Supporting Information for

Cu(II)₄L₄ Coordination-Driven Molecular Container: A Reusable Visual Colorimetric Sensor for Ag(I) Ion

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Ligand Synthesis.



Scheme S1. Synthesis of LH.

A mixture of 2, 5-bis(4-aminophenyl)-4-amino-1, 2, 4-triazole (0.50g, 2.1mmol) and acetylacetone (10 mL, large excess) in MeOH (10 mL) was refluxed for 96 h to generate **LH** as yellow crystalline solids in 65 % yield. IR (KBr pellet cm⁻¹): 3442(s), 1605(vs), 1563(s), 1537(m), 1502(m), 1475(m), 1351(m), 1327(m), 1280(vs), 1184(m), 1029(w), 925(w), 856(w), 831(w), 757(w), 706(m), 691(w), 596(w), 540(w). ¹H NMR (90MHz, DMSO, 25°C, TMS, ppm): 12.61 (s, 2H, NH), 8.04 (d, 4H, C₆H₄), 7.37 (d, 4H, C₆H₄), 6.30 (s, 2H, NH₂), 5.32 (s, 2H, CH), 2.14 (s, 6H, CH₃), 1.94 (s, 6H, CH₃). Elemental analysis (%) calcd for $C_{24}H_{26}N_6O_2$: C 66.96, H 6.09, N 19.52; Found: C 66.57, H 6.37, N 19.05.



Fig. S1 TGA trace of **1**. The weight loss below 250° C is corresponding to the loss of the encapsulated solvent molecules (4CH₃OH and 5H₂O). The observed mass loss is 10.6 % and the calculated mass loss is 10.0 %.



Fig. S2. UV-vis spectra showing the change in the absorbance for 1 (10⁻⁴ M) in the presence of above representative metal ions (3.75×10^{-4} M) in MeOH at a λ_{max} of 505 nm, and Ag⁺ with different counter ions. The picture of color change of 1 (10⁻² M) after addition of Ag⁺ was inserted.



Fig. S3 (a): Color change of **2** in the presence of various representative metal ions, from left to right: blank, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Cr³⁺, Mg²⁺, Ca²⁺, Fe³⁺, Pb²⁺, Na⁺ and K⁺. [**2**] = 10⁻⁴ M. [Metal ion] = 3.75×10^{-4} M. Solvent: MeOH; (b) and (c): UV-vis spectra and bar diagrams showing the change in the absorbance for **2** (10⁻⁴ M) in the presence of above representative metal ions (3.75×10^{-4} M) in MeOH at a λ_{max} of 505 nm. Biscally no change in the spectral pattern was observed except Cr³⁺. (d): The simulated and measured XRPD patterns of **2** and (e) The XRPD pattern of the powder generated from **1** with Cr³⁺. Based on the XRPD patterns, the Cu₄L₄ structure is destroied by Cr³⁺ ion. Therefore, compound **2** herein could be a disposable naked-eye selective sensor for Cr³⁺.



Fig. S4 Job's plot of C_{Ag}/C ($C = C_{Ag} + C_1$) versus absorbance. $K_a = (1-a)/(n^n a^{n+1}C^n)$: a = (A'-A)/A'; A' = 0.445, A = 0.340, a = 0.236; $K_a = 0.764/(256 \times 0.000732 \times 7.72 \times 10^{-17}) = 5.27 \times 10^{16}$.



Fig. S5 a) Cu₄L₄ was added to aqueous solution of AgCl; b) Cu₄L₄ was added to aqueous solution of AgBr.



Fig. S6 ORTEP figure of 2 (displacement ellipsoids drawn at the 30% probability level).





Fig. S7 Top: CSI-MS spectrum of 2 obtained from $H_2O/MeOH$. Bottom: The m/z and corresponding molecular fragments generated from 2 (the top are the analog isotope peaks, and the bottom are the corresponding measured results).

X-Ray Structure Determination of 2 {[Cu₄(C₂₄H₂₄N₆O₂)₄Ag₄(O₂)](SbF₆)₂}·4(CH₂Cl₂)·4H₂O:

A deep red block-like crystal was sealed in a glass tube. X-ray intensity data were measured at 100(2) K on a Agilent Supernova CCD-based diffractometer system (MoK α radiation, $\lambda = 0.71073$ Å).¹ The raw data frames were integrated into reflection intensity files using CrysAlisPro(Version 1.171.36.32),¹ which also applied corrections for Lorentz and polarization effects. The final unit cell parameters are based on the least-squares refinement of 4817 reflections from the data set with I > 5(σ)I. Analysis of the data showed negligible crystal decay during data collection. No correction for absorption was applied.

Systematic absences in the intensity data were consistent with the space group P2/c. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F², using the SHELXTL software package.² An asymmetry unit contains two Cu(II) centers, two Ag(I) center, two independent C₂₄H₂₄N₆O₂ ligands and guest molecules could be readily located and refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2×Ueq of the attached atom. Positions for the aquo hydrogens were located in the difference map and included as riding atoms once located. The crystal data, selective bond distances and angles for **2** are shown in Table S1 and Table S2, respectively.

2		
Empirical formula	$C_{100}H_{112}Ag_4C$	$I_8 Cu_4 F_{12} N_{24} O_{14} Sb_2$
Formula weight	3314.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P2/c	
Unit cell dimensions	a = 18.7240(8) Å	alpha = 90 deg.
	b = 11.4725(8) Å	beta = $96.363(3)$ deg.
	c = 39.3968(12) Å	gamma = 90 deg.

 Table S1.
 Crystal data and structure refinement for 2.

Volume	8410.7(7) Å ³	
Z, Calculated density	2, 1.309 Mg/m ³	
Absorption coefficient	1.455 mm ⁻¹	
F(000)	3284	
Crystal size	0.26 x 0.24 x 0.22 mm	
Theta range for data collection	1.04 to 29.23 deg.	
Limiting indices	-25<=h<=25, 0<=k<=15, 0<=l<=54	
Reflections collected / unique	71316 / 22864 [R(int) = 0.0278]	
Completeness to theta = 24.50	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7402 and 0.7035	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22864 / 0 / 938	
Goodness-of-fit on F ²	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1100	
R indices (all data)	R1 = 0.0668, wR2 = 0.1125	
Largest diff. peak and hole	2.027 and -2.115 e.A^-3	

 Table S2.
 Interatomic Distances (Å) and Bond Angles (°) with esds () for 2.

Ag(1)-N(9)	2.161(2)	Ag(1)-N(3)	2.207(3)
Ag(1)-O(5)	2.6093(7)	Ag(2)-N(2)	2.180(3)
Ag(2)-N(8)	2.225(2)	Ag(2)-O(5)	2.6388(8)
Cu(1)-N(6)	1.879(3)	Cu(1)-N(12)	1.884(3)
Cu(1)-O(4)	1.951(2)	Cu(1)-O(2)	1.964(3)
Cu(2)-N(1)	1.908(3)	Cu(2)-N(7)	1.917(2)
Cu(2)-O(1)	1.959(2)	Cu(2)-O(3)	1.962(2)
N(9)-Ag(1)-N(3)	152.17(10)	N(9)-Ag(1)-O(5)	94.85(7)
N(3)-Ag(1)-O(5)	107.72(7)	N(2)-Ag(2)-N(8)	151.23(10)
N(2)-Ag(2)-O(5)	107.16(7)	N(8)-Ag(2)-O(5)	93.92(7)
N(6)-Cu(1)-N(12)	102.99(12)	N(6)-Cu(1)-O(4)	141.46(12)
N(12)-Cu(1)-O(4)	93.22(12)	N(6)-Cu(1)-O(2)	95.12(11)
N(12)-Cu(1)-O(2)	141.90(13)	O(4)-Cu(1)-O(2)	92.96(10)
N(1)-Cu(2)-N(7)	103.00(12)	N(1)-Cu(2)-O(1)	95.52(11)
N(7)-Cu(2)-O(1)	146.50(11)	N(1)-Cu(2)-O(3)	149.36(10)
N(7)-Cu(2)-O(3)	90.95(11)	O(1)-Cu(2)-O(3)	86.82(9)

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

Reference

(1) CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171. NET). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

(2) Sheldrick, G. M. SHELXTL Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.