Electronic Supplementary Material (ESI) for *Dalton Trans.*

Syntheses, Structures, and Magnetic Properties of Three New Cyano-Bridged Complexes Based on the $[Mn(CN)_6]^{3-}$ Building Block

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Supporting Information

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X-ray crystallography

Table S1. Selected bond lengths [Å] and angles [°] for complex **1**.

Complex **1**			
Mn1-C1	1.992(2)	Mn3-C19	2.015(2)
Mn1-C2	2.003(3)	Mn3-C20	2.000(3)
Mn1-C3	2.008(3)	Mn3-C21	2.004(2)
Mn1-C1[a]	1.992(2)	Mn3-C19[p]	2.015(2)
Mn1-C2[a]	2.003(3)	Mn3-C20[b]	2.000(3)
Mn1-C3[a]	2.008(3)	Mn3-C21[b]	2.004(2)
Mn2-N1	2.210(2)	Mn4-N7	2.2346(19)
Mn2-N4	2.242(2)	Mn4-N10	2.246(2)
Mn2-N5	2.203(2)	Mn4-N11	2.212(2)
Mn2-N6	2.248(2)	Mn4-N12	2.2348(19)
Mn2-O1	2.288(2)	Mn4-O4	2.2784(18)
Mn2-O2	2.2569(18)	Mn4-O5	2.2781(18)
Mn2-O3	2.2762(19)	Mn4-O6	2.2845(16)
N1-C1-Mn1	174.7(2)	N7-C19-Mn3	178.2(2)
N2-C2-Mn1	178.5(2)	N8-C20-Mn3	179.3(3)
N3-C3-Mn1	178.5(2)	N9-C21-Mn3	179.1(2)
N5-Mn2-N4	72.01(8)	N11-Mn4-N12	70.67(7)
N5-Mn2-N6	70.67(8)	N11-Mn4-N10	70.99(8)
N6-Mn2-O2	72.57(8)	N10-Mn4-O5	71.53(8)
N4-Mn2-O1	72.24(7)	N12-Mn4-O4	73.25(7)
O2-Mn2-O1	72.33(7)	O5-Mn4-O4	72.71(7)
N1-Mn2-O3	176.85(8)	N7-Mn4-O6	171.40(7)
Mn2-N1-C1	161.4(2)	Mn4-N7-C19	168.5(2)

Symmetry code for complex **1**: a: -x, y, -z+1/2; b: -x+1/2, -y+3/2, -z+1

Table S2. Selected bond lengths [Å] and angles [°] for complex **2**.

Complex **2**			
Mn1-C1	1.985(9)	Mn4-N14	2.308(5)
Mn1-C2	2.026(10)	Mn4-N15	2.289(7)
Mn1-C3	1.994(7)	Mn4-N16	2.188(7)
Mn1-C4	1.989(9)	Mn4-N17	2.302(7)
Mn1-C5	1.962(10)	Mn4-N18	2.231(8)
Mn1-C6	1.976(7)	Mn4-N19	2.323(7)
Mn2-N6	2.268(6)	Mn4-N20	2.289(5)
Mn2-N7	2.250(12)	Mn5-C40	1.993(6)
Mn2-N8	2.159(12)	Mn5-C41	1.966(9)
Mn2-N9	2.339(10)	Mn5-C42	1.986(7)
Mn2-N10	2.333(10)	Mn5-C40[b]	1.993(6)
Mn2-N11	2.290(7)	Mn5-C41[b]	1.966(9)
Mn2-N12	2.285(5)	Mn5-C42[b]	1.986(7)
Mn3-C22	1.991(6)	Mn6-N22	2.269(6)
Mn3-C23	1.981(9)	Mn6-N23	2.328(7)
Mn3-C24	2.015(6)	Mn6-N24	2.262(6)
Mn3-C22[a]	1.991(6)	Mn6-N25	2.269(6)
Mn3-C23[a]	1.981(9)	Mn6-N26	2.298(7)
Mn3-C24[a]	2.015(6)	Mn6-N27	2.284(8)
		Mn6-N3[c]	2.250(6)
N1-C1-Mn1	177.0(8)	N16-Mn4-N17	69.7(3)
N2-C2-Mn2	178.0(8)	N16-Mn4-N15	69.7(3)
N3-C3-Mn3	173.6(6)	N18-Mn4-N17	73.4(3)
N4-C4-Mn4	173.6(6)	N18-Mn4-N19	75.6(4)
N5-C5-Mn5	176.2(9)	N15-Mn4-N19	72.0(3)
N6-C6-Mn6	172.6(7)	N20-Mn4-N14	178.8(2)
N8-Mn2-N7	74.8(5)	N20-C40-Mn5	177.0(6)
N8-Mn2-N9	66.9(5)	N21-C41-Mn5	175.8(8)
N10-Mn2-N9	68.4(5)	N22-C42-Mn5	176.2(6)
N11-Mn2-N10	76.8(4)	N24-Mn6-N23	68.6(3)
N7-Mn2-N11	74.1(4)	N24-Mn6-N25	69.3(2)
N6-Mn2-N12	174.4(2)	N25-Mn6-N26	73.1(2)
N12-C22-Mn3	177.9(6)	N27-Mn6-N26	75.6(3)
N13-C23-Mn3	178.8(9)	N27-Mn6-N23	73.9(3)
N14-C24-Mn3	178.1(6)	N22-Mn6-N3[c]	172.3(2)

Symmetry code for complex **2**: a: -x+2, -y, -z; b: -x+2, -y, -z+1; c: x-1, y-1, z

Table S3. Selected bond lengths [Å] and angles [°] for complex **3**.

Complex **3**			
Mn1-N1	2.341(6)	Mn4-C34	1.984(10)
Mn1-N2	2.374(8)	Mn4-C35	1.987(8)
Mn1-N3	2.427(8)	Mn4-C36	1.965(8)
Mn1-N4	2.368(7)	Mn4-C34[b]	1.984(10)
Mn1-N5	2.325(7)	Mn4-C35[b]	1.987(8)
Mn1-N6	2.207(7)	Mn4-C36[b]	1.965(8)
Mn1-N27	2.203(7)	Mn5-N16	2.182(7)
Mn2-C16	1.983(9)	Mn5-N17	2.309(6)
Mn2-C17	1.984(10)	Mn5-N18	2.337(8)
Mn2-C18	2.000(8)	Mn5-N19	2.293(7)
Mn2-C16[a]	1.983(9)	Mn5-N20	2.444(9)
Mn2-C17[a]	1.984(10)	Mn5-N21	2.415(9)
Mn2-C18[a]	2.000(8)	Mn5-N22	2.177(8)
Mn3-N8	2.310(6)	Mn6-C52	1.970(9)
Mn3-N9	2.271(7)	Mn6-C53	1.996(10)
Mn3-N10	2.320(8)	Mn6-C54	1.997(11)
Mn3-N11	2.398(8)	Mn6-C55	1.982(10)
Mn3-N12	2.331(7)	Mn6-C56	1.989(9)
Mn3-N13	2.368(8)	Mn6-C57	1.976(9)
Mn3-N15	2.238(6)		
N5-Mn1-N1	67.4(3)	N14-C14-Mn4	175.8(10)
N1-Mn1-N4	66.4(3)	N15-C15-Mn4	176.4(8)
N5-Mn1-N2	72.5(3)	N16-C16-Mn4	178.1(7)
N4-Mn1-N3	69.5(3)	N17-Mn5-N18	67.2(3)
N2-Mn1-N3	84.0(3)	N19-Mn5-N17	67.9(3)
N27-Mn1-N6	174.2(2)	N18-Mn5-N21	71.3(3)
N6-C16-Mn2	177.0(7)	N19-Mn5-N20	72.0(3)
N7-C17-Mn2	179.1(8)	N21-Mn5-N20	82.1(4)
N8-C18-Mn2	175.8(7)	N22-Mn5-N16	170.7(3)
N9-Mn3-N10	68.5(3)	N22-C52-Mn6	173.6(8)
N9-Mn3-N12	68.7(3)	N23-C53-Mn6	177.1(10)
N12-Mn3-N13	71.3(3)	N24-C54-Mn6	177.7(9)
N10-Mn3-N11	70.7(3)	N25-C55-Mn6	175.3(9)
N12-Mn3-N13	71.3(3)	N26-C56-Mn6	175.7(9)
N8-Mn3-N15	172.3(3)	N27[c]-C57-Mn6	168.5(8)

Symmetry code for complex **3**: a: -x+1, -y+1, -z; b: -x+1, -y+1, -z+1; c: x-1, y-1, z

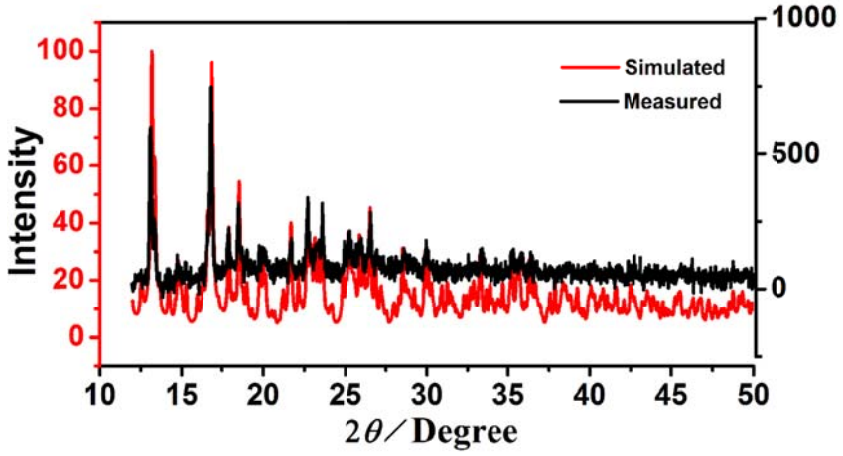

Figure S1. The powder XRD pattern of **1** in black and its simulation in red.

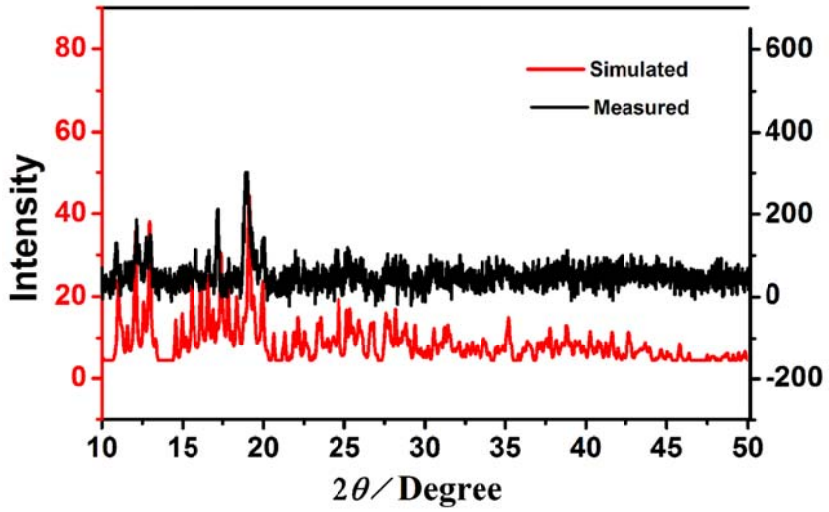

Figure S2. The powder XRD pattern of **2** in black and its simulation in red.

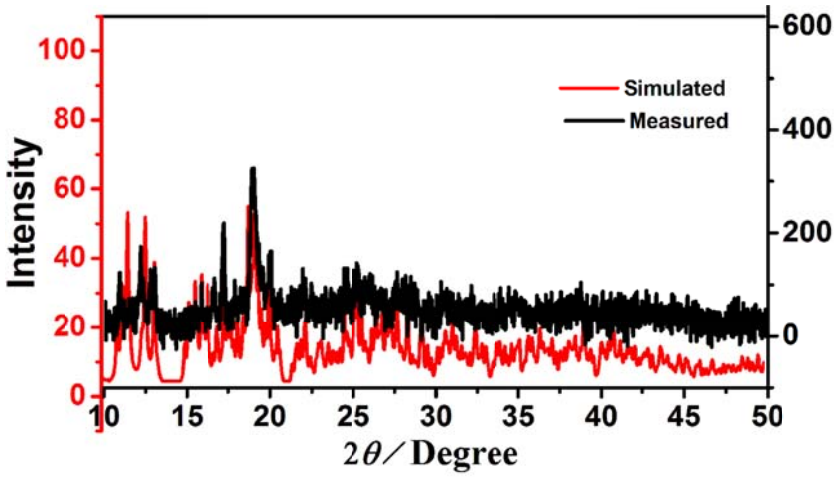

Figure S3. The powder XRD pattern of **3** in black and its simulation in red.

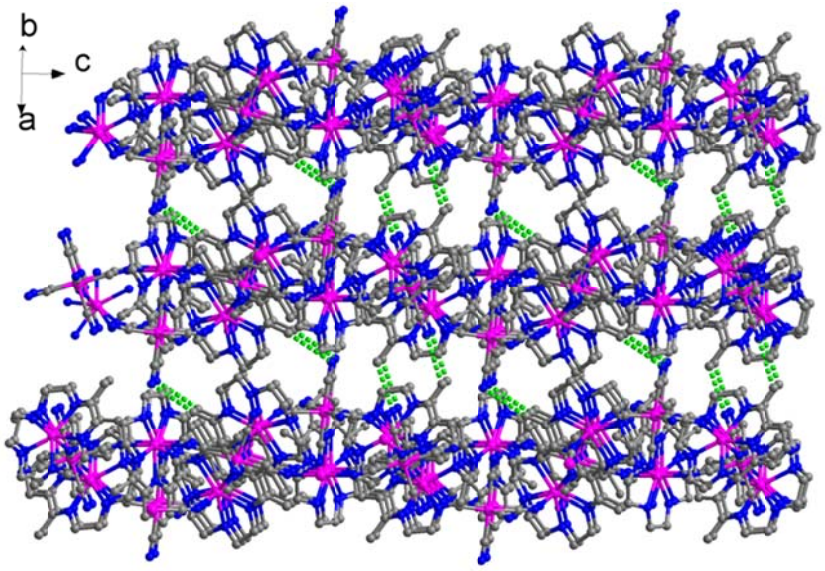

Figure S4. 3D structure of complex **2** with weak C-H···N bonds. All the H atoms have been omitted for clarity.

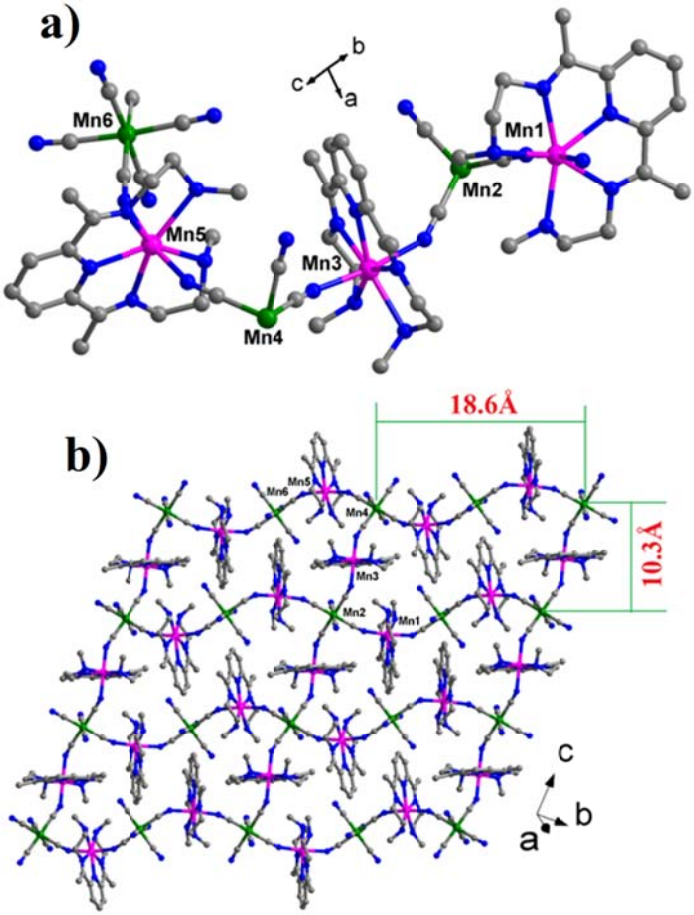

Figure S5. The asymmetry unit (a**)** and 2D (4,4) network (b) of complex **3**. The numbers in (b) represent the distances between these two vertexes. All the hydrogen atoms have been omitted for clarity.

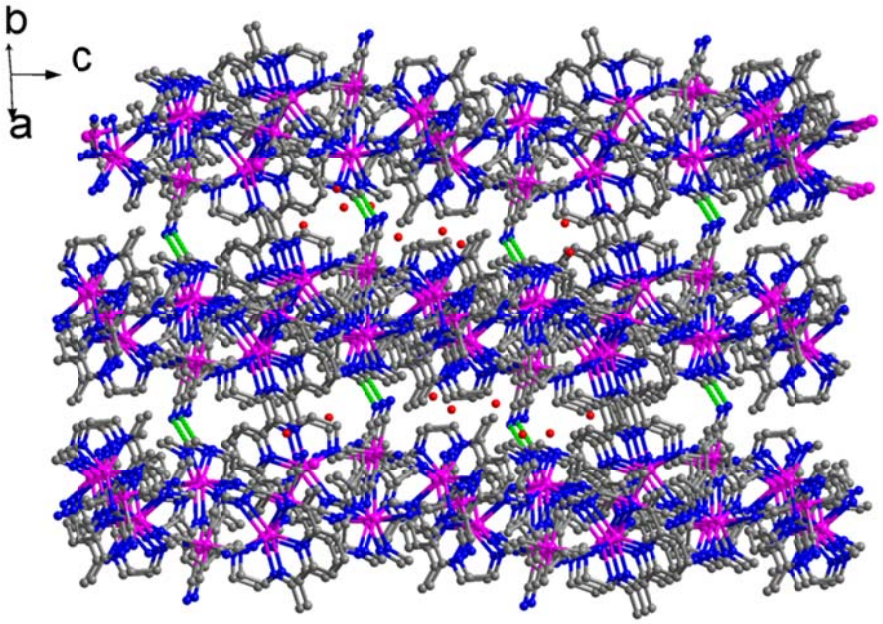

Figure S6. 3D structure of complex **3** with weak C-H···N bonds. All the H atoms have been omitted for clarity.

2. Magnetic Properties

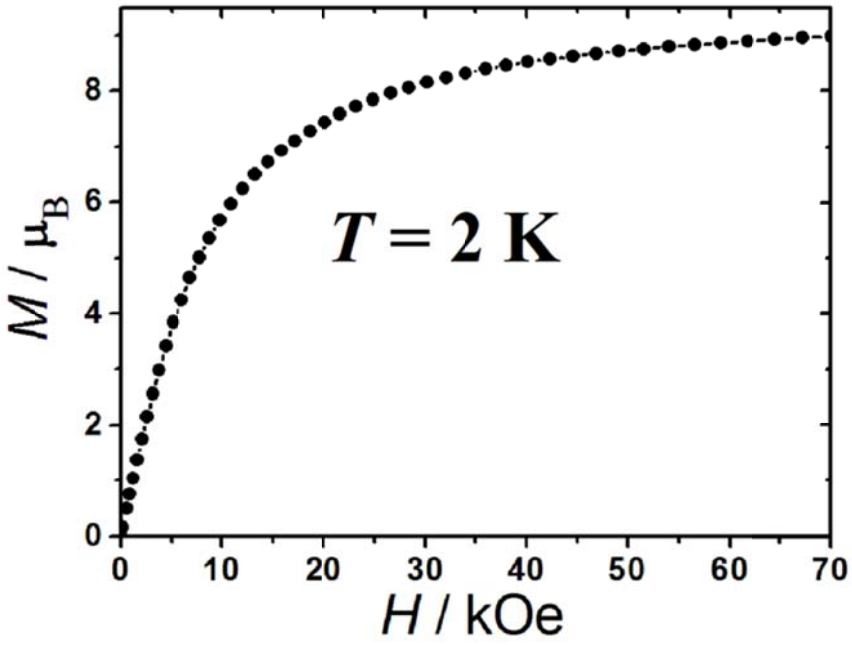

Figure S7. Field-dependent magnetization of **1** measured at 2 K.

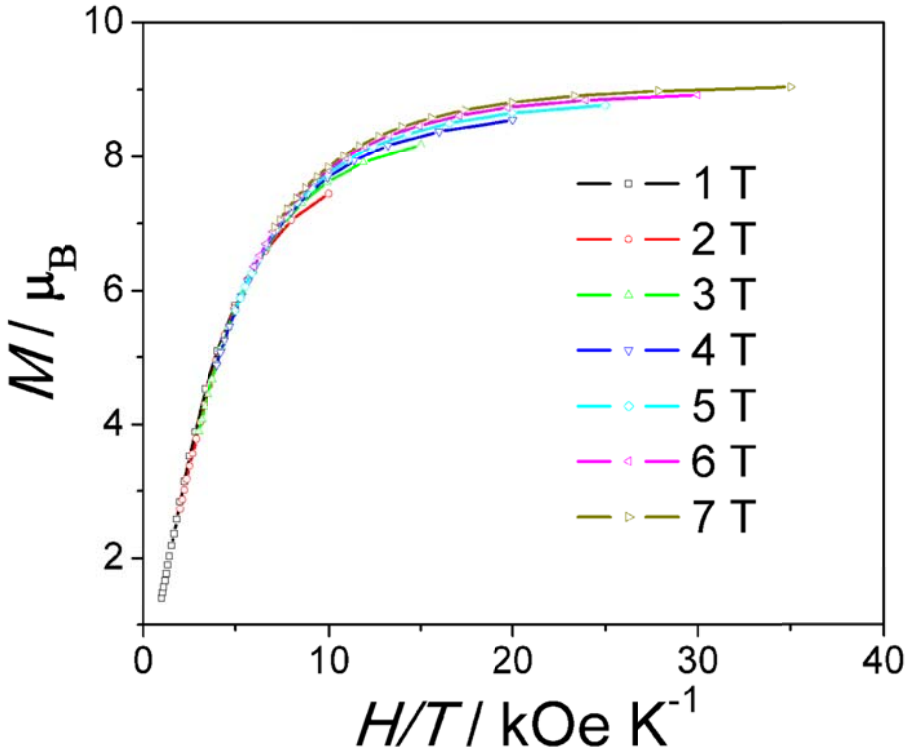

Figure S8. Reduced magnetization data for **1** collected under various applied dc fields. The lines are guides to eyes.

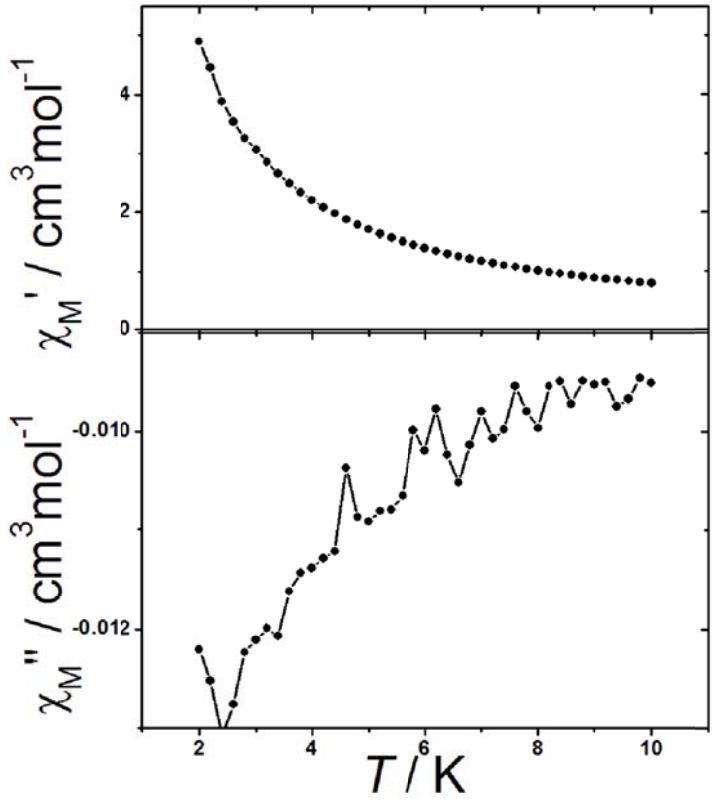

Figure S9. Temperature dependence of the ac susceptibilities for **1** at 250 Hz under H_{ac} = 2 Oe and H_{dc} = 0 Oe.

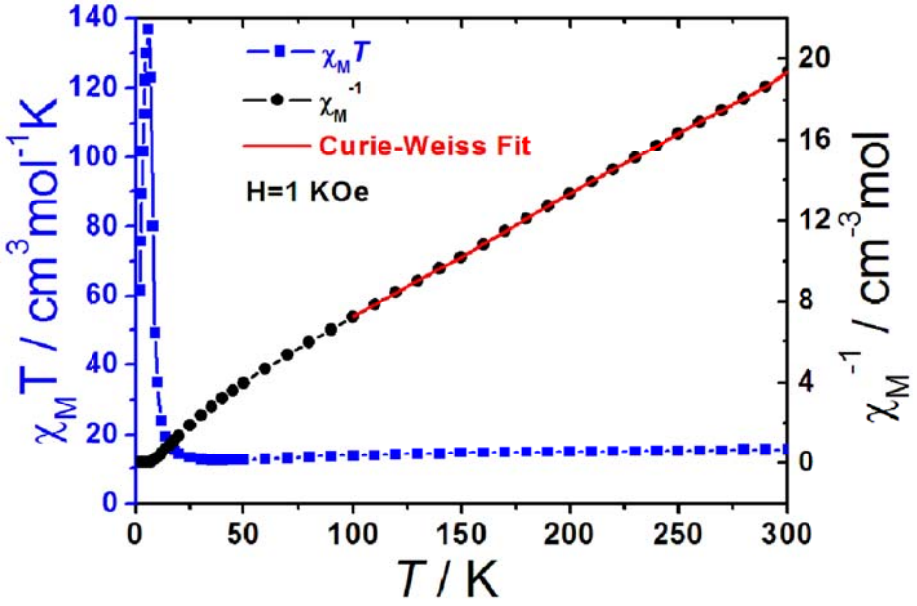

Figure S10. Temperature-dependent magnetic susceptibility of **3** measured at 1 kOe. The red line represents Curie-Weiss fitting.

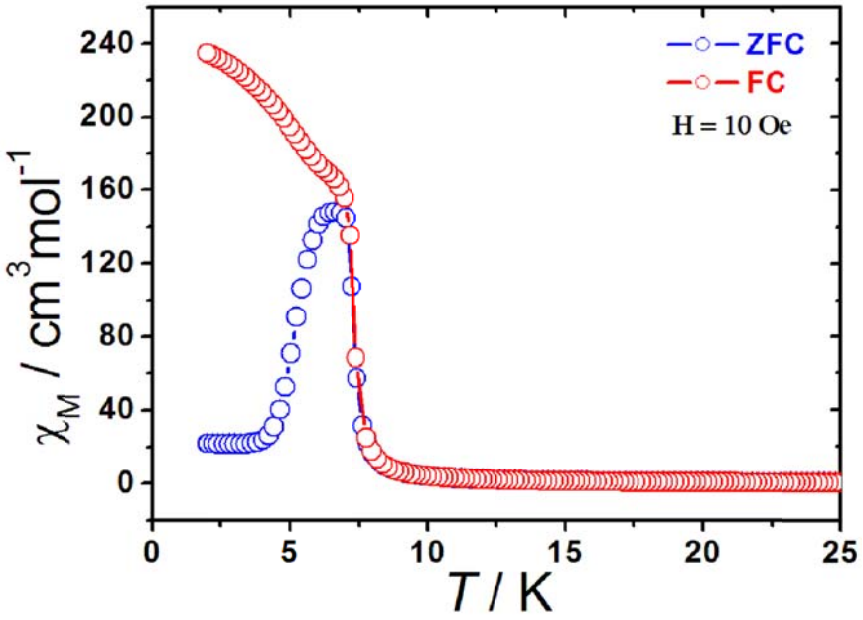

Figure S11. Zero-Field-Cooled and field-cooled (ZFC/FC) curves for compound **3** under a dc field of 10 Oe.

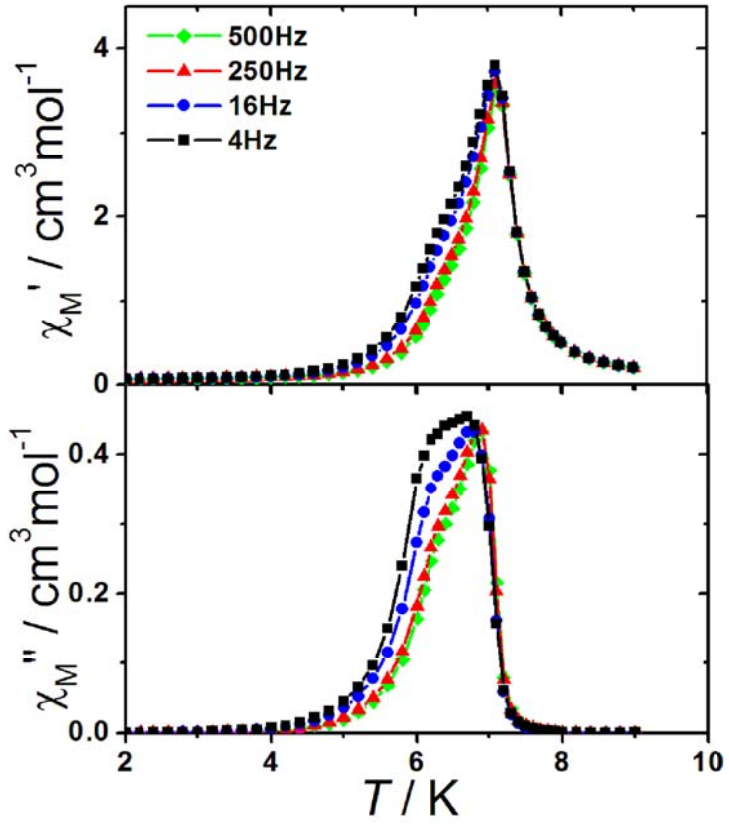

Figure S12. Temperature dependence of the ac susceptibilities for **3** at different frequencies under H_{ac} = 2 Oe and H_{dc} = 0 Oe.

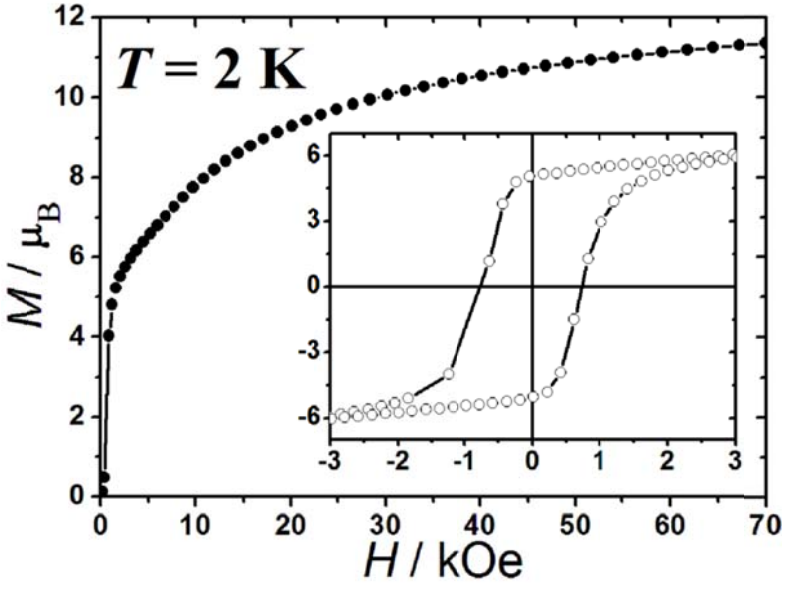

Figure S13. Field-dependence of the magnetization and the hysteresis loop (inset) of **3** measured at 2 K.