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Assembly of Infinite Silver(I) Columns, Chains, and Bridged Aggregates with Supramolecular Synthon Bearing Substituted Phenylethynides

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Dedicated to Professor Khi-Rui Tsai (also known as Qi-Rui Cai) on the occasion of his 93rd birthday

Abstract: Structural correlation in a series of eight silver(I) complexes bearing substituted phenylethynide ligands was systematically investigated through variation of the position or steric bulk of substituents on the aromatic ring. All coordination frameworks are constructed with the supramolecular synthon $Ar{-}C{\equiv}C{\supset}Ag_n$ ($Ar = 4\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, $2\text{-}MeC_6H_4$, $4\text{-}tBuC_6H_4$, $3,5\text{-}(CF_3)_2C_6H_3$; $n = 4$, 5), and the presence of coexisting ligands was found to influence the supramolecular assembly. The role of π–π stacking, C−H···π and Ag–C(aromatic) interactions in stabilizing the coordination networks is also discussed.

Keywords: argentophilicity · coordination modes · ethynides · pi interactions · silver · supramolecular chemistry

Introduction

Coordinate covalent bonding[1] and directional noncovalent interactions are two well-established essentials of crystal engineering in the construction of solid-state frameworks, the latter laying the foundation of an enormous family of supramolecular synthons.[2] The identification and summarization of such supramolecular synthons facilitate a better comprehension of the crystal structures of organic solids for the systematic design of related materials.[2,3] However, the development and exploitation of supramolecular synthons in the construction of metal–organic frameworks is still at an emerging stage due to the unpredictability of metal–ligand coordination geometries.[4]

Recently, metal–ethynide complexes have attracted much interest owing to their structural diversity[5] and potential application as precursors of nonlinear optical materials,[6] luminescence materials,[7] and rigid-rod molecular wires.[8] Spectroscopic and crystallographic evidence has amply demonstrated that the ethynide group can act as a good σ-donor and weak π-acceptor ligand to form a large variety of metal–alkynyl complexes.[5c,i] In addition, the ethynide ligand can also function as a good π donor through pπ–dπ overlap with metal atoms to engender a series of cluster complexes and multinuclear aggregates.[9] Our recent studies on silver phenylenediethynide complexes[10] and silver phenylethynide[11] complexes showed that the ethynide moieties therein consistently exhibit μ_4- or μ_5-ligation modes through σ- and π-bonding, implying that the highest ligation number[12] of the ethynide moiety is five and establishing the existence of new supramolecular synthons $Ag_n{\subset}C_2{-}R{-}C_2{\supset}Ag_n$ ($R = p$-, m-, o-C_6H_4; $n = 4$, 5) and $R{-}C_2{\supset}Ag_n$ ($R = C_6H_5$; $n = 4$, 5). To further explore various factors that influence the formation of such supramolecular synthons and establish their general utility in the construction of coordination networks, we undertake synthetic and structural studies on a series of eight silver(I) complexes of phenylethynide derivatives with different substituents (methyl, *tert*-butyl, trifluoromethyl) at variable positions (*p*-, *m*-, *o*-) on the aromatic ring: $2\,AgC{\equiv}CC_6H_4Me\text{-}4\cdot 6\,AgCF_3CO_2\cdot 1.5\,CH_3CN$ (**1**), $AgC{\equiv}CC_6H_4Me\text{-}4\cdot 3\,AgCF_3CO_2\cdot(CH_3)_3N^+CH_2CO_2^-$ (**2**), $AgC{\equiv}CC_6H_4Me\text{-}3\cdot 2\,AgCF_3SO_3$ (**3**), $AgC{\equiv}CC_6H_4Me\text{-}2\cdot 4\,AgCF_3CO_2\cdot H_2O$ (**4**), $2\,AgC{\equiv}CC_6H_4Me\text{-}2\cdot 9\,AgC_2F_5CO_2\cdot 6\,H_2O$ (**5**), $AgC{\equiv}CC_6H_4tBu\text{-}4\cdot 3\,AgCF_3CO_2\cdot CH_3CN$ (**6**), $2\,AgC{\equiv}CC_6H_4tBu\text{-}4\cdot 5\,AgCF_3CO_2$ (**7**), and $AgC{\equiv}CC_6H_3(CF_3)_2\text{-}3,5\cdot 3\,AgCF_3CO_2\cdot(Et_3NH)CF_3CO_2\cdot H_2O$ (**8**).

Results and Discussion

We have previously reported that the polymeric compound $[AgC{\equiv}CC_6H_5]_n$ dissolved in a water–acetonitrile solution of

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$AgCF_3CO_2$ produced the complex $AgC\equiv CC_6H_5\cdot 3AgCF_3CO_2\cdot CH_3CN$,[11] in which the ethynide moiety is enveloped in a square-pyramidal Ag_5 basket, and such baskets are mutually connected by sharing a square edge to yield a silver chain. The high concentration of silver ions and their aggregation by argentophilicity[13] ensure that the ethynide moiety achieves the highest ligation numbers of five, in contrast to most transition-metal phenylethynide complexes with ligation numbers ranging from one to four.[14] In the present study, complexes **1**–**8** were similarly obtained from the crystallization of the corresponding crude polymeric compounds $[AgC\equiv CC_6H_4Me\text{-}4]_n$, $[AgC\equiv CC_6H_4Me\text{-}3]_n$, $[AgC\equiv CC_6H_4Me\text{-}2]_n$, $[AgC\equiv CC_6H_4tBu\text{-}4]_n$, and $[AgC\equiv CC_6H_3(CF_3)_2\text{-}3,5]_n$ in a concentrated aqueous solution of $AgCF_3CO_2$, $AgCF_3SO_3$, or $AgC_2F_5CO_2$ plus $AgBF_4$, the last one being used to increase the silver ion concentration.[15]

$2AgC\equiv CC_6H_4Me\text{-}4\cdot 6AgCF_3CO_2\cdot 1.5CH_3CN$ (1): In the crystal structure of $2AgC\equiv CC_6H_4Me\text{-}4\cdot 6AgCF_3CO_2\cdot 1.5CH_3CN$ (**1**), both independent 4-methylphenylethynides exhibit the μ_5-η^1 mode, which is virtually identical to that of the phenylethynide moiety in $AgC\equiv CC_6H_5\cdot 3AgCF_3CO_2\cdot CH_3CN$.[11] As shown in Figure 1, each independent ethynide moiety ($C1\equiv C2$ and $C10\equiv C11$) is bound to a square-pyramidal Ag_5 basket, and fusion of adjacent baskets through sharing of one square edge generates an infinite linear silver(I) coordination column along the *b* direction. All phenyl rings protruding on the same side of the column constitute a parallel periodic array, and the centroid–centroid distance of 4.025 Å between adjacent rings is similar to the value of 4.189 Å in $AgC\equiv CC_6H_5\cdot 3AgCF_3CO_2\cdot CH_3CN$. The interplanar distance is 3.656 Å, falling within the generally accepted range of 3.3–3.8 Å for offset π–π stacking.[16] Four trifluoroacetate ligands (O1−O1A, O2−O2A, O3−O3B, and O4−O4B) lying above and below the base of the square-pyramidal Ag_5 basket bond with square edges of type Ag2−Ag2A and Ag4−Ag4B by the μ_2-*O*,*O'* coordination mode. Two peripheral silver atoms Ag5 and Ag6 bearing one or a half acetonitrile ligand, respectively, join the vertex of the corresponding Ag_5 basket (Ag1 and Ag3) by argentophilic interaction, which is further strengthened by two trifluoroacetate groups O7−O8 and O5−O6 spanning the Ag1−Ag5 and Ag3−Ag6 edges, respectively (Figure 2). The fused-basket silver columns are packed face-to-face in the *ac* plane without the connection of other intermolecular interactions, in contrast to the 3D network in $AgC\equiv CC_6H_5\cdot 3AgCF_3CO_2\cdot CH_3CN$ consolidated by weak C−H···F hydrogen bonds and Ag···Ag interactions. This may result from steric repulsion between the substituted methyl groups of proximal phenyl rings.

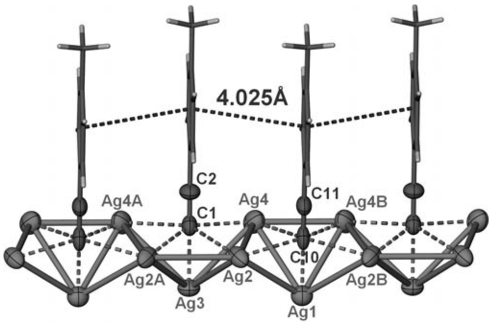


Figure 1. Atom labeling (50% thermal ellipsoids) and coordination modes of two independent 4-methylphenylethynide ligands in **1**. The linear silver(I) column is stabilized by continuous π–π stacking between completely parallel phenyl rings. Other ligands are omitted for clarity. Symmetry code: A: *x*, −*y*, *z*; B: *x*, 1−*y*, *z*. Selected bond lengths [Å]: C1−C2 1.15(3), C10−C11 1.19(3), Ag···Ag 2.975(5)–3.279(7).

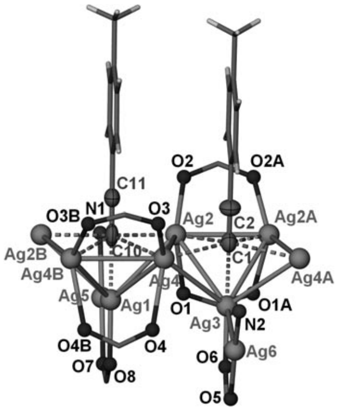


Figure 2. Coordination modes of trifluoroacetate ligands and acetonitrile groups in complex **1**. The CF_3 and CH_3 moieties are omitted for clarity. Symmetry code: A: *x*, −*y*, *z*; B: *x*, 1−*y*, *z*.

$AgC\equiv CC_6H_4Me\text{-}4\cdot 3AgCF_3CO_2\cdot (CH_3)_3N^+CH_2CO_2^-$ (2): To investigate the effect of coexisting ligands on the coordination environment of the ethynide ligand and the assembly of the silver(I) column vide supra, we synthesized the complex $AgC\equiv CC_6H_4Me\text{-}4\cdot 3AgCF_3CO_2\cdot (CH_3)_3N^+CH_2CO_2^-$ (**2**), in which the silver column connected by argentophilic interaction was found to exhibit a zigzag configuration, with a μ_3-*O*,*O'*,*O'* betaine ligand replacing a trifluoroacetate group at each turn (Figure 3).

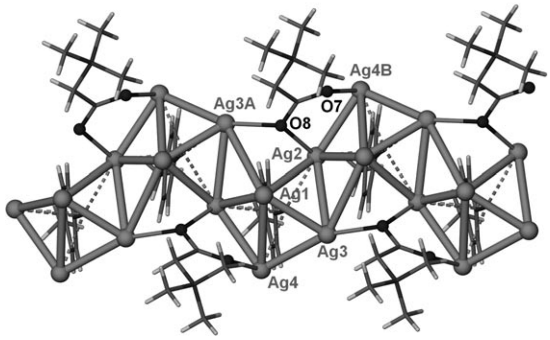


Figure 3. Zigzag silver column in **2**. Other groups are omitted for clarity. Symmetry code: A: $x-\frac{1}{2}$, $\frac{1}{2}-y$, *z*; B: $x+\frac{1}{2}$, $\frac{1}{2}-y$, *z*.

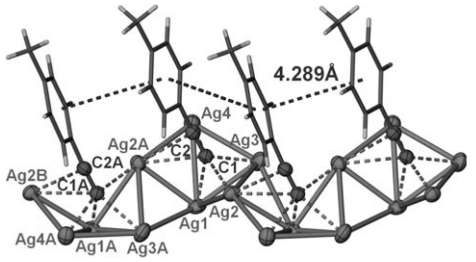


Figure 4. μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ Coordination mode of the 4-$MeC_6H_4C{\equiv}C^-$ ligand in **2** (50 % thermal ellipsoids). Other groups are omitted for clarity. Symmetry code: A: $x-\frac{1}{2}$, $\frac{1}{2}-y$, z; B: $x+\frac{1}{2}$, $\frac{1}{2}-y$, z. Selected bond lengths [Å]: C1–C2 1.228(6), Ag···Ag 2.832(1)–3.376(2).

As shown in Figure 4, all phenyl rings lean to the same side along the column, resulting in a μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ mode of the ethynide moiety. Compared with the square-edge sharing of Ag_5 baskets in complex **1**, adjacent square-pyramidal Ag_5 baskets in **2** are fused by sharing one square edge and one pyramidal edge. The deviation of the silver column from linearity causes adjacent phenyl rings to be nonparallel, forming a dihedral angle of 15.4°. Consequently two carbon atoms (C7 and C8) of one phenyl ring are inclined to the other ring with atom-to-plane distances of 3.600 and 3.626 Å, respectively, showing that significant offset π–π interaction also exists in this structure. The zigzag silver(I) columns along the *a* direction are further connected by weak hydrogen bonds of C18–H18A···O3 (H18A–O3 2.541 Å) to engender a 3D network (Figure 5).

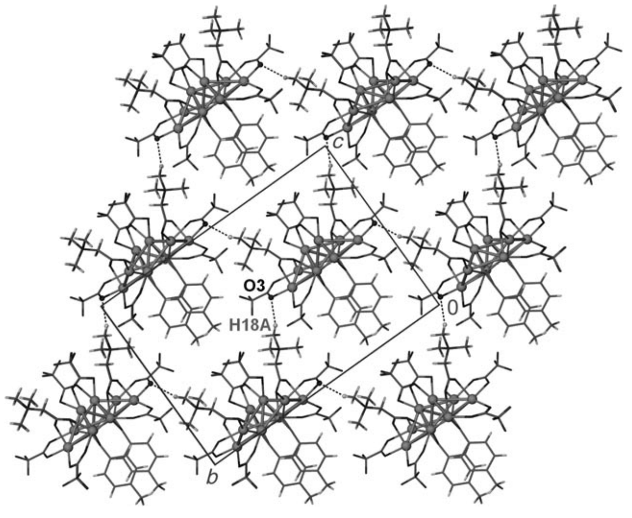


Figure 5. Zigzag silver(I) columns in complex **2** are linked by weak hydrogen bonds of the type C18–H18A···O3 (H–O 2.514 Å) to produce a 3D network.

$AgC{\equiv}CC_6H_4Me$-3·2 $AgCF_3SO_3$ (3): In the crystal structure of $AgC{\equiv}CC_6H_4Me$-3·2 $AgCF_3SO_3$ (**3**), the ethynide moiety C1≡C2 is bound to a butterfly-shaped Ag_4 basket in the μ_4-η^1 mode. Such baskets are connected along [100] by vertex-sharing to generate an infinite linear silver(I) chain. Adjacent phenyl rings lying on the silver chain are mutually parallel with a centroid–centroid distance of 4.730 Å, which indicates negligible π–π interaction. However, as shown in Figure 6a, hydrogen atom H9C of the substituted methyl group C9 points toward the centroid of the adjacent phenyl ring at 3.11 Å with a C–H···centroid angle of 148°, which lies just within the normal range of H/C_{sp^2} π interactions between 2.9 and 3.1 Å (1.2–1.4 Å for H and 1.7 Å for C_{sp^2}).[17] Hence the ordered and parallel arrangement of phenyl rings in complex **3** may be ascribed to stabilization by this C–H/π interaction.

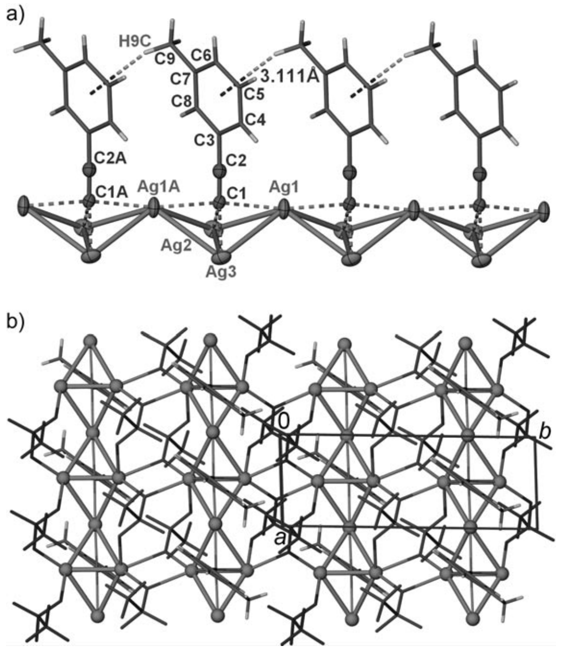


Figure 6. a) Coordination mode of the 3-$MeC_6H_4C{\equiv}C^-$ ligand in **3** (50 % thermal ellipsoids) and linear silver chain generated from vertex-sharing of Ag_4 baskets with a regular row of parallel phenyl rings protruding on the same side. Other ligands are omitted for clarity. Symmetry code: A: $x-1$, y, z. Selected bond lengths [Å]: C1–C2 1.217(6), Ag···Ag 2.853(1)–3.118(1). b) The 2D coordination network normal to [001] connected by two types of triflate ligands.

The linear silver chains are further linked by two triflate ligands (O1-O2-O3 and O4-O5-O6) at both sides to produce a 2D coordination network along the *ab* plane (Figure 6b). The phenyl rings of different chains protrude alternately above and below this plane, and steric effect leads to adjacent layers being separated by about 14.5 Å (Figure 7).

$AgC{\equiv}CC_6H_4Me$-2·4 $AgCF_3CO_2{\cdot}H_2O$ (4). In $AgC{\equiv}CC_6H_4Me$-2·4 $AgCF_3CO_2{\cdot}H_2O$ (**4**), the ethynide moiety C1≡C2 is also encapsulated in a butterfly-shaped Ag_4 basket to produce a supramolecular synthon 2-$MeC_6H_4C{\equiv}C{\supset}Ag_4$, as shown in Figure 8a. All trifluoroacetate groups in complex **4** exhibit the μ_3-*O,O′,O′* mode. Through the linkage of one trifluoroacetate group (O3–O4) along the *b* direction and the other two (O1–O2 and O7–O8) along [101], the butterfly-shaped Ag_4 baskets connect with each other to yield a 2D coordination network parallel to the (101) plane (Figure 8b).

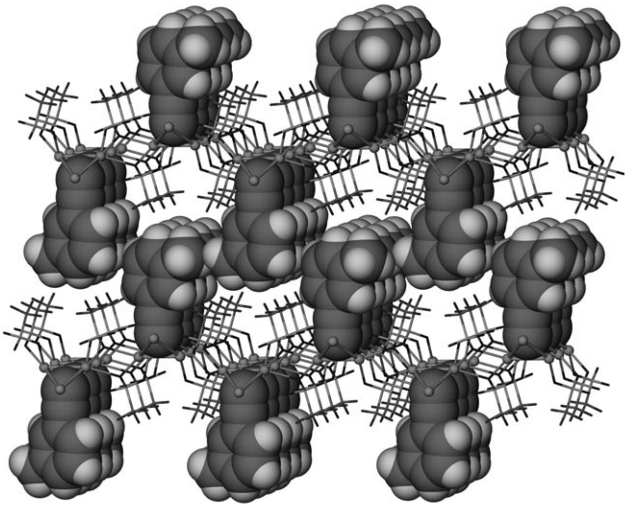


Figure 7. Packing view of 2D coordination network along the *c* direction in complex **3**. The 3-methylphenylethynide groups are indicated as space-filling models.

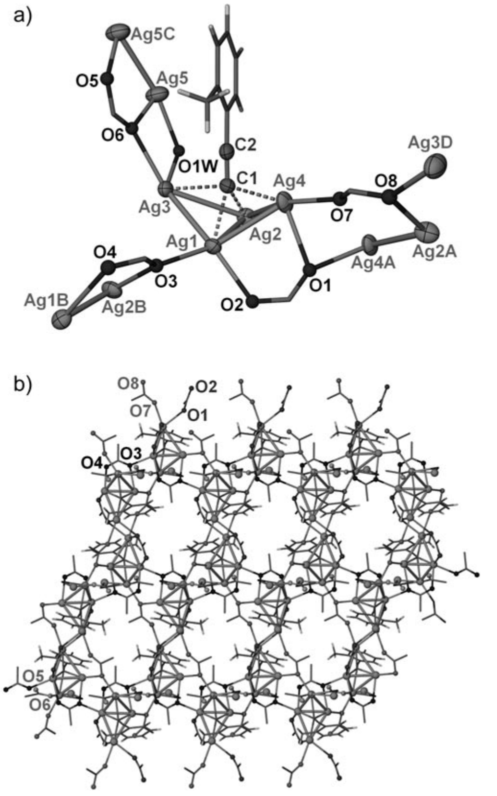


Figure 8. a) Atom labeling (50 % thermal ellipsoids) and coordination modes of the 2-MeC$_6$H$_4$C≡C$^-$ and trifluoroacetate groups in **4**. Symmetry code: A: $1-x$, $1-y$, $-z$; B: $1\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; C: $1-x$, $1-y$, $1-z$; D: $-\frac{1}{2}+x$, $1\frac{1}{2}-y$, $-\frac{1}{2}+z$. Selected bond lengths [Å]: C1−C2 1.206(6), Ag···Ag 2.853(1)–3.118(1). b) The 2D (6,3) coordination network parallel to the (1 0 1) plane connected by different trifluoroacetate groups. All fluorine atoms are omitted for clarity.

Linkage of this type of 2D networks along [1 0 1] by the bridging unit [Ag$_2$(μ$_2$-H$_2$O)$_2$(μ$_3$-CF$_3$CO$_2$)$_2$] composed of external silver atom Ag5, aqua ligand O1W, and trifluoroacetate group O5−O6 yields a 3D coordination network, in which such a bridging unit is located between adjacent phenyl rings to form a sandwich structure (Figure 9).

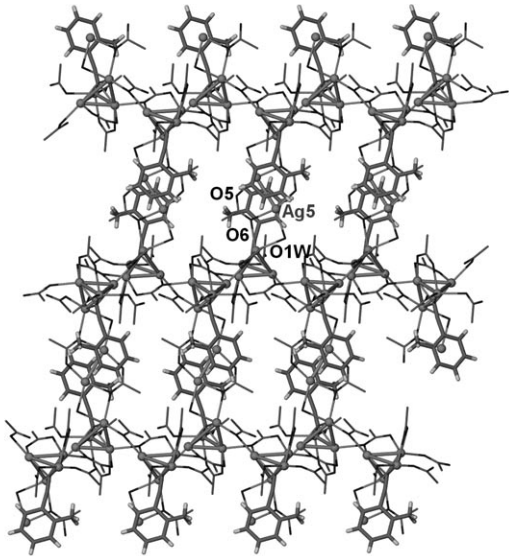


Figure 9. The 3D coordination network in complex **4** viewed along the [1 0 1] direction. All fluorine atoms are omitted for clarity.

2 AgC≡CC$_6$H$_4$Me-2·9 AgC$_2$F$_5$CO$_2$·6 H$_2$O (5): When a more bulky anionic ligand C$_2$F$_5$CO$_2$$^-$ is employed in place of CF$_3$CO$_2$$^-$ in complex **4**, two butterfly-shaped Ag$_4$ baskets each held by one 2-MeC$_6$H$_4$C≡C$^-$ ligand in 2 AgC≡CC$_6$H$_4$Me-2·9 AgC$_2$F$_5$CO$_2$·6 H$_2$O (**5**) coalesce and share one silver atom to yield a Ag$_7$ aggregate. Although the phenyl ring of one 2-methylphenylethynide ligand is disordered at two orientations, the centroid–centroid distances between two adjacent phenyl rings (**I**)–(**II**) and (**I**)–(**II′**) in the range 3.787–4.039 Å indicate the existence of offset π–π stacking. Notably, the silver atom Ag10 coordinates to three carbon atoms (C13, C14, and C15) of phenyl ring (**I**) by an unusual η$_3$-mode[18] with bond lengths of 2.839, 2.349, and 2.770 Å, respectively. Otherwise, the distances between C5′ of phenyl ring (**II′**) and disordered silver atom Ag12 lie in the range of 2.695–3.069 Å, also falling within the margin of significant silver-aromatic interactions (2.9 Å)[19] (Figure 10). This kind of columnar structure interlinked by π–π and Ag−C(aromatic) interactions occurs widely in silver complexes of polycyclic aromatic hydrocarbons (PAHs),[20] but is very rarely found for anionic organic ligands bearing only one phenyl ring.

As shown in Figure 11, four pentafluoropropionate groups (O3−O4, O5−O6, O7−O8, and O9−O10) are utilized to bridge the Ag$_7$ aggregate and two [Ag$_2$(μ$_2$-C$_2$F$_5$CO$_2$)$_2$] linking units through the μ$_3$-*O*,*O′*,*O′* mode. The other μ$_3$-*O*,*O′*,*O′* pentafluoropropionate group O13−O14 connects adjacent asymmetric units to yield a coordination column along the [1 0 1] direction, which is also bridged by an aqua ligand O4W and stabilized by the aforementioned π–π stacking and Ag−C(aromatic) π interactions. Linkage of such coordi-

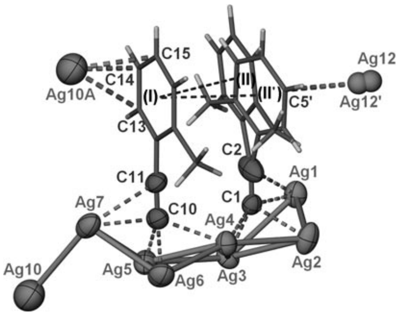


Figure 10. Atom labeling (50 % thermal ellipsoids) and coordination modes of the $2\text{-}MeC_6H_4C\equiv C^-$ ligand in **5**. Symmetry code: A: $1-x$, $2-y$, $-z$. Other ligands are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.17(1), C10–C11 1.22(1), Ag···Ag 2.874(1)–3.273(2).

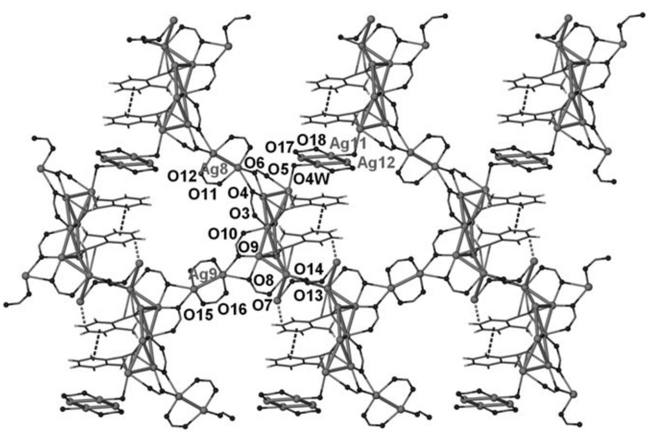


Figure 11. The 2D coordination network in complex **5** bridged by pentafluoropropionate groups and a series of $[Ag_2(\mu_2\text{-}C_2F_5CO_2)_2]$ units. All C_2F_5 moieties are omitted for clarity.

nation columns by two bridging units [(Ag8–Ag8)(O11–O12)$_2$] and [(Ag9–Ag9)(O15–O16)$_2$] thus generates a 2D coordination network parallel to the (1 0 1) plane.

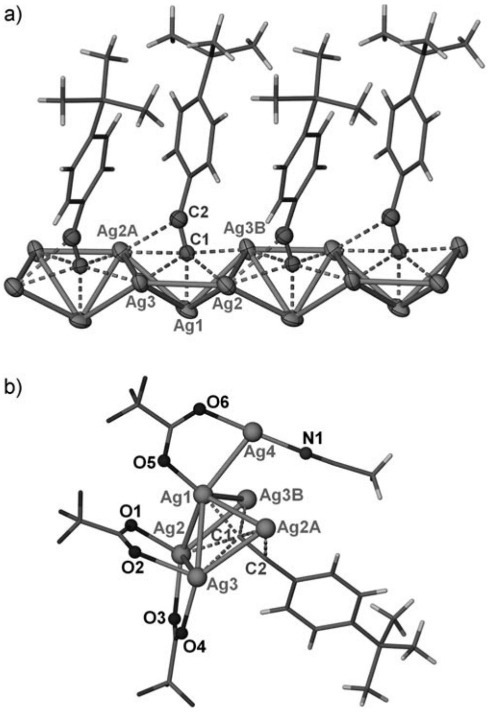


Figure 12. a) Linear silver column in **6** (50 % thermal ellipsoids) with the disordered *tert*-butylphenyl group shown in one of its possible orientations. Other ligands are omitted for clarity. Symmetry code: A: x, $^1/_2-y$, $z-^1/_2$; B: x, $^1/_2-y$, $^1/_2+z$. Selected bond lengths [Å]: C1–C2 1.22(3), Ag···Ag 2.890(9)–3.120(7). b) Coordination modes of trifluoroacetate groups and acetonitrile in **6**. Symmetry code: A: x, $^1/_2-y$, $z-^1/_2$; B: x, $^1/_2-y$, $^1/_2+z$.

$AgC\equiv CC_6H_4\mathit{t}Bu\text{-}4\cdot 3\,AgCF_3CO_2\cdot CH_3CN$ (6): Replacement of the methyl substituent at the 4-position of phenylethynide by a bulky *tert*-butyl group generates $AgC\equiv CC_6H_4\mathit{t}Bu\text{-}4\cdot 3\,AgCF_3CO_2\cdot CH_3CN$ (**6**), which is structurally analogous to the prototype complex $AgC\equiv CC_6H_5\cdot 3\,AgCF_3CO_2\cdot CH_3CN$, with an almost identical linear silver(I) column along the [001] direction composed of edge-sharing square-pyramidal Ag_5 baskets (Figure 12a). Each of the three trifluoroacetate groups (O1–O2, O3–O4, and O5–O6) in **6** similarly spans a Ag···Ag edge by the μ_2-*O,O′* mode (Figure 12b). However, interaction between aromatic rings in complex **6** is totally disrupted due to steric hindrance of the bulky *tert*-butyl group, which exhibits a disordered arrangement such that the entire $4\text{-}\mathit{t}BuC_6H_4$ moiety rotates about the $C_{ethynide}$–C_{phenyl} single bond.

The silver columns mutually interconnect through the linkage of weak hydrogen bonding (O6···H20C–C20, O–H 2.292 Å) and Ag···Ag interaction between two silver atoms of Ag4 type (Ag···Ag 3.728 Å) to generate a 2D network parallel to the *bc* plane (Figure 13).

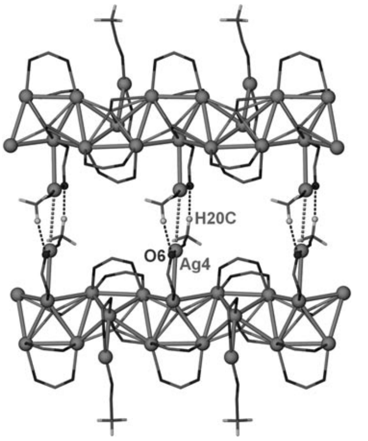


Figure 13. Coordination columns in complex **6** are connected along the *b* direction by hydrogen bond (O6···H20C–C20, O–H = 2.292 Å) and weak Ag···Ag interaction between two silver atoms of type Ag4 (Ag···Ag = 3.728 Å) to generate a 2D network. All *tert*-butylphenyl groups and CF_3 moieties are omitted for clarity.

$2\,AgC\equiv CC_6H_4\mathit{t}Bu\text{-}4\cdot 5\,AgCF_3CO_2$ (7): Complex **7** is obtained from the crystallization of $[AgC\equiv CC_6H_4\mathit{t}Bu\text{-}4]_n$ in an aqueous solution of $AgCF_3CO_2$ instead of a mixed water–acetonitrile solution of $AgCF_3CO_2$ as in complex **6**. As a result, the silver column in complex **6** transforms from a linear configuration to a zigzag one along the *b* direction, being accompanied by a change of the aforementioned μ_5-mode into μ_4- and μ_5-modes for two independent ethynide moieties.

As shown in Figure 14, 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 C13≡C14 by sharing one silver atom. All trifluoroacetate groups adopt the μ_3-*O*,*O'*,*O'* mode but play different roles: three of them (O3−O4, O5−O6, and O7−O8) link two adjacent Ag_8 aggregates to consolidate the resulting silver chain (Figure 15a), whereas O1−O2 and O9−O10 bridge adjacent silver chains to generate a 2D coordination network parallel to the (1 0 1) plane (Figure 15b).

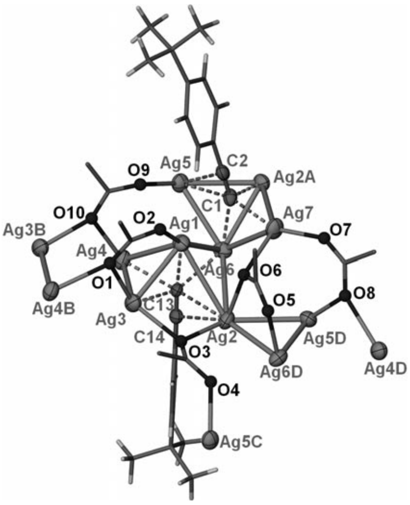


Figure 14. Coordination modes of the $tBuC_6H_4C\equiv C^-$ and trifluoroacetate groups in **7**. All fluorine atoms are omitted for clarity. Symmetry code: A: $1\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; B: $1-x$, $1-y$, $-z$; C: x, $y-1$, z; D: $1\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$.

$AgC\equiv CC_6H_3(CF_3)_2$-3,5·3 $AgCF_3CO_2\cdot(Et_3NH)CF_3CO_2\cdot H_2O$ (8): In the case of $AgC\equiv CC_6H_3(CF_3)_2$-3,5·3 $AgCF_3CO_2\cdot(Et_3NH)CF_3CO_2\cdot H_2O$ (**8**), the ethynide group C1≡C2 is likewise attached to a square-pyramidal Ag_5 basket, but in a μ_5-$\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode. Such an Ag_5 basket connects with its inversion-related one by sharing one slant edge and fusion of two silver atoms (Ag1 and Ag4) to produce a quasi-rhombic Ag_8 aggregate (Figure 16). Trifluoroacetate groups O1−O2 and O3−O4 surround this Ag_8 aggregate through the μ_3-*O*,*O'*,*O'* and μ_2-*O*,*O'* modes, respectively. The other two (O5−O6 and O7−O8) together with their inversion-related ones bridge adjacent Ag_8 aggregates to yield a coordination column along the [100] direction, which is also stabilized by a series of hydrogen bonds between O1W and two oxygen atoms of type O2 and O4.

The external counter-cation HEt_3N^+ is attached to this coordination chain through hydrogen bonding between O1W and N1, thus rendering the whole column electrically neutral (Figure 17).

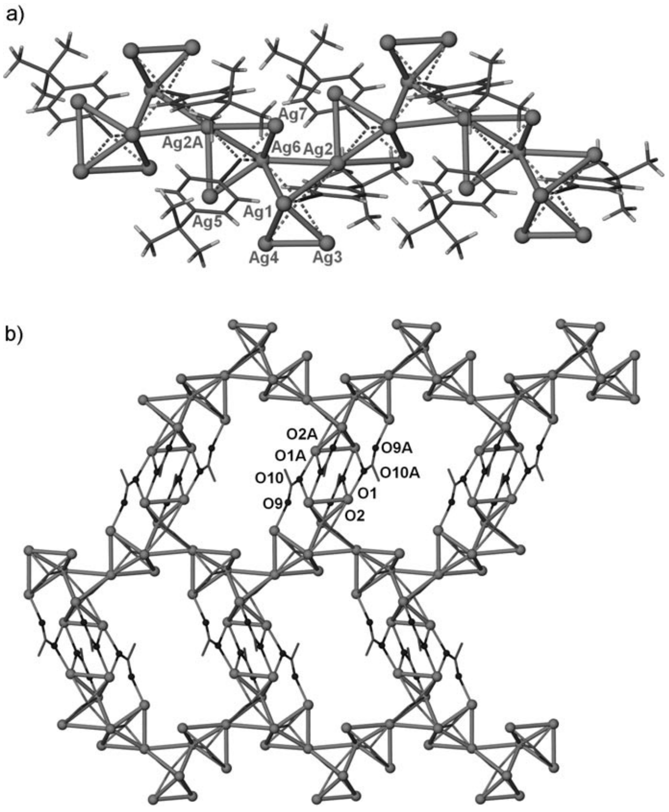


Figure 15. a) Silver column in complex **7** composed of Ag_4 and Ag_5 baskets through sharing one silver atom. Other ligands are omitted for clarity. Symmetry code: A: $1\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. Selected bond lengths [Å]: C1−C2 1.220(8), C13−C14 1.212(8), Ag···Ag 2.829(1)–3.343(1). b) The 2D coordination network in **7** through the linkage of adjacent zigzag silver chains by four trifluoroacetate groups. All fluorine atoms and *tert*-butylphenyl groups are omitted for clarity.

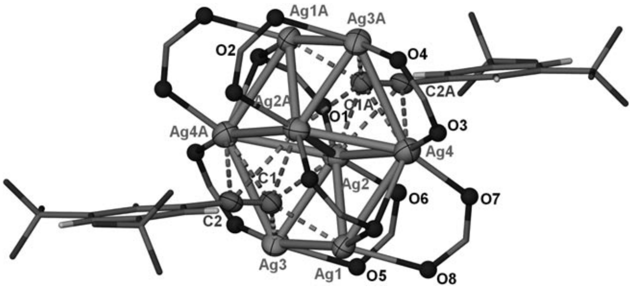


Figure 16. Coordination modes of the 3,5-$(CF_3)_2C_6H_3C\equiv C^-$ and trifluoroacetate groups in **8** (50 % thermal ellipsoids). Other ligands and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Symmetry code: A: $1-x$, $1-y$, $1-z$. Selected bond lengths [Å]: C1−C2 1.214(6), Ag···Ag 2.839(1)–3.337(1).

Supramolecular synthon: The invariable appearance of the μ_4- and μ_5- ligation modes of the ethynide moiety in the above series of eight complexes reaffirms the general utility of the silver–phenylethynide supramolecular synthon Ar−C≡C⊃Ag_n ($n=4$, 5) in the coordination network assembly.

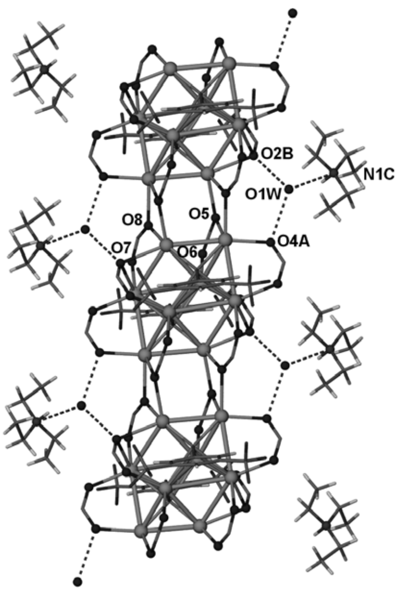


Figure 17. Coordination column in complex **8** bridged by four inter-unit trifluoroacetate groups and stabilized by two hydrogen bonds (O1W–O2B 2.846 Å, O1W–O4A 2.807 Å). The external HEt_3N^+ is attached to the column through the hydrogen bond at N1C–O1W = 2.766 Å. Symmetry code: A: 1–*x*, 1–*y*, 1–*z*; B: *x*–1, *y*, *z*; C: –*x*, 1–*y*, 1–*z*.

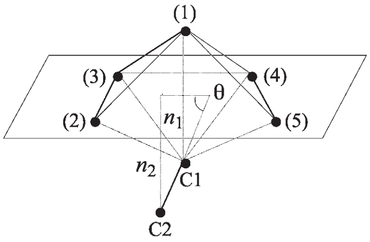
On the other hand, the coordination environment of the phenylethynide moiety can be affected by the position and steric bulk of the substituents on the aromatic ring. The coexisting anionic, neutral, and cationic ligands further influence supramolecular assembly to produce a variety of coordination networks. Weak intermolecular π–π stacking, C–H···π, and Ag–C(aromatic) interactions all contribute to stabilization of the crystal structure in these silver(I) complexes.

Linkage between silver baskets: In the crystal structures of complex **1**–**5**, stepwise placement of the methyl substituent closer to the ethynide moiety lowers its ligation number from five to four. This may be ascribed to the increasing effective steric bulk of the methyl group, which also impedes the approach of other anionic or neutral ligands to the silver atoms. Accordingly, the linkage mode between adjacent Ag_n baskets changes from edge-sharing, through vertex-sharing, to bridging by a pair of trifluoroacetate groups, to yield a silver column, a silver chain, and a linear array of bridged silver aggregates, respectively. In an analogous manner, presence of the bulky $C_6H_3(CF_3)_2$ group in **8** precludes the linkage of silver baskets into a column or chain.

Coordination environment of ethynide: As illustrated in Table 1, the μ_5 ethynide moieties in complexes **1**, **2**, **6**, **7**, and **8** are gradually shifted away from the square-pyramidal Ag_5 baskets upon increasing the steric bulk of the substituents.

Influence of coexisting carboxylate ligands: In contrast to the crystal structure of complex **1**, addition of the neutral ligand betaine in **2** causes the ethynide moiety to move away from the square-pyramidal Ag_5 basket in a slanted orientation with respect to the square plane (Table 1), leading to the transformation from a linear silver column composed of the fusion of square edges of adjacent Ag_5 baskets to a zigzag silver column through the sharing of one square edge and one pyramidal edge. As to the pair of 2-MePhC≡C^- complexes, changing the anionic ligand from $CF_3CO_2^-$ in **4** to $C_2F_5CO_2^-$ in **5** results in the fusion of two Ag_4 baskets and a 3D to a 2D network transformation. Apparently, the fusion of two Ag_4 baskets lessens the demand of anionic ligands from the charge balance point of view, which is surely favored for the bulkier $C_2F_5CO_2^-$ ligand. Likewise, $C_2F_5CO_2^-$ also hinders the linkage of adjacent 2D coordination networks into a 3D network.

Table 1. Parameters describing silver–ethynide interactions within the square-pyramidal Ag_5 basket composed of silver atoms (1)–(5): n_1 and n_2 indicate the perpendicular distance of C1 and C2 to the plane defined by silver atoms (2)–(5), respectively; θ denotes the angle between the ethynide moiety C1–C2 and the basal plane.



Complexes	n_1 [Å]	n_2 [Å]	(1)···plane [Å]	θ [°]	Deviation [Å]
$AgC{\equiv}CC_6H_5\cdot 3\,AgCF_3CO_2\cdot CH_3CN$[11]	0.266	1.471	1.788	83.0	0
1	0.276	1.426	1.853	85.2	0
	0.246	1.428	1.837	83.0	0
2	0.400	1.497	1.798	63.3	0.238
6	0.317	1.485	1.774	72.6	0.046
7	0.379	1.582	1.848	83.0	0.239
8	0.621	1.682	1.776	61.0	0.015

Weak interactions: In the present study, the abundant planar phenyl rings offer a good opportunity to probe π–π stacking and other weak interactions. The interactions between substituted phenyl rings within complex **1**–**4** are concomitantly weakened from infinite π–π stacking in **1**, incompletely parallel π–π stacking in **2**, through C–H···π interaction in **3**, to no interaction at all in **4**. Interestingly, two phenyl rings within a Ag_7 aggregate in complex **5** not only form inter-ring π–π stacking, but each bonds to a silver atom by the η^3 and η^1 mode. Moreover, a bulkier substituent in the phenyl ring impairs π–π stacking, which accounts for the variance between **1** and **6**, although these two complexes have an identical columnar structure. When this columnar structure is disturbed by the presence of other ligands in **7** and **8**, ethynide-bonded Ag_n aggregates are rearranged and π–π stacking between phenyl rings is thus totally interrupted.

Conclusion

In summary, the present work demonstrates that the ethynide moieties of five phenylethynide derivatives invariably adopt the μ_4- or μ_5-ligation mode in a series of eight silver(I) complexes, affirming that $\mathrm{Ar{-}C{\equiv}C{\supset}Ag}_n$ ($n=4$, 5) as a coordinated supramolecular synthon can be utilized in the assembly of coordination networks. The coordination environment of ethynide moieties in these silver(I) phenylethynide complexes can be fine-tuned by altering the substituents and their positions on the phenyl ring, resulting in modification of the linkage mode between $\mathrm{Ar{-}C{\equiv}C{\supset}Ag}_n$ ($n=4$, 5) supramolecular synthons to yield different infinite silver columns (**1**, **2**, and **6**), chains (**3** and **7**), or aggregates connected by bridging perfluorocarboxyalte ligands (**4**, **5**, and **8**). The supramolecular assembly process is also affected by the presence of other coexisting ligands and weak intermolecular interactions.

Experimental Section

Reagents: 4-Ethynyltoluene (Aldrich, purity >97%), 3-ethynyltoluene (Aldrich, >97%), 2-ethynyltoluene (Aldrich, >97%), 4-*tert*-butylphenylacetylene (Acros, >96%), 1-ethynyl-3,5-bis(trifluoromethyl)benzene (Aldrich, >97%), and trimethylammonioacetate (betaine) (Aldrich, >97%) were obtained commercially and used without further purification. Acetonitrile and triethylamine were purified according to standard procedures. All synthetic reactions yielding polymeric starting materials were carried out under a nitrogen atmosphere.

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

[AgC≡CC$_6$H$_4$Me-4]$_n$: This was prepared in pale yellow powdery form according to the literature method.[21] Silver nitrate (0.742 g, 4.4 mmol) was dissolved in acetonitrile (50 mL). Then 4-ethynyltoluene (0.464 g, 4.0 mmol) and triethylamine (1.83 mL, 13.2 mmol) were added with vigorous stirring and the mixture was stirred for 24 h. The pale yellow precipitate formed was collected by filtration, washed thoroughly with acetonitrile (3×10 mL) and deionized water (3×20 mL), and stored in wet form. Yield: 0.679 g (87%). IR: $\tilde{\nu}=2033\ \mathrm{cm^{-1}}$ (m, ν(C≡C)).

[AgC≡CC$_6$H$_4$Me-3]$_n$, [AgC≡CC$_6$H$_4$Me-2]$_n$, [AgC≡CC$_6$H$_4$*t*Bu-4]$_n$, and [AgC≡CC$_6$H$_3$(CF$_3$)$_2$–3,5]$_n$: These were prepared by a similar synthetic procedure employing 3-ethynyltoluene, 2-ethynyltoluene, 4-*tert*-butylphenylacetylene, and 1-ethynyl-3,5-bis(trifluoromethyl)benzene, repectively. Yield: ≈90%. [AgC≡CC$_6$H$_4$Me-3]$_n$: IR: $\tilde{\nu}=2038\ \mathrm{cm^{-1}}$ (m, ν(C≡C)); [AgC≡CC$_6$H$_4$Me-2]$_n$: IR: $\tilde{\nu}=2050\ \mathrm{cm^{-1}}$ (m, ν(C≡C)); [AgC≡CC$_6$H$_4$*t*Bu-4]$_n$: IR: $\tilde{\nu}=2048\ \mathrm{cm^{-1}}$ (w, ν(C≡C)); [AgC≡CC$_6$H$_3$(CF$_3$)$_2$–3,5]$_n$: IR: $\tilde{\nu}=2024\ \mathrm{cm^{-1}}$ (m, ν(C≡C)).

2 AgC≡CC$_6$H$_4$Me-4·6 AgCF$_3$CO$_2$·1.5 CH$_3$CN (1): AgCF$_3$CO$_2$ (0.223 g, 1 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 [AgC≡CC$_6$H$_4$Me-4]$_n$ (≈0.1 g) solid was added to the solution. After stirring for about half an hour, the solution was filtered and the filtrate stored under ambient conditions. After several days, colorless needle-like crystals of **1** were deposited in about 55% yield. Compound **1** melts from 92.7 °C to 94.2 °C. Elemental analysis calcd (%) for $\mathrm{C_{33}H_{18.5}F_{18}O_{12}N_{1.5}Ag_8}$: C 21.62, H 1.02, N 1.15; found: C 22.02, H 1.29, N 1.04. IR: $\tilde{\nu}=2021\ \mathrm{cm^{-1}}$ (w, ν(C≡C)).

AgC≡CC$_6$H$_4$Me-4·3 AgCF$_3$CO$_2$·(CH$_3$)$_3$N$^+$CH$_2$CO$_2^-$ (2): AgCF$_3$CO$_2$ (0.220 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol) were dissolved in de-ionized water (1 mL). Then [AgC≡CC$_6$H$_4$Me-4]$_n$ (≈0.1 g) was added to the solution. After stirring for an hour with the addition of trimethylammonioacetate (betaine, ≈0.15 g), the solution was filtered off. After standing for several days, colorless blocklike crystals of **2** were collected in about 30% yield. Compound **2** melts in the range of 143.5 °C to 145.2 °C. Elemental analysis calcd (%) for $\mathrm{C_{20}H_{18}F_9O_8NAg_4}$: C 23.95, H 1.81, N 1.40; C 23.62, H 1.53, N 1.18; IR: $\tilde{\nu}=2008\ \mathrm{cm^{-1}}$ (vw, ν(C≡C)).

AgC≡CC$_6$H$_4$Me-3·2 AgCF$_3$SO$_3$ (3): [AgC≡CC$_6$H$_4$Me-3]$_n$ (≈0.1 g) was added to 1 mL of a concentrated aqueous solution of AgCF$_3$SO$_3$ (0.255 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol) in a beaker with stirring until saturated. The excess amount of [AgC≡CC$_6$H$_4$Me-3]$_n$ was filtered off. The filtrate stands in the dark at room temperature for a few days. Then colorless platelike crystals of **3** were deposited in about 30% yield. Compound **3** remains as transparent crystals under heating until 240 °C and turn black very quickly over this temperature. Elemental analysis calcd (%) for $\mathrm{C_{11}H_7F_6O_6S_2Ag_3}$: C 17.93, H 0.96; found: C 17.60, H 1.01; IR: $\tilde{\nu}=2016\ \mathrm{cm^{-1}}$ (w, ν(C≡C)).

AgC≡CC$_6$H$_4$Me-2·4 AgCF$_3$CO$_2$·H$_2$O (4): AgCF$_3$CO$_2$ (0.223 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol) were dissolved in de-ionized water (1 mL). Then [AgC≡CC$_6$H$_4$Me-2]$_n$ (≈0.1 g) solid was added to the solution. After stirring for about half an hour, the solution was filtered. After several days, colorless platelike crystals of **4** were deposited in about 25% yield. Compound **4** melts from 133.1 °C to 135.1 °C. Elemental analysis calcd (%) for $\mathrm{C_{17}H_9F_{12}O_9Ag_5}$: C 18.16, H 0.81; found: C 18.20, H 0.67; IR: 2008 cm^{-1} (w, ν(C≡C)).

2 AgC≡CC$_6$H$_4$Me-2·9 AgC$_2$F$_5$CO$_2$·6 H$_2$O (5): [AgC≡CC$_6$H$_4$Me-2]$_n$ (≈0.1 g) solid was added to 1-mL aqueous solution of AgC$_2$F$_5$CO$_2$ (0.271 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol). After stirring for one hour, the solution was filtered and the filtrate stands under ambient condition for a few days. Then colorless blocklike crystals of **5** deposit in about 25% yield. Compound **5** transforms to powder over 120 °C and decomposes above 250 °C. Elemental analysis calcd (%) for $\mathrm{C_{45}H_{26}F_{45}O_{24}Ag_{11}}$: C 18.06, H 0.88; found: C 18.44, H, 0.72; IR: $\tilde{\nu}=2006\ \mathrm{cm^{-1}}$ (w, ν(C≡C)).

AgC≡CC$_6$H$_4$*t*Bu-4·3 AgCF$_3$CO$_2$·CH$_3$CN (6): [AgC≡CC$_6$H$_4$*t*Bu-4]$_n$ (≈0.1 g) was added to a 1-mL concentrated water–acetonitrile mixed solution (v/v 5:1) of AgCF$_3$CO$_2$ (0.220 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol) in a beaker with stirring until saturated. The excess [AgC≡CC$_6$H$_4$*t*Bu-4]$_n$ was filtered off. After a few days, pale yellow needle-like crystals of **6** were deposited in about 35% yield. Compound **6** has a melting point ranging from 72.2 °C to 74.0 °C. Elemental analysis calcd (%) for $\mathrm{C_{20}H_{16}F_9O_6NAg_4}$: C 24.80, H 1.66, N 1.44; found: C 25.12, H 1.46, N 1.38; IR: $\tilde{\nu}=2021\ \mathrm{cm^{-1}}$ (w, ν(C≡C)).

2 AgC≡CC$_6$H$_4$*t*Bu-4·5 AgCF$_3$CO$_2$ (7): A synthetic procedure similar to that which yielded compound **6** with de-ionized water instead of water–acetonitrile mixed solvent was utilized to obtain colorless platelike crystals of **7** in about 20% yield. Compound **7** turns black above 145 °C and melts from 184.2 °C to 186.0 °C. Elemental analysis calcd (%) for $\mathrm{C_{34}H_{26}F_{15}O_{10}Ag_7}$: C 24.98, H 1.60; found: C 24.64, H 1.34; IR: $\tilde{\nu}=2033\ \mathrm{cm^{-1}}$ (w, ν(C≡C)).

AgC≡CC$_6$H$_3$(CF$_3$)$_2$-3,5·3 AgCF$_3$CO$_2$·(Et$_3$NH)CF$_3$CO$_2$·H$_2$O (8): AgCF$_3$CO$_2$ (0.223 g, 1 mmol) and AgBF$_4$ (0.382 g, 2 mmol) were dissolved in de-ionized water (1 mL). Then [AgC≡CC$_6$H$_4$Me-2]$_n$ (≈0.1 g) solid was added to the solution. After stirring with the addition of triethylamine (0.1 mL) for about half an hour, the solution was filtered and the filtrate was placed into a −10 °C refrigerator. After several days, pale yellow blocklike crystals of **8** were deposited in about 10% yield. Compound **8** melts from 81.2 °C to 83.0 °C. Elemental analysis calcd (%) for $\mathrm{C_{24}H_{21}F_{18}O_9NAg_4}$: C 23.23, H 1.70, N 1.13; found: C 23.42, H 1.41, N 1.21; IR: $\tilde{\nu}=2020\ \mathrm{cm^{-1}}$ (w, ν(C≡C)).

X-ray crystallography: Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1.5° < \theta < 28°$. An empirical absorption correction was applied by using the SADABS program[22] to all the compounds. The structures were solved by direct methods, and non-hydrogen atoms were located from difference-Fourier maps. All the non-hydrogen atoms, unless otherwise noted, were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program.[23]

Crystal data for 1: 2 AgC≡CC$_6$H$_4$Me-4·6 AgCF$_3$CO$_2$·1.5 CH$_3$CN, $\mathrm{C_{33}H_{18.5}F_{18}O_{12}N_{1.5}Ag_8}$, $M=1832.92$, monoclinic, space group *C2m* (no. 12), $a=27.989(4)$, $b=7.312(1)$, $c=23.334(4)$ Å, $\beta=103.464(3)°$, $V=$

4644(1) Å^3, $Z=4$, $T=293$ K, $\rho_{calcd}=2.619$ g cm^{-3}. The structure, refined on F^2, converged for 4442 unique reflections ($R_{int}=0.0531$) and 2955 observed reflections with $I>2\sigma(I)$ to give $R1=0.0839$ and $wR2=0.2841$ and a goodness-of-fit = 1.050. Three atoms (F32, F51 and F52) were refined isotropically. The hydrogen atoms of the acetonitrile group (N2–C33–C34) were not added due to the disorder of this group. Three silver atoms (Ag2, Ag3, and Ag4) are disordered with 85 % occupancy in contrast to another positions (Ag2′, Ag3′ and Ag4′) of 15 %. The fluorine atoms of one trifluoroacetate group (O3–F32) were also found disordered.

Crystal data for 2: $AgC{\equiv}CC_6H_4Me$-4·3 $AgCF_3CO_2\cdot(CH_3)_3N^+CH_2CO_2^-$, $C_{20}H_{18}F_9O_8NAg_4$, $M=1002.83$, orthorhombic, space group $Pna2_1$ (no. 33), $a=7.652(1)$, $b=22.879(3)$, $c=16.243(2)$ Å, $V=2843.8(5)$ Å^3, $Z=4$, $T=293$ K, $\rho_{calcd}=2.342$ g cm^{-3}. The structure, refined on F^2, converged for 6665 unique reflections ($R_{int}=0.0305$) and 5970 observed reflections with $I > 2\sigma(I)$ to give $R1=0.0271$ and $wR2=0.0650$ and a goodness-of-fit = 1.041. Silver atom Ag3 has two disordered positions with an occupancy ration 0.9:0.1. And the disordered fluorine atoms of trifluoroacetate group (O3–O4) can be differentiated as two parts in a ratio of 0.7:0.3.

Crystal data for 3: $AgC{\equiv}CC_6H_4Me$-3 ·2 $AgCF_3SO_3$, $C_{11}H_7F_6O_6S_2Ag_3$, $M=736.90$, triclinic, space group $P1$ (no. 2), $a=4.730(1)$, $b=13.119(2)$, $c=14.547(2)$ Å, $\alpha=84.522(3)$, $\beta=87.602(3)$, $\gamma=87.510(3)$ °, $V=897.0(3)$ Å^3, $Z=2$, $T=293$ K, $\rho_{calcd}=2.728$ g cm^{-3}. The structure, refined on F^2, converged for 4365 unique reflections ($R_{int}=0.0254$) and 3651 observed reflections with $I>2\sigma(I)$ to give $R1=0.0386$ and $wR2=0.1149$ and a goodness-of-fit = 1.057. The hydrogen atom forming the C–H···π interaction was located from a difference map.

Crystal data for 4: $AgC{\equiv}CC_6H_4Me$-2·4 $AgCF_3CO_2\cdot H_2O$, $C_{17}H_9F_{12}O_9Ag_5$, $M=1124.57$, monoclinic, space group $P2_1/n$ (no. 14), $a=16.650(2)$, $b=9.230(1)$, $c=17.872(2)$ Å, $\beta=105.592(2)$°, $V=2645.5(5)$ Å^3, $Z=4$, $T=293$ K, $\rho_{calcd}=2.818$ g cm^{-3}. The structure, refined on F^2, converged for 6549 unique reflections ($R_{int}=0.0350$) and 4987 observed reflections with $I>2\sigma(I)$ to give $R1=0.0319$ and $wR2=0.0843$ and a goodness-of-fit = 1.018. Hydrogen atoms of water molecules were not included in the refinement. The fluorine atoms of every trifluoroacetate group are differentiated as two or three parts.

Crystal data for 5: 2 $AgC{\equiv}CC_6H_4Me$-2·9 $AgC_2F_5CO_2\cdot 6H_2O$, $C_{45}H_{26}F_{45}O_{24}Ag_{11}$, $M=2992.14$, triclinic, space group $P1$ (no. 2), $a=15.162(2)$, $b=15.214(2)$, $c=19.876(2)$ Å, $\alpha=92.668(2)$, $\beta=105.498(2)$, $\gamma=110.670(2)$°, $V=4082.9(8)$ Å^3, $Z=2$, $T=293$ K, $\rho_{calcd}=2.424$ g cm^{-3}. The structure, refined on F^2, converged for 14340 unique reflections ($R_{int}=0.0278$) and 9266 observed reflections with $I>2\sigma(I)$ to give $R1=0.0494$ and $wR2=0.1502$ and a goodness-of-fit = 1.010. Hydrogen atoms of water molecules were not included in the refinement. The positions and occupancy ratios of silver atoms Ag11 and Ag12 are determined by the structural refinement. Three high peaks around Ag11 and Ag12 are assigned as their corresponding disorder. The pentafluoroethyl moieties of two pentafluoropropionate groups (O13–O14 and O17–O18) have two orientations, which are processed as two disordered parts. One phenyl ring is also found disordered.

Crystal data for 6: $AgC{\equiv}CC_6H_4tBu$-4·3 $AgCF_3CO_2\cdot CH_3CN$, $C_{20}H_{16}F_9O_6NAg_4$, $M=968.82$, orthorhombic, space group $Pnc2$ (no. 30), $a=17.958(2)$, $b=20.441(2)$, $c=7.350(1)$ Å, $V=2698.0(6)$ Å^3, $Z=4$, $T=293$ K, $\rho_{calcd}=2.353$ g cm^{-3}. The structure, refined on F^2, converged for 3674 unique reflections ($R_{int}=0.0589$) and 2371 observed reflections with $I>2\sigma(I)$ to give $R1=0.0853$ and $wR2=0.2539$ and a goodness-of-fit = 1.090. Seven atoms (C9, C10, C11, C12, C18, F31, and F32) were refined isotropically. Three silver atoms (Ag1, Ag2, and Ag3) are also processed into two parts with the ratio of 0.8:0.2.

Crystal data for 7: 2 $AgC{\equiv}CC_6H_4tBu$-4·5 $AgCF_3CO_2$, $C_{34}H_{26}F_{15}O_{10}Ag_7$, $M=1634.64$, monoclinic, space group $P2_1/n$ (No. 14), $a=17.417(4)$, $b=11.245(2)$, $c=24.091(5)$ Å, $\beta=111.118(5)$°, $V=4401(2)$ Å^3, $Z=4$, $T=293$ K, $\rho_{calcd}=2.467$ g cm^{-3}. The structure, refined on F^2, converged for 10935 unique reflections ($R_{int}=0.0649$) and 5825 observed reflections with $I > 2\sigma(I)$ to give $R1=0.0458$ and $wR2=0.1145$ and a goodness-of-fit = 1.019. The fluorine atoms of trifluoroacetate group O3-O4 are differentiated as two parts in 0.65:0.35 ratio.

Crystal data for 8: $AgC{\equiv}CC_6H_3(CF_3)_2$-3,5·3 $AgCF_3CO_2\cdot$-$(Et_3NH)CF_3CO_2\cdot H_2O$, $C_{24}H_{21}F_{18}O_9NAg_4$, $M=1240.87$, monoclinic, space group $P2_1/n$ (no. 14), $a=8.848(1)$, $b=28.361(4)$, $c=15.800(2)$ Å, $\beta=105.526(3)$°, $V=3820.2(9)$ Å^3, $Z=4$, $T=293$ K, $\rho_{calcd}=2.154$ g cm^{-3}. The structure, refined on F^2, converged for 9512 unique reflections ($R_{int}=0.0344$) and 6683 observed reflections with $I>2\sigma(I)$ to give $R1=0.0408$ and $wR2=0.1105$ and a goodness-of-fit = 1.025. All fluorine atoms are processed into two disordered parts.

CCDC-632246 (**1**), CCDC-632247 (**2**), CCDC-632248 (**3**), CCDC-632249 (**4**), CCDC-632250 (**5**), CCDC-632251 (**6**), CCDC-632252 (**7**), and CCDC-632253 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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