measurements were recorded on a TA Instruments Q100 differential scanning calorimeter between 275 and 125 K.

2. X-ray Crystallography

Crystal data and data processing parameters for the structures of $[Fe(qsal\text{-}Br)_2]NO_3 \cdot 2MeOH$ are given in Table S1. X-ray quality crystals of the complex were grown by layering a solution of $Fe(NO_3)_3 \cdot 9H_2O$ in MeOH over a solution of Hqsal-Br and NEt_3 in CH_2Cl_2. Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen. The diffraction data were collected initially at 123 K on a Bruker APEXII area detector with graphite monochromated MoKα (λ = 0.71073 Å).[2] The sample was then warmed to 175, 220 and 280 K collecting data at each of these temperatures. The sample was then cooled to 175 and 123 K and data again collected. Finally, the sample was cooled to 100 K and then warmed again to 150 K with data collected at these two temperatures to confirm the reducibility of the spin crossover. After data collection, in each case an empirical absorption correction (SADABS) was applied,[3] and the structures were then solved by direct methods and refined on all F^2 data using the SHELX suite of programs.[4] 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 × (aromatic CH) or 1.5 × (CH_3, OH) the equivalent isotropic thermal parameters of their parent carbon or oxygen atoms. Pictures were generated using DIAMOND or OLEX-2.[5,6]

References

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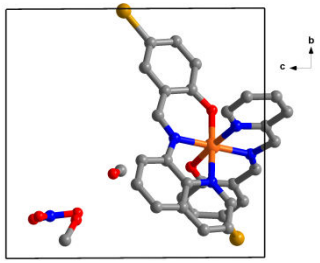
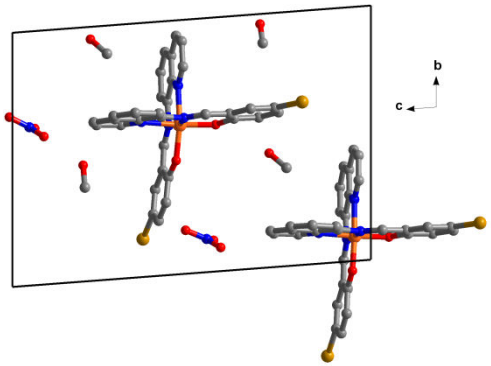
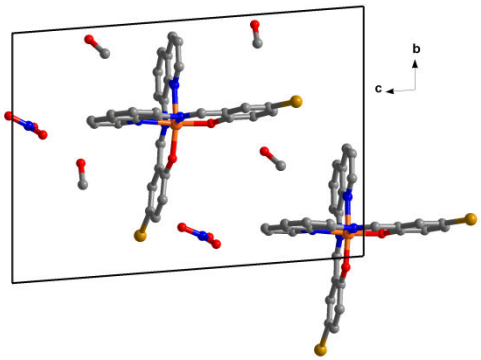
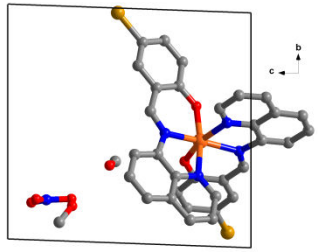
Table S1 Crystallographic data and structure refinement for **1**.

		Warm cycle 1			Cool cycle 1		Warm cycle 2	
	123 K/LS	**175 K/1LS-1HS**	**220 K/1LS-1HS**	**280 K/1HS**	**175 K/1LS-1HS**	**123 K/1LS**	**100 K/1LS**	**150 K/1LS-1HS**
Empirical Formula	$C_{34}H_{28}Br_2FeN_5O_7$							
Molecular weight/ $gmol^{-1}$	834.28							
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	12.1319 (6)	12.5838 (6)	12.6135 (11)	12.0223 (5)	12.5977 (5)	12.0359 (7)	12.0805 (10)	12.5767 (6)
b / Å	12.1588 (8)	13.7010 (7)	13.7534 (13)	12.3163 (6)	13.7134 (6)	12.1457 (7)	12.1194 (10)	13.6774 (8)
c / Å	12.5189 (8)	19.9499 (9)	19.9632 (15)	12.7577 (5)	19.9391 (9)	12.4988 (7)	12.4856 (11)	19.9247 (11)
α / °	82.798 (2)	90.858 (2)	90.999 (4)	80.991 (2)	90.838 (2)	83.175 (3)	83.110 (5)	90.818 (3)
β / °	69.275 (2)	107.360 (2)	107.339 (4)	69.414 (2)	107.328 (2)	69.400 (3)	69.235 (4)	107.363 (3)
γ / °	68.558 (2)	100.806 (2)	100.541 (4)	69.182 (2)	100.883 (2)	68.733 (3)	68.622 (5)	100.947 (3)
Cell volume / $Å^3$	1607.60 (17)	3215.4 (3)	3240.5 (5)	1651.88 (12)	3219.9 (2)	1593.75 (16)	1591.6 (2)	3202.5 (3)
Z	2	4	4	2	4	2	2	4
Absorption coefficient / mm^{-1}	3.014	3.013	2.990	2.933	3.009	3.040	3.044	3.026
Reflections collected	12104	26994	26902	17423	33875	20130	17210	38082
Independent reflections, R_{int}	7208, 0.0273	14749, 0.0410	14822, 0.0405	8939, 0.0391	14599, 0.0515	8849, 0.0409	8704, .0358	17801, 0.0558
Max. and min. transmission	0.7137 and 0.5840	0.7526 and 0.5840	0.7542 and 0.5862	0.6674 and 0.4267	0.8170 and 0.5844	0.8154 and 0.5815	0.7928 and 0.5166	0.8161 and 0.5829
Restraints/parameters	0/446	0/891	0/891	0/446	0/891	0/446	0/446	0/891
Final R indices [$I>2\sigma(I)$]: R_1, wR_2	0.0481, 0.1227	0.0493, 0.1128	0.0544, 0.1230	0.0499, 0.1292	0.0504, 0.1119	0.0462, 0.1075	0.0424, 0.0951	0.0549, 0.1242
CCDC No.	1029068	1029073	1029074	1029075	1029070	1029069	1029071	1029072

123 K	175 K	220 K	280 K
			

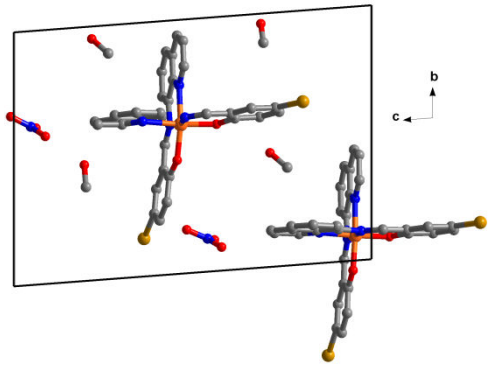
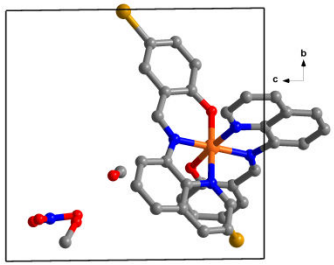
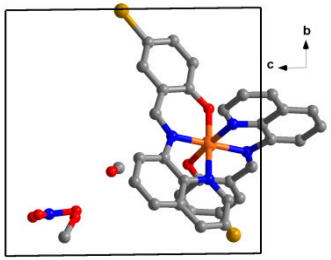
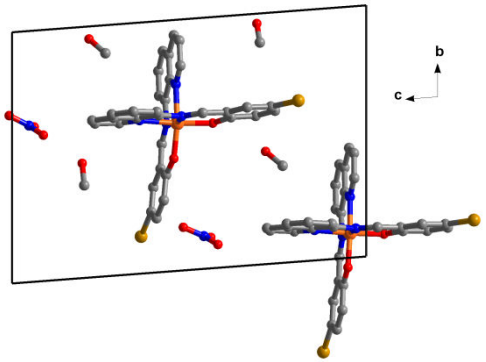
175 K	123 K	100 K	150 K
			

Table S2 Fe-N/O bond length and octahedral distortion at various temperatures for **1**.

	Warm cycle 1				Cool cycle 1		Warm cycle 2	
	123 K	**175 K**	**220 K**	**280 K**	**175 K**	**123 K**	**100 K**	**150 K**
Fe1-O1/Å	1.888(3)	1.906(2)	1.905(2)	1.905(2)	1.908(3)	1.879(2)	1.8792(19)	1.905(2)
Fe1-O2/Å	1.881(3)	1.907(3)	1.910(3)	1.905(2)	1.912(3)	1.874(2)	1.8718(18)	1.906(3)
Fe1-O_{av}/Å	1.885	1.907	1.908	1.905	1.910	1.877	1.876	1.906
Fe1-N1/Å	1.951(3)	2.101(3)	2.097(3)	2.102(2)	2.103(3)	1.943(2)	1.944(2)	2.094(3)
Fe1-N2/Å	1.990(3)	2.142(3)	2.147(3)	2.140(3)	2.145(3)	1.978(2)	1.981(2)	2.140(3)
Fe1-N3/Å	1.951(3)	2.103(3)	2.099(3)	2.104(2)	2.099(3)	1.943(2)	1.944(2)	2.094(3)
Fe1-N4/Å	1.983(3)	2.132(3)	2.137(3)	2.134(3)	2.136(3)	1.976(2)	1.972(2)	2.134(3)
Fe1-N_{av}/Å	1.969	2.120	2.120	2.120	2.121	1.960	1.960	2.120
Fe2-O3/Å		1.874(3)	1.878(3)		1.880(3)			1.875(2)
Fe2-O4/Å		1.874(2)	1.872(3)		1.874(2)			1.872(2)
Fe2-O_{av}/Å		1.874	1.875		1.877			1.874
Fe2-N5/Å		1.942(3)	1.962(3)		1.939(3)			1.935(3)
Fe2-N6/Å		1.976(3)	1.998(4)		1.980(3)			1.979(3)
Fe2-N7/Å		1.939(3)	1.959(3)		1.940(3)			1.936(3)
Fe2-N8/Å		1.976(3)	2.004(3)		1.982(3)			1.978(3)
Fe2-N_{av}/Å		1.958	1.981		1.960			1.957
Σ-Fe1, Fe2	44, -	66, 44	66, 42	63, -	65, 44	44, -	44, -	64, 45
Θ-Fe1, Fe2	65, -	189, 65	191, 73	183, -	190, 65	66, -	65, -	187, 64

Table S3 π-π and C-H···O interactions in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ which form the 1D chains at multiple temperatures.

Interactions	100 K	123 K	123C K	280 K	150 K	175 K	175C K	220 K
		1D chain along c axis				1D chain along a axis		
π-π interactions								
π-π (Type A)	3.205	3.213	3.208	3.286	3.226	3.234	3.232	3.247
π-π (Type B)	3.302	3.309	3.296	3.391	3.363	3.363	3.370	3.373
C-H···O interactions								
O1···H21	2.664(2)	2.662(2)	2.679(2)	2.729(3)	2.656(3)	2.663(3)	2.660(3)	2.679(3)
O1···C21	3.491(3)	3.492(5)	3.503(4)	3.555(5)	3.500(5)	3.505(5)	3.504(5)	3.513(6)
∠ O1···H21-C21	145.7(2)	146.2(2)	145.6(2)	148.6(2)	148.3(3)	147.9(2)	148.3(3)	148.0(3)
O2···H9	2.638(2)	2.676(3)	2.628(3)	2.594(3)	2.491(3)	2.495(3)	2.493(3)	2.523(3)
O2···C9	3.484(5)	3.517(5)	3.470(5)	3.432(5)	3.336(5)	3.344(5)	3.339(5)	3.361(6)
∠ O2···H9-C9	148.5(2)	147.9(2)	148.0(2)	150.1(3)	148.0(2)	149.0(2)	148.4(2)	148.5(3)
O2···H7	2.612(2)	2.622(3)	2.604(2)	2.808(3)	2.687(3)	2.691(3)	2.699(3)	2.722(3)
O2···C7	3.475(4)	3.480(5)	3.471(5)	3.627(5)	3.536(5)	3.536(5)	3.548(5)	3.557(5)
∠ O2···H7-C7	151.2(2)	150.3(2)	151.9(2)	147.7(2)	149.1(2)	148.6(2)	149.2(3)	148.3(3)

Table S3 π-π and C-H···O interactions in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ which form the 1D chains at multiple temperatures (Continued).

Interactions	100 K	123 K	123C K	280 K	150 K	175 K	175C K	220 K
	1D chain along c axis				1D chain along a axis			
π-π interactions								
π-π (Type A, LS)					3.218	3.230	3.232	3.242
π-π (Type B, LS)					3.295	3.300	3.302	3.311
C-H···O interactions								
O4···H37					2.701(3)	2.706(3)	2.711(3)	2.729(3)
O4···C37					3.527(5)	3.525(5)	3.536(5)	3.537(6)
∠ O4···H37-C37					145.7(2)	144.8(2)	145.6(3)	144.5(3)
O3···H57					2.689(3)	2.691(3)	2.694(3)	2.673(3)
O3···C57					3.543(5)	3.547(5)	3.544(5)	3.527(6)
∠ O3···H57-C57					149.8(2)	150.0(2)	149.5(2)	151.4(3)
O3···H55					2.638(3)	2.649(3)	2.656(3)	2.681(3)
O3···C55					3.306(5)	3.517(5)	3.525(5)	3.542(5)
∠ O3···H55-C55					152.4(2)	152.2(2)	152.5(3)	152.5(3)

Table S4 P4AE interactions within $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures.

Interactions P4AE	**100 K**	**123 K**	**123C K**	**280 K**	**150 K**	**175 K**	**175C K**	**220 K**
C-H···π	2.596	2.604	2.600	2.679	2.592	2.608	2.611	2.622
C-H···π	2.596	2.604	2.600	2.679	2.641	2.656	2.649	2.674
π-π	3.586	3.604	3.585	3.710	3.626	3.641	3.635	3.655

Table S5 Bond lengths of the NO_3 anions and MeOH solvent molecules in **1**.

	Warm cycle 1				**Cool cycle 1**		**Warm cycle 2**	
	123 K	**175 K**	**220 K**	**280 K**	**175 K**	**123 K**	**100 K**	**150 K**
N9—O5	1.242(4)	1.243(4)	1.236(5)	1.240(4)	1.241(4)	1.242(3)	1.242(3)	1.237(4)
N9—O6	1.251(5)	1.238(4)	1.235(5)	1.234(4)	1.237(4)	1.242(3)	1.245(3)	1.236(4)
N9—O7	1.272(4)	1.263(4)	1.252(5)	1.243(4)	1.257(4)	1.269(3)	1.267(3)	1.267(4)
O11—C65	1.408(5)	1.396(5)	1.386(6)	1.370(6)	1.399(5)	1.414(4)	1.415(3)	1.398(5)
O12—C66	1.421(6)	1.397(6)	1.398(7)	1.388(6)	1.401(5)	1.414(5)	1.404(4)	1.398(5)
N10—O8		1.245(4)	1.247(5)		1.248(4)			1.246(4)
N10—O10		1.239(4)	1.228(5)		1.238(4)			1.243(4)
N10—O9		1.253(4)	1.250(5)		1.258(4)			1.257(4)
O13—C67		1.409(5)	1.397(6)		1.412(5)			1.411(5)
O14—C68		1.415(5)	1.407(6)		1.412(5)			1.418(5)

Table S6 H bonding interactions within $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures.

Interactions	100 K	123 K	123C K	280 K	150 K	175 K	175C K	220 K
H11A···O12	1.868(3)	1.895(4)	1.887(2)	1.929(4)	1.851(33)	1.853(4)	1.858(3)	1.859(4)
O11···O12	2.680(3)	2.689(5)	2.683(3)	2.707(6)	2.676(5)	2.678(5)	2.675(5)	2.676(6)
∠ O11-H11A···O12	162.1(2)	157.2(3)	157.7(2)	158.1(3)	167.1(2)	166.9(2)	163.8(3)	167.8(3)
H12···O7	1.896(2)	1.903(3)	1.895(2)	1.950(2)				
O12···O7	2.727(3)	2.731(4)	2.725(3)	2.769(4)				
∠ O12-H12···O7	170.1(2)	167.8(3)	169.3(2)	176.2(3)				
H12···O9					1.904(2)	1.911(3)	1.898(3)	1.916(3)
O12···O9					2.735(4)	2.741(4)	2.736(4)	2.732(4)
∠ O12-H12···O9					169.6(2)	169.2(3)	176.0(3)	167.4(3)
H13A···O14					1.923(3)	1.898(3)	1.894(3)	1.900(4)
O13···O14					2.705(4)	2.704(5)	2.704(4)	2.712(5)
∠ O13-H13A···O14					154.5(2)	160.6(2)	161.7(2)	165.3(3)
H14A···O7					1.921(2)	1.912(2)	1.916(2)	1.936(3)
O14···O7					2.742(4)	2.750(4)	2.745(4)	2.760(4)
∠ O14-H14A···O7					165.5(2)	175.5(2)	168.1(2)	172.0(3)

Table S7 C-H···O interactions involving the nitrate anion in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures.

Interactions	100 K	123 K	123C K	280 K	150 K	175 K	175C K	220 K
O5···H7	2.849(2)	2.842(3)	2.855(2)	2.671(3)	2.649(3)	2.656(3)	2.663(3)	2.671(4)
O5···C7	3.093(3)	3.100(4)	3.096(3)	2.989(4)	2.934(5)	2.946(5)	2.950(5)	2.671(5)
∠ O5···H7-C7	95.8(2)	96.7(2)	95.6(2)	100.9(2)	97.9(3)	98.3(3)	98.0(3)	99.0(3)
O5···H18	2.439(3)	2.444(4)	2.432(3)	2.621(4)	2.532(3)	2.538(4)	2.547(4)	2.570(4)
O5···C18	3.299(4)	3.3071(7)	3.294(5)	3.520(7)	3.456(5)	3.458(6)	3.469(6)	3.479(7)
∠ O5···H18-C18	150.2(2)	151.1(3)	151.0(2)	162.9(3)	164.2(2)	163.3(3)	98.0(3)	162.6(3)
O5···H31	2.358(3)	2.382(4)	2.369(3)	2.560(4)	2.493(3)	2.512(4)	2.504(4)	2.520(4)
O5···C31	3.257(4)	3.282(6)	3.268(5)	3.447(6)	3.398(5)	3.413(6)	3.408(6)	3.413(7)
∠ O5···H31-C31	157.8(2)	158.2(2)	157.8(2)	159.4(3)	159.0(2)	158.5(254)	158.9(3)	158.7(3)
O6···H26	2.436(2)	2.432(4)	2.438(3)	2.470(4)	2.390(4)	2.392(4)	2.395(4)	2.424(4)
O6···C26	3.268(5)	3.265(6)	3.272(5)	3.309(6)	3.232(6)	3.236(7)	3.240(6)	3.263(7)
∠ O6···H26-C26	146.2(2)	146.2(3)	146.1(2)	150.2(3)	147.6(3)	147.8(3)	148.2(3)	148.5(3)
O7···H31	2.577(2)	2.601(3)	2.593(2)	2.626(3)	2.577(2)	2.600(3)	2.581(2)	2.594(3)
O7···C31	3.104(3)	3.119(5)	3.120(4)	3.199(5)	3.111(4)	3.125(5)	3.122(4)	3.137(6)
∠ O7···H31-C31	115.3(2)	114.7(2)	115.4(2)	120.4(2)	147.6(3)	115.3(3)	116.4(3)	117.2(3)

Table S7 C-H···O interactions involving the nitrate anion in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures (Continued).

Interactions	100 K	123 K	123C K	280 K	150 K	175 K	175C K	220 K
O8···H55					2.871(3)	2.878(3)	2.879(3)	2.865(4)
O8···C55					3.115(5)	3.126(5)	3.128(5)	3.117(5)
∠ O8···H55-C55					95.9(2)	96.2(3)	96.2(3)	96.7(3)
O8···H34					2.446(3)	2.377(4)	2.475(3)	2.499(4)
O8···C34					3.311(5)	3.276(6)	3.336(6)	3.360(7)
∠ O8···H34-C34					151.3(2)	151.2(3)	150.9(3)	152.6(3)
O8···H47					2.367(3)	2.377(4)	2.382(3)	2.416(4)
O8···C47					3.266(5)	3.276(6)	3.281(5)	3.306(7)
∠ O8···H47-C47					157.7(2)	157.8(3)	157.8(3)	157.8(3)
O10···H42					2.445(3)	2.449(4)	2.463(4)	2.478(4)
O10···C42					3.292(5)	3.293(7)	3.306(6)	3.315(7)
∠ O10···H42-C42					148.4(3)	147.9(3)	147.9(3)	148.4(3)
O9···H47					2.601(2)	2.606(3)	2.618(3)	2.631(3)
O9···C47					3.148(4)	3.156(5)	3.164(5)	3.178(6)
∠ O9···H47-C47					117.0(2)	117.2(3)	117.0(3)	117.6(3)

Table S8 C-H···O interactions involving MeOH in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures.

Interactions	100 K	123 K	123C K	280 K	150 K	175 K	175C K	220 K
O11···H2	2.562(2)	2.572(3)	2.558(2)	2.751(4)	2.675(4)	2.679(4)	2.697(4)	2.718(4)
O11···C2	3.377(3)	3.392(5)	3.374(4)	3.587(6)	3.518(5)	3.525(5)	3.540(5)	3.552(6)
∠ O11···H2-C2	143.8(1)	144.6(3)	144.2(2)	150.2(2)	148.1(3)	148.5(3)	148.3(3)	148.3(3)
O11···H15	2.484(2)	2.514(4)	2.504(3)	2.904(6)	2.861(3)	2.862(4)	2.854(4)	2.872(5)
O11···C15	3.390(4)	3.420(6)	3.409(5)	3.802(7)	3.389(5)	3.784(6)	3.775(7)	3.782(7)
∠ O11···H15-C15	159.1(2)	159.3(2)	159.2(2)	162.9(2)	145.5(3)	164.1(3)	163.7(3)	163.2(3)
O11···H23	2.580(3)	2.588(4)	2.575(3)	2.507(3)	2.452(3)	2.470(3)	2.471(3)	2.485(3)
O11···C23	2.889(4)	2.898(6)	2.879(5)	2.861(7)	2.833(5)	2.848(5)	2.844(5)	2.855(6)
∠ O11···H23-C23	98.7(2)	99.3(3)	98.9(2)	102.9(3)	103.8(3)	103.6(2)	103.3(2)	103.5(2)
O13···H50					2.562(3)	2.575(3)	2.579(3)	2.602(3)
O13···C50					3.389(5)	3.404(5)	3.402(5)	3.422(6)
∠ O13···H50-C50					145.5(3)	145.9(3)	145.1(3)	146.0(3)
O13···H63					2.512(4)	2.522(4)	2.528(4)	2.599(4)
O13···C63					3.409(5)	3.421(5)	3.425(6)	3.490(6)
∠ O63···H63-C63					157.6(3)	157.9(3)	157.6(3)	158.5(3)
O13···H39					2.577(3)	2.579(3)	2.570(3)	2.569(3)
O13···C39					2.863(5)	2.868(5)	2.865(5)	2.873(5)
∠ O13···H39-C39					97.6(2)	97.9(2)	98.3(2)	99.2(2)

Table S9 Additional interactions involving nitrate and MeOH in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures.

Interactions	**100 K**	**123 K**	**123C K**	**280 K**	**150 K**	**175 K**	**175C K**	**220 K**
NO_3 and MeOH interactions								
Br2···H3	3.0237(4)	3.0251(5)	3.0345(4)	3.1670(5)				
Br2···C3	3.904(3)	3.905(4)	3.908(4)	3.925(4)				
∠ Br2···H3-C3	154.7(2)	154.6(2)	153.6(2)	139.9(2)				
Br2···O12	3.138(3)	3.157(4)	3.144(3)	3.163(5)				
Br2···O14					2.974(4)	2.989(4)	2.990(3)	3.026(4)
Br3···O12					3.223(4)	3.236(4)	3.227(4)	3.236(4)
Br3···H3					3.0296(4)	3.0358(5)	3.0402(5)	3.0660(5)
Br3···C3					3.851(4)	3.855(4)	3.863(4)	3.863(4)
∠ Br3···H3-C3					145.6(2)	145.3(2)	145.9(3)	144.7(3)
O6···H29	2.720(3)	2.715(4)	2.7120(3)	2.691(5)	2.638(4)	2.660(4)	2.665(4)	2.668(4)
O6···C29	3.342(4)	3.348(6)	3.351(4)	3.327(7)	3.294(6)	3.304(6)	3.311(6)	3.312(6)
∠ O6···H29-C29	123.7(2)	125.7(3)	124.5(2)	126.3(3)	126.5(3)	125.5(3)	125.7(3)	126.2(3)

Table S9 Additional interactions involving nitrate and MeOH in $[Fe(qsal\text{-}Br)_2]\cdot NO_3\cdot 2MeOH$ at multiple temperatures (Continued).

Interactions	**100 K**	**123 K**	**123C K**	**280 K**	**150 K**	**175 K**	**175C K**	**220 K**
NO_3 and MeOH interactions								
O7···H30	2.815(2)	2.726(4)	2.692(3)	2.764(4)	2.632(3)	2.654(3)	2.628(3)	2.678(4)
O7···C30	3.218(3)	3.337(6)	3.311(5)	3.470(6)	3.316(5)	3.336(5)	3.327(5)	3.373(6)
∠ O7···H30-C30	106.6(2)	122.8(3)	123.4(2)	133.5(3)	129.3(2)	129.3(2)	130.8(2)	131.3(3)
N9···H30	3.576(3)	2.788(3)	2.780(2)	2.751(3)	2.704(4)	2.726(4)	2.702(4)	2.732(4)
N9···C30	3.979(4)	3.297(6)	3.290(4)	3.362(6)	3.261(6)	3.283(6)	3.274(6)	3.308(6)
∠ N9···H30-C30	108.4(2)	114.5(3)	114.5(2)	124.1(3)	118.1(3)	118.2(3)	119.3(3)	120.4(3)
O10···H45						2.687(3)	2.699(4)	2.709(4)
O10···C45						3.323(5)	3.334(6)	3.341(6)
∠ O10···H45-C45						124.9(2)	124.8(3)	125.3(3)
O9···H46						2.749(3)	2.760(4)	2.787(4)
O9···C46						3.387(5)	3.403(6)	3.437(6)
∠ O9···H46-C46						125.2(2)	125.8(3)	127.1(3)
N10···H46						2.775(4)	2.785(4)	2.807(4)
N10···C46						3.322(6)	3.336(6)	3.363(7)
∠ N10···H46-C46						117.5(3)	117.9(3)	118.8(3)

Table S10 Fe-Fe distance from P4AE and Br···H-C linking along b axis at 123 and bc plane at other temperatures.

	123 K	**175 K**	**220K**	**280 K**	**175 K**	**123 K**	**100 K**	**150 K**
Fe1-Fe2 (P4AE)	8.8551(9)	8.9598(8)	8.9943(10)	9.1222(9)	8.9589(8)	8.8114(8)	8.8116(9)	8.9417(9)
Fe1-Fe2 (Br···H-C)	12.159(1)	12.298(1) 12.076(1)	12.316(1) 12.127(1)	12.316(1)	12.295(1) 12.0743(9)	12.146(1)	12.119(1)	12.253(1) 11.754(1)

Table S11 ^{57}Fe Mössbauer parameters for **1**.

Temperature (K)	**Species**	**δ (mm/s)**	**ΔE_Q (mm/s)**	**Γ_L (mm/s)**	**Γ_R (mm/s)**	**I (%)**
5.1	LS	0.21	2.77	0.27	0.28	100
100	LS	0.21	2.77	0.27	0.28	100
170	LS	0.18	2.72	0.28	0.27	78
	HS	0.44	0.69	0.42	0.62	22
294	LS	0.12	2.52	0.37	0.35	61
	HS	0.33	0.53	0.44	0.63	39

Supporting Figures

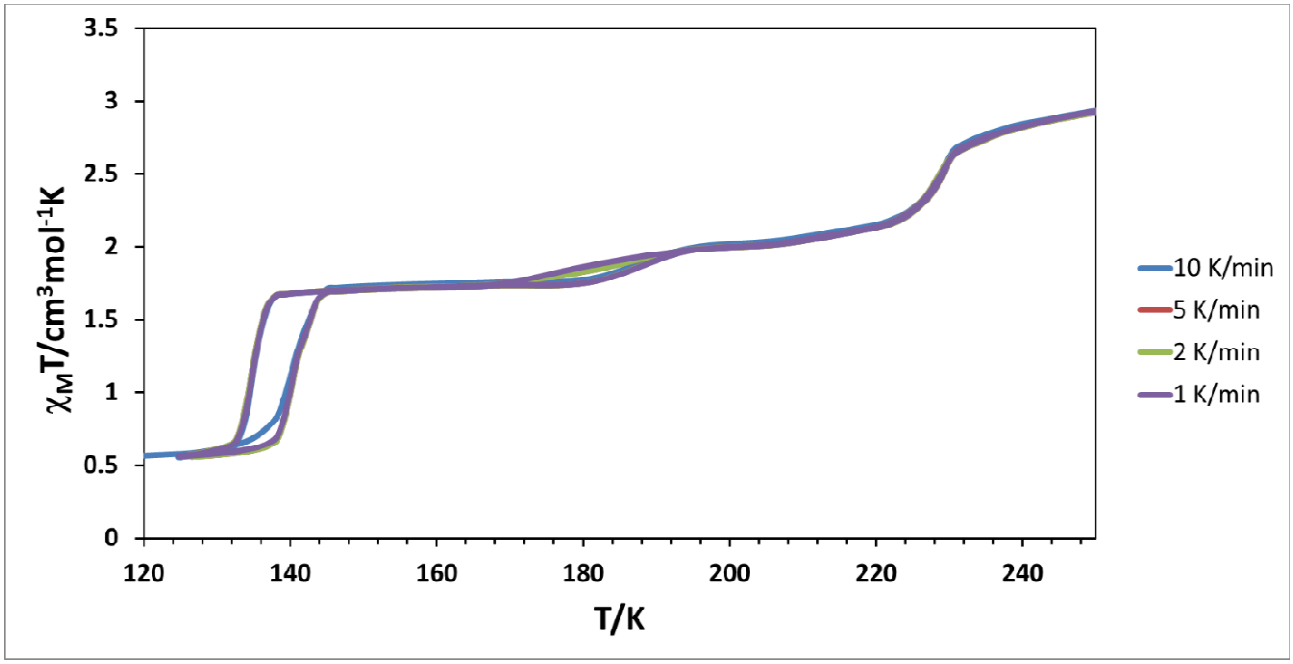


Figure S1 SQUID magnetic susceptibility studies of **1** between 2 and 400 K at scan rates of 1, 2, and 5 $Kmin^{-1}$.

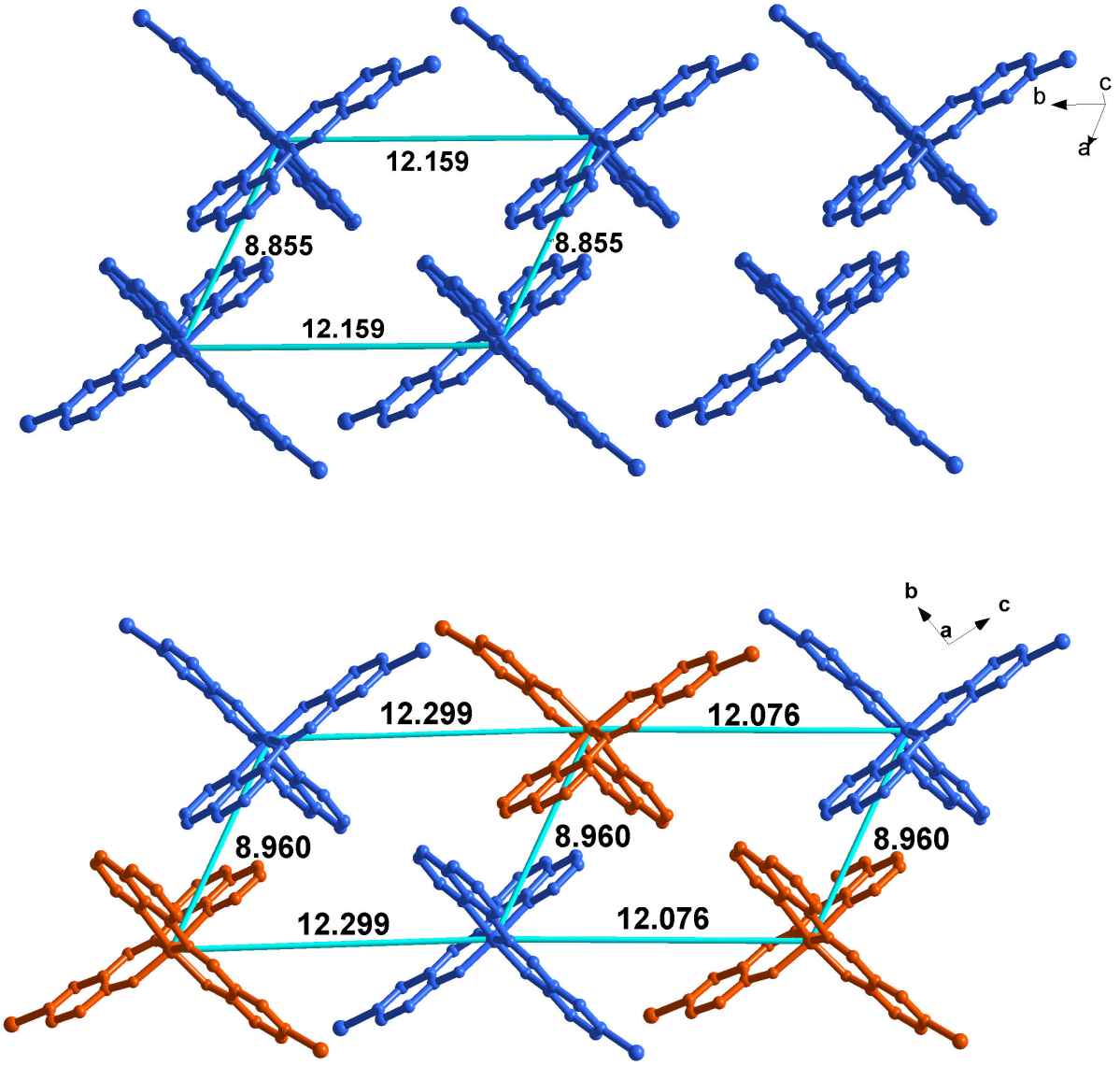


Figure S2 Partial packing diagram of the LS (top) and [LS-HS] (bottom) phases in **1** where blue and orange represent LS and HS centres, respectively. The light blue box represents the unit cell (or *pseudo*-unit cell in the [LS-HS] phase). The *pseudo*-unit cell of the intermediate [LS-HS] is deliberately divided in two to show its relationship with the unit cell of the simple LS structure and the clear doubling of the unit cell.

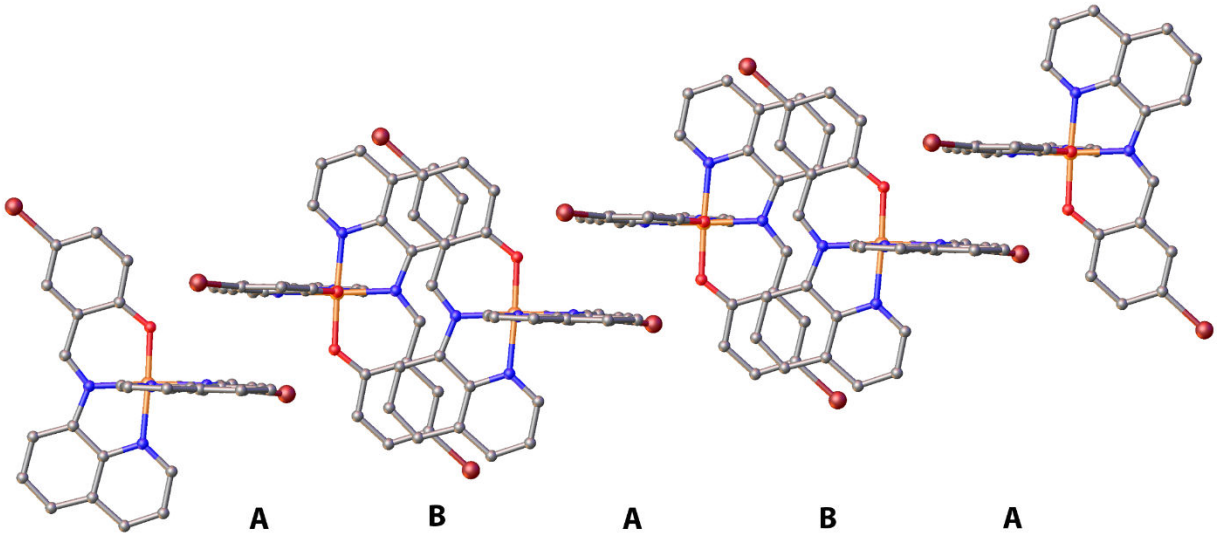


Figure S3 The perpendicular π-π interactions that form the 1D chains in **1** at 123 K.

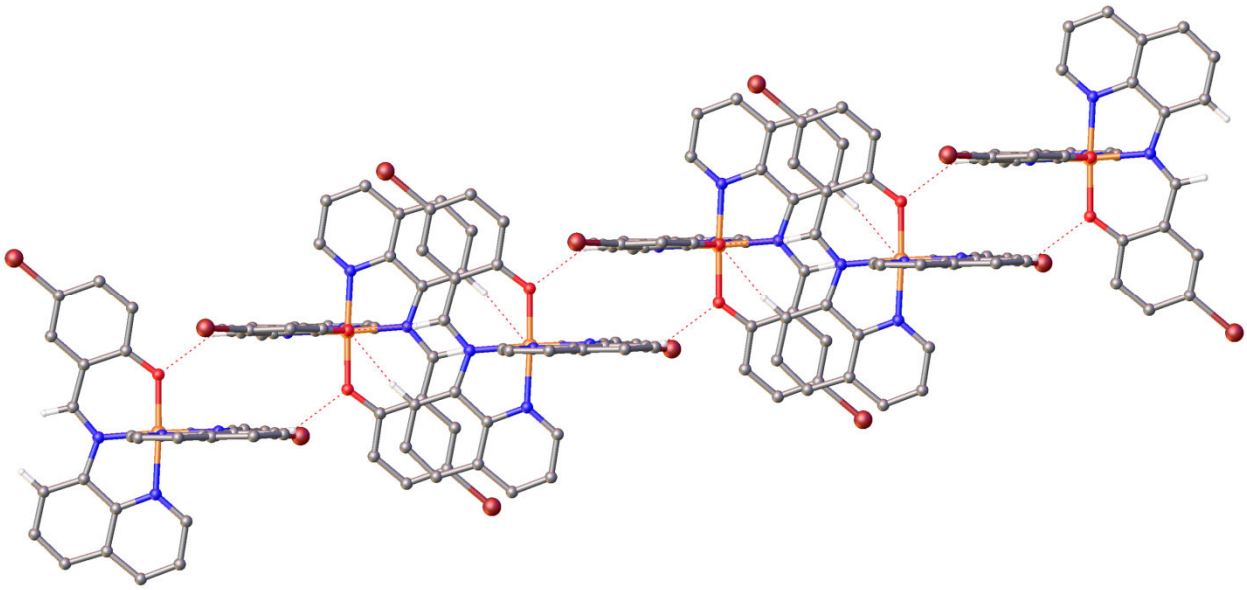
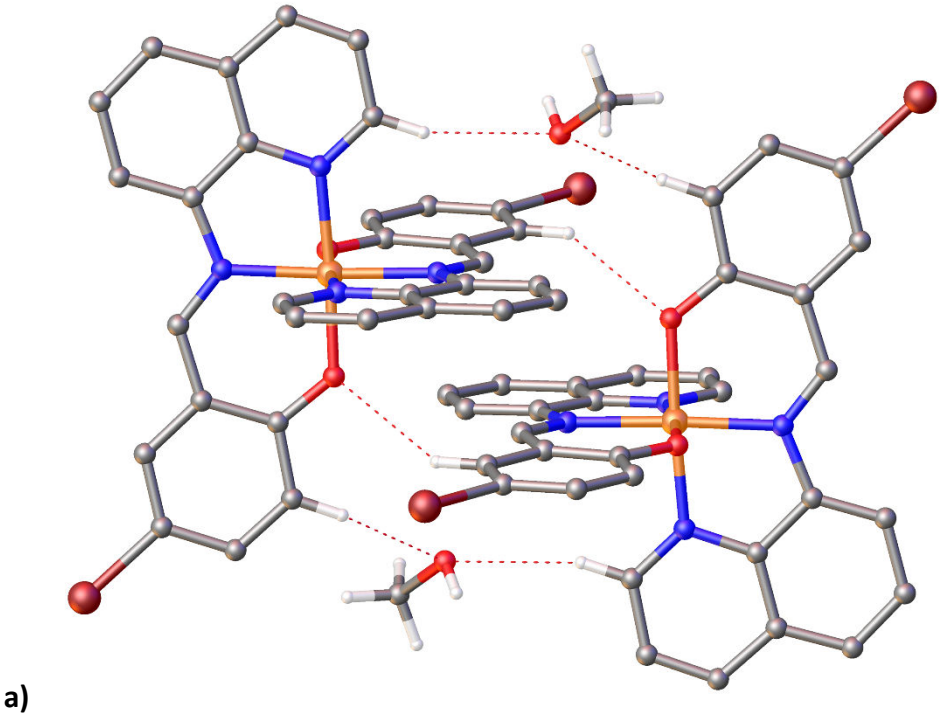
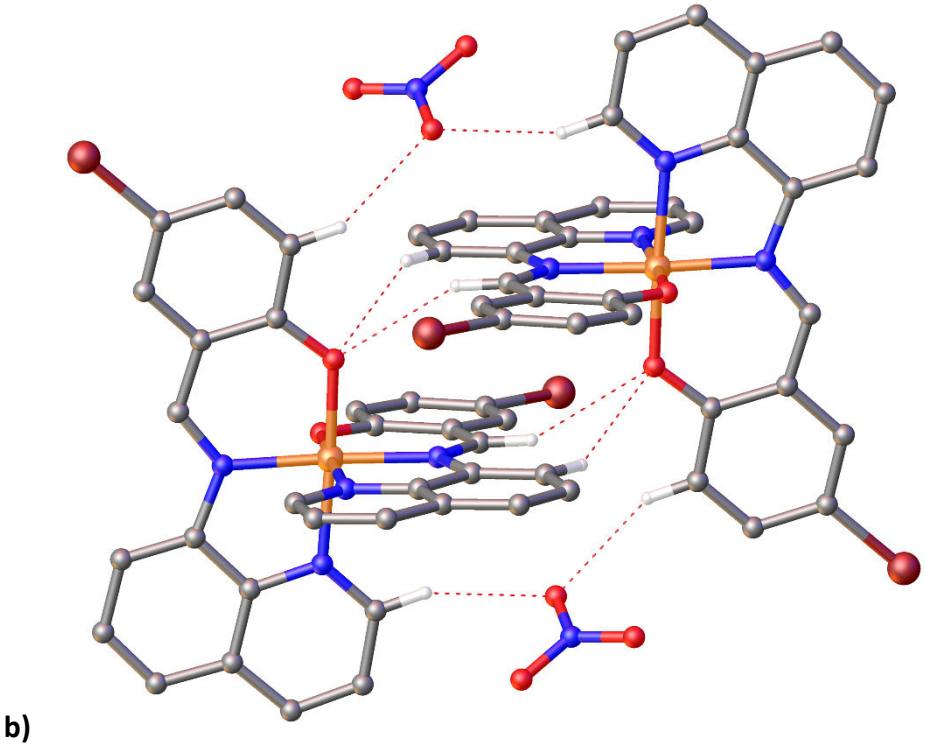


Figure S4 The supplementary C-H···O interactions between the qsal-Br C-H groups and the phenoxide O atoms at 123 K.



a)



b)

Figure S5 The C-H···O interactions forming the a) solvent (Type A) and b) anionic (Type B) embraces above and below the π-π interactions at 123 K.

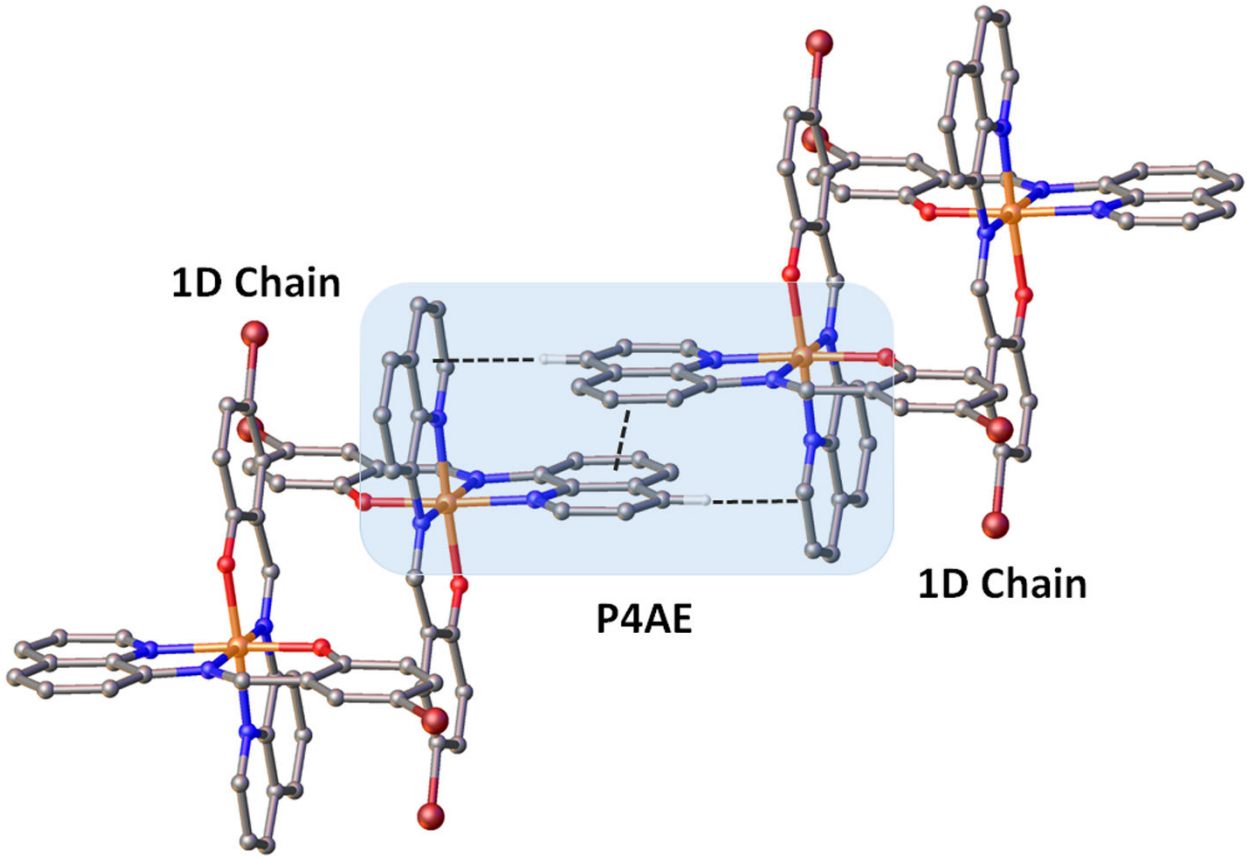


Figure S6 The P4AE interactions that link the 1D chains in **1** at 123 K.

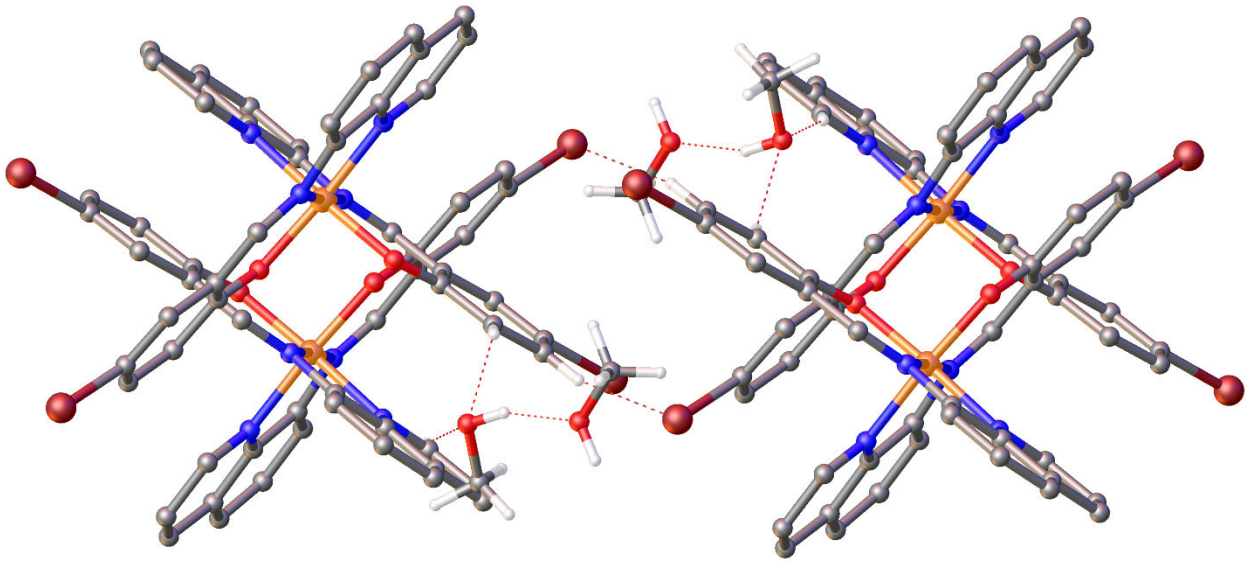


Figure S7 The C-H···Br and Br···O interactions that link the 1D chains in **1**.

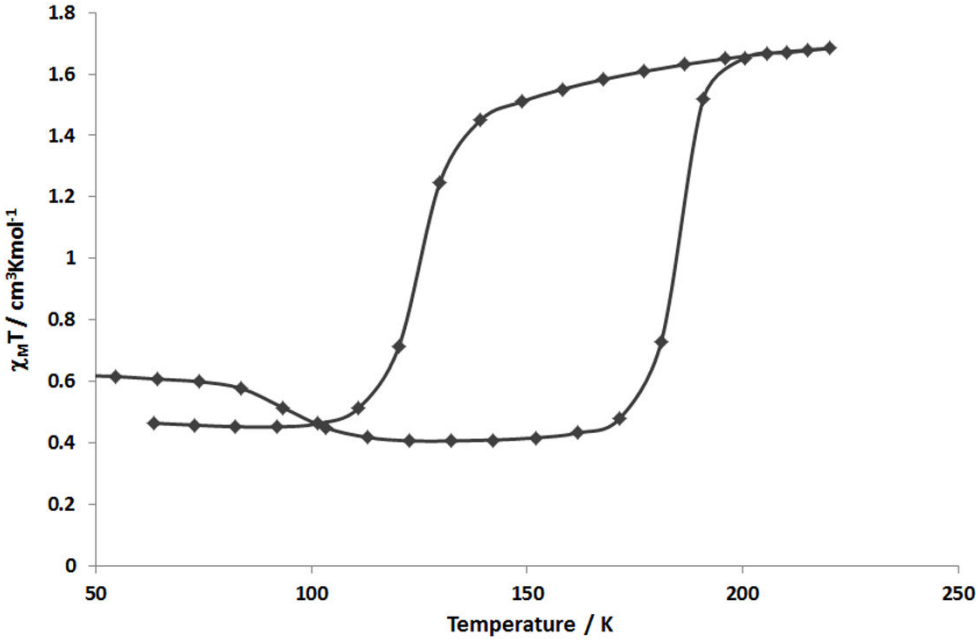


Figure S8 Thermal variation of $\chi_M T$ versus *T* plot for dried **1**.

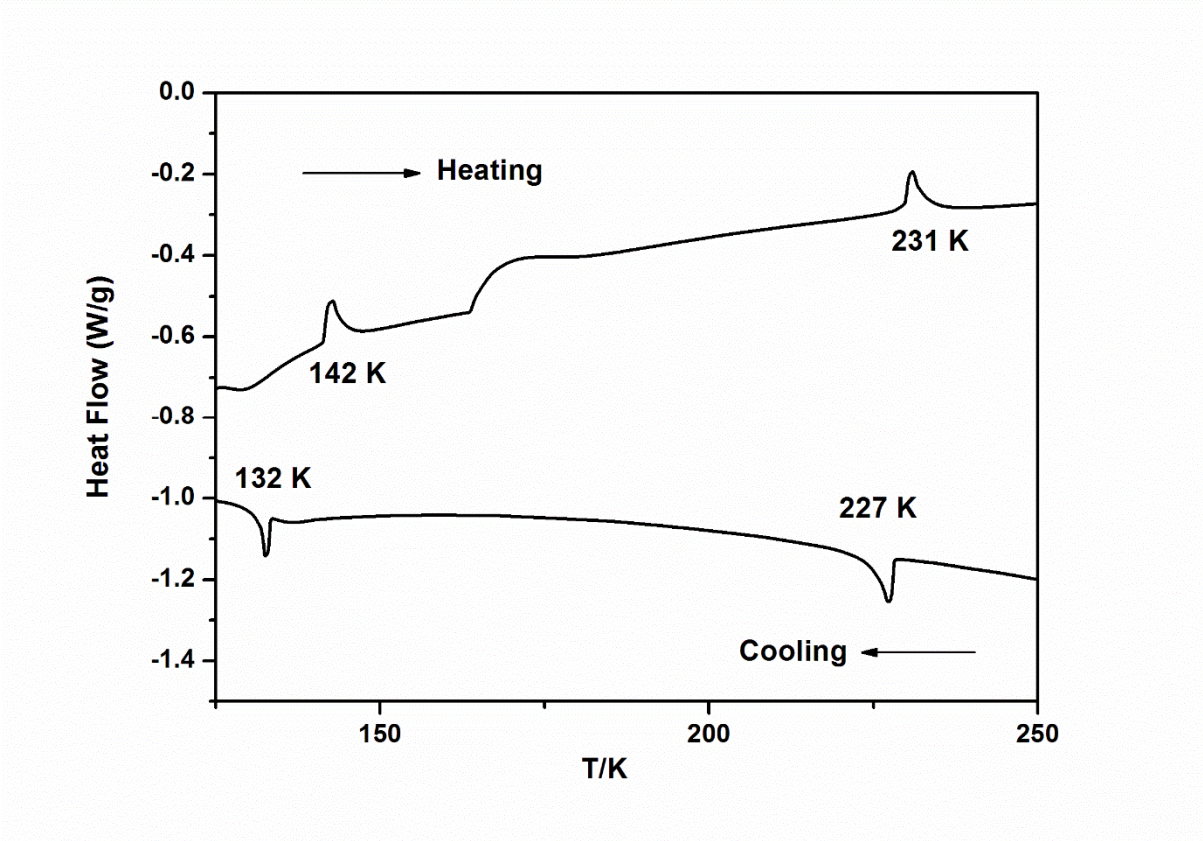


Figure S9 DSC measurements for **1**.

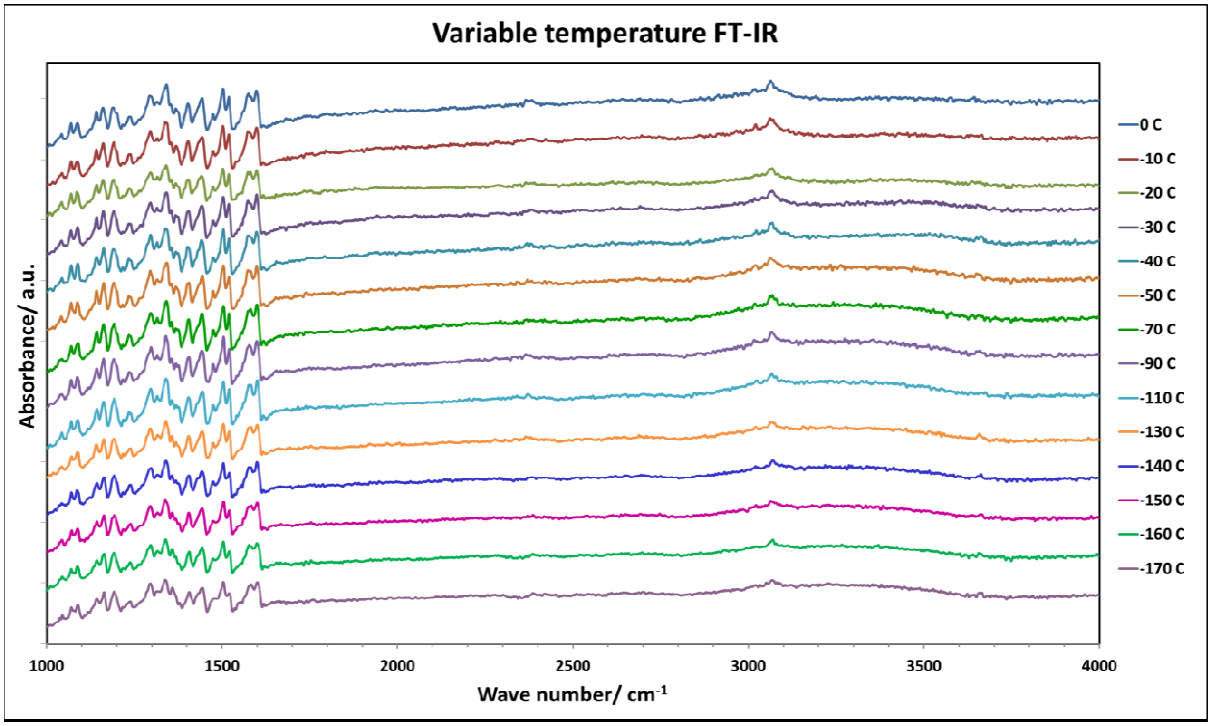


Figure S10 VT-IR spectroscopic measurements of **1**.