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Silver(I)−Organic Networks Assembled with Propargyl-Functionalized Di- and Trihydroxybenzenes

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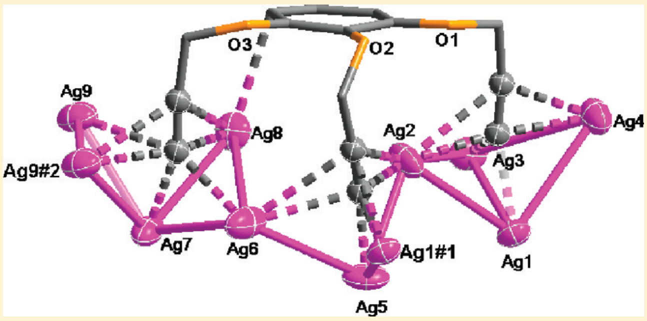
Supporting Information



ABSTRACT: A series of four new ligands bearing terminal ethynide moieties attached via pendant arms to a benzene skeleton have been used in the syntheses of four silver(I) complexes: $[(Ag_2L1)_2\cdot(AgCF_3CO_2)_{10}\cdot(CH_3CN)_2\cdot(H_2O)_4\cdot(\mu_2\text{-}H_2O)_2]\cdot(AgBF_4)$ (**1**), $[(Ag_2L2)\cdot(AgCF_3CO_2)_7\cdot(CH_3CN)\cdot(H_2O)]$ (**2**), $\{[(Ag_2L3)\cdot(AgCF_3CO_2)_{10}\cdot(CH_3CN)_6\cdot(H_2O)_2\cdot(OH)_2]\cdot(H_2O)\}$ (**3**), and $[(Ag_3L4)_2\cdot(AgCF_3CO_2)_{13}\cdot(CH_3CN)_5\cdot(H_2O)]$ (**4**) (H_2L1 = 1,2-bis(prop-2-ynyloxy)benzene, H_2L2 = 1,3-bis(prop-2-ynyloxy)benzene, H_2L3 = 1,4-bis(prop-2-ynyloxy) benzene, H_3L4 = 1,2,3-tris(prop-2-ynyloxy)benzene). In these compounds, the invariable appearance of the μ_4- and μ_5-ligation modes of the ethynide moiety affirms the general utility of the silver−ethynide supramolecular synthon $Ag_n\subset C\equiv CCH_2OC_6H_4OCH_2C\equiv C\supset Ag_n$ (n = 4, 5) in coordination network assembly. Additionally, several conventional and unconventional silver−ethynyl, argentophilic, hydrogen-bonding, silver−aromatic, and $\pi-\pi$ interactions play an important role in stabilizing their framework structures. In **1**, Ag_{15} aggregates are fused together by argentophilic interaction to yield thick silver rods, which are further linked through interchain hydrogen bonds into a 2D network. In **2**, butterfly-shaped Ag_4 baskets are fused into silver(I) columns, which are further associated by external $Ag(CF_3COO)_2$ units and argentophilic interactions to give a metal−organic sheet; adjacent layers are then linked into a 3D metal−organic framework through face-to-face aromatic $\pi-\pi$ interactions. In **3**, Ag_6−phenyl ring−Ag_6 structural units are interconnected by a pair of $\mu_4\text{-}\eta^2,\eta^2$ trifluoroacetate groups to yield silver columns, which are further united by hydrogen bonds to give a 3D metal−organic network. Two kinds of silver rods in parallel orientation are bridged by three $\mu_3\text{-}\eta^1,\eta^2$ and one $\mu_4\text{-}\eta^2,\eta^2$ trifluoroacetate groups to generate a two-dimensional metal−organic network of **4**, in which the trianion exhibits the unprecedented μ_{20}-coordination mode.

INTRODUCTION

Crystal engineering of metal−organic frameworks (MOFs) is a current trend in view of the discovery of interesting topologies and crystal-packing motifs, as well as their potential application as functional materials.[1−3] In contrast to the abundance of supramolecular architectures constructed with silver(I)−ligand coordination bonds,[4] the assembly of crystal-engineered organosilver(I) networks is much less developed. Recently, metal−ethynide complexes have attracted much interest owing to their structural diversity[5−7] and promising application as precursors of nonlinear optical materials,[8] luminescence materials,[9] and rigid-rod molecular wires.[10]

Following our investigation of the coordination chemistry of silver ethynediide (Ag_2C_2),[11] we have conducted systematic studies on various complexes containing silver(I) 1,3-butadiynediide (Ag_2C_4).[12] Furthermore, utilizing new metal−ligand supramolecular synthons of the type $R-C\equiv C\supset Ag_n$ (R = aryl or alkyl; n = 4, 5)[13] and $Ag_n\subset C\equiv C-R-C\equiv C\supset Ag_n$ (R = *o*-, *m*-, *p*-C_6H_4; n = 4, 5),[14] we have obtained a series of metal−organic networks stabilized by argentophilic[15] and silver−ethynide (σ, π and mixed σ, π) interactions. Recently, we have explored the employment of several ligands with an ethynide ethynyl group attached to a phenyl, biphenyl, or naphthyl skeleton via a flexible $-CH_2-O-$ link for the construction of MOFs consolidated by both silver(I)−ethynide and silver(I)−aromatic interactions.[16]

In continuation of our research program, we have designed four new conformational flexible ligands, 1,2-bis(prop-2-ynyloxy)benzene (H_2L1), 1,3-bis(prop-2-ynyloxy)benzene (H_2L2), 1,4-bis(prop-2-ynyloxy)benzene (H_2L3), and 1,2,3-tris(prop-2-ynyloxy)benzene (H_3L4), with two or three flexible substituents bearing terminal ethynyl groups at variable positions on the aromatic ring (Scheme 1). The reaction of crude starting materials $[Ag_2L1]_n$ (**5**), $[Ag_2L2]_n$ (**6**), $[Ag_2L3]_n$ (**7**), and $[Ag_3L4]_n$ (**8**) with water-soluble silver trifluoroacetate/tetrafluoroborate generated four new metal−organic networks, namely, $[(Ag_2L1)_2\cdot$

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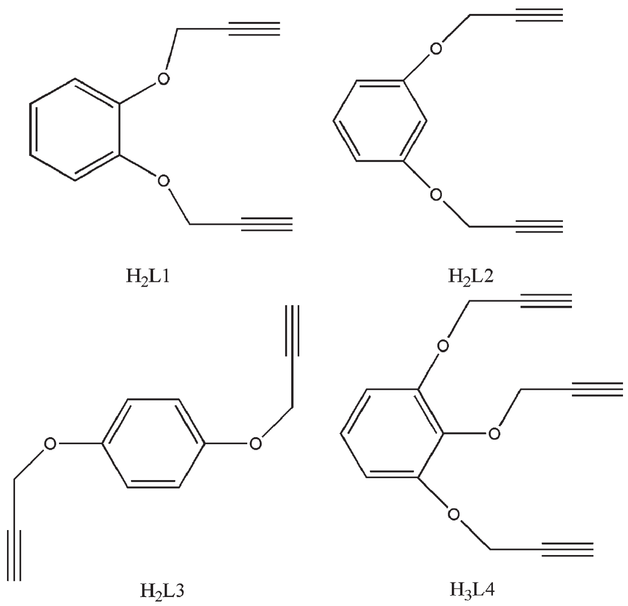
Scheme 1. Structural Formulas of Propargyl-Funtionalized Di- and Trihydroxybenzenes Used As Ligands in Forming New Silver(I)−Ethynide Complexes


H_2L1 H_2L2 H_2L3 H_3L4

$(AgCF_3CO_2)_{10}\cdot(CH_3CN)_2\cdot(H_2O)_4\cdot(\mu_2\text{-}H_2O)_2]\cdot(AgBF_4)$ (**1**), $[(Ag_2L2)\cdot(AgCF_3CO_2)_7\cdot(CH_3CN)\cdot(H_2O)]$ (**2**), $\{[(Ag_2L3)\cdot(AgCF_3CO_2)_{10}\cdot(CH_3CN)_6\cdot(H_2O)_2\cdot(OH)_2]\cdot(H_2O)\}$ (**3**), and $[(Ag_3L4)_2\cdot(AgCF_3CO_2)_{13}\cdot(CH_3CN)_5\cdot(H_2O)]$ (**4**), which are expected to be stabilized by silver(I)−ethynide and argentophilic interactions, and the phenyl ring is potentially capable of partaking in $\pi-\pi$ and silver−aromatic interactions.

EXPERIMENTAL SECTION

Reagents. Commercially available *o*-dihydroxybenzene, *m*-dihydroxybenzene, *p*-dihydroxybenzene, 1,2,3-benzenetriol, propargyl bromide (80% in toluene), and K_2CO_3 were used without further purification. Acetone, dichloromethane, ethyl acetate, *n*-hexane, acetonitrile, and triethylamine were purified according to standard procedures. All synthetic reactions yielding organic ligands and polymeric starting materials were carried out under a nitrogen atmosphere.

Caution! *Silver ethynide complexes are highly potentially explosive in the dry state when subjected to heating or mechanical shock and should be handled in small amounts with extreme care.*

1,2-Bis(prop-2-ynyloxy)benzene (H_2L1). H_2L1 was synthesized according to the literature method.[17] Propargyl bromide (2.8 mL, 25 mmol) and K_2CO_3 (3.46 g, 25 mmol) were added to a solution of *o*-dihydroxybenzene (1.10 g, 10 mmol) in acetone (30 mL). The solution was heated under reflux for 24 h under a nitrogen atmosphere. The precipitate was filtered off, and the filtrate was evaporated to dryness to yield the crude product as a yellow oil. It was purified by chromatography on silica gel to afford a pale yellow oil. Yield: 1.58 g, 85%. H NMR (300 MHz, $CDCl_3$): δ 6.61−6.79 (4H, benzene); 4.68 (4H, OCH_2); 2.52 (2H, C≡CH). IR: ν 2055 cm^{-1} (w, $\nu_{C\equiv C}$). Anal. Calcd (%) for $C_{12}H_{10}O_2$: C 77.33; H 5.41. Found: C 77.38; H 5.45.

1,3-Bis(prop-2-ynyloxy)benzene (H_2L2). H_2L2 was obtained by the above procedure except that *m*-dihydroxybenzene replaced *o*-dihydroxybenzene. Yield: 1.61 g, 87%. H NMR (300 MHz, $CDCl_3$): δ 6.61−7.26 (4H, benzene); 4.68 (4H, OCH_2); 2.53 (2H, C≡CH). IR: ν 2053 cm^{-1} (w, $\nu_{C\equiv C}$). Anal. Calcd (%) for $C_{12}H_{10}O_2$: C 77.33; H 5.41. Found: C 77.30; H 5.47.

1,4-Bis(prop-2-ynyloxy)benzene (H_2L3). H_2L3 was obtained by the same procedure using *p*-dihydroxybenzene. Yield: 1.65 g, 89%. H NMR (300 MHz, $CDCl_3$): δ 6.93 (4H, benzene); 4.65 (4H, OCH_2); 2.52 (2H, C≡CH). IR: ν 2051 cm^{-1} (w, $\nu_{C\equiv C}$). Anal. Calcd (%) for $C_{12}H_{10}O_2$: C 77.33; H 5.41. Found: C 77.40; H 5.39.

1,2,3-Tris(prop-2-ynyloxy)benzene (H_3L4). Propargyl bromide (4.2 mL, 37.5 mmol) and K_2CO_3 (5.18 g, 37.5 mmol) were added to a solution of 1,2,3-benzenetriol (1.26 g, 10 mmol) in acetone (30 mL). The solution was heated under reflux for 24 h under a nitrogen atmosphere. The precipitate was filtered off, and the filtrate was evaporated to dryness to yield the crude product as a yellow oil. It was purified by chromatography on silica gel to afford a pale yellow oil. Yield: 1.9 g, 80%. H NMR (300 MHz, $CDCl_3$): δ 6.54−6.92 (3H, benzene); 4.66−4.81 (6H, OCH_2); 2.53 (3H, C≡CH). IR: ν 2032 cm^{-1} (w, $\nu_{C\equiv C}$). Anal. Calcd (%) for $C_{15}H_{12}O_3$: C 74.99; H 5.03. Found: C 74.96; H 5.07.

*$[Ag_2L1]_n$ (**5**).* Silver nitrate (0.91 g, 5.36 mmol) was dissolved in acetonitrile (30 mL). Then H_2L1 (0.6 g, 2.68 mmol) and triethylamine (0.81 mL, 5.36 mmol) were added with vigorous stirring, and the mixture was stirred overnight under a nitrogen atmosphere in the dark. The white precipitate formed was collected by filtration, washed thoroughly with acetonitrile (2 × 10 mL) and deionized water (3 × 10 mL), and then stored in wet form at −10 °C in a refrigerator. Yield: 1.03 g, 80%. IR: ν 2038 cm^{-1} (*w*, $\nu_{C\equiv C}$).

*$[Ag_2L2]_n$ (**6**) $[Ag_2L3]_n$ (**7**), and $[Ag_3L4]_n$ (**8**).* These polymeric materials were prepared by a similar synthetic procedure using H_2L2, H_2L3, and H_3L4, respectively. Yield: 83%. $[Ag_2L2]_n$ (**6**) IR ν 2046 cm^{-1} (w, $\nu_{C\equiv C}$); $[Ag_2L3]_n$ (**7**) IR ν 2042 cm^{-1} (w, $\nu_{C\equiv C}$); $[Ag_3L4]_n$ (**8**) IR ν 2054 cm^{-1} (w, $\nu_{C\equiv C}$).

*$[(Ag_2L1)_2\cdot(AgCF_3CO_2)_{10}\cdot(CH_3CN)_2\cdot(H_2O)_4\cdot(\mu_2\text{-}H_2O)_2]\cdot(AgBF_4)$ (**1**).* $AgCF_3CO_2$ (0.44 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of water and acetonitrile (0.2 mL). Then, $[Ag_2L1]_n$ (~20 mg) solid was added to the solution. After stirring for about 2 h, the solution was filtered and the filtrate stored at −10 °C in a refrigerator. After several days, colorless block crystals of **1** were deposited in about 80% yield. Anal. Calcd (%) for $C_{48}H_{34}Ag_{15}BF_{34}N_2O_{30}$: C 16.99; H 1.01. Found: C 17.27; H 0.98. IR: ν 2086 cm^{-1} (w, $\nu_{C\equiv C}$).

*$[(Ag_2L2)\cdot(AgCF_3CO_2)_7\cdot(CH_3CN)\cdot(H_2O)]$ (**2**).* $AgCF_3CO_2$ (0.44 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of water and acetonitrile (0.2 mL). Then, $[Ag_2L2]_n$ (~20 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless needle crystals of **2** were deposited in about 90% yield. Anal. Calcd (%) for $C_{28}H_{13}Ag_9F_{21}NO_{17}$: C 16.77; H 0.65. Found: C 16.73; H 0.69. IR: ν 2075 cm^{-1} (w, $\nu_{C\equiv C}$).

*$\{[(Ag_2L3)\cdot(AgCF_3CO_2)_{10}\cdot(CH_3CN)_6\cdot(H_2O)_2\cdot(OH)_2]\cdot(H_2O)\}$ (**3**).* $AgCF_3CO_2$ (0.44 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water and acetonitrile (0.2 mL). Then, $[Ag_2L3]_n$ (~25 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **3** were deposited in about 86% yield. Anal. Calcd (%) for $C_{44}H_{34}Ag_{12}F_{30}N_6O_{27}$: C17.96; H 1.16. Found: C 17.91; H 1.11. IR: ν 2064 cm^{-1} (w, $\nu_{C\equiv C}$).

*$[(Ag_3L4)_2\cdot(AgCF_3CO_2)_{13}\cdot(CH_3CN)_5\cdot(H_2O)]$ (**4**).* $AgCF_3CO_2$ (0.44 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water and acetonitrile (0.2 mL). Then, $[Ag_3L4]_n$ (~15 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **4** were deposited in about 81% yield. Anal. Calcd (%) for $C_{66}H_{35}Ag_{19}F_{39}N_5O_{33}$: C 18.80; H 0.84. Found: C 18.77; H 0.86. IR: ν 2047 cm^{-1} (w, $\nu_{C\equiv C}$).

X-ray Crystallographic Analysis. Selected crystals were used for data collection on a Bruker SMART 1000 CCD diffractometer (**1**−**4**) at 293 K using frames of oscillation range 0.3°, with $2° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[18] The structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[19] Most of the CF_3 moieties of $CF_3CO_2^-$ groups in compounds **1**−**4** were disordered, and the SADI command was used to fix them in the refinements. In **1**, silver atoms Ag1, Ag2, Ag4, Ag7, and Ag8 are located in two disordered positions with an occupancy ratio of 0.47:0.53. In **4**, silver atoms Ag6 and Ag9 are located in two disordered positions with occupancy ratios of 0.50:0.50 and 0.90:0.10, respectively. The crystallographic data and selected bond lengths and angles for **1**−**4** are listed in Tables 1 and 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center. CCDC reference numbers: 804457−804460.

RESULTS AND DISCUSSION

Syntheses. The neutral ligands H_2L1, H_2L2, H_2L3, and H_3L4 were synthesized from the reaction of *o*-dihydroxybenzene, *m*-dihydroxybenzene, *p*-dihydroxybenzene, and 1,2,3-benzenetriol, respectively, with propargyl bromide in acetone in the presence of K_2CO_3. Silver(I) double/triple salts **1**−**4** were obtained from crystallization of the corresponding polymeric crude compounds $[AgL]_n$ (**5**−**8**) in a concentrated aqueous or water/acetonitrile solution of silver(I) trifluorocarboxylate/tetrafluoroborate. The tetrafluoroborate ion was employed to provide a high concentration of silver ions, which enhanced aggregation through argentophilicity such that the ethynide moiety is embraced within a butterfly-shaped Ag_4 or square-pyramidal Ag_5 basket.

Description of Crystal Structures. *$[(Ag_2L1)_2\cdot(AgCF_3CO_2)_{10}\cdot(CH_3CN)_2\cdot(H_2O)_4\cdot(\mu_2\text{-}H_2O)_2]\cdot(AgBF_4)$ (**1**).* In the crystal structure of compound **1**, there are two independent phenylethynide (L1) anions, each adopting a nearly planar conformation, in which the torsion angles C2−C3−O1−C4 and C11−C10−O2−C9 are −171.78° and 173.69°, respectively. The ethynide group composed of C1 and C2 is capped by a butterfly-shaped Ag_4 basket in the μ_4-$\eta^1,\eta^2,\eta^2,\eta^2$ coordination mode, and the other one comprising C11 and C12 by a different butterfly-shaped Ag_4 basket in the μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, as shown in Figure 1. Moreover, the external silver atom Ag8 is attached to the Ag_8 unit by three trifluoroacetate groups (O3−O4, O9−O10, and O11−O12) via μ_3-η^1,η^2 coordination modes to form a Ag_9 aggregate, in which the Ag−Ag distances vary from 2.782 to 3.174 Å, being shorter than twice the van der Waals radius of silver ions (3.44 Å)[20] and suggesting the presence of significant argentophilic interactions. Such symmetry-related aggregates are fused by vertex-sharing (Ag4, Ag5, and Ag4#2) to form a Ag_{15} aggregate (Figure 1 and Figure S1). Additionally, the edge-to-centroid distance between two proximal phenyl rings in the aggregate unit is 3.836 Å, indicating the existence of a significant edge-to-face π−π stacking interaction.[21]

Adjacent Ag_{15} aggregates are fused by argentophilic interaction Ag1···Ag2#1, Ag2···Ag1#1 (3.174 Å) to yield a thick silver rod, additional consolidation being provided by a pair of trifluoroacetate groups (O7−O8 and O7#1−O8#1) through the μ_3-O,O',O' mode (Figure 2a and Figure S2). The infinite silver rods are interconnected by hydrogen bonds (O3W#4···O8 2.780 Å, O1W···O11#4 2.810 Å, O1W···O10 2.786 Å) to engender a two-dimensional network parallel to the *ac* plane (Figure 2b). There is no obvious intermolecular interaction between layers.

*$[(Ag_2L2)\cdot(AgCF_3CO_2)_7\cdot(CH_3CN)\cdot(H_2O)]$ (**2**).* The asymmetric unit of **2** contains nine crystallographically independent Ag(I) ions, seven trifluoroacetate ions, one coordinated acetonitrile molecule, and one coordinated water molecule. In the crystal structure of **2**, the dianionic ligand L2 adopts a nonplanar conformation, in which the torsion angles C2−C3−O1−C4 and C11−C10−O2−C8 are −69.67° and −68.54°, respectively. As shown in Figure 3, the ethynide groups (C1≡C2 and

Table 1. X-ray Crystal Data and Structure Refinement for Compounds 1−4

	1	2	3	4
formula	$C_{48}H_{34}Ag_{15}BF_{34}N_2O_{30}$	$C_{28}H_{13}Ag_9F_{21}NO_{17}$	$C_{44}H_{34}Ag_{12}F_{30}N_6O_{27}$	$C_{66}H_{35}Ag_{19}F_{39}N_5O_{33}$
fw	3393.63	2005.22	2943.21	4216.52
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.0752(13)	11.892(2)	11.504(7)	17.0118(16)
b (Å)	30.335(3)	14.616(3)	14.494(8)	17.1524(17)
c (Å)	24.098(3)	14.813(3)	15.198(9)	17.9913(16)
α (deg)	90	107.88(3)	62.249(11)	89.850(2)
β (deg)	98.459(2)	109.19(3)	69.626(11)	79.799(2)
γ (deg)	90	95.85(3)	73.765(12)	88.085(2)
volume (Å^3)	8731.3(16)	2254.5(11)	2081(2)	5163.8(8)
Z	4	2	1	2
D_{calc} (g·cm^{-3})	2.582	2.954	2.348	2.712
$F(000)$	6368	1872	1390	3948
R(int)	0.0635	0.0635	0.0338	0.0431
GOF	1.008	1. 021	0.983	1.055
$R_1[(I > 2\sigma(I)]$	0.0738	0.0661	0.0656	0.0804
$wR_2[(I > 2\sigma(I)]$	0.2130	0.2038	0.1755	0.1720
R_1 (all data)	0.1235	0.0728	0.1106	0.1258
wR_2 (all data)	0.2436	0.2112	0.1987	0.1931
residuals (e Å^{-3})	1.648, −2.216	1.698,−1.076	1.203, −0.885	1.610, −0.937

Table 2. Selected Bond Lengths (Å) for Complexes **1**−**4**[a]

1					
C1≡C2	1.200(2)	C11≡C12	1.231(17)	Ag1−C1	2.104(12)
Ag2−C1#1	2.553(14)	Ag3−C1	2.355(13)	Ag4−C1	2.500(13)
Ag5−C12	2.487(13)	Ag5−C12#2	2.487(13)	Ag6−C12#2	2.133(13)
Ag7−C12#2	2.347(11)	Ag7−C11#2	2.438(11)	Ag1···Ag2	3.118(8)
Ag1···Ag2#1	3.174(9)	Ag1···Ag3	2.782(6)	Ag1···Ag4	3.180(16)
Ag1···Ag6	3.191(14)	Ag2···Ag1#1	2.928(18)	Ag2···Ag3	2.981(8)
Ag5···Ag6#2	2.958(10)	Ag4···Ag5	2.967(4)	Ag4···Ag6	2.848(5)
Ag5···Ag6	2.958(10)	Ag6···Ag7	3.023(5)		
2					
C1≡C2	1.216(15)	C11≡C12	1.228(15)	Ag1−C12	2.080 (11)
Ag2−C1	2.451(10)	Ag2−C2	2.536(10)	Ag2−C12	2.498 (10)
Ag3−C1	2.427(10)	Ag3−C2	2.585(10)	Ag4−C1	2.095(11)
Ag6#1−C11	2.345(10)	Ag6#1−C12	2.412(10)	Ag7−C11	2.959(12)
Ag7−C12	2.374(10)	Ag8−C1	2.297(10)	Ag8−C2	3.090(10)
Ag9−C11	2.988(14)	Ag9−C12	2.751(13)	Ag1···Ag2	2.919(16)
Ag1···Ag7	2.925(15)	Ag1···Ag9	3.315(17)	Ag2···Ag3	3.247(2)
Ag3···Ag4	2.895(16)	Ag4···Ag8	2.734(14)	Ag6#1···Ag1	3.342(19)
Ag6#1···Ag6	3.239(2)	Ag7···Ag8	3.128(2)		
3					
C1≡C2	1.201(14)	Ag1−C1	2.401(11)	Ag1−C2	2.747(16)
Ag2−C1	2.511(10)	Ag2−C2	2.526(11)	Ag3−C1	2.315(11)
Ag3−C2	3.028(1)	Ag4−C1	2.150(10)	Ag5−C1	2.312(10)
Ag1···Ag4	2.947(18)	Ag1···Ag5	3.036(18)	Ag2···Ag3	2.985(19)
Ag2···Ag4	3.059(19)	Ag3···Ag5	2.860(19)	Ag4···Ag5	2.918(2)
4					
C8≡C9	1.223(17)	C14≡C15	1.198(17)	C23≡C24	1.219(17)
C29≡C30	1.198 (9)	Ag1−C9	2.207(14)	Ag2−C9	2.272(13)
Ag2−C8	2.733(14)	Ag3−C9	2.217(12)	Ag4−C8	2.537(13)
Ag4−N1	2.168(17)	Ag4−C9	2.346(13)	Ag5−C12	2.089(12)
Ag5−N2	2.097(12)	Ag6−C15	2.359(13)	Ag7−C15	2.139(13)
Ag8−C15	2.270(13)	Ag8−N5	2.19 (2)	Ag9−C14#2	2.633(13)
Ag9−C15#2	2.467(13)	Ag10−N3	2.19(2)	Ag10−N4	2.15(2)
Ag11−C24	2.227(13)	Ag12−C23	2.725(14)	Ag12−C24	2.375(13)
Ag13−C24	2.288(13)	Ag14−C23	2.711(14)	Ag14−C24	2.308(12)
Ag15−C24	2.923(12)	Ag11#3−C26	2.594(12)	Ag11#3−C27	2.501(12)
Ag12−C27	2.258(12)	Ag15#3−C27	2.175(12)	Ag16−C26	2.794(1)
Ag16−C27	2.299(12)	Ag16−C29	2.886(13)	Ag16−C30	2.428(11)
Ag17−C29	3.081(12)	Ag17−C30	2.260(12)	Ag18−C30	2.184(10)
Ag19−C29	2.783(11)	Ag19−C30	2.625(12)	Ag19#4−C30	2.495(12)
Ag1···Ag4	3.193(17)	Ag1···Ag3	2.835(15)	Ag1···Ag5#1	2.987(16)
Ag2···Ag5	2.862(18)	Ag2···Ag3	3.270(17)	Ag1···Ag2	3.028(16)
Ag6···Ag8	3.377(4)	Ag5···Ag6	3.073(4)	Ag3···Ag4	3.249(18)
Ag7···Ag9#2	3.090(18)	Ag7···Ag9	2.999(2)	Ag6···Ag7	2.896(3)
Ag9···Ag9#2	3.094(3)	Ag9···Ag7#2	3.090(18)	Ag7···Ag8	2.997(2)
Ag11···Ag12	3.053(15)	Ag11···Ag13	2.820(15)	Ag11···Ag14	2.978(15)
Ag11···Ag15	2.848(15)	Ag12···Ag15#3	2.786(17)	Ag12···Ag16	3.056(16)
Ag13···Ag14	3.344(16)	Ag15#3···Ag16	3.067(2)	Ag15#3···Ag11#3	2.848(15)
Ag16···Ag17	3.121(18)	Ag16···Ag18	3.015(16)	Ag17···Ag18	2.823(15)
Ag17···Ag19#4	3.122(17)	Ag18···Ag19#4	3.213(16)	Ag18···Ag19	2.959(15)
Ag19···Ag19#4	3.035(2)				

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, -y + 1/2, -z + 1$; #2 $-x, y, -z + 1/2$ for **1**; #1 $-x, -y, -z$ for **2**; #1 $-x, 1 - y, 1 - z$; #2 $1 - x, 1 - y, 1 - z$; #3 $-x, 2 - y, 2 - z$; #4 $1 - x, 2 - y, 2 - z$ for **4**.

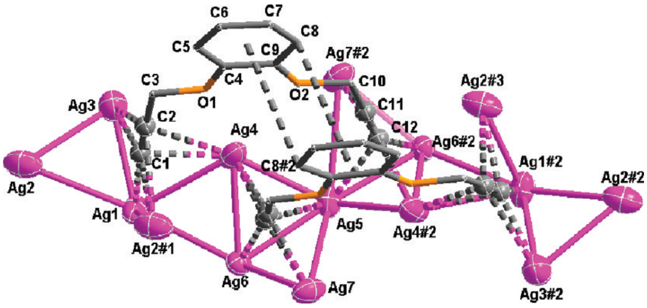


Figure 1. Atom labeling and coordination mode of L1 in **1** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms, acetonitrile molecules, BF_4^- anions, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry code: #1 $-x+1/2, -y+1/2, -z+1$; #2 $-x, y, -z+1/2$; #3 $x-1/2, -y+1/2, z-1/2$. Atom color codes: Ag purple, C gray, O orange.

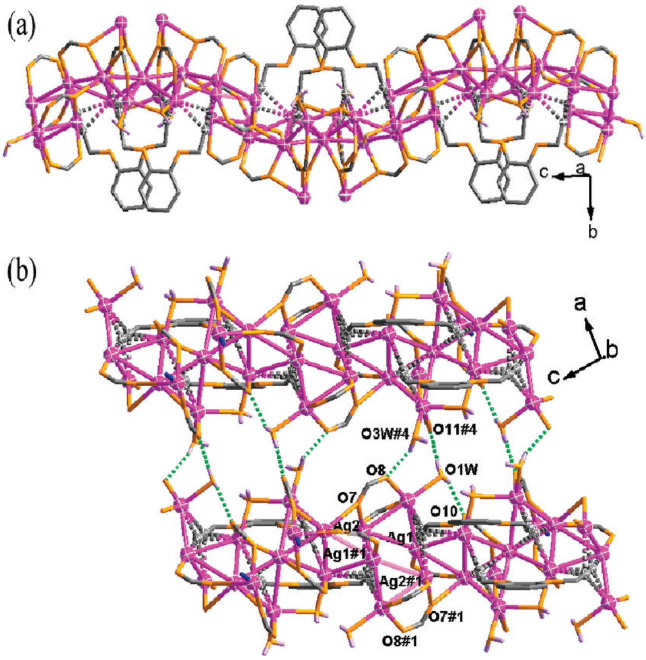


Figure 2. (a) In the crystal structure of **1**, Ag_{15} aggregates are fused by argentophilic interaction Ag1···Ag2#1, Ag2···Ag1#1 (2.928 Å) and bridging trifluoroacetate groups to yield a thick silver rod. (b) The silver rods are further interconnected through interchain hydrogen bonds to give a 2D network. All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry code: #1 $-x+1/2, -y+1/2, -z+1$; #2 $-x, y, -z+1/2$; #3 $x-1/2, -y+1/2, z-1/2$; #4 $x+1, y, z$. Color codes: Ag purple, C gray, O orange.

C11≡C12) are enveloped by a butterfly-shaped Ag_4 basket in the μ_4-$\eta^1,\eta^2,\eta^2,\eta^2$ coordination mode and a square-pyramidal Ag_5 basket in the μ_5-$\eta^1,\eta^1,\eta^2,\eta^2,\eta^2$ mode, respectively. The peripheral Ag5 atom is hitched to the Ag_4 basket by a pair of μ_3-O,O',O' and μ_4-O,O,O',O' trifluoroacetate groups (O13, O13, O14, O14 and O15, O15, O16), while atom Ag6 is attached to the Ag_5 basket by trifluoroacetate groups in μ_3-O,O',O' (O7, O8, O8) and μ_4-O,O,O',O' (O9, O9, O10, O10) modes and argentophilic interaction (Ag6—Ag6#1 3.239 Å). Adjacent Ag_4 and Ag_5 baskets coalesce by sharing one vertex (Ag2) to yield a Ag_8 aggregate. The acetonitrile molecule is attached to silver atom Ag1. The Ag_8 aggregates are further connected by a pair of inversion-related trifluoroacetate groups (O15—O16 and O15#2—O16#2) with the assistance of argentophilic interactions Ag3···Ag4#2, Ag4···Ag3#2 (3.226 Å) to produce a Ag_8—(μ_3-η^1,η^2-$CF_3CO_2)_2$—Ag_8 building unit. Such units are connected by a pair of inversion-related trifluoroacetate groups (O9—O10 and O9#1—O10#1) acting in the μ_4-η^2,η^2 mode, which together with argentophilic interactions (Ag1···Ag6#1 3.342 Å, Ag6···Ag1#1 3.342 Å, Ag6···Ag6#1 3.239 Å) generate a silver column (Figure 4 and Figure S3). As shown in Figure 5a, adjacent silver columns are associated by the external Ag5 atom, a pair of trifluoroacetate groups (O11#1—O12#1 and O11#3—O12#3), and argentophilic interaction Ag9#1···Ag9#3 (3.092 Å), resulting in a two-dimensional (2D) network, and further consolidation is provided by hydrogen bonding (O1W#2···O4#3 2.800 Å, O1W#2···O7 2.932 Å, and O1W#2···F7#3 2.968 Å).[22] Finally, association of layers through face-to-face π—π stacking interactions between adjacent phenyl rings (centroid—centroid distance 3.638 Å) leads to a 3D supramolecular framework (Figure 5b). Moreover, two phenyl carbon atoms (C4 and C9) coordinate to the silver atom Ag2 by the μ-η^2 mode with bond lengths of 3.054 and 2.668 Å, respectively, implying the presence of significant Ag(I)—π interaction.[23]

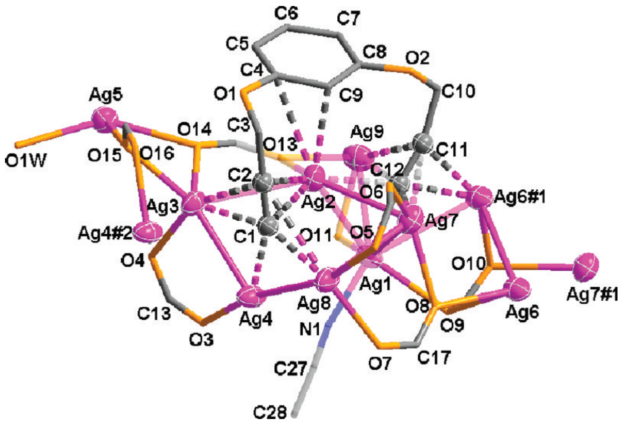


Figure 3. Atom labeling and coordination mode of L2 in **2** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: #1 $-x, -y, -z$; #2 $-x+1, -y+1, -z+1$. Atom color codes: Ag purple, C gray, N blue, O orange.

{[(Ag2L3)·(AgCF3CO2)10·(CH3CN)6·(H2O)2·(OH)2]·(H2O)} (**3**). In the crystal structure of **3**, dianionic ligand L3 located at a center of symmetry takes an *anti* conformation with a C2—C3—O1—C4 torsion angle of 55.19°. As shown in Figure 6, the ethynide group (C1≡C2) is bound to the square-pyramidal Ag_5 basket in the μ_5-$\eta^1,\eta^1,\eta^2,\eta^2,\eta^2$ coordination mode. The Ag6 atom is hitched to the Ag_5 basket through two trifluoroacetate groups (O2—O3 and O4—O5) in the μ_3-η^1,η^2 mode to give an Ag_6 cluster, within which the argentophilic Ag—Ag distances vary from 2.860 to 3.059 Å. As shown in Figure 7a, a novel Ag_6—phenyl ring—Ag_6 structural unit is formed. Such units are connected by a pair of μ_4-η^2,η^2 trifluoroacetate groups (O2—O3 and O2#2—O3#2) to yield an infinite column along the *a* axis, and such columns are further united through hydrogen bonds (O2W···O7#3 2.748 Å) to give a metal—organic layer in the *ab* plane (Figure 7a). Adjacent layers are also associated through hydrogen bonds (C22···O9#4 3.435 Å, C22···O10#4 3.611 Å, C20#1···O9#4 3.441 Å, and C20#1···O10 3.489 Å)[24] to produce a 3D supramolecular network (Figure 7b).

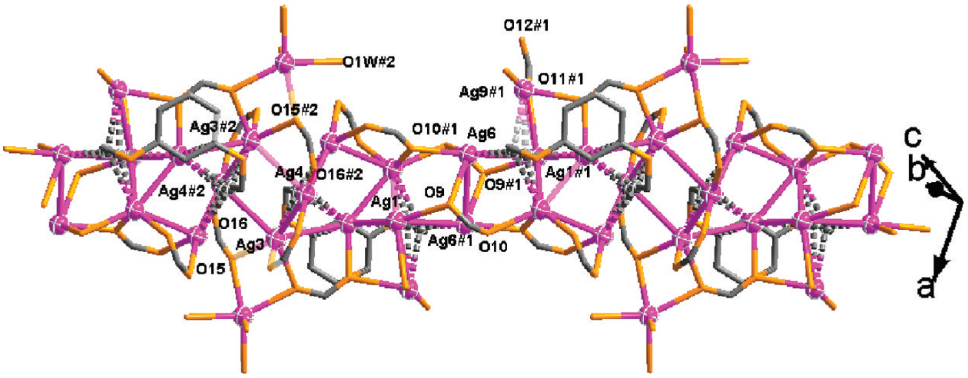


Figure 4. $Ag_7-(\mu_3-\eta^1,\eta^2-CF_3CO_2)_2-Ag_7$ building units in **2** are connected by a pair of inversion-related trifluoroacetate groups (O9—O10 and O9#1—O10#1) acting in the $\mu_3-\eta^1,\eta^2$ mode, together with argentophilic interactions (Ag1···Ag6#1 3.342 Å; Ag6···Ag1#1 3.342 Å; Ag6···Ag6#1 3.239 Å) to generate a thick silver rod. CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: #1 $-x, -y, -z$; #2 $-x+1, -y+1, -z+1$; #3 $x-1, y, z$. Color codes: Ag purple, C gray, O orange.

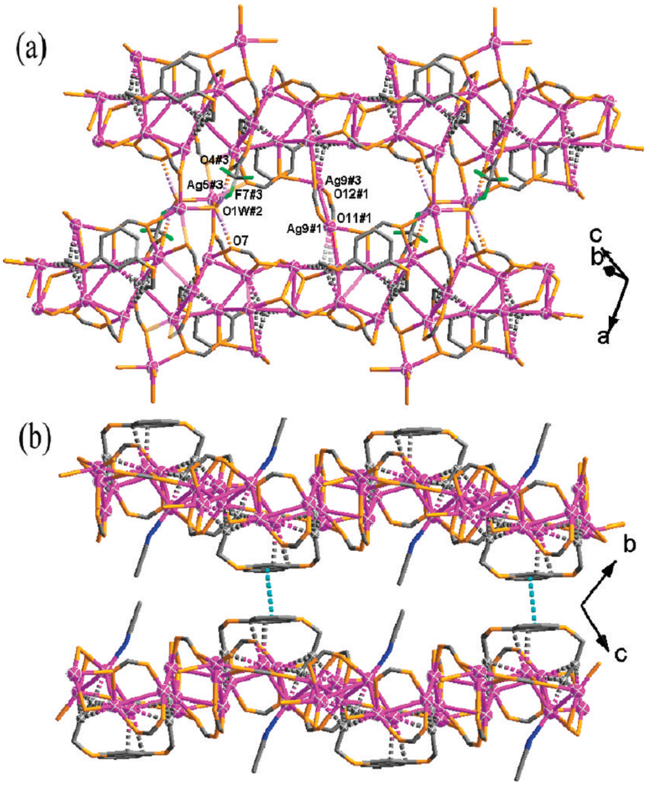


Figure 5. (a) 2D metal—organic network of **2**. (b) 3D network of **2** linked by face-to-face $\pi-\pi$ stacking interactions. All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: #1 $-x, -y, -z$; #2 $-x+1, -y+1, -z+1$; #3 $x-1, y, z$. Color codes: Ag purple, C gray, N blue, O orange.

*[(Ag$_3$L4)$_2$·(AgCF$_3$CO$_2$)$_{13}$·(CH$_3$CN)$_5$·(H$_2$O)] (**4**).* The asymmetric unit of **4** contains 19 crystallographically independent Ag(I) ions, two L4 ligands bearing bunched ethynide groups that exhibit different ligation modes **A** and **B** (Figure 8), 13 trifluoroacetate groups, one aqua ligand, and five acetonitrile ligands (Figure S4). As expected, each ethynide species in L4 is inserted into a Ag_n ($n = 4, 5$) basket. The ethynide groups acting in mode **A** are attached to a Ag_{11} aggregate in the $\mu_4-\eta^1,\eta^1,\eta^2,\eta^2$, $\mu_4-\eta^1,\eta^2,\eta^2,\eta^2$. and $\mu_5-\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ fashion, whereas those functioning in mode **B** coordinate to a Ag_{12} aggregate in the

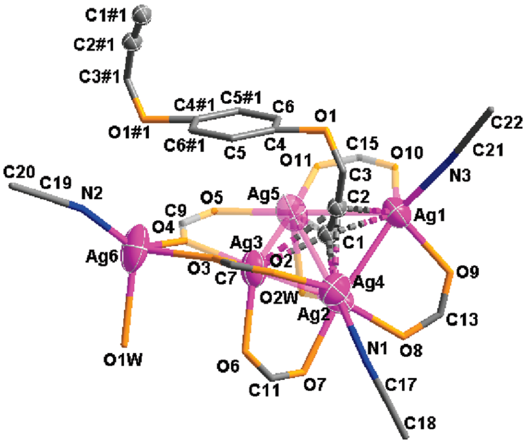


Figure 6. Atom labeling and coordination mode of L3 in **3** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms, free water molecule, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry code: #1 $-x+1, -y+2, -z+1$. Atom color codes: Ag purple, C gray, N blue, O orange.

$\mu_5-\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$, $\mu_4-\eta^1,\eta^1,\eta^2,\eta^2$, and $\mu_5-\eta^1,\eta^1,\eta^2,\eta^2,\eta^2$ manner (Figure 8). Adjacent Ag_{11} aggregates are connected by vertex-sharing to yield a novel Ag_{20} aggregate (Figure 9a), and such aggregates are fused by edge-sharing (Ag9···Ag9#2, 3.094 Å) to form a type **A** thick silver rod (Figure 9c and Figure S5). Similarly, edge-sharing between symmetry-related Ag_{12} aggregates yields a similar Ag_{20} aggregate (Figure 9b), and such aggregates are further associated through sharing of another edge (Ag19···Ag19#4, 3.035 Å) to give a type **B** silver rod (Figure 9d and Figure S6). The two kinds of silver rods in parallel orientation are bridged by three $\mu_3-\eta^1$, η^2 and one $\mu_4-\eta^2,\eta^2$ trifluoroacetate group to generate a two-dimensional metal—organic network parallel to the *ac* plane (Figure 9e and f). The remaining nine trifluoroacetate groups span edges of the Ag_n baskets to stabilize each $[Ag_nC{\equiv}C]^{(n-1)+}$ moiety.

Supramolecular Synthons. In contrast to reported silver ethynediide (Ag_2C_2), silver(I) 1,3-butadiynediide (Ag_2C_4), $R-C{\equiv}C{\supset}Ag_n$ (R = aryl or alkyl; $n = 4, 5$), and $Ag_n{\subset}C{\equiv}C-R-C{\equiv}C{\supset}Ag_n$ (R = *o*-, *m*-, *p*-C_6H_4; $n = 4, 5$) supramolecular synthons, the new $Ag_n{\subset}C{\equiv}CCH_2OC_6H_4OCH_2C{\equiv}C{\supset}Ag_n$ synthon has much longer flexible arms. Although the invariable μ_4- and

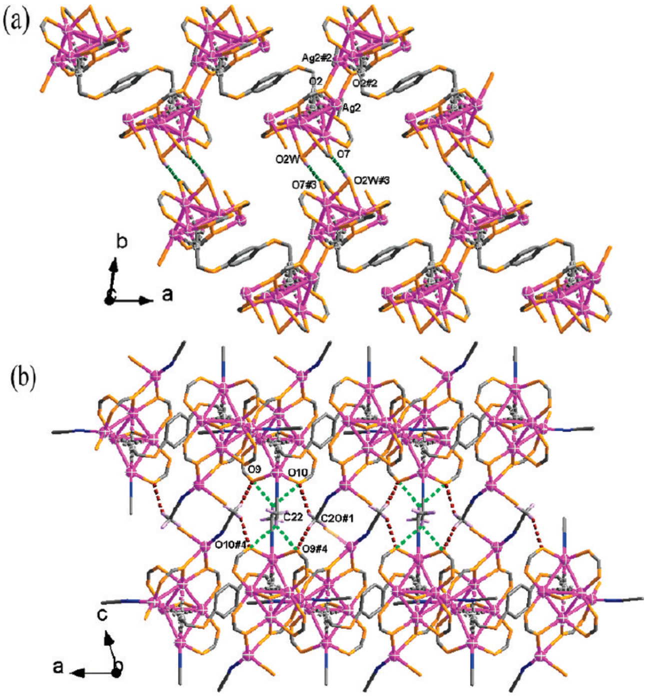


Figure 7. (a) Layer structure of **3**. All hydrogen atoms, acetonitrile molecules, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. (b) 3D network of **3**. All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: #1 $-x + 1, -y + 2, -z + 1$; #2 $-x + 2, -y + 2, -z + 1$; #3 $-x + 2, -y + 1, -z + 1$; #4 $-x + 2, -y + 2, -z$.

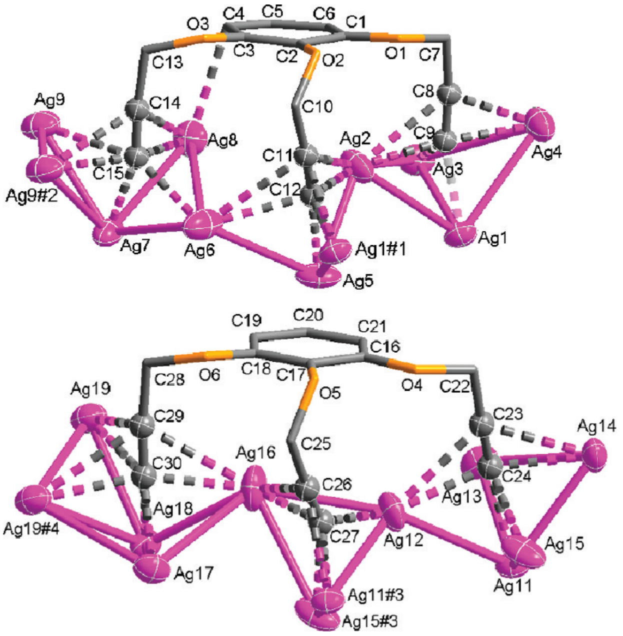


Figure 8. Coordination modes **A** (top) and **B** (bottom) of anionic L4 in Ag_{11} and Ag_{12} aggregates, respectively (50% thermal ellipsoids are drawn for silver atoms). Symmetry codes: #1 $-x, 1 - y, 1 - z$; #2 $1 - x, 1 - y, 1 - z$; #3 $-x, 2 - y, 2 - z$; #4 $1 - x, 2 - y, 2 - z$. Atom color codes: Ag purple, C gray, O orange.

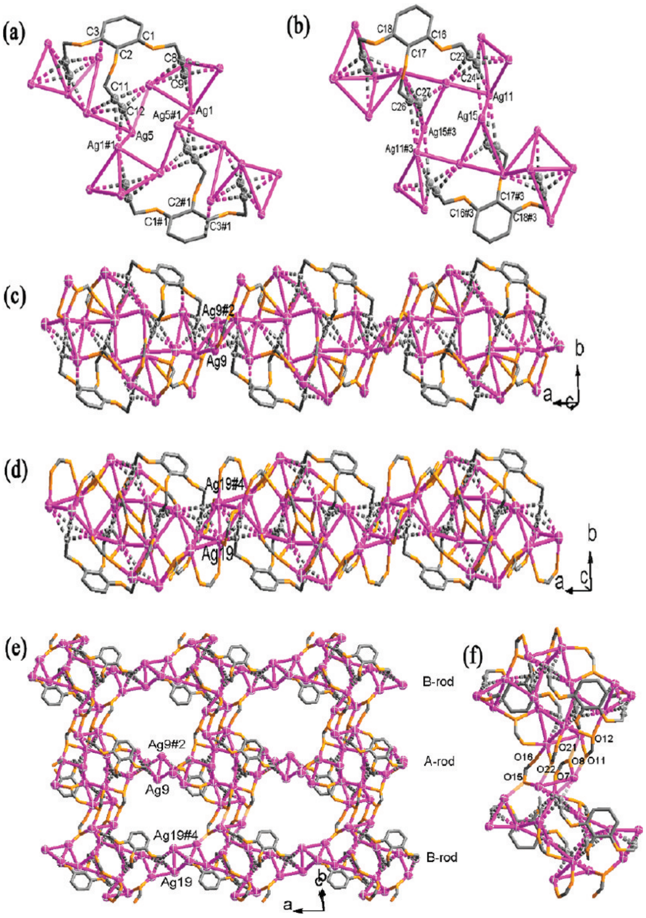
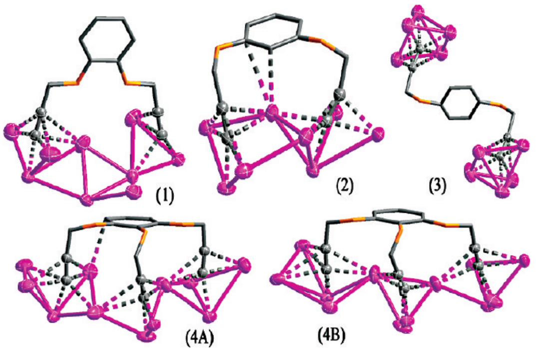


Figure 9. (a) Centrosymmetric Ag_{20} aggregate in **4** built from inversion-related L4 ligands acting in mode **A** sharing vertex silver atoms (Ag1 and Ag1#1) and stabilized by argentophilic interaction (Ag1···Ag5#1, 2.987 Å). (b) Similar Ag_{20} aggregate acting in mode **B** (Ag11···Ag15, 2.848 Å). (c) Ag_{20} aggregates are united through sharing one edge (Ag9···Ag9#2, 3.094 Å) to give a thick silver rod. (d) Ag_{20} aggregates are united through sharing one edge (Ag19···Ag19#4, 3.035 Å) to give a silver rod. (e) Two kinds of silver rods in parallel orientation are bridged by three μ_3-η^1,η^2 and one μ_4-η^2,η^2 trifluoroacetate group to generate a two-dimensional metal−organic network parallel to the *ac* plane. (f) Enlargement to show the interchain linkage through three μ_3-η^1,η^2 (O7−O8, O15−O16, and O21−O22) and one μ_4-η^2,η^2 (O11−O12) trifluoroacetate group. Acetonitrile molecules and other $CF_3CO_2^-$ groups are omitted for clarity. Symmetry codes: #1 $-x, 1 - y, 1 - z$; #2 $1 - x, 1 - y, 1 - z$; #3 $- x, 2 - y, 2 - z$; #4 $1 - x, 2 - y, 2 - z$. Atom color codes: Ag purple, C gray, O orange.

μ_5-ligation modes of the ethynide moiety appear in both the previously studied $Ag_n \subset C_2{-}C_6H_4{-}C_2 \supset Ag_n$ (n = 4, 5)[14] and present $Ag_n \subset C{\equiv}CCH_2OC_6H_4OCH_2C{\equiv}C \supset Ag_n$ (n = 4, 5) multinuclear supramolecular synthons in coordination network assembly, they give rise to very different crystal structures. No silver(I)−aromatic interaction was found in silver complexes constructed with the $Ag_n \subset C_2{-}C_6H_4{-}C_2 \supset Ag_n$ (n = 4, 5) supramolecular synthon, whereas the propargyl-functionalized di- and trihydroxybenzenes employed in the present work offer a good opportunity to introduce silver(I)−aromatic interactions in the construction of coordination networks of variable dimensions. In the crystal structure of **4**, the fully deprotonated 1,2,3-tris(prop-2-ynyloxy)benzene ligand exhibits the highest Ag_{20} aggregation reported to date for a silver(I)-ethynide metal−organic framework, which may be attributed to the presence of three neighboring pendant arms bearing terminal ethynide groups.

Scheme 2. Coordination Modes Observed for L1 (in 1), L2 (in 2), L3 (in 3), and L4 (in 4)



■ CONCLUSION

In summary, the present study has established that ethynide moieties of the flexible multifunctional ligands L1−L4 can adopt μ_4- and μ_5-ligation modes upon bonding to silver(I) centers, and the new metallo-ligand supramolecular synthon Ag_n−L−Ag_n (n = 4, 5) may be utilized for the construction of metal−organic networks (Scheme 2). In addition, a thick silver rod has been shown to exist in silver(I)-ethynide compounds **1**, **2**, and **4**. The interplay of silver−ethynide bonding, argentophilicity, and weak intermolecular interactions such as hydrogen bonding, silver−aromatic, and π−π interactions in these complexes has been shown to play a vital role in the formation and stabilization of supramolecular aggregates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic files (CIF) and diagrams of the structures of complexes **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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