

Supporting Information

Solvent Controlled Assembly of Four

Mn(II)-2,5-Thiophenedicarboxylate Frameworks with

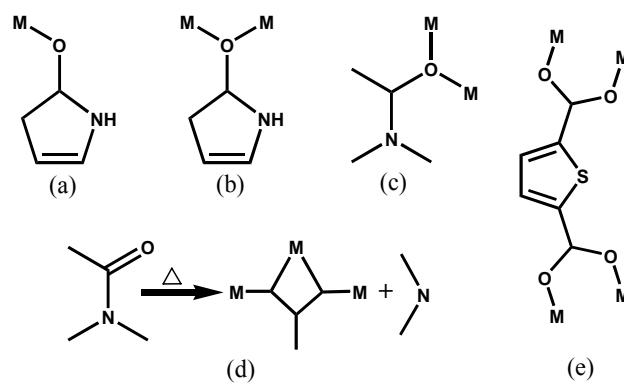
Rod-packing Architectures and Magnetic Properties

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Scheme S1. The coordination modes of the solvents (a-d) in **1-4** and THB ligands in **1-4** all adopt the same $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_4$ tetradentate coordination mode (e).

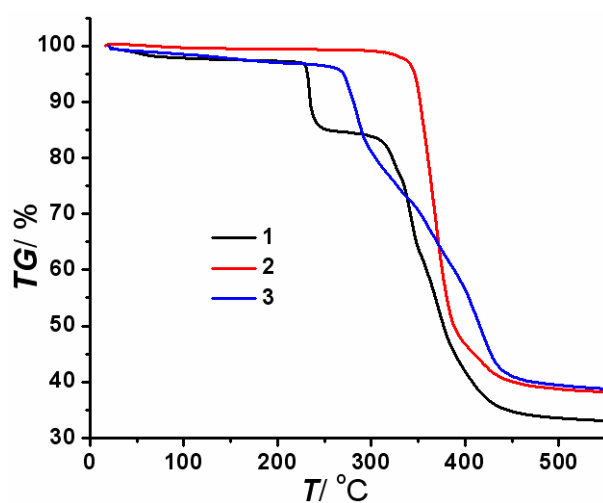


Figure S1. TG plots of compounds **1-3**.

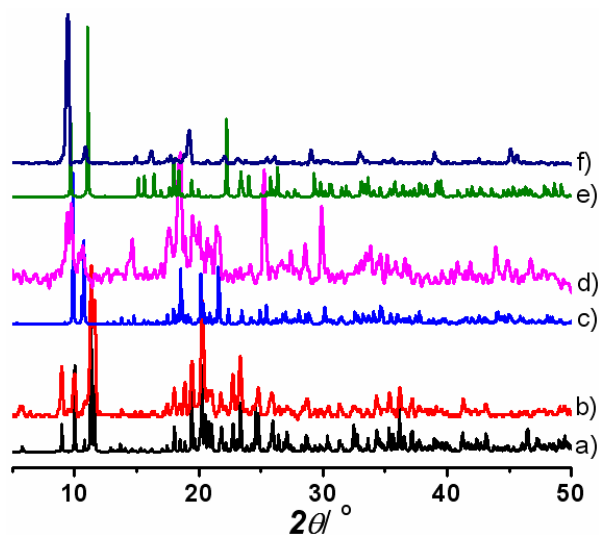


Figure S2. Powder XRD patterns: (a) simulated one of **1**, (b) as-synthesized **1**, (c) simulated one of **2**, (d) as-synthesized **2**, (e) simulated one of **3**, (f) as-synthesized **3**.

Table S1 Selected bond lengths (Å) and angles (°) for **1**

Mn1-O11#1	2.104(3)	O11#1-Mn1-O8	86.44(13)	O4#3-Mn1-O5	95.41(13)
Mn1-O8	2.144(4)	O11#1-Mn1-O3#2	85.41(13)	O2-Mn1-O5	92.34(14)
Mn1-O3#2	2.176(3)	O8-Mn1-O3#2	92.65(14)	O7-Mn2-O10#2	96.54(13)
Mn1-O4#3	2.193(3)	O11#1-Mn1-O4#3	175.95(12)	O7-Mn2-O6	100.47(13)
Mn1-O2	2.192(3)	O8-Mn1-O4#3	91.67(13)	O10#2-Mn2-O6	92.68(14)
Mn1-O5	2.222(4)	O3#2-Mn1-O4#3	91.11(12)	O7-Mn2-O9#3	103.40(12)
Mn2-O7	2.102(3)	O11#1-Mn1-O2	98.45(14)	O10#2-Mn2-O9#3	89.55(13)
Mn2-O10#2	2.133(3)	O8-Mn1-O2	83.94(14)	O6-Mn2-O9#3	155.61(13)
Mn2-O6	2.138(3)	O3#2-Mn1-O2	174.65(13)	O7-Mn2-O1	92.86(13)
Mn2-O9#3	2.197(3)	O4#3-Mn1-O2	84.90(13)	O10#2-Mn2-O1	170.25(12)
Mn2-O1	2.201(4)	O11#1-Mn1-O5	86.77(14)	O6-Mn2-O1	88.16(14)
Mn2-O4#3	2.488(3)	O8-Mn1-O5	171.69(14)	O9#3-Mn2-O1	85.73(13)
		O7-Mn2-O4#3	159.18(12)	O9#3-Mn2-O4#3	55.87(11)
		O10#2-Mn2-O4#3	82.52(12)	O1-Mn2-O4#3	87.78(12)
		O6-Mn2-O4#3	100.35(12)	Mn1#4-O4-Mn2#4	108.08(12)

Symmetry transformations used to generate equivalent atoms: #1 $x+1,y,z$; #2 $-x,-y+1,-z+1$; #3 $x,y-1,z$; #4 $x,y+1,z$.

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

Mn(1)-O(12)	2.122(3)	O(12)-Mn(1)-O(7)#1	87.46(13)	O(3)-Mn(2)-O(1)	88.62(14)
Mn(1)-O(7)#1	2.124(3)	O(12)-Mn(1)-O(6)#2	85.06(13)	O(4)#3-Mn(2)-O(11)	93.37(13)
Mn(1)-O(6)#2	2.127(3)	O(7)#1-Mn(1)-O(6)#2	101.96(13)	O(3)-Mn(2)-O(11)	87.20(13)
Mn(1)-O(5)	2.169(3)	O(12)-Mn(1)-O(5)	174.98(14)	O(1)-Mn(2)-O(11)	111.09(13)
Mn(1)-O(14)	2.253(3)	O(7)#1-Mn(1)-O(5)	97.49(13)	O(4)#3-Mn(2)-O(14)	86.46(12)
Mn(1)-O(15)	2.282(3)	O(6)#2-Mn(1)-O(5)	93.03(13)	O(3)-Mn(2)-O(14)	92.00(12)
Mn(2)-O(4)#3	2.080(3)	O(12)-Mn(1)-O(14)	86.31(12)	O(1)-Mn(2)-O(14)	89.62(12)
Mn(2)-O(3)	2.097(3)	O(7)#1-Mn(1)-O(14)	165.11(11)	O(11)-Mn(2)-O(14)	159.24(11)
Mn(2)-O(1)	2.152(3)	O(6)#2-Mn(1)-O(14)	90.96(12)	O(4)#3-Mn(2)-O(15)	87.51(13)

Mn(2)-O(11)	2.154(3)	O(5)-Mn(1)-O(14)	89.08(12)	O(3)-Mn(2)-O(15)	89.68(12)
Mn(2)-O(14)	2.305(3)	O(12)-Mn(1)-O(15)	91.78(13)	O(1)-Mn(2)-O(15)	160.62(12)
Mn(2)-O(15)	2.349(3)	O(7)#1-Mn(1)-O(15)	93.38(12)	O(11)-Mn(2)-O(15)	88.10(11)
Mn(3)-O(2)	2.078(4)	O(6)#2-Mn(1)-O(15)	164.16(12)	O(14)-Mn(2)-O(15)	71.15(10)
Mn(3)-O(8)#3	2.084(3)	O(5)-Mn(1)-O(15)	88.81(13)	O(2)-Mn(3)-O(8)#3	108.26(15)
Mn(3)-O(13)#4	2.104(3)	O(14)-Mn(1)-O(15)	73.33(11)	O(2)-Mn(3)-O(13)#4	87.63(17)
Mn(3)-O(9)#5	2.137(3)	O(4)#3-Mn(2)-O(3)	177.11(14)	O(8)#3-Mn(3)-O(13)#4	99.32(14)
Mn(3)-O(10)	2.139(3)	O(4)#3-Mn(2)-O(1)	93.82(14)	O(2)-Mn(3)-O(9)#5	154.15(15)
		O(8)#3-Mn(3)-O(9)#5	97.58(13)	O(13)#4-Mn(3)-O(10)	152.40(14)
		O(13)#4-Mn(3)-O(9)#5	87.30(14)	O(9)#5-Mn(3)-O(10)	84.73(14)
		O(2)-Mn(3)-O(10)	88.14(17)	Mn(1)-O(14)-Mn(2)	101.55(11)
		O(8)#3-Mn(3)-O(10)	107.90(13)	Mn(1)-O(15)-Mn(2)	99.38(11)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z; #2 -x+1,-y+1,-z; #3 x,y-1,z; #4 -x+1,y-1/2,-z+1/2; #5 -x,y-1/2,-z+1/2.

Table S3 Selected bond lengths (Å) and angles (°) for **3**

Mn(1)-O(2)#1	2.126(4)	O(2)#1-Mn(1)-O(2)#2	82.0(2)	O(5)-Mn(2)-O(5)#4	180.00(18)
Mn(1)-O(2)#2	2.126(4)	O(2)#1-Mn(1)-O(3)#3	92.19(17)	O(5)-Mn(2)-O(4)#5	86.98(16)
Mn(1)-O(3)#3	2.160(4)	O(2)#2-Mn(1)-O(3)#3	174.14(17)	O(5)#4-Mn(2)-O(4)#5	93.02(16)
Mn(1)-O(3)	2.160(4)	O(2)#1-Mn(1)-O(3)	174.14(17)	O(5)-Mn(2)-O(4)#2	93.02(16)
Mn(1)-O(1)#3	2.276(4)	O(2)#2-Mn(1)-O(3)	92.19(17)	O(5)#4-Mn(2)-O(4)#2	86.98(16)
Mn(1)-O(1)	2.276(4)	O(3)#3-Mn(1)-O(3)	93.6(2)	O(4)#5-Mn(2)-O(4)#2	180.00(12)
Mn(2)-O(5)	2.126(4)	O(2)#1-Mn(1)-O(1)#3	92.63(15)	O(5)-Mn(2)-O(1)#3	88.03(14)
Mn(2)-O(5)#4	2.126(4)	O(2)#2-Mn(1)-O(1)#3	91.95(15)	O(5)#4-Mn(2)-O(1)#3	91.97(14)
Mn(2)-O(4)#5	2.167(4)	O(3)#3-Mn(1)-O(1)#3	87.59(14)	O(4)#5-Mn(2)-O(1)#3	89.96(15)
Mn(2)-O(4)#2	2.167(4)	O(3)-Mn(1)-O(1)#3	88.25(15)	O(4)#2-Mn(2)-O(1)#3	90.04(15)
Mn(2)-O(1)#3	2.290(4)	O(2)#1-Mn(1)-O(1)	91.95(15)	O(5)-Mn(2)-O(1)#6	91.97(14)
Mn(2)-O(1)#6	2.290(4)	O(2)#2-Mn(1)-O(1)	92.63(15)	O(5)#4-Mn(2)-O(1)#6	88.03(14)
		O(3)#3-Mn(1)-O(1)	88.25(15)	O(4)#5-Mn(2)-O(1)#6	90.04(15)

		O(3)-Mn(1)-O(1)	87.59(15)	O(4)#2-Mn(2)-O(1)#6	89.96(15)
		O(1)#3-Mn(1)-O(1)	173.9(2)	Mn(1)-O(1)-Mn(2)#3	112.73(15)

Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, y+1/2, z$; #2 $-x+1/2, y+1/2, -z+1/2$; #3 $-x+1, y, -z+1/2$; #4 $-x+1/2, -y+1/2, -z$; #5 $x, -y, z-1/2$; #6 $x-1/2, -y+1/2, z-1/2$.

Table S4 Selected bond lengths (Å) and angles (°) for **4**

Mn(1)-O(5')#1	2.122(16)	O(5')#1-Mn(1)-O(5')#2	114.0(9)	O(5')#1-Mn(1)-O(3)#1	94.8(5)
Mn(1)-O(5')#2	2.122(16)	O(5')#1-Mn(1)-O(2)#3	93.7(6)	O(5')#2-Mn(1)-O(3)#1	151.0(5)
Mn(1)-O(2)#3	2.148(7)	O(5')#2-Mn(1)-O(2)#3	81.2(6)	O(2)#3-Mn(1)-O(3)#1	101.0(3)
Mn(1)-O(2)	2.148(7)	O(5')#1-Mn(1)-O(2)	81.2(6)	O(2)-Mn(1)-O(3)#1	87.2(3)
Mn(1)-O(5)#2	2.153(14)	O(5')#2-Mn(1)-O(2)	93.7(6)	O(5)#2-Mn(1)-O(3)#1	140.0(4)
Mn(1)-O(5)#1	2.153(14)	O(2)#3-Mn(1)-O(2)	170.8(4)	O(5)#1-Mn(1)-O(3)#1	87.7(4)
Mn(1)-O(3)#1	2.301(7)	O(5')#1-Mn(1)-O(5')#2	121.1(6)	O(5')#1-Mn(1)-O(3)#2	151.0(5)
Mn(1)-O(3)#2	2.301(7)	O(5')#2-Mn(1)-O(5')#2	15.2(5)	O(5')#2-Mn(1)-O(3)#2	94.8(5)
Mn(2)-O(4)	2.139(8)	O(2)#3-Mn(1)-O(5')#2	94.2(4)	O(2)#3-Mn(1)-O(3)#2	87.2(3)
Mn(2)-O(4)#1	2.139(8)	O(2)-Mn(1)-O(5')#2	81.9(4)	O(2)-Mn(1)-O(3)#2	101.0(3)
Mn(2)-O(1)#1	2.148(8)	O(5')#1-Mn(1)-O(5')#1	15.2(5)	O(5)#2-Mn(1)-O(3)#2	87.7(4)
Mn(2)-O(1)	2.148(8)	O(5')#2-Mn(1)-O(5')#1	121.1(6)	O(5)#1-Mn(1)-O(3)#2	140.0(4)
Mn(2)-O(3)	2.173(7)	O(2)#3-Mn(1)-O(5')#1	81.9(4)	O(3)#1-Mn(1)-O(3)#2	56.7(4)
Mn(2)-O(3)#1	2.173(7)	O(2)-Mn(1)-O(5')#1	94.2(4)	O(4)-Mn(2)-O(4)#1	180.0(4)
		O(5)#2-Mn(1)-O(5')#1	131.3(7)	O(4)-Mn(2)-O(1)#1	90.1(2)
		O(1)#1-Mn(2)-O(1)	180.0(3)	O(4)-Mn(2)-O(3)#1	91.2(2)
		O(4)-Mn(2)-O(3)	88.8(2)	O(4)#1-Mn(2)-O(3)#1	88.8(2)
		O(4)#1-Mn(2)-O(3)	91.2(2)	O(1)#1-Mn(2)-O(3)#1	85.3(2)
		O(1)#1-Mn(2)-O(3)	94.7(2)	O(1)-Mn(2)-O(3)#1	94.7(2)
		O(1)-Mn(2)-O(3)	85.3(2)	O(3)-Mn(2)-O(3)#1	180.0(3)
				Mn(2)-O(3)-Mn(1)#1	115.6(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z$; #2

$y, x, z - 1/2; \#3 -y+1, -x+1, -z-1/2.$