Electronic Supplementary Information

Manganese clusters of aromatic oximes: synthesis, structure and magnetic properties

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Table S1 Crystallographic data and structure refinement parameters for **1-3**.

	1	**2**	**3**
formula	$C_{37}H_{43}ClMn_3N_9O_{17}$	$C_{40}H_{29}Mn_3N_6O_{11}$	$C_{225}H_{168}Cl_4Mn_{12}N_{40}O_{51}$
fw	1086.07	934.51	5049.07
Temperature / K	298(2) K	153(2)	298(2)
Wavelength / Å	0.71073 A	0.71073	0.71073
Crystal system	Hexagonal	Monoclinic	Triclinic
Space group	$P6_1$	$P2_1/c$	$P\bar{1}$
a / Å	20.1846(4)	10.8393(15)	17.1115(8)
b / Å	20.1846(4)	18.418(3)	18.8978(6)
c / Å	20.1893(6)	18.329(3)	19.9978(6)
α / °	90	90	67.248(3)
β / °	90	92.871(2)	89.768(3)
γ / °	120	90	70.924(4)
V / Å^3	7123.4(3)	3654.6(9)	5580.2(4)
Z	6	4	1
D_c / g cm^{-3}	1.519	1.698	1.502
μ / mm^{-1}	0.920	1.096	0.790
θ / °	2.85 to 25.09	1.57 to 25.01	2.92 to 25.02
F(000)	3336	1896	2574
Crystal size / mm	0.28 × 0.25 × 0.19	0.29 × 0.26 × 0.19	0.28 × 0.24 × 0.20
Reflections collected	80754	26301	52316
Reflections unique	8404	6425	19658
R_{int}	0.0796	0.0314	0.0442
GOF on F^2	1.011	1.063	1.049
R_1[a] ($I > 2\sigma(I)$)	0.0510	0.0366	0.0603
wR_2[b] ($I > 2\sigma(I)$)	0.1159	0.0912	0.1642
R_1[a] (all data)	0.0785	0.0467	0.0959
wR_2[b] (all data)	0.1306	0.0983	0.1951

Table S2 Crystallographic data and structure refinement parameters for **4**-**5**.

	4	**5**
formula	$C_{123}H_{101}Mn_8N_{27}O_{25}$	$C_{177}H_{129}Mn_8N_{15}O_{37}$
fw	2796.83	3497.47
Temperature / K	153(2)	185(2)
Wavelength / Å	0.71073	0.71073
Crystal system	Triclinic	Cubic
Space group	$P\bar{1}$	$Pa\bar{3}$
a / Å	16.5792(19)	31.8857(4)
b / Å	16.8624(19)	31.8857(4)
c / Å	23.487(3)	31.8857(4)
α / °	77.380(2)	90
β / °	82.470(2)	90
γ / °	76.586(2)	90
V / Å^3	6210.3(12)	32418.1(7)
Z	2	8
D_c / g cm^{-3}	1.496	1.433
μ / mm^{-1}	0.869	0.685
θ / °	0.89 to 25.02	1.81 to 23.64 deg.
F(000)	2856	14336
Crystal size / mm	0.32 × 0.25 × 0.18	0.30 × 0.28 × 0.26
Reflections collected	48250	138386
Reflections unique	21746	7817
R_{int}	0.0489	0.1075
GOF on F^2	1.022	1.153
R_1[a] ($I > 2\sigma(I)$)	0.0493	0.0997
wR_2[b] ($I > 2\sigma(I)$)	0.1352	0.2500
R_1[a] (all data)	0.0847	0.1492
wR_2[b] (all data)	0.1634	0.2995

Table S3 Selected bond lengths / Å and bond angles / º of **1**.

Mn1–O1	1.873(3)	Mn2–O1	1.885(3)	Mn3–O9	1.896(4)
Mn1–O3	1.907(4)	Mn2–O6	1.906(4)	Mn3–O1	1.896(4)
Mn1–O5	1.941(3)	Mn2–O8	1.921(4)	Mn3–O2	1.933(4)
Mn1–N1	2.025(4)	Mn2–N3	2.030(4)	Mn3–N5	1.997(5)
Mn1–O14	2.264(5)	Mn2–O12	2.212(6)	Mn3–Cl1	2.421(2)
Mn1–O13	2.271(4)	Mn2–O11	2.232(4)		
O1–Mn1–O3	177.6(2)	O1–Mn2–O6	176.9(2)	O9–Mn3–O1	159.6(2)
O1–Mn1–O5	93.41(15)	O1–Mn2–O8	92.04(16)	O9–Mn3–O2	85.28(16)
O3–Mn1–O5	85.57(15)	O6–Mn2–O8	86.41(17)	O1–Mn3–O2	91.18(15)
O1–Mn1–N1	89.03(16)	O1–Mn2–N3	90.16(16)	O9–Mn3–N5	90.43(17)
O3–Mn1–N1	92.10(16)	O6–Mn2–N3	91.44(17)	O1–Mn3–N5	88.79(16)
O5–Mn1–N1	176.3(2)	O8–Mn2–N3	177.60(19)	O2–Mn3–N5	167.5(2)
O1–Mn1–O14	88.24(19)	O1–Mn2–O12	90.6(2)	O9–Mn3–Cl1	100.29(17)
O3–Mn1–O14	89.62(17)	O6–Mn2–O12	92.2(2)	O1–Mn3–Cl1	100.07(16)
O5–Mn1–O14	92.39(18)	O8–Mn2–O12	93.8(2)	O2–Mn3–Cl1	98.04(16)
N1–Mn1–O14	90.49(19)	N3–Mn2–O12	85.2(2)	N5–Mn3–Cl1	94.23(17)
O1–Mn1–O13	91.54(19)	O1–Mn2–O11	88.61(18)	Mn1–O1–Mn2	119.16(18)
O3–Mn1–O13	90.71(17)	O6–Mn2–O11	88.70(18)	Mn1–O1–Mn3	120.32(18)
O5–Mn1–O13	93.72(19)	O8–Mn2–O11	90.99(18)	Mn2–O1–Mn3	120.10(18)
N1–Mn1–O13	83.40(19)	N3–Mn2–O11	90.02(18)		
O14–Mn1–O13	173.88(15)	O12–Mn2–O11	175.18(19)		

Table S4 Selected bond lengths / Å and bond angles / º of **2**.

Mn1–O1	1.8800(19)	Mn1–Mn3	3.1621(7)	Mn2–O10	2.345(2)
Mn1–O2	1.881(2)	Mn2–O4	1.877(2)	Mn3–O6	1.876(2)
Mn1–O7	1.917(2)	Mn2–O1	1.9028(19)	Mn3–O1	1.9061(19)
Mn1–N2	2.007(2)	Mn2–O3	1.960(2)	Mn3–O5	1.910(2)
Mn1–O8	2.136(2)	Mn2–N4	2.001(2)	Mn3–N6	1.989(2)
		Mn2–O11	2.242(2)	Mn3–O9	2.147(2)
O1–Mn1–O2	163.59(9)	O4–Mn2–N4	90.95(9)	O6–Mn3–O5	85.31(9)
O1–Mn1–O7	93.28(8)	O1–Mn2–N4	87.90(9)	O1–Mn3–O5	90.77(8)
O2–Mn1–O7	82.32(8)	O3–Mn2–N4	171.93(10)	O6–Mn3–N6	91.16(9)
O1–Mn1–N2	89.89(9)	O4–Mn2–O11	90.21(9)	O1–Mn3–N6	90.07(9)
O2–Mn1–N2	91.16(9)	O1–Mn2–O11	86.49(8)	O5–Mn3–N6	167.55(10)
O7–Mn1–N2	167.10(10)	O3–Mn2–O11	88.35(9)	O6–Mn3–O9	99.86(9)
O1–Mn1–O8	91.24(8)	N4–Mn2–O11	99.68(9)	O1–Mn3–O9	93.01(8)
O2–Mn1–O8	104.91(9)	O4–Mn2–O10	88.55(9)	O5–Mn3–O9	106.04(9)
O7–Mn1–O8	96.03(9)	O1–Mn2–O10	94.97(8)	N6–Mn3–O9	86.32(9)
N2–Mn1–O8	96.39(9)	O3–Mn2–O10	82.79(8)	Mn1–O1–Mn2	118.49(10)
O4–Mn2–O1	176.28(10)	N4–Mn2–O10	89.18(9)	Mn1–O1–Mn3	113.27(10)
O4–Mn2–O3	89.69(9)	O11–Mn2–O10	171.07(8)	Mn2–O1–Mn3	119.48(10)
O1–Mn2–O3	91.94(8)	O6–Mn3–O1	167.13(10)		

Table S5 Selected bond lengths / Å and bond angles / º of **3**.

Mn1–O1	1.889(3)	Mn3–O6	1.926(3)	Mn5–O11	1.890(3)
Mn1–O7	1.919(3)	Mn3–O1	1.930(3)	Mn5–O10	1.917(3)
Mn1–O2	1.960(3)	Mn3–N3	1.993(4)	Mn5–O8	1.918(3)
Mn1–N5	2.000(4)	Mn3–N10	2.342(5)	Mn5–N14	1.991(4)
Mn1–N7	2.318(4)	Mn3–N9	2.368(4)	Mn5–O15	2.303(4)
Mn1–O9	2.347(3)	Mn4–O8	1.892(3)	Mn5–N18	2.337(4)
Mn2–O3	1.862(3)	Mn4–O9	1.922(3)	Mn6–O13	1.865(3)
Mn2–O1	1.879(3)	Mn4–O14	1.947(3)	Mn6–O8	1.875(3)
Mn2–O4	1.901(3)	Mn4–N12	2.008(4)	Mn6–O12	1.904(3)
Mn2–N1	1.983(4)	Mn4–N17	2.277(4)	Mn6–N16	1.987(4)
Mn2–N8	2.234(4)	Mn4–O7	2.334(3)	Mn6–N19	2.207(5)
Mn3–O5	1.891(3)				
O1–Mn1–O7	173.35(14)	O1–Mn3–N3	89.15(14)	O8–Mn5–N14	89.47(14)
O1–Mn1–O2	91.86(12)	O5–Mn3–N10	83.39(16)	O11–Mn5–O15	84.44(16)
O7–Mn1–O2	90.36(12)	O6–Mn3–N10	92.12(15)	O10–Mn5–O15	91.88(16)
O1–Mn1–N5	88.03(14)	O1–Mn3–N10	96.76(15)	O8–Mn5–O15	93.67(14)
O7–Mn1–N5	90.19(14)	N3–Mn3–N10	90.14(17)	N14–Mn5–O15	89.81(17)
O2–Mn1–N5	176.02(15)	O5–Mn3–N9	85.74(15)	O11–Mn5–N18	87.15(15)
O1–Mn1–N7	100.02(14)	O6–Mn3–N9	92.70(15)	O10–Mn5–N18	90.71(15)
O7–Mn1–N7	86.35(14)	O1–Mn3–N9	94.15(14)	O8–Mn5–N18	94.76(14)
O2–Mn1–N7	86.82(14)	N3–Mn3–N9	84.93(16)	N14–Mn5–N18	87.41(16)
N5–Mn1–N7	89.28(15)	N10–Mn3–N9	167.96(15)	O15–Mn5–N18	171.10(14)
O1–Mn1–O9	99.54(12)	O8–Mn4–O9	171.53(14)	O13–Mn6–O8	165.76(16)
O7–Mn1–O9	74.35(12)	O8–Mn4–O14	91.86(12)	O13–Mn6–O12	83.06(14)
O2–Mn1–O9	86.33(12)	O9–Mn4–O14	90.36(12)	O8–Mn6–O12	92.91(13)
N5–Mn1–O9	97.61(13)	O8–Mn4–N12	88.27(14)	O13–Mn6–N16	91.40(14)
N7–Mn1–O9	159.46(13)	O9–Mn4–N12	89.91(14)	O8–Mn6–N16	89.95(13)
O3–Mn2–O1	165.51(16)	O14–Mn4–N12	177.18(15)	O12–Mn6–N16	168.23(16)
O3–Mn2–O4	82.13(14)	O8–Mn4–N17	100.75(15)	O13–Mn6–N19	93.75(18)
O1–Mn2–O4	93.23(13)	O9–Mn4–N17	87.55(15)	O8–Mn6–N19	100.28(16)
O3–Mn2–N1	92.10(15)	O14–Mn4–N17	86.05(15)	O12–Mn6–N19	96.28(17)
O1–Mn2–N1	90.25(14)	N12–Mn4–N17	91.16(16)	N16–Mn6–N19	94.43(16)
O4–Mn2–N1	169.57(17)	O8–Mn4–O7	97.37(12)	Mn2–O1–Mn1	119.47(15)
O3–Mn2–N8	93.89(16)	O9–Mn4–O7	74.60(12)	Mn2–O1–Mn3	118.45(15)
O1–Mn2–N8	100.30(14)	O14–Mn4–O7	86.66(12)	Mn1–O1–Mn3	119.77(15)
O4–Mn2–N8	96.80(16)	N12–Mn4–O7	96.12(13)	Mn1–O7–Mn4	105.74(13)
N1–Mn2–N8	92.23(15)	N17–Mn4–O7	160.65(14)	Mn6–O8–Mn4	119.85(15)
O5–Mn3–O6	88.22(14)	O11–Mn5–O10	87.68(14)	Mn6–O8–Mn5	118.94(15)
O5–Mn3–O1	179.53(16)	O11–Mn5–O8	178.03(16)	Mn4–O8–Mn5	119.74(15)
O6–Mn3–O1	91.33(12)	O10–Mn5–O8	91.82(13)	Mn4–O9–Mn1	105.14(13)
O5–Mn3–N3	91.29(15)	O11–Mn5–N14	91.08(15)		
O6–Mn3–N3	177.61(16)	O10–Mn5–N14	177.80(17)		

Table S6 Selected bond lengths / Å and bond angles / º of **4**.

Mn1–O2	1.904(3)	Mn3–O16	2.079(3)	Mn6–O11	1.933(3)
Mn1–O5	1.906(3)	Mn3–O2	2.685(3)	Mn6–N5	2.008(4)
Mn1–O1	1.927(3)	Mn4–O4	1.895(3)	Mn6–O22	2.156(3)
Mn1–N2	2.002(3)	Mn4–O17	1.897(3)	Mn6–O5	2.649(3)
Mn1–O7	2.065(3)	Mn4–O2	1.926(3)	Mn7–O20	1.871(3)
Mn1–O3	2.684(3)	Mn4–N14	2.018(3)	Mn7–O2	1.906(3)
Mn2–O1	1.884(3)	Mn4–O19	2.068(3)	Mn7–O6	1.922(3)
Mn2–O13	1.906(3)	Mn4–O1	2.813(3)	Mn7–N15	2.011(3)
Mn2–O3	1.926(3)	Mn5–O15	1.873(3)	Mn7–O23	2.195(3)
Mn2–N10	2.028(3)	Mn5–O4	1.891(3)	Mn7–O12	2.599(3)
Mn2–O9	2.074(3)	Mn5–O18	1.934(3)	Mn8–O8	1.866(3)
Mn2–O4	2.774(4)	Mn5–N12	2.009(3)	Mn8–O1	1.892(3)
Mn3–O12	1.895(3)	Mn5–O21	2.188(3)	Mn8–O14	1.951(3)
Mn3–O3	1.898(3)	Mn5–O13	2.550(3)	Mn8–N3	2.015(4)
Mn3–O4	1.922(3)	Mn6–O10	1.869(3)	Mn8–O24	2.161(3)
Mn3–N7	2.008(3)	Mn6–O3	1.900(3)	Mn8–O17	2.626(3)
O2–Mn1–O5	161.18(13)	O4–Mn4–N14	86.59(12)	O20–Mn7–O23	93.31(14)
O2–Mn1–O1	89.19(12)	O17–Mn4–N14	88.97(13)	O2–Mn7–O23	96.19(13)
O5–Mn1–O1	92.30(13)	O2–Mn4–N14	168.75(13)	O6–Mn7–O23	95.15(14)
O2–Mn1–N2	87.00(13)	O4–Mn4–O19	103.17(13)	N15–Mn7–O23	95.11(14)
O5–Mn1–N2	89.07(13)	O17–Mn4–O19	97.83(14)	O20–Mn7–O12	93.39(12)
O1–Mn1–N2	172.03(13)	O2–Mn4–O19	90.06(12)	O2–Mn7–O12	77.87(11)
O2–Mn1–O7	101.82(13)	N14–Mn4–O19	100.89(13)	O6–Mn7–O12	92.52(12)
O5–Mn1–O7	96.96(14)	O4–Mn4–O1	86.93(10)	N15–Mn7–O12	77.58(12)
O1–Mn1–O7	89.29(11)	O17–Mn4–O1	74.18(11)	O23–Mn7–O12	170.28(12)
N2–Mn1–O7	98.34(13)	O2–Mn4–O1	66.09(10)	O8–Mn8–O1	171.14(14)
O2–Mn1–O3	86.26(10)	N14–Mn4–O1	103.53(11)	O8–Mn8–O14	86.97(12)
O5–Mn1–O3	76.92(11)	O19–Mn4–O1	154.07(10)	O1–Mn8–O14	89.64(11)
O1–Mn1–O3	68.22(10)	O15–Mn5–O4	171.07(14)	O8–Mn8–N3	91.63(14)
N2–Mn1–O3	104.51(11)	O15–Mn5–O18	86.08(12)	O1–Mn8–N3	90.52(13)
O7–Mn1–O3	156.15(11)	O4–Mn5–O18	89.85(11)	O14–Mn8–N3	171.47(14)
O1–Mn2–O13	159.12(14)	O15–Mn5–N12	92.51(13)	O8–Mn8–O24	92.09(14)
O1–Mn2–O3	88.56(12)	O4–Mn5–N12	90.84(12)	O1–Mn8–O24	96.39(13)
O13–Mn2–O3	93.12(12)	O18–Mn5–N12	174.84(15)	O14–Mn8–O24	95.69(13)
O1–Mn2–N10	86.24(12)	O15–Mn5–O21	92.29(14)	N3–Mn8–O24	92.77(14)
O13–Mn2–N10	88.76(13)	O4–Mn5–O21	96.03(13)	O–Mn8–O17	92.73(12)
O3–Mn2–N10	170.04(13)	O18–Mn5–O21	95.77(13)	O–Mn8–O17	79.13(11)
O1–Mn2–O9	103.47(13)	N12–Mn5–O21	89.23(14)	O–Mn8–O17	90.84(11)
O13–Mn2–O9	97.36(14)	O15–Mn5–O13	92.91(13)	O–Mn8–O17	80.82(12)
O3–Mn2–O9	89.75(12)	O4–Mn5–O13	79.40(11)	O–Mn8–O17	172.08(12)
N10–Mn2–O9	99.72(13)	O18–Mn5–O13	93.65(12)	Mn2–O1–Mn8	122.94(14)
O1–Mn2–O4	88.27(11)	N12–Mn5–O13	81.46(12)	Mn2–O1–Mn1	115.87(14)

O13–Mn2–O4	73.37(11)	O21–Mn5–O13	169.53(11)	Mn8–O1–Mn1	121.17(14)
O3–Mn2–O4	66.87(11)	O10–Mn6–O3	168.02(14)	Mn2–O1–Mn4	87.52(10)
N10–Mn2–O4	104.44(11)	O10–Mn6–O11	84.65(13)	Mn8–O1–Mn4	97.40(11)
O9–Mn2–O4	153.78(10)	O3–Mn6–O11	89.24(12)	Mn1–O1–Mn4	85.96(10)
O12–Mn3–O3	159.60(13)	O10–Mn6–N5	92.74(14)	Mn1–O2–Mn7	121.03(13)
O12–Mn3–O4	93.17(12)	O3–Mn6–N5	91.60(13)	Mn1–O2–Mn4	118.76(14)
O3–Mn3–O4	89.31(12)	O11–Mn6–N5	170.40(15)	Mn7–O2–Mn4	119.96(14)
O12–Mn3–N7	88.91(13)	O10–Mn6–O22	94.00(15)	Mn1–O2–Mn3	88.91(10)
O3–Mn3–N7	86.50(13)	O3–Mn6–O22	96.78(13)	Mn7–O2–Mn3	98.61(11)
O4–Mn3–N7	173.17(13)	O11–Mn6–O22	94.87(14)	Mn4–O2–Mn3	87.41(10)
O12–Mn3–O16	96.23(14)	N5–Mn6–O22	94.53(15)	Mn3–O3–Mn6	121.89(14)
O3–Mn3–O16	104.07(13)	O10–Mn6–O5	92.17(12)	Mn3–O3–Mn2	117.57(14)
O4–Mn3–O16	88.67(11)	O3–Mn6–O5	77.89(11)	Mn6–O3–Mn2	120.20(15)
N7–Mn3–O16	97.57(12)	O11–Mn6–O5	93.47(12)	Mn3–O3–Mn1	89.06(11)
O12–Mn3–O2	75.82(11)	N5–Mn6–O5	77.37(12)	Mn6–O3–Mn1	99.11(11)
O3–Mn3–O2	86.35(11)	O22–Mn6–O5	170.04(12)	Mn2–O3–Mn1	87.34(10)
O4–Mn3–O2	68.40(10)	O20–Mn7–O2	169.19(14)	Mn5–O4–Mn4	122.55(14)
N7–Mn3–O2	105.91(11)	O20–Mn7–O6	84.31(13)	Mn5–O4–Mn3	121.64(14)
O16–Mn3–O2	154.90(10)	O2–Mn7–O6	89.67(12)	Mn4–O4–Mn3	115.75(13)
O4–Mn4–O17	159.00(14)	O20–Mn7–N15	92.30(14)	Mn5–O4–Mn2	97.26(11)
O4–Mn4–O2	88.44(12)	O2–Mn7–N15	92.01(13)	Mn4–O4–Mn2	88.47(10)
O17–Mn4–O2	92.09(12)	O6–Mn7–N15	169.36(14)	Mn3–O4–Mn2	86.24(10)

Table S7 Selected bond lengths / Å and bond angles / º of **5**.

Mn1–O9	2.108(9)	Mn2–N4A	2.325(8)	Mn3–Mn4	3.020(2)
Mn1–O1A	2.239(6)	Mn2–N2	2.337(7)	Mn4–O6A	2.023(5)
Mn1–O1	2.239(6)	Mn2–N3B	2.356(7)	Mn4–O6	2.023(5)
Mn1–O1B	2.239(6)	Mn3–O10	1.972(5)	Mn4–O6B	2.023(5)
Mn1–N1A	2.342(6)	Mn3–O2A	1.988(6)	Mn4–O10B	2.027(6)
Mn1–N1	2.342(6)	Mn3–O4	1.998(6)	Mn4–O10A	2.027(5)
Mn1–N1B	2.342(6)	Mn3–O10B	1.999(5)	Mn4–O10	2.027(5)
Mn2–O10	2.088(5)	Mn3–O9	2.000(4)	Mn4–Mn3B	3.020(2)
Mn2–O5B	2.220(6)	Mn3–O8	2.021(7)	Mn4–Mn3A	3.020(2)
Mn2–O3	2.235(6)	Mn3–Mn3B	2.997(2)		
Mn2–O7A	2.238(7)	Mn3–Mn3A	2.997(2)		
O9–Mn1–O1A	132.25(16)	O5B–Mn2–N4A	149.8(3)	O9–Mn3–O8	168.9(2)
O9–Mn1–O1	132.25(16)	O3–Mn2–N4A	88.3(2)	O6A–Mn4–O6	87.5(2)
O1A–Mn1–O1	79.7(2)	O7A–Mn2–N4A	68.7(3)	O6A–Mn4–O6B	87.5(2)
O9–Mn1–O1B	132.25(16)	O10–Mn2–N2	76.6(2)	O6–Mn4–O6B	87.5(2)
O1A–Mn1–O1B	79.7(2)	O5B–Mn2–N2	86.0(2)	O6A–Mn4–O10B	88.8(2)
O1–Mn1–O1B	79.7(2)	O3–Mn2–N2	69.1(2)	O6–Mn4–O10B	167.7(2)
O9–Mn1–N1A	75.50(16)	O7A–Mn2–N2	149.5(2)	O6B–Mn4–O10B	104.0(2)
O1A–Mn1–N1A	68.5(2)	N4A–Mn2–N2	116.4(2)	O6A–Mn4–O10A	104.0(2)
O1–Mn1–N1A	148.1(2)	O10–Mn2–N3B	76.5(2)	O6–Mn4–O10A	88.8(2)
O1B–Mn1–N1A	91.3(2)	O5B–Mn2–N3B	68.8(2)	O6B–Mn4–O10A	167.7(2)
O9–Mn1–N1	75.50(16)	O3–Mn2–N3B	148.8(2)	O10B–Mn4–O10A	80.7(2)
O1A–Mn1–N1	91.3(2)	O7A–Mn2–N3B	87.0(3)	O6A–Mn4–O10	167.7(2)
O1–Mn1–N1	68.5(2)	N4A–Mn2–N3B	114.2(2)	O6–Mn4–O10	104.0(2)
O1B–Mn1–N1	148.1(2)	N2–Mn2–N3B	114.4(2)	O6B–Mn4–O10	88.8(2)
N1A–Mn1–N1	113.95(13)	O10–Mn3–O2A	169.8(2)	O10B–Mn4–O10	80.7(2)
O9–Mn1–N1B	75.50(16)	O10–Mn3–O4	90.6(2)	O10A–Mn4–O10	80.7(2)
O1A–Mn1–N1B	148.1(2)	O2A–Mn3–O4	86.9(2)	Mn3B–O9–Mn3	97.1(3)
O1–Mn1–N1B	91.3(2)	O10–Mn3–O10B	82.7(3)	Mn3B–O9–Mn3A	97.1(3)
O1B–Mn1–N1B	68.5(2)	O2A–Mn3–O10B	100.6(2)	Mn3–O9–Mn3A	97.1(3)
N1A–Mn1–N1B	113.95(13)	O4–Mn3–O10B	171.4(2)	Mn3B–O9–Mn1	120.1(2)
N1–Mn1–N1B	113.95(13)	O10–Mn3–O9	82.3(2)	Mn3–O9–Mn1	120.1(2)
O10–Mn2–O5B	130.0(2)	O2A–Mn3–O9	88.6(2)	Mn3A–O9–Mn1	120.1(2)
O10–Mn2–O3	131.8(2)	O4–Mn3–O9	102.9(2)	Mn3–O10–Mn3A	98.0(2)
O5B–Mn2–O3	80.9(2)	O10B–Mn3–O9	81.7(2)	Mn3–O10–Mn4	98.1(2)
O10–Mn2–O7A	131.8(2)	O10–Mn3–O8	103.5(2)	Mn3A–O10–Mn4	97.2(2)
O5B–Mn2–O7A	81.9(3)	O2A–Mn3–O8	86.2(2)	Mn3–O10–Mn2	119.8(3)
O3–Mn2–O7A	81.4(2)	O4–Mn3–O8	86.6(3)	Mn3A–O10–Mn2	119.1(3)
O10–Mn2–N4A	77.4(3)	O10B–Mn3–O8	89.6(2)	Mn4–O10–Mn2	119.8(3)

Symmetry codes: A) $y + 1/2, -z + 1/2, -x + 1$; B) $-z + 1, x - 1/2, -y + 1/2$.

Table S8 Bond Valence Sum (BVS) calculations for the Mn atoms in **1**-**6**.

Complex	Oxidation state*							
	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Mn7	Mn8
1	3.27 3.02	3.35 3.09	2.93 2.71					
2	3.22 2.97	3.24 2.99	3.21 2.96					
3	3.13 2.89	3.24 2.99	3.15 2.91	3.17 2.92	3.24 2.99	3.26 3.00		
4	3.29 3.03	3.27 3.00	3.30 3.04	3.27 3.01	3.26 3.01	3.25 3.00	3.23 2.98	3.24 2.99
5	1.99 1.83	2.04 1.88	3.44 3.17	3.18 2.93				

*There are two calculated results for the oxidation states of every Mn atom. The upper and below ones are obtained from the calculation based on Mn(II) and Mn(III) ions, respectively.

Table S9 Hydrogen bonds for **1-3** [Å and °].

complex	D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1	O11–H111···O15	0.85	1.89	2.730(7)	166.8
	O11–H112···O3A	0.85	1.95	2.778(5)	164.5
	O11–H112···N2A	0.85	2.54	3.202(6)	135.7
	O13–H131···O16B	0.85	1.84	2.695(8)	179.8
	O13–H132···O15	0.83	1.97	2.761(7)	156.8
	O14–H141···O6C	0.85	1.95	2.799(6)	179.5
	O14–H141···N4C	0.85	2.52	3.275(7)	148.3
	O14–H142···O12	0.84	2.28	3.025(8)	147.1
	O14–H142···Cl1	0.84	2.86	3.414(4)	124.7
	Symmetry codes: A) $x - y + 1, x + 1, z + 1/6$; B) $x - 1, y, z$; C) $y - 1, -x + y, z - 1/6$.				
2	O10–H101···O8	0.84	2.10	2.876(3)	153.5
	O11–H111···N1A	0.84	1.96	2.805(3)	174.9
	Symmetry code: A) $-x + 1, -y + 1, -z + 1$.				
3	O15–H151···N20A	0.85	1.92	2.766(8)	171.2
	O15–H152···O23	0.86	2.39	2.930(12)	121.2
	O24–H241···O17B	0.86	2.17	3.031(11)	179.5
	O24–H242···O13B	0.86	2.23	2.999(8)	148.7
	O24–H242···N15B	0.86	2.70	3.302(8)	128.6
	O25–H25···O21	0.86	2.58	3.44(4)	178.2
	O26–H261···O18C	0.87	2.56	3.43(3)	178.6
	O26–H262···O27C	0.84	1.64	2.26(4)	128.0
	O27–H271···O24B	0.85	2.58	3.44(3)	177.9
	O27–H272···O26	0.84	2.23	2.726(10)	118.3
	Symmetry codes: A) $-x + 1, -y + 1, -z + 1$; B) $-x + 1, -y + 1, -z$; C) $-x, -y + 2, -z$.				

Table S10 $\pi\cdots\pi$ interaction data of **1**–**4**.

	Two aromatic rings existing $\pi\cdots\pi$ interaction	Dihedral angle / °	Center-to-center distance / Å	Offset angle / °
1	intrachain $\pi\cdots\pi$ interaction			
	C1-C4,C9 and C22-C27 (–1 + *y*, –*x* + *y*, –1/6 + *z*)	3.782(1)	3.3948(1)	5.695(2)
	C13-C18 and C10-C13,C18 (–1 + *y*, –*x* + *y*, –1/6 + *z*)	2.895(1)	3.4699(1)	6.107(2)
	interchain $\pi\cdots\pi$ interaction			
	C22-C27 and C1-C4,C9 (*y*, −*x* + *y*, –1/6 + *z*)	2.754(2)	3.6164(1)	19.999(2)
	C19-C22,C27 and C4-C9 (*y*, −*x* + *y*, –1/6 + *z*)	2.278	3.6590(1)	20.638(2)º
2	Intra-dimer $\pi\cdots\pi$ interaction			
	C25-C29 and C3,C4,C9-C12 (1 − *x*, 1 − *y*, 1 – *z*)	2.657(2)	3.7115(5)	25.965(5)
	inter-dimer $\pi\cdots\pi$ interaction			
	C25-C29 and C15,C16,C21-C24 (−*x*, −0.5 + *y*, 0.5 – *z*)	3.076(2)	3.5927(5)	18.250(3)
	C28-C33 and C13-C17 (−*x*, −0.5 + *y*, 0.5 – *z*)	1.643(2)	3.6512(5)	19.419(4)
	C1-C12 and C13-C24 (*x*, 1.5 − *y*, 0.5 + *z*)	5.278(2)	3.5816(4)	15.105(4)
3	$\pi\cdots\pi$ interactions for the formation of 2D sheet			
	C15-C24 and C71-C80 (1 + *x*, −1 + *y*, *z*)	1.729(2)	3.7036(2)	22.190(3)
	C27-C36 and C27-C36 (1 − *x*, 1 − *y*, – *z*)	0	3.6243(1)	18.612(1)
	$\pi\cdots\pi$ interactions for the formation of 3D structure			
	C72-C77 and C4-C9 (1 − *x*, 1 − *y*, 1 – *z*)	5.801(1)	3.6731(1)	16.071(2)
	C4-C9 and C72-C77(1 − *x*, 1 − *y*, 1 – *z*)	5.801(1)	3.6731(1)	16.071(2)
	C60-C65 and C60-C65 (2 − *x*, 1 − *y*, 1 – *z*)	0	3.5574(1)	11.453(2)
4	For chain			
	C52-C57 and C52-C57 (1 − *x*, 1 − *y*, 1 – *z*)	0	3.7246(4)	26.657(2)
	C76-C81 and C76-C81 (1 − *x*, 2 − *y*, 1 – *z*)	0	3.8304(4)	25.861(2)

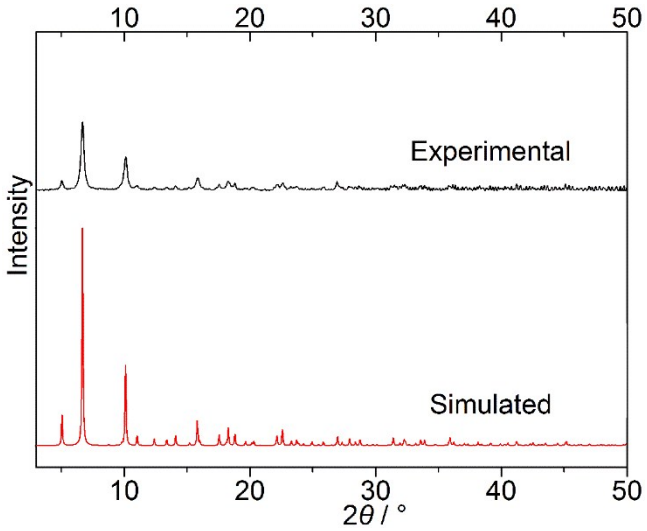


Fig. S1 PXRD patterns of **1**.

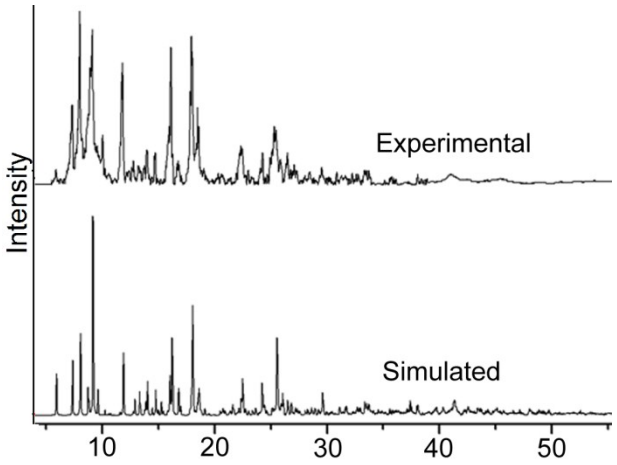


Fig. S2 PXRD patterns of **2**.

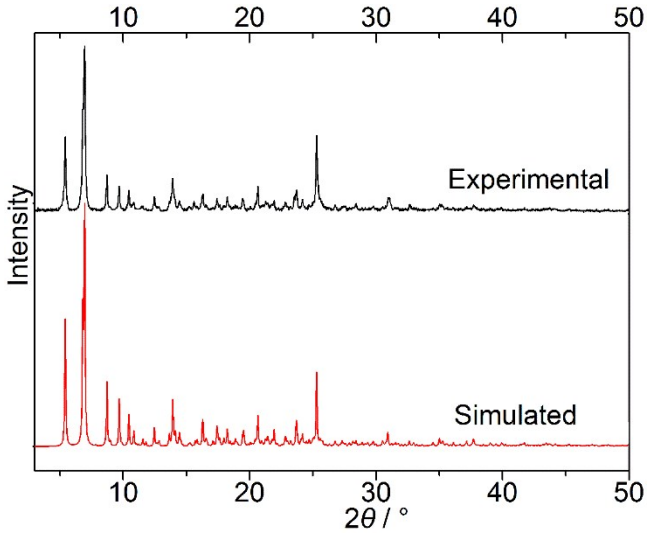


Fig. S3 PXRD patterns of **3**.

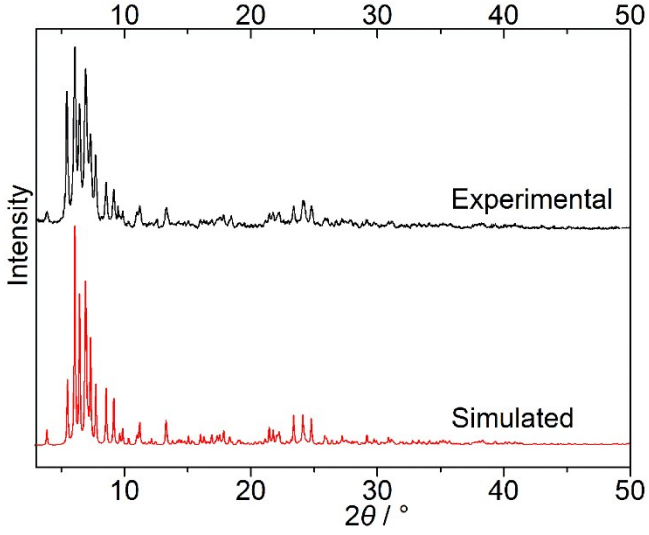


Fig. S4 PXRD patterns of **4**.

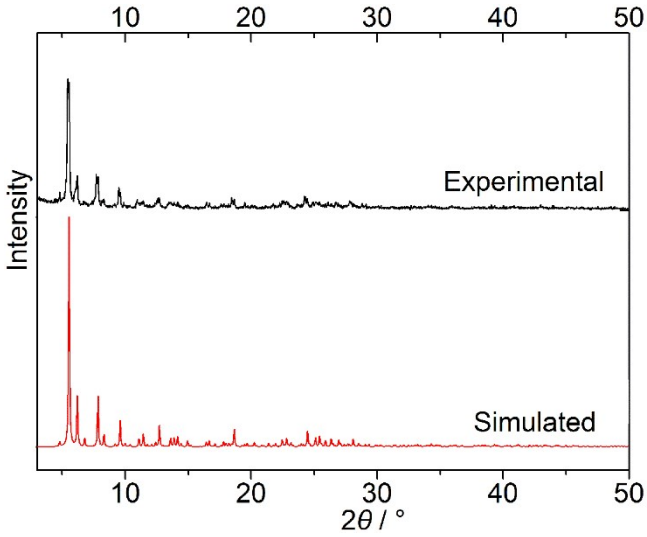


Fig. S5 PXRD patterns of **5**.

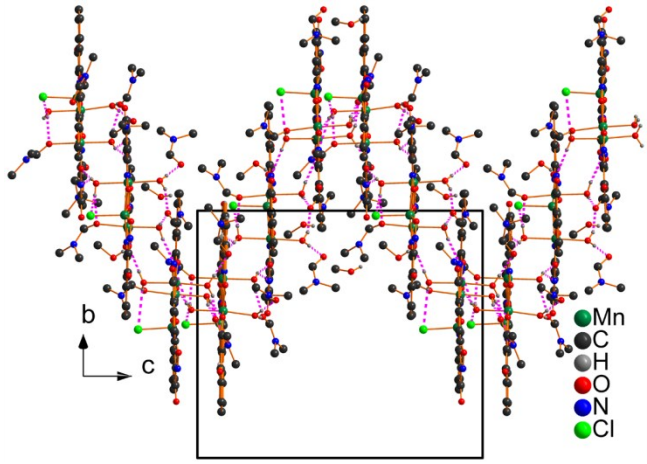


Fig. S6 One-dimensional supramolecular H-bonded chain of **1**. Purple broken lines represent hydrogen bonds.

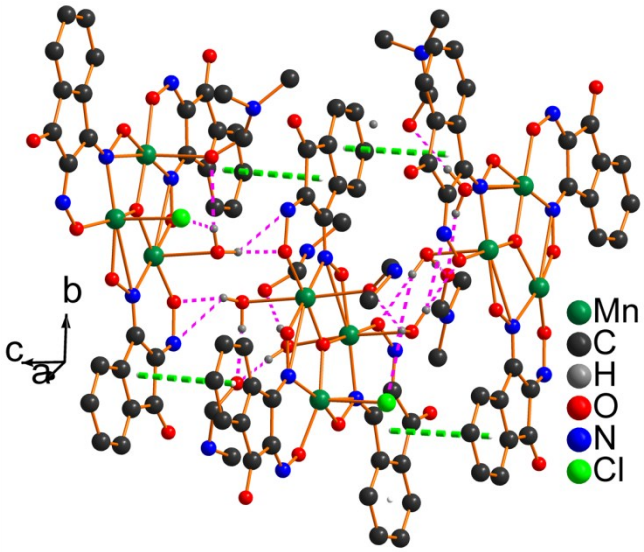


Fig. S7 A show of the hydrogen bonds (purple broken lines) and π···π stacking interactions (green broken lines) in the supramolecular one-dimensioanl chain of **1**.

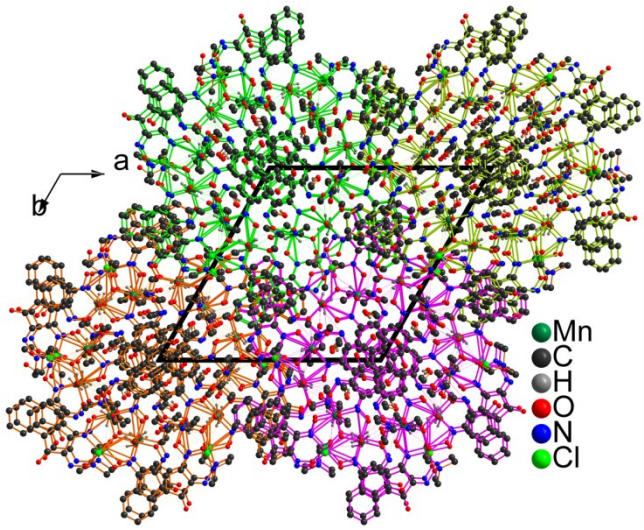


Fig. S8 A show of the three-dimensional supramolecular structure of **1** formed from one-dimensional supramolecular chains by π···π stacking interactions. The bonds in different chains are highlighted with different colors.

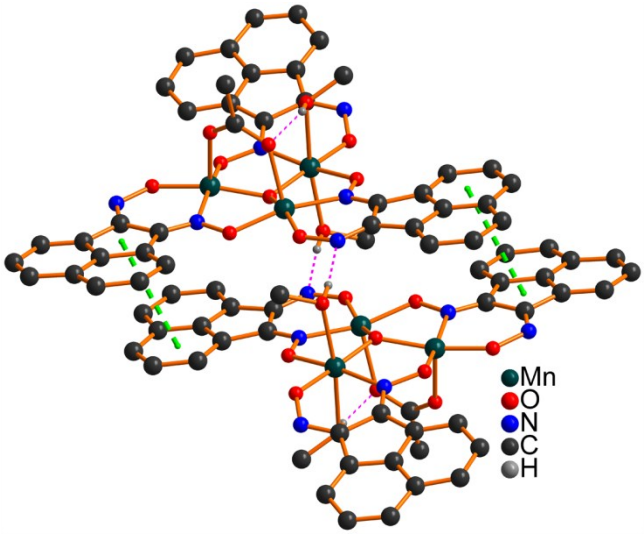


Fig. S9 The dimer of **2** formed by hydrogen bonds (purple broken lines) and π···π stacking interactions (green broken lines).

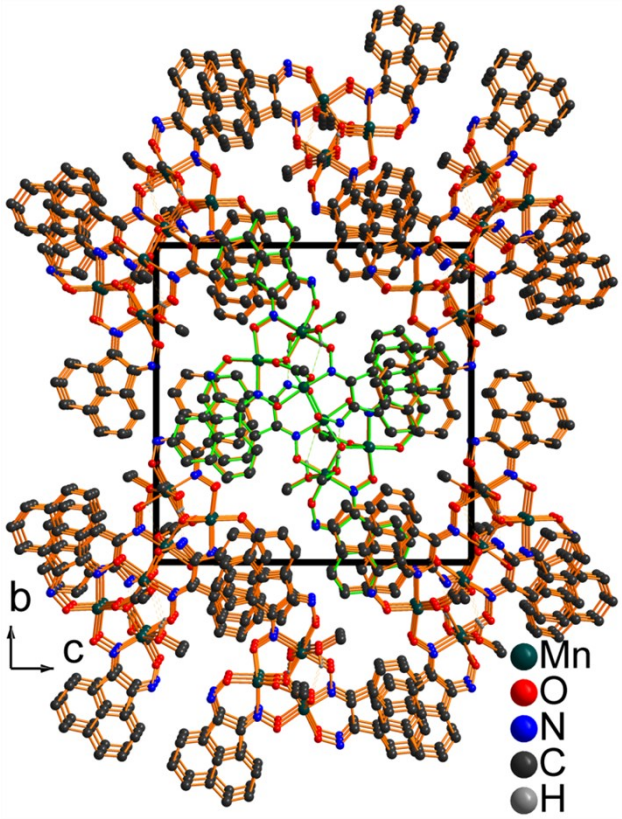


Fig. S10 Packing diagram of the dimers in **2** by π···π stacking interactions. The bonds in one dimer are highlighted with green color.

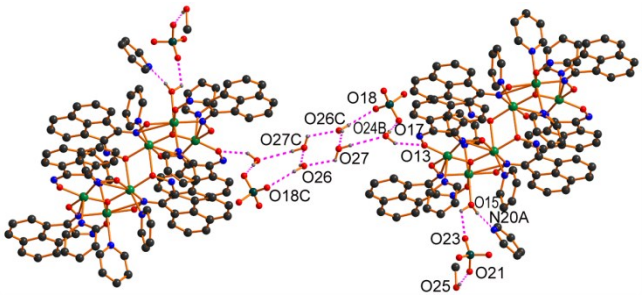


Fig. S11 The dimer of **3** formed by hydrogen bonds (purple broken lines).

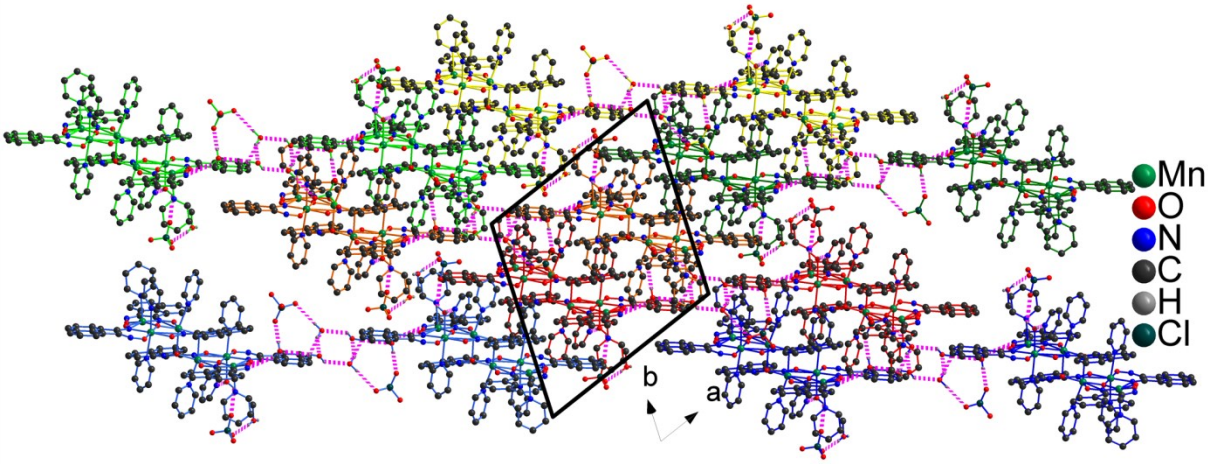


Fig. S12 Two-dimensional supramolecular sheet of **3** in the ab plane formed from the dimers through π···π stacking interactions.

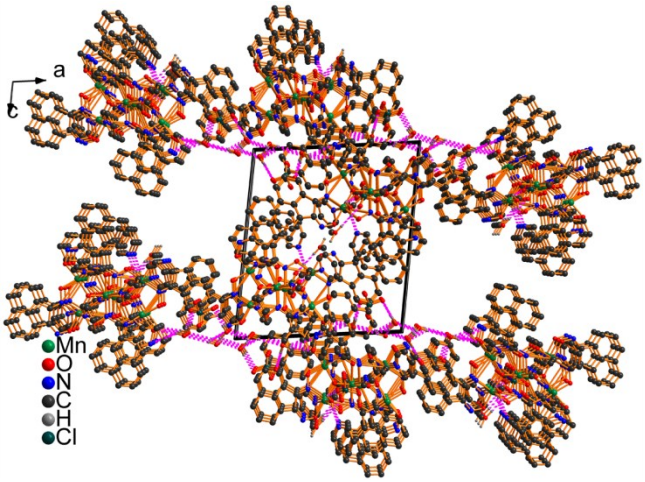


Fig. S13 Three-dimensional supramolecular structure of **3** formed from the supramolecular sheets through π···π stacking interactions.

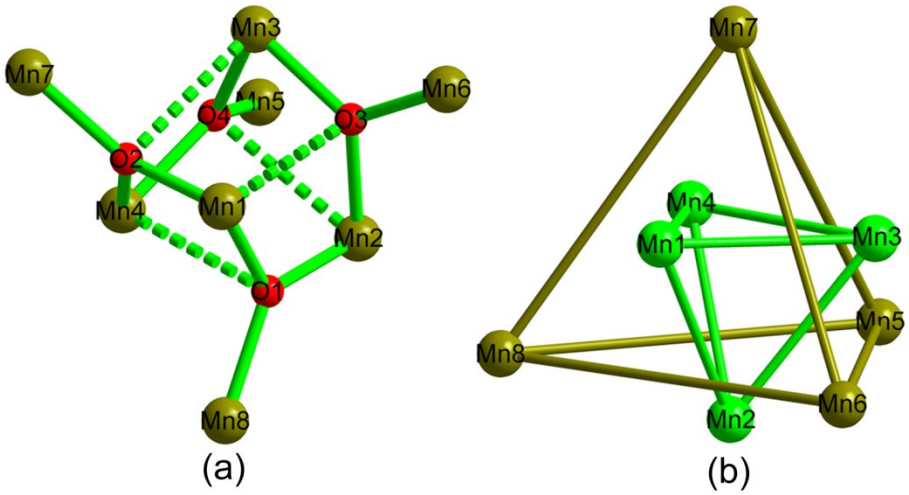


Fig. S14 a) The $Mn_8O_4^{16+}$ skeleton in **4** with the weak Mn−O bonds represented by broken lines. b) A schematic show of the inner and outer tetrahedral Mn_4 skeletons of **4**.

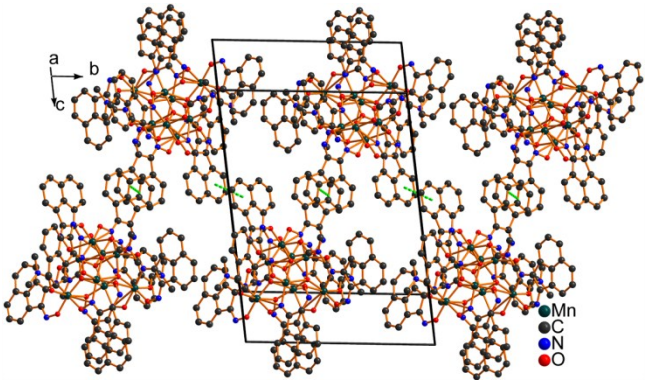
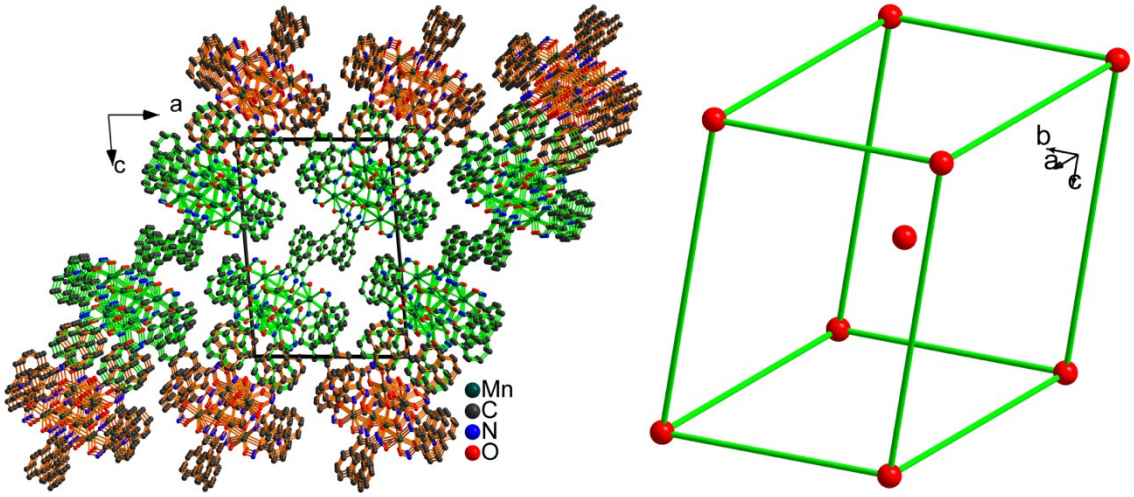
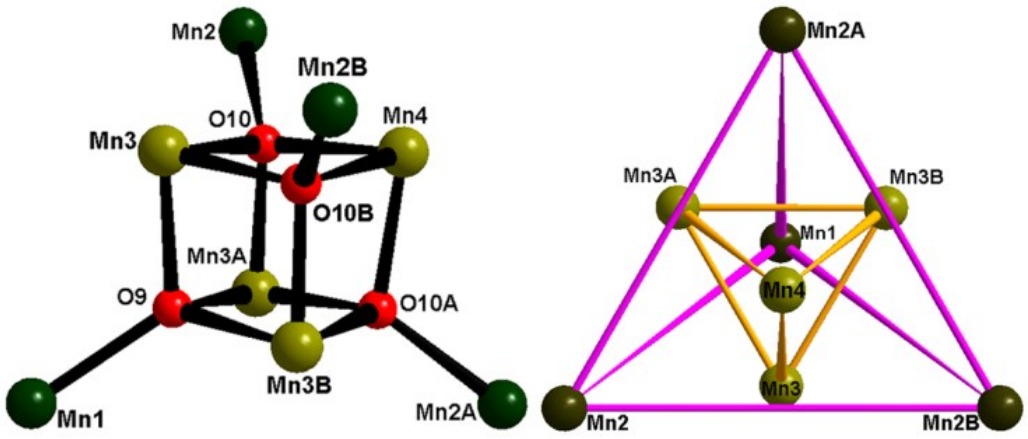


Fig. S15 One-dimensional supramolecular chain of **4** formed from octanuclear units by π···π stacking interactions (green broken lines).



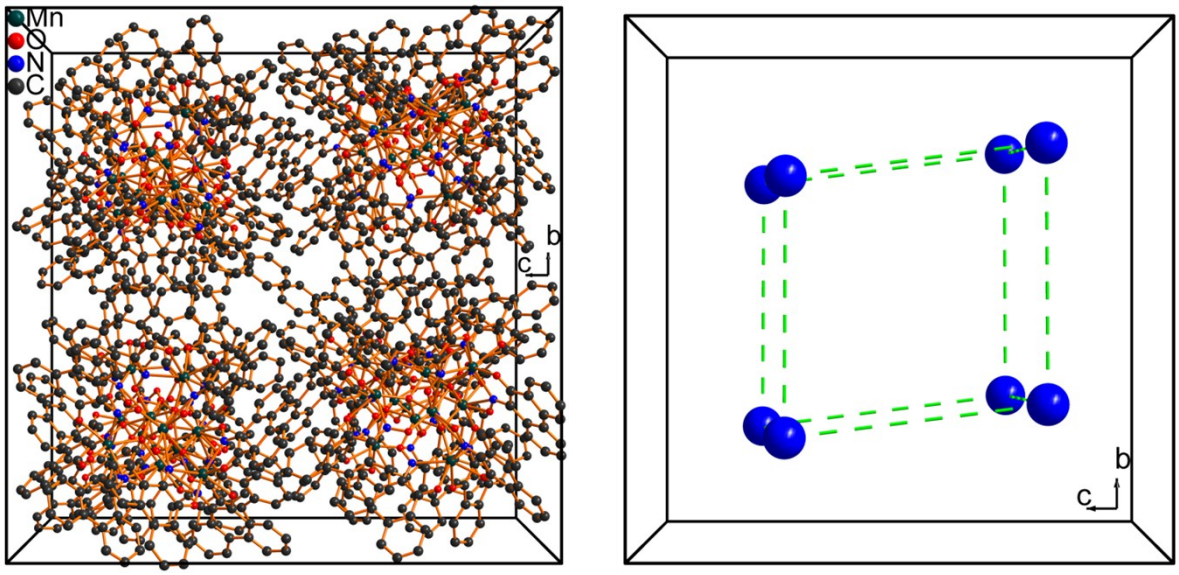
(a) (b)

Fig. S16 a) Packing diagram of **4** with the one-dimensional supramolecular chain highlighted by green colors. b) A schematic show of the packing diagram of the trinuclear units (red spheres) of **4**.



(a) (b)

Fig. S17 a) The $[Mn^{II}_4Mn^{III}_4O_4]^{12+}$ skeleton in **5**. b) A schematic show of the inner and outer tetrahedral Mn_4 skeletons of **5**.



(a) (b)

Fig. S18 a) A packing diagram of the octanuclear nuclear units of **5** with all solvent molecules and hydrogen atoms omitted. b) A schematic show of the octanuclear nuclear units (blue spheres) of **5**.

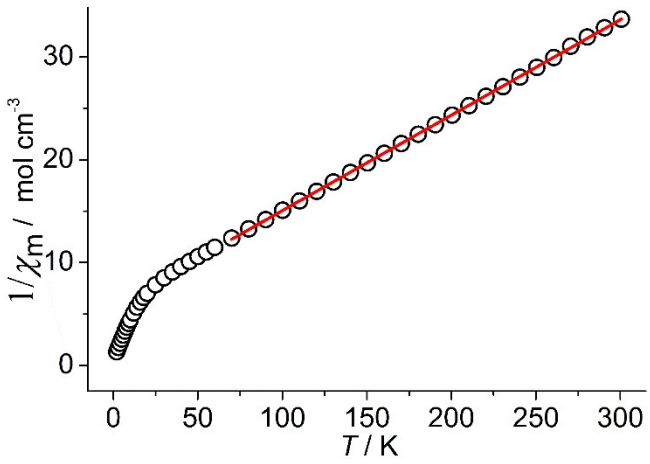


Fig. S19 The plot of χ_m^{-1} vs T for **1** in the temperature range of 2.0-300 K. The solid line represents the fitting by Curie-Weiss law in the temperature range of 70-300 K.

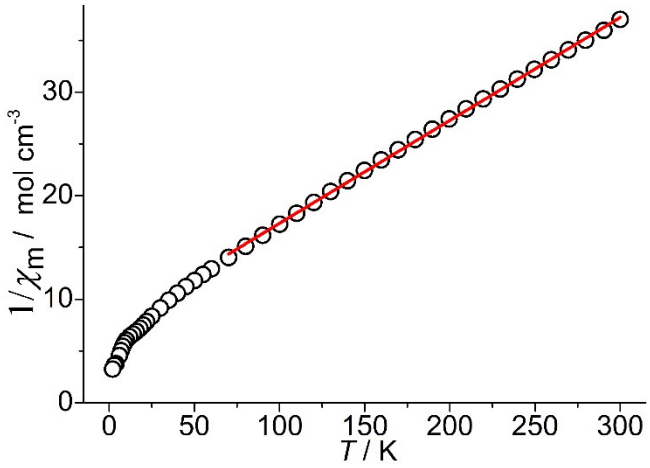


Fig. S20 The plot of χ_m^{-1} vs T for **2** in the temperature range of 2.0-300 K. The solid line represents the fitting by Curie-Weiss law in the temperature range of 70-300 K.

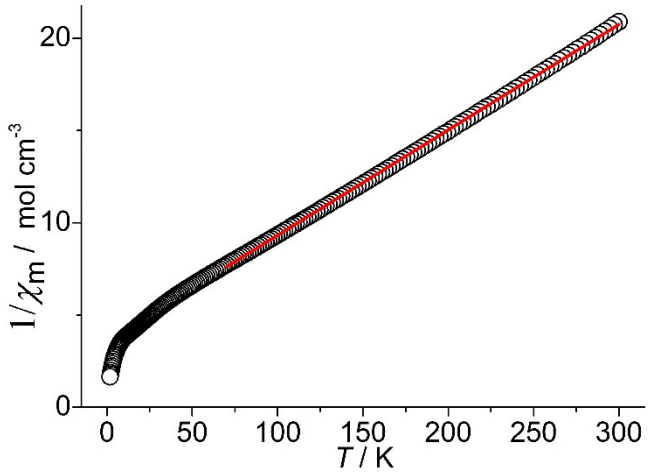


Fig. S21 The plot of χ_m^{-1} vs T for **3** in the temperature range of 1.8-300 K. The solid line represents the fitting by Curie-Weiss law in the temperature range of 70-300 K.

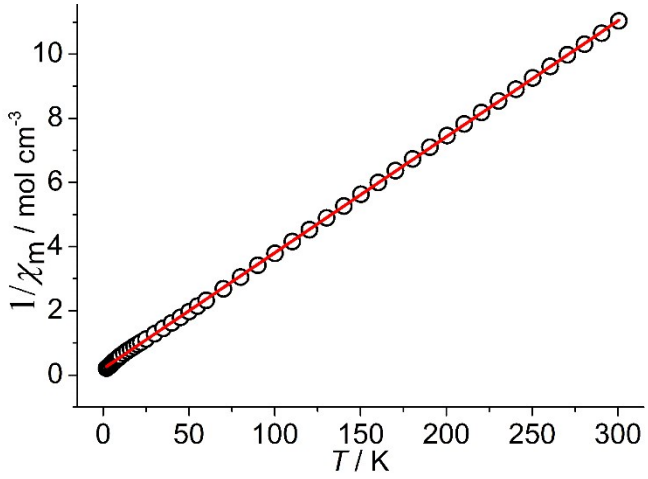


Fig. S22 The plot of χ_m^{-1} vs T for **4** in the temperature range of 2.0-300 K. The solid line represents the fitting by Curie-Weiss law.

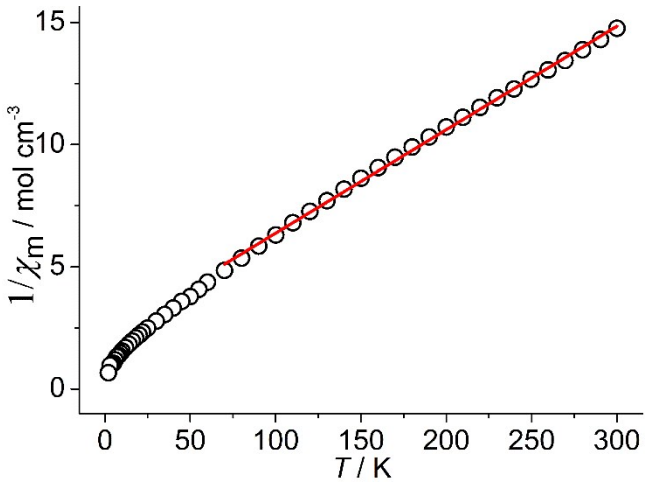


Fig. S23 The plot of χ_m^{-1} vs T for **5** in the temperature range of 2.0-300 K. The solid line represents the fitting by Curie-Weiss law.

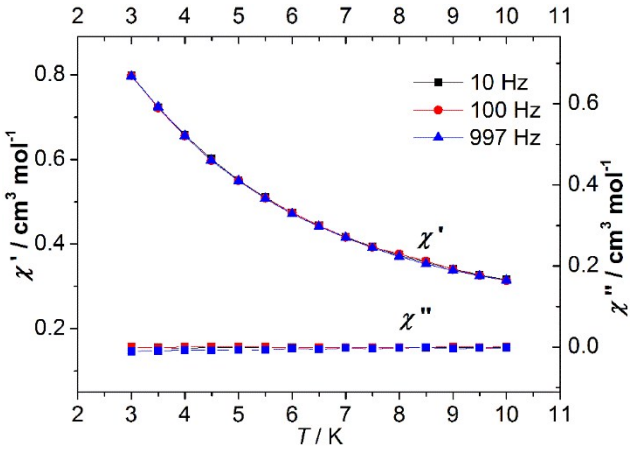


Fig. S24 Temperature-dependent ac magnetic susceptibilities of **1** under different frequencies with a zero DC field and an oscillating field of 2.5 Oe. Solid lines are guides for the eye.

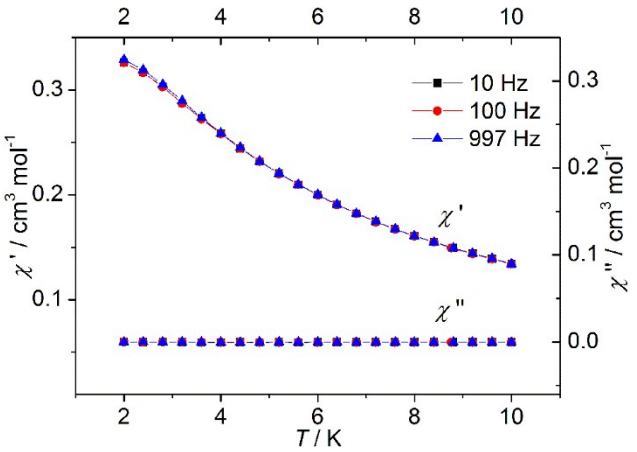


Fig. S25 Temperature-dependent ac magnetic susceptibilities of **2** under different frequencies with a zero DC field and an oscillating field of 2.5 Oe. Solid lines are guides for the eye.

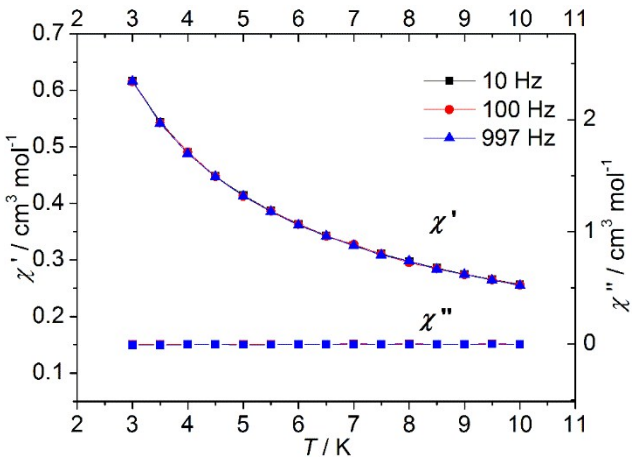


Fig. S26 Temperature-dependent ac magnetic susceptibilities of **3** under different frequencies with a zero DC field and an oscillating field of 2.5 Oe. Solid lines are guides for the eye.

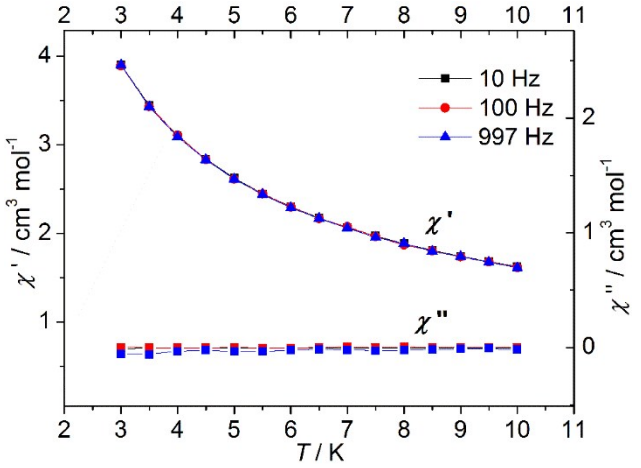


Fig. S27 Temperature-dependent ac magnetic susceptibilities of **4** under different frequencies with a zero DC field and an oscillating field of 2.5 Oe. Solid lines are guides for the eye.

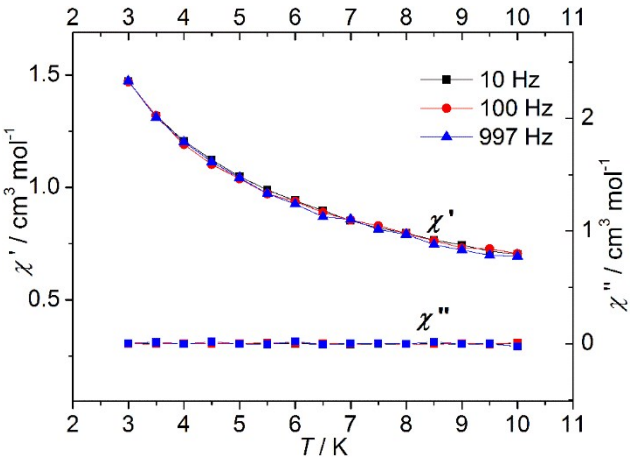


Fig. S28 Temperature-dependent ac magnetic susceptibilities of **5** under different frequencies with a zero DC field and an oscillating field of 2.5 Oe. Solid lines are guides for the eye.