A Preformed 1-D $\{Cu^{II}_2\}_n$ Helical Chain as Precursor to a Decanuclear 0-D $\{Cu^{II}_8Mn^{II}_2\}$ Cluster: Synthesis, Structure and Magnetism

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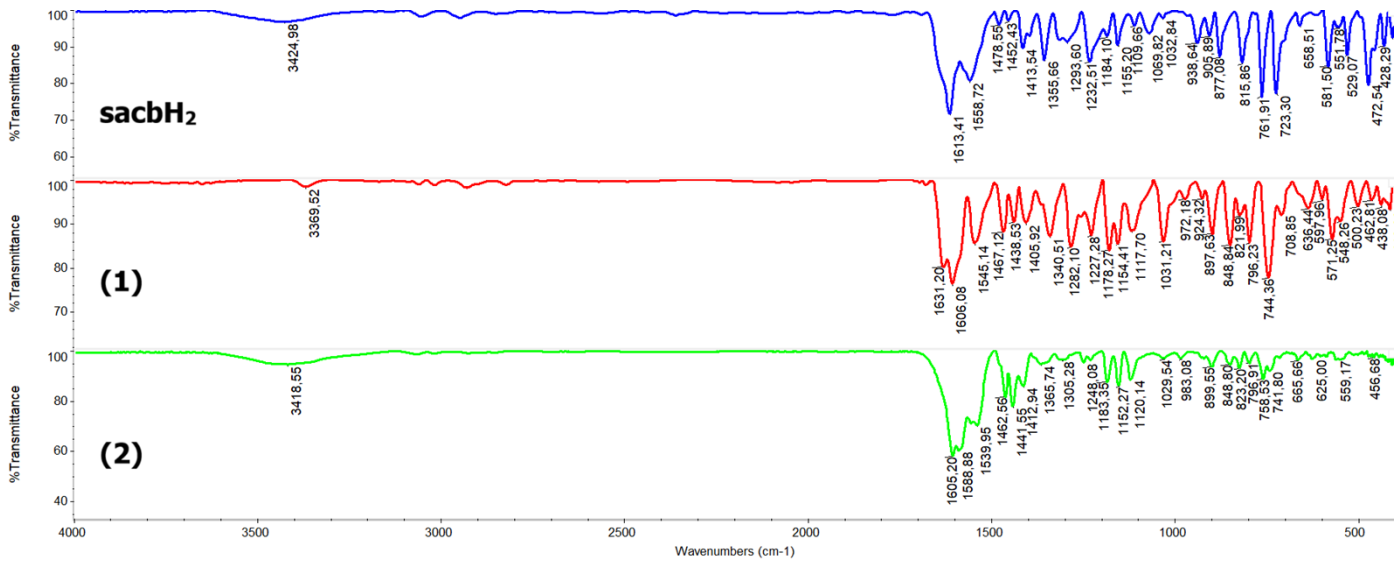

Figure S1. FT-IR spectra of the organic chelate sacbH_2, and $[Cu^{II}_2(sacb)_2(MeOH)]_n$ (**1**) and $[Cu^{II}_8Mn^{II}_2(OH)_4(sacb)_8(H_2O)_2]$ (**2**) complexes.

Table S1. Crystallographic data for compounds **1** and **2**.

Parameter	**1**	**2**
Formula	$C_{29}H_{20}Cl_2Cu_2N_2O_7$	$C_{369}Cl_{24}Cu_{24}H_{266}Mn_6N_{40.5}O_{90.25}$
F_w / g mol^{-1}	706.45	9416.61
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$
a / Å	12.8851(4)	77.1822(12)
b / Å	13.6763(4)	16.6415(4)
c / Å	14.8823(5)	29.2589(7)
α / °	90	90
β / °	90	100.799(2)
γ / °	90	90
V / Å^3	2622.57(14)	36915.4(14)
Z	4	4
T / K	102(4)	100.00
Radiation / μ (mm^{-1})	Cu Kα / 4.349	Cu Kα / 5.379
ρ_{calcd} / g cm^{-3}	1.789	1.694

Reflections collected/unique (R_{int})	9354/4999 (0.0373)	76551/32630 (0.0560)
Reflections with $I>2\sigma(I)$	4924	25788
No. of parameters	383	2463
R_1 [$I>2\sigma(I)$], wR_2 [$I>2\sigma(I)$][a,b]	0.0521, 0.1375	0.0658, 0.1637
R_1 (all data), wR_2 (all data)[a,b]	0.0525, 0.1383	0.0816, 0.1772
$(\Delta/\sigma)_{max}$	0.001	0.002
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.91/-1.38	1.21/-0.78
CCDC number	2504835	2504836

[a] $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2] / 3$; [b] $R_1 = \Sigma(|F_o| - |F_o|) / \Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected bond distances (Å) and bond angles (º) for complex **1**.

Bond Distances (Å)			
Cu1 – O2	2.289(4)	Cu2 – O3	1.923(4)
Cu1 – O3	2.007(4)	Cu2 – O41	2.333(4)
Cu1 – O5	1.898(4)	Cu2 – O1	1.891(4)
Cu1 – N2	1.950(5)	Cu2 – O6	2.012(4)
Cu1 – O6	1.933(4)	Cu1 ⋯ Cu2	3.0357(10)
Cu2 – N1	1.952(4)		
Bond Angles (º)			
O3 – Cu1 – O2	87.6(2)	N1 – Cu2 – O41	101.8(2)
O5 – Cu1 – O2	104.3(2)	N1 – Cu2 – O6	158.4(2)
O5 – Cu1 – O3	95.7(2)	O3 – Cu2 – N1	94.0(2)
O5 – Cu1 – N2	93.7(2)	O3 – Cu2 – O41	81.9(2)
O5 – Cu1 – O6	155.3(2)	O3 – Cu2 – O6	78.5(2)
N2 – Cu1 – O2	89.2(2)	O1 – Cu2 – N1	93.0(2)
N2 – Cu1 – O3	170.6(2)	O1 – Cu2 – O3	170.1(2)
O6 – Cu1 – O2	99.4(2)	O1 – Cu2 – O41	89.9(2)
O6 – Cu1 – O3	78.4(2)	O1 – Cu2 – O6	97.4(2)
O6 – Cu1 – N2	93.4(2)	O6 – Cu2 – O41	97.1(2)

Table S3. Selected bond distances (Å) and bond angles (º) for complex **2**.

Bond Distances (Å)			
Cu1 – O1	1.993(4)	Cu6 – O21	2.006(4)
Cu1 – O5	1.961(4)	Cu6 – O28	2.132(3)
Cu1 – O6	1.914(4)	Cu6 – N6	1.936(4)
Cu1 – N1	1.967(5)	Cu7 – O4	1.944(4)
Cu1 – O8	2.450(4)	Cu7 – O19	2.138(3)
Cu1 – O11	2.468(4)	Cu7 – O23	1.936(4)
Cu2 – O1	1.963(3)	Cu7 – O24	2.021(3)
Cu2 – O5	2.440(4)	Cu7 – N7	1.933(4)
Cu2 – O8	1.890(4)	Cu8 – O4	1.932(3)
Cu2 – O9	1.919(4)	Cu8 – O26	1.948(4)
Cu2 – N2	1.947(4)	Cu8 – O27	1.939(4)
Cu3 – O2	1.986(4)	Cu8 – N8	1.944(4)
Cu3 – O11	1.938(4)	Cu8 – O23	2.444(4)
Cu3 – O12	1.908(4)	Mn1 – O1	2.159(4)
Cu3 – N3	1.954(5)	Mn1 – O3	2.215(4)
Cu3 – O5	2.488(4)	Mn1 – O16	2.195(3)
Cu3 – O14	2.579(4)	Mn1 – O17	2.330(3)
Cu4 – O2	1.988(3)	Mn1 – O21	2.385(4)
Cu4 – O14	1.893(4)	Mn1 – O29	2.129(4)
Cu4 – O15	1.916(4)	Mn2 – O2	2.166(4)
Cu4 – N4	1.959(4)	Mn2 – O4	2.235(4)
Cu4 – O11	2.443(3)	Mn2 – O10	2.187(3)
Cu5 – O3	1.939(3)	Mn2 – O24	2.398(3)
Cu5 – O17	1.935(4)	Mn2 – O26	2.294(3)
Cu5 – O18	1.938(4)	Mn2 – O30	2.151(4)
Cu5 – O20	2.398(4)	Cu1 ⋯ Cu2	2.8581(10)
Cu5 – N5	1.948(4)	Cu3 ⋯ Cu4	2.9113(11)
Cu6 – O3	1.950(3)	Cu5 ⋯ Cu6	3.0800(10)
Cu6 – O20	1.937(3)	Cu7 ⋯ Cu8	3.0499(10)
Bond Angles (º)			

O5 – Cu1 – O1	89.1(2)	N5 – Cu6 – O28	88.0(2)
O5 – Cu1 – N1	93.2(2)	O4 – Cu7 – O19	93.3(1)
O6 – Cu1 – O1	83.8(2)	O4 – Cu7 – O24	84.7(1)
O6 – Cu1 – O5	171.8(2)	O23 – Cu7 – O4	89.4(2)
O6 – Cu1 – N1	93.2(2)	O23 – Cu7 – O19	128.0(2)
N1 – Cu1 – O1	169.0(2)	O23 – Cu7 – O24	131.9(2)
O1 – Cu2 – O5	77.3(1)	O24 – Cu7 – O19	100.1(1)
O8 – Cu2 – O1	81.3(2)	N7 – Cu7 – O4	172.9(2)
O8 – Cu2 – O5	82.1(1)	N7 – Cu7 – O19	89.3(2)
O8 – Cu2 – O9	167.6(2)	N7 – Cu7 – O23	94.2(2)
O8 – Cu2 – N2	95.5(2)	N7 – Cu7 – O24	88.4(2)
O9 – Cu2 – O1	88.1(1)	O4 – Cu8 – O26	82.4(1)
O9 – Cu2 – O5	89.2(1)	O4 – Cu8 – O27	88.6(1)
O9 – Cu2 – N2	95.5(2)	O4 – Cu8 – N8	176.8(2)
N2 – Cu2 – O1	175.2(2)	O27 – Cu8 – O26	158.8(2)
N2 – Cu2 – O5	105.9(2)	O27 – Cu8 – N8	94.0(2)
O11 – Cu3 – O2	88.4(2)	N8 – Cu8 – O26	95.8(2)
O11 – Cu3 – N3	94.2(2)	O1 – Mn1 – O3	88.0(1)
O12 – Cu3 – O2	84.7(2)	O1 – Mn1 – O16	92.8(1)
O12 – Cu3 – O11	170.3(2)	O1 – Mn1 – O17	88.9(1)
O12 – Cu3 – N3	92.0(2)	O1 – Mn1 – O21	158.9(1)
N3 – Cu3 – O2	173.4(2)	O3 – Mn1 – O17	67.1(1)
O14 – Cu4 – O2	83.4(1)	O3 – Mn1 – O21	72.6(1)
O14 – Cu4 – O15	170.3(2)	O16 – Mn1 – O3	87.4(1)
O14 – Cu4 – N4	95.2(2)	O16 – Mn1 – O17	154.4(1)
O15 – Cu4 – O2	88.7(1)	O16 – Mn1 – O21	78.3(1)
O15 – Cu4 – N4	93.1(2)	O17 – Mn1 – O21	91.2(1)
N4 – Cu4 – O2	175.4(2)	O29 – Mn1 – O1	123.4(2)
O3 – Cu5 – O20	75.6(1)	O29 – Mn1 – O3	147.5(1)
O3 – Cu5 – N5	176.9(2)	O29 – Mn1 – O16	98.2(1)
O17 – Cu5 – O3	81.0(1)	O29 – Mn1 – O17	102.2(1)
O17 – Cu5 – O18	159.5(2)	O29 – Mn1 – O21	77.2(1)
O17 – Cu5 – O20	102.6(1)	O2 – Mn2 – O4	87.7(1)

O17 – Cu5 – N5	96.0(2)	O2 – Mn2 – O10	92.6(1)
O18 – Cu5 – O3	90.3(1)	O2 – Mn2 – O24	156.8(1)
O18 – Cu5 – O20	93.0(1)	O2 – Mn2 – O26	86.3(1)
O18 – Cu5 – N5	92.7(2)	O4 – Mn2 – O24	70.3(1)
N5 – Cu5 – O20	105.0(2)	O4 – Mn2 – O26	68.7(1)
O3 – Cu6 – O21	87.2(2)	O10 – Mn2 – O4	88.3(1)
O3 – Cu6 – O28	92.5(1)	O10 – Mn2 – O24	79.9(1)
O20 – Cu6 – O3	87.3(2)	O10 – Mn2 – O26	157.0(1)
O20 – Cu6 – O21	128.0(2)	O26 – Mn2 – O24	92.2(1)
O20 – Cu6 – O28	126.5(2)	O30 – Mn2 – O2	126.9(1)
O21 – Cu6 – O28	105.4(2)	O30 – Mn2 – O4	144.2(1)
N6 – Cu6 – O3	176.5(2)	O30 – Mn2 – O10	98.1(1)
N6 – Cu6 – O20	95.2(2)	O30 – Mn2 – O24	76.2(1)
N5 – Cu6 – O21	89.4(2)	O30 – Mn2 – O26	100.9(1)

Table S4. Bond Valence Sum (BVS) Calculations for the Mn atoms in complex **2**.

Atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	**1.82**	1.70	1.74
Mn2	**1.80**	1.67	1.72

The underlined and boldface value is the one closest to the charge for which it was calculated. The oxidation state can be taken as the nearest whole number to the underlined value.

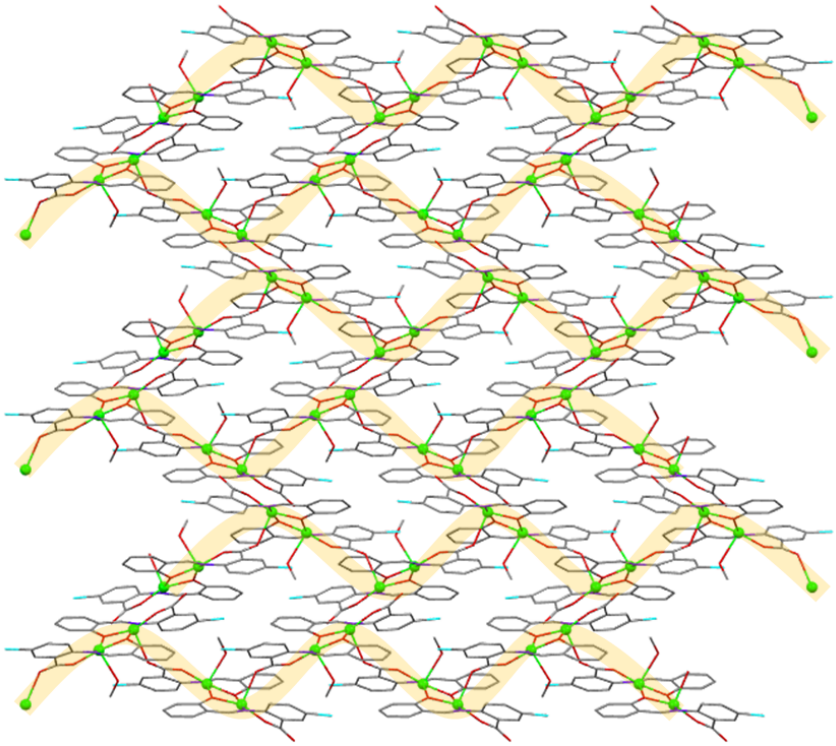

Figure S2. Representation of a section of the 1-D helical chains of **1** along the crystallographic *a*-axis. All H atoms are omitted for clarity. Color scheme: Cu^{II}, green; O, red; N, blue; C, gray; Cl, cyan.

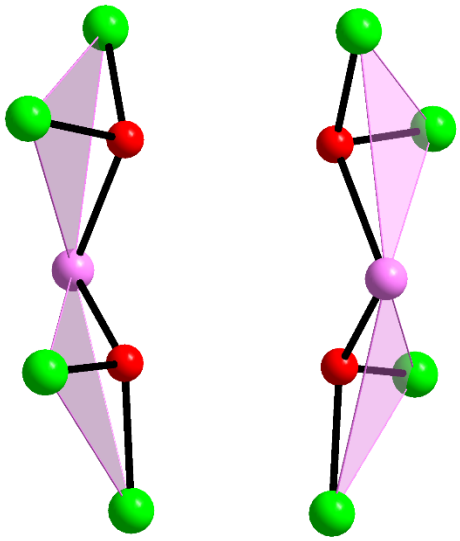

Figure S3. The four $\{Cu_2Mn(\mu_3\text{-}OH)\}^{5+}$ triangles within the structure of complex **2**. H atoms are omitted for clarity. Color scheme: Cu^{II}, green; Mn^{II}, magenta; O, red.

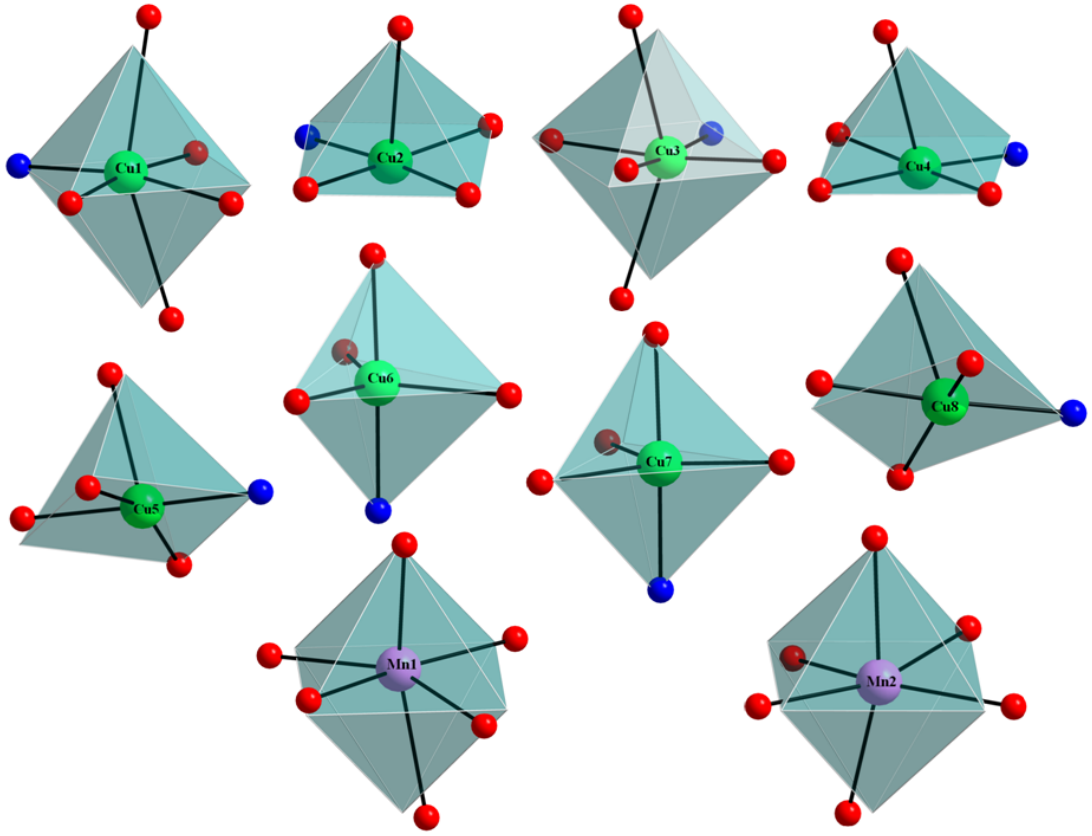

Figure S4. The distorted octahedral (for Cu1, Cu3, Mn1 and Mn2), square pyramidal (for Cu2, Cu4, Cu5 and Cu8) and trigonal bipyramidal (for Cu6 and Cu7) coordination polyhedra of the metal ions present in **2**. Points connected by the white thin lines define the vertices of the ideal polyhedron. Color scheme: Cu^{II}, green; Mn^{II}, magenta; O, red; N, blue.

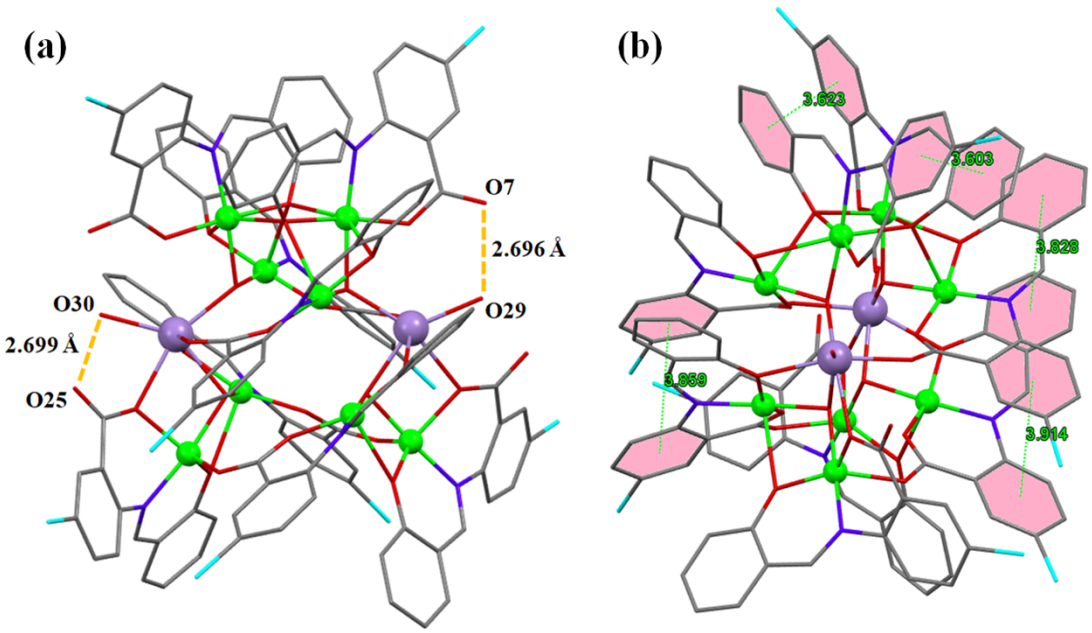

Figure S5. The intramolecular (a) hydrogen bonding interactions (indicated by yellow dashed lines) and (b) π···π stacking interactions (indicated by green dashed lines) between the aromatic rings (with pink color) within complex **2**. All H atoms are omitted for clarity. Color scheme: Cu^{II}, green; Mn^{II}, magenta; O, red; N, blue; C, gray; Cl, cyan.

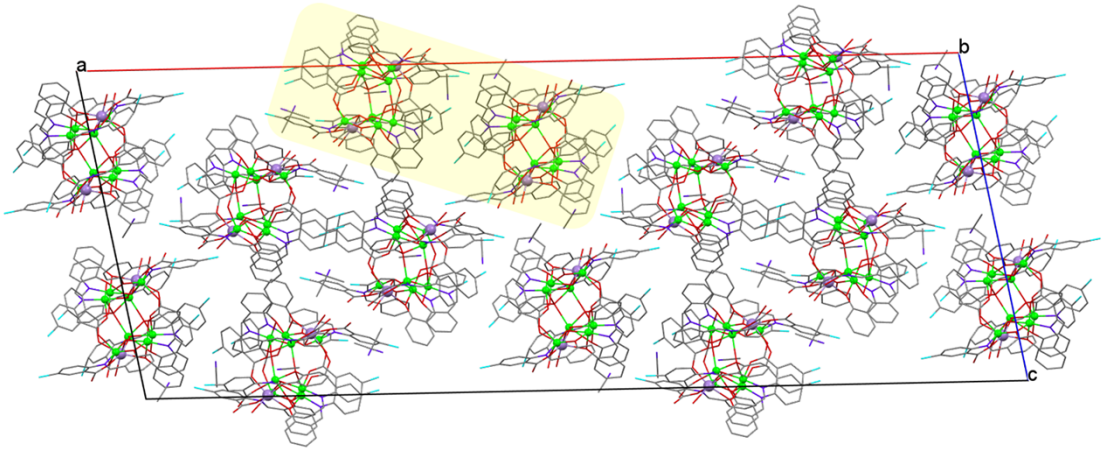

Figure S6. A part of the crystal packing of complex **2**, along the crystallographic *b*-axis, highlighting with a yellow square the two crystallographically independent decanuclear molecules. All H atoms are omitted for clarity. Color scheme: Cu^{II}, green; Mn^{II}, magenta; O, red; N, blue; C, gray; Cl, cyan.

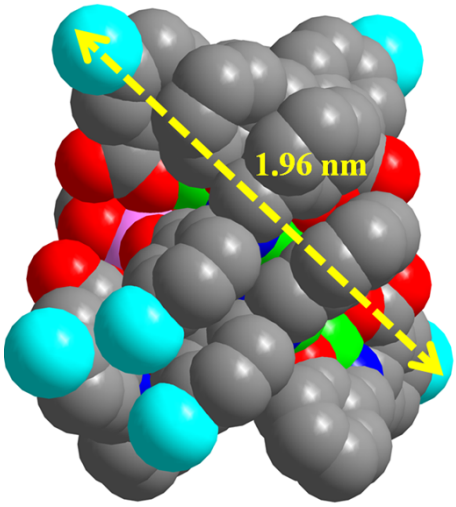

Figure S7. Space-filling representation of **2**, showing its nanosized dimensions (1.96 nm). All H atoms are omitted for clarity. Color scheme: Cu^{II}, green; Mn^{II}, magenta; O, red; N, blue; C, gray; Cl, cyan.

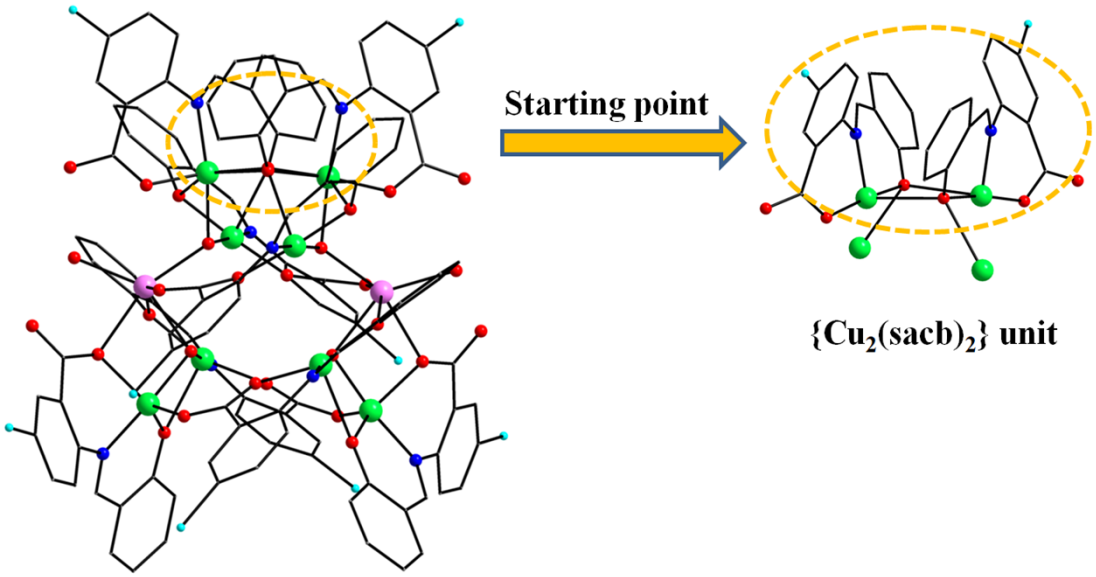

Figure S8. Representation (with yellow dashed circle) of the $\{Cu_2(sacb)_2\}$ unit as a starting point of cluster **2**, which comprises the repeating unit of the polymeric compound **1**. All H atoms are omitted for clarity. Color scheme: Cu^{II}, green; Mn^{II}, magenta; O, red; N, blue; C, gray; Cl, cyan.