Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Nuclearity Control of Manganese Polymers dependent on Structural Differences in the Coligands and Magnetic Properties Studies

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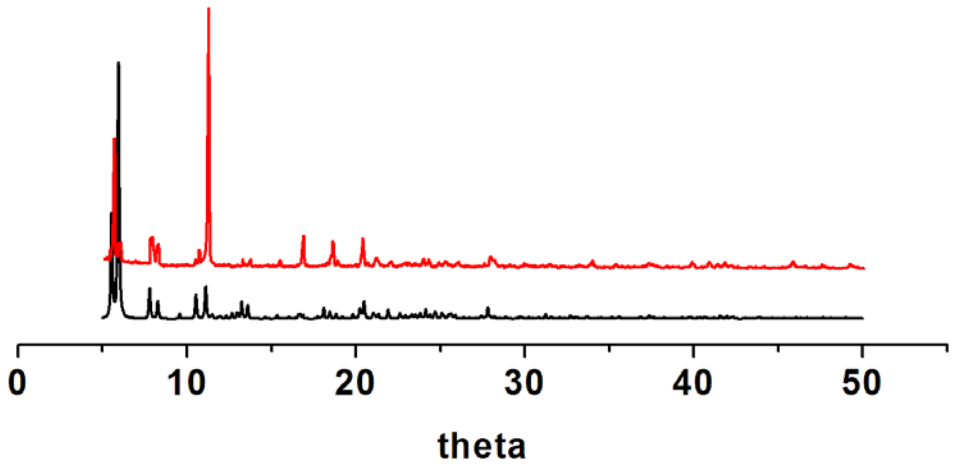

Figure S1: The PXRD patterns of polymer **1**.

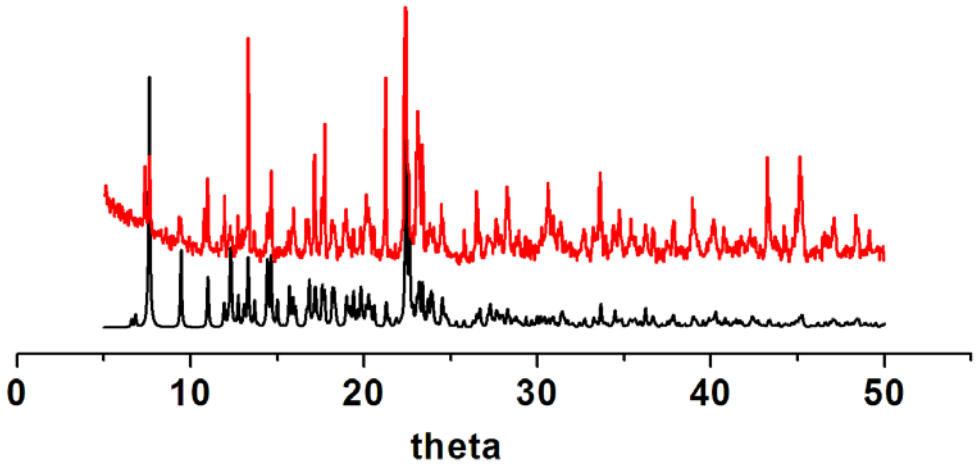

Figure S2: The PXRD patterns of polymer **2**.

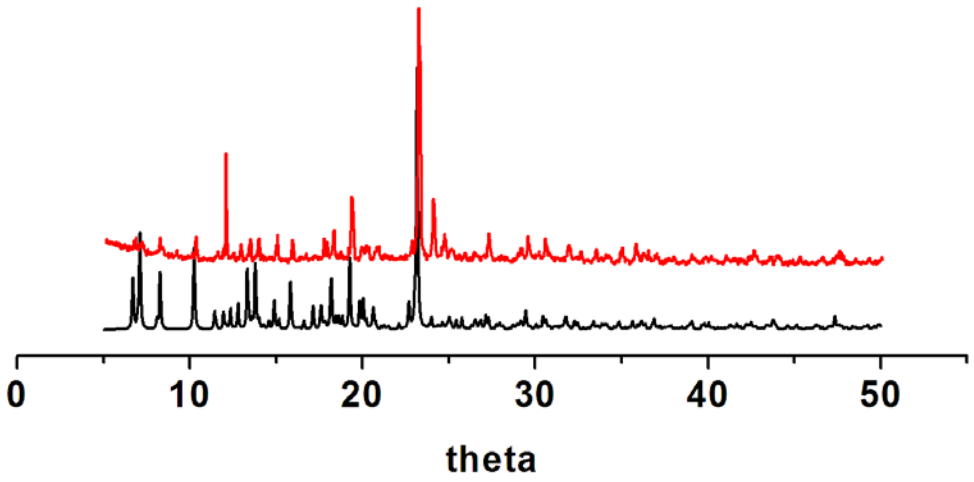

Figure S3: The PXRD patterns of polymer **3**.

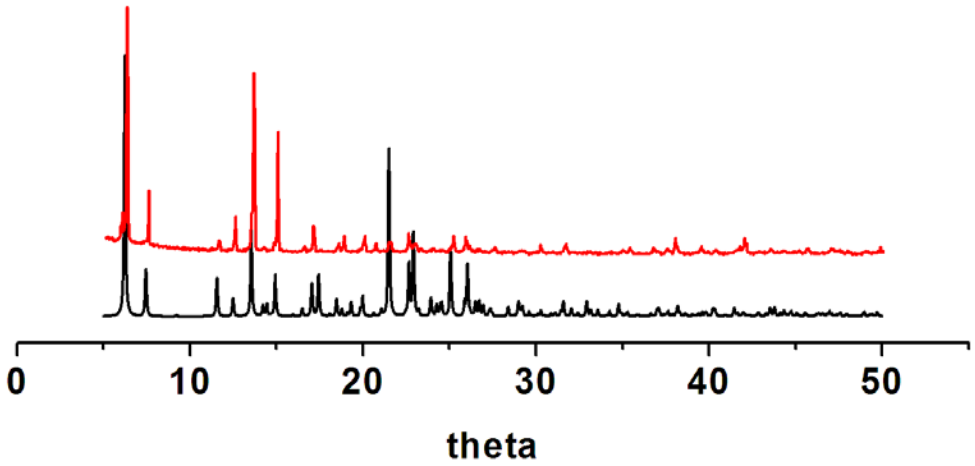

Figure S4: The PXRD patterns of polymer **4**.

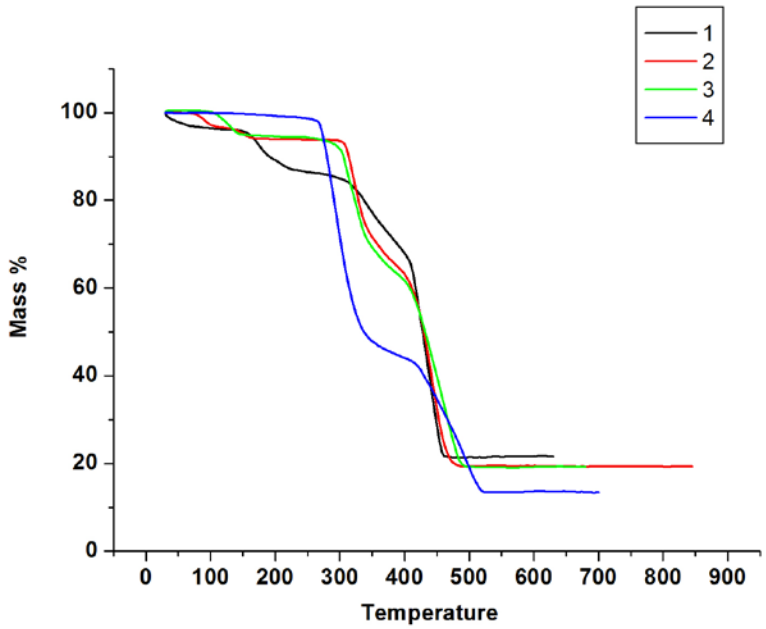

Figure S5: The TG curves of polymers **1-4.**

Thermal analysis:

The thermostability of polymers **1-4** was estimated by thermogravimetric analysis (TGA). Polymer **1** shows a weight loss of 13.87% from room temperature to 174.9 °C corresponding to the release of water molecules (13.32%). For polymer **2**, a weight loss of 6.09% occurs from 73 °C to 153.1 °C attributed to the release of four water molecules (calcd 5.88%). The overall framework of **3** begins to collapse at 96.5 °C and the water molecules (obsd, 6%, calcd, 5.9%) are lost during the storage. In the case of anhydrous polymer **4**, no obvious weight loss was observed until 278.3 °C.

Table S1. Crystal data and structure refinement for complexes **1-4**[a]

compound	1	2	3	4
Formula	$C_{58}H_{72}Mn_4N_{28}O_{32}$	$C_{43}H_{52}Mn_3N_{10}O_{22}$	$C_{42}H_{50}Mn_3N_{10}O_{22}$	$C_{25}H_{27}MnN_5O_9$
fw	1893.20	1225.77	1211.74	596.46
T/K	293(2)	293(2)	293(2)	293(2)
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
cryst syst	*orthorhombic*	*triclinic*	*triclinic*	*orthorhombic*
space group	*Pnma*	*P-1*	*P-1*	*Pna21*
a/Å	15.365(3)	13.519(3)	13.527(3)	28.334(6)
b/Å	31.833(6)	14.955(3)	14.982(3)	13.063(3)
c/Å	16.779(3)	15.356(3)	15.036(3)	6.7989(14)
α/deg	90	102.35(3)	62.09(3)	90
β/deg	90	109.47(3)	67.21(3)	90
γ/deg	90	110.99(3)	74.82(3)	90
V/Å^3	8207(3)	2529.3(9)	2470.4(9)	2516.4(9)
Z	4	2	2	4
D_{calcd}.(g·cm^{-3})	1.532	1.609	1.629	1.574
F(000)	3888	1262	1246	1160
Reflections collected	7356/7356	21412 / 8864	20504 / 8600	11500 / 4345
R(int)	0.0000	0.0237	0.0528	0.0427
$2\theta_{max}$(°)	25.00	25.00	25.00	25.50
GOF	1.104	1.089	1.067	1.037
R_1(I>2sigma(I))	0.0878	0.0402	0.0772	0.0435
wR_2 (all data)	0.2171	0.1098	0.2168	0.1107

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths /Å and angles /°for **1-4**

Complex **1**			
Mn(1)-O(2)	2.156(4)	Mn(1)-N(9)	2.293(4)
Mn(1)-O(12)	2.218(4)	Mn(1)-N(11)	2.277(4)
Mn(1)-N(10)	2.310(5)	Mn(1)-N(15)#1	2.319(5)
Mn(2)-O(6)	2.115(7)	Mn(2)-O(6)	2.115(7)
Mn(2)-O(1)	2.151(4)	Mn(2)-O(15)	2.169(5)
Mn(2)-O(13)	2.193(4)	Mn(2)-N(8)	2.193(5)
Mn(2)-N(5)	2.394(5)	O(2)-Mn(1)-O(12)	84.19(17)
O(2)-Mn(1)-N(11)	110.72(17)	O(12)-Mn(1)-N(11)	89.83(17)
O(2)-Mn(1)-N(9)	108.55(17)	O(12)-Mn(1)-N(9)	92.06(18)
N(11)-Mn(1)-N(9)	140.67(17)	N(11)-Mn(1)-N(10)	70.96(16)
O(2)-Mn(1)-N(10)	171.63(16)	O(12)-Mn(1)-N(10)	87.64(16)
N(9)-Mn(1)-N(10)	69.88(15)	O(2)-Mn(1)-N(15)#1	93.06(17)
O(12)-Mn(1)-N(15)#1	173.86(17)	N(11)-Mn(1)-N(15)#1	86.00(16)
N(9)-Mn(1)-N(15)#1	94.03(17)	N(10)-Mn(1)-N(15)#1	95.25(17)
O(6)-Mn(2)-O(15)	83.1(3)	O(1)-Mn(2)-O(15)	104.1(2)
O(6)-Mn(2)-O(13)	162.7(3)	O(1)-Mn(2)-O(13)	98.08(16)
O(15)-Mn(2)-O(13)	82.6(2)	O(6)-Mn(2)-N(8)	103.0(3)
O(1)-Mn(2)-N(8)	86.84(17)	O(15)-Mn(2)-N(8)	167.1(2)
O(13)-Mn(2)-N(8)	89.14(18)	O(6)-Mn(2)-N(5)	84.3(2)
O(1)-Mn(2)-N(5)	157.83(18)	O(15)-Mn(2)-N(5)	97.8(2)
O(13)-Mn(2)-N(5)	87.91(16)	N(8)-Mn(2)-N(5)	71.86(17)
O(1)-Co(1)-N(1)	98.24(12)	O(6)-Mn(2)-O(1)	94.9(2)
Complex **2**			
Mn(1)-O(1)	2.1482(19)	Mn(1)-O(1)#3	2.186(2)
Mn(1)-O(7)#4	2.231(2)	Mn(1)-O(6)#4	2.244(2)
Mn(1)-O(8)	2.257(2)	Mn(1)-O(9)	2.298(2)
Mn(2)-O(20)#3	2.172(2)	Mn(2)-O(15)#4	2.179(2)
Mn(2)-O(19)	2.248(2)	Mn(2)-N(10)	2.249(2)
Mn(3)-O(21)#3	2.114(2)	Mn(3)-O(14)	2.131(3)
Mn(3)-O(13)	2.201(2)	Mn(3)-O(15)#4	2.224(2)
Mn(3)-N(7)	2.262(2)	Mn(3)-O(16)#4	2.345(2)
O(1)-Mn(1)-O(1)#3	76.14(9)	O(1)-Mn(1)-O(7)#4	96.44(8)
O(1)#3-Mn(1)-O(7)#4	108.75(9)	O(1)-Mn(1)-O(6)#4	147.18(8)
O(1)#3-Mn(1)-O(6)#4	92.22(9)	O(7)#4-Mn(1)-O(6)#4	57.91(8)
O(1)-Mn(1)-O(8)	113.29(9)	O(1)#3-Mn(1)-O(8)	91.71(8)
O(7)#4-Mn(1)-O(8)	147.43(8)	O(6)#4-Mn(1)-O(8)	97.40(9)
O(1)-Mn(1)-O(9)	110.33(9)	O(1)#3-Mn(1)-O(9)	148.04(8)
O(7)#4-Mn(1)-O(9)	101.69(9)	O(6)#4-Mn(1)-O(9)	95.84(9)
O(8)-Mn(1)-O(9)	56.62(8)		
Complex **3**			
Mn(1)-O(10)	2.143(4)	Mn(1)-O(5)	2.172(4)

Mn(1)-O(20)	2.193(4)	Mn(1)-O(4)#2	109.88(11)
Mn(1)-N(1)	2.225(4)	Mn(1)-O(19)	2.232(4)
Mn(2)-O(11)	2.066(4)	Mn(2)-O(1)#3	2.158(4)
Mn(2)-O(6)#1	2.174(4)	Mn(2)-N(4)	2.251(5)
Mn(2)-O(4)#2	2.303(4)	Mn(2)-O(3)#2	2.323(4)
Mn(3)-O(2)	2.076(4)	Mn(3)-O(15)#1	2.103(5)
Mn(3)-O(21)	2.117(5)	Mn(3)-O(13)#4	2.143(6)
Mn(3)-O(12)#4	2.238(6)	Mn(3)-C(16)#4	2.541(8)
O(10)-Mn(1)-O(5)	174.24(16)	O(10)-Mn(1)-O(20)	85.34(19)
O(5)-Mn(1)-O(20)	89.81(17)	O(10)-Mn(1)-O(4)#2	90.08(17)
O(5)-Mn(1)-O(4)#2	94.42(16)	O(20)-Mn(1)-O(4)#2	172.67(16)
O(10)-Mn(1)-N(1)	89.97(17)	O(5)-Mn(1)-N(1)	93.41(16)
O(20)-Mn(1)-N(1)	93.06(18)	O(4)#2-Mn(1)-N(1)	92.65(17)
O(10)-Mn(1)-O(19)	88.12(15)	O(5)-Mn(1)-O(19)	88.50(13)
O(20)-Mn(1)-O(19)	86.79(16)	O(4)#2-Mn(1)-O(19)	87.34(16)
N(1)-Mn(1)-O(19)	178.09(16)	O(11)-Mn(2)-O(1)#3	122.84(17)
O(11)-Mn(2)-O(6)#1	88.48(17)	O(1)#3-Mn(2)-O(6)#1	83.71(16)
O(11)-Mn(2)-N(4)	88.04(18)	O(1)#3-Mn(2)-N(4)	96.90(17)
O(6)#1-Mn(2)-N(4)	176.19(17)	O(11)-Mn(2)-O(4)#2	93.53(16)
O(1)#3-Mn(2)-O(4)#2	142.20(16)	O(6)#1-Mn(2)-O(4)#2	87.69(15)
N(4)-Mn(2)-O(4)#2	94.06(17)	O(11)-Mn(2)-O(3)#2	149.05(16)
O(1)#3-Mn(2)-O(3)#2	87.69(16)	O(6)#1-Mn(2)-O(3)#2	90.26(14)
N(4)-Mn(2)-O(3)#2	93.52(16)	O(4)#2-Mn(2)-O(3)#2	55.53(13)
O(2)-Mn(3)-O(15)#1	100.1(2)	O(2)-Mn(3)-O(21)	107.2(2)
O(15)#1-Mn(3)-O(21)	91.4(2)	O(2)-Mn(3)-O(13)#4	149.1(2)
O(15)#1-Mn(3)-O(13)#4	99.2(3)	O(21)-Mn(3)-O(13)#4	96.2(2)
O(2)-Mn(3)-O(12)#4	94.1(2)	O(15)#1-Mn(3)-O(12)#4	109.1(3)
O(21)-Mn(3)-O(12)#4	147.5(3)	O(13)#4-Mn(3)-O(12)#4	56.7(3)

Complex **4**

Mn(1)-O(2)#1	2.098(3)	Mn(1)-O(1)#2	2.151(3)
Mn(1)-O(3)#3	2.180(3)	Mn(1)-N(4)	2.224(3)
Mn(1)-O(4)	2.304(3)	Mn(1)-O(3)	2.329(3)
O(2)#1-Mn(1)-O(1)#2	168.53(12)	O(2)#1-Mn(1)-O(3)#3	89.51(11)
O(1)#2-Mn(1)-O(3)#3	85.57(11)	O(2)#1-Mn(1)-N(4)	96.10(12)
O(1)#2-Mn(1)-N(4)	94.41(12)	O(3)#3-Mn(1)-N(4)	91.85(12)
O(2)#1-Mn(1)-O(4)	102.16(12)	O(1)#2-Mn(1)-O(4)	82.98(11)
O(3)#3-Mn(1)-O(4)	168.33(11)	N(4)-Mn(1)-O(4)	86.81(11)
O(2)#1-Mn(1)-O(3)	88.94(11)	O(1)#2-Mn(1)-O(3)	85.39(11)
O(3)#3-Mn(1)-O(3)	124.73(6)	N(4)-Mn(1)-O(3)	143.18(11)
O(4)-Mn(1)-O(3)	56.56(9)		

Symmetry transformations used to generate equivalent atoms: for polymer **1**: #1 x-1/2,y,-z+1/2; #2 x,-y+3/2,z; #3 x+1/2,y,-z+1/2; for polymer **2**: #1 x+1,y,z; #2 -x,-y+2,-z+1; #3 -x+1,-y+1,-z+2; #4 x-1,y,z; for polymer **3**: #1 -x+2,-y+2,-z+2; #2 -x+1,-y+2,-z+2; #3 x+1,y,z-1; #4 x-1,y+1,z+1; #5 x+1,y-1,z-1; #6 x-1,y,z+1; for

polymer **4**: #1 x,y-1,z; #2 -x,-y+1,z+1/2; #3 -x,-y,z+1/2; #4 -x,-y+1,z-1/2; #5 x,y+1,z; #6 -x,-y,z-1/2;