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Enlargement of Globular Silver Alkynide Cluster via Core Transformation

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Supporting Information

ABSTRACT: The multinuclear metal−ligand supramolecular synthon R−C≡C⊃Ag_n (R = alkyl, cycloalkyl; n = 3, 4, 5) has been employed to construct two high-nuclearity silver ethynide cluster compounds, $[Cl_6Ag_8@Ag_{30}(^tBuC{\equiv}C)_{20}(ClO_4)_{12}]{\cdot}Et_2O$ (**1**) and $[Cl_6Ag_8@Ag_{30}(chxC{\equiv}C)_{20}(ClO_4)_{10}](ClO_4)_2{\cdot}1.5Et_2O$ (chx = cyclohexyl) (**2**), that bear the same novel Cl_6Ag_8 central core. The synthesis of **1** made use of $[Cl@Ag_{14}(^tBuC{\equiv}C)_{12}]OH$ as a precursor, and its reaction with $AgClO_4$ in CH_2Cl_2 resulted in an increase in nuclearity from 14 to 38. The results presented here strongly suggest that the formation of multinuclear silver ethynide cage complexes **1** and **2** proceeds by a reassembly process in solution that involves transformation of the encapsulated chloride template within a Ag_{14} cage into a cationic pseudo-O_h Cl_6Ag_8 inner core, leading to the generation of a much enlarged $Cl_6Ag_8@Ag_{30}$ cluster within a cluster. To our knowledge, this provides the first example of the conversion of a silver cluster into one of higher nuclearity via inner-core transformation.

Anions play crucial roles in coordination network assembly by engaging in relatively strong and specific bonding interactions.[1] The established route to the construction of high-nuclearity silver ethynide[2] clusters uses facile anionic templates to induce self-assembly. In the prototypical cluster compound $[Cl@Ag_{14}(^tBuC{\equiv}C)_{12}]OH$,[3a] the chloride template occupies the center of a rhombic-dodecahedral Ag_{14} cage that is held together by a combination of bridging *tert*-butylethynide groups and argentophilic $Ag^I{\cdots}Ag^I$ interactions. Various anionic templates such as halide,[3] carbonate,[4] chromate,[5] and polyoxometalates (POMs)[6] have been employed in the generation of giant silver ethynide clusters with nuclearities ranging from 14 to 60. To date, however, this synthetic approach has resulted in clusters that encapsulate one, or rarely two or three,[6c] anionic species in the central cavity, and assembly processes involving more extensive anion templation have not been realized.

Herein we report two novel high-nuclearity silver ethynide cluster compounds, $[Cl_6Ag_8@Ag_{30}(^tBuC{\equiv}C)_{20}(ClO_4)_{12}]{\cdot}Et_2O$ (**1**) and $[Cl_6Ag_8@Ag_{30}(chxC{\equiv}C)_{20}(ClO_4)_{10}]$ $(ClO_4)_2{\cdot}1.5Et_2O$ (chx = cyclohexyl) (**2**), that were assembled using the multinuclear supramolecular synthon R−C≡C⊃Ag_n (n = 3, 4, 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.[2]

The synthesis of **1** made use of $[Cl@Ag_{14}(^tBuC{\equiv}C)_{12}]OH$ as a precursor, and presumably its reaction with $AgClO_4$ in CH_2Cl_2 resulted in cluster expansion through core transformation and reassembly.[7] Single-crystal X-ray analysis[8] revealed that complex **1** is a neutral centrosymmetric cluster with a cationic Cl_6Ag_8 inner core that is enveloped by an outer shell composed of 30 silver(I) vertices, 20 peripheral $^tBuC{\equiv}C^-$ groups (Figure 1a), and 12 perchlorate ligands together with a diethyl ether solvate molecule.

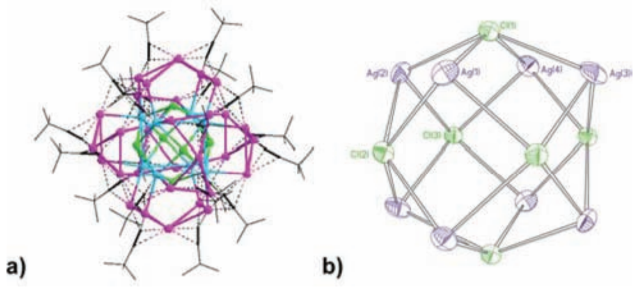

Figure 1. (a) Perspective view of the centrosymmetric cluster structure of $[Cl_6Ag_8@Ag_{30}(^tBuC{\equiv}C)_{20}(ClO_4)_{12}]{\cdot}Et_2O$ (**1**). The argentophilic Ag···Ag distances shown lie in the range 2.70−3.50 Å. Color scheme: turquoise, interior silver atoms; purple, exterior silver atoms; green, chloride ions; bold black lines, C≡C bonds; broken lines, Ag−C bonds. H atoms, perchlorate ligands, and the diethyl ether solvate molecule have been omitted for clarity. (b) Thermal ellipsoid plot (50% probability level) of the pseudo-O_h Cl_6Ag_8 inner core, with atom labeling.

The pseudo-O_h cationic Cl_6Ag_8 core comprises a cubic array of eight unconnected silver(I) ions having each square face capped by a μ_4-chloride, with Ag−Cl distances ranging from 2.601(15) to 2.785(15) Å (Figure 1b). Each $ClAg_4$ square pyramid is capped by a larger square-pyramidal Ag_5 unit to form the $Cl_6Ag_8@Ag_{30}$ "cluster within a cluster" molecular skeleton with Ag···Ag "edge distances" ranging from 2.897(7) to 3.486(11) 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[9] (Figure 2a). Each interior silver atom of the Cl_6Ag_8 core is octahedrally surrounded by three chloride ions and three exterior silver

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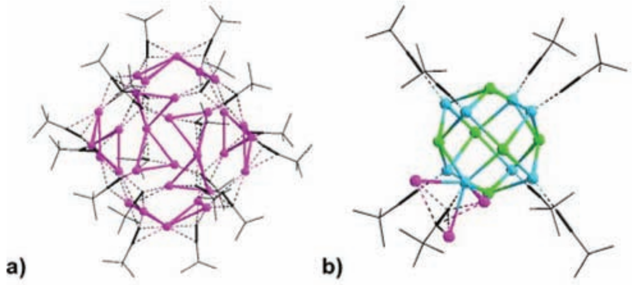

Figure 2. (a) Cluster shell of **1**, which is composed of six square-pyramidal Ag_5 aggregates and 20 peripheral *tert*-butylethynide ligands. The argentophilic Ag···Ag distances shown lie in the range 2.70−3.50 Å. (b) Perspective view showing the σ-type *tert*-butylethynide ligands directed inward toward the Cl_6Ag_8 central core. The coordination environment of one interior silver atom is illustrated. Color scheme: turquoise, interior silver atoms; purple, exterior silver atoms; green, chloride ions; bold black lines, C≡C bonds; broken lines, Ag−C bonds.

atoms (Figure 2b). Each of the 20 peripheral ethynide ligands is bonded to either three or four silver(I) centers in different ligation modes: ten μ_3-η^1,η^1,η^2; two μ_3-η^1,η^2,η^2; and eight μ_4-$\eta^1,\eta^2,\eta^2,\eta^2$. Each ethynide ligand in the last category is coordinated to an interior silver atom through a σ-type interaction, with Ag−C distances ranging from 2.161(6) to 2.194(3) Å (Figure 2b). Each of the 12 perchlorate ligands is attached to either one or two exterior silver atoms in three different ligation modes: six μ_1-*O*; two μ_2-*O*,*O*; and four μ_2-*O*,*O*,*O*′.

To explore the possible assembly of analogous clusters possessing a Ag_8Cl_6 inner core, we synthesized the new precursor $[Cl@Ag_{14}(chxC{\equiv}C)_{12}]Cl$ (**3**) by dissolving polymeric $[(chxC{\equiv}C)Ag]_n$ in tetrahydrofuran (THF) in the presence of a stoichiometric amount of $[(n\text{-}C_4H_9)_4N]Cl$ as a chloride source,[10] and crystals of good quality were obtained by slow diffusion of diethyl ether into a saturated THF solution. As expected, single-crystal X-ray analysis established that **3** is a structural analogue of $[Cl@Ag_{14}(^tBuC{\equiv}C)_{12}]OH$ in which the cyclohexyl groups replace the corresponding peripheral *tert*-butyl groups in the chloride-centered rhombic-dodecahedral Ag_{14} cluster and the counteranion is a chloride instead of a hydroxide. In fact, two polymorphic forms of **3** were obtained in separate crystallizations with the same solvent: one (**3A**) is a linear coordination polymer with each Cl^- ion bridging two adjacent $[Cl@Ag_{14}(chxC{\equiv}C)_{12}]^+$ moieties to generate an infinite chain, and the other (**3B**) is an organic salt composed of a packing of $[Cl@Ag_{14}(chxC{\equiv}C)_{12}]^+$ and Cl^- ions (Figure 3). Since the separation between the chloride ion and its closest silver(I) neighbor in **3B** (3.330 Å) was found to be much larger than that in polymorph **3A** (2.550 Å), the former has a less densely packed crystal lattice, as reflected by the larger size of its unit cell.[10]

The reaction between $[Cl@Ag_{14}(chxC{\equiv}C)_{12}]Cl$ (**3**) and $AgClO_4$ was conducted in dichloromethane to obtain crystalline complex **2**,[11] which has the same cluster-within-a-cluster $Cl_6Ag_8@Ag_{30}$ structure as in **1**. In its Cl_6Ag_8 inner cluster core, the Ag−Cl bond distances lie in the range from 2.623(2) to 2.750(2) Å, and the argentophilic Ag···Ag distances between outer-shell silver atoms lie in the range from 2.923(11) to 3.467(13) Å. The 20 peripheral cyclohexylethynide ligands in **2** can be divided into three groups on the basis of their different ligation modes: six μ_3-η^1,η^1,η^2; six μ_3-η^1,η^2,η^2; and eight μ_4-$\eta^1,\eta^2,\eta^2,\eta^2$. Each of the last group of ligands is attached to one of the eight interior silver atoms in σ fashion with a Ag−C distance in the range from 2.162(7) to 2.197(1) Å. The increased bulkiness of the cyclohexyl group relative to the *tert*-butyl group accounts for the fact that only 10 of the 12 perchlorate ions in **2** are coordinated to the exterior silver atoms (eight in a μ_1-*O* ligation mode and two in a μ_2-*O*,*O*,*O*′ mode), so the $Cl_6Ag_8@Ag_{30}$ cluster of **2** bears a net charge of +2. Of the two solvated diethyl ether molecules, one was found to exhibit 50% occupancy.

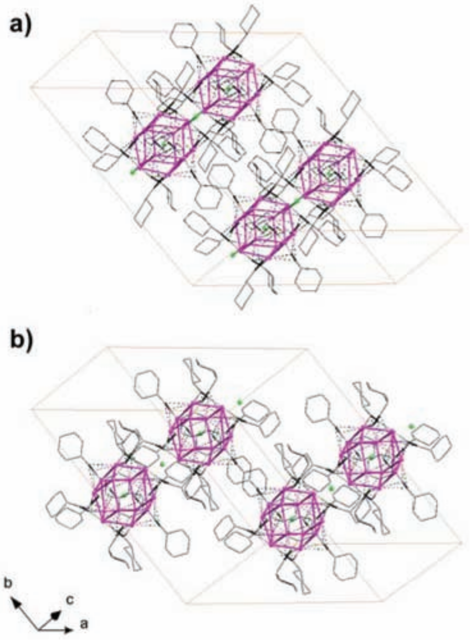

Figure 3. (a) Perspective view of the crystal packing in polymorph **3A**. It should be noted that the exopolyhedral chloride ion serves as a bridge between a pair of adjacent cationic $Cl@Ag_{14}$ cages. (b) Perspective view of the crystal packing in polymorph **3B**. In this case, the exopolyhedral chloride ion is not bound to any silver(I) center.

Complexes **1** and **2** are slightly soluble in dichloromethane, and their solution properties and formation processes were investigated using electrospray ionization mass spectrometry (ESI-MS) and NMR spectroscopy. Unfortunately, attempts to detect the molecular weight signal of either complex were unsuccessful, as the highly charged cluster cation was labile during the ESI process.[12] The ^1H NMR spectrum of **3** in CD_2Cl_2 (Figure 4) displayed clear and well-differentiated peaks for the 12 cyclohexyl ligands coordinated to different silver atoms, showing that the cluster structure of **3** remained stable in solution. The introduction of $AgClO_4$ into the solution initiated a structural change in **3**, and the onset of the rearrangement process was signaled by the downfield shift of the cyclohexyl protons and their splitting into two separate sets. When the reaction was allowed to proceed overnight, the molar concentration of complex **2** became undetectable by NMR analysis, as the rearrangement is a low-yield process. After complex **2** was isolated and redissolved in CD_2Cl_2, its ^1H NMR spectrum displayed two different sets of cyclohexyl proton signals, particularly for the proton on the tertiary carbon atom of the ligand (originally at δ 2.68 for **3**). The quintet signal was shifted to a more downfield region and divided into two separate sets (δ 2.84 and 2.99) in a 3:2 ratio, which is consistent

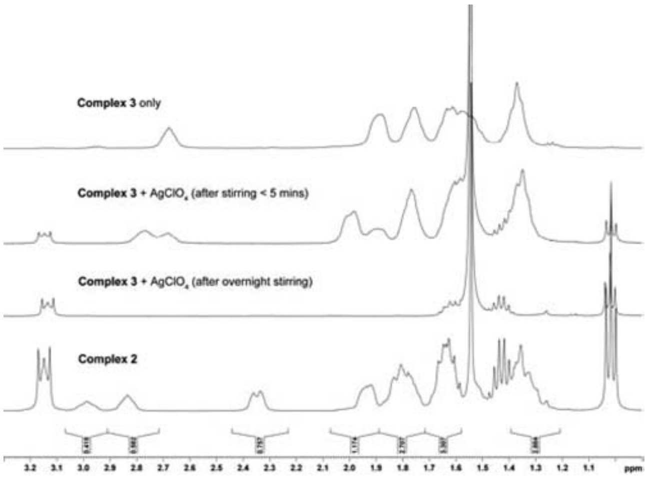

Figure 4. ^{1}H NMR spectra showing the δ 0.8−3.3 region for (top to bottom) complex **3** in CD_2Cl_2, its reaction with $AgClO_4$ in two time intervals, and isolated complex **2** redissolved in CD_2Cl_2. Each spectrum is internally referenced to residual proton solvent signals of CD_2Cl_2 at δ 5.32. The pairs of peaks located at δ 1.03 and 3.15 belong to the solvated diethyl ether residue from the preparation of complex **3**.

with the ratio of the 20 cyclohexyl ligands exhibiting distinguishable coordination modes (12 μ_3 and eight μ_4).

It is noteworthy that although the reassembly process resulting in the synthesis of **1** or **2** takes a long time to accomplish at room temperature, it is nonetheless energetically feasible and reproducible. Formation of the common Cl_6Ag_8 cluster core presumably arises from fusion of the central chloride ion in the corresponding precursor (i.e., $[Cl@Ag_{14}({}^tBuC\equiv C)_{12}]OH$ or $[Cl@Ag_{14}(chxC\equiv C)_{12}]Cl$) with silver perchlorate, rather than the abstraction of chloride from CH_2Cl_2[13] by Ag(I) ions, in view of the low yields of **1** and **2**. The Ag_{14} cage of either precursor may be envisaged to undergo partial degradation upon dissolution in CH_2Cl_2 in the presence of $AgClO_4$, thereby freeing the encapsulated chloride template for condensation with the abundant supply of Ag(I) ions from dissolved silver perchlorate. Furthermore, introducing an extra chloride source by the addition of $[(n\text{-}C_4H_9)_4N]Cl$ also failed to improve the yield of either **1** or **2**. This may be explained by a competing reaction, namely, the precipitation of silver chloride from dichloromethane. The slightly higher yield of **2** relative to **1** can be rationalized by the higher chloride content in precursor **3** versus $[Cl@Ag_{14}({}^tBuC\equiv C)_{12}]OH$. Notably, our subsequent attempt to reproduce either **1** or **2** using a non-halogenated solvent such as THF in place of dichloromethane turned out to be unsuccessful.

The generation of the high-nuclearity cluster complexes **1** and **2** presumably materializes from the choice of, and proper stoichiometric balance between, the silver ethynide, encapsulated chloride, and silver perchlorate components. The reaction was also found to be highly specific to the chloride ion as a template, as attempts to use $[Br@Ag_{14}(chxC\equiv C)_{12}]NO_3$ (**4**)[14] (Figure 5) as a starting material to synthesize similar high-nuclearity clusters proved futile; this may be due to the size mismatch for assembling a functioning Br_6Ag_8 inner core inside a silver cluster shell consolidated by peripheral ethynide groups. When less bulky $[Cl@Ag_{14}(i\text{PrC}\equiv C)_{12}]NO_3$ (**5**)[15] was used as a precursor for the intended generation of the $Ag_{38}Cl_6$ cluster unit, only tiny crystals of poor quality could be obtained, implying that the bulkiness of the ethynide ligands plays a significant role in stabilizing the molecular structure of the high-nuclearity cluster unit. The present cluster conversion reaction is also influenced by the choice of the counteranion: when silver perchlorate was replaced by silver tetrafluoroborate or silver hexafluorophosphate in the synthetic procedure, white powders of unknown composition were deposited instead of crystals of **1** or **2**. Because of the poor solubility of silver nitrate in dichloromethane, only unreacted starting material ($[Cl@Ag_{14}({}^tBuC\equiv C)_{12}]OH$ or **3**) was recovered.

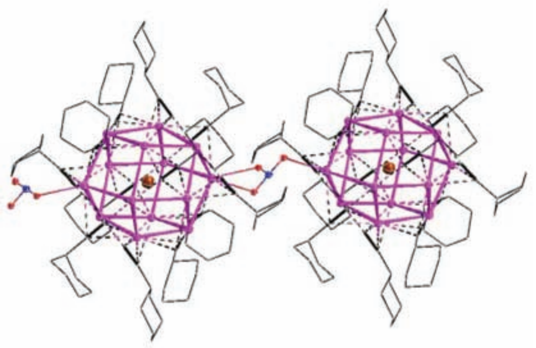

Figure 5. A portion of the infinite coordination polymeric chain in the crystal structure of $[Br@Ag_{14}(chxC\equiv C)_{12}]NO_3$ (**4**). H atoms have been omitted for clarity. The nitrate ion was found to exhibit orientational disorder, giving two sets of oxygen atoms each having 50% site occupancy. The diagram shows one orientation of the nitrate ion that links two neighboring cationic $[Br@Ag_{14}]$ clusters. Color scheme: purple, silver atoms; brown, bromide ions; blue, nitrogen atoms; red, oxygen atoms; bold black lines, C≡C bonds; broken lines, Ag−C bonds).

In summary, we have employed the multinuclear supramolecular synthon $R{-}C\equiv C\supset Ag_n$ (R = alkyl, cycloalkyl; n = 3, 4, 5) to construct two high-nuclearity silver ethynide cluster compounds, $[Cl_6Ag_8@Ag_{30}({}^tBuC\equiv C)_{20}(ClO_4)_{12}]\cdot Et_2O$ (**1**) and $[Cl_6Ag_8@Ag_{30}(chxC\equiv C)_{20}(ClO_4)_{10}](ClO_4)_2\cdot 1.5Et_2O$ (chx = cyclohexyl) (**2**), that bear the same novel Cl_6Ag_8 central core. The synthesis of **1** made use of $[Cl@Ag_{14}({}^tBuC\equiv C)_{12}]X$ (X = OH) as a precursor, and its reaction with $AgClO_4$ in CH_2Cl_2 resulted in an increase in nuclearity from 14 to 38. A similar reaction using an analogous Ag_{14} precursor with X = Cl produced compound **2**. The present results strongly suggest that the formation of **1** and **2** involves a transformation of the encapsulated chloride template within a Ag_{14} cage into a cationic Cl_6Ag_8 central core within a Ag_{30} cluster shell. To our knowledge, this provides the first example of conversion of a silver cluster into one of higher nuclearity via an inner-core transformation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional figures, ^{1}H NMR spectra, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Synthesis of $[Ag_{38}Cl_6({}^tBuC\equiv C)_{20}(ClO_4)_{12}]\cdot Et_2O$ (**1**): Silver perchlorate (50 mg, 0.25 mmol) was added to a suspension of $[Cl@Ag_{14}({}^tBuC\equiv C)_{12}]OH$ (50 mg, 0.019 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 24 h in the dark, and a white precipitate was deposited. After filtration, colorless blocklike crystals were obtained by slow diffusion of diethyl ether into the filtrate at room temperature. Yield: 4.4%.

(8) Crystallographic data for complex **1**: triclinic; a = 18.3988(14) Å, b = 18.6925(14) Å, c = 19.0757(24) Å, α = 94.796(2)°, β = 116.638(2)°, γ = 116.175(1)°; V = 4928.4(0) Å^3; T = 173 K; space group P-1 (No. 2); Z = 1; 106795 measured reflns, 17850 unique (R_{int} = 0.0435), which were used in all calculations; R_1 = 0.0338, wR_2 = 0.0799 for $I > 2\sigma$.

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(10) Synthesis of $[Cl@Ag_{14}(chxC\equiv C)_{12}]Cl$ (**3**): Polymeric $[(chxC\equiv C)Ag]_n$ (30 mg, 0.140 mmol of $(chxC\equiv C)Ag$) was dissolved in THF (3 mL) with stirring. $[(n\text{-}C_4H_9)_4N]Cl$ (3.5 mg, 0.012 mmol) was added, and a clear orange solution was obtained. After filtration, colorless blocklike crystals were deposited by slow diffusion of diethyl ether into the filtrate. Two crystalline polymorphs, **3A** and **3B**, were obtained in separate operations. Yields: 6% (**3A**); 5% (**3B**). Crystallographic data for **3A**: rhombohedral (hexagonal setting); a = 25.8259(15) Å, c = 12.3664(7) Å; V = 7143.0(7) Å^3; T = 173 K; space group R-3 (No. 148); Z = 3; 50586 reflns measured, 3259 unique (R_{int} = 0.0801), which were used in all calculations; R_1 = 0.0255, wR_2 = 0.0675 for $I > 2\sigma$. For **3B**: rhombohedral (hexagonal setting); a = 24.4626(14) Å, c = 14.0339(7) Å; V = 7273.0(1) Å^3; T = 173 K, space group R-3 (No. 148); Z = 3; 68135 reflns measured, 2935 unique (R_{int} = 0.0926), which were used in all calculations; R_1 = 0.0435, wR_2 = 0.1185 for $I > 2\sigma$. Structure plots for **3A** and **3B** are shown in Figures S2 and S3, respectively.

(11) Synthesis of $[Ag_{38}Cl_6(chxC\equiv C)_{20}(ClO_4)_{10}](ClO_4)_2\cdot 1.5Et_2O$ (**2**): Silver perchlorate (20 mg, 0.097 mmol) was added to a suspension of $[Cl@Ag_{14}(chxC\equiv C)_{12}]Cl$ (20 mg, 0.007 mmol) in dichloromethane (3 mL). The reaction mixture was stirred for 24 h in the dark, and a solution with a white precipitate was obtained. After filtration, colorless blocklike crystals were deposited by slow diffusion of diethyl ether into the filtrate at room temperature. Yield: 14.7%. Anal. Calcd for $C_{160}H_{220}Ag_{38}Cl_{18}O_{48}$: C, 25.13; H, 2.90. Found: C, 25.20; H, 2.87. Crystallographic data for **2**: monoclinic; a = 32.8837(27) Å, b = 20.3223(18) Å, c = 33.9498(29) Å, β = 91.106(2)°; V = 22683.4(9) Å^3; T = 173 K; space group $C2/c$; Z = 8; 415251 reflns measured, 20563 unique (R_{int} = 0.0945), which were used in all calculations; R_1 = 0.0393, wR_2 = 0.1121 for $I > 2\sigma$. Structure plots for **2** are shown in Figure S1.

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(14) Synthesis of $[Br@Ag_{14}(chxC\equiv C)_{12}]NO_3$ (**4**): Polymeric $[(chxC\equiv C)Ag]_n$ was synthesized via the reaction of silver nitrate with equal stoichiometric amounts of cyclohexylethyne and triethylamine in acetonitrile at room temperature. The resulting $[(chxC\equiv C)Ag]_n$ powder was contaminated with a trace amount of $AgNO_3$ as a contaminant. The synthetic procedure developed for complex **3** was repeated with polymeric $[(chxC\equiv C)Ag]_n$ powder (30 mg, 0.140 mmol of $(chxC\equiv C)Ag$ monomer) and $[(n\text{-}C_4H_9)_4N]Br$ (4.3 mg, 0.013 mmol) to obtain colorless blocklike crystals of **4**. Yield: 3%. Crystallographic data: rhombohedral (hexagonal setting); a = 24.5343(15) Å, c = 13.9815(9) Å; V = 7288.4(8) Å^3; T = 173 K, space group R-3 (No. 148); Z = 3; 80410 reflns measured, 2939 unique (R_{int} = 0.0740), which were used in all calculations; R_1 = 0.0324, wR_2 = 0.0839 for $I > 2\sigma$.

(15) Synthesis of $[Cl@Ag_{14}(iPrC\equiv C)_{12}]NO_3$ (**5**): Polymeric $[(iPrC\equiv C)Ag]_n$ was synthesized via the reaction of silver nitrate with equimolar amounts of 3-methyl-1-butyne and triethylamine in acetonitrile at room temperature. The resulting $[(iPrC\equiv C)Ag]_n$ powder was contaminated with a trace amount of $AgNO_3$. The synthetic procedure developed for complex **3** was repeated with polymeric $[(iPrC\equiv C)Ag]_n$ (30 mg, 0.170 mmol of monomer) and $[(n\text{-}C_4H_9)_4N]Cl$ (4.3 mg, 0.016 mmol) to obtain colorless blocklike crystals of **5**. Yield: 4%. Crystallographic data: rhombohedral (hexagonal setting); a = 21.4318(9) Å, c = 13.7670(6) Å; V = 5476.3(4) Å^3; T = 173 K, space group R-3 (No. 148); Z = 3; 36623 reflns measured, 2209 unique (R_{int} = 0.0726), which were used in all calculations; R_1 = 0.0259, wR_2 = 0.0662 for $I > 2\sigma$. Structure plots for **5** are shown in Figures S4 and S5.

■ NOTE ADDED AFTER ASAP PUBLICATION

Reference 9(c) and 9(d) were incorrect in the version of this Communication published ASAP February 2, 2012. The corrected version was posted February 7, 2012.