Supporting Information

Structure, magnetic properties and spin density of two alternative Mn(II) coordination polymers based on 1,4-bis(2'-carboxyphenoxy)benzene

Ai Wang,*[a] Bin Yang,[a, b] Yan Wang, [c] Zijia, Hu, [a] Zhihong Wei, [a] Miaoli Zhu [a] and Ulli Englert [a,d]

Fig. S6 (a) PXRD pattern of complex **1**; (b) PXRD pattern of complex **2**.

Fig. S7 Field dependent isothermal magnetization $M(T, H)$ for **1** at 1.8 K from 0 to 70 KOe.

Information on the reaction vessels used in the syntheses:

Solvothermal reactors were bought from Jinan Henghua Sci. & Tec. Co., Ltd, China and consist of two parts. The outer vessel is made of steel (type 316) and its wall-thickness is 4.5 mm. The inner part is a white Teflon tube with a wall-thickness of 4.5 mm. The whole device can withstand heat of 250 ° and pressure of 15 MPa.

The process of screening experiments for the different volumes of reaction system

To establish the relationship between the product yields and the volume of reaction system, the synthesis experiments have been repeated.

As shown in Table S1, with a reaction system around 8 mL ($V_{reactants+solvent}/V_{Teflon\ tube}$) for the 25 mL Teflon tubes, a mixture of crystalline products **1** and **2** is obtained. Due to the different solid particle sizes of the solid reactants ($MnCl_2{\cdot}4H_2O$, H_2bcpb and 2,2'-bipy), the volumes of the reaction mixtures (solvent and reactants) differ slightly in the five experiments. Thus, the average yields are 22.0% for **1** and 41.0% for **2**.

Table S1 Experimental results (1-5) for 25 mL Teflon tubes and product yields.

Experiments	1	2	3	4	5
$V_{Teflon\ tube}$ (mL)			25		
$V_{reactants}$[a]$_{+solvents}$[b] (mL)	7.6	7.5	8.0	7.8	8.7
Yield of **1**(%, based on Mn^{2+})	22.0	23.4	19.0	22.0	36.1
Yield of **2**(%, based on Mn^{2+})	41.0	43.2	39.8	41.0	41.5
Average Yield (%)			22.0 for **1**, 41.0 for **2**		

[a] $MnCl_2{\cdot}4H_2O$ (0.10 mmol, 19.80 mg)+H_2bcpb (0.05 mmol, 17.50 mg)+2,2'-bipy (0.10mmol, 15.60mg)

[b] **NaOH (0.5 mL, 0.25 M) and H_2O (6.0 mL)**

As shown in Table S2, addition of 6 mL of water to the mixture of solvent and reactants listed in Table S1. For the five experiments 6 - 11, the average yields slightly decrease to 20.6% for **1** and 38.5% for **2**.

Table S2 Experimental results (6-10) for 25 mL Teflon tubes and product yields.

Experiments	6	7	8	9	10
$V_{Teflon\ tube}$ (mL)			25		

$V_{reactants}$[a]+$_{solvents}$[b] (mL)	13.6	13.5	14.0	14.8	14.7
Yield of **1**(%, based on Mn^{2+})	20.1	19.6	19.0	22.0	22.3
Yield of **2**(%, based on Mn^{2+})	37.3	38.1	39.8	41.0	36.3
Average Yield (%)	20.6 for **1**, 38.5 for **2**				

[a] $MnCl_2 \cdot 4H_2O$ (0.10 mmol, 19.80 mg)+H_2bcpb (0.05 mmol, 17.50 mg)+2,2'-bipy (0.10mmol, 15.60mg)

[b] **NaOH (0.5 mL, 0.25 M) and H_2O (12.0 mL)**

When the volume of reaction system of the 25 mL Teflon tube reaches to 20 mL by addition of 6 mL water to the solvents volume in Table S2, compound **2** is obtained exclusively (seeing Table S3) and the yields of complex **2** reach to 59.3%.

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Table S3 Experimental results (11-15) for 25 mL Teflon tubes and product yields.

Experiments	11	12	13	14	15
$V_{Teflon\ tube}$ (mL)	25				
$V_{reactants}$[a]+$_{solvents}$[b] (mL)	20.0	20.5	19.5	20.6	19.4
Yield of **1**(%, based on Mn^{2+})	0	0	0	0	0
Yield of **2**(%, based on Mn^{2+})	58.0	57.6	59.0	60.3	61.6
Average Yield (%)	0 for **1**, 59.3 for **2**				

[a] $MnCl_2 \cdot 4H_2O$ (0.10 mmol, 19.80 mg)+H_2bcpb (0.05 mmol, 17.50 mg)+2,2'-bipy (0.10mmol, 15.60mg)

[b] **NaOH (0.5 mL, 0.25 M) and H_2O (18.0 mL)**

For the experiments 16-20, the same synthesis recipe as listed in Table S1 is transferred into 13 mL Teflon tubes. From 13 mL Teflon tubes, pure crystalline (**2**) could be obtained in 61.0% yield based on Mn(II) (see Table S4).

Table S4 Experimental results (16-20) for 13 mL Teflon tubes and product yields.

Experiments	16	17	18	19	20
$V_{Teflon\ tube}$ (mL)	13				
$V_{reactants}$[a]+$_{solvents}$[b] (mL)	7.0	7.3	7.0	7.2	7.2
Yield of **1**(%, based on Mn^{2+})	0	0	0	0	0
Yield of **2**(%, based on Mn^{2+})	60.0	61.3	59.3	61.8	62.6
Average Yield (%)	0 for **1**, 61.0 for **2**				

[a] $MnCl_2 \cdot 4H_2O$ (0.10 mmol, 19.80 mg)+H_2bcpb (0.05 mmol, 17.50 mg)+2,2'-bipy (0.10mmol, 15.60mg)

[b] NaOH (0.5 mL, 0.25 M) and H_2O (6.0 mL)

The product yields of complexes **1** and **2** in Table S5 are the average results based on the five experiments.

Table S5 Experimental results correlating the volume of reaction system and the product yields.

$V_{Teflon\ tube}$ (mL)	25	13

$V_{reactants}^{a}+_{solvents}^{b}$ (mL)	8	14	20	7
Yield of **1**	22.5%	20.6%	0	0
Yield of **2**	41.3%	38.5%	59.3%	61.0%

Table S6 Selected bond lengths (Å) and bond angles (°) for complex **1**.

Mn1-O4^{i}	2.1430(16)	Mn1-O4	2.1637(15)
Mn1-O2	2.1967(17)	Mn1-N1	2.2350(19)
Mn1-N2	2.2420(19)	Mn1-O1	2.3412(18)
O4^{i}-Mn1-O4	76.77(6)	O4^{i}-Mn1-O2	139.61(6)
O4-Mn1-O2	87.91(6)	O4^{i}-Mn1-N1	104.14(7)
O4-Mn1-N1	170.61(7)	O2-Mn1-N1	96.88(7)
O4^{i}-Mn1-N2	104.55(7)	O4-Mn1-N2	97.65(6)
O2-Mn1-N2	114.50(7)	N1-Mn1-N2	73.02(7)
O4^{i}-Mn1-O1	87.68(6)	O4-Mn1-O1	98.46(7)
O2-Mn1-O1	57.54(6)	N1-Mn1-O1	90.93(7)
N2-Mn1-O1	90.93(7)		

Symmetry code: (i)-x+1, -y, -z+1

Table S7 Selected bond lengths (Å) and bond angles (°) for complex **2**.

Mn1-O8	2.1337(19)	Mn1-O4	2.1633(19)
Mn1-O1	2.1990(19)	Mn1-O5	2.2028(19)
Mn1-N2	2.290(2)	Mn1-N1	2.296(2)
Mn2-O6	2.065(2)	Mn2-O9	2.0885(19)
Mn2-O11	2.2083(18)	Mn2-N4	2.243(2)
Mn2-N3	2.281(2)	Mn2-O12	2.3330(19)
O8-Mn1-O4	113.15(8)	O8-Mn1-O1	91.56(8)
O4-Mn1-O1	86.99(8)	O8-Mn1-O5	89.59(8)
O4-Mn1-O5	90.61(8)	O1-Mn1-O5	177.58(7)
O8-Mn1-N2	155.57(8)	O4-Mn1-N2	90.83(8)
O1-Mn1-N2	84.83(8)	O5-Mn1-N2	94.99(8)
O8-Mn1-N1	85.24(8)	O4-Mn1-N1	161.56(8)
O1-Mn1-N1	91.37(8)	O5-Mn1-N1	90.84(8)
N2-Mn1-N1	70.73(9)	O6-Mn2-O9	92.58(8)
O6-Mn2-O11	103.47(8)	O9-Mn2-O11	98.90(7)
O6-Mn2-N4	162.40(9)	O9-Mn2-N4	86.20(8)
O11-Mn2-N4	94.06(8)	O6-Mn2-N3	93.41(9)
O9-Mn2-N3	116.06(8)	O11-Mn2-N3	140.40(8)
N4-Mn2-N3	71.57(9)	O6-Mn2-O12	93.44(8)
O9-Mn2-O12	156.38(8)	O11-Mn2-O12	57.48(7)
N4-Mn2-O12	94.66(8)	N3-Mn2-O12	86.35(8)

Table S8 Bond valence values for manganese cations in complex **1**.

Bond	Bond distance	Bond valence (based on Mn(II))	Bond valence (based on Mn(III))
Mn1-O4^{i}	2.1430(16)	0.385	0.355
Mn1-O4	2.1637(15)	0.364	0.335
Mn1-O2	2.1967(17)	0.333	0.307
Mn1-N1	2.2350(19)	0.352	0.341
Mn1-N2	2.2420(19)	0.346	0.335
Mn1-O1	2.3412(18)	0.226	0.208
		2.005	1.881

Table S9 Bond valence values for manganese cations in complex **2**.

Bond	Bond distance	Bond valence (based on Mn(II))	Bond valence (based on Mn(III))
Mn1-O8	2.1337(19)	0.395	0.364
Mn1-O4	2.1633(19)	0.365	0.336
Mn1-O1	2.1990(19)	0.331	0.305
Mn1-O5	2.2028(19)	0.328	0.302
Mn1-N2	2.290(2)	0.304	0.294
Mn1-N1	2.296(2)	0.298	0.288
		2.019	1.890
Mn2-O6	2.065(2)	0.474	0.437
Mn2-O9	2.0885(19)	0.446	0.412
Mn2-O11	2.2083(18)	0.323	0.298
Mn2-N4	2.243(2)	0.345	0.334
Mn2-N3	2.281(2)	0.311	0.301
Mn2-O12	2.3330(19)	0.231	0.213
		2.130	1.994

Table S10 Energy comparison of ferromagnetic and antiferromagnetic states for two simplified models of compound **1**.

		1_Model I		**1_Model II**	
Functional/Basis	Energy (298.15 K)	f*	af*	f	af
B3LYP/Def2TZVP	Electronic Energy(E)/Hartree	-4974.531719	-4974.531713	-4974.527463	-4974.527827
	ΔE(kJ/mol)= E(f)-E(af)	-0.0158		-0.9557	
	ΔG(kJ/mol)= G(f)-G(af)	-5.0094		-4.9753	
B3LYP/D3BJ/Def2TZVP	Electronic Energy(E)/Hartree	-4975.380571	-4975.380606	-4975.373202	-4975.373525
	ΔE(kJ/mol)=E(f)-E(af)	-0.0919		-0.8467	

	ΔG(kJ/mol)= G(f)-G(af)	-4.9018	-5.0843
M06L/ Def2TZVP	Electronic Energy(E)/Hartree	- 4974.654273	- 4974.654248	-4974.651211	-4974.651598
	ΔE(kJ/mol)=E(f)-E(af)	-0.06695	-1.0171
	ΔG(kJ/mol)= G(f)-G(af)	-5.0606	-4.91389
MN15/ Def2TZVP	Electronic Energy(E)/Hartree	- 4972.114839	- 4972.115106	-4972.108531	-4972.108761
	ΔE(kJ/mol)=E(f)-E(af)	-0.6997	-0.6041
	ΔG(kJ/mol)= G(f)-G(af)	-4.2940	-5.3269

*af = antiferromagnetic; f = ferromagnetic

Table S11 Comparison of structural parameters of the optimized ferromagnetic geometries of the two models of compound **1**.

	1_Exp.	**1_Modle I**	**1_Modle II**
Spin-coupling	ferromagnetic	ferromagnetic	ferromagnetic
Mn1-O4(Å)	2.14	2.17	2.13
Mn1-O4^{I}(Å)	2.16	2.17	2.14
Mn1-O2(Å)	2.19	2.21	2.20
Mn1-N1(Å)	2.24	2.30	2.31
Mn1-N2(Å)	2.24	2.33	2.34
Mn1-O1(Å)	2.34	2.29	2.36
Mn1-O4-Mn2(°)	103.23	101.2	91.76
O4-Mn1-O4^{i}(°)	76.77	78.8	97.50
O4-Mn1-O2(°)	139.61	105.70	102.40
O4-Mn1-N2(°)	97.65	91.20	98.93
Mn1…Mn2(Å)	3.38	3.36	4.48
Spin-densities[a] Mn1	--	4.85	4.85
Spin-densities[a] Mn2	--	4.85	4.85
Energy/Hartree		-4974.654273	-4974.651211

[a]Mulliken spin-density. i: -*x*+1,-*y*,-*z*+1

Table S12 Energy comparison of ferromagnetic and antiferromagnetic states for 2_Model in compound **2**.

Functional/Basis	**2_Model**

	Energy (298.15 K)	f*	af*
B3LYP/Def2TZVP	Electronic Energy(E)/Hartree	-5051.00596	-5051.005842
	ΔE(kJ/mol)=E(f)-E(af)	-0.3098	
	ΔG(kJ/mol)= G(f)-G(af)	-3.0062	
B3LYP/D3BJ/Def2TZV	Electronic Energy(E)/Hartree	-5051.867583	-5051.867833
P	ΔE(kJ/mol)=E(f)-E(af)	-0.6569	
	ΔG(kJ/mol)= G(f)-G(af)	-3.9729	
M06L/Def2TZVP	Electronic Energy(E)/Hartree	**-5051.13039**	**-5051.13052**
	ΔE(kJ/mol)=E(f)-E(af)	**0.3423**	
	ΔG(kJ/mol)= G(f)-G(af)	**2.9736**	
MN15/Def2TZVP	Electronic Energy(E)/Hartree	-5048.52784	-5048.527886
	ΔE(kJ/mol)=E(f)-E(af)	-0.1210	
	ΔG(kJ/mol)= G(f)-G(af)	-3.4370	

*af = antiferromagnetic; f = ferromagnetic

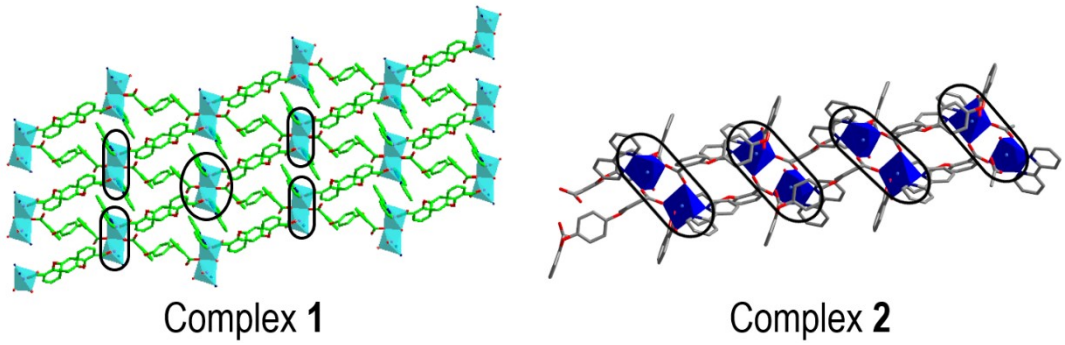

Fig. S1 The different connection ways between neighboring Mn(II) ions in complexes **1** (left) and **2** (right).

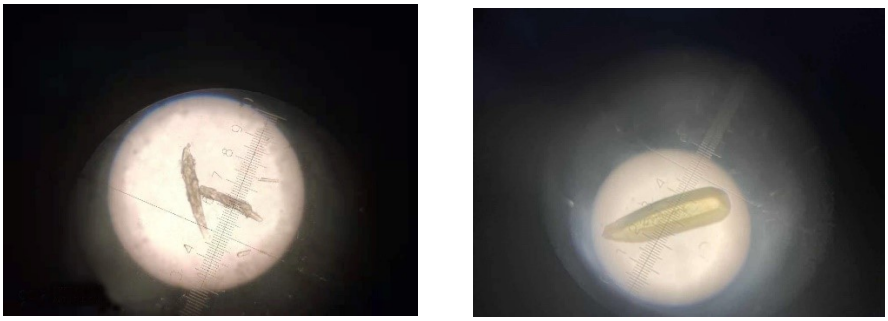

Fig. S2 Single crystals of complexes **1** (left) and **2** (right) under the microscope.

Fig. S3 Different shapes for complexes **1** and **2** stored in plastic tubes.

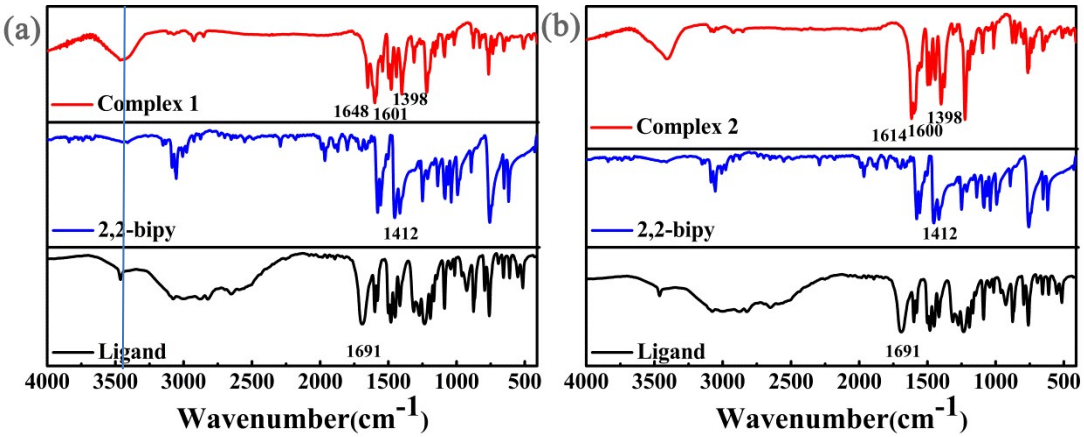

Fig. S4 (a) Infrared spectra of complex **1**; (b) Infrared spectra of complex **2**.

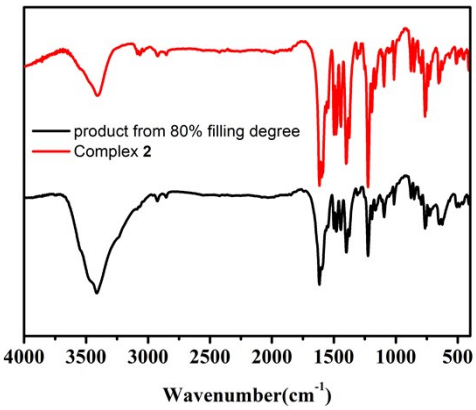

Fig. S5 Infrared spectra of complex **2** with 55% filling degree of 13 mL tube (red line); the complex **2** with 80% filling degree of 25 mL tube (black line);

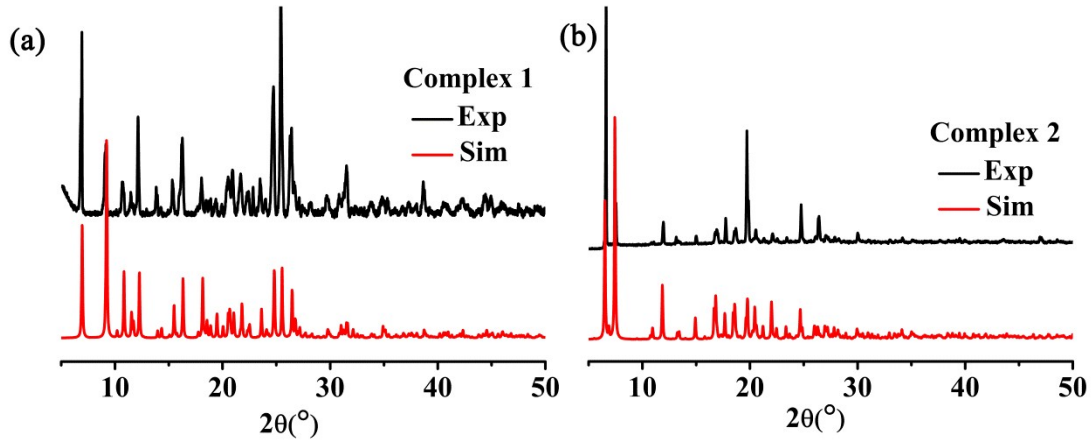

Fig. S6 (a) PXRD pattern of complex **1**; (b) PXRD pattern of complex **2**.

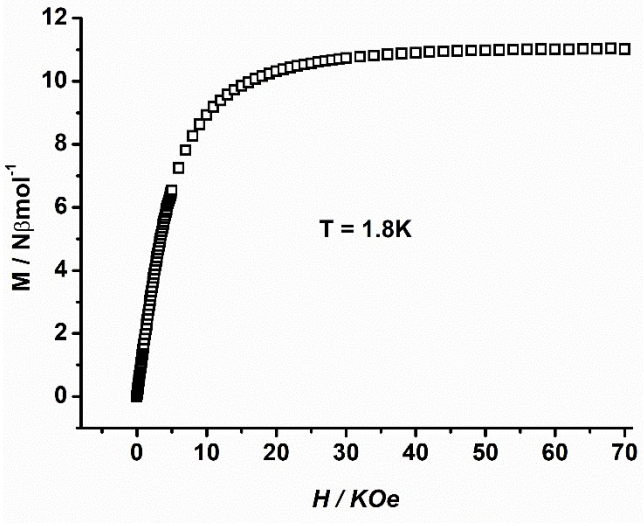

Fig. S7 Field dependent isothermal magnetization M(T, H) for 1 at 1.8 K from 0 to 70 KOe.