

Interparticle Reactions between Silver Nanoclusters Leading to Product Cocrystals by Selective Cocrystallization

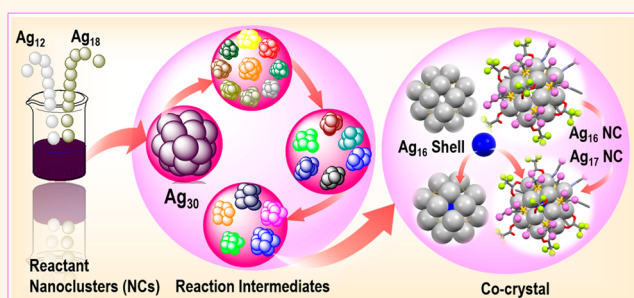
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S Supporting Information

ABSTRACT: We present an example of an interparticle reaction between atomically precise nanoclusters (NCs) of the same metal, resulting in entirely different clusters. In detail, the clusters $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$ (TBT = *tert*-butylthiolate, TFA = trifluoroacetate, CH_3CN = acetonitrile) and $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ (TPP = triphenylphosphine) abbreviated as Ag_{12} and Ag_{18} , respectively, react leading to $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$, abbreviated as Ag_{16} and Ag_{17} , respectively. The two product NCs crystallize together as both possess the same metal chalcogenolate shell, composed of Ag_{16}S_8 , making them indistinguishable. The occupancies of Ag_{16} and Ag_{17} are 66.66 and 33.33%, respectively, in a single crystal. Electrospray ionization mass spectrometry (ESI MS) of the reaction product and a dissolved crystal show the population of Ag_{16} and Ag_{17} NCs to be in a 1:1 and 2:1 ratio, respectively. This suggests selective crystallization in the cocrystal. Time-dependent ESI MS was employed to understand the formation of product clusters by monitoring the reaction intermediates formed in the course of the reaction. We present an unprecedented growth mechanism for the formation of silver NCs mediated by silver thiolate intermediates.

KEYWORDS: nanoclusters, intercluster reactions, homometallic clusters, cocrystals, Ag_{16} and Ag_{17}



Atomically precise noble metal nanoclusters (NCs) are an emerging class of materials. Studies on them are motivated by their unusual structures and associated properties.^{1–6} NCs possess exceptional geometric and electronic structures, having a core size below 3 nm, exhibiting intriguing properties due to molecule-like energy levels, strong photoluminescence, color tunability, high catalytic activity, facile surface tailorability, and good photostability, which are different from bulk nanoparticles, with diameters >3 nm.^{3–7} Scalable fabrication of the NCs results in new materials with distinctly different applications.^{8,9} Attempts to design novel NCs have been there using diverse methodologies. Clusters with varying cores can be obtained by different synthetic procedures such as size focusing methodology,^{10,11} interparticle reactions,¹² and many others.^{2–6} To understand the distinct properties of NCs, detailed knowledge of their structures is important. In the recent past, atomically precise silver (Ag) nanoclusters with a wide range of nuclearity have been characterized, including Ag_{14} ,¹³ Ag_{16} ,¹⁴ Ag_{17} ,¹⁵ Ag_{33} ,¹⁶ Ag_{20} ,¹⁷ Ag_{21} ,¹⁸ Ag_{25} ,¹⁹ Ag_{22} ,²⁰ Ag_{29} ,²¹ Ag_{40} ,²² Ag_{44} ,²³ Ag_{46} ,²² Ag_{123} ,²⁴ Ag_{320} ,²⁵ Ag_{344} ,²⁴ Ag_{352} ,²⁵ Ag_{490} ,²⁵ etc., with varying

thiols, as well as with secondary ligands, mostly phosphines. Charge is an integral part of the cluster system, with many existing in multianionic forms. Structural studies of nanoclusters revealed that the metal core is protected by an outer layer, composed of the metal and ligands. A closed-shell electronic structure makes these clusters stable, which often results in an overall charge for the system. In a few cases, an unusual possibility of two NCs of similar outer structure covering varied inner cores exist during the nucleation of a crystal, leading to the formation of multicomponent molecular solids or cocrystals.²² They have properties of both the clusters. The study of cocrystals is a well-known aspect of modern crystal engineering.²⁶ They may have several applications in pharmaceutical sciences.²⁷ Many cocrystals of noble metal NCs are known now.^{22,28–30} These have been synthesized either by reducing thiolate or phosphine complexes or by ligand-exchange-induced size transformation

Received: August 25, 2019

Accepted: November 1, 2019

Published: November 1, 2019

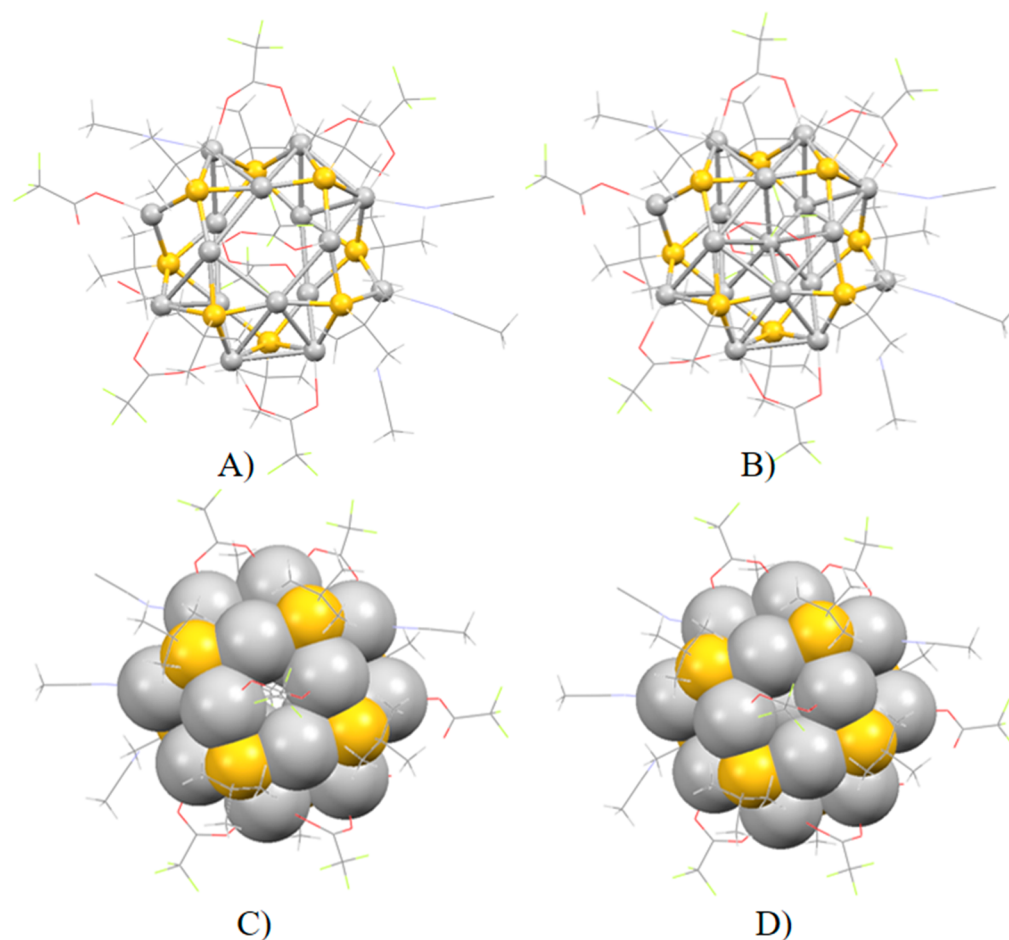


Figure 1. Total structures of (A) $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3(\text{Cl})]^+$ and (B) $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3(\text{Cl})]^+$. The Ag_{16} NC is hollow inside, and Ag_{17} contains one additional Ag atom inside. Light gray and yellow spheres in the ball-and-stick model represent Ag and S atoms, respectively, and other nonmetals are represented by a wire frame model. Space-filling models of (C) Ag_{16} and (D) Ag_{17} . Color code: Ag, light gray; S, yellow; F, light green; C, gray; N, light blue; Cl, black.

reactions (LEIST).³¹ NCs are considered as stable entities and are expected to retain their identity in solution. Chemical reactions between NCs or interparticle reactions belong to a special class of reactions introduced by our group, which typically involve the exchange of metals and ligands between different clusters, leading to product clusters.^{32–34} These reactions were performed by reacting monolayer-protected clusters composed of different metals, for example, Ag and Au NCs. Reaction between Au_{25} and Ag_{44} were reported initially followed by the reaction of Ag_{25} and Au_{25} .^{32,33} Many others were also studied subsequently.^{34–37} Here, we explored an interparticle reaction methodology between homometallic clusters to make new clusters. To understand the growth of NCs, time-dependent electrospray ionization mass spectrometry (ESI MS) studies were performed. We note that the size evolution mechanism for the formation of Ag and Au NCs *via* homoleptic thiolate-stabilized precursors has been reported recently.^{28,38,39}

We present the synthesis, optical properties, ESI MS analysis, and structures of atomically precise NCs, costabilized by TBT (*tert*-butylthiolate) and TFA (trifluoroacetate) ligands. The synthesis involves a homometallic interparticle reaction of silver NCs using $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$ and a hydride and phosphine coprotected cluster, $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$, abbreviated as Ag_{12} and Ag_{18} , respectively, as reactants, which are known previously.^{40,41} The

reaction mixture formed cocrystals of product NCs *viz.* $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ denoted as Ag_{16} and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ denoted as Ag_{17} . The two NCs are structurally similar and are indistinguishable in the lattice. We probed the mechanism of interparticle reaction using time-dependent ESI MS and UV–vis spectroscopy, which gave deep insights into the formation of the NCs mediated by silver thiolate intermediates. Our approach represents a different method of synthesizing atomically precise NC cocrystals, which could result in unusual properties and applications.

RESULTS AND DISCUSSION

The Ag_{12} NC was synthesized by dissolving silver thiolate, $\text{Ag}(\text{TBT})_n$, and CF_3COOAg in a mixture of acetonitrile and methanol. To this was added a methanolic solution of Ag_{18} (synthesized by a reported method).^{41,42} A dark brown solution along with a black precipitate was formed; the mixture was kept stirring for 1 h, and the solution was centrifuged at 8000 rpm (5868g). The black precipitate was discarded as it did not dissolve in various organic solvents. The resultant supernatant dark brown solution was initially analyzed by UV–vis absorption spectroscopy for its optical properties that displayed the characteristic molecular transitions at 439 and 611 nm. The solution obtained after

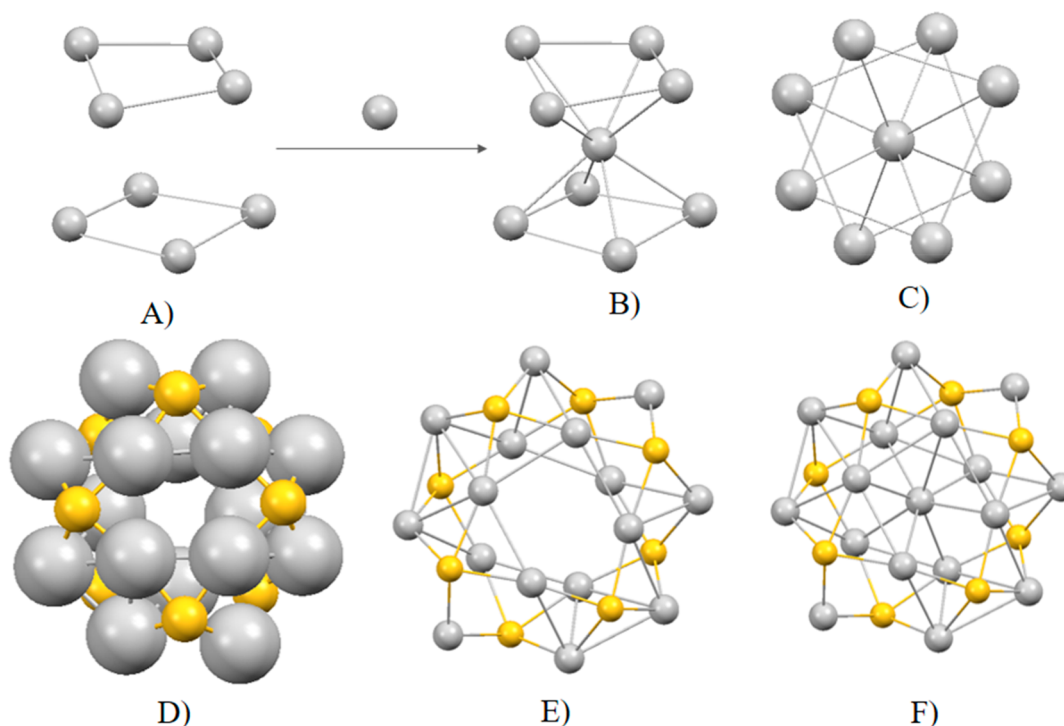


Figure 2. (A) Construction of Ag₁₇ by the addition of one silver atom between the Ag atoms, (B) showing distorted square anti-biprismatic geometry in which the central Ag atom is bonded to eight Ag atoms. (C) Top view of the Ag₉ metallic framework. (D) View of Ag₁₆S₈ shell showing Ag₄S capping around the periphery of the shell. (E) Top view of Ag₁₆ and (F) Ag₁₇ NC shells: Ag (gray) and S (yellow).

centrifugation was left for slow evaporation at 5 ± 5 °C for crystallization, and after 1 week, light brown crystals suitable for single-crystal X-ray diffraction (SCXRD) were obtained. SCXRD, ESI MS, and UV–vis spectroscopic techniques were employed to characterize the product formed.

A block-shaped single crystal was evaluated by SCXRD. Analysis of the crystallographic data showed that there exist two types of NC entities *viz.* $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$, acronymed as Ag₁₆ and Ag₁₇, respectively, in a single crystal, as shown in Figure 1. Each NC exhibits a sandwich-like molecular structure, assembled in a monoclinic $P2_1/n$ space group (Table S1). These NCs have identical outer structures, and they can easily exchange positions in a lattice. They are, therefore, not able to distinguish each other and crystallize together. The geometrical framework of the Ag₁₆ NC can be represented by surface-connected 16 Ag and 8 S atoms, thereby forming an Ag₁₆S₈ hollow shell, arranged in a layered fashion: Ag₄S₄–Ag₈–Ag₄S₄, forming a sandwich-like structure (Figure S1). For the Ag₁₇ NC, a single Ag atom is encapsulated in the Ag₁₆ shell and has an occupancy of 1/3. Thus, in the cocrystal, 2/3 NCs have 16 Ag atoms and 1/3 NCs have 17 Ag atoms. In Ag₁₆S₈ shell, each S atom is coordinated to four Ag atoms, forming Ag₄S capping around the periphery of the shell (Figure 2D). The Ag₁₆ and Ag₁₇ NCs in a cocrystal are primarily protected by the TBT ligand. In addition, seven units of TFA, three molecules of acetonitrile and one chlorine atom are coordinated to the Ag₁₆S₈ shell. One molecule of acetonitrile per unit cell is also located in the lattice. The Ag₁₆ NC structure is almost similar to the shell of a recently reported $[\text{Ag}_{16}\text{Cl}(\text{S}^t\text{Bu})_8(\text{CF}_3\text{COO})_7(\text{DMF})_4(\text{H}_2\text{O})] \cdot 1.5(\text{DMF})$ NC, although it encapsulates Cl[−] within the cluster core.⁴³ Recently, a $[\text{Ag}_{17}\text{I}_3\text{S}(\text{C}_2\text{B}_{10}\text{H}_{10}\text{S}_2)_6(\text{CH}_3\text{CN})_{11}]$ NC was reported, but it

has a different geometry.¹⁵ The construction of Ag₁₇ is shown in Figure 2A–C, in which the central Ag atom is coordinated to eight Ag atoms of the shell, resulting in a distorted square anti-biprismatic geometry. We have not seen any counterion upon solving the structure of these NCs. To identify the counterion, we have performed the IR (infrared) spectroscopy of a cocrystal. The IR spectrum exhibits a characteristic band at 1365 cm^{−1} (Figure S2), which can be assigned to N–O stretching of the NO₃[−] ion.⁴⁴ It indicates that the NO₃[−] ion is the counterion existing in a cocrystal. The NO₃[−] has its origin from AgNO₃ used in the synthesis of Ag₁₈ NCs.^{41,42}

ESI MS was performed to probe the existence of NCs in the solution. A single crystal was dissolved in acetonitrile for carrying out mass spectral measurements. Other details of the sample preparation and instrumental conditions are described in the instrumentation section of the Supporting Information (SI). The mass spectrum (MS) exhibits three major peaks at m/z 3055, 3277, and 3499 in the positive ion mode (Figure 3Ai). Expanded peaks show a characteristic peak separation of m/z 1.00, which confirms the +1 charge state. Therefore, the peaks at m/z 3499, 3277, and 3055 are assigned to $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$, $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$, and $[\text{Ag}_{15}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})_3\text{Cl}]^+$, respectively. This was further confirmed by matching the experimental (violet trace) and simulated (red trace) isotopic distributions of the peaks (Figure 3Aii). The presence of Ag₁₅ and Ag₁₆ peaks in the mass spectrum may be a result of fragmentation. To probe this, we performed collision-induced dissociation (CID) experiments of the peaks due to Ag₁₆ and Ag₁₇ by varying the laboratory collision energy. For the Ag₁₆ peak, CID results in the Ag₁₅ moiety, as a result of the loss of CF₃COOAg. Other fragmented species were also formed upon increasing the collision energy (Figure S3). CID studies of the Ag₁₇ peak

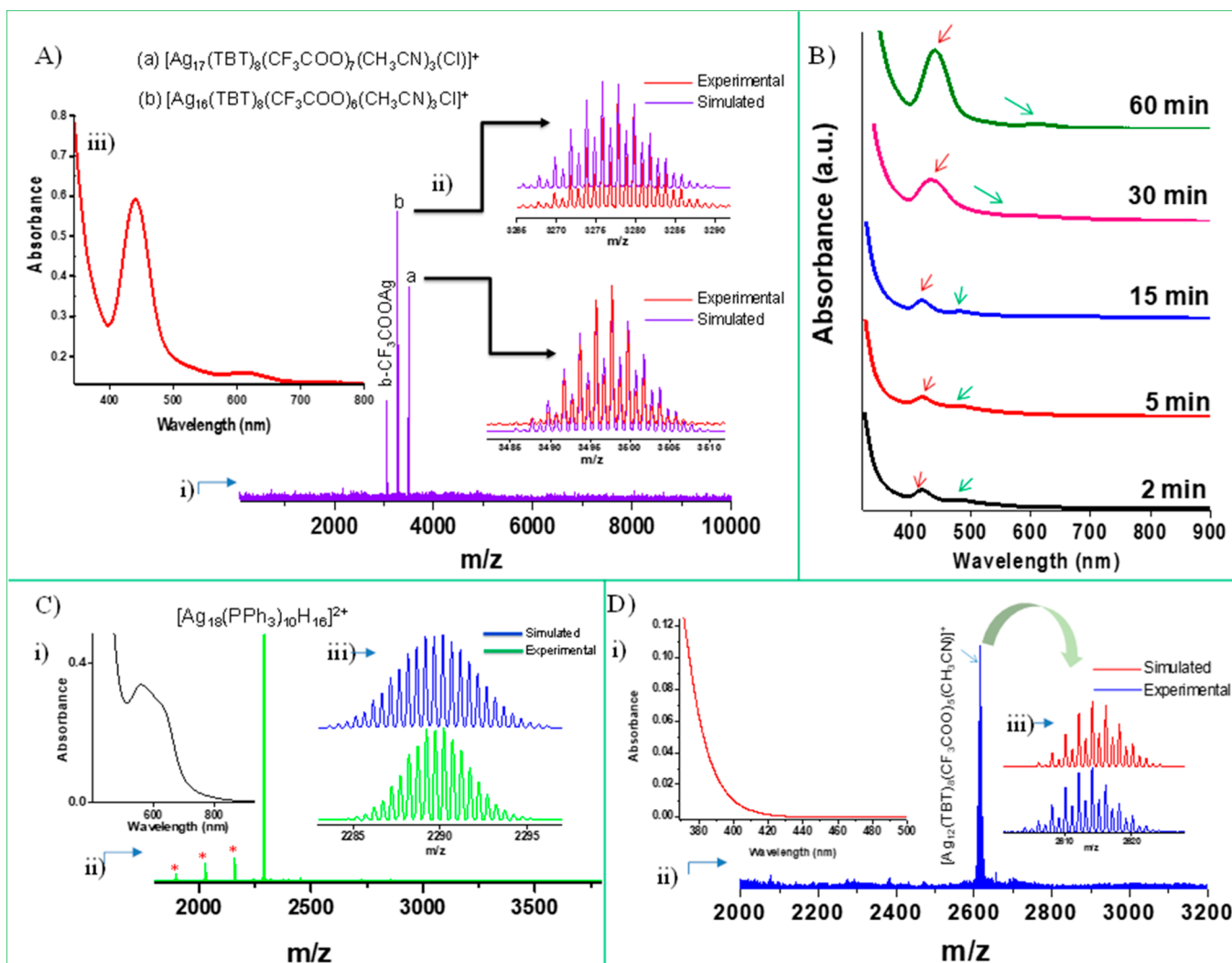


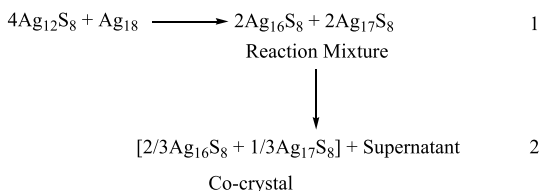
Figure 3. (A) (i) ESI MS in positive ion mode of crystals dissolved in acetonitrile solution. Peak (a) corresponds to $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3(\text{Cl})]^+$. Peak (b) corresponds to $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_6(\text{CH}_3\text{CN})_3(\text{Cl})]^+$, and another peak corresponds to $\text{b-CF}_3\text{COOAg}$. (ii) Isotopic distribution of (a) experimental spectrum (violet trace) is compared with simulated spectrum (red trace). (iii) UV-vis absorption spectrum of a crystal dissolved in acetonitrile solution. (B) UV-vis spectra of a reaction mixture in acetonitrile during $t = 2\text{--}60$ min. Arrows mark the position of absorption bands. (C) UV-vis and ESI MS of the methanolic solution of $[\text{Ag}_{18}(\text{PPh}_3)_{10}\text{H}_{16}]^{2+}$. (D) UV-vis and ESI MS of $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$ in acetonitrile. Experimental and simulated mass spectra are compared in the insets of (Ciii) and (Diii).

shows the systematic loss of TBT and TFA moieties, with an increase in collision energy, but no signature of the conversion to Ag_{16} NC was observed, as shown in Figure S4. We conclude that the peak corresponding to Ag_{16} is due to a separate entity and not arising from a fragment of Ag_{17} . The above observation proves the presence of two kinds of NCs in solution. Populations of Ag_{16} and Ag_{17} are not equal in the ESI MS (Figure 3Ai), assuming that both the species have similar ionization efficiencies. The Ag_{16} peak, whose population is more than Ag_{17} in the crystal, supports its appearance as the major NC species. Although there are additional factors such as ionization efficiency and ion transmission, which determine mass spectral intensities, the intensity ratio supports excess concentration of Ag_{16} . MS of the solution obtained after 1 h of the reaction shows the population of Ag_{16} and Ag_{17} to be almost equal (Figure S5). In order to correlate the findings of the single crystal and the reaction mixture, we carried out the MS of the supernatant left behind after crystallization. It was observed that the supernatant also contains peaks correspond-

ing to Ag_{16} and Ag_{17} (Figure S6). These findings suggest that the single crystal stabilizes with a population of 66.66 and 33.33% of Ag_{16} and Ag_{17} NCs, respectively, rather than the 1:1 ratio noted in another set of clusters,²² despite the presence of extra Ag_{17} species in the supernatant. This could be due to the minimum energy considerations.²² These results allow us to write a balanced chemical equation given below (considering the mass balance of silver and sulfur atoms only). To the best of our knowledge, this is the early observation of a homometallic interparticle reaction of silver NCs yielding cocrystals. We believe that the hydride-rich Ag_{18} is important for inducing the reaction. We suggest the following processes (Scheme 1).

The mass spectral intensities in the reaction mixture and supernatant support this conclusion. Equal intensities of Ag_{16} and Ag_{17} in the reaction mixture were changed to 2:1 for a solution prepared from the crystal. In the supernatant, the amount of Ag_{17} increased, although the ratio in the supernatant is not 1:2, which is understandable as some of the Ag_{16} and

Scheme 1



Ag_{17} may have only crystallized. To further explore the individual properties of Ag_{16} and Ag_{17} NCs, attempts were made to synthesize these separately by changing the reaction conditions, but we could not succeed in this process.

ESI MS of the reaction mixture measured at various time intervals ($t = 2, 5, 15, 30, 60$ min and 7 days) after the addition

of a methanolic solution of Ag_{18} into a solution of Ag_{12} are shown in Figure 4. These measurements show that the characteristic peaks of individual Ag_{18} and Ag_{12} NCs disappeared completely after mixing them. At $t = 2$ min (right after the reaction), a characteristic peak at m/z 4928, which could be assigned to $[\text{Ag}_{30}(\text{TBT})_9(\text{TFA})_6(\text{CH}_3\text{CN})_5]^+$, denoted as Ag_{30} , was observed. The appearance of this peak suggests that an addition reaction had taken place between Ag_{12} and Ag_{18} NCs. Many peaks were observed in the range between m/z 100 and 1000. All of these low molecular weight species ($m/z < 1000$) were assigned to thiolates and phosphines formed during the reaction, shown in Figure S7. MS recorded after 5 min of reaction show many peaks in the region between m/z 1000 and 3000, which were assigned to the heteroleptic reaction intermediates. No such peak was

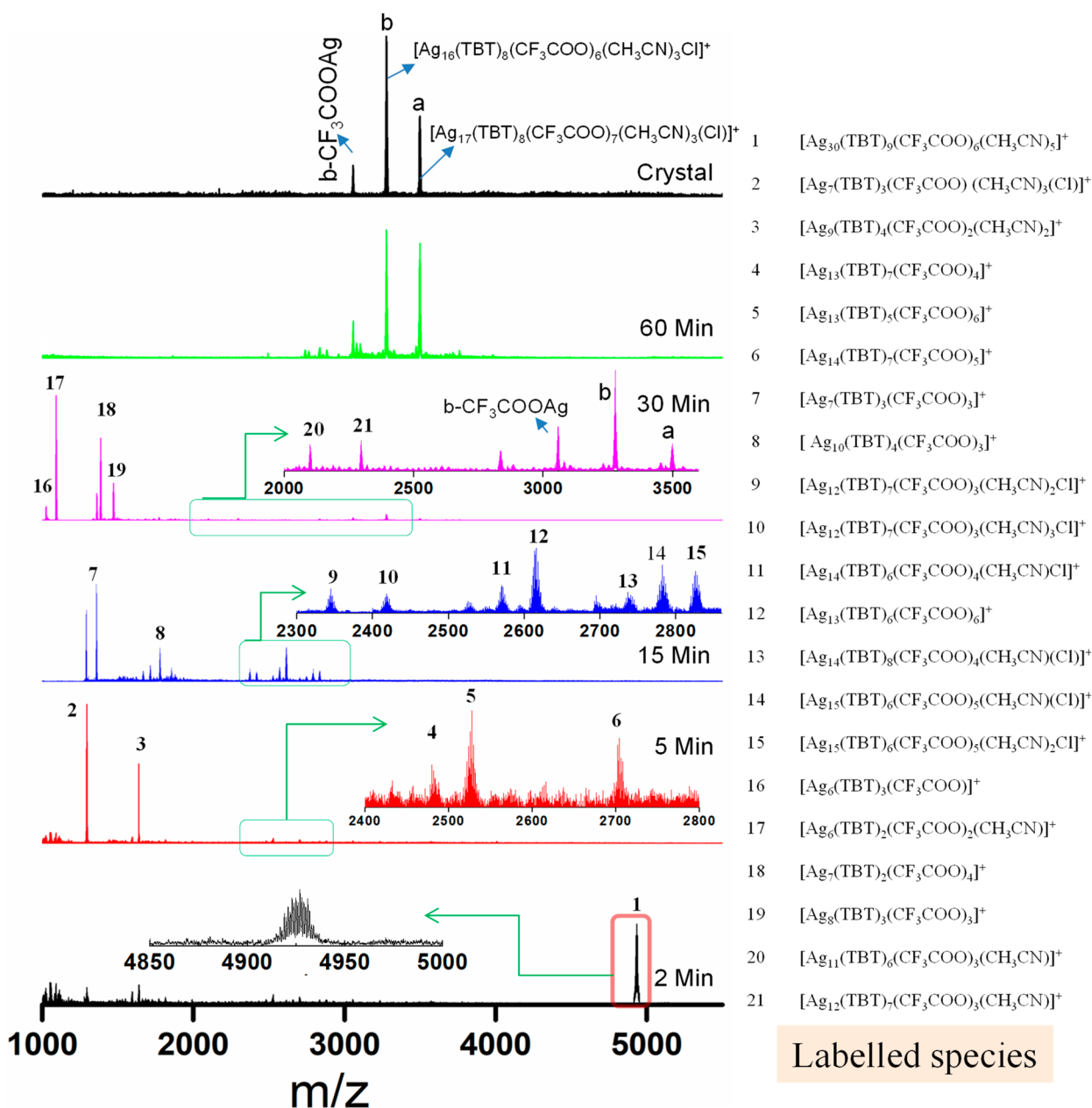


Figure 4. Time-dependent ESI MS spectra of the reaction mixture during the synthesis of $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_6(\text{CH}_3\text{CN})_3(\text{Cl})]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3(\text{Cl})]^+$ via silver-thiolate-based reaction intermediates (assigned from 1 to 21). Insets show the magnified regions of ESI MS containing intermediates. Assignments of the peaks are on the right.

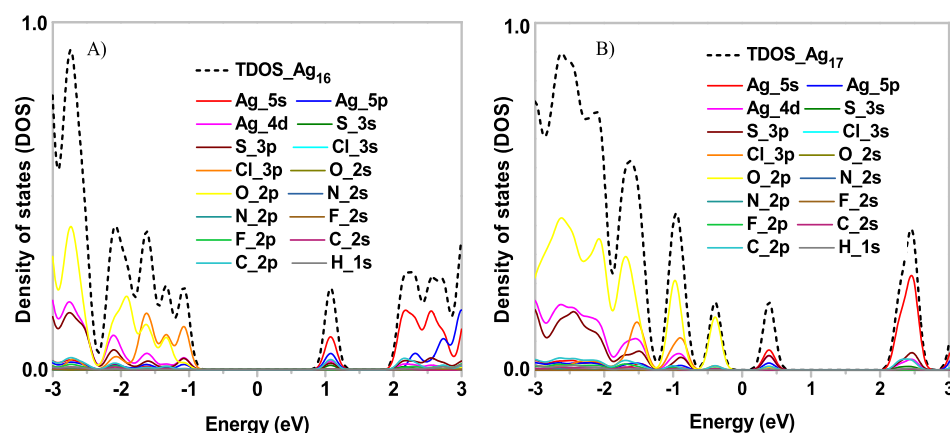


Figure 5. DOS analysis of molecular orbitals of the model cluster, (A) $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ and (B) $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$.

observed at m/z 4928. This suggests that the adduct Ag_{30} is fragmented into smaller intermediates. Therefore, it appears to be a top-down approach and is different from the reported one.^{28,38} MS monitored from time $t = 15$ –30 min shows that significant changes occur. Color of the reaction mixture changes from dark to light brown. An important aspect noticed after 30 min is the emergence of different peaks whose m/z match with the molecular mass of $[\text{Ag}_{15}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})_3\text{Cl}]^+$, $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_6(\text{CH}_3\text{CN})_3\text{Cl}]^+$, and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$. After 1 h, MS does not show the appearance of any kind of intermediate(s). Intensities of the peaks corresponding to Ag_{16} and Ag_{17} were stabilized. MS of the crystal dissolved in acetonitrile also show signatures corresponding to Ag_{15} , Ag_{16} , and Ag_{17} similar to that obtained after 1 h of the reaction, however, with different intensities. It suggests that stable NCs are formed after 1 h of the reaction. We were able to identify as many as 21 intermediates in the entire path of the reaction, which undergo dissociation and rearrangement via a “growth mechanism” which leads to the formation of Ag_{16} and Ag_{17} NCs. These intermediates can be represented by a general formula, $[\text{Ag}_p(\text{TBT})_q(\text{TFA})_r(\text{CH}_3\text{CN})_s\text{Cl}]^+$, where $p = 6$ –15 and 30, $q = 2$ –9, $r = 1$ –6, $s = 0$ –5, and $t = 0$ –1 (Table S3). We, therefore, conclude that all of the silver thiolate intermediates formed during the reaction will size-focus to stable NCs, viz. $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_6(\text{CH}_3\text{CN})_3\text{Cl}]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$. Both the NCs have zero valence electron count. A flowchart of the reaction is shown in Scheme S1.

UV–vis absorption spectra of the reaction mixture were studied at different time intervals ($t = 2, 5, 15, 30, 60$ min and 7 days) after the addition of a methanolic solution of Ag_{18} into a solution of Ag_{12} , as shown in Figure 3B. The UV–vis measurements during time $t = 2$ –15 min show a broad absorption band with λ_{max} at 419 nm, followed by a shoulder at 483 nm. The absorption features of Ag_{12} and Ag_{18} NCs disappeared completely upon mixing them (Figure 3Ci, Di). This suggests the possibility that a reaction had taken place between Ag_{18} and Ag_{12} NCs. During $t = 30$ –60 min, a notable red shift was observed, and the absorption peaks were shifted to λ_{max} 438 and 611 nm (Figure 3B). The color of the reaction mixture changed from dark to light brown. After 1 week, the UV–vis absorption features of the crystal dissolved in acetonitrile were similar to that observed after 60 min of the

reaction (Figure 3Aiii). This implies that a stable composition had formed, and the reaction products did not transform subsequently.

Time-dependent density functional theory calculations were performed on the optimized structures of Ag_{16} and Ag_{17} NCs to understand their optical transitions (Figure S8). In the optimized structures, F, C, and H atoms were relaxed, and all other atoms were kept fixed. This setup was established using the hybrid Perdew, Burke, and Ernzerhof (PBE) model without any symmetry constraints. The following PAW setups, $\text{Ag}(4d^{10}5s^1)$, $\text{Cl}(3s^23p^5)$, $\text{S}(3s^23p^4)$, $\text{F}(2s^22p^5)$, $\text{O}(2s^22p^4)$, $\text{N}(2s^22p^3)$, $\text{C}(2s^22p^2)$, and $\text{H}(1s^1)$, were used including the scalar-relativistic effects for silver. The optical absorption spectra of optimized clusters having the simplified model ligand (CH_3) were calculated using linear response time-dependent density functional theory.⁴⁵ The oscillator strengths of both Ag_{16} and Ag_{17} NCs were added in a 2:1 ratio in order to obtain the absorption spectrum of the cocrystal. The absorption spectrum was plotted with a Gaussian broadening of 0.085 eV in the energy range of 400–900 nm, and it is compared with the experimental spectrum (red trace), as shown in Figure S9. The calculated spectrum displays the molecular transitions at 356 and 742 nm. The absorption peaks were observed at 439 and 611 nm in the experiment which are blue-shifted by 43 nm and red-shifted by 103 nm, respectively, from the calculated spectrum. This difference could be due to the reduced structure utilized for theoretical calculations.^{45,46} The molecular orbitals (MOs) involved for the transitions at 356 and 742 nm are shown in Figures S10 and S11, respectively. These transitions have mainly ligand to metal character. From the density of states (DOS) analysis, it is seen that significant difference in the spectra between Ag_{16} and Ag_{17} clusters lies only in the frontier orbitals (Figure 5). HOMO of the clusters is dominated by 2p and 3p atomic orbitals (AOs) of ligands, whereas LUMO is composed of 5s of Ag. The HOMO–LUMO gap is larger for Ag_{16} than for the Ag_{17} cluster and may be due to the presence of a central Ag atom, which significantly alters its electronic structure. Therefore, to understand the role of the central Ag atom in the Ag_{17} cluster, the partial DOS spectrum was separately plotted for the central Ag atom and of the Ag_{16} shell (Figure 6). From this, it is clearly noted that the AOs of the central Ag atom were extensively populated only in the frontier orbitals, and the rest of the MOs were dominated by the AOs of the Ag_{16} shell. However, the HOMO is comparably contributed by the 4d AOs of Ag_{16} shell

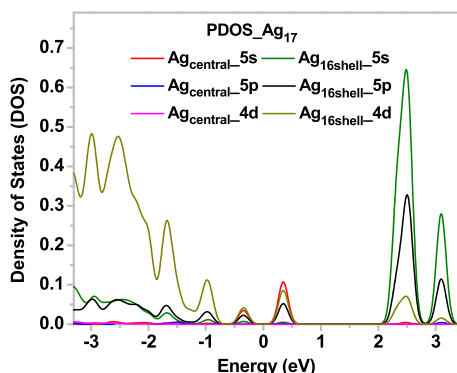


Figure 6. Partial DOS analysis of molecular orbitals of the model cluster, $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$.

and 5s AOs of the central Ag atom, whereas the near LUMOs are predominantly due to 5s AOs of the central Ag atom. Furthermore, the optical absorption transitions of both Ag_{17} and the cocrystal at a wavelength of ~ 742 nm might be significantly influenced by the high spherical symmetry of 5s AOs of the central Ag atom of Ag_{17} rather than the 4d AOs of the Ag_{16} shell. Therefore, the peaks at 742 and 356 nm are attributed to sp–sp intraband transition and pd–sp transition, respectively. Contributions of AOs to the MOs were analyzed using the Kohn–Sham MOs and DOS.

CONCLUSIONS

To summarize, we report an interparticle reaction between two atomically precise NCs $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$ and $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ abbreviated as Ag_{12} and Ag_{18} , respectively, resulting in products $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ which cocrystallize together. The reaction proceeds *via* a growth mechanism utilizing silver thiolate intermediates. Both the NCs have an identical Ag_{16}S_8 shell, arranged in a layered fashion of Ag_4S_4 – Ag_8 – Ag_4S_4 , forming a sandwich. This makes the NCs indistinguishable, and they cocrystallize. In a single crystal, the occupancies of Ag_{16} and Ag_{17} NCs are 66.66 and 33.33%, respectively. MS of the reaction product shows the population of Ag_{16} and Ag_{17} to be almost equal, whereas that of a crystal dissolved in acetonitrile shows a 2:1 ratio of their intensities. This may possibly suggest that the concentrations of Ag_{16} and Ag_{17} are almost equal in the product, but selective incorporation occurs in the crystal. For further validation, MS of the supernatant after crystallization was measured which showed peaks corresponding to Ag_{16} and Ag_{17} NCs, but with an excess of the latter. These findings support that the single crystal stabilizes with 2:1 ratio of Ag_{16} and Ag_{17} NCs, despite the presence of extra Ag_{17} species in the supernatant. Our results allowed us to write a balanced chemical equation for the reaction. We believe that our results will initiate more activities in the area of atomically precise clusters.

EXPERIMENTAL SECTION

Chemicals and Materials. *tert*-Butylthiol (TBT), silver trifluoroacetate (CF_3COOAg), triphenylphosphine (TPP), and sodium borohydride (NaBH_4 , 98%) were purchased from Aldrich. Silver nitrate (AgNO_3) was purchased from Rankem Chemicals. All chemicals were used as received without further purification. All of the solvents, such as dichloromethane (DCM), methanol (MeOH), acetonitrile (CH_3CN), and chloroform (CHCl_3), were purchased

from Rankem Chemicals and were of analytical grade. Milli-Q water was used for the synthesis.

Synthesis of a Mixture of $[\text{Ag}_{16}(\text{TBT})_8(\text{CF}_3\text{COO})_7(\text{CH}_3\text{CN})_2\text{Cl}]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{CF}_3\text{COO})_7(\text{CH}_3\text{CN})_2\text{Cl}]^+$. Synthesis of $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$: 200 mg of silver thiolate, $\text{Ag}(\text{TBT})_m$, was added to a solution of acetonitrile and methanol (3 mL each). To this was added 200 mg of CF_3COOAg upon stirring, and after some time, a clear transparent solution appeared, which resulted in the formation of $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$ denoted as Ag_{12} . About 1 mL of methanolic solution of $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ denoted as Ag_{18} (~ 5 mg/mL) was added to the above reaction mixture. Ag_{18} was synthesized by a reported procedure (see the [Supporting Information](#) for a detailed synthesis).^{41,42} A dark brown solution along with a black precipitate was formed; the mixture was kept stirring for 1 h, and the solution was centrifuged at 8000 rpm (5868g). The black precipitate was discarded. The solution obtained after centrifugation was left for slow evaporation at 5 ± 5 °C for crystallization, and after 1 week, light brown crystals were obtained. Crystals were soluble in acetonitrile, methanol, ethanol, and DCM. Yield of the synthesis was 25% in terms of silver.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b06740.

Experimental section, instrumentation, X-ray crystallographic parameters, additional experimental data (PDF)
X-ray data for compound 1 (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Department of Science and Technology (DST) for supporting our research program. We thank the Sophisticated Analytical Instruments Facility, Indian Institute of Technology Madras for SCXRD data collection. W.A.D. thanks SERB-DST for the award of a National Postdoctoral Fellowship (NPDF). M.B. and K.S.S. thank U.G.C. for their research fellowships. G.P. thanks IITM for an Institute Postdoctoral Fellowship. D.G. and E.K. thank IIT Madras for Institute Doctoral Fellowships.

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