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Ligand-Induced Assembly of Coordination Chains and Columns Containing High-Nuclearity Silver(I) Ethynide Cluster Units

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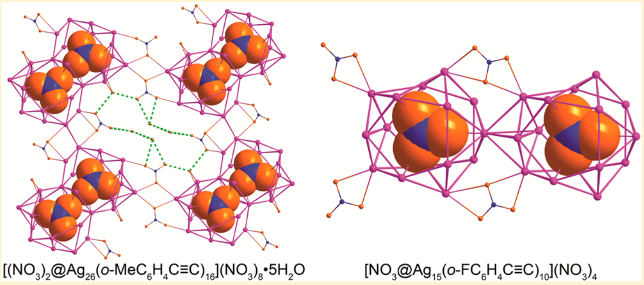
Supporting Information



ABSTRACT: The multinuclear metal–ligand supramolecular synthon $RC_6H_4C{\equiv}C{\supset}Ag_n$ (R = Me, F; n = 3–5) has been employed to construct the two high-nuclearity silver ethynide cluster compounds $[(NO_3)_2@Ag_{26}(o\text{-}MeC_6H_4C{\equiv}C)_{16}](NO_3)_8{\cdot}5H_2O$ (**1**) and $[NO_3@Ag_{15}(o\text{-}FC_6H_4C{\equiv}C)_{10}](NO_3)_4$ (**2**), which bear the same nitrate central core. The synthesis of $[CrO_4@Ag_{18}(i\text{PrC}{\equiv}C)_{12}](ClO_4)_4$ (**3**) and $[ClO_4@Ag_{18}(i\text{PrC}{\equiv}C)_{12}](ClO_4)_5$ (**4**) demonstrated the effect of variation of central anionic core size and charge on the construction of multidimensional organosilver(I) networks. The bulkiness of the peripheral ligands and the orientation of substituents with respect to the ethynide group proved to be dominant factors that direct the formation of high-nuclearity clusters and the assembly of coordination networks. To our knowledge, **1** and **2** are the first examples using the nitrate anion for templated cluster synthesis.

Inorganic anions are often employed as templates in coordination network assembly, owing to their relatively strong and directional bonding interactions with metal centers.[1] Facile anionic templates inducing self-assembly is a well-established route to construct high-nuclearity silver ethynide[2] clusters. Various anionic templates, such as halides,[3] carbonate,[4] chromate,[5] and polyoxometalates (POMs)[6] have been utilized in the synthesis of giant silver ethynide clusters, with nuclearities ranging from 14 to 70. However, the nitrate ion is rarely employed for such purposes, owing to its dominant capacity for planar coordination, which plays a major role in directing a two-dimensional argentophilic assembly. Recently, we synthesized a new series of silver(I) nitrate complexes containing new ligands, each composed of a functionalized phenyl nucleus bearing a terminal ethynyl substituent.[7]

Herein we report the two high-nuclearity silver ethynide cluster compounds $[(NO_3)_2@Ag_{26}(o\text{-}MeC_6H_4C{\equiv}C)_{16}](NO_3)_8{\cdot}5H_2O$ (**1**) and $[NO_3@Ag_{15}(o\text{-}FC_6H_4C{\equiv}C)_{10}](NO_3)_4$ (**2**), assembled by nitrate templation with the multinuclear supramolecular synthon $RC{\equiv}C{\supset}Ag_n$ (n = 3–5), which has been demonstrated to be useful in the designed synthesis of discrete molecules as well as one-, two-, and three-dimensional coordination networks. The complexes $[CrO_4@Ag_{18}(i\text{PrC}{\equiv}C)_{12}](ClO_4)_4$ (**3**) and $[ClO_4@Ag_{18}(i\text{PrC}{\equiv}C)_{12}](ClO_4)_5$ (**4**) have also been synthesized to investigate the effect of varying the bulkiness of the peripheral ligands and the central anionic template on crystal packing. Details of the synthesis of compounds **1**–**4** are given in the Supporting Information.

Single-crystal X-ray analysis revealed that $[(NO_3)_2@Ag_{26}(o\text{-}MeC_6H_4C{\equiv}C)_{16}](NO_3)_8{\cdot}5H_2O$ (**1**) features a centrosymmetric peanut-shaped Ag_{26} face-sharing double cage enclosing two nitrate templates, which is surrounded by 16 peripheral $o\text{-}MeC_6H_4C{\equiv}C^-$ groups, and charge balance is provided by eight exterior nitrate ions (Figure 1a). The Ag···Ag distances lying in the range of 2.902(3)–3.367(1) Å are comparable to those observed in a wide variety of silver double and multiple salts reported by our group and are attributed to argentophilic interactions.[8] The eight independent peripheral ethynide ligands are each bound to either three or four silver(I) centers in different ligation modes: $\mu_4\text{-}\eta^2,\eta^2,\eta^2,\eta^1$, $\mu_4\text{-}\eta^2,\eta^2,\eta^1,\eta^1$, two $\mu_3\text{-}\eta^2,\eta^2,\eta^1$, three $\mu_3\text{-}\eta^2,\eta^1,\eta^1$, and $\mu_3\text{-}\eta^1,\eta^1,\eta^1$ (Figure 1b). The four independent peripheral nitrate ligands are each attached to either two or three silver(I) atoms in different ligation modes: $\mu_2\text{-}\eta^1,\eta^2$ and three $\mu_3\text{-}\eta^1,\eta^2$. The crystal structure is also consolidated by a μ_2-coordinated aqua ligand (O1W) and two lattice water molecules (O2W and O3W), each having 0.75 site occupancy (Figure S1a in the Supporting Information).

Such Ag_{26} clusters are interconnected through argentophilic interaction between Ag4 and Ag4A to generate an infinite chain of linked clusters along the *a* axis (Figure S1b in the Supporting Information). Bridged by a pair of symmetry-related nitrate ligands (labeled by N3 and N3B), adjacent silver chains are interassociated, yielding a two-dimensional coordination layer. As illustrated in Figure 2a, the coordination layer is further stabilized by hydrogen bonds in the range of 2.59(2)–2.94(3) Å involving nitrate groups, aqua ligands, and lattice water molecules. Furthermore, adjacent metal–organic layers are interconnected through C–H···O interactions between methyl substituents of

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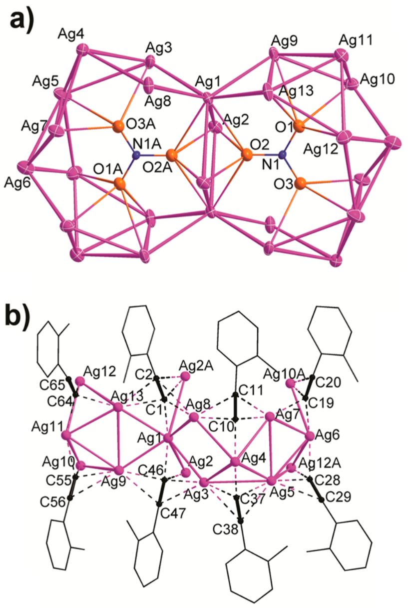

Figure 1. (a) Perspective view of the centrosymmetric Ag_{26} cluster in $[(NO_3)_2@Ag_{26}(o\text{-}MeC_6H_4C{\equiv}C)_{16}](NO_3)_8{\cdot}5H_2O$ (**1**). The argentophilic Ag···Ag distances, shown as thick rods, lie in the range 2.70−3.40 Å. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. (b) Perspective view of the coordination modes of the eight independent $o\text{-}MeC_6H_4C{\equiv}C^-$ peripheral ligands in **1**. Symmetry code: (A) 2 − *x*, 1 − *y*, 1 − *z*. In this and all other figures, the hydrogen and fluorine atoms are omitted for clarity.

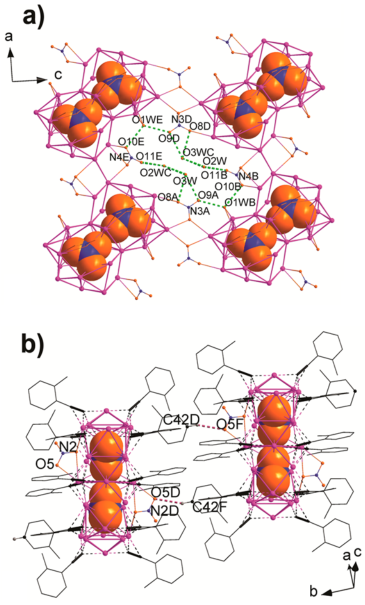

Figure 2. (a) Perspective view of the coordination layer in **1**, with all notable hydrogen bonding interactions shown by broken lines. (b) Perspective view of the 3D supramolecular framework formed by weak C−H···O interactions between methyl groups and nitrate ligands. Symmetry codes: (A) −1 + *x*, *y*, −1 + *z*; (B) 1 − *x*, 1 − *y*, 1 − *z*; (C) 1 − *x*, 1 − *y*, −*z*; (D) 2 − *x*, 1 − *y*, 1 − *z*; (E) *x*, *y*, −1 + *z*; (F) *x*, −1 + *y*, *z*.

ethynide groups and nearby nitrate ligands (C42D−H···O5F, 2.576(3) Å) to produce a 3D supramolecular network (Figure 2b).

The crystal structure of $[NO_3@Ag_{15}(o\text{-}FC_6H_4C{\equiv}C)_{10}]\text{-}(NO_3)_4$ (**2**) is composed of infinite chains of linked Ag_{15} polyhedra, each silver(I) cage having a 2-fold axis passing through atoms Ag1, N1, and O2, also the midpoint of the Ag6−Ag6A edge (Figure 3a). Such an Ag_{15} cage is consolidated by 10 $o\text{-}FC_6H_4C{\equiv}C^-$ groups, which are each bound to three silver(I) atoms in either the $\mu_3\text{-}\eta^2,\eta^2,\eta^1$ or $\mu_3\text{-}\eta^2,\eta^1,\eta^1$ mode (Figures S2 and S3a in the Supporting Information). One independent exo-polyhedral nitrate ligand is attached to a silver(I) atom via the μ_2-*O,O′* chelating mode and the other to two silver(I) atoms via the μ_2-*O,O,O′,O″* mode (Figure S3b in the Supporting Information). Adjacent Ag_{15} polyhedra are interassociated through argentophilic interactions between Ag1B and the symmetry-related atom pairs of Ag6 and Ag7 together with bridging nitrate groups (N3 and N3A) to yield an infinite chain of corner-to-face-linked Ag_{15} polyhedra along the *b* axis (Figure 3b).

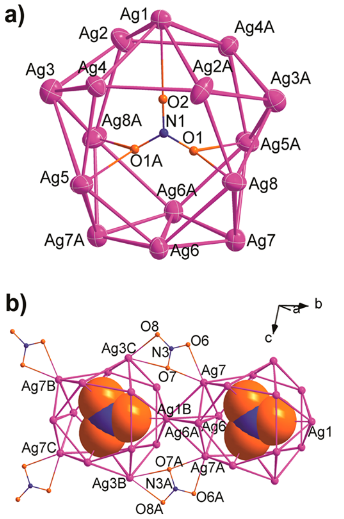

Figure 3. (a) Perspective view of the nitrate-encapsulating cluster lying on a crystallographic 2-axis in $[NO_3@Ag_{15}(o\text{-}FC_6H_4C{\equiv}C)_{10}](NO_3)_4$ (**2**). The argentophilic Ag···Ag distances, shown as thick rods, lie in the range 2.70−3.50 Å. Labeled silver(I) atoms are drawn as thermal ellipsoids at the 50% probability level. (b) Coordination mode of exo-polyhedral nitrate groups. Symmetry codes: (A) 1 − *x*, *y*, 0.5 − *z*; (B) *x*, −1 + *y*, *z*; (C) 1 − *x*, −1 + *y*, 0.5 − *z*.

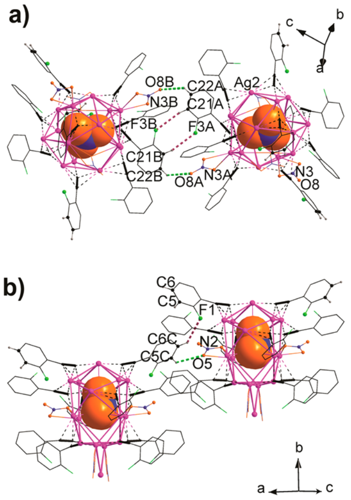

Figure 4. (a) Perspective view of interassociation between neighboring chains in **2**, showing all notable weak C−H···O and C−H···F interactions. (b) Perspective view of crystal packing in **2**, showing all notable weak C−H···O and C−H···F interactions. Symmetry codes: (A) 1 − *x*, *y*, 0.5 − *z*; (B) *x*, −1 − *y*, 0.5 + *z*; (C) 1.5 − *x*, −0.5 + *y*, 0.5 − *z*.

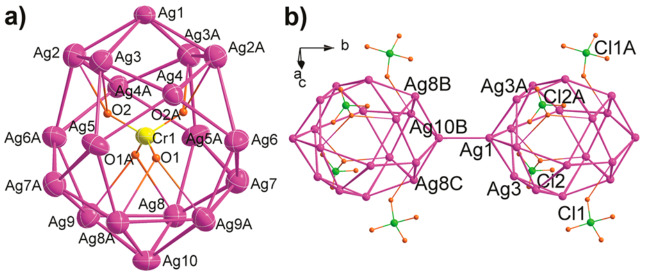

Figure 5. (a) Perspective view of the Ag_{18} cluster in [CrO$_4$@Ag$_{18}$(*i*PrC≡C)$_{12}$](ClO$_4$)$_4$ (**3**) with atom labeling. The argentophilic Ag···Ag distances, shown as thick rods, lie in the range 2.70−3.50 Å. Silver atoms are drawn as thermal ellipsoids (50% probability level). (b) Perspective view of the linkage between adjacent silver(I) polyhedra. Symmetry codes: (A) −*x*, *y*, 0.5 − *z*; (B) *x*, −1 + *y*, *z*.

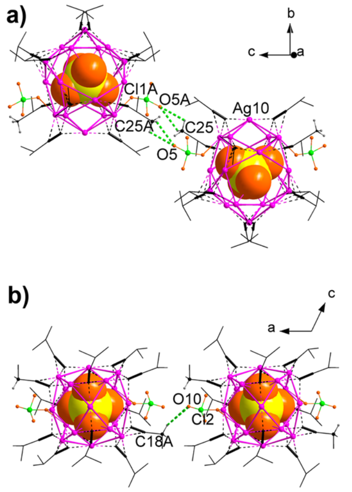

Figure 6. (a) Perspective view of interassociation between neighboring chains in **3**, showing all notable weak C−H···O interactions. (b) Perspective view of crystal packing in **3**, showing all notable weak C−H···O interactions. Symmetry codes: (A) −*x*, 1 − *y*, 1 − *z*; (B) 0.5 − *x*, −0.5 + *y*, 0.5 − *z*.

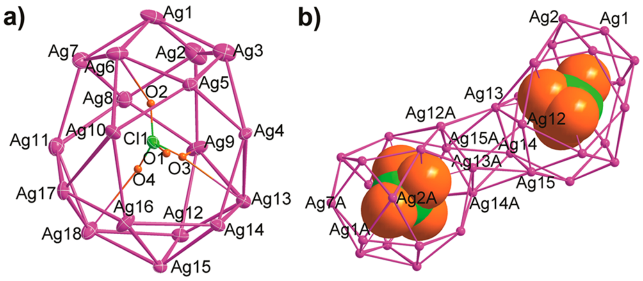

Figure 7. (a) Perspective view of the perchlorate-centered Ag_{18} cluster in [ClO$_4$@Ag$_{18}$(*i*PrC≡C)$_{12}$](ClO$_4$)$_5$ (**4**) with atom labeling. The argentophilic Ag···Ag distances, shown as thick rods, lie in the range 2.70−3.50 Å. Silver atoms are drawn as thermal ellipsoids (50% probability level). (b) Perspective view of the linkage between adjacent silver(I) polyhedra in **4**.

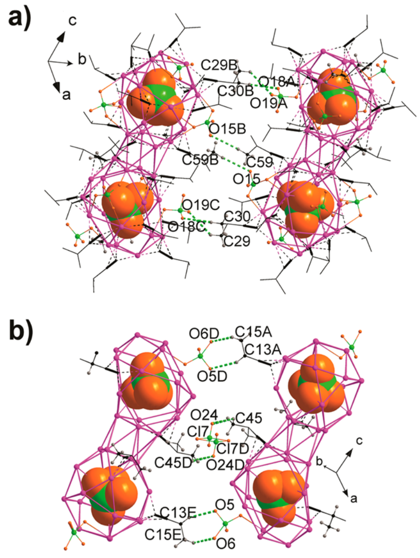

Figure 8. (a) Perspective view of interassociation between neighboring chains in **4**, showing all notable weak C−H···O interactions. (b) Perspective view of crystal packing in **4**, showing all notable weak C−H···O interactions. Symmetry codes: (A) −0.5 − *x*, *y*, 1.5 − *z*; (B) −1 − *x*, −1 − *y*, 1 − *z*; (C) −0.5 + *x*, −1 − *y*, −0.5 + *z*; (D) −1 − *x*, −*y*, 1 − *z*; (E) −0.5 + *x*, −*y*, −0.5 + *z*.

The coordination chains are further associated by weak C−H···O (C22A−H···O8B, 2.587(6) Å) and C−H···F (C21A−H···F3B, 2.667(5) Å) interactions between fluorophenyl and nitrate groups to form a supramolecular layer (Figure 4a). Neighboring layers are interconnected by additional C−H···O (C5C−H···O5, 2.674(7) Å) and C−H···F (C6C−H···F1, 2.539(6) Å) interactions, leading to generation of a supramolecular network (Figure 4b).

As illustrated in Figure 5a, [(CrO$_4$)@Ag$_{18}$(*i*PrC≡C)$_{12}$]-(ClO$_4$)$_4$ (**3**) contains an olive-shaped Ag_{18} polyhedron with a crystallographic 2-fold axis passing through the Ag1, Ag10, and Cr1 atoms. Three independent peripheral *i*PrC≡C$^-$ groups are attached to silver(I) centers in μ_3-η^2,η^2,η^1, μ_3-η^2,η^2,η^1, and μ_3-η^1,η^1,η^1 modes (Figures S4 and S5a in the Supporting Information), along with two symmetry-related pairs of μ_1-coordinated Cl1 and μ_2-coordinated Cl2 perchlorate ligands (Figure S5b in the Supporting Information). Such Ag_{16} cages are interconnected through a corner-to-corner argentophilic linkage between Ag1 and Ag10B to yield an infinite silver(I) chain along the *b* axis (Figure 5b).

As illustrated in Figure 6a, adjacent silver chains are linked through weak hydrogen bonds between perchlorate ligands and terminal methyl groups of ethynide ligands (C25−H···O5A, 2.473(5) and 2.560(4) Å) to produce a supramolecular layer (Figure 6a). Such layers are further associated by additional hydrogen bonding (C18A−H···O10, 2.832(6) Å) to yield a 3D supramolecular network (Figure 6b).

Single-crystal X-ray analysis established that [ClO$_4$@Ag$_{18}$(*i*PrC≡C)$_{12}$](ClO$_4$)$_5$ (**4**) is a structural analogue of **3**, with a perchlorate anion replacing the corresponding chromate template in the Ag_{18} cage held by argentophilic Ag···Ag distances ranging from 2.923(1) to 3.467(1) Å (Figure 7a in the Supporting Information). The four exo-polyhedral perchlorate ions in **4** are divided into three groups on the basis of their different ligation behaviors: Cl2 and Cl5 in μ_1-η^1, Cl3 in μ_3-η^2,η^1, and Cl4 in μ_3-η^1,η^1,η^1 modes (Figure S6a in the Supporting Information). In addition, the charge balance is provided by two more lattice perchlorate ligands (Cl6 and Cl7), which exhibit half-site occupancy. Twelve *i*PrC≡C$^-$ ligands are connected to the olive Ag_{18} cluster via two ligation modes: 11 μ_3-η^2,η^1,η^1 and 1 μ_3-η^2,η^2,η^1 (Figure S7 in Supporting Information). Two adjacent Ag_{18} cages are fused to form a distorted peanut-shaped dimeric Ag_{36} cluster through face-to-face argentophilic interactions between four symmetry-related atom pairs of Ag12, Ag13, Ag14, and Ag15 (Figure 7b in the Supporting Information).

With an inversion center located at the midpoint of peripheral chloride atoms Cl6 and Cl6A, which both have half-site occupancy (Figure S6b in the Supporting Information), such a dinuclear perchlorate species is bridging two neighboring Ag_{26} clusters through weak C−H···O interactions (C5A−H···O21, 2.415(3) Å; C5A−H···O22A, 2.455(5) Å) and generates an infinite wavy metal−organic supramolecular chain along the *c* axis (Figure S8 in the Supporting Information). Cross-linkage of adjacent silver-organic supramolecular chains through weak C−H···O interactions (C59B−H···O15, 2.807(3) Å; C30−H···O18C, 2.819(3) Å; C29−H···O19C, 2.976(3) Å) yields a supramolecular layer (Figure 8a). Such layers are linked by additional hydrogen bonding between terminal methyl groups of ethynide ligands and perchlorate ligands (C45−H···O24, 2.712(2) Å; C13E−H···O5, 2.566(2) Å; C15E−H···O6, 2.209(5) Å), in which Cl7 and O24 exhibit half-site occupancy, leading to the formation of a supramolecular network (Figure 8b).

The central nitrate template in both **1** and **2** reaffirms its dominant coordination capacity up to μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$. The methyl and fluoro substituents, in **1** and **2**, respectively, at the ortho position of the phenylethynide nucleus are about the same size. However, the more hydrophilic fluoro group leads to the formation of an infinite silver(I) column composed of smaller Ag_{15} cluster units, and it also forms a weak C−H···F acceptor hydrogen bond to link adjacent columns to generate a three-dimensional supramolecular network in **2**. On the other hand, the Ag_{26} cluster in **1** is enveloped by eight nitrate groups and two aqua ligands, and symmetry-related clusters are bridged by a single argentophilic interaction to give a dimeric building unit. The presence of peripheral nitrate groups facilitates the formation of a coordination layer structure in **1**, and neighboring layers are connected through weak C−H···O interactions to yield a supramolecular network. In accordance with our previously reported results,[7] the ortho position of the substituent with respect to the ethynide moiety on the phenyl nucleus is crucial for the formation of a high-nuclearity cluster. When the methyl substituent is located at the para position in $12Ag(C{\equiv}CC_6H_4Me\text{-}p)\cdot 7AgNO_3$,[7] an argentophilic silver(I) layer is obtained instead.

Complex **4** can be regarded as a structural analogue of **3** with a less symmetrical Ag_{18} cage. Since both are prepared from the same $AgC{\equiv}C\textit{i}Pr$ as a synthetic precursor, such distortion of the cage in **4** is accounted for by the relatively bulky and less negatively charged perchlorate center (Figure S9 in the Supporting Information), leading to the fusion of two adjacent Ag_{18} clusters through argentophilic interactions. The surrounding perchlorate anions play a significant role in bridging adjacent chains to form a supramolecular network through weak C−H···O interactions. In comparison to the high-nuclearity silver(I) cluster $[Ag_{22}(C{\equiv}C\textit{t}Bu)_{18}(CrO_4)](BF_4)_2$ synthesized by Wang et al.,[5] the infinite chain of clusters generated by $AgC{\equiv}C\textit{i}Pr$ in **3** implies that the bulkiness of ethynide ligands plays a significant role in influencing the packing between cluster units.

In summary, we have employed the multinuclear supramolecular synthon $RC_6H_4C{\equiv}C{\supset}Ag_n$ (R = Me, F; n = 3−5) to construct the two high-nuclearity silver ethynide cluster compounds $[(NO_3)_2@Ag_{26}(\textit{o}\text{-}MeC_6H_4C{\equiv}C)_{16}](NO_3)_8\cdot 5H_2O$ (**1**) and $[NO_3@Ag_{15}(\textit{o}\text{-}FC_6H_4C{\equiv}C)_{10}](NO_3)_4$ (**2**), which bear the same nitrate central template. The synthesis of $[CrO_4@Ag_{18}(\textit{i}PrC{\equiv}C)_{12}](ClO_4)_4$ (**3**) and $[ClO_4@Ag_{18}(\textit{i}PrC{\equiv}C)_{12}](ClO_4)_5$ (**4**) demonstrated the influence of the size and charge of the central anionic template on the construction of multidimensional silver(I) ethynide networks. The bulkiness of the peripheral ligands and the orientation of substituents with respect to the ethynide group proved to be dominant factors in directing the assembly of high-nuclearity clusters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, a table, and CIF files giving additional structures, experimental details, X-ray crystallographic data, and structure refinement parameters for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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