<Electronic Supplementary Information>

Construction of kagome-type networks via tridentate ligand: structural properties as alcohol reservoir

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Experimental

Materials and Measurements. All chemicals including $CuCl_2$ and $CuBr_2$ were purchased from Aldrich, and used as received. Elemental microanalyses (C, H, N) were performed on crystalline samples by the KBSI Pusan Center using a Vario-EL III analyzer. Thermal analyses were performed under N_2 at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer using samples prepared as KBr pellets. X-ray powder diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu Kα. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300. SEM images were taken by a VEGA 3 SEM TESCAN. Calcination of crystals was performed using a Daeheung Muffle Furnace DF-1.

Preparation of *N,N',N"*-Tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide (L).

Triethylamine (2.30 mL, 16.5 mmol) was slowly added to a 100 mL chloroform solution of 2-(2-pyridinyl)ethanamine (1.97 mL, 16.5 mmol) maintained at an ice-bath temperature. Then, an equivalent amount of 1,3,5-benzenetricarbonyl trichloride (1.35 g, 5.0 mmol) was added and refluxed for 36 h. The solution was washed with water several times, and then dried with $MgSO_4$. Removal of the solvent *N,N',N"*-tris(2-pyridinylethyl)-1,3,5-

benzenetricarboxamide (L) afforded a pale yellow solid in a 77% yield (2.02 g). Anal. Calcd

for $C_{30}H_{30}N_6O_3$: C, 68.95; H, 5.79; N, 16.08%. Found: C, 68.80; H, 5.72; N, 16.14%. IR

(KBr, cm^{-1}): 3238 (m), 3064 (m), 2935 (w), 1656 (s), 1592 (m), 1533 (s), 1477 (m), 1438 (m),

1292 (s), 765(m). ^{1}H NMR (Me$_2$SO-d_6, δ): 8.81 (s, 3H), 8.51 (d, J = 4.94 Hz, 3H), 8.36 (s,

3H), 7.71 (t, J = 7.42 Hz, 3H), 7.29 (d, J = 7.69 Hz, 3H), 7.23 (dd, J = 7.42 Hz, J = 4.94 Hz,

3H), 3.65 (m, 6H), 3.02 (t, J = 7.69 Hz, 6H). ^{13}C NMR (75 MHz, CD$_3$OD, δ): 168.34, 160.15,

149.80, 138.66, 137.52, 129.78, 125.03, 123.18, 41.07, 38.22. ^{13}C NMR (75 MHz, Me$_2$SO-d_6,

δ): 165.65, 159.18, 149.17, 136.57, 135.17, 128.53, 123.22, 121.63, 39.50, 37.34.

Synthesis of 6EtOH@[Cu$_3$Cl$_6$L$_2$]. A methanol solution (10 mL) of CuCl$_2$ (40.3 mg, 0.3

mmol) was slowly added to an ethanol solution (10 mL) of L (105 mg, 0.2 mmol). The

mixture was gradually evaporated, resulting, after 3 days in an 84.0% (145 mg) yield of blue

crystals suitable for X-ray crystallography. m.p. 332 °C (dec. of skeleton). Anal. Calcd for

$C_{72}H_{93}N_{12}O_{12}Cu_3Cl_6$: C, 50.22; H, 5.44; N, 9.76%. Found: C, 50.10; H, 5.37; N, 9.81%. IR

(KBr, cm^{-1}): 3305 (m), 3070 (m), 2937 (w), 1654 (s), 1606 (s), 1540 (s), 1488 (m), 1438 (m),

1290 (m), 769 (m).

Synthesis of 3MeOH·3EtOH@[Cu$_3$Br$_6$L$_2$]. 3MeOH·3EtOH@[Cu$_3$Br$_6$L$_2$] was prepared in

the same manner as 6EtOH@[Cu$_3$Cl$_6$L$_2$], using CuBr$_2$ instead of CuCl$_2$, for a 78.6% (153

mg) yield. m.p. 338 °C (dec. of skeleton). Anal. Calcd for $C_{69}H_{90}N_{12}O_{12}Cu_3Br_6$: C, 42.51; H,

4.65; N, 8.62%. Found: C, 42.50; H, 4.62; N, 8.86%. IR (KBr, cm^{-1}): 3288 (m), 3066 (m),

2939 (w), 1646 (s), 1606 (m), 1540 (s), 1488 (m), 1438 (m), 1292 (m), 769 (m).

Crystallographic Structure Determination. All X-ray data were collected on a Bruker

SMART automatic diffractometer with graphite-monochromated Mo Kα radiation (λ =

0.71073 Å) and a CCD detector at 170 K. The cell parameters and orientation matrix were

obtained by means of the collection and processing of 36 frames of 2D diffraction images.

The data were corrected for Lorentz and polarization effects. The absorption effects were

corrected by the multi-scan method (SADABS).[1] The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least-squares techniques (SHELXL 97).[2] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal parameters along with procedural information on the data collection and structure refinement are listed in Table S1.

References

1   G. M. Sheldrick, SADABS, A program for Empirical Absorption Correction of Srea Detector Data; University of Göttingen, Germany, 1996.

2   G. M. Sheldrick, SHELXS-97: A Program for Structure Determination; University of Göttingen, Germany, 1997; G. M. Sheldrick, SHELXL-97: A Program for Structure Refinement; University of Göttingen, Germany, 1997.

Table S1. Crystal data for 6EtOH@[$Cu_3Cl_6L_2$] and 3MeOH·3EtOH@[$Cu_3Br_6L_2$]

	6EtOH@[$Cu_3Cl_6L_2$]	3MeOH·3EtOH@[$Cu_3Br_6L_2$]
Formula	$C_{72}H_{96}N_{12}O_{12}Cu_3Cl_6$	$C_{69}H_{90}N_{12}O_{12}Cu_3Br_6$
M_w (g mol^{-1})	1724.94	1949.61
Crystal system	Trigonal	Trigonal
Space group	$R3$	$R3$
a (Å)	25.1719(5)	25.4049(3)
c (Å)	10.8188(3)	10.6802(2)
V (Å^3)	5936.7(2)	5969.5(2)
Z	3	3
d_{calcd} (Mg m^{-3})	1.447	1.627
Reflections	11925	11714
R_{int}	0.0655	0.0942
μ (mm^{-1})	1.067	3.870
GoF on F^2	1.089	1.026
R_1 [$I > 2\sigma(I)$][a]	0.0406	0.0590
wR_2 (all data)[b]	0.0686	0.1371

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b]$wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for 6EtOH@$[Cu_3Cl_6L_2]$ and

3MeOH·3EtOH@$[Cu_3Br_6L_2]$

	6EtOH@$[Cu_3Cl_6L_2]$	3MeOH·3EtOH@$[Cu_3Br_6L_2]$
Cu(1)–N(1)	2.000(4)	1.989(6)
Cu(1)–N(3)	2.005(4)	2.000(7)
Cu(1)–X(1)	2.261(2)	2.456(2)
Cu(1)–X(2)	2.283(2)	2.416(2)
Cu(1)···O(2)	2.99(2)	2.99(1)
Cu···Cu	11.352(1)	11.525(2)
	13.820(1)	13.879(2)
diagonal Cu···Cu	25.172(1)	25.405(1)
plane···plane	3.606(1)	3.560(1)
N(1)–Cu(1)–N(3)	162.6(2)	163.6(3)
X(1)–Cu(1)–X(2)	175.51(7)	174.46(6)
N(1)–Cu(1)–X(1)	90.6(1)	88.0(2)
N(3)–Cu(1)–X(1)	92.4(1)	91.7(2)
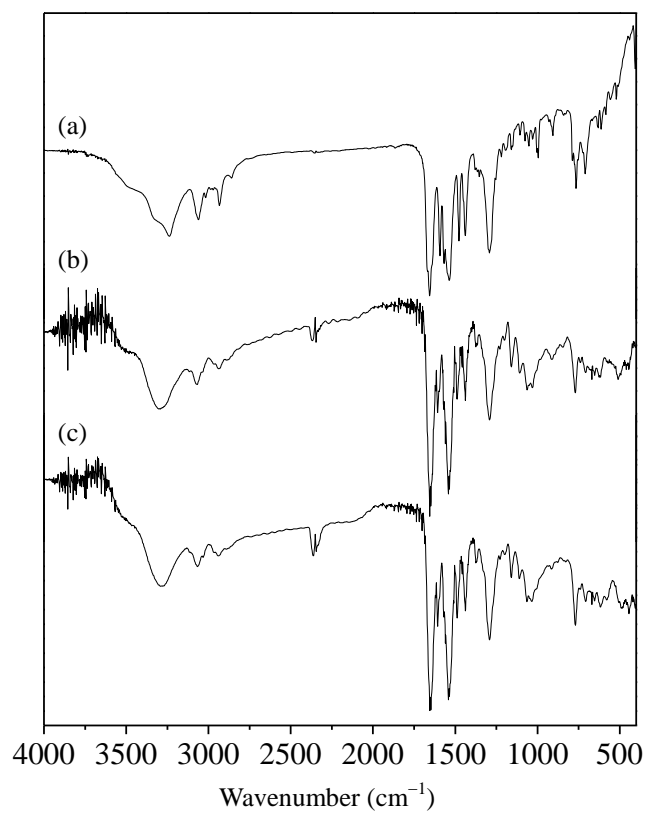
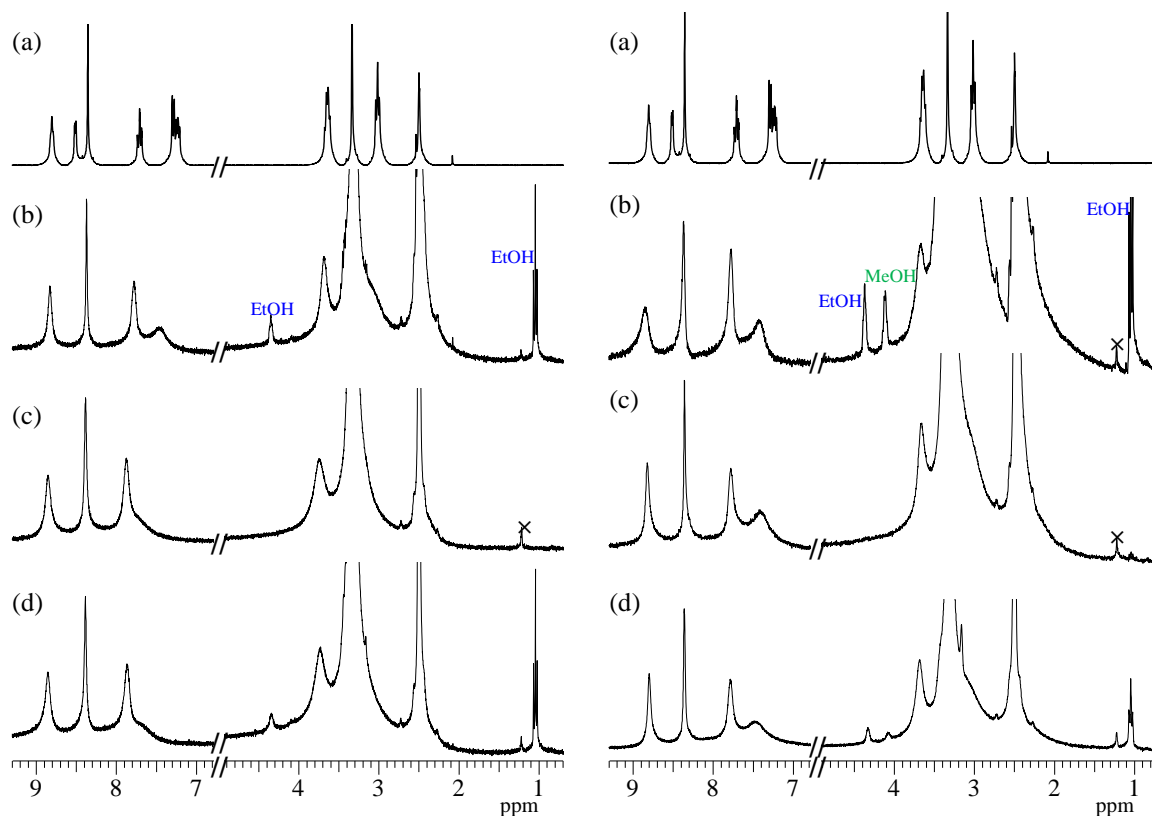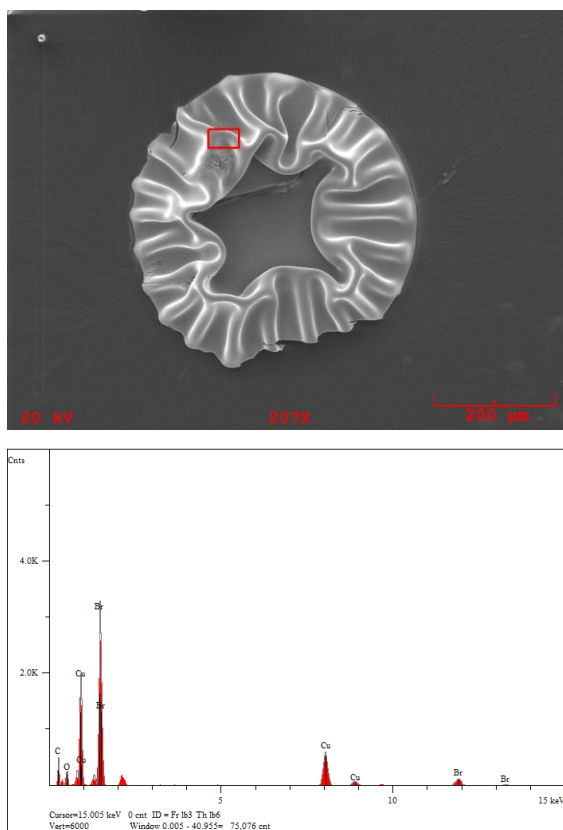**Fig. S1.** IR data of L (a), 6EtOH@[$Cu_3Cl_6L_2$] (b), and 3MeOH·3EtOH@[$Cu_3Br_6L_2$] (c).

Fig. S2. ^{1}H NMR spectra (DMSO-d_6) during the evacuation of re-absorption of the solvated molecules into [Cu$_3$X$_6$L$_2$]. Left: L (a), 6EtOH@[Cu$_3$Cl$_6$L$_2$] (b), evacuated sample at 80 °C overnight (c), and re-absorbed sample (d); right: L (a), 3MeOH·3EtOH@[Cu$_3$Br$_6$L$_2$] (b), evacuated sample at 80 °C overnight (c), and re-absorbed sample (d).

Elt.	Line	Atomic %	Conc.	Units	
C	Kα	60.863	23.882	wt.%	
O	Kα	9.284	4.853	wt.%	
Cu	Kα	12.468	25.884	wt.%	
Br	Kα	17.385	45.381	wt.%	
		100.000	100.000	wt.%	Total

Fig. S3. SEM EDX data for $3MeOH \cdot 3EtOH@[Cu_3Br_6L_2]$ after calcination at 350 °C for 1 h.
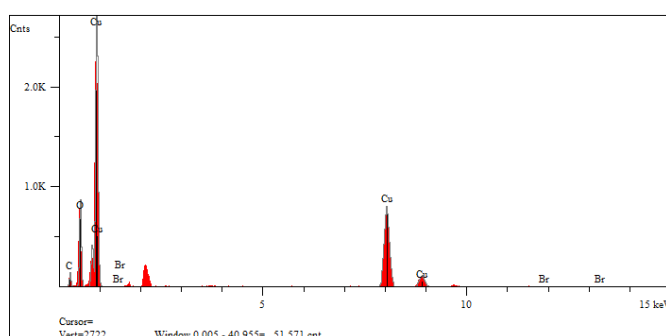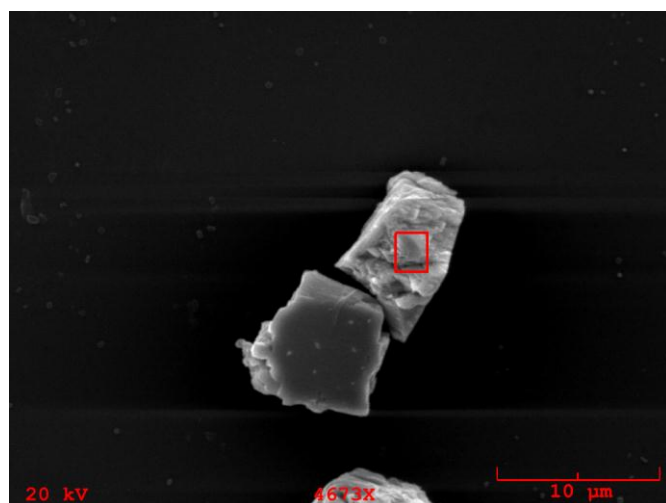
Elt.	Line	Atomic %	Conc	Units	
C	Kα	26.111	9.615	wt.%	
O	Kα	**36.929**	18.114	wt.%	
Cu	Kα	**36.429**	70.972	wt.%	
Br	Kα	0.530	1.298	wt.%	
		100.000	100.000	wt.%	Total

Fig. S4. SEM EDX data for CuO after calcination of $3MeOH \cdot 3EtOH@[Cu_3Br_6L_2]$ at 600 °C
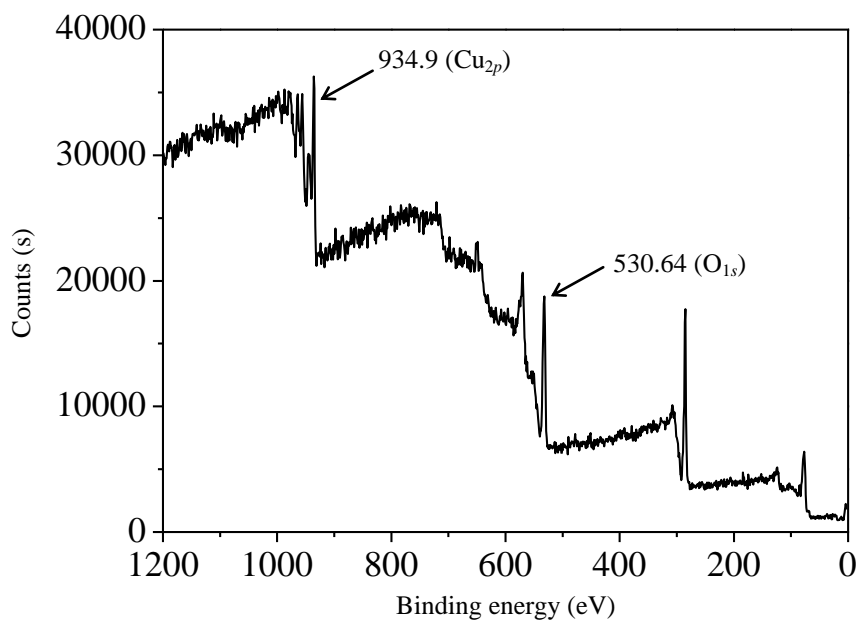
for 1 h.

Fig. S5. XPS data of CuO nanocrystals after calcination of $3MeOH·3EtOH@[Cu_3Br_6L_2]$ at 600 °C for 1 h.