Supplementary Material (ESI) for Chemical Communications

2D warp-and-woof interwoven networks constructed by helical chains with different chirality

Yuhua Feng, Yang Guo, Yan OuYang, Zhanquan Liu, Daizheng Liao, Peng Cheng, Shiping Yan and Zonghui Jiang.*

Department of Chemistry, Nankai University. Tianjin 300071, P.R. China.

Email: liaodaizheng@yahoo.com.cn

Contents:

Experimental Section

Physical Measurements: The infrared spectrum was obtained on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the 4000-400 cm^{-1} regions, using KBr pellets. Elemental analysis for C, H and N were carried out on a Perkin–Elmer elemental analyzer model 240. X-ray powder

diffraction was performed on a D/Max-2500 X-ray powder diffractometer. Variable temperature magnetic susceptibilities were measured on SQUID magnetometer between 2 and 300 K in a magnetic field of 2000 Oe. The molar magnetic susceptibility was corrected from the sample holder and diamagnetic contributions of all constituent atoms by using Pascal's constants. Single crystal X-ray diffraction data collection was collected on a AapexII CCD area detector equipped with a graphite-monochromated Mo$K\alpha$ radiation (γ = 0.71070 Å). The crystal structure was solved by a direct method and refined on F^2 by the SHELX-97 program.

Materials: All starting materials were analytical grade, purchased from commercial sources and used without further purification. $K[Au(CN)_2]$ and $K[Ag(CN)_2]$ were kindly provided by Professor Zhanquan Liu (Department of Chemistry, Nankai University).

H_2salen (salen = N, N'-ethylene bis-salicylideneaminato) was prepared by a literature method (J.H. Billman, L. Dorman, C. Linneaus, *J. Med. Chem.* 1963, **6**, 701). And $[Mn(salen)(H_2O)_2]ClO_4$ was prepared by the reaction of $Mn(OOCCH_3)_3$, H_2salen and $NaClO_4$ (molar ratio 1:1:1.5) in a solution of 1:1 methanol/H_2O. [Mn(acacen)Cl] (acacen = N,N'-ethylene bis(acetylacetonylideneiminate) was prepared according to the literature: L.J.

Boucher and V.W. Day, *Inorg. Chem.*, 1977, **16**, 1360.

Caution! Since the complexes of perchloride are potentially explosive, only small amounts of the materials should be handled with care.

Synthesis of Coordination Polymer:

{Mn(salen)[Au(CN)$_2$](H$_2$O)}$_n$ (1): An aqueous solution (5 mL) of K[Au(CN)$_2$] (0.03 g, 0.1mmol) was slowly added to a dark brown methanol solution (20 mL) of [Mn(salen)(H$_2$O)$_2$]ClO$_4$ (0.045 g, 0.1 mmol) with stirring. After the resulting solution had been filtered and evaporated slowly at room temperature for about two months in a dark place, dark brown crystals suitable for X-ray analysis were collected, washed with minimum methanol and water, dried under vacuum. Yield: 0.03 g, ca. 60% based on Mn(III). IR (KBr): $\nu_{C\equiv N}$ (cyanide) 2145 cm^{-1}, $\nu_{C=N}$(imine) 1625 cm^{-1}

{Mn(acacen)[Ag(CN)$_2$])}$_n$ (2) was prepared by the same method to 1 except that Mn(Acen)Cl (0.032 g, 0.1 mmol) and K[Ag(CN)$_2$] (0.02 g, 0.1mmol) were used. Yield: 0.02 g, ca. 50% based on Mn(III). IR (KBr): $\nu_{C\equiv N}$ (cyanide) 2148 cm^{-1}, $\nu_{C=N}$(imine) 1586 cm^{-1}. Elemental analysis: C28H36Ag2Mn2N8O4, Calcd: C 38.46, H 4.15, N 12.82, Found: C 38.18%, H 4.03%, N 12.52%.

The spin Hamiltonian of 1 and magnetic simulated formula of 1 and 2.

The susceptibility data of **1** was fitted by a formula including both single ion zero-field splitting (D) and intermolecular effects with the use of molecular field approximation (*zJ*) based on spin Hamiltonian (assume $g_{\parallel} = g_{\perp}$):

$\hat{H} = D\hat{S}_z^2 + g_{\parallel}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y) + 2zJ\langle S_z\rangle\hat{S}_z$

The equation is:

$$\chi_{ZFS} = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3}$$

$$\chi_{\parallel} = \frac{2N\beta^2g^2}{KT}\frac{\exp(-D/KT) + 4\exp(-4D/KT)}{1 + 2\exp(-D/KT) + 2\exp(-4D/KT)}$$

$$\chi_{\perp} = \frac{2N\beta^2g^2}{3D}\frac{9 - 7\exp(-D/KT) - 2\exp(-4D/KT)}{1 + 2\exp(-D/KT) + 2\exp(-4D/KT)}$$

$$\chi = \frac{\chi_{ZFS}}{1 - 2zJ\chi_{ZFS}/N\beta^2g^2}$$

And **2** was fitted by a one-dimensional chain formula with A = 2.0000, B = 71.938, C = 10.482, D = 955.56:

$$\chi = \frac{N\beta^2g^2}{KT}\frac{A + B(\frac{/J/}{KT})^2}{1 + C(\frac{/J/}{KT}) + D(\frac{/J/}{KT})^3}$$

Table S1. Crystal data and structure refinement for **1**

Empirical formula	C72H58Au4Mn4N16O9
Formula weigh	2298.97
Temperature	293(2) K
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 13.382(5) Å alpha = 94.217(3) deg.
	b = 14.081(5) Å beta = 107.932(4) deg.
	c = 20.242(8) Å gamma = 90.853(6) deg.
Volume	3616(2) $Å^3$
Z, Calculated density	2, 2.111 g/cm^3
Absorption coefficient	8.824 mm^{-1}
F(000)	2180
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	1.45 to 27.89 deg.
Reflections collected / unique	28281/17061 [R(int) = 0.0505]
Completeness to theta = 27.89	98.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.643 and 0.318
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17061/0/947
Goodness-of-fit on F^2	0.965
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1009
R indices (all data)	R1 = 0.0840, wR2 = 0.1172
Extinction coefficient	0.00066(4)
Largest diff. peak and hole	1.582 and -2.144 $e.Å^{-3}$

Table S2. Crystal data and structure refinement for **2**

Empirical formula	C28H36Ag2Mn2N8O4
Formula weight	874.27
Temperature	294(2) K
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 20.388(4) Å alpha = 90 deg.
	b = 20.161(4) Å beta = 105.690(3) deg.
	c = 17.384(3) Å gamma = 90 deg.
Volume	6880(2) $Å^3$
Z, Calculated density	8, 1.688 g/cm^3
Absorption coefficient	1.883 mm^{-1}
F(000)	3488
Crystal size	0.22 x 0.18 x 0.16 mm
Theta range for data collection	1.45 to 25.01 deg.
Reflections collected / unique	17294 / 6047 [R(int) = 0.0405]
Completeness to theta = 27.89	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7527 and 0.6821
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6047 / 0 / 407
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0661
R indices (all data	R1 = 0.0881, wR2 = 0.0857
Extinction coefficient	0.00049(2)
Largest diff. peak and hole	0.281 and -0.353 $e.Å^{-3}$

Table S3. Bond lengths [Å] and angles [deg] for **1**.

Au(1)-C(2)	1.978(8)	Mn(3)-O(5)	1.869(5)
Au(1)-C(1)	1.996(8)	Mn(3)-O(6)	1.869(5)
Au(1)-Au(4)$^{\#1}$	3.1497(13)	Mn(3)-N(13)	1.969(6)
Au(2)-C(4)	1.985(8)	Mn(3)-N(14)	1.971(7)
Au(2)-C(3)	2.000(8)	Mn(3)-N(8)#4	2.303(7)
Au(2)-Au(3)	3.0959(13)	Mn(3)-N(5)	2.382(7)
Au(3)-C(5)	2.010(8)	Mn(4)-O(7)	1.879(5)
Au(3)-C(6)	2.011(8)	Mn(4)-O(8)	1.881(5)
Au(4)-C(8)	1.976(8)	Mn(4)-N(15)	1.977(6)
Au(4)-C(7)	1.987(7)	Mn(4)-N(16)	1.988(6)
Au(4)-Au(1)$^{\#2}$	3.1497(13)	Mn(4)-N(6)	2.318(6)
Mn(1)-O(1)	1.866(5)	Mn(4)-N(7)	2.328(6)
Mn(1)-O(2)	1.867(5)	N(1)-C(1)	1.141(10)
Mn(1)-N(9)	1.979(6)	N(2)-C(2)	1.150(9)
Mn(1)-N(10)	1.982(5)	N(3)-C(3)	1.125(9)
Mn(1)-N(1)	2.346(7)	N(4)-C(4)	1.134(9)
Mn(1)-N(4)$^{\#3}$	2.397(7)	N(4)-Mn(1)#5	2.397(7)
Mn(2)-O(4)	1.851(5)	N(5)-C(5)	1.128(9)
Mn(2)-O(3)	1.860(5)	N(6)-C(6)	1.107(8)
Mn(2)-N(12)	1.979(6)	N(7)-C(7)	1.136(8)
Mn(2)-N(11)	1.994(6)	N(8)-C(8)	1.155(9)
Mn(2)-N(2)	2.318(7)	N(8)-Mn(3)#6	2.303(7)
Mn(2)-N(3)	2.457(7)		
C(2)-Au(1)-C(1)	175.8(3)	O(7)-Mn(4)-N(16)	174.0(2)
C(2)-Au(1)-Au(4)#1	91.6(2)	O(8)-Mn(4)-N(16)	92.2(2)
C(1)-Au(1)-Au(4)#1	84.4(2)	N(15)-Mn(4)-N(16)	81.4(3)
C(4)-Au(2)-C(3)	175.1(3)	O(7)-Mn(4)-N(6)	90.9(2)
C(4)-Au(2)-Au(3)	91.1(2)	O(8)-Mn(4)-N(6)	93.4(2)
C(3)-Au(2)-Au(3)	84.1(2)	N(15)-Mn(4)-N(6)	88.7(3)
C(5)-Au(3)-C(6)	175.2(3)	N(16)-Mn(4)-N(6)	89.5(2)
C(5)-Au(3)-Au(2)	90.6(2)	O(7)-Mn(4)-N(7)	93.9(2)
C(6)-Au(3)-Au(2)	85.5(2)	O(8)-Mn(4)-N(7)	90.8(2)
C(8)-Au(4)-C(7)	176.2(3)	N(15)-Mn(4)-N(7)	86.6(2)
C(8)-Au(4)-Au(1)#2	87.0(2)	N(16)-Mn(4)-N(7)	85.4(2)
C(7)-Au(4)-Au(1)#2	90.1(2)	N(6)-Mn(4)-N(7)	173.5(2)
O(1)-Mn(1)-O(2)	92.6(2)	C(1)-N(1)-Mn(1)	154.2(7)
O(1)-Mn(1)-N(9)	92.6(2)	C(2)-N(2)-Mn(2)	149.7(6)
O(2)-Mn(1)-N(9)	174.2(2)	C(3)-N(3)-Mn(2)	151.7(7)
O(1)-Mn(1)-N(10)	173.7(2)	C(4)-N(4)-Mn(1)#5	149.4(7)
O(2)-Mn(1)-N(10)	92.7(2)	C(5)-N(5)-Mn(3)	148.8(7)
N(9)-Mn(1)-N(10)	82.3(3)	C(6)-N(6)-Mn(4)	155.8(7)
O(1)-Mn(1)-N(1)	92.3(2)	C(7)-N(7)-Mn(4)	154.5(6)
O(2)-Mn(1)-N(1)	95.1(2)	C(8)-N(8)-Mn(3)#6	147.1(7)
N(9)-Mn(1)-N(1)	87.2(3)	C(15)-N(9)-C(16)	122.4(7)
N(10)-Mn(1)-N(1)	83.9(2)	C(15)-N(9)-Mn(1)	124.4(6)
O(1)-Mn(1)-N(4)#3	98.2(2)	C(16)-N(9)-Mn(1)	113.2(5)
O(2)-Mn(1)-N(4)#3	93.3(2)	C(18)-N(10)-C(17)	122.8(6)
N(9)-Mn(1)-N(4)#3	83.4(3)	C(18)-N(10)-Mn(1)	125.5(5)
N(10)-Mn(1)-N(4)#3	84.8(2)	C(17)-N(10)-Mn(1)	111.6(5)
N(1)-Mn(1)-N(4)#3	166.2(2)	C(31)-N(11)-C(32)	123.4(7)
O(4)-Mn(2)-O(3)	92.4(2)	C(31)-N(11)-Mn(2)	125.7(5)
O(4)-Mn(2)-N(12)	91.9(2)	C(32)-N(11)-Mn(2)	110.9(5)
O(3)-Mn(2)-N(12)	172.8(2)	C(34)-N(12)-C(33)	122.5(7)
O(4)-Mn(2)-N(11)	175.0(2)	C(34)-N(12)-Mn(2)	126.0(5)
O(3)-Mn(2)-N(11)	92.6(2)	C(33)-N(12)-Mn(2)	111.2(5)
N(12)-Mn(2)-N(11)	83.1(3)	C(47)-N(13)-C(48)	122.8(7)
O(4)-Mn(2)-N(2)	95.4(2)	C(47)-N(13)-Mn(3)	124.3(6)
O(3)-Mn(2)-N(2)	94.9(2)	C(48)-N(13)-Mn(3)	112.9(5)

N(12)-Mn(2)-N(2)	90.5(2)	C(50)-N(14)-C(49)	122.1(7)
N(11)-Mn(2)-N(2)	84.8(2)	C(50)-N(14)-Mn(3)	125.1(6)
O(4)-Mn(2)-N(3)	95.4(2)	C(49)-N(14)-Mn(3)	112.7(5)
O(3)-Mn(2)-N(3)	90.6(2)	C(63)-N(15)-C(64)	120.9(7)
N(12)-Mn(2)-N(3)	83.2(2)	C(63)-N(15)-Mn(4)	125.5(5)
N(11)-Mn(2)-N(3)	83.9(2)	C(64)-N(15)-Mn(4)	113.4(6)
N(2)-Mn(2)-N(3)	167.7(2)	C(66)-N(16)-C(65)	121.1(7)
O(5)-Mn(3)-O(6)	93.0(2)	C(66)-N(16)-Mn(4)	125.6(5)
O(5)-Mn(3)-N(13)	93.3(3)	C(65)-N(16)-Mn(4)	113.0(5)
O(6)-Mn(3)-N(13)	173.6(3)	C(9)-O(1)-Mn(1)	127.7(5)
O(5)-Mn(3)-N(14)	175.0(2)	C(24)-O(2)-Mn(1)	129.4(4)
O(6)-Mn(3)-N(14)	91.7(3)	C(25)-O(3)-Mn(2)	128.0(5)
N(13)-Mn(3)-N(14)	82.0(3)	C(40)-O(4)-Mn(2)	129.9(4)
O(5)-Mn(3)-N(8)#4	94.1(3)	C(41)-O(5)-Mn(3)	128.6(5)
O(6)-Mn(3)-N(8)#4	94.5(3)	C(56)-O(6)-Mn(3)	126.8(5)
N(13)-Mn(3)-N(8)#4	84.8(3)	C(57)-O(7)-Mn(4)	128.5(5)
N(14)-Mn(3)-N(8)#4	87.4(3)	C(72)-O(8)-Mn(4)	129.1(4)
O(5)-Mn(3)-N(5)	92.4(2)	N(1)-C(1)-Au(1)	171.3(8)
O(6)-Mn(3)-N(5)	96.5(2)	N(2)-C(2)-Au(1)	173.7(7)
N(13)-Mn(3)-N(5)	83.6(2)	N(3)-C(3)-Au(2)	172.5(8)
N(14)-Mn(3)-N(5)	85.3(3)	N(4)-C(4)-Au(2)	172.6(7)
N(8)#4-Mn(3)-N(5)	167.0(3)	N(5)-C(5)-Au(3)	173.5(8)
O(7)-Mn(4)-O(8)	93.8(2)	N(6)-C(6)-Au(3)	174.4(8)
O(7)-Mn(4)-N(15)	92.6(3)	N(7)-C(7)-Au(4)	172.3(7)
O(8)-Mn(4)-N(15)	173.2(2)	N(8)-C(8)-Au(4)	172.7(8)

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

Table S4. Bond lengths [Å] and angles [deg] for **2**.

Ag(1)-C(4)	2.054(6)	Mn(2)-N(2)#2	2.304(4)
Ag(1)-C(1)	2.066(6)	Mn(3)-O(4)	1.909(3)
Ag(1)-Ag(2)	3.0967(8)	Mn(3)-O(4)#3	1.909(3)
Ag(2)-C(2)	2.062(5)	Mn(3)-N(8)#3	1.986(4)
Ag(2)-C(3)	2.065(5)	Mn(3)-N(8)	1.986(4)
Mn(1)-O(1)	1.908(3)	Mn(3)-N(3)#3	2.298(4)
Mn(1)-O(2)	1.909(3)	Mn(3)-N(3)	2.298(4)
Mn(1)-N(6)	1.980(4)	O(1)-C(6)	1.291(5)
Mn(1)-N(5)	1.986(4)	O(2)-C(15)	1.299(5)
Mn(1)-N(4)#1	2.298(4)	O(3)-C(18)	1.290(5)
Mn(1)-N(1)	2.302(4)	O(4)-C(24)	1.303(5)
Mn(2)-O(3)#2	1.913(3)	N(1)-C(1)	1.127(5)
Mn(2)-O(3)	1.913(3)	N(2)-C(2)	1.127(5)
Mn(2)-N(7)	1.989(4)	N(3)-C(3)	1.129(5)
Mn(2)-N(7)#2	1.989(4)	N(4)-C(4)	1.128(5)
Mn(2)-N(2)	2.304(4)	N(4)-Mn(1)#4	2.298(4)
C(4)-Ag(1)-C(1)	175.25(19)	O(4)#3-Mn(3)-N(8)#3	92.59(17)
C(4)-Ag(1)-Ag(2)	83.69(13)	O(4)-Mn(3)-N(8)	92.59(17)
C(1)-Ag(1)-Ag(2)	91.57(14)	O(4)#3-Mn(3)-N(8)	175.70(16)
C(2)-Ag(2)-C(3)	176.08(18)	N(8)#3-Mn(3)-N(8)	84.2(3)
C(2)-Ag(2)-Ag(1)	89.91(13)	O(4)-Mn(3)-N(3)#3	89.93(13)
C(3)-Ag(2)-Ag(1)	86.18(13)	O(4)#3-Mn(3)-N(3)#3	91.27(14)
O(1)-Mn(1)-O(2)	91.48(13)	N(8)#3-Mn(3)-N(3)#3	87.26(15)
O(1)-Mn(1)-N(6)	92.91(15)	N(8)-Mn(3)-N(3)#3	91.47(15)
O(2)-Mn(1)-N(6)	175.06(15)	O(4)-Mn(3)-N(3)	91.27(14)
O(1)-Mn(1)-N(5)	175.73(14)	O(4)#3-Mn(3)-N(3)	89.93(13)
O(2)-Mn(1)-N(5)	92.19(15)	N(8)#3-Mn(3)-N(3)	91.47(15)
N(6)-Mn(1)-N(5)	83.52(17)	N(8)-Mn(3)-N(3)	87.26(15)
O(1)-Mn(1)-N(4)#1	89.12(14)	N(3)#3-Mn(3)-N(3)	178.3(2)
O(2)-Mn(1)-N(4)#1	91.71(14)	C(6)-O(1)-Mn(1)	126.9(3)
N(6)-Mn(1)-N(4)#1	90.64(14)	C(15)-O(2)-Mn(1)	126.6(3)
N(5)-Mn(1)-N(4)#1	88.58(15)	C(18)-O(3)-Mn(2)	126.5(3)
O(1)-Mn(1)-N(1)	90.40(14)	C(24)-O(4)-Mn(3)	127.2(3)
O(2)-Mn(1)-N(1)	89.23(14)	C(1)-N(1)-Mn(1)	152.9(5)
N(6)-Mn(1)-N(1)	88.46(15)	C(2)-N(2)-Mn(2)	153.5(4)
N(5)-Mn(1)-N(1)	91.84(15)	C(3)-N(3)-Mn(3)	157.4(4)
N(4)#1-Mn(1)-N(1)	178.95(16)	C(4)-N(4)-Mn(1)#4	157.5(4)
O(3)#2-Mn(2)-O(3)	92.1(2)	C(13)-N(5)-C(11)	121.4(4)
O(3)#2-Mn(2)-N(7)	174.40(16)	C(13)-N(5)-Mn(1)	126.5(3)
O(3)-Mn(2)-N(7)	92.28(17)	C(11)-N(5)-Mn(1)	111.9(3)
O(3)#2Mn(2)-N(7)#2	92.28(17)	C(8)-N(6)-C(10)	121.9(4)
O(3)-Mn(2)-N(7)#2	174.41(16)	C(8)-N(6)-Mn(1)	125.0(3)
N(7)-Mn(2)-N(7)#2	83.5(3)	C(10)-N(6)-Mn(1)	112.9(3)
O(3)#2-Mn(2)-N(2)	88.80(14)	C(20)-N(7)-C(22)	121.9(5)
O(3)-Mn(2)-N(2)	90.55(14)	C(20)-N(7)-Mn(2)	125.8(4)
N(7)-Mn(2)-N(2)	87.70(15)	C(22)-N(7)-Mn(2)	111.7(4)
N(7)#2-Mn(2)-N(2)	93.00(16)	C(26)-N(8)-C(28)	123.1(5)
O(3)#2-Mn(2)-N(2)#2	90.55(14)	C(26)-N(8)-Mn(3)	124.9(4)
O(3)-Mn(2)-N(2)#2	88.80(14)	C(28)-N(8)-Mn(3)	111.5(4)
N(7)-Mn(2)-N(2)#2	93.01(16)	N(1)-C(1)-Ag(1)	172.7(5)
N(7)#2-Mn(2)-N(2)#2	87.70(15)	N(2)-C(2)-Ag(2)	173.3(5)
N(2)-Mn(2)-N(2)#2	179.1(2)	N(3)-C(3)-Ag(2)	172.6(4)
O(4)-Mn(3)-O(4)#3	90.73(19)	N(4)-C(4)-Ag(1)	171.1(5)
O(4)-Mn(3)-N(8)#3	175.69(16)		

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

Supporting figures

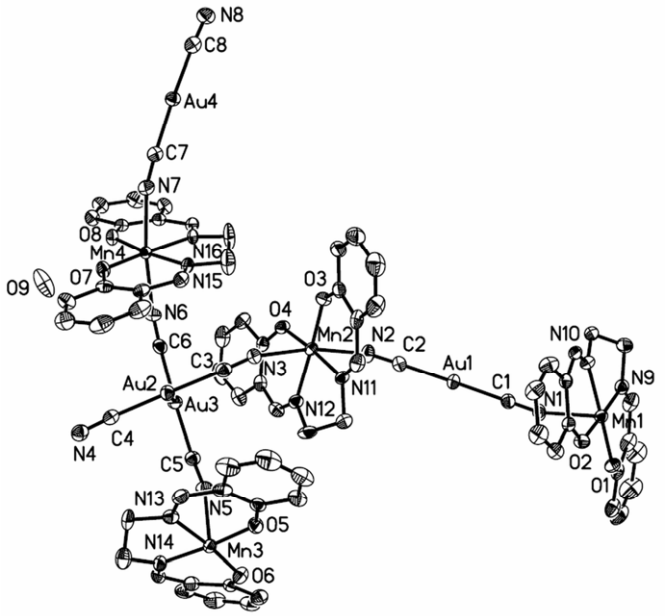

Figure S1. ORTEP diagram for **1** with partial atom labeling. (30% ellipsoids).

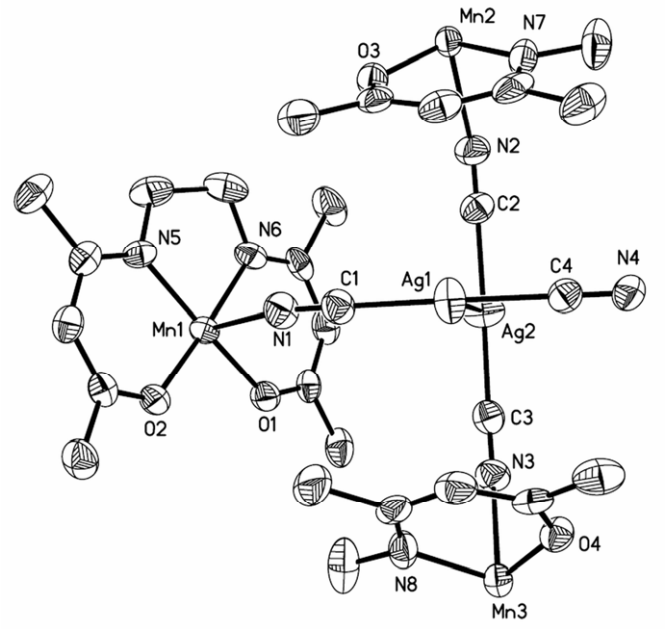

Figure S2. ORTEP diagram for **2** with partial atom labeling. (30% ellipsoids).

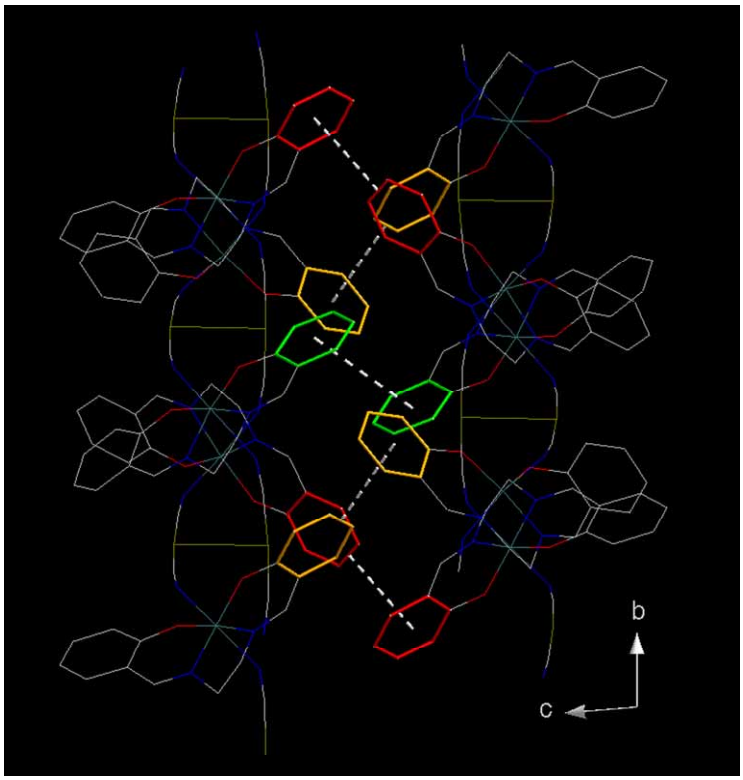

Figure S3. π-π interactions between adjacent 2D layers of **1**.

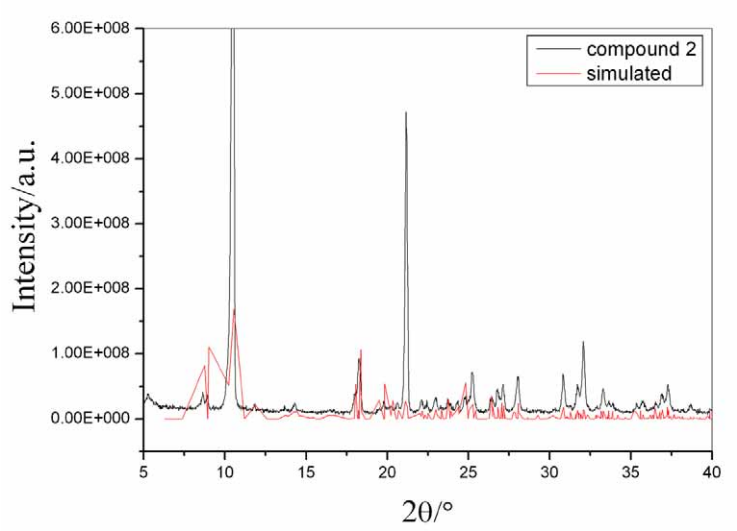

Figure S4. X-ray powder diffraction patterns for **2**. (Black line: bulk sample of **2**; Red line: simulated patterns obtained from single-crystal structural data. The intensity of black line was adjusted for clarity)

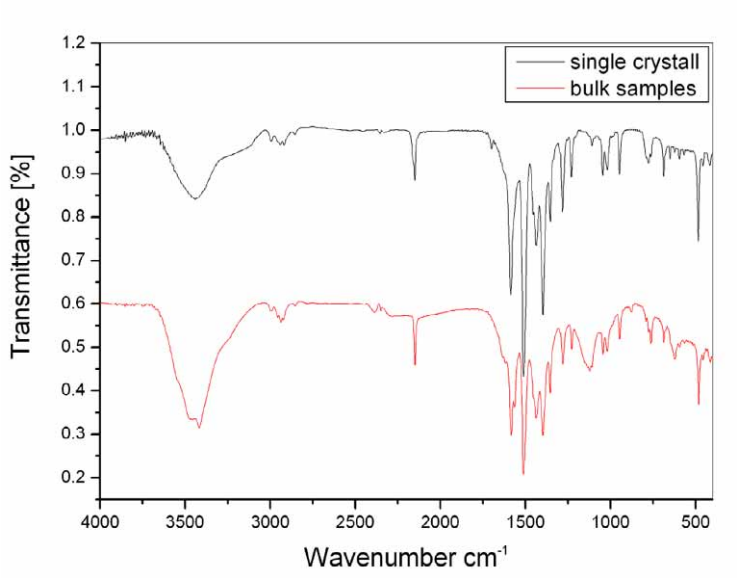

Figure S5. IR spectrum of **2**. (Red line: bulk material, black line: single crystal. The red line has been shifted along Y-axes for clarity)