Supplementary material (ESI) for *Chemical Communications*

For paper (Ref. B314221C) entitled "**$Mn_3(HCOO)_6$: a 3D porous magnet of diamond framework with nodes of Mn-centered $MnMn_4$ tetrahedron and guest-modulated ordering temperature**" by Z. M. Wang, *et al.*

Satisfied elemental analysis results were obtained for **1-7**. **1**: Calc: C, 17.34; H, 2.49%. Found: C, 17.20, H, 2.32%. **2**: Calc: C, 16.57, H, 1.39%. Found: C, 16.40, H, 1.59%. **3**: Calc: C, 21.24, H, 2.38%. Found: C, 21.38, H, 2.42%. **4**: Calc: C, 21.28, H, 2.58, N, 2.76%. Found: C, 21.14, H, 2.60, N, 2.69%. **5**: Calc: C, 23.88, H, 2.00%. Found: C, 23.25, H, 1.97%. **6**: Calc: C, 28.09, H, 2.36%. Found: C, 27.01, H, 2.43%. **7**: Calc: C, 10.99, H, 0.92%. Found: C, 10.97, H, 1.03%.

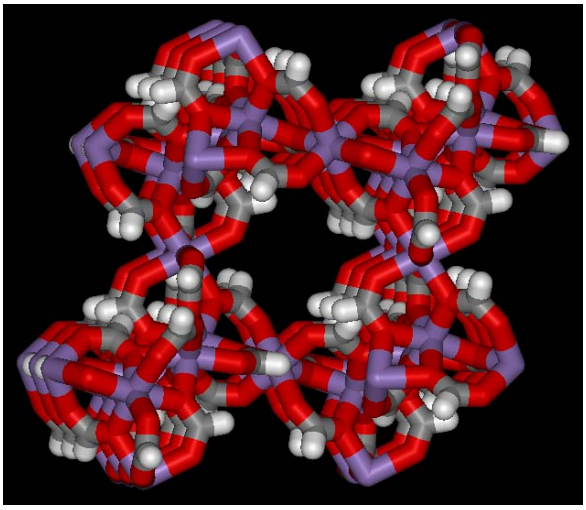

Fig. S1. One channel showing the structural details. Colour scheme: C gray, H white, O red, and Mn purple.

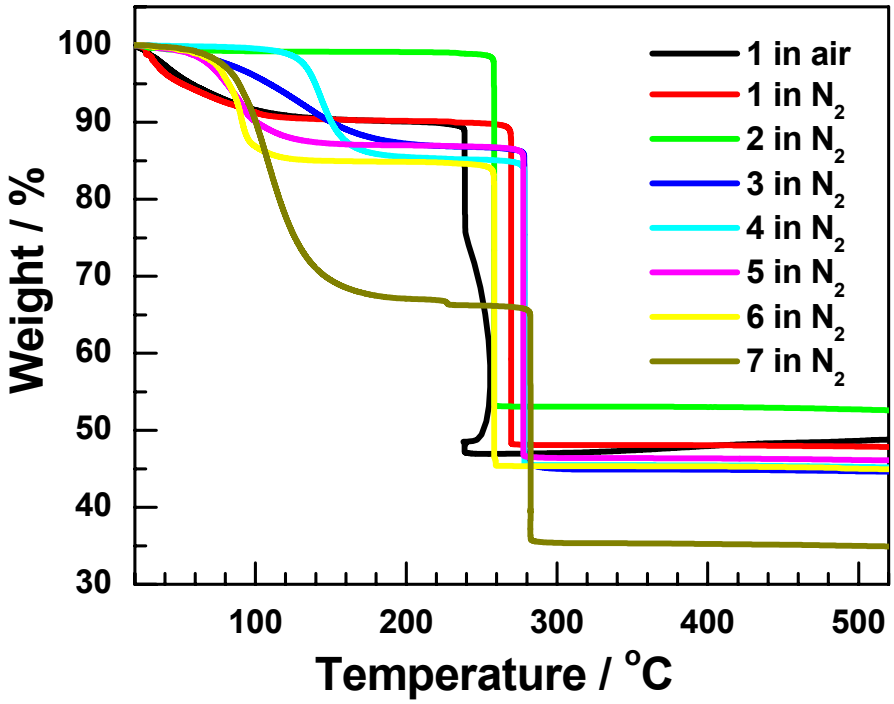

Fig. S2. TGA results for **1**-**7**. The framework of **1** is also stable up to 250 °C in air. When the framework decomposed around this temperature in air atmosphere, rapidly burning might cause the excessive overshoot of temperature during TGA measurement (black line) and this was avoided when the measurements were carried in N_2 atmosphere. Experimental weight lost values (%) for guest lost, with calculated values in parentheses, were 9.9(10.3), 0.8(0.0), 12.2(11.8), 14.4(14.5), 13.0(13.5), 15.1(15.2) and 33.8(33.7) for **1**, **2**, **3**, **4**, **5**, **6** and **7**, respectively. The values of weight lost for framework decomposition are within 2% of the calculated values based on Mn_2O_3 residue.

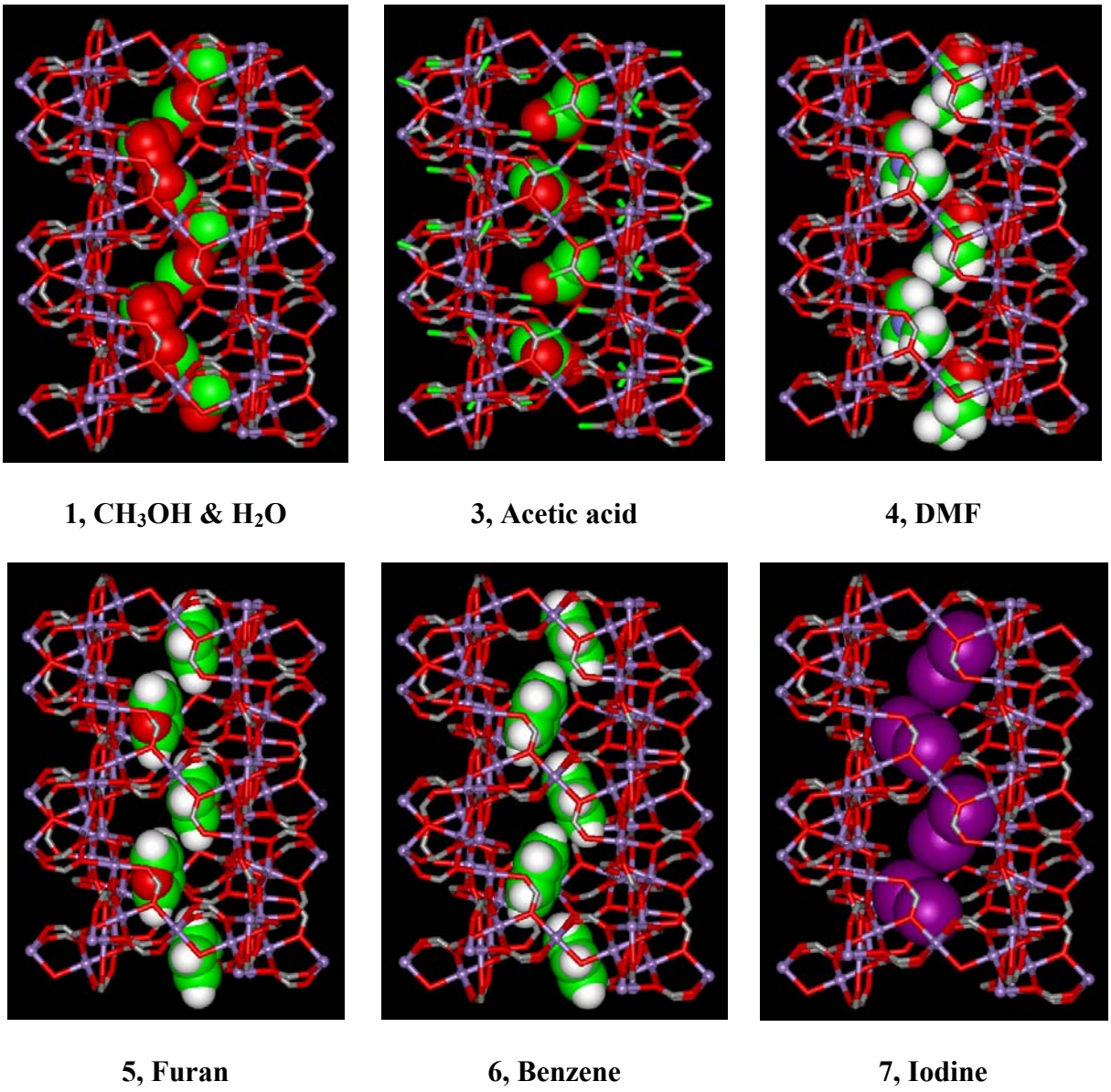

Fig. S3. One channel with occupied guest molecules in **1**, **3-7**, with frameworks in ball-stick model and same framework orientation and guests highlighted in space filling model. Colour scheme for frameworks is the same as **Fig. S1**, and for guest: C green, H white, O red, N blue, and I purple. H atoms of frameworks are omitted, and green sticks in the framework of **3** are methyl C of CH_3COO groups that random replace HCOO groups. In **1**, the guests are severely disordered.

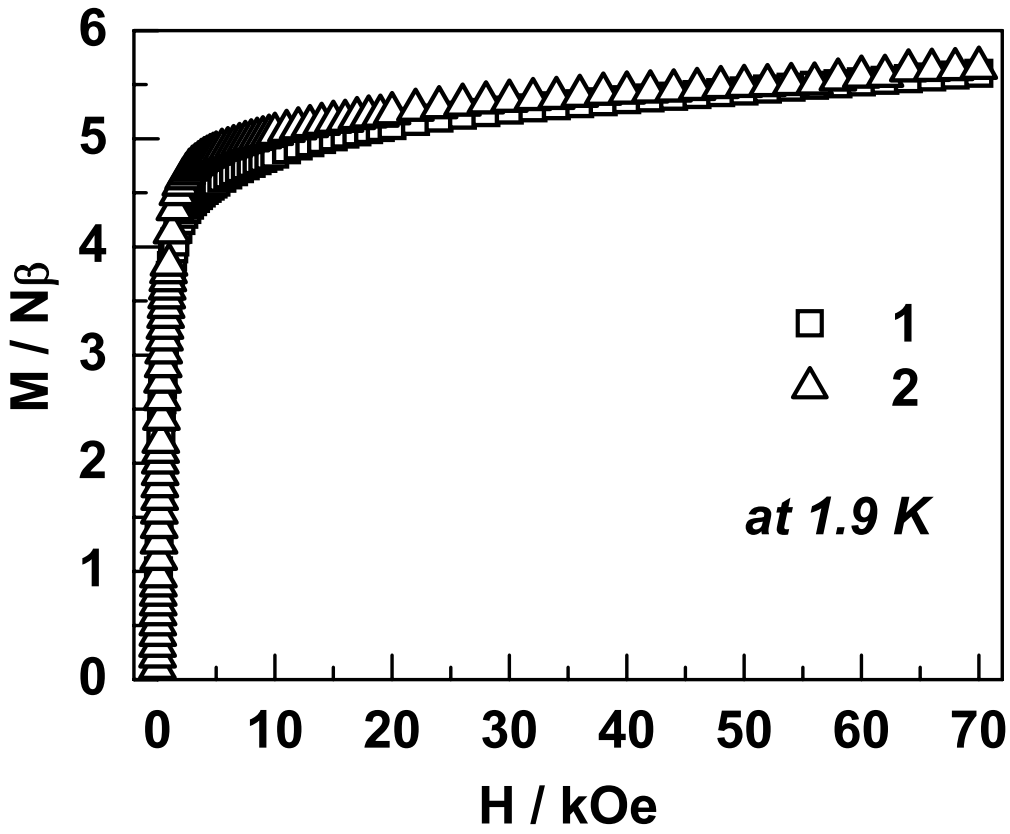

Fig. S4. Isothermal field dependent magnetization at 1.9 K for **1** and **2**. Magnetizations at 70 kOe are 5.61, 5.66 Nβ for **1** and **2**, respectively.

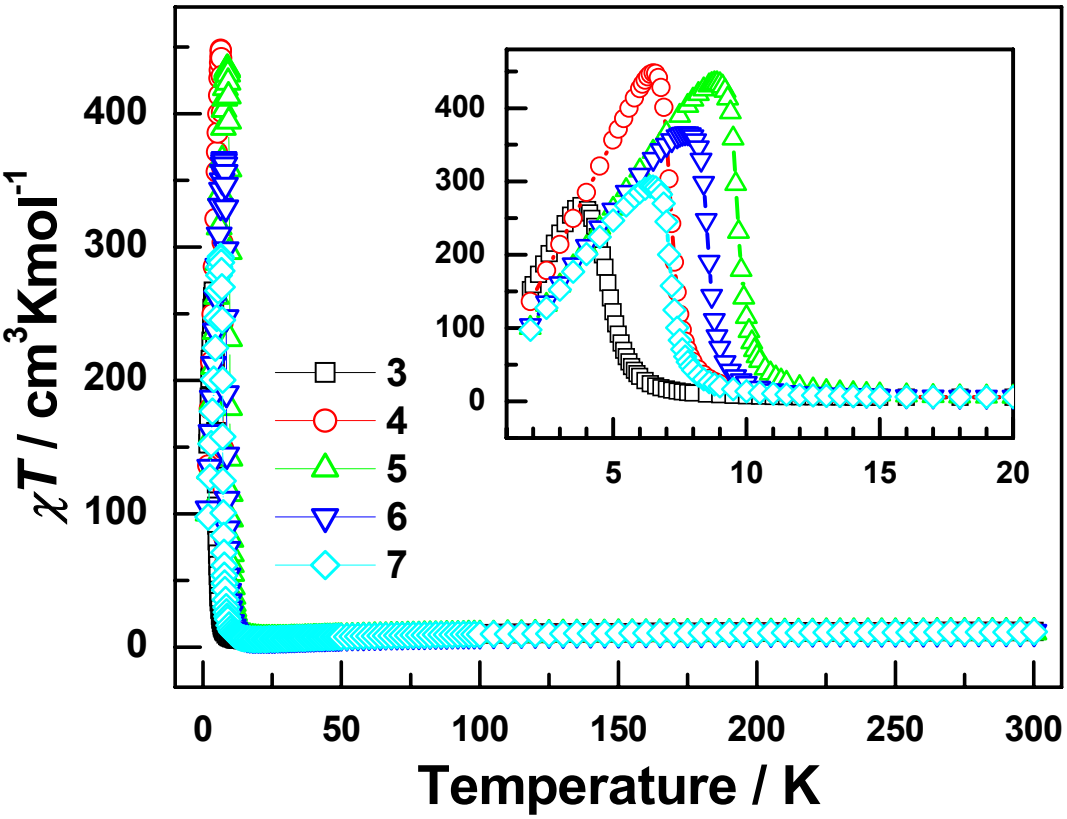

Fig. S5. The temperature dependence of the magnetic susceptibility of **3-7** in an applied field of 100 Oe, inset: low temperature region. The data above 40 K fit Curie-Weiss law with C=12.94, 12.83, 12.69, 12.26 and 12.41 cm^3Kmol^{-1}; and θ= -30.1, -33.5, -36.7, -27.0, and -29.4 K for **3**, **4**, **5**, **6** and **7**, respectively.

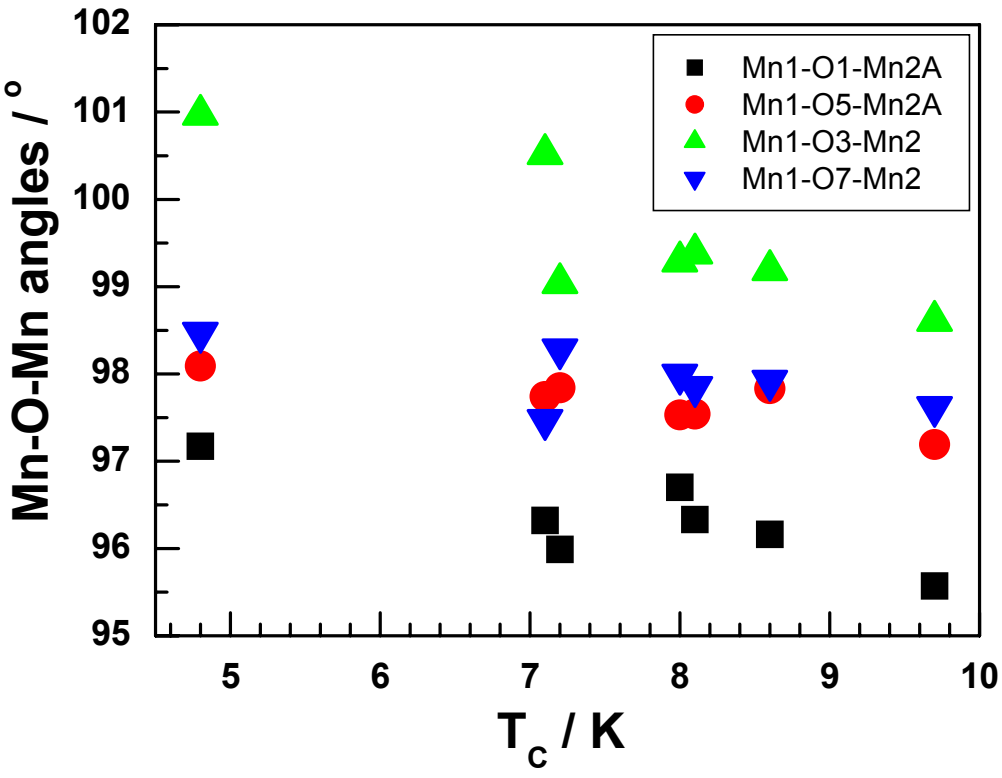

Fig. S6. The plot of the important Mn1-O-Mn2 bond angles *vs* T_C for compounds **1-7**, from left to right: **3**, **7**, **4**, **2**, **1**, **6**, and **5** according to the increase of T_C. The Mn1-O-Mn2 bond angles show the trend described in the manuscript.

Table S1. The important Mn-O-Mn bond angles (°) and T_C (K) for compounds **1-7**

Compd.	T_c	angle1	angle5	angle3	angle7	angle9	angle11
1	8.1	96.33	97.54	99.38	97.85	113.06	110.38
2	8.0	96.70	97.53	99.29	97.99	113.81	110.63
3	4.8	97.17	98.09	100.97	98.47	113.28	110.72
4	7.2	95.99	97.84	99.04	98.28	113.14	110.38
5	9.7	95.57	97.19	98.61	97.62	113.14	109.90
6	8.6	96.16	97.83	99.19	97.92	114.11	111.69
7	7.1	96.32	97.74	100.52	97.47	114.08	112.35

angle1: Mn1-O1-Mn2A; angle5: Mn1-O5-Mn2A; angle3: Mn1-O3-Mn2;
angle7: Mn1-O7-Mn2; angle9: Mn1-O9-Mn3; angle11: Mn1-O11-Mn4