Electronic Supplementary Information for:

Two-Step Relaxation in the 3D Spin-Canted Manganese Phosphate with High P-O-Mn Connectivity

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$[Mn^{II}_7(HPO_4)_4(PO_4)_2]_n$ (**1**): $MnSO_4 \cdot H_2O$ (0.5 mmol), morpholine (0.3 mmol), and 85% phosphoric acid (0.1 mmol) in 10 ml water were mixed together and stirred for 30 min at the ambient temperature. The pH value of the mixture was adjusted to be 4.75 using the additional 85% phosphoric acid (ca. 0.1 mmol) during stirring. Then the consequent suspension was moved into the Teflon-lined steel autoclave, heated at 433 K for 72 h, and then slowly cooled to the ambient temperature. X-ray quality colorless needlelike crystals were washed using distilled water and collected by filtration. After the reaction, the pH value of the residue solution was down to 3.0. Yield: 60 % (based on metal ions).

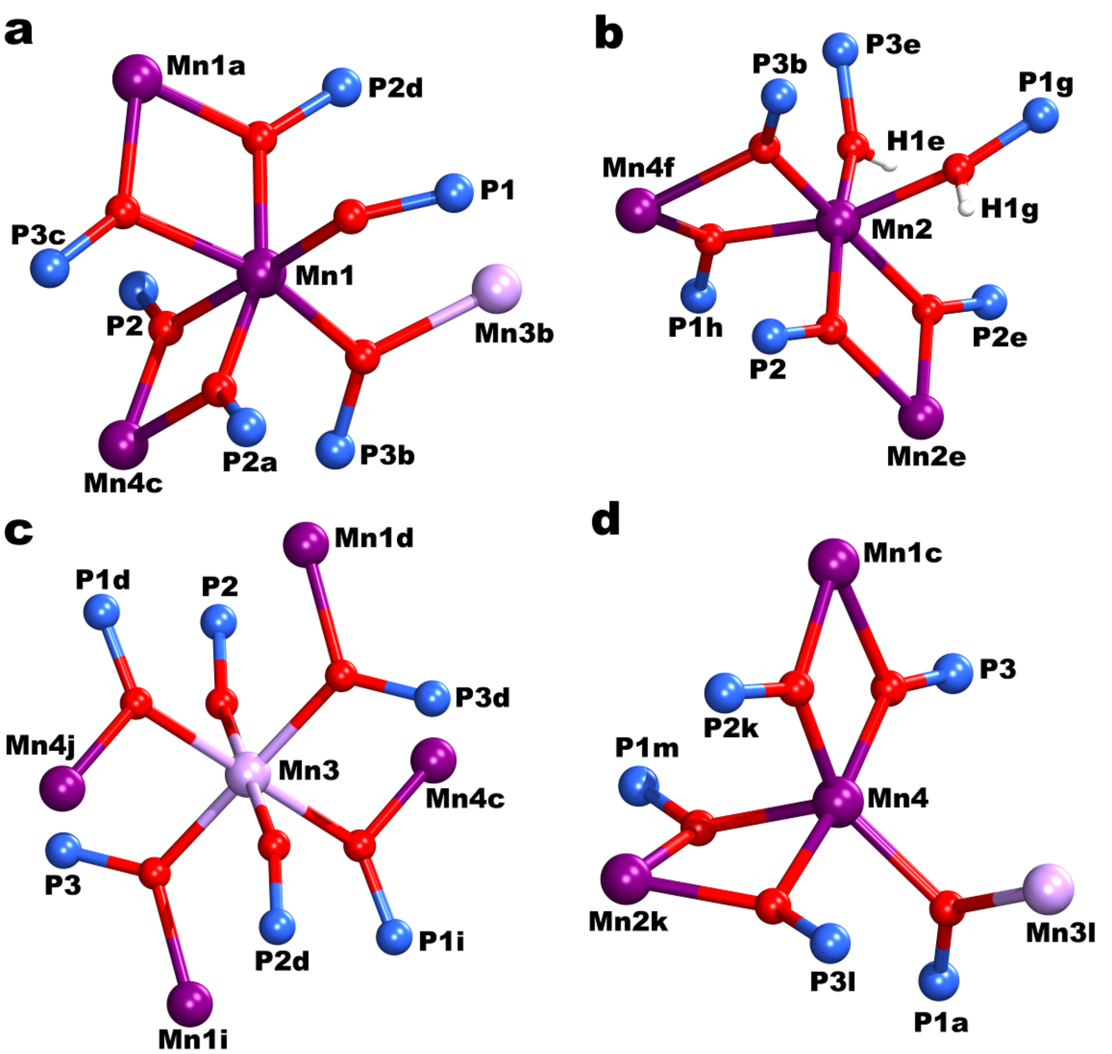

Fig. S1. The coordination geometries of manganese ions in complex 1. The plots of the coordination environment of (a) Mn(1), (b) Mn(2), (c) Mn(3), and (d) Mn(4) ions, respectively (purple, Mn(1), Mn(2), and Mn(4) atoms; lavender, the Mn(3) atom; red, oxygen atoms; blue, phosphorus atoms; white, hydrogen atoms). a, b, c, d, e, f, g, h, i, j, k, l, and m represent the symmetry transformations used to generate equivalent atoms: 1-x, 2-y, -z; x, 1+y, z; 1-x, 1-y, -z; 2-x, 2-y, -z; 2-x, 2-y, 1-z; 1+x, 1+y, z; x, y, 1+z; 1+x, y, 1+z; x, -1+y, z; 1+x, y, z; -1+x, -1+y, z; -1+x, y, z and x, -1+y, 1+z respectively.

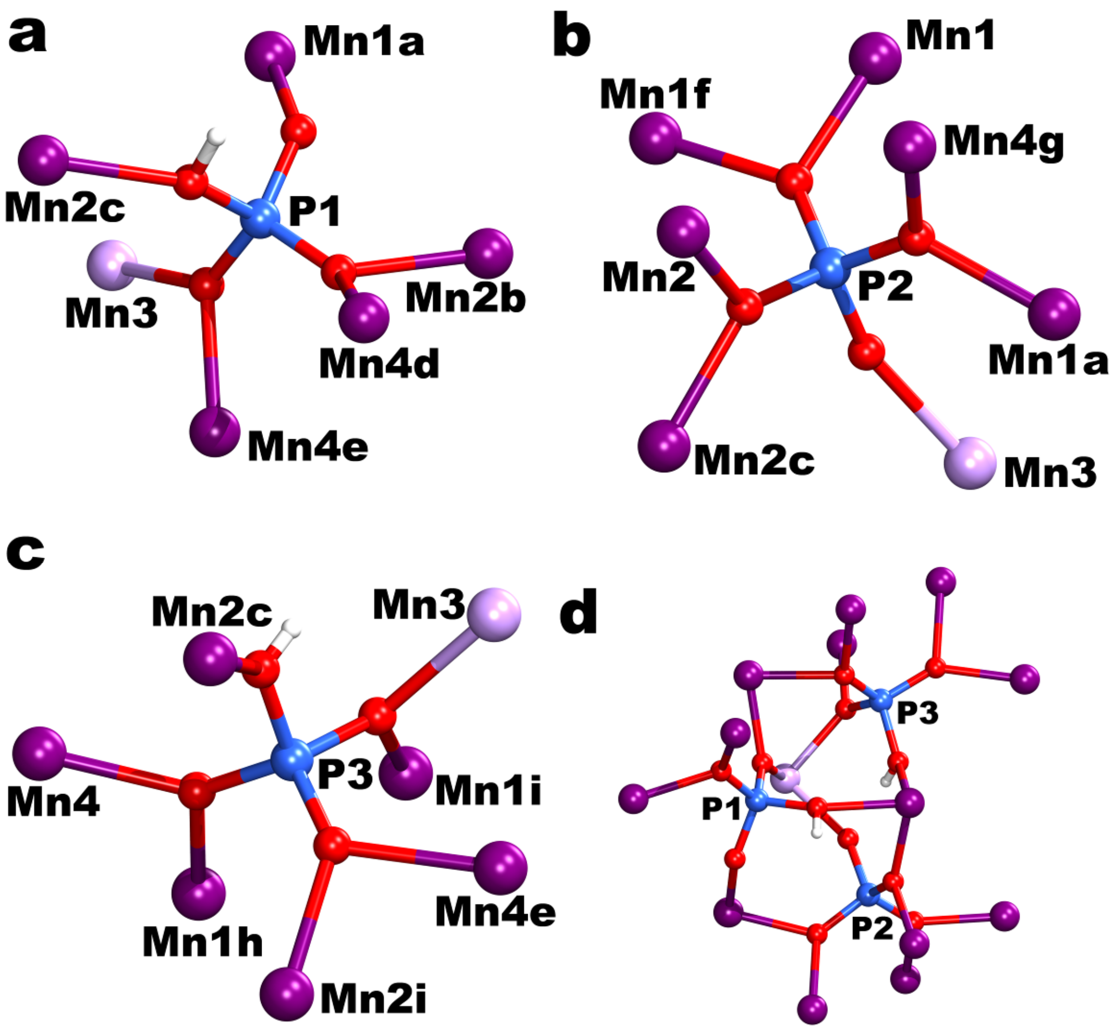

Fig. S2. The connection modes of the phosphate ions. (a) The P1 containing phosphate ion connects Mn and H atoms in $\eta^1:\eta^2:\eta^2:\eta^2:\mu_7$ mode. (b) The P2 containing phosphate ion connects Mn atoms in $\eta^1:\eta^2:\eta^2:\eta^2:\mu_7$ mode. (c) The P3 containing phosphate ion connects Mn and H atoms in $\eta^2:\eta^2:\eta^2:\eta^2:\mu_8$ mode. (d) The overall manganese phosphate connectivity (a, b, c, d, e, f, g, h and I represent the symmetry transformations used to generate equivalent atoms: 2-x, 2-y, -z; 3-x, 2-y, 1-z; 2-x, 2-y, 1-z; 2-x, 1-y, 1-z; 1+x, y, z; 1-x, 2-y, -z; 1+x, 1+y, z; 1-x, 1-y, -z and x, -1+y, z respectively.).

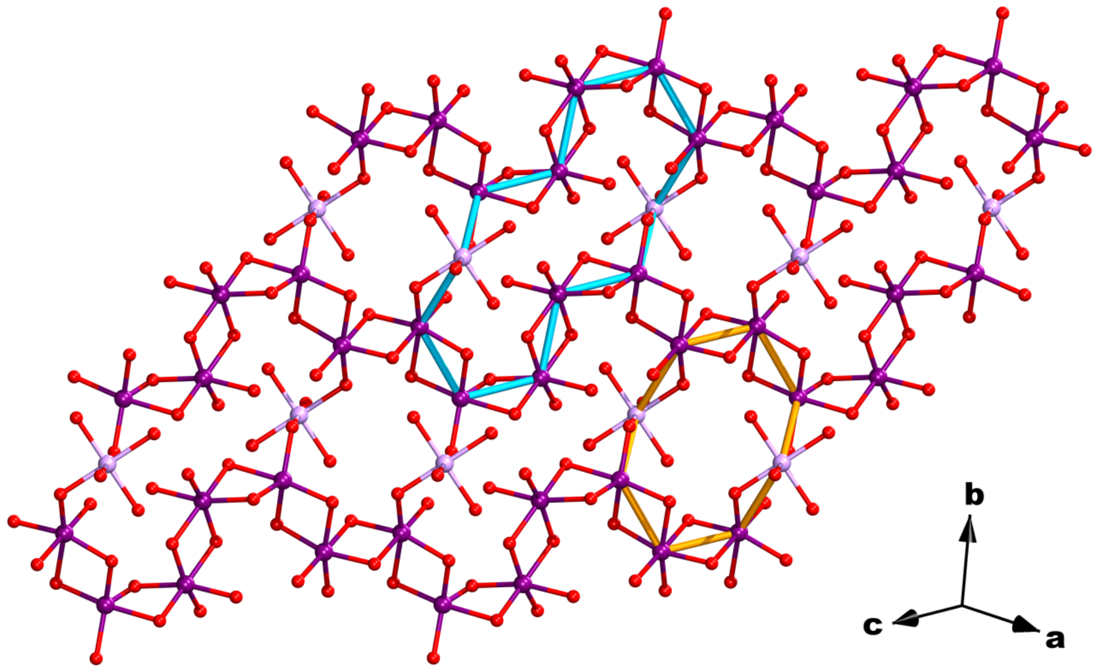

Fig. S3. The 2D layer in complex 1. The representation of the 2D layer consists of 12-membered (blue) and 8-membered (orange) rings.

Table S1. Selected bond distances (Å) and bond angles (°) for complex 1.

Mn(1)-O(1)	2.161(3)	O(8)#2-Mn(1)-O(11)#4	78.23(10)
Mn(1)-O(5)#1	2.161(3)	O(9)#3-Mn(1)-O(11)#4	162.18(9)
Mn(1)-O(5)	2.162(3)	O(1)-Mn(1)-Mn(1)#1	135.84(8)
Mn(1)-O(8)#2	2.166(3)	O(5)#1-Mn(1)-Mn(1)#1	42.68(7)
Mn(1)-O(9)#3	2.177(3)	O(5)-Mn(1)-Mn(1)#1	42.67(7)
Mn(1)-O(11)#4	2.312(3)	O(8)#2-Mn(1)-Mn(1)#1	130.52(7)
Mn(1)-Mn(1)#1	3.178(1)	O(9)#3-Mn(1)-Mn(1)#1	87.06(7)
Mn(2)-O(12)#3	2.137(3)	O(11)#4-Mn(1)-Mn(1)#1	77.47(7)
Mn(2)-O(6)	2.143(3)	O(12)#3-Mn(2)-O(6)	90.55(10)
Mn(2)-O(10)#5	2.151(3)	O(12)#3-Mn(2)-O(10)#5	106.74(11)
Mn(2)-O(6)#5	2.191(3)	O(6)-Mn(2)-O(10)#5	161.23(11)
Mn(2)-O(2)#6	2.201(3)	O(12)#3-Mn(2)-O(6)#5	165.50(11)
Mn(2)-O(3)#7	2.202(3)	O(6)-Mn(2)-O(6)#5	78.14(11)
Mn(3)-O(7)	2.191(3)	O(10)#5-Mn(2)-O(6)#5	85.80(11)
Mn(3)-O(7)#8	2.191(3)	O(12)#3-Mn(2)-O(2)#6	92.59(10)
Mn(3)-O(9)	2.196(2)	O(6)-Mn(2)-O(2)#6	97.50(11)
Mn(3)-O(9)#8	2.196(2)	O(10)#5-Mn(2)-O(2)#6	89.12(12)
Mn(3)-O(4)#2	2.259(3)	O(6)#5-Mn(2)-O(2)#6	80.09(10)

Mn(3)-O(4)#9	2.259(3)	O(12)#3-Mn(2)-O(3)#7	79.19(10)
Mn(4)-O(8)#10	2.107(3)	O(6)-Mn(2)-O(3)#7	94.99(10)
Mn(4)-O(4)#1	2.128(3)	O(10)#5-Mn(2)-O(3)#7	81.51(11)
Mn(4)-O(11)	2.139(3)	O(6)#5-Mn(2)-O(3)#7	110.51(10)
Mn(4)-O(3)#11	2.146(3)	O(2)#6-Mn(2)-O(3)#7	165.11(11)
Mn(4)-O(12)#12	2.265(3)	O(7)-Mn(3)-O(7)#8	180
P(1)-O(4)	1.525(3)	O(7)-Mn(3)-O(9)	90.58(10)
P(1)-O(1)	1.525(3)	O(7)#8-Mn(3)-O(9)	89.42(10)
P(1)-O(3)	1.530(3)	O(7)-Mn(3)-O(9)#8	89.42(10)
P(1)-O(2)	1.577(3)	O(7)#8-Mn(3)-O(9)#8	90.58(10)
P(2)-O(5)	1.527(3)	O(9)-Mn(3)-O(9)#8	180.00(12)
P(2)-O(6)	1.536(3)	O(7)-Mn(3)-O(4)#2	87.03(10)
P(2)-O(8)	1.544(3)	O(7)#8-Mn(3)-O(4)#2	92.97(10)
P(2)-O(7)	1.553(3)	O(9)-Mn(3)-O(4)#2	86.53(9)
P(3)-O(11)	1.528(3)	O(9)#8-Mn(3)-O(4)#2	93.47(9)
P(3)-O(12)	1.535(3)	O(7)-Mn(3)-O(4)#9	92.97(10)
P(3)-O(9)	1.545(3)	O(7)#8-Mn(3)-O(4)#9	87.03(10)
P(3)-O(10)	1.574(3)	O(9)-Mn(3)-O(4)#9	93.47(9)
O(1)-Mn(1)-O(5)#1	93.23(10)	O(9)#8-Mn(3)-O(4)#9	86.53(9)
O(1)-Mn(1)-O(5)	176.93(11)	O(4)#2-Mn(3)-O(4)#9	180
O(5)#1-Mn(1)-O(5)	85.35(10)	O(8)#10-Mn(4)-O(4)#1	137.87(11)
O(1)-Mn(1)-O(8)#2	89.71(10)	O(8)#10-Mn(4)-O(11)	83.52(10)
O(5)#1-Mn(1)-O(8)#2	160.48(11)	O(4)#1-Mn(4)-O(11)	105.10(10)
O(5)-Mn(1)-O(8)#2	90.74(10)	O(8)#10-Mn(4)-O(3)#11	96.22(11)
O(1)-Mn(1)-O(9)#3	99.54(10)	O(4)#1-Mn(4)-O(3)#11	121.24(11)
O(5)#1-Mn(1)-O(9)#3	92.41(10)	O(11)-Mn(4)-O(3)#11	101.29(10)
O(5)-Mn(1)-O(9)#3	83.25(10)	O(8)#10-Mn(4)-O(12)#12	88.62(10)
O(8)#2-Mn(1)-O(9)#3	106.14(10)	O(4)#1-Mn(4)-O(12)#12	82.05(10)
O(1)-Mn(1)-O(11)#4	97.73(10)	O(11)-Mn(4)-O(12)#12	171.91(10)
O(5)#1-Mn(1)-O(11)#4	82.25(10)	O(3)#11-Mn(4)-O(12)#12	77.62(10)
O(5)-Mn(1)-O(11)#4	79.39(10)		

#1-#12 represent the symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+2, -z; #2 -x+2, -y+2, -z; #3 x, y+1, z; #4 -x+1, -y+1, -z; #5 -x+2, -y+2, -z+1; #6 x, y, z+1; #7 x+1, y, z+1; #8 -x+2, -y+1, -z; #9 x, y-1, z; #10 x-1, y-1, z; #11 x, y-1, z+1; #12 x-1, y, z.

Magnetic Measurement.

DC and AC magnetic susceptibility measurements on polycrystalline samples of complex **1** were carried out with Quantum Design SQUID

MPMS XL-7 instruments.

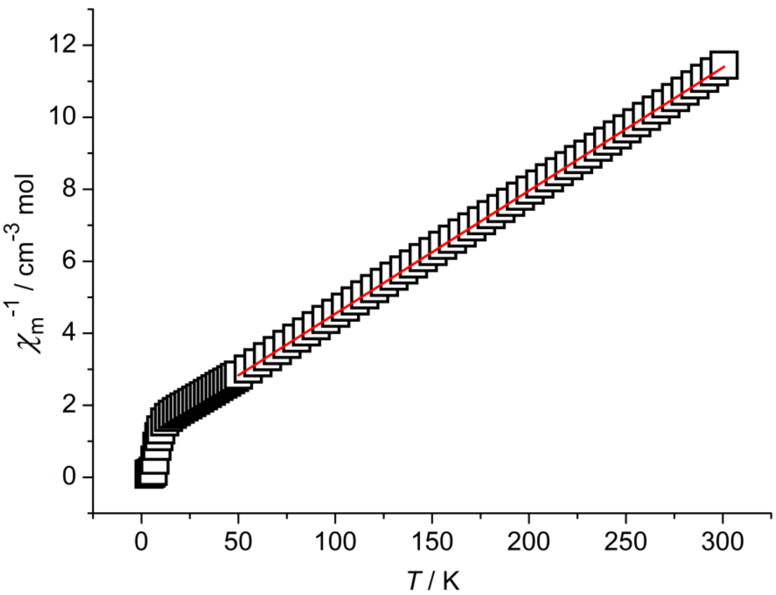

Fig. S4. Reciprocal magnetic susceptibility versus temperature of complex 1. Plot of χ_m^{-1} versus T for polycrystalline samples of **1** in an applied field of 1 kOe from 2 to 300 K. (red solid line corresponds to the best theoretical fitting resulting in C = 29.25 cm^3 K mol^{-1} and θ = -32.83 K)

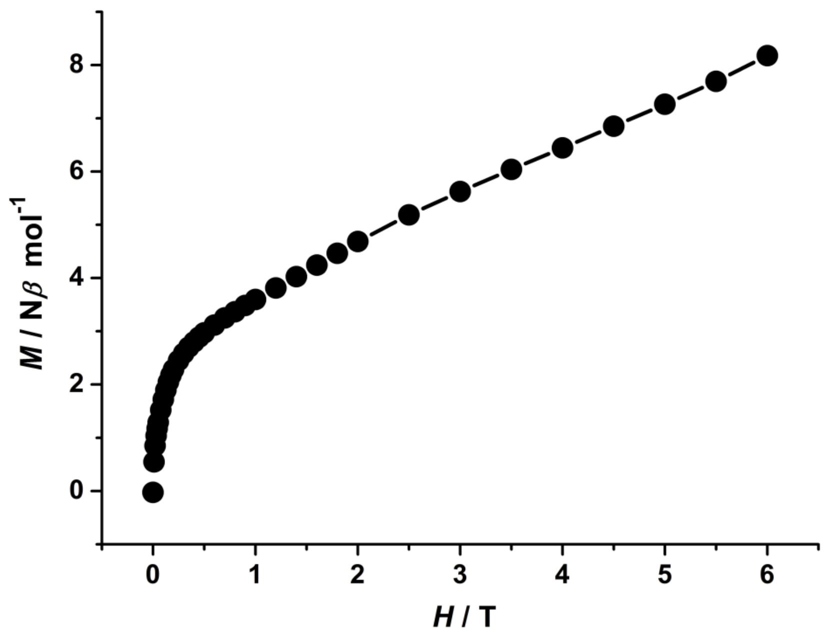

Fig. S5. Field dependence of magnetization of 1. The plot of M-H measured at 2 K from 0 to 6 T.

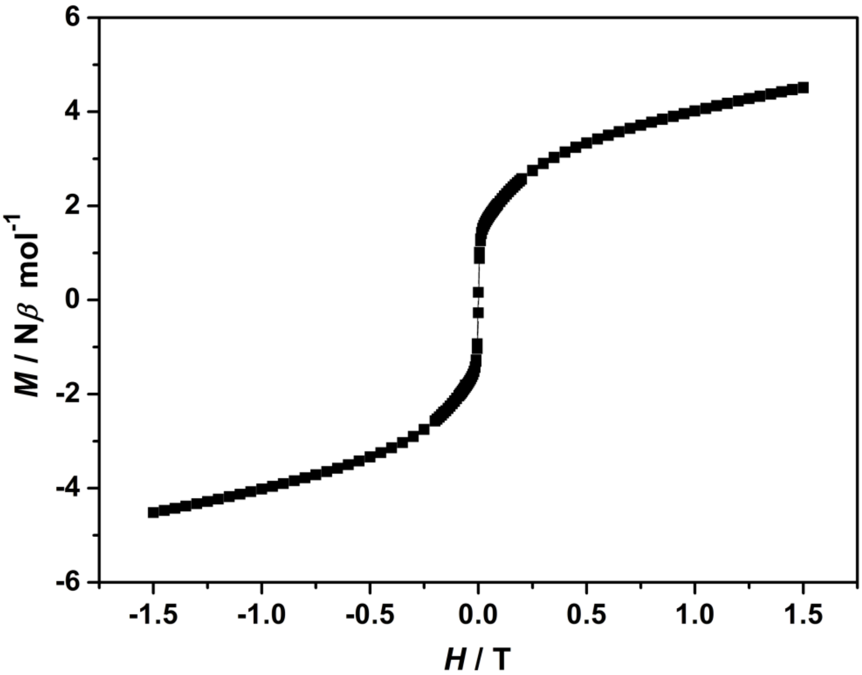

Fig. S6. The *M* versus *H* plot of 1. The plot of field dependent magnetization was measured at 2 K from -1.5 to 1.5 T.