Electronic Supplementary Material

Preparation of a Magnetic Metal-Organic Square and Metal-Organic Cubes using 4,5-Bis(2-imidazolinyl)imidazolate: Slow Magnetization Relaxation Behavior in Mixed-Valent Octamanganese(II/III) Clusters

Hajime Kamebuchi,[a] Hiroki Murakami,[b] Ryosuke Shiga[b] and Makoto Tadokoro*[b]*

[a] Department of Chemistry, College of Humanities and Sciences, Nihon University, Sakurajosui 3-25-40, Setagaya-ku, Tokyo 156-8550, Japan

[b] Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

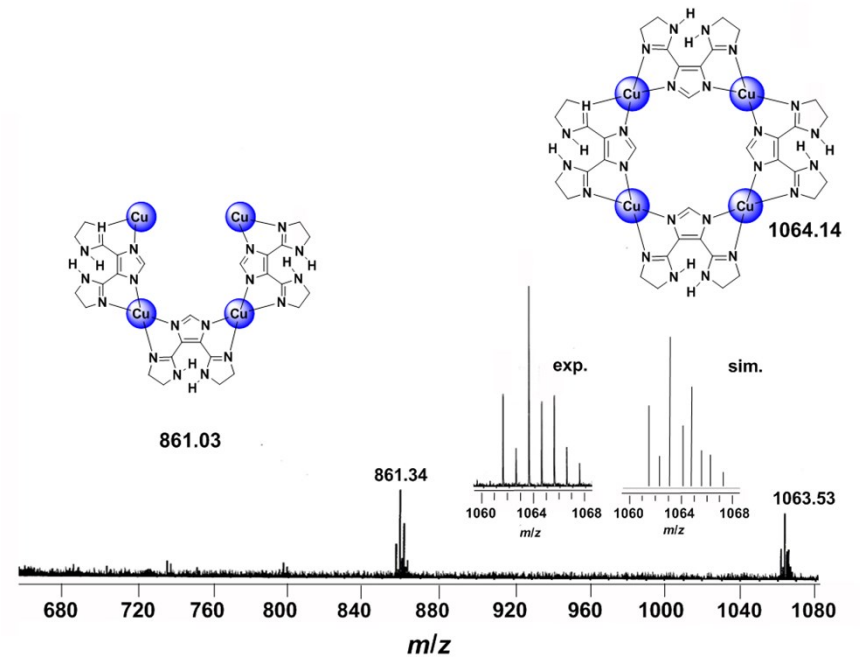

Fig. S1 MALDI-TOF-MS spectrum for **1**. Inset is an expanded view of $[Cu_4(im\text{-}H_2bizn)_4]^+$ cluster and the corresponding simulated isotope pattern.

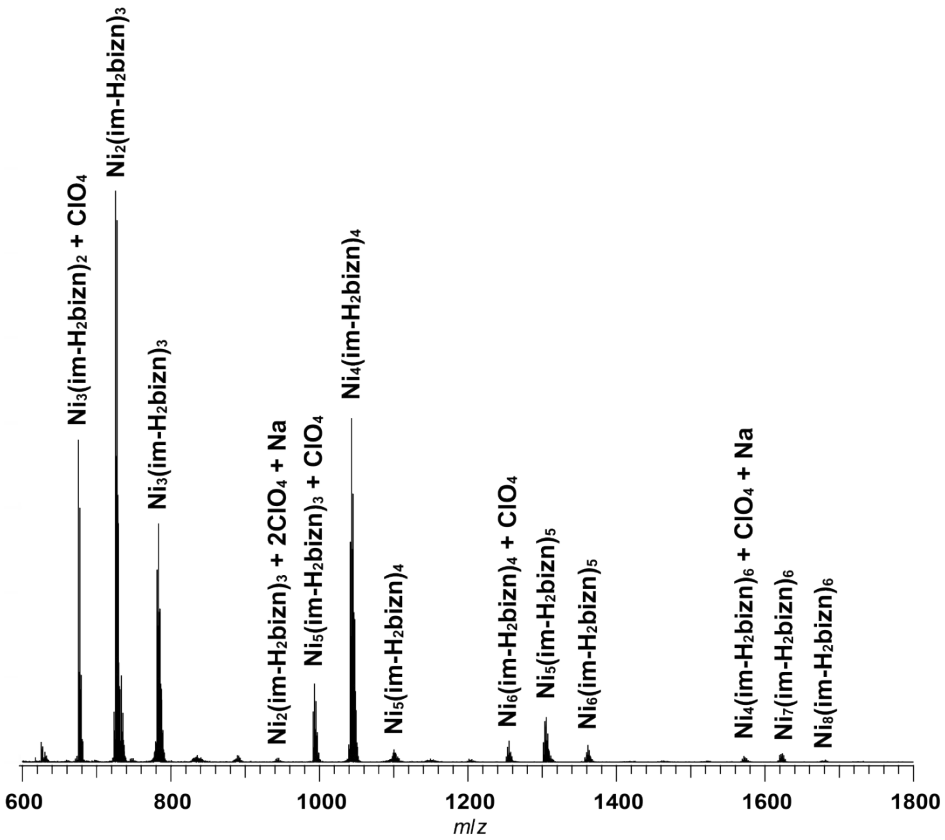

Fig. S2 MALDI-TOF-MS spectrum for **2**.

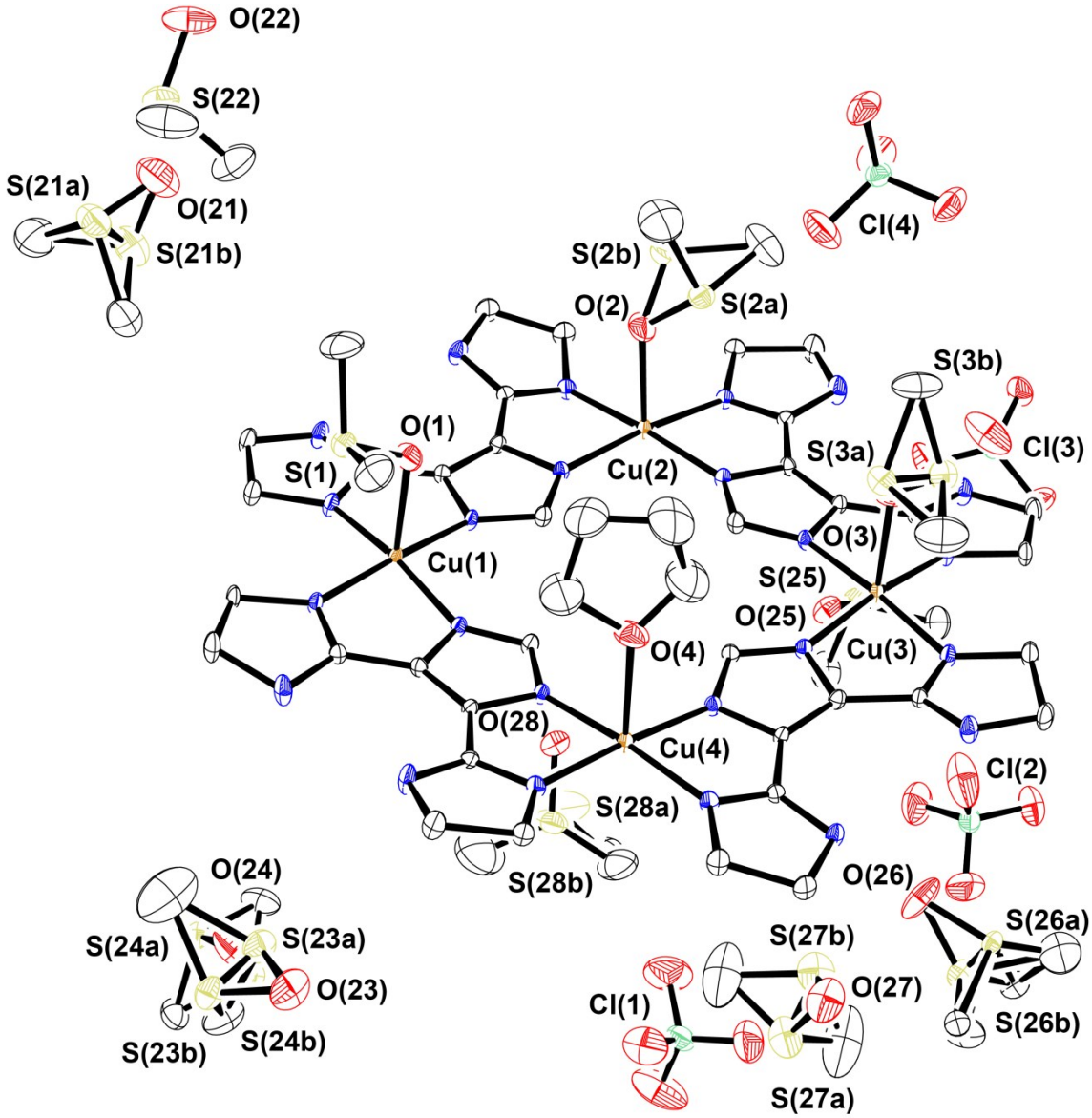

Fig. S3 ORTEP image of **1** with thermal ellipsoids at the 30% probability level. The disorder of DMSO molecules is also shown.

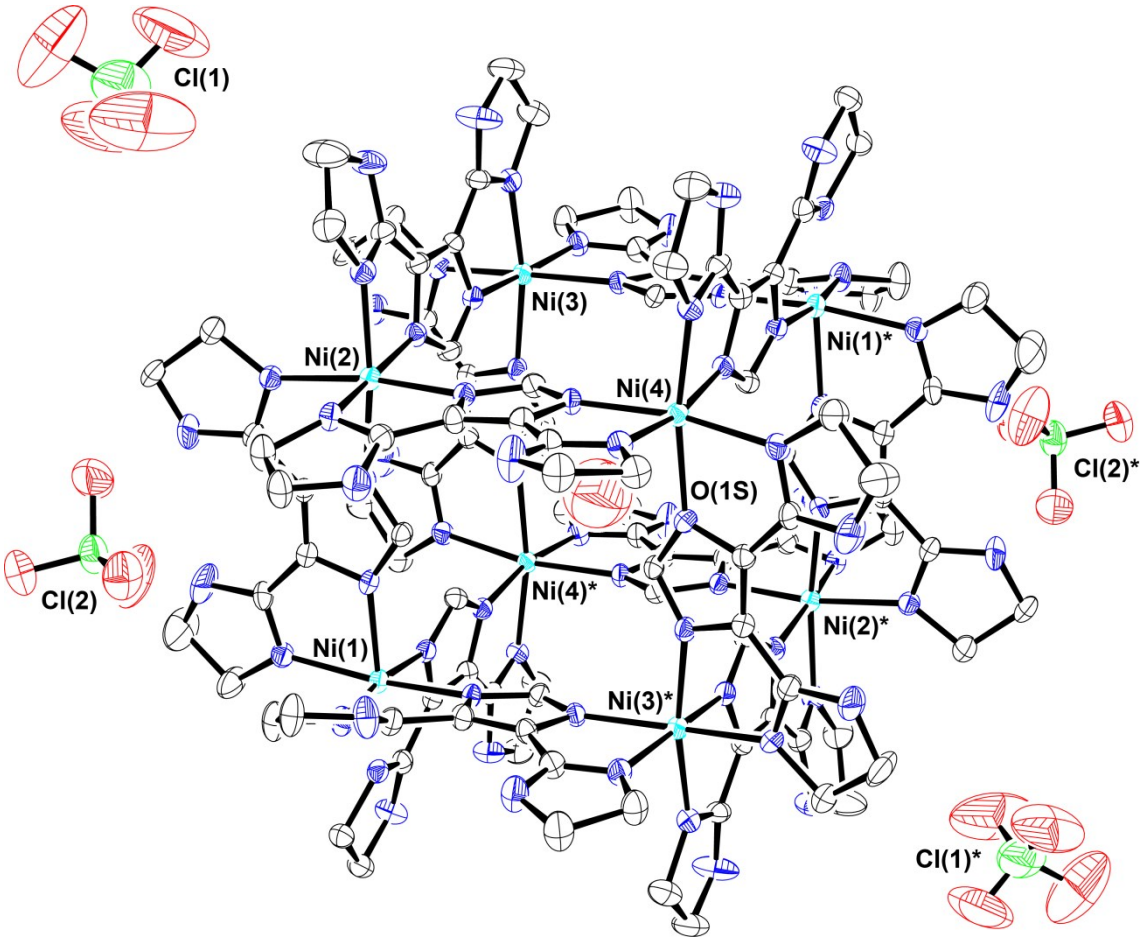

Fig. S4 ORTEP image of **2** with thermal ellipsoids at the 30% probability level.

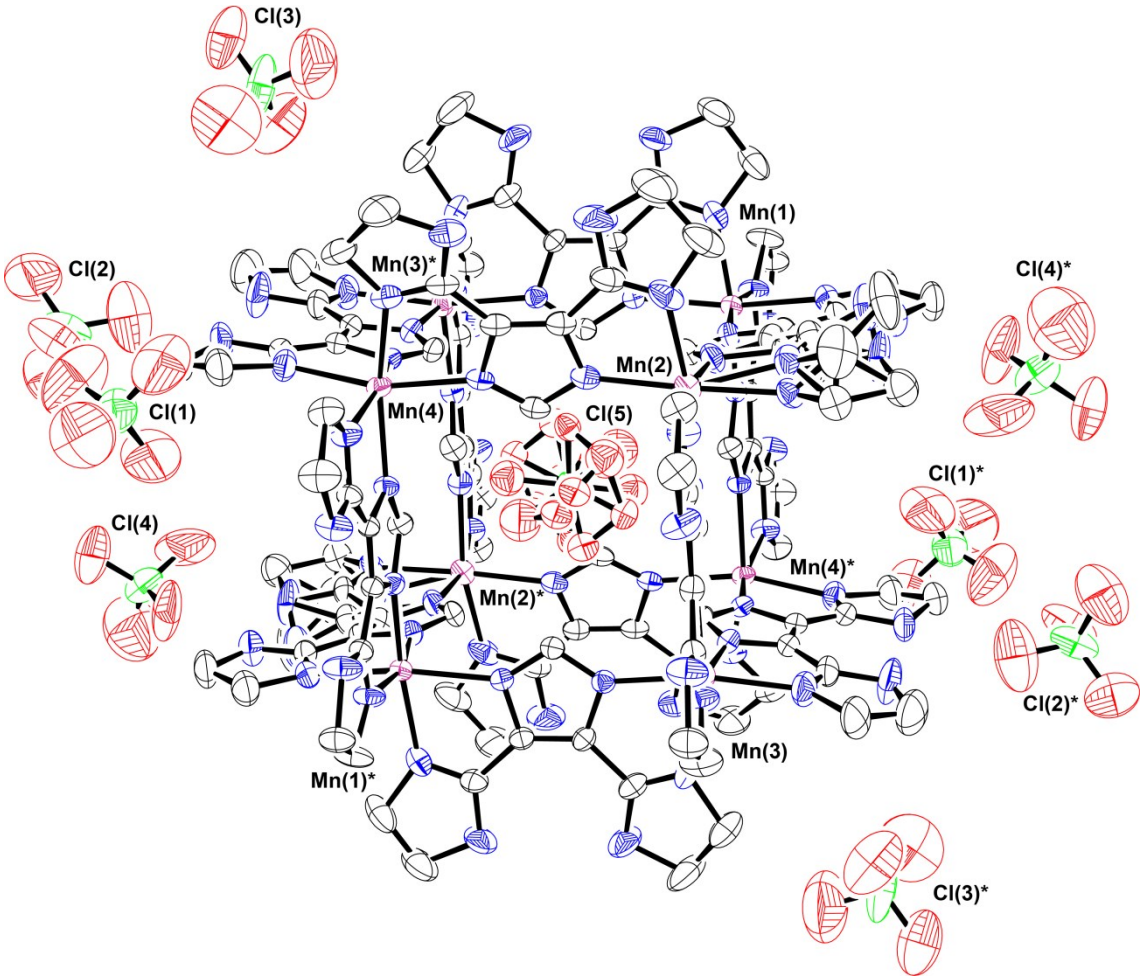

Fig. S5 ORTEP image of **3** with thermal ellipsoids at the 30% probability level. The disorder of the ligand and perchlorate ion is also shown. The three perchlorate ions, Cl(2)-Cl(4), were refined to have a total occupancy of 2.5.

Table S1 Selected Bond Lengths (Å) of **1**.

Cu(1)-N(1)	1.981(4)	Cu(3)-N(13)	1.990(4)
Cu(1)-N(23)	1.994(4)	Cu(3)-N(11)	2.012(4)
Cu(1)-N(22)	1.998(4)	Cu(3)-N(10)	2.017(4)
Cu(1)-N(3)	2.010(4)	Cu(3)-N(15)	2.017(4)
Cu(1)-O(1)	2.322(5)	Cu(3)-O(3)	2.299(4)
Cu(2)-N(7)	1.999(4)	Cu(4)-N(19)	1.979(4)
Cu(2)-N(5)	2.004(4)	Cu(4)-N(17)	2.003(4)
Cu(2)-N(4)	2.009(4)	Cu(4)-N(16)	2.005(4)
Cu(2)-N(9)	2.009(4)	Cu(4)-N(21)	2.010(4)
Cu(2)-O(2)	2.268(4)	Cu(4)-O(4)	2.353(5)

Table S2 Selected Bond Angles (°) of **1**.

N(1)-Cu(1)-N(23)	97.32(18)	N(13)-Cu(3)-N(11)	97.95(18)
N(1)-Cu(1)-N(22)	170.1(2)	N(13)-Cu(3)-N(10)	172.66(19)
N(23)-Cu(1)-N(22)	81.22(17)	N(11)-Cu(3)-N(10)	80.97(17)
N(1)-Cu(1)-N(3)	81.20(17)	N(13)-Cu(3)-N(15)	80.83(17)
N(23)-Cu(1)-N(3)	174.19(19)	N(11)-Cu(3)-N(15)	169.13(18)
N(22)-Cu(1)-N(3)	99.26(17)	N(10)-Cu(3)-N(15)	98.85(17)
N(1)-Cu(1)-O(1)	94.6(2)	N(13)-Cu(3)-O(3)	92.82(19)
N(23)-Cu(1)-O(1)	92.29(18)	N(11)-Cu(3)-O(3)	95.02(18)
N(22)-Cu(1)-O(1)	95.24(19)	N(10)-Cu(3)-O(3)	94.51(18)
N(3)-Cu(1)-O(1)	93.43(17)	N(15)-Cu(3)-O(3)	95.83(17)
N(7)-Cu(2)-N(5)	98.58(18)	N(19)-Cu(4)-N(17)	98.06(18)
N(7)-Cu(2)-N(4)	172.73(18)	N(19)-Cu(4)-N(16)	175.27(18)
N(5)-Cu(2)-N(4)	81.10(17)	N(17)-Cu(4)-N(16)	81.48(17)
N(7)-Cu(2)-N(9)	81.35(17)	N(19)-Cu(4)-N(21)	81.34(17)
N(5)-Cu(2)-N(9)	174.87(19)	N(17)-Cu(4)-N(21)	173.35(19)
N(4)-Cu(2)-N(9)	98.31(17)	N(16)-Cu(4)-N(21)	98.56(17)
N(7)-Cu(2)-O(2)	94.59(18)	N(19)-Cu(4)-O(4)	91.98(19)
N(5)-Cu(2)-O(2)	87.9(2)	N(17)-Cu(4)-O(4)	95.5(2)
N(4)-Cu(2)-O(2)	92.66(18)	N(16)-Cu(4)-O(4)	92.74(18)
N(9)-Cu(2)-O(2)	97.2(2)	N(21)-Cu(4)-O(4)	91.1(2)

Table S3 Hydrogen Bond Distances (Å) of **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(26)#1	0.88	2.12	2.842(6)	138.6
N(6)-H(6)...O(27)#1	0.88	2.39	2.942(7)	121.2
N(8)-H(8)...O(24)#1	0.88	2.25	2.797(7)	120
N(8)-H(8)...O(16)	0.88	2.6	3.285(10)	135.6
N(12)-H(12)...O(16)	0.88	2.32	3.059(8)	141.8
N(14)-H(14A)...N(18)	0.88	2.65	3.317(7)	133.1
N(14)-H(14A)...O(23)#2	0.88	2.28	3.027(6)	142.3
N(18)-H(18)...N(14)	0.88	2.63	3.317(7)	135.5
N(18)-H(18)...O(23)#2	0.88	2.33	3.010(5)	133.7
N(18)-H(18)...O(26)	0.88	2.28	2.844(6)	122.1
N(20)-H(20)...N(24)	0.88	2.6	3.323(7)	139.6
N(20)-H(20)...O(25)#1	0.88	2.33	2.780(7)	111.7
N(24)-H(24)...N(20)	0.88	2.7	3.323(7)	128.9
N(24)-H(24)...O(13)#1	0.88	2.36	3.070(8)	137.6
C(5)-H(5)...O(28)#1	0.95	2.51	3.168(7)	126.4
C(10)-H(10B)...O(22)#3	0.99	2.62	3.283(8)	124.8
C(14)-H(14)...O(28)#1	0.95	2.41	3.193(7)	140.1
C(17)-H(17A)...O(10)#4	0.99	2.56	3.351(10)	137.1
C(19)-H(19B)...O(14)#4	0.99	2.43	3.372(11)	159.6
C(23)-H(23)...O(28)#1	0.95	2.41	3.148(6)	134.1
C(28)-H(28B)...O(22)#7	0.99	2.54	3.310(8)	134.9
C(29)-H(29A)...O(22)#7	0.99	2.62	3.349(9)	130.7
C(32)-H(32)...O(28)#1	0.95	2.5	3.129(7)	123.8
C(35)-H(35B)...O(14)#1	0.99	2.6	3.340(9)	131.3
C(39)-H(39C^a)...O(21)#3	0.98	2.58	3.268(14)	127.6
C(40)-H(40C^a)...O(6)#1	0.98	2.5	3.247(12)	133.3
C(45)-H(45B)...O(8)#8	0.99	2.54	3.366(16)	141.3
C(48)-H(48B^a)...O(16)#9	0.98	2.54	3.371(13)	142.7
C(49)-H(49C)...O(7)#1	0.98	2.6	3.338(14)	132.1
C(51)-H(51C^a)...O(18)#6	0.98	2.51	3.387(7)	149.2
C(52)-H(52B^a)...O(15)#1	0.98	2.57	3.388(8)	140.5
C(57A^a)-H(57C^a)...O(17)#7	0.98	2.26	3.212(9)	165.3
C(58A^a)-H(58A^a)...O(18)#7	0.98	2.37	3.208(10)	142.6
C(57B^b)-H(57E^b)...O(17)#7	0.98	2.46	3.292(11)	142.5
C(57B^b)-H(57E^b)...O(18)#7	0.98	2.1	3.022(12)	156.8
C(58B^b)-H(58D^b)...O(18)#7	0.98	2.57	3.351(12)	136.5
C(60)-H(60B^a)...O(7)	0.98	2.45	3.355(12)	152.5
C(60)-H(60C^a)...O(21)#1	0.98	2.58	3.253(11)	126.2
C(61A^a)-H(61A^a)...S(2A^a)#1	0.98	2.22	3.14(2)	156.7
C(62A^a)-H(62A^a)...O(1)#1	0.98	2.27	3.249(17)	172.8
C(62B^b)-H(62F^b)...O(8)	0.98	2.41	3.141(12)	131

#1 -x+1,-y+1,-z+1 #2 -x+2,-y,-z+1 #3 -x+1,-y+2,-z+1 #4 -x+1,-y+1,-z

#5 -x+2,-y+1,-z #6 -x+2,-y+1,-z+1 #7 x,y-1,z #8 x+1,y,z #9 x,y,z+1

Table S4 Selected Bond Lengths (Å) of **2**.

Ni(1)-N(7)	2.084(6)	Ni(3)-N(27)	2.082(5)
Ni(1)-N(9)	2.086(5)	Ni(3)-N(24)	2.088(5)
Ni(1)-N(1)	2.087(5)	Ni(3)-N(12)#1	2.091(5)
Ni(1)-N(13)	2.090(6)	Ni(3)-N(10)#1	2.098(6)
Ni(1)-N(3)	2.102(6)	Ni(3)-N(22)	2.099(5)
Ni(1)-N(15)	2.109(5)	Ni(3)-N(25)	2.108(6)
Ni(2)-N(33)	2.056(5)	Ni(4)-N(36)	2.077(5)
Ni(2)-N(19)	2.097(5)	Ni(4)-N(34)	2.082(5)
Ni(2)-N(21)	2.101(5)	Ni(4)-N(28)#1	2.089(5)
Ni(2)-N(18)	2.101(5)	Ni(4)-N(4)#1	2.103(5)
Ni(2)-N(16)	2.112(5)	Ni(4)-N(30)#1	2.108(5)
Ni(2)-N(31)	2.154(6)	Ni(4)-N(6)#1	2.109(5)

#1 -x+1,-y+1,-z+1

Table S5 Selected Bond Angles (°) of **2**.

N(7)-Ni(1)-N(9)	79.0(2)	N(27)-Ni(3)-N(24)	95.4(2)
N(7)-Ni(1)-N(1)	93.9(2)	N(27)-Ni(3)-N(12)#1	95.3(2)
N(9)-Ni(1)-N(1)	94.5(2)	N(24)-Ni(3)-N(12)#1	95.4(2)
N(7)-Ni(1)-N(13)	95.8(2)	N(27)-Ni(3)-N(10)#1	94.6(2)
N(9)-Ni(1)-N(13)	172.8(2)	N(24)-Ni(3)-N(10)#1	169.0(2)
N(1)-Ni(1)-N(13)	90.8(2)	N(12)#1-Ni(3)-N(10)#1	79.2(2)
N(7)-Ni(1)-N(3)	169.3(2)	N(27)-Ni(3)-N(22)	169.6(2)
N(9)-Ni(1)-N(3)	93.3(2)	N(24)-Ni(3)-N(22)	79.0(2)
N(1)-Ni(1)-N(3)	79.1(2)	N(12)#1-Ni(3)-N(22)	93.9(2)
N(13)-Ni(1)-N(3)	92.5(2)	N(10)#1-Ni(3)-N(22)	91.8(2)
N(7)-Ni(1)-N(15)	92.1(2)	N(27)-Ni(3)-N(25)	79.4(2)
N(9)-Ni(1)-N(15)	96.0(2)	N(24)-Ni(3)-N(25)	90.5(2)
N(1)-Ni(1)-N(15)	168.7(2)	N(12)#1-Ni(3)-N(25)	172.5(2)
N(13)-Ni(1)-N(15)	79.1(2)	N(10)#1-Ni(3)-N(25)	95.8(2)
N(3)-Ni(1)-N(15)	96.2(2)	N(22)-Ni(3)-N(25)	91.8(2)
N(33)-Ni(2)-N(19)	94.8(2)	N(36)-Ni(4)-N(34)	78.4(2)
N(33)-Ni(2)-N(21)	94.6(2)	N(36)-Ni(4)-N(28)#1	168.6(2)
N(19)-Ni(2)-N(21)	78.7(2)	N(34)-Ni(4)-N(28)#1	92.1(2)
N(33)-Ni(2)-N(18)	92.7(2)	N(36)-Ni(4)-N(4)#1	94.8(2)
N(19)-Ni(2)-N(18)	168.2(2)	N(34)-Ni(4)-N(4)#1	92.2(2)
N(21)-Ni(2)-N(18)	91.6(2)	N(28)#1-Ni(4)-N(4)#1	91.9(2)
N(33)-Ni(2)-N(16)	171.4(2)	N(36)-Ni(4)-N(30)#1	95.56(19)
N(19)-Ni(2)-N(16)	93.5(2)	N(34)-Ni(4)-N(30)#1	95.1(2)
N(21)-Ni(2)-N(16)	89.1(2)	N(28)#1-Ni(4)-N(30)#1	78.8(2)
N(18)-Ni(2)-N(16)	79.3(2)	N(4)#1-Ni(4)-N(30)#1	168.4(2)
N(33)-Ni(2)-N(31)	78.3(2)	N(36)-Ni(4)-N(6)#1	97.1(2)
N(19)-Ni(2)-N(31)	91.9(2)	N(34)-Ni(4)-N(6)#1	169.8(2)
N(21)-Ni(2)-N(31)	167.8(2)	N(28)#1-Ni(4)-N(6)#1	93.3(2)
N(18)-Ni(2)-N(31)	98.6(2)	N(4)#1-Ni(4)-N(6)#1	79.0(2)
N(16)-Ni(2)-N(31)	99.4(2)	N(30)#1-Ni(4)-N(6)#1	94.5(2)

#1 -x+1,-y+1,-z+1

Table S6 Hydrogen Bond Distances (Å) of **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8)...N(11)	0.88	2.65	3.335(7)	135.9
N(11)-H(11)...N(8)	0.88	2.66	3.335(7)	134.5
N(26)-H(26)...N(29)	0.88	2.68	3.312(4)	129.6
N(29)-H(29)...N(26)	0.88	2.62	3.312(4)	136.1
N(14)-H(14)...O(5)#2	0.88	2.51	2.984(10)	114.7
N(14)-H(14)...N(17)	0.88	2.6	3.301(4)	137.4

#2 -x+2,-y+2,-z+2

Table S7 Selected Bond Lengths (Å) of **3**.

Mn(1)-N(2)	2.084(5)	Mn(3)-N(17)	2.108(5)
Mn(1)-N(4)	2.090(4)	Mn(3)-N(20)	2.169(5)
Mn(1)-N(6)	2.120(4)	Mn(3)-N(16)	2.173(5)
Mn(1)-N(9)	2.133(5)	Mn(3)-N(23)	2.174(6)
Mn(1)-N(1)	2.224(4)	Mn(3)-N(21)	2.191(5)
Mn(1)-N(7)	2.230(5)	Mn(3)-N(19)	2.220(4)
Mn(2)-N(13)	2.087(5)	Mn(4)-N(35)	2.146(4)
Mn(2)-N(10)	2.131(6)	Mn(4)-N(31)	2.153(5)
Mn(2)-N(25)	2.154(6)	Mn(4)-N(32)	2.180(5)
Mn(2)-N(11B)	2.16(3)	Mn(4)-N(29)	2.195(5)
Mn(2)-N(15)	2.164(5)	Mn(4)-N(28)	2.198(4)
Mn(2)-N(27)	2.185(5)	Mn(4)-N(34)	2.203(4)
Mn(2)-N(11A)	2.194(12)		

Table S8 Selected Bond Angles (°) of **3**.

N(2)-Mn(1)-N(4)	90.20(17)	N(15)-Mn(2)-N(11A)	103.7(4)
N(2)-Mn(1)-N(6)	163.30(17)	N(27)-Mn(2)-N(11A)	159.6(4)
N(4)-Mn(1)-N(6)	77.16(16)	N(17)-Mn(3)-N(20)	164.0(2)
N(2)-Mn(1)-N(9)	99.06(18)	N(17)-Mn(3)-N(16)	75.77(17)
N(4)-Mn(1)-N(9)	165.79(18)	N(20)-Mn(3)-N(16)	96.52(16)
N(6)-Mn(1)-N(9)	95.51(16)	N(17)-Mn(3)-N(23)	90.4(2)
N(2)-Mn(1)-N(1)	75.69(16)	N(20)-Mn(3)-N(23)	100.03(18)
N(4)-Mn(1)-N(1)	99.78(17)	N(16)-Mn(3)-N(23)	160.66(17)
N(6)-Mn(1)-N(1)	95.52(14)	N(17)-Mn(3)-N(21)	92.8(2)
N(9)-Mn(1)-N(1)	92.97(16)	N(20)-Mn(3)-N(21)	75.0(2)
N(2)-Mn(1)-N(7)	93.11(18)	N(16)-Mn(3)-N(21)	102.2(2)
N(4)-Mn(1)-N(7)	92.6(2)	N(23)-Mn(3)-N(21)	91.8(2)
N(6)-Mn(1)-N(7)	98.26(17)	N(17)-Mn(3)-N(19)	99.95(19)
N(9)-Mn(1)-N(7)	76.29(18)	N(20)-Mn(3)-N(19)	94.47(16)
N(1)-Mn(1)-N(7)	163.24(18)	N(16)-Mn(3)-N(19)	93.79(15)
N(13)-Mn(2)-N(10)	165.3(2)	N(23)-Mn(3)-N(19)	75.09(16)
N(13)-Mn(2)-N(25)	91.3(2)	N(21)-Mn(3)-N(19)	161.7(2)
N(10)-Mn(2)-N(25)	98.9(2)	N(35)-Mn(4)-N(31)	162.54(17)
N(13)-Mn(2)-N(11B)	86.7(8)	N(35)-Mn(4)-N(32)	93.3(2)
N(10)-Mn(2)-N(11B)	80.7(8)	N(31)-Mn(4)-N(32)	75.3(2)
N(25)-Mn(2)-N(11B)	102.8(8)	N(35)-Mn(4)-N(29)	89.26(17)
N(13)-Mn(2)-N(15)	76.91(17)	N(31)-Mn(4)-N(29)	104.25(17)
N(10)-Mn(2)-N(15)	94.68(18)	N(32)-Mn(4)-N(29)	92.87(19)
N(25)-Mn(2)-N(15)	164.2(2)	N(35)-Mn(4)-N(28)	98.79(17)
N(11B)-Mn(2)-N(15)	87.2(8)	N(31)-Mn(4)-N(28)	95.31(16)
N(13)-Mn(2)-N(27)	97.74(18)	N(32)-Mn(4)-N(28)	163.09(19)
N(10)-Mn(2)-N(27)	94.98(18)	N(29)-Mn(4)-N(28)	75.63(17)
N(25)-Mn(2)-N(27)	76.11(19)	N(35)-Mn(4)-N(34)	76.22(15)
N(11B)-Mn(2)-N(27)	175.4(8)	N(31)-Mn(4)-N(34)	92.89(15)
N(15)-Mn(2)-N(27)	94.81(16)	N(32)-Mn(4)-N(34)	101.44(17)
N(13)-Mn(2)-N(11A)	94.8(4)	N(29)-Mn(4)-N(34)	160.05(17)
N(10)-Mn(2)-N(11A)	75.3(4)	N(28)-Mn(4)-N(34)	92.91(14)
N(25)-Mn(2)-N(11A)	87.6(4)		

Table S9 Hydrogen Bond Distances (Å) of **3**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(12A^a)-H(12A^a)...N(8)	0.87	2.38	3.073(12)	136.4
N(12B^b)-H(12B^b)...O(14)#1	0.87	2.3	2.95(2)	130.7
N(12B^b)-H(12B^b)...N(8)	0.87	2.69	3.35(2)	132.9
N(5)-H(5)...O(14)#3	0.87	2.51	3.141(8)	130.3
N(5)-H(5)...O(16)#3	0.87	2.6	3.065(8)	114.1
N(5)-H(5)...N(36)#1	0.87	2.43	3.154(7)	140.5
N(14)-H(14)...O(7)#2	0.87	2.57	3.080(10)	118.1
N(14)-H(14)...N(18)	0.87	2.54	3.245(8)	138.9
N(18)-H(18)...N(14)	0.87	2.52	3.245(8)	141.4
N(3)-H(3)...N(24)#1	0.87	2.46	3.163(9)	138.3
N(8)-H(8)...N(12A^a)	0.87	2.44	3.073(12)	130
N(8)-H(8)...N(12B^b)	0.87	2.6	3.35(2)	145.1
N(8)-H(8)...O(14)#1	0.87	2.29	3.019(7)	141.1
N(22)-H(22)...O(8)	0.87	2.33	2.966(7)	130.4
N(22)-H(22)...N(33)#1	0.87	2.39	3.120(10)	141.9
N(24)-H(24)...O(3)#6	0.87	2.32	2.952(10)	129.3
N(24)-H(24)...N(3)#1	0.87	2.45	3.163(9)	139.9
N(30)-H(30)...O(9)#5	0.87	2.6	3.041(12)	112.3
N(30)-H(30)...N(26)	0.87	2.37	3.079(10)	138.5
N(26)-H(26A)...N(30)	0.87	2.37	3.079(10)	138.6
N(33)-H(33)...O(8)#1	0.87	2.46	3.197(9)	142.6
N(33)-H(33)...N(22)#1	0.87	2.41	3.120(10)	139.4
N(36)-H(36)...O(14)#8	0.87	2.55	3.163(10)	127.9
N(36)-H(36)...N(5)#1	0.87	2.43	3.154(6)	141.5

#1 -x+1,-y+1,-z+1 #2 -x+1,-y+1,-z+2 #3 x,y+1,z

#4 -x+1,-y+2,-z+1 #5 x-1,y,z #6 -x+2,-y+1,-z+1

#7 x,y,z+1 #8 -x+1,-y,-z+1

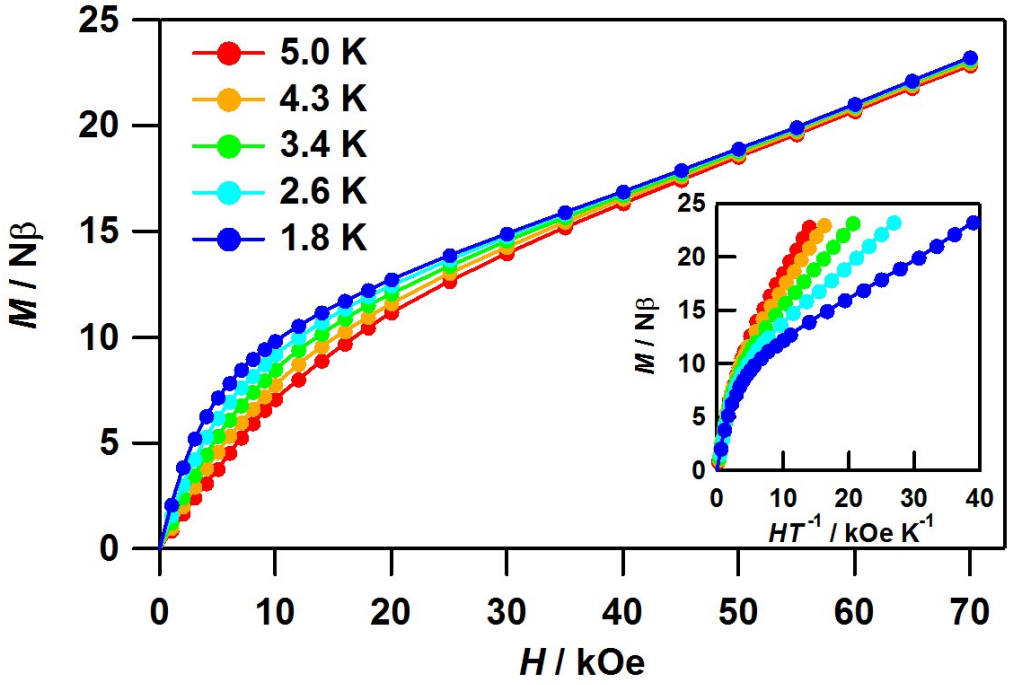

Fig. S6 *M*-*H* curve in the temperature range of 1.8-5 K. Inset is *M* vs. *H*/*T* plot.

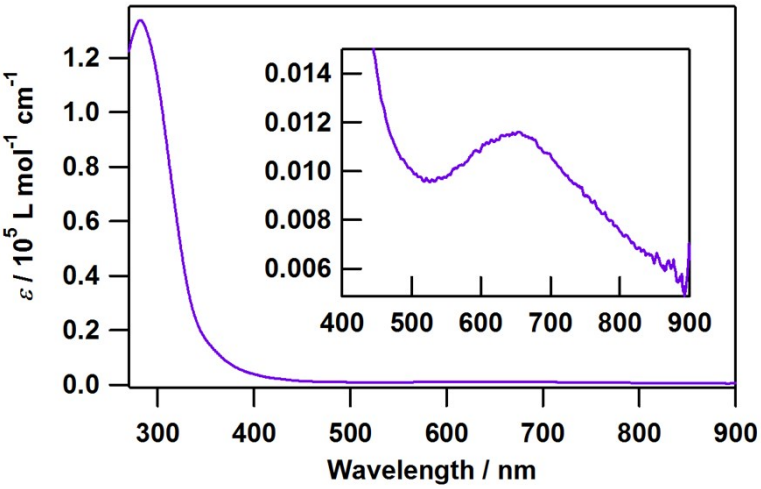

Fig. S7 UV-vis spectrum of **1** in DMSO (1.0×10^{-5} M). Inset is an expanded view.

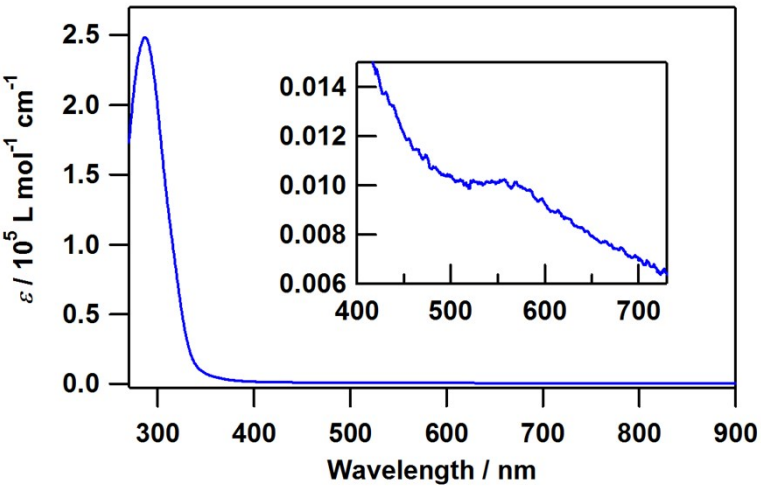

Fig. S8 UV-vis spectrum of **2** in DMSO (0.5×10^{-5} M). Inset is an expanded view.

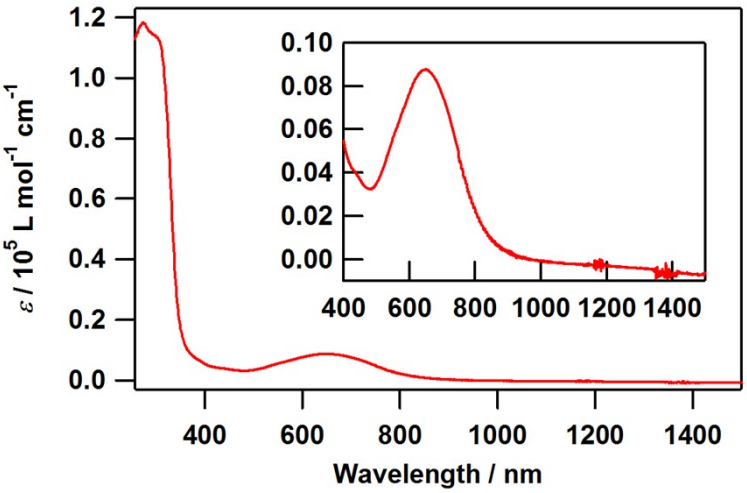

Fig. S9 UV-vis-NIR spectrum of **3** in DMSO (1.0×10^{-5} M). Inset is an expanded view.

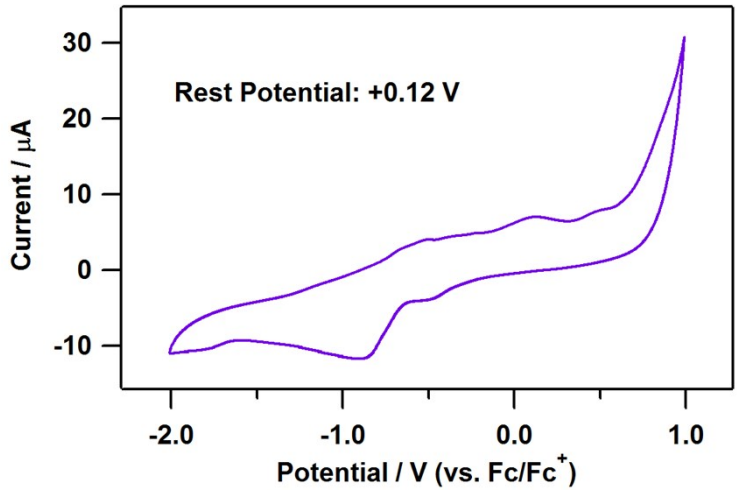

Fig. S10 Cyclic voltammogram of **1** in DMSO (1.0 mM). Scan rate, 100 mV/s; electrolyte, 0.1 M $^{n}Bu_4NPF_6$; working electrode, glassy carbon (ϕ = 3.0 mm); counter electrode, Pt wire.