

## **SUPPORTING INFORMATION**

### **Syntheses, crystal structures and magnetic properties of a novel family of penta-manganese complexes derived from an assembly system containing polydentate hydroxy-rich Schiff-base ligands**

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**Table S1.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 1.

Mn(1)-O(5)	2.233(5)	Mn(2)-O(10)	1.979(5)	Mn(4)-O(2)	1.912(5)
Mn(1)-O(6)	2.145(5)	Mn(3)-O(9)	2.195(5)	Mn(4)-N(1)	1.999(6)
Mn(1)-O(15)	1.869(5)	Mn(3)-O(5)	2.284(5)	Mn(5)-O(13)	2.149(6)
Mn(1)-O(16)	1.917(5)	Mn(3)-O(4)	1.875(5)	Mn(5)-O(12)	2.256(6)
Mn(1)-O(14)	1.955(5)	Mn(3)-O(3)	1.902(5)	Mn(5)-O(15)	1.900(5)
Mn(1)-N(3)	2.059(7)	Mn(3)-O(16)	1.934(5)	Mn(5)-O(7)	1.904(5)
Mn(2)-O(2)	2.132(5)	Mn(3)-N(2)	1.983(7)	Mn(5)-O(8)	1.910(5)
Mn(2)-O(4)	2.188(5)	Mn(4)-O(8)	2.207(5)	Mn(5)-N(4)	1.999(6)
Mn(2)-O(15)	1.895(5)	Mn(4)-O(17)	2.319(6)	Mn(1)...Mn(2)	2.843(2)
Mn(2)-O(16)	1.920(5)	Mn(4)-O(1)	1.904(6)	Mn(1)...Mn(3)	3.1589(16)
Mn(2)-O(11)	1.955(5)	Mn(4)-O(6)	1.905(5)	Mn(2)...Mn(3)	2.9333(16)
O(15)-Mn(1)-O(16)	83.4(2)	O(2)-Mn(2)-O(4)	170.26(19)	N(1)-Mn(4)-O(17)	88.8(2)
O(15)-Mn(1)-O(14)	98.5(2)	O(4)-Mn(3)-O(3)	173.5(2)	O(8)-Mn(4)-O(17)	177.9(2)
O(16)-Mn(1)-O(14)	171.7(2)	O(4)-Mn(3)-O(16)	86.7(2)	O(15)-Mn(5)-O(7)	90.9(2)
O(15)-Mn(1)-N(3)	169.8(2)	O(3)-Mn(3)-O(16)	99.5(2)	O(15)-Mn(5)-O(8)	97.5(2)
O(16)-Mn(1)-N(3)	91.9(2)	O(4)-Mn(3)-N(2)	82.2(2)	O(7)-Mn(5)-O(8)	171.2(2)
O(14)-Mn(1)-N(3)	87.5(2)	O(3)-Mn(3)-N(2)	91.8(3)	O(15)-Mn(5)-N(4)	178.1(3)
O(15)-Mn(1)-O(6)	91.4(2)	O(16)-Mn(3)-N(2)	168.5(2)	O(7)-Mn(5)-N(4)	88.3(2)
O(16)-Mn(1)-O(6)	94.2(2)	O(4)-Mn(3)-O(9)	92.2(2)	O(8)-Mn(5)-N(4)	83.3(2)
O(14)-Mn(1)-O(6)	93.9(2)	O(3)-Mn(3)-O(9)	90.2(2)	O(15)-Mn(5)-O(13)	91.5(2)
N(3)-Mn(1)-O(6)	80.0(2)	O(16)-Mn(3)-O(9)	86.8(2)	O(7)-Mn(5)-O(13)	89.8(2)
O(15)-Mn(1)-O(5)	104.3(2)	N(2)-Mn(3)-O(9)	91.0(2)	O(8)-Mn(5)-O(13)	92.8(2)
O(16)-Mn(1)-O(5)	80.9(2)	O(4)-Mn(3)-O(5)	91.0(2)	N(4)-Mn(5)-O(13)	90.2(2)
O(14)-Mn(1)-O(5)	90.7(2)	O(3)-Mn(3)-O(5)	88.1(2)	O(15)-Mn(5)-O(12)	95.0(2)
N(3)-Mn(1)-O(5)	83.7(2)	O(16)-Mn(3)-O(5)	79.3(2)	O(7)-Mn(5)-O(12)	87.3(2)
O(6)-Mn(1)-O(5)	162.79(19)	N(2)-Mn(3)-O(5)	103.4(2)	O(8)-Mn(5)-O(12)	89.1(2)
O(15)-Mn(2)-O(16)	82.6(2)	O(9)-Mn(3)-O(5)	165.5(2)	N(4)-Mn(5)-O(12)	83.2(2)
O(15)-Mn(2)-O(11)	99.1(2)	O(1)-Mn(4)-O(6)	93.8(2)	O(13)-Mn(5)-O(12)	172.9(2)
O(16)-Mn(2)-O(11)	169.4(2)	O(1)-Mn(4)-O(2)	170.0(2)	Mn(1)-O(5)-Mn(3)	88.75(19)
O(15)-Mn(2)-O(10)	175.0(2)	O(6)-Mn(4)-O(2)	94.5(2)	Mn(3)-O(4)-Mn(2)	92.1(2)
O(16)-Mn(2)-O(10)	92.7(2)	O(1)-Mn(4)-N(1)	89.0(2)	Mn(4)-O(2)-Mn(2)	130.7(2)
O(11)-Mn(2)-O(10)	85.9(2)	O(6)-Mn(4)-N(1)	176.0(2)	Mn(4)-O(6)-Mn(1)	127.0(3)
O(15)-Mn(2)-O(2)	88.5(2)	O(2)-Mn(4)-N(1)	82.5(2)	Mn(5)-O(8)-Mn(4)	123.8(2)
O(16)-Mn(2)-O(2)	91.9(2)	O(1)-Mn(4)-O(8)	92.0(2)	Mn(1)-O(15)-Mn(2)	98.1(2)
O(11)-Mn(2)-O(2)	98.6(2)	O(6)-Mn(4)-O(8)	89.5(2)	Mn(1)-O(15)-Mn(5)	129.7(3)
O(10)-Mn(2)-O(2)	89.8(2)	O(2)-Mn(4)-O(8)	93.7(2)	Mn(2)-O(15)-Mn(5)	125.4(3)
O(15)-Mn(2)-O(4)	92.9(2)	N(1)-Mn(4)-O(8)	93.3(2)	Mn(1)-O(16)-Mn(2)	95.6(2)
O(16)-Mn(2)-O(4)	78.73(19)	O(1)-Mn(4)-O(17)	87.9(3)	Mn(1)-O(16)-Mn(3)	110.2(2)
O(11)-Mn(2)-O(4)	90.7(2)	O(6)-Mn(4)-O(17)	88.3(2)	Mn(2)-O(16)-Mn(3)	99.1(2)
O(10)-Mn(2)-O(4)	88.0(2)	O(2)-Mn(4)-O(17)	86.7(2)		

**Table S2.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 2.

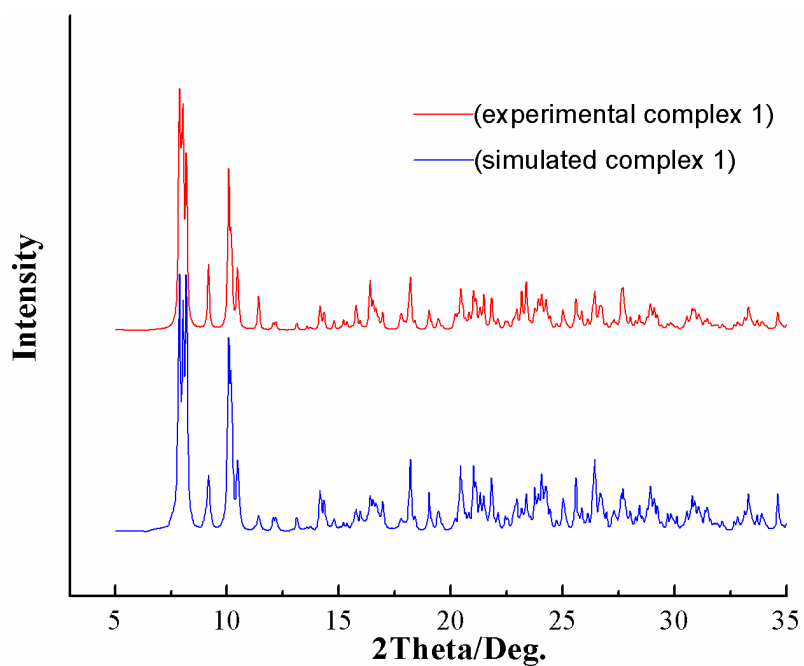
Mn(1)-O(16)	1.896(6)	Mn(2)-O(3)	2.329(6)	Mn(4)-O(8)	2.174(5)
Mn(1)-O(15)	1.922(5)	Mn(3)-O(16)	1.890(5)	Mn(4)-O(17)	2.324(6)
Mn(1)-O(10)	1.937(5)	Mn(3)-O(15)	1.910(6)	Mn(5)-O(7)	1.900(6)
Mn(1)-O(11)	1.978(6)	Mn(3)-O(13)	1.942(6)	Mn(5)-O(8)	1.912(6)
Mn(1)-O(6)	2.141(6)	Mn(3)-N(2)	2.058(6)	Mn(5)-O(16)	1.917(5)
Mn(1)-O(2)	2.177(6)	Mn(3)-O(4)	2.168(5)	Mn(5)-N(4)	2.026(7)
Mn(2)-O(2)	1.866(5)	Mn(3)-O(3)	2.197(5)	Mn(5)-O(14)	2.182(7)
Mn(2)-O(1)	1.899(5)	Mn(4)-O(4)	1.887(5)	Mn(5)-O(9)	2.243(6)
Mn(2)-O(15)	1.945(5)	Mn(4)-O(5)	1.914(6)	Mn(1)···Mn(2)	2.9682(19)
Mn(2)-N(1)	1.980(7)	Mn(4)-O(6)	1.918(6)	Mn(2)···Mn(3)	3.150(2)
Mn(2)-O(12)	2.199(6)	Mn(4)-N(3)	1.990(7)	Mn(1)···Mn(3)	2.8237(19)
O(16)-Mn(1)-O(15)	84.0(2)	O(12)-Mn(2)-O(3)	165.2(2)	N(3)-Mn(4)-O(17)	89.2(3)
O(16)-Mn(1)-O(10)	97.8(2)	O(16)-Mn(3)-O(15)	84.5(2)	O(8)-Mn(4)-O(17)	179.7(3)
O(15)-Mn(1)-O(10)	168.2(2)	O(16)-Mn(3)-O(13)	98.9(2)	O(7)-Mn(5)-O(8)	170.6(2)
O(16)-Mn(1)-O(11)	175.4(2)	O(15)-Mn(3)-O(13)	173.5(2)	O(7)-Mn(5)-O(16)	92.1(2)
O(15)-Mn(1)-O(11)	91.9(2)	O(16)-Mn(3)-N(2)	170.4(2)	O(8)-Mn(5)-O(16)	97.3(2)
O(10)-Mn(1)-O(11)	86.6(2)	O(15)-Mn(3)-N(2)	93.4(3)	O(7)-Mn(5)-N(4)	88.4(3)
O(16)-Mn(1)-O(6)	89.9(2)	O(13)-Mn(3)-N(2)	84.2(3)	O(8)-Mn(5)-N(4)	82.3(3)
O(15)-Mn(1)-O(6)	92.1(2)	O(16)-Mn(3)-O(4)	90.6(2)	O(16)-Mn(5)-N(4)	178.9(3)
O(10)-Mn(1)-O(6)	99.6(2)	O(15)-Mn(3)-O(4)	92.5(2)	O(7)-Mn(5)-O(14)	91.5(3)
O(11)-Mn(1)-O(6)	88.1(2)	O(13)-Mn(3)-O(4)	93.0(2)	O(8)-Mn(5)-O(14)	89.2(3)
O(16)-Mn(1)-O(2)	94.6(2)	N(2)-Mn(3)-O(4)	80.1(2)	O(16)-Mn(5)-O(14)	92.4(2)
O(15)-Mn(1)-O(2)	77.8(2)	O(16)-Mn(3)-O(3)	105.0(2)	N(4)-Mn(5)-O(14)	86.6(3)
O(10)-Mn(1)-O(2)	90.5(2)	O(15)-Mn(3)-O(3)	82.9(2)	O(7)-Mn(5)-O(9)	85.6(2)
O(11)-Mn(1)-O(2)	86.7(2)	O(13)-Mn(3)-O(3)	90.8(2)	O(8)-Mn(5)-O(9)	92.6(2)
O(6)-Mn(1)-O(2)	168.4(2)	N(2)-Mn(3)-O(3)	83.9(2)	O(16)-Mn(5)-O(9)	94.0(2)
O(2)-Mn(2)-O(1)	173.5(2)	O(4)-Mn(3)-O(3)	163.1(2)	N(4)-Mn(5)-O(9)	87.0(3)
O(2)-Mn(2)-O(15)	85.2(2)	O(4)-Mn(4)-O(5)	94.1(3)	O(14)-Mn(5)-O(9)	173.1(2)
O(1)-Mn(2)-O(15)	101.3(2)	O(4)-Mn(4)-O(6)	94.3(3)	Mn(2)-O(2)-Mn(1)	94.1(2)
O(2)-Mn(2)-N(1)	82.8(3)	O(5)-Mn(4)-O(6)	169.6(3)	Mn(3)-O(3)-Mn(2)	88.1(2)
O(1)-Mn(2)-N(1)	90.7(3)	O(4)-Mn(4)-N(3)	176.3(3)	Mn(4)-O(4)-Mn(3)	127.8(3)
O(15)-Mn(2)-N(1)	167.6(3)	O(5)-Mn(4)-N(3)	88.8(3)	Mn(4)-O(6)-Mn(1)	129.0(3)
O(2)-Mn(2)-O(12)	90.0(2)	O(6)-Mn(4)-N(3)	82.6(3)	Mn(5)-O(8)-Mn(4)	125.2(3)
O(1)-Mn(2)-O(12)	90.7(2)	O(4)-Mn(4)-O(8)	91.6(2)	Mn(3)-O(15)-Mn(1)	94.9(2)
O(15)-Mn(2)-O(12)	86.5(2)	O(5)-Mn(4)-O(8)	92.2(2)	Mn(3)-O(15)-Mn(2)	109.6(3)
N(1)-Mn(2)-O(12)	96.7(3)	O(6)-Mn(4)-O(8)	93.7(2)	Mn(1)-O(15)-Mn(2)	100.3(2)
O(2)-Mn(2)-O(3)	90.7(2)	N(3)-Mn(4)-O(8)	90.6(3)	Mn(3)-O(16)-Mn(1)	96.5(2)
O(1)-Mn(2)-O(3)	90.4(2)	O(4)-Mn(4)-O(17)	88.5(2)	Mn(3)-O(16)-Mn(5)	129.2(3)
O(15)-Mn(2)-O(3)	78.8(2)	O(5)-Mn(4)-O(17)	88.1(2)	Mn(1)-O(16)-Mn(5)	126.8(3)
N(1)-Mn(2)-O(3)	98.1(3)	O(6)-Mn(4)-O(17)	86.0(2)		

**Table S3.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 3.

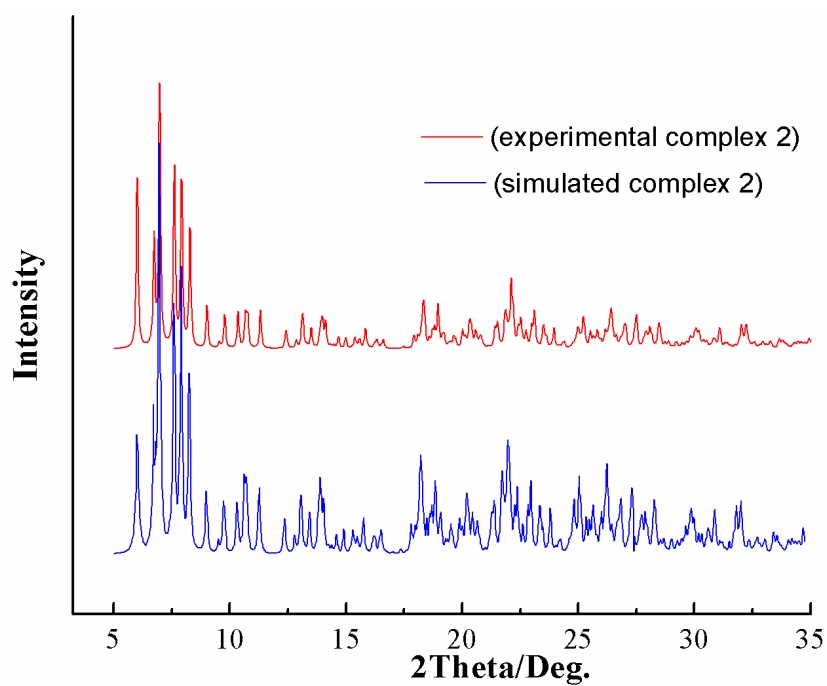
Mn(1)-O(2)	1.854(6)	Mn(2)-O(14)	2.102(7)	Mn(4)-O(8)	1.944(6)
Mn(1)-O(1)	1.876(6)	Mn(2)-O(6)	2.400(7)	Mn(4)-N(3)	1.979(8)
Mn(1)-O(5)	1.929(6)	Mn(3)-O(16)	2.118(6)	Mn(4)-O(19)	2.090(6)
Mn(1)-N(1)	1.991(7)	Mn(3)-O(11)	2.141(6)	Mn(4)-O(9)	2.471(7)
Mn(1)-O(15)	2.189(7)	Mn(3)-O(17)	2.144(7)	Mn(5)-O(11)	1.851(6)
Mn(1)-O(13)	2.194(8)	Mn(3)-O(2)	2.145(6)	Mn(5)-O(10)	1.867(6)
Mn(2)-O(12)	1.833(6)	Mn(3)-O(12)	2.198(6)	Mn(5)-O(8)	1.933(6)
Mn(2)-O(4)	1.878(6)	Mn(3)-O(3)	2.209(6)	Mn(5)-N(4)	1.960(8)
Mn(2)-O(5)	1.937(6)	Mn(4)-O(3)	1.830(6)	Mn(5)-O(20)	2.169(6)
Mn(2)-N(2)	1.989(8)	Mn(4)-O(7)	1.868(6)	Mn(5)-O(18)	2.286(7)
O(2)-Mn(1)-O(1)	173.7(3)	O(5)-Mn(2)-O(6)	73.3(2)	N(3)-Mn(4)-O(19)	96.6(3)
O(2)-Mn(1)-O(5)	91.2(3)	N(2)-Mn(2)-O(6)	81.4(3)	O(3)-Mn(4)-O(9)	87.9(3)
O(1)-Mn(1)-O(5)	94.5(3)	O(14)-Mn(2)-O(6)	166.4(3)	O(7)-Mn(4)-O(9)	100.9(3)
O(2)-Mn(1)-N(1)	83.6(3)	O(16)-Mn(3)-O(11)	141.3(3)	O(8)-Mn(4)-O(9)	71.7(2)
O(1)-Mn(1)-N(1)	91.0(3)	O(16)-Mn(3)-O(17)	82.9(3)	N(3)-Mn(4)-O(9)	74.8(3)
O(5)-Mn(1)-N(1)	171.9(3)	O(11)-Mn(3)-O(17)	92.7(2)	O(19)-Mn(4)-O(9)	162.0(2)
O(2)-Mn(1)-O(15)	94.3(3)	O(16)-Mn(3)-O(2)	90.5(2)	O(11)-Mn(5)-O(10)	173.9(3)
O(1)-Mn(1)-O(15)	88.4(3)	O(11)-Mn(3)-O(2)	115.9(2)	O(11)-Mn(5)-O(8)	90.3(3)
O(5)-Mn(1)-O(15)	87.9(3)	O(17)-Mn(3)-O(2)	139.0(2)	O(10)-Mn(5)-O(8)	95.8(3)
N(1)-Mn(1)-O(15)	86.3(3)	O(16)-Mn(3)-O(12)	141.0(2)	O(11)-Mn(5)-N(4)	83.3(3)
O(2)-Mn(1)-O(13)	89.8(3)	O(11)-Mn(3)-O(12)	74.9(2)	O(10)-Mn(5)-N(4)	90.6(3)
O(1)-Mn(1)-O(13)	87.6(3)	O(17)-Mn(3)-O(12)	80.9(3)	O(8)-Mn(5)-N(4)	171.5(3)
O(5)-Mn(1)-O(13)	91.4(3)	O(2)-Mn(3)-O(12)	79.3(2)	O(11)-Mn(5)-O(20)	92.8(3)
N(1)-Mn(1)-O(13)	94.8(3)	O(16)-Mn(3)-O(3)	82.2(2)	O(10)-Mn(5)-O(20)	87.0(3)
O(15)-Mn(1)-O(13)	175.8(3)	O(11)-Mn(3)-O(3)	78.7(2)	O(8)-Mn(5)-O(20)	93.0(2)
O(12)-Mn(2)-O(4)	91.4(3)	O(17)-Mn(3)-O(3)	143.1(3)	N(4)-Mn(5)-O(20)	92.9(3)
O(12)-Mn(2)-O(5)	96.2(3)	O(2)-Mn(3)-O(3)	74.6(2)	O(11)-Mn(5)-O(18)	94.0(3)
O(4)-Mn(2)-O(5)	167.4(3)	O(12)-Mn(3)-O(3)	129.3(2)	O(10)-Mn(5)-O(18)	86.4(3)
O(12)-Mn(2)-N(2)	169.5(3)	O(3)-Mn(4)-O(7)	90.8(3)	O(8)-Mn(5)-O(18)	85.4(2)
O(4)-Mn(2)-N(2)	88.4(3)	O(3)-Mn(4)-O(8)	94.5(3)	N(4)-Mn(5)-O(18)	89.5(3)
O(5)-Mn(2)-N(2)	82.3(3)	O(7)-Mn(4)-O(8)	170.7(3)	O(20)-Mn(5)-O(18)	173.0(3)
O(12)-Mn(2)-O(14)	97.4(3)	O(3)-Mn(4)-N(3)	162.4(3)	Mn(1)-O(2)-Mn(3)	119.6(3)
O(4)-Mn(2)-O(14)	95.4(3)	O(7)-Mn(4)-N(3)	89.8(3)	Mn(4)-O(3)-Mn(3)	123.7(3)
O(5)-Mn(2)-O(14)	93.6(3)	O(8)-Mn(4)-N(3)	82.9(3)	Mn(1)-O(5)-Mn(2)	127.6(3)
N(2)-Mn(2)-O(14)	93.1(3)	O(3)-Mn(4)-O(19)	100.9(3)	Mn(5)-O(8)-Mn(4)	127.1(3)
O(12)-Mn(2)-O(6)	88.2(3)	O(7)-Mn(4)-O(19)	94.7(3)	Mn(5)-O(11)-Mn(3)	118.7(3)
O(4)-Mn(2)-O(6)	96.9(3)	O(8)-Mn(4)-O(19)	91.8(2)	Mn(2)-O(12)-Mn(3)	124.4(3)

**Table S4.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 4.

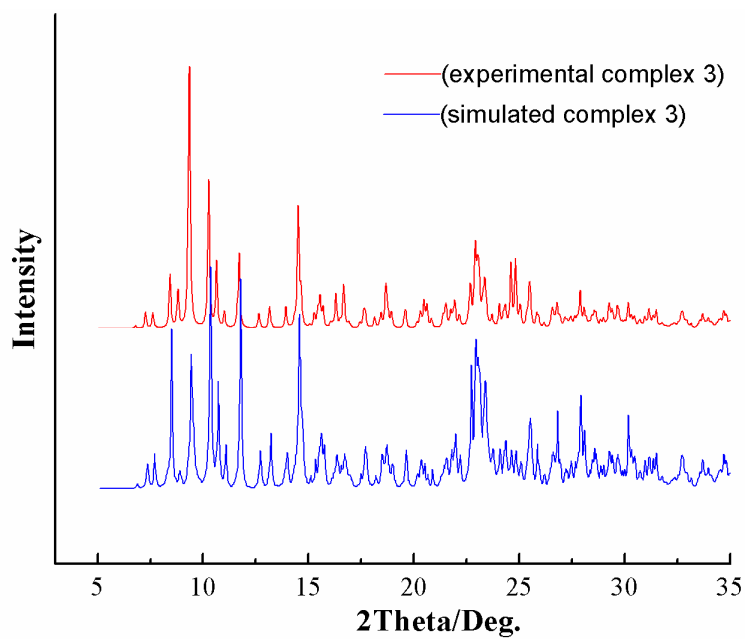
Mn(1)-O(19)	2.139(9)	Mn(2)-O(18)	2.122(12)	Mn(4)-N(3)	1.949(11)
Mn(1)-O(2)	2.146(10)	Mn(2)-O(15)	2.172(11)	Mn(4)-O(8)	1.975(10)
Mn(1)-O(13)	2.155(11)	Mn(3)-O(12)	1.818(9)	Mn(4)-O(21)	2.083(10)
Mn(1)-O(16)	2.237(11)	Mn(3)-O(4)	1.855(12)	Mn(4)-O(9)	2.403(10)
Mn(1)-O(3)	2.267(10)	Mn(3)-N(2)	1.957(14)	Mn(5)-O(19)	1.866(9)
Mn(1)-O(12)	2.280(11)	Mn(3)-O(5)	1.971(11)	Mn(5)-O(10)	1.873(10)
Mn(2)-O(1)	1.854(10)	Mn(3)-O(17)	2.108(12)	Mn(5)-O(8)	1.946(10)
Mn(2)-O(2)	1.872(9)	Mn(3)-O(6)	2.364(12)	Mn(5)-N(4)	1.995(13)
Mn(2)-O(5)	1.957(11)	Mn(4)-O(3)	1.839(9)	Mn(5)-O(20)	2.168(11)
Mn(2)-N(1)	1.965(15)	Mn(4)-O(7)	1.877(10)	Mn(5)-O(14)	2.259(11)
O(19)-Mn(1)-O ( 2 )	113.4(4)	O(5)-Mn(2)-O(15)	90.0(4)	O(8)-Mn(4)-O(21)	94.8(4)
O(19)-Mn(1)-O(13)	93.3(4)	N(1)-Mn(2)-O(15)	91.2(5)	O(3)-Mn(4)-O(9)	89.4(4)
O(2)-Mn(1)-O(13)	140.4(4)	O(18)-Mn(2)-O(15)	174.3(4)	O(7)-Mn(4)-O(9)	98.5(4)
O(19)-Mn(1)-O(16)	142.0(4)	O(12)-Mn(3)-O(4)	92.1(5)	N(3)-Mn(4)-O(9)	79.7(4)
O(2)-Mn(1)-O(16)	92.5(4)	O(12)-Mn(3)-N(2)	171.7(6)	O(8)-Mn(4)-O(9)	72.9(4)
O(13)-Mn(1)-O(16)	81.7(4)	O(4)-Mn(3)-N(2)	89.3(6)	O(21)-Mn(4)-O(9)	166.3(4)
O(19)-Mn(1)-O(3)	80.5(4)	O(12)-Mn(3)-O(5)	94.6(5)	O(19)-Mn(5)-O(10)	174.7(4)
O(2)-Mn(1)-O(3)	73.2(4)	O(4)-Mn(3)-O(5)	165.5(5)	O(19)-Mn(5)-O(8)	89.5(4)
O(13)-Mn(1)-O(3)	142.8(4)	N(2)-Mn(3)-O(5)	82.2(5)	O(10)-Mn(5)-O(8)	95.8(4)
O(16)-Mn(1)-O(3)	81.2(4)	O(12)-Mn(3)-O(17)	95.8(5)	O(19)-Mn(5)-N(4)	84.4(5)
O(19)-Mn(1)-O(12)	72.1(3)	O(4)-Mn(3)-O(17)	94.9(5)	O(10)-Mn(5)-N(4)	90.3(5)
O(2)-Mn(1)-O(12)	80.8(4)	N(2)-Mn(3)-O(17)	92.3(5)	O(8)-Mn(5)-N(4)	172.6(4)
O(13)-Mn(1)-O(12)	80.5(4)	O(5)-Mn(3)-O(17)	97.2(5)	O(19)-Mn(5)-O(20)	88.5(4)
O(16)-Mn(1)-O(12)	142.3(4)	O(12)-Mn(3)-O(6)	89.1(4)	O(10)-Mn(5)-O(20)	91.6(4)
O(3)-Mn(1)-O(12)	130.4(4)	O(4)-Mn(3)-O(6)	94.1(5)	O(8)-Mn(5)-O(20)	94.2(4)
O(1)-Mn(2)-O(2)	173.8(5)	N(2)-Mn(3)-O(6)	82.6(5)	N(4)-Mn(5)-O(20)	89.9(5)
O(1)-Mn(2)-O(5)	95.6(4)	O(5)-Mn(3)-O(6)	73.3(4)	O(19)-Mn(5)-O(14)	92.2(4)
O(2)-Mn(2)-O(5)	90.6(4)	O(17)-Mn(3)-O(6)	169.6(5)	O(10)-Mn(5)-O(14)	87.6(4)
O(1)-Mn(2)-N(1)	89.5(5)	O(3)-Mn(4)-O(7)	92.0(4)	O(8)-Mn(5)-O(14)	86.3(4)
O(2)-Mn(2)-N(1)	84.3(5)	O(3)-Mn(4)-N(3)	169.1(5)	N(4)-Mn(5)-O(14)	89.7(5)
O(5)-Mn(2)-N(1)	174.8(5)	O(7)-Mn(4)-N(3)	90.2(5)	O(20)-Mn(5)-O(14)	179.1(4)
O(1)-Mn(2)-O(18)	88.5(5)	O(3)-Mn(4)-O(8)	93.7(4)	Mn(2)-O(2)-Mn(1)	116.7(5)
O(2)-Mn(2)-O(18)	90.4(4)	O(7)-Mn(4)-O(8)	169.6(4)	Mn(4)-O(3)-Mn ( 1 )	121.6(5)
O(5)-Mn(2)-O(18)	90.7(5)	N(3)-Mn(4)-O(8)	82.6(4)	Mn(2)-O(5)-Mn ( 3 )	126.5(5)
N(1)-Mn(2)-O(18)	88.6(5)	O(3)-Mn(4)-O(21)	97.5(4)	Mn(5)-O(8)-Mn ( 4 )	127.2(5)
O(1)-Mn(2)-O(15)	85.9(4)	O(7)-Mn(4)-O(21)	93.1(4)	Mn(3)-O(12)-Mn ( 1 )	122.7(5)
O(2)-Mn(2)-O(15)	95.2(4)	N(3)-Mn(4)-O(21)	93.1(4)	Mn(5)-O(19)-Mn ( 1 )	118.5(5)



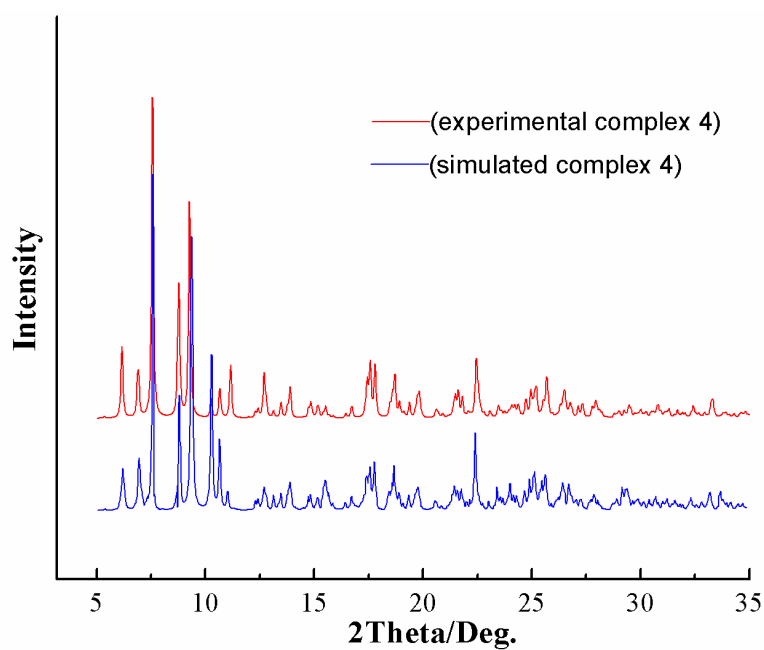
**Figure S1.** The XRD patterns of complex 1.



**Figure S2.** The XRD patterns of complex 2.

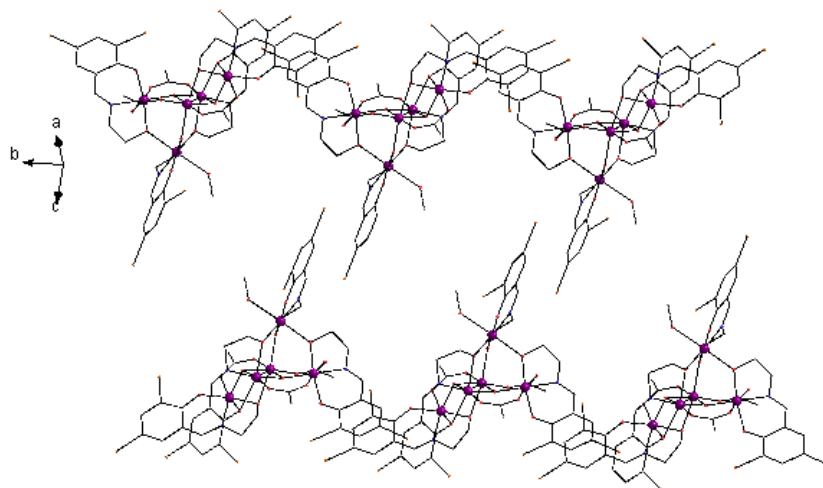


**Figure S3.** The XRD patterns of complex 3.

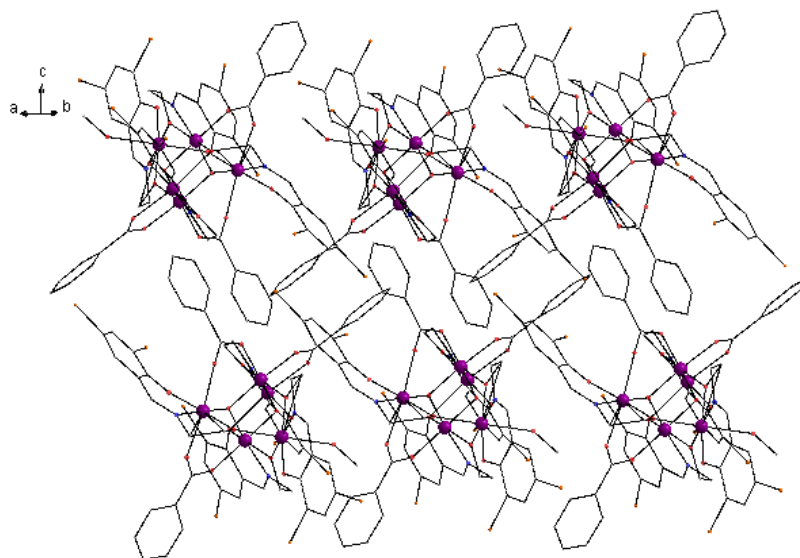


**Figure S4.** The XRD patterns of complex 4.

Packing diagrams (Fig. S5 to Fig. S8) reveal the presence of intercluster  $\pi$ - $\pi$  supramolecular interaction between the phenyl rings of the neighboring clusters in complexes **1-4**.

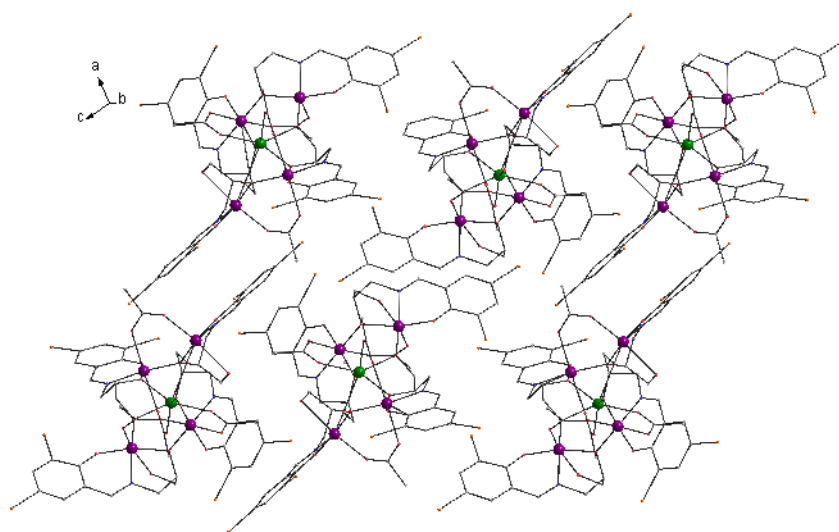


**Fig. S5.** The molecular packing structure of complex **1** (H atoms and solvent molecules are omitted for clarity).

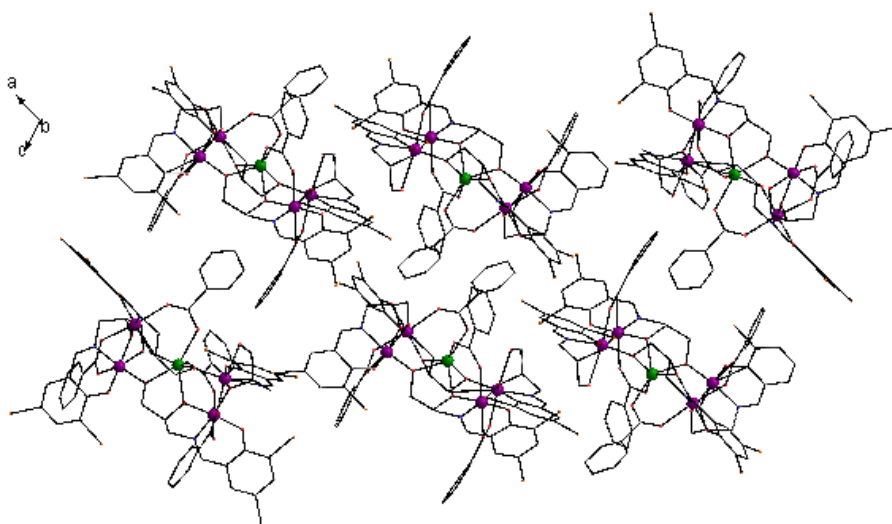


**Fig. S6.** The molecular packing structure of complex **2** (H atoms and solvent molecules are omitted for clarity).

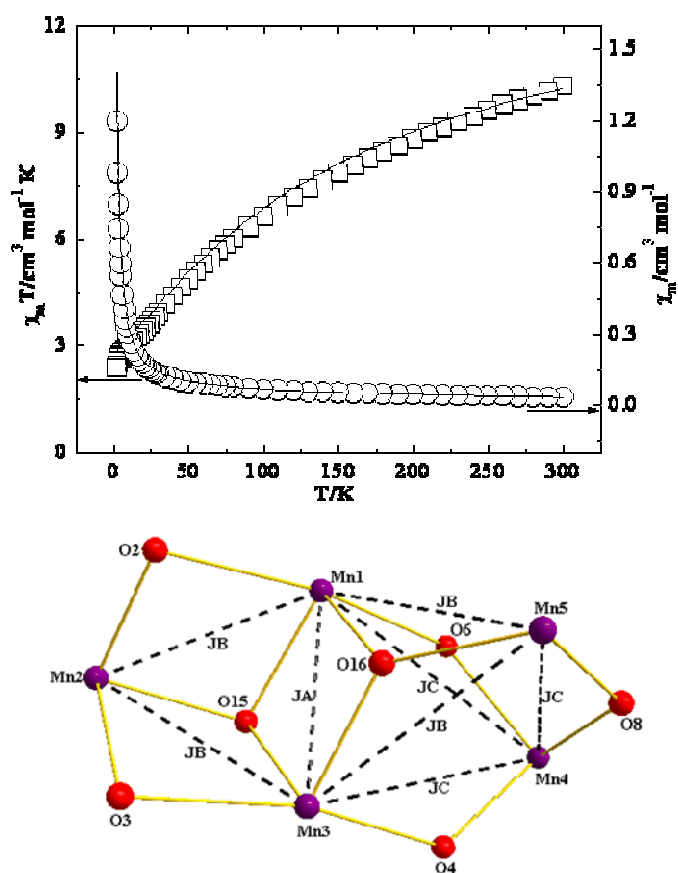




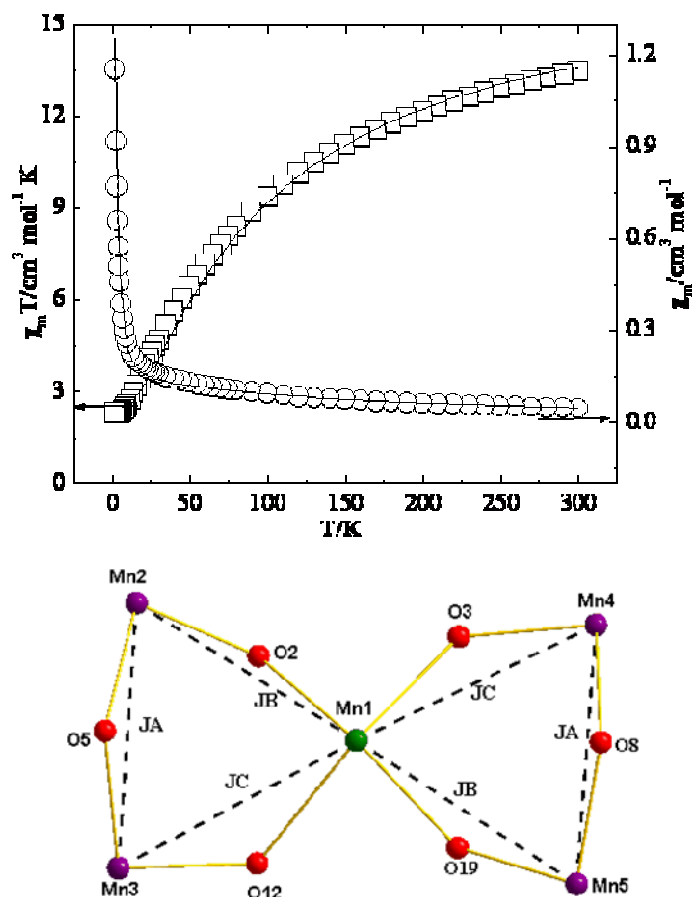
**Fig. S7.** The molecular packing structure of complex **3** (H atoms and solvent molecules are omitted for clarity).



**Fig. S8.** The molecular packing structure of complex **4** (H atoms and solvent molecules are omitted for clarity).



**Fig. S9.** (top) Temperature dependence of  $\chi_m$  ( $\circ$ ) and  $\chi_m T$  ( $\square$ ) values for **2**. The solid lines correspond to the best-fit curves using the parameters described in the text. (bottom) Spin topology for **2** assuming three different  $J$  values.



**Fig. S10.** (top) Temperature dependence of  $\chi_m$  ( $\circ$ ) and  $\chi_m T$  ( $\square$ ) values for **4**. The solid lines correspond to the best-fit curves using the parameters described in the text. (bottom) Spin topology for **4** assuming three different  $J$  values.