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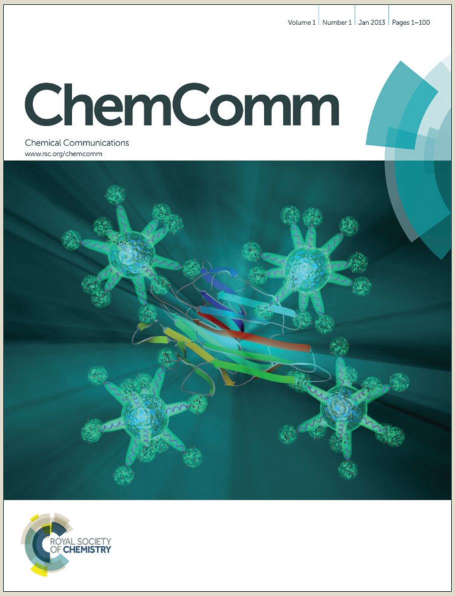

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Cu(II)$_4$L$_4$ coordination-driven molecular container: a reusable visual colorimetric sensor for Ag(I) ion

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Jian-Ping Ma,† Shen-Qing Wang,† Chao-Wei Zhao, Hai-Ying Wang, and Yu-Bin Dong*

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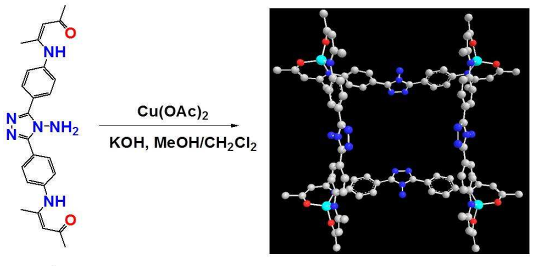
A Cu_4L_4 square-like molecular container which can be a reusable visual sensor for Ag^+ is reported. The present results can be a useful stepwise approach for the construction of heterometallic supramolecular complexes with potential applications.

Metal-directed self-assembly of discrete two- and three-dimensional molecular containers can accommodate various guest species such as neutral molecules and ionic species, and often draw them to reveal some new properties.[1] Among various coordination-driven molecular containers, molecular square can be the most typical and representative of coordination-driven containers. Since the first spontaneous formation of square-like Pd^{2+}-complex in 1990,[2] numerous squares and related metal-cornered structures have been successfully synthesized. In general, the end-capped M-components (M = Pd^{2+} and Pt^{2+}) used for construction of molecular squares based on linear rigid bidentate ligands are usually four-coordinated square planar, which is naturally required by the formation of square-like metallamacrocycles. Besides Pd^{2+} and Pt^{2+}, the other kinds of metal-cornered squares, however, have attracted much less attention.[3] The preparation of other metallasquares such as Cu^{2+} molecular squares are very hard, which might be limited by the preferred metal node coordination geometry together with the specific ligand design.[4]

In most cases, the organic linkers used for construction of metallasquares are 4, 4'-bipy-type of organic ligands which contain no free heteroatomic donors except the coordinating sites. On the other hand, the insertion of uncoordinated heteroatoms such as N, O and S would endow the resulted molecular containers more functionalities. The synthesis of such ligands, however, is very difficult due to the inherent difficulty in preparation of the multidentate organic spacers with specific recognizing sites for the metal ions. Furthermore, the reported metallamacrocycles are mainly used to trap and recognize organic guest molecules and sometimes counter ions,[1d] meanwhile they are rarely used as a host to incorporate heavy metal cations, furthermore, to be the sensors to detect heavy metal cations.

As we know, Ag^+ is very harmful to human health as an environmental heavy metal pollutant.[5] Therefore, the development of Ag^+ sensor, especially direct, convenient and selective Ag^+-detector is very significant. Up to now, various methods, for example atomic absorption spectroscopy, inductively coupled plasma-mass spectroscopy, and electrochemical methods based on ion-selective electrodes, have been developed.[6] More recently, organic species,[7] molecular complexes,[8] nanomaterials,[9] quantum dots[10] and DNA-based materials[11] are adopted as the fluorescent and electrochemical sensors to detect Ag^+. To our knowledge, the sensors for metal cations based on discrete coordination-driven molecular containers are extremely rare. As we know, the most practical and convenient sensor candidates are naked-eye colorimetric ones. Compared to the fluorescent and electrochemical sensors, discrete coordination-driven molecular containers that exhibit naked-eye colorimetric response after incorporating specific type of metal ions are unprecedented.



Scheme 1. Synthesis and the 3D molecular modeling of **1** (The model structure was obtained by the Gauss View program).

In this contribution, we describe a triazole-bridged ligand (**LH**) capped by NO cheating groups[12] which can bind Cu^{2+} ions into a square-like metallamacrocycle (**1**) with uncoordinated nitrogen donors and amino groups (Scheme 1). Moreover, compound **1** can be a reusable naked-eye colorimetric sensor to detect Ag^+ ion. The sensing mechanism is also investigated.

Ligand **LH**, generated from 2,5-bis(4-aminophenyl)-4-amino-1,2,4-triazole and acetylacetone, is capped by two terminal N, O-chelating groups (SI). Neutral macrocyclic compound **1** was isolated as light brown powder by mixing **LH** and $Cu(OAc)_2$ (molar ratio, 1:1) in a mixture of MeOH and CH_2Cl_2 in presence of KOH in quantitative yield (‡, Scheme 1).

Cold-spray ionization mass spectroscopy (CSI-MS) provides substantial evidence for the formation of a Cu_4L_4 structure. As shown in Fig. 1, molecular peak at *m/z* 2185.8 was observed due to the formation of the $[Cu_4L_4{\cdot}4CH_3OH{\cdot}5H_2O + H^+]$ species, thereby confirming that the Cu^{2+} cations in solution are chelated by four deprotoned ligand **L** (Scheme1). The existence of co-crystallized MeOH and H_2O solvent molecules was further confirmed by thermogravimetric analysis (TGA). TGA revealed that the observed solvent molecule weight loss is 10.6% (calculated 10.0 % based on $Cu_4L_4{\cdot}4CH_3OH{\cdot}5H_2O$, Fig. S1).

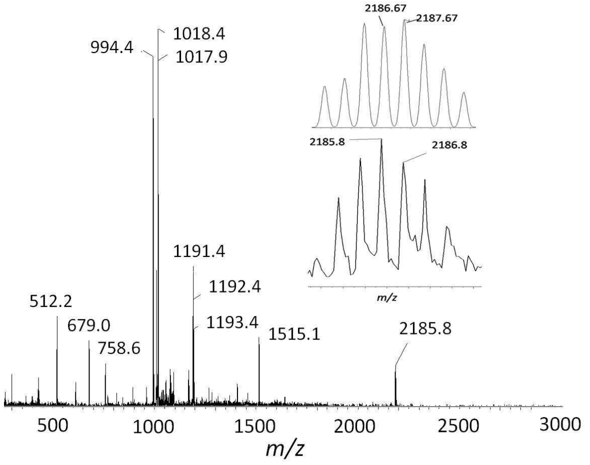


Fig. 1 CSI-MS spectrum of **1** obtained from $MeOH/CH_2Cl_2$. The inset shows the calculated (top) and the experimental (bottom) isotopic distribution of the square species $[Cu_4L_4{\cdot}4CH_3OH{\cdot}5H_2O + H^+]$.

As mentioned above, the obtained Cu_4L_4 metallamacrocycle contains four triazole moieties with uncoordinated N atoms. Such nucleophilic molecular pocket would be expected to be an ideal receptor to trap specific type of metal cations based on their size and charge. Follow this idea, compound **1** was used a macrocyclic host to bind different metal cations, including IA, IIA and other some other common transition metal ions.

Interestingly, our initial investigations showed that the color change of the methanol solution of **1** from light green to red upon addition of Ag^+ aqueous solution was readily visible to the naked eyes (Fig. S2). It suggested that Ag^+ ions were trapped by the heteroatom-rich Cu_4L_4 host. It is different from Ag^+, the color of methanol solution containing **1** did not show basically no color change upon addition of each metal cation, i.e., Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Pb^{2+}, Na^+ and K^+, which is further confirmed by the absorption spectra (Fig. 2 and Fig. S2). To determine if the counter ions used can affect the Ag^+ recognition based on **1**, the different silver salts such as $AgSbF_6$, $AgNO_3$, $AgSO_3CF_3$, $AgClO_4$, and $AgCOOCF_3$ were used to perform the parallel reactions. The adsorption spectra showed that the different anions have no interaction with **1** in methanol solution (Fig. 2). Furthermore, the UV-vis absorption spectra of **1** in the presence of other kinds of metal ions mentioned above were also performed. No change in the spectral pattern was observed except Cr^{3+}, indicating that Cu_4L_4 binds preferentially to Ag^+ (Fig. S3 and S4). Based on above observation, the metallamacrocycle of **1** could be a selective visual sensor for Ag^+ ion.

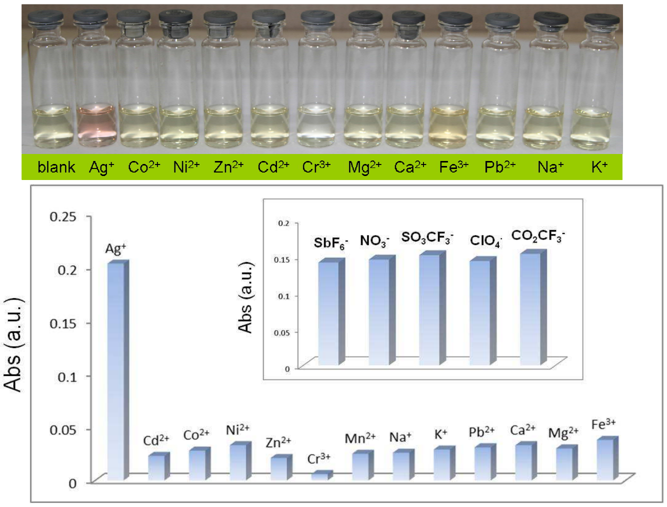


Fig. 2 Up: Color change of **1** in the presence of various representative metal ions, from left to right: blank, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Pb^{2+}, Na^+ and K^+. $[\mathbf{1}] = 10^{-4}$ M. [Metal ion] = 3.75×10^{-4} M. Solvent: MeOH; Bottom: UV-vis bar diagrams 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.

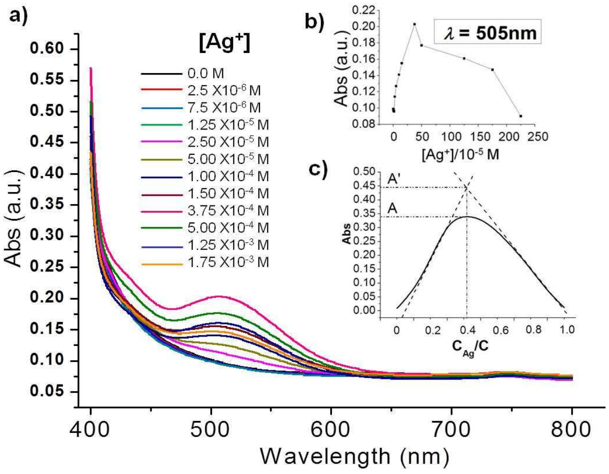


Fig. 3 a) Absorption spectral response of **1** upon addition of Ag^+ ions in methanol; b) the diagram of absorption variation with $[Ag^+]$ and c) Job's plot of C_{Ag}/C ($C = C_{Ag} + C_1$) versus absorbance.

As indicated above, the color of methanol solution of **1** immediately changed to red as Ag^+ was added to it. However, the red color did not deepen with increasing Ag^+ concentration when the ratio of Ag^+ to **1** exceeded 4:1. A detailed absorption titration study of Ag^+ was conducted using a 9.37×10^{-5} M solution of **1** in MeOH. As shown in Fig. 3a, at the concentration range of 0 to 3.75×10^{-4} M, the absorption at 505 nm of **1** increased in intensity upon the addition of Ag^+ ions. The absorption intensity, however, gradually decreased when the concentrations of Ag^+ higher than 3.75×10^{-4} M. So, the maximum absorption was observed at the Ag^+ concentration of 3.75×10^{-4} M. At this point, the molar ratio between Cu_4L_4 (**1**) and Ag^+ is 1:4 (Fig. 3b). The binding constant, K_a, of the Ag^+ to Cu_4L_4 host was found to be 5.27×10^{16} based on Job's plot (Fig. 3c and Fig. S4).[13]

Notably, the Ag^+-responded color change is reversible (Fig. 4a). As shown in Fig. 4b, upon addition of Br^- (4 equiv to **2**) to **2**, the maximum absorbance in UV-vis spectrum at 505nm disappeared. Meanwhile, the color of the system went back to light green (Fig. 4a), indicating that the Cu_4L_4 host was regenerated. On the other hand, the maximum absorbance was completely recovery upon addition of Ag^+ (4 equiv to **1**) to above system, and the corresponding red color of the solution reappeared (Fig. 4a). It is noteworthy that the empty Cu_4L_4 host cannot be regenerated upon addition of Cl^- (4 equiv to **2**), which is resulted from the K_{sp} (1.8×10^{-10}) of AgCl is much larger than that of AgBr ($K_{sp} = 5.35\times10^{-13}$) (Fig. S5).

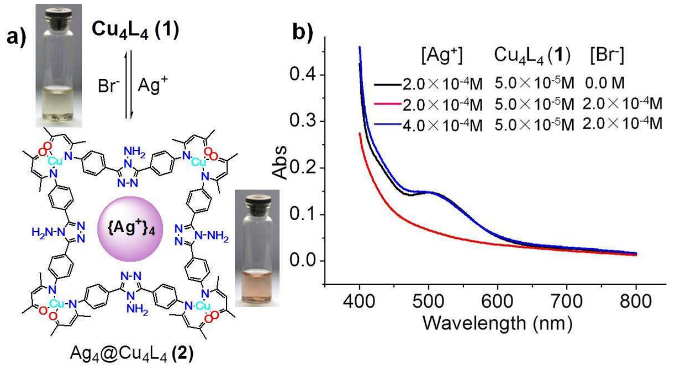


Fig. 4 a) Reversible Ag^+ encapsulation based on **1** in $MeOH/H_2O$; and b) corresponding UV-vis spectra. The corresponding photographs of **1** and **2** are inserted.

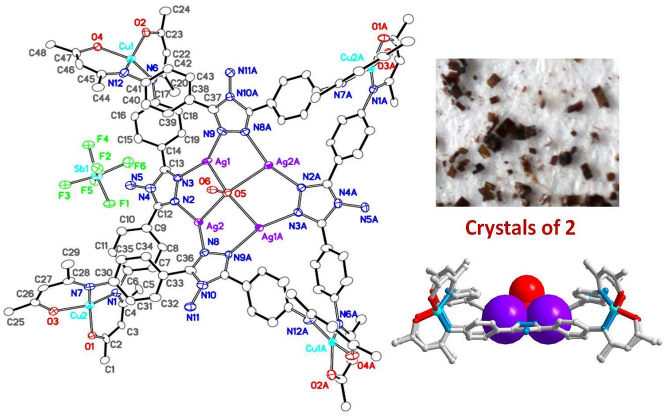


Fig. 5 ORTEP figure (displacement ellipsoids drawn at the 30% probability level) and side view of **2**. The photograph of crystals **2** is inserted.

In order to understand the mechanism for this interesting visual colorimetric Ag^+ sensing, supramolecular complex $Ag^+@Cu_4L_4$ (**2**) was isolated and its structure was determined by single-crystal X-ray diffraction analysis (ESI and Fig. S6). The deep red single crystals (Fig. 5) of **2** ($\{[Cu_4L_4Ag_4(O_2)](SbF_6)_2\}\cdot4(CH_2Cl_2)\cdot4H_2O$) were obtained by the combination of **1** and $AgSbF_6$ (molar ratio = 1 : 4) in a $MeOH/CH_2Cl_2$ mixed-solvent system at ambient temperature(‡). Complex **2** crystallizes in the monoclinic space group *P2/c*. As shown in Fig. 5, the four tetrahedral Cu^{2+} nodes are bridged by four bis-didentate deprotonated ligands into a square-like molecular square, in which the $Cu^{2+}\cdots Cu^{2+}$ distances are in a range of 14.353-14.763 Å. The eight N-donors on the central 1,2,4-triazole moieties face toward the center of the square, furthermore, bind a $\{Ag_4O_2\}^{2+}$ cluster core through eight Ag-N bonds. The Ag-N bond distances are in a range of 2.161(2) - 2.225(2) Å. The geometry of $\{Ag_4O_2\}^{2+}$ cluster core is sort of tetragonal pyramid, in which one oxygen donor occupies the axial positions with a long Ag-O bond distance of 2.6388(8) Å. A side view of **2** (Fig. 5) reveals that the $\{Ag_4O_2\}^{2+}$ cluster core is situated in the center of the macrocycle, and deviates from the square plane ca. 1 Å. The SbF_6^- ions are at the side of the molecular square. Besides single-crystal analysis, the ESI-MS spectrum (Fig. S7) of **2** recorded in DMSO/MeOH displays multiply charged cations verifying the formation of the Cu^{2+}-Ag^+ heterometallic species.

As mentioned above (Fig. 3), the maximum UV-vis absorbance of **2** was observed when the ratio of Cu_4L_4 to Ag^+ reached 1:4, which is well consistent with the single crystal structure. Upon addition of more Ag^+, the UV-vis absorption intensity gradually decreased which might be caused by the Cu_4L_4 macrocyclic structure collapse due to the ion-exchange between Cu^{2+} nodes and the excess of Ag^+ ions.

Conclusions

In summary, we have shown that the formation of a soluble tetrametallic square-like Cu^{2+}-macrocycle based on a triazole bridging bis-didentate ligand is possible. The obtained Cu^{2+}-macrocycle with eight uncoordinated heterocyclic N-donors is very sensitive and selective toward Ag^+ over twelve other important ions as demonstrated by UV-vis titrations. More importantly, it can be a naked-eye sensor to clearly detect Ag^+ (visual limit, 10^{-4} M) under ambient conditions. In addition, this selective sensing mechanism is studied. Single-crystal analysis reveals that the Ag^+-species was trapped in the Cu^{2+}-host as a $\{Ag_4O_2\}^{2+}$ cluster core, which well agrees with the UV-vis titration. Notably, the adsorption of Ag^+-species based on **1** is reversible, and the empty Cu_4L_4 host can be easily regenerated. On the other hand, the present results can be a useful stepwise approach for construction of the heterometallic supramolecular complexes with potential applications.

Notes and references

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, P. R. China. Email: yubindong@sdnu.edu.cn

† These authors contributed equally to this work.

‡**Synthesis of $Cu_4L_4·4CH_3OH·5H_2O$ (1).** A solution of $Cu(OAc)_2·H_2O$ (80 mg, 0.4 mmol) in MeOH (30 mL) was added to a solution of **LH** (172 mg, 0.4mmol) and KOH (22.4 mg, 0.4 mmol) in CH_2Cl_2/MeOH (20/20 mL). The mixture was stirred for 3 h at room temperature. After removal of most solvent under vacuum, Et_2O (50 mL) was added to precipitate **1** as brown crystalline powder in 96% yield. IR (KBr pellet cm^{-1}): 3279(m), 1599(vs), 1563(vs), 1510(vs), 1474(m), 1396(vs), 1331(vs), 1276(vs), 1185(s), 1017(s), 927(m), 940(m), 831(w), 747(m). Elemental analysis (%) calcd for $C_{100}H_{122}N_{24}O_{17}Cu_4$: C 54.89, H 5.58, N 15.37; Found: C 54.67, H 5.39, N 15.45.

Synthesis of $\{[Cu_4L_4Ag_4(O_2)](SbF_6)_2\}·4(CH_2Cl_2)·4H_2O$ (2). A solution of $AgSbF_6$ (20mg, 0.058 mmol) in MeOH (8 mL) was slowly added to a solution of **1** (32mg, 0.015mmol) in MeOH/CH_2Cl_2 (10 mL, V_{CH2Cl2}: V_{MeOH} = 9:1), and the red solutions were left for about ten days at ambient temperature, and the deep red crystals of **2** were obtained. IR (KBr pellet cm^{-1}): 3422(s), 2025 (w), 1627(m), 1504 (w), 1467(w), 1471(w), 1362(w), 1310(w), 1160(s), 1105(s), 1056(s), 931(w), 806(w), 788(w), 750(w). Element alanalysis (%) calcd for $\{[Cu_4L_4Ag_4(O_2)](SbF_6)_2\}·1.5H_2O$ ($C_{96}H_{99}N_{24}O_{11.5}Cu_4Ag_4Sb_2F_{12}$): C 39.35, H 3.41, N 11.47; Found: C 39.33, H 3.38, N 11.52.

X-ray single-crystal analysis was performed on a Aglent Supernova CCD-based diffractometer system (Mo Kα radiation, λ = 0.71073 Å). The raw data frames were integrated into reflection intensity files using CrysAlisPro (Version 1.171.36.32), 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. These data can be obtained from supplementary materials for this paper. Crystal data for **2**: $\{[Cu_4(C_{24}H_{24}N_6O_2)_4Ag_4(O_2)](SbF_6)_2\}·4(CH_2Cl_2)·4H_2O$, Mr = 1453.57, monoclinic, $P2/c$, a = 18.7240(8) Å, b = 11.4725(8) Å, c = 39.3968(12) Å, β = 96.363(3)°, V = 8912(5) $Å^3$, Z = 4, T = 100(2) K, ρ_{calcd} = 1.309 g cm^{-3}, final R [I>2sigma(I)]: R_1 = 0.0534, ${}_wR_2$ = 0.1100. CCDC 978498 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic Supplementary Information (ESI) available: **LH** synthesis, ORTEP figure of **2**, UV-vis spectra, TGA, CSI-MS spectrum of **2**, Job's plot and crystal data of **2**. See DOI: 10.1039/c000000x/

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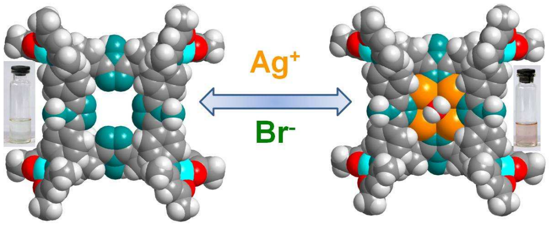

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