Electronic Supplementary Information

Homochiral and heterochiral Mn(II) coordination frameworks: spontaneous resolution dependent on dipyridyl ligands

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Materials and physical measurements. Reagents and solvents were purchased commercially and used without further purification. Elemental analyses for C, H, and N were performed on a Elementar Vario ELIIICHN elemental Analyzer. The FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrophotometer using KBr pellets in the 400–4000 cm^{-1} range. Powder X-ray diffraction data were collected on a Bruker D8–ADVANCE diffractometer equipped with Cu-Kα radiation (λ= 1.5418 Å) over the 2θ range of 4-40^{o} at room temperature. Solid-state circular dichroism (CD) spectra were recorded on a JASCO J-815 spectropolarimeter. A mixture of 1 mg bulk sample and 40 mg dried KBr powder is well-ground and pressed into a disk. Temperature-dependent and field-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-XL5 magnetometer. Diamagnetic corrections were made with Pascal's constants. Thermogravimetric (TG) measurements were performed on Mettler TGALSDTA851e/5FL1100 Thermogravimetric Analyzer under a nitrogen flow at a typical heating rate of 10.0 ℃·min^{-1}.

X-ray Crystallography. Single-crystal X-ray diffraction data of **1-3** were collected at 293K on a Bruker Apex II CCD area detector equipped with graphite-monochromatic Mo Kα radiation (by ω scan mode). The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using SHELXTL-2014 program.[1] All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located in calculated positions and refined using the riding model. The hydrogen atoms of water molecules, except those associated with disordered water, were placed from difference Fourier maps and refined with distance restraints. Each structure contains a disordered water molecule (O13) in the asymmetric unit, for which the occupancy is set at 0.5 and the hydrogen atom is not located. The selected bond lengths and angles are listed in Table S3-5.

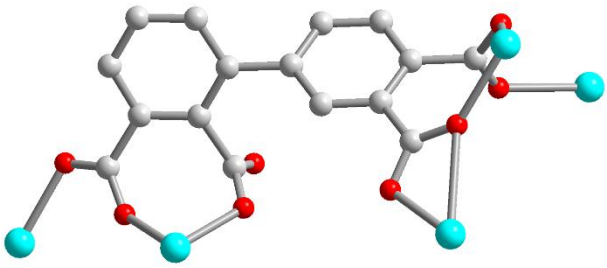
Synthesis of $[Mn_2(\alpha\text{-bptc})(bipy)_{0.5}(H_2O)_4]\cdot 1.5H_2O$ (1). A mixture of $MnCl_2$ $4H_2O$ (0.0197 g, 0.1 mmol), α-H_4bptc (0.0165 g, 0.05 mmol), bipy (0.0156 g, 0.1 mmol), 0.1 mol/L KOH solution (1ml) and water (3ml) was sealed in a 20 ml Telflon–lined stainless steel autoclave and heated at 120 ℃ for 3 days, which was followed by slow cooling (a descent rate of 20 ℃/h) to room temperature. Colorless block crystals of **1** suitable for single crystal X-ray diffraction analysis were collected by filtration. Yield: 48 % based on Mn. Anal. calcd (%) for $C_{21}H_{21}NO_{13.5}Mn_2$ (M_r = 613.27): C, 41.13; H, 3.45; N, 2.28; found C, 40.98; H, 3.66; N, 2.25. IR (cm^{-1}): 3349(s), 2363(w), 1633(s), 1585(s), 1463(m), 1400(s), 1138(w), 1099(w), 842(m), 765(w), 725(m), 681(w), 513(w).

Synthesis of $[Mn_2(\alpha\text{-bptc})(bpee)_{0.5}(H_2O)_4]\cdot 1.5H_2O$ (2).The preparation of **2** was similar to that of **1** except that bpee (0.0182 g, 0.1 mmol) was used instead of bipy. Colorless block crystals of **2** were collected in 42 % yield (based on Mn). Anal. calcd (%) for $C_{22}H_{22}NO_{13.5}Mn_2$ (M_r = 626.26): C, 42.19; H, 3.54; N, 2.24; found C, 41.53; H, 3.81; N, 2.16. IR (cm^{-1}): 3313(s), 1606(s), 1547(s), 1453(s), 1402(s), 1097(w), 1070(w), 1017(m), 841(m), 762(m), 703(w), 637(w), 559(w), 467(w), 409(m).

Synthesis of $[Mn_2(\alpha\text{-bptc})(bpea)_{0.5}(H_2O)_4]\cdot 2H_2O$ (3). **3** was synthesized though the same synthetic procedure as that of **1** except that bpea (0.0184 g, 0.1 mmol) was used instead of bipy. Colorless block crystals of **3** were collected in a yield 50 % (based on Mn). Anal. calcd (%) for $C_{22}H_{24}O_{14}NMn_2$ (M_r = 636.30): C, 41.53; H, 3.80; N, 2.20; found C, 41.30; H, 3.94; N, 2.15. IR (cm^{-1}): 3302(s), 1612(s), 1543(s), 1453(m), 1411(s), 1216(w), 1154(w), 1097(w), 1071(m), 1016(m), 937(w), 875(w), 833(m), 771(m), 710(m), 632(w), 549(w), 477(w).

References

1 (*a*) G. M. Sheldrick, *SHELXTL NT, Version 5.1 (Program for Solution and Refinement of Crystal Structures)*, Germany, 1997; (*b*) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3.



Scheme S1. The coordinated type of α-bptc^{4-} ligand.

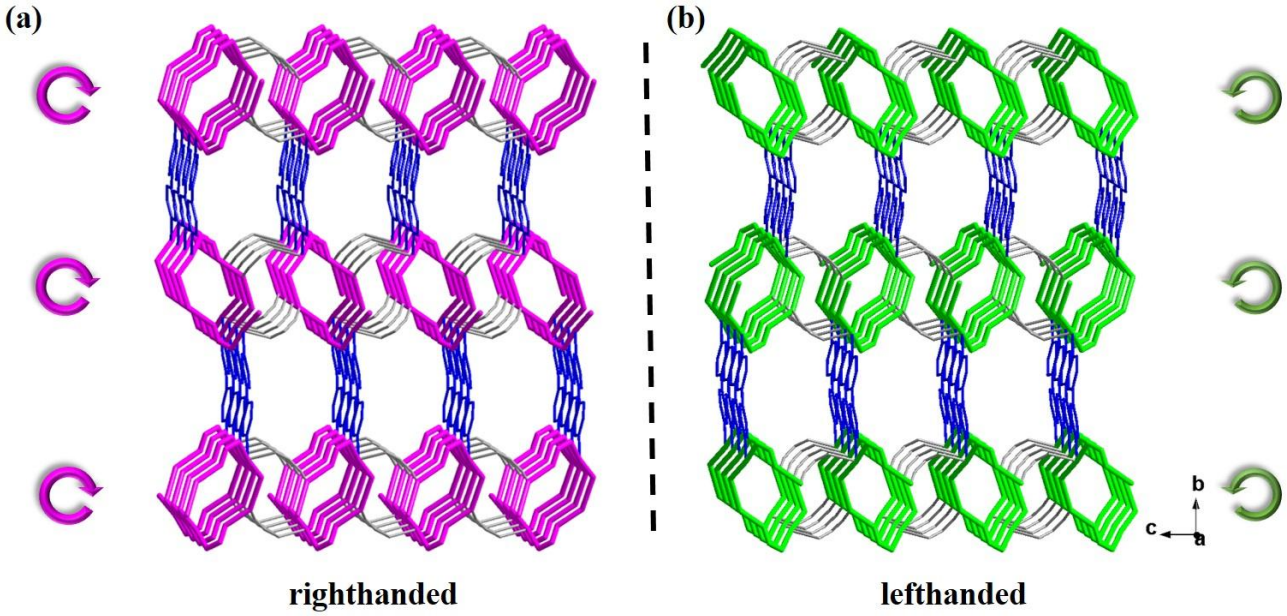


Fig. S1. The righthanded (a) and lefthanded (b) frameworks of **1**.

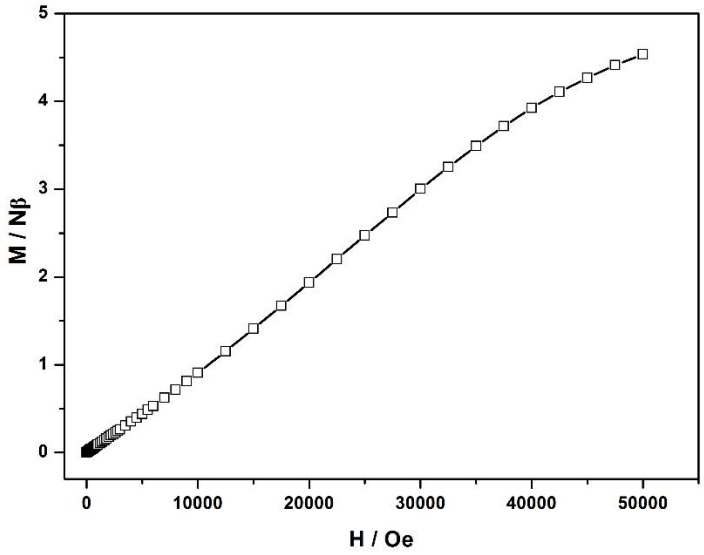


Fig. S2. *M* vs. *H* curve of **1** at 2 K.

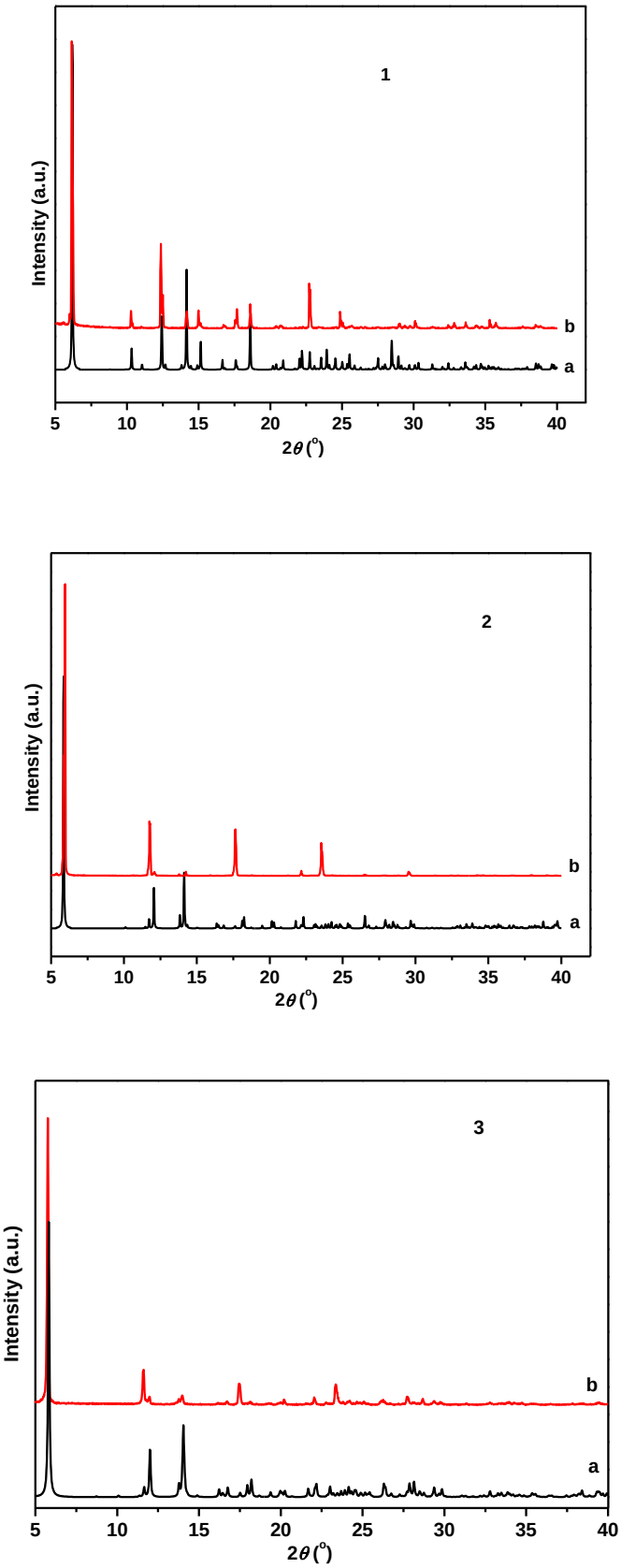


Fig. S3. PXRD patterns of compounds **1**-**3.** a) Simulated from single crystal structure data. b) Experimental data. The differences between the calculated and observed patterns in intensity may be due to the preferential orientation of the crystals.

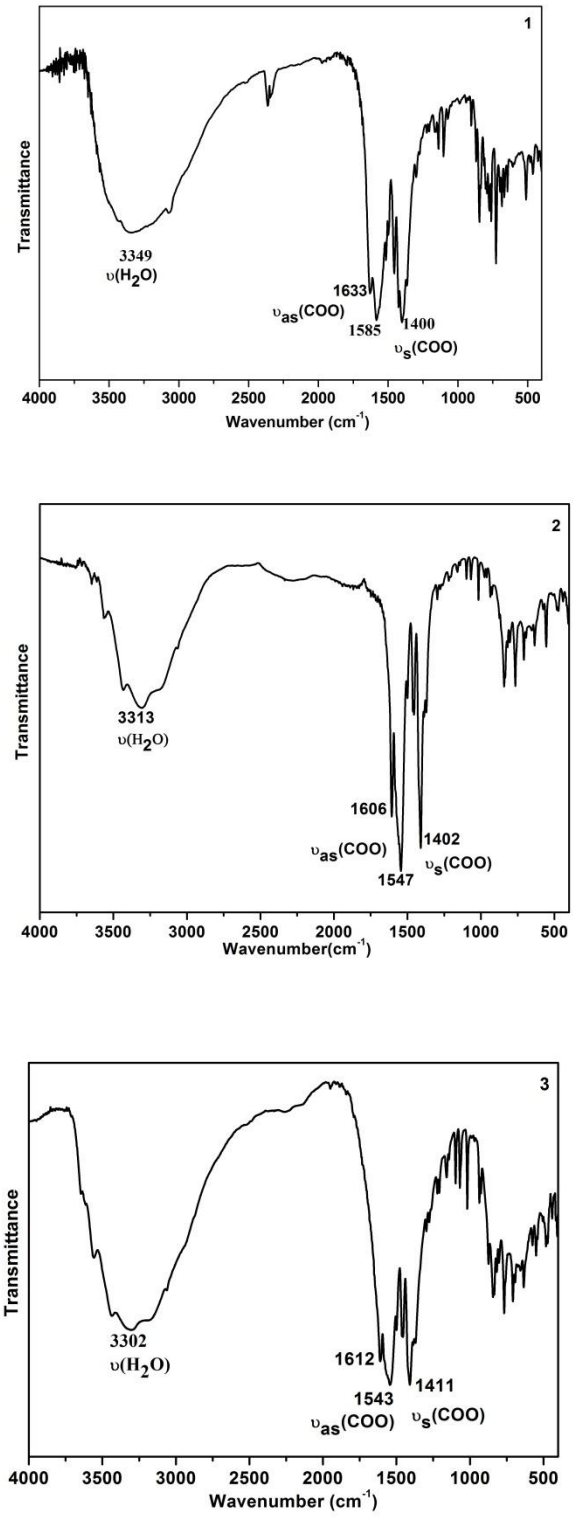


Fig. S4. FT-IR spectra for compounds **1-3**.

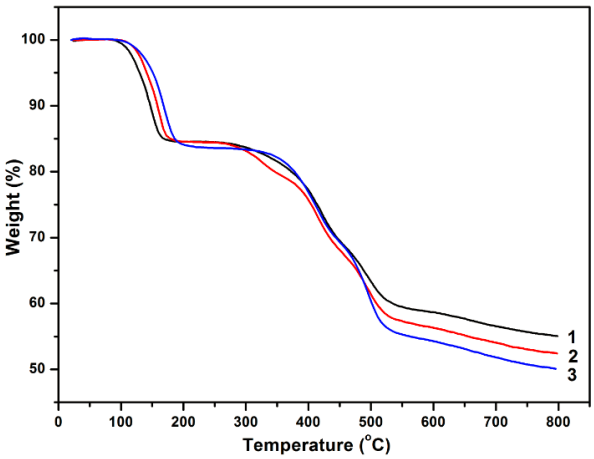


Fig. S5. TGA plots of compounds **1**, **2** and **3**. The Y-axis is the percentages of residual weight. The three compounds show similar thermal stability. The first weight loss occurs in the range of 90-200℃, attributable to the loss of all lattice and coordinated water molecules: observed (calculated), 15.2% (16.2%), 15.4% (15.8%) and 16.3% (17.0%) for **1**-**3**, respectively. The weight loss above 300 ℃ is due to the decomposition of the organic components of the compounds.

Table S1. Crystal data and structure refinements for compounds **1-3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{21}H_{21}O_{13.5}NMn_2$	$C_{22}H_{22}O_{13.5}NMn_2$	$C_{22}H_{24}O_{14}NMn_2$
M_r	613.27	626.26	636.30
T/K	293(2)	296(2)	296(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12$	$P2_1/n$	$P2_1/n$
a/Å	10.7074(3)	7.9630(4)	8.0116(4)
b/Å	28.5474(8)	10.7340(5)	10.7378(5)
c/Å	8.0000(2)	30.1664(13)	30.3601(15)
α (°)	90	90	90
β (°)	90	90.4870(10)	91.0040(10)
γ (°)	90	90	90
V/Å^3	2445.35(11)	2578.4(2)	2611.4(2)
Z	4	4	4
D_c/Mg m^{-3}	1.666	1.613	1.618
μ/mm^{-1}	1.105	1.050	1.039
F(000)	1248	1276	1300
Crystal size/mm	0.30 × 0.20 × 0.15	0.25 × 0.23 × 0.20	0.29 × 0.25 × 0.20
θ range for data/°	1.427 to 28.320	2.014 to 28.171	2.012 to 28.363
Reflns collected/unique	33633/5807	34458/6281	34862/6315
R_{int}	0.0461	0.0400	0.0461
Data/restraints/parameters	5807 / 15 / 384	6281 / 15 / 395	6315 / 12 / 396
Goodness-of-fit on F^2	1.179	1.053	1.157
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0363, wR_2 = 0.0824	R_1 = 0.0352, wR_2 = 0.0895	R_1 = 0.0594, wR_2 = 0.1408
R indices (all data)	R_1 = 0.0390, wR_2 = 0.0834	R_1 = 0.0463, wR_2 = 0.0949	R_1 = 0.0686, wR_2 = 0.1447
Flack parameter	0.03(2)	-	-
Peak and hole /e.A^{-3}	0.316,-0.382	0.705, -0.226	1.095, -0.594

Table S2. A summary of structure determinations of five randomly selected crystals of compound **1** from the same crystallization.

Complex	**1-1**(lefthanded)	**1-2**	**1-3** (lefthanded)	**1-4**	**1-5**
Formula	$C_{21}H_{21}Mn_2NO_{13.5}$	$C_{21}H_{21}Mn_2NO_{13.5}$	$C_{21}H_{21}Mn_2NO_{13.5}$	$C_{21}H_{21}Mn_2NO_{13.5}$	$C_{21}H_{21}Mn_2NO_{13.5}$
M	613.27	613.27	613.27	613.27	613.27
T/K	293(2)	296(2)	296(2)	296(2)	296(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12$	$P2_12_12$	$P2_12_12$	$P2_12_12$	$P2_12_12$
a/Å	10.7082(3)	10.7080(3)	10.7072(2)	10.7072(2)	10.7085(2)
b/Å	28.5518(8)	28.5500(7)	28.5471(6)	28.5488(6)	28.5480(6)
c/Å	7.9997(2)	7.9991(2)	8.0001(2)	8.0008(2)	7.9990(2)
V/Å^3	2445.82(11)	2445.43(11)	2445.31(9)	2445.67(9)	2445.34(9)
Z	4	4	4	4	4
D_c/Mg m^{-3}	1.666	1.690	1.666	1.666	1.690
μ/mm^{-1}	1.106	1.105	1.105	1.104	1.105
F(000)	1248	1248	1248	1248	1248
Crystal size/mm	0.34×0.21×0.13	0.35×0.20×0.15	0.33×0.23×0.16	0.34×0.20×0.15	0.36×0.27×0.20
θ range for data/°	1.43 to 28.25	1.43 to 28.24	1.43 to 28.25	1.43 to 28.32	0.71 to 28.27
Reflections collected	33732	33803	33867	33738	33665
Data/parameters	5869 / 384	5927 / 384	5946 / 384	5771 / 384	5979 / 384
R_{int}	0.0356	0.0483	0.0477	0.0426	0.0333
GOF on F^2	1.165	1.091	1.043	1.172	1.165
R_1 ($I > 2\ \sigma(I)$)	0.0383	0.0375	0.0385	0.0379	0.0349
wR_2 ($I > 2\ \sigma(I)$)	0.1051	0.0831	0.0821	0.0897	0.0892
R_1 (all data)	0.0429	0.0442	0.0466	0.0420	0.0379
wR_2 (all data)	0.1150	0.0859	0.0855	0.0913	0.0906
Flack parameter	**0.03(3)**	**0.02(2)**	**0.03(2)**	**0.035(17)**	**0.00(2)**
Residues /e.A^{-3}	0.702, -0.666	0.341,-0.306	0.387,-0.294	0.370, -0.401	0.357, -0.312

Table S3. Selected bond lengths and bond angles for compound **1**.

Mn(1)-O(10)	2.118(3)	Mn(2)-O(11)	2.167(3)
Mn(1)-O(1)	2.168(3)	Mn(2)-O(6)#2	2.176 (3)
Mn(1)-O(8)#1	2.171(3)	Mn(2)-O(7)#2	2.189(3)
Mn(1)-O(9)	2.251(2)	Mn(2)-O(4)	2.208(3)
Mn(1)-N(1)	2.272(3)	Mn(2)-O(12)	2.223(3)
Mn(1)-O(3)	2.297(3)	Mn(2)-O(2)#3	2.297(3)
		Mn(2)-O(3)	2.778(3)
O(11)-Mn(2)-O(7)#2	108.87(13)	O(11)-Mn(2)-O(6)#2	83.88(11)
O(10)-Mn(1)-O(1)	165.66(11)	O(6)#2-Mn(2)-O(7)#2	81.08(11)
O(10)-Mn(1)-O(8)#1	105.31(13)	O(11)-Mn(2)-O(4)	89.35(13)
O(1)-Mn(1)-O(8)#1	89.02(12)	O(6)#2-Mn(2)-O(4)	124.23(11)
O(10)-Mn(1)-O(9)	86.10(12)	O(7)#2-Mn(2)-O(4)	151.07(12)
O(1)-Mn(1)-O(9)	89.78(11)	O(11)-Mn(2)-O(12)	175.16(12)
O(8)#1-Mn(1)-O(9)	104.63(11)	O(6)#2-Mn(2)-O(12)	92.47(11)
O(10)-Mn(1)-N(1)	92.45(13)	O(7)#2-Mn(2)-O(12)	73.56(11)
O(1)-Mn(1)-N(1)	88.25(12)	O(4)-Mn(2)-O(12)	90.09(11)
O(8)#1-Mn(1)-N(1)	89.13(12)	O(11)-Mn(2)-O(2)#3	85.83(11)
O(10)-Mn(1)-O(3)	82.38(11)	O(6)#2-Mn(2)-O(2)#3	151.89(10)
O(1)-Mn(1)-O(3)	83.29(10)	O(7)#2-Mn(2)-O(2)#3	77.65(12)
O(8)#1-Mn(1)-O(3)	172.31(13)	O(4)-Mn(2)-O(2)#3	81.63(11)
O(9)-Mn(1)-O(3)	75.55(9)	O(12)-Mn(2)-O(2)#3	98.85(11)
N(1)-Mn(1)-O(3)	90.52(11)	O(9)-Mn(1)-N(1)	166.07(11)

Symmetry transformations used to generate equivalent atoms:

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

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

#5 -x+1, -y, z

Table S4. Selected bond lengths and bond angles for compound **2**.

Mn(1)-O(9)	2.1221(15)	Mn(2)-O(5)#2	2.1735(14)
Mn(1)-O(1)	2.1693(14)	Mn(2)-O(11)	2.1744(16)
Mn(1)-O(8)#1	2.1782(15)	Mn(2)-O(7)#2	2.1874(15)
Mn(1)-O(10)	2.2474(14)	Mn(2)-O(4)	2.2008(14)
Mn(1)-N(1)	2.2587(17)	Mn(2)-O(12)	2.2262(14)
Mn(1)-O(3)	2.3105(15)	Mn(2)-O(2)#3	2.2893(14)
		Mn(2)-O3	2.8021(15)
O(1)-Mn(1)-N(1)	88.49(6)	O(5)#2-Mn(2)-O(11)	83.94(6)
O(8)#1-Mn(1)-N(1)	88.40(6)	O(5)#2-Mn(2)-O(7)#2	81.03(6)
O(10)-Mn(1)-N(1)	165.03(6)	O(11)-Mn(2)-O(7)#2	108.43(6)
O(9)-Mn(1)-O(3)	82.12(6)	O(5)#2-Mn(2)-O(4)	123.08(5)
O(9)-Mn(1)-O(1)	164.71(6)	O(11)-Mn(2)-O(4)	89.81(6)
O(9)-Mn(1)-O(8)#1	106.61(6)	O(7)#2-Mn(2)-O(4)	151.91(6)
O(1)-Mn(1)-O(8)#1	88.68(6)	O(5)#2-Mn(2)-O(12)	92.43(6)
O(9)-Mn(1)-O(10)	85.47(6)	O(11)-Mn(2)-O(12)	175.26(6)
O(1)-Mn(1)-O(10)	90.35(5)	O(7)#2-Mn(2)-O(12)	73.88(6)
O(8)#1-Mn(1)-O(10)	106.50(6)	O(4)-Mn(2)-O(12)	89.62(6)
O(9)-Mn(1)-N(1)	91.77(7)	O(5)#2-Mn(2)-O(2)#3	152.29(6)
O(1)-Mn(1)-O(3)	82.59(5)	O(11)-Mn(2)-O(2)#3	85.80(6)
O(8)#1-Mn(1)-O(3)	171.18(6)	O(7)#2-Mn(2)-O(2)#3	77.93(6)
O(10)-Mn(1)-O(3)	74.96(5)	O(4)-Mn(2)-O(2)#3	82.47(5)
N(1)-Mn(1)-O(3)	90.09(6)	O(12)-Mn(2)-O(2)#3	98.79(5)

Symmetry transformations used to generate equivalent atoms:

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

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

#5 -x, -y, -z

Table S5. Selected bond lengths and bond angles for compound **3**.

Mn(1)-O(10)	2.128(3)	Mn(2)-O(6)#2	2.173(3)
Mn(1)-O(1)	2.170(3)	Mn(2)-O(11)	2.182(3)
Mn(1)-O(8)#1	2.184(3)	Mn(2)-O(7)#2	2.196(3)
Mn(1)-O(9)	2.247(3)	Mn(2)-O(12)	2.230(3)
Mn(1)-N(1)	2.254(3)	Mn(2)-O(2)#3	2.278(3)
Mn(1)-O(3)	2.324(3)	Mn(2)-O(4)	2.206(3)
		Mn(2)-O3	2.799(3)
O(10)-Mn(1)-O(1)	164.57(11)	O(6)#2-Mn(2)-O(11)	83.98(11)
O(10)-Mn(1)-O(8)#1	106.79(12)	O(6)#2-Mn(2)-O(7)#2	81.20(11)
O(1)-Mn(1)-O(8)#1	88.62(11)	O(11)-Mn(2)-O(7)#2	108.03(12)
O(10)-Mn(1)-O(9)	84.86(11)	O(6)#2-Mn(2)-O(4)	123.30(10)
O(1)-Mn(1)-O(9)	90.16(10)	O(11)-Mn(2)-O(4)	89.94(12)
O(8)#1-Mn(1)-O(9)	105.75(11)	O(7)#2-Mn(2)-O(4)	151.73(11)
O(10)-Mn(1)-N(1)	91.99(12)	O(6)#2-Mn(2)-O(12)	92.13(11)
O(1)-Mn(1)-N(1)	88.86(12)	O(11)-Mn(2)-O(12)	175.51(11)
O(8)#1-Mn(1)-N(1)	89.94(12)	O(7)#2-Mn(2)-O(12)	73.45(11)
O(9)-Mn(1)-N(1)	164.25(11)	O(4)-Mn(2)-O(12)	90.34(10)
O(10)-Mn(1)-O(3)	82.77(10)	O(6)#2-Mn(2)-O(2)#3	152.16(10)
O(1)-Mn(1)-O(3)	81.83(10)	O(11)-Mn(2)-O(2)#3	85.79(10)
O(8)#1-Mn(1)-O(3)	170.43(11)	O(7)#2-Mn(2)-O(2)#3	77.50(11)
O(9)-Mn(1)-O(3)	74.98(10)	O(4)-Mn(2)-O(2)#3	82.43(10)
N(1)-Mn(1)-O(3)	89.33(11)	O(12)-Mn(2)-O(2)#3	98.69(10)

Symmetry transformations used to generate equivalent atoms:

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

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

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