

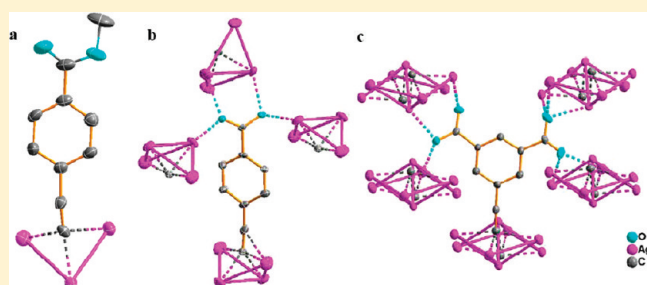
## Two- and Three-Dimensional Silver(I)-Organic Networks Generated from Mono- and Dicarboxylphenylethyne

Ying Zhao,<sup>†</sup> Peng Zhang,<sup>†</sup> Bao Li,<sup>†</sup> Xianggao Meng,<sup>‡</sup> and Tianle Zhang<sup>\*,†</sup><sup>†</sup>College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China<sup>‡</sup>College of Chemistry, Central China Normal University, Wuhan, Hubei 430079, P. R. China

## Supporting Information

**ABSTRACT:** Three phenylethyne bearing methyl carboxylate (HL1), monocarboxylate (H<sub>2</sub>L2), and dicarboxylate (H<sub>2</sub>L3) groups were utilized as ligands to synthesize a new class of organometallic silver(I)-ethynide complexes as bifunctional building units to assemble silver(I)-organic networks. X-ray crystallographic studies revealed that in [Ag<sub>2</sub>(L1)<sub>2</sub>·AgNO<sub>3</sub>]<sub>∞</sub> (1) (L1 = 4-C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>CH<sub>3</sub>), one ethynide group interacts with three silver ions to form a complex unit. These units aggregate by sharing silver ions with the other three units to afford a silver column, which are further linked through argentophilic interaction to generate a two-dimensional (2D)

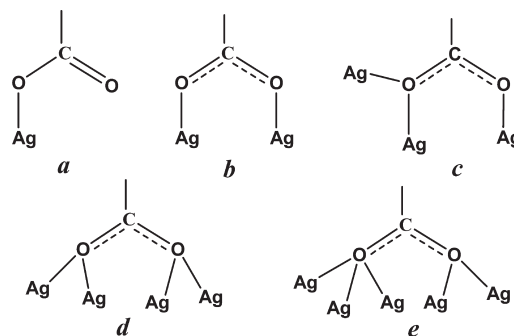
silver(I) network. In [Ag<sub>2</sub>(L2)·3AgNO<sub>3</sub>·H<sub>2</sub>O]<sub>∞</sub> (2) (L2 = 4-CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>), the ethynide group coordinates to four silver ions to form a building unit (Ag<sub>4</sub>C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>), which interacts through silver(I)-carboxylate coordination bonds to generate a wave-like 2D network and is subsequently connected by nitrate anions as bridging ligands to afford a three-dimensional (3D) network. In [Ag<sub>3</sub>(L3)·AgNO<sub>3</sub>]<sub>∞</sub> (3) (L3 = 3,5-(CO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C<sub>2</sub>), the building unit (Ag<sub>4</sub>C<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>) aggregates to form a dimer [Ag<sub>8</sub>(L3)<sub>2</sub>] through argentophilic interaction. The dimeric units interact through silver(I)-carboxylate coordination bonds to directly generate a 3D network. The obtained results showed that as a building unit, silver(I)-ethynide complexes bearing carboxylate groups exhibit diverse binding modes, and an increase in the number of carboxylate groups in the silver(I)-ethynide complex unit leads to higher level architectures. In the solid state, all of the complexes (1, 2, and 3) are photoluminescent at room temperature.



## INTRODUCTION

The construction of coordination polymers is of great interest due to their intriguing topologies and potential applications as functional materials by using single metal<sup>1</sup> and polynuclear metal centers<sup>2</sup> as building blocks. In the past decades, a number of silver chalcogenide nanoclusters have been synthesized and structurally characterized.<sup>3</sup> Interestingly, silver(I)-ethynide complexes have also been intensively investigated to prepare giant silver clusters<sup>4</sup> and luminescent materials<sup>5</sup> and serve as novel polynuclear building units to assemble organometallic networks.<sup>6</sup> Recently, it was proposed that silver-ethynide complexes could be modified by the incorporation of coordination groups, such as pyridyl or pyrimidyl rings to become bifunctional building blocks to rationally assemble two-dimensional (2D) and three-dimensional (3D) coordination networks through Ag–N coordination bonds and argentophilic and silver-ethynide interactions.<sup>7,8</sup> In these kinds of networks, each N atom in the pyridyl or pyrimidyl groups usually prefers to coordinate to one silver ion in the silver-ethynide complex unit in a simple way<sup>7,8</sup> or binds to a single silver ion if the steric hindrance of the ligands attached to the silver-ethynide complexes is large.<sup>7</sup> Compared to pyridyl and pyrimidyl groups, organic ligands containing carboxylate groups are extensively

## Scheme 1. Binding Modes in Silver(I) Carboxylate Complexes



used to construct supramolecules and coordination polymers.<sup>2</sup> Furthermore, carboxylate groups of organic ligands usually exhibit relatively weak capability to coordinate to silver(I) ions<sup>9</sup> and diverse binding modes, which may interact with one, two, or

Received: June 14, 2011

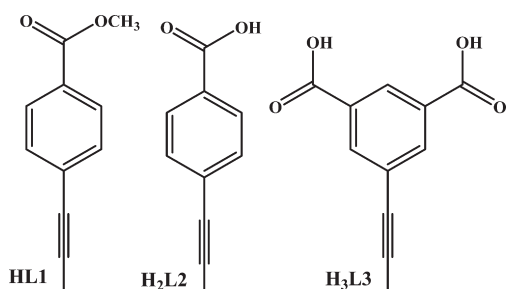
Published: August 22, 2011

even five silver(I) ions (Scheme 1).<sup>10</sup> Therefore, one could imagine that phenylethyne ligands bearing carboxylate groups could make a silver(I) phenylethyne complex unit interact with more silver(I) ions or silver-ethynide complex units and thus lead to diverse and high-level organometallic architectures. In this work, three phenylethyne bearing one or two carboxylic groups, as well as one methyl carboxylate for comparison purposes (Scheme 2), are utilized as ligands to construct a new class of silver-organic networks and to investigate the relationship between the structure of the network and the number of carboxylate groups attached to the phenylethyne ligands.

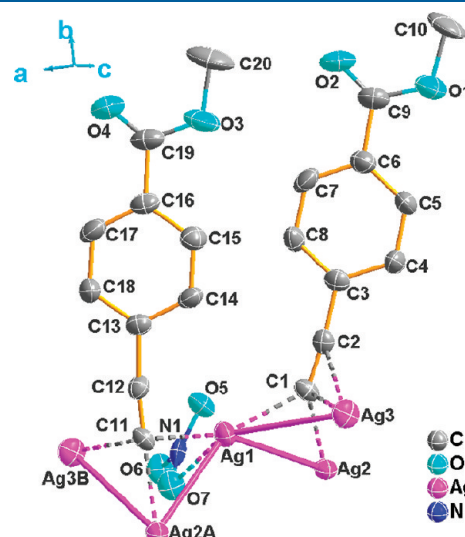
## EXPERIMENTAL SECTION

**Materials.** Methyl 4-ethynylbenzoate (HL1), 4-ethynylbenzoic acid (H<sub>2</sub>L2), and 5-ethynyl-1,3-benzenedicarboxylic acid (H<sub>2</sub>L3) were

**Scheme 2. Ligands Used to Construct Silver-Organic Networks**



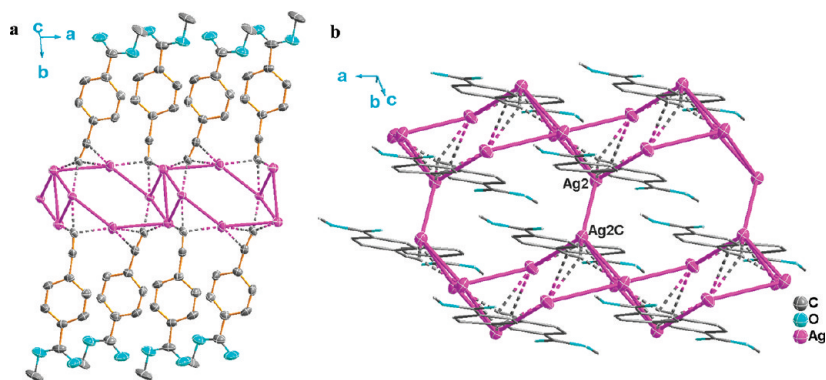
prepared according to literature methods.<sup>11</sup> AgNO<sub>3</sub> was purchased from commercial sources and used without further purification.



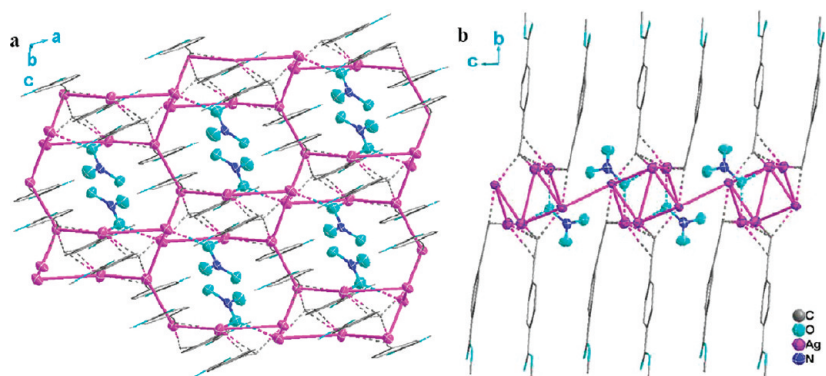
**Figure 1.** Coordination modes of the methyl 4-carboxylatephenylethyne ligand in **1** (50% thermal ellipsoids). All of the hydrogen atoms are omitted for clarity. Symmetry code: A is  $2 - x, -y, 2 - z$ ; B is  $1 + x, y, z$ . Selected bond lengths (Å) and angles (deg): C1–C2 1.205(9), C1–Ag1 2.182(7), C1–Ag2 2.194(7), C1–Ag3 2.318(6), C2–Ag3 2.544(6), C11–C12 1.205(8), C11–Ag1 2.268(7), C11–Ag2A 2.160(7), C11–Ag3B 2.301(6), O7–Ag1 2.587(5), Ag1–Ag2 2.9143(9), Ag1–Ag3 3.2681(10), Ag1–Ag2A 2.9774(8), Ag2A–Ag3B 3.0558(8), C1–C2–C3 171.8(7), and C11–C12–C13 174.4(8).

**Table 1. Crystal Data and Collection Parameters for Complexes 1, 2, and 3**

cmpd ref	1	2	3
empirical formula	C <sub>20</sub> H <sub>14</sub> Ag <sub>3</sub> NO <sub>7</sub>	C <sub>18</sub> H <sub>12</sub> Ag <sub>10</sub> N <sub>6</sub> O <sub>24</sub>	C <sub>10</sub> H <sub>3</sub> Ag <sub>4</sub> NO <sub>7</sub>
formula weight	703.93	1775.04	680.61
temperature (K)	273(2)	298(2)	298(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	6.6447(10)	20.917(4)	16.9809(13)
<i>b</i> (Å)	44.942(7)	9.0810(15)	10.0515(8)
<i>c</i> (Å)	6.9234(10)	17.963(3)	15.0429(12)
$\alpha$ (deg)	90.00	90.00	90.00
$\beta$ (deg)	109.998(3)	92.633(3)	109.966(1)
$\gamma$ (deg)	90.00	90.00	90.00
volume (Å <sup>3</sup> )	1942.8(5)	3408.4(10)	2413.3(3)
<i>Z</i>	4	4	8
density (calculated) (g·cm <sup>-3</sup> )	2.407	3.459	3.747
<i>F</i> (000)	1798	3296	2512
crystal size	0.20 × 0.10 × 0.10 mm	0.20 × 0.10 × 0.05 mm	0.12 × 0.10 × 0.10 mm
$\mu$ (mm <sup>-1</sup> )	3.040	3.459	6.432
reflections collected	13509	25080	7857
unique reflections [ <i>R</i> (int)]	4781 [ <i>R</i> (int) = 0.0761]	8350 [ <i>R</i> (int) = 0.1086]	2957 [ <i>R</i> (int) = 0.1053]
absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max and min transmission	0.745 and 0.708	0.7607 and 0.5210	0.5402 and 0.4711
data/restraints/parameters	4781/0/282	8350/0/523	2957/0/199
final <i>R</i> <sub>1</sub> [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.0598	0.0641	0.0556
<i>wR</i> <sub>2</sub> (all data)	0.1130	0.1522	0.1479
GOF	1.051	1.108	1.103



**Figure 2.** (a) 1D silver column in **1**, showing silver rings formed by six silver ions. (b) 2D network in **1**, showing linkage of the silver columns through argentophilic interaction ( $\text{Ag}_2\text{-Ag}_2\text{C}$  3.1727(11) Å).



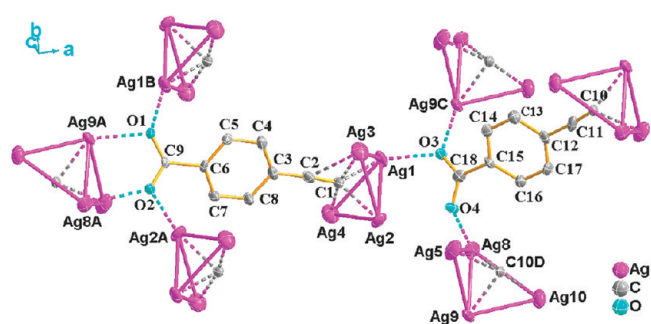
**Figure 3.** (a) 2D silver network and locations of nitrate anions in **1**, viewed along the *b* direction. (b) 2D silver network viewed along the *a* direction.

**Caution!** Silver ethynide complexes are potentially explosive and should be handled in small amounts with extreme care.

**{Ag<sub>2</sub>(L1)<sub>2</sub>·AgNO<sub>3</sub>}<sub>∞</sub> (1).** To a 4 mL vial containing solid methyl 4-ethynylbenzoate (**HL1**) (0.0025 g, 0.016 mmol) were added a few drops of distilled water and excess solid silver nitrate (0.0040 g, 0.024 mmol). This mixture was stirred for 20 min to generate a white precipitate. After washing twice with distilled water to remove the excess AgNO<sub>3</sub> and nitric acid released from the reaction, a white solid was obtained. This solid was dissolved in a concentrated solution of silver nitrate (0.2 mL of distilled water, 0.21 g of AgNO<sub>3</sub>, 1.24 mmol) to generate a clear solution. Diffusion of water to this solution at 333 K over 1–2 days afforded **1** as colorless flakes in about 85% yield. Elemental analysis calcd (%) for C<sub>20</sub>H<sub>14</sub>Ag<sub>3</sub>NO<sub>7</sub>: C, 34.13; H, 2.00; N, 1.99. Found: C, 33.89; H, 2.02; N, 1.85. IR (cm<sup>-1</sup>): 2000 (vw, ν(C≡C)), 1725 (s, ν(COO<sup>-</sup>)), 1279 (s, ν(NO<sub>3</sub><sup>-</sup>)).

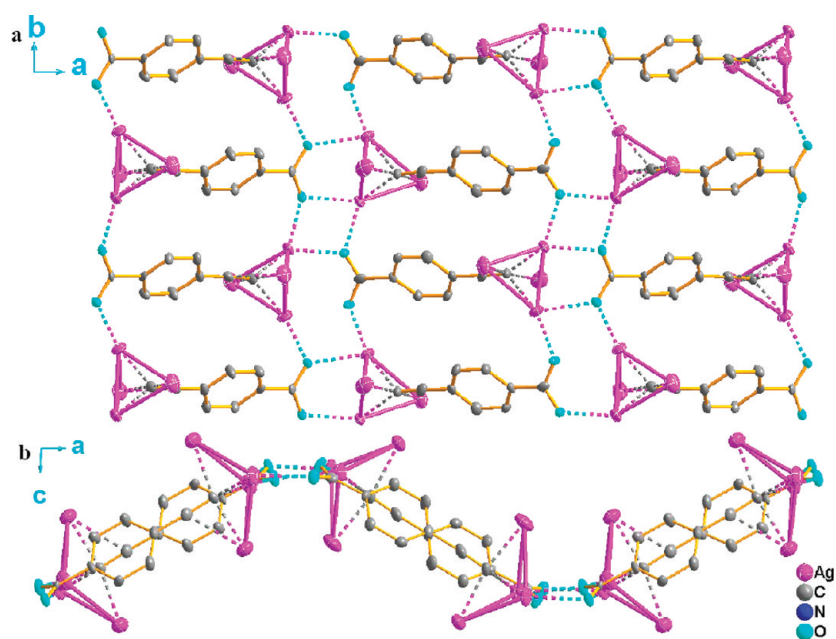
**{Ag<sub>2</sub>(L2)·3AgNO<sub>3</sub>·H<sub>2</sub>O}<sub>∞</sub> (2).** To a 4 mL vial containing solid 4-ethynylbenzoic acid (**H<sub>2</sub>L2**) (0.0008 g, 0.0055 mmol) were added a few drops of distilled water and excess solid silver nitrate (0.0025 g, 0.015 mmol). This mixture was stirred for 20 min to generate a pale-pink precipitate. After washing twice with distilled water to remove the excess AgNO<sub>3</sub> and nitric acid released from the reaction, an off-white solid was obtained. This solid was dissolved in a concentrated solution of silver nitrate (0.2 mL of distilled water, 0.20 g of AgNO<sub>3</sub>, 1.18 mmol) to generate a clear solution. Diffusion of water to this solution at 333 K over 2–3 days afforded **2** as colorless needles in about 70% yield. Elemental analysis calcd (%) for C<sub>18</sub>H<sub>12</sub>Ag<sub>10</sub>N<sub>6</sub>O<sub>24</sub>: C, 12.18; H, 0.68; N, 4.73. Found: C, 12.01; H, 0.71; N, 4.58. IR (cm<sup>-1</sup>): 1991 (vw, ν(C≡C)), 1762 (s, ν(COO<sup>-</sup>)), 1508, 1380, 1284 (s, ν(NO<sub>3</sub><sup>-</sup>)).

**{Ag<sub>3</sub>(L3)·AgNO<sub>3</sub>}<sub>∞</sub> (3).** To a 4 mL vial containing solid 5-ethynyl-1,3-benzenedicarboxylic acid (**H<sub>2</sub>L3**) (0.0007 g, 0.0037 mmol) were



**Figure 4.** Coordination modes of the 4-carboxylatophenylethyne ligand in **2** (50% thermal ellipsoids). All hydrogen atoms are omitted for clarity. Symmetry code: A is  $1 - x, 1 - y, 2 - z$ . B is  $1 - x, 2 - y, 2 - z$ . C is  $x, 1 + y, z$ . D is  $2 - x, 1 - y, 2 - z$ . Selected bond lengths (Å) and angles (deg): C1–C2 1.213(12), C1–Ag1 2.148(8), C1–Ag2 2.154(8), C1–Ag3 2.331(9), C1–Ag4 2.348(9), C2–Ag3 2.620(9), C9–O1 1.262(9), C9–O2 1.266(9), C10–C11 1.185(12), C18–O3 1.263(9), C18–O4 1.267(9), C10D–Ag5 2.331(8), C10D–Ag8 2.186(8), C10D–Ag9 2.184(8), C10D–Ag10 2.331(8), Ag1–Ag2 2.8233(11), Ag1–Ag3 3.0318(12), Ag1–Ag4 3.0069(13), Ag2–Ag3 3.0392(12), Ag2–Ag4 3.1009(13), Ag5–Ag8 3.0067(12), Ag5–Ag9 3.1827(13), Ag8–Ag9 2.7367(11), Ag8–Ag10 3.1834(11), Ag9–Ag10 2.8959(11), O1–Ag1B 2.287(5), O1–Ag9A 2.426(5), O2–Ag2A 2.191(5), O2–Ag8A 2.543(5), O3–Ag1 2.338(6), O3–Ag9C 2.277(5), O4–Ag8 2.207(5), C1–C2–C3 176.2(9), C10–C11–C12 175.9(9), O1–C9–O2 122.1(7), and O3–C18–O4 121.6(8).

added a few drops of distilled water and excess solid silver nitrate (0.0025 g, 0.015 mmol). This mixture was stirred for 20 min to generate a pale-yellow



**Figure 5.** (a) 2D coordination network viewed along the *c* direction in **2**; (b) 2D wave-like layer along the *b* direction in **2**.

precipitate. After washing twice with distilled water to remove the excess  $\text{AgNO}_3$  and nitric acid released from the reaction, a pale-yellow solid was obtained. This solid was dissolved in a concentrated solution of silver nitrate (0.2 mL of distilled water, 0.18 g of  $\text{AgNO}_3$ , 1.06 mmol) to generate a clear solution. Diffusion of water to this solution at 333 over 2–3 days afforded **3** as brown blocks in about 61% yield. Elemental analysis calcd (%) for  $\text{C}_{10}\text{H}_3\text{Ag}_4\text{NO}_7$ : C, 17.74; H, 0.45; N, 2.07. Found: C, 17.51; H, 0.52; N, 1.91. IR ( $\text{cm}^{-1}$ ): 1977 (vw,  $\nu(\text{C}\equiv\text{C})$ ), 1596 (s,  $\nu(\text{COO}^-)$ ), 1533, 1356, 1282 (s,  $\nu(\text{NO}_3^-)$ ).

**Physical Measurements.** 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.

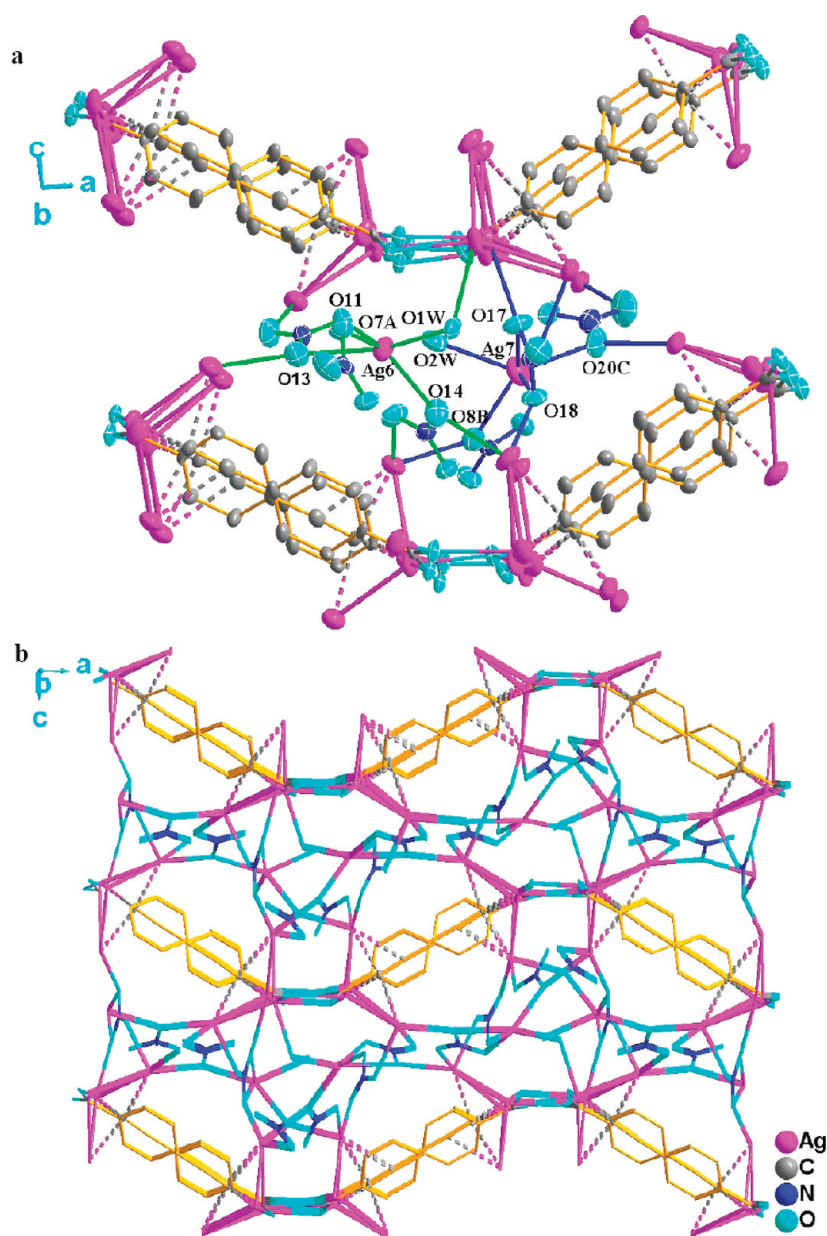
**X-ray Structure Determinations.** Suitable single crystals were selected and mounted onto the end of a thin glass fiber. X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073$  Å) at 273 or 298 K. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software package.<sup>12</sup> Anisotropic displacement parameters were applied to all nonhydrogen atoms. In all cases, hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms. Crystal data for the compounds **1**, **2**, and **3** are listed in Table 1.

## RESULTS AND DISCUSSION

**Synthesis.** Three ligands **HL1**, **H<sub>2</sub>L2**, and **H<sub>3</sub>L3** were synthesized conveniently according to a method reported by Lau and his co-workers three decades ago.<sup>11</sup> A reaction of methyl 4-iodobenzoate with trimethylsilylene under standard conditions for Sonogashira reactions afforded methyl 4-trimethylsilylbenzoate, which was treated subsequently using anhydrous potassium carbonate in anhydrous methanol at room temperature to generate **HL1**. De-esterification of **HL1** with sodium hydroxide, followed by a treatment with hydrochloric acid, gave **H<sub>2</sub>L2**. In a similar way, **H<sub>2</sub>L3** can be also prepared. Three ligands (**HL1**, **H<sub>2</sub>L2**, and **H<sub>2</sub>L3**) directly react with silver nitrate to generate organometallic polymers as intermediate products,<sup>7</sup>

which can be dissolved in a concentrated solution of silver nitrate to afford clear solutions. Complexes **1**, **2**, and **3** were obtained as crystals by slow diffusion of water into these solutions at 333 K in moderate yields, which are stable at room temperature in the solid state, but slowly decompose while exposed to light. The weak absorptions of ethynide groups located at 2000, 1991, and 1977  $\text{cm}^{-1}$ , respectively, in infrared spectra of **1**, **2**, and **3**, and the peaks related to carboxylate and nitrate groups also appear at their corresponding positions, indicative of the formation of silver(I)-ethynide complexes.

**Structure of  $\{\text{Ag}_2(\text{L1})_2 \cdot \text{AgNO}_3\}_\infty$  (**1**).** In order to investigate the effect of the number of carboxylate groups on the structures of silver(I)-ethynide complexes and assembled network, **1** was synthesized and structurally characterized. In **1**, there are two kinds of binding modes for **L1**, where one ethynide group (C2–C3) coordinates to three silver ions with a  $\mu_3\text{-}\eta^2, \eta^1, \eta^1$  bonding mode to form a complex unit ( $\text{CAG}_3$ ), but another (C11–C12) interacts with three silver ions with a  $\mu_3\text{-}\eta^1, \eta^1, \eta^1$  mode (Figure 1). The triple bond lengths of C2–C3 and C11–C12 are similar (1.205 Å), and the C–Ag and Ag···Ag distances are in the range of 2.160(7)–2.544(6) and 2.9143(9)–3.2681(10) Å, respectively, close to the values in the literature.<sup>6</sup> The values for C1–C2–C3 (171.8(7)°) and C11–C12–C13 (174.4(8)°) indicate the deviation from perfect linearity. Both silver-ethynide units ( $\text{CAG}_3$ ) exhibit a distorted tetrahedral geometry, where three silver ions are arranged in an asymmetrical triangle pattern.<sup>7a</sup> Unexpectedly, in the solid state, each silver-ethynide unit is connected with three neighboring units by sharing silver ions to afford a silver column, which is constructed by aggregation of six-membered silver rings with a chairlike geometry through argentophilic interaction (Figure 2a). These silver columns are further linked through unsupported  $\text{Ag}\cdots\text{Ag}$  interaction to generate a two-dimensional silver network (Figure 2b, Figure 3a) ( $\text{Ag}_2\text{–Ag}_2\text{C}$  3.1727(11) Å), where large silver rings constructed by eight silver ions are observed, whose structure is similar to that of cyclo- $\text{S}_8$  to some extent (Figure 2b). In the solid state, the nitrate groups are located in

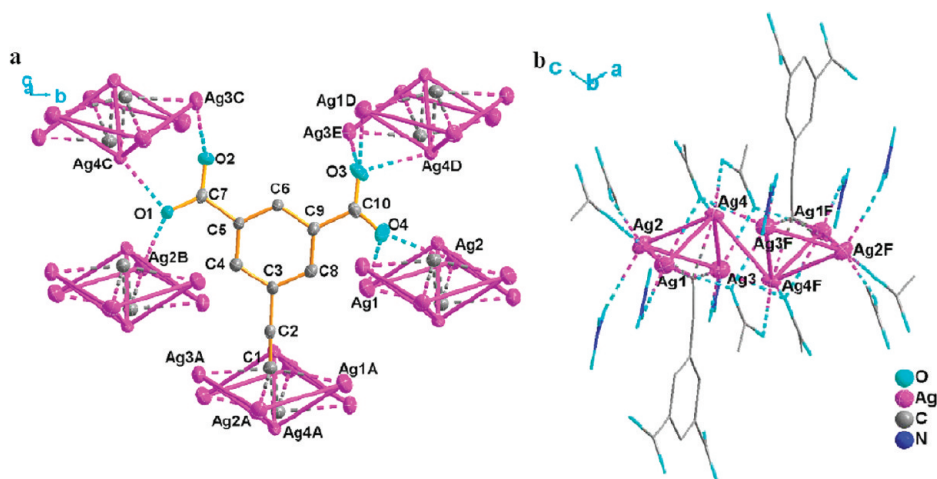


**Figure 6.** (a) 2D wave-like layers in **2** are linked by two kinds of  $\text{AgNO}_3$  units, which are marked by turquoise and blue colors, respectively (50% thermal ellipsoids). Symmetry code: A is  $x, 0.5 - y, -0.5 + z$ . B is  $x, 1.5 - y, -0.5 + z$ . C is  $2 - x, 0.5 + y, 1.5 - z$ ; Selected bond lengths ( $\text{\AA}$ ): Ag6–O1W 2.480(6), Ag6–O7A 2.529(7), Ag6–O11 2.572(7), Ag6–O13 2.576(8), Ag6–O14 2.448(7), Ag7–O2W 2.510(8), Ag7–O8B 2.427(8), Ag7–O17 2.538(7), Ag7–O18 2.579(8), and Ag7–O20C 2.428(8). (b) 3D coordination network viewed along the  $b$  direction. All of the hydrogen atoms are omitted for clarity.

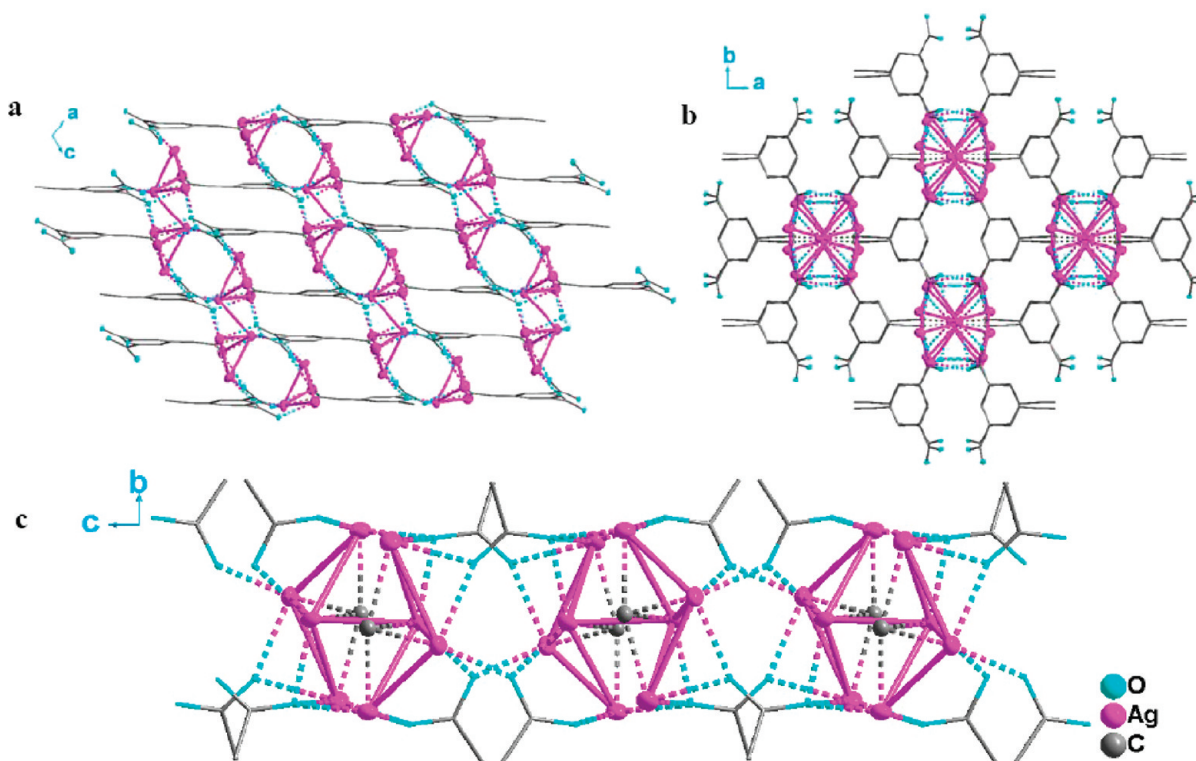
the large cavities formed by eight-membered silver rings and phenyl rings perpendicular to the silver rings, and each anion interacts with two silver ions by using one oxygen atom (O7) in a bridging mode with 2.470(5) and 2.587(5)  $\text{\AA}$  of Ag–O distances (Figure 3). It is well documented that  $\text{R}-\text{C}\equiv\text{C}\text{Ag}_n$  (R = alkyl or aryl) complex units usually interact to generate silver(I) columns, chains, and aggregates,<sup>6</sup> but 2D silver(I) networks were not observed in the past. However, in silver(I)-phenyldiethynides or pyridyldiethynides, two 2D silver layers were found in the literature: one was observed in a silver 1,2-phenylenediethynide complex,<sup>13</sup> and another was reported by us in silver 2,5-pyridyldiethynide.<sup>14</sup> Because methyl 4-carboxylphenylethylene is similar to other arylyethylene ligands to some extent, what

controls the structure of the assembled network is not clear, but possibly the weakly steric hindrance of nitrate anions is an important factor in this process.<sup>14</sup> All the ligands are arranged almost parallel and located on both sides of this layer as shown in Figure 3b. There are two kinds of interplanar distances between these phenyl rings, 3.409 and 3.436  $\text{\AA}$ , respectively, and the centroid–centroid distances are in the range of 3.881–4.055  $\text{\AA}$ , indicating that no strong offset  $\pi-\pi$  stacking exists. In the solid state, no significant interaction is observed between these 2D networks (see Figure S1 in the Supporting Information).

**Structure of  $\{\text{Ag}_2(\text{L}2) \cdot 3\text{AgNO}_3 \cdot \text{H}_2\text{O}\}_\infty$  (**2**).** Crystallographic studies revealed that in **2** there are also two coordination modes for **L2**, and each ligand interacts with four butterfly shaped



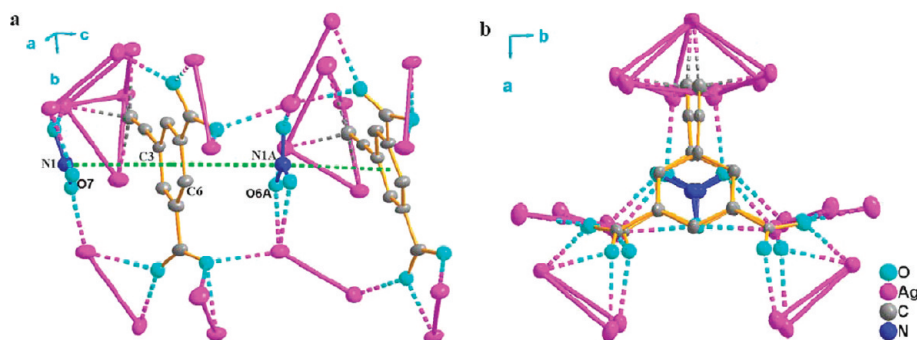
**Figure 7.** (a) Coordination mode for the 3,5-dicarboxylatophenylethyne ligand in **3** (50% thermal ellipsoids). (b) Ag<sub>8</sub> unit generated from two Ag<sub>4</sub>-ethynide units through argentophilic interaction. All the hydrogen atoms are omitted for clarity. Symmetry code: A is  $0.5 - x, 0.5 - y, 1 - z$ . B is  $x, -1 + y, z$ . C is  $1 - x, -1 + y, 1.5 - z$ . D is  $1 - x, y, 1.5 - z$ . E is  $x, 1 - y, 0.5 + z$ . F is  $1 - x, 1 - y, 1 - z$ . Selected bond lengths (Å) and angles (deg): C1–C2 1.193(10), C1–Ag1A 2.465(8), C1–Ag2A 2.223(8), C1–Ag3A 2.341(8), C1–Ag4A 2.240(8), C7–O1 1.273(9), C7–O2 1.238(9), C10–O3 1.257(9), C10–O4 1.243(10), O1–Ag2B 2.204(5), O1–Ag4C 2.339(5), O2–Ag3C 2.380(6), O3–Ag1D 2.579(6), O3–Ag4D 2.425(6), O3–Ag3E 2.483(6), O4–Ag1 2.513(8), O4–Ag2 2.476(6), Ag1–Ag2 3.2753(10), Ag1–Ag4 2.9958(9), Ag2–Ag3 2.9991(10), Ag2–Ag4 2.8899(10), Ag3–Ag4 3.1102(8), Ag4–Ag4F 2.9600(12), C1–C2–C3 174.0(8), O1–C7–O2 123.4(7), and O3–C10–O4 125.7(7).



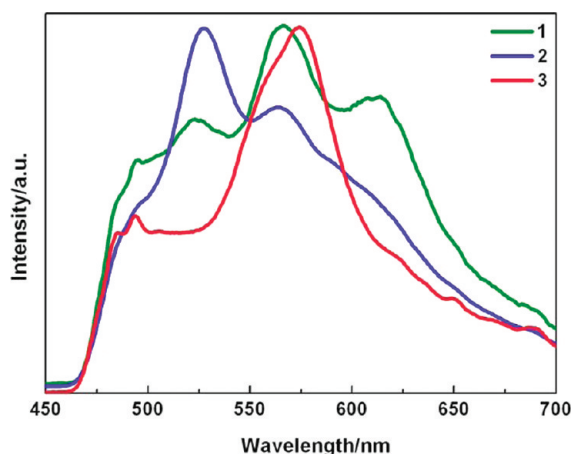
**Figure 8.** (a) 3D network viewed along the *b* direction in **3**. (b) 3D network viewed along the *c* direction in **3**. (c) Silver column in **3** generated from the linkage of Ag<sub>8</sub> cluster units by the bridging carboxylato groups.

Ag<sub>4</sub> units, which are depicted in Figure 4. One mode is that one ethynide group (C2–C3) of one ligand coordinates to four silver ions with a  $\mu_4\text{-}\eta^2, \eta^1, \eta^1, \eta^1$  bonding mode, and each oxygen atom (O1, O2) of the carboxylate group interacts with two silver ions in a bridging mode (mode *d* in Scheme 1) (O1–Ag1B 2.287(5), O1–Ag9A 2.426(5), O2–Ag2A 2.191(5),

O2–Ag8A 2.543(5) Å, O1–C9–O2 122.1(7)°). However, the ethynide group of another ligand exhibits a  $\mu_4\text{-}\eta^1, \eta^1, \eta^1, \eta^1$  bonding mode, and the carboxylate group interacts with silver ions in a different way, where one oxygen atom (O3) interacts with two silver ions (O3–Ag1 2.338(6), O3–Ag9C 2.277(5) Å, O3–C18–O4 121.6(8)°) belonging to two different R–C≡C–Ag<sub>4</sub>



**Figure 9.** (a) Nitrate- $\pi$  interaction in **3**. (b) Linear  $\pi$ - $\pi$  stacking viewed along the  $c$  direction. Symmetry code: A is  $x, -y, 0.5 + z$ . All the hydrogen atoms are omitted for clarity.



**Figure 10.** Solid state emission spectra of **1** ( $\lambda_{em}$  567 nm), **2** ( $\lambda_{em}$  527 nm), and **3** ( $\lambda_{em}$  574 nm) at room temperature.

units, but another oxygen atom (O4) coordinates to one silver ion (O4–Ag8 2.207(5) Å). The two triple bond distances are 1.213(12) (C1–C2) and 1.185(12) (C10–C11) Å, respectively, which are typical values found in silver-ethynide complexes.<sup>6</sup> Both C–Ag and Ag $\cdots$ Ag distances (in the ranges of 2.148(8)–2.620(9) and 2.7367(11)–3.1834(11) Å, respectively) are also normal, indicating the existence of silver-ethynide and argentophilic interactions.<sup>6,15</sup> Compared to that observed in **1**, the angles of C1–C2–C3 (176.2(9)°) and C10–C11–C12 (175.9(9)°) are just slightly bent. As shown in Figure 5, the O<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub>–C≡CAg<sub>4</sub> complex units are linked to each other to generate a wave-like two-dimensional network through O–Ag coordination bonds.

In **2**, all the nitrate anions are located between the layers, which not only connect the layers through O–Ag coordination bonds but also bind to single silver ions (Ag6, Ag7), as shown in Figure 6a. Both silver ions (Ag6, Ag7) are coordinated by five oxygen atoms, four of which are from three nitrate anions, and one from a water molecule. In such way, a three-dimensional network is constructed (Figure 6b).

**Structure of {Ag<sub>3</sub>(L3)·AgNO<sub>3</sub>}<sub>∞</sub> (**3**).** From the structural analysis of **1** and **2**, it has been shown that the coordination ability of the carboxylate group could lead to the aggregation of Ph–C≡CAg<sub>4</sub> units to generate coordination networks. In **3**, one ethynide group of H<sub>2</sub>L3 interacts with four silver ions, which are arranged in a butterfly shape in a  $\mu_4$ - $\eta^1, \eta^1, \eta^1, \eta^1$  bonding

mode, which was also observed in **2**. Two carboxylate groups interact with four Ph–C≡CAg<sub>4</sub> units in different binding modes, as depicted in Figure 7a. Two oxygen atoms of one carboxylate group (O1 and O2) coordinate to three silver atoms belonging to two ethynide-Ag<sub>4</sub> units in mode  $c$  (Scheme 1) (O1–Ag2B 2.204(5), O1–Ag4C 2.339(5), and O2–Ag3C 2.380(6) Å; O1–C7–O2 123.4(7)°), and another carboxylate group interacts with five silver ions in mode  $e$  (Scheme 1) (O3–Ag1D 2.579(6), O3–Ag4D 2.425(6), O3–Ag3E 2.483(6), O4–Ag1 2.513(8), and O4–Ag2 2.476(6) Å; O3–C10–O4 125.7(7)°). The triple bond distance (C1–C2) is 1.193(10) Å, and the value for C1–C2–C3 is 174.0(8)°, close to that observed in **1** and **2**; however, in **3**, two Ph–C≡CAg<sub>4</sub> units aggregate through argentophilic interaction (Ag4–Ag4F 2.9600(12) Å) to form a dimeric unit containing eight silver ions, which is shown in Figure 7b. The Ag $\cdots$ Ag distances are in the range of 2.8899(10)–3.2753(10) Å, indicating the existence of argentophilic interaction.<sup>15</sup>

As shown in Figure 8a,b, the dimeric [(O<sub>2</sub>C)<sub>2</sub>-Ph–C≡C]<sub>2</sub>Ag<sub>8</sub> units are linked through silver(I)-carboxylate interactions (Ag–O coordination bonds) to generate a three-dimensional network in the solid state. It is also clearly shown that the Ag<sub>8</sub> units are bridged by carboxylate groups to form silver columns in Figure 8a,b,c, which are often found in silver(I)-ethynide complexes.<sup>6</sup>

It has been demonstrated that the anion- $\pi$  interactions with aromatic rings is an important factor in controlling the structures of complexes in the solid state.<sup>16</sup> In **3**, it is observed that the nitrate anions coordinated to silver ions are almost arranged parallel with phenyl rings to form an infinite linear chain, which is depicted in Figure 9a,b. The shortest distances between nitrates and phenyl rings are 3.215 (N1–C3) and 3.279 (O6A–C6) Å, and the distances between oxygen atoms in nitrate groups and the ring centroids are 3.364 (O7 $\cdots$ centroid) and 3.571 (O6A $\cdots$ centroid) Å, respectively, comparable with that of the values for the anion-pyrimidine ring<sup>17</sup> and chloride-pyridine ring<sup>18</sup> reported in the literature, indicating the existence of a weak anion- $\pi$  interaction.

**Photoluminescence Properties.** Compared to copper(I)-ethynide complexes, the photoluminescence properties of silver(I)-ethynide complexes are relatively less investigated, and their emissions mainly originate from intraligand  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions.<sup>5,7b</sup>

In the solid state, all of the complexes in this work are emissive at room temperature, as shown in Figure 10. Their broad emission bands for complexes **1**, **2**, and **3** are located in the

range of 470–700 nm with several peaks and exhibit somewhat similar characteristics regardless of the carboxylate groups attached to the phenylethyne ligands. The solid sample of **1** displays a broad band with three peaks at 523, 567, and 614 nm, and the maximum is at 567 nm on excitation at 370 nm. There are two peaks located at 528 and 564 nm and two shoulders around ~500 and ~620 nm for **2**, and **3** exhibits one maximum peak at 574 nm and two shoulders at ~500 and ~620 nm. Their relatively long lifetimes, 0.12, 0.20, and 0.76 ms for **1**, **2**, and **3**, respectively, indicate phosphorescence characteristics. For assignment purposes, the emission spectra of the ligands, **HL1**, **H<sub>2</sub>L2**, and **H<sub>2</sub>L3** were also measured (Figure S2 in the Supporting Information). Obviously, these bands are somewhat similar to that observed for complexes **1**, **2**, and **3** in the solid state, which also spread in the range of 470–720 nm. These results indicate that the emissions mainly originate from ligand-centered excited states and are not possibly related to metal centers.<sup>5a,19</sup> Therefore, it is reasonable to attribute these emissions as intraligand transitions, perturbed by silver(I)-ligand interactions based on the comparisons.

## CONCLUSIONS

By utilizing mono- and dicarboxylphenylethyne ligands, a series of new silver(I)-ethynide complexes have been synthesized and structurally characterized. These kinds of complexes bearing carboxylate groups could serve as new building units to assemble novel silver(I)-organic networks, which exhibit diverse coordination modes and are capable of interacting with more silver(I) ions or silver(I)-ethynide complex units compared to silver(I) pyridyl or pyrimidylethyne complexes and thus lead to high-level organometallic networks through silver(I)-carboxylate coordination bonds. The obtained results demonstrate that the structure of the assembled network constructed from silver(I)-ethynide complexes is highly dependent upon the number of carboxylate groups attached to the phenylethyne ligands. In the solid state, all the complexes synthesized in this work are emissive at room temperature, which mainly originate from intraligand  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions.

## ASSOCIATED CONTENT

**S** Supporting Information. X-ray crystallographic data for **1**, **2**, and **3** in CIF format, packing diagram for **1**, and excitation and emission spectra for **HL1**, **H<sub>2</sub>L2**, and **H<sub>2</sub>L3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*Fax: 86-27-87543632. E-mail: [tlzhang@mail.hust.edu.cn](mailto:tlzhang@mail.hust.edu.cn).

## ACKNOWLEDGMENT

This research was supported by the National Natural Science Foundation of China (Grant No. 20871049) and the Analytical and Testing Center, Huazhong University of Science and Technology.

## REFERENCES

- (a) Inokuma, Y.; Kawano, M.; Fujita, M. *Nat. Chem.* **2011**, *3*, 349–358. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369–378. (c) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (d) Merlau, M. L.; Del Pilar Mejia, M.; Nguyen, S. T.; Hupp, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4239–4242. (e) Gianneschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825–837. (f) Boyer, J. L.; Kuhlman, M. L.; Rauchfuss, T. B. *Acc. Chem. Res.* **2007**, *40*, 233–242. (g) Yoshizawa, M.; Fujita, M. *Pure Appl. Chem.* **2005**, *77*, 1107–1112. (h) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349–358. (i) Jiang, H.-L.; Tatsu, Y.; Lu, Z.-H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586–5587.
- (2) (a) Kuppler, R. J.; Timmons, D. J.; Fang, Q.; Li, J.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H.-C. *Coord. Chem. Rev.* **2009**, *253*, 3042–3066. (b) Férey, G.; Mellot-Drazniewski, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225. (c) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714. (d) Furukawa, H.; Ko, N.; Go, Y.; Aratani, N.; Choi, S.; Choi, E.; Yazaydin, A. Ö.; Snurr, R. Q.; O’Keeffe, M.; Kim, J.; Yaghi, O. M. *Science* **2010**, *329*, 424–428. (e) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357–5361. (f) Song, F.; Wang, C.; Falkowski, J. M.; Ma, L.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 15390–15398. Yi, F.-Y.; Lin, Q.-P.; Zhou, T.-H.; Mao, J.-G. *Inorg. Chem.* **2010**, *49*, 3489–3500.
- (3) (a) Anson, C. E.; Eichhöfer, A.; Issac, I.; Fenske, D.; Fuhr, O.; Sevillano, P.; Persau, C.; Stalke, D.; Zhang, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1326–1331. (b) Fenske, D.; Anson, C. E.; Eichhöfer, A.; Fuhr, O.; Ingendoh, A.; Persau, C.; Richert, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 5242–5246. (c) Fenske, D.; Persau, C.; Dehnen, S.; Anson, C. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 305–309. (d) Wang, X.-J.; Langetepe, T.; Person, C.; Kang, B.-S.; Sheldrick, G. M.; Fenske, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3818–3822. (e) Fenske, D.; Zhu, Y.; Langetepe, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 2640–2644. (f) Li, G.; Lei, Z.; Wang, Q.-M. *J. Am. Chem. Soc.* **2010**, *132*, 17678–17679. (g) Tang, K.; Xie, X.; Zhang, Y.; Zhao, X.; Jin, X. *Chem. Commun.* **2002**, 1024–1025.
- (4) (a) Qiao, J.; Shi, K.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2010**, *49*, 1765–1767. (b) Bian, S.-D.; Wu, H.-B.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5363–5365. (c) Bian, S.-D.; Jia, J.-H.; Wang, Q.-M. *J. Am. Chem. Soc.* **2009**, *131*, 3422–3423. (d) Xie, Y.-P.; Mak, T. C. W. *J. Am. Chem. Soc.* **2011**, *133*, 3760–3763. (e) Gao, G.-G.; Cheng, P.-S.; Mak, T. C. W. *J. Am. Chem. Soc.* **2009**, *131*, 18257–18259. (f) Gruber, F.; Jansen, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4924–4926. (g) Koshevoy, I. O.; Lin, C.-L.; Karttunen, A. J.; Janis, J.; Haukka, M.; Tunik, S. P.; Chou, P.-T.; Pakkanen, T. A. *Inorg. Chem.* **2011**, *50*, 2395–2403. (h) Koshevoy, I. O.; Karttunen, A. J.; Shakirova, J. R.; Melnikov, A. S.; Haukka, P. M.; Tunik, P. S. P.; Pakkanen, T. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 8864–8866.
- (5) (a) Chui, S. S. Y.; Ng, M. F. Y.; Che, C.-M. *Chem.—Eur. J.* **2005**, *11*, 1739–1749. (b) Lin, Y.-Y.; Lai, S.-W.; Che, C.-M.; Cheung, K.-K.; Zhou, Z.-Y. *Organometallics* **2002**, *21*, 2275–2282. (c) Wei, Q.-H.; Yin, G.-Q.; Zhang, L.-Y.; Chen, Z.-N. *Inorg. Chem.* **2006**, *45*, 10371–10377.
- (6) (a) Mak, T. C. W.; Zhao, L. *Chem.—Asian J.* **2007**, *2*, 456–467. (b) Zhao, L.; Wong, W.-Y.; Mak, T. C. W. *Chem.—Eur. J.* **2006**, *12*, 4865–4872. (c) Zhao, L.; Zhao, X.-L.; Mak, T. C. W. *Chem.—Eur. J.* **2007**, *13*, 5927–5936. (d) Zhao, L.; Mak, T. C. W. *Organometallics* **2007**, *26*, 4439–4448. (e) Zang, S.-Q.; Mak, T. C. W. *Inorg. Chem.* **2008**, *47*, 7094–7105. (f) Zhao, L.; Chen, X.-D.; Mak, T. C. W. *Organometallics* **2008**, *27*, 2483–2489. (g) Zang, S.-Q.; Zhao, L.; Mak, T. C. W. *Organometallics* **2008**, *27*, 2396–2398. (h) Zhao, L.; Wan, C.-Q.; Han, J.; Chen, X.-D.; Mak, T. C. W. *Chem.—Eur. J.* **2008**, *14*, 10437–10444. (i) Zang, S.-Q.; Han, J.; Mak, T. C. W. *Organometallics* **2009**, *28*, 2677–2683. (j) Li, B.; Zang, S.-Q.; Liang, R.; Wu, Y.-J.; Mak, T. C. W. *Organometallics* **2011**, *30*, 1710–1718.
- (7) (a) Zhang, T.-L.; Kong, J.-X.; Hu, Y.-J.; Meng, X.-G.; Yin, H.-B.; Hu, D.-S.; Ji, C.-P. *Inorg. Chem.* **2008**, *47*, 3144–3149. (b) Zhang, T.-L.; Hu, Y.-J.; Kong, J.-X.; Meng, X.-G.; Dai, X.-M.; Song, H.-B. *CrystEngComm* **2010**, *12*, 3027–3032.
- (8) Zhao, L.; Mak, T. C. W. *Inorg. Chem.* **2009**, *48*, 6480–6489.
- (9) Sun, D.; Wang, D.-F.; Han, X.-G.; Zhang, N.; Huang, R.-B.; Zheng, L.-S. *Chem. Commun.* **2011**, 746–748.
- (10) (a) Awaleh, M. O.; Brisse, F.; Soubaneh, Y. D.; Maris, T. *Polyhedron* **2010**, *29*, 2966–2975. (b) Bian, S.-D.; Wang, Q.-M. *Chem.*



*Commun.* **2008**, 5586–5588. (c) Liu, S.-Q.; Konaka, H.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G.-L.; Munakata, M. *Inorg. Chim. Acta* **2005**, 358, 919–926. (d) Sun, D.; Wang, D.-F.; Zhang, N.; Liu, F.-J.; Hao, H.-J.; Huang, R.-B.; Zheng, L.-S. *Dalton Trans.* **2011**, 5677–5679.

(11) (a) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, 46, 2280–2286. (b) Sabourin, E. T.; Onopchenko, A. *J. Org. Chem.* **1983**, 48, 5135–5137.

(12) (a) Sheldrick, G. M. SADABS; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXS97 and SHELXL97; University of Göttingen: Göttingen, Germany, 1997.

(13) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2005**, 127, 14966–14967.

(14) Zhang, T.-L.; Song, H.-B.; Dai, X.-M.; Meng, X.-G. *Dalton Trans.* **2009**, 7688–7694.

(15) (a) Pyykkö, P. *Chem. Rev.* **1997**, 97, 597–636. (b) Che, C.-M.; Tse, M.-C.; Chan, M. C. W.; Cheung, K.-K.; Phillip, D. L.; Leung, K.-H. *J. Am. Chem. Soc.* **2000**, 122, 2464–2468. (c) Reiß, P.; Weigend, F.; Ahlrichs, R.; Fenske, D. *Angew. Chem., Int. Ed.* **2000**, 39, 3925–3929.

(16) (a) Schottel, B. L.; Chifotides, H. T.; Shatruk, M.; Chouai, A.; Péres, L. M.; Bacsa, J.; Dunbar, K. R. *J. Am. Chem. Soc.* **2006**, 128, 5895–5912. (b) Demeshko, S.; Dechert, S.; Meyer, F. *J. Am. Chem. Soc.* **2004**, 126, 4508–4509.

(17) (a) Garcia-Raso, A.; Albertí, F. M.; Fiol, J. J.; Tasada, A.; Barceló-Oliver, M.; Molins, E.; Escudero, D.; Frontera, A.; Quinero, D.; Deyá, P. M. *Eur. J. Org. Chem.* **2007**, 5821–5825. (b) Zaccheddu, M.; Filippi, C.; Buda, F. *J. Phys. Chem. A* **2008**, 112, 1627–1632.

(18) (a) de Hoog, P.; Games, P.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Angew. Chem., Int. Ed.* **2004**, 43, 5815–5817.

(19) Lu, W.; Zhu, N.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2003**, 125, 16081–16088.