CrystEngComm

PAPER

Cite this: DOI: 10.1039/c3ce40230d

Assembly of silver(I)–organic frameworks from flexible supramolecular synthons with pendant ethynide arm attached to biphenyl and phenoxybenzene skeletons†

Bo Li,^a Ren-Wu Huang,^a Shuang-Quan Zang*^a and Thomas C. W. Mak^{ab}

A series of six silver(I) complexes bearing terminal ethynide moiety attached *via* pendant arm to biphenyl and phenoxybenzene skeletons of two new ligands have been synthesized. In these compounds, the invariable appearance of the μ_{3^-} , μ_{4^-} and μ_5 -ligation modes of the ethynide moiety reaffirms the general utility of the silver–ethynide supramolecular synthons L \supset Ag_n (n = 3-5) in coordination network assembly. In complexes **1**, **2**, **4**, and **5**, silver(I)–aromatic interactions play important roles in assembling a series of silver–organic frameworks. Notably, an unusual $\pi \cdots Ag_4 \cdots \pi$ sandwich unit makes it appearance in complex **2**, which is the first example in silver–ethynide complexes. An argentophilic layer is found in complex **3**. In addition, a two-fold interpenetrating 3D supramolecular framework based on discrete Ag₈ aggregate is found in complex **6**. In the solid state, their luminescence behaviors have been studied.

Received 3rd February 2013, Accepted 18th March 2013 DOI: 10.1039/c3ce40230d

www.rsc.org/crystengcomm

Introduction

Silver(I)-ethynide complexes have attracted much interest owing to their structural diversity¹⁻³ and promising application as luminescent materials.⁴ The diverse coordination modes of the alkynyl moiety together with argentophilic interaction lead to the formation of giant silver clusters,² or extended solid-state architectures.3 In the past decade, our group has engaged in the designed construction of coordination networks based on new silver-ethynide supramolecular synthons. By utilizing them, a series of silver(I)-organic networks stabilized by argentophilic and silver-ethynide (σ , π and mixed σ , π) interactions have been obtained.^{3,5-7} Recently, Zhang and co-workers have studied the bonding and structures of silver-ethynide complexes incorporating pyridyl, pyrimidyl and carboxylate groups.³ⁱ With the aim of constructing unusual architectures, we have explored the employment of several ligands with one or more ethynyl groups attached to a phenyl, biphenyl, or naphthyl skeleton via a flexible -CH2-O- link for the construction of MOFs consolidated by both silver(I)-ethynide and silver(I)-aromatic interactions. Indeed, compared to rigid organic ligands,

flexible ones can change their conformations to meet the coordination requirement of the metal ion, which facilitates the formation of silver(I)-aromatic interactions and other intermolecular interactions.

In continuation of our research program and with the aim of constructing silver(I)-organic networks stabilized by both silver-ethynide, silver-aromatic and argentophilic interactions, we have designed two new conformational flexible ligands, 1-phenyl-4-(prop-2-ynyloxy)benzene (HL1), and 1-phenoxy-4-(prop-2-ynyloxy)benzene (HL2), with one substituent bearing terminal ethynyl group on the aromatic ring, and the phenyl ring is potentially capable of partaking in π - π and silver-aromatic interactions. The reaction of crude starting materials $[AgL]_n$ with water, water-acetonitrile, methanolsoluble silver trifluoroacetate-tetrafluoroborate generated six new metal-organic networks, namely, [(AgL1)·(AgCF₃CO₂)₂]_n $[(AgL1) \cdot (AgCF_3CO_2)_5 \cdot (CH_3CN) \cdot (H_2O)]_n$ (1), (2), $[(AgL1)_4 \cdot (AgNO_3)_2]_n$ (3), $[(AgL2) \cdot (AgCF_3CO_2)_4]_n$ (4), $[(AgL2)_2 \cdot (AgCF_3CO_2)_3]_n$ (5), and $[(AgL1) \cdot (AgCF_3CO_2)_3 \cdot (bpy)_2]_n$ (6), which are expected to be stabilized by silver(1)-ethynide and argentophilic interactions.

Experimental section

Materials and physical measurements

Commercially available 4-phenylphenol, 4-phenoxyphenol, propargyl bromide (80% in toluene), and K_2CO_3 were used without further purification. All synthetic reactions yielding organic ligands and polymeric starting materials were carried out under a nitrogen atmosphere. Elemental analysis for C, H,

RSCPublishing

View Article Online

^aThe College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, People's Republic of China. E-mail: zangsqzg@zzu.edu.cn; Fax: +86-371-67780136

^bDepartment of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China

[†] Electronic supplementary information (ESI) available: Solid-state excitation and emission spectra for compounds **1–6**. CCDC 910770–910775. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c3ce40230d

and N were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 $\rm cm^{-1}$ on a Bruker VECTOR22 spectrometer. Luminescence spectra for the solid samples were recorded on a FluoroMax-4 fluorescence spectrophotometer.

Caution! Silver ethynide complexes are highly potentially explosive in the dry state when subjected to heating or mechanical shock, and should be handled in small amounts with extreme care.

X-ray crystallographic analysis

Selected crystals were used for data collection on an OXFORD Diffraction Gemini Single Crystal diffractometer. An empirical absorption correction was applied using the SADABS program.⁸ The structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.⁹ Most of the CF₃ moieties of CF₃CO₂⁻ groups in these compounds were disordered, and the SADI command was used to fix them in the refinements. In **6**, silver atom Ag4 is located in two disordered positions with occupancy ratios of 0.82 : 0.18. The crystallographic data and selected bond lengths and angles for **1–6** are listed in Tables S1–S3, ESI.[†]

Synthesis of $[(AgL1) \cdot ((AgCF_3CO_2)_2]_n$ (1). AgCF₃CO₂ (0.22 g, 1 mmol) and AgBF₄ (0.382 g, 2 mmol) were dissolved in 1 mL of water. Then, $[AgL1]_n$ (0.025 g, 0.083 mmol) solid was added to the solution. After stirring for about 1 h, the solution was filtered. After several days, colorless block crystals of 1 were deposited in about 60% yield. Anal. calcd for C₁₉H₁₁Ag₃F₆O₅: C, 30.15; H, 1.46. Found: C, 30.21; H, 1.54. IR spectrum: 2065 cm⁻¹ (w, $v_{C=C}$).

Synthesis of $[(AgL1) \cdot (AgCF_3CO_2)_5 \cdot (CH_3CN) \cdot (H_2O)]_n$ (2). The procedure is similar to the synthesis of **1** except that acetonitrile (0.2 mL) was added. After several days, colorless needle crystals of **2** were deposited in about 55% yield. Anal. calcd for C₂₇H₁₆Ag₆F₁₅NO₁₂: C, 21.93; H, 1.09; N, 0.95. Found: C, 21.87; H, 1.14; N, 1.02. IR spectrum: 2069 cm⁻¹ (w, $v_{C=C}$).

Synthesis of $[(\text{AgL1})_4 \cdot (\text{AgNO}_3)_2]_n$ (3). AgNO₃ (0.34 g, 2 mmol) was dissolved in 1 mL DMSO. $[\text{AgL1}]_n$ (0.020 g, 0.066 mmol) was added to the solution. After stirring for about half an hour, the solution was filtered and transferred to a test tube. And then, water was layered over the solution. After several days, pale yellow needle crystals of **3** were obtained in about 45% yield. Anal. calcd for C₆₀H₄₄Ag₆N₂O₁₀: C, 45.03; H, 2.77; N, 1.75. Found: C, 45.09; H, 2.83; N, 1.83. IR spectrum: 2066 cm⁻¹ (w, $v_{C=C}$).

Synthesis of $[(AgL2) \cdot (AgCF_3CO_2)_4]_n$ (4). The procedure is similar to the synthesis of 1 except that $[AgL2]_n$ (0.020 g, 0.060 mmol) was added instead of $[AgL1]_n$. After several days, colorless block crystals of 4 were deposited in about 65% yield. Anal. calcd for $C_{23}H_{11}Ag_5F_{12}O_{10}$: C, 22.74; H, 0.91. Found: C, 22.79; H, 0.99. IR spectrum: 2112 cm⁻¹ (w, $v_{C=C}$).

Synthesis of $[(AgL2)_2 \cdot (AgCF_3CO_2)_3]_n$ (5). The procedure is similar to the synthesis of 2 except that $[AgL2]_n$ (0.020 g, 0.060 mmol) was added instead of $[AgL1]_n$. After several days, colorless block crystals of 5 were deposited in about 60% yield. Anal. calcd for $C_{36}H_{22}Ag_5F_9O_{10}$: C, 32.64; H, 1.67. Found: C, 32.67; H, 1.61. IR spectrum: 2109 cm⁻¹ (w, $v_{C=C}$).

Synthesis of $[(AgL1) \cdot (AgCF_3CO_2)_3 \cdot (bpy)_2]_n$ (6). $[AgL1]_n$ (0.011 g, 0.035 mmol) was dissolved in methanol solution (1.5 mL) of AgCF₃CO₂ (0.22 g, 1 mmol). To the resulting solution bpy (0.008 g, 0.05 mmol) was added, a clear solution was obtained, which was evaporated slowly in the air. Colorless crystals were isolated in *ca*. 63% yield. Anal. calcd for C₈₂H₅₄Ag₈F₁₈N₈O₁₄: C, 38.17; H, 2.11; N, 4.34. Found: C, 38.11; H, 2.08; N, 4.40. IR spectrum: 2069 cm⁻¹ (w, $v_{C=C}$).

Results and discussion

Syntheses

The neutral ligands HL1 and HL2 were synthesized according to the literature method.¹⁰ Reaction of 4-phenylphenol and 4-phenoxyphenol, respectively, with propargyl bromide in acetone in the presence of K₂CO₃ afforded 1-phenyl-4-(prop-2-ynyloxy)benzene (HL1) and 1-phenoxy-4-(prop-2-ynyloxy)benzene (HL2). Polymeric starting materials $[AgL]_n$ were prepared according to the literature method.¹¹ While sufficiently crystalline materials of 1, 2, 4-6 have been obtained by slow evaporation of crude polymeric compounds $[AgL]_n$ in a concentrated aqueous, water-acetonitrile, or methanol solution of $AgBF_4/AgCF_3CO_2$, respectively, growing crystals of 3 in a size and quality suitable for single-crystal X-ray diffraction required us to run precipitation under diffusion control. The tetrafluoroborate ion was employed to provide a high concentration of silver ions, which enhanced aggregation through argentophilicity such that the ethynide moiety is embraced within a trigonal Ag₃, butterfly-shaped Ag₄ or square-pyramidal Ag₅ basket. All of the complexes 1-6 are stable at room temperature in the solid state.

Description of crystal structures

[(AgL1)·(AgCF₃CO₂)₂]_n (1). In the crystal structure of 1, the ethynide moiety C1 and C2 taking the μ_4 - η^1 , η^1 , η^2 , η^2 coordination mode lies perpendicular to the plane comprising silver atoms Ag1#1, Ag2, and Ag3, pointing almost linearly at Ag1 (C2–C1–Ag1 177.05(5)°) to give rise to a butterfly-shaped Ag₄ basket (Fig. 1). In 1, the anionic ligand L1 adopts a non-planar conformation, in which the torsion angel C4–O1–C3–C2 is $-70.01(1)^\circ$, which facilitate to the formation of silver(I)–



Fig. 1 Atom labeling and coordination mode of L1 in **1** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry codes: #1 - x, -y, 2 - z; #2 - x, y, 1.5 - z. Atom color codes: Ag purple, C gray, O red.



Fig. 2 (a) Ag₆ aggregate in **1**. (b) Ag₆ aggregates are fused together through two pairs of trifluoroacetate groups and argentophilic interactions to produce a silver column in **1**. (c) 3D supramolecular structure of **1** linked by face-to-face π - π stacking interactions. All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry codes: #1 -*x*, -*y*, 2 - *z*; #2 -*x*, *y*, 1.5 - *z*; #3 *x*, -*y*, 0.5 + *z*. Atom color codes: Ag purple, C gray, O red.

aromatic interaction. Phenyl ring I takes η^1 and η^2 modes to coordinate to two independent silver atoms (Ag2 and Ag3#2) with bond lengths of 2.989(9) Å (Ag2...C9), 2.498(8) Å (Ag3#2...C5), and 2.690(8) Å (Ag3#2...C6), respectively, implying the presence of significant Ag(1)– π interaction.¹² Such butterfly-shaped Ag₄ baskets share one edge (Ag1...Ag1#1 3.134(8) Å) to produce a Ag₆ aggregate, and further united through two pairs of trifluoroacetate groups (O2–O3, O2#2– O3#2, O4–O5 and O4#2–O5#2) *via* μ_3 - η^1 , η^2 and μ_4 - η^1 , η^3 coordination modes with the assistance of argentophilic interactions Ag1...Ag1#2 (3.250(1) Å), Ag1...Ag2#2 (3.108(9) Å), Ag3...Ag2#2 (3.268(1) Å), Ag2...Ag1#2 (3.108(9) Å), Ag2...Ag3#2 (3.268(1) Å), respectively, to form a silver column along the *c* axis (Fig. 2a and b). The infinite columns arranged in a



Fig. 3 Atom labeling and coordination mode of L1 in **2** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry code: #1 2 - x, 2 - y, -z. Atom color codes: Ag purple, C gray, O red.

hexagonal array are interconnected by face-to-face π - π stacking interactions between adjacent phenyl rings I with the distances of 3.686(2) Å to form a three-dimensional supramolecular network (Fig. 2c).

 $[(AgL1) \cdot (AgCF_3CO_2)_5 \cdot (CH_3CN) \cdot (H_2O)]_n$ (2). The asymmetric unit of 2 contains six crystallographically independent Ag(I)ions, five trifluoroacetate ions, one coordinated acetonitrile molecule, and one coordinated water molecule. In 2, there are one independent anionic ligand L1, adopting a non-planar conformation, in which the torsion angle C3-O1-C25-C2 is $-96.47(7)^{\circ}$. The ethynide group composed of C1 and C2 is capped by a square-pyramidal Ag₅ basket in the μ_5 - $\eta^1, \eta^2, \eta^2, \eta^2, \eta^2$ coordination mode, as shown in Fig. 3. Utilizing two μ_3 - η^1 , η^2 and μ_2 - η^1 , η^1 trifluoroacetate groups (O2-O3 and O10-O11) as linkage components, together with the argentophilic interactions (Ag3…Ag6 2.938(2) Å), the external silver atom Ag6 is hitched to the Ag5 basket, within which the argentophilic Ag-Ag distances vary from 2.787(2) to 3.324(2) Å, being shorter than twice the van der Waals radius of silver ions (3.44 Å)13 and suggesting the presence of significant argentophilic interactions. The Ag6 atom coordinates to two carbon atoms (C4 and C5) of phenyl ring I in the η^2 mode with bond lengths of 2.893(8) and 2.908(7) Å (Fig. 3). Phenyl ring II takes a μ_2 - η^1 , η^1 mode to coordinate to two independent silver atoms (Ag3#1 and Ag6#1) with bonds lengths of 2.776(9) (Ag3#1...C12) and 3.026(8) Å (Ag6#1...C14), respectively. Through such Ag-aromatic interactions, adjacent anionic ligands sandwich multiple silver atoms to produce a π ···Ag₄··· π structure, which is also consolidated by trifluoroacetate groups, as shown in Fig. 4a. Although metal-organic macrocycle has been obtained,¹⁴ the π ···Ag₄··· π sandwich unit is still rarely constructed with flexible supramolecular synthons. These moieties are further associated together through coordination interactions between silver atoms and trifluoroacetate groups (O4-O5, O6-O7, O4#2-O5#2 and O6#2-O7#2), affording a silver column with the μ_4 -O,O',O',O' and μ_3 -



Fig. 4 (a) π ···Ag₄··· π sandwich structure in **2**. (b) 2D network of **2**. Symmetry codes: #1 2 - x, 2 - y, -z; #2 1 - x, 1 - y, 1 - z; #3 1 - x, 2 - y, 1 - z. Atom color codes: Ag purple, C gray, O red, N blue.



Fig. 5 Atom labeling and coordination mode of L1 in **3** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms are omitted for clarity. Symmetry codes: #1 x, 1 + y, z; #2 - x, 2 - y, -z; #3 1 - x, 2 - y, -z; #4 - 1 + x, y, z; #5 - x, 1 - y, -z. Atom color codes: Ag purple, C gray, O red, N blue.

O,O',O' modes, respectively. The infinite silver columns are also interconnected together by trifluoroacetate groups (O8–O9 and O8#2–O9#2) to engender a two-dimensional network *via* the μ_3 -O,O',O' mode (Fig. 4b). There is no obvious intermolecular interaction between layers.

[(AgL1)₄·(AgNO₃)₂]_n (3). The asymmetric unit of 3 contains six crystallographically independent Ag(I) ions, and two coordinated nitrate anions. As shown in Fig. 5, the ethynide groups (C1=C2, C16=C17, C31=C32 and C46=C47) are enveloped by three trigonal Ag₃ aggregate in the μ_3 - η^1 , η^2 , η^2 coordination modes and two butterfly-shaped Ag₄ baskets in the μ_4 - η^1 , η^1 , η^2 , η^2 coordination modes, respectively. Such aggregates share Ag2 and their symmetry-related atoms to produce an infinite silver column, as illustrated in Fig. 6a. Different from complexes 1 and 2, there is no silver–aromatic interaction, which is possibly due to each of four independent L1 anions adopting a nearly planar conformation, in which the torsion angels C4–O1–C3–C2, C19–O2–C18–C17, C35–O3–C33–



Fig. 6 (a) View of silver column in **3** along the *b* axis. (b) 2D network of **3** parallel to the *ab* plane. Symmetry codes: #1 x, 1 + y, z; #2 - x, 2 - y, -z; #3 1 - x, 2 - y, -z. Atom color codes: Ag purple, C gray, O red, N blue.

C32, C49–O4–C48–C47 are 173.67(5)°, 174.03(6)°, 169.84(6)°, 175.39(6)°, respectively. These silver columns are further associated together through the linkage of Ag3, Ag6, their symmetry-related atoms to generate an infinite double chain along the *b* axis. Such double chains are linked together through Ag···Ag interaction (Ag1–Ag5#3) to form a 2D silver layer parallel to the *ab* plane with the anion ligand protruding on both sides (Fig. 6b). Owing to the phenyl ring appended on both sides of this silver(i) layer, there is no obvious intermolecular interaction between layers. To the best of our knowledge, this is the first silver layer in flexible silver– ethynide complexes although there are several examples in rigid ones.^{3b,h,i,k}

 $[(AgL2) \cdot (AgCF_3CO_2)_4]_n$ (4). The asymmetric unit of 4 contains five crystallographically independent Ag(I) ions and four trifluoroacetate ions. In the crystal structure of 4, the anionic ligand L2 adopts a non-planar conformation, in which the C3 and O1 atoms nearly lie in the plane of the corresponding phenyl ring, and the torsion angle C4-O1-C3-C2 is 65.34(8)°. As shown in Fig. 7, the ethynide group (C1=C2) is enveloped by a square-pyramidal Ag₅ basket in the μ_5 - η^1 , η^1 , η^2 , η^2 , η^2 mode. The peripheral Ag5 atom is hitched to the Ag₅ basket by a pair of µ₃-O,O,O' trifluoroacetate groups (O5, O5, O6 and O9, O10, O10). Adjacent square-pyramidal Ag₅ baskets coalesce together by sharing one edge (Ag2…Ag2#3 2.820(1) Å) to give rise to a Ag₈ aggregate, and such aggregates are further united together through trifluoroacetate groups (O3-O4, O7-O8 and O9-O10) and their symmetry-related atoms via μ_3 - η^1 , η^2 and μ_4 - η^1 , η^3 coordination modes, respectively, to form a silver column along the a axis (Fig. 8a and b). Moreover, the phenyl rings I and II of the independent anionic L2 ligand are both attached to silver atoms though the η^2 mode. The Ag4#1 atom coordinates to two carbon atoms (C5 and C6) of phenyl ring I with bond lengths of 2.683(7) and 2.955(8) Å. Silver atom Ag5#4 coordinates to two carbon atoms (C13 and C14) of phenyl ring II with bond lengths of 2.505(2) and 2.503(2) Å, which extended the silver column to lead to the formation of a three-dimensional supramolecular architecture along the b and c directions (Fig. 8c).

 $[(AgL2)_2 \cdot (AgCF_3CO_2)_3]_n$ (5). In the crystal structure of 5, anionic ligand L2 also adopts a non-planar conformation, in



Fig. 7 Atom labeling and coordination mode of L2 in **4** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry codes: #1 1 + *x*, *y*, *z*; #2 - *x*, 2 - *y*, 1 - *z*; #3 1 - *x*, 2 - *y*, 1 - *z*; #4 1 + *x*, 3/2 - *y*, 1/2 + *z*. Atom color codes: Ag purple, C gray, O red.

CrystEngComm



Fig. 8 (a) Ag₈ aggregates in **4**. (b) Silver column formed from Ag₈ aggregates through sharing one edge in **4**. (c) 3D supramolecular structure of **4**. All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry codes: #1 1 + *x*, *y*, *z*; #2 - *x*, 2 - *y*, 1 - *z*; #3 1 - *x*, 2 - *y*, 1 - *z*; #4 1 + *x*, 3/2 - *y*, 1/2 + z; #5 - *x*, 1/2 + y, 1/2 - z. Atom color codes: Ag purple, C gray, O red.

which the C3 and O3, C18 and O1 atoms nearly lie in the plane of the corresponding phenyl ring, and the torsion angles C4– O3–C3–C2 and C19–O1–C18–C17 are 77.87(2) and $60.45(2)^{\circ}$, respectively. As shown in Fig. 9, the ethynide groups (C1=C2 and C16=C17) are enveloped by a trigonal Ag₃ aggregate in the μ_3 - η^1 , η^2 , η^2 coordination mode and a butterfly-shaped Ag₄ basket in the μ_4 - η^1 , η^1 , η^2 , η^2 coordination mode, respectively. Notably, the silver atom Ag3#2 coordinates to two carbon atoms (C8 and C9) of phenyl ring **I** *via* the η^2 -mode with bond lengths of 2.780(2) and 2.887(2) Å. Phenyl ring **III** takes a μ_2 - η^1 , η^1 mode to coordinate two independent silver atoms (Ag2 and Ag4) with bond lengths of 2.957(2) Å (Ag2···C24) and



Fig. 9 Atom labeling and coordination mode of L2 in **5** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry codes: #1 1/2 - x, -1/2 + y, 1/2 - z; #2 1/2 - x, 1/2 + y, 1/2 - z. Atom color codes: Ag purple, C gray, O red.



Fig. 10 (a) Silver column formed from Ag₆ aggregates, and further consolidated by the trifluoroacetate groups and Ag–aromatic interaction in **5**. (b) 2D structure of **5** linked by face-to-face π – π stacking interactions. All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry code: #1 1/2 - x, -1/2 + y, 1/2 - z. Atom color codes: Ag purple, C gray, O red.

2.821(1) Å (Ag4····C20), respectively. Adjacent Ag₃ and Ag₄ baskets coalesce together by sharing one vertex (Ag2) to yield a Ag₆ aggregate, within which the argentophilic Ag–Ag distances vary from 2.901(2) to 3.323(2) Å. Such aggregates connected together by sharing the Ag5 and its symmetry-related atoms to give rise to a silver column along the *b* axis direction, which is further consolidated by the trifluoroacetate groups and Ag–aromatic interaction (Fig. 10a). Finally, association of chains through face-to-face π - π stacking interactions between adjacent phenyl rings with the distances of 3.732(2) Å furnishes a 2D network (Fig. 10b). There is no obvious intermolecular interaction between layers.

 $[(AgL1) \cdot (AgCF_3CO_2)_3 \cdot (bpy)_2]_n$ (6). In addition, we have carried out exploratory studies on structural control by introducing nitrogen-donor ancillary ligands to direct the assembly process, which led to the formation of supramolecular structure 6. The asymmetric unit of 6 contains four crystallographically independent Ag(I) ions, one anionic L1 ligand, three trifluoroacetate ions and two bpy molecules. In 6, anionic ligand L1 adopts a non-planar conformation, in which the C3 and O1 atoms nearly lie in the plane of the phenyl ring, and the torsion angle C4-O1-C3-C2 is 71.92(4)°. As shown in Fig. 11, the ethynide group (C1≡C2) is bound to the butterflyshaped Ag₄ basket in the μ_4 - η^1 , η^1 , η^2 , η^2 coordination mode. Two bpy molecules are associated to the Ag₄ basket with Ag1 and Ag4, respectively. Such butterfly-shaped Ag4 baskets are fused by argentophilic interaction Ag3...Ag2#1, Ag2...Ag3#1 (3.091(4) Å) to yield a Ag₈ aggregate, additional consolidation being provided by two pairs of trifluoroacetate groups (O2-O3, O2#1-O3#1, O4-O5 and O4#1-O5#1) through the μ_2 -O,O' and μ_3 -O,O',O' mode, respectively. Adjacent Ag₈ aggregates are united together through weak $\pi \cdots \pi$ stacking (centroid-centroid distance 4.073(3) Å) interaction to furnish a one-dimensional chain along the c axis. Notably, the infinite chains are interconnected by hydrogen bond C14#3-H14#3…F3 (H14#3…F3 2.589(3) Å) to yield a three-dimensional supramolecular architecture with a hole (*ca.* 16.24 \times 17.65 Å²), as shown in Fig. 12b. Notably, the presence of the large voids in this supramolecular framework facilitate the formation of





Fig. 11 Atom labeling and coordination mode of L1 in **6** (50% thermal ellipsoids are drawn for silver atoms). All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. Symmetry code: #1 -x, -y + 1, -z + 1. Atom color codes: Ag purple, C gray, O red, N blue.

interpenetrations. The channels are filled by another identical framework in a typical 2-fold interpenetration fashion (Fig. 12c).

Photoluminescence properties

Compared to gold-ethynide and copper(I)-ethynide complexes, the photoluminescence properties of silver(1)-ethynide complexes are relatively less well investigated, and their emissions mainly originate from intraligand $n \rightarrow \pi^*$ and π $\rightarrow \pi^*$ transitions.^{3i,4e,15} Therefore, in the present work, the luminescent properties of the free ligands and complexes 1-6 were investigated in the solid state at room temperature (Fig. S1-S8, ESI[†]). As shown in Fig. S3-S8, ESI,[†] all of the complexes in this work displayed weak luminescence in the solid state at room temperature, and the maximum excitation and emission wavelengths are listed in Table S4, ESI.[†] The emission spectra of complexes 1-6 display maxima peaks at 396 nm (1), 373 nm (2), 367 nm (3), 396, 415 nm (4), 438 nm (5), and 373 nm (6), respectively. Complexes 1, 4, and 5 show red shifts, while others (2, 3, and 6) show no shifts or slight blue shifts. In complexes 1, 4 and 5, there are strong Ag $\cdots\pi$ interactions, while complexes 3 and 6 show no Ag^{\dots} π interactions and complex 2 shows a relatively longer Ag $\cdots \pi$ distance. This fact is clear that the absorption bands of complexes 1-6 mainly originate from ligand-centered excited states and Ag $\cdots\pi$ interactions within the complexes.

Influence of solvent and neutral ligands

It should be noted that the solvent molecules affect the coordination ability of the anionic component, and lead to the diversity of the final structures. For example, the structural differences of **1–3** and **4**, **5** are mainly caused by changes of the solvent. Polymeric starting material $[AgL]_n$ dissolves in a concentrated aqueous solution of silver salts. To improve the solubility of $[AgL]_n$, a mixed solvent of water and acetonitrile was used. In complex **3**, we even use DMSO in place of water and acetonitrile. When the ancillary ligand 2,2'-bpy was employed, the steric effect of the chelating 2,2'-bpy is reflected in the generation of a discrete molecular cluster, which is further associated by the intermolecular interaction to form a 2-fold interpenetrated 3D framework in complex **6**.



Fig. 12 (a) One-dimensional chain of **6** linked by $\pi \cdots \pi$ stacking interaction. All hydrogen atoms and CF₃ moieties of CF₃CO₂⁻ are omitted for clarity. (b) The chains are also further interconnected through inter-chain hydrogen bonds to give a 3D network. (c) A space-filling view of the 2-fold interpenetration framework. Symmetry codes: #1 -x, -y + 1, -z + 1; #2 -x + 1, y - 1/2, -z + 5/2 for **6**.

Weak intermolecular interactions

In the construction of solid-state frameworks, coordinate covalent bonding and noncovalent interactions are two wellestablished essentials of crystal engineering. Indeed, the latter one lays the foundation of an enormous family of supramolecular synthons. The new metallo–ligand supramolecular synthon $R-C_6H_4OCH_2C\equiv C \supset Ag_n$ ($R = C_6H_5$ or C_6H_5O , n = 3, 4, 5) offers a good opportunity to introduce silver(I)–aromatic and $\pi-\pi$ interactions in the construction of metal–organic networks of variable dimensions. Silver(I)–aromatic interactions provide a powerful tool for the building of novel molecular architectures. As we reported in this work, common weak intermolecular interactions such as $Ag^{...}\pi$ (1 and 5) and hydrogen bonding (6) have been employed as available cohesive forces in the consolidation of such supramolecular architectures.

Conclusions

In summary, two flexible supramolecular synthons are herein employed to construct silver(I)–organic frameworks by virtue of changing the groups from phenyl ring to phenoxy group. In the series of six complexes, the invariable appearance of the μ_3 -, μ_4 - and μ_5 -ligation modes of the ethynide moiety are obtained. The diversities of the present structures indicate that controlled synthesis by adjusting the silver-ethynide supramolecular synthons, silver salts or synthetic methods is a facile and effective approach to the designed construction of new supramolecular assemblies with distinct structural features. Silver(I)-aromatic interaction was successfully introduced into the silver-ethynide system, which play important roles in series of silver-organic assembling а frameworks. Interestingly, it is the first example of an unusual $\pi \cdots Ag_4 \cdots \pi$ interaction in silver-ethynide complexes. In the solid state, all the complexes synthesized in this work are emissive at room temperature, which mainly originates from intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

Acknowledgements

We gratefully acknowledge financial support by the National Natural Science Foundation of China (No. 20901070), Zhengzhou University, and the Hong Kong Research Grants Council (Ref. No. CUHK 402408).

Notes and references

- (a) M. I. Bruce, *Chem. Rev.*, 1991, 91, 197; (b) S. Lotz, P. H. Van Rooyen and R. Meyer, *Adv. Organomet. Chem.*, 1995, 37, 219; (c) H. Lang, D. S. A. George and G. Rheinwald, *Coord. Chem. Rev.*, 2000, 206–207, 101; (d) F. Gruber, M. Schulz-Dobrick and M. Jansen, *Chem.–Eur. J.*, 2010, 16, 1464.
- 2 (a) M.-L. Chen, X.-F. Xu, Z.-X. Cao and Q.-M. Wang, Inorg. Chem., 2008, 47, 1877; (b) S.-D. Bian and Q.-M. Wang, Chem. Commun., 2008, 5586; (c) S.-D. Bian, J.-H. Jia and Q.-M. Wang, J. Am. Chem. Soc., 2009, 131, 3422; (d) S.-D. Bian, H.-B. Wu and Q.-M. Wang, Angew. Chem., Int. Ed., 2009, 48, 5363; (e) G.-G. Gao, P.-S. Cheng and T. C. W. Mak, J. Am. Chem. Soc., 2009, 131, 18257; (f) J.-H. Jia and Q.-M. Wang, J. Am. Chem. Soc., 2009, 131, 16634; (g) J. Qiao, K. Shi and Q.-M. Wang, Angew. Chem., Int. Ed., 2010, 49, 1765; (h) F. Gruber and M. Jansen, Angew. Chem., Int. Ed., 2010, 49, 4924; (i) Y.-P. Xie and T. C. W. Mak, J. Am. Chem. Soc., 2011, 133, 3760; (j) S. C. K. Hau, P.-S. Cheng and T. C. W. Mak, J. Am. Chem. Soc., 2012, 134, 2922.
- 3 (a) G.-C. Guo, G.-D. Zhou and T. C. W. Mak, J. Am. Chem. Soc., 1999, 121, 3136; (b) L. Zhao and T. C. W. Mak, J. Am. Chem. Soc., 2005, 127, 14966; (c) T. C. W. Mak, X.-L. Zhao, Q.-M. Wang and G.-C. Guo, Coord. Chem. Rev., 2007, 251, 2311; (d) T. C. W. Mak and L. Zhao, Chem.-Asian J., 2007, 2, 456; (e) S.-Q. Zang and T. C. W. Mak, Inorg. Chem., 2008, 47, 7094; (f) S.-Q. Zang, L. Zhao and T. C. W. Mak, Organometallics, 2008, 27, 2396; (g) S.-Q. Zang, J. Han and T. C. W. Mak, Organometallics, 2009, 28, 2677; (h) T.-L. Zhang, H.-B. Song, X.-M. Dai and X.-G. Meng, Dalton Trans., 2009, 7688; (i) Y. Zhao, P. Zhang, B. Li, X. G. Meng and T.-L. Zhang, Inorg. Chem., 2011, 50, 9097; (j) B. Li, S.-

Q. Zang, R. Liang, Y.-J. Wu and T. C. W. Mak, *Organometallics*, 2011, **30**, 1710; (*k*) P.-S. Cheng, S. Marivel, S.-Q. Zang, G.-G. Gao and T. C. W. Mak, *Cryst. Growth Des.*, 2012, **12**, 4519.

- 4 (a) V. W.-W. Yam, Acc. Chem. Res., 2002, 35, 555; (b) Y.-Y. Lin, S.-W. Lai, C.-M. Che, K.-K. Cheung and Z.-Y. Zhou, Organometallics, 2002, 21, 2275; (c) Q.-H. Wei, L.-Y. Zhang, G.-Q. Yin, L.-X. Shi and Z.-N. Chen, J. Am. Chem. Soc., 2004, 126, 9940; (d) Q.-H. Wei, G.-Q. Yin, L.-Y. Zhang and Z.-N. Chen, Inorg. Chem., 2006, 45, 10371; (e) Z.-N. Chen, N. Zhao, Y. Fan and J. Ni, Coord. Chem. Rev., 2009, 253, 1; (f) I. O. Koshevoy, Y. C. Lin, A. J. Karttunen, M. Haukka, P. T. Chou, S. P. Tunik and T. A. Pakkanen, Chem. Commun., 2009, 2860; (g) H.-B. Wu, Z.-J. Huang and Q.-M. Wang, Chem.-Eur. J., 2010, 16, 12321.
- 5 (a) L. Zhao, W. Y. Wong and T. C. W. Mak, *Chem.-Eur. J.*, 2006, **12**, 4865; (b) L. Zhao, X.-L. Zhao and T. C. W. Mak, *Chem.-Eur. J.*, 2007, **13**, 5927.
- 6 L. Zhao and T. C. W. Mak, J. Am. Chem. Soc., 2005, 127, 14966.
- 7 (a) M. Jansen, Angew. Chem., Int. Ed. Engl., 1987, 26, 1098;
 (b) P. Pyykkö, Chem. Rev., 1997, 97, 597; (c) C.-M. Che and S.-W. Lai, Coord. Chem. Rev., 2005, 249, 1296.
- 8 G. M. Sheldrick, SADABS, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.
- 9 (a) G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs, Bruker Analytical X-ray Systems Inc., Madison, WI, 1997; (b) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- B. Peter, N. Karolina, W. Andreas, B. Udo, G. H. Lance, P. Alecia, S. Tor, O. Krister, K. David, B. Maria and W. David, *Bioorg. Med. Chem. Lett.*, 2006, 16, 4792.
- 11 B. K. Teo, Y.-H. Xu, B.-Y. Zhong, Y.-K. He, H.-Y. Chen, W. Qian, Y.-J. Deng and Y. H. Zou, *Inorg. Chem.*, 2001, 40, 6794.
- 12 (a) M. Munakata, L.-P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, G.-L. Ning and T. Kojima, J. Am. Chem. Soc., 1998, **120**, 8610; (b) M. Munakata, G.-L. Ning, Y. Suenaga, T. Kuroda-Sowa, M. Maekawa and T. Ohta, Angew. Chem., Int. Ed., 2000, 39, 4555; (c) M. Munakata, L.-P. Wu and G.-L. Ning, Coord. Chem. Rev., 2000, 198, 171; (d) S.-Q. Liu, T. Kuroda-Sowa, H. Konaka, Y. Suenaga, M. Maekawa, T. Mizutani, G.-L. Ning and M. Munakata, Inorg. Chem., 2005, 44, 1031; (e) Y.-B. Dong, Y.-Y. Jiang, J. Li, J.-P. Ma, F.-L. Liu, B. Tang, R.-Q. Huang and S. R. Batten, J. Am. Chem. Soc., 2007, 129, 4520; (f) L.-M. Chiang, C.-W. Yeh, Z.-K. Chan, K.-M. Wang, Y.-C. Chou, J.-D. Chen, J.-C. Wang and J. Y. Lai, Cryst. Growth Des., 2008, 8, 470; (g) J. T. Lenthall and J. W. Steed, Coord. Chem. Rev., 2007, 251, 1747; (h) M. A. Petrukhina, Angew. Chem., Int. Ed., 2008, 47, 1550; (i) Z.-P. Deng, M.-S. Li, Z.-B. Zhu, L.-H. Huo, H. Zhao and S. Gao, Organometallics, 2011, 30, 1961.
- 13 A. Bondi, J. Phys. Chem., 1964, 68, 441.
- 14 S.-Q. Zang, P.-S. Cheng and T. C. W. Mak, *CrystEngComm*, 2009, **11**, 1061.
- (a) Y.-Y. Lin, S.-W. Lai, C.-M. Che, K.-K. Cheung and Z.-Y. Zhou, *Organometallics*, 2002, 21, 2275; (b) S. S. Y. Chui, M. F. Y. Ng and C.-M. Che, *Chem.-Eur. J.*, 2005, 11, 1739; (c) Q.-H. Wei, G.-Q. Yin, L.-Y. Zhang and Z.-N. Chen, *Inorg. Chem.*, 2006, 45, 10371.