Supporting Information

A Luminescent 3D Organometallic Network Based on Silver Clusters and Star-Like Tri(4-ethynylphenyl)amine

Bao Li, and Tianle Zhang*

School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China

Corresponding Author: Tianle Zhang, E-mail: tlzhang@hust.edu.cn

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General Procedures

All synthetic procedures were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried and distilled by using standard methods. The chemicals and reagents were obtained commercially and were used without further purification. Tri(4-ethynylphenyl)amine was prepared according to literature methods[1]. Elemental analysis was performed with a Perkin-Elmer elemental analyzer. FT-IR and emission spectra were measured on a Bruker VERTEX 70 and FP-6500 spectrometers, respectively. Excitation and emission spectra at room temperature were measured on a Jasco FP-6500 spectrometer，and emission spectra at low temperatures were recorded on LabRam HR800 (excited at 325nm) spectrometer. FT-IR spectrum was recorded on a Bruker VERTEX 70 spectrometer. Elemental analysis (C, H, N) was performed on a Perkin-Elmer elemental analyser.

Preparation of $\{[N(4\text{-}C_6H_4\text{-}C{\equiv}C)_3Ag_3]_6{\cdot}29AgNO_3\ 14H_2O\}_n$ (2)

To a 4 mL vial containing 0.0100g solid tri(4-ethynylphenyl)amine (0.0315 mmol) was added about 0.2 mL distilled water and excess solid silver nitrate (0.0935g, 5.886 mmol). This mixture was stirred for 20 min to generate an orange solution. Then distilled water was added to this solution to produce an orange precipitate, which was washed three times with distilled water to remove excess $AgNO_3$ and nitric acid released from the reaction and dried in air (**1**) (0.0191g, yield: 95.5%). Elemental analysis calcd (%) for proposed formula $C_{24}H_{12}NAg_3$: C 45.18, H 1.90, N 2.20; found: C, 42.32; H, 1.71; N, 2.55. However elemental analysis results for **1** could change if the samples prepared from different experiments were analyzed because the samples always contain excess $AgNO_3$ to some extent. IR: 1384 cm^{-1} (m, $\nu(NO_3^-)$).

0.0050g (**1**) was dissolved in about 0.2 mL of concentrated silver nitrate solution (0.6000g $AgNO_3$) to generate a clear orange solution. Slow diffusion of water to this solution at 328 K afforded **2** as dark red plates (0.0015g, yield: 11.8%). Elemental analysis calcd (%) for $C_{144}H_{100}N_{35}O_{101}Ag_{47}$: C 19.20, H 1.12, N 5.44; found: C, 18.91; H, 1.20; N, 5.22. IR: 1384 cm^{-1} (s, $\nu(NO_3^-)$).

X-Ray Structure Determination.

X-ray diffraction measurements were performed at 123 K on a Bruker AXS machine equipped with an Apex II CCD. The multi-scan method was used for absorption corrections. The structure was solved by direct methods and refined by full-matrix least squares using the *SHELXTL*

crystallographic software package.[2-3] Anisotropic displacement parameters were applied to all non-hydrogen atoms. The hydrogen atoms were placed at calculated positions using the riding model. Three silver atoms (Ag3, Ag4 and Ag6) have two disordered positions with an occupancy ratio of 0.9:0.1. Two oxygen atoms (O4 and O14) have two disordered positions with an occupancy ratio of 0.6:0.4, and one oxygen atom with half occupancy (O12) has two disordered positions with an occupancy ratio of 0.3:0.2.

References:

1. Niamnont, N.; Kimpitak, N.; Wongravee, K.; Rashatasakhon, P.; Baldridge, K. K.; Siegel, J. S.; Sukwattanasinitt, M., *Chem. Commun.,* **2013**, 49, 780.
2. SADABS, *Area Detector Absorption Correction Program*; Bruker Analytical X-Ray; Madison, WI, USA, **1997**.
3. G. M. Sheldrick, *SHELXTL-PLUS, Crystal Structure Analysis Package*; Bruker Analytical X-Ray; Madison, WI, USA, **1997**.

Table S1 Crystal data and collection parameters for compound 2

Compound reference	**2**
Chemical formula	$C_{144}H_{100}Ag_{47}N_{35}O_{101}$
Formula Mass	9006.48
Crystal system	Trigonal
a/Å	18.0608(5)
b/ Å	18.0608(5)
c/ Å	104.861(5)
α/°	90.00
β/°	90.00
γ/°	120.00
Unit cell volume/Å^3	29622.4(19)
Temperature/K	123(2)
Space group	*R*-3*c*
No. of formula units per unit cell, *Z*	6
No. of reflections measured	26632
No. of independent reflections	5592
R_{int}	0.1783
GOOF	1.038
Final R_1 values ($I > 2\sigma(I)$)	0.0902
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2178
Final R_1 values (all data)	0.1415
Final $wR(F^2)$ values (all data)	0.2434

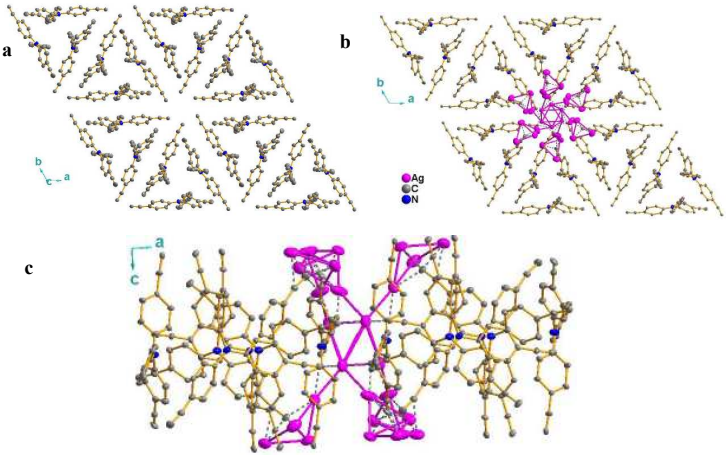

Figure S1. (a) Arrangement of ligands in one layer along *c* axis; (b) 2D organometallic network in **2** along *c* axis, showing that the ligands are connected by Ag_{30} cluster units; (c) 2D organometallic network in **2** along *b* axis.

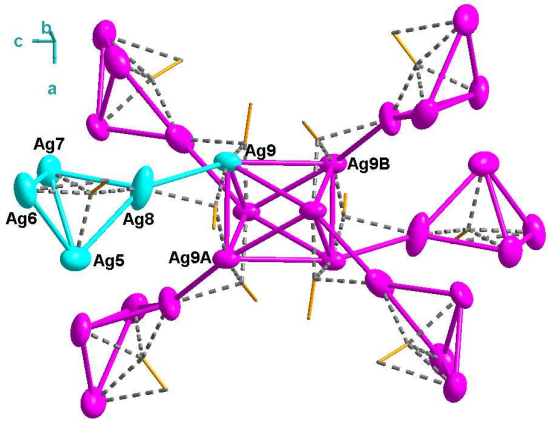

Figure S2. Thirty nuclear silver cluster unit (Ag_{30}) in **2**. Selected bond lengths (Å): Ag9-Ag9A 2.932(2), Ag9-Ag9B 3.334(3). Symmetry code: A 2-x+y, 1-x, z; B x-y, -1+x, -z.

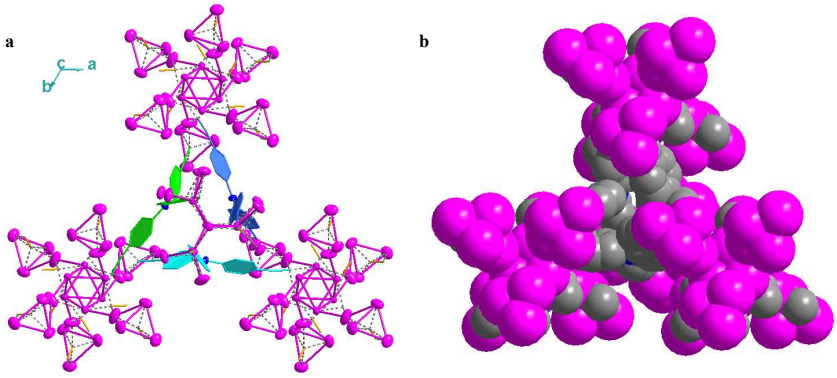

Figure S3. (a) A cage formed by three star-like ligands and silver cluster units; (b) the space-filling model of a cage formed by three ligands and silver cluster units, showing a very small cavity in this cage.

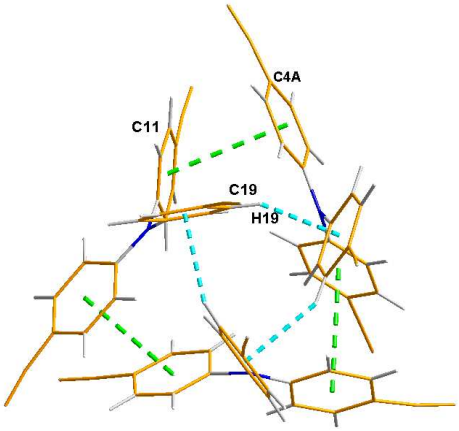

Figure S4. Aromatic C-H/π (turquoise line) and π/π (green line) interactions between the ligands in the cage. Symmetry code: A –y, -1+x-y, z.

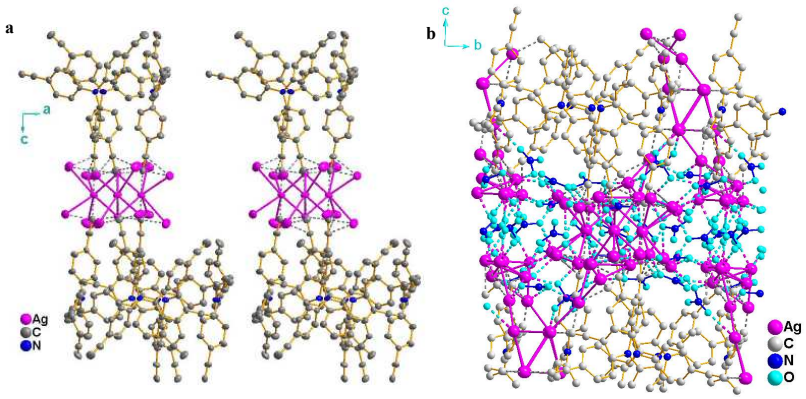

Figure S5. Bridging Ag_{17} cluster units and nitrate anions in **2**. (a) Bridging mode of Ag_{17} cluster units in **2**; (b) Bridging nitrate anions in **2**.

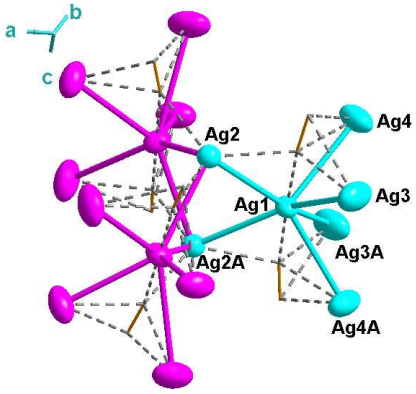

Figure S6. Seventeen nuclear silver cluster unit (Ag_{17}) in **2**. Selected bond lengths (Å): Ag1-Ag2 2.905(2), Ag1-Ag2A 2.905(2), Ag1-Ag3 3.255(3), Ag1-Ag3A 3.255(3), Ag1-Ag4 2.958(2), Ag1-Ag4A 2.958(2). Symmetry code: A 0.33333+x-y, 0.6667-y, 0.16667-z.

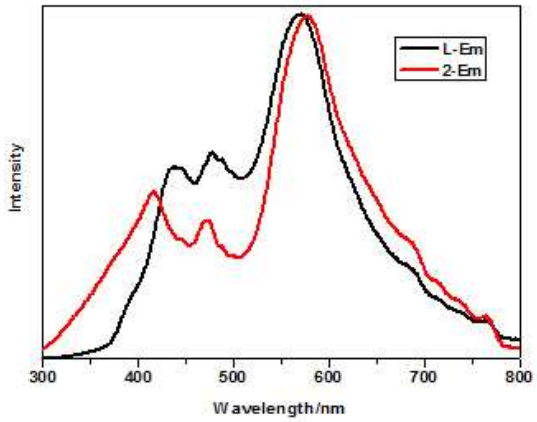

Figure S7. Solid state emission spectra of free ligand and **2** at room temperature.

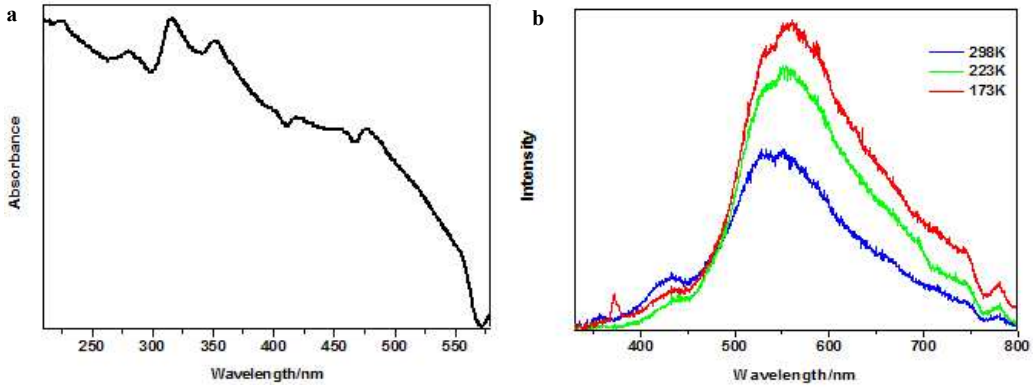

Figure S8. (a) Solid state UV spectrum of **2** at room temperature; (b) Solid state emission spectra of **2** at low temperatures.