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Assembly of organosilver(I) frameworks with terminal ethynide and ethenyl groups on separate pendent arms attached to an aromatic ring

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1. Introduction

Metal-ethynyl complexes have caught much attention in recent years owing to their structural diversity [1–3] and potential applications as precursors of nonlinear optical materials [4], luminescence materials [5] and rigid-rod molecular wires [6]. Utilizing appropriate metal-ligand supramolecular synthons, the designed engineering of organometallic frameworks has come of age [7]. Our systematic studies on the syntheses and characterization of silver(I) ethynide [8] complexes have led to the recognition and demonstrated utility of two kinds of multinuclear supramolecular synthons symbolized by Ar–C \equiv C \supset Ag_n and Ar–OCH₂C \equiv C \supset Ag_n [9]. Making use of such rigid and flexible metal-ligand supramolecular synthons in combination with various anionic and/or neutral ancillary ligands, we have achieved the construction of a wide variety of two- and three-dimensional silver(I) coordination networks exhibiting an interplay of argentophilicity, silver(I)-ethynide, silver(I)–aromatic, hydrogen bonding, π – π and anion– π interactions [9]. In addition, we have undertaken a systematic study of bi-/tri-dentate phenylethynide [10] or heteroaromatic ethynide silver(I) complexes [11].

As the ethenyl functional group $-CH=CH_2$ is known to serve as a π -ligand site [12], our conceived idea is to investigate the coordination behavior of newly designed ligands **HLn** (n = 1-7) each having ethynyl and ethenyl groups at the terminals of separate pendent arms attached to two variable positions on an aromatic skeleton (Scheme 1). By tuning the relative separation and orienta-

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ABSTRACT

A series of eight silver(I) trifluoroacetate complexes based on aromatic ligands bearing terminal ethynyl and ethenyl groups on separate pendent arms has been synthesized. Single-crystal X-ray analysis of the complexes provided detailed information on the influence of argentophilicity, ligand disposition and orientation, and the co-existence of three types of silver–carbon bonding (silver–ethynide, silver–ethenyl and silver–aromatic) in coordination network construction, as well as the roles played by weak π - π stacking and anion– π interactions in supramolecular assembly.

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tion of these two functional groups on the aromatic system, we aim to investigate their combination with silver(I) trifluorocarboxylate for the construction of new metal–organic frameworks (MOFs) consolidated by silver(I)–ethynide plus silver(I)–olefin binding.

Herein, we report our synthetic and structural studies of a series of eight silver(I) complexes of phenyl/naphthylethynide-based ligands with an ethenyl group tethered to a pendent arm at variable positions on the aromatic ring: AgL1·6AgCF₃CO₂·3H₂O (1), AgL2·7AgCF₃CO₂·2H₂O·CH₃CN (2), AgL3·6AgCF₃CO₂·5H₂O (3), AgL3· 3AgCF₃CO₂·H₂O·CH₃CN (4), AgL4·4AgCF₃CO₂·H₂O (5), AgL5·3AgCF₃ CO₂ (6), AgL6·6AgCF₃CO₂·H₂O (7), AgL7·7AgCF₃CO₂·4H₂O (8) (Scheme 1). On the basis of our previous experience, the reaction of crude starting materials [AgL1]_n (9), [AgL2]_n (10), [AgL3]_n (11), [AgL4]_n (12), [AgL5]_n (13), [AgL6]_n (14) and [AgL7]_n (15) with water-soluble silver salts is expected to generate MOFs stabilized by argentophilic, silver(I)–ethynide and silver(I)–ethenyl interactions, and the naphthyl or phenyl ring is potentially capable of partaking in weaker silver–aromatic, π – π stacking and anion– π interactions.

2. Experimental

All reagents and solvents used were reagent grade. Further purification and drying followed the guidelines of Armarego [13] when necessary. Organic solvents were concentrated under reduced pressure on a rotary evaporator. Chromatographic purification of the products was performed on Macherey Nagel Kieselgel 60 M (230–400 mesh). Thin-layer chromatography (TLC) was conducted on E. Merck silica gel 60 F_{254} (0.1 mm thickness) coated on aluminum plates. Visualization of the developed chromatogram





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Scheme 1. Ligands HL1-HL7 synthesized for the present study.

was performed by a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. Melting points (uncorrected) were measured with a Reichert apparatus in degrees Celsius. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker ADVANCE-III NMR spectrometer at 400 MHz (¹H) and 100 MHz (¹³C). All NMR measurements were carried out at room temperature in deuterated solution and were internally referenced to residual proton solvent signals (note: CDCl₃ referenced at δ 7.26 in ¹H, and δ 77.16 for central line of the triplet in ¹³C). Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s, singlet; d, doublet; t, triplet; brs, broad singlet; dd, doublet of doublets; m, multiplet), integration, coupling constant (Hz) and assignment. Mass spectrometry (MS) and high resolution mass spectrometry (HRMS) measurements were made on a ThermoFinnigan MAT 95XL instrument.

2.1. Synthesis of ligands (HL1-HL7)

2.1.1. Synthesis of 2-(prop-2-ynyloxy)benzaldehyde

2-Hydroxybenzaldehyde (1.7 mL, 16.4 mmol) was dissolved in acetone (40 mL) in a round bottom flask followed by the addition of K₂CO₃ (4.5 g, 32.8 mmol) at 25 °C. After stirring for 10 min, propargyl bromide solution (2.8 mL, 24.6 mmol) was injected. The reaction mixture was then heated for reflux until TLC monitoring indicated the disappearance of starting material. Followed by cooling to room temperature, the mixture was filtered through a small pad of silica gel and the pad was further washed with dichloromethane (3×40 mL). The collected filtrate was concentrated and purified by column chromatography (EtOAc/n-hexanes, 1:12). The desired product was collected as white solids (2.5 g, 15.3 mmol). Yield: 93%; $R_f = 0.5$ (EtOAc/*n*-hexanes, 1:10); ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta 2.57 \text{ (t, } I = 2.4 \text{ Hz}, 1 \text{ H}), 4.81 \text{ (d, } I = 2.4 \text{ Hz}, 2 \text{ H}),$ 7.04–7.11 (m. 2H), 7.53–7.57 (m. 1H), 7.84 (dd, *I* = 1.7, 7.7, 1H), 10.46 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 56.5, 76.6, 77.8, 113.3, 121.8, 125.6, 128.6, 135.8, 159.8, 189.6; HRMS (ESI) m/z Calc. for C₁₀H₈O₂ [M+H]⁺ 161.0597. Found: 161.0598.

2.1.2. Synthesis of 1-(prop-2-ynyloxy)-2-vinylbenzene (HL1)

As shown in Scheme 2, methyltriphenylphosphonium iodide (3.0 g, 7.5 mmol) was added to a THF solution (15 mL) in a round bottom flask. The white suspension was cooled to 0 °C in an ice bath. After 5 min, ^tBuOK (806 mg, 7.2 mmol) was added to the mixture to form yellow slurry. The mixture was stirred for another 30 min followed by the slow injection of a solution of 2-(prop-2ynyloxy)benzaldehyde (1.0 g, 6.3 mmol) in THF (5 mL). TLC monitoring indicated the completion of the reaction. The heterogeneous mixture was diluted with diethyl ether and filtered through a pad of silica gel, which was further washed with diethyl ether (40 mL). The collected filtrate was concentrated and purified by column chromatography (EtOAc/n-hexanes, 1:20) to give the desired product as white powder (900 mg, 6.0 mmol). Yield: 96%; $R_f = 0.4$ (EtOAc/n-hexanes, 1:15); ¹H NMR (CDCl₃, 400 MHz) δ 2.52 (t, *J* = 2.4 Hz, 1H), 4.73 (d, *J* = 2.4 Hz, 2H), 5.27 (dd, *J* = 1.3, 11.2 Hz, 1H), 5.75 (dd, J = 1.4, 17.8 Hz, 1H), 6.98–7.11 (m, 3H), 7.23–7.27 (m, 1H), 7.51 (dd, J = 1.3, 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 56.4, 75.6, 78.8, 112.8, 114.9, 121.8, 126.8, 127.6, 128.8, 131.5, 154.8.



Table 1

Crystallography data and structure refinement parameters of complex 1-8.

Complex	1	2	3	4
Structural formula	C ₂₃ H ₁₅ Ag ₇ F ₁₈ O ₁₆	C ₂₇ H ₁₆ Ag ₈ F ₂₁ NO ₁₇	C ₂₃ H ₁₉ Ag ₇ F ₁₈ O ₁₈	$C_{19}H_{14}Ag_4F_9NO_8$
Formula weight	1644.40	1888.32	1680.43	986.77
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1 (No. 2)
a (Å)	12.583(6)	11.458(6)	13.091(6)	9.987(4)
b (Å)	13.233(6)	13.707(8)	13.528(6)	11.554(5)
<i>c</i> (Å)	13.396(6)	17.101(9)	14.144(6)	13.113(9)
α (°)	76.965(1)	71.392(1)	97.664(1)	103.869(1)
β(°)	78.434(1)	75.057(1)	106.305(1)	101.074(1)
γ (°)	64.796(1)	66.680(1)	116.085(1)	107.193(1)
V (Å ³)	1952.6(1)	2310.8(2)	2061.3(16)	1346.0(12)
Ζ	2	2	2	2
$ ho_{c} (g \text{ cm}^{-3})$	2.797	2.714	2.708	2.435
$\mu (\mathrm{mm}^{-1})$	3.589	3.467	3.406	2.973
$R_1^a (I > 2\sigma)$	0.0248	0.0249	0.0408	0.0292
wR_2^{b} (all data)	0.0637	0.0632	0.1157	0.0746
Goodness-of-fit (GOF) on F ²	1.097	1.033	1.055	1.037
	5	6	7	8
Structural formula	$C_{24}H_{15}Ag_5F_{12}O_{11}$	$C_{22}H_{13}Ag_4F_9O_8$	$C_{28}H_{15}Ag_7F_{18}O_{15}$	$C_{30}H_{21}Ag_8F_{21}O_{20}$
Formula weight	1246.69	1007.79	1688.46	1963.40
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	P1 (No. 2)	P2/n (No. 13) ^c	<i>P</i> 1̄ (No. 2)	<i>P</i> 1 (No. 2)
a (Å)	10.486(7)	14.551(1)	13.516(6)	12.494(7)
b (Å)	10.969(8)	12.076(1)	13.829(6)	12.763(7)
c (Å)	13.574(9)	15.220(1)	14.144(6)	17.126(9)
α (°)	83.833(1)	90	82.156(1)	81.747(1)
β(°)	82.421(1)	105.959(2)	69.040(1)	89.677(1)
γ (°)	77.626(1)	90	71.419(1)	69.244(1)
V (Å ³)	1506.8(1)	2571.5(5)	2339.4(1)	2524.5(2)
Ζ	2	4	2	2
$ ho_{\rm c} ({\rm g}{\rm cm}^{-3})$	2.748	2.603	2.397	2.583
$\mu (\mathrm{mm}^{-1})$	3.326	3.115	2.998	3.185
$R_1^a (I > 2\sigma)$	0.0230	0.0368	0.0408	0.0760
wR2 ^b (all data)	0.0576	0.0875	0.1090	0.2417
Goodness-of-fit (GOF) on F^2	1.094	1.110	1.080	1.049

b

$$\begin{split} R_1 &= \sum ||F_0| - |F_c|| / \sum |F_0|, \\ wR_2 &= \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}. \end{split}$$

Space group P2/n is equivalent to standard P2/b by an axial transformation.

2.1.3. Synthesis of 3-(prop-2-ynyloxy)benzaldehyde

3-(Prop-2-ynyloxy)benzaldehyde was prepared from 3-hydroxybenzaldehyde (2.0 g, 16.4 mmol) according to the synthetic procedures for 2-(prop-2-ynyloxy)benzaldehyde and purified as colorless oil (2.3 g, 14.3 mmol). Yield: 87%; R_f = 0.5 (EtOAc/n-hexanes, 1:15); ¹H NMR (CDCl₃, 400 MHz) δ 2.55 (t, J = 2.2 Hz, 1H), 4.76 (d, J = 2.1 Hz, 2H), 7.25 (d, J = 1.0 Hz, 1H), 7.46–7.53 (m, 3H), 9.98 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 56.1, 76.3, 78.0, 113.6, 122.3, 124.3, 130.3, 137.9, 158.2, 192.1; HRMS (ESI) m/z Calc. for C₁₀H₈O₂ [M+H]⁺ 161.0597. Found: 161.0595.

2.1.4. Synthesis of 1-(prop-2-ynyloxy)-3-vinylbenzene (HL2)

HL2 was prepared from 3-(prop-2-ynyloxy)benzaldehyde (1.0 g, 6.25 mmol) as the preparation of 1-(prop-2-ynyloxy)-2vinylbenzene and purified as white solids (808 mg, 5.11 mmol). Yield: 82%; $R_f = 0.4$ (DCM/*n*-hexanes, 1:3); ¹H NMR (CDCl₃, 400 MHz) δ 2.53 (t, J = 2.4 Hz, 1H), 4.71 (d, J = 2.4 Hz, 2H), 5.27 (d, J = 10.8 Hz, 1H), 5.75 (dd, J = 0.6, 17.6 Hz, 1H), 6.66–6.73 (m, 1H), 6.88-6.90 (m, 1H), 7.03-7.07 (m, 2H), 7.24-7.28 (m, 1H); ^{13}C NMR (CDCl_3, 100 MHz) δ 56.0, 75.7, 78.7, 112.8, 114.4, 114.5, 119.9, 129.7, 136.7, 139.3, 157.9.

2.1.5. Synthesis of 1-(prop-2-ynyloxy)-4-vinylbenzene (HL3) HL3 was prepared according to literature procedures [14].

2.1.6. Synthesis of 7-(allyloxy)naphthalen-2-ol

2,7-Dihydroxynaphthalene (800 mg, 5.0 mmol) was dissolved in acetone (15 mL) followed by the addition of K₂CO₃ (759 mg,

5.5 mmol) at 25 °C. After stirring for 10 min, allyl bromide (475 µL, 5.5 mmol) was added dropwise to the solution mixture. The mixture was allowed to stir for an overnight. TLC indicated the disappearance of the starting material. The mixture was then filtered through a small pad of silica gel, which was further washed



Fig. 1. Coordination environment of the silver(1) atoms in the double salt AgL1 6AgCF₃CO₂ 3H₂O (1). The argentophilic Ag ... Ag distances shown as thick rods lie in the range 2.70-3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. Color scheme: dark gray, silver atoms; gray, oxygen atoms; broken line, Ag-C bond.



Fig. 2. (a) Perspective view of the crystal packing in **1** viewed from the direction of the *a*-axis, showing all notable H-bond between water molecules and trifluoroacetate ligands, Symmetry code: A: 1 - x, 1 - y, 2 - z; B: 1 - x, 2 - y, 2 - z; (b) perspective view of crystal packing of **1** from the direction of the *c*-axis, indicating the additional H-bonds (O3WB-..O9A) within metal–organic layers, which lead to the formation of a 3D supramolecular structure. (b) Perspective view of the crystal packing viewed from the direction of the *c*-axis. Symmetry code: A: x, y, 1 + z; B: -x, 2 - y, 2 - z; C: 1 - x, 1 - y, 2 - z; D: x, -1 + y, z. The hydrogen atoms and fluorine atoms are omitted for clarity. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; black line, C=C bond; black broken line, Ag–C bond; gray broken line, H-bond interactions.

with dichloromethane. After that, the collected filtrate was concentrated and purified by column chromatography to give the product as colorless oil (346 mg, 1.7 mmol). Yield: 34%; R_f = 0.5 (EtOAc/*n*-hexanes, 1:6); ¹H NMR (CDCl₃, 400 MHz) δ 4.63 (d, J = 5.3 Hz, 2H), 5.13 (brs, 1H), 5.32 (dd, J = 0.9, 10.5 Hz, 1H), 5.47 (dd, J = 1.3, 17.3 Hz, 1H), 6.07–6.17 (m, 1H), 6.94 (dd, J = 2.4, 8.8 Hz, 1H), 6.98–7.04 (m, 3H), 7.66 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 68.9, 106.0, 108.9, 115.4, 116.7, 118.0, 124.5, 129.4, 129.7, 133.3, 136.0, 154.1, 157.3; HRMS (ESI) *m*/*z* Calc. for C₁₃H₁₂O₂ [M+H]⁺ 201.0910. Found: 201.0913.

2.1.7. Synthesis of 2-(allyloxy)-7-(prop-2-ynyloxy)naphthalene (HL4)

7-(Allyloxy)naphthalen-2-ol (346 mg, 1.7 mmol) was dissolved in acetone (5 mL) followed by the addition of K₂CO₃ (287 mg, 2.1 mmol) at 25 °C (Scheme 3). After stirring for 15 min, propargyl bromide (233 μ L, 2.1 mmol) was injected slowly to the solution mixture. The mixture was then heated to reflux until TLC monitoring indicated the disappearance of the starting material. The mixture was cooled to room temperature and filtered through a small pad of silica gel. The collected filtrate was concentrated and purified by column chromatography to give the



Fig. 3. Perspective view of the coordination geometry in the silver double salt Ag**L2**.7AgCF₃CO₂·2H₂O·CH₃CN (**2**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.7O–3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. Symmetry code: -1 - x, -y, -1 - z. Color scheme: dark gray, silver atoms; gray, oxygen atoms, broken line, Ag–C bond.

desired product as white solids (294 mg, 1.2 mmol). Yield: 71%; R_f = 0.6 (EtOAc/*n*-hexanes, 1:8); ¹H NMR (CDCl₃, 400 MHz) δ 2.57 (t, *J* = 2.3 Hz, 1H), 4.65 (dd, *J* = 1.3, 4.0 Hz, 2H), 4.80 (d, *J* = 2.4 Hz, 2H), 5.34 (dd, *J* = 1.3, 10.5 Hz, 1H), 5.48 (dd, *J* = 1.5, 17.2 Hz, 1H), 6.09–6.19 (m, 1H), 7.04–7.08 (m, 3H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 2.6, 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 55.9, 68.9, 75.7, 78.7, 106.7, 107.0, 116.3, 116.9,



2.1.8. Synthesis of 6-(allyloxy)naphthalen-2-ol

6-(Allyloxy)naphthalen-2-ol was prepared from 2,6-dihydroxynaphthalene (500 mg, 3.1 mmol) according to the synthetic procedures for 7-(allyloxy)naphthalene-2-ol and purified as colorless oil (272 mg, 1.4 mmol). Yield: 45%; R_f = 0.4 (EtOAc/*n*-hexanes, 1:3); ¹H NMR (CDCl₃, 400 MHz) δ 4.63 (d, *J* = 5.3 Hz, 2H), 4.90 (brs, 1H), 5.32 (dd, *J* = 1.3, 10.5 Hz, 1H), 5.47 (dd, *J* = 1.5, 17.3 Hz, 1H), 6.07–6.17 (m, 1H), 7.06–7.17 (m, 4H), 7.61 (dd, *J* = 9.0, 15.7 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 69.1, 107.5, 109.8, 117.9, 118.2, 119.7, 127.9, 128.6, 129.8, 130.1, 133.5, 152.0, 155.2.

2.1.9. Synthesis of 2-(allyloxy)-6-(prop-2-ynyloxy)naphthalene (HL5)

HL5 was prepared from 6-(allyloxy)naphthalen-2-ol (272 mg, 1.4 mmol) as the preparation of 2-(Allyloxy)-7-(prop-2-ynyl-oxy)naphthalene and purified as white solids (257 mg, 1.1 mmol). Yield: 79%; R_f = 0.7 (EtOAc/*n*-hexanes, 1:6); ¹H NMR (CDCl₃, 400 MHz) δ 2.55 (t, *J* = 2.3 Hz, 1H), 4.63 (d, *J* = 5.2 Hz, 2H), 4.79 (d, *J* = 2.3 Hz, 2H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.47 (dd, *J* = 1.2, 17.3 Hz, 1H), 6.08–6.17 (m, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 7.16–7.21 (m, 3H), 7.66 (dd, *J* = 6.2, 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 56.1, 69.0, 75.7, 78.8, 107.4, 108.0, 117.9, 119.2, 119.5, 128.4, 128.5, 129.7, 130.3, 133.4, 154.2, 155.5; HRMS (ESI) *m*/*z* Calc. for C₁₆H₁₄O₂ [M+H]⁺ 239.1067. Found: 239.1064.

2.1.10. Synthesis of 3-(allyloxy)naphthalen-2-ol

3-(Allyloxy)naphthalen-2-ol was prepared from 2,3-dihydroxynaphthalene (2.0 g, 12.5 mmol) according to the synthetic procedures for 7-(allyloxy)naphthalene-2-ol and purified as colorless oil (1.8 g, 9.1 mmol). Yield: 72%; R_f = 0.5 (EtOAc/*n*-hexanes, 1:3); ¹H NMR (CDCl₃, 400 MHz) δ 4.74 (dt, *J* = 1.3, 5.5 Hz, 2H), 5.38 (dd, *J* = 1.2, 10.5 Hz, 1H), 5.48 (dq, *J* = 1.4, 17.2 Hz, 1H), 5.96 (brs, 1H), 6.09–6.19 (m, 1H), 7.13 (s, 1H), 7.28 (s, 1H), 7.29–7.36 (m, 2H), 7.66 (dd, *J* = 1.6, 4.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 69.8,



Fig. 4. Perspective view of the centrosymmetric silver-organic cycle in the crystal structure of **2**, showing that it is further stabilized by the existence of H-bonds between water molecules and trifluoroacetate ligands (01W...06A and 01W...012A), as well as the significant anion- π interaction. Symmetry code: A: -1 - x, -y, -1 - z. The hydrogen atoms and fluorine atoms are omitted for clarity. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; bold black line, C=C bond; black broken line, Ag–C bond; gray broken line, H-bond interactions; light gray broken line, anion- π interactions.

107.1, 109.7, 118.9, 124.0, 124.5, 126.5, 126.6, 129.0, 129.9, 132.5, 145.9, 146.4; HRMS (ESI) m/z Calc. for $C_{13}H_{12}O_2$ [M+H]⁺ 201.0910. Found: 201.0910.

2.1.11. Synthesis of 2-(allyloxy)-3-(prop-2-ynyloxy)naphthalene (HL6)

HL6 was prepared from 3-(allyloxy)naphthalen-2-ol (1.8 g, 9.1 mmol) as the preparation of 2-(Allyloxy)-7-(prop-2-ynyl-oxy)naphthalene and purified as white solids (1.9, 7.9 mmol). Yield: 87%; R_f = 0.4 (EtOAc/*n*-hexanes, 1:20); ¹H NMR (CDCl₃, 400 MHz) δ 2.55 (t, *J* = 2.3 Hz, 1H), 4.73 (d, *J* = 5.4 Hz, 2H), 4.89 (d, *J* = 2.3 Hz, 2H), 5.35 (dd, *J* = 1.0, 10.5 Hz, 1H), 5.49 (dd, *J* = 1.3,

17.3 Hz, 1H), 6.12–6.22 (m, 1H), 7.17 (s, 1H), 7.32–7.38 (m, 3H), 7.67–7.73 (m, 2H); 13 C NMR (CDCl₃, 100 MHz) δ 56.7, 69.7, 76.2, 78.5, 108.6, 109.6, 118.3, 124.4, 124.7, 126.5, 126.7, 129.1, 129.8, 133.1, 147.6, 148.8; HRMS (ESI) *m*/*z* Calc. for C₁₆H₁₄O₂ [M+Na]⁺ 261.0886. Found: 261.0886.

2.1.12. Synthesis of 5-(allyloxy)naphthalen-1-ol

5-(Allyloxy)naphthalen-1-ol was prepared from 1,5-dihydroxynaphthalene (2.0 g, 12.5 mmol) according to the synthetic procedures for 7-(allyloxy)naphthalene-2-ol and purified as yellowish oil (638 mg, 3.21 mmol). Yield: 26%; R_f = 0.3 (EtOAc/*n*-hexanes,



Fig. 5. (a) Perspective view of the grid-like metal-organic network layer structure in **2**. The zigzag infinite silver chains are separated into two groups labeled in gray and light gray color, respectively. Symmetry code: A: x, y, z; B: x, y, 1 + z. (b) Perspective view of the crystal packing along the a-axis, indicating the additional H-bonds (C27–H27A···O2A) and off-set π - π stacking interaction within metal-organic layers, which lead to the formation of the supramolecular network structure. Symmetry code: A: 1 + x, 1 + y, z; B: -x, 1 - y, 1 - z. The hydrogen atoms and fluorine atoms are omitted for clarity. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; bold black line, C=C bond; black broken line, Ag-C bond; gray broken line, H-bond interactions; light gray broken line, π - π stacking interactions.



Fig. 6. Perspective view of the coordination geometry in the silver double salt Ag**L3**·6AgCF₃CO₂·5H₂O (**3**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atom Ag4 exhibits twofold positional disorder, and only that the atom position with a higher occupancy (51%) is shown. Silver atoms are represented as thermal ellipsoids (30% probability level) with atom labeling. Symmetry code: A: -x, -y, 1-z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; broken line, Ag–C bond.

1:5); ¹H NMR (CDCl₃, 400 MHz) δ 4.72 (d, *J* = 5.1 Hz, 2H), 5.37 (d, *J* = 10.5 Hz, 1H), 5.55 (dd, *J* = 1.0, 16.8 Hz, 1H), 6.15–6.25 (m, 2H), 6.84–6.87 (m, 2H), 7.32 (t, *J* = 8 Hz, 1H), 7.39 (t, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 69.1, 105.9, 109.6, 114.1, 114.7, 117.5, 125.2, 125.3, 125.6, 127.2, 133.4, 151.4, 154.3; HRMS (ESI) *m/z* Calc. for C₁₃H₁₂O₂ [M+H]⁺ 201.0910. Found: 201.0912.

2.1.13. Synthesis of 5-(allyloxy)-1-(prop-2-ynyloxy)naphthalene (**HL7**)

HL7 was prepared from 5-(allyloxy)naphthalen-1-ol (638 mg, 3.21 mmol) as the preparation of 2-(allyloxy)-7-(prop-2-ynyl-oxy)naphthalene and purified as yellowish oil (600 mg, 2.53 mmol). Yield: 79%; R_f = 0.6 (EtOAc/*n*-hexanes, 1:15); ¹H NMR (CDCl₃, 400 MHz) δ 2.55 (t, *J* = 2.3 Hz, 1H), 4.71 (d, *J* = 5.1 Hz, 2H), 4.89 (d, *J* = 2.3 Hz, 2H), 5.34 (dd, *J* = 1.3, 10.6 Hz, 1H), 5.53 (dd, *J* = 1.5, 17.3 Hz, 1H), 6.13–6.23 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 7.36–7.41 (m, 2H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 56.3, 69.1, 75.7, 78.8, 106.0, 106.4, 114.5, 115.5, 117.5, 125.0, 125.5, 126.9,

127.0, 133.4, 153.3, 154.2; HRMS (ESI) m/z Calc. for C₁₆H₁₄O₂ [M+H]⁺ 239.1067. Found: 239.1066.

2.2. Preparation of polymeric silver ethynides as synthetic precursors

Caution: Silver ethynides are potentially explosive and should be handled in small amounts with extreme care!

Ligand **HL1** (1 mmol) was first dissolved in acetonitrile (10 mL). Silver nitrate (1 mmol) and triethylamine (1 mmol) were added subsequently with vigorous stirring, and the mixture was allowed to stir for 2 h in darkness. The resulted pale yellow slurry was diluted with methanol (20 mL) and filtered by suction filtration to collection a pale yellow precipitate of polymeric [AgL1]_n (**9**), which was washed thoroughly with methanol (3× 10 mL) and then stored in wet form at -10 °C in a refrigerator. Silver complexes of **HL2– HL7** were prepared in the same manner, the yields and infra-red absorption data are displayed below:

$[AgL1]_n$ (9) yield: 95%; IR: v 2054 cm ⁻¹ (w , $v_{C=C}$).
$[AgL2]_n$ (10) yield: 93%; IR: v 2052 cm ⁻¹ (w , $v_{C=C}$).
$[AgL3]_n$ (11) yield: 85%; IR: v 2045 cm ⁻¹ (w , $v_{C=C}$).
$[AgL4]_n$ (12) yield: 91%; IR: v 2038 cm ⁻¹ (w , $v_{C=C}$).
$[AgL5]_n$ (13) yield: 90%; IR: v 2046 cm ⁻¹ (w , $v_{C=C}$).
$[AgL6]_n$ (14) yield: 88%; IR: v 2006 cm ⁻¹ (w , $v_{C=C}$).
$[AgL7]_n$ (15) yield: 83%; IR: v 2045 cm ⁻¹ (w, $v_{C=C}$).

2.3. Synthesis of silver ethynide complexes

2.3.1. Synthesis of $AgL1 \cdot 6AgCF_3CO_2 \cdot 3H_2O(1)$

AgCF₃CO₂ (440 mg, 2 mmol) and AgBF₄ (38 mg, 0.2 mmol) were dissolved in a mixed solution of methanol (1 mL) and deionized water (0.1 mL). Complex **9** (16 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **1** were deposited in about 60% yield. *Anal.* Calc. for C₂₃H₁₅Ag₂F₁₈O₁₆: C, 16.80; H, 0.92. Found: C, 16.92; H, 1.06%; IR: v 2026 cm⁻¹ (w, v_{C=C}).

2.3.2. Synthesis of AgL2 7AgCF₃CO₂·2H₂O·CH₃CN (2)

AgCF₃CO₂ (440 mg, 2 mmol) and AgBF₄ (76 mg, 0.4 mmol) were dissolved in a mixed solution of methanol (1 mL) and deionized water (0.2 mL). Complex **10** (11 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **2** were deposited in about 53% yield. *Anal.* Calc. for $C_{27}H_{16}Ag_8F_{21}NO_{17}$: C,



Fig. 7. Perspective view of the silver–organic cycle in **3** with an inversion center between Ag2 and Ag2A. Symmetry code: A: –*x*, –*y*, 1 – *z*. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; bold black line, C=C bond; black broken line, Ag–C bond; gray broken line, H-bond interactions; light gray broken line, anion–π interactions.

17.17; H, 0.85; N, 0.74. Found: C, 17.15; H, 1.14; N, 0.58%. IR: ν 2040 cm⁻¹ (w, $v_{C=C}$). (Powder of complex **10** prepared may contain some acetonitrile as contaminates.)

2.3.3. Synthesis of $AgL3 \cdot 6AgCF_3CO_2 \cdot 5H_2O(3)$

AgCF₃CO₂ (440 mg, 2 mmol) and AgBF₄ (382 mg, 2 mmol) were dissolved in deionized water (1 mL). Complex **11** (40 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and stored at $-10 \,^{\circ}$ C in a refrigerator. After several days, colorless block crystals of **3** were deposited in about 60% yield. *Anal.* Calc. for C₂₃H₁₉Ag₇F₁₈O₁₈: C, 16.44; H, 1.14. Found: C, 16.60; H, 0.92%. IR: ν 2016 cm⁻¹ (*w*, $\nu_{C=C}$).

2.3.4. Synthesis of AgL336AgCF₃CO₂·H₂O·CH₃CN (4)

AgCF₃CO₂ (440 mg, 2 mmol) and AgBF₄ (382 mg, 2 mmol) were dissolved in a mixed solution of acetonitrile (0.2 mL) and deionized water (1 mL). Complex **11** (40 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and stored at -10 °C in a refrigerator. After several days, colorless block crystals of **4** were deposited in about 80% yield. *Anal.* Calc. for C₁₉H₁₄Ag₄F₉NO₈: C, 23.13; H, 1.43; N, 1.42. Found: C, 23.28; H, 1.71; N, 1.65%. IR: ν 2039 cm⁻¹ (w, $\nu_{C=C}$).

2.3.5. Synthesis of $AgL4 \cdot 4AgCF_3CO_2 \cdot H_2O(5)$

AgCF₃CO₂ (440 mg, 2 mmol) were dissolved in a mixed solution of methanol (1 mL) and deionized water (0.5 mL). Complex **12** (15 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **5** were deposited in about 54% yield. *Anal.* Calc. for $C_{24}H_{15}Ag_5F_{12}O_{11}$: C, 21.44; H, 0.37. Found: C, 21.65; H, 0.61%. IR: v 2039 cm⁻¹ (w, v_{C=C}).

2.3.6. Synthesis of AgL5 3AgCF₃CO₂ (6)

AgCF₃CO₂ (220 mg, 1 mmol) were dissolved in deionized water (1 mL). Complex **13** (8 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **6** were deposited in about 23% yield. *Anal.* Calc. for C₂₂H₁₃Ag₄F₉O₈: C, 23.90; H, 0.27%. Found: C, 24.21; H, 0.34%. IR: v 2043 cm⁻¹ (w, $v_{C=C}$).

2.3.7. Synthesis of $AgL6 \cdot 6AgCF_3CO_2 \cdot H_2O(7)$

 $AgCF_3CO_2$ (440 mg, 2 mmol) were dissolved in a mixed solution of methanol (3 mL) and deionized water (0.5 mL). Complex **14** (12 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and left to stand in the dark at room temperature. After several



Fig. 8. (a) Perspective view of a portion of the grid-like metal–organic layer structure in the crystal packing of **3**, showing notable H-bonds. Symmetry code: A: -x, -y, -z; B: -x, -1 - y, -z. (b) Perspective view of the crystal packing of **3** from the direction of the *c*-axis, indicating the additional H-bond (O3W…O7A) and aromatic π - π stacking interaction within metal–organic layers. Symmetry code: A: 1 - x, -y, 1-z. The hydrogen atoms and fluorine atoms are omitted for clarity. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; bold black line, C=C bond; black broken line, Ag–C bond; gray broken line, H-bond interactions; light gray broken line, π - π stacking interaction.

days, colorless block crystals of **7** were deposited in about 64% yield. *Anal.* Calc. for $C_{28}H_{15}Ag_7F_{18}O_{15}$: C, 19.92; H, 0.90. Found: C, 20.15; H, 1.05%. IR: v 2035 cm⁻¹ (w, $v_{C==C}$).

2.3.8. Synthesis of $AgL7 \cdot 7AgCF_3CO_2 \cdot 4H_2O(\mathbf{8})$

AgCF₃CO₂ (440 mg, 2 mmol) and AgBF₄ (382 mg, 2 mmol) were dissolved in deionized water (1 mL). Complex **15** (15 mg) was then added to the solution mixture with stirring until all the solids were dissolved. After that, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless block crystals of **8** were deposited in about 35% yield. *Anal.* Calc. for $C_{30}H_{21}Ag_8F_{21}O_{20}$: C, 18.35; H, 1.08. Found: C, 18.55; H, 1.33%. IR: ν 2135 cm⁻¹ (w, $\nu_{C=C}$).

2.4. X-ray crystallography

Selected crystals were used for data collection on a Bruker AXS Kappa ApexII Duo diffractometer at 123 K (**1** and **2**), at 150 K (**5**), at 173 K (**6** and **7**), and at 293 K (**3**, **4** and **8**) using frames of oscillation range 0.3°, with $2^{\circ} < \theta < 28^{\circ}$. An empirical absorption correction was applied using the sADABS program [15]. The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL program package [16]. The crystal-lographic data are summarized in Table 1.

3. Results

3.1. Crystallization

The neutral ligands **HL1–HL7** were synthesized from the respective reactions using the corresponding hydroxybenzaldehyde and dihydoxynaphthalene as starting materials. Double salts **1–8** were obtained from room-temperature crystallization of the corresponding crude polymeric compounds [AgL1]_n (9), [AgL2]_n (**10**), [AgL3]_n (**11**), [AgL4]_n (**12**), [AgL5]_n (**13**), [AgL6]_n (**14**) and [AgL7]_n (**15**) in a concentrated aqueous, water/acetonitrile or water/methanol solution of AgCF₃CO₂/AgBF₄ (1:1 or 5:1). AgCF₃-CO₂ and AgBF₄ were used to provide the auxiliary CF₃CO₂⁻ ligand and increase the silver(I) ion concentration, respectively.

The high concentration of silver ions and their aggregation through argentophilicity ensure that the ethynide moiety mostly achieves a high ligation number of 4 or 5 within a butterfly-shaped Ag₄ or square-pyramidal Ag₅ basket [17], as opposed to most transition-metal alkyl and aryl ethynide complexes with ligation numbers ranging from 1 to 4, and such baskets can be mutually connected by bridging trifluoroacetate ligands to yield higher-dimensional MOFs.

3.2. Description of crystal structures

3.2.1. $AgL1 \cdot 6AgCF_3CO_2 \cdot 3H_2O(1)$

In the crystal structure of **1**, the vinyl group is conjugated with the phenyl ring with a torsion angle C8–C9–C10–C11 = 1.7(6)°. As expected, the 3-(2-vinylphenoxy)propynide chain adopts a nonplanar conformation, in which the C3 and O1 atoms are nearly co-planar with the phenyl ring, and the torsion angles C5–C4– O1–C3 and C4–O1–C3–C2 are $-12.4(5)^{\circ}$ and $-63.7(4)^{\circ}$, respectively (Fig. 1). The ethynide group is encapsulated in a Ag₄ butterfly-shaped basket in the $\mu_4-\eta^1,\eta^1,\eta^1,\eta^2$ coordination mode. The silver atom Ag5 is connected to the Ag₄ silver aggregates through argentophilic interaction to form a Ag₅ segment, with Ag…Ag bond distances range from 2.801(4) to 3.337(4) Å, which are comparable to those observed in a wide variety of silver double and multiple salts reported by our group and attributed to argentophilic interactions [18]. The peripheral silver atoms Ag6 and Ag7 are attached to this Ag₅ segment through five trifluoroacetate groups, O2^O3, O6^O7, O8^O9, O10^O11 and O12^O13 via the $\mu_4-\eta^2, \eta^2, \mu_{2-}\eta^1, \eta^1, \mu_3-\eta^1, \eta^2, \mu_3-\eta^1, \eta^2$ and $\mu_4-\eta^2, \eta^2$ modes, respectively. Carbon atom C5 of the phenyl ring is attached to Ag2 at a bond distance of 2.815(4) Å, which is indicative of significant silver–aromatic interaction (under 2.9 Å) [19–24]. Furthermore, silver atom Ag6 is coordinated by the vinyl group in the η^2 mode with a bond length of 2.218(3) Å, which indicates a strong silver–ethenyl interaction (under 2.7 Å) [7a,25–31]. All three independent water molecules are coordinated to this segment in the μ_1 mode.

The Ag₅ segments are linked together by two pairs of inversion-related trifluoroacetate groups (O2^O3 and O12^O13) in $(\mu_4 - \eta^2, \eta^2 - CF_3CO_2)_2$ mode to form an infinite zigzag chain along the *c*-axis (Fig. 2a; also see Fig. S1 in Supplementary Information). Adjacent silver(I) chains are further cross-bridged by the external silver atoms (Ag7 and Ag7A) and trifluoroacetate groups [μ_2 -(O6^O7) and μ_2 -(O6^O7A)] to give a two-dimensional coordination network parallel to the *bc* plane, which is stabilized by hydrogen bonds (O1W···O6, 2.801(3) Å; O2W···O7, 2.915(3) Å; O1W···O4B, 2.867(4) Å). Such metal–organic layers are further associated together through formation of additional hydrogen bonding (O3WB···O9A, 2.771(4) Å) to form a 3D supramolecular structure (Fig. 2b).

3.2.2. AgL2·7AgCF₃CO₂·2H₂O·CH₃CN (2)

In the crystal structure of 2, 3-(2-vinylphenoxy)propynide also adopts a non-planar conformation, in which the torsion angles C5-C4-O1-C3 and C4-O1-C3-C2 are 123.1(4)° and -67.2(4)°, respectively (Fig. 3). The vinyl group is twisted out of the plane of the phenyl ring, the torsion angle C7-C8-C10-C11 being 23.5(6)°. As shown in Fig. 3, the ethynide group $(C1 \equiv C2)$ is bound to a square-pyramidal Ag₅ basket in the $\mu_5 - \eta^1, \eta^1, \eta^2, \eta^2$ coordination mode with Ag... Ag bond distances with a range of 2.845(5) to 3.017(5) Å. Two peripheral silver(I) atoms (Ag7 and Ag8) are hitched to the Ag₅ basket by two pairs of trifluoroacetate groups (02^03 and 014^015 for Ag7; 06^07 and 010^011 for Ag8) in the $\mu_3 - \eta^1, \eta^2$ mode, and the μ_1 acetonitrile (N1) and aqua (O2W) ligands coordinate to the Ag8 atom. The Ag6 atom is attached to the Ag₅ basket by two $\mu_3 - \eta^1, \eta^2$ trifluoroacetate groups (04^05) and O8^O9) and bridging water molecule O1W in the μ_2 mode. Silver atom Ag6A is also bonded to the vinyl group (C10=C11), with bond length 2.245(4) Å to form a centrosymmetric silver-organic



Fig. 9. Perspective view of the coordination geometry in the silver double salt AgL3·3AgCF₃CO₂·H₂O·CH₃CN (**4**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are represented as thermal ellipsoids (30% probability level) with atom labeling. Symmetry code: A: 1 - x, 1 - y, -z; B: 1 - x, 1 - y, -z; B: 1 - x, A_{z} -C bond.

cycle, which is stabilized by the formation of hydrogen bonds $O1W \cdots O6A$ (2.705(4) Å) and $O1W \cdots O12A$ (2.758(4) Å). Within this cycle, the distance between O6 and the center of the phenyl ring is about 3.681(3) Å, implying the possibility of significant anion- π interaction (Fig. 4).

The association of silver–organic cycles by a pair of inversionrelated trifluoroacetate groups (O12^O13 and O12B^O13B) produces an infinite zigzag chain along the *c*-axis direction (Fig. 5a). Such chains are connected together by two types of $\mu_3-\eta^1,\eta^2$ trifluoroacetate groups (O2^O3 and O14^O15) to give a grid-like metal–organic layer corresponding to the *ac* plane (Fig. 5a), and such networks are further united together through off-set faceto-face $\pi-\pi$ interactions (inter-centroid distance 3.879(2) Å) between adjacent phenyl rings and C27–H27A···O2A hydrogen bonding (2.245(3) Å) to give a 3D supramolecular structure (Fig. 5b).

3.2.3. AgL3 · 6AgCF₃CO₂ · 5H₂O (3)

In the crystal structure of **3**, 3-(4-vinylphenoxy)propynide adopts a non-planar conformation, in which the C3 and O1 atoms are nearly perpendicular to the benzene ring with torsion angles $C5-C4-O1-C3 = -177.6(7)^{\circ}$ and $C4-O1-C3-C2 = -73.8(9)^{\circ}$. As show in Fig. 6, the ethynide group (C1=C2) is bound to a

square-pyramidal Ag₅ basket in the $\mu_5-\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, and the argentophilic Ag...Ag interactions range from 2.806(1) to 3.169(5) Å. Atom Ag6 is attached to the Ag₅ basket by two μ_3 -0,0',0' trifluoroacetate groups (O2^O3 and O6^O7) and one η^2 -bridged water ligand (O1W). Silver atom Ag4 is also found to exhibit site-occupancy disorder in a ratio of 51:49. Symmetryrelated atom Ag6A from a neighboring chain is coordinated by the conjugated vinyl group in the η^2 mode with a bond length of 2.286(8) Å. The exterior silver atom Ag7 is linked with the Ag₅ segment through coordination by two trifluoroacetate ligands (O4^O5 and O6^O7) via the μ_3 -0,0',0' mode and one trifluoroacetate ligand (O12^O13) by the μ_2 -0,0' binding mode.

As shown in Fig. 7, the silver atom Ag6 is bonded simultaneously to the vinyl group (C10B and C11B) to form a silverorganic cycle with an inversion center between Ag2 and Ag2B. This cycle is stabilized by the formation of hydrogen bonds O1W···O8B (2.732(8) Å) and O1W···O10B (2.815(9) Å). Notably, the short distance between the oxygen atom O10B of the coordinated trifluoroacetate group (O10B^O11B) and the center of the benzene ring (3.570(5) Å) indicate the existence of weak anion- π interaction. The remaining water molecules are coordinated to different silver atoms via the μ_1 mode (O2W to Ag4 and O3W to Ag5).



Fig. 10. (a) Perspective view of a portion of the infinite chain structure in **4** along the *a*-axis, showing notable H-bond and anion– π interaction. Symmetry code: A: 1 – *x*, 1 – *y*, –*z*; B: 1 – *x*, 1 – *y*, 1 – *z*; C: –*x*, 1 – *y*, –*z*. (b) Crystal packing of **4** viewed from the direction of the *a*-axis, indicating the additional C–H… π interaction between metal-organic layers, which leads to the formation of a three-dimensional supramolecular structure. The hydrogen atoms and fluorine atoms are omitted for clarity. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; black line, C=C bond; black broken line, Ag–C bond; gray broken line, H-bond interactions; light gray broken line, anion– π interactions; dark gray broken line, C–H… π interactions.



Fig. 11. Perspective view of the coordination geometry in the silver double salt Ag**L4** 4AgCF₃CO₂·H₂O (**5**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40 Å. The hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are shown as thermal ellipsoids (50% probability level) with atom labeling. Symmetry code: A: -1 - x, 1 - y, -z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; broken line, Ag–C bond.

Two pairs of inversion-related trifluoroacetate groups (O2^O3, O4^O5, O2A^O3A, and O4A^O5A) are utilized to bridge two adjacent cycles to yield a metal–organic chain along the *c*-axis. Adjacent chains are associated through a pair of inversion-related trifluoroacetate groups (O12^O13 and O12D^O13D) acting in the μ_2 –O,O' mode on silver atoms Ag7 and Ag7D to produce a grid-like layer structure. And such layer structure is further stabilized by additional hydrogen bonding between water molecules and trifluoroacetate ligands (O2W···O9A, 2.978(1)Å; O2W···O5W, 2.704(3)Å; O4W···O5W, 2.693(3)Å; O4W···O12, 2.877(1)Å) (Fig. 8a).

Adjacent sheets are further linked together through the hydrogen bond (O3W···O7 2.901(6) Å) and weak aromatic π - π stacking interaction between the phenyl rings from different layers (4.134(1) Å) to generate a 3D supramolecular structure (Fig. 8b).

3.2.4. AgL3·3AgCF₃CO₂·H₂O·CH₃CN (4)

By changing the crystal-growing medium from a concentrated aqueous solution of AgCF₃CO₂ to a mixed water–acetonitrile solution of AgCF₃CO₂, complex **4** was obtained from the crystallization of Ag**L3**.

In the crystal structure of **4**, 3-(4-vinylphenoxy)propynide adopts a nearly co-planar conformation, and the torsion angles C5-C4-O1-C3 and C4-O1-C3-C2 are $-1.4(7)^{\circ}$ and $-170.0(3)^{\circ}$, respectively. As shown in Fig. 9, the ethynide group (C1=C2) is bound to a square-pyramidal Ag₅ basket in the $\mu_5-\eta^1,\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, and the argentophilic Ag···Ag bond distances



Fig. 12. (a) A portion of the infinite column of linked Ag₈ fragments in **5** along the *b*-axis. The hydrogen atoms and fluorine atoms are omitted for clarity. Symmetry code: A: -1 - x, 1 - y, -z; B: -1 - x, 2 - y, -z. (b) Perspective view of packing in **5** from the direction of the *b*-axis. The hydrogen atoms and fluorine atoms are omitted for clarity. Symmetry code: A: -1 - x, 1 - y, -1 - z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; bold black line, C=C bond; black broken line, Ag-C bond; gray broken line, H-bond interactions; light gray broken line, anion- π interactions; pale gray broken line, $\pi - \pi$ stacking interactions.



Fig. 13. Perspective view of the coordination geometry in the silver double salt Ag**L5**·3AgCF₃CO₂ (**6**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are represented as thermal ellipsoids (50% probability level) with atom labeling. Symmetry code: A: 0.5 + x, 1 - y, 0.5 + z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; broken line, Ag–C bond.



Fig. 14. (a) Perspective view of the crystal packing of **6**. Symmetry code: A: 1.5 - x, y, 0.5 - z; B: 1 - x, 1 - y, -z. (b) Perspective view of the crystal packing of **6** showing the existence of weak π - π stacking interaction (3.775 Å), which leads to the formation of layer structure. The hydrogen atoms and fluorine atoms are omitted for clarity. Symmetry code: A: 1.5 - x, y, 0.5 - z; B: -1 + x, y, z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, $C \equiv C$ bond; black line, C = C bond; black broken line, Ag–C bond; light gray broken line, π - π stacking interactions.

are in a range of 2.818(6) to 3.186(5)Å. The vinyl group (C10=C11), which is slightly twisted out of the plane of the phenyl ring with a torsion angle (C6-C7-C10-C11) of 164.5(5)°, coordinates to atom Ag4B by the η^2 mode with a bond distance of 2.352(5)Å.

As shown in Fig. 10a, with an inversion center located at the center of the Ag2–Ag2A bond, two Ag₅ baskets share an edge to engender a Ag₈ aggregate. Two adjacent Ag₈ aggregates are linked by an inversion-related pair of trifluoroacetate ligands (O2^O3 and O2B^O3B) via μ_3 –O,O,O' mode to generate an infinite metal–organic column along the *a* axis. The column is further stabilized by additional hydrogen bonds of type O4···O1WB at a distance of 2.823(6) Å.

Such columns are cross-bridged through silver–olefin interaction to form a metal–organic layer with an inversion center between Ag4 and Ag4B. (Fig. 10a). Notably, the short distance (O1…ring center, 3.649(4)Å) between oxygen atom O1 of the prop-2-ynyloxy group and the proximal phenyl ring indicates the existence of a weak anion– π interaction.

Water molecule O1W and molecule N1 are coordinated to silver atoms Ag1 and Ag3, respectively (Fig. 10a). Adjacent layers are further linked together through C-H··· π interaction (C19– H19A···ring center, 3.003(1)Å) between acetonitrile methyl and phenyl groups to generate a three-dimensional supramolecular network (Fig. 10b).

3.2.5. AgL4·4AgCF₃CO₂·H₂O (5)

In the crystal structure of **5**, ligand **I4** exhibits a non-planar conformation with both the prop-2-ynyloxy group and the allyloxy group twisted out of the plane of the naphthyl ring, and the torsion angles C5–C4–O1–C3, C4–O1–C3–C2, C9–C8–O2–C14, C8–O2–C14–C15 and O2–C14–C15–C16 are 135.8(3)°, –56.2(3)°, 161.9(3)°, –79.7(3)° and –19.6(5)°, respectively. As shown in Fig. 11, the ethynide group composed of C1 and C2 is bound to a Ag₄ basket (Ag1–Ag4) in the $\mu_4-\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode with Ag…Ag interaction distances in the range of 2.814(4)–



Fig. 15. Perspective view of the coordination geometry in the silver double salt AgL6-6AgCF₃CO₂·H₂O (**7**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are shown as thermal ellipsoids (50% probability level) with atom labeling. Symmetry code: A: -x, 2 - y, 1 - z; B: 1 - x, 2 - y, -z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; broken line, Ag–C bond.

3.163(5) Å. Inversion-related silver atom Ag4A is linked with the Ag₄ basket by three trifluoroacetate groups (05^{\chi}06, 07^{\chi}08 and 09^{010} via μ_4 -0,0,0',0', μ_2 -0,0' and μ_2 -0,0' coordination modes, respectively. An exterior silver atom Ag5 is attached to the Ag2-Ag1-Ag4A segment through two trifluoroacetate groups (03^04 and O5^O6) via the μ_3 -0,0',0' and μ_4 -0,0,0',0' coordination modes, respectively (Fig. 11). Notably, silver atom Ag2 is η^2 -coordinated by C12 and C13 of the naphthyl ring with a Ag-C_{cent} bond distance of 2.601(3) Å. Atom Ag5 is coordinated by the η^2 -ethenyl group (C15 and C16) with a Ag-C_{cent} bond length of 2.288(3) Å; it also interacts with the naphthyl ring via the η^1 mode at a Ag5–C7 bond distance of 2.843(3) Å. Adjacent Ag₈ aggregates with an inversion center located at the center of the Ag4 Ag4A bond are linked by trifluoroacetate group (03^04) via the μ_4 -0,0,0',0' coordination mode to generate an infinite chain composed of linked Ag₈ segments along the *b*-axis (Fig. 12a). Viewing from the direction of the *b*-axis (Fig. 12b), adjacent infinite chains are seen to be connected by π - π stacking interactions (3.842(3)Å) between naphthyl rings of **L4** ligands, together with an anion- π interaction between oxygen atom O2A of the allyloxy group and a C₆ aromatic ring (O2A···ring center = 3.417(2) Å), leading to the formation of a close-packed layer structure, which is further stabilized by additional H-bonding (O1W···O9, 2.766(3) Å).

3.2.6. AgL5·3AgCF₃CO₂ (6)

In the crystal structure of complex **6**, the ethynide moiety C1–C2, which is also twisted out of the plane of the naphthyl ring with torsion angles (C5–C4–O1–C3, C4–O1–C3–C2) of 142.6(6)° and -160.0(5)°, respectively, is capped by a butterfly-shaped Ag₄ segment taking the $\mu_4-\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode with Ag…Ag distances in a range of 2.789(7) to 3.000(5) Å. The allyloxy moiety is twisted out of the plane of the naphthyl ring with torsion angles C8–C9–O2–C14 = 170.8(5)°, C9–O2–C14–C15 = -91.6(6)° and O2–C14–C15–C16 = -12.9(8)°. Utilizing three μ_3 –O,O,O' trifluoroacetate groups as linkage components, external silver atom Ag5 is connected with the trigonal pyramidal Ag₄ basket. Silver atom Ag2A is coordinated by the ethenyl group (C15 and C16) in the η^2 mode with a Ag–C_{cent} bond distance of 2.335(5) Å (Fig. 13).



Fig. 16. (a) Perspective view of interconnection between the infinite chains through Ag–aromatic interactions in the crystal structure of **7** viewed from the direction of the *c*-axis. (b) Perspective view of the crystal packing showing the aromatic π – π stacking interactions (3.665 Å) between the naphthalene rings. The hydrogen atoms and fluorine atoms are omitted for clarity. Symmetry code: A: –x, 2 – y, –z; B: 1 – x, 2 – y, –z. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C=C bond; black line, C=C bond; black broken line, Ag–C bond; gray broken line, H-bond interactions; light gray broken line, π – π stacking interactions.

With Ag4 lying on a C₂ axis, two Ag₄ baskets share a common vertex to form a Ag₇ aggregate (Fig. 14a). Linkage of adjacent Ag₇ aggregates by a pair of inversion-related trifluoroacetate groups (O5^O6 and O5B^O6B) produce a Ag₇– $(\mu_4 - \eta^2, \eta^2 - CF_3CO_2)_2 - Ag_7$ building unit, which leads to the formation of a zigzag infinite chain along the *a*-axis direction (see Fig. S2 in Supplementary Information). With the presence of aromatic π - π stacking interactions (3.775(3)Å) between proximal naphthyl rings, adjacent infinite zigzag silver chains are interconnected to form a wavy layer structure (Fig. 14b).

3.2.7. AgL6.6AgCF₃CO₂.H₂O (7)

As shown in Fig. 15, the alkyl ethynide moiety $(C1 \equiv C2)$ of L7 in the crystal structure of AgL6·6AgCF₃CO₂·H₂O (7) is capped by a square-pyramidal Ag₅ (Ag1–Ag5) basket in a $\mu_5-\eta^1,\eta^1,\eta^2,\eta^2$ coordination mode, and the Ag. Ag interaction distances range from 2.843(6) to 3.176(8) Å. Besides, the prop-2-ynyloxy group deviates from the plane of the naphthyl ring by torsion angles $C5-C4-O1-C3 = -6.0(8)^{\circ}$ and $C4-O1-C3-C2 = 74.3(6)^{\circ}$, while the torsion angles between the allyloxy group and the naphthyl ring are C4-C13-O2-C14 = -168.2(5)°, C13-O2-C14-C15 = 163.0(5)° and $O2-C14-C15-C16 = -19.8(9)^{\circ}$. The silver atom Ag6 is connected to the Ag₅ silver aggregates through argentophilic interaction to form a Ag₆ segment. A peripheral silver atom Ag7 is attached to this Ag₆ segment through two trifluoroacetate groups and an aqua ligand, O3^O4, O5^O6 and O1W via the μ_3 -0.0.0'. μ_4 –0,0,0',0' and μ_2 –0,0 modes, respectively. Silver atom Ag7B is n^2 -coordinated by the center of the C9–C10 edge of the naphthyl ring with a bond distance of 2.428(6) Å. In addition, symmetryrelated atom Ag6A is η^2 -coordinated by the ethenyl group (C15 and C16) with a bond distance of 2.252(7) Å.

Two independent Ag_6 aggregates are connected together through two different pairs of inversion-related trifluoroacetate ligands (05^06 and 07^08) to engender a Ag_{12} segment. Such Ag_{12} segments are further interconnected by another pairs of inversion-related trifluoroacetate ligands (013^014 and 013a^014a) to generate an infinite chain of linked Ag_{12} segments (Fig. S3 in Supporting Information). Adjacent chains are seen to associate with each other by silver aromatic interaction between



Fig. 17. Perspective view of the coordination geometry in the silver double salt $AgL7.7AgCF_3CO_2.4H_2O$ (**8**). The argentophilic Ag...Ag distances shown lie in the range 2.70–3.40 Å, and the hydrogen atoms and fluorine atoms are omitted for clarity. Silver atoms are represented by thermal ellipsoids (20% probability level) with atom labeling. The silver atom Ag7 exhibits site-occupancy disorder, and only position Ag7 with the higher occupancy (86%) is shown. Similarly, water molecule O2W exhibits site-occupancy disorder, and only position O2W with the higher occupancy (59%) is shown. Color scheme: dark gray, silver atoms; gray, oxygen atoms; broken line, Ag–C bond; gray broken line, H-bond interactions.

Ag7 atoms and the naphthyl rings to assemble a silver layer structure (Fig. 16a). Such association is further supported by notable H-bonding between water molecule and trifluoroacetate ligands (O1W···O9B, 2.775(5) Å and O1W···O11B, 2.744(5) Å). In between the silver layer structures, notable aromatic π - π stacking interactions (3.665(1) Å) are found to support such three-dimensional supramolecular structure (Fig. 16b).

3.2.8. AgL7.7AgCF₃CO₂.4H₂O (8)

In the crystal structure of **8**, both the prop-2-ynyloxy group $(torsion angles C5-C4-O1-C3 = -22.4(16)^{\circ} and C4-O1-C3 C2 = -76.7(11)^{\circ}$) and the allyloxy group (torsion angles $C8-C9-O2-C14 = -178.3(1)^{\circ}$, $C9-O2-C14-C15 = 168.0(1)^{\circ}$ and $O2-C14-C15-C16 = -16.4(3)^{\circ}$ are twisted out of the naphthalene plane (Fig. 17). The ethynide group is capped by a Ag₅ square-pyramidal basket in a $\mu_5 - \eta^1, \eta^1, \eta^2, \eta^2$ coordination mode, and the distance of Ag. . . Ag argentophilic interaction ranges from 2.847(1) to 3.116(1) Å. Atom Ag6 is attached to the Ag₅ silver basket through two trifluoroacetate groups O9^O10 and O11^O12 via the $\mu_3 - \eta^1, \eta^2$ mode, and is also η^2 -coordinated by the center of the C11–C12 edge of the naphthyl ring at a bond distance of 2.363(1) Å. Atom Ag7 exhibits site-occupancy disorder in a ratio of 86:14; it is coordinated by aqua ligand O3W and the ethenyl group (C15=C16) in the η^2 mode at a bond length of 2.206(2) Å. Furthermore, silver atom Ag8 is coordinated to the Ag₅ aggregates through coordination by two trifluoroacetate groups O3^O4 and O7^O8 via the μ_3 - η^1 , η^2 mode and two water molecules O1W and O2W in the μ_2 and μ_1 modes, respectively. A solvated water molecule O4W contributes to stabilization of the crystal structure via hydrogen bonding.

Adjacent Ag₅ segments are linked together by a pair of inversion-related trifluoroacetate group (O13^O14) in $(\mu_4 - \eta^2, \eta^2 - CF_3CO_2)_2$ mode to form an infinite zigzag chain composed of Ag₅ segments along the *b*-axis (Fig. 18a). Water molecule O1W shows strong H-bond interactions with adjacent trifluoroacetate ligands (O1WB···O5B, 3.084(1) Å; O1WB···O5C, 2.864(1) Å; O1W···O7C, 3.007(1) Å). Similarly, water molecule O2W has rather strong H-bond interaction with trifluoroacetate ligand (O2W···O13, 2.857(2) Å) and it is found to exhibit site-occupancy disorder in a ratio of 59:41. Water molecule O3W is interacted with adjacent trifluoroacetate ligands through H-bondings (O3WD···O6C, 2.791(3) Å; O3WD···O10C, 3.102(3) Å). Finally, water molecule O4W exhibits notable H-bond interaction with a nearby trifluoroacetate ligand (O15^O16) at a distance of 2.865(3) Å.

Adjacent silver(I) chains are further cross-bridged by the coordination of O1W with silver atoms Ag4B and Ag8A to assemble a wavy metal–organic supramolecular layer structure (Fig. S4 in Supporting Information). Silver atoms Ag7 are bonded to the allyloxy group simultaneously, which generate a centrosymmetric metal–organic cycle (Fig. S5 in Supporting Information shows that an inversion center is located between Ag7A and Ag7B). As a result, such cyclic structural elements act as cross-linkers to join two adjacent layers to generate a three-dimensional supramolecular framework. This network structure is further supported by the additional H-bondings between water molecules and trifluoroacetate ligands (O4WB···O16C, 2.865(3) Å) (Fig. 18b).

4. Discussion

4.1. Silver–carbon linkage modes

Systematic investigation of the present series of eight silver complexes (1-8) reaffirms the general utility of the silver–ethynide supramolecular synthon $R-C \equiv C \supset Ag_n$ (n = 4, 5) in coordination network assembly [32]. The coordination modes of ethynide ligands **L1–L8** in their silver double-salts are displayed in Fig. 19.



Fig. 18. (a) Perspective view of a portion of the zigzag chains composed of Ag_5 segments in **8**, showing all notable H-bondings within water molecules and those between water molecules and trifluoroacetate ligands. Symmetry code: A: 2 - x, 1 - y, -z; B: 1 - x, 1 - y, -1 - z; C: -1 + x, y, z; D: 1 - x, 1 - y, -z. (b) Perspective view of wavy metalorganic layer structure viewed from the direction of the *a*-axis, adjacent layer structures are differentiated by purple and turquoise colors, showing notable H-bondings within water molecules and those between water molecules and trifluoroacetate ligands. Symmetry code: A: 1 - x, 1 - y, -1 - z; B: -1 + x, y, z; C: 2 - x, 1 - y, -z. The hydrogen atoms and fluorine atoms are omitted for clarity. Color scheme: dark gray, silver atoms; gray, oxygen atoms; black ball and stick, C to bond; block line, C=C bond; block line, H-bond interactions.



Fig. 19. Coordination modes of anionic ligands in their corresponding silver complexes: L1 in 1(a), L2 in 2(b), L3 in 3(c) and 4(d), L4 in 5(e), L5 in 6(f), L6 in 7(g) and L7 in 8(h).

In each complex, the terminal olefinic group of the **L** ligand is π bonded to a silver atom at a Ag–ethenyl bond distance that varies from 2.206(2) to 2.352(5) Å. This finding shows that an ethenyl moiety at the end of either a pendant arm or directly attached to an aromatic ring invariably serves as a η^2 ligation site for the supramolecular assembly of silver(I) coordination chains and layers.

Among the eight complexes reported herein, half are found to exhibit significant silver–aromatic (Ag···Ar) interactions ranging from 2.363(1) to 2.843(3) Å in either the η^1 or η^2 coordination

Table 2	
Summary of the different types of silver(I)-carbon interactions and other weak interactions that exist in comple	x 1-8.

Complex	1	2	3	4
Solvated molecules in the crystal structure (No.)	H ₂ O (3)	H ₂ O (2); CH ₃ CN (1)	H ₂ O (5)	H ₂ O (1); CH ₃ CN (1)
Silver-ethynide Silver-ethenyl Silver-aromatic	$\begin{array}{l} \mu_{4}-\eta^{1},\eta^{1},\eta^{1},\eta^{2}\\ \eta^{2} \left(2.218(3)\text{\AA}\right)\\ \eta^{1} \left(2.815(4)\text{\AA}\right) \end{array}$	$ \begin{array}{l} \mu_{5}-\eta^{1},\eta^{1},\eta^{1},\eta^{2},\eta^{2}\\ \eta^{2} \ (2.245(4) \text{ Å}) \\ - \end{array} $		$ \begin{array}{l} \mu_{5}-\eta^{1},\eta^{1},\eta^{1},\eta^{2},\eta^{2}\\ \eta^{2} \ (2.352(5) \text{ \AA}) \\ - \end{array} $
Hydrogen bonding π - π Stacking Anion- π interaction C-H··· π interaction	√ - -	√ 3.879(2) Å 3.681(3) Å -	√ 4.134(1) Å 3.570(5) Å -	√ - 3.649(4) Å 3.003(1) Å
Complex	5	6	7	8
Solvated molecules in the crystal structure (No.)	H ₂ O (1)	-	H ₂ O (1)	H ₂ O (4)
Silver-ethynide Silver-ethenyl Silver-aromatic	$\begin{array}{l} \mu_4 - \eta^1, \eta^1, \eta^2, \eta^2 \\ \eta^2 \ (2.288(3) \ \text{\AA}) \\ \eta^2 \ (2.601(3) \ \text{\AA}) \\ \eta^1 \ (2.843(3) \ \text{\AA}) \end{array}$	$ \begin{array}{l} \mu_{4}-\eta^{1},\eta^{1},\eta^{2},\eta^{2}\\ \eta^{2} \left(2.335(5)\text{\AA}\right)\\ - \end{array} $	$\begin{array}{l} \mu_{5}-\eta^{1},\eta^{1},\eta^{1},\eta^{2},\eta^{2}\\ \eta^{2}\;(2.252(7)\;\text{\AA})\\ \eta^{2}\;(2.428(6)\;\text{\AA}) \end{array}$	$\begin{array}{l} \mu_{5}-\eta^{1},\eta^{1},\eta^{1},\eta^{2},\eta^{2}\\ \eta^{2} \ (2.206(2) \ \text{\AA})\\ \eta^{2} \ (2.363(1) \ \text{\AA}) \end{array}$
Hydrogen bonding π - π Stacking Anion- π interaction C-H \cdots π interaction	√ 3.842(3) Å 3.417(2) Å -	- 3.775(3) Å - -	√ 3.665(1) Å - -	√ - -

mode, and an interesting structure-dependent relationship is observed. Comparing the results of complex **5–8**, it is noted that when the prop-2-ynyloxy and allyloxy groups are far apart (complex **6**, substitution at 2,6-positions in the naphthalene ring), coordination network construction is dominated by π – π stacking to yield a centrosymmetric metal–organic cycle, making it unfavorable for silver atoms to get close to the aromatic system for significant Ag···Ar interaction. When both functional moieties are suitably oriented and closely spaced (complex **7** and **8**, 2,3and 1,5-positions, respectively), the possibility of Ag···Ar interaction will be enhanced. In complex **1** and **5**, the pendant arm bearing the terminal ethynide group of the respective ligand (L1 and L4, respectively) attached to the 2-position is favorably oriented to facilitate both silver–ethynide and silver–aromatic binding to the same Ag₅ basket.

The size of the aromatic skeleton in the **L** ligand also plays a significant role in influencing the onset of silver–aromatic interaction. In comparison with the phenyl ring, the naphthyl ring has a more extensive delocalized π -electron system that facilitates stronger Ag. Ar interaction. This is reflected by the shorter Ag. Ar distances observed in complex **5**, **7** and **8** in comparison that in **1**.

The coordination mode of the trifluoroacetate groups varies from the common $\mu_2 - \eta^1, \eta^1, \mu_3 - \eta^1, \eta^2$ and $\mu_4 - \eta^2, \eta^2$ varieties. The trifluoroacetate ligand generally plays two important roles: one type spans an edge of the Ag_n basket to stabilize the [Ag_nC \equiv C]⁽ⁿ⁻¹⁾⁺ cationic moiety, whereas the other type bridges adjacent Ag_n baskets or Ag atoms coordinated to the olefin/aromatic moieties to generate an infinite chain or a layer-type network.

4.2. Weak intermolecular interactions

With the lone exception of **6**, all other complexes incorporate solvated water molecules or acetonitrile or both in their crystalline lattices. In these solvent-containing complexes, hydrogen-bonds confer extra stability to a coordination layer structure or connect the layers into a three-dimensional supramolecular network.

When a crystal structure contains a centrosymmetric metal–organic cycle as a building block, as in complex **2**, **3**, and **6**, offset face-to-face π – π stacking interactions (ring center-to-center distance in the range 3.3–4.2 Å) [33] serve to associate adjacent coordination layers to yield a three-dimensional supramolecular network. On the other hand, π – π stacking interaction is usually absent in those complexes that show strong Ag.··Ar (<2.4 Å) or

dominant hydrogen-bonding interactions, such as in complex 1 and 8. In such crystal structures, the aromatic systems are much engulfed within the coordination network by silver atoms and bridging trifluoroacetate ligands, which prevent them from coming into close contact. When the crystal structures exhibit rather weak Ag···Ar interactions (>2.6 Å), as in complex **5** and **7**, significant $\pi - \pi$ stacking interactions can co-exist. In the crystal structure of 7, notable aromatic π - π stacking serves as the only interaction to associate adjacent layers by forming a distorted centrosymmetric metal-organic cycle. In the structure of 5, both ethynide and ethenyl functional moieties lie above the same face of the naphthyl ring, exposing the other face (β -side) for π - π stacking interactions. Moreover, the occurrence of aromatic π - π stacking is abetted by the co-existence of uncommon anion- π interactions; for instance, complex 2-4 each possesses a centrosymmetric metal-organic cycle in their crystal structures, so that the phenyl rings are constrained to be close to the oxygen atoms of the pendant arms. In the structure of **4**, significant C-H··· π interaction with the acetonitrile ligand as the donor serves to connect adjacent layers.

5. Conclusion

The present work reports the synthesis and structural characterization of a series of eight silver(I) trifluoroacetate complexes containing newly designed ligands each composed of an aromatic nucleus with two flexible pendant arms attached to variable positions: one bearing a terminal ethynyl group and the other an ethenyl group. Single-crystal X-ray analysis of the complexes provided detailed information on the influence of ligand disposition and orientation, the onset and co-existence of three types of silver–carbon bonding (silver–ethynide, silver–ethenyl and silver–aromatic) in coordination network construction, as well as the roles played by weak interactions in supramolecular assembly. Different types of silver(I)–carbon interactions and other weak interactions that exist in complex **1–8** are summarized in Table 2.

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Appendix A. Supplementary data

CCDC 873473-873480 contain the supplementary crystallographic data for **1–8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.06.082.

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