Conversion Reactions of Atomically Precise Semiconductor Clusters

Max R. Friedfeld, Jennifer L. Stein, Andrew Ritchhart, Brandi M. Cossairt*

Department of Chemistry, University of Washington, Seattle, WA 98195-1700.

*cossairt@uw.edu

Conspectus

Clusters are unique molecular species that can be viewed as a bridge between phases of matter, and thus between disciplines of chemistry. The structural and compositional complexity observed in cluster chemistry serves as an inspiration to the material science community and motivates our search for new phases of matter. Moreover, the formation of kinetically persistent cluster molecules as intermediates in the nucleation of crystals, makes these materials of great interest for determining and controlling mechanisms of crystal growth. Our lab developed a keen interest in clusters insofar as they relate to the nucleation of nanoscale semiconductors and the modeling of post-synthetic reaction chemistry of colloidal materials. In particular, our discovery of a structurally unique $In_{37}P_{20}X_{51}$ (X = carboxylate) cluster *en route* to InP quantum dots has catalyzed our interest in all aspects of cluster conversion, including the use of clusters as precursors to larger nanoscale colloids and as platforms for examining post-synthetic reaction chemistry.

This accounts article is presented in four parts. First, we introduce cluster chemistry in a historical context with a focus on main group, metallic, and semiconductor clusters. We put

forward the concept of rational, mechanism-driven design of colloidal semiconductor nanocrystals as the primary motivation for the studies we have undertaken. Second, we describe the role of clusters as intermediates both in the synthesis of well-known material phases and in the discovery of unprecedented nanomaterial structures. The primary distinction between these two approaches is one of kinetics – in the case of well-known phases, we are often operating under high temperature thermolysis conditions, whereas for materials discovery, we are discovering strategies to template the growth of kinetic phases as dictated by the starting cluster structure. Third, we describe reactions of clusters as model systems for their larger nanomaterial progeny, with a primary focus on cation exchange. In the case of InP, cation exchange in larger nanostructures has been challenging due to the covalent nature of the crystal lattice. However, in the higher energy, strained cluster intermediates, cation exchange can be accomplished even at room temperature. This opens opportunities for accessing doped and alloyed nanomaterials using post-synthetically modified clusters as single-source precursors. Finally we present surface chemistry of clusters as the gateway to subsequent chemistry and reactivity and as an integral component of cluster structure and stability. Taken as a whole, we hope to make a compelling case for using clusters as a platform for mechanistic investigation and materials discovery.

Introduction

A cluster can be defined as a collection of atoms, in a precise number and with a precise structure, that is intermediate in size between a typical small molecule and a bulk solid. Because of their existence in this unique size regime, clusters have been viewed as bridges between phases of matter, and therefore, between disciplines of chemistry.[1,2] From the structurally and compositionally expansive examples of main group clusters that are both naturally occurring and that have been synthetically developed over the past several decades,[3–6] to kinetically stabilized intermediates that have recently emerged in the realm of colloidal metal and semiconductor nanoscience,[7,8] cluster chemistry is a diverse and impactful area of science (Figure 1).

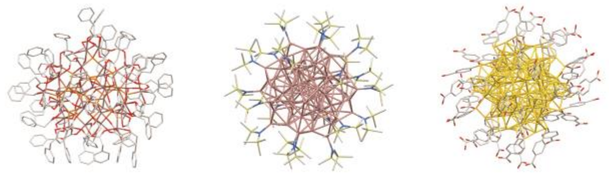


Figure 1. Single crystal X-ray diffraction structures of semiconductor, metalloid and metal clusters. $In_{37}P_{20}(O_2CCH_2C_6H_5)_{51}$ (left), $[Ga_{84}(N(SiMe_3)_2)_{20}]^{4-}$ (middle), $Au_{102}(S(C_6H_4)CO_2H)_{44}$ (right).

Our interest in clusters arose specifically in the context of colloidal nanoscience, wherein their role as intermediates, precursors, and models for examining post-synthetic modification is of immense interest.[8] Colloidal nanocrystals are not molecular species - when a collection of nanocrystals is prepared via solution-phase chemistry, a range of stoichiometries and structures is obtained even in the most well-controlled syntheses. This presents a challenge for both characterizing and devising chemical transformations of these intriguing inorganic compounds. We, and many others, therefore have viewed cluster intermediates as a gateway to understanding the structure and chemical reactivity of their larger nanoscale progeny. This viewpoint has led to a proliferation of, in particular, metal nanocluster syntheses and chemistries, which have in turn informed our understanding of the structural variability and reactivity of this class of cluster materials.[5] Semiconductor nanoclusters, insofar as they are relevant to the field of colloidal semiconductor nanocrystals, have been much less systematically examined.

CdSe has the richest history and development with respect to both the nanocrystal and cluster forms. Clusters of CdSe were first prepared by combining $CdCl_2(PPh_3)_2$ with $PhSeSiMe_3$, which resulted in the precipitation of a $Cd_{32}Se_{14}$ cluster bearing 36 $^{-}$SePh ligands.[9] These roughly pyramidal structures looked like excerpts of the bulk zincblende lattice, furthering their analogy as intermediaries of molecules and nanocrystals. Since this first synthesis, discretely sized CdSe clusters have been identified as intermediates *en route* to larger nanomaterials in a range of sizes and stoichiometries,[10–12] and in all the structurally characterized examples, the pyramidal structure is conserved.[13]

As industry has pivoted toward less-toxic semiconductor nanocrystals for emissive applications, InP was identified as perhaps the leading candidate for a direct replacement in CdSe-based technologies. The synthesis of InP, however, was far less developed, which spurred our interest in the mechanism of nucleation and growth of this material.[14–17] Our lab demonstrated that kinetically persistent cluster intermediates with well-defined compositions and structures play a key role in the nucleation of this more covalent material. In the case of carboxylate-ligated InP clusters, the most stable and easily isolated of these species has a composition of $In_{37}P_{20}(O_2CR)_{51}$, and was characterized by single-crystal X-ray diffraction (XRD) to have a low-symmetry pseudo C_{2v} structure.[18] This cluster has been verified as a robust precursor to crystalline, size-uniform InP quantum dots and has proven to be an amazing platform for examining a variety of surface-initiated transformations of InP. This accounts article will highlight our work in all areas of cluster conversion, including the use of clusters as precursors to larger nanoscale colloids and as platforms for examining the post-synthetic reaction chemistry of InP nanocrystals.

Clusters as precursors for nanomaterials

a. “Traditional” Nucleation and Growth

The first observation of the intermediacy of InP clusters during the synthesis of quantum dots (QDs) was reported in 2009 where the formation of these nanoclusters was explained by precursor-controlled kinetics, shedding light on the first step in the crystallization of InP.[19] In this work the clusters were viewed as a model for InP QDs and the observations were taken to signify a departure from classical nucleation models being relevant in the synthesis of this material. These same clusters were later observed again in the synthesis of InP QDs from indium carboxylate and $P(SiMe_3)_3$,[20] however, neither of these early studies verified these nanoclusters as on-pathway intermediates along the reaction trajectory.

In our group's studies on the synthesis of InP nanomaterials, we sought to temporally isolate the formation of clusters and larger QDs by pursuing a low temperature synthesis in a similar fashion to making ultra-small nanocrystals previously reported.[7] In this manner, adding $P(SiMe_3)_3$ at 100 °C to a solution of indium myristate in a 1:2 ratio resulted in the formation of a species with a high-energy excitonic feature (λ_{max} = 386 nm).[16] Using phenylacetate stabilizing ligands rigidified the ligand shell and enabled the determination of the single-crystal X-ray structure of the cluster (Figure 2A).[18] The structure of this cluster, $In_{37}P_{20}(O_2CR)_{51}$, is characterized by the non-stoichiometric $[In_{21}P_{20}]^{3+}$ core, the indium-rich surface, multiple carboxylate binding modes, and full ligand passivation at the surface. Clusters with myristate or oleate ligands proved suitable as single-source precursors in the synthesis of InP QDs upon rapidly injecting a solution of clusters into squalane at 400 °C (Figure 2B,C). It was determined that increasing the cluster concentration results in larger QDs, suggesting that nucleation is impacted by the concentration of liberated monomer.

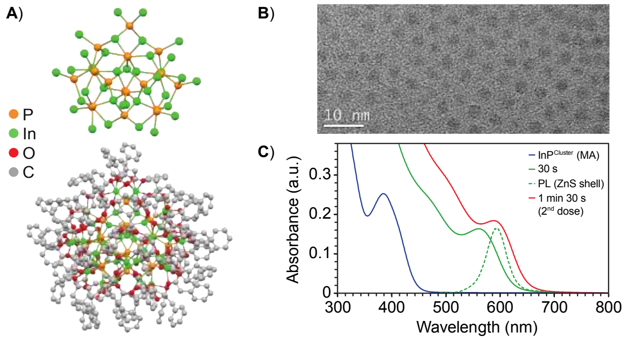
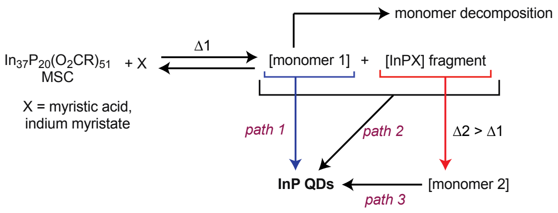


Figure 2. (A) Two views of the single crystal X-ray diffraction structure of $In_{37}P_{20}(O_2CH_2Ph)_{51}$ (H atoms omitted for clarity). (B) TEM and (C) UV-Vis images that demonstrate the use of $In_{37}P_{20}(O_2CR)_{51}$ ($R = C_{13}H_{27}$) as a single-source precursor for the synthesis of crystalline InP QDs with narrow size distribution.

Having developed a robust and reproducible method for synthesizing InP QDs using clusters as single-source precursors, we sought to consider the various mechanisms by which these clusters could convert to larger nanomaterials. To do this, we turned to *in-situ* UV-Vis spectroscopy to observe changes to the absorbance features of the nanomaterials during nucleation and growth across a range of reaction conditions.[21] Over the temperature range of 200 - 300 °C, the conversion of InP clusters to larger nanomaterials was demonstrated to occur with a monotonic increase in QD concentration in less than 20 minutes. The particles grown at 250 °C and 300 °C display a narrower and blue-shifted excitonic feature compared to the lower-temperature syntheses. While transmission electron microscopy revealed that the nanomaterials grown at 150 °C had an ill-defined morphology compared to the uniform particles (2.6 +/- 0.5 nm) grown at 250 °C, both products display an XRD pattern consistent with zincblende InP nanoparticles. These data are consistent with dissolution of the original cluster phase during the reaction.

Measuring the rate of product formation at different concentrations at 250 °C and 300 °C revealed that the rate increased linearly as a function of concentration, indicating a first-order dependence. Studies of cluster evolution in the presence of myristic acid and indium myristate, species of potential relevance in this process, revealed that the rate of reaction increases as a function of increasing additive concentration. We hypothesize that this occurs by accelerating surface ligand exchange and stabilizing reactive intermediates and monomer species in solution. This stands in contrast to an example of a CdSe cluster converting to nanorods, in which the presence of exogenous ligands *decreased* the rate of cluster conversion.[10] Overall this analysis revealed that while MSCs are competent single source precursors for InP QD synthesis, their dissolution involves the release of multiple monomer species with varying reactivities (Scheme 1). This process is further altered by the addition of exogenous myristic acid or indium myristate, which promote monomer generation in a temperature-dependent manner.



Scheme 1. Proposed competing pathways for MSC conversion to InP QDs are dependent on temperature and additive.

b. Templating non-thermodynamic phases

Nanoscale synthesis offers new opportunities in materials discovery, giving rise to compounds with novel properties and phases that may be otherwise inaccessible. Most crystal phases seen in the bulk can be reproduced on the nanoscale and principles for controlling particle size and shape have been well-developed for many material classes (i.e., metal NPs, CdSe). Beyond this there is a growing body of knowledge on novel structures that exist only at the nanoscale and only for specific materials.[22–24] Principles for accessing new phases remain under developed, and we propose that progress will be underpinned by elucidating non-classical nucleation mechanisms for nanoscale materials.

As discussed previously, early work in our lab characterized the growth of an InP cluster as a locally stable intermediate in the synthesis of InP QDs. This cluster was noteworthy both for its high local stability and, less obviously, the deviance of its phase. As evidenced by powder XRD, this cluster species does not index to either the zincblende phase seen exclusively in other InP colloidal syntheses, or to wurtzite, the only other phase of InP seen at atmospheric pressures. Many atomically-precise clusters, including those of the metalloid elements such as Ge and Al also display this phenomenon and are well-visualized as core-shell structures with complex or unusual bonding patterns that would be impossible to predict *ab initio*.[25] Other clusters such as Si,[26] Zn_3P_2,[27] and InP appear relatively more crystalline than these but with unit cells not found in the bulk.

In the case of $In_{37}P_{20}$, the *pseudo* C_{2v} symmetry does not display an obviously repeatable bonding pattern or unit cell that could be easily extended into a regular bulk structure. Initially we rationalized the structure as being nearly wurtzite as it appeared to be comprised of strained boat conformation rings, but in time we realized that these rings were actually adopting the lesser known 'twist' conformer. In one dimension, the repetition of this conformer is known as polytwistane and has been pursued, but not isolated, in the carbon nanotube literature.[28,29] Within the cluster we see that it is composed of a complex 3D network of numerous chirally-consistent, intersecting polytwistane units – an unprecedented structure type in solid state matter (Figure 3A). The result is a non-thermodynamic phase comprised of a strained structure with lower symmetry than normally seen in InP that does not confer an obvious unit cell but is infinitely repeatable along any one of the polytwistane axes.

The existence of this atomically precise and structurally unique intermediate motivated our exploration of templating the growth of non-thermodynamic InP phases. A variety of strategies using highly monodisperse nanoscale building blocks and clusters have been studied for templated growth, including using transition metal clusters as 'super atoms' to create lattices that are not obtainable through a thermodynamic strategy.[30] More commonly in the colloidal semiconductor literature is the strategy of oriented attachment.[31] The use of highly monodisperse building blocks to create nanorods, nanowires, and more complex structures has the potential to create useful and novel materials difficult to access through colloidal growth or vapor deposition.

We hypothesize that the novel crystal structure of the InP cluster is well suited for kinetically-controlled oriented attachment along its primary axis. We selected $P(SiMe_3)_3$ to promote this conversion as it serves dual purposes of stripping the tightly bound X-type ligands and adding P_{3-} to bridge the In-rich surfaces between two clusters. The titration of $P(SiMe_3)_3$ into a cluster solution was monitored using *in-situ* UV-Vis and revealed a continuous growth profile at temperatures as low as 35 °C, significantly below the temperature for cluster thermolysis and re-nucleation.

This strategy results in primarily spherical, 3 nm diameter QDs and is size-tunable based on the amount of $P(SiMe_3)_3$ added, observations which are contrary to the expectations of a stepwise-oriented attachment mechanism. Despite this, the cluster phase was preserved as determined by powder XRD and Raman and $_{31}P$ solid-state NMR spectroscopies. A closer examination of the absorbance data reveals three distinct reaction regimes as a function of $P(SiMe_3)_3$ concentration: induction, growth, and loss of colloidal stability. To investigate how the growth was deviating from our hypothesis we replicated the induction stage at lower temperature and concentration. Upon completion we observed a blueshift of 0.3 eV and, by $_{31}P$ NMR spectroscopy, determined that the original cluster had converted to a smaller and more symmetric cluster which we assign $In_{29}P_{14}$. The spherical morphology and absence of unassigned phosphorus species in the $_{31}P$ NMR suggests that particle growth results from these etched cores aggregating with each other and with liberated monomer species, ultimately templating the initial non-thermodynamic phase.

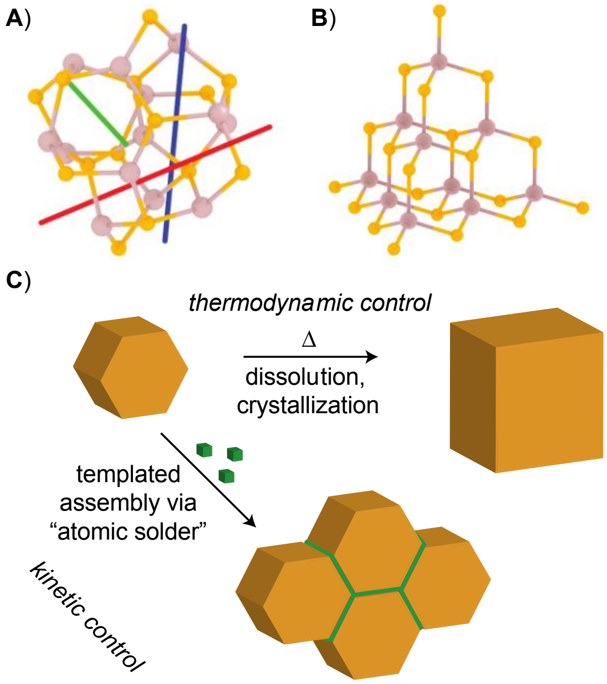


Figure 3. A) The structure of the cluster-phase with selected polytwistane axes shown. B) The bulk phase zincblende lattice. C) Scheme differentiating traditional thermally-driven re-nucleation of InP clusters to QDs (thermodynamic control) versus the templated assembly (cluster etching and aggregation) observed in the low-temperature, $P(SiMe_3)_3$ route (kinetic control).

Clusters as models for post-synthetic reaction chemistry

Beyond the application of clusters as nanomaterial precursors, atomically precise clusters provide a unique opportunity to take advantage of the spectroscopic handles that accompany a well-defined inorganic core and organic ligand network. In particular, compositional tailoring of nanoscale colloids has been highlighted as an aspect of synthetic chemistry that can lead to emergent properties of materials that would normally be unattainable in the binary semiconductor. Atomically precise clusters serve as ideal, mono-disperse and well defined models for elucidating the mechanism of ion exchange and assessing the properties of the resulting doped and alloyed structures.

With respect to InP nanocrystals, attempts to tune the cationic composition through alloying have taken two distinct approaches, the first of which involves the mixing of multiple metallic monomer species before the QD nucleation event (Figure 4A), which necessitates that the reactivity of the precursors be well-matched.[32] Thus far, this approach has sacrificed control of the dopant atom location in favor of a facile synthetic method that offers control over InP optical properties. The second method takes a reverse approach to InP cation exchange by utilizing pre-formed metal phosphide nanostructures as the anionic template for insertion of indium (Figure 4B). These examples include $Cu_{3-x}P$ and Cd_3P_2 as the foundation for this reverse-type cation exchange where nearly composition-pure InP nanostructures were achieved.[33,34] In the case of the Cd_3P_2 to InP phase transformation, the reverse ion exchange reaction (InP to Cd_3P_2) were highly unfavored, highlighting the inertness of the InP lattice to cation exchange.[33] Our related work with Z-type (neutral Lewis acid) ligand exchange of cadmium and zinc Lewis acids on InP QDs also demonstrated this activation barrier towards cation exchange.[35] We observed cation exchange occurring predominantly on the surface of the particles and in the case of cadmium, evidence of coincident alloying to a minor degree. More recently, the Talapin group has reported cation exchange in InP at high temperature (450 °C) in molten salts.[36] This method was used to gain access to alloyed III-V nanostructures.

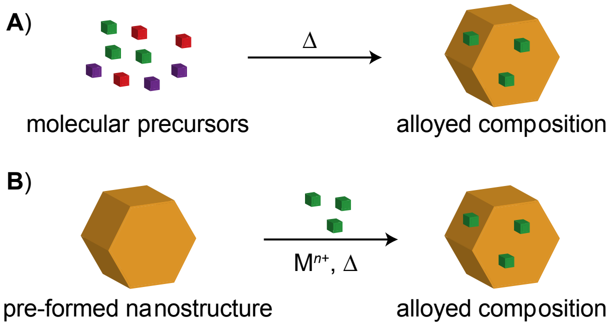


Figure 4. Bottom-up (A) and top-down (B) approaches to accessing mixed cationic compositions in InP nanostructures.

The advent of an atomically precise InP nanocluster was appealing to further probe the potential of cation exchange in materials with more covalent character. In our initial study,[37] cation exchange with Cd^{2+} did not result in atomically precise alloyed intermediates due to the non-site selective nature of addition, thus, the homogeneity of the starting material was essential in assigning the most probable reaction pathway. A complementary host of tools was employed in the analysis of intermediate structures, including optical and NMR spectroscopies and structural characterization (MS/PXRD/PDF/XPS). One of the unique aspects of this work was that full conversion to Cd_3P_2 nanoclusters was observed upon the room temperature addition of excess cadmium. This was an unexpected finding given the extreme reaction conditions alluded to in larger InP nanomaterial cation exchange reactions.

We were able to identify that the first site of exchange occurs at the so-called apical indium atoms (when the cluster is oriented along the molecular C_2 axis) by analyzing distinct changes observed in the ^{31}P NMR and UV-Vis spectra and supporting DFT calculations. From the initial reaction at this position, we hypothesized that the remaining surface-bound indium carboxylates would primarily undergo Z-type ligand exchange precluding core incorporation of cadmium (Figure 5). Nanocrystals in general can endure rather drastic changes in surface ligation while the bulk of the inorganic core is retained. The unmistakable cluster crystal phase, which serves as a structural fingerprint, allowed us to conclude that the inorganic core was conserved, which falls in line with the more traditional cation exchange reactions that are topotactic, i.e., the anion framework remains intact.[38]

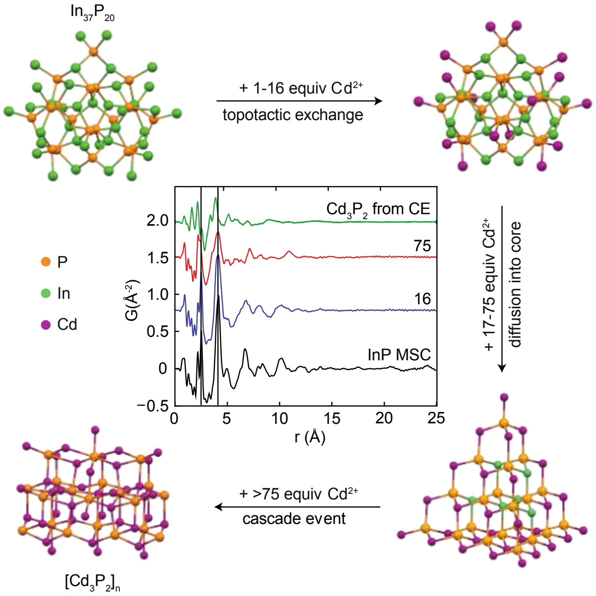


Figure 5. Schematic representation of the conversion of InP clusters to Cd_3P_2 clusters via cation exchange initiated by topotactic Z-type ligand exchange, followed by a series of cation concentration-dependent structural rearrangements, as supported in part by the included powder X-ray diffraction pair distribution function data. Adapted with permission from ref. 37. Copyright 2017 American Chemical Society.

If we consider the tetragonal Cd_3P_2 unit cell as an extension of the cubic lattice then it is not surprising that following surface exchange, the InP clusters progress in a semi-continuous manner to Cd_3P_2.[39,40] The next step in this conversion involves the exchange of additional cadmium ions into the InP lattice, leading to relaxation of the nanocluster phase to a zincblende form, as observed through pair distribution function analysis.[13] The final stage of the reaction was most analogous to the phenomenon of cooperative cation exchange that is observed with the substitution of Cu^+ and Ag^+ in cadmium chalcogenide lattices.[41,42] As the level of incorporated cadmium reaches a critical level in the alloyed InP, an abrupt cascade of exchange reactions accelerated the structure towards tetragonal Cd_3P_2.

In order for a cation exchange reaction and structural transformation of this nature to be plausible at room temperature, we refer to other examples of room temperature cation exchange and find that in several cases, the reorganization of the lattice tends to occur to relieve existing strain.[43,44] In the context of the InP nanocluster, our characterization has made it clear that there is a degree of strain that is the predominant driving force of these reactions following disruption of the surface via Z-type ligand exchange. Within the known InP cation exchange chemistry, these results demonstrate a unique avenue to alloyed materials that may be useful in either evaluating the properties conferred by more complex compositions, or more directly, in accessing a variety of compositional alloys in larger nanocrystals via use of these clusters as single-source precursors.

Among the number of cation exchange reactions performed on nanoclusters, the only other examples of truly atomically precise starting materials are based on tetrameric metal thiolate clusters.[45] Kittilstved and co-workers were able to assign the site-specific incorporation of dopant Mn^{2+} ions (surface vs core) and accompanying outward-diffusion of dopants over time, contributing valuable insight to the rational design of larger doped nanocrystals.[46] Other noteworthy research has centered on the doping and alloying of stoichiometric CdSe nanocluster species, whose specific compositions are inferred by non-crystallographic methods. These clusters have been examined as not only Mn^{2+}-doped and alloyed precursors to nanomaterials,[47] but as a model to probe the cooperative nature of Cu^{+} cation exchange observed in larger CdSe nanocrystals.[48]

Surface chemistry

At the heart of all cluster conversion chemistry are reactions initiated at the surface of the cluster. From cluster dissolution *en route* to QD formation, or cation exchange within the intact cluster lattice, the understanding and control of surface chemistry is essential in synthesizing high-performance materials. The well-defined crystalline structure, known stoichiometry, and presence of both X-type and Z-type stabilizing ligands make the $In_{37}P_{20}$ cluster an ideal model system for studying nanomaterial surface chemistry. The complex coordination network that results from the exclusively bridging carboxylate ligands precludes straightforward predictions on the outcomes of simple ligand addition or exchange reactions (reactions summarized in Figure 6). Therefore, our lab has begun to study the role of surface chemistry in controlling the structure and reactivity of these InP clusters.

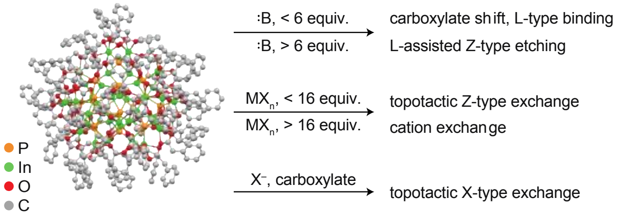


Figure 6. Examples of L, X, and Z-type ligand reactions at the $In_{37}P_{20}(O_2CR)_{51}$ cluster surface.

With a surface composed primarily of Lewis acidic indium carboxylate, the cluster is likely to react with L-type Lewis bases. In fact, the cluster reacts with adventitious water, resulting in a selective ligand rearrangement at the apical indium site in which a carboxylate ligand goes from bidentate to monodentate to accommodate water coordination.[18] This bidentate-to-monodentate rearrangement is the first step upon exposure to primary amines as well.[49] Upon addition of four equivalents of added amine, exfoliation of the two apical surface indium atoms resulted in a smaller, higher-symmetry cluster phase. This is analogous to the cluster etching process observed in the first step of the templated growth of polytwistane-phase InP discussed previously, which gave rise to a T-symmetry cluster intermediate, although in this case the product clusters appear less homogeneous in structure.

The addition of Lewis or Brønsted acids on the other hand, does not immediately result in deviation from the cluster crystal phase. Addition of 1-10 eq. of phenylacetic acid to a toluene solution of $In_{37}P_{20}(O_2CCH_2C_6H_5)_{51}$ resulted in only a slight blue-shift of the cluster excitonic feature. A similar blue shift is observed upon adding 50 equivalents of indium carboxylate to the cluster, similar to the etching process we have previously described for Zn_3P_2 nanocrystals.[50]

To learn more about the dynamics at the cluster surface, an isotopically labelled cluster was synthesized using isotopically pure $PhCH_2{}^{13}CO_2H$.[21] The ^{13}C NMR spectrum of the labeled cluster displays resonances only of the carboxylate carbons, in a range from 180-185 ppm in a static exchange regime at room temperature. The ^{13}C NMR spectrum coalesces upon heating to 80 °C, indicating intramolecular ligand rearrangement and exchange. The low-exchange regime is reestablished upon cooling to room temperature. Variable temperature *in-situ* UV-Vis spectra of the cluster from 25 - 100 °C indicates redshifts consistent with thermal expansion but not with chemical or physical rearrangement, an observation that is also consistent with the variable temperature ^{31}P NMR spectrum. Taken together, these data indicate that at temperatures below 100 °C, the cluster core remains intact, while the surface is in dynamic exchange. The degenerate exchange of phenylacetic acid with surface phenylacetate was also examined by ^{13}C NMR spectroscopy by adding increasing equivalents of $PhCH_2{}^{13}CO_2H$ to natural abundance $In_{37}P_{20}(O_2CH_2Ph)_{51}$ cluster. Upon addition of only one equivalent of the labeled carboxylic acid, non-selective exchange is observed, indicating that even at low concentrations of exogenous acid relative to cluster, surface chemistry exchange is facile at room temperature.

Upon changing the surface ligands of the cluster from carboxylate to phosphonate, a significant departure in reactivity is observed. Octadecylphosphonate-ligated clusters (ODPA clusters) can be prepared directly from the carboxylate clusters and are significantly more thermally stable, and are also structurally distinct.[16] The ^{31}P NMR spectrum for the ODPA cluster indicates a broad resonance in the phosphide region (-200 to -250 ppm), and broad resonances from 10-40 ppm, which we assign to a mixture of multiply chelating phosphonate and phosphonic anhydride ligands on the cluster surface that contribute to the cluster stability. The high thermal stability of the phosphonate cluster precludes its use as single-source precursors to make InP QDs, highlighting the importance of surface chemistry in QD synthesis. Furthermore, the crystal phase of the phosphonate clusters matches well with zincblende InP, as opposed to the unique cluster phase seen with the carboxylate clusters. A similar structure difference is observed in InP QDs, where QDs synthesized using carboxylate ligands generally tend to be spherical, while InP QDs synthesized using halide and amine ligands are tetrahedral.[51,52]

The cation exchange process detailed in the previous section is also initiated via surface ligand exchange. In a similar way that indium carboxylate interacts with the cluster surface, cadmium carboxylate also interacts, initiating the process of cation exchange. This process of In^{3+} for Cd^{2+} exchange is accompanied by an overall reduction in ligand density at the cluster surface, which inevitably renders the material less stable and more prone to further transformation. This trend is consistent with observations in larger InP nanocrystals, although the degree of cation diffusion is significantly more limited following Z-type ligand exchange with zinc and cadmium.[35] Compositional analysis and ^1H NMR spectroscopy indicated that the exchanged Z-type ligands were robustly bound to the InP surface following column purification and further X-type ligand exchange.[53] Intriguingly, in the larger InP nanocrystals, this Z-type ligand exchange was observed to have a remarkable impact on the optical properties of the QDs. While the role of surface chemistry on optical properties and reactivity has been extensively explored within the metal chalcogenide family,[54,55] similar trends with InP are generally lacking.

Conclusions and Prospectus

Hopefully we have convinced you that cluster science is a structurally rich and mechanistically insightful area of chemistry. When it comes to the synthesis of colloidal nanocrystals, like semiconductor QDs, clusters represent not only intermediates along the crystallization pathway, but also robust and atomically-precise models for reaction chemistry. In order for this approach to studying semiconductor nanomaterials to flourish, additional synthetic and theoretical effort is needed to deduce the principles that govern cluster stability and structure. This includes developing a quantitative understanding of ligand exchange chemistries at cluster surfaces. In addition, generalizable methods for rigidifying the ligand shell are needed to enable characterization by single crystal X-ray diffraction methods. If these two challenges are met, then a whole field of cluster science will open up that will enable the discovery of new nanoscale phases and compositions, as well as quantitative and precise mechanistic understanding of colloid surface chemistry.

Biographical Information

Dr. Max Friedfeld obtained his B.S. in Chemistry from the University of Virginia in 2011. Max went on to receive his Ph.D. in Chemistry from Princeton University in 2016 under the mentorship of Professor Paul Chirik where he studied cobalt-catalyzed asymmetric hydrogenation reactions. He is currently a Washington Research Foundation postdoctoral fellow at the University of Washington, studying nanomaterial nucleation and growth mechanisms under the mentorship of Professor Brandi Cossairt.

Jennifer Stein obtained her B. S. in Chemistry in 2013 from Pacific Lutheran University, a small liberal arts university located in the tranquil Pacific Northwest. Jennifer journeyed north to the

University of Washington where she received her Ph.D. in 2018 working under the guidance of Professor Brandi Cossairt. Jennifer has recently joined Professor Jill Millstone’s lab at the University of Pittsburgh as a postdoctoral associate to focus on the role that precursor complexes play in dictating metal nanoparticle structures.

Andrew Ritchhart obtained his B.S. in Chemistry from the University of Illinois in 2015. There he studied thermodynamic binding processes of proteins to gold nanoparticles in Professor Catherine Murphy’s lab. Since 2015 he has been pursuing his Ph.D. at the University of Washington as a member of Professor Brandi Cossairt’s lab where he studies non-classical growth and surface chemistry of nanoscale InP.

Dr. Brandi Cossairt received her B. S. in Chemistry from the California Institute of Technology in 2006 as a first-generation college graduate. Brandi went on to receive her Ph.D. in 2010 from the Massachusetts Institute of Technology under the guidance of Professor Christopher Cummins. She then continued her academic training as an NIH NRSA Postdoctoral Fellow at Columbia University in the laboratory of Professor Jonathan Owen. Brandi joined the Department of Chemistry at the University of Washington as an Assistant Professor in 2012. She has received a number of awards for her research including a Packard Fellowship, a Sloan Research Fellowship, and an NSF CAREER Award. Brandi is an associate editor at Inorganic Chemistry and is the co-founder of the Chemistry Women Mentorship Network.

Acknowledgments

We would like to gratefully acknowledge support from the National Science Foundation (CHE-1552164, BMC and AR; DMR-1719797, JLS), the David and Lucile Packard Foundation, and the Washington Research Foundation (MRF) for support during the writing of this accounts article.

References

(1) Castleman, A. W.; Jena, P. Clusters: A Bridge between Disciplines. *Proc. Natl. Acad. Sci.* **2006**, *103*, 10552–10553.

(2) Castleman, A. W. J.; Bowen, K. H. J. Clusters: Structure, Energetics, and Dynamics of Intermediate States of Matter. *J. Phys. Chem.* **1996**, *100*, 12911–12944.

(3) Schnockel, H. Structures and Properties of Metalloid Al and Ga Clusters Open Our Eyes to the Diversity and Complexity of Fundamental Chemical and Physical Processes During Formation and Dissolution of Metals. *Chem. Rev.* **2010**, *110*, 4125–4163.

(4) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C60: Buckminsterfullerene. *Nature* **1985**, *318*, 162–163.

(5) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116*, 10346–10413.

(6) Corrigan, J. F.; DeGroot, M. W. Large Semiconductor Molecules. In *The Chemistry of Nanomaterials: Synthesis, Properties and Applications*; Rao, C. N. R., Muller, A., Cheetham, A. K., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 418–451.

(7) McBride, J. R.; Dukes, A. D. I.; Schreuder, M. A.; Rosenthal, S. J. On Ultrasmall Nanocrystals. *Chem. Phys. Lett.* **2010**, *498*, 1–9.

(8) Friedfeld, M. R.; Stein, J. L.; Cossairt, B. M. Main-Group-Semiconductor Cluster Molecules as Synthetic Intermediates to Nanostructures. *Inorg. Chem.* **2017**, *56*, 8689–8697.

(9) Behrens, S.; Bettenhausen, M.; Deveson, A. C.; Eichhöfer, A.; Fenske, D.; Lohde, A.; Woggon, U. Synthesis and Structure of the Nanoclusters [Hg$_{32}$Se$_{14}$(SePh)$_{36}$], [Cd$_{32}$Se$_{14}$(SePh)$_{36}$(PPh$_3$)$_4$],[P(Et)$_2$(Ph)C$_4$H$_8$OSiMe$_3$]$_5$[Cd$_{18}$I$_{17}$(PSiMe$_3$)$_{12}$], and [N(Et)$_3$C$_4$H$_8$OSiMe$_3$]$_5$[Cd$_{18}$I$_{17}$(PSiMe$_3$)$_{12}$]. *Angew. Chem. Int. Ed.* **1996**, *35*, 2215–2218.

(10) Jiang, Z.-J.; Kelley, D. F. Role of Magic-Sized Clusters in the Synthesis of CdSe Nanorods. *ACS Nano* **2010**, *4*, 1561–1572.

(11) Kudera, S.; Zanella, M.; Giannini, C.; Rizzo, A.; Li, Y.; Gigli, G.; Cingolani, R.; Ciccarella, G.; Spahl, W.; Parak, W. J.; et al. Sequential Growth of Magic-Size CdSe Nanocrystals. *Adv. Mater.* **2007**, *19*, 548–552.

(12) Liu, Y.-H.; Wang, F.; Wang, Y.; Gibbons, P. C.; Buhro, W. E. Lamellar Assembly of Cadmium Selenide Nanoclusters into Quantum Belts. *J. Am. Chem. Soc.* **2011**, *133*, 17005–17013.

(13) Beecher, A. N.; Yang, X.; Palmer, J. H.; LaGrassa, A. L.; Juhas, P.; Billinge, S. J. L.; Owen, J. S. Atomic Structures and Gram Scale Synthesis of Three Tetrahedral Quantum Dots. *J. Am. Chem. Soc.* **2014**, *136*, 10645–10653.

(14) Cossairt, B. M. Shining Light on Indium Phosphide Quantum Dots: Understanding the Interplay among Precursor Conversion, Nucleation, and Growth. *Chem. Mater.* **2016**, *28*, 7181–7189.

(15) Gary, D. C.; Glassy, B. A.; Cossairt, B. M. Investigation of Indium Phosphide Quantum Dot Nucleation and Growth Utilizing Triarylsilylphosphine Precursors. *Chem. Mater.* **2014**, *26*, 1734–1744.

(16) Gary, D. C.; Terban, M.; Billinge, S. J. L.; Cossairt, B. M. Two-Step Nucleation and Growth of InP Quantum Dots via Magic-Sized Cluster Intermediates. *Chem. Mater.* **2015**, *27*, 1432–1441.

(17) Gary, D. C.; Cossairt, B. M. Role of Acid in Precursor Conversion During InP Quantum Dot Synthesis. *Chem. Mater.* **2013**, *25*, 2463–2469.

(18) Gary, D. C.; Flowers, S. E.; Kaminsky, W.; Petrone, A.; Li, X.; Cossairt, B. M. Single Crystal and Electronic Structure of a 1.3 nm Indium Phosphide Nanocluster. *J. Am. Chem. Soc.* **2016**, *138*, 1510–1513.

(19) Xie, R.; Li, Z.; Peng, X. Nucleation Kinetics vs Chemical Kinetics in the Initial Formation of Semiconductor Nanocrystals. *J. Am. Chem. Soc.* **2009**, *131*, 15457–15466.

(20) Yang, X.; Zhao, D.; Leck, K.; Tan, S.; Tang, Y.; Zhao, J.; Demir, H.; Sun, X. Full Visible Range Covering InP/ZnS Nanocrystals with High Photometric Performance and Their Application to White Quantum Dot Light-Emitting Diodes. *Adv. Mater.* **2012**, *24*, 4180–4185.

(21) Friedfeld, M. R.; Johnson, D. A.; Cossairt, B. M. On the Conversion of InP Clusters to Quantum Dots. *Under Review*.

(22) Norako, M. E.; Brutchey, R. L. Synthesis of Metastable Wurtzite $CuInSe_2$ Nanocrystals. *Chem. Mater.* **2010**, *22*, 1613–1615.

(23) Deng, Z.; Han, D.; Liu, Y. Colloidal Synthesis of Metastable Zinc-Blende IV–VI SnS Nanocrystals with Tunable Sizes. *Nanoscale* **2011**, *3*, 4346.

(24) Osorio-Cantillo, C.; Perales-Perez, O. Synthesis and Characterization of Metastable Nanocrystalline Cobalt. *J. Appl. Phys.* **2009**, *105*, 07A332.

(25) Schnöckel, H. Structures and Properties of Metalloid Al and Ga Clusters Open Our Eyes to the Diversity and Complexity of Fundamental Chemical and Physical Processes during Formation and Dissolution of Metals. *Chem. Rev.* **2010**, *110*, 4125–4163.

(26) Ganguly, S.; Kazem, N.; Carter, D.; Kauzlarich, S. M. Colloidal Synthesis of an Exotic Phase of Silicon: The BC_8 Structure. *J. Am. Chem. Soc.* **2014**, *136*, 1296–1299.

(27) Glassy, B. A.; Cossairt, B. M. Resolving the Chemistry of Zn_3P_2 Nanocrystal Growth. *Chem. Mater.* **2016**, *28*, 6374–6380.

(28) Barua, S. R.; Quanz, H.; Olbrich, M.; Schreiner, P. R.; Trauner, D.; Allen, W. D. Polytwistane. *Chem. – Eur. J.* **2014**, *20*, 1638–1645.

(29) Olbrich, M.; Mayer, P.; Trauner, D. Synthetic Studies toward Polytwistane Hydrocarbon Nanorods. *J. Org. Chem.* **2015**, *80*, 2042–2055.

(30) Vossmeyer, T.; Reck, G.; Katsikas, L.; Haupt, E. T. K.; Schulz, B.; Weller, H. A "Double-Diamond Superlattice" Built Up of $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ Clusters. *Science* **1995**, *267*, 1476–1479.

(31) Quan, Z.; Valentin-Bromberg, L.; Loc, W. S.; Fang, J. Self-Assembly of Lead Chalcogenide Nanocrystals. *Chem. Asian J.* *6*, 1126–1136.

(32) Tamang, S.; Lincheneau, C.; Hermans, Y.; Jeong, S.; Reiss, P. Chemistry of InP Nanocrystal Syntheses. *Chem. Mater.* **2016**, *28*, 2491–2506.

(33) Beberwyck, B.; Alivisatos, A. Ion Exchange Synthesis of III–V Nanocrystals. *J. Am. Chem. Soc.* **2012**, *134*, 19977–19980.

(34) De Trizio, L.; Gaspari, R.; Bertoni, G.; Kriegel, I.; Moretti, L.; Scotognella, F.; Maserati, L.; Zhang, Y.; Messina, G. C.; Prato, M.; et al. $Cu_{3-x}P$ Nanocrystals as a Material Platform for Near-Infrared Plasmonics and Cation Exchange Reactions. *Chem. Mater.* **2015**, *27*, 1120–1128.

(35) Stein, J. L.; Mader, E. A.; Cossairt, B. M. Luminescent InP Quantum Dots with Tunable Emission by Post-Synthetic Modification with Lewis Acids. *J. Phys. Chem. Lett.* **2016**, *7*, 1315–1320.

(36) Srivastava, V.; Kamysbayev, V.; Hong, L.; Dunietz, E.; Klie, R. F.; Talapin, D. V. Colloidal Chemistry in Molten Salts: Synthesis of Luminescent $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ Quantum Dots. *J. Am. Chem. Soc.* **2018**, *140*, 12144–12151.

(37) Stein, J. L.; Steimle, M. I.; Terban, M. W.; Petrone, A.; Billinge, S. J. L.; Li, X.; Cossairt, B. M. Cation Exchange Induced Transformation of InP Magic-Sized Clusters. *Chem. Mater.* **2017**, *29*, 7984–7992.

(38) De Trizio, L.; Manna, L. Forging Colloidal Nanostructures via Cation Exchange Reactions. *Chem. Rev.* **2016**, *116*, 10852–10887.

(39) Adolphi, N. L.; Stoddard, R. D.; Goel, S. C.; Buhro, W. E.; Gibbons, P. C.; Conradi, M. S. The ^{31}P NMR Spectra of Cd_3P_2 and Zn_3P_2. *J. Phys. Chem. Solids* **1992**, *53*, 1275–1278.

(40) Wang, R.; Ratcliffe, C. I.; Wu, X.; Voznyy, O.; Tao, Y.; Yu, K. Magic-Sized Cd_3P_2 II−V Nanoparticles Exhibiting Bandgap Photoemission. *J. Phys. Chem. C* **2009**, *113*, 17979–17982.

(41) Ott, F. D.; Spiegel, L. L.; Norris, D. J.; Erwin, S. C. Microscopic Theory of Cation Exchange in CdSe Nanocrystals. *Phys. Rev. Lett.* **2014**, *113*, 156803.

(42) White, S. L.; Smith, J. G.; Behl, M.; Jain, P. K. Co-Operativity in a Nanocrystalline Solid-State Transition. *Nat. Commun.* **2013**, *4*, 2933.

(43) Xie, Y.; Bertoni, G.; Riedinger, A.; Sathya, A.; Prato, M.; Marras, S.; Tu, R.; Pellegrino, T.; Manna, L. Nanoscale Transformations in Covellite (CuS) Nanocrystals in the Presence of Divalent Metal Cations in a Mild Reducing Environment. *Chem. Mater.* **2015**, *27*, 7531–7537.

(44) Min, Y.; Moon, G. D.; Park, J.; Park, M.; Jeong, U. Surfactant-Free $CuInSe_2$ Nanocrystals Transformed from In_2Se_3 Nanoparticles and Their Application for a Flexible UV Photodetector. *Nanotechnology* **2011**, *22*, 465604.

(45) Pittala, S.; Kittilstved, K. R. Cation Exchange in Small ZnS and CdS Molecular Analogues. *Inorg. Chem.* **2015**, *54*, 5757–5767.

(46) Kato, F.; Kittilstved, K. R. Site-Specific Doping of Mn^{2+} in a CdS-Based Molecular Cluster. *Chem. Mater.* **2018**, *30*, 4720–4727.

(47) Yang, J.; Muckel, F.; Baek, W.; Fainblat, R.; Chang, H.; Bacher, G.; Hyeon, T. Chemical Synthesis, Doping, and Transformation of Magic-Sized Semiconductor Alloy Nanoclusters. *J. Am. Chem. Soc.* **2017**, *139*, 6761–6770.

(48) White, S. L.; Banerjee, P.; Chakraborty, I.; Jain, P. K. Ion Exchange Transformation of Magic-Sized Clusters. *Chem. Mater.* **2016**, *28*, 8391–8398.

(49) Gary, D. C.; Petrone, A.; Li, X.; Cossairt, B. M. Investigating the Role of Amine in InP Nanocrystal Synthesis: Destabilizing Cluster Intermediates by Z-Type Ligand Displacement. *Chem. Commun.* **2016**, *53*, 161–164.

(50) Glassy, B. A.; Cossairt, B. M. Resolving the Chemistry of Zn_3P_2 Nanocrystal Growth. *Chem. Mater.* **2016**, *28*, 6374–6380.

(51) Kim, K.; Yoo, D.; Choi, H.; Tamang, S.; Ko, J.-H.; Kim, S.; Kim, Y.-H.; Jeong, S. Halide–Amine Co-Passivated Indium Phosphide Colloidal Quantum Dots in Tetrahedral Shape. *Angew. Chem. Int. Ed.* **2016**, *55*, 3714–3718.

(52) Tessier, M. D.; Dupont, D.; De Nolf, K.; De Roo, J.; Hens, Z. Economic and Size-Tunable Synthesis of InP/ZnE (E = S, Se) Colloidal Quantum Dots. *Chem. Mater.* **2015**, *27*, 4893–4898.

(53) Roberge, A.; Stein, J. L.; Shen, Y.; Cossairt, B. M.; Greytak, A. B. Purification and In Situ Ligand Exchange of Metal-Carboxylate-Treated Fluorescent InP Quantum Dots via Gel Permeation Chromatography. *J. Phys. Chem. Lett.* **2017**, *8*, 4055–4060.

(54) Anderson, N. C.; Owen, J. S. Soluble, Chloride-Terminated CdSe Nanocrystals: Ligand Exchange Monitored by ^{1}H and ^{31}P NMR Spectroscopy. *Chem. Mater.* **2013**, *25*, 69–76.

(55) Kroupa, D. M.; Vörös, M.; Brawand, N. P.; McNichols, B. W.; Miller, E. M.; Gu, J.; Nozik, A. J.; Sellinger, A.; Galli, G.; Beard, M. C. Tuning Colloidal Quantum Dot Band Edge Positions through Solution-Phase Surface Chemistry Modification. *Nat. Commun.* **2017**, *8*, 15257.