Mixed-valence $\{Fe^{II}_2Fe^{III}_4\}$ hexanuclear complexes with thermally induced spin crossover behavior

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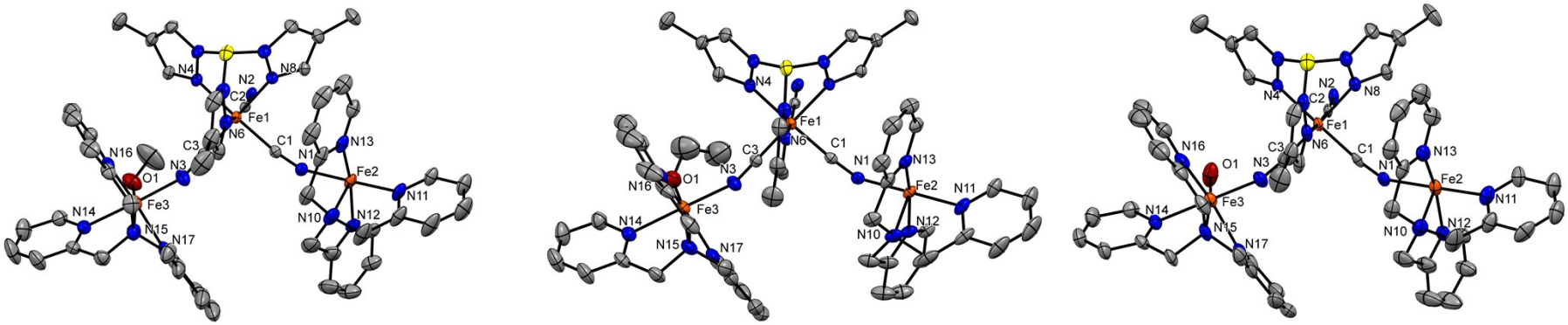

Figure S1. The asymmetric unit of **1**, **2** and **3** at 100 K, anions and hydrogen atoms are omitted for clarity.

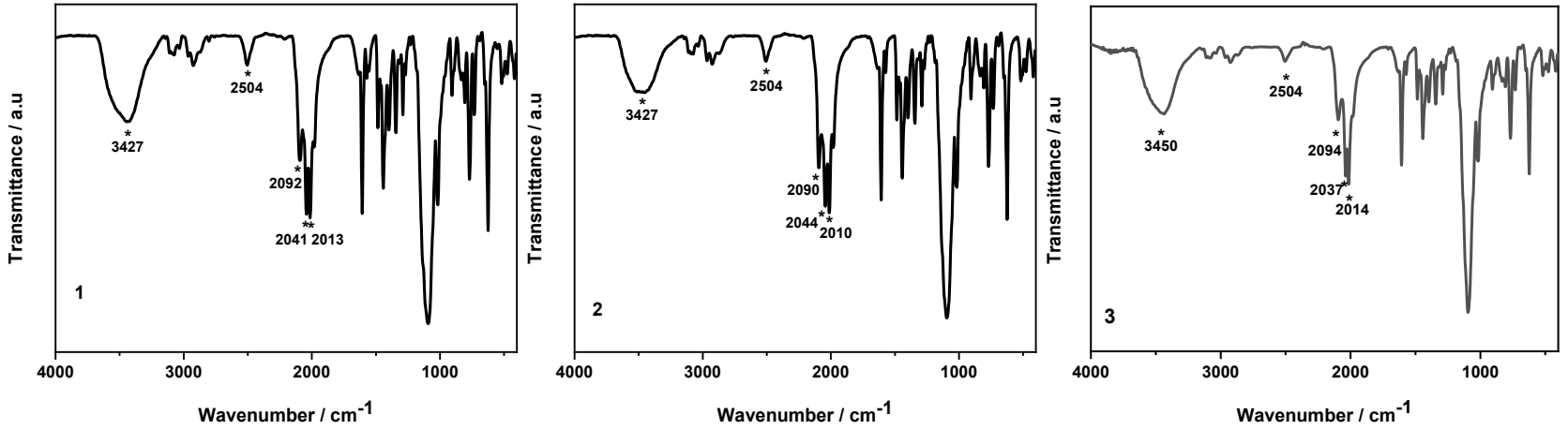

Figure S2. FT-IR transmission spectrum of **1, 2** and **3** at 298 K.

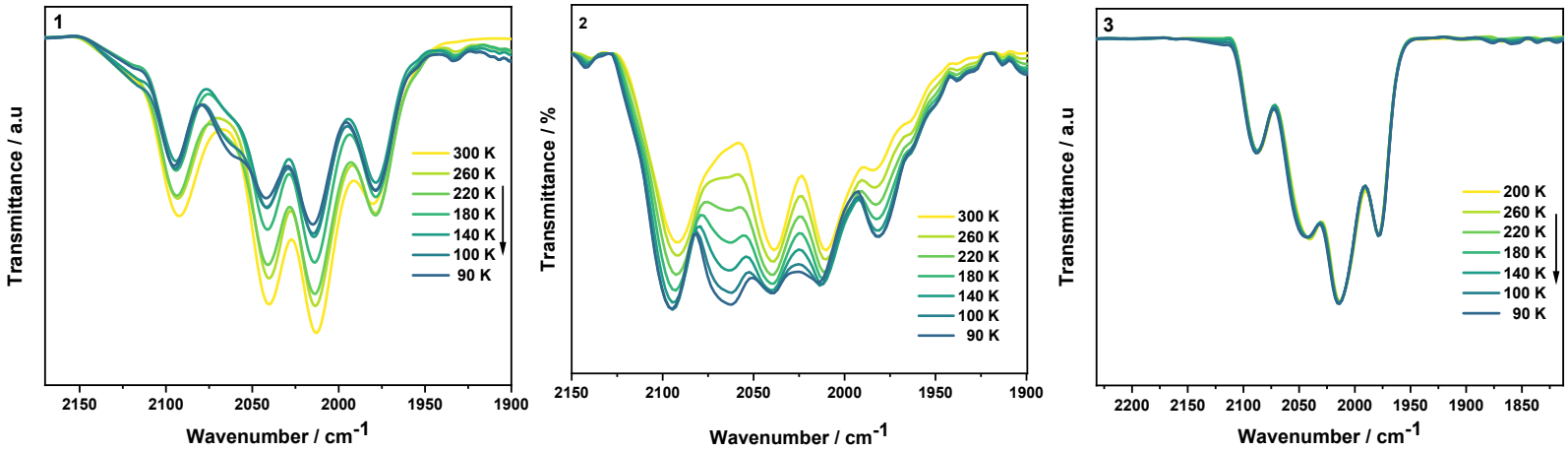

Figure S3. The variable-temperature IR spectra of compounds **1, 2**, and **3**.

Table S1. Crystal data and structure refinement for **1**, **2** and **3** at different tempterature.

	$\mathbf{1}^{298K}$	$\mathbf{1}^{150K}$	$\mathbf{1}^{100K}$	$\mathbf{2}^{298K}$	$\mathbf{2}^{100K}$	$\mathbf{3}^{298K}$	$\mathbf{3}^{100K}$
CCDC	2126714	2126715	2126716	2126718	2126717	2126720	2126719
Temperature /K	298	150	100	298	100	298	100
Formula	$C_{112}H_{142}B_2Cl_6Fe_6N_{34}O_{34}$			$C_{118}H_{150}B_2Cl_6Fe_6N_{34}O_{32}$		$C_{102}H_{122}B_2Cl_6Fe_6N_{34}O_{34}$	
Formula weight	3077.96	3077.96	3077.96	3127.10	3127.10	3005.72	3005.72
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
Z	4	4	4	4	4	4	4
a /Å	25.421 (5)	25.026 (2)	25.019 (3)	25.5260 (11)	25.057 (2)	25.260 (3)	24.824 (3)
b /Å	22.267 (4)	22.1299 (19)	22.076 (3)	22.3469 (10)	22.1418 (18)	22.226 (3)	21.984 (3)
c /Å	24.753 (5)	24.392 (2)	24.338 (3)	24.7393 (11)	24.2605 (19)	24.363 (3)	23.864 (3)
α /°	90	90	90	90	90	90	90
β /°	96.334 (4)	96.767 (2)	96.654 (2)	95.456 (2)	95.759 (1)	96.680 (2)	97.145 (2)°

γ /°	90	90	90	90	90	90	90
V / Å^3	13926 (4)	13415 (2)	13352 (3)	14048.0 (11)	13392.1 (19)	13585 (3)	12922 (3)
D_{calc} (mg/m^3)	1.345	1.397	1.404	1.250	1.411	1.366	1.482
μ /mm^{-1}	0.80	0.83	0.83	0.75	0.83	0.82	0.86
F(000)	5781	5792	5792	5440	5838	5728	5896
Collected reflections	72480	65550	57305	64778	62711	59617	43836
Unique reflections(Rint)	21208(0.046)	21995(0.030)	15884(0.056)	16924(0.036)	19464(0.039)	16367(0.051)	11354(0.050)
Goodness-of-fit on F^2	1.01	1.02	1.02	1.04	1.03	1.03	1.09
R_1 [I >2σ (I)]	0.063	0.046	0.054	0.056	0.054	0.069	0.079
wR_2 [I >2σ (I)]	0.210	0.134	0.169	0.188	0.164	0.232	0.250

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond lengths (Å) for **1**, **2** and **3** at different temperature.

	$\mathbf{1}^{298K}$	$\mathbf{1}^{150K}$	$\mathbf{1}^{100K}$	$\mathbf{2}^{298K}$	$\mathbf{2}^{100K}$	$\mathbf{3}^{298K}$	$\mathbf{3}^{100K}$
Fe1–C1	1.865 (3)	1.894 (2)	1.900 (3)	1.863 (3)	1.866 (2)	1.862 (4)	1.882 (6)
Fe1–C2	1.856 (3)	1.897 (2)	1.893 (3)	1.857 (3)	1.879 (2)	1.844 (4)	1.887 (5)
Fe1–C3	1.870 (3)	1.882 (2)	1.877 (3)	1.870 (3)	1.864 (3)	1.866 (4)	1.865 (6)
Fe1–$C_{average}$	1.864 (3)	1.891 (2)	1.890 (3)	1.863 (3)	1.869 (2)	1.857 (4)	1.878 (6)
Fe1–N4	1.994 (2)	1.976 (2)	1.970 (2)	2.009 (2)	1.991 (2)	2.008 (3)	1.986 (4)
Fe1–N6	1.986 (3)	1.969 (2)	1.960 (2)	1.999 (3)	1.986 (2)	2.000 (3)	1.980 (5)
Fe1–N8	1.988 (2)	1.984 (2)	1.981 (2)	2.005 (2)	1.999 (2)	2.000 (3)	1.995 (4)
Fe1–$N_{average}$	1.989 (2)	1.976 (2)	1.970 (2)	2.004 (2)	1.992 (2)	2.003 (3)	1.987 (4)
Fe2–N10	2.108 (3)	1.959 (2)	1.977 (3)	2.136 (3)	1.985 (2)	2.168 (4)	2.027 (5)
Fe2–N11	2.067 (3)	1.981 (2)	1.957 (3)	2.097 (3)	1.966 (2)	2.141 (4)	2.000 (5)
Fe2–N12	2.057 (3)	1.970 (2)	1.970 (3)	2.078 (3)	1.966 (2)	2.130 (4)	2.014 (5)
Fe2–N13	2.040 (3)	1.959 (2)	1.953 (3)	2.076 (3)	1.966 (2)	2.089 (4)	1.974 (5)
Fe2–N_{TPa}	2.068 (3)	1.967 (2)	1.964 (3)	2.096 (3)	1.970 (2)	2.132 (4)	2.003 (5)
Fe2–$N1^{i}$	1.973 (2)	1.929 (2)	1.926 (3)	1.985 (3)	1.914 (2)	1.999 (3)	1.946 (5)
Fe2–N2	1.947 (3)	1.915 (2)	1.915 (3)	1.957 (3)	1.920 (2)	1.958 (3)	1.924 (5)
Fe2–$N_{cyanide}$	1.96 (3)	1.922 (2)	1.920 (3)	1.971 (3)	1.917 2)	1.979 (3)	1.935 (5)
Fe3–N14	2.119 (3)	2.076 (2)	2.082 (3)	2.113 (3)	2.117 (2)	2.150 (3)	2.123 (5)
Fe3–N15	2.220 (3)	2.183 (2)	2.182 (3)	2.213 (3)	2.216 (3)	2.230 (4)	2.217 (5)
Fe3–N16	2.132 (3)	2.102 (2)	2.108 (3)	2.130 (3)	2.128 (3)	2.141 (4)	2.145 (5)
Fe3–N17	2.122 (3)	2.101 (2)	2.094 (4)	2.130 (3)	2.126 (3)	2.121 (4)	2.119 (5)
Fe3–N_{Tpa}	2.148 (3)	2.115 (2)	2.117 (3)	2.125 (3)	2.124 (3)	2.161 (4)	2.151 (5)
Fe3–N3	2.052 (3)	2.041 (2)	2.044 (3)	2.039 (3)	2.034 (2)	2.050 (3)	2.058 (5)
Fe3–O1	1.783 (3)	1.789 (2)	1.802 (3)	1.795 (3)	1.815 (3)	1.838 (4)	1.859 (5)

Symmetry code: $\mathbf{1}^{298K}$: (i) -*x*+1/2, -*y*+1/2, -*z*+1; $\mathbf{1}^{150K}$: (i) -*x*+3/2, -*y*+1/2, -*z*+1; $\mathbf{1}^{100K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{2}^{298K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{2}^{100K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{3}^{298K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{3}^{100K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1.

Table S3. Selected bond lengths (Å) for **1**, **2** and **3** at different temperature.

Avg. bond distance (Å)		$\mathbf{1}^{298K}$	$\mathbf{1}^{100K}$	change	$\mathbf{2}^{298K}$	$\mathbf{2}^{100K}$	change	$\mathbf{3}^{298K}$	$\mathbf{3}^{100K}$	change
FeC_3N_3	Fe1–$C_{average}$	1.864 (3)	1.890 (3)	+0.026 Å	1.863 (3)	1.869 (2)	+0.006 Å	1.857 (4)	1.878 (6)	+0.021 Å
	Fe1–$N_{average}$	1.989 (2)	1.970 (2)	-0.019 Å	2.004 (2)	1.992 (2)	-0.012 Å	2.003 (3)	1.987 (4)	-0.016 Å
FeN_6	Fe2–$N_{cyanide}$	1.960 (3)	1.920 (3)	-0.040 Å	1.971 (3)	1.917 (2)	-0.054 Å	1.979 (3)	1.935 (5)	-0.044 Å
	Fe2–N_{Tpa}	2.068 (3)	1.964 (3)	-0.104 Å	2.096 (3)	1.970 (2)	-0.126 Å	2.132 (4)	2.003 (5)	-0.129 Å
FeN_5	Fe3–N3	2.052 (3)	2.044 (3)	-0.006 Å	2.039 (3)	2.034 (2)	-0.005 Å	2.050 (3)	2.058 (5)	-0.008 Å
	Fe3–N_{Tpa}	2.148 (3)	2.117 (3)	-0.031 Å	2.125 (3)	2.124 (3)	-0.001 Å	2.161 (4)	2.151 (5)	-0.001 Å

Table S4. Selected bond angles (°) for **1**, **2** and **3** at different temperature.

Bond Angles	**1** 298K	**1** 150K	**1** 100K	**2** 298K	**2** 100K	**3** 298K	**3** 100K
C1–Fe1–C2	93.54 (11)	93.78 (12)	93.85 (7)	94.12 (12)	95.01 (10)	93.88 (15)	94.2 (2)
C1–Fe1–N4	175.95 (11)	176.10 (11)	175.84 (7)	175.58 (12)	175.08 (10)	175.88 (14)	176.2 (2)
C1–Fe1–N6	90.91 (11)	91.01 (11)	90.90 (7)	90.82 (11)	90.51 (10)	89.34 (14)	90.4 (2)
C1–Fe1–N8	88.76 (11)	88.11 (11)	88.11 (7)	88.88 (11)	88.55 (9)	92.85 (15)	89.1 (2)
C2–Fe1–N4	89.33 (11)	88.85 (11)	89.01 (7)	89.00 (11)	88.70 (10)	89.50 (14)	89.0 (2)
C2–Fe1–N6	174.58 (12)	173.91 (12)	173.83 (7)	174.01 (12)	172.71 (10)	88.57 (14)	174.1 (2)
C2–Fe1–N8	88.49 (11)	87.36 (11)	87.19 (7)	88.56 (11)	86.99 (9)	174.72 (15)	87.3 (2)
C3–Fe1–C1	91.41 (12)	90.74 (13)	90.84 (8)	90.84 (13)	90.68 (11)	93.03 (15)	92.6 (2)
C3–Fe1–C2	90.82 (12)	89.99 (12)	89.99 (8)	91.50 (13)	91.62 (11)	89.58 (15)	89.2 (2)
C3–Fe1–N4	91.41 (11)	92.14 (12)	92.19 (7)	92.21 (12)	92.44 (10)	89.34 (15)	89.5 (2)
C3–Fe1–N6	92.16 (12)	93.71 (12)	93.88 (8)	91.82 (12)	93.08 (10)	90.68 (14)	94.2 (2)
C3–Fe1–N8	179.30 (12)	177.03 (12)	176.92 (7)	179.71 (13)	178.34 (10)	177.09 (15)	176.2 (2)
N4–Fe1–N8	88.46 (10)	89.13 (10)	89.00 (6)	88.07 (10)	88.43 (9)	85.83 (14)	88.89 (18)
N6–Fe1–N4	86.07 (11)	86.18 (10)	86.05 (7)	85.89 (11)	85.53 (9)	88.39 (13)	86.31 (19)
N6–Fe1–N8	88.52 (11)	89.05 (10)	89.03 (7)	88.15 (11)	88.40 (9)	88.82 (13)	89.07 (19)
N11–Fe2–N10	81.55 (12)	85.24 (12)	85.47 (8)	80.76 (12)	85.08 (11)	79.82 (16)	83.9 (2)
N11–Fe2–N12	88.85 (13)	91.15 (12)	91.16 (8)	88.72 (13)	91.51 (10)	87.09 (16)	88.7 (2)
N11–Fe2–N13	88.73 (12)	89.74 (11)	89.93 (7)	88.63 (11)	89.32 (10)	88.48 (15)	90.1 (2)
N12–Fe2–N10	79.77 (12)	83.15 (12)	82.98 (8)	78.56 (12)	82.60 (10)	78.24 (16)	82.1 (2)
N13–Fe2–N10	80.12 (12)	84.60 (12)	84.74 (8)	79.73 (12)	84.64 (10)	77.41 (16)	82.3 (2)
N13–Fe2–N12	159.88 (11)	167.60 (12)	167.54 (8)	158.27 (11)	167.09 (10)	155.65 (15)	164.4 (2)
N1–Fe2–N10	91.62 (11)	92.24 (11)	91.94 (7)	91.80 (11)	91.87 (10)	92.76 (15)	93.54 (19)
N1–Fe2–N11	172.76 (11)	175.35 (11)	175.36 (7)	172.25 (12)	174.96 (10)	172.42 (15)	175.9 (2)
N1–Fe2–N12	92.30 (12)	92.43 (11)	92.35 (7)	91.94 (12)	92.08 (10)	88.42 (13)	94.1 (2)
N1–Fe2–N13	87.74 (11)	86.13 (11)	86.00 (7)	87.91 (11)	86.39 (9)	88.42 (13)	86.29 (19)
$N2^{i}$–Fe2–N1	93.12 (10)	87.90 (10)	88.23 (6)	93.75 (11)	88.99 (9)	94.70 (13)	89.26 (18)
$N2^{i}$–Fe2–N10	175.17 (11)	177.57 (12)	177.46 (8)	174.39 (12)	177.56 (10)	172.51 (15)	176.7 (2)
$N2^{i}$–Fe2–N11	93.76 (11)	94.79 (11)	94.52 (7)	93.72 (12)	94.21 (10)	92.74 (15)	93.38 (19)
$N2^{i}$–Fe2–N12	99.07 (12)	94.42 (11)	94.49 (7)	100.43 (12)	95.09 (9)	100.65 (14)	95.9 (2)
$N2^{i}$–Fe2–N13	101.02 (12)	97.83 (11)	97.80 (7)	101.26 (12)	97.70 (9)	103.48 (15)	99.7 (2)
N3–Fe3–N14	165.81 (12)	166.64 (12)	166.62 (8)	165.97 (13)	165.16 (10)	163.00 (16)	163.1 (2)
N3–Fe3–N15	89.02 (12)	88.85 (12)	88.67 (8)	89.68 (12)	88.94 (10)	86.73 (15)	86.06 (18)
N3–Fe3–N16	86.33 (12)	85.94 (11)	85.87 (7)	85.51 (12)	85.75 (10)	87.50 (16)	87.3 (2)
N3–Fe3–N17	89.34 (12)	89.56 (12)	89.68 (8)	90.43 (12)	89.79 (10)	88.12 (15)	87.3 (2)
N14–Fe3–N15	78.94 (11)	80.26 (11)	80.35 (7)	78.94 (12)	78.89 (10)	78.26 (14)	78.78 (18)
N14–Fe3–N16	83.72 (12)	84.27 (11)	84.43 (7)	84.05 (12)	83.35 (9)	81.49 (14)	82.07 (18)
N14–Fe3–N17	94.80 (11)	95.28 (11)	95.11 (7)	94.56 (12)	95.22 (9)	95.82 (14)	96.18 (18)
N16–Fe3–N15	77.32 (13)	78.08 (11)	78.26 (7)	77.46 (13)	77.36 (11)	77.21 (17)	76.9 (2)

N17–Fe3–N15	75.35 (13)	76.27 (13)	76.46 (9)	75.46 (13)	75.34 (11)	75.93 (16)	76.1 (2)
N17–Fe3–N16	152.39 (13)	154.04 (13)	154.42 (9)	152.63 (14)	152.41 (11)	152.99 (17)	152.7 (2)
O1–Fe3–N14	93.48 (13)	93.36 (12)	92.82 (8)	92.76 (13)	92.66 (11)	95.34 (17)	95.4 (2)
O1–Fe3–N15	172.02 (12)	173.44 (12)	172.98 (8)	171.30 (12)	171.09 (10)	173.42 (17)	174.1 (2)
O1–Fe3–N16	104.56 (14)	102.95 (13)	102.83 (8)	104.51 (15)	104.67 (12)	103.52 (19)	103.4 (2)
O1–Fe3–N17	103.05 (14)	102.99 (14)	102.74 (9)	102.85 (15)	102.92 (12)	103.49 (18)	103.9 (2)
O1–Fe3–N3	98.81 (13)	97.68 (13)	98.32 (9)	98.90 (13)	99.83 (11)	99.81 (18)	99.9 (2)

Symmetry code: $\mathbf{1}^{298K}$: (i) -*x*+1/2, -*y*+1/2, -*z*+1; $\mathbf{1}^{150K}$: (i) -*x*+3/2, -*y*+1/2, -*z*+1; $\mathbf{1}^{100K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{2}^{298K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{2}^{100K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{3}^{298K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1; $\mathbf{3}^{100K}$: (i) -*x*+1/2, -*y*+3/2, -*z*+1.

Table S5. Structural parameters for **1**, **2** and **3** at 298 K high and 100 K.

Compd.		Σ_{Fe}(°)	ζ_{Fe}	Θ_{Fe}(°)	
1 298 (100) K	Fe1	20.62 (23.26)	1.93 (0.26)	52.81 (71.31)	[FeC3N3] [(Tpa)Fe(NC)3]
	Fe2	64.11 (44.89)	2.03 (0.12)	161.82 (117.86)	[FeN6] [(pzTp)Fe(CN)3]
	Fe3	94.68 (88.08)	2.07 (0.53)	211.27 (193.25)	
2 298 (100) K	Fe1	22.54 (26.73)	0.42 (0.37)	57.73 (73.69)	[FeC3N3] [(Tpa)Fe(NC)3]
	Fe2	68.22 (45.47)	0.34 (0.14)	173.43 (118.13)	[FeN6] [(pzTp)Fe(CN)3]
	Fe3	92.90 (95.87)	0.61 (0.59)	213.90 (215.17)	
3 298 (100) K	Fe1	21.05 (23.01)	0.44 (0.33)	55.91 (66.37)	[FeC3N3] [(Tpa)Fe(NC)3]
	Fe2	77.81 (53.87)	0.41 (0.20)	197.35 (145.32)	[FeN6] [(pzTp)Fe(CN)3]
	Fe3	102.76 (104.28)	0.58 (0.51)	208.47 (210.01)	

[a] Σ_{Fe}: the sum of |90-a| for the 12 *cis*-N-Fe-N angles around the iron atom; [b] ζ_{Fe}: the average of the sum of the deviation of 6 unique metal-ligand bond lengths around the central metal atom (Fe) from the average value. [c] Θ_{Fe}: the sum of the deviation of 24 unique torsional angles between the ligand atomson opposite triangular faces of the octahedron viewed along the pseudo-threefold axis (θi) from 60°. All of these data are obtained through the OctaDist software.

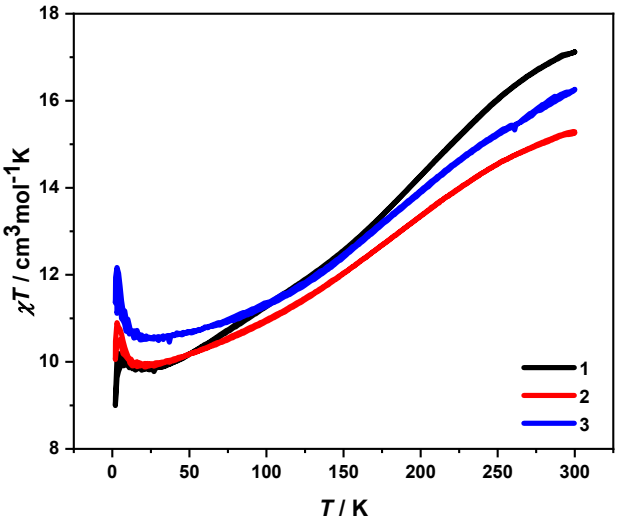

Figure S4. Temperature dependence of $\chi_M T$ plots for **1**, **2**, and **3** (from 300 K to 2 K to 300 K).

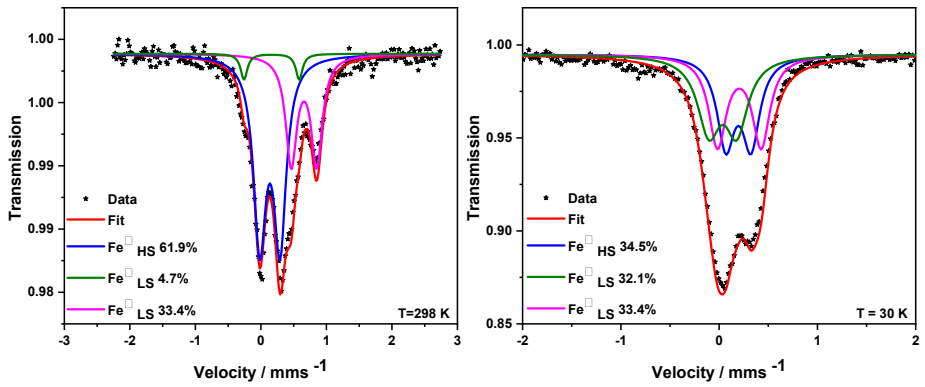

Figure S5. ^{57}Fe Mössbauer spectra of **2** at 298 K and 30 K.

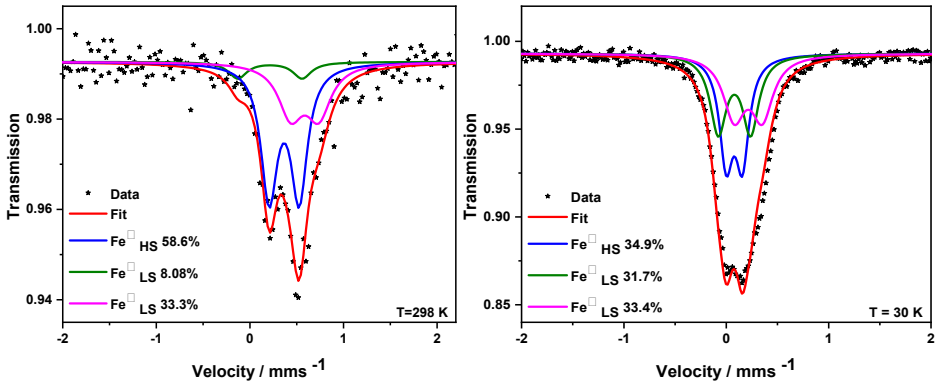

Figure S6. ^{57}Fe Mössbauer spectra of **3** at 298 K and 30 K.

Table S5. ^{57}Fe Mössbauer parameters for **1**, **2** and **3** at different tempterature.

	T (K)	Fe site	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Aera (%)
1	298 K	Fe^{III}_{HS}	0.02	0.95	66.8
		Fe^{II}_{LS}	0.35	0.29	33.1
	30 K	Fe^{III}_{HS}	0.11	0.35	33.7
		Fe^{III}_{LS}	0.12	0.19	33.6
		Fe^{II}_{LS}	0.19	0.29	32.5
2	298 K	Fe^{III}_{HS}	0.14	0.31	61.9
		Fe^{III}_{LS}	0.16	0.84	4.68
		Fe^{II}_{LS}	0.66	0.39	33.3
	30 K	Fe^{III}_{HS}	0.03	0.28	34.5
		Fe^{III}_{LS}	0.19	0.26	32.1
		Fe^{II}_{LS}	0.21	0.44	33.4
3	298 K	Fe^{III}_{HS}	0.37	0.32	58.6
		Fe^{III}_{LS}	0.21	0.69	8.08
		Fe^{II}_{LS}	0.58	0.29	33.3
	30 K	Fe^{III}_{HS}	0.08	0.16	34.9
		Fe^{III}_{LS}	0.08	0.32	31.7
		Fe^{II}_{LS}	0.21	0.27	33.4

δ = isomer shift, ΔE_Q = quadrupole splitting, [b] with the estimated standard deviations (esd) given in brackets.

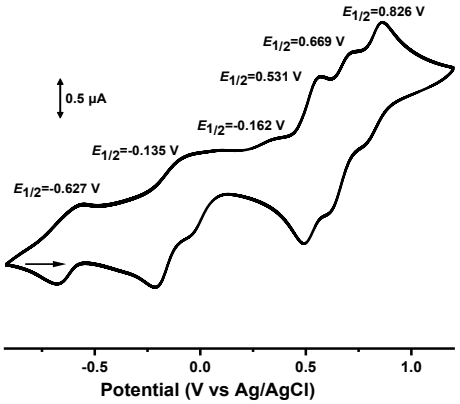

Figure S7. Cyclic voltammogram of **1** (potential *vs* Ag/AgCl, 1 mM, 0.1 M Bu_4NPF_6 in CH_2Cl_2, glassy carbon working electrode, Pt wire counter electrode, and a scan rate of 50 mV/s).

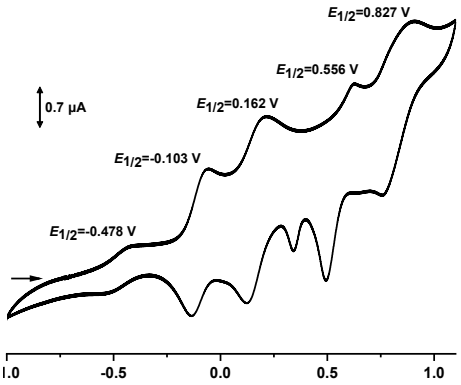

Figure S8. Cyclic voltammogram of **2** (potential vs Ag/AgCl, 1 mM, 0.1 M Bu_4NPF_6 in CH_2Cl_2, glassy carbon working electrode, Pt wire counter electrode, and a scan rate of 50 mV/s).

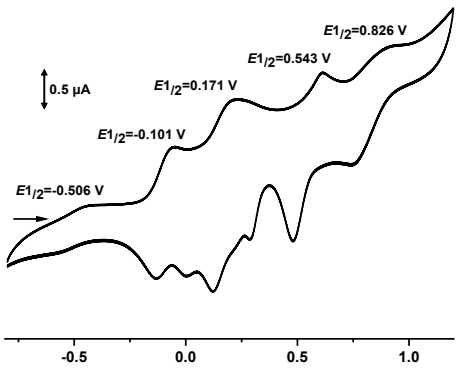

Figure S9. Cyclic voltammogram of **3** (potential vs Ag/AgCl, 1 mM, 0.1 M Bu_4NPF_6 in CH_2Cl_2, glassy carbon working electrode, Pt wire counter electrode, and a scan rate of 50 mV/s).

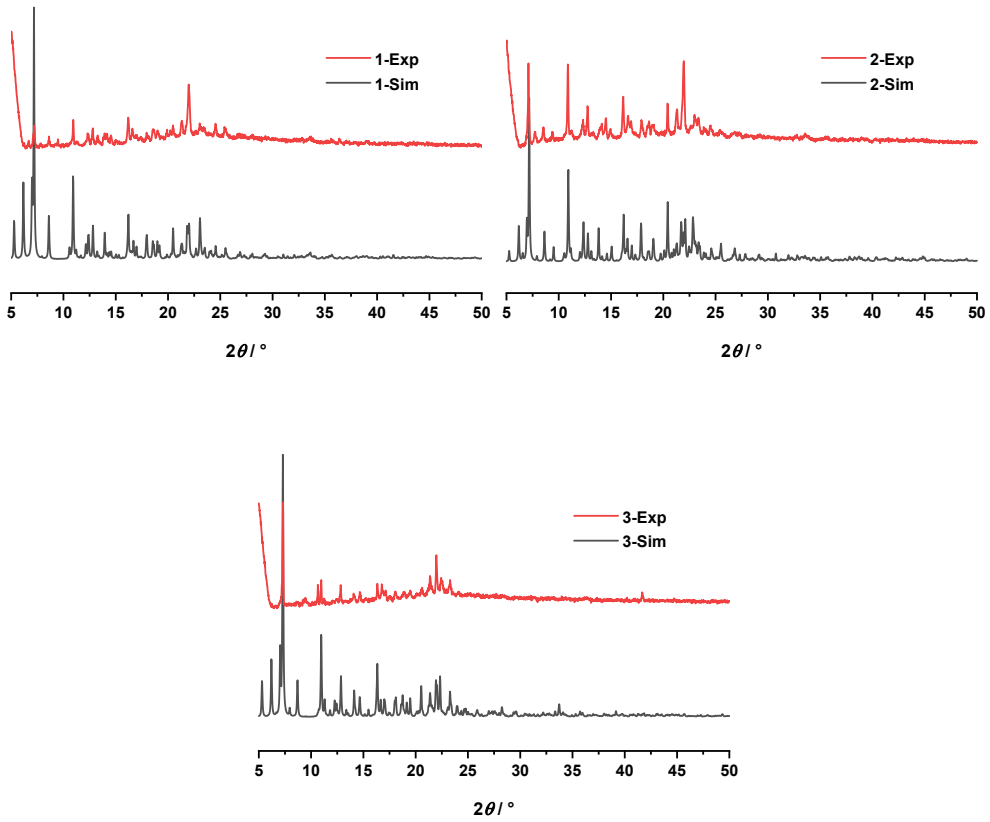

Figure S10. PXRD profiles of **1**, **2** and **3**: simulation results (Sim) and experimental results (Exp).

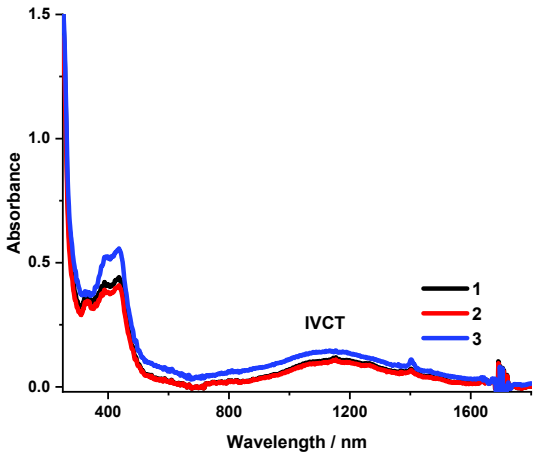

Figure S11. UV-Vis-NIR spectrum of **1**, **2** and **3** (c = 2.0 mmol·L^{-1}, CH_2Cl_2).