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Silver(I)−Ethynide Supramolecular Synthons in the Assembly of $\pi-\pi$ Stacked Infinite Columns[⊥]

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In a series of four silver(I) complexes containing nitrate and ethynide ligands attached to different aromatic rings, namely, $[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 5AgNO_3\cdot 3H_2O$ (**1**), $2[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]\cdot 10AgNO_3$ (**2**), $[(AgC{\equiv}C)\text{-}3\text{-py}]\cdot 3AgNO_3$ (**3**), and $2[(AgC{\equiv}C)\text{-}2\text{-pyz}]\cdot 6AgNO_3\cdot 3H_2O$ (**4**) (py = pyridine; pyz = pyrazine), intermolecular $\pi-\pi$ interaction dominates the assembly of supramolecular synthons $Ag_4{\subset}C{\equiv}C{-}R{-}C{\equiv}C{\supset}Ag_4$ and $R{-}C{\equiv}C{\supset}Ag_4$ to give infinite columnar structures exhibiting distinct $\pi-\pi$ stacking modes. The decrease in aromaticity of the ring moieties in **1**, **3**, and **4** is accompanied by weakened $\pi-\pi$ stacking, transforming from the parallel face-to-face mode in **1**, through a displaced stacked arrangement in **3**, to the edge-to-face contact in **4**. Replacement of one ethynide moiety of *m*-phenylenediethynide ligand in **1** by nitrogen coordination sites on the aromatic ring in **3** and **4** was found to have a limited effect on interrupting the whole $\pi-\pi$ stacking infinite column.

Introduction

$\pi-\pi$ stacking is an important noncovalent intermolecular interaction,[1] which not only plays a pivotal role in the self-assembly of building blocks with aromatic moieties in crystal engineering[2] but also contributes much to the binding and conformational relationship between biological molecules.[3] Aromatic−aromatic stacking in complexes generally occurs in three distinctive modes: face-to-face (perfect alignment or offset), edge-to-face, and T-shaped, which can enhance the stability of the complexes both in solution and in the solid state. In particular, it can combine with coordination bonds to build up elaborate supramolecular architectures.[2] Furthermore, recent research efforts to investigate organic field-effect transistors (OFET)[4] and molecular conducting materials[5] also concentrate on enhancing the efficiency of $\pi-\pi$ stacking between aromatic rings, thus leading to a large transfer integral between molecules that is crucial for high carrier mobility.[6] However, as the aromatic−aromatic interaction is weakly directional, controlled packing of aromatic rings in a given crystal lattice remains a formidable challenge.

Our recent structural studies of a series of silver double salts containing phenylethynide[7] or isomeric phenylenediethynide[8] metal−ligand supramolecular synthons[9] indicate that the phenyl or phenylene rings invariably partake in continuous or discontinuous $\pi-\pi$ stacking. To elucidate the effect of $\pi-\pi$ interaction in coordination network assembly and compare the efficiency of stacking between different kinds of aromatic rings, we utilized an aqueous solution of silver nitrate to crystallize four kinds of polymeric starting materials $[Ag_2(C{\equiv}C{-}R{-}C{\equiv}C)]_n$ ($R = m\text{-}C_6H_4$, $2,3\text{-}C_4H_2S$) and $[R{-}C{\equiv}CAg]_n$ (R = 3-pyridyl, 2-pyrazinyl). In contrast to frequently used anions such as trifluoroacetate and pentafluoropropionate in our previous work,[7,8] the nitrate group stabilizes the silver−ethynide aggregate through coordination, and its diminished steric bulk favors $\pi-\pi$ stacking of

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[⊥] Dedicated to Prof. Wei-Yuan Huang on the occasion of his 87th birthday.

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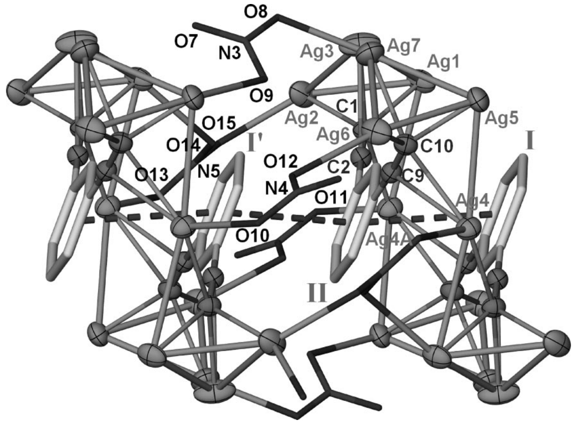

Figure 1. Atom labeling (50% thermal ellipsoids) and coordination modes of ligands in $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 5AgNO_3\cdot 3H_2O$, **1**. The infinite columnar tube is composed of $(m\text{-}C{\equiv}CC_6H_4\text{-}C{\equiv}C)_2@Ag_{14}$ units bridged by nitrate groups and stabilized by continuous $\pi-\pi$ stacking. Other ligands are omitted for clarity. Symmetry code: A $1-x, -y, 1-z$. Selected bond lengths and distances (Å): C1−C2 1.214(6), C9−C10 1.220(6), Ag···Ag 2.718(4)−3.140(3).

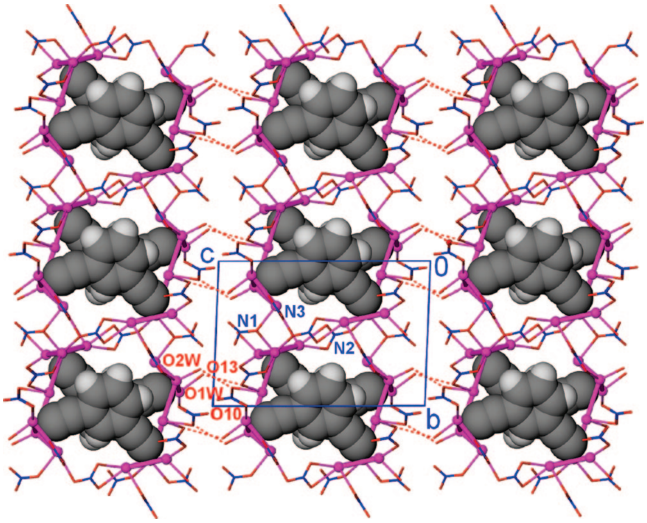

Figure 2. 3-D network in **1** composed of coordination layers cross-linked by hydrogen bonds between aqua ligands (O1W and O2W) and nitrate groups (N4 and N5). Selected hydrogen bonds (Å): O1W···O13 2.927, O2W···O10 2.753. Ag, purple; C, black; H, gray; O, red; N, blue.

adjacent aromatic rings in supramolecular assembly via the metal−ligand synthons $Ag_4{\subset}C{\equiv}C{-}R{-}C{\equiv}C{\supset}Ag_4$ (R = $m\text{-}C_6H_4$, $2,3\text{-}C_4H_2S$) and $R{-}C{\equiv}C{\supset}Ag_4$ (R = 3-pyridyl, 2-pyrazinyl). Herein we report the synthesis and structural characterization of four silver(I) double salts containing arylethynide anions, namely, $[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 5AgNO_3\cdot 3H_2O$ (**1**), $2[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]\cdot 10AgNO_3$ (**2**), $[(AgC{\equiv}C)\text{-}3\text{-}py]\cdot 3AgNO_3$ (**3**), and $2[(AgC{\equiv}C)\text{-}2\text{-}pyz]\cdot 6AgNO_3\cdot 3H_2O$ (**4**) (py = pyridine; pyz = pyrazine), in which $\pi-\pi$ stacking induces the formation of a columnar structure and can be fine-tuned by the electronic effect of the aromatic rings.

Results and Discussion

Complexes **1**−**4** were deposited from crystallization of the corresponding crude polymeric compounds $[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]_n$,[8] $[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]_n$, $[(AgC{\equiv}C)\text{-}3\text{-}py]_n$ and $[(AgC{\equiv}C)\text{-}2\text{-}pyz]_n$, in a concentrated aqueous solution of $AgNO_3$. The latter three new polymeric starting materials were prepared from the reaction of $AgNO_3$ with their respective alkynyl ligands in the presence of NEt_3. The synthetic procedures are based on the fact that silver−ethynide complexes have poor solubility in common solvents and can be easily separated by precipitation.

In the double salt $[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot 5AgNO_3\cdot 3H_2O$, **1**, the *m*-phenylenediethynide ligand adopts a μ_8 bonding mode, each terminal ethynide being surrounded by a butterfly-shaped Ag_4 basket (Figure 1). This silver−phenylenediethynide aggregate coalesces with its inversion-related one in a face-to-face fashion by sharing two silver atoms to constitute a building unit, which is further stabilized by $\pi-\pi$ stacking between two completely parallel phenylene rings ($I-II_{cent-cent}$ = 3.655 Å). This $(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)_2@Ag_{14}$ (the symbol @ means encapsulated by) unit also occurs in our previously reported complex $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)\cdot 6AgCF_3CO_2\cdot 3CH_3CN\cdot 2.5H_2O$,[8] in which each similar $\pi-\pi$ interaction stabilized unit is extended by an argentophilic Ag···Ag interaction[10] to form a silver double chain. Herein, such $[Ag_{14}(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)_2]$ units are linked together by bridging nitrate groups of type N3, N4, and N5 and an interunit $\pi-\pi$ interaction ($II-I'_{cent-cent}$ = 3.636 Å) to engender an infinite 1.1 × 1.1 nm columnar tube (Figure 1). With reference to $Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)\cdot 6AgCF_3CO_2\cdot 3CH_3CN\cdot 2.5H_2O$,[8] replacing the trifluoroacetate counteranion by nitrate breaks up the silver double chain, and the $\pi-\pi$ interaction between *m*-phenylene rings is converted from pairwise to continuous. Adjacent infinite tubes are interconnected through the linkage of nitrate groups N1, N2, and N3 via different μ_2-*O,O*, μ_3-*O,O′,O″*, and μ_3-*O,O′,O′* bonding modes, respectively (Figure S1), to generate a 2-D coordination network parallel to the *ab* plane, and such networks are further bridged by hydrogen bonding between the aqua ligands (O1W and O2W) and nitrate groups N4 and N5 to produce a 3-D network (Figure 2).

We subsequently grafted ethynide moieties on the 2- and 3-positions of the thiophene ring to generate the double salt $2[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]\cdot 10AgNO_3$ (**2**), in which each ethynide moiety of three independent thiophene-2,3-diethynide ligands is bound to different Ag_4 baskets (Figure 3). The 12 independent nitrate groups (N1 to N12) in this complex play diverse roles in building up the crystal structure, ranging from being a free anion (N12) to a bridging ligand in the complex μ_4-*O,O,O′,O′* coordination mode (Figure S2). Two Ag_4 baskets attached to the same thiophene-2,3-diethynide ligand coalesce by sharing one vertex to produce a $C_4H_2S\text{-}2,3\text{-}(C{\equiv}C)_2{\supset}Ag_7$ aggregate, and such aggregates are bridged by a series of nitrate groups (N3, N5, N10, and N11) to engender a coordination ribbon along the *a* direction (Figure 4). The thiophene rings on this coordination ribbon extend outward

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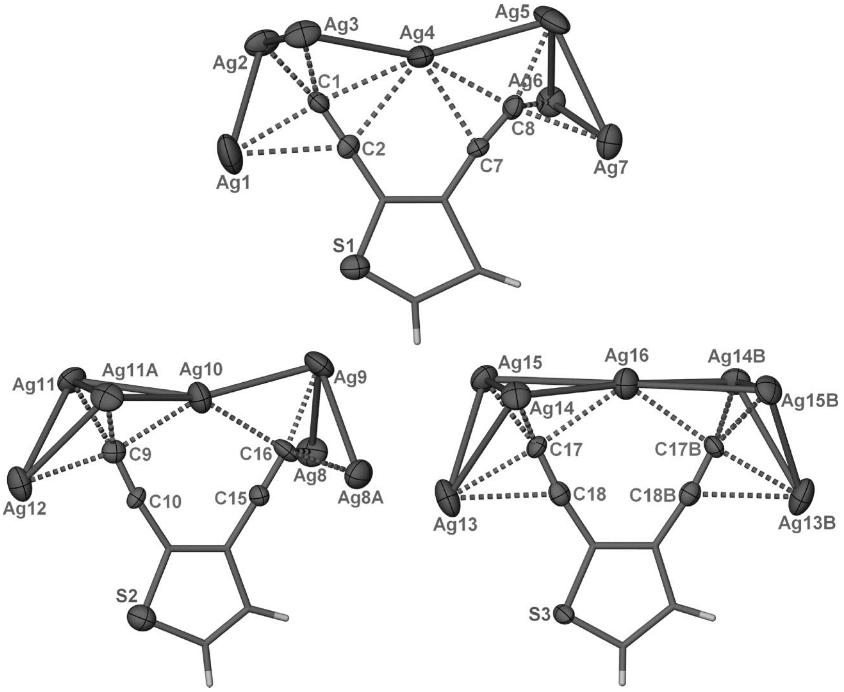

Figure 3. Atom labeling (50% thermal ellipsoids) and coordination modes of three independent thiophene-2,3-diethynide ligands in $2[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]\cdot 10AgNO_3$, **2**. Other ligands are omitted for clarity. Symmetry code: A 1/2 −*x*, *y*, *z*; B −*x*, −*y*, *z*. Selected bond lengths and distances (Å): C1−C2 1.202(12), C7−C8 1.215(12), C9−C10 1.223(17), C15−C16 1.204(17), C17−C18 1.203(12), Ag···Ag 2.830(1)−3.339(1).

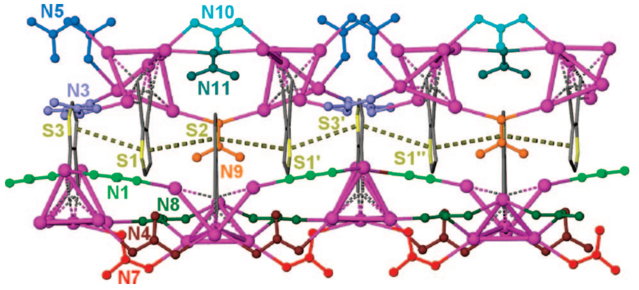

Figure 4. Composite column in **2** composed of two coordination ribbons, which are bridged by different nitrate groups (indicated in different colors).

Table 1. Contact Parameters between Adjacent Aromatic Rings in 1−4

	ring	cent−cent distance (Å)	interplanar separation (Å)	dihedral angle (deg)	shortest C−C distance (Å)
1	I−II	3.655	3.337	0	3.381
	II−I′	3.636	3.347	0	3.351
2	S3−S1	3.786	3.511	0.7	3.500
	S1−S2	3.756	3.522	6.9	3.516
	S2−S1′	3.801	3.541	6.8	3.516
3	I−II	3.912	3.529	0	3.597
	II−I′	4.639	3.675	0	3.706
4	I−II	4.062		25.6	3.322
	II−I′	4.019		25.6	3.333

and interdigitate with those belonging to an adjacent ribbon bridged by nitrate groups (N1, N4, N7, and N8), yielding a composite column stabilized by continuous $\pi-\pi$ stacking between nearly parallel thiophene rings (Figure 4). As tabulated in Table 1, the centroid−centroid distances (3.756−3.801 Å) between three independent thiophene rings (S1, S2, and S3) are somewhat longer than typical values of 3.6−3.7 Å in numerous reported thiophene and polythiophene complexes.[11] These composite columns are arranged in a pseudohexagonal array and interlinked by the remaining coordination sites of nitrate groups to generate a robust 3-D coordination network relative to the hybrid coordination-hydrogen-bonded 3-D network in **1** (Figure 5).

Next, we replaced *m*-phenylenediethynide by 3-pyridylethynide to alter the coordination environment of the central aromatic ring, thereby probing the $\pi-\pi$ stacking between electron-deficient pyridyl rings. In the crystal structure of $[(AgC{\equiv}C)\text{-}3\text{-py}]\cdot 3AgNO_3$ (**3**), the ethynide moiety is bound to a butterfly-shaped Ag_4 basket (atoms Ag1 to Ag4) and the nitrogen atom of the pyridine ring to silver atom Ag1A (Figure 6). As shown in Figure 7a, these $Ag{-}NC_5H_4{-}C{\equiv}C{\supset}Ag_4$ units are linked by three types of nitrate groups (N2, N3, and N4) that adopt different coordination modes, μ_2-*O,O′*, μ_2-*O,O*, and μ_3-*O,O′,O″*, respectively, and further stabilized by continuous $\pi-\pi$ stacking between adjacent pyridyl rings to produce a 1.4 × 1.4 nm infinite column along the *a* direction (Figure 7b). Although the centroid−centroid distances (3.92 and 4.64 Å) are longer than the upper limit of 3.8 Å for pyridyl rings,[2] relatively close interplanar separations between two completely parallel pyridyl rings of 3.53−3.68 Å indicate that weak continuous zigzag $\pi-\pi$ interaction stabilizes the whole structure (Figure 7a). These columns are arranged in a pseudohexagonal array with the Ag_4 aggregates serving as nodes to produce a 3-D coordination network (Figure 8).

Finally, we explore the effect of using the more electron-deficient pyrazine ring on the $\pi-\pi$ interaction. As shown in Figure 9, two independent 2-pyrazinylethynide ligands are involved in the crystal structure of $2[(AgC{\equiv}C)\text{-}2\text{-pyz}]\cdot 6\text{-}$

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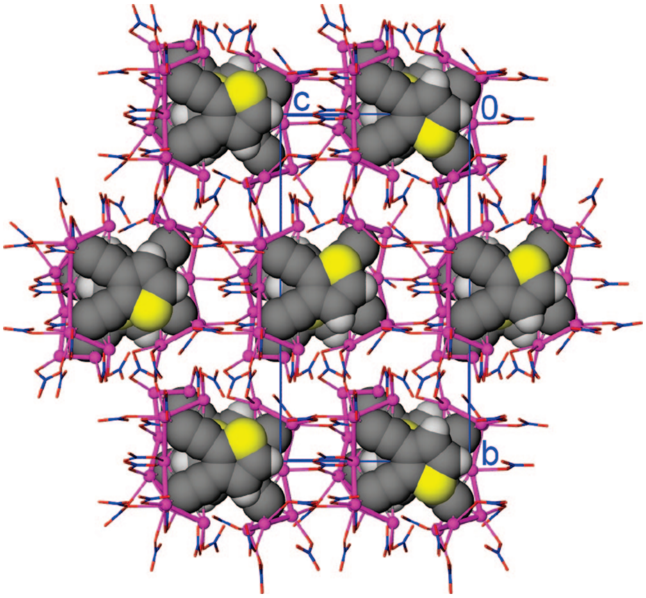

Figure 5. Pseudohexagonal array of composite columns in **2** cross-linked by a series of nitrate groups to yield a 3-D coordination network. The thiophene-2,3-diethynide ligands are illustrated in space-filling type. Ag, purple; C, black; H, gray; O, red; N, blue.

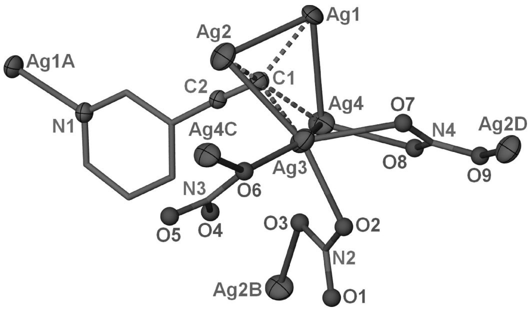

Figure 6. Atom labeling (50% possibility) and coordination modes of 3-pyridylethynide and nitrate groups in [(AgC≡C)-3-py]·3AgNO$_3$, **3**. Symmetry code: A $1/2 - x$, $1/2 + y$, $3/2 - z$; B $1/2 + x$, $1/2 - y$, $1/2 + z$; C $x - 1$, y, z; D $-x$, $-y$, $1 - z$. Selected bond lengths and distances (Å): C1−C2 1.216(4), Ag···Ag 2.864(4)−3.130(4).

AgNO$_3$·3H$_2$O (**4**), with each ethynide moiety (C1≡C2 and C7≡C8) bonding to a butterfly-shaped Ag$_4$ aggregate and every nitrogen atom (N1, N2, N3, and N4) coordinating to a silver vertex of one independent Ag$_4$ aggregate. Consequently, five neighboring Ag$_4$ silver aggregates are congregated through the linkage of anionic ethynide terminals and nitrogen atoms of such two pyz-2-C≡C$^-$ anions. Among the six independent nitrate groups, three (N5, N6, and N10) adopt a simple μ-*O* mode to bridge silver atoms Ag2 and Ag3 of one butterfly-shaped Ag$_4$ basket (Figure S3). By analogy to the structure of complex **3**, a similar coordination column linked by the other two nitrate groups N8 and N9 via respective μ_2-*O,O* and μ_3-*O,O′,O′* mode and stabilized by continuous $\pi-\pi$ stacking between adjacent pyrazinyl rings occurs in **4** (Figure 9). Due to the more electron-deficient nature and the ligation of an additional coordination site of the pyrazinyl ring as compared to the pyridyl ring, adjacent pyrazinyl rings in **4** are not parallel but make a dihedral angle of 25.6°, and the centroid−centroid distances (4.02−4.06 Å) are comparable with the average value in a few reported crystalline compounds of pyrazinyl ligands.[12] These $\pi-\pi$ stabilized coordination columns are further linked by the nitrate groups (N7, N8, and N9) to generate a 3-D coordination network (Figure 10).

Since a hydrophilic polar solvent (aqueous AgNO$_3$) was used in the crystallization of complexes **1**−**4**, it is expected that the aromatic rings tend to be accommodated in a hydrophobic environment constructed by the silver−ethynide supramolecular synthons and nitrate groups. By analogy to the bilayer emulsion of polymeric molecules, the aromatic moieties are prone to congregation, thus facilitating the manifestation of $\pi-\pi$ interaction. Although the ligation of nitrate groups can partially account for continuous $\pi-\pi$ stacking in complex **1**, formation of the composite column in **2** stabilized only by interdigitating thiophene rings means that $\pi-\pi$ stacking plays a pivotal role to generate the infinite columnar structure in **1**−**4**. The decrease in aromaticity of the ring moieties in **1**, **3**, and **4** is accompanied by weakened $\pi-\pi$ stacking, transforming from the parallel face-to-face mode in **1**, through a displaced stacked arrangement in **3**, to the edge-to-face contact in **4**. Replacement of one ethynide moiety of the *m*-phenylenediethynide ligand in **1** by nitrogen coordination sites on the aromatic ring in **3** and **4** was found to have a limited effect on interrupting the whole $\pi-\pi$ stacking infinite column.

As silver ethynide complexes are potentially explosive, we did not attempt to measure the conduction properties of compounds **1**−**4**.

Conclusion

In summary, we have synthesized and characterized a series of four silver(I) complexes containing nitrate and ethynide ligands attached to various aromatic rings, which feature infinite columns stabilized by aromatic $\pi-\pi$ interaction. Intermolecular $\pi-\pi$ stacking in these complexes dominates supramolecular assembly, and distinct modes can be tuned by altering the electron-richness or -deficiency of the aromatic moiety. This affords a rationale for the frequent occurrence of $\pi-\pi$ interaction in silver aryl-ethynide and related complexes, thereby pointing the way to future designs of multidimensional metal−organic frameworks with this weak intermolecular interaction. Since the synthetic operations were conducted in aqueous media, the present findings are of relevance to aqueous organometallic chemistry.

Experimental Section

Reagents. 1,3-[Bis(trimethyl)silylethynyl]benzene (Lancaster, 98%), 3-ethynylpyridine (Aldrich, 98%), 2-chloropyrazine (Aldrich, 97%), 2,3-dibromothiophene (International Laboratory, +98%), trimethylsilylacetylene (Alfa Aesar, 98%), and *n*-BuLi in hexane (Merck, 1.6 M) were commercially available and used without further purification. Tetrahydrofuran (THF) was purified by refluxing over sodium and benzophenone. 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.

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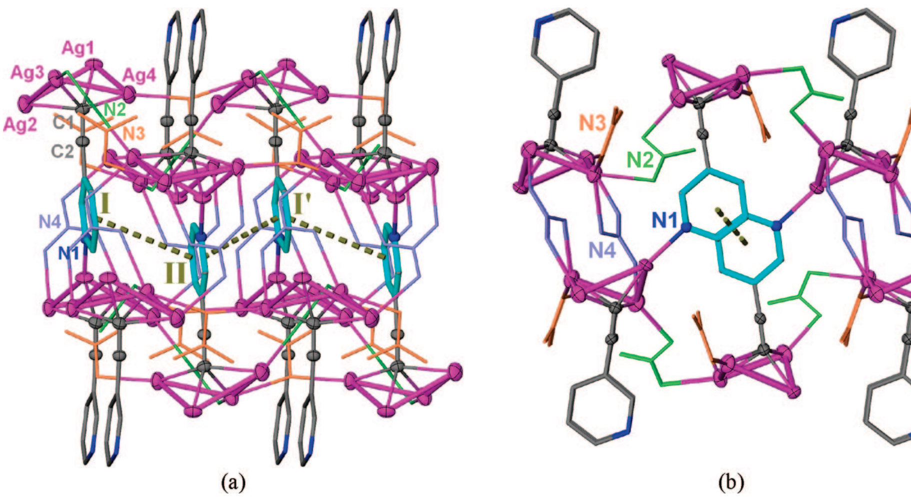

Figure 7. (a) Infinite coordination column in **3** linked by nitrate groups (N2, N3, and N4) and stabilized by continuous zigzag $\pi-\pi$ stacking between adjacent 3-pyridyl rings located within this column. (b) Side view of the 1.4 × 1.4 nm infinite coordination column in **3** along the *a* direction.

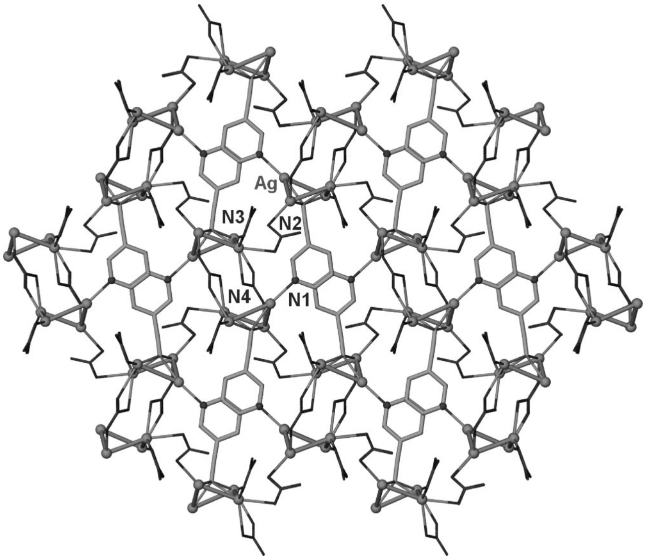

Figure 8. 3-D coordination network in **3** viewed along the *a* direction. A series of infinite coordination columns are arranged in a hexagonal array.

[Ag_2(*m*-C≡CC_6H_4C≡C)]$_n$. In a 100 mL Schlenk flask, THF (20 mL) was cooled to −78 °C in a cold bath. Then *n*-BuLi (1.6 M in *n*-hexane, 4.4 mmol) was added via a syringe, and the mixture was stirred for 15 min at −78 °C. 1,3-[Bis(trimethyl)silylethynyl-]benzene (0.541 g, 2.0 mmol) dissolved in 5 mL of THF solution was added dropwise. The cold bath was then replaced by an ice−water bath, and the mixture was stirred for 3 h. Under a stream of nitrogen, $AgNO_3$ crystals (0.680 g, 4.0 mmol) were added to the flask and dissolved gradually while the mixture was stirred overnight. A dark brown powdery precipitate of crude [Ag_2(*m*-C≡CC_6H_4C≡C)]$_n$ was isolated by filtration and washed several times with THF and finally with deionized water. Yield: 0.402 g (60%). IR spectrum: 2018, 2149 cm^{-1} (w, υ C≡C).

[(AgC≡C)$_2$-2,3-C_4H_2S]$_n$. 2,3-Bis(trimethylsilylethynyl)thiophene was synthesized according to the literature method with 2,3-dibromothiophene reacting with trimethylsilylacetylene in the presence of [$PdCl_2(PPh_3)_2$] and CuI.[13] Then 2,3-bis(trimethylsilylethynyl)thiophene was desilylated using K_2CO_3 in methanol to yield 2,3-diethynylthiophene, which was mixed with $AgNO_3$ and Et_3N in acetonitrile to produce a yellow powder of [(AgC≡C)$_2$-2,3-C_4H_2S]$_n$ via the synthetic procedure described below. IR spectrum: 2045 cm^{-1} (m, υ C≡C).

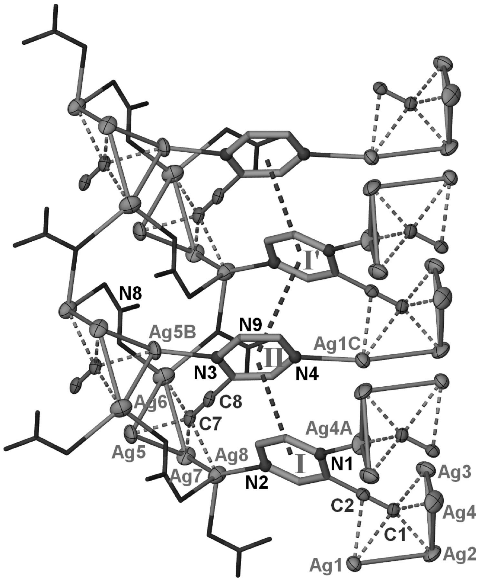

Figure 9. Coordination modes of 2-pyrazinylethynide ligands with atom labeling (50% probability) in 2[(AgC≡C)-2-pyz]·6AgNO_3·3H_2O, **4**. Symmetry code: A −*x*, 1 − *y*, −*z*; B 1 − *x*, −*y*, 1 − *z*; C 1 + *x*, *y*, *z*. Selected bond lengths and distances (Å): C1−C2 1.210(7), C7−C8 1.220(8), Ag···Ag 2.786(4)−3.343(3).

[(AgC≡C)-3-py]$_n$. Silver nitrate (0.342 g, 2.0 mmol) was dissolved in 30 mL of acetonitrile. Then 3-ethynylpyridine (0.207 g, 2.0 mmol) and triethylamine (3.6 mL, 26 mmol) were added with vigorous stirring for 24 h. The pale yellow precipitate formed was collected by filtration, washed thoroughly with 3 × 10 mL of acetonitrile and 3 × 20 mL deionized water, and stored in wet form. IR spectrum: 2007 cm^{-1} (w, υ C≡C).

[(AgC≡C)-2-pyz]$_n$. 2-Ethynylpyrazine was synthesized by the literature method through the reaction of 2-chloropyrazine with trimethylsilylacetylene catalyzed [$PdCl_2(PPh_3)_2$] and CuI in a mixture of THF and triethylamine, followed by the deprotected reaction with the process of K_2CO_3 in methanol.[14] Silver nitrate (0.690 g, 4.0 mmol) was added to 50 mL of acetonitrile. Then a 10 mL acetonitrile solution of 2-ethynylpyrazine (0.416 g, 4.0

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(13) Lewis, J.; Long, N. J.; Raithby, P. R.; Shields, G. P.; Wong, W.-Y.; Younus, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4283–4288.

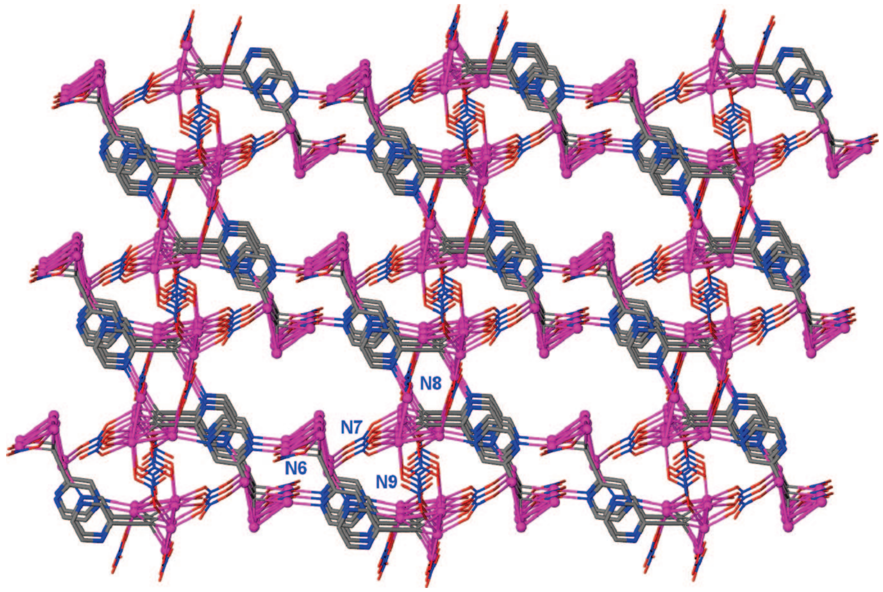

Figure 10. 3-D coordination network in **4** through the linkage of $\pi-\pi$ stabilized coordination columns by the nitrate groups (N7, N8, and N9).

mmol) and triethylamine (3.0 mL) was added with vigorous stirring for 24 h. The pale yellow precipitate formed was collected by filtration, washed thoroughly with 3 × 10 mL of acetonitrile and 3 × 20 mL deionized water, and stored in wet form. IR spectrum: 2013 cm^{-1} (m, υ C≡C).

$[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot5AgNO_3\cdot3H_2O$ (1). $[Ag_2(m\text{-}C{\equiv}C-C_6H_4-C{\equiv}C)]_n$ (~0.1 g) was added to 1 mL of a concentrated aqueous solution of $AgNO_3$ (0.510 g, 3 mmol) in a beaker with stirring until saturated. The excess $[Ag_2(m\text{-}C{\equiv}C-C_6H_4-C{\equiv}C)]_n$ was filtered off. The filtrate was then placed in the dark. After a few days, pale yellow prismatic crystals of **1** were deposited in ~30% yield. Compound **1** melts from 167.2 to 169.9 °C. Anal. for $C_{10}H_{10}O_{18}N_5Ag_7$, found (calcd): C, 9.54 (9.66); H, 0.64 (0.81); N, 5.07 (5.63). IR spectrum: 2062 cm^{-1} (w, υ C≡C).

$2[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]\cdot10AgNO_3$ (2). To 1 mL of an aqueous solution of $AgNO_3$ (0.511 g, 3 mmol) was added solid $[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]_n$ (~0.1 g). After stirring for 1 h, the solution was filtered and the filtrate allowed to stand under ambient conditions for several days. Then yellow crystals of **2** were deposited in ~60% yield. Compound **2** decomposes over 230 °C. Anal. for $C_{16}H_4N_{10}O_{30}S_2Ag_{14}$, found (calcd): C, 8.32 (8.04); H, 0.11 (0.17); N, 6.04 (5.86). IR spectrum: 2011 cm^{-1} (vw, υ C≡C).

$[(AgC{\equiv}C)\text{-}3\text{-py}]\cdot3AgNO_3$ (3). $[(AgC{\equiv}C)\text{-}3\text{-py}]_n$ (~0.1 g) was added to 1 mL of a concentrated aqueous solution of $AgNO_3$ (0.510 g, 3 mmol) in a beaker with stirring until saturated. The excess $[(AgC{\equiv}C)\text{-}3\text{-py}]_n$ was filtered off. The filtrate was then placed in the dark. After a few days, pale yellow crystals of **3** were deposited in ~30% yield. Compound **3** melts with decomposition from 208.2 to 210.4 °C. Anal. for $C_7H_4O_9N_4Ag_4$, found (calcd): C, 11.69 (11.68); H, 0.43 (0.56); N, 7.51 (7.78). IR spectrum: 1975 cm^{-1} (w, υ C≡C).

$2[(AgC{\equiv}C)\text{-}2\text{-pyz}]\cdot6AgNO_3\cdot3H_2O$ (4). $[(AgC{\equiv}C)\text{-}2\text{-pyz}]_n$ (~0.1 g) was added to 1 mL of a concentrated aqueous solution of $AgNO_3$ (0.510 g, 3 mmol) in a beaker with stirring until saturated. The excess $[(AgC{\equiv}C)\text{-}2\text{-pyz}]_n$ was filtered off. The filtrate was then placed in the dark. After a few days, pale yellow crystals of **4** were deposited in ~65% yield. Compound **4** melts from 103.8 to 105.2 °C. Anal. for $C_{12}H_{12}O_{21}N_{10}Ag_8$, found (calcd): C, 9.68 (9.64); H, 0.63 (0.81); N, 9.20 (9.37). IR spectrum: 2046 cm^{-1} (w, υ C≡C).

X-ray Crystallographic Analysis. 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 using the SADABS program.[15] 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.[16]

(a) Crystal data for $[Ag_2(m\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\cdot5AgNO_3\cdot3H_2O$ (**1**): $C_{10}H_{10}O_{18}N_5Ag_7$, $M = 1243.27$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.2360(7)$ Å, $b = 10.635(1)$ Å, $c = 15.585(2)$ Å, $\alpha = 87.661(2)°$, $\beta = 89.882(2)°$, $\gamma = 86.547(2)°$, $V = 1196.2(2)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 3.435$ g cm^{-3}. The structure, refined on F^2, converged for 5832 unique reflections ($R_{int} = 0.0248$) and 4708 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0321$ and $wR_2 = 0.0827$ and a goodness-of-fit = 1.039. Three silver atoms (Ag1, Ag2, and Ag3) are each disordered at two positions and refined with an assigned site-occupancy ratio of 0.8:0.2. Hydrogen atoms of water molecules were not included in the refinement.

(b) Crystal data for $2[(AgC{\equiv}C)_2\text{-}2,3\text{-}C_4H_2S]\cdot10AgNO_3$ (**2**): $C_{16}H_4N_{10}O_{30}S_2Ag_{14}$, $M = 2390.59$, orthorhombic, space group $Ima2$ (No. 46), $a = 28.477(3)$ Å, $b = 22.881(2)$ Å, $c = 12.458(1)$ Å, $V = 8118(2)$ Å^3, $Z = 8$, $T = 293$ K, $D_c = 3.912$ g cm^{-3}. The structure, refined on F^2, converged for 8560 unique reflections ($R_{int} = 0.0425$) and 6923 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0349$ and $wR_2 = 0.0817$ and a goodness-of-fit = 1.035. Three silver atoms (Ag1, Ag7, and Ag12) are each disordered at two positions and refined with a set site-occupancy ratio of 0.8:0.2, 0.7:0.3, and 0.4:0.1, respectively. Two thiophene rings (S1 and S3) have two completely reversed orientations each, which are treated as separate components and refined according to a set site-occupancy ratio of 0.6:0.4 and 0.5:0.5, respectively.

(c) Crystal data for $[(AgC{\equiv}C)\text{-}3\text{-py}]\cdot3AgNO_3$ (**3**): $C_7H_4O_9N_4Ag_4$, $M = 719.62$, monoclinic, space group $P2_1/n$ (No. 14), $a = 7.2997(9)$ Å, $b = 16.077(2)$ Å, $c = 11.782(1)$ Å, $\beta = 92.056(2)°$, $V = 1381.8(3)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 3.459$ g cm^{-3}. The structure, refined on F^2, converged for 3429 unique reflections ($R_{int} = 0.0255$) and 3091 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0219$ and $wR_2 = 0.0526$ and a goodness-of-fit = 1.068. Two

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[14] Schultheiss, N.; Barnes, C. L.; Bosch, E. *Cryst. Growth Des.* **2003**, *3*, 573–580.

[15] Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; Univ. of Göttingen: Germany, 1996.

[16] Sheldrick, G. M. *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*; Bruker Analytic X-Ray Systems, Inc.: Madison, WI, 1997.

silver atoms (Ag3 and Ag4) are each disordered at two positions with a ratio of 0.62:0.38.

(d) Crystal data for 2[(AgC≡C)-2-pyz]·6AgNO$_3$·3H$_2$O (**4**): $C_{12}H_{12}O_{21}N_{10}Ag_8$, $M = 1495.23$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.535(1)$ Å, $b = 11.464(1)$ Å, $c = 17.235(2)$ Å, $\alpha = 82.286(2)°$, $\beta = 88.016(2)°$, $\gamma = 84.343(2)$ °, $V = 1467.6(3)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 3.370$ g cm^{-3}. The structure, refined on F^2, converged for 7144 unique reflections ($R_{int} = 0.0290$) and 5088 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0388$ and $wR_2 = 0.0968$ and a goodness-of-fit = 1.023. Two silver atoms (Ag2 and Ag3) are each disordered at two positions and refined with a set site-occupancy ratio of 0.8:0.2. Hydrogen atoms of water molecules were not included in the refinement.

CCDC-663464 (**1**), -637959 (**2**), -663465 (**3**), and -663466 (**4**) 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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Supporting Information Available: X-ray crystallographic data for **1**−**4** in CIF format and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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