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Silver(I)−Thiophene π Interaction in the Assembly of Coordination Networks with the Supramolecular Synthons R−C≡C⊃Ag$_n$ (R = 2- or 3-thienyl; n = 4)[†]

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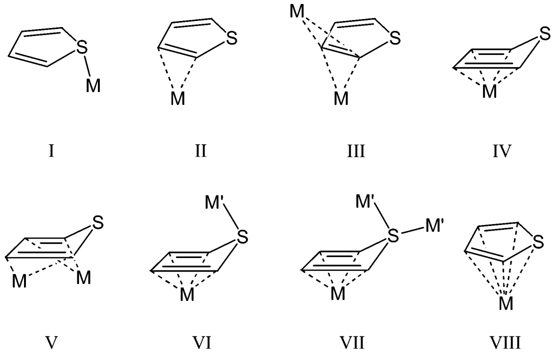
Silver−thiophene π interactions in two bonding modes, namely, η^2-(C=C) and κ-(C,S), have been observed for the first time in crystalline silver(I) complexes $(C_4H_3S\text{-}2)C{\equiv}CAg{\cdot}4AgCF_3CO_2$ (**1**), $2[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}CH_3CN$ (**2**), and $(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}4AgCF_3CO_2$ (**4**), bearing thiophene ligands with an ethynide substituent at the 2- or 3-position. Introduction of an additional betaine component in $3[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}Me_3N^+CH_2CO_2^-{\cdot}4.5H_2O$ (**3**) and replacement of trifluoroacetate by pentafluoropropionate in $(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}5AgC_2F_5CO_2{\cdot}4H_2O$ (**5**) were found to interrupt these silver−thiophene π interactions and instead form an infinite π−π-stacked silver chain and a π−π-stacking-stabilized Ag_8 aggregate, respectively. The establishment of a new kind of silver−ethynide supramolecular synthon, R−C≡C⊃Ag$_n$ (R = 2-, 3-thienyl; n = 4), highlights the potential of building metal−organic frameworks utilizing the π-coordination capacity of a heterocyclic ring.

Introduction

Although significant interaction between the silver(I) atom and aromatic compounds was reported in 1921,[1a] nearly three decades were to pass before the first X-ray crystallographic analysis of a silver−aromatic complex, $C_6H_6{\cdot}AgClO_4$.[1b] Recent interest in silver−aromatic π complexes is prompted by their structural diversity for the construction of crystalline solid-state devices as electrical conductors and chemical sensors.[2] Each silver(I) center thereof is mostly η^1- or η^2-bound to a wide variety of aromatic ligands, including benzenoid[2b,3] and polycyclic aromatic hydrocarbons (PAH).[2] However, in contrast to the plethora of silver−arene complexes, to our knowledge there are as yet only sporadic reports of significant silver−aromatic π interaction involving heterocyclic rings.[4]

The coordination chemistry of thiophene and related compounds has attracted much attention in recent decades owing to its relevance to metal-catalyzed hydrodesulfurization (HDS) of fossil fuels.[5] The known coordination modes of thiophene and its derivatives[6] in transition metal complexes are illustrated in Scheme 1. In mode I, the sulfur atom bonds to a variety of metal centers via its lone-pair electrons.[6−12] In another commonly occurring mode (mode II), transition metal atoms lying

Scheme 1. Coordination Modes of Thiophene Ligands in Transition Metal Complexes[a]



[a] The dashed line represents the metal−thiophene π interaction.

[†] Dedicated to Prof. Cun-Hao Zhang on the occasion of his 80th birthday.

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above or below the thiophene ring exhibit a η^2-($C{=}C$) bonding type,[13−15] and an unusual η^2,η^2-mode (mode III) exists in (μ_4-phenylphosphido)-(μ_4-η^2,η^2,σ^2-thienyl)bis(μ_2-carbonyl)-nonacarbonyltetraruthenium.[14a] As to the η^4-mode, versatile bonding patterns including η^4-($C{=}C{-}C{=}C$) (mode IV),[16] μ_2-η^2,η^2-($C{=}C{-}C{=}C$) (mode V),[17] μ_2-S,η^4-($C{=}C{-}C{=}C$) (mode VI),[18] and μ_3-S,S,η^4-($C{=}C{-}C{=}C$) (mode VII)[19] have been reported. The thiophene ring can also act as a Cp-like η^5-ligand toward a metal atom (mode VIII).[20] Elfeninat and co-workers have studied the interaction between thiophene and some group 11 metals employing quantum-chemical methods, showing that the sulfur atom bonds to the copper atom to a very small extent, and there is no significant interaction between thiophene and gold.[21]

Our recent studies on the synthesis and characterization of silver(I) ethynide complexes led to the recognition of two new kinds of coordinated supramolecular synthons[22] symbolized by $\mathrm{R{-}C{\equiv}C{\supset}Ag}_n$ (R = aryl or alkyl, n = 4 or 5)[23] and $\mathrm{Ag}_n\mathrm{{\subset}C{\equiv}C{-}R{-}C{\equiv}C{\supset}Ag}_n$ (R = p-, m-, o-$\mathrm{C_6H_4}$; n = 4 or 5),[24] and $\pi-\pi$ stacking between adjacent aryl groups tends to dominate the molecular packing in the solid state. To explore the possibility of silver−aromatic interactions involving heterocyclic compounds, we embarked on a study of the ligand behavior of ethynyl-functionalized thiophenes, since it is well-known that the hetero sulfur atom has poor σ-coordination ability, so that the thiophene ring may be expected to coordinate to a silver(I) center via the π mode. We herein report the establishment of a new kind of supramolecular synthons $\mathrm{R{-}C{\equiv}C{\supset}Ag}_n$ (R = $\mathrm{C_4H_3S}$-2 or $\mathrm{C_4H_3S}$-3; n = 4) based on the synthesis and structural characterization of five silver(I) ethynylthiophene complexes, namely, $\mathrm{(C_4H_3S\text{-}2)C{\equiv}CAg{\cdot}4AgCF_3CO_2}$ (**1**), $\mathrm{2[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}CH_3CN}$ (**2**), $\mathrm{3[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}Me_3N^+CH_2CO_2^-{\cdot}4.5H_2O}$ (**3**), $\mathrm{(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}4AgCF_3CO_2}$ (**4**), and $\mathrm{(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}5AgC_2F_5CO_2{\cdot}4H_2O}$ (**5**), in which the silver−thiophene π interaction is substantiated for the first time and it can be further affected by the bulk of carboxylate ligands.

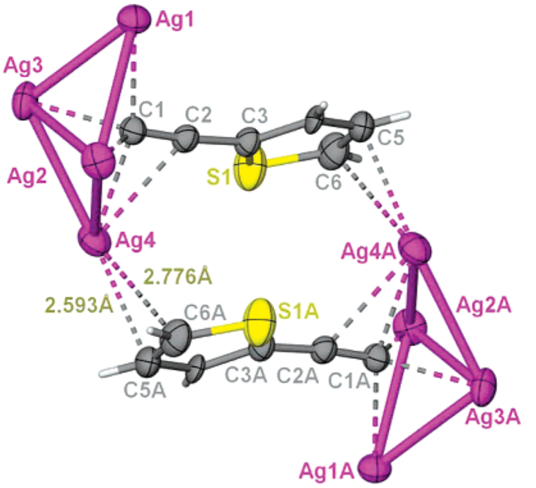

Figure 1. Atom labeling (atoms shown as 50% thermal ellipsoids) and coordination mode of the thiophene-2-ethynide ligand in $\mathrm{(C_4H_3S\text{-}2)C{\equiv}CAg{\cdot}4AgCF_3CO_2}$ (**1**). Two inversion-related $\mathrm{(C_4H_3S\text{-}2){-}C{\equiv}C{\supset}Ag_4}$ units are connected by the silver−thiophene π interaction to yield a 10-membered metallacycle. Other ligands bond to the silver(I) centers are omitted for clarity. Symmetry code: A $1-x$, $1-y$, $1-z$.

Results and Discussion

Complexes **1**−**5** were obtained from crystallization of the corresponding crude polymeric compounds $\mathrm{[(C_4H_3S\text{-}2)C{\equiv}CAg]}_n$ and $\mathrm{[(C_4H_3S\text{-}3)C{\equiv}CAg]}_n$, which were synthesized for the first time, in a concentrated aqueous solution of $\mathrm{AgCF_3CO_2}$, $\mathrm{AgC_2F_5CO_2}$, and $\mathrm{AgBF_4}$, with the addition of acetonitrile and betaine

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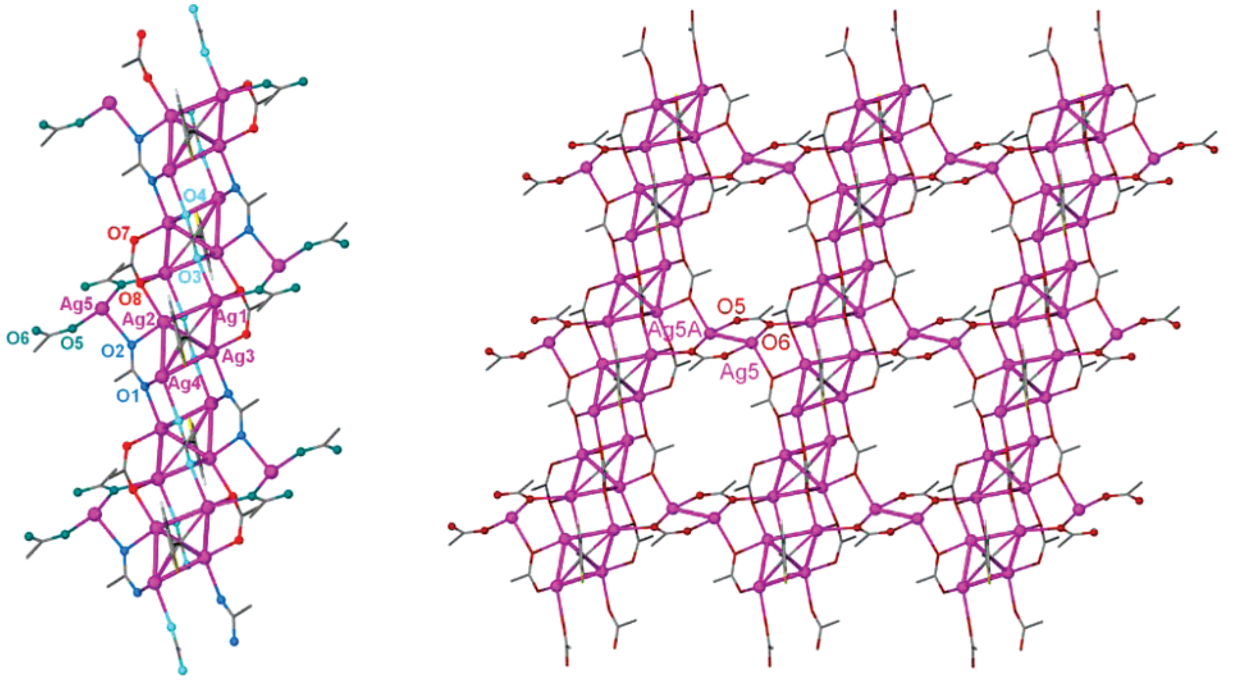

(a) (b)

Figure 2. (a) Coordination column along the *a* direction in complex **1** assembled from the linkage of (C_4H_3S-2)−$C_2 \supset Ag_4$ synthons by four types of trifluoroacetate groups. Oxygen atoms are indicated by different colors, and all fluorine atoms are omitted for clarity. (b) 2-D coordination network parallel to the *ac* plane in complex **1** bridged by [$Ag_2(\mu_3\text{-}CF_3CO_2)_2$] units. All fluorine atoms are omitted for clarity. Color scheme for atoms: Ag purple, C gray, O red, S yellow.

in the case of complexes **2** and **3**. Herein $AgBF_4$ was used to increase the concentration of silver ions.[25] The polymeric starting material [(C_4H_3S-2)C≡CAg]$_n$ was synthesized by the reaction of 2-lithioethynylthiophene (generated *in situ* from 2-[(trimethylsilyl)ethynyl]thiophene and *n*-BuLi) with $AgNO_3$ in THF under an inert atmosphere of nitrogen at room temperature, and [(C_4H_3S-3)C≡CAg]$_n$ was prepared from the reaction of $AgNO_3$ with 3-ethynylthiophene 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 crystal structure of (C_4H_3S-2)C≡CAg·4$AgCF_3CO_2$ (**1**) (Figure 1), the separation of Ag4 from the mean plane of the thiophene ring (C3A−C4A−C5A−C6A−S1A) is 2.45 Å, which is in good agreement with the reported values for Ag−arene complexes (2.41 ± 0.05 Å).[3a] Furthermore, the Ag−C bond distances with C5A−C6A lie in the range 2.593(5)−2.776(5) Å, respectively, being well below the upper limit of 2.92 Å for effective π interaction between silver(I) and an aryl carbon atom.[2a] The hapticity of this coordination is calculated as $\eta^{1.79}$,[26] indicating the first observation of a silver−thiophene η^2-(*C*=*C*) π interaction. The angle between the vector from Ag4 to the C5A−C6A bond center and the vector from C3A to the C5A−C6A bond center is 106.5°, in good agreement with the corresponding value of 113.0° in the complex TpRe(CO)(tBuNC)(η^2-thiophene) (Tp = hydridotris(pyrazolyl)borate).[27]

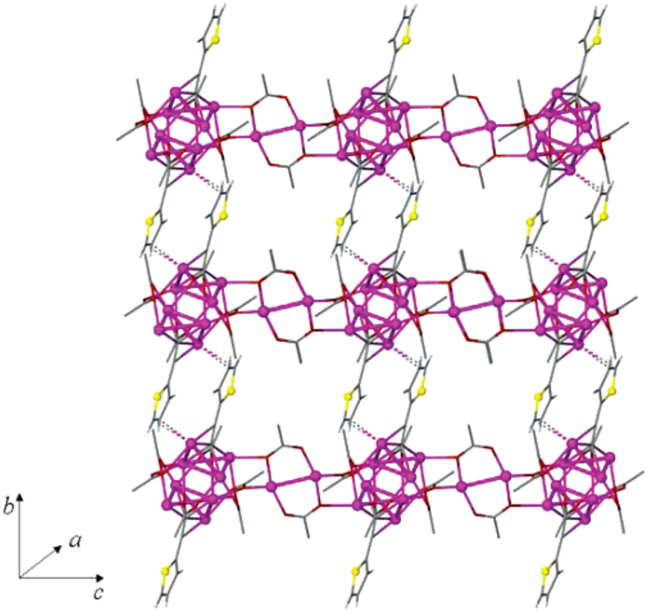

Figure 3. 3-D network in complex **1** constructed from linkage of 2-D coordination networks normal to [010] by silver−thiophene π interaction via the η^2-(C=C) mode. All fluorine atoms are omitted for clarity. Color scheme for atoms: Ag purple, S yellow, O red, C gray.

Moreover, the silver atom Ag4 is coordinated not only by the thiophene ring but also by the triple bond C1≡C2 via π interaction, thereby giving rise to the first (C≡C)Ag(C≡C) bent-sandwich configuration observed among silver(I) complexes. The ethynide moiety C1≡C2 is surrounded by a butterfly-shaped Ag_4 basket through σ-type bonds ranging from 2.196(4) to 2.334(4) Å, and a π bond at Ag4−C2 = 2.661(4) Å to produce a new supramolecular synthon (C_4H_3S-2)−C≡C$\supset Ag_4$. The

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[25] Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, *123*, 7594−7600.

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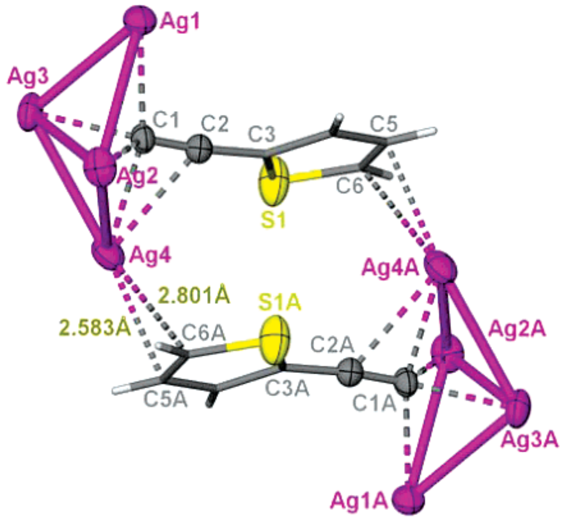
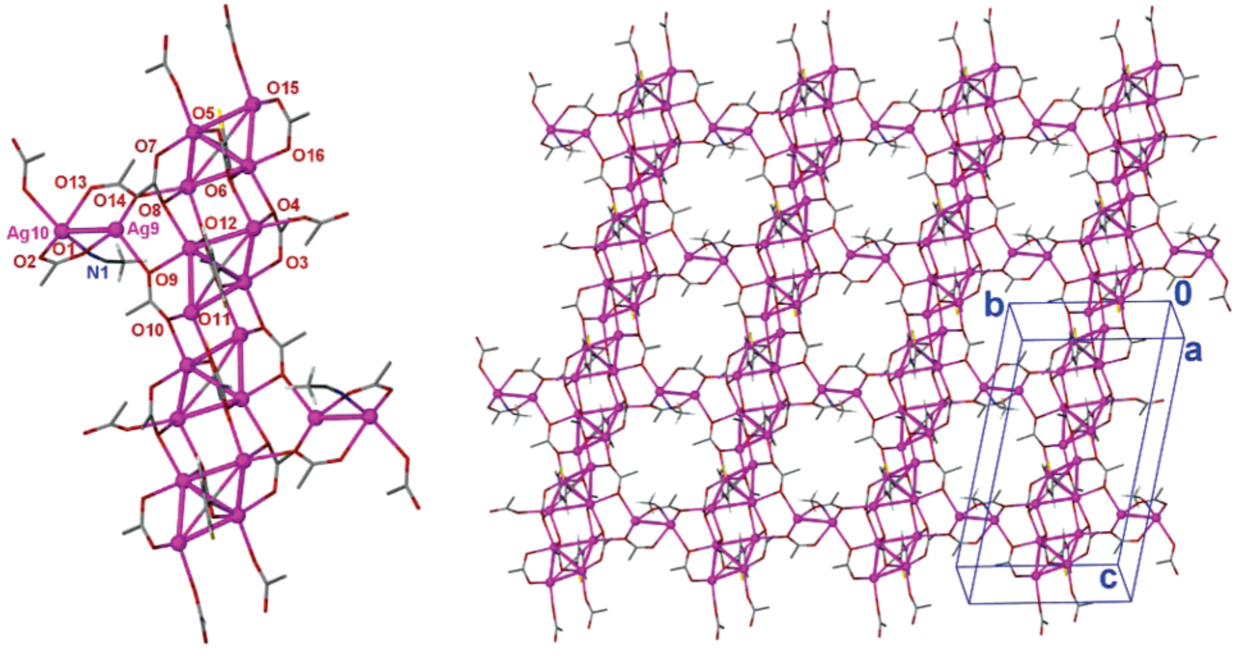


Figure 4. Atom labeling (50% thermal ellipsoids) and coordination modes of two independent $(C_4H_3S\text{-}2){-}C{\equiv}C^-$ ligands in $2[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}CH_3CN$ (**2**). Other ligands are omitted for clarity. Symmetry code: A $1-x$, $1-y$, $1-z$; B $1-x$, $1-y$, $-z$. Selected bond distances (Å): C1−C2 1.223(6); C7−C8 1.216(6); Ag···Ag 2.778(1)−3.152(1).



(a) (b)

Figure 5. (a) Coordination column in $2[(C_4H_3S\text{-}2)C[{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}CH_3CN$ (**2**) assembled from the linkage of $(C_4H_3S\text{-}2){-}C_2{\supset}Ag_4$ synthons by eight different trifluoroacetate groups. All fluorine atoms are omitted for clarity. (b) 2-D coordination network of complex **2** parallel to the (100) plane through the linkage of coordination columns by $[Ag_2(\mu_3\text{-}CF_3CO_2)_2]$ units. All fluorine atoms are omitted for clarity.

C1≡C2 bond distance is 1.221(5) Å, falling within the range 1.181−1.252 Å in the reported μ_1-ethynyl complex *trans*-$[(Et_3P)_2PhPt{-}C{\equiv}CRC{\equiv}C{-}PtPh(PEt_3)_2]$ (R = 2,5-thiophenediyl).[28] The Ag···Ag distances within the Ag_4 basket range from 2.795(1) to 3.072(1) Å, being shorter than twice the van der Waals radius of the silver(I) ion (3.4 Å), suggesting the existence of significant argentophilic interaction.[29] Furthermore, two centrosymmetrically related $(C_4H_3S\text{-}2){-}C{\equiv}C{\supset}Ag_4$ units are interconnected by the silver−thiophene π interaction to yield a 10-membered metallacycle containing two completely parallel thiophene rings without $\pi-\pi$ stacking (interplanar distance = 3.847 Å). The long S···S separation of 4.635 Å indicates the absence of significant sulfur−sulfur interaction in **1**, although such interaction plays a pivotal role in reported thiophene $\pi-\pi$-stacked complexes.[30]

The $(C_4H_3S\text{-}2){-}C{\equiv}C{\supset}Ag_4$ units are mutually bridged by three independent trifluoroacetate groups (O1−O2, O3−O4, and O7−O8) via μ_4-*O,O,O′,O′*, μ_4-*O,O,O′,O′*, and μ_3-*O,O′,O′* modes, respectively, to generate an infinite silver column along the *a* direction. By utilizing the linking unit $[Ag_2(\mu_3\text{-}\eta^1,\eta^2\text{-}CF_3\text{-}$

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[29] (a) Pyykkö, P. *Chem. Rev*. **1997**, *97*, 597−636. (b) Zhao, X.-L.; Wang, Q.-M.; Mak, T. C. W. *Chem.−Eur. J*. **2005**, *11*, 2094−2102, and references therein.

[30] (a) Zhang, X.; Johnson, J. P.; Kampf, J. W.; Matzger, A. J. *Chem. Mater*. **2006**, *18*, 3470−3476. (b) Yamazaki, D.; Nishinaga, T.; Tanino, N.; Komatsu, K. *J. Am. Chem. Soc*. **2006**, *128*, 14470−14471. (c) Nakao, K.; Nishimura, M.; Tamachi, T.; Kuwatani, Y.; Miyasaka, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc*. **2006,** *128*, 16740−16747.

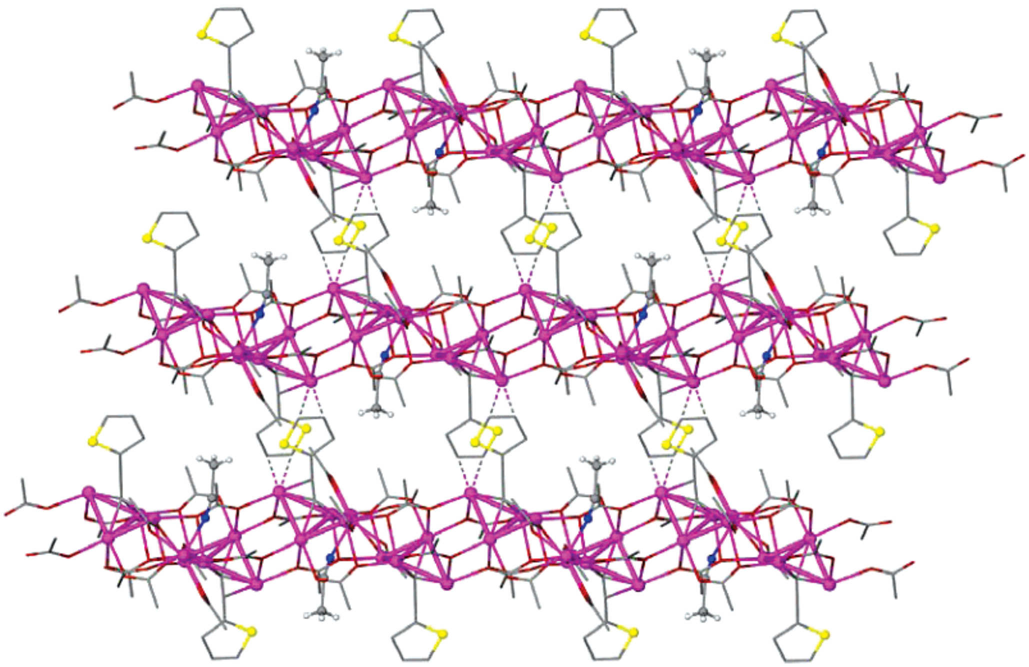

Figure 6. 3-D coordination network in **2** composed of 2-D coordination networks linked by silver−thiophene π interaction via the η^2-(*C*═*C*) mode. All fluorine atoms are omitted for clarity. Color scheme for atoms: Ag purple, C gray, O red, N blue, S yellow.

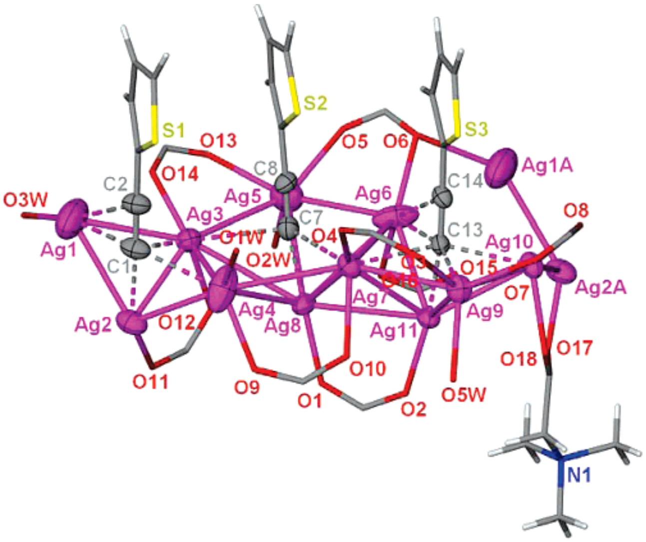

Figure 7. Atom labeling (50% thermal ellipsoids) and coordination modes of three independent (2-thienyl)ethynide and carboxylate ligands in $3[(C_4H_3S\text{-}2)C{\equiv}CAg]\cdot 8AgCF_3CO_2\cdot Me_3N^+CH_2CO_2^-\cdot 4.5H_2O$ (**3**). Trifluoromethyl moieties and some other ligands are omitted for clarity. Symmetry code: A 1+*x*, *y*, *z*. Selected bond distances (Å): C1−C2 1.21(2); C7−C8 1.21(2); C13−C14 1.26(2); Ag···Ag 2.770(4)−3.337(3).

$CO_2)_2$] composed of the external silver atom Ag5 and trifluoroacetate group O5−O6, adjacent infinite silver columns are cross-linked along the *c* direction to generate a two-dimensional network orientated parallel to the *ac* plane (Figure 2). Packing of these 2-D coordination networks along the *b* direction via bridging silver−thiophene π interaction leads to a three-dimensional coordination network (Figure 3).

Addition of acetonitrile into the solution during the crystallization of complex **1** yielded another complex containing the η^2-(*C*═*C*) silver−thiophene π interaction, namely, $2[(C_4H_3S\text{-}2)C{\equiv}CAg]\cdot 8AgCF_3CO_2\cdot CH_3CN$ (**2**), in which two independent (2-thienyl)ethynide ligands are involved (Figure 4). The Ag−C distances within the silver−thiophene π interaction are in the range 2.583(5)−2.801(5) and 2.615(5)−2.731(5) Å for Ag4−(C5A═C6A) and Ag8−(C11B═C12B), respectively. Thus their corresponding hapticity can be calculated as 1.76 and 1.86 according to the atom-to-plane distances of 2.44 and 2.45 Å, respectively. The vectors from the silver atoms Ag4 and Ag8 to the midpoints of the corresponding C═C double bonds make an angle of 107.1° and 107.9°, respectively, with the thiophene rings. Ag4 and Ag8 are likewise each embraced by an ethynide moiety and a thiophere ring via π bonding. The interplanar distances of 3.899 and 3.960 Å for the pair of thiophene rings S1−S1A and S2−S2B preclude the existence of π−π stacking.

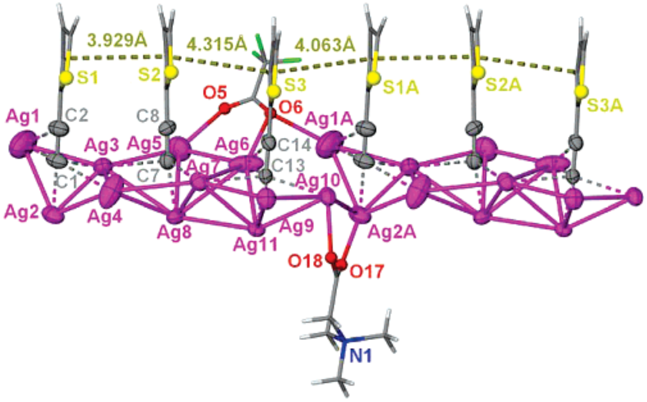

Figure 8. Silver column in complex **3** along the *a* direction bridged by the argentophilic interaction Ag10−Ag2A and two μ_3-*O,O,O′* carboxylate ligands (O5−O6 and O17−O18). Other ligands are omitted for clarity. Symmetry code: A 1+*x, y, z*.

Four μ_4-*O,O,O′,O′* trifluoroacetate groups (O5−O6, O9−O10, O11−O12, and O15−O16) are involved in the crystal structure of complex **2**, acting in the same role as in complex **1** to yield a similar coordination column (Figure 5a). The other two (O3−O4 and O7−O8) play a secondary role to consolidate this columnar structure via the μ_3-*O,O,O′* mode. Two independent trifluoroacetate groups (O1−O2 and O13−O14) bridge the silver atoms of type Ag9 and Ag10 bearing a coordinated acetonitrile group to connect all these columns into a 2-D coordination network (Figure 5b). Through additional consolidation via η^2-

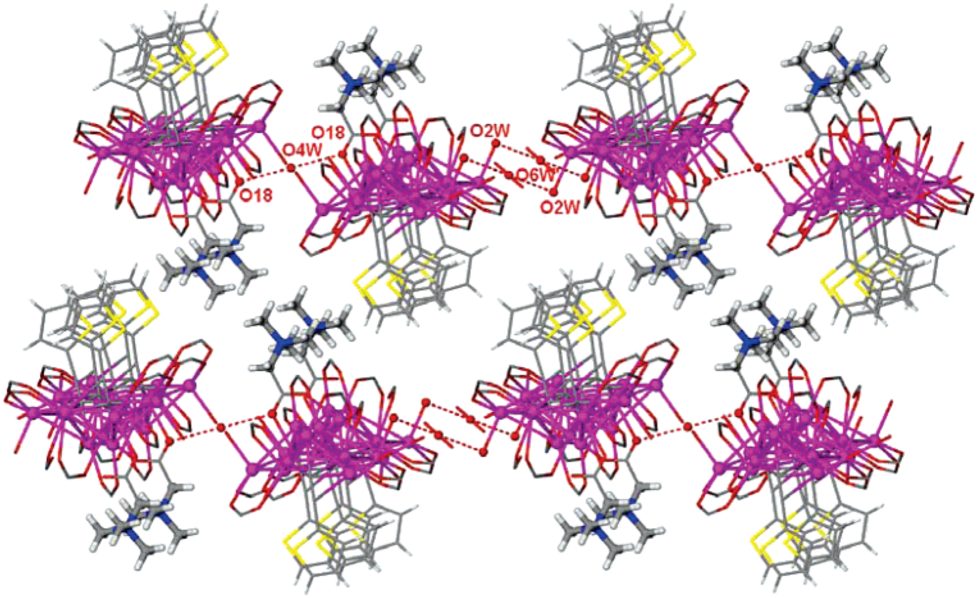

Figure 9. 2-D networks in complex **3** constructed from the linkage of silver column by hydrogen bonding. Hydrogen bonds (Å): O4W−O18 2.728; O2W−O6W′ 3.001; O6W′ indicates the central position of two disordered sites of water molecule O6W. Color scheme for atoms: Ag purple, S yellow, O red, C gray, N blue, H white.

Table 1. Structural Parameters between Adjacent Thiophene Rings in Complex 3

ring	cent−cent (Å)	interplanar separation (Å)	dihedral angle (deg)	S−S distance (Å)	shortest C−C(S) distance (Å)
S1−S2	3.929	3.845	4.9	3.951	3.894
S2−S3	4.315	3.688	3.9	4.191	3.719
S3−S1A	4.063	3.727	2.1	4.100	3.863

($C{=}C$) silver−thiophene π interaction, adjacent 2-D networks are connected to form a 3-D coordination network (Figure 6).

Employment of an additional betaine ligand, $Me_3N^+CH_2CO_2^-$, results in the generation of $3[C_4H_3S\text{-}2)C{\equiv}CAg]\cdot 8AgCF_3CO_2\cdot Me_3N^+CH_2CO_2^-\cdot 4.5H_2O$ (**3**), in which this silver−thiophene π interaction is totally interrupted. As shown in Figure 7, three independent (2-thienyl)ethynide ligands are involved in this structure, in which three ethynide moieties ($C1{\equiv}C2$, $C7{\equiv}C8$, and $C13{\equiv}C14$) adopt different kinds of coordination modes, μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$, μ_4-η^1, and μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$, respectively, to bond to a Ag_{11} silver aggregate. In contrast to the simple μ_2-*O,O′* mode of six trifluoroacetate groups and the μ-*O* mode of trifluoroacetate group O7−O8, trifluoroacetate group O5−O6 and betaine ligand O17−O18 link adjacent Ag_{11} aggregates via the μ_3-*O,O,O′* mode to generate a silver column along the [100] direction (Figure 8). Notably, all thiophene rings of this silver column protrude on the same side and are stabilized by continuous $\pi-\pi$ stacking, which bears much similarity to that between phenyl rings in $AgC{\equiv}CC_6H_5\cdot 3AgCF_3CO_2\cdot CH_3CN$,[23a] $2AgC{\equiv}CC_6H_4Me\text{-}4\cdot 6AgCF_3CO_2\cdot 1.5CH_3CN$, and $AgC{\equiv}CC_6H_4\text{-}Me\text{-}4\cdot 3AgCF_3CO_2\cdot (CH_3)_3N^+CH_2CO_2^-$.[23b] As tabulated in Table 1, all thiophene rings are almost parallel to each other, with interplanar separations in the range 3.69−3.84 Å, which are somewhat longer than typical values of 3.6−3.7 Å in numerous reported thiophene and polythiophene complexes.[30,31]

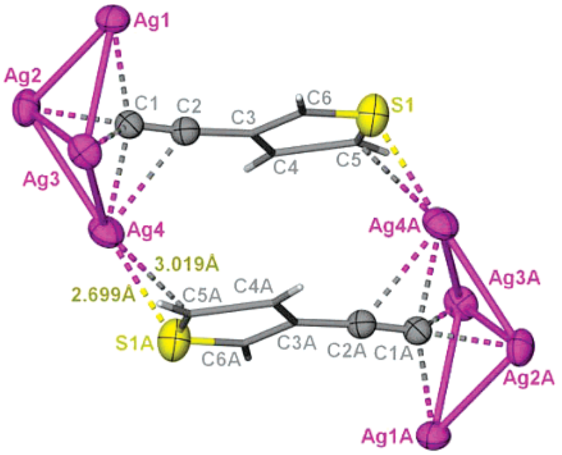

Figure 10. Atom labeling (50% thermal ellipsoids) and coordination mode of the thiophene-3-ethynide ligand in $(C_4H_3S\text{-}3)C{\equiv}CAg\cdot 4AgCF_3CO_2$ (**4**). The κ-(*C,S*) silver−thiophene π interaction links two inversion-related $(C_4H_3S\text{-}3)\text{−}C{\equiv}C{\supset}Ag_4$ units to engender a 10-membered dinuclear metallacycle. Other ligands are omitted for clarity. Symmetry code: A $-x$, $-y$, $-z$. Selected bond distances (Å): C1−C2 1.219(7); Ag···Ag 2.794(1)−3.036(1).

The silver columns are further linked by hydrogen bonding between O18 and water molecule O4W at one side and between aqua ligand O2W and water molecule O6W on the other to construct a 2-D network. As shown in Figure 9, adjacent 2-D networks are packed along the *b* direction and separated by the betaine ligands, thereby leading to the absence of internetwork interaction between thiophene rings.

Employment of the thiophene-3-ethynide ligand in the ensuing study leads to the observation of an unprecedented κ-(*C,S*) silver−thiophene interaction in the crystal structure of $(C_4H_3S\text{-}3)C{\equiv}CAg\cdot 4AgCF_3CO_2$ (**4**) (Figure 10). We differentiate this

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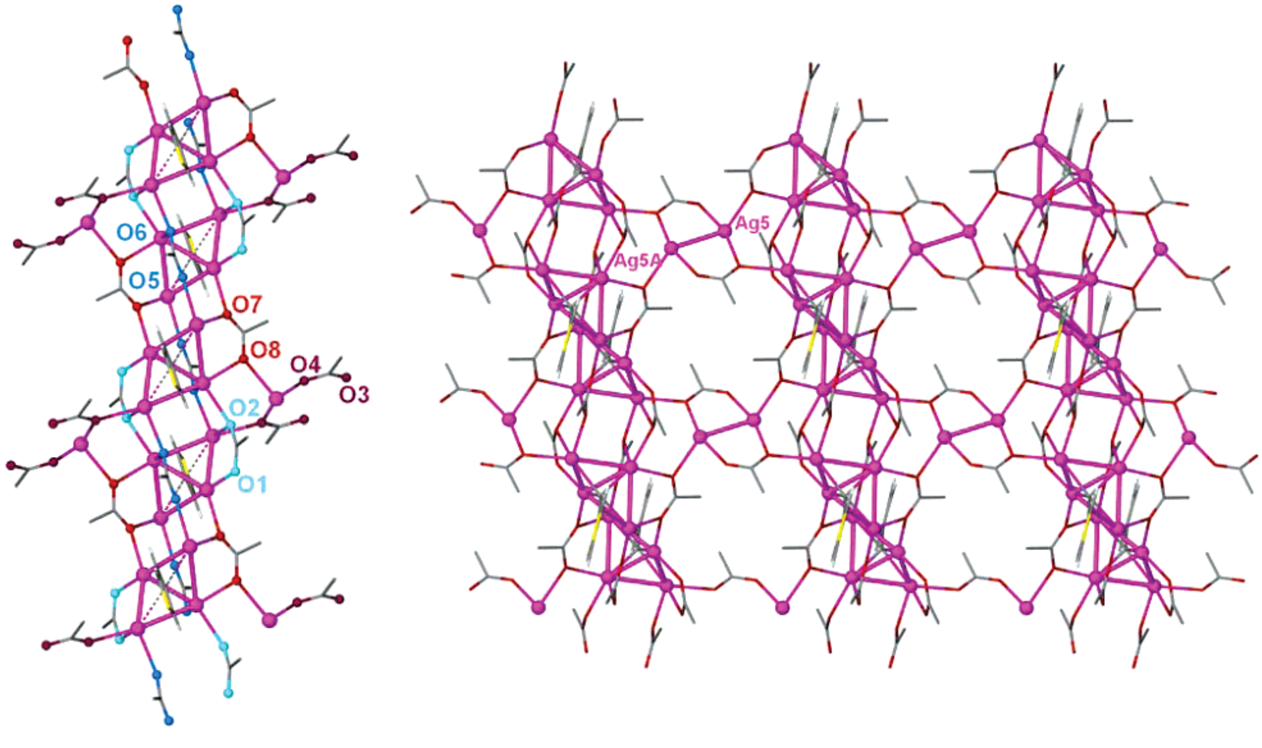

(a) (b)

Figure 11. (a) Coordination column in **4** assembled from the linkage of $(C_4H_3S\text{-}3){-}C_2{\supset}Ag_4$ synthons by four independent trifluoroacetate groups, which are indicated by different colors. All fluorine atoms are omitted for clarity. (b) 2-D coordination network of complex **4** normal to [010] through the bridging of adjacent silver columns by $[Ag_2(\mu_3\text{-}CF_3CO_2)_2]$ units.

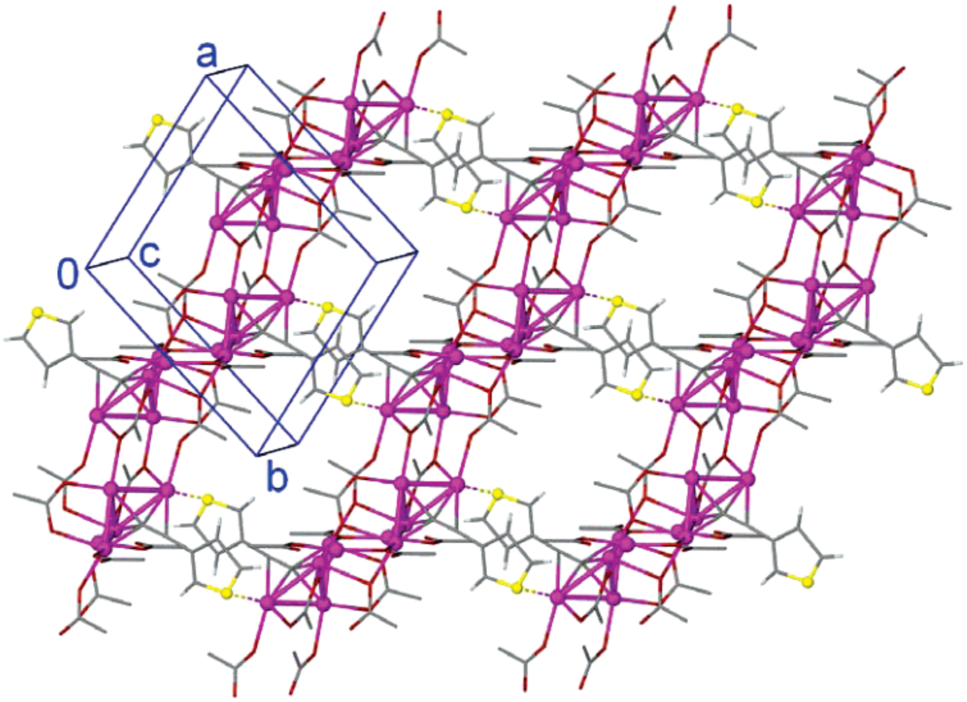

Figure 12. 3-D network in **4** (viewed from the *c* direction) composed of 2-D coordination networks linked by silver−thiophene π interaction. All fluorine atoms are omitted for clarity. Color scheme for atoms: Ag purple, S yellow, O red, C gray.

Ag−(*C*,*S*) interaction as a silver−aromatic π interaction, in contrast to σ-coordination bonding via the lone-pair electrons of the sulfur atom, on the basis of the following considerations: (i) the bond distance of Ag4A−S1 (2.699(2) Å) is significantly shorter than bond distances of 2.768−2.995 Å in the reported silver−thiophene σ-bonded complexes;[7] (ii) the distance between Ag4 and carbon atom C5A is 3.019 Å, being shorter than the sum of van der Waals radii (3.11 Å) of the Ag(I) ion and a carbon atom,[32] and also smaller than the values ranging from 3.281 to 3.884 Å in the aforementioned silver−thiophene σ-bonded complexes; (iii) the angle between the

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[32] Dean, J. A. Ed. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985.

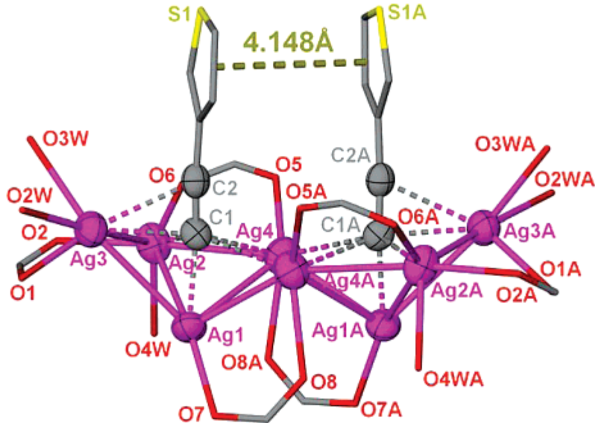


Figure 13. Atom labeling (50% thermal ellipsoids) and coordination mode of the $(C_4H_3S\text{-}3)C\equiv C^-$ ligand in $(C_4H_3S\text{-}3)C\equiv CAg\cdot 5AgC_2F_5CO_2\cdot 4H_2O$ (**5**). $\pi-\pi$ stacking occurs in a pair of C_2-related thiophene rings. C_2F_5 moieties of pentafluoropropionate groups and other ligands are omitted for clarity. Symmetry code: A *x*, 1/2−*y*, 1−*z*. Selected bond distances (Å): C1−C2 1.23(1); Ag···Ag 2.805(2)−3.151(3).

Ag4A−S1 vector and the vector from S1 to the C3−C4 midpoint is 110.2°, being smaller than the values in reported transition metal thiophene σ-bonding complexes ranging from 117.1° to 153.0°.[8−12]

Although Ag4 is coordinated by both sulfur and carbon atoms and its atom-to-ring distance is 2.46 Å (within the range 2.41 ± 0.05 Å), the long Ag−C distance of 3.019 Å indicates that the hapticity of this kind of silver−thiophene interaction is much closer to 1 rather than 2 as found in **1** and **2**. The interplanar distances between two thiophene rings and the sulfur−sulfur separation are 4.00 and 6.22 Å, respectively.

Through the Ag−(*C,S*) π linkage, a pair of inversion-related $(C_4H_3S\text{-}3)-C\equiv C\supset Ag_4$ units are consolidated into a dinuclear 10-membered metallacycle (Figure 10). Along the [100] direction, the $(C_4H_3S\text{-}3)-C\equiv C\supset Ag_4$ units are linked by three types of trifluoroacetate groups (O1−O2, O5−O6, O7−O8) via μ_3-*O,O′,O′*, μ_3-*O,O′,O′*, and μ_4-*O,O,O′,O′* modes, respectively, to yield an infinite coordination column. Bridged by the $[Ag_2(\mu_3\text{-}CF_3CO_2)_2]$ unit composed of inversion-related silver atom Ag5 and a trifluoroacetate group of the O3−O4 type, these columns are connected mutually to form a 2-D coordination network parallel to the (010) plane (Figure 11). Utilizing the κ-(*C,S*) silver−thiophene π interaction, adjacent 2-D coordination networks are linked along the *b* direction to generate a 3-D network with a series of infinite channels running parallel to the *c* direction (Figure 12).

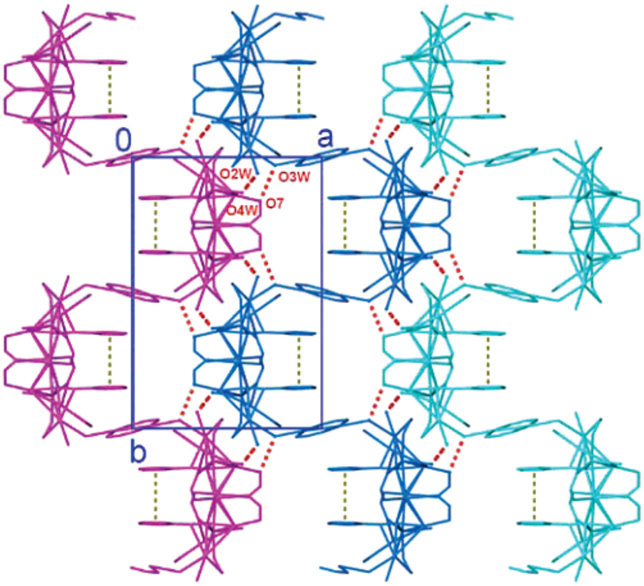
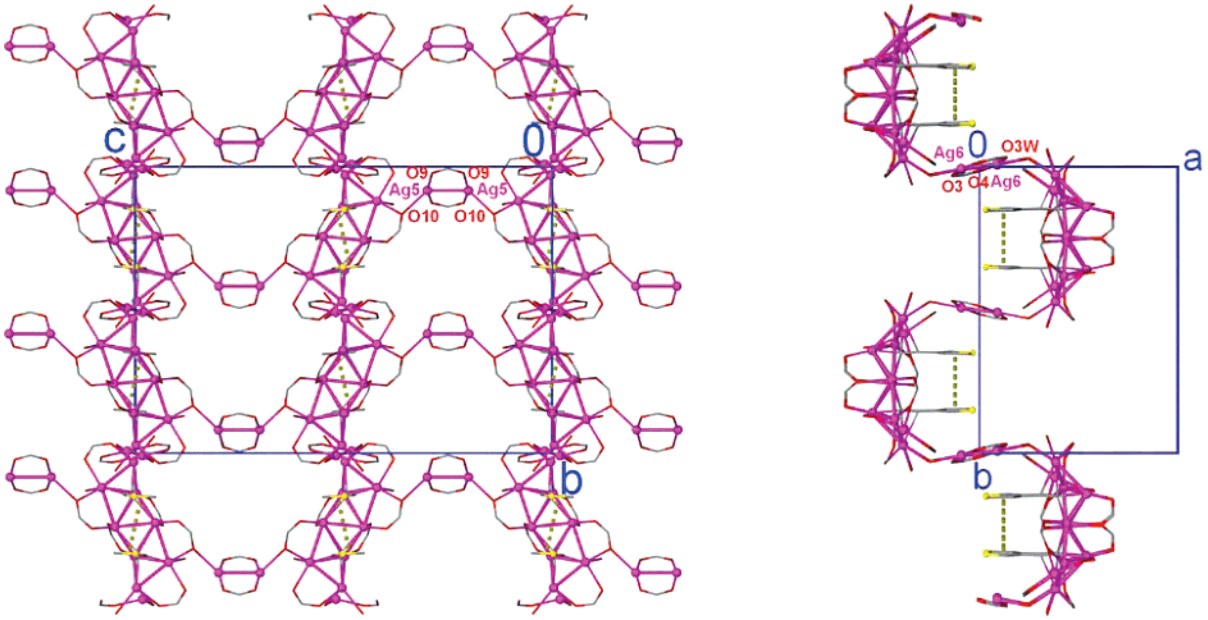


Figure 15. 3-D network in complex **5** constructed by the connection of a 2-D coordination network (indicated by different colors) by hydrogen bonding. Hydrogen bonds (Å): O2W−O4W 2.833; O3W−O7 2.903.

In the crystal structure of $(C_4H_3S\text{-}3)C\equiv CAg\cdot 5AgC_2F_5CO_2\cdot 4H_2O$ (**5**), two C_2-related (3-thienyl)ethynide ligands each adopts a μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ bonding mode to bond to a square-pyramidal



(a) (b)

Figure 14. (a) Zigzag coordination chain in **5** linked by a bridging unit $[Ag_2(\mu_2\text{-}C_2F_5CO_2)_2]$ composed of two silver atoms of Ag5 type and two pentafluoropropionate groups (O9−O9 and O10−O10). Linkage of these coordination chains by a $\{(\mu_2\text{-}H_2O)[Ag_2(\mu_2\text{-}C_2F_5CO_2)_2](\mu_2\text{-}H_2O)\}$ unit to form a 2-D undulating coordination network. (b) 2-D coordination network viewed along the *c* direction.

Ag_5 aggregate. Sharing of one basal edge between two such Ag_5 aggregates leads to the formation of a Ag_8 segment (Figure 13). Notably, weak $\pi-\pi$ interaction also occurs in the pair of thiophene rings with a centroid−centroid distance of 4.148 Å. These two thiophene rings are almost parallel to each other (2.3°), with an interplanar separation of 4.097 Å, and the separation between two sulfur atoms is 4.042 Å, longer than the sum of the van der Waals radius of sulfur (3.45−3.5 Å).[33] This $\pi-\pi$-stacking-stabilized $[(C_4H_3S\text{-}3)C{\equiv}C]_2Ag_8$ silver−ethynide aggregate is further coordinated by aqua ligands (O2W, O3W, and O4W) and a series of μ_2-*O,O′* pentafluoropropionate groups (O1−O2 and O7−O8) through spanning of a Ag···Ag edge. Linkage of $[(C_4H_3S\text{-}3)C{\equiv}C]_2Ag_8$ silver-ethynide aggregates by a μ_3-*O,O,O′* pentafluoropropionate group O5−O6 and a mirror-related bridging unit $[Ag_2(\mu_2\text{-}C_2F_5CO_2)_2]$ composed of silver atom Ag5 and two pentafluoropropionate groups (O9−O9A and O10−O10A) yields a zigzag coordination chain along the [001] direction (Figure 14a). These coordination chains are then bridged by a $\{(\mu_2\text{-}H_2O)[Ag_2(\mu_2\text{-}C_2F_5CO_2)_2](\mu_2\text{-}H_2O)\}$ linking unit to generate an undulating 2-D coordination layer normal to [100] (Figure 14). As shown in Figure 15, these 2-D coordination layers are packed along the *a* direction and linked by a series of hydrogen-bonding interactions between two aqua ligands (O2W−O4W) and between aqua ligand O3W and oxygen atom O7 to construct a 3-D network.

Conclusion

In the present study, the establishment and utilization of a new class of supramolecular synthons, $R-C{\equiv}C{\supset}Ag_n$ ($R = C_4H_3S$-2 or C_4H_3S-3; $n = 4$), in the construction of metal−organic networks, has revealed an precedented silver(I)−thiophene π interaction via two coordination modes: η^2-(*C*≡*C*) and κ-(*C,S*). The prevalence of the silver(I)−thiophene π interaction in **1**, **2**, and **4** may result from energetically favorable configurations that incorporate the hydrophobic thiophene rings into a dinuclear metallacyclic system. Employment of bulkier carboxylate ligands, such as the betaine ligand $Me_3N^+CH_2CO_2^-$ in **3** and the pentafluoropropionate group in **5**, hinders the close approach of the thiophene ring to a silver aggregate to form a significant silver(I)−thiophene π interaction, resulting in the occurrence of $\pi-\pi$ stacking between adjacent thiophene rings.

Experimental Section

Reagents. 2-[(Trimethylsilyl)ethynyl]thiophene (Aldrich, purity >97%) and 3-ethynylthiophene (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.*

$[(C_4H_3S\text{-}2)C{\equiv}CAg]_n$. 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. 2-[(Trimethylsilyl)ethynyl]thiophene (0.721 g, 4.0 mmol) dissolved in 10 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 black precipitate of crude $[(C_4H_3S\text{-}2)C{\equiv}CAg]_n$ contaminated with some metallic silver was isolated by filtration and washed several times with THF and finally with deionized water. Yield: 0.370 g (43%). IR spectrum: 2047 cm^{-1} (w, ν C≡C).

$[(C_4H_3S\text{-}3)C{\equiv}CAg]_n$. Silver nitrate (0.742 g, 4.4 mmol) was dissolved in 50 mL of acetonitrile. Then 3-ethynylthiophene (0.433 g, 4.0 mmol) and triethylamine (1.83 mL, 13.2 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. Yield: 0.723 g (84%). IR spectrum: 2051 cm^{-1} (w, ν C≡C).

$(C_4H_3S\text{-}2)C{\equiv}CAg{\cdot}4AgCF_3CO_2$ (1). $AgCF_3CO_2$ (0.223 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then $[(C_4H_3S\text{-}2)C{\equiv}CAg]_n$ (∼0.1 g) solid was added to the solution. After stirring for about half an hour, the solution was filtered and the filtrate was allowed to stand at room temperature in the dark. After several days, pale yellow block crystals of **1** were deposited in ∼70% yield. Compound **1** gradually turns black above 166 °C and melts from 214.7 to 216.5 °C. Elemental analysis for $C_{14}H_3F_{12}O_8SAg_5$, found (calcd): C, 15.02 (15.31); H, 0.49 (0.28). IR spectrum: 2008 cm^{-1} (w, ν C≡C).

$2[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}CH_3CN$ (2). $[(C_4H_3S\text{-}2)C{\equiv}CAg]_n$ (∼0.1 g) was added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ (0.220 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) in a beaker with stirring until saturated. The excess $[(C_4H_3S\text{-}2)C{\equiv}CAg]_n$ was filtered off. Then 0.1 mL of acetonitrile was added to the filtrate, which was then placed at room temperature in the dark. After a few days, yellow block-like crystals of **2** were deposited in ∼65% yield. Compound **2** has a melting point ranging from 198.2 to 200.4 °C with color darkening over 155 °C. Elemental analysis for $C_{30}H_9F_{24}O_{16}NS_2Ag_{10}$, found (calcd): C, 16.51 (16.10); H, 0.46 (0.40); N, 0.38 (0.62). IR spectrum: 2008 cm^{-1} (w, ν C≡C).

$3[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}Me_3N^+CH_2CO_2^-{\cdot}4.5H_2O$ (3). $AgCF_3CO_2$ (0.220 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then $[(C_4H_3S\text{-}2)C{\equiv}CAg]_n$ (∼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, yellow prismatic crystals of **3** were collected in ∼60% yield. Compound **3** melts in the range 72.9 to 74.4 °C. Elemental analysis for $C_{39}H_{29}F_{24}O_{22.5}NS_3Ag_{11}$, found (calcd): C, 17.66 (17.94); H, 1.36 (1.12); N, 0.46 (0.54). IR spectrum: 1996 cm^{-1} (w, ν C≡C).

$(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}4AgCF_3CO_2$ (4). $AgCF_3CO_2$ (0.220 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in 1 mL of deionized water. Then $[(C_4H_3S\text{-}3)C{\equiv}CAg]_n$ (∼0.1 g) was added to the solution. After stirring for about 10 min, the solution was filtered off. After crystallization under ambient condition in the dark for several days, colorless plate crystals of **4** were collected in ∼80% yield. Compound **4** turns dark over 150 °C and melts in the range 213.7 to 215.0 °C. Elemental analysis for $C_{14}H_3F_{12}O_8SAg_5$, found (calcd): C, 15.60 (15.31); H, 0.69 (0.28). IR spectrum: 2009 cm^{-1} (vw, ν C≡C).

$(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}5AgC_2F_5CO_2{\cdot}4H_2O$ (5). To 1 mL of an aqueous solution of $AgC_2F_5CO_2$ (0.271 g, 1 mmol) and $AgBF_4$ (0.382 g, 2 mmol) was added solid $[(C_4H_3S\text{-}3)C{\equiv}CAg]_n$ (∼0.1 g). After stirring for 1 h, the solution was filtered and the filtrate allowed to stand under ambient condition for several days. Then colorless block-like crystals of **5** were deposited in ∼45% yield. Compound **5** melts in the range 53.4−55.0 °C. Elemental analysis for $C_{21}H_{11}F_{25}O_{14}SAg_6$, found (calcd): C, 15.58 (15.36); H, 0.73 (0.68). IR spectrum: 1992 cm^{-1} (w, ν 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° < θ < 28°. An empirical absorption correction was applied using the SADABS program.[34] The structures were solved by direct methods, and non-

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[33] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

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

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.[35]

(a) Crystal data for $(C_4H_3S\text{-}2)C{\equiv}CAg{\cdot}4AgCF_3CO_2$ (**1**): $C_{14}H_3F_{12}O_8SAg_5$, $M = 1098.57$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.213(2)$ Å, $b = 11.269(3)$ Å, $c = 12.049(3)$ Å, $\alpha = 89.426(4)°$, $\beta = 78.679(4)°$, $\gamma = 74.408(4)°$, $V = 1308.4(5)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.788$ g cm^{-3}. The structure, refined on F^2, converged for 6373 unique reflections ($R_{int} = 0.0237$) and 5315 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0319$ and $wR_2 = 0.0897$ and a goodness-of-fit = 1.016. All four independent trifluoroacetate groups exhibit orientational disorder in a 0.54:0.46 ratio.

(b) Crystal data for $2[(C_4H_3S\text{-}2)C{\equiv}CAg]{\cdot}8AgCF_3CO_2{\cdot}CH_3CN$ (**2**): $C_{30}H_9F_{24}O_{16}NS_2Ag_{10}$, $M = 2238.20$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.338(1)$ Å, $b = 12.250(1)$ Å, $c = 20.313(2)$ Å, $\alpha = 77.610(2)°$, $\beta = 73.911(2)°$, $\gamma = 88.355(2)°$, $V = 2646.3(5)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.809$ g cm^{-3}. The structure, refined on F^2, converged for 12 862 unique reflections ($R_{int} = 0.0226$) and 10 246 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0349$ and $wR_2 = 0.0982$ and a goodness-of-fit = 1.045. All eight independent trifluoroacetate groups exhibit orientational disorder in a 0.64:0.36 ratio.

(c) Crystal data for $3[(C_4H_3S\text{-}2)C{\equiv}CAg{\cdot}8AgCF_3CO_2{\cdot}Me_3N^+\text{-}CH_2CO_2^-{\cdot}4.5H_2O$ (**3**): $C_{39}H_{29}F_{24}O_{22.5}NS_3Ag_{11}$, $M = 2610.33$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.278(2)$ Å, $b = 13.870(3)$ Å, $c = 22.812(4)$ Å, $\alpha = 73.065(4)°$, $\beta = 79.733(4)°$, $\gamma = 80.770(4)°$, $V = 3336(1)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.589$ g cm^{-3}. The structure, refined on F^2, converged for 11 724 unique reflections ($R_{int} = 0.0312$) and 6974 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0866$ and $wR_2 = 0.2918$ and a goodness-of- fit = 1.029. Five silver atoms of the Ag_{11} silver aggregate exhibit positional disorder with an occupancy ratio of 0.9:0.1 for Ag2, Ag4, and Ag10 and 0.8:0.2 for Ag5 and Ag6. The site occupancy of water molecules O5W and O6W was derived from the elemental analysis results and X-ray structure analysis. Hydrogen atoms of water molecules were not included in the refinement.

(d) Crystal data for $(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}4AgCF_3CO_2$ (**4**): $C_{14}H_3F_{12}O_8SAg_5$, $M = 1098.57$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.283(2)$ Å, $b = 11.458(2)$ Å, $c = 11.989(3)$ Å, $\alpha = 91.137(2)°$, $\beta = 101.018(2)°$, $\gamma = 105.768(3)°$, $V = 1330.6(5)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.742$ g cm^{-3}. The structure, refined on F^2, converged for 6480 unique reflections ($R_{int} = 0.0299$) and 4979 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0374$ and $wR_2 = 0.1105$ and a goodness-of-fit = 1.025. All four independent trifluoroacetate groups exhibit orientational disorder in a 0.5:0.5 ratio. The carbon atom C5 on the thiophene ring has two disordered positions with an occupancy ratio of 0.65:0.35.

(e) Crystal data for $(C_4H_3S\text{-}3)C{\equiv}CAg{\cdot}5AgC_2F_5CO_2{\cdot}4H_2O$ (**5**): $C_{21}H_{11}F_{25}O_{14}Sag_6$, $M = 1641.53$, orthorhombic, space group *Pbcm* (No. 57), $a = 14.146(2)$ Å, $b = 20.208(2)$ Å, $c = 29{,}490(4)$ Å, $V = 8430(2)$ Å^3, $Z = 8$, $T = 293$ K, $D_c = 2.574$ g cm^{-3}. The structure, refined on F^2, converged for 8454 unique reflections ($R_{int} = 0.0442$) and 5362 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0541$ and $wR_2 = 0.1847$ and a goodness-of-fit = 1.035. Two carbon atoms (C21 and C24) were refined isotropically. Fluorine atom F51 of the pentafluoropropionate group located on a mirror symmetry has two disordered positions with an occupancy ratio of 0.55:0.45. Silver atom Ag4 is disordered at two positions in a 0.9:0.1 ratio. Hydrogen atoms of water molecules were not included in the refinement.

CCDC-637956 (**1**), -637957 (**2**), -651308 (**3**), -637958 (**4**), and -651309 (**5**) 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**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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