Supporting Information

Crystal transformation in Mn(II) metal-organic frameworks based on a one-dimensional chain precursor

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Experimental Section

Materials and Methods

All analytic reagents and chemical materials are commercially available and used directly without any further purification. Powder X-ray diffraction (PXRD) data were acquired via a Shimadzu XRD-6000 powder diffractometer equipped with Cu-Kα radiation tube (λ= 1.5418 Å), in the 2θ range of 4–40° with a speed of 6° min^{-1} at 40 kV and 30 mA. Elemental analysis (C, H, and N) was conducted on an Elementary Vario EL cube CHNOS elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded in the range of 4000–400 cm-1 on a Bruker Nicolet IS5 spectrometer using the KBr pellet method. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA499F3 QMS403D thermogravimetric analyzer from 50 to 800 °C at a ramp heating rate of 10 °C min^{-1} in an air atmosphere. ^{1}H NMR spectra were measured on Bruker Avance III 400 console at a frequency of 400 MHz. Inductively coupled plasma optical emission spectrometer (ICP-OES) analysis was performed on an Agilent 725 instrument. N_2 adsorption isotherms were measured using a Micromeritics ASAP 2020 surface area analyzer at 77 K

Determination of Crystal Structure

The crystallographic data of **1-3** were acquired using a Bruker D8 VENTURE diffractometer with graphite-monochromated Mo-Kα (λ= 0.71073 Å) sealed tube radiation at room temperature. No obvious decay was discovered during the data collection. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 values using OLEX-2 equipped with SHELXTL-2014 program.[1] The assignment of space groups were done with the XPREP program. All of the non-hydrogen atoms were located in the Fourier maps and refined with anisotropic displacement parameters. The Mn atom was first located in the Fourier maps and other atoms were located, subsequently. All the ordered non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms connected to the C and O atoms were generated geometrically and their positions were calculated using a riding model. The contribution of the electron density connected with the disordered solvent molecules was removed through the SQUEEZE program in PLATON software.[2] The final empirical formula was determined by combined crystallographic data, elemental and thermogravimetric analysis. The selected crystallographic data and refinement details of **1-3** are listed in Table S1, and selected bond lengths and angles data are presented in Table S2-S4. CCDC 2062075-2062077 contain the supplementary crystallographic data for this paper.

(1) G. M. Sheldrick, SHELXL-2014: Program for Structure Solution; University of Göttingen, Göttingen, Germany, 2014.

(2) A. L. Spek, Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. 2003, **36**, 7–13.

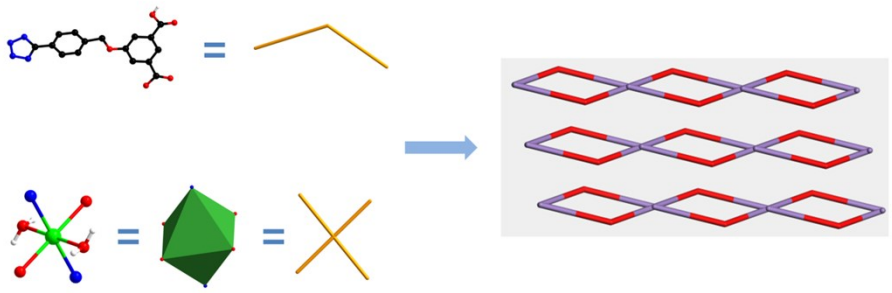

Fig. S1 Simplify of the structure of **1**.

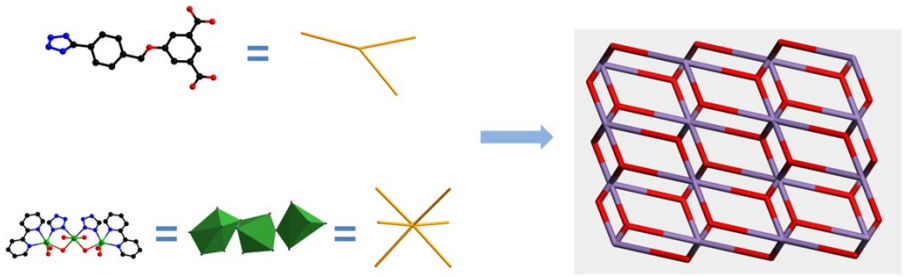

Fig. S2 Simplify of the structure of **2**.

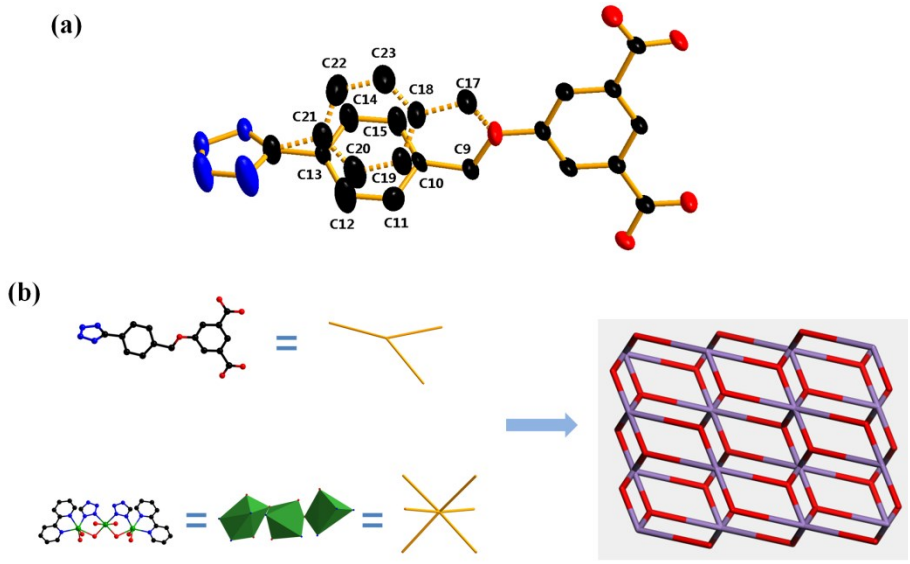

Fig. S3 (a) The disordered ligand in **3**, (b) simplify of the structure of **3**.

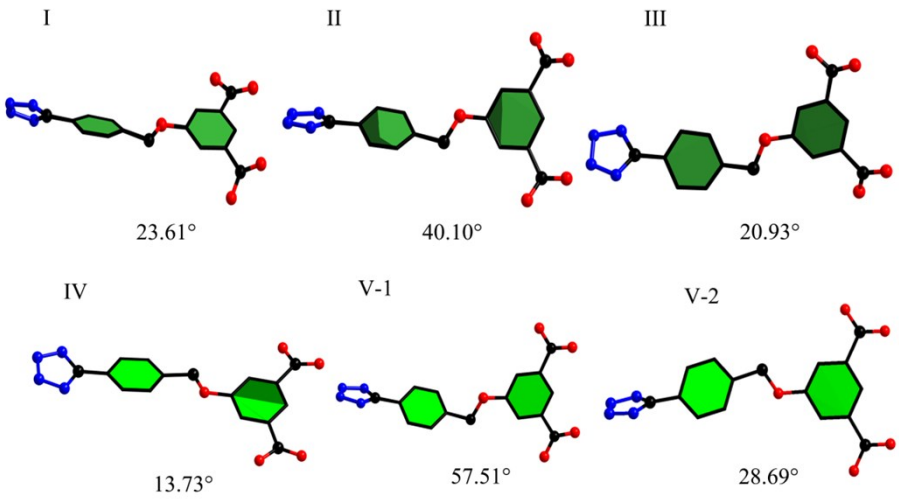

Fig. S4 The conformation of the ligand.

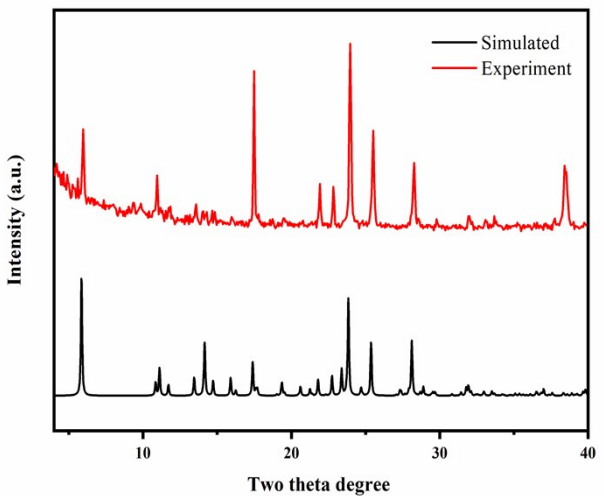

Fig. S5 PXRD pattern of **1**.

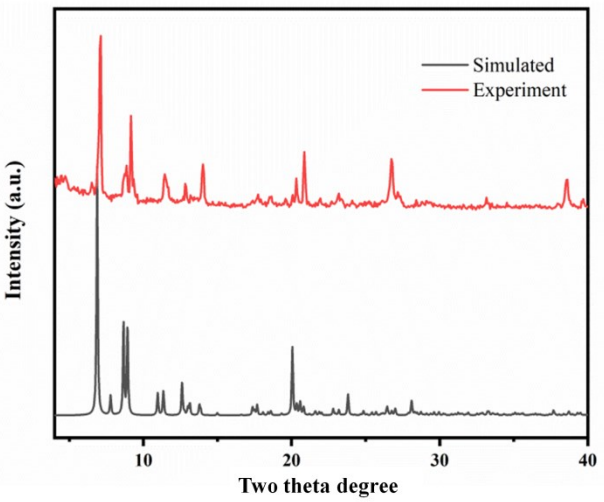

Fig. S6 PXRD pattern of **2**.

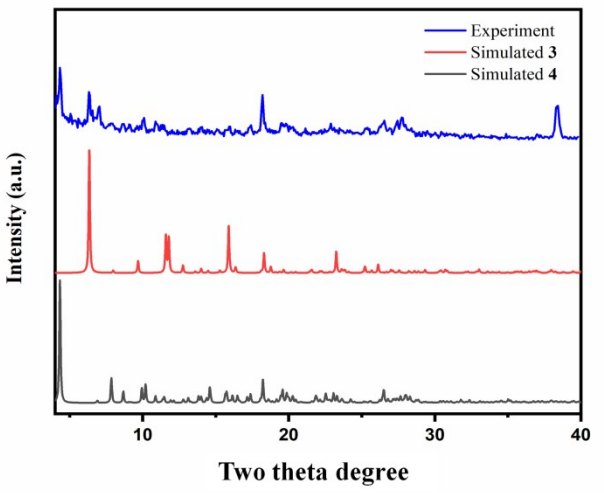

Fig. S7 PXRD pattern of the mixture of **3** and **4**.

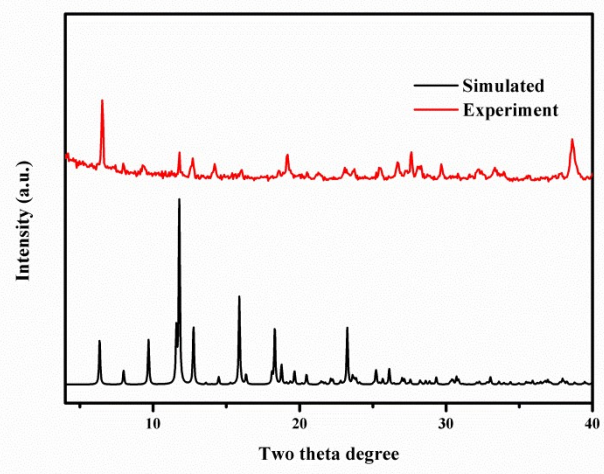

Fig. S8 PXRD pattern of **3**.

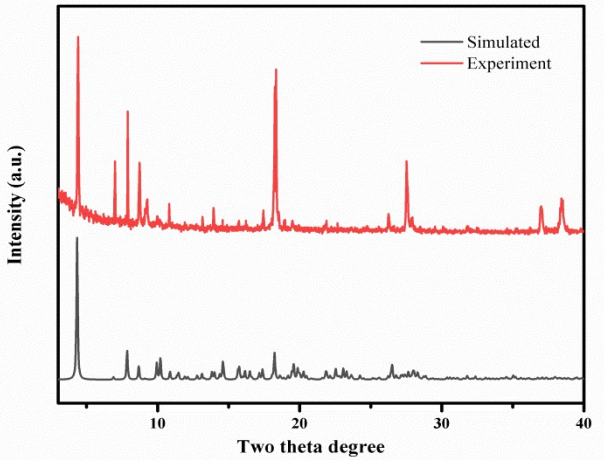

Fig. S9 PXRD pattern of **4**.

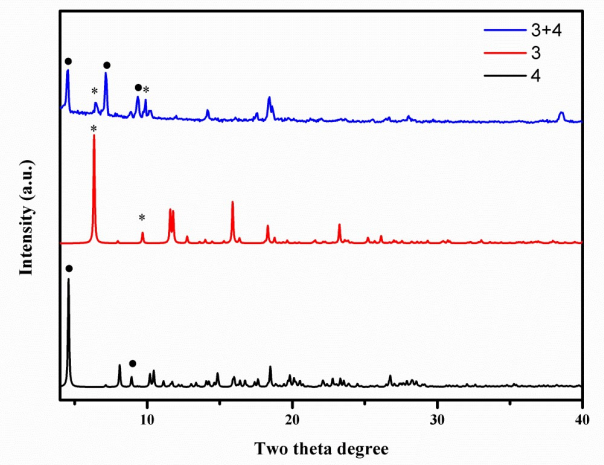

Fig. S10 PXRD patterns of the product of **3** after 7 d transformation.

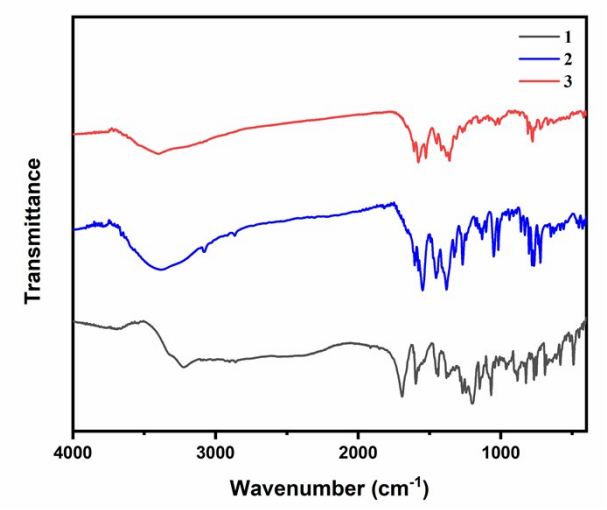

Fig. S11 FT-IR spectra.

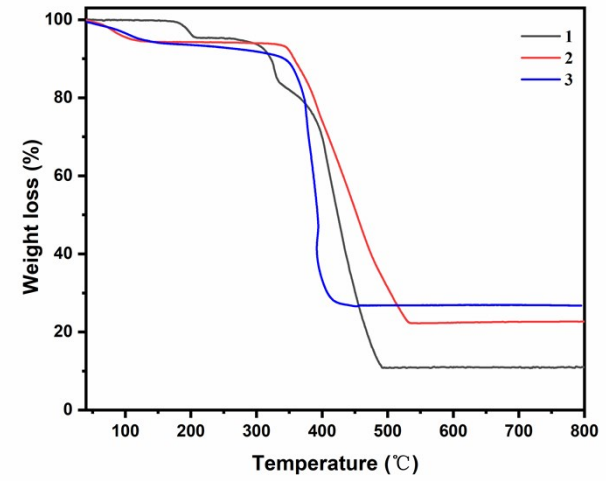

Fig. S12 TG curves.

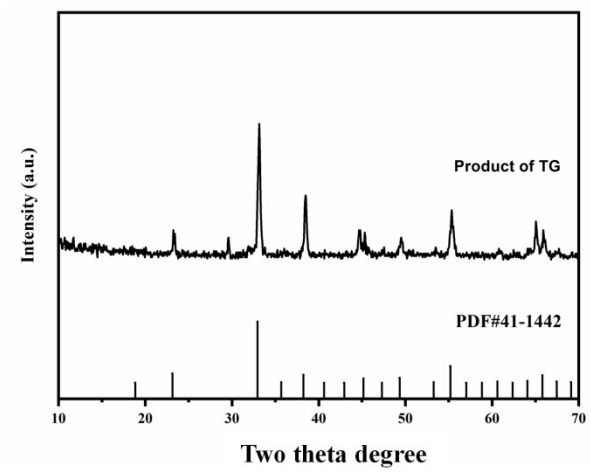

Fig. S13 PXRD patterns of the product after TGA.

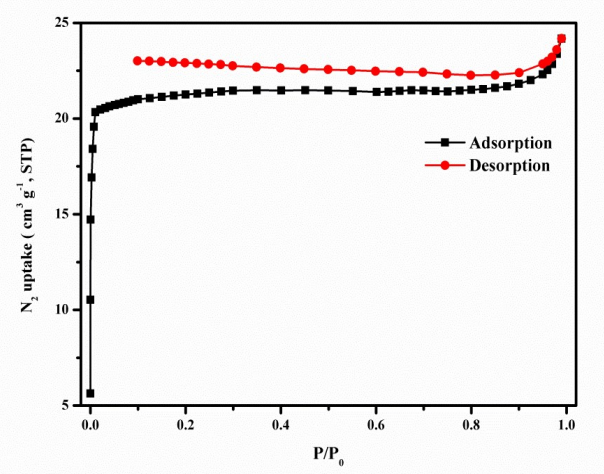

Fig. S14 N_2 adsorption/desorption isomers.

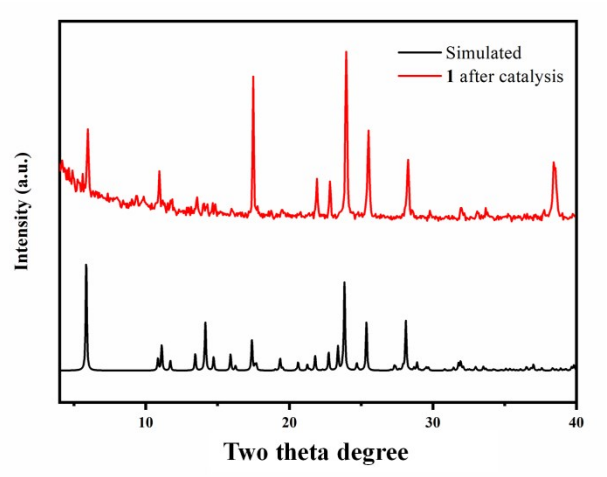

Fig. S15 PXRD patterns of **1** after catalysis.

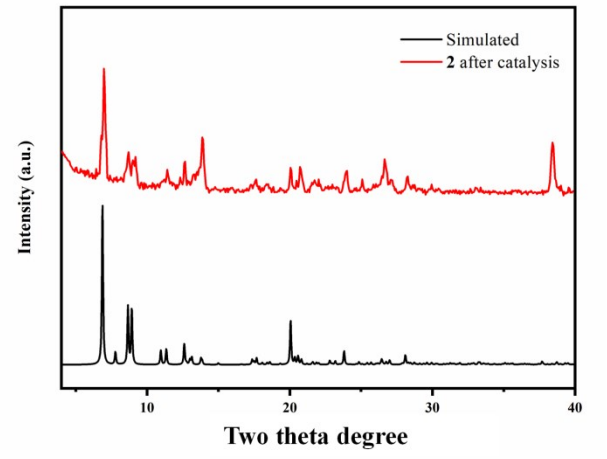

Fig. S16 PXRD patterns of **2** after catalysis.

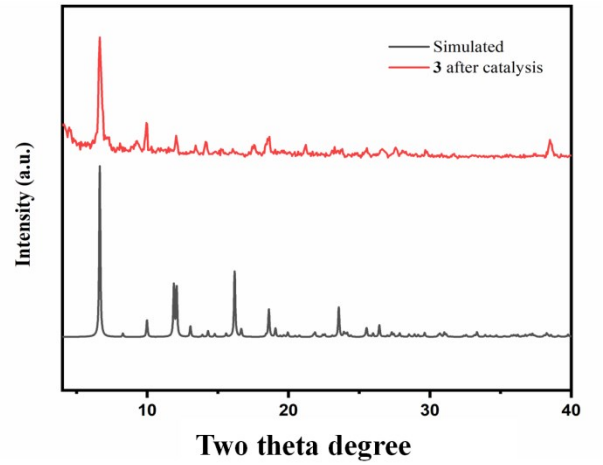

Fig. S17 PXRD patterns of **3** after catalysis.

Table S1 The crystal data and structure refinement details for **1-3**.

	1	**2**	**3**
Empirical formula	$C_{32}H_{26}MnN_8O_{12}$	$C_{52}H_{34}Mn_3N_{12}O_{10}$	$C_{32}H_{26}Mn_3N_8O_{14}$
Formula weight	769.55	1151.73	911.43
Temperature/K	293	293(2)	296.99
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	C_2/c	$P2_1/c$
a/Å	6.3618(5)	22.729(2)	14.0220(10)
b/Å	8.4580(5)	15.5808(13)	18.2487(13)
c/Å	15.5130(10)	16.1471(10)	8.2913(5)
α/°	102.196(5)	90.00	90.00
β/°	93.997(6)	93.157(7)	96.976(2)
γ/°	99.130(6)	90.00	90.00
Volume/Å^3	800.93(9)	5709.5(8)	2105.9(2)
Z	1	4	2
ρ_{calc}g/cm^3	1.595	1.340	1.437
μ/mm^{-1}	0.493	0.717	0.955
F(000)	395.0	2340.0	922.0
Crystal size/mm^3	0.4 × 0.2 × 0.2	0.4 × 0.1 × 0.1	0.4 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.78 to 58.38	6.76 to 59	5.86 to 50
Index ranges	-8 ≤ h ≤ 7, -11 ≤ k ≤ 9, -21 ≤ l ≤ 20	-28 ≤ h ≤ 20, -20 ≤ k ≤ 16, -16 ≤ l ≤ 21	-16 ≤ h ≤ 16, -18 ≤ k ≤ 21, -7 ≤ l ≤ 9
Reflections collected	5923	12645	13354
Independent reflections	3636 [R_{int} = 0.0228, R_{sigma} = 0.0482]	6610 [R_{int} = 0.0531, R_{sigma} = 0.0916]	3582 [Rint = 0.0321, Rsigma = 0.0344]
Data/restraints/parameters	3636/4/252	6610/0/348	3582/48/301
Goodness-of-fit on F^2	1.019	0.955	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.0937	R_1 = 0.0584, wR_2 = 0.1251	R1 = 0.0485, wR2 = 0.1318
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.1067	R_1 = 0.0948, wR_2 = 0.1442	R1 = 0.0568, wR2 = 0.1363
Largest diff. peak/hole / e Å^{-3}	0.34/-0.41	0.82/-0.50	0.87/-0.32

Table S2 The selected bond lengths and angles for **1**.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Mn01	O1[1]	2.1033(14)	O1[1]	Mn01	O1	180.00(8)
Mn01	O1	2.1033(14)	O1	Mn01	O2[1]	88.71(6)
Mn01	O2[1]	2.2180(14)	O1	Mn01	O2	91.29(6)
Mn01	O2	2.2180(14)	O1[1]	Mn01	O2[1]	91.29(6)
Mn01	N2[2]	2.3323(16)	O1[1]	Mn01	O2	88.71(6)
Mn01	N2[3]	2.3323(16)	O1	Mn01	N2[2]	93.10(6)
N2	Mn01[4]	2.3323(16)	O1	Mn01	N2[3]	86.90(6)
			O1[1]	Mn01	N2[3]	93.10(6)
			O1[1]	Mn01	N2[2]	86.90(6)
			O2[1]	Mn01	O2	180.000(1)
			O2[1]	Mn01	N2[2]	84.60(6)
			O2	Mn01	N2[3]	84.60(6)
			O2[1]	Mn01	N2[3]	95.40(5)
			O2	Mn01	N2[2]	95.40(5)

[1]2-X,2-Y,2-Z; [2]1-X,2-Y,1-Z; [3]1+X,+Y,1+Z; [4]-1+X,+Y,-1+Z

Table S3 The selected bond lengths and angles for **2**.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Mn01	O003[1]	2.175(2)	O003[1]	Mn01	O003[2]	173.97(12)
Mn01	O003[2]	2.175(2)	O003[1]	Mn01	N009[3]	88.47(9)
Mn01	O004	2.169(2)	O003[1]	Mn01	N009[4]	87.81(9)
Mn01	O004[3]	2.169(2)	O003[2]	Mn01	N009[3]	87.81(9)
Mn01	N009[4]	2.252(3)	O003[2]	Mn01	N009[4]	88.47(9)
Mn01	N009[5]	2.252(3)	O004[5]	Mn01	O003[1]	103.42(8)
Mn02	O004[6]	2.438(2)	O004	Mn01	O003[1]	80.95(8)
Mn02	O005	2.1272(19)	O004[5]	Mn01	O003[2]	80.95(8)
Mn02	O006[6]	2.243(2)	O004	Mn01	O003[2]	103.42(8)
Mn02	N008[7]	2.230(3)	O004	Mn01	O004[5]	89.30(11)
Mn02	N00A	2.246(3)	O004	Mn01	N009[3]	84.74(9)
Mn02	N00B	2.273(3)	O004[5]	Mn01	N009[3]	165.72(9)
O003	Mn01[2]	2.175(2)	O004	Mn01	N009[4]	165.72(9)
O003	C00I	1.257(4)	O004[5]	Mn01	N009[4]	84.74(9)
O004	Mn02[1]	2.438(2)	N009[3]	Mn01	N009[4]	103.86(14)
O004	C00H	1.274(3)	O005	Mn02	O004[6]	83.67(8)
O005	C00I	1.262(4)	O005	Mn02	O006[6]	114.83(9)
O006	Mn02[1]	2.243(2)	O005	Mn02	N008[7]	133.39(9)
O006	C00H	1.261(3)	O005	Mn02	N00A	100.80(9)
O007	C00J	1.368(4)	O005	Mn02	N00B	86.23(9)
O007	C00R	1.430(4)	O006[6]	Mn02	O004[6]	55.77(7)
N008	Mn02[8]	2.230(3)	O006[6]	Mn02	N00A	86.66(9)
N008	N009	1.349(3)	O006[6]	Mn02	N00B	153.04(9)
N008	C00M	1.341(4)	N008[7]	Mn02	O004[6]	79.75(8)
N009	Mn01[9]	2.252(3)	N008[7]	Mn02	O006[6]	90.62(9)
N00B	C00T	1.338(4)	N008[7]	Mn02	N00A	119.98(10)
			N008[7]	Mn02	N00B	85.71(10)
			N00A	Mn02	O004[6]	139.11(9)
			N00A	Mn02	N00B	72.34(11)

[1]+X,1-Y,-1/2+Z; [2]1-X,1-Y,1-Z; [3]1-X,+Y,1/2-Z; [4]3/2-X,1/2+Y,1/2-Z; [5]-1/2+X,1/2+Y,+Z; [6]+X,1-Y,1/2+Z; [7]-1/2+X,1/2-Y,1/2+Z; [8]1/2+X,1/2-Y,-1/2+Z; [9]1/2+X,-1/2+Y,+Z

Table S4 The selected bond lengths and angles for **3**.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Mn1	O4[1]	2.185(2)	O4[1]	Mn1	O4[2]	180.00(9)
Mn1	O4[2]	2.185(2)	O4[2]	Mn1	N3[3]	94.50(11)
Mn1	O2	2.122(2)	O4[1]	Mn1	N3[3]	85.50(11)
Mn1	O2[3]	2.122(2)	O4[2]	Mn1	N3[4]	85.50(11)
Mn1	N3[4]	2.284(3)	O4[1]	Mn1	N3[4]	94.50(11)
Mn1	N3[5]	2.284(3)	O2[5]	Mn1	O4[2]	87.38(10)
Mn2	O4[2]	2.372(2)	O2	Mn1	O4[2]	92.62(10)
Mn2	O1	2.088(3)	O2[5]	Mn1	O4[1]	92.62(10)
Mn2	O3[2]	2.217(2)	O2	Mn1	O4[1]	87.38(10)
Mn2	N4[5]	2.241(3)	O2[5]	Mn1	O2	180.0
Mn2	O6	2.193(4)	O2	Mn1	N3[3]	92.70(11)
Mn2	O7	2.130(3)	O2[5]	Mn1	N3[4]	92.70(11)
O4	Mn1[6]	2.185(2)	O2[5]	Mn1	N3[3]	87.30(11)
O4	Mn2[6]	2.372(2)	O2	Mn1	N3[4]	87.30(11)
O4	C5	1.272(4)	N3[3]	Mn1	N3[4]	180.00(15)
O2	C1	1.250(4)	O1	Mn2	O4[1]	101.85(9)
O1	C1	1.250(4)	O1	Mn2	O3[1]	158.46(9)
O3	Mn2[6]	2.217(2)	O1	Mn2	N4[3]	89.05(12)
O3	C5	1.252(4)	O1	Mn2	O6	86.53(15)
N4	Mn2[7]	2.241(3)	O1	Mn2	O7	104.77(18)
N4	N3	1.342(4)	O3[1]	Mn2	O4[1]	56.73(8)
N4	C16	1.339(6)	O3[1]	Mn2	N4[3]	91.80(11)
N3	Mn1[7]	2.284(3)	N4[3]	Mn2	O4[1]	87.08(10)
			O6	Mn2	O4[1]	82.46(12)
			O6	Mn2	O3[1]	88.10(15)
			O6	Mn2	N4[3]	167.56(12)
			O7	Mn2	O4[1]	151.08(19)

[1]+X,3/2-Y,-1/2+Z; [2]2-X,-1/2+Y,1/2-Z; [3]2-X,1-Y,-Z; [4]1+X,3/2-Y,-1/2+Z; [5]1-X,-1/2+Y,1/2-Z; [6]2-X,1/2+Y,1/2-Z; [7]1-X,1/2+Y,1/2-Z

Table S5 Specified hydrogen bonds for **1**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1A	O4[1]	0.836(15)	1.924(16)	2.755(2)	173(2)
O1	H1B	N3[2]	0.852(15)	1.991(16)	2.818(2)	164(2)
O5	H5	N4[3]	0.82	1.95	2.696(2)	150.6

[1]1-X,1-Y,2-Z; [2]2+X,+Y,1+Z; [3]-1-X,1-Y,1-Z