High temperature spin crossover behaviour of mononuclear bis-(thiocyanato)iron(II) complexes with judiciously designed bidentate N-donor Schiff bases with varying substituent

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Supporting Information

Table S1 Mössbauer spectral data of **1-3** at 296 K

Compound	Isomer Shift (δ) (mm/sec)	Quadrupole splitting (ΔEQ) (mm/sec)
1	0.3163±0.01196	0.6668±0.02131
2	0.0626±0.024	0.282±0.071
3	0.2992±0.01517	0.6308±.0259

Figure S1 Mössbauer spectra of complexes 1-3 at 296 K

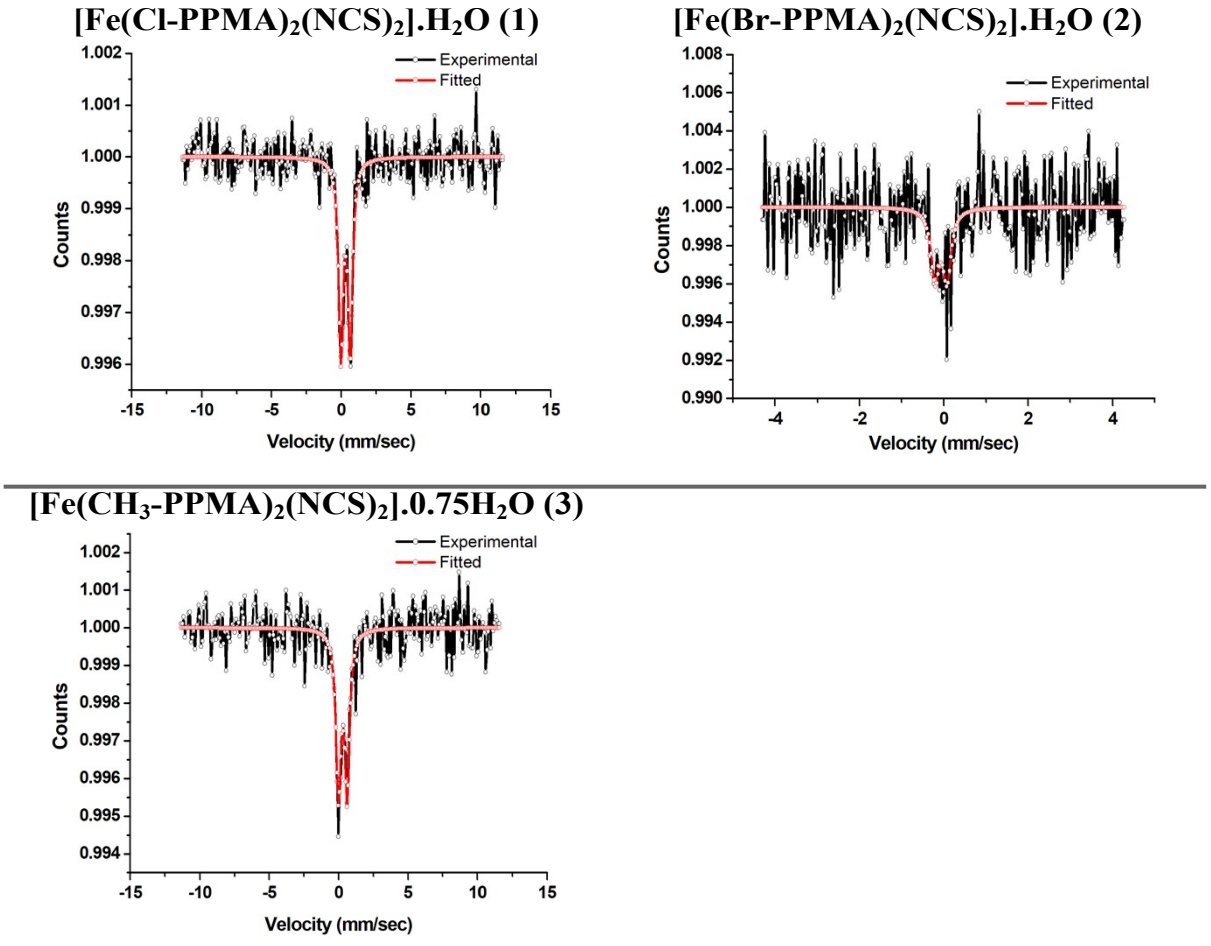


Table S2 Crystal data and structure refinement parameters for **1-3** at RT

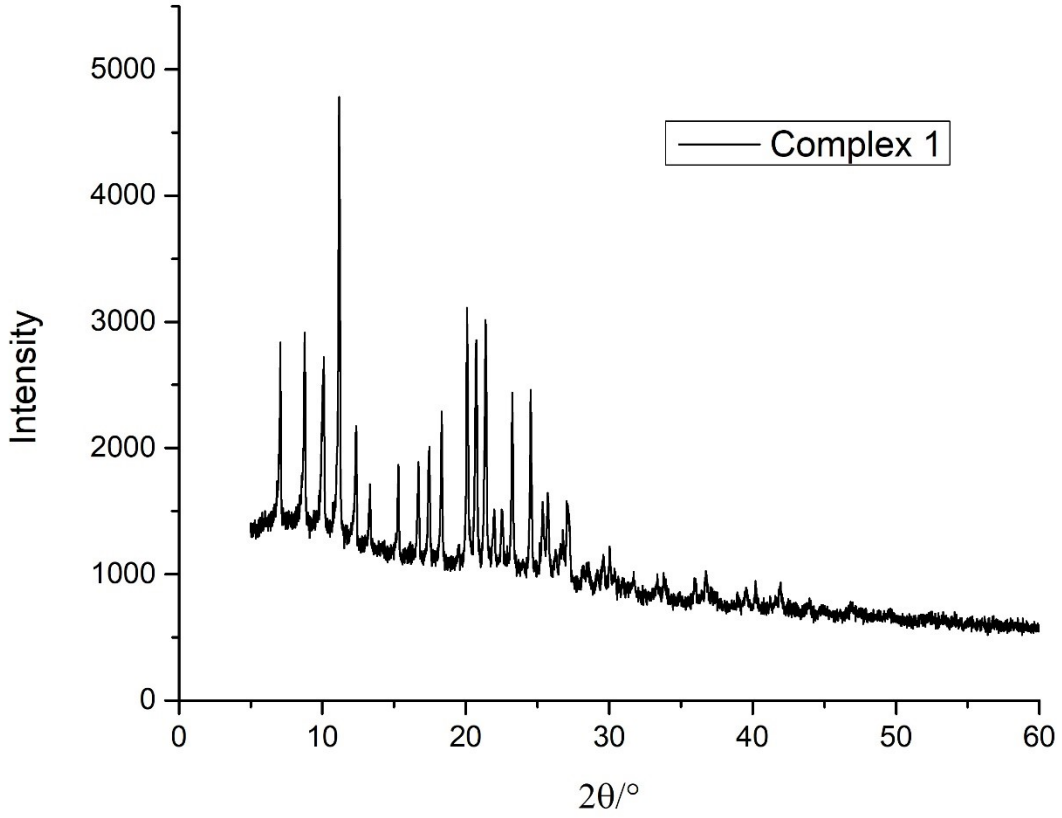
	$\mathbf{1^{RT}}$	$\mathbf{2^{RT}}$	$\mathbf{3^{RT}}$
Formula	$C_{36}H_{26}N_6S_2Cl_2Fe$	$C_{38}H_{26}N_6S_2Br_2Fe$	$C_{40}H_{32}N_6S_2Fe$
Formula Weight (g/mol)	757.52	846.44	716.68
Size (mm^3)	0.60×0.20×0.18	0.60×0.40×0.12	0.45×0.15×0.12
Crystal system	Tetragonal		
Space group	$P4_32_12$ (No. 96)	$P4_12_12$ (No. 92)	$P4_12_12$ (No. 92)
a (Å)	17.6439(7)	17.7700(8)	17.7428(6)
c (Å)	12.2291(5)	12.1810(5)	12.2100(4)
Volume ($Å^3$)	3807.0(3)	3846.4(4)	3843.8(3)
ρ_{calc} **($g.cm^{-3}$)**	1.322	1.462	1.238
μ (mm^{-1})	0.681	2.613	0.536
GOF on F^2	1.028	1.009	1.015
R_1, wR_2 [$I>2\sigma(I)$]	0.0372 0.0726	0.0430 0.0736	0.0386 0.0768
***R_1, wR_2* [all data]**	0.0609 0.0828	0.0823 0.0850	0.0597 0.0848
Largest diff. peak/hole ($e.Å^{-3}$)	0.238/-0.207	0.339/-0.365	0.282/-0.153
Flack value	-0.005(9)	-0.024(6)	-0.014(8)
CCDC	1978235	1978236	1978237

Table S3 The coordination sphere parameters for **1-3** at RT

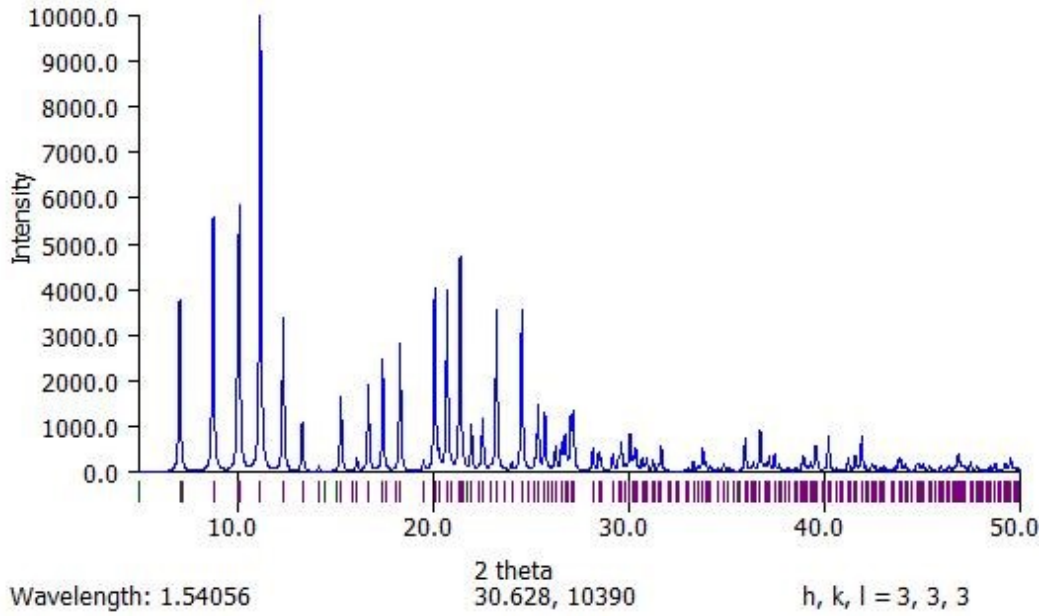
	$\mathbf{1^{RT}}$	$\mathbf{2^{RT}}$	$\mathbf{3^{RT}}$
Fe1-N1(pyridine)/Å	1.977(2)	1.977(3)	1.971(2)
Fe1-N2(imine)/Å	1.970(2)	1.965(4)	1.958(2)
Fe1-N3(NCS)/Å	1.956(3)	1.967(4)	1.962(3)
<Fe-N>/Å	1.966	1.969	1.963
ζ/Å	0.041	0.027	0.033
Σ/º	43.8	44.5	42.8
Θ/º	136	136	138
Spin state	LS	LS	LS

Symmetry code: (i) y, x, $-z + 1$. LS = Low spin.

Figure S2 (a) Experimental and (b) simulated powder-XRD plots of complex **1** at 300 K.

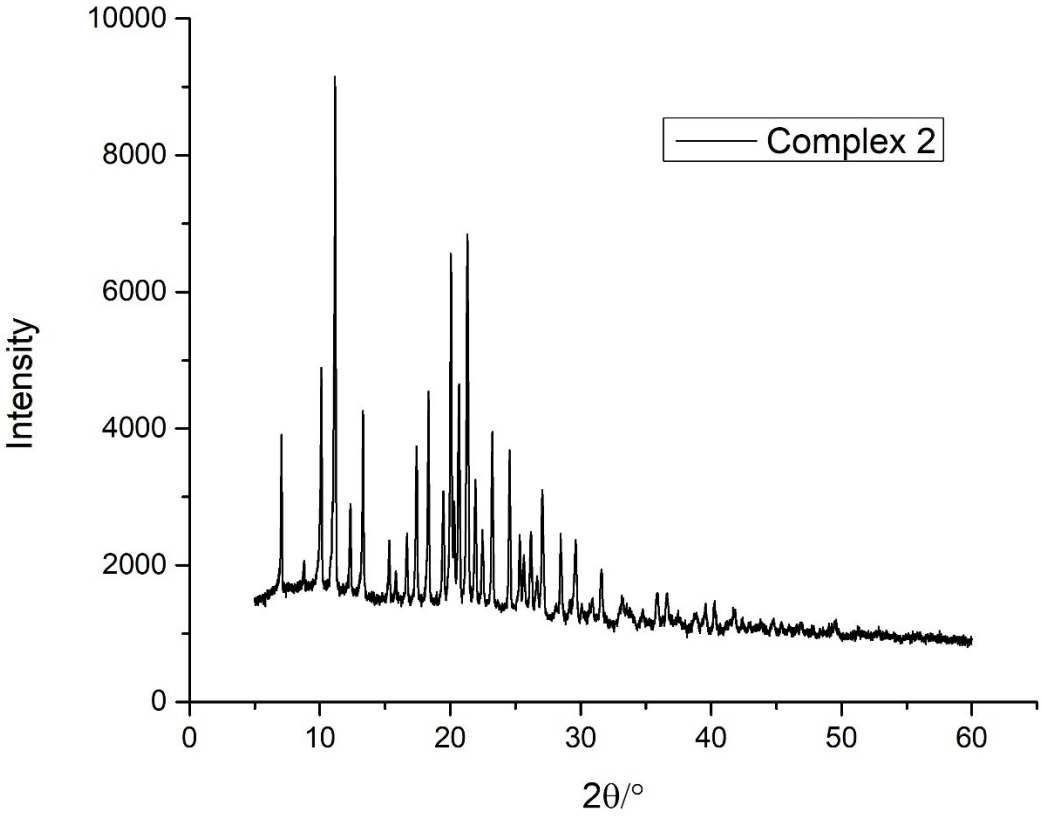


(a)

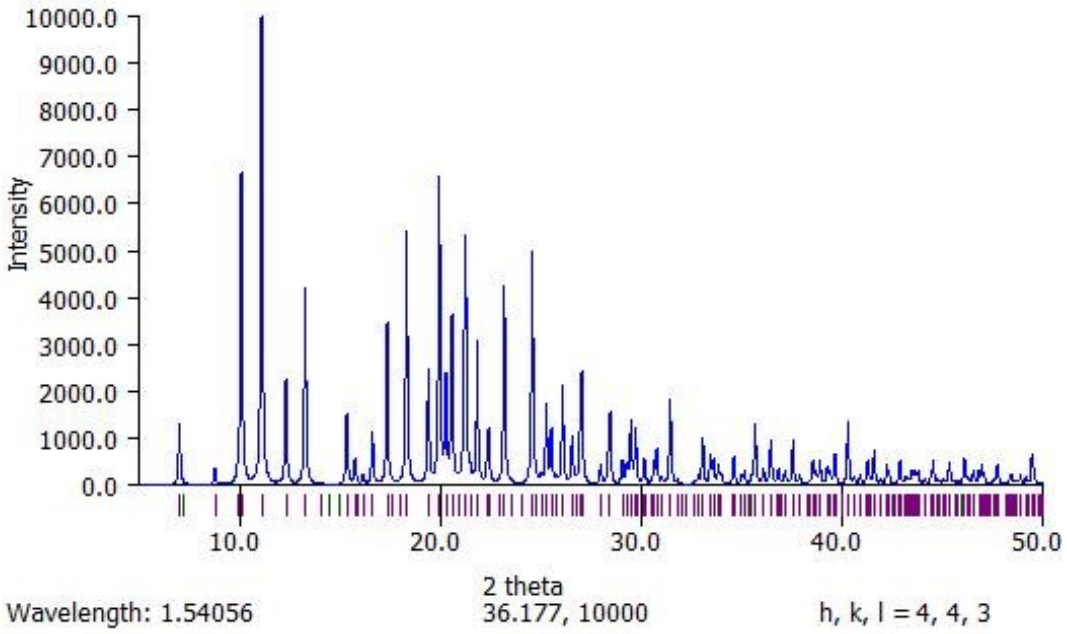


(b)

Figure S3 (a) Experimental and (b) simulated powder-XRD plots of complex **2** at 300 K.

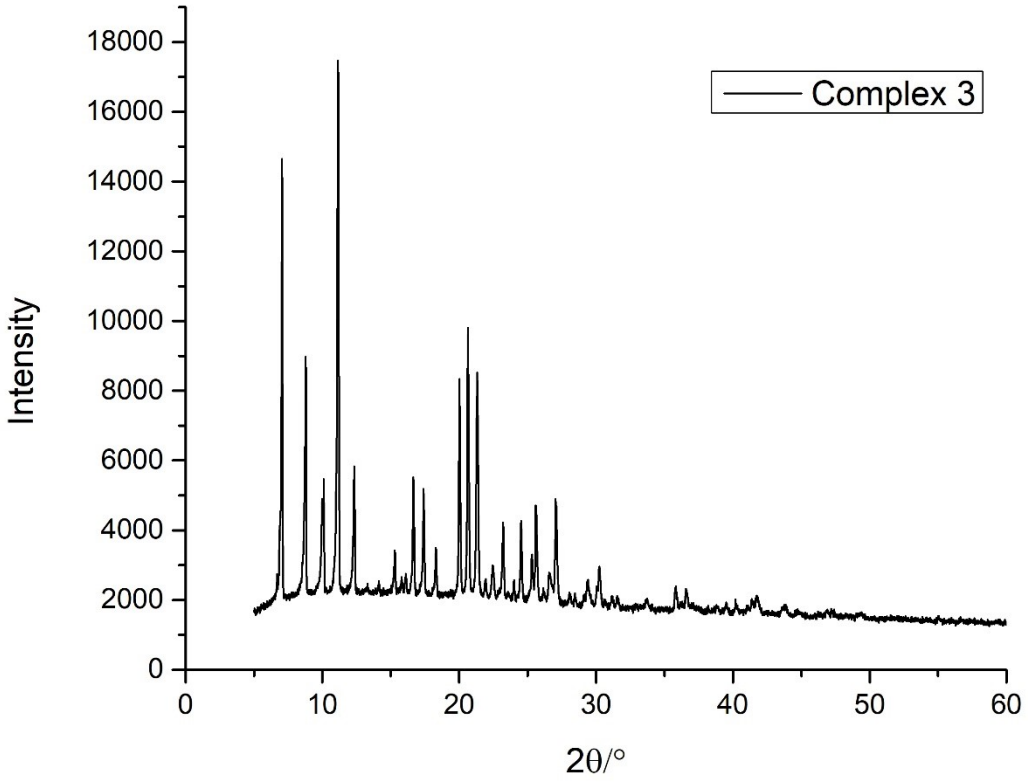


(a)

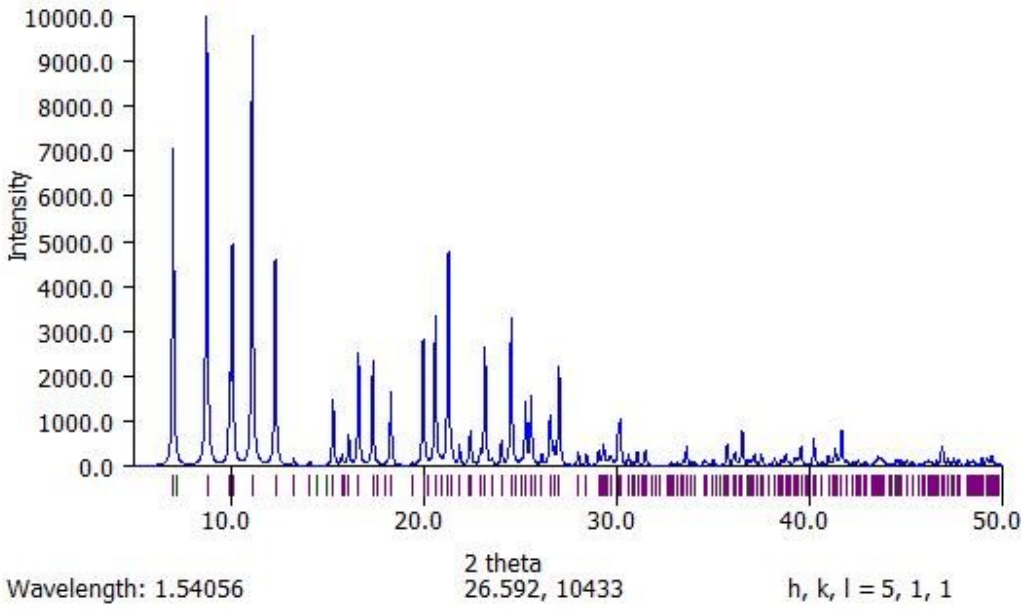


(b)

Figure S4 (a) Experimental and (b) simulated powder-XRD plots of complex **3** at 300 K.



(a)



(b)

Figure S5 TGA plot of complexes **1-3** in the temperature range 30-800 ºC.

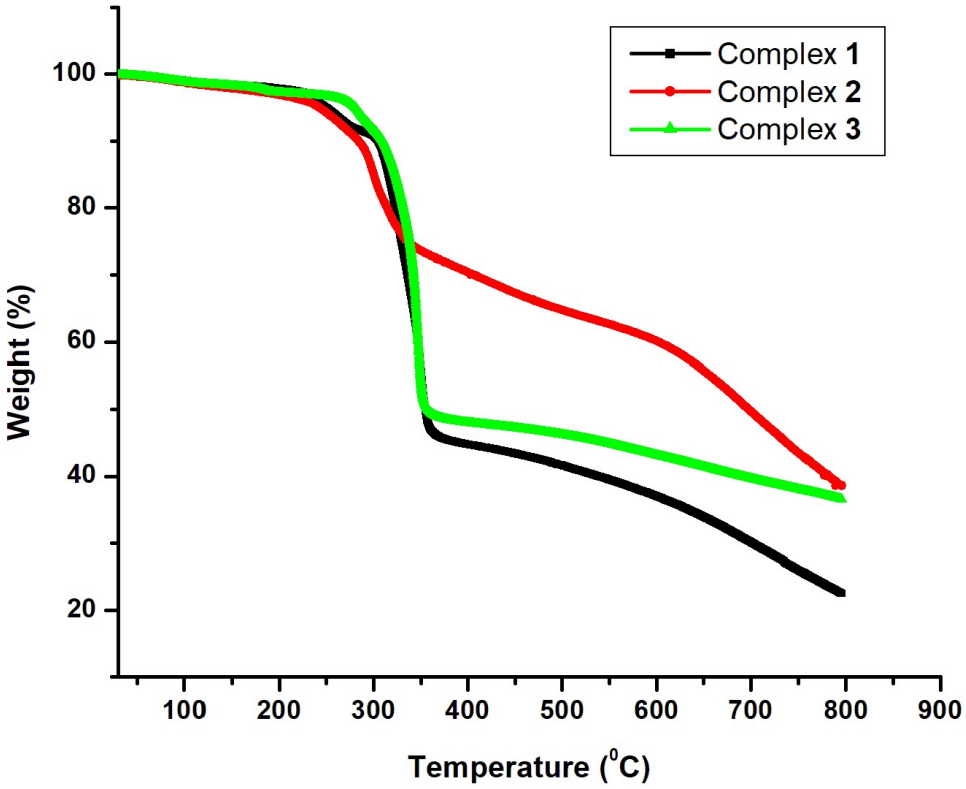


Figure S6 TGA plot and loss of water in complex **1**.

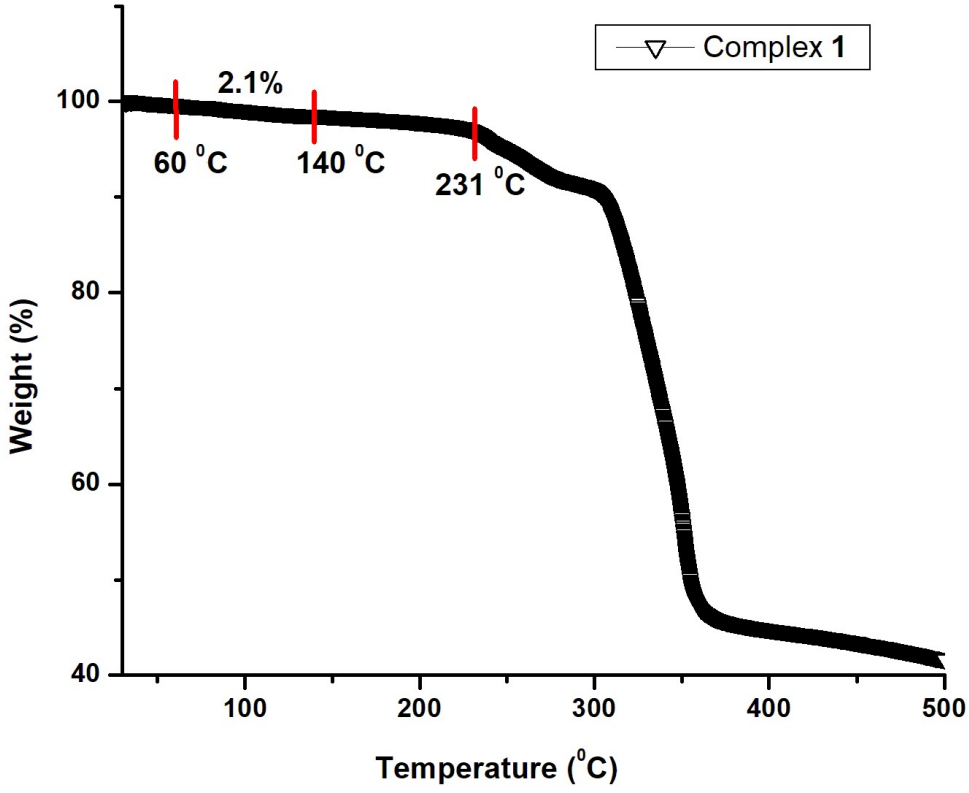


Figure S7 TGA plot and loss of water in complex **2**.

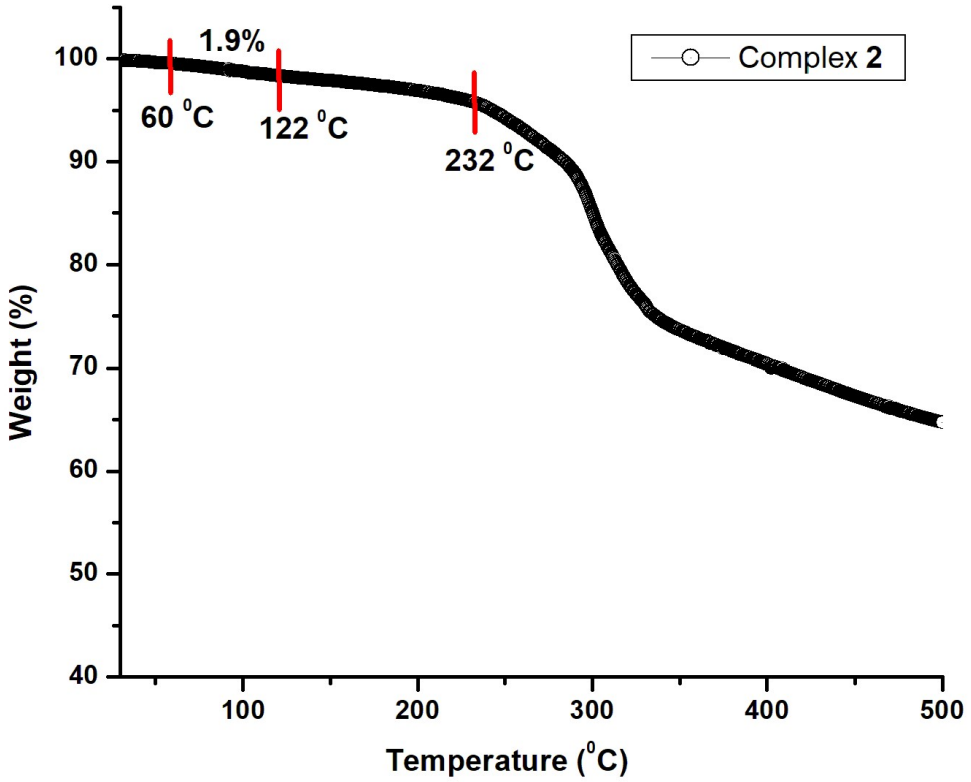


Table S4 Selected crystallographic parameters at various temperatures for **1**

	$\mathbf{1}^{150K}$	$\mathbf{1}^{250K}$	$\mathbf{1}^{300K}$	$\mathbf{1}^{350K}$	$\mathbf{1}^{400K}$	$\mathbf{1}^{450K}$
Formula	$C_{76}H_{52}N_{12}S_4Cl_4Fe_2$				$C_{76}H_{52}N_{12}S_4Cl_4Fe_2$	
F. W. (g/mol)	1515.03				1515.03	
Size (mm^3)	0.20×0.06×0.06					
Space group	$P4_32_12$					
a (Å)	17.4989(11)	17.586(3)	17.6150(6)	17.6560(7)	17.6740(7)	17.7562(15)
c (Å)	12.1221(11)	12.194(2)	12.2291(5)	12.3860(6)	12.5284(6)	12.5703(13)
Volume ($Å^3$)	3711.9(6)	3771.2(14)	3794.5(3)	3861.1(4)	3913.5(4)	3963.2(8)
ρ_{calc} **($g.cm^{-3}$)**	1.356	1.334	1.326	1.303	1.286	1.270
μ (mm^{-1})	0.698	0.687	0.683	0.671	0.662	0.654
GOF on F^2	0.969	1.049	1.023	1.040	1.049	1.124
R_1, wR_2 [I>2σ(I)]	0.0354 0.0706	0.0324 0.0691	0.0384 0.0873	0.0424 0.0936	0.0523 0.1217	0.0810 0.1783
***R_1, wR_2* [all data]**	0.0498 0.0741	0.0403 0.0726	0.0498 0.0929	0.0632 0.1065	0.0921 0.1466	0.1290 0.2117
Largest diff. peak/hole ($e.Å^{-3}$)	0.270/-0.295	0.318/-0.329	0.285/-0.314	0.213/-0.218	0.32/-0.21	0.40/-0.23
Flack value	0.002(10)	0.03(2)	0.007(4)	0.000(4)	0.004(5)	0.019(6)
CCDC	1979597	1979599	2009216	1979600	1979604	1979602

Table S5 Selected crystallographic parameters at various temperatures for **2**

	$\mathbf{2}^{150K}$	$\mathbf{2}^{250K}$	$\mathbf{2}^{300K}$	$\mathbf{2}^{350K}$	$\mathbf{2}^{400K}$	$\mathbf{2}^{450K}$
Formula	$C_{38}H_{26}N_6S_2Br_2Fe$	$C_{76}H_{52}N_{12}S_4Br_4Fe_2$		$C_{76}H_{52}N_{12}S_4Br_4Fe_2$		
F. W.(g/mol)	846.44	1692.87		1692.87		
Size (mm^3)	0.24×0.10×0.06					
Space group	$P4_12_12$					
a (Å)	17.6160(17)	17.6816(11)	17.7390(4)	17.6859(12)	17.7629(19)	17.834(4)
c (Å)	12.106(2)	12.1451(11)	12.1851(4)	12.3676(13)	12.4907(14)	12.571(3)
Volume ($Å^3$)	3756.8(10)	3797.0(6)	3834.3(2)	3868.5(7)	3941.1(10)	3998(2)
ρ_{calc} **($g.cm^{-3}$)**	1.497	1.481	1.466	1.453	1.427	1.406
μ (mm^{-1})	2.675	2.647	2.621	2.598	2.550	2.514
GOF on F^2	1.055	1.047	1.030	1.103	1.111	1.103
R_1, wR_2 [I>2σ(I)]	0.0309 0.0892	0.0453 0.0715	0.0450 0.0777	0.0688 0.1001	0.0759 0.1060	0.0892 0.1176
***R_1, wR_2* [all data]**	0.0339 0.0911	0.0600 0.0755	0.0596 0.0821	0.1539 0.1190	0.1728 0.1269	0.1943 0.1414
Largest diff. peak/hole ($e.Å^{-3}$)	0.314/-0.596	0.418/-0.391	0.362/-0.371	0.95/-0.86	0.85/-0.66	0.61/-0.30
Flack value	0.003(2)	0.033(14)	0.046(16)	0.016(3)	0.029(5)	0.032(5)
CCDC	1979605	1979607	2009217	1979608	1979609	1979611

Table S6 Evolution of the coordination sphere parameters as a function of temperature for **1**

	$\mathbf{1}^{150K}$	$\mathbf{1}^{250K}$	$\mathbf{1}^{300K}$	$\mathbf{1}^{350K}$	$\mathbf{1}^{400K}$	$\mathbf{1}^{450K}$
Fe-$N_{pyridine}$ (Å)	1.963(3)	1.968(2)	1.977(3)	2.037(3)	2.109(4)	2.151(7)
Fe-N_{imine} (Å)	1.954(2)	1.942(19)	1.962(3)	2.044(3)	2.144(4)	2.201(6)
Fe-N_{NCS} (Å)	1.950(3)	1.957(2)	1.950(3)	1.983(4)	2.039(6)	2.071(10)
<Fe-N> (Å)	1.955(2)	1.956(2)	1.963(3)	2.021(3)	2.097(5)	2.141(8)
ζ (Å)	0.031	0.032	0.058	0.158	0.235	0.281
Σ (°)	41.6	42.4	43.6	52.3	65.1	71.4
Φ (°)	131	133	138	158	190	208
V(FeN_6) $Å^3$	9.861	9.935	9.977	10.858	12.005	12.703
Spin state	LS	LS (95%)	LS (94%)	HS (34%)	HS (71%)	HS (94%)

Table S7 Evolution of the coordination sphere parameters as a function of temperature for **2**

	$\mathbf{2}^{150K}$	$\mathbf{2}^{250K}$	$\mathbf{2}^{300K}$	$\mathbf{2}^{350K}$	$\mathbf{2}^{400K}$	$\mathbf{2}^{450K}$
Fe-N (Å)	1.967(3) 1.957(3) 1.960(3)	1.970(3) 1.961(3) 1.957(3)	1.977(4) 1.968(3) 1.966(4)	2.040(8) 2.067(8) 1.996(10)	2.161(9) 2.108(10) 2.026(11)	2.206(10) 2.135(11) 2.044(12)
<Fe-N> (Å)	1.961(3)	1.963(4)	1.970(4)	2.0349(9)	2.098(10)	2.128(11)
ζ (Å)	0.025	0.030	0.031	0.157	0.289	0.34
Σ (°)	42	43	45	55	66	71
Φ (°)	133	134	138	160	188	198
V(FeN_6) Å^3	9.950	9.986	10.099	11.044	12.010	12.502
Spin state	LS (95%)	LS (94%)	LS (90%)	HS (40%)	HS (71%)	HS (87%)

Table S8 Selected crystallographic parameters at various temperatures for **3**

Temperature/K	$\mathbf{3}^{150K}$	$\mathbf{3}^{250K}$	$\mathbf{3}^{400K}$	$\mathbf{3}^{420K}$	$\mathbf{3}^{250Kcooling}$	$\mathbf{3}^{90Kcooling}$
Formula	$C_{80}H_{64}N_{12}S_4Fe_2$		$C_{80}H_{64}N_{12}S_4Fe_2$			
F. W. (g/mol)	1433.37		1433.37			
Size (mm^3)	0.16×0.08×0.04					
Space group	$P4_12_12$					
a (Å)	17.5623(8)	17.6315(3)	17.6961(5)	17.725(3)	17.5254(7)	17.3815(7)
c (Å)	12.1023(8)	12.1717(3)	12.5406(5)	12.578(2)	12.2143(6)	12.1164(5)
Volume (Å^3)	3732.8(4)	3783.8(16)	3927.1(3)	3951.7(15)	3751.5(4)	3660.6(3)
ρ_{calc} **(g.cm^{-3})**	1.275	1.258	1.212	1.205	1.269	1.300
μ (mm^{-1})	0.552	0.545	0.525	0.521	0.549	0.563
GOF on F^2	1.067	1.020	1.011	0.935	0.982	1.049
R_1, wR_2 [I>2σ(I)]	0.0264 0.0651	0.0461 0.0922	0.0491 0.0983	0.0463 0.0905	0.0502 0.0766	0.0434 0.0684
***R_1, wR_2* [all data]**	0.0288 0.0667	0.0883 0.0922	0.1171 0.1159	0.1867 0.1159	0.1240 0.0903	0.0697 0.0730
Largest diff. peak/hole (e.Å^{-3})	0.418/-0.178	0.591/-0.392	0.21/-0.16	0.18/-0.17	0.34/-0.48	0.48/-0.61
Flack value	0.009(15)	0.003(7)	0.022(8)	0.036(12)	0.007(9)	0.018(8)
CCDC	1979617	1979618	1979620	1979621	1979622	1979623