Supporting Information

Synthesis and magnetic properties of Two Mn-based coordination polymers constructed by mixed-ligand strategy

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Comment S1: X-ray crystallography

Intensity data collection was carried out on a Siemens SMART diffractometer equipped with a CCD detector using Mo-$K\alpha$ monochromatized radiation (λ=0.71073 Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program [1]. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL package [2]. Crystallographic data for complexes **1** and **2** is given in Table S1. Selected bond lengths and angles for **1** and **2** are listed in Table S2.

Comment S2: Theoretical calculation of spin-only value

The theoretical spin-only value ($\chi_M T$, cm^3 K mol^{-1}) was calculated according to the following Eqs. S1.

$$\chi_M T = 0.1253n(n+2) \quad \text{.....(S1)}$$

where *n* represented the single electron numbers (For Mn^{2+} ions, n=5).

Refs:

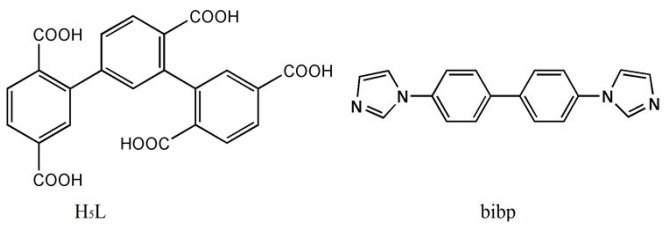
[1] H.L. Buckley and W.A. Chomitz, *Chem Commun.*, 2012, 48, 10766-107768.
[2] G.M. Sheldrick, *Acta Cryst A*., 2008, 64, 112-122.

Table S1. Crystallographic data for **1** and **2**.

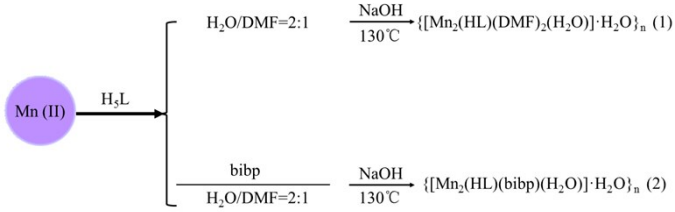
Complex	**1**	**2**
Formula	C_{29} H_{28} Mn_2 N_2 O_{14}	C_{41} H_{28} Mn_2 N_4 O_{12}
Formula weight	738.41	878.55
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/n$	$P\,2_1/c$
a (Å)	13.2419 (7)	15.6867 (16)
b (Å)	15.4637 (7)	14.8573 (15)
c (Å)	18.8598 (9)	18.9889 (19)
α (°)	90	90
β (°)	107.908 (2)	93.799 (4)
γ (°)	90	90
V (Å^3)	3674.8 (3)	4415.9 (8)
Z	4	4
D_{calcd} (Mg/m^3)	1.335	1.321
μ (mm^{-1})	0.749	0.634
F (000)	1512	1792
R_{int}	0.1895	0.0423
R_1 [$I > 2\sigma(I)$][a]	0.0685	0.0403
wR_2 [$I > 2\sigma(I)$][b]	0.1391	0.0994
Gof	1.005	1.035
CCDC number	1974347	1956742

Table S2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex **1**					
Mn(1)-O(1)	2.432(3)	Mn(1)-O(3)$^{\#1}$	2.282(3)	Mn(2)-O(7)	2.163(3)
Mn(1)-O(2)	2.306(3)	Mn(1)-O(4)$^{\#1}$	2.258(3)	Mn(2)-O(8)	2.197(3)
Mn(1)-O(5)	2.126(3)	Mn(2)-O(1)$^{\#1}$	2.230(3)	Mn(2)-O(9)	2.169(3)
Mn(2)-O(6)	2.156(3)	Mn(2)-O(3)$^{\#1}$	2.185(3)	Mn(1)-O(12)$^{\#2}$	2.126(3)
O(2)-Mn(1)-O(1)	55.19(10)	O(5)-Mn(1)-O(1)	88.94(11)	O(5)-Mn(1)-O(2)	87.15(12)
O(4)$^{\#1}$-Mn(1)-O(2)	90.866(13)	O(4)$^{\#1}$-Mn(1)-O(3)$^{\#1}$	57.63(13)	O(3)$^{\#1}$-Mn(1)-O(1)	153.98(10)
O(4)$^{\#1}$-Mn(1)-O(1)	111.64(11)	O(5)-Mn(1)-O(4)$^{\#1}$	153.23(12)	O(3)$^{\#1}$-Mn(1)-O(2)	99.52(10)
O(12)$^{\#2}$-Mn(1)-O(1)	81.30(11)	O(5)-Mn(1)-O(3)$^{\#1}$	96.39(11)	O(12)$^{\#2}$-Mn(1)-O(3)$^{\#1}$	118.85(12)
O(12)$^{\#2}$-Mn(1)-O(4)$^{\#1}$	86.88(14)	O(12)$^{\#2}$-Mn(1)-O(2)	131.89(12)	O(12)$^{\#2}$-Mn(1)-O(5)	113.98(13)
O(6)-Mn(2)-O(7)	86.79(13)	O(6)-Mn(2)-O(9)	83.42(12)	O(6)-Mn(2)-O(8)	95.87(13)
O(6)-Mn(2)-O(1)$^{\#1}$	164.72(12)	O(6)-Mn(2)-O(3)$^{\#1}$	89.02(11)	O(7)-Mn(2)-O(1)$^{\#1}$	92.48(12)
O(7)-Mn(2)-O(3)$^{\#1}$	88.67(12)	O(7)-Mn(2)-O(8)	174.77(14)	O(7)-Mn(2)-O(9)	93.79(13)
O(3)$^{\#1}$-Mn(2)-O(8)	86.89(12)	O(3)$^{\#1}$-Mn(2)-O(1)$^{\#1}$	106.22(11)	O(8)-Mn(2)-O(1)$^{\#1}$	86.13(12)
O(9)-Mn(2)-O(8)	90.99(13)	O(9)-Mn(2)-O(1)$^{\#1}$	81.40(12)	O(9)-Mn(2)-O(3)$^{\#1}$	171.90(12)
Symmetry codes: #1 -x+3/2,y+1/2,-z+1/2, #2 x-1/2,-y+1/2,z-1/2.					
Complex **2**					
Mn(1)-O(1)	2.1586(14)	Mn(1)-O(7)	2.2437(15)	Mn(1)-O(1)$^{\#1}$	2.2900(15)
Mn(1)-O(2)$^{\#1}$	2.5393(14)	Mn(1)-O(5)$^{\#2}$	2.1904(15)	Mn(1)-O(6)$^{\#2}$	2.3270(17)
Mn(1)-O(8)$^{\#1}$	2.2081(14)	Mn(2)-O(2)	2.3160(14)	Mn(2)-O(3)	2.1481(14)
Mn(2)-O(12)	2.2374(16)	Mn(2)-O(4)$^{\#3}$	2.1666(14)	Mn(2)-N(1)	2.2055(16)
Mn(2)-N(4)$^{\#4}$	2.2136(17)	O(1)-Mn(1)-O(6)$^{\#2}$	98.27(6)	O(1)-Mn(1)-O(1)$^{\#1}$	87.69(5)
O(1)-Mn(1)-O(7)	82.10(6)	O(1)-Mn(1)-O(2)$^{\#1}$	140.01(5)	O(1)-Mn(1)-O(5)$^{\#2}$	138.02(6)
O(1)-Mn(1)-O(8)$^{\#1}$	82.63(5)	O(1)$^{\#1}$-Mn(1)-O(2)$^{\#1}$	53.47(5)	O(1)$^{\#1}$-Mn(1)-O(6)$^{\#2}$	157.72(6)
O(3)-Mn(2)-O(2)	100.85(5)	O(3)-Mn(2)-N(1)	99.91(6)	O(3)-Mn(2)-O(12)	171.30(6)
O(3)-Mn(2)-O(4)$^{\#3}$	91.59(5)	O(4)$^{\#3}$-Mn(2)-N(1)	89.35(6)	O(4)$^{\#3}$-Mn(2)-O(2)	167.09(5)
O(4)$^{\#3}$-Mn(2)-N(4)$^{\#4}$	85.88(6)	O(4)$^{\#3}$-Mn(2)-O(12)	88.46(6)	O(5)$^{\#2}$-Mn(1)-O(2)$^{\#1}$	81.18(5)
O(5)$^{\#2}$-Mn(1)-O(6)$^{\#2}$	57.20(6)	O(5)$^{\#2}$-Mn(1)-O(1)$^{\#1}$	128.56(5)	O(5)$^{\#2}$-Mn(1)-O(8)$^{\#1}$	119.94(6)
O(6)$^{\#2}$-Mn(1)-O(2)$^{\#1}$	114.48(6)	O(7)-Mn(1)-O(2)$^{\#1}$	97.69(5)	O(7)-Mn(1)-O(1)$^{\#1}$	79.48(6)
O(7)-Mn(1)-O(6)$^{\#2}$	122.50(6)	O(8)$^{\#1}$-Mn(1)-O(1)$^{\#1}$	79.68(5)	O(8)$^{\#1}$-Mn(1)-O(2)$^{\#1}$	81.34(5)
O(8)$^{\#1}$-Mn(1)-O(7)	154.56(5)	O(8)$^{\#1}$-Mn(1)-O(6)$^{\#2}$	79.83(6)	O(12)-Mn(2)-O(2)	79.76(6)
N(1)-Mn(2)-O(2)	85.17(6)	N(1)-Mn(2)-O(12)	88.80(6)	N(1)-Mn(2)-N(4)$^{\#4}$	173.05(7)
N(4)$^{\#4}$-Mn(2)-O(2)	98.44(6)	N(4)$^{\#4}$-Mn(2)-O(12)	86.02(7)		
Symmetry codes: #1 -x,-y+1,-z+1, #2 -x,y-1/2,-z+1/2, #3 -x,-y+2,-z+1, #4 x-1,-y+3/2,z-1/2.					



Scheme S1 Ligands H_5L and bibp used.



Scheme S2 Synthesis scheme of CPs **1** and **2**.

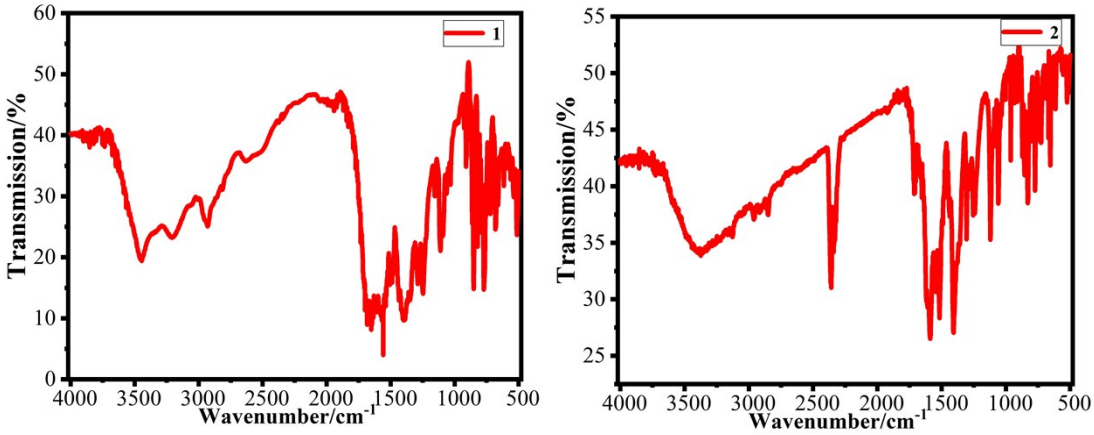


Fig. S1 IR spectra of CPs **1** and **2**.

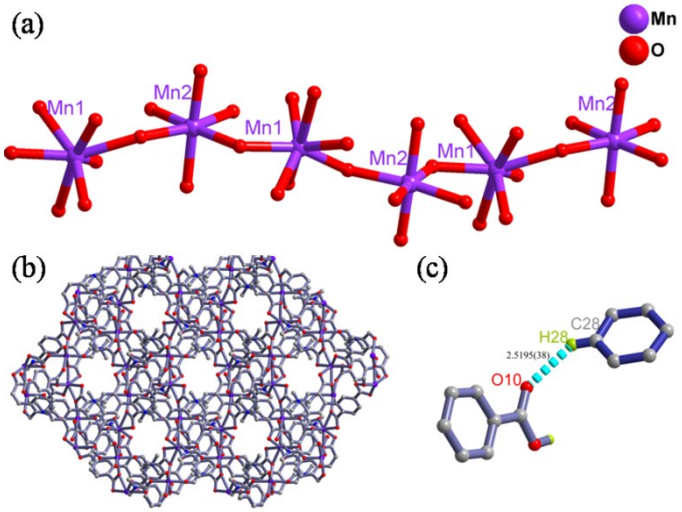


Fig. S2 (a) The 1D {MnO} chain of **1**. (b) The 2D lawyed structure in the direction of c axis for **1**. (c) The hydrogen bonding of **1**.

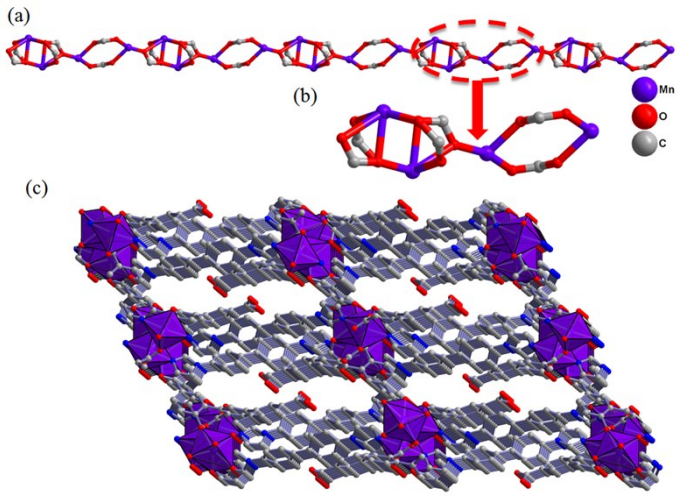


Fig. S3 (a) 1D paddle-wheel $\{Mn_2O_4C_2\}$ chain of **2**; (b) paddle-wheel $\{Mn_2O_4C_2\}$ of **2**; (c) 3D network framework of **2**.

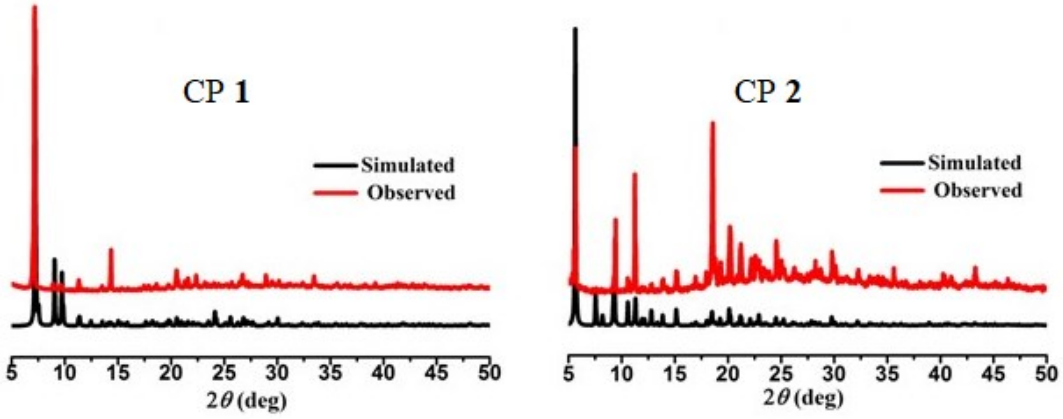


Fig. S4 PXRD patterns of CPs **1** and **2**. Dark: calculated from the X-ray single-crystal data; Red: observed for the as-synthesized samples.

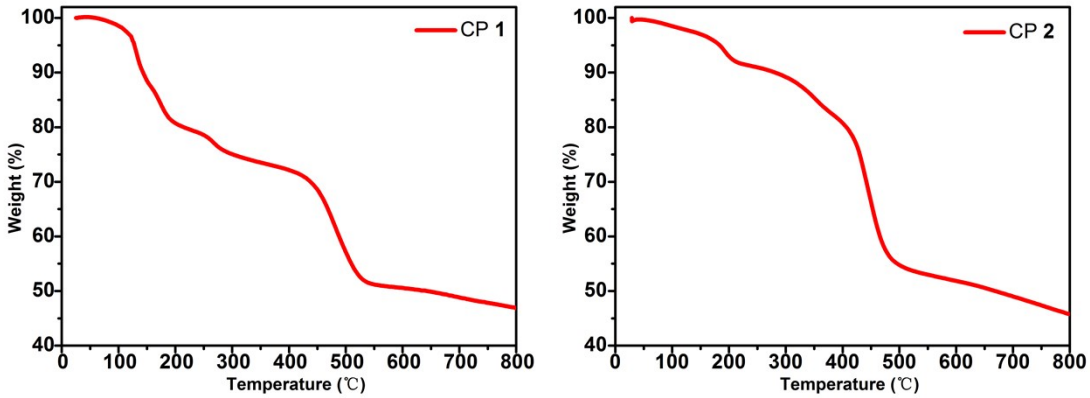


Fig. S5 TGA curves of **1** and **2**.