Supporting information

Deliberate Design of a 3D Homochiral Cu^{II}/L-met/Ag^{I} Coordination Network Based on the Distinct Soft-Hard Recognition Principle

Tzuoo-Tsair Luo,† Liang-Yu Hsu,† Chan-Cheng Su,‡ Chuen-Her Ueng,‡ Tseng-Chang Tsai,§ and Kuang-Lieh Lu*,†

†Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, ‡Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan, and §Department of Applied Chemistry, National Kaohsiung University, Kaohsiung 811, Taiwan

Experimental Section

General Details: $Cu(NO_3)_2{\cdot}3H_2O$, $AgNO_3$ and L-methionine were purchased commercially and used as received without further purification. Thermogravimetric analyses were performed under nitrogen with a Perkin–Elmer TGA-7 analyzer. Powder-diffraction measurements were recorded with a Siemens D-5000 diffractometer at 40 kV (30 mA) with Cu-K_α radiation (λ = 1.5406 Å), with a step size of 0.02° in θ and s scan speed of 1s per step size. IR spectra were recorded with a Perkin-Elmer Paragon 1000 FTIR Spectrophotometer. DSC measurements were carried out with a Mettler Toledo DSC822 calorimeter.

Synthesis of $[Ag_3Cu_3$(L-methioninato)$_6(NO_3)_3(H_2O)_3]{\cdot}7H_2O$ (1). A solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.5 mmol) and $AgNO_3$ (0.5 mmol) in C_2H_5OH (6 mL) was carefully layered onto a solution of L-methionine (1 mmol) in water (6 mL). It was then allowed to stand at room temperature in dark for about four weeks, whereupon deep-blue rod-like crystals were formed in 62% yield (based on L-

methionine). The solid product was washed with deionized water and ethanol, and dried in air. Elemental analysis (%) calcd for $C_{30}H_{80}Ag_3Cu_3N_9O_{31}S_6$: C 20.36, H 4.56, N 7.12; found: C 20.73, H 4.15, N 7.08. The formula $[Ag_3Cu_3(\text{L-methioninato})_6(NO_3)_3(H_2O)_3]\cdot 7H_2O$ was in good agreement with thermogravimetric analysis and single-crystal X-ray diffraction studies.

Detailed reversible dehydration–rehydration studies

The existence of a wide plateau area in the TGA plot of **1** indicates that compound **1** would be amenable to a dehydration-rehydration study (Figure S6). A freshly ground sample of **1** was heated at 110 °C for 1 h until a stable flat baseline of the TGA curve was observed, which indicates that all hosted water molecules were eliminated (weight loss about 10.2%, Figure S10). The sample was then naturally cooled to room temperature by exposure to a moist atmosphere for 24 h. TGA analysis of the rehydrated samples (weight loss of water is about 9.8%, Figure S10) reveals that the rehydration process is almost complete. The XRPD patterns for compound **1** at 110 °C do not show any significant peak, but the crystallinity of **1** was recovered after rehydration. Using the same sample, the cycle of dehydration–rehydration process can be repeated many times as monitored by XRPD (Figure S8–S9).

Crystal structure determination

$[Ag_3Cu_3(\text{L-methioninato})_6(NO_3)_3(H_2O)_3]\cdot 7H_2O$ (1). A suitable single crystal of **1** with dimensions of 0.30 × 0.20 × 0.20 mm^3 was mounted on the tip of a glass fiber and placed onto the goniometer head for indexing and intensity data collection using a Nonius Kappa CCD diffractometer ($Mo_{K\alpha}$ = 0.71073 Å). The raw frame data for **1** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects with the Denzo program.[1] An empirical absorption correction was applied by using the Multiscan method. The structure of **1** was solved by direct methods and refined against F^2 by the full-matrix least-squares technique, using the WINGX,[2] PLATON,[3] and SHELX[4] software packages. The non-hydrogen atoms were refined with anisotropic displacement parameters,

and the hydrogen atoms of the framework were calculated and refined as riding modes. The hydrogen atoms of water molecules were found in difference Fourier maps but not refined. Crystal data for **1**: $C_{30}H_{80}Ag_3Cu_3N_9O_{31}S_6$ $\{[Ag_3Cu_3(\text{L-methioninato})_6(NO_3)_3(H_2O)_3]\cdot 7H_2O\}_n$, M_r = 1769.62, orthorhombic, $P2_12_12_1$, a = 15.8730(1) Å, b = 16.9061(1) Å, c = 22.8297(2) Å, V = 6126.36(8) Å^3, Z = 4, ρ_{calcd} = 1.919 g cm^{-3}, μ = 2.258 mm^{-1}, λ ($Mo_{K\alpha}$) = 0.71073 Å, F(000) = 3580, T = 293(2) K, A total of 44653 reflections were collected in the range of 4.13° ≤ θ ≤ 27.48°, of which 13889 were unique (R_{int} = 0.0446). Final R indices: R_1 = 0.0363, wR_2 = 0.0786 for 11509 reflections [$I > 2\sigma(I)$]; R_1 = 0.0498, wR_2 = 0.0831 for 13889 independent reflections (all data) and 775 parameters, GOF = 1.053.

References

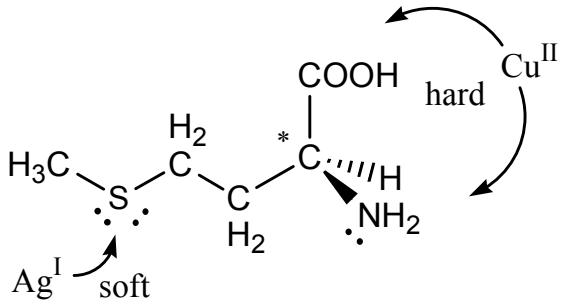
(1) Otwinowski, Z.; Minor, W. "*Processing of X-ray Diffraction Data Collected in Oscillation Mode*", *Methods in Enzymology*, Volume 276: Macromolecular Crystallography, part A, pp. 307–326, 1997, Carter, Jr. C. W. and Sweet, R. M. Eds., Academic Press.

(2) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(3) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(4) Sheldrick, G. M. *SHELX-97*, University of Göttingen, 1997**.**

Scheme S1. The soft-hard interaction between Ag^{I}, Cu^{II}, and bifunctional ligand of L-methionine.



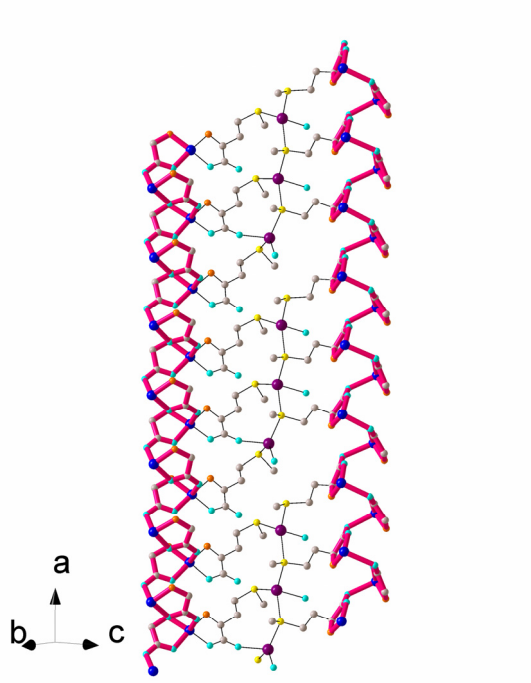


Figure S1. Side view of the linkage between Ag-trimer units and two Cu_{∞}-helix units. (Water guest molecules and nitrate anions inside the channels have been omitted for clarity. Color codes as in Figure 1)

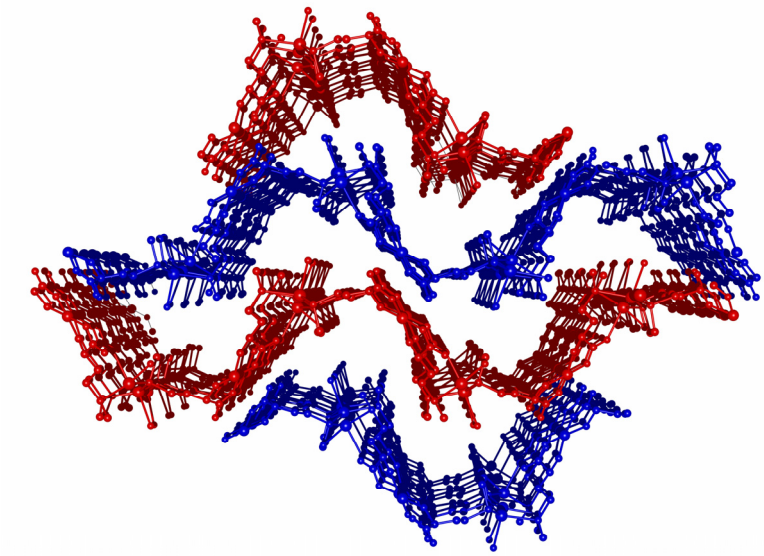


Figure S2. Ball-and-stick representation of **1** shows the undulated layers stacking along the *b* axis.

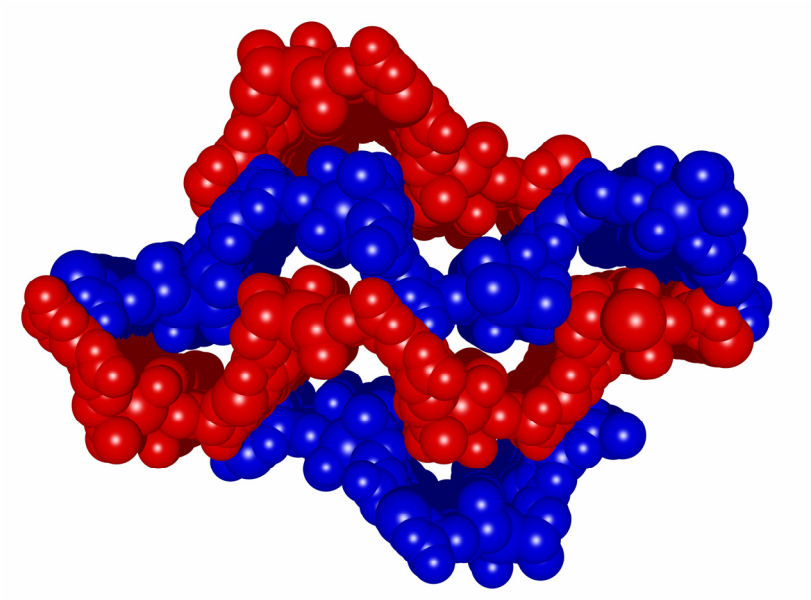


Figure S3. Space-filling representation of **1** shows the undulated layers stacking along the *b* axis.

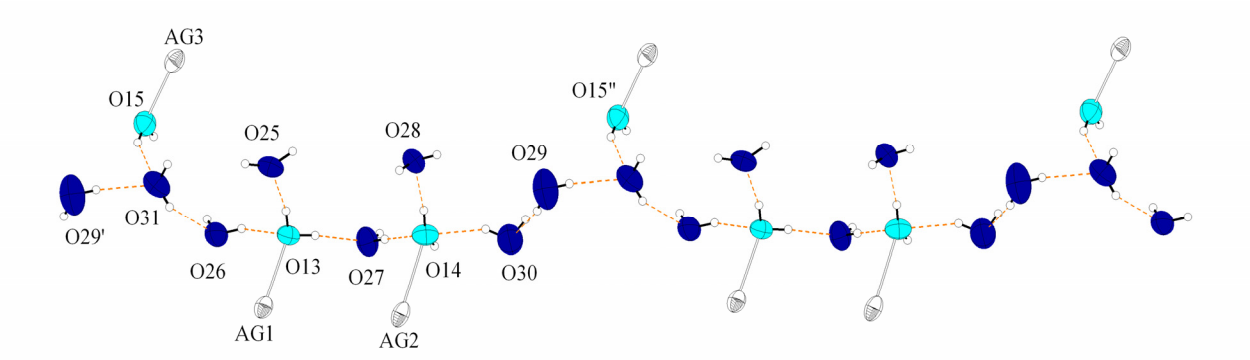


Figure S4. View of the water chains showing coordinated and uncoordinated water molecules.

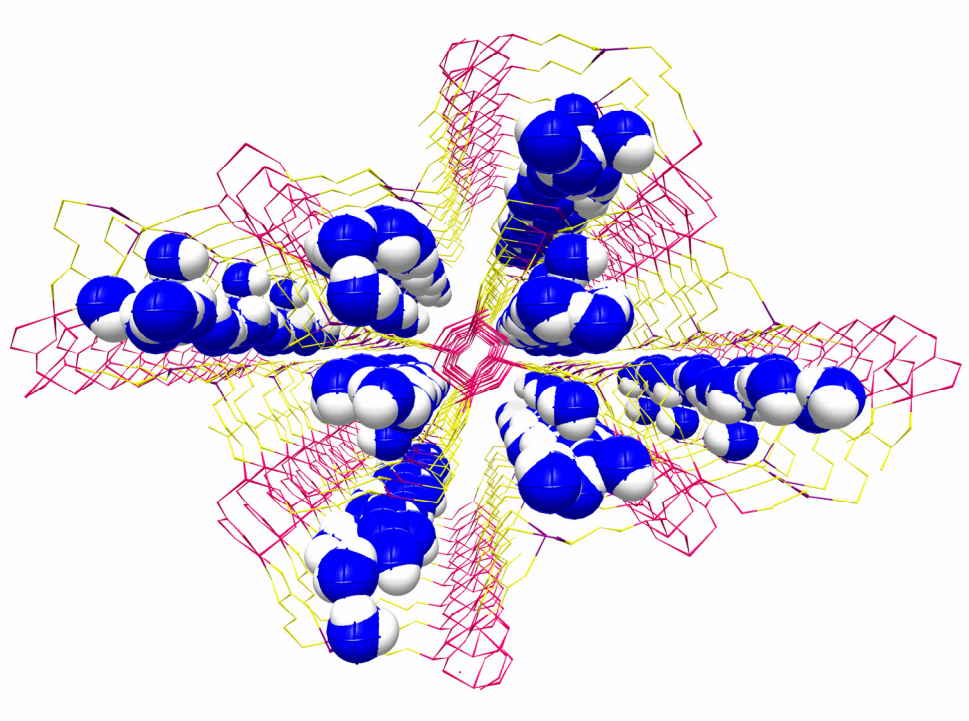


Figure S5. Top view of the water chains in helical channels of **1**.

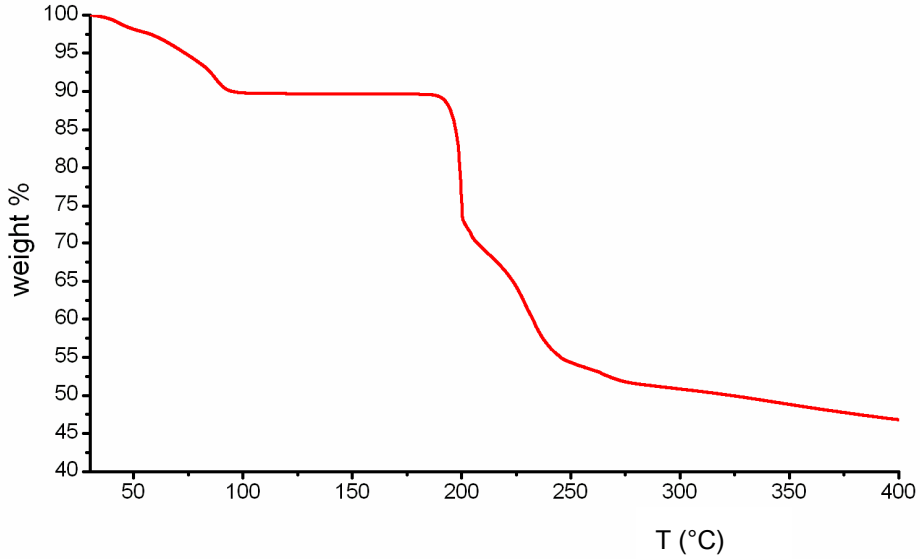


Figure S6. TGA plot of **1**.

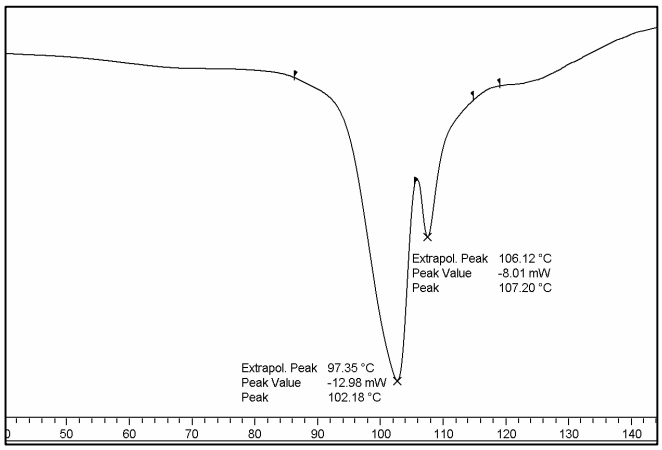


Figure S7. DSC plot of **1** (The lability of the water molecules was further examined by the DSC, which showed two endotherms at 102 °C and 107 °C in accord with the existence of two types of water molecules in uncoordinated and coordinated environments).

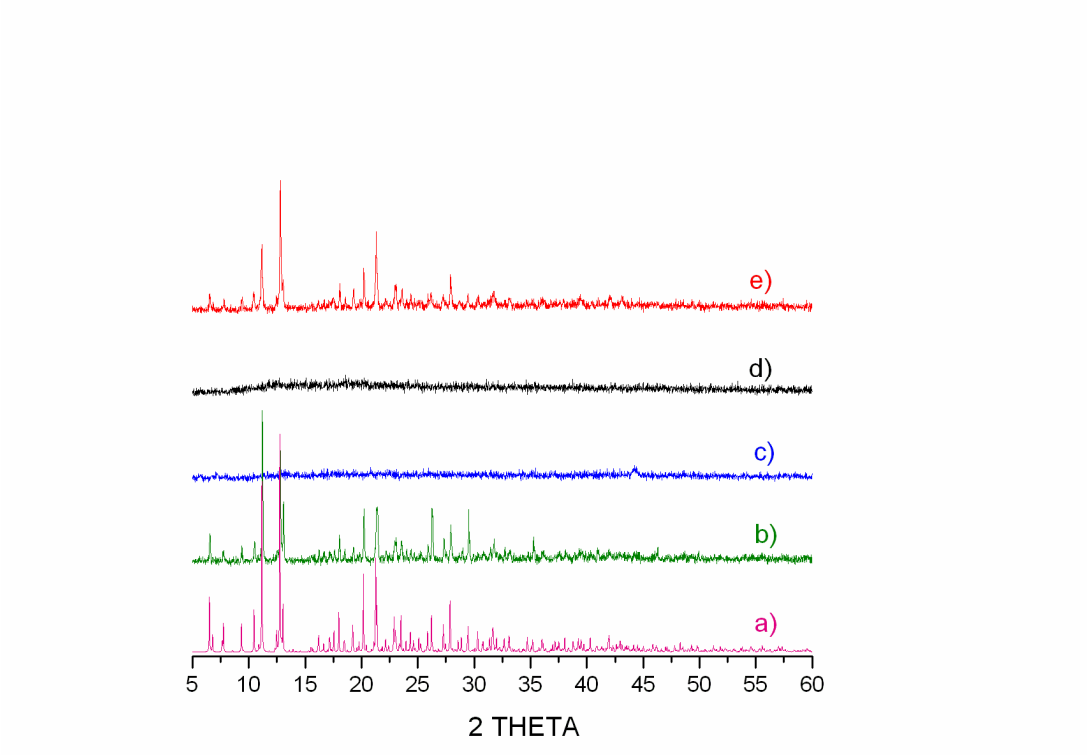


Figure S8. XRPD patterns of **1**: (a) simulated, (b) as synthesized (RT), (c) at 50 °C, (d) at 110 °C, e) after rehydration.

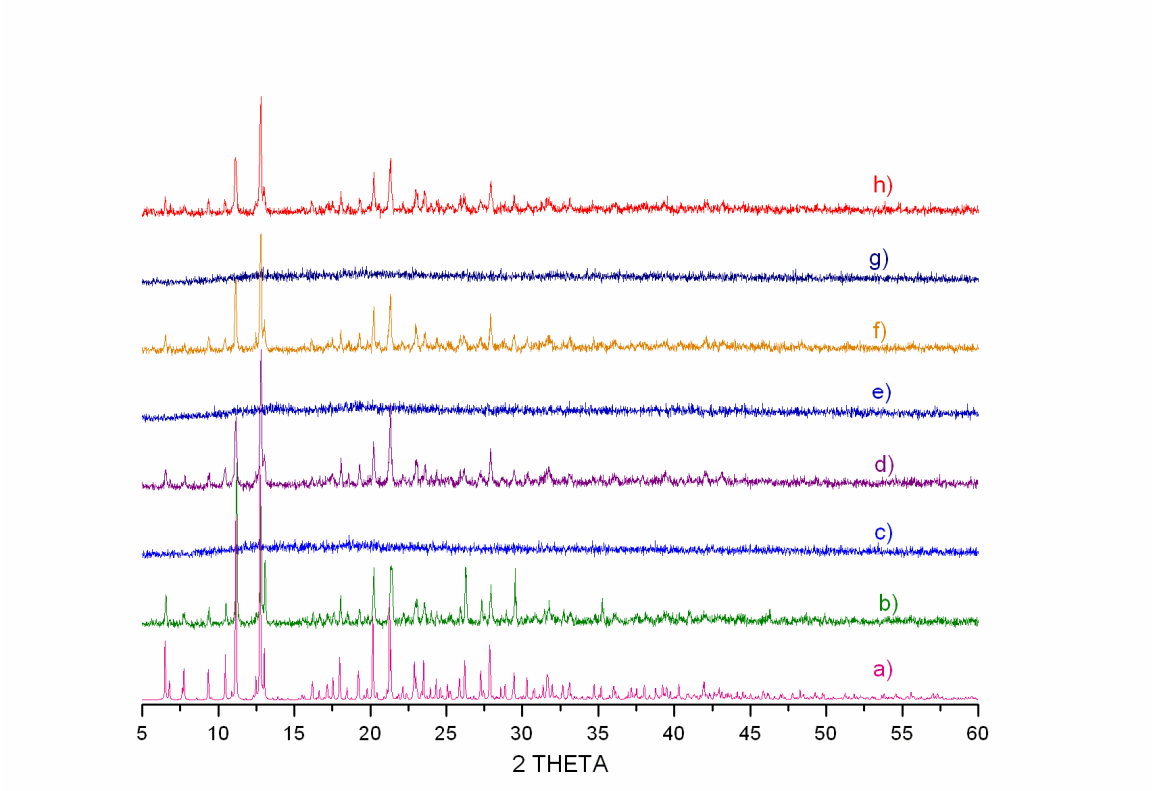


Figure S9. XRPD patterns of **1**, (a) simulated, (b) as-synthesized (RT), and (c)–(h): three reversible cycles of dehydration (110 °C) and rehydration (24 h, at RT).

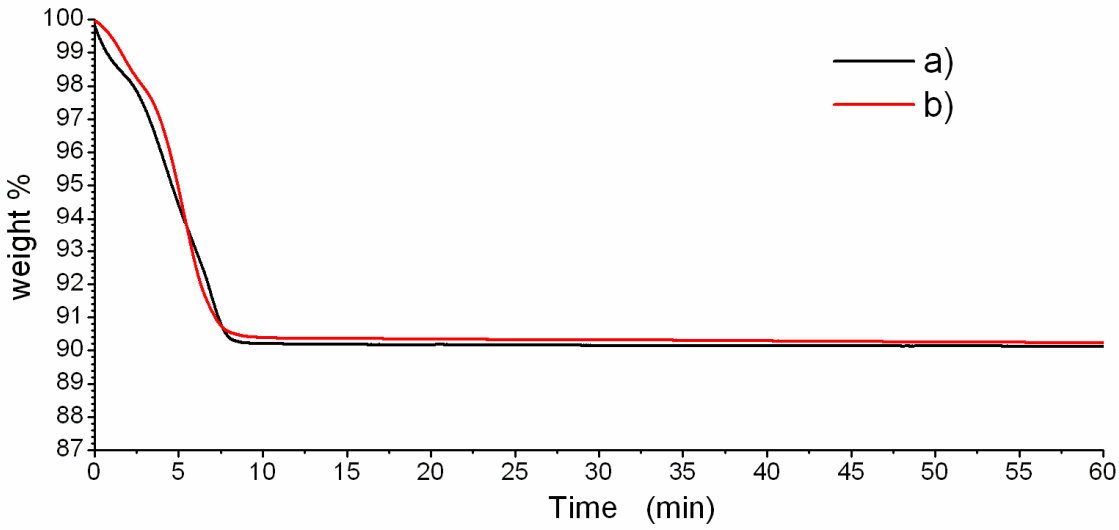


Figure S10. TGA curves of **1** treated at 110 °C, (a) fresh compound, (b) after rehydration for 24 h.

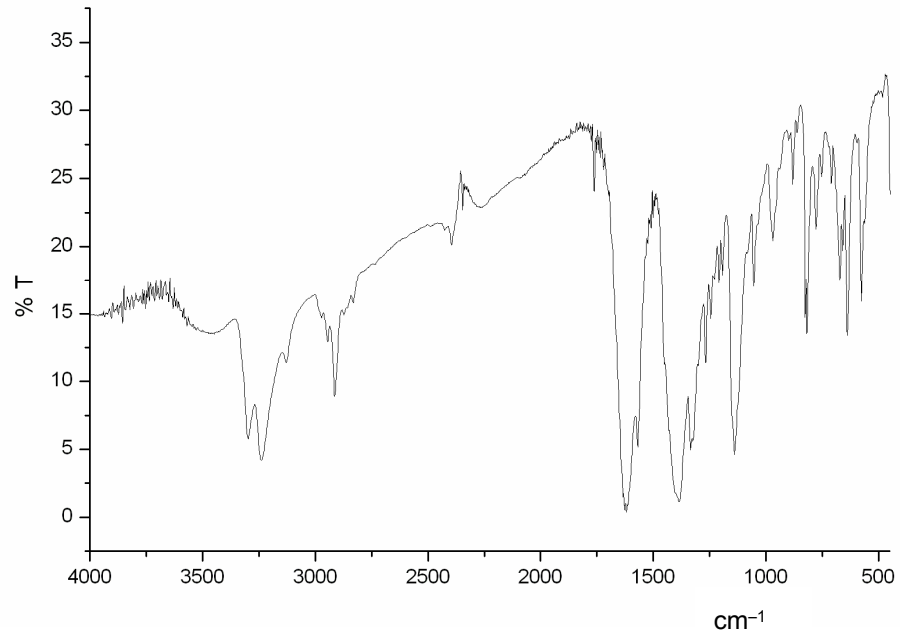


Figure S11. IR Spectrum of **1** (KBr pellet).

Table S1. Selected geometrical parameters of the water chain (Å, deg) for **1**

O13···O25	2.764(6)	O13···O26···O31	111.6(2)
O13···O26	2.802(6)	O13···O27···O14	114.2(2)
O13···O27	2.769(6)	O14···O30···O29	108.0(2)
O14···O27	2.751(6)	O15···O31···O26	100.3(2)
O14···O28	2.738(6)	O25···O13···O26	96.8(2)
O14···O30	2.814(7)	O25···O13···O27	116.7(2)
O15···O31	2.802(7)	O26···O31···O29’	131.3(2)
O26···O31	2.820(6)	O27···O14···O28	108.6(2)
O29···O30	2.872(7)	O27···O14···O30	128.2(2)
O29···O31	2.812(7)	O30···O29···O31”	114.0(2)

Table S2. Selected bond lengths (Å) and bond andgles (deg) for **1**

Bond lengths (Å)			
Ag1–S1	2.514(1)	Cu1–O8	1.954(3)
Ag1–S2	2.613(1)	Cu1–N1	1.993(3)
Ag1–S4	2.586(1)	Cu1–N4	1.998(4)
Ag1–O13	2.519(4)	Cu2–O3	1.952(3)
Ag2–S2	2.550(1)	Cu2–O12	1.957(3)
Ag2–S3	2.617(1)	Cu2–N2	2.005(3)
Ag2–S5	2.549(1)	Cu2–N6#2	1.988(4)
Ag2–O14	2.671(4)	Cu2–O2	2.561(3)
Ag3–S3	2.536(1)	Cu3–O4#3	2.411(3)
Ag3–S6#1	2.443(1)	Cu3–O5	1.943(3)
Ag3–O10	2.536(3)	Cu3–O9	1.952(3)
Ag3–O15	2.369(4)	Cu3–N3	2.003(3)
Cu1–O1	1.944(3)	Cu3–N5	1.994(3)
Cu1–O6	2.387(3)		
Bond Angles (º)			
S1–Ag1–S2	126.96(4)	O1–Cu1–N4	168.2(2)
S1–Ag1–S4	105.56(4)	O1–Cu1–N1	84.5(1)
S2–Ag1–S4	120.49(3)	O1–Cu1–O8	93.4(1)
S1–Ag1–O13	113.4(1)	O1–Cu1–O6	100.4(1)
S2–Ag1–O13	85.9(1)	N1–Cu1–O8	176.2(1)
S2–Ag2–S3	123.59(4)	O3–Cu2–N6#2	175.0(2)
S2–Ag2–S5	121.20(4)	O3–Cu2–N2	84.7(1)
S3–Ag2–S5	111.27(4)	O3–Cu2–O12	93.8(1)
S2–Ag2–O14	106.73(9)	O3–Cu2–O2	95.2(1)
S3–Ag2–O14	82.44(9)	N2–Cu2–O12	176.1(1)
S3–Ag3–S6#1	137.44(4)	O5–Cu3–N5	169.2(1)
S3–Ag3–O10	96.15(8)	O5–Cu3–N3	84.6(1)
S3–Ag3–O15	96.3(1)	O5–Cu3–O9	92.3(1)
O10–Ag3–O15	82.1(1)	O5–Cu3–O4#3	98.6(1)
S6–Ag3–O15	125.5(1)	N3–Cu3–O9	175.3(1)

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

Table S3. Crystal data and structure refinement for **1**

Formula	$\{[Ag_3Cu_3(L\text{-methioninato})_6(NO_3)_3(H_2O)_3]\cdot 7H_2O\}_n$	
Empirical formula	$C_{30}H_{80}Ag_3Cu_3N_9O_{31}S_6$	
Formula weight	1769.62	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 15.8730(1) Å	α = 90°
	b = 16.9061(1) Å	β = 90°
	c = 22.8297(2) Å	γ = 90°
Volume	6126.36(8) $Å^3$	
Z	4	
Density (calculated)	1.919 Mg/m^3	
Absorption coefficient	2.258 mm^{-1}	
F(000)	3580	
Crystal size	0.3 × 0.2 × 0.2 mm^3	
Theta range for data collection	4.13 to 27.48°	
Index ranges	–16<=h<=20, –21<=k<=14, –29<=l<=27	
Reflections collected	44653	
Independent reflections	13889 [R(int) = 0.0446]	
Completeness to theta = 27.48°	99.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6053 and 0.5568	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13889 / 0 / 775	
Goodness-of-fit on F^2	1.053	
Final R indices [I > 2sigma(I)]	R1 = 0.0363, wR2 = 0.0786	
R indices (all data)	R1 = 0.0498, wR2 = 0.0831	
Absolute structure parameter	–0.014(11)	
Extinction coefficient	0.00032(5)	
Largest diff. peak and hole	0.733 and –0.794 e $Å^{-3}$	