

Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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CONSPECTUS: Supramolecular chemistry is a major area of chemistry that utilizes weaker non-covalent interactions between molecules, including hydrogen bonding, van der Waals, electrostatic, $\pi \cdots \pi$, and C-H $\cdots \pi$ interactions. Such forces have been the basis of several molecular self-assemblies and host-guest complexes in organic, inorganic, and biological systems. Atomically precise nanoclusters (NCs) are materials of growing interest that display interesting structure-property correlations. The evolving science of such systems reaffirms their molecular behavior. This gives a possibility of exploring their supramolecular chemistry, leading to assemblies with similar or dissimilar cluster molecules. Such assemblies with compositional, structural, and conformational precision may ultimately result in cluster-assembled hybrid materials. In this Account, we present recent advancements on different possibilities of supramolecular interactions in atomically precise cluster systems that can occur at different length scales. We first present a brief discussion of the aspicule model of clusters, considering $Au_{25}(SR)_{18}$ as an example, that can explain various aspects of its atomic precision and distinguish the similar or dissimilar interacting sites in their structures. The supramolecular interaction of 4-tert-butylbenzyl mercaptan (BBSH)-protected [Au₂₅(SBB)₁₈]⁻ NCs with cyclodextrins (CD) to form $Au_{25}SBB_{18}\cap CD_n$ (n = 1-4) and that of $[Ag_{29}(BDT)_{12}]^{3-}$ with fullerenes to form $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n = 1-9) (BDT = 1,3-benzenedithiolate) are discussed subsequently. The formation of these adducts was studied by electrospray ionization mass spectrometry (ESI MS), optical absorption and NMR spectroscopy. In the subsequent sections, we discuss how variation in intercluster interactions can lead to polymorphic crystals, which are observable in single-crystal X-ray diffraction. Taking $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ (TPP = triphenylphosphine) clusters as an example, we discuss how the different patterns of $C-H\cdots\pi$ and $\pi\cdots\pi$ interactions between the secondary ligands can alter the packing of the NCs into cubic and trigonal lattices. Finally, we discuss how the supramolecular interactions of atomically precise clusters can result in their hybrid assemblies with plasmonic nanostructures. The interaction of p-mercaptobenzoic acid (p-MBA)-protected Ag₄₄(p-MBA)₃₀ NCs with tellurium nanowires (Te NWs) can form crossed-bilayer precision assemblies with a woven-fabric-like structure with an angle of 81° between the layers. Similar crossed-bilayer assemblies show an angle of 77° when Au₁₀₂(p-MBA)₄₄ clusters are used to form the structure. Such assemblies were studied by transmission electron microscopy (TEM). Precision in these hybrid assemblies of Te NWs was highly controlled by the geometry of the ligands on the NC surface. Moreover, we also present how $Ag_{44}(p-MBA)_{30}$ clusters can encapsulate gold nanorods to form cage-like nanostructures. Such studies involved TEM, scanning transmission electron microscopy (STEM), and three-dimensional tomographic reconstructions of the nanostructures. The hydrogen bonding interactions of the -COOH groups of the p-MBA ligands were the major driving force in both of these cases. An important aspect that is central to the advancement of the area is the close interplay of molecular tools such as MS with structural tools such as TEM along with detailed computational modeling. We finally conclude this Account with a future perspective on the supramolecular chemistry of clusters. Advancements in this field will help in developing new materials with potential optical, electrical, and mechanical properties.

INTRODUCTION

Atomically precise nanoclusters (NCs) present rich diversity in their structures and properties.^{1,2} A large variety of clusters made of noble metals like Au, Ag, etc. and protected by ligands^{3,4} such as thiols and phosphines are known in the literature, and many of their structures have been determined from single-crystal studies. Precise composition, precision in molecular structure,

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Figure 1. Representation of the $Au_{25}(SMe)_{18}$ cluster in the Borromean ring model. Three ellipses encompassing six $Au_2(SR)_3$ staples are represented as nearly coplanar rings. These staples are labeled as D1 to D6. The rings include core Au atoms (numbered 1 to 12). The atoms in the staples are numbered 1 to 5 in the clockwise direction. Inset (i) shows these aspicule rings in the standard structure of $Au_{25}(SMe)_{18}$. The three rings are shown in red, green, and blue, while the Au atoms in the icosahedron are shown in gold. Inset (ii) shows an expanded view of the icosahedral core, where the icosahedral central atom alone is shown in gold. A cluster composed of Au (green, orange, and gray) and S (yellow) atoms is shown in inset (iii), and a photograph of a Borromean ring structure is shown in inset (iv). The ring structure enables the cluster to be disassembled completely just by detaching one bond; a break in one ring separates the other two. Reproduced from ref 12. Copyright 2015 American Chemical Society.

electronic energy levels, optical absorption and emission, chemical reactivity,^{5,6} catalysis,³ and an expanding body of emerging properties increasingly reaffirm the molecular nature of such systems. This expanding science makes one wonder about the distinct possibilities of supramolecular chemistry of such molecules. While supramolecular interactions play important roles in cluster crystallization, phase transfer, reaction chemistry, etc., these interactions can also be important for the synthesis of new cluster compounds, e.g., in the formation of cluster assemblies. Recently, Jin and co-workers reported that protecting ligands on clusters can organize in specific patterns that may direct their assembly, which can match the level of atomic precision in biomolecules.⁷ The forces guiding the organization of the NCs may vary from weak intermolecular forces like C–H··· π , π ··· π , van der Waals, hydrogen bonding, and electrostatic interactions to strong covalent bonding. While molecular interactions between clusters result in their crystallization, interactions with heteromolecules as well as those between clusters forming homomolecular adducts such as dimers,⁸ trimers,⁸ and polymers⁹ can create specific building blocks. Clusters, which have nanometric dimensions, can interact with other systems to form supramolecular architectures of larger dimensions. Such assemblies could also occur in organized biological systems such as viruses and bacteria, leading to bio-nano conjugates or synthetic superstructures of unprecedented diversity.^{10,11} This Account briefly illustrates this emerging body of science and projects its growth to suggest future possibilities.

The precision in structures is captured elegantly in the aspicule nomenclature,¹² wherein the cluster is composed of a core and distinct staples having precise labels. The overall structure of $Au_{25}(SMe)_{18}$ can be drawn precisely, leading to the name 18(methylthiolato)-auro-25 aspicule(1–) to represent the molecule, as shown in Figure 1. This molecular structure presents symmetry-equivalent sites where interactions are similar or dissimilar. It also indicates the limits or limitations of molecular access and presents the possibilities of interactions

at distinct sites leading to structural transformation, particularly ligand exchange,¹³ exchange of core atoms, creation of alloys,^{5,14} and supramolecular functionalization.¹⁵ Intercluster interactions between similar or different clusters as well as those with nanoparticles may also be visualized. In this Account, we discuss the different possibilities of supramolecular interactions in the atomically precise clusters and classify them into the following specific categories:

- (A) single cluster interactions (with small molecules)
- (B) intercluster interactions
- (C) cluster-nanoparticle assembly and supersystems

In each of these, the essential interaction is intermolecular in nature, but they occur at different length scales. Consequently, they are explored with different tools. In the first case, single cluster interactions, supramolecular interactions of the clusters with molecules like cyclodextrins (CDs) and fullerenes are studied principally using mass spectrometry (MS). Such results are supplemented by complementary studies using optical and NMR spectroscopy. In the second case, supramolecular interactions lead to intercluster organizations, which are observed by single-crystal diffraction. In the third case, interactions occur on substrates or at surfaces of much larger (bulk-like) phases, so the integrated systems are currently above the limit of regular MS. Here the formation of assemblies around nanostructures such as nanowires and nanorods mediated by supramolecular interactions with NCs is discussed.¹⁶ Such systems are examined with microscopy. All of these systems are examined with computational methods with varying degrees of sophistication. Each of these subclasses is separately presented below, and Scheme 1 presents a schematic of the possible types of supramolecular interactions in the atomically precise clusters, as discussed above. While the interactions and structures derived are atomically precise in detail, a thorough understanding of structural and conformational precision has been possible only for A and B. We hope that more definitive understanding of all three types will be available in the years ahead.

Scheme 1. Schematic Capturing Some of the Supramolecular Interactions Possible in Atomically Precise Clusters^a



"New directions shown at the periphery are not captured in this Account. The size of each component is not to scale.



Figure 2. (A) Negative ion ESI MS spectra for the $Au_{25}SBB_{18}$ cluster and its CD adducts. Spectra a, b, and c are at SBB/CD molar ratios of 1:1.2, 1:1, and 1:0, respectively. Part of a spectrum is expanded in (b). (B) Schematic representations of $Au_{25}SBB_{18}\cap CD_n$ (n = 1-4). (C) Computed structure of $Au_{25}SBB_{18}\cap CD_4$ with nearly tetrahedral binding of the four CDs (shown in cyan). H atoms of the SBB ligands have been omitted for clarity. (D) Aspicule representation of $Au_{25}SBB_{18}\cap CD_4$. (E, F) BBSH \cap CD inclusion complexes where the *tert*-butyl group of BBSH undergoes complexation through the (E) narrower and (F) wider rims of β -CD. In (E) and (F), all of the atoms of BBSH are colored cyan for clarity, whereas atoms of CD are colored differently. Reproduced from ref 15. Copyright 2014 American Chemical Society.

A. SINGLE CLUSTER INTERACTIONS

Supramolecular Interactions of NCs with CDs

The interactions of a cluster with other molecules may be tuned to precisely functionalize the surface of the NCs. We used the 4tert-butylbenzyl mercaptan (BBSH)-protected [Au₂₅(SBB)₁₈]⁻ cluster¹⁵ and studied its supramolecular functionalization with β -CD. CDs are water-soluble cyclic oligosaccharides having hydrophobic cavities that form inclusion complexes with specific molecules.¹⁷ Several host-guest complexes of β -CDs with inorganic complexes containing thiol groups like BBSH have been reported in the literature.¹⁸ We utilized such a molecular recognition process to synthesize $Au_{25}SBB_{18}\cap CD_n$ (n = 1-4), where $X \cap Y$ denotes an inclusion complex between the substrate X and receptor Y.¹⁵ The CD-encapsulated clusters were synthesized from a mixture of the cluster and β -CD in THF/ water medium by constant stirring followed by intermittent sonication, and they were characterized using different techniques such as UV-vis, fluorescence, and NMR spectroscopy. The formation of Au₂₅SBB₁₈ \cap CD_n (n = 1-4) was observed in electrospray ionization mass spectrometry (ESI MS) (Figure 2A). Schematic structures of $Au_{25}SBB_{18}\cap CD_n$ (n =1-4) are presented in Figure 2B. Although a mixture of adducts (n = 1-4) existed in solution, the amount of Au₂₅SBB₁₈ \cap CD₄ was increased by careful control of the SBB/CD molar ratio at 1:1.2. The nature of the interaction was explained using computational studies. In the structure of Au₂₅SBB₁₈, surrounding the icosahedral core there are six $Au_2(SR)_3$ staples, corresponding to the six staples D1 to D6 in the aspicule model (Figure 1). In each staple, there are two nonbridging S (positions 1 and 5) joining a core Au to a staple Au and one bridging S (position 3) joining only two exterior Au atoms. The ligands anchored at positions 1 and 5, being less crowded, remain more accessible for encapsulation with CDs. This appears to be counterintuitive, as position 3 appears to be less crowded in the aspicule picture. However, Figure 1(iv) suggests that positions 1 and 5 are indeed accessible. NMR data also revealed the interactions between aromatic protons of SBB and H^3 and H^5 (inner protons) of CD. The theoretical structure of $Au_{25}SBB_{18}\cap CD_4$ (Figure 2C) shows four CDs bound at tetrahedral locations, minimizing the inter-CD interactions. A representation in the aspicule model is shown in Figure 2D. Complexation through the narrower rim of CD facing the cluster core was more favorable than complexation through the wider rim (Figure 2E,F).

The formation of these inclusion complexes was specific to the precise orientation of the SBB ligands, which pointed outward from the core. In the case of $Au_{25}(PET)_{18}$ (PET = 2phenylethyl thiolate),^{19,20} which presents a different orientation of the PET ligands, no CD inclusion was observed. CD encapsulation resulted in an enhancement in the luminescence of the cluster and shielded the metal core from incoming ions or ligands and consequently increased its stability. Inclusion complexes of other thiols such as adamantanethiol (SAdm) with CD are also well-known.^{21–23} Yan et al.²⁴ showed the surface functionalization of $Au_{38}S_2(SAdm)_{20}$ NCs with α -, β -, and γ -CD. This unfolds the possibility of functionalizing other Adm-protected clusters like $Au_{30}(SAdm)_{18}$,²⁵ Pt₁Ag₂₈-(SAdm)₁₈(PPh₃)₄,²⁶ Au₂₄(SAdm)₁₆,²⁷ etc. with CDs in a similar fashion. In a recent report, Au NC-grafted CD superstructures were used to develop fluorescence on–off composites.²⁸ Xie and co-workers used a CD–AuNC–TiO₂ hybrid system to enhance photocatalytic decomposition of organic pollutants.²⁹

Supramolecular Interactions of NCs with Fullerenes

Fullerenes are another important class of molecules for exploration of the supramolecular chemistry of clusters. Fullerenes show electron-accepting properties and form a wide range of supramolecular self-assembled structures.³⁰ We observed the formation of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ $(n = 1-9)^{31}$ (BDT = 1,3-benzenedithiolate) adducts in solution through the interaction of $[Ag_{29}(BDT)_{12}]^{3-}$ NCs³² with C₆₀. Twelve Ag atoms cover the icosahedral core, forming four trigonal prisms. The Ag₁₃ core is further covered by four Ag atoms at tetrahedral positions.³² Addition of C₆₀ to the cluster at a cluster:C₆₀ molar ratio of 1:4 resulted in the formation of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n = 1-4) adducts, which were observed by ESI MS (Figure 3). The BDT ligands are arranged



Figure 3. ESI MS spectra of (A) $[Ag_{29}(BDT)_{12}]^{3-}$ and (B) $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n = 1-4). Experimental and theoretical isotopic distributions of the peaks are compared in the insets. Reproduced from ref 31. Copyright 2018 American Chemical Society.

in such a way that they form a cavity, encapsulating the curved surface of fullerenes (Figure 4A,B). This structural compatibility facilitated the supramolecular host-guest complexation. Detailed insights into the structures of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n = 1-4) were obtained from computational studies. In the structure of $[Ag_{29}(BDT)_{12}(C_{60})]^{3-}$ (Figure 4A), C₆₀ has weak binding interactions with the vertex Ag atom at a distance of about 3.40–3.53 Å and stabilizes the unpassivated Ag atom by η^2 interactions. The adduct $[Ag_{29}(BDT)_{12}(C_{60})_4]^{3-}$ (Figure 4C) retains a tetrahedral symmetry in its structure with four C₆₀ molecules bound at four vertex sites. The primary interactions are $\pi \cdots \pi$ and van der Waals interactions between the π surface of the fullerene and the aromatic rings of BDT. In the crystal structure of the NC, triphenylphosphine (TPP) ligands are bound at the vertex Ag sites.³² When TPP was added to $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (*n* = 1-4), TPP replaced C₆₀, forming $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ (*n* = 1-4), which reaffirmed the binding sites of the fullerenes to the cluster. Addition of excess C_{60} resulted in an even higher number of C_{60} additions to the cluster (n > 4). Additional C₆₀ may bind over the four trigonal faces formed by the Ag₃S₃ motifs. The likely structure of $[Ag_{29}(BDT)_{12}(C_{60})_8]^{3-}$ (Figure 4D) shows fullerenes bound at all of the face and vertex positions of the cluster with a slightly distorted cube-like overall geometry. Additional fullerene-



Figure 4. (A) Results of DFT calculations on the minimum-energy geometry of $[Ag_{29}(BDT)_{12}(C_{60})]^{3-}$. Interaction distances (in Å) are marked in the figure. (B) Interactions between the fullerene and the ligands are shown in an expanded view. (C–E) Lowest-energy structures of (C) $[Ag_{29}(BDT)_{12}(C_{60})_4]^{3-}$, (D) $[Ag_{29}(BDT)_{12}(C_{60})_8]^{3-}$, and (E) $[Ag_{29}(BDT)_{12}(C_{60})_9]^{3-}$. Color code: yellow, S; gray, Ag of the icosahedral core; red, tetrahedral sites of four Ag atoms; blue, $Ag_{3}S_3$ staple motifs composed of 12 Ag atoms making four trigonal planes; green, BDT ligands; black, C_{60} at vertex positions; cyan, C_{60} at face positions; purple, an additional fullerene located between the face and vertex positions. Reproduced from ref 31. Copyright 2018 American Chemical Society.

fullerene interactions may also favor further attachment of C_{60} (Figure 4E) such that the latter may form a sphere covering the entire cluster surface. Similar results were observed with C_{70} , which exhibited stronger $\pi \cdots \pi$ interactions and closer contacts with the aromatic ligands of the cluster. The importance of intermolecular interactions in the formation of intercluster compounds of fullerides with gold NCs, $[Au_7(PPh_3)_7]C_{60}$.THF and $[Au_8(PPh_3)_8](C_{60})_2$, was also demonstrated by Schulz-Dobrick et al.³³ The interactions of a cluster may also be utilized to form atomically precise supramolecular assemblies with other molecules such as catenanes, calixarenes, rotaxanes, porphyrins, etc.

B. INTERCLUSTER INTERACTIONS

Supramolecular interactions also play a crucial role in arranging the NCs in their crystal lattice. In the crystal lattice of *p*mercaptobenzoic acid (*p*-MBA)-protected Ag₄₄(*p*-MBA)₃₀ NCs, the –COOH groups of the *p*-MBA ligands show strong hydrogen bonding between the neighboring NCs.³⁴ Similar non-covalent interactions have also been observed in the crystal lattices of Au₁₀₂,³⁵ Au₂₄₆,⁷ Au₁₀₃,³⁶ etc. Interesting packing patterns such as the 4H phase array of Au₉₂(TBBT)₄₄ NCs³⁷ and the 6H left-handed helical arrangement of Au₆₀S₆(SCH₂Ph)₃₆ NCs³⁸ in their crystal lattices were also observed. Considering $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ NCs³² as an example, we demonstrated how the intercluster interactions may be tuned to create polymorphic crystals. In the structure reported by Bakr and coworkers,³² evaporation of DMF formed orange crystals in a cubic (C) lattice with space group $Pa\overline{3}$ (Figure 5A). In our vapor diffusion method (MeOH diffusing into DMF solution of the NCs), dark-red crystals in a trigonal (T) lattice with space group $R\overline{3}$ were formed (Figure 5D).³⁹ The difference in packing of the two polymorphic forms is largely due to the difference in the supramolecular interactions of the BDT and TPP ligands. These interactions for the T and C systems may be classified into two categories:

(i) In a single NC, the C–H groups of the TPP subunits interact with the π system of the aromatic rings of BDT in an intracluster fashion. Moreover, the C–H groups of BDT and the aromatic rings of TPP also interact strongly through intercluster C–H… π interactions in both the C



Figure 5. (A) Cubic unit cell of $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$ NCs. (B) Packing of the TPP subunits viewed from the Z axis in the C system. (C) Strong C-H… π interactions (T-shaped) between the eight TPP subunits forming a hexagonal shape in the C system. (D) Trigonal unit cell of the NCs. (E) C-H… π interactions between the TPP subunits in the T system. (F) Emission spectra obtained from single crystals of the C and T lattices. The C structure exhibits stronger and slightly red-shifted (~30 nm) luminescence compared with the T structure. Reproduced with permission from ref 39. Copyright 2018 Royal Society of Chemistry.

and the T systems at distances of \sim 3.07–3.39 and 2.92 Å, respectively.

(ii) In the C lattice, the C–H… π interactions within the TPP subunits are stronger, forming polymeric chains (Figure 5B) to directly or indirectly connect every NC with others. These distances are comparable to the C–H… π distances of 2.88 ± 0.42 Å seen in Au₂₄₆ NCs protected by –SPh-*p*-CH₃ ligands⁷ but slightly longer than the interaction distances of 2.76 ± 0.05 Å in Au₁₀₃ NCs protected by –S-Nap.³⁶ The interaction distances for the TPP subunits are larger in the T system (Figure 5E) compared with the C system, and hence, these interactions are discontinuous and do not form polymeric chains.

It is evident from the crystal packing of the two polymorphs of the clusters that the intercluster interactions of TPP ligands are more favored in C than in T. The C lattice, being more rigid, exhibits a higher luminescence efficiency than the T NCs with a slight red shift (30 nm) (Figure 5F). This also reveals how the luminescence efficiencies of the NCs in the solid state are controlled by interactions of their secondary ligands.

C. CLUSTER-NANOPARTICLE ASSEMBLY AND SUPERSYSTEMS

Cluster-Mediated Precision Assemblies of Nanowires

The interactions of NCs are very different from those of nanoparticles or ionic salts of metals.⁴⁰ Small thiol-protected clusters like $Ag_{32}(SG)_{19}^{41}$ tend to coalesce on the surface of one-dimensional (1D) nanomaterials like tellurium nanowires (Te NWs). This finally leads to the decoration of the NWs with Ag nodules, whereas the interactions of Ag(I) ions and Ag NPs lead

to the formation of Ag_2 Te NWs.⁴⁰ Inspired by this result, in a particular study we modified the surface of Te NWs with $Ag_{44}(p-1)$ MBA)₃₀⁴² (abbreviated as Ag₄₄). Next, the Ag₄₄@Te NWs were dispersed in 1-butanol, which was then spread over water, followed by solvent evaporation.¹⁶ The pristine Te NWs formed the usual monolayer assembly when subjected to this process, whereas Ag₄₄@Te NWs led to a crossed-bilayer structure. Upon detailed TEM investigation, the pattern was found to be a woven-fabric-like structure in which NWs in the same layer were parallel but adjacent layers were arranged at an unusual angle of 81° (Figure 6C). To explain the origin of the unusual assembly, we modeled the hydrogen bonding between neighboring Ag₄₄ units in the cluster superlattice. The p-MBA ligands on individual Ag44 clusters are present in the form of bundles of two (L_2) or three (L_3) units (Figure 6D). Either two L_2 pairs or two L₃ pairs are known to form hydrogen bonds in the Ag₄₄ crystal. In Ag₄₄@Te NWs, the clusters attach themselves on the surfaces of the Te NWs via the $-COO^{-}$ groups of some of their p-MBA ligands (Figure 6A). Upon solvent evaporation, the Ag₄₄@Te NWs come closer, and hydrogen bonding may occur between free *p*-MBA ligands, which are not bound on the NWs, of two neighboring Ag44 clusters attached to adjacent NWs. Computational modeling further explained that the greatest number of hydrogen bonds was possible when the two layers were arranged at an angle of 81°, thereby giving the most stable and most symmetrical structure (Figure 6E). When Au₁₀₂(p- $MBA)_{44}^{35}$ was used instead of $Ag_{44}(p-MBA)_{30}$, a similar crossedbilayer structure was observed with an angle of 77° between the two layers, which is due to the difference in the geometrical arrangement of the ligands of the two clusters. Thus, precise angular control between highly ordered Te NW assemblies could be achieved by using atomically precise NCs.



Figure 6. (A) Schematic of the bonding of $Ag_{44}(p-MBA)_{30}$ clusters to Te NWs. (B) Structure of $Ag_{44}(p-MBA)_{30}$ modeled from its crystal structure. (C) TEM image of the crossed bilayer assembly of $Ag_{44}(p$ Te NWs. A schematic showing the crossed-bilayer structure of the assembly is presented in the inset. (D) Hydrogen bonding between the –COOH groups of the *p*-MBA ligands of neighboring NCs in the $Ag_{44}(p-MBA)_{30}$ superlattice. The neighboring clusters interact via hydrogen bonding with L_2 (inset a) and L_3 (inset b) types of ligands. (E) (a) Schematic of the crossed bilayer assembly. (b) Expanded view of the region modeled in (a). Further details are shown in (c). Clusters assembled on the surfaces of the Te NWs, which were kept at a distance of 3.4 nm, in three different planes, labeled as C_1 , C_2 , and C_3 . Reproduced with permission from refs 16 and 45. Copyright 2016 and 2018 Wiley.

Nanoparticle-Templated Cluster Supersystems

Once the clusters were known to interact with anisotropic nanoparticles leading to structures of interesting morphology, we expanded the study using similar nanomaterials. Gold nanorods (GNRs) have been at the center of interest for decades because of their unique surface plasmonic properties. Recent studies have revealed that because of their nanometric dimensions, GNRs can accommodate quantum dots on their surfaces and significantly alter the optoelectronic properties of the quantum dots by plasmon-exciton coupling in these systems.⁴³ Using *p*-MBA-protected gold NCs, Nonappa and coworkers demonstrated the formation of monolayer-thick 2D nanosheets and spherical capsids by tuning the supramolecular interactions such as intercluster hydrogen bonding.44,45 We placed atomically precise clusters on GNRs to explore the possibility of supramolecular-chemistry-driven hybrid nanostructures.⁴⁶ Specifically, GNRs were functionalized with p-MBA at neutral pH. These GNRs were then incubated with $Ag_{44}(p-MBA)_{30}$ in DMF for 20 h, during which the p-MBA groups of the clusters formed hydrogen bonds within themselves as well as with the *p*-MBA groups on the GNR surface (scheme in Figure 7A). This created a multilayer shell encapsulating the individual GNRs within a cage-like nanostructure. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and 3D tomographic reconstructions of these nanostructures revealed that the final morphology of the hybrid material is octahedral (Figure 7C-E), possibly because of the preferable anchoring of the clusters on the four alternative $\langle 110 \rangle$ facets over the $\langle 100 \rangle$ facets on the octagonal GNR

surfaces. Interestingly, the intrinsic properties of the constituent materials, namely, the GNR and Ag44, were retained in the final nanostructure which shows remarkable ambient stability. Next, we reacted the p-MBA-functionalized GNRs with waterdispersible $\operatorname{Au}_{102}(p-\text{MBA})_{44}^{35}$ and $\operatorname{Au}_{250}(p-\text{MBA})_n^{47}$ in a similar fashion to check the generic nature of the scheme in terms of the NCs and the solvents used. Here also we observed encapsulation of the GNRs by the NCs, although in these cases the cluster moieties were less closely packed (Figure 7F). This was attributed to the fact that in the water-soluble state, some of the *p*-MBA ligands of the gold clusters had to be deprotonated, making fewer ligands available for hydrogen bonding and thus making the final structures less compact. We expect that with the rightly chosen NC, this hybrid system can significantly improve the stability and detection limit of cluster-based sensing devices by plasmon-assisted enhancement of cluster properties.

FUTURE PERSPECTIVES

In this Account, we have presented a glimpse into the various supramolecular interactions possible in atomically precise clusters. While supramolecular functionalization of the NCs with molecules like CD and C_{60} highlights the precision in their structures to selectively favor the formation of the host–guest complexes, exploring such composite structures in the solid state would lead to new materials. Although we have observed a mixture of adducts in solution, better control of the polydispersity of the supramolecular adducts to accomplish atomic precision and consequent crystallization are challenging areas. Furthermore, the site of attachment and binding modes of



Figure 7. (A) Assembly of Ag_{44} NCs on the GNR@*p*-MBA surface. The ESI MS spectrum of Ag_{44} is shown as the inset. (b) TEM image of GNR@*p*-MBA. HRTEM image of the tip of a GNR is shown in the inset. (C) TEM image of GNR@ Ag_{44} . A dark-field STEM image is shown in the inset. (D, E) TEM tomographic and dark-field STEM images of GNR@ Ag_{44} . The image shows that the clusters make a nanocage and encapsulate the GNR. A theoretical model of the assembly of Ag_{44} clusters forming an octahedral shape is presented in the inset. (F) TEM image of GNR@ Au_{250} . (G, H) 3D reconstructed structures and 3D graphical representation of GNR@ Au_{250} , respectively. Reproduced with permission from ref 46. Copyright 2018 Wiley-VCH.

CD and C₆₀ to the clusters may vary, which may lead to isomerism in the resulting structures. Such isomerism could extend to novel optical properties as well. With an appropriate choice of the host and guest molecules, chirality may also be introduced in supramolecular assemblies of certain clusters. Functionalized fullerenes or CDs may also be used to modify cluster binding. The development of functional cluster-based materials may also include modifying the ligand shell of the cluster with suitable bidentate or multidentate linkers, allowing the creation of cluster-assembled metal-organic frameworks. The observation of polymorphic crystal lattices of NCs also enfolds a new area in nanoparticle engineering. Supramolecular interactions may also favor crystallization of dimers or oligomers of clusters. Furthermore, the self-organization of nanostructures with macrostructures leading to architectures of larger dimensions constitutes new types of precision hybrids with diverse possibilities. These derived materials, especially lowdimensional building blocks, may lead to anisotropic solids with unprecedented properties. The self-assembly of NCs leading to spherical capsids^{44,45} is a direction toward larger assemblies similar to biological systems. Cluster-assembled hybrid materials may result in a new paradigm of conductive or magnetic luminescent materials.

The choice of supramolecular building blocks presented here has been dominated by the consideration of interactions. However, such building blocks can also be chosen on the basis of new properties such as magnetism, chirality, energy transfer, etc. that they provide. A unique aspect of clusters is that their size is comparable to the dimensions of biomolecules, which are also building blocks with atomic precision. Thus, structures incorporating biomolecules or synthetic polymers along with clusters is another strategy to create functional materials. In comparison with supramolecular assemblies solely composed of biomolecules, cluster-based assemblies can introduce new optical, magnetic, or electrical properties.

A closer analysis of this area shows that the molecule– materials interface is enriched by MS in its diverse forms. Compositional precision revealed by MS, in conjunction with structural and conformational precision revealed by diffraction and spectroscopy, coupled with computational studies enabling better insights into the properties, are essential components of this area. Several of the finer details of these materials such as the atomistic steps involved in the formation of these assemblies and their time scales are not accessible presently by experimental methods, and therefore, computations become the only credible methodology for exploration. This MS–diffraction–theory combination in the context of novel properties of atomically precise matter is expected to expand into even more larger systems in the years ahead, which should result in a fuller appreciation of materials with atomic precision.

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