Electronic Supporting Information

Magnetostructural relationship for μ_2-phenoxido bridged ferric dimers

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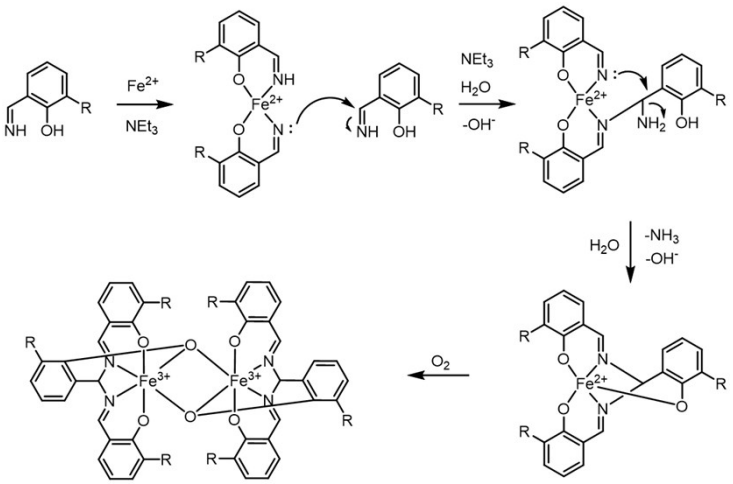
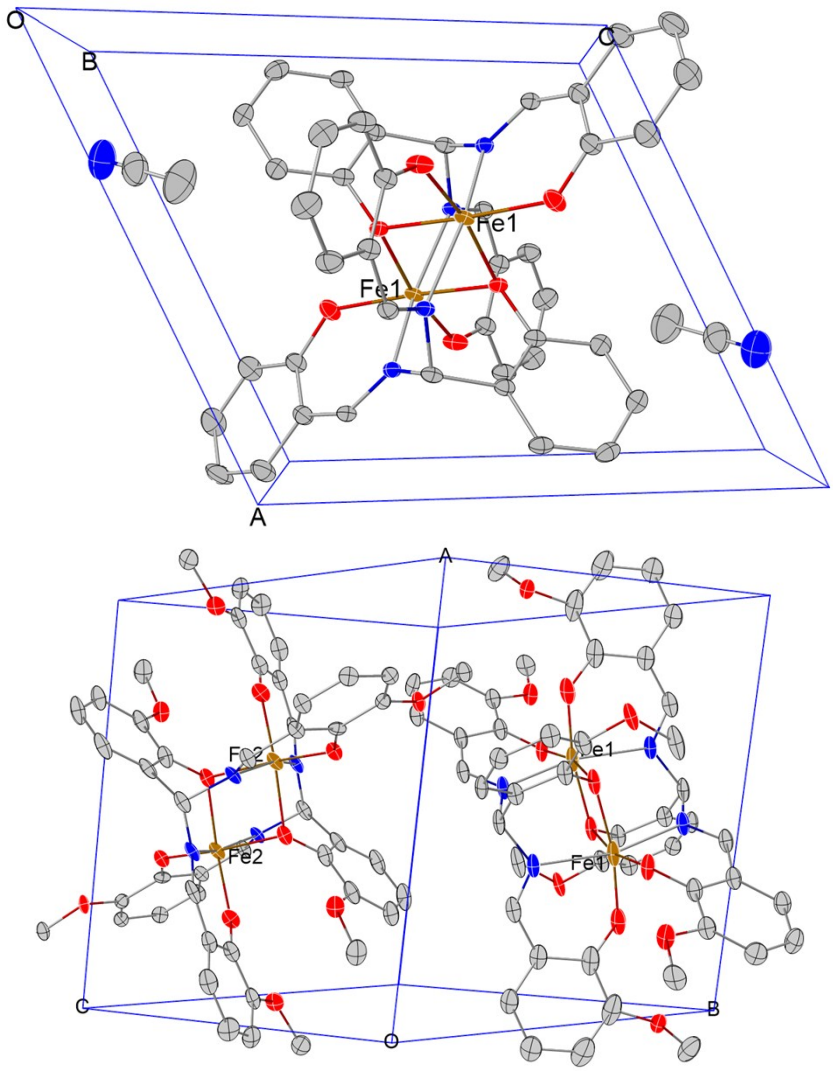
Caption of Content



Scheme S1. Proposed Reaction Leading to ligands H_2L-R (H_2L-H, H_2L-OCH_3 and H_2L-OC_2H_5) for complexes **1**, **2** and **3**.



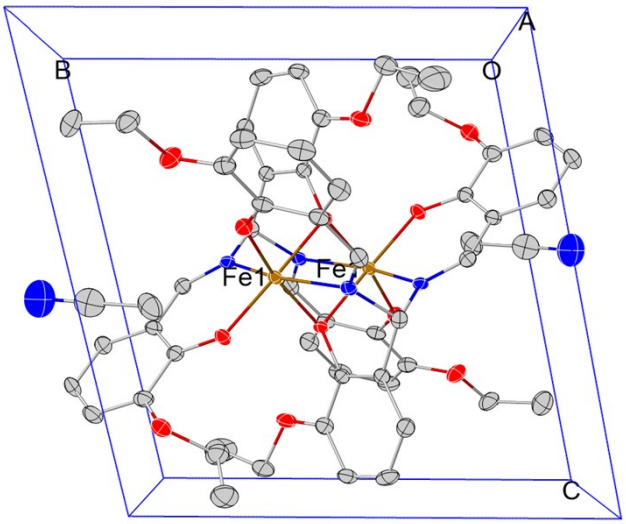


Fig. S1 Structures of the molecular units in **1**, **2** and **3**.

Table S1 Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

		1	
Fe1-O1	2.026 (1)	Fe1-O1^{i}	2.061 (2)
Fe1-O2	1.903 (1)	Fe1-O3^{i}	1.915 (2)
Fe1-N1	2.161(2)	Fe1-N2^{i}	2.147(2)
Fe1^{i}-O1-Fe1	98.01(6)	O1-Fe1-O2	169.81(6)
O1-Fe1-O3^{i}	91.86(6)	O1-Fe1-O1^{i}	81.99(6)
O1-Fe1-N1	82.34(6)	O1-Fe1-N2^{i}	86.34(6)
O1^{i}-Fe1-N1	81.80 (6)	O1^{i}-Fe1-O2	93.66(6)
O1^{i}-Fe1-O3^{i}	167.39(6)	O2-Fe1-O3^{i}	94.10(7)
O2-Fe1-N2^{i}	102.23(6)	O2-Fe1-N1	87.94(6)
O3^{i}-Fe1-N1	108.39(6)	O3^{i}-Fe1-N2^{i}	86.75(6)
N1-Fe1- N2^{i}	161.28(6)	O1^{i}-Fe1-N2^{i}	81.90 (6)
		2	
Fe1-O1	2.040(3)	Fe1-O1^{i}	2.066(2)
Fe1-O3	1.905(3)	Fe1-O5^{i}	1.930(3)
Fe1-N1	2.164(3)	Fe1-N2^{i}	2.129(3)
Fe1^{i}-O1	2.066(2)	Fe1^{i}-O5	1.930(3)
Fe1^{i}-N2	2.129(3)	Fe2-O11^{ii}	1.911(3)
Fe2-O9	1.904(3)	Fe2-O7	2.020(3)
Fe2-O7^{ii}	2.091(3)	Fe2-N4^{ii}	2.124(3)
Fe2-N3	2.137(3)	Fe2^{ii}-O7	2.091(3)
Fe2^{ii}-O11	1.912(3)	Fe2^{ii}-N4	2.124(3)
Fe1-O1-Fe1^{i}	97.03(12)	Fe2-O7-Fe2^{ii}	97.17(11)
O1-Fe1-O3	168.83(7)	O1-Fe1-O5^{i}	91.90(12)
O1-Fe1-N1	81.97(12)	O1-Fe1-O1^{i}	82.97(12)
O1^{i}-Fe1-N1	82.67(11)	O1-Fe1-N2^{i}	87.59(12)
O1^{i}-Fe1-O5^{i}	167.10(12)	O1^{i}-Fe1-O3	94.89(12)
O3-Fe1-O1	169.33(11)	O3-Fe1-O5^{i}	92.26(12)
O3-Fe1-N2^{i}	102.47(13)	O1^{i}-Fe1-N2^{i}	81.51(11)
O5^{i}-Fe1-N1	108.41(11)	O3-Fe1-N1	87.39(13)
N1-Fe1- N2^{i}	161.99(12)	O5^{i}-Fe1-N2^{i}	86.48(11)

O9-Fe2-O11^{ii}	95.24(12)	O9-Fe2-O7	169.89(11)
O11^{ii}-Fe2-O7	93.25(11)	O9-Fe2-O7^{ii}	89.64(11)
O11^{ii}-Fe2-O7^{ii}	169.92(10)	O7-Fe2-O7^{ii}	82.83(11)
O9-Fe2-N4^{ii}	99.16(12)	O11^{ii}-Fe2-N4^{ii}	88.79(11)
O7-Fe2-N4^{ii}	86.46(11)	O7^{ii}-Fe2-N4^{ii}	81.72(11)
O9-Fe2-N3	89.10(12)	O11^{ii}-Fe2-N3	107.96(12)
O7-Fe2-N3	83.08(11)	O7^{ii}-Fe2-N3	80.88(11)
N4^{ii}-Fe2-N3	160.67(12)		
	3		
Fe1-O1	2.049(2)	Fe1-O1^{i}	2.048(2)
Fe1-O3	1.913(2)	Fe1-O5^{i}	1.919(2)
Fe1-N1	2.166(2)	Fe1-N2^{i}	2.146(2)
Fe1^{i}-O1-Fe1	98.53(7)	O1-Fe1-O3	168.83(7)
O1-Fe1-O5^{i}	92.41(7)	O1-Fe1-O1^{i}	81.47(7)
O1-Fe1-N1	81.78(7)	O1-Fe1-N2^{i}	84.83(7)
O1^{i}-Fe1-N1	81.74(7)	O1^{i}-Fe1-O3	94.49(7)
O1^{i}-Fe1-O5^{i}	168.27(7)	O3-Fe1-O5^{i}	93.29(8)
O3-Fe1-N2^{i}	105.03(8)	O3-Fe1-N1	87.34(8)
O5^{i}-Fe1-N1	107.41(7)	O5^{i}-Fe1-N2^{i}	87.22(7)
N1-Fe1- N2^{i}	160.49(8)	O1^{i}-Fe1-N2^{i}	82.28 (7)

Symmetry codes for **1**: Symmetry code: (i) -*x*+1, -*y*+1, -*z*+1; **2**: Symmetry code: (i) -*x*+1, -*y*+1, -*z*+2; (ii) -*x*+1, -*y*, -*z*+1.; **3**: Symmetry code: (i) -*x*+1, -*y*+1, -*z*+1.

Table S2 Hydrogen-bond geometry (Å, º) for (**2**). (D, donor atom; A, acceptor atom).

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C7—H7*B*···O5^{i}	0.98	2.40	3.304(6)	154
C23—H23*C*···O10^{ii}	0.98	2.64	3.187(4)	115
C39—H39*C*···O9^{iii}	0.98	2.52	3.409(5)	151
C40—H40···O2^{i}	0.95	2.48	3.338(5)	150
C47—H47*C*···O3^{iv}	0.98	2.51	3.395(5)	150

C47—H47···*C*O4′^{iv}	0.98	2.45	3.191(8)	132

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+2; (ii) -*x*+1, -*y*, -*z*+1; (iii) -*x*+2, -*y*, -*z*+1; (iv) -*x*+1, -*y*, -*z*+2.

Table S3 Hydrogen-bond geometry (Å, º) for (**3**). (D, donor atom; A, acceptor atom).

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C25—H25*B*···O5	0.99	2.36	2.922(3)	115
C27—H27···N3^{ii}	0.95	2.45	3.399(4)	172
C29—H29*A*···O6	0.98	2.46	3.201(4)	133
C29—H29*B*···O3^{i}	0.98	2.39	3.330(4)	162
C29—H29*B*···O5	0.98	2.60	3.275(4)	126
C29—H29*C*···N3^{iii}	0.98	2.50	3.335(5)	143

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*, -*z*+1; (iii) -*x*, -*y*, -*z*+1.

Table S4 Structural and magnetic data for *bis*(μ_2-oxido)diiron(III) complexes with separation ferromagnetic and antiferromagnetic ($H = -2J\, S_1 \cdot S_2$).

Complex	Fe···Fe/Å	Fe–O–Fe/°	*P*/Å [a]	J_{exp}/ cm^{-1}	J_{eq}/ cm^{-1} [b]	Ref.
bis(μ_2-phenoxido)diiron(III) complexes						
$[Fe_2(L\text{-}H)_2]\cdot 2CH_3CN$	3.085	98.02	2.044	+0.47	-4.85	This work
$Fe_2(L\text{-}OCH_3)_2$	3.076	97.03	2.066	+0.86	-3.82	This work
$[Fe_2(L\text{-}OC_2H_5)_2]\cdot 2CH_3CN$	3.105	98.53	2.048	-0.72	-4.79	This work
$Fe_2(salmp)_2$[c]	3.062	97.02	2.064	+1.21	-3.91	1
$[FeL^1Cl]_2$[d]	3.248	105.0	2.044	-6.51	-5.02	2
$[FeL^2(MeOH)Cl]_2$[e]	3.216	105.1	2.025	-7.71	-6.43	2
$[FeL^3Cl]_2$[f]	3.186	105.6	1.999	-10.92	-8.91	2
$[FeL^4(MeOH)Cl]_2$[g]	3.163	104.7	1.997	-8.02	-9.23	3
$[Fe_2L_2]$[h]	3.321	108.9	2.043	-12.71	-5.11	4
$[Fe_2L_2]$[i]	3.341	103.8	2.12	-6.44	-1.92	5
bis(μ_2-alkoxido)diiron(III) complexes						

$[Fe_2(L_2)]$ [j]	3.125	101.05	2.024	-2.2	-6.5	6
$[Fe(heidi)(H_2O)]_2$ [k]	3.119	104.3	1.9755	-13.4	-12.0	7
$[Fe\{(N(PL)_2)_2ala\}]_2^{2+}$ [l]	3.180	103.8	2.0205	-5.2	-6.8	8
$[Fe_2(acac)_4(OEt)_2]$ [m]	3.116	103.6	1.982	-11.0	-11.0	9
$[Fe_2L(OEt)Cl_2]$ [n]	3.114	104.3	1.991	-15.4	-9.9	9
$[Fe_2L(OMe)Cl_2]$ [o]	3.106	103.0	1.995	-16.3	-9.4	10
$[Fe(cupf)_2(OMe)]_2$ [p]	3.075	102.4	1.9725	-14.0	-12.5	11
bis(μ_2-hydroxido)diiron(III) complexes						
$[Fe(L)(OH)]_2$ [q]	3.085	100.7	2.002	-5.5	-7.7	12
$[Fe(chel)(H_2O)(OH)]_2$ [r]	3.078	103.2	1.964	-7.3	-14.6	13
$[Fe(L)(OH)]_2$ [s]	3.155	102.8	2.021	-10.4	-6.9	14
$[Fe(dipic)(H_2O)(OH)]_2$ [t]	3.098	103.6	1.965	-11.4	-14.4	13
$[Fe(Me_2Npic)(H_2O)(OH)]_2$ [u]	3.118	105.3	1.962	-11.7	-16.2	15

[a] Half of the shortest super-exchange pathway between two Fe(III) ions.
[b] Calculated using the exponential relationship $-J_{eq} = A \exp(BP)$ and the reported values $A = 8.763 \times 10^{11}$ and $B = -12.662$.[11]
[c] H_3salmp = 2-bis(salicylideneamino) methylphenol.
[d] H_2L^1 = *N*-2-hydroxyphenyl-3-hydroxy-2-naphthaldimine.
[e] H_2L^2 = *N*-2-hydroxy-4-chlorophenylsalicylaldimine.
[f] H_2L^3 = *N*-2-hydroxyphenylsalicylaldimine.
[g] H_2L^4 = *N*-2-hydroxy-4-chlorophenyl-3-hydroxy-2-naphthaldimine.
[h] $H_3L = C_6H_2(CH_3)(OH)\{[C(CH_3)_3]_2(OH)NCH\}_2$.
[i] *N,N'*-bis-(5-chlorosalicylidene)-2-methylpropane-1,2-diamine.
[j] H_3L = 1-Salicylideneamino-3-salicylaminopropan-2-ol.
[k] H_3heidi = [N,N′-Di(2-acetate)-N-2-(hydroxyethyl)]amine.
[l] $H_2N(PL)_2ala$ = α,3-Dihydroxy-β-{[(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridyl)methylene]amino}-5-hydroxymethyl-α,2 dimethyl-4-pyridylpropanoic acid.
[m] acac = Pentane-2,4-dionate.
[n] H_3L = 1,4-Piperazinediyl-bis(N-ethylenesalicylaldimine).
[o] H_2L = pimelyl-bis(N-isopropylhydroxamic acid).
[p] Hcupf = PhN(OH)NO (cupferron).
[q] H_2L = macrocyclic tetraaminodiphenol ligand.
[r] H_2chel = 4-hydroxo-2,6-pyridine-dicarboxylate.
[s] H_2L = *N,N'*-ethylenebis(salicylamine).
[t] H_2dipic = 2,6-pyridinedicarboxylate.
[u] H_2Me_2Npic = 4-(dimethyl-amino)-2,6-pyridinedicarboxylate.

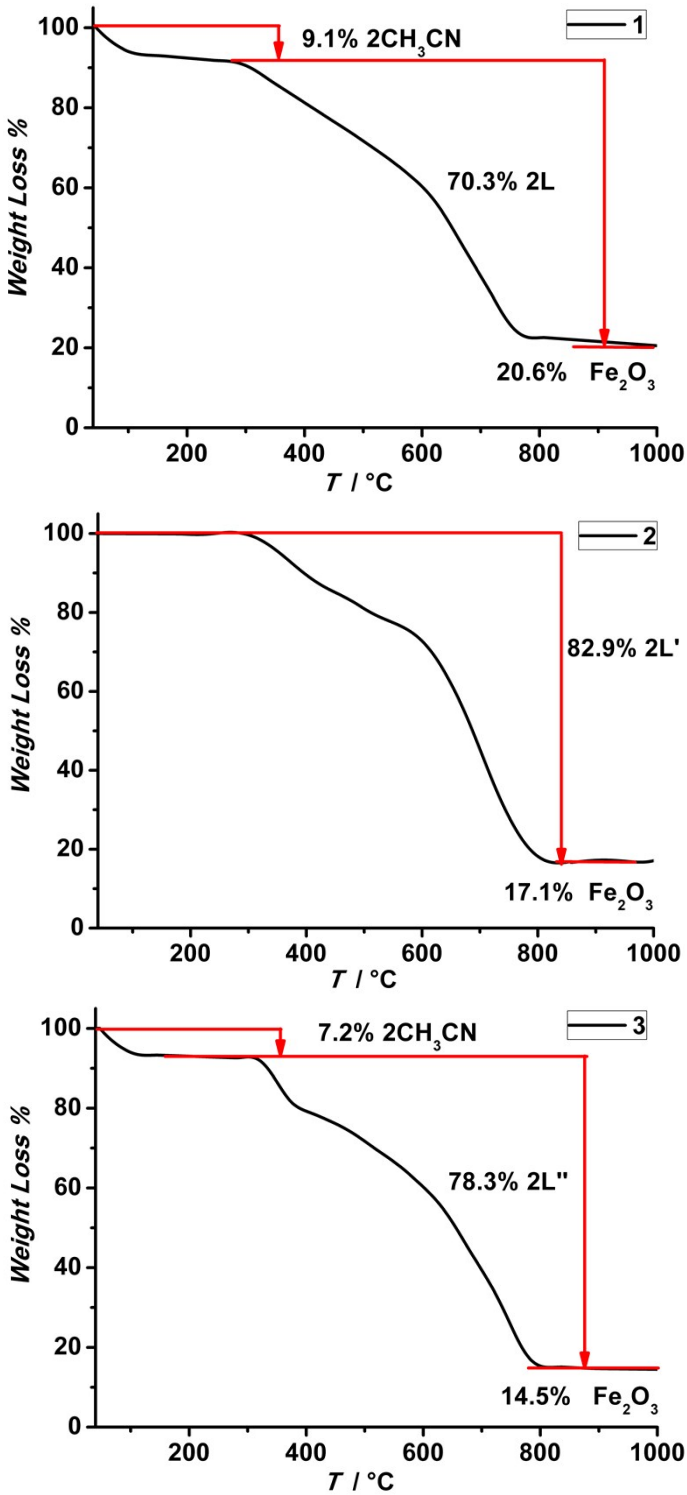
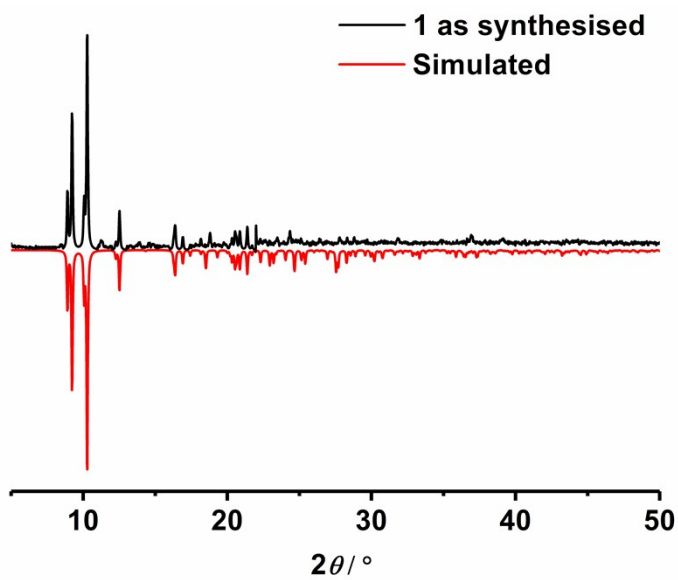
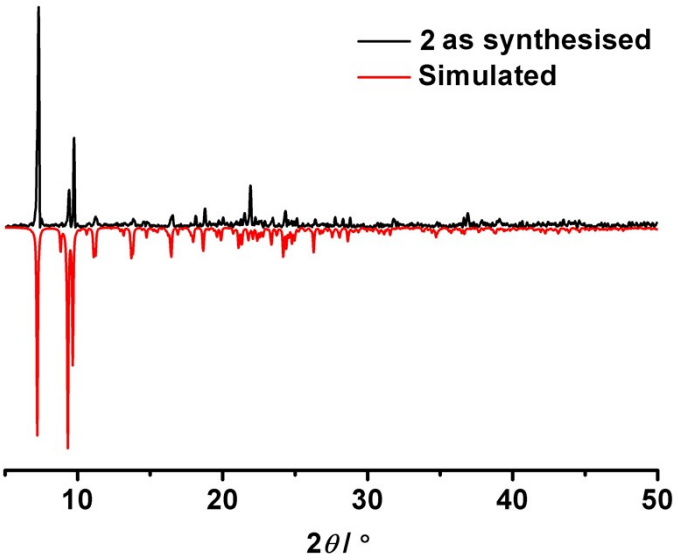


Fig. S2 TGA plots for **1**, **2** and **3**. For **1**, there are two steps of weight loss. The first one from 40 to 310 °C corresponds to the loss of the acetonitrile molecule (obs. 9.1 %, calc. 9.3 %), Then the desolvated network becomes unstable above 310 °C. The second weight loss of 70.3 % (calc. for Fe_2O_3 72.6 %) from 410 to 800 °C corresponds to the decomposition of the compound. For **2**, the complex is stable until 310 °C. The weight loss of 82.9 % in the range of 310 to 820 ºC corresponds to the

decomposition to Fe_2O_3 (calc. 83.7%). For **3**, there are two steps of weight loss. The first one from 40 to 315 °C corresponds to the loss of the acetonitrile molecule (obs. 7.2 %, calc. 7.1 %). Then the desolvated network becomes unstable above 315 °C. The second weight loss of 78.3 % (calc. for Fe_2O_3 78.9 %) from 410 to 800 °C corresponds to the decomposition of the compound.





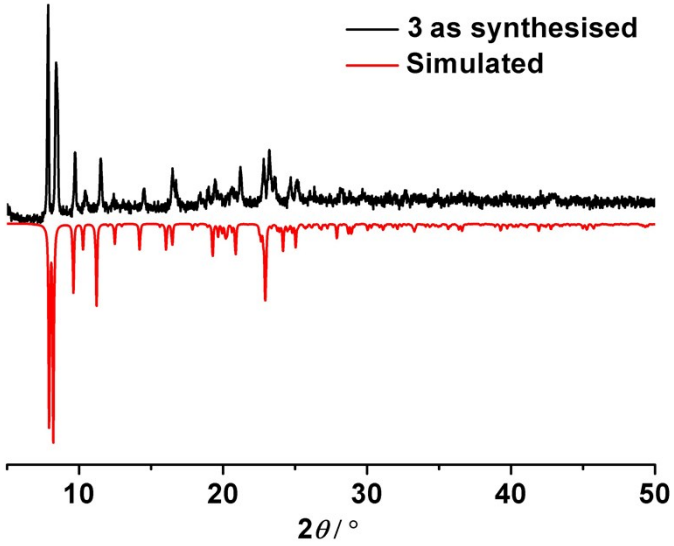


Fig. S3 PXRD patterns simulated from single crystal data and of polycrystalline samples of freshly synthesized of **1**, **2** and **3**.

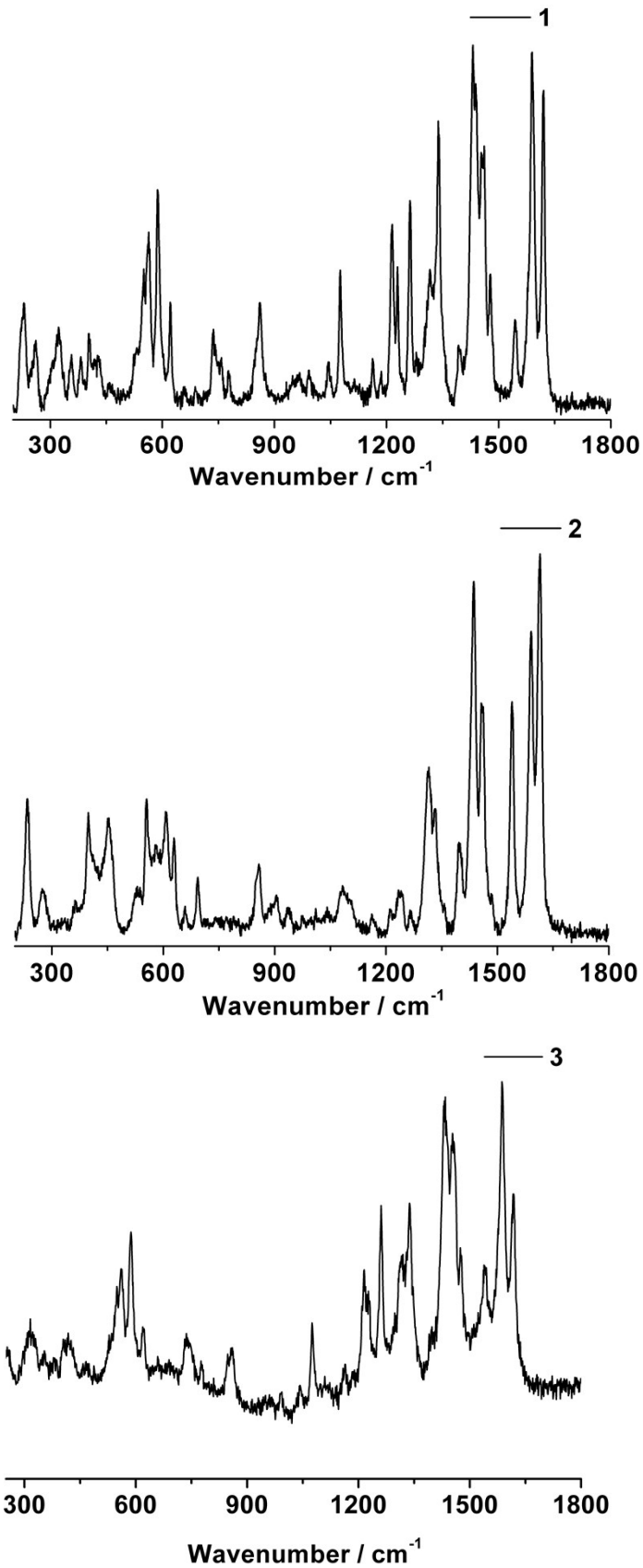


Fig. S4 Raman spectra of **1**, **2** and **3** (λ = 514.5 nm).

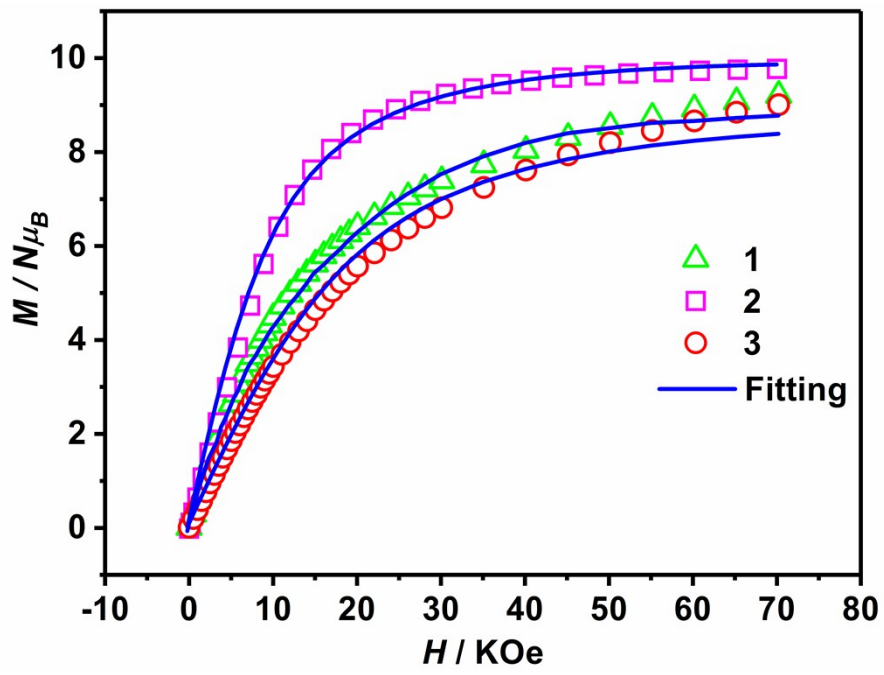


Fig. S5 Isothermal magnetizations for **1**, **2** and **3** at 1.8 K.

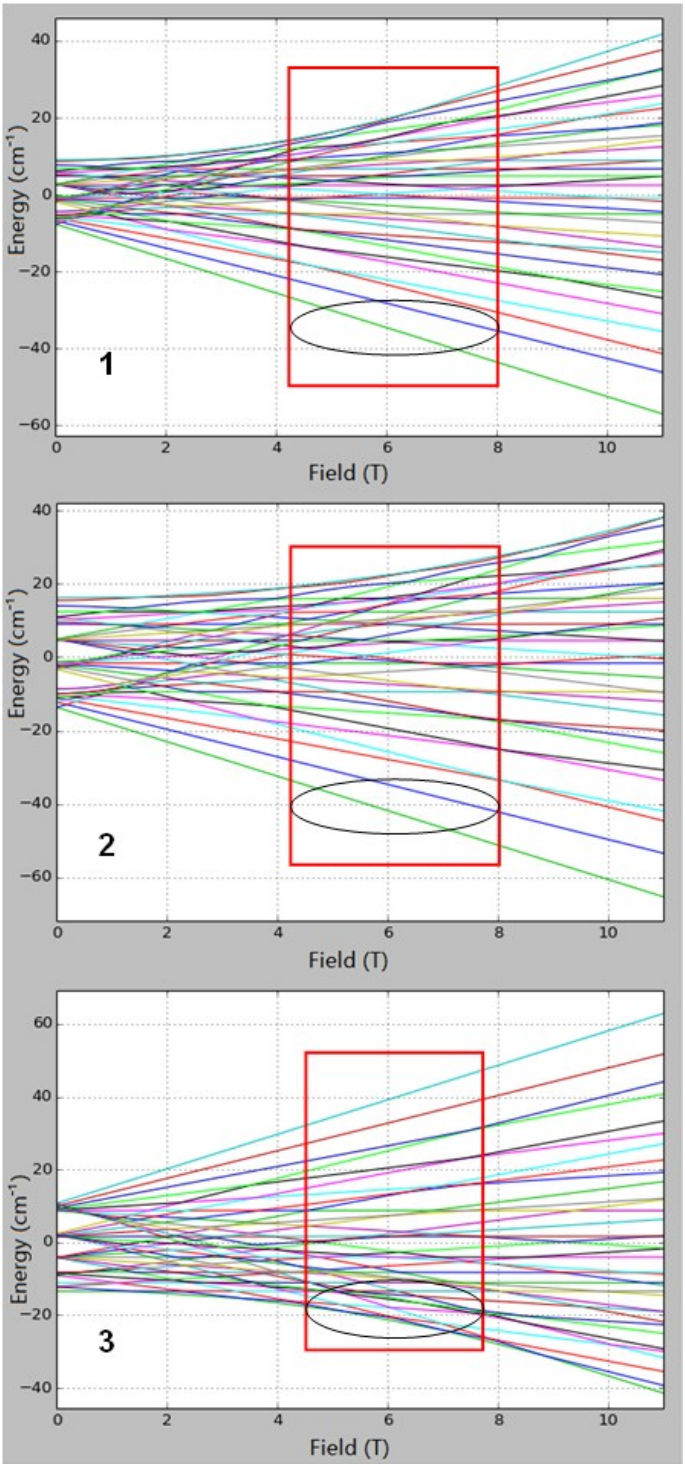


Fig. S6 Zeeman splitting of the Energy levels (in cm^{-1}) of **1**, **2**, and **3** with spin Hamiltonian parameters used in Fig. 4. Magnetic field is along the Fe-Fe directions. Red rectangle areas indicate the field ranges where the HF-EPR transitions can happen. Black circles point out the populated energy levels at 2 K. For **1** and **2**, the large dominate J values (+0.47 and +0.86 cm^{-1}, respectively) result in the S = 5 as

pure ground states, hence the EPR spectrum at 2 K could be well described by $S = 5$, while for **3**, the dominate J (–0.72 cm^{-1}) results in severe crossing of low-lying energy states, and the EPR spectrum at 2 K is contributed by several low spin states ($S = 1$, 2...), making it difficult to simulate the spectra.

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