Stepwise Crystallization: Illustrative Examples of the Use of Metalloligands, $[Cu_6(mna)_6]^{6-}$ and $[Ag_6(Hmna)_2(mna)_4]^{4-}$ (H_2mna = 2–mercapto nicotinic acid), in the Formation of Heterometallic Two and Three Dimensional Assemblies with *brucite*, *pcu* and *sql* Topologies.

Tanaya Kundu, Ajay Kumar Jana and Srinivasan Natarajan*

Framework solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India.

Electronic Supporting Information

* Corresponding author, E-mail: snatarajan@sscu.iisc.ernet.in

Table S1. Crystallographic data for Cu_6(*Hmna*)$_6$

	Cu_6(*Hmna*)$_6$
formula	$C_{36}H_{18}N_6O_{12}S_6Cu_6$
formula weight	1300.16
crystal system	triclinic
space group	*P*-1
a (Å)	12.3691(5)
b (Å)	12.3715(9)
c (Å)	15.6775(11)
α (deg)	90.070(6)
β (deg)	113.174(5)
γ (deg)	119.983(6)
volume (Å^3)	1850.4(2)
Z	1
temperature (K)	120(2)
ρ_c (gcm^{-3})	1.167
μ (mm^{-1})	1.903
θ range (deg)	2.72- 25.99
wavelength (Å)	0.71073
total reflns	13103
unique reflns	7258
R_1, wR_2 [I>2σ(I)]	0.0668, 0.1901
R_1, wR_2 (all data)	0.1019, 0.2189

Table S2. Selected bond lengths (Å) and bond angles (deg) for Cu_6(*Hmna*)$_6$

bond length		bond angle	
Cu(1)-N(1)	2.031(6)	N(1)-Cu(1)-S(3)#1	115.52(14)
Cu(1)-S(3)#1	2.2355(16)	N(1)-Cu(1)-S(2)	117.62(13)
Cu(1)-S(2)	2.2408(17)	S(3)#1-Cu(1)-S(2)	117.42(7)
Cu(1)-Cu(2)	2.7917(10)	N(1)-Cu(1)-Cu(2)	88.74(15)
Cu(1)-Cu(3)#1	2.7937(10)	S(3)#1-Cu(1)-Cu(2)	134.80(5)
Cu(2)-N(2)	2.019(5)	S(2)-Cu(1)-Cu(2)	76.41(5)
Cu(2)-S(1)	2.2375(18)	N(1)-Cu(1)-Cu(3)#1	87.69(14)
Cu(2)-S(3)	2.2433(18)	S(3)#1-Cu(1)-Cu(3)#1	76.45(5)
Cu(2)-Cu(3)	2.7925(11)	S(2)-Cu(1)-Cu(3)#1	134.61(6)
Cu(3)-N(3)	2.016(6)	Cu(2)-Cu(1)-Cu(3)#1	66.58(3)
Cu(3)-S(2)	2.2324(17)	N(2)-Cu(2)-S(1)	115.19(15)
Cu(3)-S(1)#1	2.2420(17)	N(2)-Cu(2)-S(3)	117.60(14)
Cu(3)-Cu(1)#1	2.7937(10)	S(1)-Cu(2)-S(3)	117.57(7)
		N(2)-Cu(2)-Cu(1)	87.78(15)
		S(1)-Cu(2)-Cu(1)	76.45(5)
		S(3)-Cu(2)-Cu(1)	134.69(5)
		N(2)-Cu(2)-Cu(3)	89.08(16)
		S(1)-Cu(2)-Cu(3)	134.86(5)
		S(3)-Cu(2)-Cu(3)	76.36(5)
		Cu(1)-Cu(2)-Cu(3)	66.63(3)
		N(3)-Cu(3)-S(2)	115.36(14)
		N(3)-Cu(3)-S(1)#1	117.86(15)
		S(2)-Cu(3)-S(1)#1	117.50(7)
		N(3)-Cu(3)-Cu(2)	87.23(16)
		S(2)-Cu(3)-Cu(2)	76.52(5)
		S(1)#1-Cu(3)-Cu(2)	134.66(5)
		N(3)-Cu(3)-Cu(1)#1	88.66(15)
		S(2)-Cu(3)-Cu(1)#1	134.83(6)
		S(1)#1-Cu(3)-Cu(1)#1	76.34(5)
		Cu(2)-Cu(3)-Cu(1)#1	66.59(3)

Table S3. Selected bond lengths (Å) and bond angles (deg) for 1–3

bond length		bond angle	
1			
Cu1–N1#1	2.004(3)	N1#1–Cu1–S1	119.91(8)
Cu1–S1	2.2288(9)	N1#1–Cu1–S1#2	121.65(8)
Cu1–S1#2	2.2345(9)	S1–Cu1–S1#2	113.18(4)
Cu1–Cu1#3	2.8528(7)	N1#1–Cu1–Cu1#3	88.17(8)
Cu1–Cu1#1	2.8528(7)	S1–Cu1–Cu1#3	72.26(2)
Mn1–O1#4	2.177(2)	S1#2–Cu1–Cu1#3	131.29(2)
Mn1–O1#5	2.177(2)	N1#1–Cu1–Cu1#1	89.15(8)
Mn1–O1	2.177(2)	S1–Cu1–Cu1#1	131.42(2)
Mn1–O3#4	2.185(3)	S1#2–Cu1–Cu1#1	72.19(2)
Mn1–O3#5	2.185(3)	Cu1#3–Cu1–Cu1#1	70.699(19)
Mn1–O3	2.185(3)	O1#4–Mn1–O1#5	92.70(8)
Mn2–O4#6	2.195(3)	O1#4–Mn1–O1	92.70(8)
Mn2–O4	2.195(3)	O1#5–Mn1–O1	92.70(8)
Mn2–O4#7	2.195(3)	O1#4–Mn1–O3#4	88.86(10)
Mn2–O4#8	2.195(3)	O1–Mn1–O3 #4	177.04(10)
Mn2–O4#9	2.195(3)	O1–Mn1–O3#4	89.74(9)
Mn2–O4 #10	2.195(3)	O1#4–Mn1–O3#5	89.74(9)
		O1#5–Mn1–O3#5	88.86(10)
		O1–Mn1–O3#5	177.04(10)
		O3#4–Mn1–O3#5	88.63(11)
		O1#4–Mn1–O3	177.04(10)
		O1#5–Mn1–O3	89.74(9)
		O1–Mn1–O3	88.86(10)
		O3#4–Mn1–O3	88.63(11)
		O3#5–Mn1–O3	88.63(11)
		O4#6–Mn2–O4	90.14(10)
		O4#6–Mn2–O4#7	90.14(10)
		O4–Mn2–O4#7	90.14(10)
		O4#6–Mn2–O4#8	180.0
		O4–Mn2–O4 #8	89.86(10)
		O4#7–Mn2–O4 #8	89.86(10)
		O4#6–Mn2–O4 #9	89.86(10)
		O4–Mn2–O4#9	180.0
		O4#7–Mn2–O4#9	89.86(10)
		O4#8–Mn2–O4#9	90.14(10)
		O4#6–Mn2–O4 #10	89.86(10)
		O4–Mn2–O4#10	89.86(10)
		O4#7–Mn2–O4#10	179.999(1)
		O4#18–Mn2–O4#10	90.14(10)
		O4#9–Mn2–O4 #10	90.14(10)

2			
Cu1–N1	2.031(3)	N1–Cu1–S2	111.02(8)
Cu1–S2	2.2525(9)	N1–Cu1–S3	113.91(8)
Cu1–S3	2.2535(9)	S2–Cu1–S3	122.42(3)
Cu1–Cu2	2.7929(6)	N1–Cu1–Cu2	86.42(8)
Cu1–Cu3	2.8042(6)	S2–Cu1–Cu2	79.02(3)
Cu1–Cu2#1	2.8798(6)	S3–Cu1–Cu2	136.60(3)
Cu1–Cu3#1	2.9114(6)	N1–Cu1–Cu3	87.80(8)
Cu2–N2	2.040(3)	S2–Cu1–Cu3	137.29(3)
Cu2–S3#1	2.2357(9)	S3–Cu1–Cu3	78.49(2)
Cu2–S1	2.2389(9)	Cu2–Cu1–Cu3	63.757(15)
Cu2–Cu3#1	2.7883(6)	N1–Cu1–Cu2 #1	143.50(8)
Cu2–Cu1#1	2.8798(6)	S2–Cu1–Cu2#1	104.04(3)
Cu2–Cu3	2.9560(6)	S3–Cu1–Cu2 #1	49.82(2)
Cu3–N3	2.030(3)	Cu2–Cu1–Cu2#1	90.614(18)
Cu3–S1	2.2334(9)	Cu3–Cu1–Cu2#1	58.735(14)
Cu3–S2#1	2.2403(9)	N1–Cu1 Cu3 #1	140.54(8)
Cu3–Cu2#1	2.7883(6)	S2–Cu1–Cu3#1	49.42(2)
Cu3–Cu1#1	2.9114(6)	S3–Cu1–Cu3#1	104.53(3)
Mn1–O8	2.146(2)	Cu2–Cu1–Cu3#1	58.481(14)
Mn1–O1	2.176(2)	Cu3–Cu1–Cu3#1	91.470(16)
Mn1–O8#2	2.201(2)	Cu2#1–Cu1–Cu3 #1	61.381(15)
Mn1–O6#3	2.207(2)	N2–Cu2–S3#1	112.37(8)
Mn1–O7	2.212(3)	N2–Cu2–S1	114.47(8)
Mn1–O3#2	2.254(2)	S3#1–Cu2–S1	121.41(3)
Mn1–Mn1#3	3.2386(10)	N2–Cu2–Cu3#1	86.34(8)
Mn2–O8	2.117(2)	S3#1–Cu2–Cu3#1	79.12(2)
Mn2–O5#3	2.135(3)	S1–Cu2–Cu3#1	135.89(3)
Mn2–O11	2.175(3)	N2–Cu2–Cu1	87.81(8)
Mn2–O10	2.189(3)	S3#1–Cu2–Cu1	135.93(3)
Mn2–O9	2.242(3)	S1–Cu2–Cu1	78.78(3)
Mn2–O12	2.262(3)	Cu3#1–Cu2–Cu1	62.885(16)
		N2–Cu2–Cu1#1	142.27(8)
		S3#1–Cu2–Cu1 #1	50.37(2)
		S1–Cu2–Cu1 #1	101.79(3)
		Cu3#1–Cu2–Cu1#1	59.278(14)
		Cu1–Cu2–Cu1#1	89.386(18)
		N2–Cu2–Cu3	142.61(8)
		S3#1–Cu2–Cu3	103.62(3)
		S1–Cu2–Cu3	48.55(2)
		Cu3#1–Cu2–Cu3	90.856(18)
		Cu1–Cu2–Cu3	58.308(15)
		Cu1#1–Cu2–Cu3	59.836(14)
		N3–Cu3–S1	113.84(8)

		N3–Cu3–S2#1	114.58(8)
		S1–Cu3–S2#1	120.50(3)
		N3–Cu3–Cu2 #1	87.80(8)
		S1–Cu3–Cu2#1	134.43(3)
		S2#1–Cu3–Cu2 #1	79.31(2)
		N3–Cu3–Cu1	87.63(8)
		S1–Cu3–Cu1	78.62(3)
		S2#1–Cu3–Cu1	134.87(3)
		Cu2#1–Cu3–Cu1	61.986(15)
		N3–Cu3–Cu1#1	143.40(8)
		S1–Cu3–Cu1 #1	100.98(3)
		S2#1–Cu3–Cu1#1	49.79(2)
		Cu2#1–Cu3–Cu1#1	58.634(15)
		Cu1–Cu3–Cu1	88.530(16)
		N3–Cu3–Cu2	141.96(8)
		S1–Cu3–Cu2	48.71(2)
		S2#1–Cu3–Cu2	102.02(3)
		Cu2#1–Cu3–Cu2	89.144(18)
		Cu1–Cu3–Cu2	57.934(15)
		Cu1#1–Cu3–Cu2	58.783(14)
		O8–Mn1–O1	94.20(9)
		O8–Mn1–O8#2	83.66(9)
		O1–Mn1–O8 #2	88.44(9)
		O8–Mn1–O6#3	96.17(9)
		O1–Mn1–O6#3	86.54(9)
		O8#2–Mn1–O6#3	174.95(9)
		O8–Mn1–O7	95.06(10)
		O1–Mn1–O7	170.45(10)
		O8#2–Mn1–O7	94.92(10)
		O6#3–Mn1–O7	90.12(10)
		O8–Mn1–O3#4	177.36(9)
		O1–Mn1–O3#4	87.92(8)
		O8#2–Mn1–O3 #4	94.83(8)
		O6#3–Mn1–O3#4	85.52(9)
		O7–Mn1–O3#4	82.89(9)
		O8–Mn1–Mn12#2	42.48(6)
		O1–Mn1–Mn1#2	91.72(6)
		O8#2–Mn1–Mn1#2	41.19(6)
		O6#3–Mn1–Mn1#2	138.42(7)
		O7–Mn1–Mn1#2	96.70(8)
		O3#4–Mn1–Mn1 #2	135.98(6)
		O8–Mn2–O5#3	101.73(9)
		O8–Mn2–O11	90.31(11)
		O5#3–Mn2–O11	167.96(12)
		O8–Mn2–O10	174.06(12)

		O5#3–Mn2–O10	84.07(12)
		O11–Mn2–O10	83.90(14)
		O8–Mn2–O9	89.93(9)
		O5#3–Mn2–O9	87.32(11)
		O11–Mn2–O9	92.49(12)
		O10–Mn2–O9	91.60(12)
		O8–Mn2–O12	89.78(11)
		O5#3–Mn2–O12	87.93(11)
		O11–Mn2–O12	92.43(13)
		O10–Mn2–O12	89.19(13)
		O9–Mn2–O12	175.07(11)
3			
Ag1–N1	2.280(5)	N1–Ag1–S2	121.73(13)
Ag1–S2	2.4853(14)	N1–Ag1–S3#1	121.22(13)
Ag1–S3#1	2.4938(14)	S2–Ag1–S3#1	112.70(5)
Ag1–Ag3	2.9530(6)	N1–Ag1–Ag3	85.00(12)
Ag1–Ag2#2	2.9689(6)	S2–Ag1–Ag3	75.61(3)
Ag2–N3#3	2.280(5)	S3#1–Ag1–Ag3	130.72(4)
Ag2–S1#2	2.4636(14)	N1–Ag1–Ag2#2	86.29(12)
Ag2–S2	2.4801(15)	S2–Ag1–Ag2#2	131.64(4)
Ag2–Ag3	2.9439(6)	S3#1–Ag1–Ag2#2	72.68(3)
Ag2-Ag1#2	2.9689(6)	Ag3–Ag1–Ag2#2	68.082(15)
Ag2–Ag3#2	3.3151(6)	N3#3–Ag2–S1#2	118.40(12)
Ag3–N2	2.306(5)	N3#3–Ag2–S2	118.22(12)
Ag3–S1	2.4871(15)	S1#1–Ag2–S2	112.95(5)
Ag3–S3#3	2.4881(15)	N3#3–Ag2–Ag3	87.87(12)
Ag3–Ag2#2	3.3151(6)	S1#2–Ag2–Ag3	137.39(4)
Mn1–O3	2.152(4)	S2–Ag2–Ag3	75.86(4)
Mn1–O4	2.152(4)	N3#3–Ag2–Ag1#2	86.77(11)
Mn1–O7	2.167(4)	S1#2–Ag2–Ag1#2	76.32(3)
Mn1–O9	2.180(5)	S2–Ag2–Ag1#2	138.32(4)
Mn1–O6	2.202(4)	Ag3–Ag2–Ag1#2	72.169(16)
Mn1–O8	2.278(3)	N3#3–Ag2–Ag3 #2	141.03(11)
		S1#2–Ag2 Ag3 #2	48.26(3)
		S2–Ag2–Ag3#2	98.78(4)
		Ag3–Ag2–Ag3#2	89.858(17)
		Ag1#2–Ag2–Ag3 #2	55.732(13)
		N2–Ag3–S1	114.60(12)
		N2–Ag3–S3#3	122.40(12)
		S1–Ag3–S3#3	115.94(5)
		N2–Ag3–Ag2	87.88(12)
		S1–Ag3–Ag2	137.08(4)
		S3#3–Ag3–Ag2	73.21(3)
		N2–Ag3–Ag1	79.96(11)

		S1–Ag3–Ag1	76.28(4)
		S3#3–Ag3–Ag1	137.59(4)
		Ag2–Ag3–Ag1	72.238(16)
		N2–Ag3–Ag2#2	134.29(12)
		S1–Ag3–Ag2#2	47.66(3)
		S3#3–Ag3–Ag2#2	100.41(4)
		Ag2–Ag3–Ag2#2	90.142(17)
		Ag1–Ag3–Ag2#2	56.187(13)
		O3–Mn1–O4	171.01(19)
		O3–Mn1–O7	101.60(17)
		O4–Mn1– O7	86.60(19)
		O3–Mn1–O9	87.49(17)
		O4–Mn1–O9	85.08 (18)
		O7–Mn1–O9	166.79(18)
		O3–Mn1–O6	91.44(16)
		O4–Mn1–O6	93.63 (17)
		O7–Mn1 O6	80.04(17)
		O9–Mn1–O6	90.26(19)
		O3–Mn1–O8	91.08(12)
		O4–Mn1–O8	85.51(13)
		O7–Mn1–O8	87.77(15)
		O9–Mn1–O8	101.76(18)
		O6–Mn1–O8	167.81(16)

Symmetry transformations used to generate equivalent atoms:

For **1**: #1 x-y+1,x+1,-z, #2 -y+1,x-y+2,z, #3 y-1,-x+y,-z, #4 -x+y-1,-x,z, #5 -y,x-y+1,z, #6 -y+1,x-y+1,z, #7 -x+y,-x+1,z, #8 y-1/3,-x+y+1/3,-z+1/3, #9 -x+2/3,-y+4/3,-z+1/3, #10 x-y+2/3,x+1/3,-z+1/3, #11 -x+y-1,-x+1,z

For **1**: #1 -x+2,-y+1,-z+1, #2 -x+2,-y,-z, #3 -x+3,-y+1,-z+1, #4 -x+2,-y,-z+1

For **3**: #1 -x+2,y-1,-z+3/2, #2 -x+2,-y+1,-z+1, #3 x,-y+2,z-1/2, #4 x,-y+2,z+1/2, #5 -x+2,y+1,-z+3/2, #6 -x+2,y,-z+3/2

Table S4. Bond Valence sum for compound 2 and 3

compound **2**		compound **3**	
bond	bond valence	bond	bond valence
Mn1-O5 ($)	0.39	Mn1-O3	0.37
Mn1-O8	0.41	Mn1-O4	0.37
Mn1-O9	0.29	Mn1-O6	0.32
Mn1-O10	0.34	Mn1-O7	0.36
Mn1-O11	0.35	Mn1-O8	0.26
Mn1-O12	0.28	Mn1-O9	0.34
Valence Sum	**2.06**	**Valence Sum**	**2.02**
Mn2-O1	0.35		
Mn2-O3 ($)	0.28		
Mn2-O6 ($)	0.32		
Mn2-O7	0.32		
Mn2-O8	0.38		
Mn2-O8 ($)	0.33		
Valence Sum	**1.98**		

The bond valence sum of O(8) in compound **2** is 0.41 + 0.38 + 0.33 = 1.12, which indicates that the O(8) is oxygen of hydroxyl group. The bond valence sum of O(8) in compound **3** is 0.26 + 0.26 = 0.52 as O8 is bridged by two Mn1; which indicates that the O(8) is oxygen of water molecule.

Table S5. Hexanuclear silver clusters with 2-mercaptonicotinic acid

compounds	cluster unit	cluster connectivity	dimensionality	ref.
$[Ag(Hmna)]_6 \cdot 4H_2O$	$[Ag(Hmna)]_6$	none	0D	14a
$\{4Na^+ \cdot 2[C_4O_3H_{12}N^+] \cdot [Ag(mna)]_6^{6-} \cdot 10H_2O\}$	$[Ag(mna)]_6^{6-}$	Counter ions: Na^+, $(HOCH_2)_3C\text{-}NH_3^+$	0D	14b
$\{[(Et_3NH)^+]_2 \cdot [Ag_6(Hmna)_4(mna)_2]^{2-} (DMSO)_2 \cdot (H_2O)\}$	$[Ag_6(Hmna)_4(mna)_2]^{2-}$	Counter ions: Et_3NH^+	0D	14c
$\{[Cu(en)_2(H_2O)_2]_3 \cdot [Ag_6(mna)_6] \cdot 9H_2O\}$ en=ethylenediamine	$[Ag(mna)]_6^{6-}$	Counter ions: $[Cu(eda)_2(H_2O)_2]^{2+}$		13c
(i) $\{[Cu_3(bpy)_3(H_2O)_5][Ag_6(mna)_6] \cdot 11.5H_2O\}_n$, (bpy = 2,2′-bipyridine) (ii) $\{[Zn_3(en)_3(H_2O)_4][Ag_6(mna)_6] \cdot 8H_2O\}_n$	$[Ag(mna)]_6^{6-}$	(i) connected to $[Cu(bpy)(H_2O)]^{2+}$, binding mode: $\mu_4\text{-}\eta^1:\eta^1:\eta^1:\eta^1$ Counter ions: $[Cu(bpy)(H_2O)_3]^{2+}$ (ii) connected to $[Zn(eda)_{0.5}(H_2O)_2]^{2+}$ and $[Zn(eda)_2]^{2+}$ binding mode: $\mu_4\text{-}\eta^1:\eta^1:\eta^1:\eta^1$	(i) 1D (ii) 2D	13a
$(NH_4)_2\{[Zn_2(phen)_2(H_2O)_4][Ag_6(mna)_6]\} \cdot 2H_2O \cdot 2CH_3CH_2OH$ (phen=1,10-phenanthroline)	$[Ag(mna)]_6^{6-}$	connected to $[Zn(phen)(H_2O)_2]^{2+}$, binding mode: $\mu_2\text{-}\eta^1:\eta^1$ Counter ions: NH_4^+	0D	13b
$\{[Mn_2(H_2O)_5][Ag_6(Hmna)_2(mna)_4]. 20H_2O\}$	$[Ag_6(Hmna)_2(mna)_4]^{4-}$	connected to $[Mn_2(H_2O)_5]^{4+}$ dimer units, binding mode: $\mu_6\text{-}\eta^2:\eta^2:\eta^1:\eta^1$	2D	present work

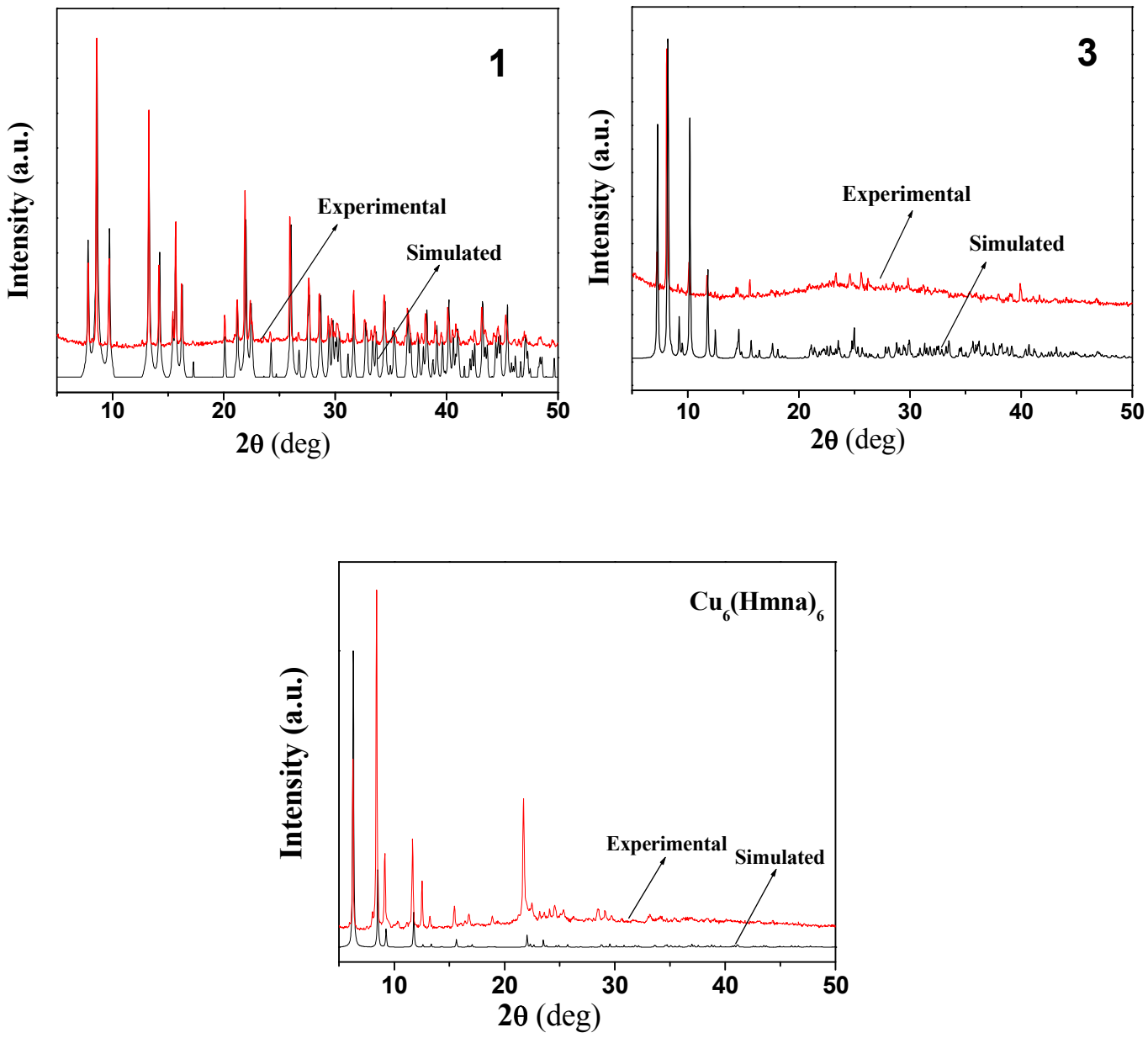


Figure S1. Simulated and experimental powder XRD patterns of compounds **1**, **3** and $Cu_6(Hmna)_6$.

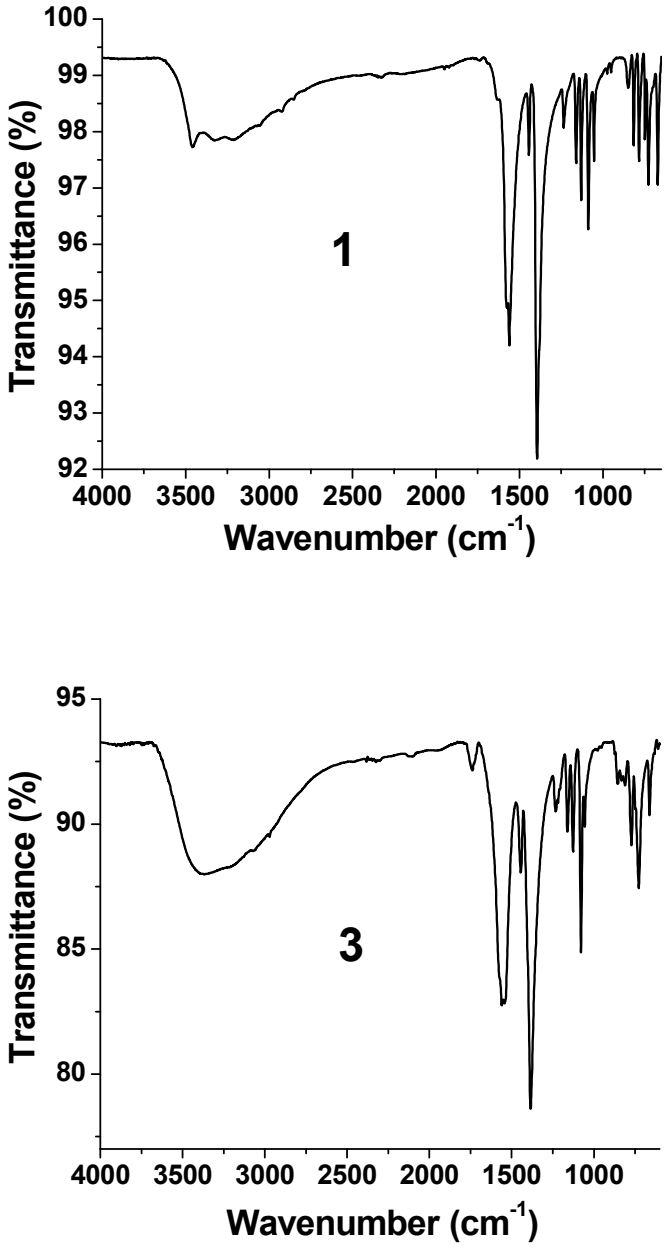
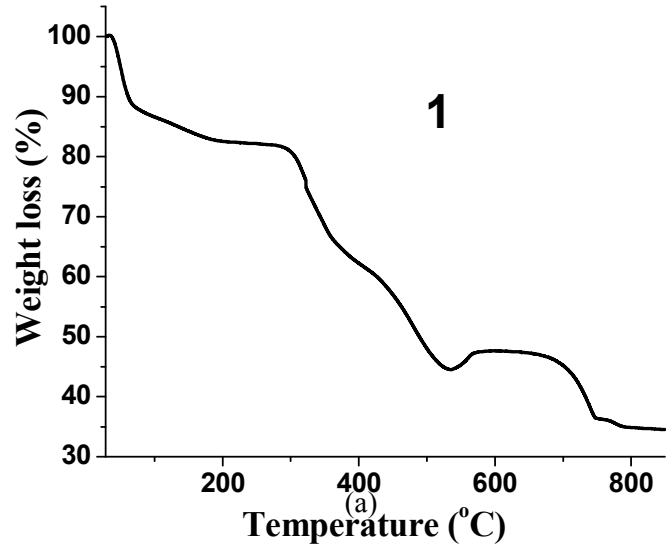
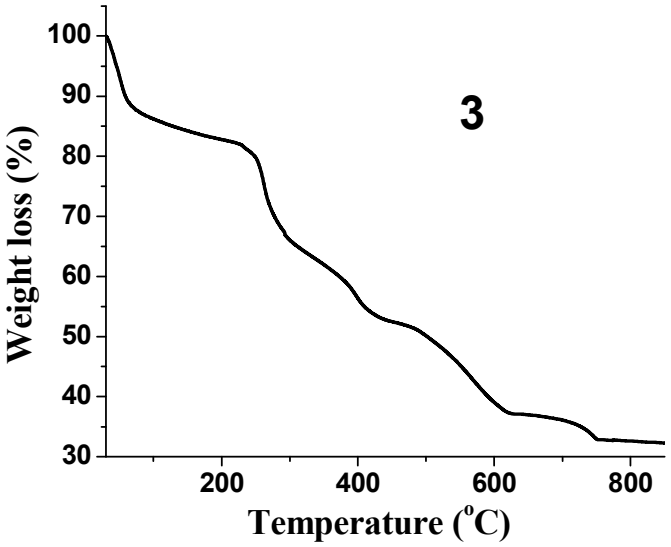


Figure S2. IR Spectra of compounds **1** and **3**.



(a)



(b)

Figure S3. TGA of compounds **1** (a) and **3** (b).

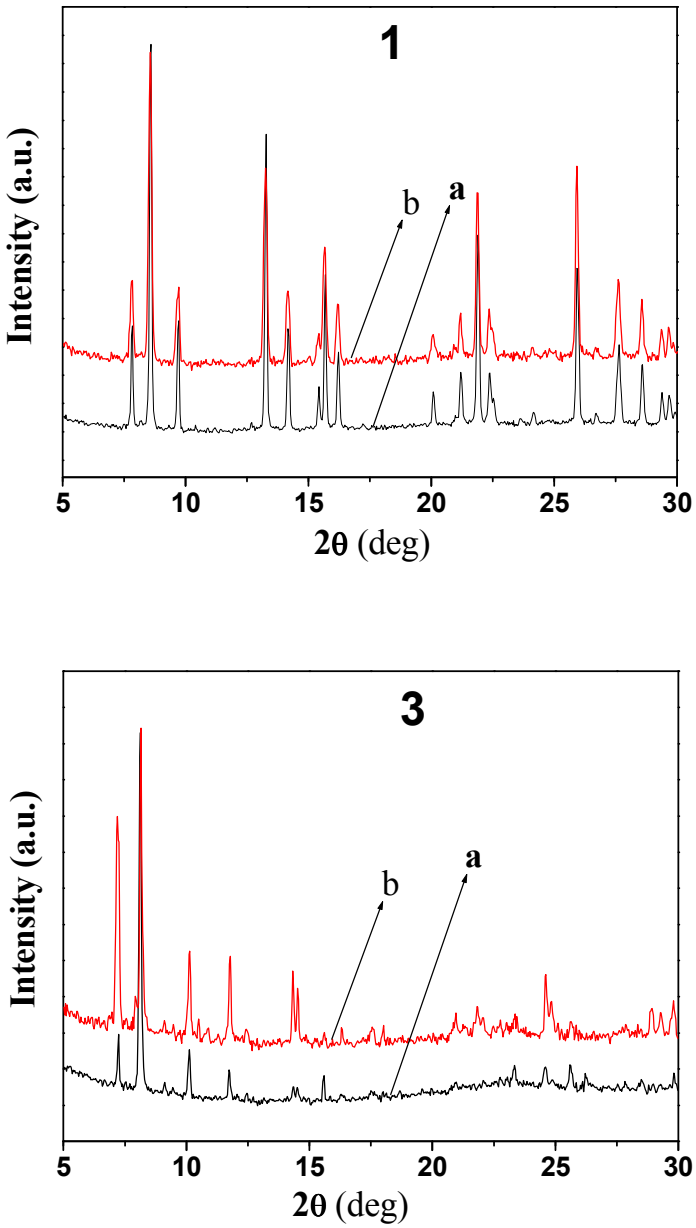
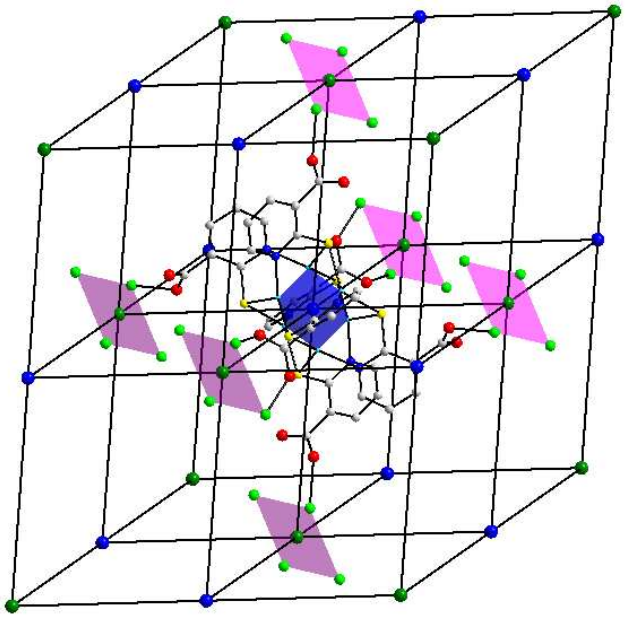
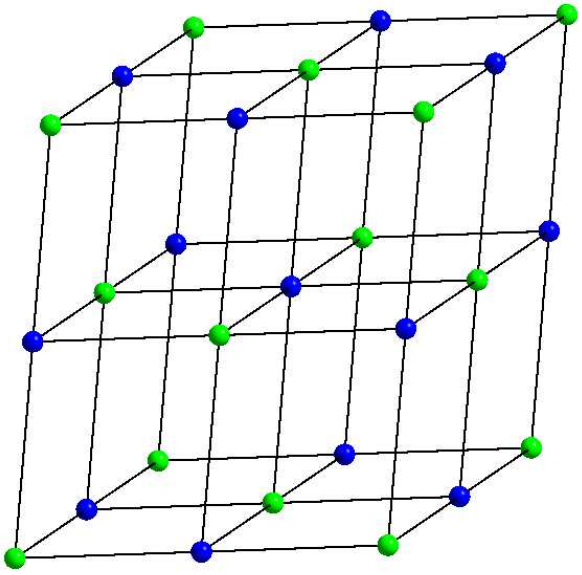


Figure S4. Powder XRD patterns for compounds **1** and **3**, (a) before and (b) after exposing to 98% RH for 24 hrs.

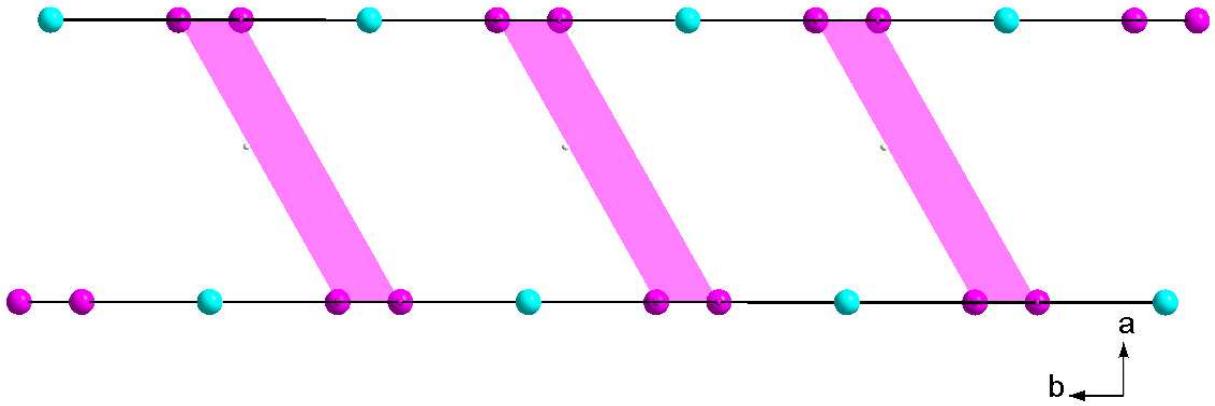


(a)

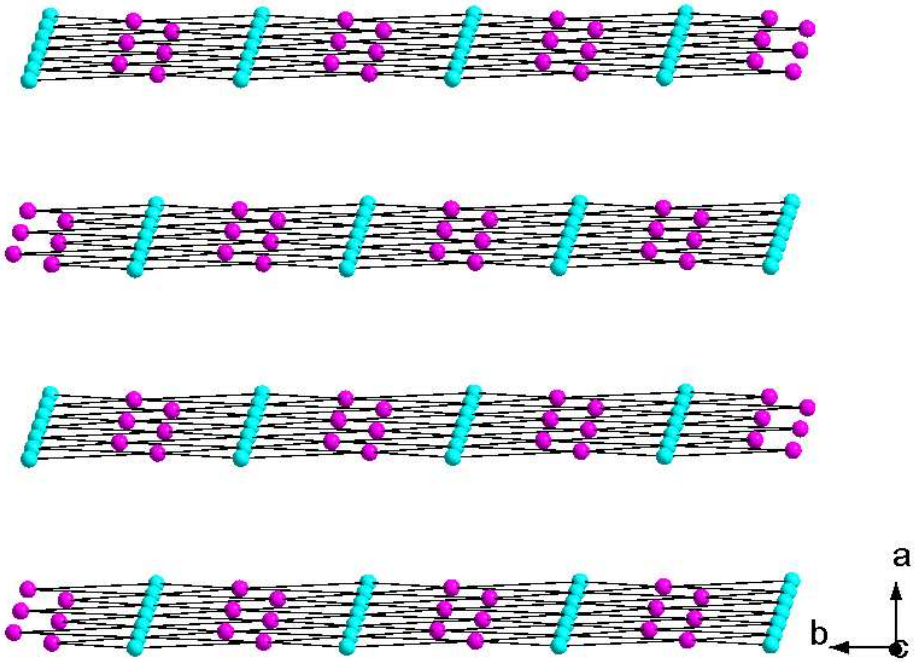


(b)

Figure S5. Connectivity of $Cu_6S_6N_6$ cluster with Mn_4 clusters forming (6,6) net in **2**, blue and green points are representing $Cu_6S_6N_6$ and Mn_4 clusters, respectively.

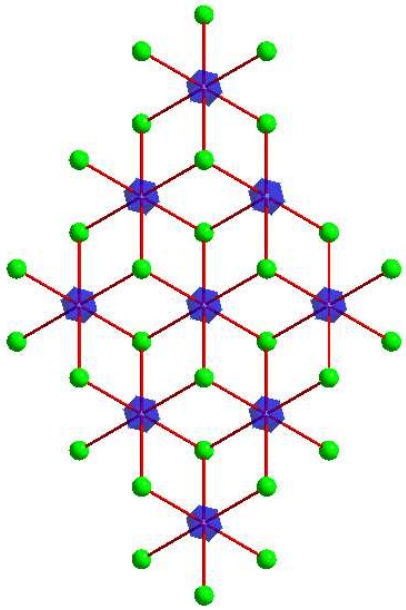


(a)

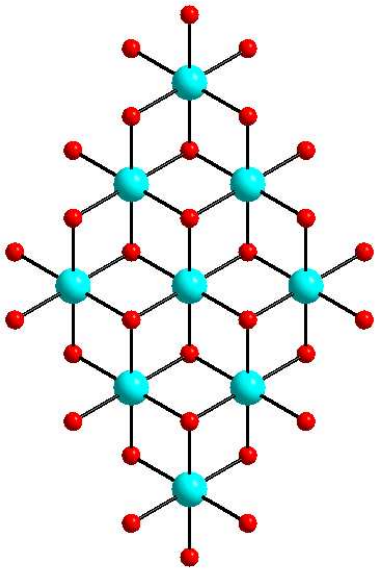


(b)

Figure S6. (a) Schematic representation of the orientation of two–dimensional water sheets with the layers in **3**. (b) The stacking of layers in **3**. Note the ABAB…stacking.

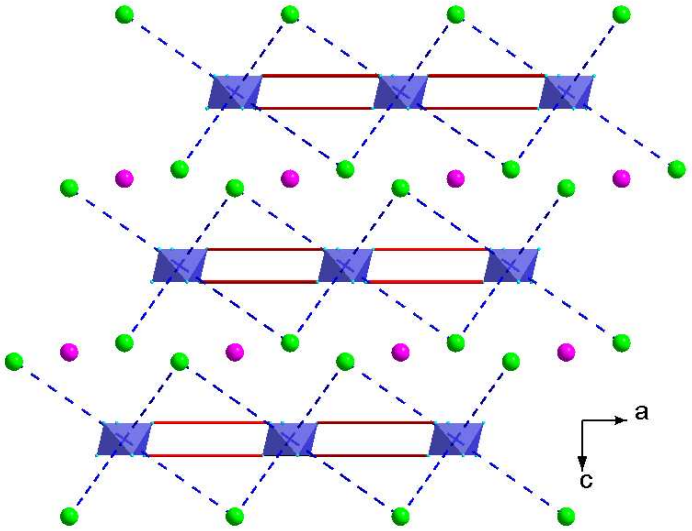


(a)

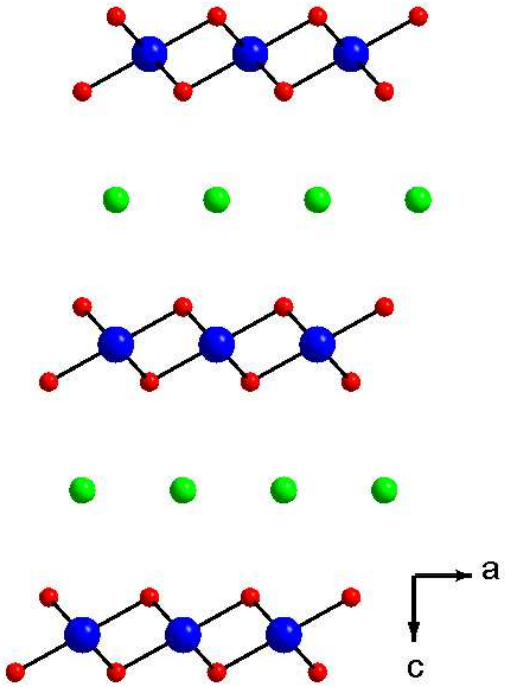


(b)

Figure S7. (a) Figure shows the arrangement of the layers in **1**. The $Cu_6S_6N_6$ clusters are shown as hexagons and Mn(1) as green ball. (b) The layers observed in brucite, $Mg(OH)_2$. Note the close similarity between the two layer arrangements (see text).



(a)



(b)

Figure S8. (a) Figure shows the layer arrangements in compound **1**, the dashed line represent the connectivity between the Cu_6 core and Mn atoms within the layer. (b) Structure of the layered double hydroxide $[Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.165}]$. Note the similarity in the positioning of the interlayer ions.

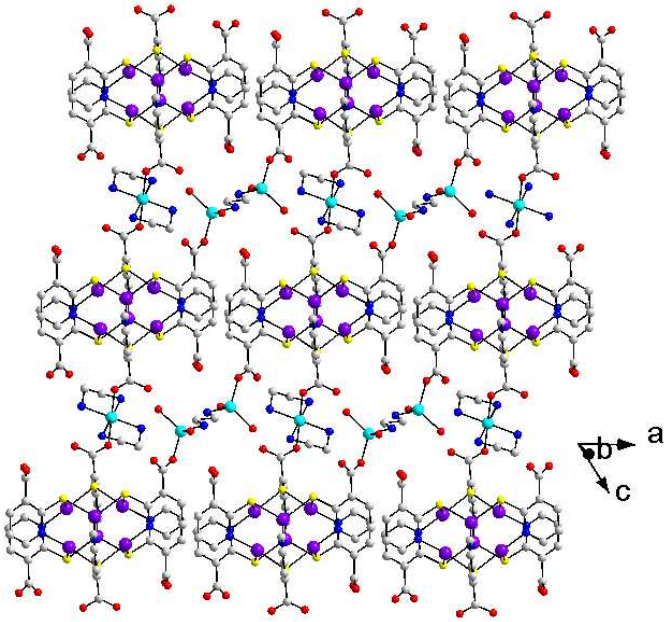
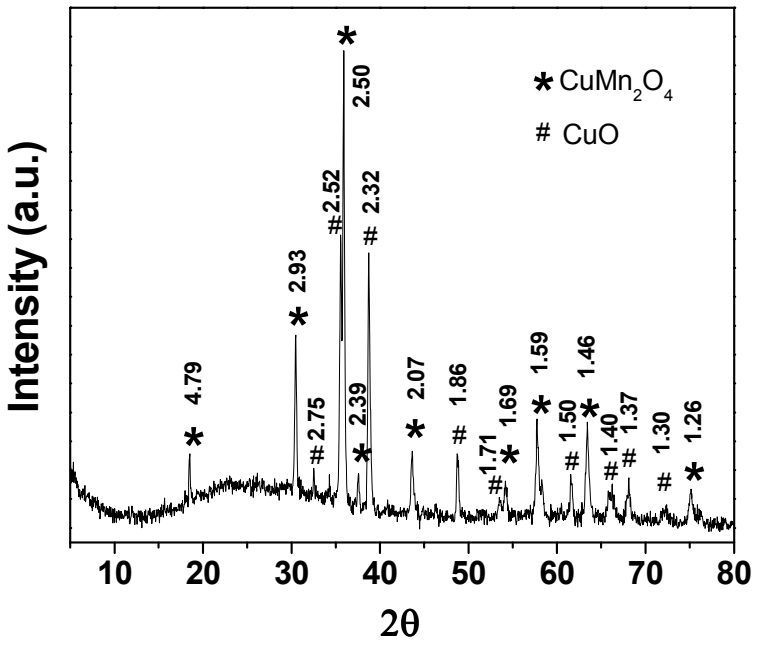
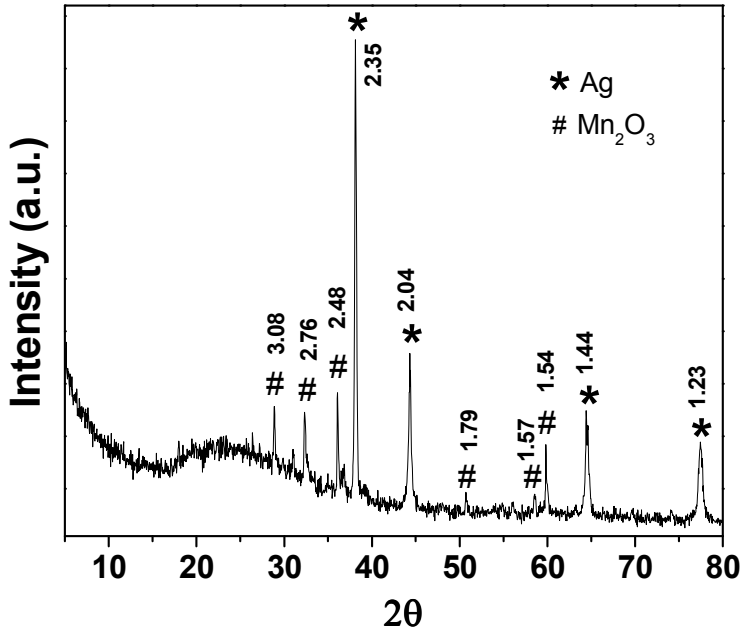


Figure S9. 2D layered structure of reported $\{[Zn_3(en)_3(H_2O)_4][Ag_6(mna)_6]\cdot 8H_2O\}_n$.



(a)



(b)

Figure S10. Powder XRD patterns of the final products of the compounds **1** (a) and **3** (b) after TGA analysis. The numbers denote the d spacing of the peaks.

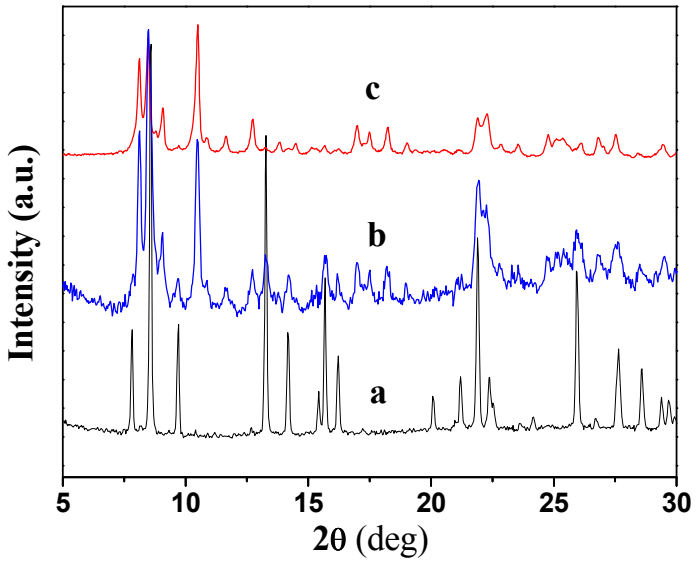


Figure S11. Powder XRD patterns of (a) pale yellow native compound **1**, (b) dark red compound after heating compound **1** at 70°C and (c) dark red compound produced by applying vacuum on compound **1**.

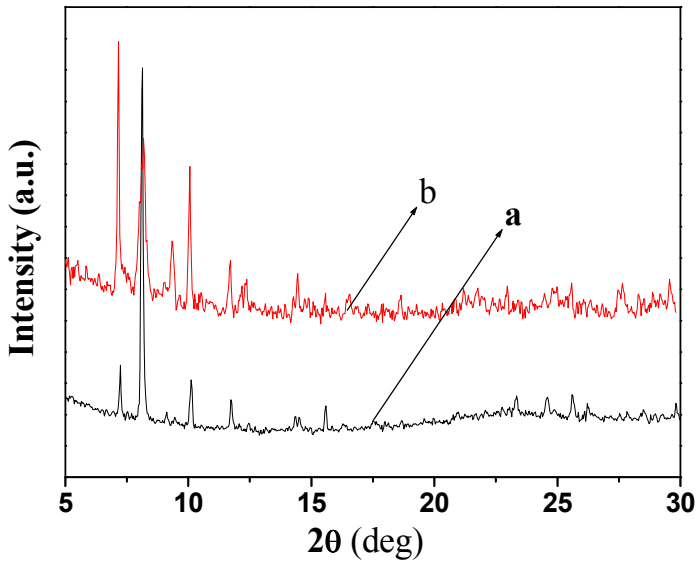


Figure S12. Powder XRD patterns of (a) compound **3** and (b) after heating the compound **3** at 70°C.

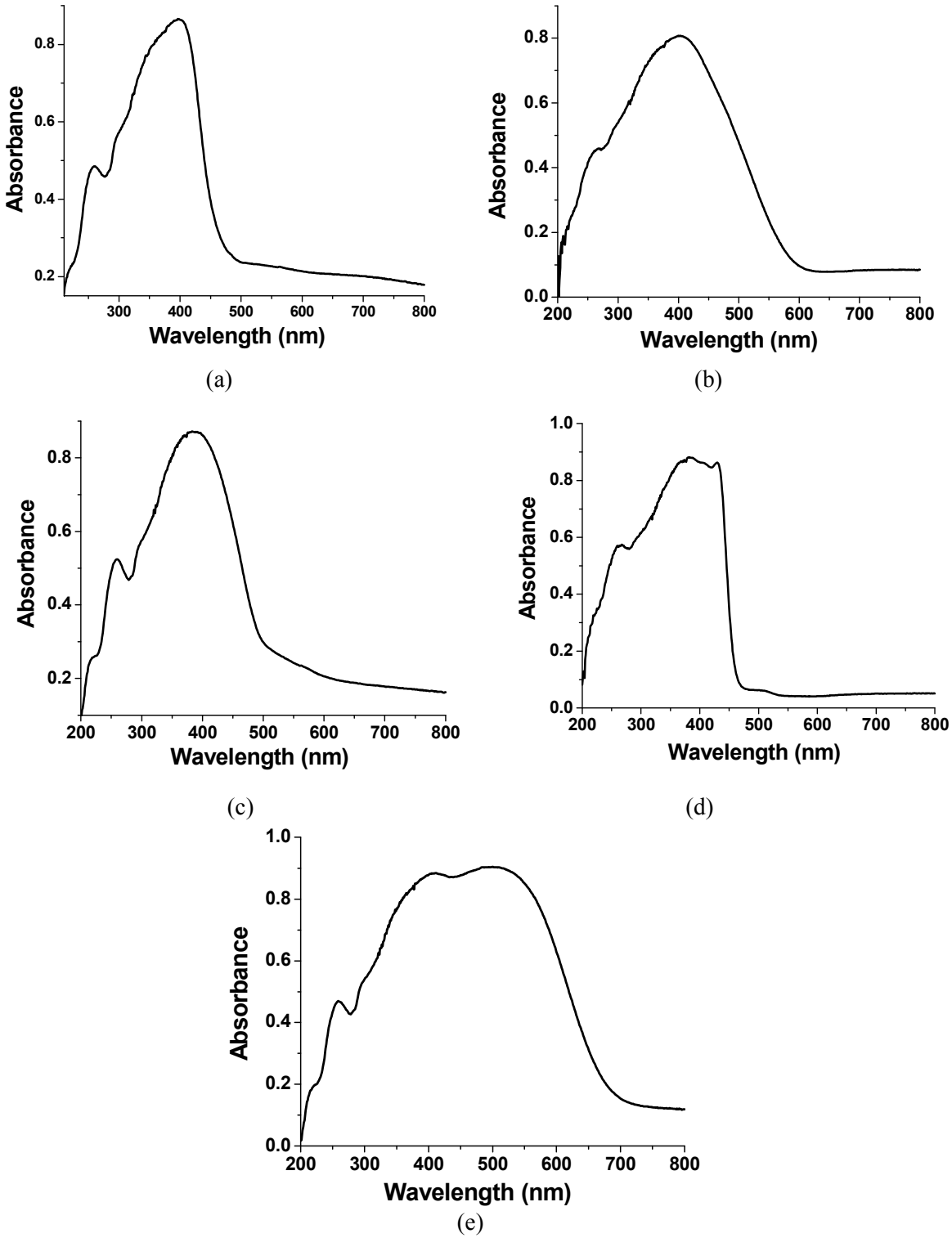


Figure S13. The solid state UV–Vis absorption spectrum of (a) compound **1**, (b) $[Cu_6(Hmna)_6]$, (c) compound **3**, (d) free H_2mna ligand and (e) red color phase of compound **1** at room temperature.

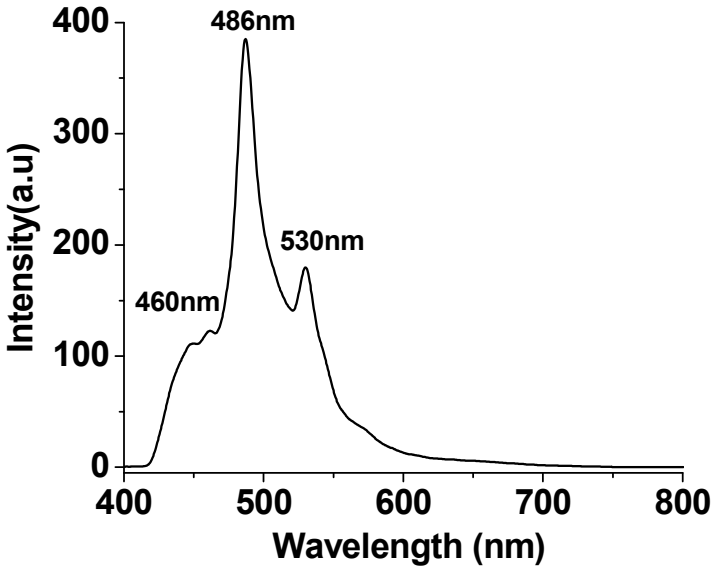


Figure S14. Room temperature solid–state photoluminescence spectrum of **3.**

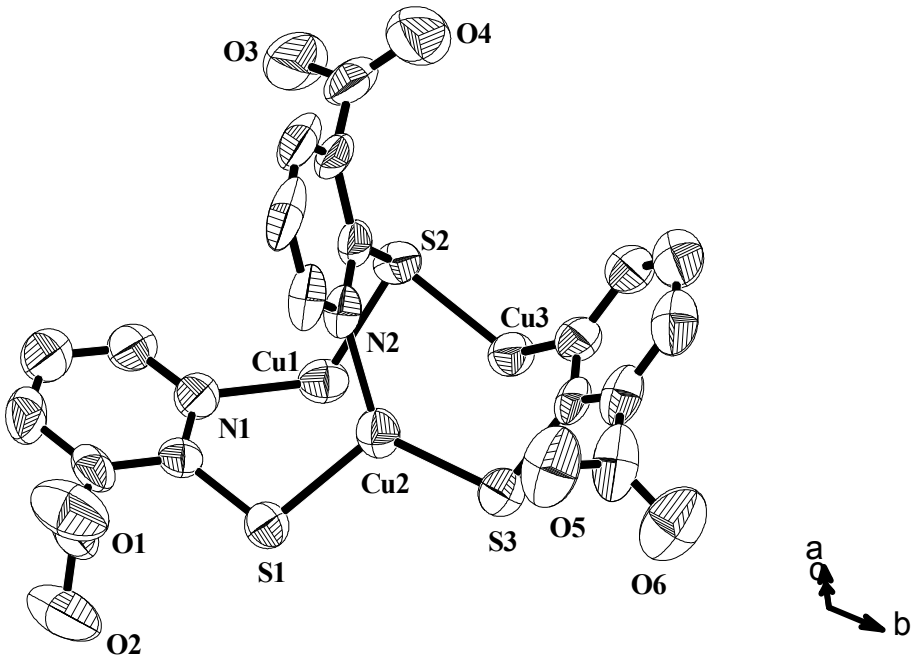


Figure S15. Asymmetric unit of the structure of compound $Cu_6(Hmna)_6$ (thermal ellipsoids with 50% probability).

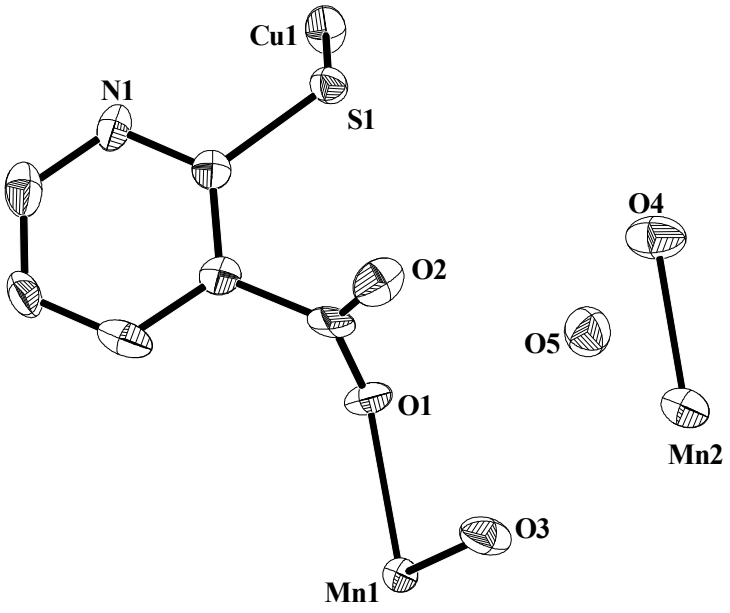


Figure S16. Asymmetric unit of the structure of compound **1** (thermal ellipsoids with 50% probability).

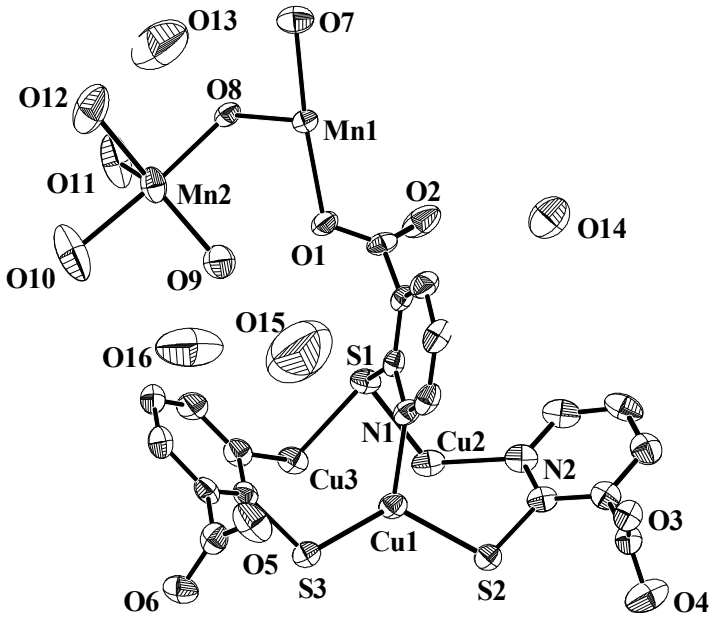


Figure S17. Asymmetric unit of the structure of compound **2** (thermal ellipsoids with 50% probability).

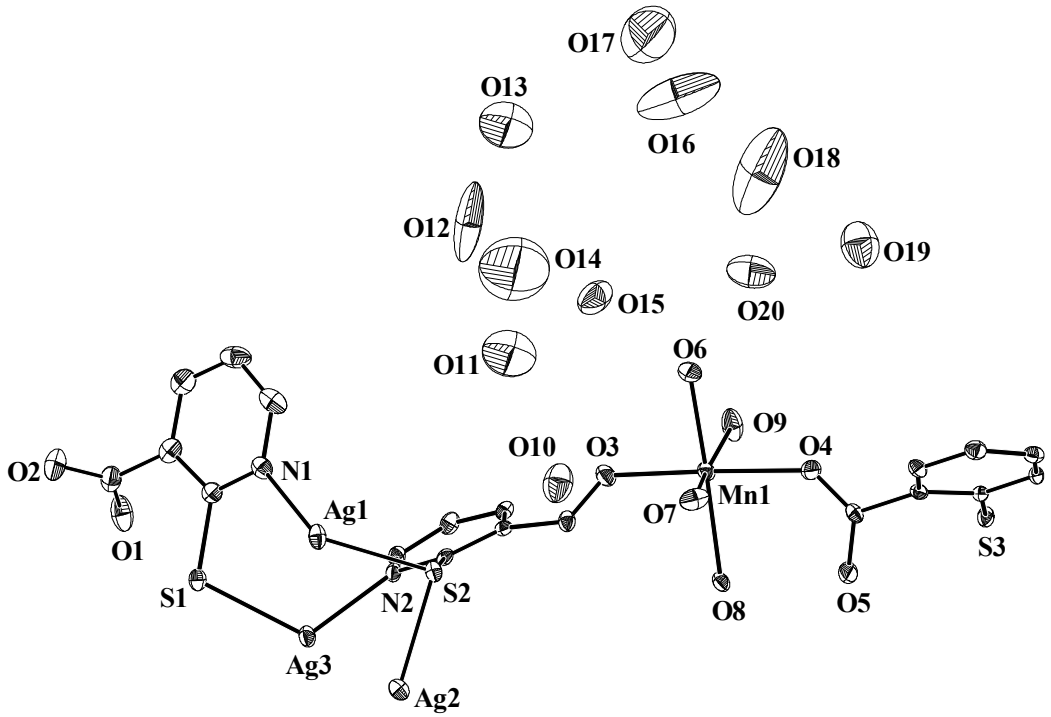


Figure S18. Asymmetric unit of the structure of compound **3** (thermal ellipsoids with 50% probability)