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Supporting Information

Syntheses, Structures, and Magnetic Properties of Cyano- and Phenoxide-Bridged Fe(III)-Mn(III) Tetrameric Assemblies Formed by Blocked *fac*-Fe Tricyanide with Aliphatic Rings

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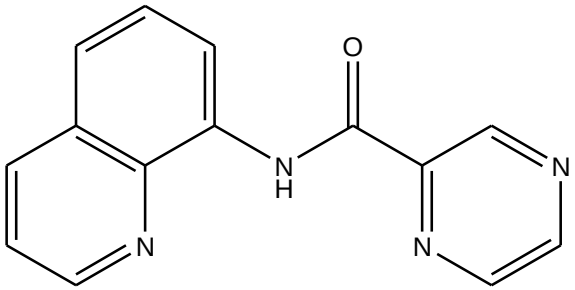

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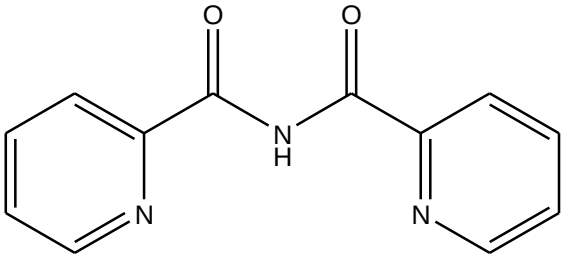

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Scheme S1. Tridentate ligands.

Table S1. Crystallographic data for **1** – **3**

	1	**2**	**3**
formula	$C_{86}H_{92}B_2Cl_4Fe_2Mn_2N_{22}O_4$	$C_{84}H_{96}B_2Cl_4Fe_2Mn_2N_{22}O_8$	$C_{88}H_{108}B_2Fe_2Mn_2N_{22}O_{12}$
Mr	1882.82	1926.83	1909.16
T (K)	100	100	100
crystal system	Triclinic	Monoclinic	Monoclinic
space group	P-1	$P2_1/c$	$P2_1/c$
a (Å)	12.711(3)	9.6040(19)	9.5060(19)
b (Å)	13.004(3)	14.817(3)	15.152(3)
c (Å)	15.439(3)	30.988(6)	31.398(6)
α (^{o})	107.70(3)	90	90
β (^{o})	101.74(3)	93.56(3)	92.33(3)
γ (^{o})	112.78(3)	90	90
V (Å^3)	2086.4(7)	4401.2(15)	4518.7(16)
Z	1	2	2
ρ_{calc} (g cm^{-3})	1.498	1.454	1.403
μ (mm^{-1})	0.832	0.794	0.661
F(000)	974	1996	1996
reflections collected	6175	26835	8642
GOF	1.036	1.056	1.026
R1[a] (I≥2σ(I))	0.0724	0.0615	0.0589
wR2[b] (I≥2σ(I))	0.1989	0.1576	0.1464

[a] $R1=\Sigma||F_O|-|F_C||/\Sigma|F_C|$, [b] $wR2 = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2]^{1/2}$.

Table S2. Bond lengths (Å) and angles (°) for **1 - 3**[a]

		1	
Fe(1)-C(1)	1.909(7)	N(1)-Mn(1)	2.210(6)
Fe(1)-C(2)	1.936(8)	Mn(1)-O(2)	1.847(5)
Fe(1)-C(3)	1.973(8)	Mn(1)-O(1)	1.897(4)
Fe(1)-N(6)	1.981(6)	Mn(1)-N(11)	1.986(6)
Fe(1)-N(8)	2.007(6)	Mn(1)-N(10)	1.990(6)
Fe(1)-N(4)	2.037(6)	Mn(1)-O(1)a	2.505(4)
O(1)-Mn(1)a	2.505(4)		
C(1)-Fe(1)-C(2)	84.7(3)	N(9)-N(8)-Fe(1)	117.0(4)
C(1)-Fe(1)-C(3)	87.9(3)	O(2)-Mn(1)-O(1)	95.0(2)
C(2)-Fe(1)-C(3)	83.6(3)	O(2)-Mn(1)-N(11)	91.1(2)
C(1)-Fe(1)-N(6)	93.0(3)	O(1)-Mn(1)-N(11)	162.7(2)
C(2)-Fe(1)-N(6)	94.0(3)	O(2)-Mn(1)-N(10)	174.6(2)
C(3)-Fe(1)-N(6)	177.4(3)	O(1)-Mn(1)-N(10)	89.5(2)
C(1)-Fe(1)-N(8)	91.3(3)	N(11)-Mn(1)-N(10)	85.5(2)
C(2)-Fe(1)-N(8)	174.6(3)	O(2)-Mn(1)-N(1)	93.5(2)
C(3)-Fe(1)-N(8)	92.7(3)	O(1)-Mn(1)-N(1)	98.8(2)
N(6)-Fe(1)-N(8)	89.7(2)	N(11)-Mn(1)-N(1)	97.0(2)
C(1)-Fe(1)-N(4)	177.6(3)	N(10)-Mn(1)-N(1)	82.9(2)
C(2)-Fe(1)-N(4)	93.4(3)	O(2)-Mn(1)-O(1)a	87.11(19)
C(3)-Fe(1)-N(4)	90.5(3)	O(1)-Mn(1)-O(1)a	77.64(19)
N(6)-Fe(1)-N(4)	88.5(2)	N(11)-Mn(1)-O(1)a	86.47(19)
N(8)-Fe(1)-N(4)	90.5(2)	N(10)-Mn(1)-O(1)a	96.8(2)
N(1)-C(1)-Fe(1)	178.6(6)	N(1)-Mn(1)-O(1)a	176.43(18)
N(2)-C(2)-Fe(1)	176.2(6)	C(29)-N(10)-Mn(1)	125.7(5)
N(3)-C(3)-Fe(1)	177.6(6)	C(26)-N(10)-Mn(1)	111.6(4)
C(1)-N(1)-Mn(1)	159.1(6)	C(37)-N(11)-Mn(1)	128.4(5)
C(5)-N(4)-N(5)	107.5(5)	C(27)-N(11)-Mn(1)	109.5(4)
C(5)-N(4)-Fe(1)	136.1(5)	C(35)-O(1)-Mn(1)	118.1(4)
N(5)-N(4)-Fe(1)	116.1(4)	C(35)-O(1)-Mn(1)a	127.4(4)
C(12)-N(6)-Fe(1)	135.8(5)	Mn(1)-O(1)-Mn(1)a	102.36(19)
N(7)-N(6)-Fe(1)	117.3(4)	C(43)-O(2)-Mn(1)	127.4(5)

C(19)-N(8)-Fe(1)	136.4(4)		

2

Fe(1)-C(1)	1.904(4)	N(1)-Mn(1)	2.172(3)
Fe(1)-C(3)	1.922(4)	Mn(1)-O(2)	1.865(3)
Fe(1)-C(2)	1.934(4)	Mn(1)-O(1)	1.913(2)
Fe(1)-N(4)	1.974(3)	Mn(1)-N(11)	1.985(3)
Fe(1)-N(8)	1.994(3)	Mn(1)-N(10)	1.988(3)
Fe(1)-N(6)	2.013(3)	Mn(1)-O(1)b	2.482(3)
O(1)-Mn(1)b	2.482(3)		
C(1)-Fe(1)-C(3)	85.84(16)	N(9)-N(8)-Fe(1)	116.8(2)
C(1)-Fe(1)-C(2)	82.83(15)	O(2)-Mn(1)-O(1)	97.01(11)
C(3)-Fe(1)-C(2)	91.20(16)	O(2)-Mn(1)-N(11)	90.70(11)
C(1)-Fe(1)-N(4)	95.40(14)	O(1)-Mn(1)-N(11)	164.32(11)
C(3)-Fe(1)-N(4)	89.49(15)	O(2)-Mn(1)-N(10)	170.85(11)
C(2)-Fe(1)-N(4)	178.04(15)	O(1)-Mn(1)-N(10)	88.38(11)
C(1)-Fe(1)-N(8)	93.48(15)	N(11)-Mn(1)-N(10)	82.37(12)
C(3)-Fe(1)-N(8)	178.03(15)	O(2)-Mn(1)-N(1)	96.62(12)
C(2)-Fe(1)-N(8)	90.55(14)	O(1)-Mn(1)-N(1)	93.71(11)
N(4)-Fe(1)-N(8)	88.73(13)	N(11)-Mn(1)-N(1)	98.96(12)
C(1)-Fe(1)-N(6)	172.66(14)	N(10)-Mn(1)-N(1)	90.37(12)
C(3)-Fe(1)-N(6)	89.22(15)	O(2)-Mn(1)-O(1)b	92.80(10)
C(2)-Fe(1)-N(6)	91.86(15)	O(1)-Mn(1)-O(1)b	81.09(10)
N(4)-Fe(1)-N(6)	89.98(13)	N(11)-Mn(1)-O(1)b	84.93(10)
N(8)-Fe(1)-N(6)	91.63(13)	N(10)-Mn(1)-O(1)b	80.70(10)
N(3)-C(3)-Fe(1)	177.7(3)	N(1)-Mn(1)-O(1)b	169.75(10)
N(2)-C(2)-Fe(1)	175.1(3)	C(33)-O(1)-Mn(1)	121.9(2)
N(1)-C(1)-Fe(1)	173.3(3)	C(33)-O(1)-Mn(1)b	114.0(2)
C(1)-N(1)-Mn(1)	159.2(3)	Mn(1)-O(1)-Mn(1)b	98.91(10)
C(5)-N(4)-Fe(1)	135.3(2)	C(40)-O(2)-Mn(1)	130.4(2)
N(5)-N(4)-Fe(1)	116.6(2)	C(27)-N(10)-Mn(1)	125.2(3)
C(12)-N(6)-Fe(1)	134.5(3)	C(26)-N(10)-Mn(1)	112.4(2)
N(7)-N(6)-Fe(1)	117.6(2)	C(34)-N(11)-Mn(1)	127.4(3)
C(19)-N(8)-Fe(1)	136.4(3)	C(25)-N(11)-Mn(1)	112.9(2)

3

Fe(1)-C(1)	1.903(8)	N(1)-Mn(1)	2.178(6)

Fe(1)-C(2)	1.905(6)	Mn(1)-O(2)	1.860(3)
Fe(1)-C(3)	1.906(6)	Mn(1)-O(1)	1.899(4)
Fe(1)-N(6)	1.968(4)	Mn(1)-N(10)	1.982(4)
Fe(1)-N(4)	1.988(5)	Mn(1)-N(11)	1.984(4)
Fe(1)-N(8)	2.008(5)	Mn(1)-O(1)c	2.497(4)
O(1)-Mn(1)c	2.497(4)		

C(1)-Fe(1)-C(2)	85.7(2)	N(9)-N(8)-Fe(1)	118.1(3)
C(1)-Fe(1)-C(3)	82.8(2)	O(2)-Mn(1)-O(1)	96.37(15)
C(2)-Fe(1)-C(3)	91.8(2)	O(2)-Mn(1)-N(10)	90.72(16)
C(1)-Fe(1)-N(6)	95.6(2)	O(1)-Mn(1)-N(10)	163.98(18)
C(2)-Fe(1)-N(6)	90.0(2)	O(2)-Mn(1)-N(11)	171.00(17)
C(3)-Fe(1)-N(6)	177.5(2)	O(1)-Mn(1)-N(11)	88.66(16)
C(1)-Fe(1)-N(4)	93.9(2)	N(10)-Mn(1)-N(11)	82.60(18)
C(2)-Fe(1)-N(4)	178.0(2)	O(2)-Mn(1)-N(1)	96.36(17)
C(3)-Fe(1)-N(4)	90.1(2)	O(1)-Mn(1)-N(1)	94.27(17)
N(6)-Fe(1)-N(4)	88.08(18)	N(10)-Mn(1)-N(1)	99.21(19)
C(1)-Fe(1)-N(8)	172.1(2)	N(11)-Mn(1)-N(1)	90.69(18)
C(2)-Fe(1)-N(8)	88.9(2)	O(2)-Mn(1)-O(1)c	94.00(15)
C(3)-Fe(1)-N(8)	91.6(2)	O(1)-Mn(1)-O(1)c	80.82(14)
N(6)-Fe(1)-N(8)	90.20(19)	N(10)-Mn(1)-O(1)c	84.38(16)
N(4)-Fe(1)-N(8)	91.74(19)	N(11)-Mn(1)-O(1)c	79.39(16)
N(1)-C(1)-Fe(1)	173.5(5)	N(1)-Mn(1)-O(1)c	168.97(14)
N(2)-C(2)-Fe(1)	177.6(5)	C(27)-N(10)-Mn(1)	127.2(4)
N(3)-C(3)-Fe(1)	175.2(5)	C(26)-N(10)-Mn(1)	112.9(3)
C(1)-N(1)-Mn(1)	158.4(4)	C(34)-N(11)-Mn(1)	125.9(4)
C(5)-N(4)-N(5)	106.7(4)	C(25)-N(11)-Mn(1)	112.1(3)
C(5)-N(4)-Fe(1)	136.7(4)	C(33)-O(2)-Mn(1)	130.6(3)
N(5)-N(4)-Fe(1)	116.5(3)	C(40)-O(1)-Mn(1)	121.5(3)
C(12)-N(6)-Fe(1)	135.3(4)	C(40)-O(1)-Mn(1)c	112.0(3)
N(7)-N(6)-Fe(1)	117.1(3)	Mn(1)-O(1)-Mn(1)c	99.18(14)
C(19)-N(8)-Fe(1)	135.3(4)		

[a]Symmetry transformations used to generate equivalent atoms: (a) -x,-y+1,-z+1; (b) -x,-y+1,-z; (c) -x,-y+1,-z.

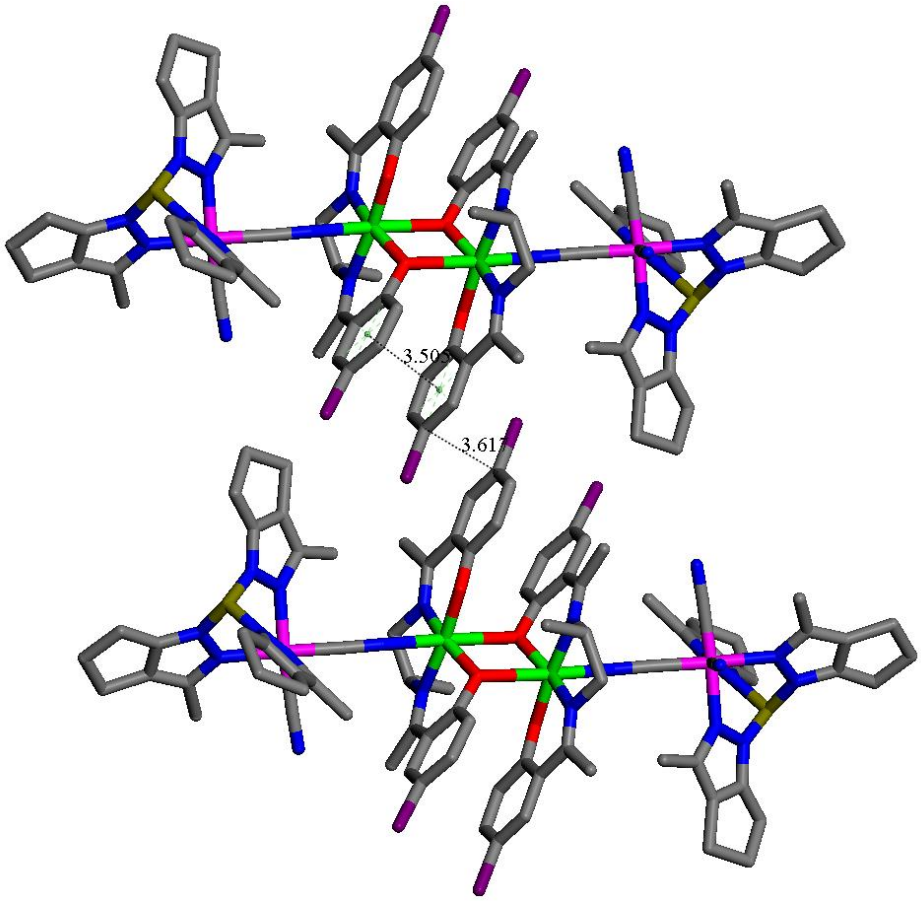

Figure S1. Extended structure of **1** showing π-π interactions between benzene rings of Schiff bases ligands (centroid distance = 3.505 Å) and a weak π-π contact between single C atoms with a distance of 3.617 Å.

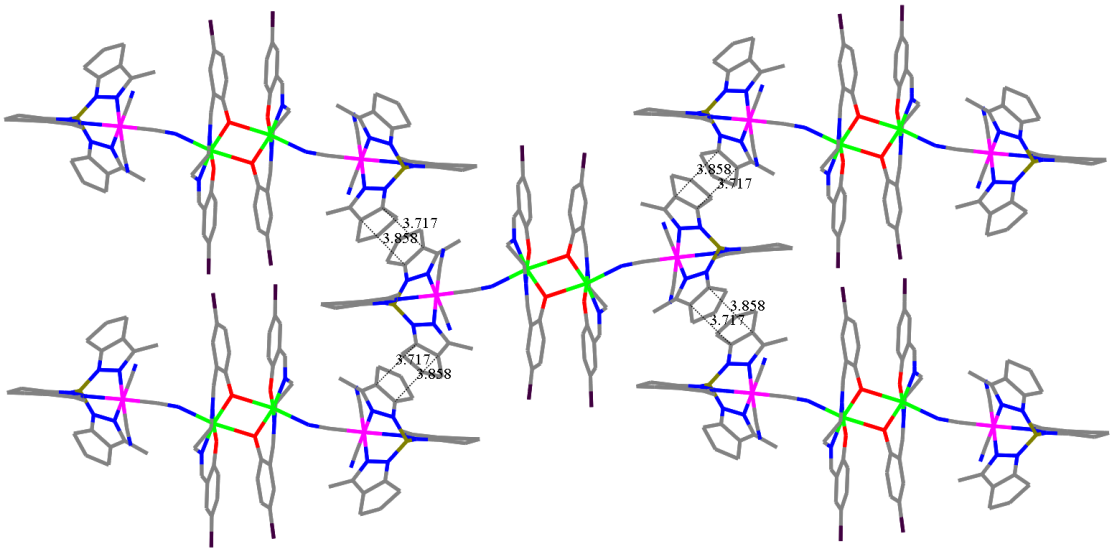

Figure S2. Extended structure of **2** showing π-π interactions between pyrazole C atoms of $Tp^{Me,mt3}$ ligands (C---C = 3.717 and 3.858 Å). The shortest Fe-Fe distance is 9.358 Å through the intermolecular contact.

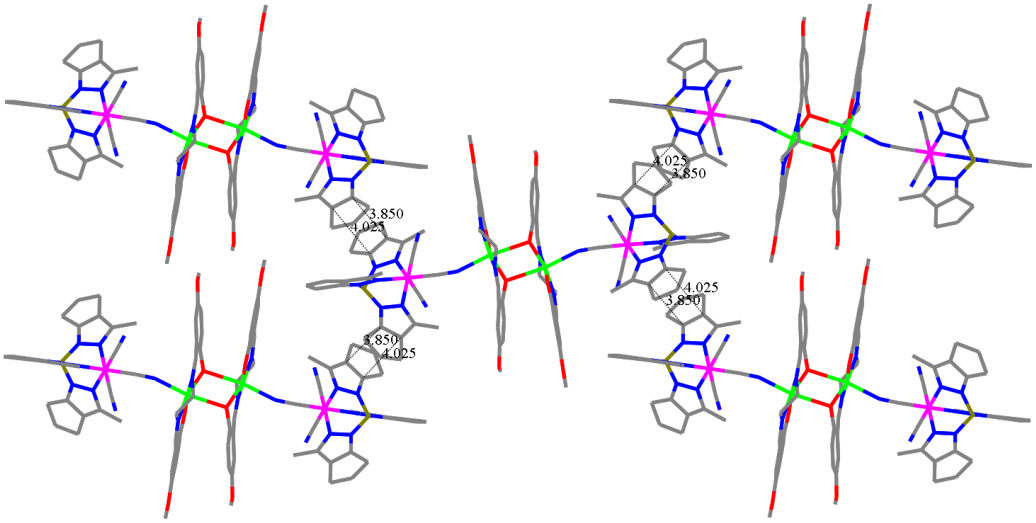

Figure S3. Extended structure of **3** showing π-π interactions between pyrazole C atoms of $Tp^{Me,mt3}$ ligands (C---C = 3.850 and 4.025 Å). The shortest Fe-Fe distance is 9.612 Å through the intermolecular contact.

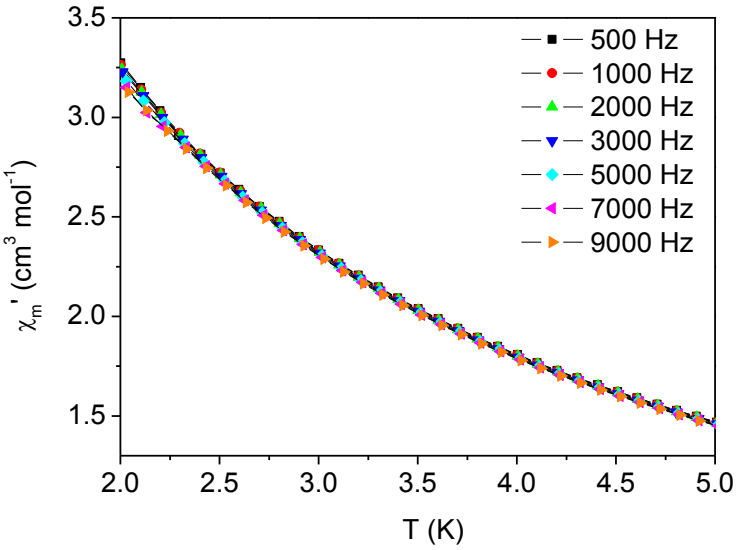

Figure S4. Plots of χ_m' versus T for **1** at indicated frequencies.

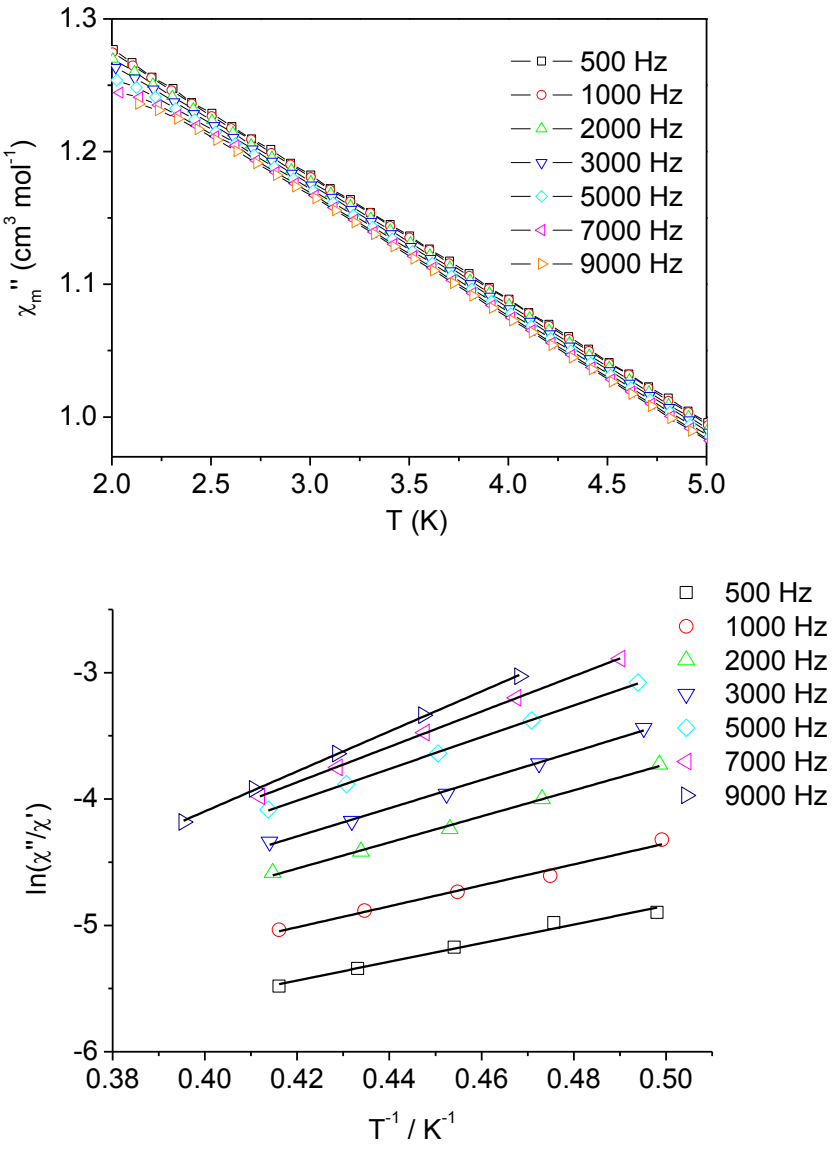

Figure S5. Plots of χ_m' versus T (top) and natural logarithm of the ratio of χ_m'' to χ_m' versus 1/T for **2** (bottom).

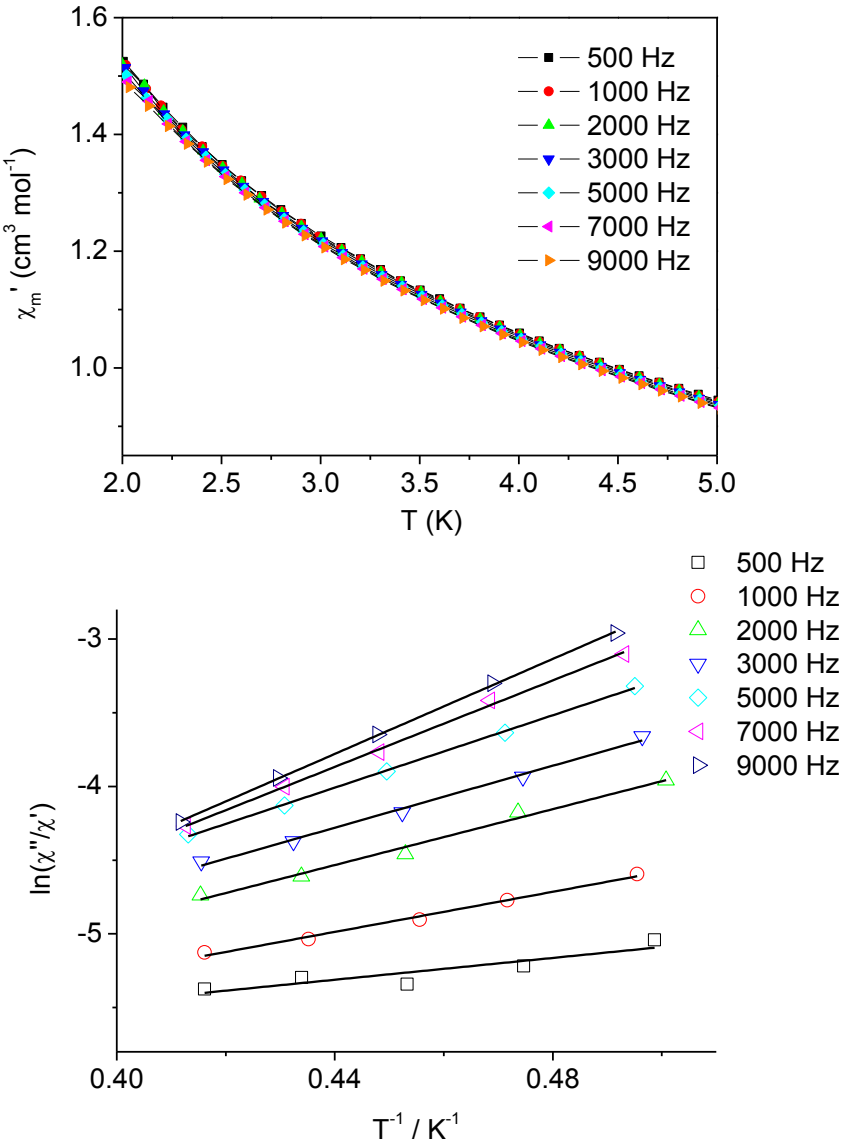

Figure S6. Plots of χ_m' versus T (top) and natural logarithm of the ratio of χ_m'' to χ_m' versus 1/T for **3** (bottom).

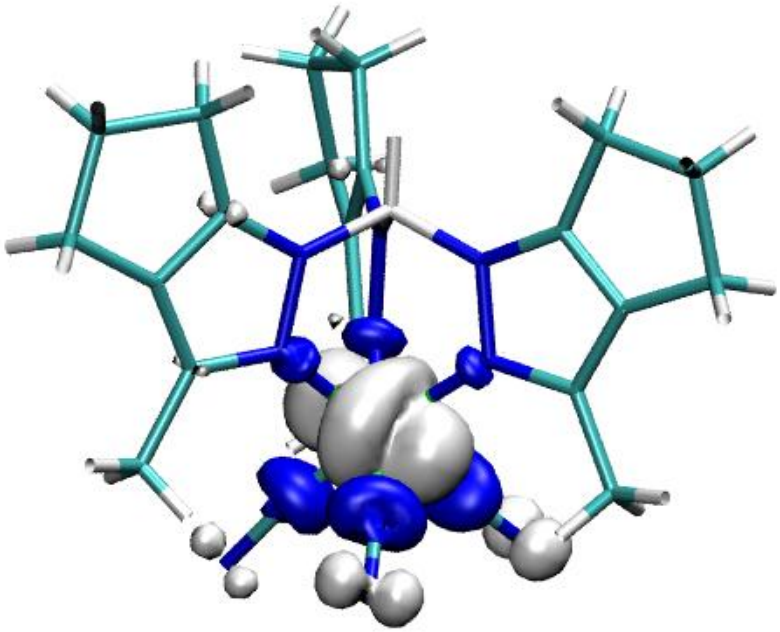

Figure S7. Spin density of the $[(Tp^{Me,mt3})Fe(CN)_3]^-$ precursor with a Fe d_{z2} type magnetic orbital, derived from B3LYP DFT calculations performed with Gaussian 09. The 6-311G* basis set is used for Fe and the 6-31G(d, p) basis set is taken for the other atoms.