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Article

Assembly of Silver(I)−Organic Networks from Flexible Supramolecular Synthons with Pendant Ethynide Arms Attached to a Naphthyl Skeleton

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Five new ligands bearing terminal ethynide moieties attached *via* pendant arms to a naphthyl skeleton have been used in the synthesis of eight silver(I) complexes. In these compounds, the invariable appearance of the μ_4 and μ_5 ligation modes of the ethynide moiety reaffirms the general utility of the silver−ethynide supramolecular synthons $R-C\equiv C\supset Ag_n$ and $Ag_n\subset C\equiv C-R-C\equiv C\supset Ag_n$ ($n = 4, 5$) in coordination network assembly, even when the R group is conformationally flexible. Besides the silver−ethynyl and silver−aromatic interactions, several unconventional intermolecular interactions (argentophilicity, anion−π, C−H$\cdots\pi$, and C≡N$\cdots\pi$) also make their appearance.

Introduction

The recent upsurge in crystal engineering of metal−organic frameworks is prompted by the discovery of interesting topologies and crystal packing motifs, as well as by their potential application as functional materials.[1–3] The design of supramolecular synthons with multicenter binding sites for constructing new kinds of nonclassical metal−organic frameworks (MOFs) poses an interesting challenge.[4]

Compared to the assembly of supramolecular architectures with metal−ligand coordination bonds, designed engineering of organometallic networks is much less developed.[5] Recently, metal−ethynide complexes have attracted much interest owing to their structural diversity[4,6,7] and potential 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 acetylenediide (Ag_2C_2),[11] we have conducted systematic studies on various complexes containing silver(I) 1,3-butadiynediide (Ag_2C_4).[12] Furthermore, by utilizing new metal−ligand supramolecular synthons of the types $R-C\equiv C\supset Ag_n$ (R = aryl or alkyl; $n = 4, 5$)[13] and $Ag_n\subset C\equiv C-R-C\equiv C\supset Ag_n$ (R = *p*-, *m*-, *o*-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 and π) interactions.

The π-electron system of polycyclic aromatic hydrocarbons (PAHs) is known to be capable of bonding to metal ions. The exploitation of such cation−π interactions provides a potentially fruitful approach to building novel molecular architectures that may exhibit a wide variety of useful electrical and electrochemical properties.[4a,16–19] For instance,

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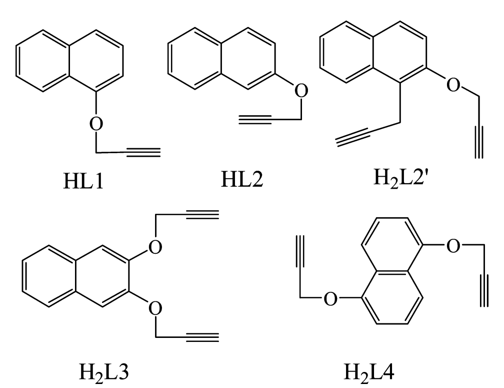
the co-deposition of volatile metal complexes with PAHs in a solvent-free environment allowed Petrukhina's group to effectively utilize directional metal$-\pi-$arene interactions in the formation of novel crystalline organometallic products, especially in the construction of extended networks.[18] A number of organosilver(I) complexes of PAHs with remarkable features such as W-type sandwiches; helical structures; and double-, triple-, and multidecker frameworks have also been obtained by Munakata's group.[19] Enlightened by such exploits, our conceived idea is to attach pendant arms bearing terminal ethynide moieties to a naphthyl skeleton for the construction of MOFs consolidated by both silver(I)−ethynyl binding[11–14] and silver(I)−aromatic[16–19] interactions.

Scheme 1



In this paper, we report synthetic and structural studies of a series of eight silver(I) complexes of naphthalene-based ligands with one or two flexible substitutents bearing terminal ethynide groups at variable positions on the aromatic ring: $[\mathrm{AgL1}\cdot(\mathrm{AgCF_3CO_2})_5\cdot(\mathrm{H_2O})_2]$ (**1**), $[\mathrm{AgL1}\cdot(\mathrm{AgCF_3CO_2})_7\cdot(\mathrm{H_2O})_3\cdot(\mathrm{CH_3CN})]$ (**2**), $[\mathrm{AgL2}\cdot(\mathrm{AgCF_3CO_2})_6\cdot(\mathrm{H_2O})_{3.25}]$ (**3**), $[\mathrm{Ag_2L2'}\cdot(\mathrm{AgCF_3CO_2})_7\cdot(\mathrm{H_2O})_4]\cdot(\mathrm{H_2O})_{1.5}$ (**4**), $[\mathrm{Ag_2L3}\cdot(\mathrm{AgCF_3CO_2})_8\cdot(\mathrm{H_2O})_3]\cdot\mathrm{H_2O}$ (**5**), $[\mathrm{Ag_2L3}\cdot(\mathrm{AgCF_3CO_2})_5\cdot(\mathrm{CH_3CN})_5]$ (**6**), $[\mathrm{AgL4_{0.5}}\cdot(\mathrm{AgCF_3CO_2})_6\cdot(\mathrm{H_2O})_2\cdot(\mathrm{CH_3CN})]$ (**7**), and $[\mathrm{Ag(L4)_{0.5}}\cdot(\mathrm{AgCF_3CO_2})_5\cdot(\mathrm{H_2O})_3]$ (**8**) (HL1 = 1-prop-2-ynyloxy-naphthalene, HL2 = 2-prop-2-ynyloxy-naphthalene, H$_2$L2′ = 1-prop-2-ynyl-2-prop-2-ynyloxy-naphthalene, H$_2$L3 = 2,3-bis-prop-2-ynyloxy-naphthalene, H$_2$L4 = 1,5-bis-prop-2-ynyloxy-naphthalene) (Scheme 1). On the basis of our previous experience, the reaction of crude starting materials $[\mathrm{AgL1}]_n$ (**9**), $[\mathrm{AgL2}]_n$ (**10**), $[\mathrm{Ag_2L3}]_n$ (**11**), and $[\mathrm{Ag_2L4}]_n$ (**12**) with water-soluble silver salts is expected to generate MOFs stabilized by silver(I)−ethynyl and argentophilic interactions, and the naphthyl ring is potentially capable of partaking in $\pi-\pi$ and silver−aromatic interactions.

Results and Discussion

Syntheses. The neutral ligands HL1, HL2, H$_2$L3, and H$_2$L4 (Scheme 1) were synthesized from the respective reactions

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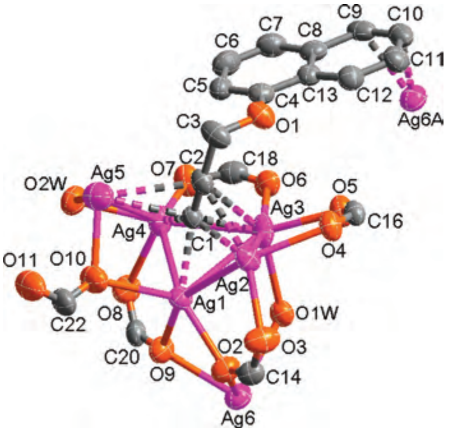

Figure 1. Atom labeling and coordination mode of L1 in **1** (50% thermal ellipsoids). All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.201, Ag1−C1 2.213, Ag2−C1 2.416, Ag2−C2 2.538, Ag3−C1 2.341, Ag3−C2 2.916, Ag4−C1 2.278, Ag5−C1 2.677, Ag5−C2 2.806, Ag6A−C9 2.417, Ag6A−C10 2.408, Ag1···Ag2 2.825, Ag1···Ag3 3.010, Ag1···Ag4 2.777, Ag2···Ag3 3.011, Ag3···Ag4 2.873, Ag4···Ag5 3.335. Symmetry code: A 1 − *x*, 1 − *y*, 1 − *z*.

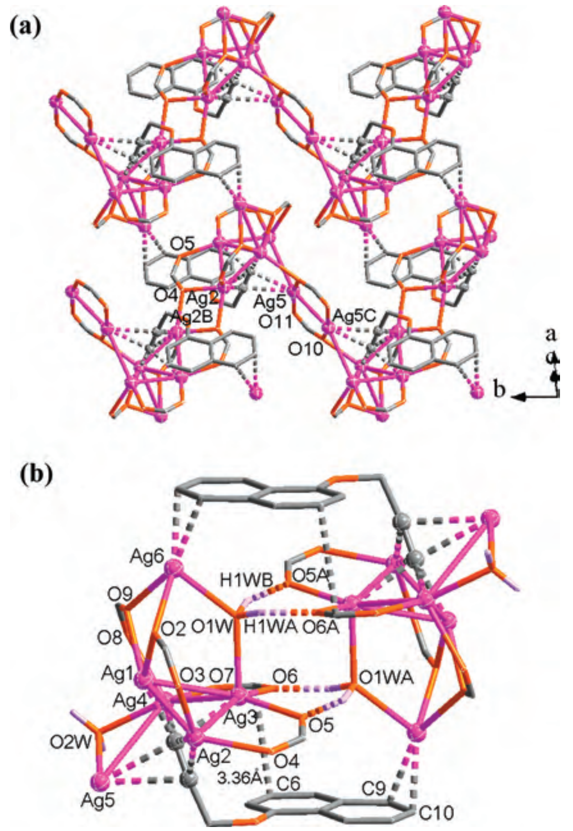

Figure 2. (a) In the crystal structure of **1**, Ag_5 baskets are fused together through two independent trifluoroacetate groups (O4−O5 and O10−O11) to form an infinite zigzag silver(I) chain along the *b* axis, and interchain silver(I)−aromatic interaction gives a 2D network. (b) Silver(I)−organic cycle formed *via* silver(I)−aromatic interactions. This cycle is stabilized by the formation of hydrogen bonding and anion−π interactions. All irrespective hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: A 1 − *x*, 1 − *y*, 1 − *z*; B −*x*, 1 − *y*, 1 − *z*; C −*x*, − *y*, 1 − *z*.

between 1-naphthol, 2-naphthol, 2,3-dihydroxynaphthalene, or 1,5-dihydroxynaphthalene and propargyl bromide in acetone in the presence of K_2CO_3. Double salts **1**−**8** were obtained from crystallization of the corresponding crude polymeric compounds $[AgL1]_n$ (**9**), $[AgL2]_n$ (**10**), $[Ag_2L3]_n$ (**11**), and $[Ag_2L4]_n$ (**12**) in a concentrated aqueous or water/acetonitrile solution of $AgCF_3CO_2/AgBF_4$. $AgCF_3CO_2$ and $AgBF_4$ were used to provide the auxiliary $CF_3CO_2^-$ ligand and increase the silver(I) ion concentration, respectively.[11b] Compounds **1**−**3** and **5**−**8** were obtained at lower temperatures (−10 °C), whereas **4** was unexpectedly obtained as a minor product involving synchronous ligand transformation from L2 to L2′ at room temperature.

The high concentration of silver ions and their aggregation through argentophilicity[11–15,20] ensure that the ethynide moiety achieves a high ligation number of 4 or 5 within a butterfly-shaped Ag_4 or square-pyramidal Ag_5 basket, as opposed to most transition-metal alkyl and aryl ethynide complexes with ligation numbers ranging from 1 to 4,[6–10] and such baskets are mutually connected by sharing a vertex or edge and/or are connected by bridging trifluoroacetate ligands to yield higher-dimensional metal−organic frameworks.

Crystal Structures. $[AgL1\cdot(AgCF_3CO_2)_5\cdot(H_2O)_2]$ (1). In the crystal structure of **1**, anionic ligand L1 adopts a nonplanar conformation, in which the C3 and O1 atoms nearly lie in the plane of the naphthyl ring, and the torsion angle C4−O1−C3−C2 is 73.81°. As shown in Figure 1, the ethynide group (C1≡C2) is bound to a square-pyramidal Ag_5 basket in an unprecedented μ_5-$\eta^1,\eta^1,\eta^2,\eta^2,\eta^2$ coordination mode, which differs from the μ_5-η^1, μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ and μ_5-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ modes reported previously.[12,13]

With two inversion centers located at the center of the Ag2···Ag2B and Ag5···Ag5C (2.961 Å), the Ag_5 baskets are linked together through two types of μ_3-*O*,*O*′,*O*′ trifluoroacetate groups (O4−O5 and O10−O11) to generate an infinite zigzag silver(I) chain along the *b* axis (Figure 2a). As shown in Figures 1 and 2, one trifluoroacetate group (O6−O7) bridges one Ag3···Ag4 edge of the basket by the μ_2-*O*,*O*′ mode. The two other remaining μ_3-*O*,*O*′,*O*′ trifluoroacetate groups (O8−O9 and O3−O2) are both bonded to three silver atoms (Ag4, Ag1, Ag6; Ag2, Ag1, Ag6), and the two independent bridging water molecules (OW1 and OW2) each coordinate to two silver atoms (Ag3, Ag6; Ag4, Ag5). Notably, silver atom Ag6A from the neighboring chain is coordinated by two carbon atoms (C9 and C10) of the naphthyl ring by the η^2 mode with Ag−C bond lengths of 2.407 and 2.417 Å, respectively. The Ag6 atom is bonded simultaneously to the C9A and C10A atoms to form a silver−organic cycle with an inversion center between Ag3 and Ag3A (Figure 2b). This cycle is stabilized by the formation of hydrogen bonds O1W−H1WB···O5A (H1WB−O5A 1.832 Å) and O1W−HW1A···O6A (H1WA−O6A 1.846 Å). The intracycle distance between C18 and C6 is about 3.36 Å, being shorter than the sum of van der Waals radii (3.4 Å) of two carbon atoms,[21] which implies significant anion−π interaction.[22] Though intermolecular interaction

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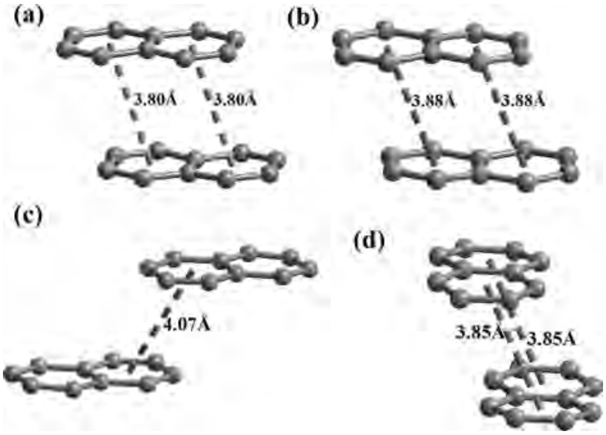
Scheme 2. $\pi-\pi$ Stacking between Naphthyl Rings in Adjacent Sheets in **1**−**4**



between electron-deficient (π-acidic) aromatic rings and anionic species has become a rapidly expanding area of supramolecular chemistry owing to its relevance to anion recognition and transport with medicinal and environmental applications,[23,24] it has not been found for an anionic organic ligand interacting with a nearly neutral naphthyl ring. In compound **1**, it may be rationalized that the π-electron density of the ring is polarized upon bonding to a positively charged silver(I) ion. The formation of the above-mentioned silver−organic cycle links the zigzag silver(I) chains to give a 2D metal−organic network parallel to the *ab* plane (Figure 2a).

Such layers are associated together through offset, face-to-face $\pi-\pi$ stacking interactions (intercentroid distance 3.80 Å) between adjacent naphthyl rings to give a 3D supramolecular structure (Scheme 2a). It is noted that a coexistence of cation(Ag^{I})−π, anion−π, and $\pi-\pi$ interactions in **1** has not been observed for the reported organosilver(I) complexes. Recent calculation has made it clear that very favorable interaction energies, short equilibrium distances, and strong synergic effects can be achieved when different noncovalent interactions (cation−π, anion−π, and/or $\pi-\pi$) coexist in the same system.[25]

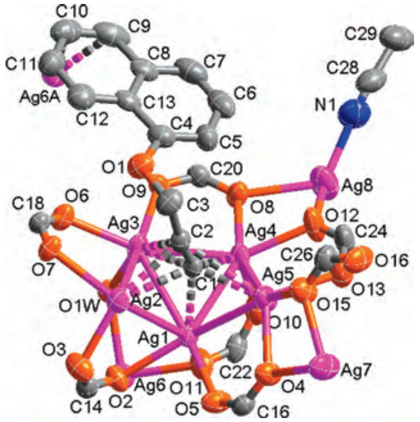


Figure 3. Atom labeling and coordination mode of L1 in **2** (50% thermal ellipsoids). All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.204, Ag1−C1 2.225, Ag2−C1 2.461, Ag2−C2 2.436, Ag3−C1 2.386, Ag3−C2 2.902, Ag4−C1 2.271, Ag5−C1 2.354, Ag5−C2 2.894, Ag6A−C9 2.507, Ag6A−C10 2.430, Ag1⋯Ag2 2.873, Ag1⋯Ag3 2.950, Ag1⋯Ag4 2.803, Ag1⋯Ag5 3.006, Ag2⋯Ag3 2.984, Ag3⋯Ag4 2.887, Ag4⋯Ag5 2.930. Symmetry code: A 1 − *x*, 1 − *y*, 1 − *z*.

[AgL1·$(AgCF_3CO_2)_7$·$(H_2O)_3$·(CH_3CN)] (2). In order to investigate the effect of solvent on the coordination environment of the ethynide, we obtained complex **2** from the crystallization of $[AgL1]_n$ (**8**) in a mixed water−acetonitrile solution of $AgCF_3CO_2$, instead of an aqueous solution of $AgCF_3CO_2$ as in complex **1**. In the crystal structure of **2**, anionic ligand L1 also adopts a nonplanar conformation, in which the C3 and O1 atoms are nearly coplanar with the naphthyl ring, and the torsion angle C4−O1−C3−C2 is −72.21°. As shown in Figure 3, the ethynide group (C1≡C2) is bound to a square-pyramidal Ag_5 basket in the μ_5-$\eta^1,\eta^1,\eta^2,\eta^2,\eta^2$ coordination mode. Two peripheral silver(I) atoms (Ag7 and Ag8) are hitched to the Ag_5 basket by both μ_3-η^1,η^2-$CF_3CO_2^-$ groups (O4,O4,O5 and O15,O16,O16 for Ag7; O8,O9,O9 and O12,O12,O13 for Ag8). The linkage of two square-pyramidal Ag_5 baskets by a pair of inversion-related trifluoroacetate groups (O6−O7 and O6B−O7B) produces a Ag_5−(μ_3-η^1,η^2-CF_3CO_2)$_2$−Ag_5 building unit, and such units and [Ag_2(μ_2-CF_3CO_2)$_2$] (Ag7⋯Ag7C, 2.910 Å) moieties are connected by two types of μ_3-*O*,*O′*,*O′* trifluoroacetate groups (O4−O5 and O15−O16) to generate an infinite zigzag chain along the *c* direction (Figure 4a). The remaining two μ_3-*O*,*O′*,*O′* trifluoroacetate groups (O2−O3 and O10−O11) each bridge one edge of the Ag_5 basket to stabilize the $[Ag_5C1{\equiv}C2]^{4+}$ moiety, with both the acetonitrile and water (O2W) ligands coordinated to the Ag8 atom.

As found in **1**, silver atom Ag6A from a neighboring chain coordinates to two carbon atoms (C9 and C10) of the η^2-naphthyl ring with bond lengths of 2.507 and 2.430 Å, respectively. The Ag6 atom is bonded simultaneously to C9A and C10A to form a centrosymmetric silver−organic cycle, which is also stabilized by the formation of hydrogen bonds OW1−H1WB⋯O6 (H1WB−O6A 1.907 Å) and O1W−H1WA⋯O9 (H1WA−O9 1.762 Å) (Figure 4b). Within this cycle, the distance between C20 (C20A) and C6 (C6A) is about 3.4 Å, implying the possibility of significant anion−π interactions. The formation of the silver−organic cycles links the zigzag silver(I) chains to give 2D grid networks in the *ac* plane (Figure 4a and b), and such networks are united together through off-set face-to-face $\pi-\pi$ interactions (intercentroid distance 3.88 Å) between adjacent naphthyl rings to give a 3D supramolecular structure (Scheme 2b).

[AgL2·$(AgCF_3CO_2)_6$·$(H_2O)_{3.25}$] (3). In the crystal structure of **3**, anionic ligand L2 also adopts a nonplanar

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(22) (a) Black, C. A.; Hanton, L. R.; Spicer, M. D. *Inorg. Chem.* **2007**, *46*, 3669–3679. (b) Yang, X.; Wu, D.; Ranford, J. D.; Vittal, J. J. *Cryst. Growth Des.* **2005**, *5*, 41–43. (c) Zhou, X.-P.; Zhang, X.-J.; Lin, S.-H.; Li, D. *Cryst. Growth Des.* **2007**, *7*, 485–487.

(23) (a) Quiñonero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3389–3392. (b) Alkorta, I.; Rozas, I.; Elguero, J. *J. Am. Chem. Soc.* **2002**, *124*, 8593–8598. (c) Mascal, M.; Armstrong, A.; Bartberger, M. *J. Am. Chem. Soc.* **2002**, *124*, 6274–6276. (d) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210–1250.

(24) (a) Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. *Acc. Chem. Res.* **2007**, *40*, 435–444. (b) Schottel, B. L.; Chifotides, H. T.; Dunbar, K. R. *Chem. Soc. Rev.* **2008**, *37*, 68–83.

(25) Quiñonero, D.; Frontera, A.; Garau, C.; Ballester, P.; Costa, A.; Deyà, P. M. *ChemPhysChem* **2006**, *7*, 2487–2491.

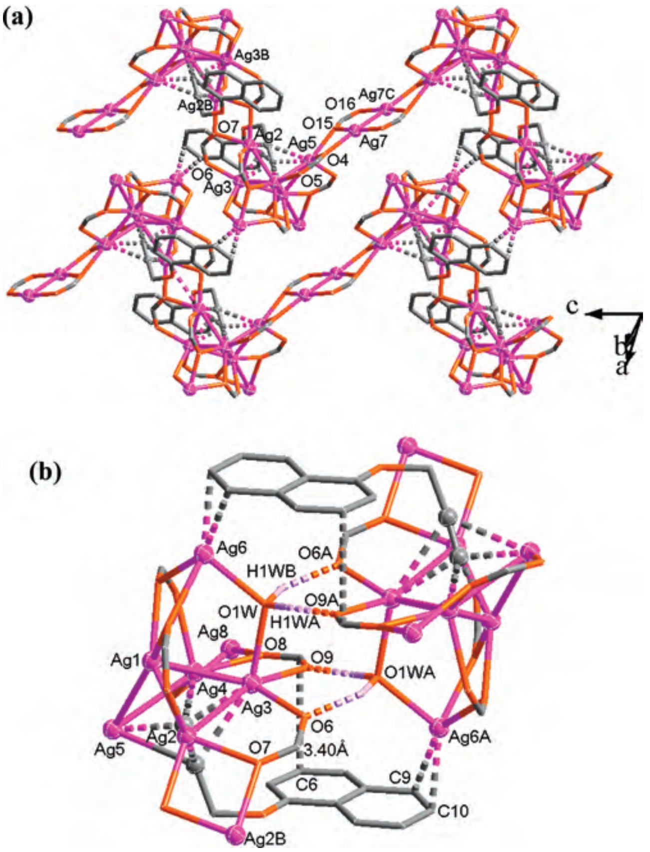

Figure 4. (a) $Ag_5-(\mu_3-\eta^1,\eta^2-CF_3CO_2)_2-Ag_5$ and $[Ag_2(\mu_2-CF_3CO_2)_2]$ building units in **2** associated together through two types of trifluoroacetate groups (O4−O5 and O15−O16) to give a zigzag chain. These are further fused together through silver(I)−aromatic interaction and hydrogen bonding to give a 2D metal−organic network. (b) Silver(I)−organic cycle formed *via* silver(I)−aromatic interactions stabilized by the formation of hydrogen bonds and anion−-π interactions. All irrespective hydrogen atoms, acetonitrile, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: A 1 − *x*, 1 − *y*, 1 − *z*; B −*x*, 1 − *y*, 1 − *z*; C −*x*, 1 − *y*, −*z*.

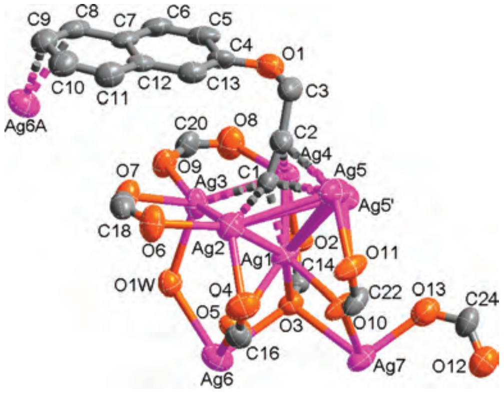

Figure 5. Atom labeling and coordination mode of L2 in **3** (50% thermal ellipsoids). All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.203, Ag1−C1 2.203, Ag2−C1 2.266, Ag3−C1 2.333, Ag4−C1 2.475, Ag4−C2 2.585, Ag5−C1 2.397, Ag5−C2 2.523, Ag5′−C1 2.274, Ag5′−C2 2.423, Ag6A−C8 2.560, Ag6A−C9 2.375, Ag1⋯Ag2 2.807, Ag1⋯Ag3 2.920, Ag1⋯Ag4 2.877, Ag1⋯Ag5 3.080, Ag1⋯Ag5′ 2.681, Ag2⋯Ag3 2.857, Ag2⋯Ag5 3.091, Ag3⋯Ag4 2.973. Symmetry code: A 1 − *x*, 1 − *y*, 1 − *z*.

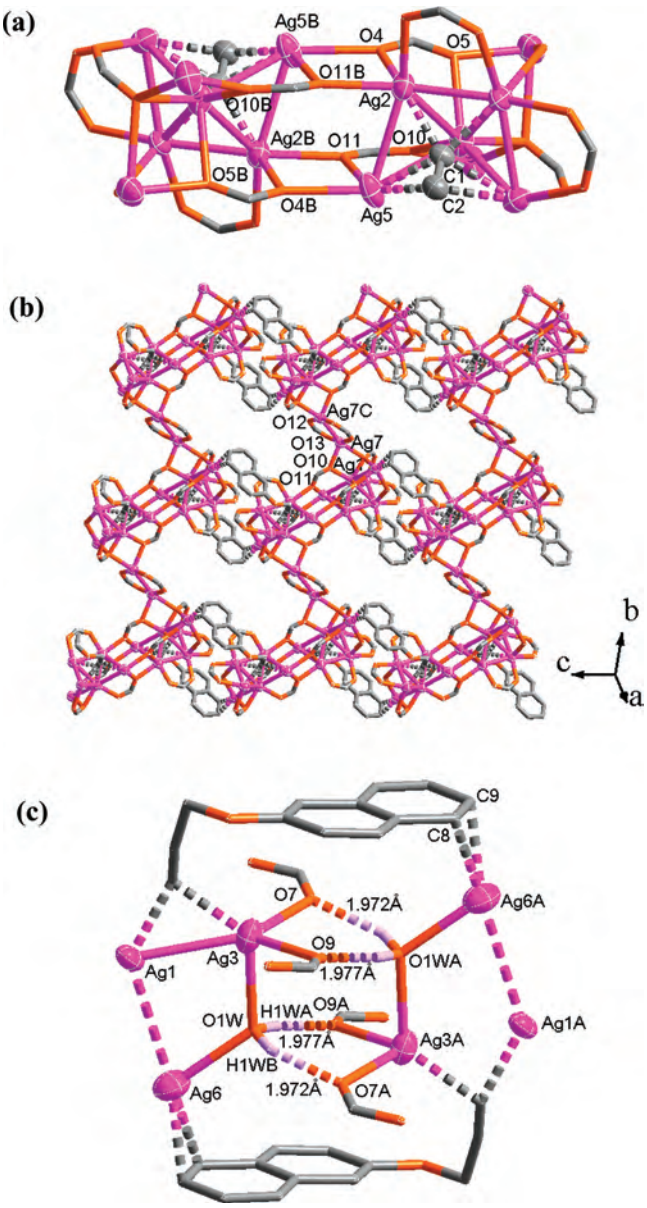

Figure 6. (a) $Ag_5-(\mu_4-\eta^2,\eta^2-CF_3CO_2)_4-Ag_5$ building unit in **3**. (b) 2D metal−organic network of **3**. (c) The metal−organic cycle formed *via* silver(I)−aromatic interactions. This cycle is stabilized by the formation of hydrogen bonds. All irrespective hydrogen atoms, acetonitrile, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: A 1 − *x*, 1 − *y*, − *z*; B 1 − *x*, 1 − *y*, 1 − *z*; C 1 − *x*, 2 − *y*, 1 − *z*.

conformation, in which the C3 and O1 atoms are nearly coplanar with the naphthyl ring, and the torsion angle C4−O1−C3−C2 is 74.24°. As shown in Figure 5, the ethynide group (C1≡C2) is bound to a square-pyramidal Ag_5 basket in the $\mu_5-\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode. The Ag6 atom is attached to the Ag_5 basket by two trifluoroacetate groups (O2−O3 and O4−O5) in the $\mu_4-\eta^1,\eta^3$ and $\mu_3-\eta^1,\eta^2$ modes and the bridging water ligand (O1W). Each of the remaining two trifluoroacetate groups (O6−O7 and O8−O9) in **3** similarly spans a Ag⋯Ag edge by the μ_2-*O*,*O*′ mode. The linkage of two square-pyramidal Ag_5 baskets by two pairs of inversion-related trifluoroacetate groups (O4−O5, O10B−O11B, O4B−O5B, and O10−O11) produces a $Ag_5-(\mu_4-\eta^2,\eta^2-CF_3CO_2)_4-Ag_5$ building unit (Figure 6a).

As shown in Figure 6b, $Ag_5-(\mu_4-\eta^2,\eta^2-CF_3CO_2)_4-Ag_5$ building units are further united together through $[Ag_2(\mu_4-CF_3CO_2)_2]$ (Ag7⋯Ag7C 2.906 Å) linkers to yield a zagzig chain along the *b* axis. Adjacent chains are joined together through silver(I)−aromatic interactions (Ag−C8, 2.560 Å; Ag−C9, 2.376 Å) and hydrogen bonds to form a 2D grid

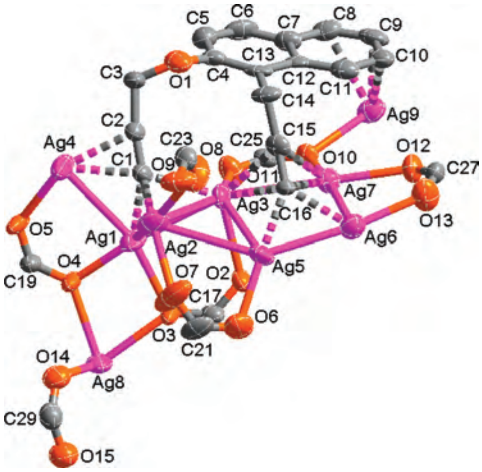

Figure 7. Atom labeling and coordination mode of L2′ in **4** (50% thermal ellipsoids). All hydrogen atoms, CF_3 moieties of $CF_3CO_2^-$, and water molecules are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.224, C15≡C16 1.217, Ag1−C1 2.177, Ag2−C1 2.194, Ag3−C1 2.3383, Ag3−C16 2.453, Ag3−C15 2.637, Ag4−C1 2.372, Ag4−C2 2.396, Ag5−C16 2.094, Ag6−C16 2.257, Ag7−C16 2.394, Ag7−C15 2.615, Ag9−C8 2.740, Ag9−C9 2.411, Ag9−C10 2.877, Ag1···Ag2 2.841, Ag1···Ag3 2.848, Ag1···Ag4 2.921, Ag2···Ag3 2.990, Ag2···Ag5 3.219, Ag3···Ag5 2.947, Ag3···Ag7 3.100, Ag5···Ag6 2.712, Ag6···Ag7 2.938.

network (Figure 6c and b). The shortest C···C distance between the trifluoroacetate group and naphthyl ring is about 3.43 Å, indicating negligible anion−π interaction. Such layers are also united together through offset face-to-face π−π stacking interactions (intercentroid distance 4.07 Å) between adjacent naphthyl rings to give a 3D supramolecular structure (Scheme 2c).

$[Ag_2L2'\cdot(AgCF_3CO_2)_7\cdot(H_2O)_4]\cdot(H_2O)_{1.5}$ (4). Complex **4** was obtained by crystallization at room temperature, which unexpectedly resulted in ligand transformation from monoanionic L2 to dianionic L2′. In complex **4**, ethynide C1≡C2 is grasped by a butterfly-shaped Ag_4 (Ag1, Ag2, Ag3, and Ag4) basket, whereas the other ethynide C15≡C16 is bound to a nearly planar Ag_4 (Ag3, Ag5, Ag6, and Ag7) square. As shown in Figure 7, these two kinds of $C_2\supset Ag_4$ synthons share one silver atom (Ag3) and interact through argentophilic interaction (Ag2···Ag5 3.21 Å) to yield a Ag_7 aggregate.

Two pairs of inversion-related trifluoroacetate groups (O6−O7, O8−O9, O6A−O7A, O8A−O9A) are utilized to bridge two adjacent Ag_7 aggregates to yield a $Ag_7-(CF_3CO_2)_4-Ag_7$ building unit (Figure 8a). Linkage of such $Ag_7-(CF_3CO_2)_4-Ag_7$ units by bridging unit [(Ag8−Ag8B)(O14−O15)$_2$] through two μ_3-η^1,η^2-CF_3CO_2 groups (O2−O3 and O4−O5) thus generates a coordination column along the *c* axis (Figure 8b). Notably, as shown in Figures 7 and 8c, the silver atom Ag9 coordinates to three carbon atoms (C8, C9, and C10) of a naphthyl ring from an adjacent coordination column by an unusual η^3 mode[26] with Ag−C bond lengths of 2.740, 2.411, and 2.877 Å, respectively.

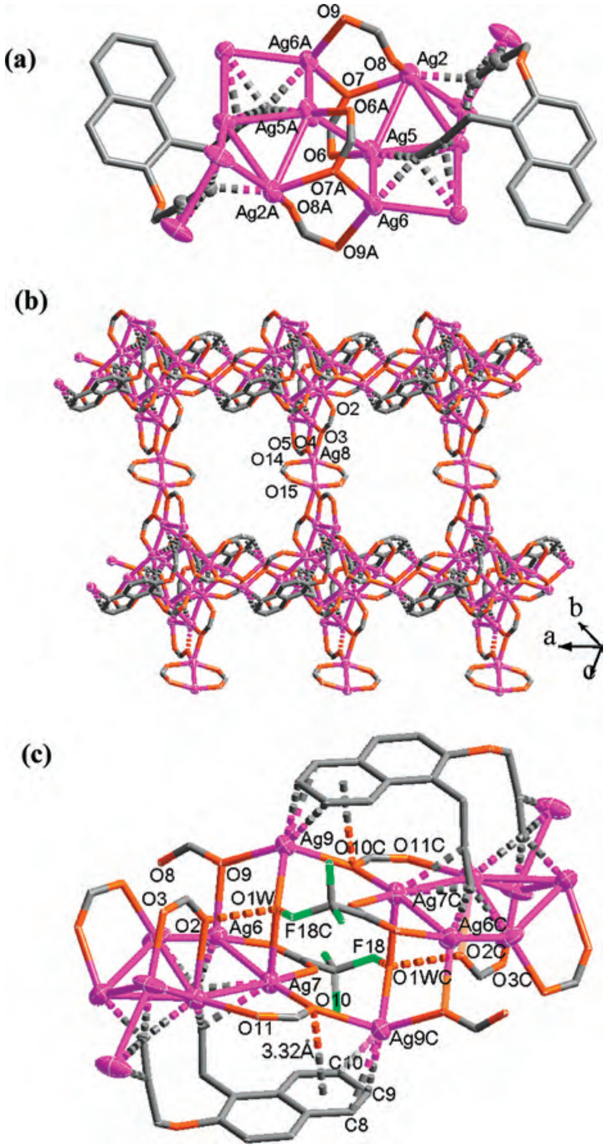

Figure 8. (a) $Ag_7-(CF_3CO_2)_4-Ag_7$ building unit in **4**. (b) 2D metal−organic network. All hydrogen atoms, water molecules, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. (c) Interchain linkage through coordination bonds and silver−aromatic interaction with unusual η^3 mode. All hydrogen atoms and irrespective CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: A $1-x$, $1-y$, $-z$; B $1-x$, $-y$, $1-z$; C $-x$, $1-y$, $-z$.

Adjacent chains are associated through a pair of inversion-related trifluoroacetate groups (O10−O11 and O10C−O11C) acting in the μ_3-η^1,η^2 mode, together with silver−aromatic interactions along the *a* axis, to produce a 2D grid structure (Figure 8b and c), which is further stabilized by the formation of O1W···F18C (3.36 Å) and O1W···O2 (2.73 Å) hydrogen bonds (Figure 8c). The shortest distance of O10 from the center of the naphthyl ring is about 3.32 Å, indicating the existence of anion−π interaction. Adjacent sheets are also associated through offset face-to-face π−π stacking interactions (intercentroid distance 3.85 Å) between adjacent naphthyl rings to give a 3D supramolecular structure (Scheme 2d).

$[Ag_2L3\cdot(AgCF_3CO_2)_8\cdot(H_2O)_3]\cdot H_2O$ (5). In the crystal structure of **5**, torsion angles in dianionic ligand L3 are

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[26] (a) Schmidbaur, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1089–1090. (b) Krossing, I. *Chem.—Eur. J.* **2001**, *7*, 490–502. (c) Wang, Q.-M.; Mak, T. C. W. *Chem. Commun.* **2002**, *2682*, 2683. (d) Chiang, L.-M.; Yeh, C.-W.; Chan, Z.-K.; Wang, K.-M.; Chou, Y.-C.; Chen, J.-D.; Wang, J.-C.; Lai, J.-Y. *Cryst. Growth Des.* **2008**, *8*, 470–477.

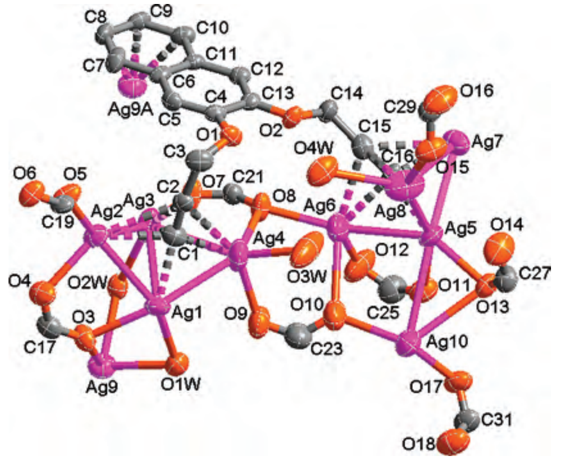

Figure 9. Atom labeling and coordination mode of L3 in **5** (50% thermal ellipsoids). All hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.184, C15≡C16 1.211, Ag1−C1 2.175, Ag2−C1 2.354, Ag2−C2 2.769, Ag3−C1 2.222, Ag3−C2 2.941, Ag4−C1 2.274, Ag4−C2 2.854, Ag5−C16 2.130, Ag6−C16 2.410, Ag6−C15 2.637, Ag7−C16 2.210, Ag7−C15 2.789, Ag8−C16 2.185, Ag8−C15 2.817, Ag9A−C8 2.902, Ag9A−C9 2.379, Ag9A−C10 2.653, Ag1···Ag2 2.868, Ag1···Ag3 2.937, Ag1···Ag4 2.909, Ag2···Ag3 2.944, Ag3···Ag4 2.929, Ag5···Ag6 2.870, Ag5···Ag7 2.871, Ag5···Ag8 2.855, Ag5···Ag10 3.265, Ag7···Ag8 3.331. Symmetry code: A 1 − *x*, −*y*, −*z*.

C3−O1···O2−C14 = 5.15°, C2−C3−O1−C4 =72.00°, C3−O1−C4−C5 = 18.92°, C15−C14−O2−C13 = −154.49°, and C14−O2−C13−C12 = −8.77° (Figure 9). The independent ethynide groups coordinate to two butterfly-shaped Ag_4 baskets in a similar μ_4-$\eta^1,\eta^2,\eta^2,\eta^2$ mode. Two Ag_4 baskets are fused together through two μ_3-*O,O′,O′* trifluoroacetate groups (O7−O8 and O9−O10) to generate a Ag_8 aggregate. As shown in Figure 10a, adjacent Ag_4 baskets of ethynide C15≡C16 are associated together through three pairs of inversion-related trifluoroacetate groups (O11−O12, O11B−O12B, O17−O18, and O17B−O18B in the μ_3-η^1,η^2 mode; O13−O14 and O13B−O14B in the μ_4-η^1,η^3 mode) to produce a $Ag_4-(CF_3CO_2)_6-Ag_4$ building unit, which is further united together with an adjacent Ag_4 basket of ethynide C1≡C2 through type O17−O18 μ_3-*O,O′,O′* trifluoroacetate groups to give a metal−organic ribbon along the *b* axis (Figure 10a and c). Such ribbons are linked together by two types of μ_3-η^1,η^2 trifluoroacetate groups (O5−O6 and O15−O16) to give a double-layer network parallel to the *ab* plane (Figure 10b). Unusual silver−aromatic interaction is found for Ag9, which is bound by three carbon atoms (C8, C9, and C10) of the naphthyl ring from an adjacent ribbon with bond lengths of 2.902, 2.369, and 2.653 Å, respectively. Compared to the π−π stacking interactions in the third direction in complexes **1**−**4**, adjacent sheets in **5** are associated together through interlayer silver−aromatic interactions along the *c* axis to give a 3D network (Figure 10c).

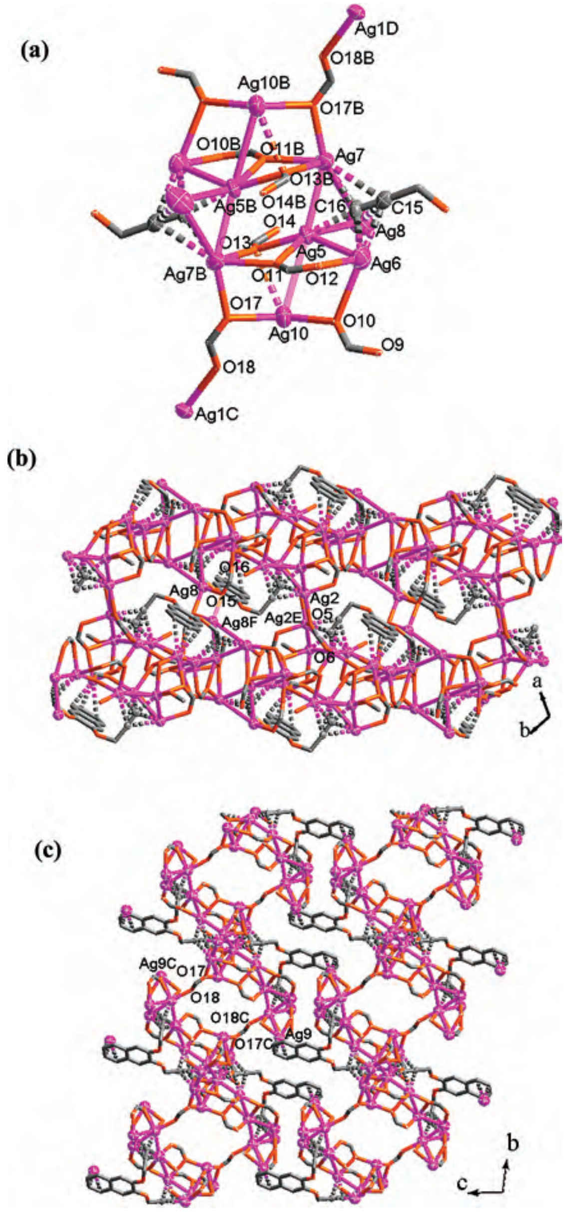

Figure 10. (a) Adjacent Ag_4 baskets of ethynide C15≡C16 are first fused together through three pairs of inversion-related trifluoroacetate groups in **5**. (b) Adjacent ribbons are linked together through trifluoroacetate groups of O5−O6 and O15−O16 types to give a robust 2D sheet. (c) 3D network of **5**. All hydrogen atoms, water, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: A 1 − *x*, −*y*, −*z*; B 2 − *x*, 1 − *y*, 1 − *z*; C 1 − *x*, −*y*, 1 − *z*; D 1 + *x*, 1 + *y*, *z*; E −*x*, −*y*, −*z*; F 1 − *x*, 1 − *y*, 1 − *z*.

$[Ag_2L3\cdot(AgCF_3CO_2)_5\cdot(CH_3CN)_5]$ (6). In order to investigate the effect of solvent on the coordination environment of the ethynide, complex **6** was obtained from the crystallization of $[Ag_2L3]_n$ (**10**) in a mixed water−acetonitrile solution of $AgCF_3CO_2$ instead of an aqueous solution of $AgCF_3CO_2$ as in complex **5**. Torsion angles in L3 are C3−O1···O2−C14 = 45.47°, C2−C3−O1−C4 = −67.96°, C3−O1−C4−C5 = −5.10°, C15−C14−O2−C13 = −78.93°, and C14−O2−C13−C12 = 1.26°. The independent ethynide groups display different μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ and μ_5-$\eta^1,\eta^1,\eta^2,\eta^2,\eta^2$ coordination modes (Figure 11). In this crystal structure, short distances between the nearly parallelly aligned acetonitrile ligand and naphthyl ring indicate weak C−H···π[27] and C≡N···π[28] stacking interactions (Figure 11), which are comparable with similar results in the literature. Though the first experimental proof for significant interactions between

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[27] (a) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction: Evidence, Nature and Consequences*; Wiley-VCH: Weinheim, Germany, 1998. (b) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: New York, 1999; pp 122−201.

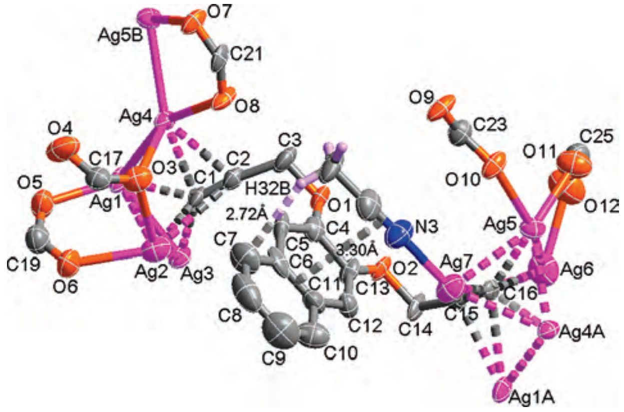

Figure 11. Atom labeling and coordination mode of L3 in **6** (50% thermal ellipsoids). All irrespective hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.180, C15≡C16 1.166, Ag1−C1 2.286, Ag1A−C16 2.827, Ag1A−C15 2.698, Ag2−C1 2.241, Ag2−C2 3.041, Ag3−C1 2.230, Ag4−C1 2.647, Ag4−C2 2.652, Ag4A−C16 2.298, Ag5−C16 2.221, Ag6−C16 2.410, Ag6−C15 2.647, Ag7−C16 2.309, Ag7−C15 2.865, Ag1···Ag2 2.931, Ag1···Ag3 2.787, Ag1···Ag4 2.838, Ag2···Ag3 2.933, Ag4···Ag5B 2.806, Ag4A···Ag7 2.989, Ag5···Ag6 2.987, Ag5···Ag7 2.970. Symmetry codes: A *x*, 1 + *y*, *z*; B *x*, −1 + *y*, *z*.

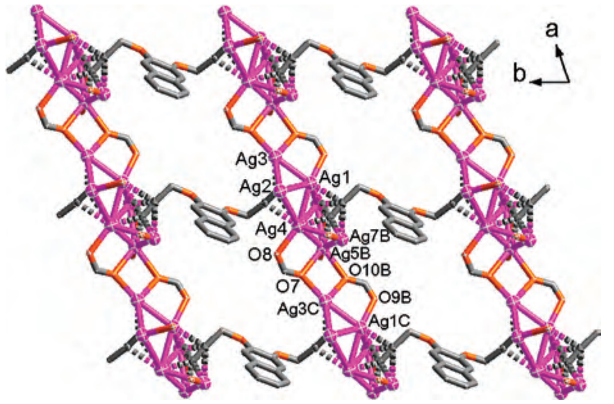

Figure 12. 2D metal−organic network of **6** parallel to the *ab* plane. All hydrogen atoms, water, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: A *x*, 1 + *y*, *z*. B *x*, −1 + *y*, *z*; C: −1 + *x*, *y*, *z*.

neutral electron-rich acetonitrile and the electron-deficient aromatic ring has been reported recently,[29] the concurrence of C−H···π and C≡N···π interactions involving one acetonitrile molecule is an interesting mode in the context of its host−guest supramolecular chemistry.[30]

As shown in Figures 11 and 12, the ethynide moiety C1≡C2 is bound to a butterfly-shaped Ag_4 basket, which is connected to the square-pyramidal Ag_5 basket of ethynide C15≡C16 from adjacent molecules by sharing one edge (Ag1 and Ag4) to give a 1D staircase structure along the *b* axis. Such staircases are associated together through two μ_3-η^1,η^2 trifluoroacetate groups (O7−O8 and O9−O10) to produce a 2D wavelike metal−organic network in the *ab* plane (Figure 12).

$[Ag(L4)_{0.5}\cdot(AgCF_3CO_2)_6\cdot(H_2O)_2\cdot(CH_3CN)]$ (7). In the crystal structure of **7**, dianionic ligand L4 lies on an inversion

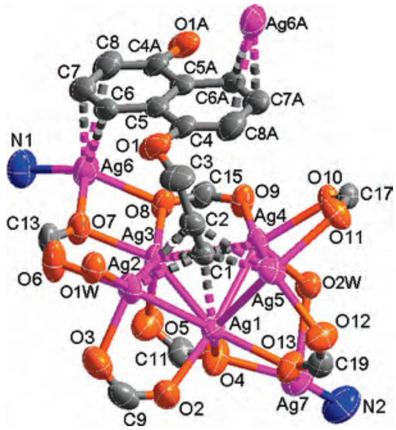

Figure 13. Atom labeling and coordination mode of L4 in **7** (50% thermal ellipsoids). All irrespective hydrogen atoms, CH_3 groups of acetonitrile, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: C1≡C2 1.189, Ag1−C1 2.203, Ag2−C1 2.410, Ag2−C2 2.506, Ag3−C1 2.364, Ag3−C2 3.089, Ag4−C1 2.279, Ag5−C1 2.335, Ag5−C2 2.622, Ag6A−C6 2.852, Ag6A−C7 2.544, Ag6A−C8 2.976, Ag1···Ag2 2.928, Ag1···Ag3 2.890, Ag1···Ag4 2.909, Ag1···Ag5 2.923, Ag2···Ag3 2.960, Ag3···Ag4 2.902, Ag4···Ag5 3.042. Symmetry code: A − *x*, 1 − *y*, 1 − *z*.

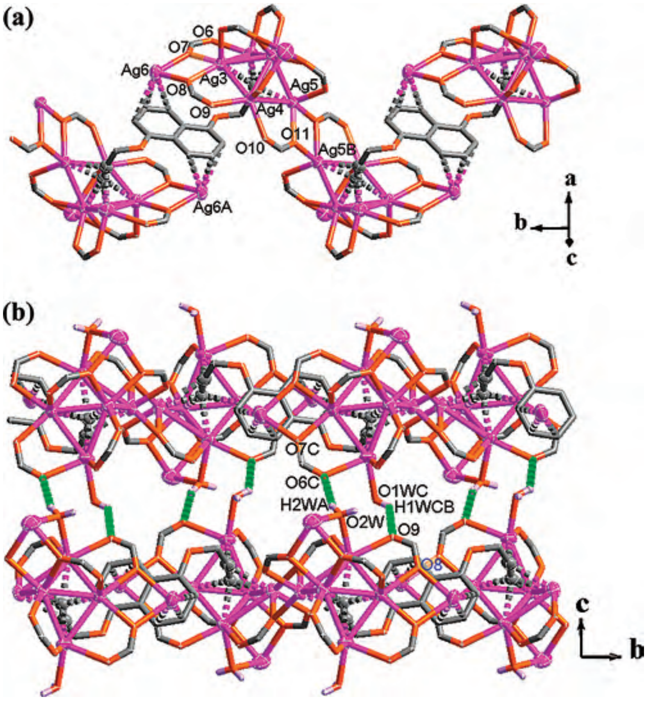

Figure 14. (a) 1D zigzag chain structure of **7** along the *b* axis. All hydrogen atoms, water, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. (b) 2D supramolecular structure built from interchain hydrogen bonds. All irrespective atoms are omitted for clarity. Symmetry codes: A −*x*, 1 − *y*, 1 − *z*; B −*x*, −*y*, 1 − *z*; C *x*, 1/2 − *y*, 1/2 + *z*.

center and takes a symmetric *anticlinal* conformation with a C2−C3−O1−C4 torsion angle of −68.40°. The ethynide group C1≡C2 coordinates to a square-pyramidal Ag_5 basket with the μ_5-η^1,η^1,η^1,η^2,η^2 coordination mode (Figure 13). Ag6 and Ag7 atoms are attached to the Ag_5 basket through trifluoroacetate groups [O6−O7 and O8−O9 for Ag6; O4−O5 and O12−O13 and bridged water (O2W) for Ag7] to give a Ag_7 cluster.

As shown in Figures 13 and 14, the centrosymmetrical naphthyl ring takes a novel μ_2-η^3,η^3 coordination mode with

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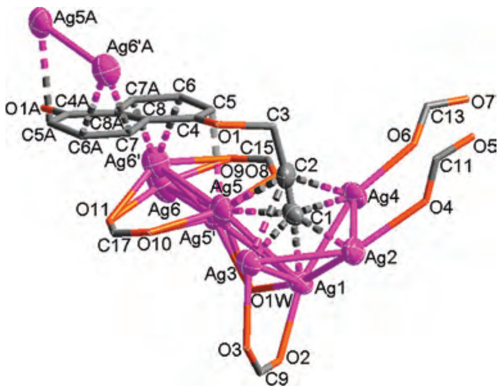

Figure 15. Atom labeling and coordination mode of L4 in **8** (50% thermal ellipsoids). All irrespective hydrogen atoms and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å]: $C1\equiv C2$ 1.106, Ag1−C1 2.221, Ag2−C1 2.336, Ag3−C1 2.268, Ag3−C2 2.934, Ag4−C1 2.353, Ag4−C2 2.572, Ag5−C1 2.856, Ag5−C2 2.975, Ag6′−C6 2.518, Ag6′−C7A 2.510, Ag1···Ag2 2.836, Ag1···Ag3 2.819, Ag1···Ag4 2.920, Ag1···Ag5 3.183, Ag2···Ag3 2.961, Ag2···Ag4 3.160, Ag5···Ag6 2.958, Ag5···Ag6′ 3.040. Symmetry code: A 1 − *x*, 1 − *y*, 1 − *z*.

six carbon atoms (C6, C7, C8; C6A, C7A, C8A) linking to a pair of inversion-related Ag6 atoms with bond lengths of 2.852, 2.544, and 2.976 Å, respectively. Through these silver−aromatic interactions, a novel Ag_7−naphthyl ring−Ag_7 sandwich structure unit is formed. Such units are united together through inversion-related μ_3-η^1,η^2 trifluoroacetate groups (O10−O11) to yield a zigzag chain (Figure 14a) and are further united together through the formation of O2W−H2WA···O6B (H2WA−O6C, 1.964 Å) and O1WC−H1WCB···O9 (H1WCB−O9, 2.252 Å) hydrogen bonds along the *c* axis to give a layer-type supramolecular structure (Figure 14b). There is no other obvious intermolecular interaction between layers.

$[Ag(L4)_{0.5}\cdot(AgCF_3CO_2)_5\cdot(H_2O)_3]$ (8). In the crystal structure of **8**, dianionic ligand L4 also lies on a center of symmetry and takes a symmetric up-and-down conformation with a C2−C3−O1−C4 torsion angle of −76.76°. The ethynide group $C1\equiv C2$ coordinates to a square-pyramidal Ag_5 basket (Ag1, Ag2, Ag3, Ag4, and Ag5) in the μ_5-η^1,η^1,η^2,η^2,η^2 coordination mode (Figure 15). In this structure, the naphthyl ring takes an unprecedented μ_4-η^1,η^1,η^2,η^2 coordination mode in linking to two pairs of inversion-related Ag5 (Ag−C5 2.888 Å) and disorder Ag6′ (Ag6′−C6 2.518; Ag6′−C7A 2.510 Å) atoms. Through such silver−aromatic interactions, a novel Ag_2−naphthyl ring−Ag_2 slipped sandwich structure unit is formed.

Adjacent square-pyramidal Ag_5 baskets are connected together by two pairs of μ_3-η^1,η^2 trifluoroacetate groups (O4−O5, O4B−O5B, O6−O7, and O6B−O7B) to give a staircase structure. Such staircases are associated together through a pair of μ_3-η^1,η^2 trifluoroacetate groups (O2−O3 and O2C−O3C) to produce a 2D wavelike metal−organic network in the *bc* plane (Figure 16a). Adjacent sheets are further linked together through the formation of the Ag5−[Ag6−(μ_3-η^1,η^2-O8−O9)$_2$−Ag6D]−Ag5D bridging unit to form a robust 3D metal−organic network (Figure 16b and c), which is also reinforced through silver−aromatic interactions.

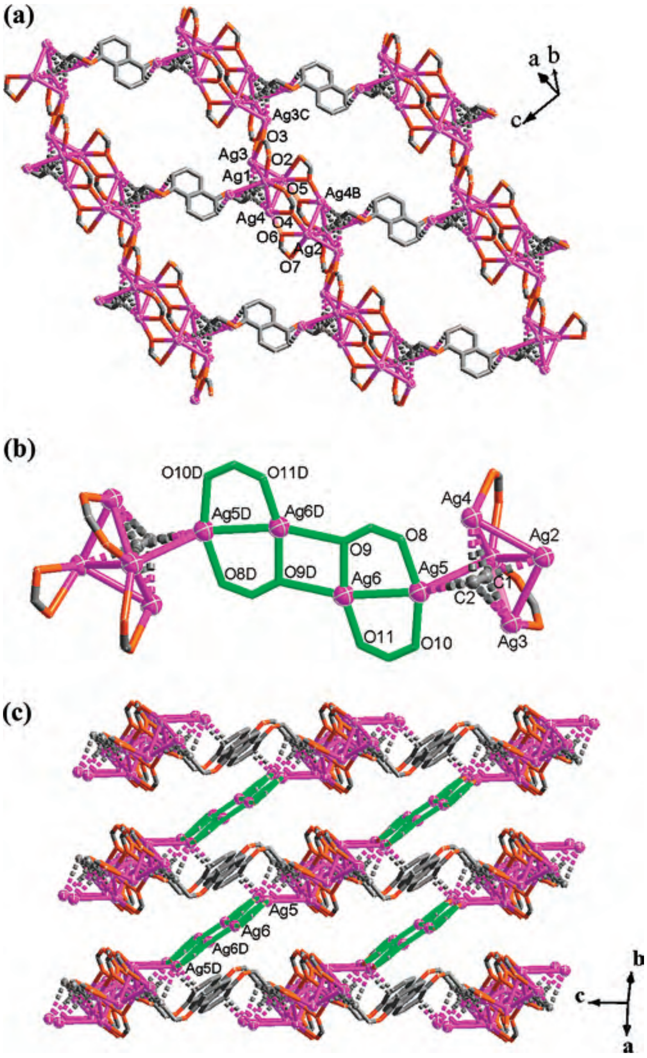

Figure 16. (a) 2D network of **8** along the *bc* plane. (b) Formation of the Ag5−[Ag6−(μ_3-η^1,η^2−O8−O9)$_2$−Ag6D]−Ag5D bridging unit. (c) Adjacent 2D networks are associated together to give a robust 3D metal−organic network. All hydrogen atoms, water, the Ag6′ atom, and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry codes: B −*x*, −*y*, −*z*; C 1 − *x*, 1 − *y*, −*z*; D 1 −*x*, −*y*, 1 − *z*.

Ligand Transformation. At low temperatures (−10 °C), $[AgL2\cdot(AgCF_3CO_2)_6\cdot(H_2O)_4]$ (**3**) can be nearly quantitatively obtained as colorless blocklike crystals from the reaction of $[AgL2]_n$ (**10**) with silver salts. Unexpectedly, we obtained a small amount of single crystals of $[Ag_2L2'\cdot(AgCF_3CO_2)_7\cdot(H_2O)_4]\cdot(H_2O)_2$ (**4**) among black unknown materials from the reaction of $[AgL2]_n$ (**10**) with silver salts at room temperature. While several reactions involving silver salts as catalysts or silver acetylides have been reported very recently,[31] the mechanism of ligand transformation from L2 to L2′ is not known at this time.

Supramolecular Synthon and Its Linkage. The invariable appearance of the μ_4 and μ_5 ligation modes of the ethynide moiety in the present series of eight complexes reaffirms the general utility of the silver−ethynide supramolecular synthons $R-C\equiv C\supset Ag_n$ and $Ag_n\subset C\equiv C-R-C\equiv C\supset Ag_n$ (n = 4, 5) in coordination network assembly,[13,14] despite the fact that the R group is conformationally nonrigid

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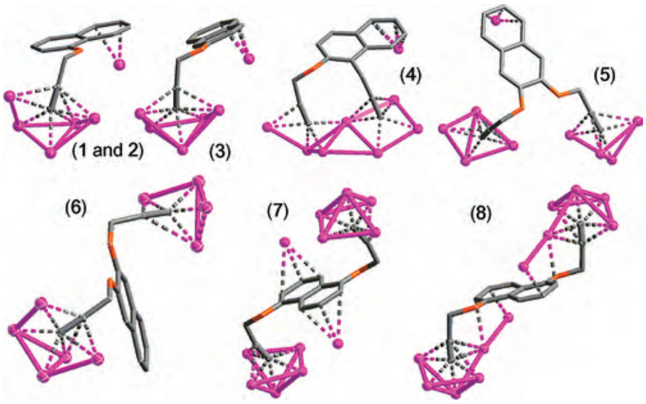
Scheme 3. Coordination Modes for L1 (in **1** and **2**), L2 (in **3**), L2′ (in **4**), L3 (in **5** and **6**), and L4 (in **7** and **8**)



(Scheme 3). The coordination mode of the trifluoroacetate groups varies from the common μ_2-η^1,η^1, μ_3-η^1,η^2, and μ_4-η^1,η^2 types to an unfamiliar μ_4-η^1,η^3 mode.[32] It generally plays two important roles: one type of trifluoroacetate group spans an edge of the Ag_n basket to stabilize the $[Ag_nC{\equiv}C]^{(n-1)+}$ cation moiety, whereas another type bridges adjacent Ag_n baskets to generate 1D or 2D coordination networks.

Weak Interactions. In the present series of complexes, the presence of the planar naphthyl ring offers a good opportunity to probe π-related stacking interactions. As expected, the naphthyl ring usually coordinates to silver atoms to form silver−aromatic interactions, except in the case of compound **6** (Scheme 3). Though this kind of interaction has been used in the assembly of metal−organic frameworks, it is *purposely* applied to ethynide−silver chemistry for the first time. The common coordination modes involving this interaction are η^1 and η^2 (**1**, **2**, **3**, and **8**); however, the unusual η^3 mode is found in **4**, **5**, and **7**. Through this kind of interaction, the network can achieve a higher dimensionality (for compounds **1**−**5**) or exhibit novel Ag_7−naphthyl ring−Ag_7 (**7**) and Ag_2−naphthyl ring−Ag_2 (**8**) sandwich structures.

The occurrence of anion−π interactions between the carboxylate group and naphthyl ring in **1**, **2**, and **4** is unexpected, since they have only been found between electron-deficient (π-acidic) aromatic systems and anions. Synergic effects among silver(I)−aromatic, π−π, and anion−π interactions may be invoked to interpret this phenomenon. The reason that neither silver−aromatic nor anion−π interactions have been found in **6** is attributed to the parallel arrangement of acetonitrile over the naphthyl ring, which impedes the approach of other anionic species or silver atoms. However, the concurrence of C−H$\cdots\pi$ and C≡N$\cdots\pi$ interactions for one acetonitrile ligand in **6** is an interesting new mode that arises because of synergism among different noncovalent interactions.

Metallophilic interactions[15a,33] between coinage metal centers (Cu, Ag, and Au) have been exploited in constructing macrocycles, catenanes, and polymers.[7,34] Indeed, some silver−silver distances in our complexes are well below the sum of the van der Waals radii of two silver atoms, that is, 3.44 Å,[22] and the measured values bracket the separation of silver atoms in silver metal, 2.884 Å.[35] In our complexes, diverse coordination modes of the ethynide moiety, abetted by argentophilic interactions, led to the formation of clusters, multinuclear aggregates, or extended solid-state architectures.

Besides the above-mentioned unfamiliar noncovalent interactions, the naphthyl ring also participates in π−π interactions in compounds **1**−**4** to yield higher-dimensional supramolecular structures. The intercentroid distance between two adjacent naphthyl rings from adjacent sheets varies from 3.80 to 4.07 Å in compounds **1**−**4**, all falling within the generally accepted range of 3.3−4.2 Å for offset face-to-face π−π stacking (Scheme 2).[36]

Conclusion

The present work reports the synthesis and structural characterization of a series of silver(I) trifluoroacetate complexes containing new ligands composed of terminal ethynides each attached by a pendant arm to a naphthalene nucleus. The ethynide moiety invariably adopts the μ_4 or μ_5 ligation mode, affirming that the new metalloligand supramolecular synthons $R{-}C{\equiv}C{\supset}Ag_n$ or $Ag_n{\subset}C{\equiv}C{-}R{-}C{\equiv}C{\subset}Ag_n$ (n = 4, 5) may be utilized for the construction of metal−organic networks. The interplay of ethynide−silver bonding, argentophilicity, hydrogen bonding, silver(I)−aromatic, anion−π, and π−π interactions in these complexes highlights the complexity and challenge in programming the supramolecular assembly of metal−organic networks.

Experimental Section

Reagents. 1-Naphthol, 2-naphthol, 2,3-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, propargyl bromide (80% in toluene), and K_2CO_3 were obtained commercially and 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.

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

1-Prop-2-ynyloxy-naphthalene (HL1). Propargyl bromide (1.4 mL, 12.5mmol) and K_2CO_3 (1.727 g, 25 mmol) were added to a

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solution of 1-naphthol (1.44 g, 10 mmol) in acetone (50 mL). The solution was heated under reflux for 24 h under a nitrogen atmosphere, during which a yellow precipitate formed. The precipitate was filtered off, and the filtrate was evaporated to dryness to yield the crude product as a yellow oil. Subsequent purification by chromatography on silica gel afforded a pale yellow solid. Yield: 1.56 g, 86%. H NMR (300 MHz, $CDCl_3$): δ 6.94−8.26 (7H, naphthyl ring); 4.95(2H, OCH_2); 2.55 (1H, $C\equiv CH$). IR (Nujol): $\nu_{C\equiv C}$ 2054(*w*) cm^{-1}. Elem anal. calcd (%) for $C_{13}H_{10}O$: C 85.68; H 5.53. Found: C 85.70; H 5.51%.

2-Prop-2-ynyloxy-naphthalene (HL2). HL2 was obtained by the same procedure empolying 2-naphthol instead of 1-naphthol. Yield: 1.66 g, 91%. H NMR (300 MHz, $CDCl_3$): δ 7.17−7.79 (7H, naphthyl ring); 4.81 (2H, OCH_2); 2.55 (1H, $C\equiv CH$). IR (Nujol): $\nu_{C\equiv C}$ 2013(*w*) cm^{-1}. Elem anal. calcd (%) for $C_{13}H_{10}O$: C 85.68; H 5.53. Found: C 85.65; H 5.55%.

2,3-Bis-prop-2-ynyloxy-naphthalene (H_2L3). Propargyl bromide (2.8 mL, 25 mmol) and K_2CO_3 (3.455 g, 25 mmol) were added to a solution of 2,3-dihydroxynaphthalene (1.6 g, 10 mmol) in acetone (50 mL). The solution was heated under reflux for 24 h under a nitrogen atmosphere, during which a yellow precipitate formed. The precipitate was filtered off, and the filtrate was evaporated to dryness, yielding the crude product as a yellow solid. It was purified by chromatography on silica gel to afford a pale yellow solid. Yield: 2.12 g, 90%. H NMR (300 MHz, $CDCl_3$): δ 7.32−7.74 (6H, naphthyl ring); 4.87 (4H, OCH_2^a); 2.55 (2H, $C\equiv CH$). IR (Nujol): $\nu_{C\equiv C}$ 2005(*w*) cm^{-1}. Elem anal. calcd (%) for $C_{16}H_{12}O_2$: C 81.33; H 5.12. Found: C 81.31; H 5.12%.

1,5-Bis-prop-2-ynyloxy-naphthalene (H_2L4). H_2L4 was obtained by the same procedure used for H_2L3 except that 1,3-dihydroxynaphthalene was employed instead of 2,3-dihydroxynaphthalene. Yield: 1.96 g, 83%. H NMR (300 MHz, $CDCl_3$): δ 6.97−7.92 (6H, naphthyl ring); 4.88 (4H, OCH_2); 2.54 (2H, $C\equiv CH$). IR (Nujol): $\nu_{C\equiv C}$ 2056(*w*) cm^{-1}. Elem anal. calcd (%) for $C_{16}H_{12}O_2$: C 81.33; H 5.12. Found: C 81.35; H 5.09%.

$[AgL1]_n$ (9). Silver nitrate (0.778 g, 4.58 mmol) was dissolved in acetonitrile (50 mL). Then, HL1 (0.833 g, 4.58 mmol) and triethylamine (0.634 mL, 4.58 mmol) were added with vigorous stirring, and the mixture was stirred overnight under a nitrogen atmosphere in darkness. The pale yellow precipitate formed was collected by filtration, washed thoroughly with acetonitrile (3 × 10 mL) and deionized water (2 × 10 mL), and then stored in wet form at −10 °C in a refrigerator. Yield: about 2.48 g, 86%. IR: ν 2052 cm^{-1} (*w*, $\nu_{C\equiv C}$).

$[AgL2]_n$ (10), $[Ag_2L3]_n$ (11), and $[Ag_2L4]_n$ (12). These were prepared by a similar synthetic procedure employing HL2, H_2L3, and H_2L4, respectively. Yield: ~85%. $[AgL2]_n$ (**10**) IR: ν 2035 cm^{-1} (*w*, $\nu_{C\equiv C}$). $[Ag_2L3]_n$ (**11**) IR: ν 2065 cm^{-1} (*w*, $\nu_{C\equiv C}$). $[Ag_2L4]_n$ (**12**) IR: ν 2038 cm^{-1} (*w*, $\nu_{C\equiv C}$).

$[AgL1\cdot(AgCF_3CO_2)_5\cdot(H_2O)_2]$ (1). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then, $[AgL1]_n$ (≈ 15 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. One day later, colorless block crystals of **1** were deposited in about 95% yield. Elem anal. calcd (%) for $C_{23}H_{13}Ag_6F_{15}O_{13}$: C, 19.32; H, 0.92. Found: C, 19.35; H, 0.89. IR: ν 2121 cm^{-1} (*w*, $\nu_{C\equiv C}$). Upon heating, compound **1** melts from 95 to 97 °C and then turns black and explodes.

$[AgL1\cdot(AgCF_3CO_2)_7\cdot(H_2O)_3\cdot(CH_3CN)]$ (2). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in a mixture of deionized water (1 mL) and acetonitrile (0.2 mL). Then, $[AgL1]_n$ (≈ 25 mg) solid was added to the solution. After stirring for about an hour, the solution was filtered and the filtrate stored at −10 °C in a refrigerator. After several days, colorless platelike crystals of **2** were deposited in about 85% yield. Elem anal. calcd (%) for $C_{29}H_{16}Ag_8F_{21}NO_{17}$: C, 18.21; H, 0.84; N, 0.73. Found: C, 18.26; H, 0.91; N, 0.69. IR: ν 2085 cm^{-1} (*w*, $\nu_{C\equiv C}$). Compound **2** melts from 87 to 88 °C and decomposes above 150 °C.

$[AgL2\cdot(AgCF_3CO_2)_6\cdot(H_2O)_{3.25}]$ (3). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then, $[AgL2]_n$ (≈ 20 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered, and the filtrate stored at −10 °C in a refrigerator. After several days, colorless block crystals of **3** were deposited nearly in quantitative yield in a clear solution. Elem anal. calcd (%) for $C_{25}H_{15.5}Ag_7F_{18}O_{16.25}$: C, 17.95; H, 0.93. Found: C, 17.87; H, 1.02. IR: ν 2014 cm^{-1} (*w*, $\nu_{C\equiv C}$). Compound **3** melts from 126 to 128 °C.

$[Ag_2L2'\cdot(AgCF_3CO_2)_7\cdot(H_2O)_4]\cdot(H_2O)_{1.5}$ (4). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then, $[AgL2]_n$ (≈ 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, a few colorless block crystals of **4** were deposited in about 3% yield, concomitant with black unknown materials. Elem anal. calcd (%) for $C_{30}H_{10}Ag_9F_{21}O_{20.50}$: C, 17.42; H, 0.49. Found: C, 17.49; H, 0.52. IR: ν 2058 cm^{-1} (*w*, $\nu_{C\equiv C}$). Compound **4** melts from 114 to 115 °C.

$[Ag_2L3\cdot(AgCF_3CO_2)_8\cdot(H_2O)_3]\cdot H_2O$ (5). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then, $[Ag_2L3]_n$ (≈ 25 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered and the filtrate stored at −10 °C in a refrigerator. After several days, colorless platelike crystals of **5** were deposited in about 86% yield. Elem anal. calcd (%) for $C_{32}H_{18}Ag_{10}F_{24}O_{22}$: C, 16.79; H, 0.79. Found: C, 16.76; H, 0.81. IR: ν 2001 cm^{-1} (*w*, $\nu_{C\equiv C}$). Compound **5** melts from 103 to 104 °C.

$[Ag_2L3\cdot(AgCF_3CO_2)_5\cdot(CH_3CN)_5]$ (6). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in a mixture of deionized water (1 mL) and acetonitrile (0.2 mL). Then, $[Ag_2L3]_n$ (≈ 30 mg) solid was added to the solution. After stirring for about half an hour, the solution was filtered and the filtrate stored at −10 °C in a refrigerator. After several days, colorless needle crystals of **6** were deposited in about 90% yield. Elem anal. calcd (%) for $C_{36}H_{25}Ag_7F_{15}N_5O_{12}$: C, 24.57; H, 1.43; N, 3.98. Found: C, 24.55; H, 1.46; N, 4.02. IR: ν 2093 cm^{-1} (*w*, $\nu_{C\equiv C}$). Compound **6** melts from 101 to 102 °C.

$[Ag(L4)_{0.5}\cdot(AgCF_3CO_2)_6\cdot(H_2O)_2\cdot(CH_3CN)]$ (7). $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in a mixture of deionized water (1 mL) and acetonitrile (0.2 mL). Then, $[Ag_2L4]_n$ (≈ 30 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 needle crystals of **7** were deposited in about 80% yield. Elem anal. calcd (%) for $C_{24}H_{15}Ag_7F_{18}N_2O_{15}$: C, 17.28; H, 0.91; N, 1.68. Found: C, 17.26; H, 1.71; N, 1.65. IR: ν 2039 cm^{-1} (*w*, $\nu_{C\equiv C}$). Compound **7** melts from 78 to 79 °C.

$[Ag(L4)_{0.5}\cdot(AgCF_3CO_2)_5\cdot(H_2O)_3]$ (8). $AgCF_3CO_2$ (0.440 g, 2 mmol) was dissolved in 1 mL of deionized water. Then, $[Ag_2L4]_n$ (≈ 15 mg) solid was added to the solution. After stirring for about 4 h, the solution was filtered and the filtrate stored at −10 °C in a refrigerator. After several days, colorless plate crystals of **8** were deposited in about 50% yield with unknown black solids. Elem anal. calcd (%) for $C_{18}H_{11}Ag_6F_{15}O_{14}$: C, 15.63; H, 0.80. Found: C, 15.56; H, 0.71. IR: ν 2032 cm^{-1} (*w*, $\nu_{C\equiv C}$). Upon heating, compound **8** turns to black above 118 °C and explodes at 156 °C.

X-Ray Crystallographic Analysis. Selected crystals were used for data collection on a Bruker SMART 1000 CCD diffractometer (**1**−**7**) and an APEX-II (**8**) at 293 K using frames of oscillation range 0.3°, with $2° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[37] The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[38]

Crystal Data for 1. $[AgL1\cdot(AgCF_3CO_2)_5\cdot(H_2O)_2]$, $C_{23}H_{13}Ag_6F_{15}O_{13}$, $M = 1429.55$, triclinic, space group $P\bar{1}$, $a = 11.084(1)$ Å, $b = 12.726(2)$ Å, $c = 13.761(2)$ Å, $\alpha = 73.603(2)°$, $\beta = 71.572(2)°$, $\gamma = 89.353(2)°$, $V = 1760.1(4)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.697$ g cm^{-3}. The structure, refined on F^2, converged for 6864 unique reflections ($R_{int} = 0.0209$) and 5496 observed reflections with $I < 2\sigma(I)$ to give $R_1 = 0.0409$ and $wR_2 = 0.1068$ and a goodness of fit = 1.066.

Crystal Data for 2. $[AgL1\cdot(AgCF_3CO_2)_7\cdot(H_2O)_3\cdot(CH_3CN)]$, $C_{29}H_{16}Ag_8F_{21}NO_{17}$, $M = 1912.39$, triclinic, space group $P\bar{1}$, $a = 11.461(2)$ Å, $b = 13.914(3)$ Å, $c = 17.293(3)$ Å, $\alpha = 69.805(4)°$, $\beta = 75.392(4)°$, $\gamma = 67.898(4)°$, $V = 2374.1(8)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.675$ g cm^{-3}. The structure, refined on F^2, converged for 8302 unique reflections ($R_{int} = 0.0229$) and 6612 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0466$ and $wR_2 = 0.1036$ and a goodness of fit = 1.055.

Crystal Data for 3. $[AgL2\cdot(AgCF_3CO_2)_6\cdot(H_2O)_{3.25}]$, $C_{50}H_{31}Ag_{14}F_{36}O_{32.5}$, $M = 3345.93$, triclinic, space group $P\bar{1}$, $a = 13.115(3)$ Å, $b = 13.768(3)$ Å, $c = 14.203(3)$ Å, $\alpha = 98.865(4)°$, $\beta = 105.901(4)°$, $\gamma = 116.223(4)°$, $V = 2097.1(7)$ Å^3, $Z = 1$, $T = 293$ K, $D_c = 2.649$ g cm^{-3}. The structure, refined on F^2, converged for 7355 unique reflections ($R_{int} = 0.0362$) and 4677 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0598$ and $wR_2 = 0.1528$ and a goodness of fit = 1.015. Silver atom Ag5 has two disordered positions with an occupancy ratio of 0.9:0.1.

Crystal Data for 4. $[Ag_2L2'\cdot(AgCF_3CO_2)_7\cdot(H_2O)_4]\cdot(H_2O)_{1.5}$, $C_{60}H_{20}Ag_{18}F_{42}O_{40.1}$, $M = 4136.42$, triclinic, space group $P\bar{1}$, $a = 13.295(6)$ Å, $b = 13.388(6)$ Å, $c = 16.043(7)$ Å, $\alpha = 73.074(8)°$, $\beta = 85.741(9)°$, $\gamma = 70.121(9)°$, $V = 2568.1(19)$ Å^3, $Z = 1$, $T = 293$ K, $D_c = 2.675$ g cm^{-3}. The structure, refined on F^2, converged for 8942 unique reflections ($R_{int} = 0.0467$) and 5488 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0889$ and $wR_2 = 0.2185$ and a goodness of fit = 1.034. The Ag5 atom has two disordered positions with an occupancy ratio of 0.9:0.1. The solvent water (OW5 and OW6) hydrogen atoms were not included in the structure model.

Crystal Data for 5. $[Ag_2L3\cdot(AgCF_3CO_2)_8\cdot(H_2O)_3]\cdot H_2O$, $C_{32}H_{18}Ag_{10}F_{24}O_{22}$, $M = 2289.16$, triclinic, space group $P\bar{1}$, $a = 11.119(2)$ Å, $b = 14.684(2)$ Å, $c = 17.842(2)$ Å, $\alpha = 95.827(3)°$, $\beta = 95.088(3)°$, $\gamma = 110.444(3)°$, $V = 2691.4(6)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.825$ g cm^{-3}. The structure, refined on F^2, converged for 9407 unique reflections ($R_{int} = 0.0351$) and 6385 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0649$ and $wR_2 = 0.1695$ and a goodness of fit = 1.032. Two silver atoms (Ag1 and Ag3) are also processed into two parts with a ratio of 0.9:0.1.

Crystal Data for 6. $[Ag_2L3\cdot(AgCF_3CO_2)_5\cdot(CH_3CN)_5]$, $C_{36}H_{25}Ag_7F_{15}N_5O_{12}$, $M = 1759.70$, triclinic, space group $P\bar{1}$, $a = 9.828(2)$ Å, $b = 12.052(2)$ Å, $c = 22.890(4)$ Å, $\alpha = 84.868(4)°$, $\beta = 85.005(4)°$, $\gamma = 70.265(4)°$, $V = 2537.2(8)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.760$ g cm^{-3}. The structure, refined on F^2, converged for 8888 unique reflections ($R_{int} = 0.0633$) and 4682 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0573$ and $wR_2 = 0.0864$ and a goodness of fit = 0.948. Silver atom Ag3 has two disordered positions with an occupancy ratio of 0.9:0.1.

Crystal Data for 7. $[Ag(L4)_{0.5}\cdot(AgCF_3CO_2)_6\cdot(H_2O)_2\cdot(CH_3CN)]$, $C_{24}H_{15}Ag_7F_{18}N_2O_{15}$, $M = 1668.47$, monoclinic, space group $P2_1/c$, $a = 16.600(2)$ Å, $b = 14.045(1)$ Å, $c = 19.332(2)$ Å, $\beta = 106.925(2)°$, $V = 4311.9(8)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 2.570$ g cm^{-3}. The structure, refined on F^2, converged for 7591 unique reflections ($R_{int} = 0.0493$) and 5287 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0533$ and $wR_2 = 0.1325$ and a goodness of fit = 1.031.

Crystal Data for 8. $[Ag(L4)_{0.5}\cdot(AgCF_3CO_2)_5\cdot(H_2O)_3]$, $C_{18}H_{11}Ag_6F_{15}O_{14}$, $M = 1383.49$, triclinic, space group $P\bar{1}$, $a = 10.8639(3)$ Å, $b = 11.2248(3)$ Å, $c = 14.0899(4)$ Å, $\alpha = 98.805(1)°$, $\beta = 92.317(1)°$, $\gamma = 110.405(1)°$, $V = 1583.22(8)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.902$ g cm^{-3}. The structure, refined on F^2, converged for 5604 unique reflections ($R_{int} = 0.0219$) and 4976 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0442$ and $wR_2 = 0.1235$ and a goodness of fit = 1.036. Silver atoms Ag5 and Ag6 have two disordered positions with occupancy ratios of 0.9:0.1 and 0.8:0.2, respectively. The disordered fluorine atoms of trifluoroacetate groups (O2−O3 and O10−O11) can be differentiated as two parts in a ratio of 0.7:0.3.

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Supporting Information Available: Crystallographic data for complexes **1**−**8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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