

Cluster-Assembled Materials

Shelley A. Claridge,^{†,‡} A. W. Castleman, Jr.,^{†,‡,*} Shiv N. Khanna,^{§,*} Christopher B. Murray,^{||,*} Ayusman Sen,^{†,*} and Paul S. Weiss^{†,‡,*}

[†]Department of Chemistry and [‡]Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802-6300, [§]Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284-2000, and ^{||}Departments of Chemistry and Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

ABSTRACT Cluster-assembled materials offer the ability to tune component properties, lattice parameters, and thus coupling of physical properties through the careful selection and assembly of building blocks. Multi-atom clusters have been found to exhibit physical properties beyond those available from the standard elements in the periodic table; classification of the properties of such clusters effectively enables expansion of the periodic table to a third dimension. Using clusters as superatomic building blocks for hierarchically assembled materials allows these properties to be incorporated into designer materials with tailored properties. Cluster-assembled materials are currently being explored and methods developed to control their design and function. Here, we discuss examples of building block syntheses, assembly strategies, and property control achieved to date.

KEYWORDS: cluster-assembled materials · artificial atoms · nanoparticles · superatoms · clusters · hierarchical assembly · fullerenes · nanocrystals · superlattices · self-assembly

Cluster-assembled materials offer the attractive proposition of creating materials with tailored properties using building blocks outside the normal range of atomic elements.^{1–3} However, building such materials presents its own set of challenges, related to making and characterizing a new array of superatomic building blocks and understanding the rules that govern their assembly and their assembled material properties. The building blocks used in cluster-assembled materials to date range from fullerenes and clusters with precisely controlled numbers of atoms to much larger, nearly monodisperse nanoparticles (Figure 1). In examining smaller building blocks, such as fullerenes and clusters of precise composition and size, properties can be treated theoretically and tested directly by experiment. With larger nanoparticles, shapes, surface interactions, and relative sizes of components can already be used to control lattice symmetries and spacings with remarkable diversity.

In this review, we discuss key aspects of the development and understanding of clusters as superatomic building blocks, as

well as recent findings relating to the control of cluster-assembled materials' geometries and physical properties. Examining cluster synthesis and assembly across diverse cluster sizes from 1 to more than 10 nm provides a wealth of material choices. We focus primarily on three classes of building blocks: fullerenes, small atomically precise inorganic clusters with diameters on the order of 1–2 nm (up to tens of atoms), and larger, nearly monodisperse inorganic nanocrystals with diameters up to tens of nanometers (thousands of atoms). In the context of assembly, we highlight examples of geometric control over superatom molecules and materials, particularly cases in which theory can be used as a predictive basis for guiding experiment. Examples of collective physical properties are given for materials assembled from superatomic building blocks at each length scale; such examples are largely drawn from the literature on electronic materials, which depend critically on cluster spacing and geometry to control electronic coupling. In each area, we anticipate dramatic expansion of the libraries of available building blocks and thus the properties accessible through cluster-assembled materials.

Fullerene-Based Materials. Fullerenes have a number of virtues that have made them excellent building blocks for nanostructured materials.⁴ The canonical fullerene, C₆₀, has a discrete and highly symmetric structure comprising 60 carbon atoms arranged with icosahedral symmetry and with a bonding structure similar to that of graphene.⁴ Although the nearly spherical cage structure creates a substantial amount of s-character in the carbon–carbon bonds relative to planar graphene,⁵ the structure has no dangling bonds, in contrast with inorganic clus-

*Address correspondence to awc@psu.edu (A.W.C.), snkhanna@vcu.edu (S.N.K.), cbmurray@sas.upenn.edu (C.B.M.), asen@chem.psu.edu (A.S.), stm@psu.edu (P.S.W.).

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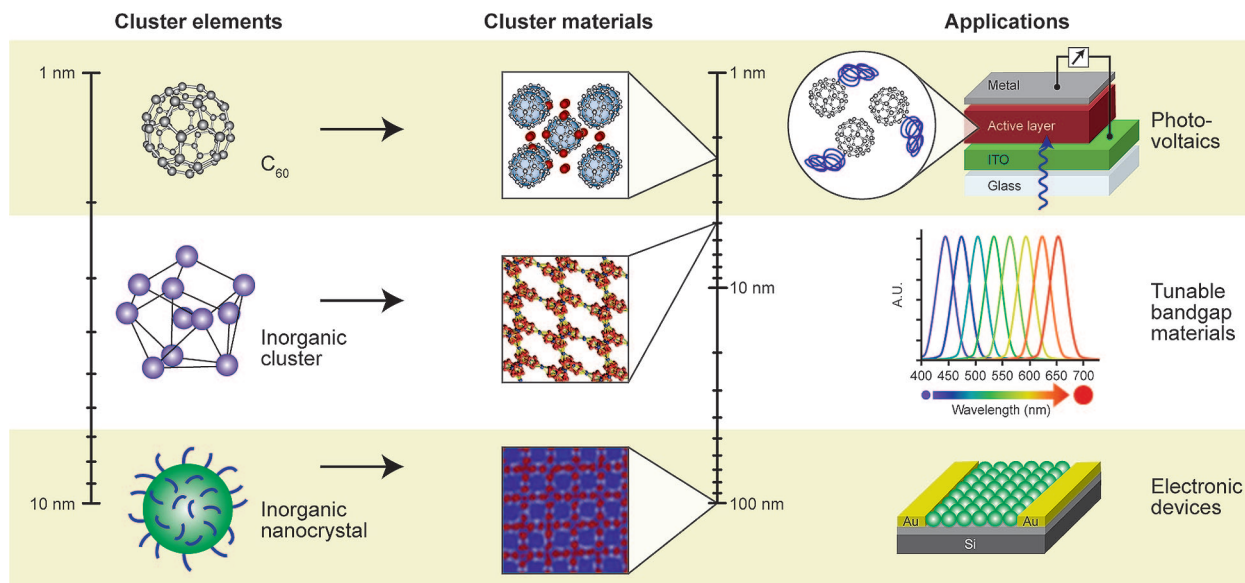


Figure 1. Fullerenes, atomic clusters, and larger inorganic nanocrystals can be used as assembly elements for creating materials with tailored properties.

ters of a similar size. The relatively high electron affinity and large numbers of π -orbitals radiating from their surfaces confer electronic properties that make fullerenes promising as components for self-assembled electronic materials.^{5,6}

Fullerenes were first discovered in 1985,⁷ but their use as active components in nanostructured materials was made possible in 1990 by Krätschmer and Huffman,⁸ who found that it was possible to isolate fullerenes in bulk quantities from carbon soot either by dissolving them in benzene or by subliming them at 400 °C. The ability to perform initial purification steps through sublimation obviates the need for solvent, which is desirable for some materials applications, particularly those involving crystallization. For other applications, the materials can be further purified using chromatographic techniques.^{9–11}

The basic fullerene architecture is capable of producing a surprisingly large array of building blocks for functional materials.¹² As shown in Figure 2, the cage structure may be doped with atoms such as boron or nitrogen, modulating its electronic properties. Metal atoms or small clusters may be intercalated into the cage, also affecting the electronic structure¹³ and magnetic properties.¹⁴ Fullerenes readily undergo external func-

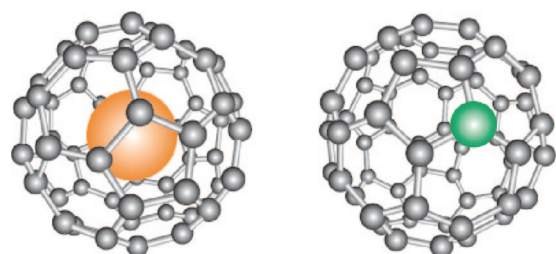


Figure 2. Endohedral (left) and on-site (right) doping of fullerenes can change their material properties. Adapted from ref 13.

tionalization (Figure 3),¹⁵ and the additional chemical handles can be used to modify their solubility or to direct their assembly. Remarkably, given the high initial symmetry of the cage, it is fairly easy to obtain fullerenes monofunctionalized with a single carboxylate, amine, or alkene, which facilitates controlled incorporation with other materials.^{15–17}

Both pure and doped fullerenes are capable of forming highly crystalline arrays with material properties that arise from interactions between their constituents. Films of C₆₀ fullerenes have a characteristic nearest-neighbor distance on the order of 10 Å;⁷ of particular interest are close-packed arrays of fullerenes

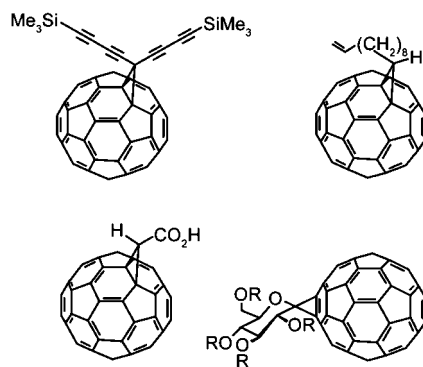


Figure 3. Covalent chemical modification of fullerenes. Silane, alkene, carboxylate, and carbohydrate modifications facilitate material assembly. Adapted from ref 15.

VOCABULARY: **superatom** – cluster consisting of more than one atom, but acting as a stable unit in some ways analogous to an atom • **cluster** – a small stable or metastable grouping of atoms, often exhibiting collective physical properties distinct from its component atoms • **hierarchical material** – one in which primary superatomic building blocks (such as clusters) are arranged to create a regular secondary structure • **superlattice** – the lattice structure describing the arrangement of primary building blocks in a hierarchical material; often refers to regular arrays of inorganic nanocrystals • **fullerene** – a hollow carbon superatom with bonding similar to that of graphite; C₆₀ (buckminsterfullerene) is the canonical example

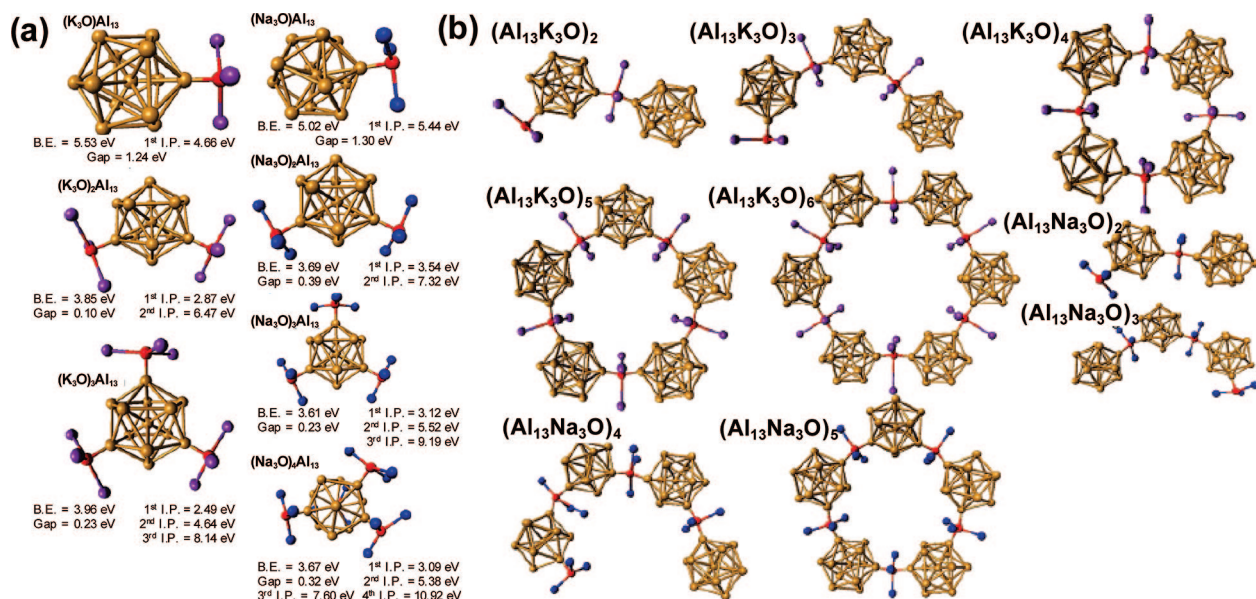


Figure 4. (a) Calculated binding energies and ionization potentials for discrete molecules created from ultrahalogen Al₁₃ clusters and K₃O and Na₃O units. (b) Larger molecular assemblies with ultra-alkali K₃O and Na₃O motifs. Adapted from ref 50.

reductively intercalated with alkali metals.^{18–20} Intercalation can occur in both tetrahedral (1.1 Å radius) and octahedral (2.06 Å) interstitial sites, forming an alkali fulleride material with the stoichiometry A₃C₆₀ if all such sites are filled. A variety of cations (including Na⁺, K⁺, Rb⁺, and Cs⁺) can be used to form such cluster-assembled materials, with the number, size, and electronegativity of the cations influencing the electronic properties of the material.¹⁹ Many alkali fullerides are

superconducting, and the use of larger cations such as Cs⁺ increases the interfullerene spacing, which raises the superconducting transition temperature, T_c ,^{21–23} due to an increased density of states at the Fermi level. Currently, the highest reported T_c for Cs fulleride materials is 38 K under ambient conditions²³ and 40 K at high pressure (14 kbar).²⁴

Another particularly successful application of fullerene materials has been in thin-film organic solar cells, in which fullerene assemblies have been found to have excellent *n*-type charge transport properties; they have been especially advantageous in this regard since there are relatively few *n*-type conducting polymers.^{25,26} Polymer solar cells employing fullerenes often take advantage of chemical functionalization strategies to attach an organic molecule to the fullerene to enhance its solubility for solution processing; the most widely used of these derivatives is PCBM (1-(3-methoxy-carbonyl)propyl-1-phenyl[6,6]C₆₁).^{25,27} The fullerene is then processed with a *p*-type conducting polymer, such as a polythiophene, to form a device in which exposure to light results in the formation of excitons, which can be separated to generate a photocurrent.²⁵

The literature on organic solar cells incorporating PCBM highlights the importance of experimental considerations in addition to theoretical evaluation of material properties.^{25,27–34} Even in using a relatively simple and well-studied building block such as PCBM, successful incorporation into a device requires stringent control over fullerene/polymer interfaces and domain sizes. This is crucial because the exciton diffusion length in such materials is typically on the order of 10 nm,³⁵ meaning that successful charge separation is most likely if the exciton is formed very near a fullerene/polymer interface. Careful tuning of a number of experimental

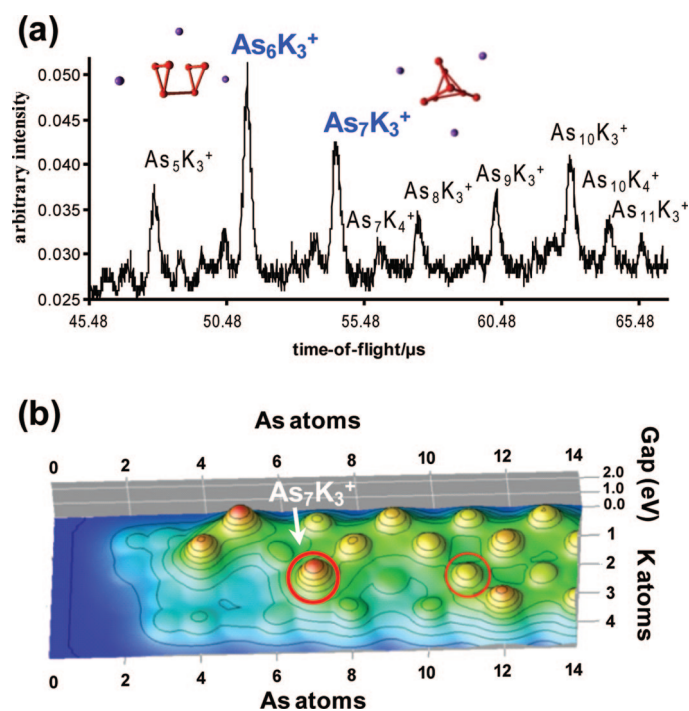


Figure 5. Identification of arsenic cluster building blocks for material assembly. (a) Time-of-flight mass spectra of As_{*n*}K_{*m*}⁺ clusters generated in molecular beams. (b) Calculated fragmentation energy for As_{*n*}K_{*m*}⁺ cluster units. In both analyses, As₇K₃⁺ appears to have high stability, appropriate for use as a cluster material building block. Adapted from ref 68.

parameters, such as solvent,³⁰ processing and annealing temperature,³¹ and polymer regioregularity,^{33,34} helps drive the fullerenes to form small phase-segregated domains for effective charge separation and transport.

Fullerene-based materials have provided both proof-of-principle and inspiration for the development of further cluster-assembled materials. Next, we discuss the development and application of inorganic cluster building blocks with sizes similar to fullerenes.

Cluster-Based Materials. Many other elements can also form small discrete clusters with characteristic physical properties. Fullerenes represent a specialized case since all their surface atoms have a full shell of valence electrons. However, clusters of other elements are known to exhibit “magic number” behavior,^{36–45} meaning that clusters with certain characteristic numbers of atoms are more stable. Importantly, this suggests that the physical properties of the cluster arise from the aggregate rather than simply mirroring the properties of their constituent atoms. Thus, it is possible to consider some inorganic clusters as “superatoms”⁴⁶ with their own physical properties that can be studied and classified, ultimately creating a periodic table of cluster elements.^{1,47}

Understanding Chemical Characteristics of Superatom Building Blocks. The jellium model³⁶ is a simple but valuable guiding principle in searching for and identifying new “cluster elements”. In this model, the charges of all nuclei and core electrons in the cluster are assumed to be distributed uniformly throughout a sphere the size of the cluster and maintained with a specific potential. The energy levels for electrons interacting with such a charge distribution correspond to $1s^2$, $1p^6$, $1d^{10}$, $2s^2$, $1f^{14}$, $2p^6$, and so on; note that, in contrast to atomic energy levels, even the first valence shell contains s, p, d, and f orbitals. Similar to the manner in which a filled electron shell correlates with the stability of an atom, the numbers of electrons in “magic number” clusters known to be exceptionally stable also correspond to filled electronic shells in the jellium model.

A newly synthesized cluster system is characterized in much the same way that nuclear researchers determine the properties of a new element, associating it with a group in the periodic table based on its chemistry.^{48,49} Investigations of cluster reactivities have revealed clusters that mimic rare gases,³⁷ alkaline earth elements,⁴¹ alkali metals,⁵⁰ and multivalent elements.⁴⁷ Some cluster elements also exhibit nonstandard chemistry, such as superhalogenic clusters with extremely high electron affinities (for example, $EA(\text{Al}_{13}) = 3.57$ eV).⁵¹ Such clusters are expected to be particularly valuable in a materials context, as they will impart properties not available from standard atomic building blocks, effectively expanding the periodic table.^{1,47}

One key example is that of aluminum clusters, which paved the way for the superatom concept.³⁷ The chemi-

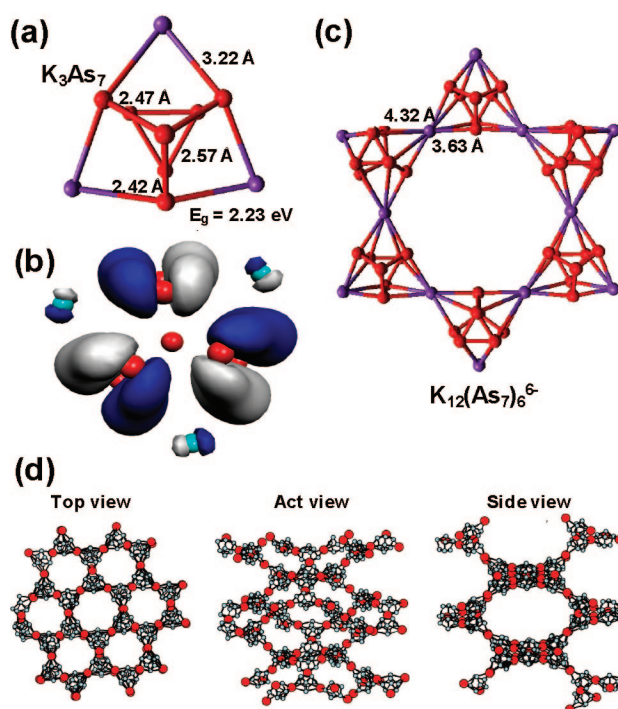


Figure 6. (a) Calculated spacings (in Å) for K_3As_7 . (b) Electron distributions for K_3As_7 . (c) Calculated stable assembly of As_7^{3-} units used in constructing material and electronic structures. (d) Experimental X-ray crystal structure for a honeycomb-like material assembled from As_7^{3-} clusters. Adapted from ref 68.

cally stable Al_{13}^- cluster has 40 valence electrons; thus, its inertness can be understood in terms of a closed electronic shell using the jellium model. Theoretical studies by Khanna and Jena⁵² suggested a high electron affinity for the cluster, comparable to that of a Cl atom. Subsequent calculations⁵² indicated that Al_{13}K was an ionically bound molecule, analogous to KCl, and led to a number of studies demonstrating that cluster assemblies could be formed using such motifs.^{53–60} Later experimental measurements by Wang and co-workers⁶¹ confirmed the theoretical finding that Al_{13} had an electron affinity (3.62 eV) close to that of a Cl atom; negative ion photodetachment spectra of Al_{13}K obtained by Bowen and co-workers⁶² have supported the ionic nature of the Al_{13}K bond.

It is also possible to create larger discrete molecules from cluster building blocks, making use of their unique properties. Recent experimental and theoretical studies by Bergeron and co-workers^{41,51} showed that it was possible to react Al_{13} clusters with I_2 , yielding $\text{Al}_{13}\text{I}_x^-$ “polyhalides” in which the extra electron was held by the aluminum motif, supporting the idea that its electron affinity is higher than that of iodine. Oxygen etching experiments demonstrated that only superatom polyhalide species with even numbers of iodine atoms were stable enough to resist etching, in agreement with expected polyhalide reactivity. Due to the small size of K relative to Al_{13} , attempts to assemble ionic solids^{53–60} using Al_{13}K and other building blocks have led to strong

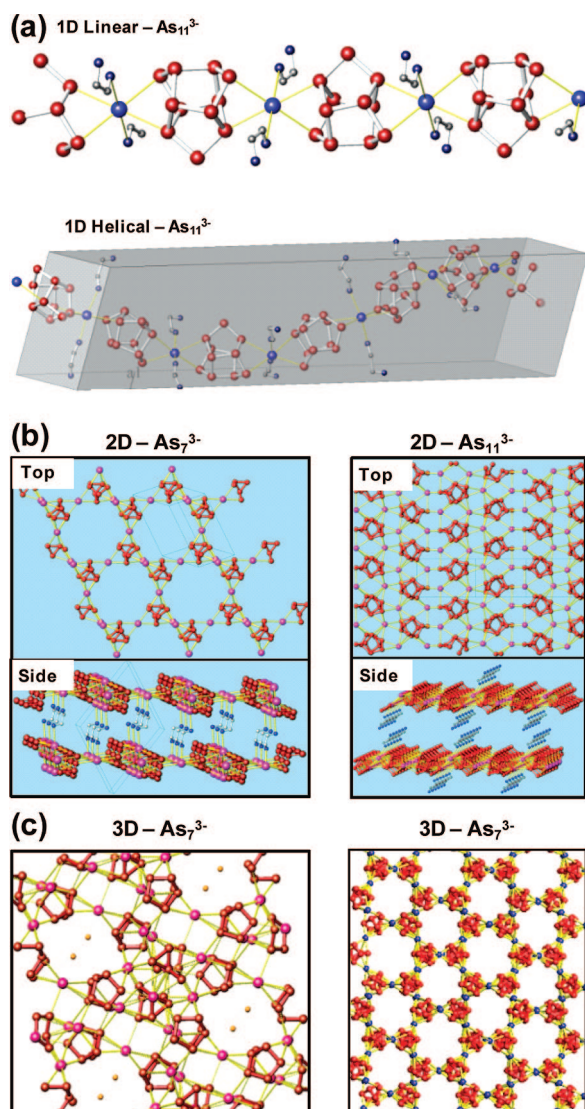


Figure 7. Controlled dimensionality in cluster-assembled materials. (a) One-dimensional linear and helical As_{11}^{3-} chain with one K^+ linker and two sequestered K^+ ions. (b) Two-dimensional cluster-assembled arsenic materials (As_7^{3-} and As_{11}^{3-} , respectively) with two Cs^+ linkers and one sequestered K^+ ion. (c) Three-dimensional cluster-assembled arsenic materials from As_7^{3-} clusters linked with Cs^+ and K^+ , respectively. Adapted from refs 1, 68, and 69.

interactions between the Al_{13} units, substantially changing their behavior.

Experimental studies of Al_{13} cluster chemistry have also led to theoretical explorations of the ability to use such clusters as building blocks for further cluster “molecules” making use of the cluster’s nonstandard properties. For example, combining ultrahalogenic Al_{13} clusters with an ultra-alkali K_3O motif results in a calculated cluster binding energy of 5.53 eV, much larger than that for $Al_{13}K$ (2.51 eV).⁵⁰ Further modeling suggests that it may also be possible to create discrete $(Al_{13}K_3O)_n$ and $(Al_{13}Na_3O)_n$ molecules, shown in Figure 4. Importantly, the use of larger alkali motifs such as K_3O reduces interactions between Al_{13} units, relative to the assemblies with smaller cations described above, allowing

the units to maintain more of their discrete superatomic character.

The above example describes the development of a class of new cluster molecules, in which discrete numbers of cluster superatoms with novel properties are combined with other elements to form new discrete species. Next we consider what happens when the connecting geometry is chosen with the goal of forming an extended solid made of cluster building blocks.

Cluster Building Blocks and Nanoscale Assembly. Controlling the assembly of cluster building blocks into extended solids is the next step toward achieving superatom materials with tunable physical properties. Many of the guiding principles are similar to those governing the formation of materials in which even smaller metallic centers (one or two atoms) form the nodes for connection by organic or inorganic linkers. A number of excellent reviews discuss the rich literature on zeolites,^{63,64} metal-organic frameworks,^{65,66} and related assembly strategies.⁶⁷ In the context of the cluster materials discussed below, identification of stable cluster building blocks for self-assembly is of crucial importance, as many clusters at these small sizes have lifetimes too short for controlled assembly into materials.

Both theory and experiment can help target the choice of suitable cluster superatoms and linkers for building materials with controlled geometry. Stabilities of potential building blocks may be verified directly through flow tube, beam, or other experiments, while first principles theoretical investigations in conjunction with photoelectron spectroscopy may aid in elucidating the structures of clusters. Finally, synthetic chemical approaches can verify the nature of candidate superatoms and linkers.

Arsenic–metal cluster materials developed by Castleman, Khanna, Sen, and co-workers provide a practical example of the success of this approach.⁶⁸ Clusters of $As_nK_m^+$ species were generated in molecular beams, and relative populations were evaluated by mass spectrometry (Figure 5a). Peaks at $As_6K_3^+$ and $As_7K_3^+$ suggested these clusters as stable building block candidates. Theoretical electronic structure analysis indicated that the ionization potential of As_7K_3 was 5.07 eV, while that of As_6K_3 was only 3.96 eV, suggesting As_7K_3 as a more stable superatom building block.

Further theoretical investigations of arsenic–potassium clusters were also used to guide the choice of targets with consideration given to both stability and desired assembly geometry.⁶⁸ These studies included compositional energy diagrams of fragmentation energy, modeling of fragmentation patterns, and calculations of the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Figure 5b shows a compositional diagram displaying the minimum energy required to break a cluster into two fragments; As_5K , As_7K_3 , and $As_{11}K_3$ have the highest fragmentation ener-

gies, suggesting their stability as building blocks. The planar structure of As_5 made it unsuitable for three-dimensional assemblies, leaving As_7 and As_{11} as potential motifs. For As_7 , theoretical studies further indicated that the cluster could be regarded as an As_7^{3-} anion and that the role of the coordinated alkali atoms was to donate charge. Thus, different materials could be generated by changing the alkali atom or by using cryptated alkali atoms, which are partially sequestered by coordination to macrocyclic donor molecules, in order to facilitate electron transfer by reducing the ionization potential. Figure 6 shows the calculated structure, electron density mapping, and HOMO–LUMO gap for an As_7K_3 superatom, as well as the structure of one calculated stable assembly state in which a circular geometry is formed by sharing two of the three potassium atoms coordinated to each cluster.

Experimental solution-phase assembly and X-ray diffraction studies by Sen and co-workers confirm the geometric control that may be achieved using As_7 and As_{11} with a small library of free and cryptated alkali atoms and other linkers as building blocks.⁶⁹ Figure 6d shows one such assembly made from K and cryptated K atoms, with a core motif similar to that shown in Figure 6c.

Controlling Dimensionality in Cluster-Assembled Materials. Further examples of one-, two-, and three-dimensional structures built using As_7 and As_{11} superatoms are shown below.^{1,68,69} They illustrate the considerable latitude possible in building discrete cluster assemblies using solution-based bulk synthesis procedures.

The one-dimensional case in which each As_{11}^{3-} cluster is combined with one K^+ linker and two sequestered K^+ cryptands provides an excellent example of the critical role linkers play in assembly geometry. When the K^+ and As_{11}^{3-} components were crystallized in the presence of bidentate amine linkers (Figure 7a), both linear and helical geometries could be produced by controlling the stoichiometry between linker and cluster.

Two- and three-dimensional structures exhibit similar tunability based on the choice of building block and linker. Very different two-dimensional sheet structures can be obtained by using As_7^{3-} or As_{11}^{3-} clusters as primary building blocks with two Cs^+ linkers and one sequestered K^+ ion, as shown in Figure 7b. In three dimensions, an even richer set of geometries can be achieved by linking As_7^{3-} clusters with Cs^+ and K^+ cations, while using Li^+ and sequestered K^+ ions as charge-balancing cations (Figure 7c).

Theoretical electronic structure investigations reveal that cluster-assembled materials of this type are marked by filled bands of energy levels separated by unoccupied bands, leading to the appearance of cluster-based semiconductors, in which the band gap can be tuned by changing the alkali atom. This modulation substantiates a key promise of cluster-assembled

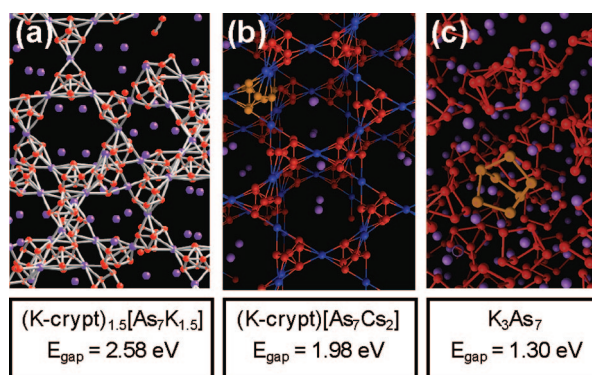


Figure 8. Cluster-assembled materials based on As_7 building blocks. Altering the cationic linker and its state of cryptation results in changes in the band gap of the material, as calculated from first principles. Adapted from ref 1, 68, and 69.

materials: properties can be varied by the choice of components. Figure 8 shows selected assemblies based on As_7 motifs and the band gaps calculated using first principles electronic structure calculations where exchange correlation effects were incorporated using a density functional approach. By altering the coordinating cation or its state of cryptation, the calculated band gap could be tuned between 1.35 and 2.60 eV.¹ Experimental studies by Weiss, Sen, and co-workers have verified that the cluster-assembled material band gaps can indeed be tuned in this way.⁷⁰

The successful synthesis of cluster-assembled materials with novel physical properties stems from the joint application of theoretical, synthetic, and analytical methods. In the above discussion, we have outlined the rational design of a class of arsenic-based materials

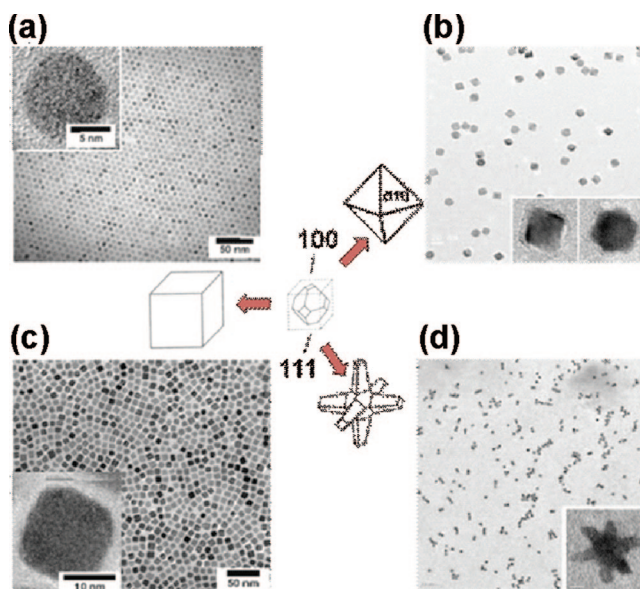


Figure 9. Shape control of PbSe nanocrystals. Control of nanocrystal shape offers greater directionality to the interactions of nanocrystal building blocks and offers richer architectures than the packing of uniform spheres would provide. The shape control of PbSe nanocrystals with adjustments in temperature and surfactants allows the growth rates of the different facets of the rock-salt crystal structures to be adjusted to allow isolation of (a) spheres, (b) octahedra, (c) cubes, and (d) six-pointed stars. Adapted from ref 81.

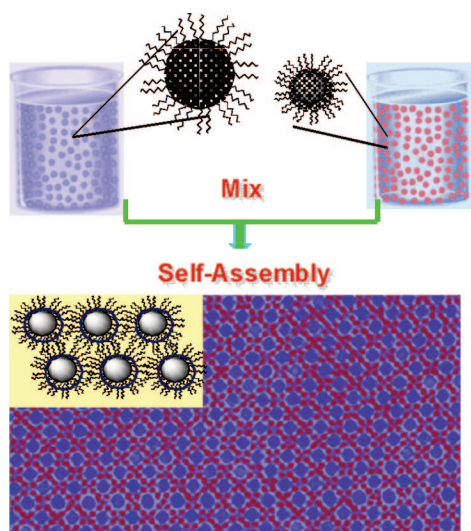


Figure 10. Formation of a binary nanocrystal superlattice. Magnetic 11-nm $\gamma\text{Fe}_2\text{O}_3$ nanocrystals (blue) and semiconducting 6-nm PbSe nanocrystals (red) are depicted forming a binary colloidal crystal or nanocrystal superlattice by drop casting. Adjusting the ratios of the particle sizes and concentrations and ensuring compatibility of the surfactant stabilizers yields a solid with an overall stoichiometry of 1 $\gamma\text{Fe}_2\text{O}_3$ for each 13 PbSe. The image shows a colored plane-view transmission electron micrograph imaged down the $\langle 100 \rangle$ axis. Figure adapted from ref 90.

with tunable band gaps founded on the theoretical work of Castleman, Khanna, and co-workers, the synthetic methods of Sen and co-workers, and the analytical work of Weiss and co-workers. Similar principles have also been applied by others in developing diverse structures based on other Zintl ions of groups

13–16.^{71–74} Early studies such as these will provide a framework to facilitate future development of other classes of cluster-assembled materials.

Nanocrystal Superlattices. Larger inorganic nanocrystals also can be used as building blocks for cluster-assembled materials.^{75–79} Although conceptually similar to the cluster superatoms described in the previous section, there are important physical differences that shape their suitability as material components. Although samples of nanocrystals with diameters larger than 1–2 nm lack perfect precision in the number of atoms per cluster, their sizes may nonetheless be tightly controlled (standard deviation $<5\%$) through careful synthetic procedures.⁷⁵ Nanocrystals can be readily synthesized out of a wide variety of inorganic materials (Au, Ag, CdSe, PbS, Fe_2O_3 , and many others) and in an array of morphologies, such as spheres, pyramids, cubes, and branched structures,^{75,80–86} that can be used to direct their self-assembly. Like the inorganic clusters discussed previously, atoms in the outermost shell typically have unsaturated coordination geometries; however, in solution-phase synthesis, organic ligands are used to passivate the crystal surface, making it more stable.⁸⁴ Superlattices of nanocrystals with diameters on the order of 10 nm can be crystallized with domains on the order of 10 μm , large enough to be relevant for individual devices and other applications; assembly procedures are being investigated for wafer-scale growth.⁸⁷ In superlattices, unlike the cluster molecules described previously, the particles are not covalently or ionically bound, but instead interact

through van der Waals and dipole or induced dipole interactions between particles, as described below. In the size regime of a few nanometers to a few tens of nanometers, most of the interactions are of comparable strength, making it difficult to predict theoretically how a superlattice will form;⁸⁸ thus, studies of superlattice growth are often largely phenomenological.

Synthesis of Nanocrystal Building Blocks.

Inorganic nanocrystals can be synthesized from a wide array of materials with practical physical properties that are often tunable with the size of the particle and provide the foundations for control over properties of nanocrystal superlattice materials.^{75,83,85,86,89} Gold and silver nanocrystals exhibit strong size-dependent plasmon resonances, making them suitable for optical applications;⁸³ semiconductors such as CdSe, CdS, and

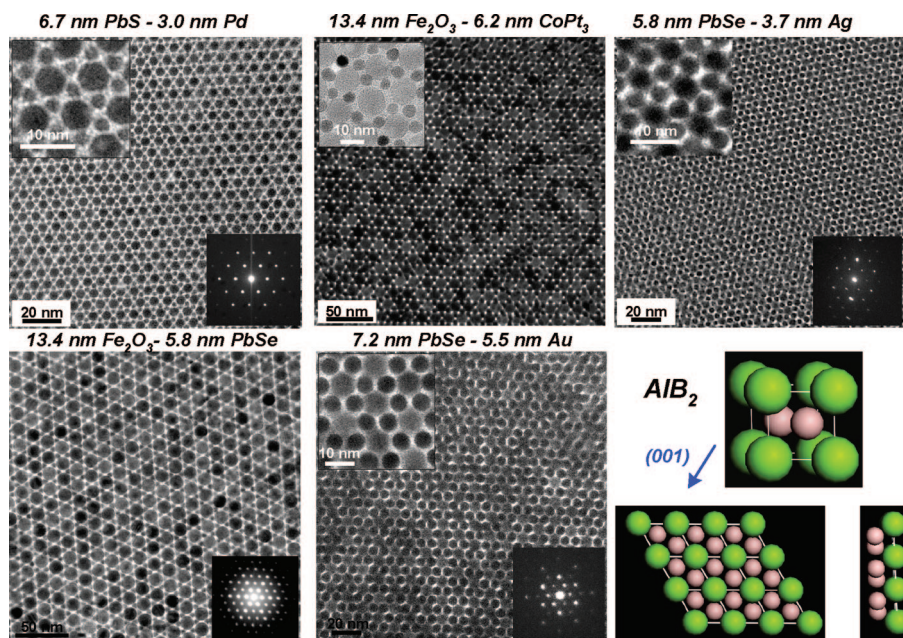


Figure 11. Examples of a series of binary superlattices with stoichiometries of one large particle for each two small particles are shown above. A wide range of semiconducting, metallic, magnetic, and plasmonic building blocks can be captured, while retaining a constant stoichiometry and symmetry. With dozens of monodisperse building blocks available, tunable in size increments of as little as one atomic layer, and with more than 25 binary crystal structures, the available combinations to explore now number in the tens of thousands. Figure adapted from ref 79.

PbS are photoluminescent, often with quantum efficiencies higher than 50% when prepared with a thin overlayer of a high band gap material.⁷⁵ Materials such as Fe₂O₃ have size-dependent magnetic properties, including transitions from superparamagnetism to ferromagnetism.⁸⁹ Many studies have demonstrated that plasmonic, magnetic, luminescent, and other properties can couple in a distance-dependent manner, making nanocrystal superlattices attractive target materials for devices and other applications in which it may be desirable to combine and to augment the properties of nanocrystal materials in a controlled fashion.

Particle growth conditions are key to determining both individual particle properties and how they may couple in a superlattice, by controlling their size, morphology, and surface chemistry. Nanocrystals used in self-assembled materials are typically synthesized in the solution phase using a shell of organic ligands such as alkanethiols, alkylamines, or phosphonic acids to stabilize the surface.⁷⁵ The choice of ligand, solvent, and reaction conditions can influence both the size and morphology of the resulting crystals, which in turn impacts their self-assembly. The case of PbSe provides an excellent example of the influence of ligands and reaction conditions on morphology. In the growth of PbSe crystals (Figure 9),⁸¹ altering growth temperature and the mixture of surface ligands can result in crystallization of spheres, octahedra, cubes, or six-pointed stars. Growth in a ligand mixture of oleic acid (OA) and trioctyl phosphine (TOP) at moderately high temperature (precursor injection at 180 °C, particle growth at 140 °C) results in spherical particles (Figure 9a), whereas growth at somewhat lower temperatures (injection 120 °C, growth at 110 °C) yields octahedra (Figure 9b). The addition of small amounts of long-chain alkylamine ligands creates cubes (Figure 9c) when the ligand is a 12-carbon dodecylamine and six-pointed stars (Figure 9d) when it is 16-carbon hexadecylamine. The choice of ligand is also significant as it determines the hydrophobicity and surface chemistry of the particles, which influence the type of interparticle induced dipole, dipole, and ionic interactions that determine particle assembly.

Preparation of Nanocrystal Superlattices. Nanocrystal superlattices can be prepared simply by slowly evaporating solvent from a solution of nanocrystals. This technique can be applied to a variety of sizes and shapes of particles to create single-component superlattices.⁷⁵ Here, however, we primarily consider the formation of binary superlattices (Figure 10),⁹⁰ in which two different types of nanocrystals are co-precipitated.

In analogy to the formation of a binary atomic crystal such as NaCl or CsCl₂, the relative sizes of the two types of nanocrystals play an important role in determining their lattice structure, a phenomenon referred to as “radius ratio rules” in molecular solids.⁹¹ A critical difference is that, for nanocrystal superlattices, the individual crystals may or may not be charged, and thus

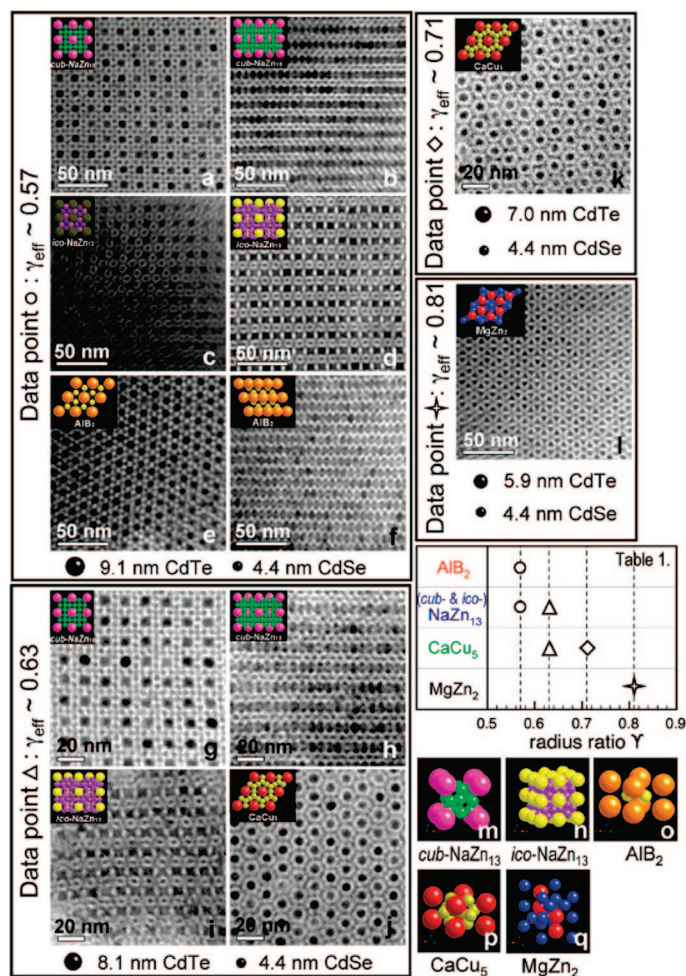


Figure 12. Binary superlattices can be assembled in a number of stoichiometries. One way in which assembly can be modulated is by varying the relative sizes of the two building components, in a manner analogous to the radius ratio rules that help predict assembly in binary atomic crystals. Adapted from ref 91.

the stoichiometry is not typically restricted by valency considerations. Figure 11 shows a variety of binary superlattices that assume the AB₂ lattice structure.⁷⁹ Other experiments have also demonstrated the formation of intermetallic AB, AB₅, and AB₁₃ binary lattices; the colored micrograph in Figure 10 illustrates the structure of a superlattice of 11-nm Fe₂O₃ and 6-nm PbSe with AB₁₃ stoichiometry.⁹⁰ O’Brien and co-workers have recently explored the formation of lattice structures based on ratio rules explicitly, generating superlattices in all four intermetallic structures mentioned above (Figure 12).⁹¹

Both shape and surface chemistry also influence superlattice formation. Three different examples of superlattices formed from LaF₃ wedges and noble metal (Au or Ag) spheres are presented in Figure 13.⁷⁸ In all three cases, the particles are coated with hydrophobic ligands. In Figure 13a, the particles assemble on a surface that is also hydrophobic, and the LaF₃ wedges orient to maximize their contact with the surface. Panels b and c in Figure 13 show superlattices assembled on a

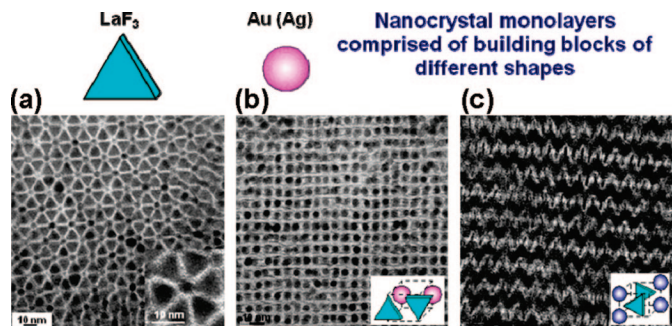


Figure 13. Nanocrystal shape and surface wetting can control binary superlattice structure. The packing of nanocrystals with different compositions and complementary shapes can further expand the structures accessible. In the panels above, wedges of LaF_3 have been co-assembled with spheres of either Ag or Au. The arrangements of the particles in the panels from left to right in the series are dictated by the energetic interaction with the surface on which the nanocrystals have been assembled. (a) On a hydrophobic amorphous surface, all particles “wet” the surface. (b) A silicon nitride membrane support provides a less hydrophobic surface, causing LaF_3 wedges to orient to reduce the contact of their organic stabilizers with the surface. (c) A SiO_2 substrate presents a hydrophilic surface; particles arrange to reduce the contact of the organic stabilizers further. Thus, shape and surface interactions can both be employed along with control of particle size and composition to engineer the superlattice structure. Adapted from ref 78.

silicon nitride membrane (somewhat hydrophilic) and a SiO_2 surface (hydrophilic), respectively. In these lattices, the LaF_3 wedges orient to minimize interactions between their hydrophobic ligands and the surface, changing the overall lattice structure substantially.

Characterization of Nanocrystal Superlattice Physical Properties.

The ability to produce highly ordered co-assemblies of nanocrystals with tunable physical properties is one of

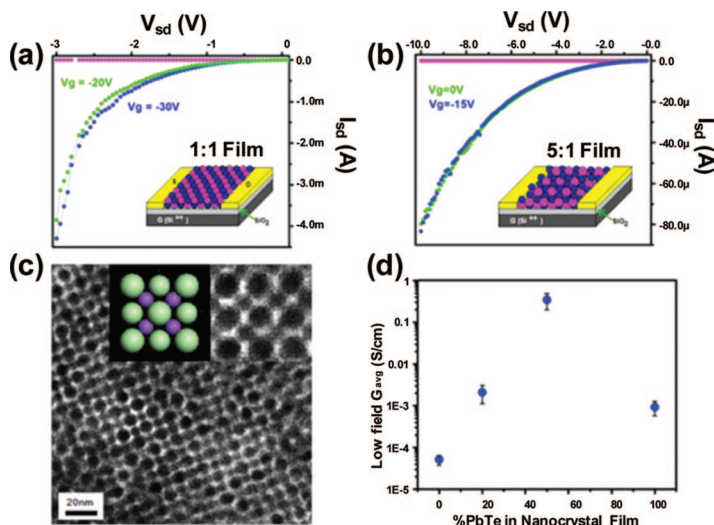


Figure 14. Synergistic effects in electron transport. (a,b) Synergistic interactions of PbTe and Ag_2Te nanocrystals when they are assembled into binary superlattices of differing compositions and symmetries are reflected in (a) and (b) for 1:1 and 5:1 Ag_2Te to PbTe ratios, respectively. The corresponding current versus voltage (I_{sd} vs V_{ds}) curves show that these materials conduct with a high concentration of mobile positive charges (holes), in contrast to the electron transport evident in separated components. (c) Plane-view transmission electron micrograph shows the binary packing of Ag_2Te (green) and PbTe (purple), after annealing to remove the organic surface ligands. (d) Conductivity of the binary films is enhanced relative to single-component films of the same constituents. Adapted from ref 92.

the great promises of custom nanostructured materials. Initial studies of the physical properties of superlattices show that aggregate properties of the superlattice can indeed be tuned by varying such properties as stoichiometry. Figure 14 shows the results of electron transport studies performed on superlattices of PbTe and Ag_2Te nanocrystals at $\text{PbTe}/\text{Ag}_2\text{Te}$ ratios of 1:1 and 5:1.⁹² Gate voltages were decreased for the 5:1 film relative to the 1:1 film, and both films evinced high conductivities and hole mobilities relative to single-component films of the same constituents.

Challenges and Open Questions. The work described above represents the first steps toward establishing a library of superatomic building blocks, characterizing their chemical properties and reactivities, and assembling them into both discrete cluster molecules and extended cluster-assembled materials. Nevertheless, many open questions remain at each stage of the process, some of which we discuss briefly here.

Although empirical paths have been discovered that allow cluster and nanocrystal building blocks to be synthesized with exquisite control over size, morphology, and surface chemistry, even relatively straightforward procedures can give striking batch-to-batch variations, especially in different laboratories. In at least one recent case,⁹³ such results have eventually been attributed to uncontrolled impurity levels in reagents; this is particularly problematic as many reported syntheses rely on one or more technical-grade (low-purity) reagents. A more complete understanding of these effects will improve reproducibility of synthetic procedures. In small clusters, which are not typically stabilized by bulky ligands, coordination chemistry must be chosen especially carefully to avoid losing the chemical identity of the cluster element. Research is underway to provide robust synthetic strategies for such control.

Nanocrystal and cluster surface chemistry, although controlled through the choice of ligand additives, is not always well-characterized or understood and can be extremely important in predicting and controlling self-assembly. Careful ligand binding studies such as the recent work of Alivisatos and co-workers⁹⁴ will ultimately provide a firm basis for predicting and controlling the assembly of superatom building blocks as it relates to surface chemistry.

Important issues also remain open regarding large-scale assemblies for device applications. One example is the need to control registration with macroscale objects, a critical concern for integration with existing manufacturing strategies. It will also be imperative to develop an understanding of the relationship between defects (both in clusters and superlattices), interfaces, and device performance.

CONCLUSIONS AND PROSPECTS

The ultimate goal of studies such as those presented here is to enable materials scientists to specify

a desired set of properties and to predict one or more sets of superatom building blocks that could be synthesized and self-assembled into such a material. While such an ambitious goal may never be fully realized, even modest subsets of such capabilities would have substantial impacts on the material science community.

We have discussed a number of key examples of the synthesis and characterization of cluster and nanocrystal superatoms and their assembly into functional materials with tunable properties. For smaller building blocks such as fullerenes and discrete atomic clusters, both theory and experiment have been used to develop a small periodic table of superatom building blocks, some of which extend the range of properties available from traditional elements and ions. Since such efforts have also allowed selection for spatial properties such as coordination geometry, it has been possible to create a variety of materials with controlled dimensionality and tunable electronic properties. A wide variety of larger nanocrystal assembly components can also be synthesized; their shape, size, and surface chemistry determine both their individual physical properties and how they will assemble into superlattices. Ongoing efforts can be expected both to expand the library of available building blocks and to improve control over all aspects of cluster-assembled material creation, from synthesis and characterization to assembly.

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