Formation Mechanism of Monodisperse Colloidal Semiconductor Quantum Dots

A Study of Nanoscale Nucleation and Growth

Matthew William Greenberg

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy under the Executive Committee of the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2020
ABSTRACT

Formation Mechanism of Monodisperse Colloidal Semiconductor Quantum Dots

A Study of Nanoscale Nucleation and Growth

Matthew William Greenberg

Since the fortuitous discovery of the existence of quantum size effects on the band structure of colloidal semiconductor nanocrystals, the development of synthetic methods that can form nanoscale crystalline materials of controllable size, shape, and composition has blossomed as an empirical scientific achievement. The fact that the term “recipe” is commonly used within the context of describing these synthetic methods is indicative of the experimentally driven nature of the field. In this respect, the highly attractive photophysical properties of semiconductor nanocrystals—as cheap wavelength tunable and high quantum yield absorbers and emitters of light for various applications in lighting, biological imaging, solar cells, and photocatalysis—has driven much of the interest in these materials. Nevertheless, a more rigorously predictive first-principles-grounded understanding of how the basic processes of nanocrystal formation (nucleation and growth) lead to the formation of semiconductor nanocrystals of desired size and size dispersity remains an elusive practical and fundamental goal in materials chemistry. In this thesis, we describe efforts to directly study these dynamic nucleation and growth processes for lead chalcogenide nanoparticles, in many cases in-situ, using a mixture of X-ray scattering and UV-Vis/NIR spectroscopy.

The lack of a rigorously predictive and verified mechanism for nanocrystal formation in solution for many material systems of practical interest is due both to the inherent kinetic
complexity of these reactions, as well as the spectroscopic challenge of finding in-situ probes that can reliably monitor nanoscale crystal growth. In particular, required are direct time-resolved structural probes of metastable inorganic amorphous and crystalline intermediates formed under the high temperature inert conditions of nanocrystal synthesis. It is, at the very least, highly challenging to apply many of the standard spectroscopic tools of mechanistic inorganic and organic chemistry such as \(^1\)H NMR spectroscopy, IR vibrational spectroscopy, and mass spectrometry to this task. A notable counterexample is, of course, UV-vis/NIR absorbance and emission spectroscopies, which are of great value to the studies described herein. Nevertheless, to address this relative dearth of conventional spectroscopic probes, here we explore the use of X-ray Total Scattering real space Pair Distribution Function (PDF) analysis and Small Angle X-ray Scattering (SAXS) techniques to directly probe the crystallization process in-situ. Time-resolved measurements of the small angle reciprocal space scattering data allow mapping of the time evolution of the colloidal size and concentration of the crystals during synthesis, while the Fourier transform of scattering data over a wide range of reciprocal space provides direct insight into the local structure. Through this approach, we compare direct observations of these nucleation and growth processes to the widely cited theoretical models of these processes (Classical Nucleation Theory and LaMer “Burst Nucleation”) and find a number of stark differences between these widely cited theories and our experiments.

The first two chapters cover the results of these in-situ diffraction studies. Chapter 1 focuses on small angle X-ray scattering data collection and modeling. Chapter 2 focuses upon lead sulfide and lead selenide real space PDF analysis of local structural evolution during synthesis. Finally, Chapter 3 discusses a project in which we examine the origins of emergent semiconducting electronic structure in an increasing size series of atomically precise oligomers of
[Ru₆C(CO)₁₆]²⁻ bridged by Hg²⁺ and Cd²⁺ atoms. Using an atomically well-defined series of molecules that bridge the small molecule and nanoscale size regimes, we discuss the factors that give rise to controllable semiconductor electronic structure upon assembly into extended periodic structures in solution. In all these projects, we seek to highlight the value of applying concepts of molecular inorganic chemistry—ligand binding models, relative bond strengths, in addition to kinetics and thermodynamics—to explain our observations regarding nanocrystal nucleation and growth. Consideration of the chemistry of nanocrystal formation processes provides a valuable compliment to the physics-based classical models of nucleation and growth that do not explicitly consider the system specific molecular structure and bonding.
# TABLE OF CONTENTS

Acknowledgments (ii)

Dedication (v)

**Chapter 1. Small Angle Scattering Measurements of PbS Nanocrystal Nucleation and Growth** (1)

**Chapter 2. Total Scattering Real Space Pair Distribution Function Analysis Measurements of PbS and PbSe Nanocrystal Nucleation and Growth** (81)

**Chapter 3. Emergence of Semiconductor Electronic Structure in Hg$^{2+}$- and Cd$^{2+}$-Linked [Ru$_6$C(CO)$_{16}$]$^{2-}$ Oligomers** (139)
Acknowledgments

I will begin my acknowledgments with an unspecific but undoubtedly necessary apology: sorry to whoever I forget to thank! When my time as a graduate student at Columbia working in the Owen group felt successful (or the many different useful flavors of life outside of successful we’ll call “interesting”) it was always in part due to the active advice, support, and friendship of many different people in this community. With this in mind, I will start by thanking my advisor Jonathan Owen for supporting me these last five years and imparting on me the value of taking one’s work and the truth of one’s work seriously. Jonathan Owen directed me towards many exciting directions and avenues in my research that I would never have thought of myself and probably would not have had a chance to experience in many other labs. He pushes his students to embrace the unfamiliar as guideposts for where science that hasn’t been done and is worth doing should point, and there’s a lot of value to that. It has been a pleasure.

There are many colleagues in the lab who I am happy to get a chance to thank as well. When I started out at Columbia, Alex Beecher was tasked with teaching me right from wrong in lab. He is an almost impossibly easy guy to get along with, and was always willing to talk through a new experiment with me even as he was getting ready to graduate. I appreciated his advice and friendship, and am very happy he did finally get his Carhaart jacket back. Peter Chen and Mike Campos were just below Beecher in the lab during my early years. Campos was always an estimable combination of inspiring focus and drive in lab combined with an endless thirst for bizarre memes. Describing Peter Chen to outside observers would likely require years of study and a separate chapter in this thesis, so I will merely observe that I really enjoyed our trips to metal bars and I still need to fix those speakers… Leslie Hamachi was another early mentor and friend
in lab, and I am glad we are still close today. She is one of the most hardest working people I have ever met. Looking forward to hearing about your exploits as you open up your lab this fall. I shared many laughs with Trevor and Iva over the years who were both really decent people to work with and always willing to engage with my societal polemics. Ellie and Brandon have also been a pleasure to work with. Brandon has been an awesome guy since I met him on his visiting weekend and has really stepped up in helping run the lab the last couple of years. Ellie is a pleasure to work with, and has loomed the halls of Brookhaven National Laboratory with me many a time. Natalie is an authentically warm and friendly person and has made our lab a much nicer place to be.

There were also many postdocs in the lab who I learned a lot from. Jonathan De Roo was a powerhouse of diffusion NMR, nanocrystal surface chemistry, and enfant terrible behavior. Anindya Swarnakar was a worthy foe in curry cook offs and a very knowledgeable synthetic chemist. Abe and Dan are our new resident synthetic inorganic transplants and are both great new additions to the lab. A number of collaborators also made this work possible. Sanjit Ghose helped facilitate a number of very challenging X-ray scattering experiments at BNL and I am looking forward to continuing to work with him in the years to come. Similarly, Benjamin Abécassis taught me a lot about small angle scattering and was part of the team working at ESRF. Plenty of other collaborators including Soham Banerjee, Max Terban, John Trunk, Jia Chen, Daniel Paley, and Vivekananda Bal also helped make this work possible. Friends in the department including Alex Radtke, Isaac Hughes, and David Sambade were also big sources of support and scientific advice. I also want to thank the chemistry department staff who help make the department run every day. Friends outside the department Alexander D’Alisera and Bryan Harris are acknowledged for their friendship and support. Craig Anderson, my undergraduate advisor and friend has been a great
source of support throughout grad school. Finally, thanks to my family for all of their love and support throughout the years.
Dedication

For Hope, Henry, Sarah, and Brian Greenberg
Chapter 1. Small Angle Scattering Measurements of PbS Nanocrystal Nucleation and Growth

Table of Contents

1.1. Introduction 3

1.1.1 Theory of Monodisperse Nanocrystal Synthesis: Nucleation 3
1.1.2 Theory of Monodisperse Nanocrystal Synthesis: Growth 8
1.1.3 Measuring Nanocrystal Nucleation and Growth 10
1.1.4 Small Angle Scattering of Nanocrystals 12

1.2. Acquisition of in-Situ SAXS during PbS Nanocrystal Formation 15

1.2.1 Synthesis of PbS Nanocrystals 15
1.2.2 Beamline Experimental Design and Setup 24
1.2.3 Data Collection and Reduction 26
1.2.4 Time Series Data Results 28

1.3. SAXS Data Modeling and Methods 32

1.3.1 Development and Implementation of Model 32
1.3.2 Analysis of Model and Assumptions 35
1.3.3 Model Results and Significance 43

1.4. Comparison to other Measurements 54

1.4.1 UV-Vis NIR/Aliquoting 54
1.4.2 NMR monitoring of Precursor Conversion 60
1.4.3 Comparison of UV-Vis, NMR kinetics 63

1.5. Population Balance Modeling of SAXS Results 65

1.5.1 Framework of PBM 65

1
1.5.2 Results of 1D PBM treatment

1.6. Summary

1.7. Experimental Details

1.7.1 Materials and Methods

1.7.2 Small Angle Scattering Beamline Experiments

1.7.3 Small Angle Scattering Modeling

1.7.4 Synthesis

1.7.5 UV-Vis/NIR Aliquoting of PbS Reactions

1.7.6 $^{13}$C NMR Aliquoting of PbS Reactions

1.7.7 1D PBE Modeling

1.8. References

Reproduced in part from

Prof. Benjamin Abécassis and Dr. Michael Campos are recognized for valuable contributions in helping carry out X-ray scattering experiments and Prof. Abécassis for data model development and modeling as is Dr. Vivekanada Bal and Prof. Baron Peter for population balance modeling of particle formation parameters extracted from diffraction data.
1.1. Introduction

1.1.1 Theory of Monodisperse Nanocrystal Synthesis: Nucleation

For nanocrystal synthesis in general, and particularly for quantum confined semiconductor nanocrystals, the ability to control nanocrystal ensemble average size and size dispersity produced by a given synthetic procedure is of paramount importance. With regard to controlling the light absorption and emission properties of a nanocrystal by the quantum confinement effect, control of the average size and size dispersity of the ensemble of nanocrystals produced by a synthesis provides control of both the position and linewidth of light absorption and photoluminescence.\(^1\)\(^-\)\(^3\) Furthermore, the importance of predictive synthetic control over average size and size dispersity is not limited to applications of nanocrystal science involving absorption or emission of light. For instance, the size dependent surface faceting, surface energy, and surface area fraction of nanocrystals makes synthetic control over nanoscale size of key importance to applications of nanocrystals in catalysis.\(^4\)\(^-\)\(^5\) Another motivation for such synthetic control is that the realization of novel collective electronic structure from ordered hierarchical assemblies of nanocrystal superlattices - including Dirac cone band structure - requires tight control over the size distribution of the individual building blocks.\(^6\)\(^-\)\(^7\)

Understanding the physical processes by which the initial nuclei of the final crystalline phase are formed, and then how these initial nuclei of the crystalline phase add further structural units to achieve their terminal size, is essential to a predictive science of nanocrystal synthesis. These processes are known as nucleation and growth respectively. The development of the dominant paradigms regarding how these nucleation and growth processes occur in the synthesis of monodisperse nanocrystals has been shaped by the historical experimental difficulty of measuring these dynamic processes directly, and the theoretical difficulty of modeling them \textit{ab}
initio at an atomic level. As such, the foundational theories of these processes were developed in the absence of corroborating in-situ measurements of the initial stages of nucleation and growth.

![Graph showing the time evolution of solute concentration during nanocrystal formation.](image)

**Figure 1.1.1** Solute concentration during solution formation of monodispersed particles as described by LaMer.⁸,⁹

Shown above in Figure 1.1.1 is perhaps the most recognizable visual representation of the modern theory of nanocrystal nucleation and growth – the largely qualitative representation of the time evolution of solute concentration during nanocrystal formation as described in the seminal work of LaMer and Dinegar.⁸,⁹ This highly influential work detailed the growth and size dispersity of sulfur sols on the 0.1-1 micron size scale generated by the decomposition of sodium thiosulfate in dilute hydrochloric acidic conditions and measured by modeling the visible light scattering of these particles using Mie theory.⁹⁻¹¹ The key significance of this work was their explanation of how the monodispersed colloidal particles could be formed. Briefly, sulfur is presumed to build up in concentration (I) until it reaches a “critical concentration” and nucleation of sulfur sols (II) begins at an effectively infinite rate rapidly plunging the sulfur concentration back below the critical concentration leading to a period of uniform growth (III) on the existing nuclei (Figure
1.1.1). In the LaMer mechanism, monodispersed particles are formed since the nuclei are all formed in a single “burst” that is effectively instantaneous, and temporally separated from the growth period.\textsuperscript{10}

The assumption that the nucleation rate is essentially a step function of the solute concentration resulting in a “burst” nucleation is a key part of the LaMer mechanism and the theoretical grounding for such an assumption was explicitly given by LaMer by referencing the Classical Nucleation Theory.\textsuperscript{9,10} Classical Nucleation Theory or CNT refers to a collection of theoretical results regarding the thermodynamics of phase transitions through the initial formation of small nuclei of the final stable phase, and the kinetic rates of such processes. Gibbs is acknowledged for first recognizing that formation of a new phase is related to the work required to create a “critical nucleus,” and the derivation of the rate of this process was then worked on decades later by Volmer, Weber, Becker, Döring, and Frenkel.\textsuperscript{12-15} The key result of the CNT is an expression for the nucleation rate $J$, which is derived from consideration of the kinetic barrier to form the smallest sized particle which is in thermodynamic equilibrium with the solution \textit{vide infra}.

The Gibbs free energy change of forming a nucleus of a nanocrystal can be expressed as the sum of a positive interfacial energy term and a negative bulk energy term (Eq. 1.1.1).

$$
\Delta G = \Delta G_{\text{bulk}} + \Delta G_{\text{surface}}
$$

\text{Eq. 1.1.1}

For a spherical nucleus one can write this expression as:

$$
\Delta G = -\frac{4\pi r^3 k_b T \ln(S)}{3 \nu} + 4\pi r^2 \gamma
$$

\text{Eq. 1.1.2}
where $\gamma$ is the surface free energy, $S = \frac{C}{C_{eq}}$ is the supersaturation or ratio of solute concentration $C$ to its equilibrium concentration $C_{eq}$, $\nu$ is molar volume, $r$ is the radius, and $k_BT$ is the product of the Boltzmann constant and temperature. The two competing functions in Eq. 1.1.2 lead to a global maxima $\Delta G_{\text{crit}}$ in $\Delta G$ as a function of $r$ as is illustrated in Figure 1.1.2. The maxima represents the “critical nucleus” which is the smallest size $r_{\text{crit}}$ for which further growth is thermodynamically downhill, and the formation of which represents the thermodynamic barrier to nucleation of the new phase.$^{16,17}$ Similar competing function arguments in the total $\Delta G$ can also be constructed without the assumption of a spherical geometry.$^{17,18}$

![Figure 1.1.2](image)

**Figure 1.1.2** $\Delta G$ of formation of a spherical nucleus around the critical nucleus size highlighting balance between $\Delta G_{\text{bulk}}$ and $\Delta G_{\text{surface}}$ contributions to the total free energy change.

The nucleation rate $J$ is the key result of CNT, and resembles the Arhennius equation with an activation barrier equal to the Gibbs free energy of forming the critical nucleus (Eq. 1.1.3).
\[ J = A \exp\left( -\frac{\Delta G_{\text{crit}}}{k_B T} \right) = A \exp\left( -\frac{16\pi \gamma^3 \nu^2}{3k_B^3T^3(\ln(S))^2} \right) \]  \hspace{1cm} \text{Eq. 1.1.3}

The preexponential factor \( A \) can be calculated within Becker-Döring theory in analogy to Transition State Theory.\(^{19}\) The terms within the exponential represent the main parameters which can be adjusted to influence the rate of nucleation temperature \( T \), supersaturation \( S \), and surface energy \( \gamma \).\(^ {16}\) Below in Figure 1.1.3 we plot the influence of supersaturation on the relative nucleation rate and see that the variation of this parameter results in a step-function like response of the nucleation rate at a critical threshold value of the solution supersaturation. This is the essence of the theoretical grounding of LaMer’s assumption of “Burst Nucleation” to explain the formation monodisperse ensembles of colloidal particles.\(^ {20}\)

**Figure 1.1.3** Normalized nucleation rate \( J \) from CNT as a function of the supersaturation around the “critical concentration.”
1.1.2 Theory of Monodisperse Nanocrystal Synthesis: Growth

While the concept of “Burst Nucleation” in the LaMer model of monodisperse nanocrystal formation is commonly invoked, it is important to note that the LaMer model makes assumptions about both nucleation and growth processes. A complete description of the time evolution of the particle size distribution must involve consideration of both the nucleation and growth processes. The widely cited basis for size distribution focusing during the growth process is due to growth by rate limiting diffusion of particles as described by Reiss and cited by LaMer.9-10,21 The classical mathematical theory of nanoparticle growth has been summarized in great detail by Tadao Sugimoto in numerous publications as well as a textbook.8,17,22-23 In general, these theories assume a colloidal particle grows by two limiting processes – the diffusion of solute towards the surface and the surface reaction of solute on that surface to add to the growing particles.24-26

For particles of submicron size undergoing Brownian motion during growth, a “diffusion layer” with a thickness δ forms around the particle, in which a gradient of solute concentration is formed between the solute concentration at the solid/liquid interface of the particle \( (C_i) \) with respect to the bulk solution concentration \( (C_b) \). It is further assumed that the size dependence of the nanocrystal solubility follows the Gibbs-Thomson equation (Equation 1.1.4) and diffusion of the solute to the surface follows Fick’s law of diffusion (Equation 1.1.5). 22,24-26

\[
C_r = C_\infty \exp\left(\frac{2\gamma v}{r k_b T}\right) \quad \text{Eq. 1.1.4}
\]

\[
\dot{n} = 4\pi x^2 D \frac{dC(x, t)}{dx} \quad \text{Eq. 1.1.5}
\]

Above, \( \dot{n} \) is the flux of solute that passes through a spherical surface with a radius \( x \), \( D \) is the diffusion coefficient, \( C \) is the concentration, and \( C_r \) is the solubility of a particle with a radius \( r \).
If diffusion is the rate limiting process the expression for the radial growth rate is (Eq. 1.1.6)

\[
\frac{dr}{dt} = D \nu \frac{(C_b - C_r)}{r}
\]  
Eq. 1.1.6

And for a rate limiting first order surface reaction the radial growth rate is (Eq. 1.1.7)

\[
\frac{dr}{dt} = k \nu (C_b - C_r)
\]  
Eq. 1.1.7

Clearly, these two expressions are limiting cases of the same general expression where either \( \frac{D}{k} \gg r \) or vice versa. In the latter case we clearly see that when diffusion of solute to the surface is the rate limiting process the radial growth rate is inversely dependent to the radius which leads to a focusing of the size distribution (decrease in the dispersity of the ensemble as the particles grow) in the size regime where the Gibbs-Thomson effect does not dominate (specifically the term \( C_b - C_r \)). In contrast, the expression for surface reaction limiting growth (Eq. 1.1.7) suggests that the size distribution will always be broadening in time.\(^{16,23}\)

The considerations above have led to a largely empirically untested belief that diffusion limited growth is operative in nanocrystal syntheses which produce monodisperse products\(^{20}\), as this was invoked explicitly in the studies of LaMer and leads to an analytical expression with an inverse radius dependence of the radial growth rate (Eq. 1.1.6).\(^9,10\) Ultimately, these expressions are derived from pencil and paper theory and the simplifying assumptions used to derive them may not be applicable to all systems. For instance, Eq. 1.1.7 assumes a single unimolecular reaction rate constant in solute for the surface reaction rate constant independent of particle size which is not obviously the case. Nevertheless, just like Classical Nucleation Theory, the simple qualitative results of the classical theory of growth have had a large influence on the dominant hypotheses used by nanocrystal scientists to explain outcomes of syntheses. The presence of diffusion limited
growth, where $\frac{dr}{dt}$ is inversely proportional to $r$, is often put forward to explain the narrowing of a size distribution during the growth process.\(^{20}\)

### 1.1.3 Measuring Nanocrystal Nucleation and Growth

The main theoretical underpinnings of nanocrystal nucleation and growth processes discussed above were developed largely in the absence of corroborating *in-situ* experimental observations.\(^{20}\) Developing a quantitative or even qualitative experimental measurement of the nucleation and growth process requires spectroscopic probes which can reliably measure nanocrystal structure, concentration, average size, and size dispersity as a function of time during a synthesis. The most commonly used techniques to provide time resolved measurements of these quantities are UV-Vis/NIR absorption and emission,\(^{27-31}\) X-ray diffraction and absorption techniques,\(^{32-35}\) and electron microscopy.\(^{36-38}\) Furthermore, the molecular reaction or series of molecular reactions that provide the rarely characterized metastable soluble material (or “solute”) that proceeds nucleation of the crystalline product is also an essential feature of these reactions to understand. These molecular reactions are often probed with NMR spectroscopy – in many cases by the use of heteronuclear NMR such as $^{31}$P NMR when possible thereby avoiding the need for large quantities of expensive perdeuterated derivatives of hydrocarbon solvents such as hexadecane used in nanocrystal synthesis.\(^{39,40}\) In addition to the references in the paragraph above that highlight examples of the use of various spectroscopic probes to measure nanocrystal nucleation and growth, it is also worth noting there are several recent reviews which address this topic.\(^{16,41,42}\)

UV-Vis/NIR absorption and emission spectroscopies are arguably the most widely used techniques for studying semiconductor nanocrystal and plasmonic noble metal nanocrystal
nucleation and growth due to their superior experimental time resolution, ease of measurement, and ability to measure key observables needed to understand these processes. Size dependence of the excitonic or plasmonic peak position allows in principle for the extraction of average size and size dispersity from relatively easily acquired measurements.\textsuperscript{43} Knowledge of the size dependent or size independent extinction coefficient further allows for calculation of concentration of the material of interest. The ability to practically perform these measurements is largely based on the availability and accuracy of empirical sizing curves which relate electronic transition energy to particle size in addition to size dependent and size independent extinction coefficients for the material system of interest in the literature.\textsuperscript{44-46}

Despite the advantages listed above, extracting polydispersity from UV-Vis/NIR data requires knowledge of the size dependence of the inherent linewidth of the electronic transitions which is not trivially measured, predicted, or widely available for many material systems.\textsuperscript{47} Moreover, one cannot use these optical measurements as direct probes of atomic level crystalline or amorphous structure without practically inaccessible \textit{ab initio} theory and sample purity for these systems. However, electron microscopy and diffraction techniques are able to provide complimentary evidence of the atomic level structure and polydispersity. TEM/STEM are often used and can provide size, size dispersity, and even atomic structure in some measurements although the statistical significance of these measurements as being representative of the entire ensemble of particles is problematic. Rigorously statistical ensemble measurements of Bragg and diffuse X-ray or neutron scattering are much more easily carried out in order to reveal atomic level structural details through either real or reciprocal space analysis.\textsuperscript{41,42} The colloidal size scale average size, nanocrystal average size and size dispersity, can be measured with Small Angle Scattering which we will address in some detail.\textsuperscript{48}
1.1.4 Small Angle Scattering of Nanocrystals

One of the essential features of any light scattering process, as is seen clearly in the well-known formula for the Bragg diffraction condition for periodic ordered crystal lattices, \( n\lambda = 2d \sin \theta \), is an inverse relationship between the repeat ordered distance \( d \) and the scattering angle \( \theta \) where diffraction is observed at a given wavelength of incident light \( \lambda \). The colloidal size regime which spans sizes between tens and thousands of angstroms is substantially larger than the X-ray wavelengths used in lab scale X-ray crystallography such as the Cu K-alpha of 1.54 angstroms that is used to probe unit cells of standard sized molecular crystals. As such, the characteristic scattering associated with repeat ordered distances of colloidal size scales will occur at scattering angles which are relatively “small” with respect to those seen in diffraction from atomic crystal lattices. To paraphrase Kratky in his textbook on the subject, we may say that the presence of small angle X-ray (SAXS) scattering in a diffraction experiment is both a necessary and sufficient condition of repeat ordered electron density inhomogeneities of colloidal size existing in the system under observation.\(^{49}\)
Figure 1.1.4 Schematic of Wide Angle X-ray Scattering (WAXS) from repeat ordered distances between atomic lattice planes, and Small Angle X-ray Scattering (SAXS) from a repeat ordered distance of a colloidal sized particle in solution with some electron density contrast $\Delta \rho$ (log-log plot to highlight form factor oscillations).

In describing the scattering of X-ray light by electrons, it is valuable to define a scattering vector $q = \frac{4\pi \sin \theta}{\lambda}$ which is used to describe the amplitude of the secondary waves emitted by electrons as $e^{iq \cdot R}$. In small angle scattering, we consider the concept of electrons per unit volume, $\rho$, to effectively describe the distribution of a large number of electrons contained
within the objects under consideration. We then can calculate the observed amplitude as the sum of all scattered secondary waves as a volume integral which we can also recognize as the Fourier transform of the real space electron density distribution $\rho(r)$ as is shown in Eq. 1.1.8

$$A(q) = \int \int \int \rho(r) e^{-iqr} dV$$

Eq. 1.1.8

Experimentally we observe the squared amplitude or intensity as a function of scattering vector, $I(q)$, and the colloidal object is always dispersed in some background medium of electron density $\Delta \rho_1$. Therefore, we only really “see” the square of the electron density difference $(\Delta \rho_2 - \Delta \rho_1)^2 = \Delta \rho^2$ between the colloidal object and the medium in which it is dispersed.\textsuperscript{48-50}

In general, for a monodisperse system of particles of volume $V$ in a solution of concentration $n$, with an electron density difference $\Delta \rho$ with respect to the solvent we may write:

$$I(q) = n\Delta \rho^2 V^2 P(q) S(q)$$

Eq. 1.1.9

where $S(q)$ is a structure factor describing interparticle order and $P(q)$ is a form factor describing the geometrical shape of the particle. For dilute solutions of particles where there is no significant supramolecular colloidal interparticle order $S(q)$ is equal to unity. The term $n\Delta \rho^2 V^2$ is effectively a measure of the number of scatterers and we abbreviate this as $n\Delta \rho^2 V^2 = I(0)$. The expression above in Eq. 1.1.9 can be generalized to dilute polydisperse systems where particle size is treated as a continuous variable given by a statistical distribution function $D(r)$ (Eq. 1.1.10).

$$I(q) = n\Delta \rho^2 \int_0^\infty V(r)^2 D(r) P(q) \, dr$$

Eq. 1.1.10

We will conclude this introduction by noting that Equation 1.1.10 suggests that the following information that is essential to mechanistic study of nanocrystal nucleation and growth is contained
within the SAXS curve – particle average size, particle polydispersity, particle shape, and particle concentration.\textsuperscript{48,50}

1.2. Acquisition of in-Situ SAXS during PbS Nanocrystal Formation

1.2.1 Synthesis of PbS Nanocrystals

In order to practically perform time resolved measurements of colloidal nanocrystal nucleation and growth by SAXS at X-ray synchrotron facilities there are several important considerations about the reaction system chemistry to take into account. The signal intensity is directly proportional to $\Delta \rho^2$, and substantial electron density contrast between the reaction medium and the growing particles is desirable for improving signal to noise in time-resolved experiments.\textsuperscript{48} Secondly, the feasibility of performing \textit{in-situ} experiments is highly dependent on developing chemistry that can be carried out with a reasonable degree of safety at a X-ray synchrotron facility. Historically, the prototypical metal chalcogenide semiconductor nanocrystals such as cadmium selenide have been synthesized at very high temperatures (300°C) using highly toxic, volatile, and reactive reagents such as dimethyl cadmium and bis(trimethylsilyl)selenide which pose an intolerable risk for synchrotron work outside of a chemical fume hood.\textsuperscript{51} Finally, the time scale of the dynamic processes under consideration should be ideally orders of magnitude faster than the time resolution of the experiment. For our studies we focus on a recently reported synthesis of PbS nanocrystals from lead carboxylates and disubstituted thioureas.\textsuperscript{52} The relatively mild reaction conditions, tunable reaction kinetics by precursor selection, and high electron density of PbS fulfill the requirements detailed above.

Lead (II) chalcogenide (E = S, Se, Te) nanoparticles have attracted substantial research attention for their use as near-infared (NIR) light absorbers with applications in various solar cell
architectures and tissue imaging in the NIR biological window.\textsuperscript{53} In addition to applied interest in understanding their synthesis, lead chalcogenide nanoparticles are an excellent model system for studying solution crystal growth by X-ray diffraction due to the relatively large atomic number $Z$ of lead and the heavier chalcogens which should result in very strong electron density contrast.\textsuperscript{48}

The synthesis of these particles was pioneered using a variety of chalcogen sources including bis(trimethylsilyl)sulfide, tertiary phosphine chalcogenides, SeO$_2$, and elemental sulfur and selenium. The Pb$^{2+}$ source has almost always been a lead (II) carboxylate (particularly lead (II) oleate) or lead (II) halide alongside coordinating amines. Representative reactions of lead sulfide nanoparticle synthesis discussed above are shown below in Figure 1.2.1.\textsuperscript{54}

\begin{align*}
\text{A.} \quad & \text{Pb}(X)_2 + S(\text{SiMe}_3)_2 \rightarrow \text{PbS} + 2 \text{Me}_3\text{Si-X} \\
& \text{X = Halide, Carboxylate} \\
\text{B.} \quad & \text{R-H + S}_8 \rightarrow \text{R-S}_n\text{-H} + \text{R-S}_n\text{-R} + \text{H}_2\text{S}_n \\
& \text{Pb}(X)_2 + \text{H}_2\text{S} \rightarrow \text{PbS} + 2 \text{HX} \\
& \text{R = Alkyl, Allyl}
\end{align*}

\textbf{Figure 1.2.1} Representative precursor chemistry for lead (II) sulfide nanoparticle synthesis by $S^2$-transfer. \textbf{A.} Reaction of bis(trimethylsilyl)sulfide with lead salts. \textbf{B.} Radical activation of hydrocarbons to generate reactive H$_2$S in particle synthesis using elemental sulfur as precursor.\textsuperscript{54}

While bis(trimethyl)silyl sulfides generally react quantitatively with lead (II) chloride and lead (II) carboxylates at mild temperatures to form highly favorable Si-O or Si-Cl bonds and a PbS lattice, it is an extremely toxic and very malodorous substance. In contrast, tertiary phosphine chalcogenides are sluggish to react, and convert in low yield (Figure 1.2.2.). Finally, precursors
that convert via ill-defined radical reactions with the hydrocarbon solvent such as \( \text{S}_8 \) to yield \( \text{H}_2\text{S} \) as the active \( \text{S}^{2-} \) source are often problematic as their reaction kinetics and yields are highly sensitive to impurities.\(^5\) An excellent alternative to these precursor classes for the synthesis of PbS and PbSe nanocrystals is the recently established thiourea and selenourea precursor libraries of Hendricks and Campos. These compounds convert to lead chalcogenide nanoparticles with high yields at mild temperatures (70-150°C), and proceed with reproducible and tunable kinetics, and are not volatile or sources for volatile byproducts. These features make these precursor classes especially attractive for in-situ synchrotron work as is the control over fairly reproducible overall reaction kinetics over several orders of magnitude.\(^5\)\(^2\)\(^5\)\(^5\)\(^6\)

**Figure 1.2.2** A. Trioctylchalcogenide \( \text{E}^{2-} \) precursor used in synthesis of PbS, PbSe, and PbTe nanocrystals. B. Proposed reduction of lead carboxylate by secondary phosphine impurities to yield reactive \( \text{Pb}^0 \) species by Steckel.\(^5\)
Figure 1.2.3 Synthesis of PbS nanocrystals using disubstituted thioureas and lead (II) oleate. A. Scope of reaction conditions for PbS formation by conversion of disubstituted thioureas and lead oleate to lead oleate capped PbS nanoparticles. B. Approximate overall reaction rates of different precursors derived from a first order ansatz rate equation fit to the dip-probe absorbance at 400 nm tracking the yield \([\text{PbS}]_n\) in particles by the extinction coefficient of Moreels.\(^{44}\) C. UV-Vis/NIR electronic absorbance spectroscopy showing the size dependent first excitonic transition of different sized particles. D. UV-vis dip probe kinetics of different precursors. Figures adapted from Ref. 52.

Figure 1.2.3 above summarizes the principal features of the recently demonstrated synthesis of PbS nanoparticles by a dissubstituted thiourea precursor library by Hendricks and Owen.\(^{52}\) In general, the reaction is performed by the hot injection of a dissubstituted thiourea dissolved in an ethereal solvent into a solution of lead (II) oleate in a high boiling point alkane or
alkene solvent conducted at relatively benign temperatures for nanocrystal synthesis (150°C at most). As discussed in more detail below, the reaction consists of relatively air stable and non-volatile precursor molecules and only produces air stable and non-volatile organic coproducts and in this regard is relatively safe within the context of lead chalcogenide nanoparticle synthesis.

Figure 1.2.4. Synthesis of PbS nanocrystal precursors. A. Synthesis of disubstituted thioureas from addition reaction of primary amines and isothiocyanates. B. Synthesis of lead (II) oleate from lead (II) trifluoroacetate.

Preparation of the disubstituted thiourea and lead (II) oleate S²⁻ and Pb²⁺ precursors is summarized in Figure 1.2.4. The disubstituted thioureas are prepared by the virtually quantitative room temperature addition reaction of a primary amine with an isothiocyanate, and generally do not require purification after solvent evaporation although they may be easily purified further by hot recrystallization from lower alcohols (MeOH, EtOH). For the mixed aryl/alkyl species the use of an alkyl amine and an aryl isothiocyanate is preferred as the reverse combination leads to substantially slower reaction kinetics and poor yield in some cases. The lead (II) oleate is synthesized from the reaction of oleic acid with in-situ generated lead (II) trifluoroacetate in MeCN.
which precipitates upon addition of oleic acid dissolved in isopropanol (IPA) and can be recovered on a fine frit and washed with polar solvent (MeCN/MeOH) to remove residual lead (II) trifluoroacetate and triethylammonium trifluoroacetate coproduct. The isolated product can be further purified by hot recrystallization in isopropanol and dried under high vacuum until no trifluoroacetate signal can be detected in $^{19}$F NMR, and no evidence of hydroxide/water/oleic acid is observed by $^1$H NMR and FT-IR spectroscopies.$^{52}$

The absorbance at 400nm can be related to the total concentration of PbS units [PbS], by the size independent extinction coefficient of Moreels, and thus the overall kinetics of the appearance of [PbS] can be monitored.$^{44}$ To compare the relative kinetics of different precursors we assume the kinetics of [PbS] appearance roughly follow the functional form of a unimolecular first order irreversible reaction as an ansatz to approximate the immense kinetic complexity of the hundreds to thousands of underlying elementary steps such a crystallization process would entail. Strictly, this could be justified from first principles if we assumed a first order irreversible precursor conversion step was the rate determining step in the overall process. We will discuss in more detail what evidence exists to support precursor conversion as the rate determining step of the overall process later in this chapter, although we will stress now that this kinetic treatment is merely a simplifying approximation rather than a real mechanistic assertion.

The various disubstituted thiourea substrates in this study show a large range in conversion rates depending on both steric and electronic—but mostly electronic within this group of compounds—factors. As is seen in the table in Figure 1.2.3 the general trend in overall relative reaction rates of appearance of [PbS] seen for the disubstituted thioureas is a clear dependence on the electron withdrawing character of the thiourea with a dramatic reactivity rate trend of N,N’ diaryl > N,N’ mixed alkyl/aryl > N,N’ dialkyl thioureas spreading orders of magnitude. Further,
the electron donating character of substituents within a given subclass (e.g. N,N’ mixed alkyl/aryl) of precursors provides a more fine control over the conversion kinetics.

![Chemical structure of thiourea derivative](image)

*Figure 1.2.5* Hammett plot showcasing the impact of the electronics of the thiourea molecule on its precursor conversion rate, adapted from ref 52.

The Hammett series of para substituted N-p-X-Phenyl-N’-n-dodecylthioureas has a positive slope ($\rho = 1.24$) plotting the logarithm of the extracted rate constants versus the Hammett sigma parameter (Figure 1.2.5). This suggests a buildup of negative charge during the transition state. We can rationalize this by several elementary steps including rate limiting deprotonation of the thiourea or rate limiting nucleophilic attack on the thiocarbonyl carbon by a carboxylate. The organic co-products observed in different reactions are consistent with decomposition of a reactive O-acylisourea intermediate to form urea and anhydride or oleic acid and N-acylurea coproducts.\(^{55}\)
Reaction of a disubstituted thiourea with lead (II) oleate to form PbS and putative O-acylisourea intermediate.

Decomposition of putative O-acylisourea to two sets of observed reaction coproducts.

The low polydispersity, high chemical yield, and low relative cost of the reagents used in this synthesis make this synthesis very attractive from an applications standpoint, although perhaps the most interesting feature of this chemistry is the fine control of reaction kinetics and particle yield afforded by the use of different disubstituted thiourea substrates. The impact of the precursor conversion rate or “solute supply” rate on final nanoparticle size under precursor conversion limited conditions was recently investigated by Sugimoto and applied to his study of AgCl nanoparticle formation. This nucleation theory based on the LaMer model assumes (1) a mass
balance (Eq. 1.2.1) between the solute supply \((R_S)\), nucleation \((R_N)\) and growth \((R_G)\) rates during the nucleation phase, (2) a constant solute supply rate \(Q_o\) during the nucleation phase (3) and a nucleation rate which only depends on the growth rate for a given solute supply rate. The conditions above are valid for a burst nucleation process where the rate limiting step in the reaction is precursor conversion or solute supply and the result is the equation below relating final particle number \(n_f\), solute supply rate \(Q_o\) during the nucleation period, molar volume \(v\), and mean volume growth rate \(v_+\) (Eq. 1.2.2).\(^8\)

\[
R_N + R_G - R_S = 0 \quad \text{Eq. 1.2.1}
\]

\[
n_f = \frac{Q_o v}{v_+} \quad \text{Eq. 1.2.2}
\]

Notwithstanding that the conditions above are somewhat limiting, qualitatively the conclusion that a faster precursor conversion rate results in a larger number of smaller particles at full reaction yield is seen in a number of nanoparticle syntheses including the Hendrick’s PbS synthesis.\(^{8,52,54}\) Certainly, \(R_N, R_G, R_S\) are expected to be functions of solute concentration (see Eq. 1.1.3 for instance) and so the assumptions of this model are clearly approximations only appropriate for a precursor conversion limited burst nucleation process. In general, one can understand Eq. 1.2.1 by consideration of the fact that under the conditions of Sugimoto’s mass balance in the nucleation phase, nucleation rates and growth rates are in competition for a fixed solute supply rate. It is the increased number \(n\) of crystals growing at a fixed rate \(v_+\) that eventually equals \(Q_o v\) sending the nucleation rate \(\frac{dn}{dt}\) to zero.\(^8\)
1.2.2 Beamline Experimental Design and Setup

The in-situ time resolved SAXS/WAXS experiments were performed primarily at the ESRF-ID02 beamline at the ESRF, which has been specially designed to perform time-resolved X-ray scattering experiment of dynamic phenomenon with up to millisecond time resolution over a wide range of scattering vector $0.001 \leq q \leq 50 \text{ nm}^{-1}$. The high brilliance of this beamline and simultaneous measurements of a large range of scattering vector in reciprocal space allows for time resolved experiments of nanoparticle growth with temporal resolution on the order of a single second or less. The utility of this beamline to study nanoscale growth in situ has already been demonstrated by Abécassis and coworkers by their in situ studies of CdSe nanoplatelet and gold nanoparticle formation. The ability to perform both SAXS and WAXS experiments on the same beamline simultaneously allows a view into both colloidal level of the particles in addition to the atomic level crystalline structure. The simultaneous measurements of WAXS and SAXS are made possible by multiple in line sample to detector distances.

The basic contours of the experimental setup used for collecting time resolved diffraction experiments of PbS nanocrystal formation at the ESRF-ID02 are shown in the Figure 1.2.8. Briefly, a lead(II) oleate solution in hexadecane is prepared in a 3-necked flask plunged in an oil bath at the reaction temperature with magnetic stirring under flowing argon. A UV-Vis dip probe is also plunged into the solution allowing for simultaneous measurement of the absorbance at 400 nm. The reaction is initiated remotely by a pressurized air triggered injection of a tetruglyme or diglyme solution of the thiourea precursor which causes the temperature of the reaction to drop approximately 2-3°C. Injection of the thiourea precursor initiates a peristaltic pump to draw up the reaction solution through a needle into thermally stable Viton tubing which pulls the reaction media into a glass capillary that is positioned in a flow cell which passes in front of the beampath.
Experiments have been performed in both recirculating and non-recirculating configurations with the latter requiring a much larger sample volume as the reaction media is flowed out directly into a waste container in that case after passing by the X-ray beam.

**Figure 1.2.8** in-situ setup at ESRD-ID-02 beamline to collect time resolved SAXS/WAXS measurements of nanoparticle nucleation and growth. Annotated image of recirculating setup highlighting principal components of in situ setup.
Figure 1.2.9 (Left) Same setup as shown in 1.2.8 for non-recirculating conditions illustrating larger reaction volume used in this case. (Right) preparation of lead (II) oleate solutions at the beamline – lead (II) oleate suspension in dry hexadecane is prepared in a glovebox and brought under inert gas and then heated to dissolve (70 °C) and transferred by metal cannula into the beamline reaction vessel under N₂.

1.2.3 Data Collection and Reduction

Small angle X-ray scattering and wide-angle X-ray scattering patterns are collected on the in-line two detector setup described above. 2D diffraction images using are corrected for background dark current, normalized to an absolute intensity scale, and are azimuthally integrated using the ID-02 beamlines automated data reduction pipeline. The reduced 1D datasets were corrected for the background solvent scattering by subtracting a solvent blank which is acquired directly prior to each reaction sequence. The batch background subtraction and normalization to the capillary thickness was performed using custom designed python code implemented in Jupyter notebooks as the number of datasets produced per sequence is 1000+.
An acquisition time of 0.3 seconds with a 0.7 dark between frames was seen to provide substantial signal to noise using this high brilliance beamline. The $q$ range chosen for the small angle scattering measurements was $0.05 \leq q \leq 5 \text{ nm}^{-1}$ which was chosen to provide full coverage of the asymptotic behavior as $q$ approaches 0 for these small ($d > 10 \text{ nm}$) particles. Given the small size of the particles in the experiment the full USAXS capabilities of this beamline were not deemed necessary. The Bragg condition can also be stated as $q = \frac{2\pi}{d}$ which qualitatively can be used a guide for the length scale of repeated ordered distances being probed at a given scattering vector. The $q$ range for the wide angle scattering measurements were similarly chosen to be able to see PbS rock-salt lattice (111), (002), (022), (113) Bragg reflections which occur at scattering vectors of $q = 18.33, 21.17, 29.94, 35.11 \text{ nm}^{-1}$ respectively.

The simultaneous measurement of colloidal size scale growth by small angle X-ray scattering and appearance of the rock salt crystal lattice by wide angle X-ray scattering is important for understanding how colloidal crystal growth occurs as it is not necessarily the case that colloidal growth is crystalline growth although in this system that appears to be true for the most part. Shown below in Figure 1.2.10 are representative 1D SAXS and WAXS data plots following background subtraction of the solvent scattering of late timepoints in the reaction. At this point the first (111), (002), (022), (113) Bragg reflections for a PbS rock salt lattice are seen (compare to calculated PXRD from the CIF in Figure 1.1.4), and the appearance of an approximately spheroidal particle with multiple form factor oscillations is evident in the SAXS. As is shown in Figure 1.2.10, the SAXS is traditionally plotted on a log-log axis in order to highlight the form factor oscillations over a large range of $q$ as these are highly significant to modeling the SAXS curve although they would superficially appear to be insignificant with respect to the intensity at lower $q$ on a linear axis.
1.2.4 Time Series Data Results

The time series data were collected on precursors and reaction conditions that fulfilled several conditions. Firstly, it was important that the overall reaction kinetics of nanocrystal formation were much larger than the experimental time resolution of the experiment such that the individual diffraction images could reveal meaningful dynamic changes between images. Secondly, the particular reaction condition and precursor combination used were known to produce monodisperse crystalline materials in high yield. Thirdly, the time scale of the reaction itself was suitably short such that many experiments could be performed in a single beamtime (the setup of each reaction and cleanup between reactions is itself very time consuming). The Hammett series of para substituted N-p-X-Phenyl-N’-n-dodecylthioureas proved very useful towards this end as they possessed total reaction times spanning between 1-30 minutes at relatively mild

![SAXS and WAXS plots](image-url)

**Figure 1.2.10** 1D reduced and solvent background subtracted small angle X-ray scattering (left) and wide angle X-ray scattering (left) curves for representative late reaction timepoints showing the crystallinity of the synthesized particles (right) and their monodispersity (left).
conditions. Below is shown a representative data sequence of time series data for such an experiment.

![Reaction stoichiometry and conditions](image)

**Figure 1.2.11** Representative in-situ SAXS data collected with precursor and temperature conditions above. Data is from non-recirculating conditions.

From a model free standpoint there are several features of the data that can be gleaned from direct inspection of the dataset plotted in Figure 1.2.11 that make this reciprocal space data easy to “read” as representing the nucleation and growth of an ensemble of nanocrystals. Recalling Equation 1.1.9, we may note the asymptotic intensity of scattering vector as $q$ approaches zero is related to the total number of scatterers and we can write this as $n \Delta \rho^2 V^2 = I(0)$. Also, the particle number itself as a function of time $n_{np}(t)$ can be expressed as $n_{np}(t) = \frac{I(0)}{\Delta \rho^2 (V^2)}$. Consequently,
the monotonic increase of scattering intensity at lower $q$ in Figure 1.2.11 is directly related to the increase in concentration of [PbS] contained in particles as the reaction proceeds. The origin of the oscillations of the scattering data are related to the $q$ dependent terms in the equation for the SAXS of a dilute solution of nanoparticles $I(q) = n\Delta\rho^2V^2P(q)$ or the form factor oscillations.\textsuperscript{49,50} The equation for the form factor for a sphere, and simulated 1D small angle scattering for a 5nm radius spherical particle using this equation are shown below in Equation 1.2.3 and Figure 1.2.12.\textsuperscript{49}

$$P(Q) = \left[ 3 \frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right]^2$$

Eq. 1.2.3

\textbf{Figure 1.2.12} Simulated SAXS for 5nm spherical particles with a polydispersity $PDI = \frac{\sigma}{R_0}$ using SASview software.\textsuperscript{60}

We can see that the numerator in Equation 1.2.3 leads to an oscillating function with zeros wherever $\sin(QR) - QR \cos(QR) = 0$. As is seen in Figure 1.2.12, the sum of a number of different sized particles leads to a “blurring” of the form factor oscillations – only when a truly monodisperse ensemble is formed with approximately $\frac{\sigma}{R_0} < 10\%$ would one expect to see more
than one clearly pronounced form factor oscillation at this length scale. Finally, the simultaneously acquired in-situ WAXS demonstrates the growth of the crystalline rock salt structure crystalline phase concurrent with the colloidal growth (Figure 1.2.13). The visibly decreasing width of the Bragg reflections during the time series also corroborates the growth of the crystallites as is predicted by the Scherrer equation.\footnote{61}

\[ \beta = \frac{K \lambda}{\cos(\theta) \tau} \quad \text{Eq. 1.2.4} \]

\textbf{Figure 1.2.13} Representative in-situ WAXS with reaction conditions of Figure 1.2.11.

Where \( \beta \) is the FWHM subtracting instrumental broadening, \( K \) is a dimensionless shape factor close to unity, \( \theta \) is the Bragg angle and \( \tau \) is the crystallite dimension. At this length scale it is likely other factors give rise to the peak broadening (largely a subject of Chapter 2) but the increase in
the sharpness of the Bragg reflections is certainly reflective of the increasing crystallite size as the particle grows.

1.3. SAXS Data Modeling and Methods

1.3.1 Development and Implementation of Model

**Figure 1.3.1** Comparison of early time and late time SAXS data highlighting differences in higher q end of the SAXS detector during a time series (left) and lead (II) oleate.

One feature of the time series data that we do not address but that motivates our discussion of the model we have developed for this data is the non-monotonic behavior of the intensity at higher scattering vector ($q > 1$). While at lower $q$ a monotonic trend of increasing intensity over time is observed, the behavior at higher scattering vector is more interesting – it appears to be at its highest intensity overall during the early reaction points and then oscillates according to the form factor oscillations of the particles at later time points. This weaker extra scattering consistent with small polydisperse spheres that is most pronounced at early times can be assigned to the lead oleate, and is identically seen when diffraction data of the hot lead oleate precursor solution is
taken alone. That lead oleate would self-assemble into a micelle in hot alkane solvent is not at all surprising and it would indeed be more surprising if its structure were simply monomeric. To better assign the self-assembly of dissolved lead oleate in hot alkane solvents small angle neutron scattering was performed in perdeuterated tetradecane to enhance the scattering contrast between the alkyl chains and the solvent. The resulting pattern could be fit to a spherical model with an average radius of 1.74 nm and roughly 20% polydispersity. This is consistent with a small molecular aggregate of several lead (II) oleate units as the radius is approximately the size of the two oleate alkyl chains end to end.

![Small Angle Neutron Scattering of lead (II) oleate in perdeuterated tetradecane to enhance scattering contrast between solvent and alkyl chains](image)

**Figure 1.3.2** Small Angle Neutron Scattering of lead (II) oleate in perdeuterated tetradecane to enhance scattering contrast between solvent and alkyl chains

To model the SAXS intensity $I(q, t)_{calc}$ during a data series we have implemented a two-phase model consisting of scattering from an ensemble of polydisperse spherical nanoparticles and an ensemble of polydisperse lead (II) oleate micelles. Recalling Equation 1.1.10, $I(q) =$
\( n \Delta \rho^2 \int_0^\infty V(r)^2 D(r)P(q) \, dr \), we select a Schulz distribution function \( D(r) \) for each component of the fit (Eq. 1.3.1). In this equation \( Z \) is a parameter of the distribution related to the polydispersity, and \( r_0 \) is the average radius

\[
D(r) = \frac{(Z + 1)^{Z+1} r^Z e^{-\frac{r(z+1)}{r_0} - \frac{r_0}{1}}}{\Gamma(Z + 1)}.
\]

Eq. 1.3.1

The principal advantage of this distribution function from a computational perspective is the fact that the form factor integral \( \int_0^\infty V(r)^2 D(r)P(Q)\,dr \) can be evaluated analytically for a spherical form factor.\(^6\) Furthermore, it is not significantly different from a gaussian population distribution for small values of the standard deviation and it is identically zero at \( r = 0 \). The standard deviation and polydispersity is easily calculated from the distribution parameters \( r_0 \) and \( Z \) (Eq.1.3.2).

\[
PD = \frac{\sigma}{r_0} = \frac{1}{(Z + 1)^{1/2}}.
\]

Eq. 1.3.2

After the onset of nanoparticle formation, the time dependent \( I(q, t)_{\text{calc}} \) SAXS intensity is fit as the sum of scattering contribution from nanoparticles and lead (II) oleate micelles as Eq. 1.3.3.

\[
I(q, t)_{\text{calc}} = I_{\text{calc}}^{NP}(q, r_0(t), Z(t)) + I_{\text{calc}}^{Micelle}(t)P_s(q, r_0', Z')
\]

Eq. 1.3.3

\( P_s \) is the form factor \( \int_0^\infty V(r)^2 D(r)P(Q)\,dr \) for a Schulz distribution of particle radii of average radius \( r \) with polydispersity parameter \( Z \). We assume here that the particles have a time dependent average radius, polydispersity, and concentration while the lead (II) oleate micelles merely have a time dependent concentration. From a mathematical standpoint this assumption seems necessary as there would be no way to distinguish the particles from the micelles in Eq. 1.3.3, but it is also somewhat logical for a particle growth process that consumes lead (II) oleate as a reactant and produces particles undergoing growth as products. This yields four free parameters which must be
optimized \( I_0^{NP}(t) \), \( I_0^{Micelle}(t) \), \( r_0(t) \), \( Z(t) \) to maximize agreement between \( I(q,t)_{\text{calc}} \) and \( I(q,t)_{\text{expt}} \). This is a non-linear least squares problem which was solved by maximizing agreement of the model to the data using the Levenberg-Marquadt Algorithm Implemented by the LMFIT package in Python.\(^{63}\) While there is user friendly software with plugins for performing such sum of form factor fitting, we found these inefficient for handling the very large number of total datasets involved in our experiments.\(^{60,64}\) Using the model outlined above we can account for the small angle scattering throughout the entirety of the time series data in each experiment.

Figure 1.3.3 Small Angle X-Ray Scattering and fits (dark lines) for data in Figure 1.2.1.

1.3.2 Analysis of Model and Assumptions

In modeling this data, we preferred the concept of a purposefully simplistic 2-component model with limited assumptions, free parameters, and analytic functional representation due to the complexity of the underlying dynamic process which could easily allow for many solutions with
comparable agreement to the experimental data. Perhaps the most fundamental rule of small angle X-ray scattering modeling is that “the fact that a model fits the data does not necessarily mean the model is right,” and with this in mind we must consider whether we should expect the simplistic one we have developed to accurately capture the dynamics of the system during the synthesis. As an example, In Equation 1.3.3. we could imagine adding further terms to account for solute intermediates of the general form \([\text{PbS}]_n[\text{Pb(Oleate)}]_m\) or relaxing more constants as variables, but attempts to do so generally led to large variations in refined parameters in the parameter space which did not seem to be physical. Within the discussion of simplifying assumptions in our model, the choice of assuming sphericity for the particles to afford use of the analytic sphere form factor is one that deserves special attention given the relationship between colloidal shape, size, and polydispersity in SAXS.\(^{48-50}\)

A fundamental problem in the modeling of small angle scattering data is that the influences of particle shape anisotropy and polydispersity cannot unambiguously be separated. In particular, the choice of a shape function and a statistical distribution function allows one to determine average size and size dispersity but does not mean that the choice of the latter or the former are justified assumptions.\(^{48-50}\) While we cannot fully obviate this uncertainty in this work, as it is inherent to small angle scattering research, there are a number of pieces of information about the system that make it a reasonable assumption in addition to filling the basic condition of being able to reproduce the experimentally observed scattering. Finally, we will note that in nanoparticle science most measurements used to determine exact structural information about heterogenous ensembles of particles are based on potentially flawed simplifying assumptions and it is best practice to overcome the limitations of a particular spectroscopic technique by showing that a result can be confirmed by more than one type of measurement. We shall argue more specifically
for our own attempts to consider multimodal characterization in this particular system later in the chapter to verify the results of the X-ray scattering modeling.

Figure 1.3.4 Simulations of the small angle X-ray scattering of a 3nm radius sphere and an isovolumic hexahedron illustrating the form factor effects for different shapes. ⁶⁰

A basic starting point for our analysis is: what other experimental evidence exists that justifies our assumption that the particles can be approximated as spherical during this synthesis? Firstly, we can note that Transmission Electron Micrographs reported in the original publication of this work show fairly clearly that the final particles produced in this synthesis do not show any pronounced shape anisotropy in aggregate and appear roughly spherical. ⁵² However, it is not necessarily the case that the smaller metastable sizes have the same morphology as the final product. The most thorough study of PbS nanoparticle morphology in the 1.5 and 7.5 nm size regime synthesized with lead (II) oleate as the passivating ligand was carried out by Choi and coworkers who used a combination of XPS to measure Pb:S ratios and DFT calculations to measure ligand binding energies to different surface facets. This work concluded that for particle
dimensions smaller than approximately 4 nm, octahedral particles containing only (111) facets which are passivated by lead (II) oleate are formed while larger particles up to about 7.5 nm become cuboctahedral with both (111) and (100) facets.\textsuperscript{65} This was further echoed by Zherebetskky and coworkers who proposed for nanocrystal shapes on the 4-5 nm length scale a Wulff construction model which contained both (111) and (100) facets (See Figure 1.3.5).\textsuperscript{66} While there do exist synthetic conditions that can form anisotropic\textsuperscript{67,68} and cubic\textsuperscript{69} nanostructures the overwhelming evidence from the literature cited above suggests that under the synthesis conditions of our experiment, the particles are likely to be polyhedral structures with (111) and (100) facets and a reasonably high degree of sphericity during synthesis.\textsuperscript{52,65,66}

\textbf{Figure 1.3.5} Lead rich Pb\textsubscript{1804}S\textsubscript{1481} \textasciitilde 5.4 nm inorganic particle structure proposed by Zherbetskky and coworkers with ligands removed for clarity. Excess Pb(II) ions are bound as Z-type ligands with oleate ligands providing charge balance. XYZ coordinate matrix taken from supporting information of ref. 66 and space filling model generated using Crystal Maker software.\textsuperscript{70}
With the above consideration of likely particle shape in mind, we can consider what small angle scattering theory itself suggests about our assumptions. As is shown in Figure 1.3.3, the scattering curve of even a cube and a sphere show a reasonably high degree of similarity for the first few form factor oscillations observed at this length scale although a dampening of the minima is also clearly seen. This was recently considered by Xin Li and coworkers who calculated the scattering functions of a number of platonic solids and considered both the reciprocal space form factor oscillations as well as the real space distance distribution functions. Briefly, they concluded that differences in the distance distribution function, $P(r)$, in real space from inverse fourier transform of SAXS data (Eq. 1.3.4 and discussed extensively in Chapter 2.) were barely discernable even in theory for dodecahedral and icosahedral particles as compared to an isovolumic sphere and could be experimentally difficult to resolve for even the case of a hexahedron.\textsuperscript{49,71}

$$P(r) = \frac{1}{2\pi^2} \int_{0}^{\infty} I(q)qr \sin(qr)dq$$ \hspace{1cm} \text{Eq. 1.3.4}

In contrast, dampening of the minima is seen in $P(q)$ as well as differences in the position and width of the higher form factor oscillations were more clear. Again, however, finite instrumental resolution can lead to this smearing even for a perfectly spherical object and this was predicted to be difficult to resolve without \textit{a priori} knowledge of the particle geometry for any object with a higher degree of sphericity than a hexahedron.\textsuperscript{71}

Finally we can consider whether the scattering from the proposed atomistic models of PbS nanoparticles is consistent with the analysis above. Using CRYSTOL software to calculate the amplitude directly from the Fourier relationship between the amplitude and the real space electron density (see Equation 1.1.8), we can evaluate the correspondence between spherical models and
atomistic nanoparticle shapes. Shown below in Figure 1.3.6 we evaluate the calculated SAXS intensity of the polyhedral model in Figure 1.3.5 in comparison to a best fit spherical model. In general we arrive at the same conclusion that we arrived at from consideration of the form factors of increasingly higher order polyhedral objects above.\textsuperscript{71} For the proposed atomistic models of PbS nanoparticles in reciprocal space there are minor differences between a roughly isovolumic best fit sphere model and a realistic nanoparticle model that would be difficult to resolve experimentally and even less difference in the pair distance distribution functions from inverse fourier transform.

![Graphs showing intensity and pair distance distribution](image)

**Figure 1.3.6** CRYSOL simulations\textsuperscript{72} of the reciprocal space SAXS from the atomistic model of a PbS nanoparticle and the real space inverse Fourier transform from ATSAS\textsuperscript{73} in addition to best fit homogenous sphere model (2.8 nm radius).

This corroborates the prior finding that real space inverse fourier transform structure modeling from SAXS data of small (<10 nm) highly symmetrical polyhedral structures is not likely to provide a unique assignment of polyhedral shape.\textsuperscript{71} While there are clear differences in reciprocal space, most notably the smearing of the form factor oscillations which could effect estimates of the polydispersity (see Figure 1.3.7), these are suspected to be difficult to tease out experimentally. This is especially true given the dynamic nature of the nanocrystal surface and its
ligands\textsuperscript{3,6}, and solvation layer around the particle inherently complicate the idea that they are perfect platonic polyhedra from the perspective of SAXS. Again, this is due to the relative high sphericity of the PbS particles formed in this case. For anisotropic or certain lower sphericity polyhedra (particularly a tetrahedron which does not possess form factor oscillations) the above analysis would potentially be more problematic.\textsuperscript{48,71}

\textbf{Figure 1.3.7} CRYSOL simulations\textsuperscript{72} of the reciprocal space SAXS from the atomistic model of a PbS nanoparticle and a polydisperse ensemble of spheres which better mimics the dampened form factor oscillations relative to an idealized sphere.

One can anticipate that a likely parameter to be influenced by this shape assumption would be the polydispersity of the ensemble, given that the smearing of the form factor oscillations is observed both for polyhedra with a finite number of parallel faces and also for polydisperse ensembles of spheres. Indeed, we show above in Figure 1.3.7 that a small polydispersity is refined (4.8\%) if it is allowed to be floated as a free parameter to the fit to the simulations in Figure 1.3.6, which also has a minor effect on the refined average radius (2.80 v.s. 2.77 nm). We consider this
an acceptable degree of potential systematic error in estimating these quantities particularly in consideration of the fact that it is not obvious what experimental technique can more more accurately measure the “real” relative polydispersity \( \frac{\sigma_{\text{PbS units per NP}}}{\text{Average PbS units per NP}} \) in this very small size regime (less than 10nm). More conventional TEM analysis for sizing of static reaction products, for instance, generally consists of taking a questionably statistically significant grouping of hundreds to thousands of ideally well separated particles in various orientations on the grid and measuring the boundary of electron density contrast of the particle with the grid in an image editing software to extract a size parameter \( r \) and then fitting a statistical distribution to a histogram plot of binned sizes of that parameter. While it should be acknowledged that the introduction of systematic error by the assumptions stated above is possible, and it is very plausible that the polydispersity is overestimated by approximately 5%, we are measuring particle radii of approximately 1.0–4.0 nm in these experiments and this error amounts a couple of angstroms which is not a trivial length scale to resolve experimentally in general for nanocrystallite dimensions.

Finally, we will note that one of the parameters of key interest \( n_{np}(t) = \frac{I(0)}{\Delta \rho^2(V^2)} \) is unlikely to be heavily affected by our assumptions. From SAXS theory we know that the excluded volume of the particles \( V = \frac{2\pi^2 I(0)}{Q} \) is a model independent quantity depending on \( I(0) \) and the Porod invariant integral \( Q \) which itself depends only on the excess scattering length density.\(^{48-50}\) While the choice of a more complex form factor of a faceted polyhedron would change the numerical value of our size parameter \( r \) (or introduce more than one size parameter depending on choice of polyhedron) and our polydispersity it, in principle, should not change our estimate of the particle concentration assuming each model is itself a good fit to the data (from arguments above this would almost certainly not be the case unless the polyhedron itself was isovolumic with the
sphere). A large meta-analysis of sizing metal chalcogenide nanoparticles on the sub 10 nm length scale by Abécassis and coworkers has also suggested that the choice of the distribution function among standard distribution functions used to described nanocrystal populations (Gaussian, Log-Normal, Schulz) has a trivial effect (less than 1%) on values of the polydispersity and average radius for polydispersity of the distribution less than 20%. For all of these reasons we consider the model described above to be acceptable due to its simplicity, fit to the experimental data, and lack of a clear fundamental motivation for the introduction of a more complex model with more parameters.

1.3.3 Model Results and Significance

The results of our modeling give the time evolution of three key quantities of the nucleation and growth processes—particle concentration, the average size, and the size dispersity or the refined parameters of our model $I_0(t), r(t), Z(t)$. Below in Figure 1.3.8 are the time evolution of the concentrations of nanocrystals in addition to the concentration of PbS units that are contained within particles plotted for a reference sequence displayed in Figure 1.2.1. The time evolution of [PbS] and [QD] displayed below is logical for a nucleation and growth process where [QD] quickly grows in during the beginning of the reaction during the nucleation period, and then undergoes a longer period of growth where [PbS] is increasing as more monomer units are added on to existing particles. What is immediately most interesting in this data is the length of the nucleation period where the [QD] is clearly increasing and is evidently not a classical step function but persists for a sizeable fraction of the reaction time.
Figure 1.3.8 Time evolution of the [PbS] and the concentration of particles during synthesis with recirculation.

Figure 1.3.9 Concentration of particles during the nucleation period which accounts for approximately 10% to 15% of the entire reaction time.

The average size and size dispersity also follow a logical time evolution. After a brief dead time (normally less than a minute prior to the nucleation of particles depending the precursor and reaction conditions), the radius—and in general all the parameters of the fit as they are correlated—
shows a large degree of scatter. This is reasonable because at early times when the particles are very small and polydisperse and in low concentration the model has difficulty “knowing” the difference between the lead (II) oleate micelles and the particles themselves leading to a large parameter space of acceptable fits. However, the average radius begins to develop a monotonically rising behavior as a function of time with the first well resolved sizes at this point showing up around 1.5 nm under these conditions. The relative polydispersity, which is directly derived from the fit parameter $Z$ as $\frac{1}{(Z+1)^{1/2}}$ is shown to quickly rise and then fall as the growth period proceeds. This can be intuitively explained, as the polydispersity should be increasing as new particles are borne during nucleation while existing particles are actively growing during the finite width of the nucleation period.

Figure 1.3.10 Time evolution of the average radius and relative polydispersity during the synthesis showing growth of the particles and narrowing of the relative size distribution during the synthesis
At later times the origin of the decrease in the relative polydispersity is not obvious, as there are multiple factors that might contribute to this. First, assuming the set of unique particles which are present at the conclusion of the reaction is determined during the nucleation period (and whatever growth occurs during the nucleation period itself sets the standard deviation of the size within that set of particles) one would expect that the relative polydispersity $\sigma / r_0$ should decrease simply because the denominator $r_0$ should increase. Alternatively, the size dispersity could be decreasing during the growth period because the growth process itself possessed some size-focusing character—we have already noted the well cited example of the inverse radius dependence of the radial growth rate under diffusion-controlled conditions. By plotting the absolute standard deviation which is simply the product of $\frac{1}{(Z+1)^{1/2}}$ and the fit parameter $r_0$ we see convincing evidence that indeed the absolute standard deviation in size is also decreasing during the synthesis during the growth period suggesting some form of size focusing behavior.

![Figure 1.3.11](image.png)

**Figure 1.3.11** Time evolution of the absolute standard deviation during the synthesis showing narrowing of the absolute size distribution.
Finally, it is important to confirm that the designed two component model behaves in a way that actually conforms to the physical reality of the reaction equation of the synthesis. To analyze this, we can look at the concentration of [PbS] which is directly related to the free model parameter $I_{ONP}(t)$ corrected to the known scattering length density of PbS and the free model parameter $I_{OMicelle}(t)$ which is directly proportional to the concentration of lead (II) oleate micelles as is shown in Figure 1.3.12. The result is very much consistent with a reaction that consumes lead oleate in order to form PbS which is contained in colloidal crystals. The sum of the two normalized intensities appears to remain constant within a roughly 10% range during the reaction. In general, we should observe that the weak featureless scattering at high $q$ that the $I_{OMicelle}(t)$ term in our model measures could possibly account for some amount of the scattering from a diversity of small oligomeric molecular structures formed as metastable intermediates (in particular “solute” of the general formula [Pb(Oleate)$_2$]$_n$[PbS]$_m$ or byproducts in the reaction). This could explain the small variation in the sum of normalized $I_{OMicelle}(t)$ and $I_{ONP}(t)$, although the generally good agreement and reasonably monotonic behavior of both intensities as a function of time is a good testament to the overall physicality of the two-component model.
Figure 1.3.12 Time evolution of the refined parameters $I_0^{\text{Micelle}}(t)$ and $I_0^{\text{NP}}(t)$ normalized for relative comparison taking into account different scattering length densities. The blue trace on the right is the sum of the two traces on the left.

From the aforementioned discussion we see the principal features that are seen in all of our measurements of PbS nucleation and growth – a nucleation period that persists for a non-trivial fraction of the total reaction time, and a steady growth period during which there is a progressive decline in both the absolute and the relative polydispersity of the nanocrystal ensemble. As mentioned earlier, in attempting to confirm that this observed behavior is truly a feature of the synthesis and not an experimental artifact we have performed these experiments under both recirculating and non-recirculating conditions and have observed comparable qualitative results between syntheses (i.e. the above points still hold). As was argued earlier, the measurement of the particle number $n_{np}(t)$ is likely reasonably accurate despite the convolution of shape and polydispersity effects potentially affecting the polydispersity estimate and so these measurements are likely to provide a good estimate for the time scale of the nanoscale nucleation event in these
syntheses. Moreover, even if the SAXS model has systematic error in estimating different parameters, the extracted radii and the results for the size and polydispersity are comparable when isolated particles synthesized in lab tested for monodispersity by UV-Vis/NIR are measured as ex-situ samples in comparison to the end result of sequences under in-situ conditions.

That the timescale of the nucleation event should be approximately two orders of magnitude larger than the time resolution of the scattering measurement (approximately 1 second) is of course very surprising given the discussion earlier about the prevalence of “burst nucleation” as a mechanistic rationale for explaining monodisperse nanoparticle synthesis. It is important to remember that the original study of sulfur sol nucleation by LaMer and coworkers was really only a study of particle growth as the nanometer length scale nucleation event could not be probed by the visible light scattering techniques used in this study.9,20 In experimental studies where the nucleation period of nanocrystals is actually measured experimentally by either diffraction or absorbance spectroscopy, it has generally been observed to persist for seconds to minutes.32-34,40,75 The pervasive untested citation of the LaMer model in nanoparticle science for instantaneous nucleation was recently “colorfully” described by Finke as citing “the physically most unreasonable assumption [of the model], a practice that makes little sense and should be discontinued.”20
Figure 1.3.13 Time evolution of the [QD] and the concentration of particles and focus on the nucleation period (right) for lower temperatures reaction conditions shown in scheme above.

In addition, we have found that under lower temperature conditions with a slower precursor the time scale for all of these processes is even slower. In Figure 1.3.13 above we see the nucleation period here clearly persists for several minutes resulting in an initially polydisperse particle ensemble. Another remarkable thing about this sequence is how the relative polydispersity and absolute polydispersity both “fix” themselves over the course of hours resulting in a relatively monodisperse ensemble. As mentioned earlier, the relative polydispersity decreasing over time is inherently partially related to the increase of the average particle radius over time. This simple mathematical fact nonetheless is a very essential part of the explanation of how a monodisperse particle ensemble is formed. This is particularly true for reactions that consist of a nucleation period and a growth period that are not fully temporally overlapped (even if the nucleation period
is finite and overlapped with the growth period to some extent the principle still applies). Fundamentally, the idea that a finite nucleation period that is overlapped with growth should result in an increase in polydispersity is experimentally seen here at early reaction timepoints. However, the decrease in the absolute polydispersity is again indicative of the fact that some size focusing process is occurring during the growth process itself that is leading to the decrease in the absolute standard deviation.

**Figure 1.3.14** Time evolution of the absolute polydispersity in terms of radius for reaction in Figure 1.3.13
**Figure 1.3.15** Comparison of total [PbS] measured by SAXS or UV-Vis for N-\(p\)-Cl-Phenyl-N’-\(n\)-dodecylthiourea at 110°C under recirculating conditions.

A common feature of reactions studied by our in-situ approach is shown above in Figure 1.3.15 comparing UV-Vis and SAXS measurements of the concentration of PbS measured either by absorbance at 400 nm for which the extinction coefficient is independent of size for particles or from the intensity of the scattering and known scattering length density of PbS. We see that at early times there is less normalized intensity seen for [PbS] by SAXS than by UV-Vis. This could suggest that there exists some metastable form of [PbS] in solution which absorbs light that is not in the particles. This would be what is conventionally known as “solute” in crystallization theory, although from this experiment alone it is hard to decisively identify the difference of the two traces as a direct form of measurement of this quantity. We will identify further evidence for the buildup of solute in solution by other multimodal techniques soon and also in Chapter 2.

Finally, we can remark how the experiments are consistent with the original proposal of Hendricks that the control over the thiourea precursor conversion rate leads to control over particle
number in the model of Sugimoto. The relationship of Sugimoto, strictly correct for a burst nucleation with rate limiting solute supply, is \( n_f = \frac{Q_0 v}{v_+} \) and we expect the number of particles to scale with the solute supply rate \( Q_0 \). While a relationship between \( Q_0 \) and \( n_f \) for this synthesis has been reported\(^5\), we further corroborate this principle by our in situ SAXS measurements. Ultimately, the Sugimoto model’s quantitative relationship is based on an approximate mass balance equation (strictly accurate for burst nucleation and a rate limiting solute supply rate) which allows a facile solution of the coupled differential equations of growth, nucleation, and solute supply to give a strictly linear relationship and real systems like the one below often show sublinear relationships.\(^7\)

**Figure 1.3.16** A Hammett series of N-\( p \)-X-Phenyl-N’-n-dodecylthioureas and their [QD] and radius at 20 mL recirculating reaction scale where (X = Cl (red), H (green), MeO (blue)) illustrating that faster precursors make a larger number of smaller nanocrystals. Relative rates of these precursors are listed in Figure 1.2.3.
1.4 Comparison to other Measurements

1.4.1 UV-Vis NIR/Aliquoting

In considering the results of the experiments above, we must acknowledge that there is inherent uncertainty in assuming the refined model parameters above actually represent physical reality. As such, to attempt to provide corroboration for our conclusions above we turn to see if we can verify aspects of the data by another technique. Due to the quantum confinement effect, in principle, we can measure the size of the particle during growth by light absorption – using the empirical sizing formula of Moreels.\(^4^4\)

\[
E_0 = 0.41 + \frac{1}{0.025d^2 + 0.283d}
\]

Eq. 1.4.1

Here \(E_0\) is in eV and was measured at energies between 0.71 and 1.28 eV (970-1740) nm which is within the Near-IR. While our UV-vis dip probe could not capture this low energy light, the higher end visible light contains wavelengths well above the band gap where the extinction coefficient of the transition depends only on the total volume of the particle or total number of PbS units. This absorbance can therefore be used as an independent measurement of \([\text{PbS}]\) or the chemical yield of the reaction. Finally, within the NIR we can measure particle concentration using the empirical extinction coefficient for the 1\(S_e\) \(-\) 1\(S_h\) transition peak position as a function of particle radius to concentration of Cademartiri.\(^4^5\)

\[
\varepsilon (M^{-1}cm^{-1}) = 19600r^{2.32}
\]

Eq. 1.4.2

Using these equations, we can in principle measure the concentration of particles as a function of time by measuring the UV-Vis/NIR absorbance. Probably the most surprising result of our SAXS measurements is the long duration of the nucleation period, so this is of substantial value for confirming this finding. We can perform this experiment by quantitative aliquoting
experiments where a small quantity of the reaction mixture is removed from the reaction, added to
a pre weighed test tube and immediately quenched by freezing in dry ice/acetone mixture, and then
weighed. Reaction conditions were optimized to allow for kinetics which were sufficiently slow
to be effectively measured with aliquoting and an example is shown below in Figure 1.4.2. In the
NIR where the $1S_e - 1S_h$ electronic transition takes place we see the expected red shifting
behavior of this transition indicating the growth of the particles.

$$
1.2 \text{Pb(Oleate)$_2$} + \text{NH}_2\text{NHCH}_3\text{S} \xrightarrow{19:1 \text{Hexadecane:DPE}} \text{100°C, Argon} \rightarrow \text{[PbS]$_n$[Pb(Oleate)$_2$]$_m$}
$$

**Figure 1.4.1** Aliquoting of a PbS reaction. Approximately 200 $\mu$l aliquots taken every minute.
Noise around 860 nm is due to a detector change on the instrument at that wavelength. The small signals at around 1250 nm and 1400 nm can be assigned to NIR C-H overtone and combination bands as is discussed below.

An interesting feature of these reactions that is not observed by in situ dip probe UV-vis measurements is that upon freezing the reactions and allowing them to thaw – previously clear reaction aliquots turn a light yellow/red color alongside noticeable quantities of a precipitated white solid which we presume are precursors/reaction products. Upon measuring the aliquots, we see absorbance through the visible and a noticeable peak around 600nm where we would otherwise see no absorbance in an in-situ experiment. This peak noticeably decreases after the first few scans, as the NIR peak for the particles grows in intensity. We assign this peak to a self-assembled cluster of \([\text{PbS}]_n[\text{Pb(Oleate)}_2]_m\) that forms from pre-nucleation solute that builds up during the beginning of the reaction period. The formation can be rationalized by lead oleate precipitating upon cooling
which could function as a stabilizing Z-type ligand on solute coordination sites (this will be discussed more substantially in Chapter 2, and will just be posited as a hypothesis for now).

An experimental difficulty associated with this measurement is the appearance of NIR absorbances for organic molecules within the range of interest for quantum confined PbS. An excellent reference on this subject is the textbook of Workman and Weyer. The second overtone region for aliphatic C-H stretches in the NIR occurs at around 1150-1210 nm, and an important combination region of C-H stretches/bends occurs at around 1300-1500 nm both of which are visible in the baseline of Figure 1.4.1. To perform these measurements, care must be taken to prepare a solvent background that contains the same ratio of tetrachloroethylene/hexadecane as the experimental aliquots to subtract out this signal otherwise these overtones will be comparable in magnitude to the measured particle excitonic features. This clearly lends some uncertainty to these measurements although many of the earliest aliquots of highest interest below 1200 nm are unaffected.

At lower temperatures we see a rather dramatic extension of the period where solute builds up in the reaction prior to the appearance of particles. In order to attempt to compare the effects independently of precursor conversion rate we tried to identify two precursors with roughly the same precursor conversion rates at two significantly different temperatures that both produced monodisperse particles. The precursors N-p-CF₃-Phenyl-N’-n-dodecylthioureas at 80°C and N-Phenyl-N’-n-dodecylthiourea at 100°C were found to convert into PbS at roughly the same rate which we characterized by fitting a first order expression of the form \( A(1 - e^{-kt}) \) to the concentration of [PbS] as measured in the aliquots absorbance at 400 nm according to Moreels and Hendricks. It is possible that this could be a better measurement of the quantity [PbS]_{tot} than the dip probe UV-Vis originally used by Hendricks which seems to fail to capture some amount
of converted [PbS] that has not yet nucleated by only measuring absorbance at 400 nm.\textsuperscript{52} Shown below is the kinetics traced for the 100°C reaction condition which gives a fit of \( k = 3.99 \times 10^{-3} \). A similar fit for the 80°C condition gave \( k = 1.69 \times 10^{-3} \). While generally good agreement is seen, this disagreement is not insubstantial, and could perhaps be improved by screening more thiourea substrates.

\[ \text{Figure 1.4.3. Early time [PbS] detectable in solution by UV-Vis spectroscopy of absorption at 400 nm in aliquots removed from solution and frozen at time t.} \]

\[ \text{Shown in Figure 1.4.4 are the UV-vis and NIR regions of a times series of 1-minute aliquots now of the 80°C reaction condition detailed above. In this case, the discrete cluster absorbance around 600 nm is present for many more aliquots than at 100°C during which the reaction solution is colorless prior to being cooled. The resulting particles are also much smaller than those in Figure 1.4.2 which could be explained either by incomplete growth relative to the 100°C condition or a larger number of particles being formed. By using the size dependent extinction coefficient in Eq. 1.4.2 as is shown Figure 1.4.4, it appears as though the latter is the case. Notably this result is not} \]
consistent with the normal positive relationship between conversion rate and final size at a given temperature and reaction condition. However, here we are in effect presumably lowering the growth rate constant in addition to changing the precursor conversion rate constant by changing the temperature between these two measurements. The longer nucleation period at a given precursor conversion rate at lower temperature could be due to a smaller growth rate constant which requires more particles to be formed before the growth solute consumption can shut off nucleation as the dominant process consuming solute. Under both of these conditions it appears as though there is an extended period of nucleation as is seen in Figure 1.4.5. This effect is particularly noticeable at lower temperatures as was seen in the SAXS experiments. While UV-vis/NIR and SAXS are each potentially problematic for measuring particle concentration the fact that a persistent nucleation process is seen in both cases attests to the likelihood of it being a physical reality rather than an artifact due to faulty assumptions in one of the techniques.

\[
\begin{align*}
&\text{F}_3\text{C} \quad \text{S} \\
&\text{NH} \quad \text{NH} \quad \text{C}_{11}\text{H}_{23} \\
&\text{1.2 Pb(Oleate)}_2 + 19:1 \text{Hexadecane:DPE} \quad 80^\circ\text{C, Argon} \\
&\rightarrow [\text{PbS}]_n[\text{Pb(Oleate)}_2]_m
\end{align*}
\]

**Figure 1.4.4** Visible (left) and NIR regions of the time series data for 80°C reaction conditions
1.4.2 NMR Monitoring of Precursor Conversion

One difficulty with analyzing our PbS reactions is we have thus far only discussed indirect methods of studying the conversion of the precursor itself. In previous publications on the PbS from thioureas synthesis the *de facto* kinetic assumption is that precursor conversion is a purely rate limiting step in the process. Thus, we can measure the appearance of absorbance at 400 nm arising from crystals adding units of PbS as a proxy for the precursor conversion rate as this is assumed to be completely determined by the precursor conversion rate. This is qualitatively consistent with this systems Sugimoto-like direct relationship (although not linear) between precursor conversion rate and number of particles. However, if precursor conversion were purely rate limiting it is not clear why solute should build up in solution for any period during the reaction as the nucleation and growth rate should both be instantaneously fast relative to the precursor conversion.
In order to provide a spectroscopic handle to help monitor the reaction, a $^{13}$C thiocarbonyl labeled thiourea was prepared from $^{13}$CS$_2$ by way of the known reaction for the decomposition of a dithiocarbamic acid salt to an isothiocyanate by the action of tosyl chloride (Figure 1.4.6).$^{78}$

$$\text{S}^{13}\text{C} = \text{S} + \text{NH}_2 \xrightarrow{3.3 \text{ Eq. TEA}} \text{THF, Ar} \xrightarrow{-10^\circ\text{C Addition 24 Hours, RT}} \text{TEA = Triethylamine}$$

**Figure 1.4.6.** Synthesis of labeled isothiocyanate from CS$_2$ by previously reported chemistry.$^{78}$

Using the labeled molecule, we can directly observe the reaction progress in the protio hexadecane/tetraglyme reaction environment by running an aliquot style experiment where a portion of the reaction is drawn up every 30 seconds and quickly quenched in a pre-weighed test tube in dry ice/acetone mixture. When it is ready to be measured, a reaction time point is thawed and diluted in a known volume of C$_6$D$_6$, brought down to the spectrometer locked/shimmed and run for a set number of scans (usually 100 to get good signal to noise under these conditions) using an inverse gated pulse sequence with a relatively long delay time between pulses ($d_1 = 10s$). While almost certainly not a rigorously QNMR experiment, very approximate kinetics can be extracted by observing the decay in the intensity of the same peak with respect to itself under a given set of NMR parameters as a function of time as has been reported previously.$^{79}$

The observed time series provides evidence for mechanism regarding the precursor conversion reaction. The $^{13}$C time series data collected and shown in Figure 1.4.7. shows a clear disappearance of the thiourea precursor around $\delta = 181$ ppm and formation of what we can assign...
as the N-acyl urea coproduct $\delta = 154$ ppm by comparison of both proton and carbon NMR to independent synthesis and previous work within our group.$^{55,80,81}$

![Figure 1.4.7](image)

**Figure 1.4.7.** Reaction of $^{13}$C N-Phenyl-N’-n-dodecylthiourea with lead oleate monitored by $^{13}$C NMR spectroscopy. Here $R_1$ is phenyl and $R_2$ is dodecyl according to the scheme on the left.

As is reported for the N-acylation of thioureas via their oxidative desulfurization by lead (II) acetate, the N-acylation will proceed with regioselective preference for acylating the amine moiety with the lower pKa attached to the thiourea.$^{80,81}$ At early reaction timepoints we also see evidence for a transient carbodiimide by comparison with carbon NMR by independent synthesis at around $\delta = 136$ ppm.$^{82}$ The presence of an N-acylurea logically suggests as a prior step O-N acyl migration from an O-acylisourea intermediate (See Figure 1.2.7). The O-acylisourea itself could be formed by reaction of the carbodiimide we observe with oleic acid, or conceivably by nucleophilic attack of a carboxylate on a thiocarbonyl carbon.$^{83}$ We imagine the disubstituted thioureas used in PbS nanocrystal synthesis convert by deprotonation of a lead (II) thioureate intermediate with an idealized monomeric form of this molecule and its decomposition to form carbodiimide, oleic acid, and PbS shown in Figure 1.4.8. This could provide a very simple rationale for the dramatic difference in reactivity between trisubstituted thioureas and disubstituted thioureas.
as the former only have one proton to give up where the latter have two and thereby can break the C=S double bond by two sequential deprotonation steps to (i) form a thioureate intermediate and then (ii) decompose this thioureate intermediate to form PbS and the carbodiimide by proton transfer.

\[
\begin{align*}
\text{Oleyl} & \quad \text{Pb} - \text{S} - \text{N} = \text{N} - \text{H} \\
\rightarrow & \quad [\text{PbS}]_n^+ + n(\text{Oleic Acid}) + n\text{R}_2\text{N} = \text{C} = \text{N} - \text{R}_1
\end{align*}
\]

**Figure 1.4.8.** Proposed decomposition of lead thioureate intermediate to carbodiimide and oelic acid

1.4.3 Comparison of UV-Vis, NMR kinetics

As was mentioned earlier, it has previously been assumed that precursor conversion is a purely rate limiting step in the synthesis of lead sulfide nanocrystals from disubstituted thioureas and lead oleate. While the kinetics derived from watching the decay of the \(^{13}\text{C}\) NMR signal intensity are clearly prone to systematic error, they do provide at least some direct measurement to test this hypothesis with. As is shown in Figure 1.4.9, comparing the appearance of absorbance at 400 nm by an in-situ UV-vis dip probe measurement and the disappearance of \(^{13}\text{C}\) NMR signal intensity by an aliquoting experiment with labeled precursor the results are comparable within a factor of two. Given the substantial experimental differences between the in situ versus ex situ experiments and general difficulty in getting reproducible kinetics given temperature fluctuations and inhomogeneities of several degrees Celsius in colloidal synthesis reactions we do not expect
to be able to resolve a $^{12}$C/$^{13}$C carbon kinetic isotope effect in this reaction. However, these results firstly suggest that the prior assumption of rate limiting precursor conversion by Hendricks was fairly reasonable as an approximation.

$$\text{1.2 Pb(Oleate)$_2$ + } \text{19:1 Hexadecane:DPE} \xrightarrow{110^\circ\text{C, Argon}} [\text{PbS}]_n[\text{Pb(Oleate)$_2$}]_m$$

**Figure 1.4.9** Measurement of the rate of precursor conversion by (left) appearance of absorbance at 400 nm measured by in situ UV-vis and (right) disappearance of signal intensity from labeled $^{13}$C NMR peak intensity. When fit to a first order rate constant approximation they are the same within a factor of two.

What is almost certainly the case based on this experiment is that there is no elementary step of the reaction much slower than the precursor conversion rate, given the relatively close agreement within a factor of two between direct precursor conversion rate and appearance of [PbS]
in particles. A more complex kinetic picture than absolute rate limiting precursor conversion could be the case as there are hundreds to thousands of kinetically coupled elementary steps one could imagine writing out in the formation of a crystal of \( n \) formula units by sequential addition of monomers as was explored recently by Finke (this is not even considering various ligand association/dissociation equilibria at particle surfaces that could be important).\(^{20}\) One could interpret the difference between these rates as consist with buildup of [PbS], solute in the reaction which is evidenced by the induction delay between thiourea addition and observed nucleation, difference between SAXS and in-situ UV-vis, the appearance and disappearance of a cluster intermediate in the UV-Vis NIR aliquoting experiments, and further X-ray total scattering experiments we will describe in Chapter 2. This is likely the correct interpretation here, and the precursor conversion has substantial impact on the overall reaction kinetics as the slowest individual step, but not quite slow enough that it fully describes the complex overall kinetics of particle formation which involve hundreds to thousands of coupled individual elementary steps of nucleation and growth.

1.5. Population Balance Modeling of SAXS Results

1.5.1 Framework of PBM

To account for our results, we turned to the framework of population balance equations which are applied to describe crystallization phenomena in chemical engineering by treating an ensemble of particles by a number density state vector \( n(x_1, x_2, \ldots x_n) \) that is a function of various possible internal and external spatial and time coordinates.\(^{85-87}\) In the simple case of anisotropic particles uniformly distributed throughout a continuous medium we can describe the number density as a function of a size parameter \( r \) and time \( t \) or \( n(r, t) \). For a system with no nucleation or aggregation one can imagine at time \( t \) the number density of particles is distributed along a size
coordinate $r$ which deforms with a velocity equal to the growth rate $G(r, t)$. In general, the population balance framework is useful as it allows us to write differential equations relating the various properties of the particle system in terms of this state vector describing its internal (or external) coordinates. Here we utilize the 1D population balance equation in Equation 1.5.1 for which a derivation can be found in Ramkrishna. To construct a PBE, we require a nucleation rate $J(t)$, the rate law for particle growth $G(r, t)$, and the concentration of PbS units that remain dissolved in solution. Here $B(n, r, t)$ is the net generation of particles through all events including nucleation, agglomeration, and breakup of particles.

\[
\frac{\partial n(r, t)}{dt} + \frac{\partial [n(r, t)G(r, t)]}{dr} = B(n, r, t) \tag{Eq. 1.5.1}
\]

Here we get $J(t)$ from the SAXS experimental measurement of [QD]. We also define the concentration of PbS in solution $[\text{PbS}_{\text{dissolved}}]$ by the $[\text{PbS}_{\text{solid}}]$ in particles measured in SAXS as $[\text{PbS}_{\text{dissolved}}] = [\text{PbS}]_{\text{total}} - [\text{PbS}]_{\text{solid}}$. $[\text{PbS}]_{\text{total}}$ is approximated as the first order fit to the dip probe UV-Vis data. Given the experimental inputs and a model for $G(r, t)$, the PBE predicts particle average size and polydispersity which are experimental parameters we can compare our model to. Thus, we can ask the question: what growth law is consistent with our experimental results?

1.5.2 Results of 1D PBM Treatment

A survey of empirical growth laws confirm that a $1/r$-type growth law $G = \frac{C[\text{PbS}]_{\text{dissolved}}}{r}$ accurately reproduces the experimentally measured mean size, and polydispersity as a function of time as is shown in Figure 1.5.1 where $C$ is a refined parameter. Empirical growth laws that did not include this inverse size dependence failed substantially. The model captures the evolving
polydispersity which increases substantially at early times as nucleation is persistent and concurrent with growth then decreases. Further, this the model with a 1/r-type growth law consistently described the data the best over multiple different precursor conversion rates and temperature conditions and temporal length scales of reactions another example of which is shown in Figure 1.5.2.

**Figure 1.5.1** Experiment and simulation for N-\(p\)-Cl-Phenyl-N'-'-dodecylthiourea at 110°C under recirculating conditions using either a size dependent growth law dependent on \([PbS]_{\text{dissolved}}\) (above) or one mererly dependent on \([PbS]_{\text{dissolved}}\) (below).
This inverse radius dependence of the growth rate in the classical theory of growth for diffusion limited growth is well known and often cited in nanoparticle formation mechanisms. If we interpret our model in this way, we get a value for the diffusion coefficient of the solute that is $3.46 \times 10^{-11}$ m$^2$/s, nearly 1-2 orders of magnitude smaller than that of small molecules. By the Stokes-Einstein equation, $D = \frac{k_B T}{6\pi \eta r}$, this would also suggest a size on the order of ten nanometres which is larger than the final PbS nanocrystals themselves. As a comparison, DOSY diffusion NMR measurements were performed on lead oleate in $d_8$-toluene and found a diffusion coefficient of $3.61 \times 10^{-10}$ m$^2$/s. This suggests that the size dependence of the growth rate we observe likely does not arise from the conditions of at least traditional diffusion limited growth. We could imagine other sources of the size dependence such as the radius dependence of the number of edge sites or an effectively slower diffusion through the ligand shell of the particle that must be overcome for growth. It also is possible that a size dependent reactivity could arise from a more reactive particle surface at smaller sizes causing a smaller barrier to activation and thus faster growth in the model of a linear free energy relationship. Distinguishing between these various possibilities will be a difficult, but potentially highly rewarding source of future inquiry.
1.6. Summary

In this work we have studied the nucleation and growth of monodisperse PbS nanoparticles during synthesis and discovered a highly non-classical mode of formation where nanocrystals are formed during an extended period of nucleation and then decrease in polydispersity during a period of size focusing growth. Much of the appeal of the LaMer model to modern nanocrystal synthesis lies in its simplicity and economy of explanation: every particle is borne at the same time, and all grow the same way, so they end up the same size. We provide evidence for an alternative explanation for how monodisperse ensembles could arise in solution which can also be stated simply: the smaller particles grow faster than the larger ones.

1.7 Experimental Details

1.7.1 Materials and Methods

Toluene (99.5%), isopropanol (≥99.7%), triethylamine (≥99%), 4-methoxyphenyl isothiocyanate (98%), 4-chlorophenyl isothiocyanate (99%), 4-(trifluoromethyl)phenyl isothiocyanate (97%), trifluoroacetic acid (99%), trifluoroacetic anhydride (99%), were obtained from Sigma Aldrich and used without further purification. 3,5- bis(trifluoromethyl)phenyl isothiocyanate (97+) was obtained from Maybridge and used without further purification. Dodecylamine (99%) was obtained from Sigma Aldrich and purified by vacuum distillation at 100°C. Diphenyl ether (≥99%), hexadecane (99%), tetraethylene glycol dimethyl ether (“tetraglyme,” ≥ 99%) were obtained from Aldrich, stirred with calcium hydride overnight, distilled and stored in a glove box over activated 3Å molecular sieves for 24 h prior to use. Oleic acid (99%) was obtained from Aldrich stored in a –20 °C freezer, and used without further purification. Benzene-d₆ and Toluene-
were obtained from Cambridge Isotope Laboratories and stored in a glovebox over activated 3Å molecular sieves for 24 h prior to use. Lead(II) oxide (99.999+%) was obtained from Strem or Alfa Aesar and used without further purification. UV-Vis-NIR spectra were obtained using a Perkin-Elmer Lambda 950 spectrophotometer equipped with deuterium and halogen lamps and either a PbS or InGaAs detector. UV-Vis-NIR spectra were corrected with a linear baseline correction and an offset at the detector change (860 nm).

1.7.2 Small Angle X-Ray Scattering Beamline Experiments

The SAXS/WAXS experiments were performed on the ID2 beamline of the ESRF at an energy of 11.5 keV (wavelength of 1.08). The sample to SAXS detector distance was 1.29707 m which yields a q-range of 0.067 to 5.33 nm⁻¹. For recirculating conditions 19 mL of a 10.8 M solution of lead oleate in hexadecane are poured in a three-neck round bottom flask under argon. An oil bath is used to set the temperature to 110°C. For non-recirculating conditions this reaction scale was increased by a factor of 7.5. While differences exist between these modes of operation, in particular the polydispersity at earlier times for non-recirculating conditions is normally larger, the same qualitative evolution of the reaction parameters are observed and the difference between final refined parameters is within around 20%. The reacting fluid is pumped through a glass capillary using a peristaltic pump (drive 5201 from Heidolph with a SP Quick head). The connection between the needles plunging in the liquid and the X-ray capillary is made with equipped with MASTERFLEX Viton tube FDA LS Size 14 with an inner diameter of 1.6 mm. The flow rate within the fluidic circuit is 24.5 mL/min and around 2m of tube are used which correspond to around 4 mL circulating outside the flask during the reaction.
1.7.3 Small Angle Scattering Modeling

Starting from the intensity versus wavevector files, all data handling was performed using Ipython and Ipython Notebooks. The non-linear fits were performed using the Levenberg-Marquardt algorithm implemented in the LMFIT module in Python. Scattering length density of PbS was taken from the NIST website.

1.7.4 Synthesis

Lead oleate and thioureas were prepared from lead trifluoroacetate according to Hendricks et al. on 80-100 mmol scale. Purity of thioureas was confirmed by $^1$H NMR comparison to literature data. Purity of lead (II) oleate was confirmed by $^1$H NMR as well as $^{19}$F NMR to assure trifluoroacetate salts had been successfully removed. $^{13}$C Labeled N-phenyl-N’-dodecylthiourea was prepared according to Hendricks et al. by $^{13}$C enriched phenyl isothiocyanate prepared from $^{13}$CS$_2$ (97-99%) by the procedure of Wong et al.

($^{13}$C) N-phenyl-N’-dodecylthiourea (3d). White powder. $^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 0.92$ (t, 3H, -CH$_3$), 1.01-1.35 (m, 20H, (CH$_2$)$_{10}$), 3.48 (b, 2H, N-CH$_2$), 5.67 (b, 1H, NH), 6.78-6.87 (m, 3H, p-CH + o-CH), 6.87 (d, 2H,), 6.94 (t, 2H, m-CH), 8.42 (b, 1H, NH); $^{13}$C{$^1$H} (125 MHz, C$_6$D$_6$): $\delta = 14.40$ (-CH$_3$), 23.15 (CH$_2$), 27.20 (CH$_2$), 29.26 (CH$_2$), 29.66 (CH$_2$), 29.85 (CH$_2$), 29.98 (CH$_2$), 30.04 (CH$_2$), 30.14 (CH$_2$), 30.15 (CH$_2$), 32.36 (CH$_2$), 45.48 (NCH$_2$), 124.98 (oC), 126.34 (p-C), 129.96 (m-C), 137.51 (i-C), 181.34 (C=S)
1.7.5 UV-vis/NIR Aliquoting of PbS Reactions

Lead oleate (.166 grams/.000216 moles) is loaded into a 3 neck 50 mL flask with a glass thermowell with 19 mL of hexadecane in a glovebox. The thiourea is dissolved in 1.2 mL of diphenyl ether by a volumetric syringe. Solvents are filtered with a 0.2 micron filter to remove sieve dust which can affect reaction outcomes. The lead oleate suspension is brought out to a Schlenk line and degassed by 3X vac cycles and then left under flowing Ar and given 30 minutes to equilibrate at the reaction temperature. Then 1.0 mL of the thiourea solution is injected into the stirring solution at reaction temperature. This makes a solution that is 10.8 mM in Pb and 9.0 mM in S (1.2/1 Pb/S). 200 uL aliquots are then removed, injected into pre-weighed test tubes which are quenched by immediately dipping into dry/ice acetone to quench. All aliquots are then diluted in 2 mL tetrachloroethylene prior to measurement from 400 to 1600 nm. The solvent blank in the UV-vis/NIR experiment must be 2.2 mL 2mL/.2mL TCE/Hexadecane to correctly subtract some C-H overtone and combination region bands from the NIR.

1.7.6 $^{13}$C NMR Aliquoting of PbS Reactions

The reaction procedure is identical to 1.7.4. although here labeled precursors are used. 300 uL aliquots are taken and diluted in 300 uL C$_6$D$_6$ for each aliquot. While locking can be done with less deuterated solvent, changing this ratio too much can lead to precipitation of thiourea and/or urea coproducts. The reaction aliquots are brought down to a 500 MHZ NMR spectrometer, locked, shimmed and 100 scans with a d1 value of 10s are taken for each timepoint.
1.7.7 1D PBE Methodology

Numerical methods were applied to simulate the 1D Population Balance Equation. The 1D PBE is discretized first in the particle radius domain, generating a set of ODEs with time derivatives. These ODEs are then discretized in the time domain using a fourth order Runge-Kutta method with variable time stepping giving a set of algebraic equations, which are solved using iterative method. This finally gives the number density distribution as a output, from which we calculate the mean radius and polydispersity directly. Polydispersity is calculated as the ratio of standard deviation to the mean radius.
1.8. References


(22) Sugimoto, T. Effects of Convection and Brownian Motion on Particle Growth Rate in Colloidal Dispersions. *AIChE J.* 1978, 24, 6, 1125-1127.


(89) [https://www.ncnr.nist.gov/resources/](https://www.ncnr.nist.gov/resources/)
Chapter 2. Total Scattering Real Space Pair Distribution Function Analysis Measurements of PbS and PbSe Nanocrystal Nucleation and Growth

Table of Contents

2.1. Introduction 83

2.1.1 Theory of Real Space Pair Distribution Function Analysis 83
2.1.2 Modeling the Pair Distribution Function for Nanocrystals 87
2.1.3 Previous in-Situ work on Local Structure during Nanoparticle Synthesis 91

2.2. Acquisition of in-Situ Total Scattering during PbS Nanocrystal Formation 93

2.2.1 Beamline Experimental Design and Setup 93
2.2.2 Data Collection and Reduction 98
2.2.3 Time Series Data Results 100

2.3. Attenuated Crystal PDF Data Modeling and Methods 104

2.3.1 Attenuated Crystal Modeling 104
2.3.2 Pearson Analysis 109

2.4. Interpretation of PDF Results 112

2.4.1 Effects of Ligand Chemistry on the Local Structure at Early Times 112
2.4.2 Analysis and Interpretation of the Induction Delay 121
2.4.3 Comparison of PbS and PbSe Induction Delay 123

2.5. Other Multimodal Experiments 125

2.5.1 In-line PDF/UV-Vis 125

2.6. Summary 127

2.7. Experimental Details 128
2.7.1 Materials and Methods

2.7.2 Total Scattering Measurements

2.7.3 Pair Distribution Function Analysis Data Processing and Modeling

2.7.4 Synthesis

2.8. References

Reproduced in part from


Ellie Bennett, Natalie Saenz, Dr. Daniel DeRosha, Dr. Abraham Jordan, Prof. Benjamin Abécassis, Prof. Jonathan de Roo, and Dr. Sanjit Ghose are recognized for valuable contributions in helping carry out X-ray total scattering experiments. Dr. Sanjit Ghose is recognized for assistance with data reduction and processing. Prof. Jonathan de Roo, Dr. Michael Campos, and Brandon McMurtry are acknowledged for work on in-situ UV-Vis spectroscopy, and data collection and analysis methods for PbS and PbSe formation. Prof. Simon Billinge, Dr. Soham Banerjee, Dr. Maxwell Terban, and Dr. Gihan Kwon are acknowledged for valuable discussions on handling PDF data.
2.1 Introduction

2.1.1 Theory of Real Space Pair Distribution Function Analysis

Structural analysis of nanocrystalline materials by X-ray diffraction poses a unique experimental challenge. While a nanocrystal possesses some degree of atomic order in real space, and hence some in reciprocal space, the fundamental crystallographic assumption of lattice periodicity breaks down on this length scale. The broad and poorly resolved X-ray diffraction patterns that nanocrystals produce in diffraction experiments are due to their inherently limited periodicity and disordered surface structure which rules out the application of the powerful techniques of single crystal X-ray crystallography.\(^1,2\) Although there are examples where nanoparticles have themselves been successfully crystallized into bulk single crystals, these crystallizations are by no means straightforward, and the results often have poor atomic resolution in comparison to routine small molecule crystal structure solutions due to the large number of atoms contained in the unit cell.\(^3\) - 6 The Pair Distribution Function (PDF) method provides valuable real space structural information from X-ray diffraction for nanoscale atomic systems without the presumption of bulk periodicity that is essential to the application of Bragg’s law.\(^1,7\)

Most of the essential physics underlying the real space PDF analysis technique is captured in the equation which gives the wave function amplitude \(\psi(Q)\) of a wave scattered by a system of \(v\) atoms with atomic form factors \(f(Q)\) with positions vectors given by \(R_v\) as a function of momentum transfer \(Q\) (Eq. 2.1.1)

\[
\psi(Q) = \frac{1}{\langle f(Q) \rangle} \sum_v f_v(Q) e^{-iQ \cdot R_v}
\]

Eq. 2.1.1

The equation above considers single scattering of X-rays and an intuitive derivation is given by Egami and Billinge as well as elsewhere.\(^8,9\) The momentum transfer or scattering vector \(Q\) is here
defined as $Q = k_{\text{final}} - k_{\text{initial}} = \frac{4\pi \sin(\theta)}{\lambda}$ where $k$ is the wavevector of the wave of magnitude $|k| = \frac{2\pi}{\lambda}$ and is identical to the $q$ defined in Chapter 1 for small angle scattering although we will refer to it as $Q$ for consistency with the PDF literature. $\langle f(Q) \rangle$ is a compositional average of the atomic form factor of the system of atoms. From Equation 2.1.1 we see what we already concluded earlier from Equation 1.1.8—the amplitude of a wave scattered by a system of atoms is simply the Fourier transform of the real space atomic position $R_v$. While we cannot directly obtain $R_v$ by inverse Fourier transform of experimentally measured intensity due to loss of the phase information, the underlying principle of the PDF method is the Fourier relationship between $Q$ and atomic position.\textsuperscript{8}

The coherent single scattering intensity $I_{\text{coh}}(Q)$ is the principal source of experimentally observed intensity in standard X-ray diffraction described herein and is related to a scattering cross section $\frac{d\sigma}{d\Omega}$ where $d\Omega$ is the angle the detector subtends with respect to the origin. PDF analysis considers a real space function $G(r)$ which is related to a normalized form of this observed scattering intensity by a Fourier transform. In this case the normalized form of the scattering intensity is what is known as the total scattering structure function $S(Q)$ as defined in Eq. 2.1.2.

$$S(Q) = \frac{I(Q)}{\langle f(Q) \rangle^2} = \frac{I_{\text{coh}}(Q) - \langle f(Q) \rangle^2 + \langle f(Q) \rangle^2}{\langle f(Q) \rangle^2} \quad \text{Eq. 2.1.2}$$

PDF analysis consists of taking a sine Fourier transform of a normalized experimentally observed scattering intensity (specifically the reduced total scattering structure function $F(Q)$ as defined in Eq. 2.1.3) that yields a distribution function in real space $G(r)$ that can be used to describe the structure of a system of atoms as defined and explained in detailed below.\textsuperscript{8}
For a macroscopically isotropic system of $N$ atoms in a volume $V$ one can define a real space function $g(r)$ that describes the system in terms of relative interatomic distances (Eq. 2.1.4)

$$
\rho(r) = \rho_0 g(r) = \frac{1}{4\pi Nr^2} \sum_v \sum_{u \neq v} f(Q)_v f(Q)_u \langle f(Q) \rangle^2 \delta(r - r_{vu}) = \frac{R(r)}{4\pi r^2}
$$

Here $\rho_0$ is the average number density, $\rho(r)$ is the pair density at interatomic distance $r$, and $r_{vu}$ is the distances separating the $v$th and $u$th atom with the double sum running over all the pairs of $N$ atoms in the system and $\delta$ is the Dirac delta function. This function $g(r)$ is known as the pair distribution function and is peaked at interatomic distances within the sample. It can be thought of as a histogram of interatomic bond distances. The relation of $g(r)$ to the more physically intuitive radial distribution function $R(r)$ is also given in Eq. 2.1.4, for which the coordination number $N_c$ of an atom in the coordination shell between $r_1$ and $r_2$ is $N_c = \int_{r_1}^{r_2} R(r) dr$.

The atomic pair distribution function is directly related to the reduced pair distribution function $G(r)$ which is accessible directly from the Fourier transform of the properly normalized scattering intensity (Eq. 2.1.5).

$$
G(r) = \frac{2}{\pi} \int_0^{\infty} F(Q) \sin(Qr) dQ
$$

In actual experiments, the range of the integral in Eq. 2.1.5 for $G(r)$ is constrained to a finite limit of scattering vectors $Q_{\text{min}} \leq Q \leq Q_{\text{max}}$ due to both the inherent angular range of the detector as well as further considerations about data quality we will discuss in detail later. For bulk materials the equation reduces to the commonly used (but not strictly correct for finite objects) expression for the reduced pair distribution function $G(r)$ in Eq. 2.1.6. This equation highlights the general features of the experimental $G(r)$: it is a function that contains peaks at average interatomic

$$
F(Q) = Q(S(Q) - 1)
$$
separations which represent deviations from the average number density of the system and asymptotically approaches zero in the limit as \( r \) approaches zero and infinity.

\[
G(r) = \int_{Q_{\text{min}}}^{Q_{\text{max}}} F(Q) \sin(Qr) dQ = 4\pi r \rho_0 (g(r) - 1)
\]

Eq. 2.1.6

As was just indicated, the commonly written expression for \( G(r) \) requires some correction for nanoscale objects as was recently demonstrated by Farrow and Billinge when considering the small angle scattering, but in general the equation in 2.1.6 is sufficient to interpret the meaning of the \( G(r) \) as a measure of the deviation from the average number density at a pair distance \( r \). We will now discuss in detail the principles for calculating \( G(r) \) from discrete nanoscale objects. Considering the above Eq. 2.1.6, we can note that the fastest oscillating component that we will use to build our \( G(r) \) by our sine Fourier series is determined by \( Q_{\text{max}} \) giving us an effective real
space resolution $\Delta r = \frac{\pi}{Q_{\text{max}}}$ for which no finer real space feature can be resolved. This is why diffraction experiments that can generate a $G(r)$ that can be analyzed for substantial real space information require measuring a large range of scattering vector and are called “total scattering” measurements.\textsuperscript{12}

2.1.2 \textit{Modeling the Pair Distribution Function for Nanocrystals}

While we have not yet discussed the experimental details of acquiring the 1D azimuthally integrated intensity $I(Q)$, and from this the total scattering structure factor $S(Q)$, we will temporarily take for granted that such quantities have been acquired over a large range of $Q$ and Fourier transformed to $G(r)$. With this in mind, how can we model such data and extract from it real space parameters of interest? In the previous chapter we considered a procedure by which we sought a model which was equivalent in scattering in reciprocal space to the observed data and then assumed that the refined parameters of that model (size, polydispersity, concentration, etc.) were the physical reality of the system. The procedure of PDF modeling is identical except we search for a model in real space which is equivalent to the produced $G(r)$ in our system.

While one could argue that fundamentally no new information is created in the Fourier transformation, the value of our natural physical intuition for real space for both model construction and interpretation is substantial and can lend insight into results of analysis that would otherwise be unavailable. This is particularly true for “diffuse scattering” contributions to the total scattering between the Bragg peaks which arise from various forms of deviation from ideal crystallinity which are normally curve-fit and discarded in traditional crystallographic or PXRD analysis.\textsuperscript{8,13} For very small nanostructures (<10 nm) that contain only hundreds of unit cells this is
especially important as assumptions of the relevant space group symmetry become increasingly inappropriate at smaller and smaller sizes.\(^7\)

One can separate paradigms of modeling into two predominant approaches which we shall call “large-box,” and “small-box” modeling. Large-box modeling seeks to find a system of atoms with a defined set of interatomic positions \(R_v\) with an identical \(G(r)\) to the measured system. In general the large number of potential degrees of freedom for a system of hundreds or even dozens of atoms cannot all be refined as free parameters simultaneously and free variables in fitting such a model would normally include anisotropic thermal parameters for a given atom type, and a stretching factor for the interatomic distance matrix to account for changes in bond lengths. In some examples, Reverse Monte Carlo algorithms have been implemented to attack the possible solution space for \(R_v\) allowing more of the atom’s translational degrees of freedom to be refined while still arriving at a solution in an acceptable amount of time.\(^8,14-16\) Small-box modeling on the other hand seeks to define a limited unit cell with periodic boundary conditions attenuated by an appropriate factor for finite size which can describe \(G(r)\) using a minimum of free parameters (lattice parameters, thermal parameters, particle size, unit cell positions and others).

For small box modeling, in real space we can calculate theoretical reduced pair distribution function \(G(r)\) of any object (including nanoparticles now) according to Eq. 2.1.7.

\[
G(r) = 4\pi r \rho_0 g(r) - 4\pi r \rho_0 \gamma(r) \quad \text{Eq. 2.1.7}
\]

Here \(\gamma(r)\) is a characteristic function and is a correction for finite particle shape which is equal to unity for bulk objects. For nanoscale objects, an approach which has been referred to as the “attenuated crystal approximation” is often applied to model the \(G(r)\) where a finite nanocrystal of coherent crystallite size \(d\) is treated as a “cutout” from the bulk crystal lattice as in Eq. 2.1.8.\(^17,18\)
These attenuation factors for nanocrystals of size \(d\) have been calculated for various simple shapes and the most commonly used one is the spherical envelope function \(f(r, d)_{sp}\) (Eq. 2.1.9)

\[
f(r, d)_{sp} = \left[ 1 - \frac{3r}{2d} + \frac{1}{2} \left( \frac{r}{d} \right)^3 \right] h(d - r)
\]

Eq. 2.1.9

Here, \(h(d - r)\) is the Heaviside step function which is zero for \(r\) greater than \(d\), and 1 for \(r \leq d\). This simple treatment of nanoparticles vastly reduces the computational complexity of the modeling and has been applied in many different contexts to both metal and semiconductor nanoparticles. By constraining the structural problems down to the atoms in the unit cell of the particle and a size parameter of the particle we in principle can model many valuable parameters such as particle size, shape, polydispersity, strain, crystal phase and faulting, and thermal parameters may be obtained. The effects of finite size on the pair distribution function, are illustrated in Figure 2.1.2

**Figure 2.1.2** Illustration of the spherical envelope function (left) and impact of finite size on \(G(r)\) assuming Equation 2.1.9.
Alternatively, modeling of $G(r)$ can be performed by consideration of a discrete set of interatomic positions. While Eq. 2.1.7 is general, for discrete calculations of small molecules or clusters of atoms it is generally easier to calculate the reduced total scattering structure function in reciprocal space due to the ambiguity of knowing $\rho_0$ and $\gamma(r)$ for a molecule $a priori$ without PBC. This approach is based on the Debye Scattering Equation (DSE) shown in Eq 2.1.10 with a Debye-Waller correction for loss of Bragg peak intensity in reciprocal space due to thermal motion.\textsuperscript{27,28}

$$F(Q) = \frac{1}{N(f)^2} \sum_{\nu} \sum_{\nu \neq u} f_{\nu}(Q)f_{u}(Q)(e^{-\frac{1}{2}\sigma_{\nu u}^2 Q^2}) \frac{\sin(Qr_{\nu u})}{r_{\nu u}}$$

Eq. 2.10

From here the generation of the $G(r)$ is simply Eq. 2.1.6 with the experimental $Q_{\text{min}}$ and $Q_{\text{max}}$. The DSE method has been applied to model the local structure of many molecular clusters, nanoparticles, and amorphous solids with poor long-range order.\textsuperscript{15,16,29-32} The limitation of this modeling is of course its computational complexity scaling with increasing number of atoms which makes modeling systems of even larger nanoparticles containing many hundreds to thousands of atoms practically impossible.

While many computer programs and open source code have been developed for both large box and small box approaches to calculation of $G(r)$ we have used PDFgui and the DiffPy-CMI complex modeling framework for the calculations herein.\textsuperscript{10,28,33-35} Within our modeling we characterize the goodness of fit of the model by a quantity called the fit residual or $R_w$ (Eq. 2.1.11).

$$R_w = \frac{\sum_{i=1}^{n}[G_{\text{obs}}(r_i) - G_{\text{calc}}(r_i)]^2}{\sum_{i=1}^{n}G_{\text{obs}}(r_i)^2}$$

Eq. 2.1.11

By inspection, this is a quantity that will equal 1 if you fit nothing to the data and is a real positive number for an incorrect model. While the standards for what constitutes a “good” fit to data are
nowhere near as mature as they are for single crystal X-ray diffraction, the literature has taken nanocrystal fits with $R_w$ between .10 and .30 as representing a reasonable degree of agreement although this is about an order of magnitude higher than measurements of bulk metals such as Ni which is commonly used as a beamline calibrant.\textsuperscript{17,20-22}

2.1.3 Previous in-Situ Work on Local Structure during Nanoparticle Synthesis

Prior work related to the study of solution nanocrystal formation processes using the X-ray total scattering real space PDF method have largely been pioneered by the research group of Bo Iversen and were reviewed recently.\textsuperscript{36} The main focus of these PDF studies has been an attempt to characterize the atomic level local structure and bonding that defines different parts of the crystallization process from pre-nucleation to nucleation to growth. Even though conventional wide-angle X-ray scattering measures the d-spacings of interatomic distances, it is often used only qualitatively for nanocrystal structural analysis to identify a majority nanocrystal phase by the observation of broad peaks roughly centered at Bragg reflections for the corresponding bulk crystal phase. The application of more quantitative analyses such as Rietveld refinement are problematic for small nanocrystals around 5 nm or less as diffraction peak lineshapes increasingly reflect nanoscale disorder and deviation from the average structure of the bulk phase.\textsuperscript{37-39} Further, these methods say nothing about the various forms of atomic order that are not a crystalline lattice and are important parts of the crystal formation process and are captured in the $G(r)$. A notable counterexample to this is wide angle x-ray total scattering modeling which is a DSE approach that simply performs the fitting of models in reciprocal rather than real space and is quite similar to PDF analysis.\textsuperscript{7,39}

Prior work on measuring the local structure during nanoparticle formation by total scattering have focused on the solvothermal synthesis of nanocrystals using a custom designed
reactor setup consisting of a thin silica tube capillary which is held by Swagelock fittings, injected with precursor, pressurized hydrostatically, and then heated to the reaction temperature rapidly by an external jet of hot air and then measured using Synchrotron X-rays.\textsuperscript{40} Using this approach, the solvothermal formation of SnO\textsubscript{2},\textsuperscript{41} CeO\textsubscript{2},\textsuperscript{42} WO\textsubscript{3},\textsuperscript{43} TiO\textsubscript{2},\textsuperscript{44} ZrO\textsubscript{2},\textsuperscript{45,46} ZnWO\textsubscript{4},\textsuperscript{47} γ-Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{48} and Pt/Pt\textsubscript{3}Gd\textsuperscript{49} nanocrystals have been studied. Outside of traditional binary/ternary nanocrystals, phase nucleation phenomena have also been studied by the PDF method for ZIF-8\textsuperscript{31} and UiO-66\textsuperscript{50} metal organic frameworks in solution and the formation of different FeSb\textsubscript{x}\textsuperscript{51} phases in the solid state. X-ray total scattering beamlines that have carried out these studies include the P02.1 at the PETRA III, 11-ID-B at the APS, (XPD)-28-ID-2 at the NSLS-II, and ID11 at the ESRF.\textsuperscript{36}

These total scattering studies have attempted to characterize the local structure and bonding of the system and how it evolves during pre-nucleation/nucleation/growth stages of the reaction. This knowledge of local structure is especially important for transient metastable structures which are thought to play a role in formation of the final phase in many systems in accordance with Ostwald’s rule of stages.\textsuperscript{52,53} In contrast, classical nanocrystal nucleation and growth theories like those discussed in Chapter 1 do not consider the crystallization process from the viewpoint of atomic structure explicitly. Although these models do contain free parameters, such as the surface energy γ, that could serve as a means to account for the different chemical structure and bonding between different nanocrystal systems, this is not particularly satisfying from the standpoint of structural chemistry. Total scattering studies of nucleation and growth phenomena have therefore been an attempt to update these more “physics-based” classical models of these processes with what has been dubbed the “chemistry of nucleation.”\textsuperscript{36,50}

The time evolution of $G(r)$ during a nanoparticle formation process is normally characterized by a pre-nucleation period where small metastable pre-nucleation precursor
structures are observed followed by nucleation and then growth of the final crystalline phase. The nucleation and growth of the particles can be directly read from the \( G(r) \) by the increasingly intense correlations at higher pair distances \( r \).\textsuperscript{36} The modeling frameworks applied to characterize such data have included both small box modeling and large box modeling. The nanocrystalline phase identity and growth process has been modeled largely using the small box attenuated crystal modeling framework described earlier. The DSE approach implemented in the DiffPy-CMI framework has proven very popular to aid in assignment of the inherently aperiodic molecular precursor or other metastable structures formed during the synthesis which do not possess long range order.\textsuperscript{31,43,47} The specific conclusions that have been drawn from this analysis about the evolution of the local atomic structure for different nanocrystal systems during synthesis that have been studied are detailed extensively in the review of Iversen and interested readers are referred to this work.\textsuperscript{36}

2.2. Acquisition of in-Situ Total Scattering during PbS Nanocrystal Formation

2.2.1 Beamline Experimental Design and Setup

The in-situ time resolved total scattering experiments were performed primarily at the (XPD)-28-ID-2 beamline at NSLS-II, which has been specifically designed for total scattering experiments of in situ dynamic structure evolution under various out of equilibrium conditions.\textsuperscript{54} The large instrumental \( Q \) coverage possible allows for a large range of scattering vectors to be collected for purposes of accurate PDF real space analysis of interatomic distances. The utility of this beamline to study solution crystallization has been demonstrated in a previously mentioned study on ZIF MOF formation in solution.\textsuperscript{31} However, the high temperature colloidal solution synthesis of PbS quantum dots required the development of some new in situ reactor components for the beamline we shall detail below. The experimental setup used for collecting time resolved
diffraction experiments of PbS and PbSe nanocrystal formation at NSLS-II is shown in Figure 2.2.1. The setup we developed here is analogous to the setup used at the ESRF-ID02 beamline discussed in Chapter 1 although many of the reactor components and reaction protocols had to be developed newly for the facility at XPD.

As in Chapter 1, a lead (II) oleate solution in hexadecane is prepared in a 3-necked flask plunged in an oil bath at the reaction temperature with magnetic stirring under flowing argon, and the reaction is initiated remotely by a pressurized air triggered injection of the thiourea precursor. Injection of the thiourea precursor initiates a peristaltic pump to quickly draw up the reaction solution through a needle into thermally stable Viton tubing which pulls the reaction media in front of the beamline where a Kapton capillary is positioned in a custom designed flow cell sealed with Teflon or graphite Ferrules which passes in front of the beampath. Kapton capillaries proved useful in this context for a few reasons. Firstly, they could be easily replaced in the cell with new tubing at the end of a reaction sequence (the cell used at ESRF was cleaned with aqua regia between runs). Secondly, it was generally found that the scattering was less substantial from the polyimide than comparably sized glass capillaries and it was desirable in these experiments to amplify the relative signal intensity from the particles as much as possible. A relatively large Kapton capillary of 0.0575'' ID x 0.0615'' OD (about 1.5 mm) was used to help enhance the signal intensity which we found to be of substantial value experimentally. A closer look at the custom designed X-ray flow cell is shown in Figure 2.2.2 and Figure 2.2.3.
**Figure 2.2.1** Custom designed X-Ray Flow Cell benchmarked at NSLS-II 28-ID-2 beamline. A remotely triggered injector initiates the nanoparticle reaction by injecting a syringe of the chalcogenoureia precursor into a hot lead oleate solution. Then, a peristaltic pump flows the nanocrystal solution through Viton tubing in front of the X-Ray beam path allowing for time resolved diffraction measurements of the evolving nanocrystal reaction solution.
Figure 2.2.2 Solution is flowed through X-ray flow cell which is aligned with the X-Ray beam.

Figure 2.2.3 Custom designed X-Ray Flow Cell, reaction is flowed through replaceable Kapton capillary in front of the beam bath held in place by a magnetic mount.

X-ray total scattering measurements at XPD were taken over a wide range of $Q$ space with a representative range $0.1 \leq Q \leq 27$ X-ray in rapid acquisition (RA-PDF) mode$^{55}$, using a 2D PerkinElmer amorphous silicon detector. A typical incident wavelength of the X-rays used in these experiments was $\lambda = 0.1877$ Å (66.05 keV). Calibration of the experimental setup was performed.
using a nickel standard sample. The sample-to-detector distance is calibrated using a nickel metal calibrant using FIT2D.\textsuperscript{56} The raw 2D intensity was corrected for experimental effects and 1D azimuthally integrated and converted to 1D intensity versus Q plots in FIT2D. Frames are integrated for 28s with a 2s dark time between collection periods. The integration time used reflects a tradeoff between signal to noise and ability to meaningfully resolve different time periods of the reaction. Although the time resolution achieved here is not ideal for resolving certain features of the nanocrystal formation reaction – for instance polydispersity estimates would be highly unreliable – reaction kinetics were designed by manipulating precursor chemistry with this limitation in mind. A sample 2D diffraction image from a time series data point showing scattering in solution is shown below. As is clear from the image, the solvent scattering defines much of the strongest diffraction intensity observed during these measurements. One of the core challenges of correctly analyzing in situ total scattering measurements resides in proper data subtraction and reduction steps towards the desired reduced total scattering structure function.

![Figure 2.2.4 2D Diffraction image from a lead sulfide nanoparticle in hexadecane solution (left) and 1D azimuthally integrated intensity (right)](image_url)
2.2.2 Data Collection and Reduction

In order to perform the background subtraction and normalization to get to the total scattering function the program xPDFsuite\textsuperscript{57} with PDFgetX3\textsuperscript{58} were used. The visualization features of these Python language-based programs are especially useful for processing low scattering data such as relatively dilute solutions of nanoparticles as they allow visual inspection of the reciprocal space structure functions and real space PDF as processing parameters such as \( Q_{\text{max}} \) are varied. Particularly for early reaction time points it was found to be beneficial to perform the background subtraction manually adjusting the scale factor of the background subtraction \( I(Q)_{\text{sample}} = I(Q)_{\text{obs}} - a \times I(Q)_{\text{background}} \) to avoid background over or under subtraction. The parameter \( a \) should be close to unity assuming proper functioning of the beamline and flow cell apparatus but can often deviate meaningfully by 1-2\% during a time series. A good approach is to line up the most intense peak which largely corresponds to solvent scattering in \( I(Q) \) as a first approximation, and adjust \( a \) within 1\% of its values and observe the resulting \( S(Q) \), \( F(Q) \), \( G(r) \). The resulting generated \( S(Q) \) should obey the appropriate asymptotic behavior of the function approaching a limiting value of unity and not containing negative values after the \textit{ad hoc} corrections implemented in PDFgetX3.\textsuperscript{58}

After the solvent subtraction, the key parameters that must be adjusted are the value of \( Q_{\text{max}} \) and \( Q_{\text{min}} \) to perform the Fourier transform. \( Q_{\text{min}} \) should be determined largely by the beamstop and care must be taken to avoid raising it over a key Bragg reflection or other major structural feature in reciprocal space as this will substantially affect \( G(r) \). It is not advisable to bring this value above 1 in most cases. As was discussed \( Q_{\text{max}} \) is an essential parameter in determining the real space resolution of the experiment. Time resolved scattering from solution crystallization, often involving amorphous intermediates, does not permit the large \( Q_{\text{max}} \) values
preferable for highly accurate structural parameters from real space PDF. In our experiments, by the time mature crystallites have appeared $Q_{max}$ values of around 14-18 Å$^{-1}$ can be comfortably accessed without comprising the integrity of $G(r)$ by Fourier transforming noise. This begins to become increasingly untenable for $Q_{max}$ values above around 20 Å$^{-1}$. For early reaction timepoints containing either low or no concentration of crystalline material rather low $Q_{max}$ values between 10-12 Å$^{-1}$ are reliably used without introducing noise consistent with prior work at XPD.$^{31}$ This is represented in Figure 2.2.5 where we show the same data processed with varying $Q_{max}$ values of 5, 10, 15 and 20 Å$^{-1}$. By the time we are substantially below 10 Å$^{-1}$ we have evidently substantially lost major structural features in $G(r)$ to poor real space resolution and by 20 Å$^{-1}$ we are seeing corruption of the signal by Fourier transforming artifact noise from the weak overall signal of the dilute solution of nanocrystals.

**Figure 2.2.5** Lead sulfide nanoparticle reaction timepoint at late times processed with varying ranges of $F(Q)$ (left) used in the Fourier transform to generate $G(r)$ (right). A $Q_{max}$ of 10 Å$^{-1}$ is accessible throughout the reaction.
2.2.3 Time Series Data Results

Using the setup discussed above we have recorded a number of X-ray total scattering measurements of both lead (II) sulfide and lead (II) selenide nanocrystal formation. The data most immediately available live at the synchrotron without the processing steps discussed above is shown in Figure 2.2.6, the 1D azimuthally integrated intensity. While perhaps hard to discern at first glance, the reaction can be visually observed by zooming in on the clear appearance of several prominent Bragg reflections of the rock salt lattice which monotonically increase as the particles are formed as was observed by our WAXS experiments at the ESRF described in Chapter 1.

![Graphs showing time series data](image)

**Figure 2.2.6** Representative time series of I(Q) of a lead (II) sulfide nanoparticle formation reaction (Reaction scheme in Figure 2.2.7). Data points from every 5 scans to highlight contrast between scans.

Once processed, our results by inspection are qualitatively largely similar to the solvothermal oxide nanocrystal total scattering measurements discussed earlier where a clear particle growth process can be read directly from the increase of pair correlation intensities at
increasingly large real space distances. The results of the reference PbS synthesis from the N-p-MeO-Phenyl-N’-n-dodecylthiourea compound are displayed below in Figure 2.2.7. The choice of thiourea and temperature was based on the time resolution for the total scattering experiment. In this respect, the tunable kinetics of precursor libraries are valuable for designing reaction conditions that can be probed by different spectroscopies with different time resolutions.

\[
\text{1.2 Pb(Oleate)}_2 + \text{(N-r-MeO-Phenyl-N’-n-dodecylthiourea)} \rightarrow [\text{PbS}]_n[\text{Pb(Oleate)}]_m
\]

**Figure 2.2.7** Time evolution of \(G(r)\) during PbS nanocrystal synthesis (first ten points). Each of the 10 plots from the bottom are sequential data points from 28 second integration of frames + 2 second dark period as described in Section 2.2.1. Other plots of data are the same unless indicated.
We have also measured PbSe nanocrystal formation with our reactor and a sequence with similar overall kinetics to the sequence in Figure 2.2.7 is displayed in Figure 2.2.8. A notable feature of these reactions is the appearance of mature crystallites with extended correlations at high $r$ happens more rapidly for PbSe in comparison to PbS. This is somewhat clear by visual inspection of the reaction conditions displayed in Figure 2.2.7 and Figure 2.2.8. As we shall see, this effect becomes much more pronounced at lower temperatures. In both cases, we see a transition from a poorly ordered local structure during early reaction timepoints to the final crystalline phase.

\[
\begin{align*}
1.2 \text{Pb(Oleate)}_2 + & \quad \text{Se} \\
& \quad \text{Hexadecane:Diglyme} \\
& \quad 110^\circ\text{C, Argon} \\
\rightarrow & \quad [\text{PbSe}]_n[\text{Pb(Oleate)}_2]_m
\end{align*}
\]

Figure 2.2.8 Time evolution of $G(r)$ during PbSe nanocrystal synthesis (first ten data points).
The changes to the local structure at early times can be more clearly visualized by overlaying the time series data. For the first five integrated scans for the PbS sequence in Figure 2.2.7 we see the expected monotonic increase in many of the prominent correlations past the first set of nearest neighbor peaks suggesting growth of the coherent crystallite domain sizes in Figure 2.2.9. A closer look at the region between around 2 and 8 Å containing much of the local structure show a number of non-monotonic peak intensity and position trends at early times suggested substantial structural change in addition to crystallite size increase at early reaction timepoints. In particular, the first nearest neighbor correlation does not obey a monotonic increase in intensity at early times. Overall, this is suggestive of the transition between the less ordered pre-nucleation stage containing what has been referred to as “solute” by nanocrystal science and the development of the extended ordered nanocrystalline rock salt phase. Similar behavior is also seen for PbSe in Figure 2.2.10. We will discuss more sequences we have recorded under various conditions and their significance to understanding nanocrystal formation, however, the sequences we have shown are representative of the data we acquire from our in situ total scattering measurements.

![Graph](image)

**Figure 2.2.9** Time evolution of $G(r)$ for a PbS nanocrystal reaction at local length scales during early reaction timepoints.
2.3. Attenuated Crystal PDF Data Modeling and Methods

2.3.1 Attenuated Crystal Modeling

As a first order approximation to reproduce our observed $G(r,t)$, we considered a simple small box model by calculating the theoretical pair distribution function as the convolution of a bulk crystal lattice with a spherical envelope function as described in Section 2.1.2. In our total scattering experiment, we anticipated that the scattering from the nanocrystalline particles would dominate any other aspect of the reaction mixture after the particles had formed and this approach was likely to give us a good fit and description of the data for nearly all of the reaction time. Moreover, observing when and how this model fails to account for the local structure at early reaction times is in itself a valuable piece of information we can obtain from this approach. This is particularly true as the deviations from the model are in real space and can thereby be directly interpreted in terms of the structural failings of a model at a given pair distance $r$. 

Figure 2.2.10 Time evolution of $G(r)$ for a PbSe nanocrystal reaction at local length scales during early reaction timepoints.
To model the time dependent evolution of the crystallites in the PDF $G(r,t)$, we have applied the attenuated crystal model to describe the finite size effects of nanocrystals on the pair distribution function. The PDF is modeled as the PDF of the bulk lattice multiplied by a spherical envelope function $f(r, d)$ dependent on nanocrystal diameter $d$. In this case, $G(r)_{\text{bulk}}$ is the known crystal lattice under ambient conditions which for the lead (II) chalcogenides is the rock salt structure.\textsuperscript{59,60} Fitting parameters related to experimental resolution - the finite Q space resolution gaussian dampening factor $Q_{\text{damp}}$ as well as the empirical broadening factor $Q_{\text{broad}}$ - were acquired by fitting the PDF of a Ni standard taken in the same size Kapton tubing as that used in the flow cell in the same sample orientation. Correlated atomic motion was treated by optimizing a previously proposed empirical quadratic correlated atomic motion correction factor $\delta_2$ which was fit using the PDF of the final nanocrystal product.\textsuperscript{61} Since it seemed impossible to differentiate among various other contributions to the peak width observed in these experiments including strain, static disorder, and changing sample composition during acquisition periods, we viewed this as an empirical correction rather than any concrete measurement of phonon properties. The resulting real space Gaussian peak width correction factor to a correlation at an interatomic separation $r_{vu}$ is $\sigma_{vu} = \sigma_{ij}' \sqrt{1 - \frac{\delta_2}{r_{vu}^2} + Q_{\text{broad}}^2 \cdot r_{vu}^2}$ where $\sigma_{ij}'$ is the uncorrelated peak width calculated from the atomic displacement parameters of the atoms at positions $v$ and $u$.

In order to fit each timepoint to best match the experimental data in the reaction, three parameters are refined using least-squares refinement implemented in PDFgui - a scale factor, a nanocrystal diameter $d$, and a single lattice constant in accordance with the space group symmetry of the FCC structure. Lead chalcogenides have been the focus of a number of pair distribution function studies mostly focused on the proposed relation of local structural distortions to their
thermal and electronic properties in the bulk and the real space Rietveld refinement of PDFGui has been used in this context.\textsuperscript{62,63} The resulting fits of the particles in solution are excellent for nanoparticles after the first few minutes of the reaction and the fit for the final product of a PbS run was used below. Fit of the final product was used to get the anisotropic atomic displacement parameters of Pb and S/Se atoms and $\delta_2$ correction factor to prevent overparameterization of the model for a time series. In principle these could be size dependent quantities, but the result of allowing them to refine freely during a run was large, non-monotonic variations in the fitting parameters over a series and clearly non-physical results at early times.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.3.1}
\caption{Representative $G(r)$ and fit using attenuated crystal modeling of a data point near the end of a time series showing a high-quality fit.}
\end{figure}

Below in Figure 2.3.2 we show the time evolution of the fit and the data during the first 3 minutes of a reaction where the model shows its greatest deviations from the data (and the reactions signal is at its weakest). Despite these limitations, we can see that the model is increasingly capable of accounting for the data at increasingly high pair correlations over time. We quantify this using
the fit residual parameter described earlier in Eq. 2.1.11 $R_w(p_1, p_2, p_3, t)$ where $p_n$ is the nth free parameter in the least squares fitting. We plot in Figure 2.3.3 the fit residual alongside the spherical envelope function (SEF) refined crystallite diameter for the rock salt phase during the reaction.

![Graph showing data points and fits](image-url)

**Figure 2.3.2** Data (blue points) and PDFGui fits (red lines) of the first six datapoints during the first three minutes of the PbS reaction in Figure 2.2.7.

At early times, we see a sharp jump up between data points in the agreement of the model to the data concurrent with a sudden increase in the refined crystal size up to around 2.1 nm. Also, at this point the refined cubic lattice constant jumps up to a value of 5.94 Å from which it doesn’t change during the rest of the time series within a factor of about $\pm 0.01$ Å which is well beyond our real space resolution. In comparison, the bulk phase for PbS has been measured at 5.934 Å which is virtually indistinguishable in our experiment. The dramatic changes in refined parameters can be interpreted as a structural transition from the pre-nucleation stage to the nucleation stage. Following this jump, the fit residual continues to go down as the refined particle radius continues.
to go up during the growth period. A small increase in the fit residual is seen in many sequences at late timepoints in the reaction – in the example in Figure 2.3.3 at around 30 minutes. We believe this is likely due to the formation of very small gas bubbles forming within the flow cell after it has run for some time. Nevertheless, this is a small change, and only happens once the reaction is largely complete.

**Figure 2.3.3** Time evolution of the fit residual and SEF during the synthesis. Here the x axis point assigned to each integrated data point is the end of the full 30s period between unique data points.

Data for PbSe sequences are analyzed by an analogous procedure and produce results that are qualitatively similar. The quality of the fit at late times is quite good for the PbSe particles with a $R_w = .22$ which compares favorably to a prior study of the PDF of PbSe nanocrystals by Hens and Petkov.\textsuperscript{30} Plotted again are the first three minutes of this reaction and accompanying fits to the data for the first three minutes of the PbSe reaction in Figure 2.2.8. What can be correctly observed in the case of this PbSe reaction in comparison to the earlier PbS reaction is
that the attenuated rock salt crystal model much more rapidly begins to account for the observed structure in solution. Said more simply, the PbSe nanocrystals seem to nucleate more quickly and the buildup of concentration of any pre-nucleation phase seems to be less pronounced in the case of PbSe.

Figure 2.3.4 Data (blue points) and PDFGui fits (red lines) of the first six datapoints during the first three minutes of the PbSe reaction in Figure 2.2.8.

2.3.2 Pearson Analysis

The results of the attenuated crystal modeling described above suggest the local structure we observe in this experiment seems to be dominated by two overlapping regimes – a pre-nucleation period where some poorly ordered cluster species persists and a period where the rock salt phase grows continuously. This seems fairly evident from the argument made earlier about the sudden change in the lattice constant, fit quality, and refined size of the nanocrystal fit. However, another way to observe this and more broadly compare the structural evolution of the
particle to itself over a period of time from a model free perspective is by the use of the Pearson product-moment correlation coefficient. For two variables X,Y the Pearson correlation coefficient is defined as in Eq. 2.3.1

$$r = \rho_{x,y} = \frac{\text{Cov}(X,Y)}{\sigma_X \sigma_Y}$$  

Eq. 2.3.1

For two variables X,Y of N discrete items we may write this as

$$r = \frac{1}{N-1} \sum_{i=1}^{N} \frac{(y_i - \bar{x})(y_i - \bar{x})}{\sigma_X \sigma_Y}$$  

Eq. 2.3.2

The Pearson correlation coefficient is a measure of the linear dependence of one variable against another, a r value of 1 implies a perfect direct linear relationship, 0 implies no relationship, and -1 a perfect inverse linear relationship. This method has previously been applied as a fingerprinting technique to compare the local structure of amorphous pharmaceuticals. The Pearson correlation between two G(r) curves consisting of N discrete values is a measure of the self-similarity between the ordered distances observed in two samples. In particular this comparison of two G(r) curves is only sensitive to the relative scaling and positions of peaks but is insensitive to the absolute scaling. We reasoned that this would be a good way to quantify whether the overall structure during two different time points within the reaction was roughly the same as two traces for a larger and a smaller PbS particle should be highly correlated.

Displayed below is the application of this technique to the first ten data point in the in situ PbS sequence show in Figure 2.2.7. We chose here a real space range of .01-50 Å to perform the analysis which should cover nearly all meaningful real space structure of the particles during this period. Other regions can be chosen to highlight certain regions of real space although the results displayed below were pretty consistent as long as the local correlations within the range from about
2-15 Å were included in the range. We schematically organize the correlations in the form of a matrix where $i,j$th element is the Pearson correlation between time point $i$ and $j$. Since the operations in Eq. 2.3.1 are commutative we do not show the terms across the diagonal of trivial correlations. In agreement with our prior conclusions, we see that the two first data points differ most dramatically in comparison to later data points and there is generally a smooth transition across a given row or column as might be expected for a progressive time series of a reaction. We visualize the matrix with the aid of a heatmap corresponding to values of the coefficient which are positive and always reasonably correlated as the structure throughout the reaction contains similar lead chalcogen bonds.

![Pearson Correlation Matrix](image.png)

**Figure 2.3.5** Pearson correlation of some early timepoints of the PbS reactions shown in Figure 2.2.7. “30 seconds” is the end of the first data point integration.
2.4. Interpretation of PDF results

2.4.1 Effects of Ligand Chemistry on the Local Structure at Early Times

Our PDF measurements can be explained by a schematic breakdown of the reaction sequence in terms of precursor conversion, nucleation, and growth. The traditional description of nanocrystal formation as detailed in Chapter 1. begins with a period where the concentration of a pre-nucleation form of the crystallite, somewhat imprecisely referred to as a “monomer,” increases up to a threshold critical concentration. We prefer the term “solute” for our lead chalcogenide synthesis over “monomers” as we do not regard the stable existence of a linear Pb=E diatomic in solution to be energetically plausible. Once solute has built up to a critical concentration the time evolution of the nanoparticle ensemble size and size dispersity is then determined by the competitive rates of nucleation and growth which are traditionally presumed to themselves be reversible processes. These can be written as schematic chemical equations as in Figure 2.4.1

\[
PbX_2 + ER_2 \xrightleftharpoons[k_{\text{conv}}]{1/i} 1/i [PbE]_i + 2 RX
\]  
\[
n[PbE]_i \xrightarrow[k_{\text{nuc}}]{[PbE]_{\text{NC}}}
\]  
\[
[PbE]_{\text{NC}} + [PbE]_i \xrightleftharpoons[k_{\text{growth}}]{[PbE]_{\text{NC}}'}
\]

**Figure 2.4.1** Schematic reaction equations for a “classical” description of the traditional phases of lead chalcogenide (E) nanocrystal formation where “solute” is slowly supplied to the system in an irreversible process (here a chemical reaction between precursors) and nucleation and growth proceed as reversible reactions. Note that the final equation refers to many distinct reactions of different sizes of nanocrystals which do not necessarily have the same growth rate constant \(k_{\text{growth}}\).
Looking at this traditional formulation of nanocrystal formation it can be said that there a few questionable things about the schemes in Figure 2.4.1. First, if one is to read the equations literally the proposal that a molecule like a simple cubane of lead chalcogenide “Pb₄E₄” is building up in concentration without coordinating more ligands is somewhat doubtful as coordination numbers of below four are uncommon for lead (II) complexes with sulfur and selenium donor atom ligands. As the valence of both the chalcogen and lead are satisfied in these charge balanced [PbE]ₙ structures, it is reasonable to invoke some form of a donor-acceptor L or Z ligand binding motif at lead or the chalcogen respectively. This Z-type ligation of metal carboxylates on nanocrystal surfaces has been discussed in detail in work on CdSe nanocrystal surface chemistry by Anderson and Chen and is known for both PbS and PbSe. It is reasonable to assume such Z-type ligation of lead carboxylates also plays a role for the smallest metastable sizes of metal chalcogenides that proceed the formation of particles in the solution.

Another objection to the traditional scheme in Figure 2.4.1. is that there is no obvious reason why the growth and nucleation reactions should be reversible processes a priori. In fact, given the high bond dissociation energy of lead chalcogen bonds (322/261 kJ/mole for Pb-S/Pb-Se) a good argument could be made that n primitive monomers of PbE coming together to make an n-mer of formula [PbE]ₙ should not be expected to be a reversible reaction as the highly endothermic reverse reaction of dissociation to monomers would have a prohibitive activation barrier. This point was made by Finke recently who argued that Classical Nucleation Theory which assumes such reversibility should not be applied to systems that are held together by strong covalent/ionic/metalllic bonds. Such an argument would presumably apply to growth as well.

In order to stabilize the “solute” in PbS synthesis - to study it - we considered the argument above that the structure of such a species would almost certainly contain ligation and probably is
of some general formula $[\text{PbS}]_n[\text{Pb(Oleate)}_2]_m$. It seemed reasonable that dissociation of Pb(Oleate)$_2$ from the particle surface would be a necessary step in further growth of these smaller clusters. Therefore, we might expect we could slow down the growth by adding more Pb(Oleate)$_2$ to push the dissociation equilibrium backwards in accordance with the reaction equation in Scheme 2.4.1. Indeed, this hypothesis proved to be quickly verifiable “by eye” as the use of more lead oleate in otherwise identical reaction conditions led to a much longer time period between the injection of precursor and the appearance of color in the solution. Using our total scattering experiment, we could directly see evidence, as the use of more lead oleate under otherwise identical reaction conditions lead to a prolonged appearance of the more poorly ordered pre-nucleation structure as is shown comparing the early reaction timepoints in Figure 2.4.2.

\[
\text{[PbS]}_n[\text{Pb(Oleate)}_2]_m \leftrightarrow \text{[PbS]}_n[\text{Pb(Oleate)}_2]_{m-1} + \text{Pb(Oleate)}_2
\]

\[
2 \text{[PbS]}_n[\text{Pb(Oleate)}_2]_{m-1} \rightarrow \text{[PbS]}_{2n}[\text{Pb(Oleate)}_2]_{2m-2}
\]

**Scheme 2.4.1** Reaction equation of ligand dissociation to yield a vacant coordination site for further growth.
Figure 2.4.2 Early time data points with 3.0 equivalents lead (left) and 1.2 equivalents lead (right).

This could also be seen by applying our attenuated crystal modeling procedure to the reactions shown in Figure 2.4.2. In the case of 3.0 equivalents of lead oleate, the refined crystallite size of the rock salt phase takes much a much longer time to increase, and the fit residual does not descend as quickly as in the case of 1.2 equivalents of lead oleate. This is consistent with a description where the “solute” in the synthesis consists of a cluster of some general molecular formula \([\text{PbS}]_n[\text{Pb(Oleate)}_2]_m\) in direct analogy to the lead rich surfaces of the final nanocrystals. Moreover, these results suggest that the addition of more lead oleate has a stabilizing effect on the clusters conversion to the nanocrystalline rock salt phase which we attribute to the ligand binding equilibrium shown in the reaction equation in Scheme 2.4.1.
Early time data points of an in situ reaction using 3.0 equivalents Pb or 1.2 equivalents on attenuated crystal model size and fit residual.

A fairly obvious control here clearly would be to show that the structure we observe is not simply lead oleate. The structures of long chain lead (II) carboxylates have been explored by a number of techniques including single crystal X-ray diffraction, $^{13}$C and $^{207}$Pb ssNMR, and PDF analysis. Interestingly, despite its importance to nanocrystal science, lead oleate itself has not been structurally characterized very well prior to this work to our knowledge. The known crystal structures of long chain lead carboxylates consist of a lamellar structural arrangement of the alkyl chains and a polymeric 2D network of interlocked Pb centers linked by Pb-O-Pb attachments. The coordination geometry at lead in most cases is best described as heptacoordinate with different polymorphs existing that differ in the stereochemical anisotropy of the lead 6s$^2$ lone pair. “Hemidirected” structures show a noticeable void in the coordination of ligands for large ranges of polar and azimuthal angles within a sphere containing the first coordination shell where the 6s$^2$ lone pair is thought to reside. “Holodirected” structures are distributed more evenly throughout the
area around the atom.\textsuperscript{73-74} Below visualized is a plot of the lamellar stacking of the alkyl chains for the crystal structure of lead (II) nonanoate with the network of Pb-O bonds coming towards us.

![Lamellar structure of Pb(Nonanoate)$_2$. CIF From ref. 71 and visualized with Mercury software.\textsuperscript{11}](image)

In PDF measurements of our own lead oleate powders we observe a structure consistent with the polymeric ordered lamellar structure well know for shorter lead carboxylates with extensive long-range structural order extending at least several nm as is illustrated in Figure 2.4.5.

![Solid state PDF measurements of lead oleate. Full $r$ (left) and low $r$ (right) distances.](image)

\textbf{Figure 2.4.4} Lamellar structure of Pb(Nonanoate)$_2$. CIF From ref. 71 and visualized with Mercury software.\textsuperscript{11}

\textbf{Figure 2.4.5} Solid state PDF measurements of lead oleate. Full $r$ (left) and low $r$ (right) distances.
We attempted to characterize the structure of the micelle of lead oleate by recording diffraction images of the hot hexadecane solution in flow to compare to our early time points. It proved much more difficult to collect data of just lead oleate at the starting reaction conditions with substantial signal to noise in comparison to the early reaction timepoints. By acquiring fifteen minutes of diffraction data we could resolve a low scattering molecular structure that appears to have Pb-O and Pb-Pb interatom distances that had a similar qualitative appearance to the local structure of the solid. The lack of long-range order observed here for the solution structure is fairly consistent with a poorly ordered micellar structure with little structural coherence past the first few correlations. It is also clearly distinct from the real space patterns that are seen at early time points in the reaction solution in both structure and intensity although unsurprisingly they are somewhat similar.

![Figure 2.4.6](image)

**Figure 2.4.6** Hexadecane solution state and solid state measurements of lead oleate. Full r (left) and low r (right) distances.

Having failed to find an appropriate structural description for the early time pre-nucleation data using the attenuated crystal model we used a Debye Scattering Equation approach to fitting
the PDF using a discrete structure model with open boundary conditions. As a first pass we attempted to first simply fit simple oligomers of [PbS]$_n$. We optimize a simple fit that allows relaxation of a scale factor, ADPs on Pb and S, and an overall stretch factor that can adjust bond lengths without changing any relative interatomic distance. Clearly as shown below in Figure 2.4.7, a structure like a simple Pb$_4$S$_4$ cubane is incapable of accounting for the local structure even within the first two correlations. The ratio of first nearest neighbor to second nearest neighbor correlations in the nanocrystalline phase is related to both the higher coordination number of second nearest neighbors to first nearest neighbor distances in rock salt in addition to the effects of the different Debye-Waller factors at different lattice sites and is clearly distinct from the solute.

**Figure 2.4.7** (Top) DSE fit of a Pb$_4$S$_4$ cubane to early time data. (Bottom) number of first nearest neighbor distances versus second nearest neighbor distances visualized for the rock salt lattice.
To try to account for the local structure of our solute we wondered if we could take our suggestion that the solute consists of lead oleate binding the surface of primitive clusters of lead sulfide seriously. As such, we sought out a few simple structural models of lead acetate bound to simple PbS structures by preliminary optimization via molecular mechanics in Avogadro followed by DFT optimization at the LACVP**/MO6-2X level of theory. Two examples that were found to be minima by the absence of negative vibrational frequencies, and their respectably good fits to an early time data point are shown below. While, neither can capture all of the local structure seen in $G(r)$ during the pre-nucleation they clearly represent a better local structural description than either a discrete or a periodic treatment that treats the pre-nucleation structure as “[PbS]**.”

**Figure 2.4.8** Fits to early time data in left panel of Figure 2.4.2 (3 eq. Pb(Oleate)$_2$) using DSE and lead acetate passivated [PbS]$_n$ models. $R_w$ of 0.31 and 0.41 were seen for the top and bottom structure respectively.
2.4.2 Analysis and Interpretation of the Induction Delay

As was discussed in the first chapter, following injection of the chalcogenourea precursor there is a brief delay between injection and appearance of visible absorbance that we have referred to as the “induction delay.” This been hypothesized to represent a pre-nucleation period where concentration of some metastable “solute” builds up in concentration until it reaches a point where nucleation of this solute into the nanocrystalline phase becomes kinetically accessible. Figure 2.4.9 illustrates this with N-p-CF$_3$-Phenyl-N'-n-dodecylthiourea at 80 degrees with the period before absorption onset. These PbS and PbSe reactions have been explored by UV-vis spectroscopy in previous work in the group by Michael Campos and Jonathan DeRoo. Over a large series of reactions, it is generally observed that this pre-nucleation period is much shorter for PbSe than it is for PbS for a given precursor conversion rate and much longer at lower temperature for both precursors.

![Graph showing absorbance at 400 nm](image)

**Figure 2.4.9** Absorbance at 400 nm studied by in-situ dip probe measurement of N-p-CF$_3$-Phenyl-N'-n-dodecylthiourea at 80 degrees
If we interpret this delay as corresponding to a buildup of solute in solution, we can define a procedure to estimate the fraction of the total precursor concentration that has converted during this period as $f_{ind} = 1 - e^{(-k_{obs}t_{ind})}$ where $k_{obs}$ is the first order rate constant from a single exponential fit to the data. The concentration of PbS or PbSe that builds up in solution prior to nucleation is then just $M_{ind} = f_{ind}M_{total}$. Plotted below are the results of this analysis for a number of different disubstituted thioureas and trisubstituted selenoureas. We see that in general for a given temperature and conversion rate $M_{ind}$ is higher for PbS than for PbSe and increases with decreasing temperature.  

![Figure 2.4.10 Plot of [M]_{ind} as a function of conversion rate and temperature as defined above.](image)

Our PDF measurements as described already give support to this general proposition regarding the meaning of this induction delay as we see through both direct inspection of the $G(r)$ curves and attenuated crystal modeling as a structural transition from a prenucleation stage to a nucleation stage that is distinct from simply being lead oleate. One alternative hypothesis to the structure being “solute” that could be posed is that the thiourea forms a dative complex or an anionic thioureate complex with lead oleate that is building up in concentration in solution during
this pre-nucleation period and this compound is the pre-nucleation structure rather than some form of \([\text{PbS}]_n[\text{Pb(Oleate)}]_m\) from precursor conversion. While we cannot affirmatively rule this out, it is not the preferred hypothesis at this time as the labeled \(^{13}\text{C}\) NMR study in Chapter 1 does not show any compelling evidence of thiourea complex formation or thioureate formation.

2.4.3 Comparison of PbS and PbSe Induction Delay

As we discussed earlier, the two reference PbS and PbSe sequences at 110°C from \(\text{N-}p\)-\text{MeO-Phenyl-N’-n-dodecylthiourea}\) and \(\text{N-butylpyrrolidine-1-carboselеноamide}\) in Figures 2.2.7 and Figures 2.2.8 represented two precursors that were chosen for their relatively similar kinetic profile with lab measured UV-vis \(k_{\text{obs}}\) values of \(1.53 \times 10^{-3}\) and \(2.38 \times 10^{-3}\) for Se and S respectively.

![Graphs showing G(r) vs r for PbS and PbSe](image)

**Figure 2.4.11** First five timepoints of data at 110°C reaction conditions for PbS (left, \(\text{N-}p\)-\text{MeO-Phenyl-N’-n-dodecylthiourea}\)) and PbSe (right, \(\text{N-butylpyrrolidine-1-carboselеноamide}\)).

Teasing out the differences at early time between this pair of compounds at this temperature proved difficult given the limited time resolution of the experiment. At lower temperatures at a given precursor conversion rate the induction delay should be substantially longer as \([M_{\text{ind}}]\)
increases with decreasing temperature. We therefore explored lower temperature conditions to see if we could more cleanly see the difference between PbS and PbSe nucleation characteristics with our total scattering method. At 80°C we found N-(3,5-bis(trifluoro)phenyl)-N’-dodecylthiourea and N-cyclohexyl-2-methylpyrrolidine-1-carboselenoamide to possess well matched precursor conversion kinetics for such a comparison with in lab measured UV-vis rate constants of 1.69 *10^{-3} and 2.21*10^{-3} respectively and induction delays of 182 seconds and 29 seconds respectively. The result below clearly suggests the difference in induction delay between PbS and PbSe in this case arises from a longer period where a pre-nucleation structure persists in solution for PbS vs. PbSe. Interestingly, the local structure of pre-nucleation consistently appears very different at 110°C versus 80°C.

Figure 2.4.12 First five timepoints of data at 80°C reaction conditions for PbS (left, N-(3,5-bis(trifluoro)phenyl)-N’-dodecylthiourea) and PbSe (right, N-cyclohexyl-2-methylpyrrolidine-1-carboselenoamide).
2.5. Other Multimodal Experiments

2.5.1 In-line PDF/UV-Vis

Finally, at XPD beamline we have benchmarked a new multimodal dual UV-vis/PDF measurement where a sample can be analyzed by UV-vis spectroscopy by an in-line flow cell directly before measurement by X-ray diffraction. Preliminary experiments were complicated by some issues with lead oleate precipitation in the Teflon tubing leading up to the UV-vis flow cell over time, but a number of successful runs were completed with this new setup. The setup is quite similar to the one already described except now the reaction solution is pulled from the reactor by Teflon which is fed into a UV-vis flow cell which is connected to optical fibers which are connected to a nearby OceanOptics UV-vis spectrometer. This reactor orientation should allow direct comparison between UV-vis and PDF data as the solution passes from the flow cell to the X-ray beam in around a second.

![In-line UV-vis flow cell and x-ray cell flow](image)

**Figure 2.5.1.** In-line UV-vis flow cell and x-ray cell flow
**Figure 2.5.2.** (left) path from flask to UV-vis flow via Teflon tubing. (right) Spectrometer hooked up to UV-vis flow cell.

**Figure 2.5.3** 150s, 300s, 450s, 600s data points for dual measurement of synthesis of PbS from N-p-4-CF3-Phenyl-N’-n-dodecylthiourea at 80°C

An example data set for a slow PbS reaction at 80°C reaction conditions for a PbS is shown in Figure 2.5.3 with a lab measured UV-vis induction time of 301s. The plotted data at
150s, 300s, 450s and 600s seems reasonably consistent with what is expected for this precursor, and the end of the induction period again seems to represent the transition from a locally ordered solute into a crystalline material. This is consistent with DFT calculations and experimental work on discrete [PbS]ₙ clusters smaller than 1 nm which suggest even oligomers up to a nonamer will have an optical band gap below 400 nm.⁷⁷,⁷⁸

2.5. Summary

Through this work we have developed a reactor system to perform X-ray total scattering real space pair distribution functions analysis on colloidal PbS and PbSe nanocrystal growth at the XPD beamline at NSLS-II. Our results are consistent with a standard nanocrystal formation mechanism where a poorly ordered solute builds up in concentration by precursor conversion until it reaches a sufficient concentration to nucleate into the final nanocrystalline phase. Our observations are consistent with the idea that this solute is stabilized by surface ligands, in our reaction Pb(Oleate)₂. The importance of ligand chemistry in affecting the evolution of metastable solute intermediates is likely a broadly important feature of nanocrystal formation reactions and the PDF method can be applied to help shed light on these poorly ordered structures. The importance of ligand chemistry to particle formation is currently being recognized by a number of different groups performing in situ studies.⁷⁹,⁸⁰ We expect these total scattering measurements to become more popular within the community as dedicated user facilities continue to be improved.
2.7 Experimental Details

2.7.1 Materials and Methods  Toluene (99.5%), acetone (≥99.8%), isopropanol (≥99.7%), triethylamine (≥99%), selenium (pellets, < 4 mm, ≥99.99%), 4-methoxyphenyl isothiocyanate (98%), 4-(trifluoromethyl)phenyl isothiocyanate (97%), Trifluoroacetic acid (99%), trifluoroacetic anhydride (99%), were obtained from Sigma Aldrich and used without further purification. bis(trifluoromethyl)phenyl isothiocyanate (97+%%) was obtained from Maybridge and used without further purification. Dodecylamine (99%) was obtained from Sigma Aldrich and purified by vacuum distillation at 100°C. Diethylene glycol dimethyl ether (“diglyme,” anhydrous, 99.5%) was obtained from Aldrich, transferred to a glovebox, shaken with activated alumina, filtered, and stored over activated 3Å molecular sieves for 24 h prior to use. Oleic acid (99%) was obtained from Aldrich stored in a −20 °C freezer, and used without further purification. Benzene-d₆ was obtained from Cambridge Isotope Laboratories and stored in a glovebox over activated 3Å molecular sieves for 24 h prior to use. Pyrrolidine (≥99.5%, purified by distillation), was obtained from Aldrich, stirred with calcium hydride overnight, distilled and stored in a glove box. 2-methylpyrrolidine (98%) was obtained from Acros Organics, stirred with calcium hydride overnight, distilled and stored in a glove box. Lead(II) oxide (99.999+%%) was obtained from Strem or Alfa Aesar and used without further purification. n-butyl isocyanide (98+%) and cyclohexyl isocyanide (98+%) was obtained from Acros Organics, degassed by the freeze-pump-thaw method, and stored in a glovebox.

2.7.2 Total scattering measurements

Experiments were carried out using beamline 28-ID-2 at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. X-ray scattering data were collected at room temperature, in rapid acquisition mode⁵⁵, using a 2D PerkinElmer amorphous silicon detector
(2048 × 2048 pixels and 200 × 200 μm pixel size) with a sample-to-detector distance of 202.444 mm. The incident wavelength of the X-rays was $\lambda = 0.1877 \, \text{Å} (66.05 \, \text{keV})$. Calibration of the experimental setup was performed using a nickel standard sample. In situ x-ray scattering experiments were performed using a custom designed reactor consisting of a remotely controlled injector, a three neck flask equipped with a temperature probe, a magnetic stirrer, an argon inlet, and submerged in an oil bath. A Hei-FLOW Precision 01 peristaltic pump, and Viton tubing (Cole-Parmer, 1/16"ID x 1/8"OD) connects a stainless steel syringe needle to a custom Kapton X-Ray flow cell. Precursor injection and triggering of the peristaltic pump were both controlled remotely, allowing diffraction patterns to be collected with the shortest time delay possible following mixing of precursors.

The reaction is initiated by a remotely triggered injection of 7 mL of a 190 mM diglyme solution of an N,N disubstituted thiourea or N,N,N’ trisubstituted selenourea (1.33 mmol) into 143 mL of a 11.3 mM solution of lead oleate (1.62 mmol) at 80 °C or 110 °C under argon with stirring. The resulting solution is 10.8 mM (1.2 equiv.) in lead and 8.90 mM (1.0 equiv.) in chalcogen immediately following injection. Following the precursor injection, the peristaltic pump is run at maximum speed for ten seconds to ensure the reaction mixture has reached the X-Ray beam and passed through the remainder of the Viton tubing into a waste container that is also under Ar. Following this 10 second period, the flow rate is immediately automatically set to a slower setting. After reducing the pumping speed, the acquisition of 30 second X-Ray diffraction patterns is initiated. Based on the pump rates and reaction volume in the contained in the Viton tubing, the early scan dead time which contain only reaction that was pumped during the fast-flowing period are discarded. An X-ray scattering pattern of the lead (II) oleate precursor solution was acquired over 15 minutes at the reaction temperature by circulating the precursor through the flow cell. The
long acquisition was needed to obtain sufficient diffuse scattering signal. Attempts to collect scattering patterns from solutions of the chalcogenourea precursors did not yield substantial signal relative to signal from the solvent, which is likely due to the relatively small electron density difference between the organic solvent reaction medium and the chalcogenoureas. The in-line dual in situ PDF/UV-vis measurements were performed with a similar setup except that the solution is pumped through Teflon first into a FIA-labs SMA-Z UV-vis connected an OceanPro Ocean Optics spectrometer by optical fibers.

2.7.3 Pair Distribution Function Analysis Data Processing and Modeling

Raw 2D data were corrected for geometrical effects and polarization, then azimuthally integrated to produce 1D scattering intensities versus the magnitude of the momentum transfer $Q$ (where $Q = 4\pi \sin \theta / \lambda$ for elastic scattering) using the program Fit2D. The program xPDFsuite with PDFgetX3 was used to perform the background subtraction, further corrections, and normalization to obtain the reduced total scattering structure function $F(Q)$, and Fourier transformation to obtain the pair distribution function (PDF), $G(r)$. The $Q_{\text{min}}$ is determined by the beamstop. PDFs were processed with a low $Q_{\text{max}}$ ($Q_{\text{max}} = 10.0 \ \text{Å}^{-1}$) to reduce statistical noise in order to evaluate low-amplitude signals during early reaction time points, although once mature particles have formed following nucleation this can be extended up to $Q_{\text{max}} = 15.0 \ \text{Å}^{-1}$. Attenuated crystal modeling of PbS nanoparticle growth was performed using PDFGui. Fits of discrete particles was performed in PDFGui. Discrete Debye Scattering Equation based calculations were performed using DiffpyCMI using DebyePDFGenerator. Structural optimizations were carried out using DFT implemented in the Jaguar 9.1 suite of \textit{ab initio} quantum chemistry programs. Geometry optimizations were performed with the MO6-2X functional using the LACVP** basis
set. Initial geometry guess was generated using either crystallographic data molecular mechanics as implemented in Avogadro version 1.2.0 using the UFF force field.

2.7.4 Synthesis

Selenoureas were synthesized from isocyanides, elemental selenium, and amines according to Campos et al. Thioureas were prepared from amines and isothiocyanates and lead oleate was prepared from lead trifluoroacetate according to Hendricks et al.
2.8. References


(4) Fenske, D.; Persau, C.; Dehnen, S.; Anson, C. E. Syntheses and Crystal Structures of the Ag-S Cluster Compounds [Ag70S20(SPh)20(dpdm)10](CF3CO2)2 [Ag326S100(SiBu)62(dppb)6] *Angew. Chem.* 2004, 43, 305-309.


(36) Chapter 1. Ref. 41.


(68) See Chapter 1. Refs. 52, 56, 65


(70) See Chapter 1. Ref. 20.


(83) See Chapter 1. Ref. 56.

(84) See Chapter 1. Ref 52.
Chapter 3. Emergence of Semiconductor Electronic Structure in Hg\(^{2+}\) and Cd\(^{2+}\)-Linked \([\text{Ru}_6\text{C(CO)}_{16}]^{2-}\) Oligomers

Table of Contents

3.1. Introduction 141

3.1.1 Emergent Properties in Cluster Assembly 141

3.1.2 Cluster Assembly of [Ru\(_6\text{C(CO)}_{16}\)]\(^{2-}\) 142

3.2. Synthesis and Characterization of [Ru\(_6\text{C(CO)}_{16}\)]\(^{2-}\) Oligomers 144

3.2.1 Synthesis and NMR/IR Characterization 144

3.2.3 Single Crystal X-ray Diffraction 149

3.2.2. Pair Distribution Function Measurements 152

3.2.4 UV-Vis Absorbance Spectroscopy 153

3.3. Density Functional Theory Calculations on [Ru\(_6\text{C(CO)}_{16}\)]\(^{2-}\) Oligomers 155

3.3.1 Density of States of Hg Linked Oligomers 155

3.3.2 Comparison of Hg linked Oligomers 157

3.3.3 Comparison of Hg and Cd Linked Oligomers 159

3.4. Density Functional Theory calculations on [Ru\(_6\text{C(CO)}_{16}\)]\(^{2-}\) Polymers 160

3.4.1 Semiconductor Band Structure of 1D Polymers 160

3.4.2 Effect of the Orbital Alignment on the Electronic Structure 161

3.5. Summary 164

3.6. Experimental Details 165

3.6.1 Materials and Methods 165

3.6.2 Synthesis 166
3.6.3 Single Crystal X-ray Diffraction 168

3.6.4 DFT Modeling and Computational Methods 169

3.6.5 X-ray Total Scattering Measurements 169

3.7. References 171

3.8. Supplementary Data and Figures 176

3.8.1 SCXRD 176

3.6.2 NMR Characterization 179

3.6.3 FT-IR 183

3.6.4 Carbide $^{13}$C NMR Comparison Monomer/ Dimer 184

Reproduced in part from


Dr. Jia Chen is acknowledged for Density Functional Theory calculations and Dr. Alexander Beecher for synthesis and X-ray crystallography contributions to this project. Dr. Daniel Paley is acknowledged for assistance with X-Ray crystallography. Dr. Maxwell Terban is acknowledged for collecting total scattering data at CHESS.
3.1. Introduction

3.1.1 Emergent Properties in Cluster Assembly

In the first two chapters of this thesis we focused on the mechanism by which a colloidal crystalline semiconductor structure emerges from its constituent building blocks by the processes of nucleation and growth. In this final chapter we will address a related question which is how the electronic structure of an assembly of atoms is formed from its constituent building blocks. Our model system for this study is a series of single metal atom bridged [Ru$_6$C(CO)$_{16}$]$^2$- oligomers, a highly symmetrical octahedral cage of ruthenium atoms encapsulating a central carbide that is decorated with carbonyl ligands which satisfy the overall valence electron count of 86 ubiquitous for such octahedral structures.$^{1-3}$ The linker chemistry developed here allows us to synthesize and isolate a molecularly precise size series of compounds and attempt to identify the governing factors which determine how their electronic structure changes as more units are added.

Ordered assemblies of atomically precise clusters or “superatoms” can generate materials with exotic electronic properties not observed in conventional atomic solids. In principle, orbital interactions between the cluster subunits can broaden electronic bands composed of cluster orbitals and support high charge carrier mobilities that are desirable for optoelectronic applications. However, it has proven difficult to obtain linked cluster assemblies with the desired electronic coupling between subunits.$^{4-14}$ For example, superatomic solids have been prepared from As$_7$$^3$- salts by Khanna and coworker that possess band gaps that vary with the counter cation and dimensionality of the assembly. However, only minimal dispersion in the energy bands results, which was attributed to minimal direct cluster–cluster interactions.$^{9,14}$ Another study where [Co$_6$Se$_8$] clusters were assembled into small superatomic oligomers by a ditopic 1,4-phenylene diisocyanide ligand only resulted in weak cluster–cluster interactions.$^{15}$ In contrast, more recent
work on direct fusion of [Co₆Se₈] cores suggests far stronger intercluster interactions can be achieved when the subunits are linked by covalent bonds. This work suggests that direct covalent linkages between cluster subunits facilitate emergent electronic structure in these assemblies.

3.1.2 Cluster Assembly of [Ru₆C(CO)₁₆]²⁻.

![Cluster Assembly Diagram](image)

**Figure 3.1.1** Representative metal atom bridged oligomers of [Ru₆C(CO)₁₆]²⁻ (above) and new structures reported in this work.²⁶-³¹

Among superatomic building blocks of interest, polyhedral transition metal carbonyl clusters have been extensively studied as model catalysts for heterogenous catalytic processes such as the Fischer-Tropsch process. In particular, the dianionic hexanuclear ruthenium cluster
[Ru₆C(CO)₁₆]²⁻ is an attractive building block²⁰⁻²⁵, as there are many examples of metal atom (M = Hg, Ag, Cu, Pt, Pd, Tl) linked oligomers and polymers of [Ru₆C(CO)₁₆]²⁻ (Figure 3.1.1).²⁶⁻³¹ While the studies above showcase a rich diversity of [Ru₆C(CO)₁₆]²⁻ cluster assembly synthesis by linking clusters with single metal atoms, they have not addressed how the electronic structure of the assembly changes during oligomerization. Given the recently noted promise of directly covalently linking clusters to generate collective electronic interactions between cluster subunits, we anticipated that fusing clusters by single metal atom bridges would also yield so-called “strongly-coupled” assemblies.⁴,¹⁶,³²

Additionally, we reasoned that modifying the linker atom in these assemblies could affect the extent of intercluster orbital interaction, thereby providing means of controlling the electronic properties of the assembly. To address the previously unexplored influence of the atomic bridge on the orbital interaction strength in [Ru₆C(CO)₁₆]²⁻ cluster assemblies, we have synthesized new oligomeric assemblies of [Ru₆C(CO)₁₆]²⁻ clusters bridged by Hg²⁺ and Cd²⁺ and compared these to the known dimeric Hg²⁺ bridged assembly and monomeric [Ru₆C(CO)₁₆]²⁻ building block. Using density functional theory (DFT) we calculate the electronic structure of these synthesized oligomeric assemblies and analogous infinite linear polymeric assemblies to illustrate how the choice of linker and cluster can affect the dispersion in the electronic band structure. These studies indicate that single atom bridges can lead to broad electronic bands provided the orbital overlap and ionization energies are appropriately matched with the cluster subunit. This result suggests molecular design principles that can be used to tune electronic structure in superatomic assemblies by linking atomically precise clusters with single atoms.
3.2. Synthesis and Characterization of \([\text{Ru}_6\text{C(CO)}_{16}]^{2-}\) Oligomers

3.2.1 Synthesis and NMR/IR Characterization

Following Hayward’s preparation, the \(\text{bis} (\text{triphenylphosphine})\text{iminium (}[\text{PPN}]^+\) salt of \([\text{Ru}_6\text{C(CO)}_{16}]^{2-}\) is synthesized from triruthenium dodecacarbonyl and sodium in diglyme as is shown in Scheme 3.2.1.\(^{33}\)

\[
2 \text{eq. } \text{Ru}_3(\text{CO})_{12} + 2.04 \text{eq. Na} \xrightarrow{\text{Reflux, } 3\text{h}} \text{ Na}_2[\text{Ru}_6\text{C(CO)}_{16}] + \text{CO}_2 + 6 \text{ CO}
\]

\[
\text{Na}_2[\text{Ru}_6\text{C(CO)}_{16}] + 2.06 \text{eq. PPNCl} \xrightarrow{\text{H}_2\text{O}} \text{ PPN}_2[\text{Ru}_6\text{C(CO)}_{16}] + 2 \text{ NaCl}
\]

**Scheme 3.2.1** Synthesis of \([\text{Ru}_6\text{C}]\).

![SCXRD Structure of \([\text{PPN}]_2[\text{Ru}_6\text{C(CO)}_{16}]\)](image)

**Figure 3.2.1** SCXRD Structure of \([\text{Ru}_6\text{C(CO)}_{16}]^{2-}\) showing carbonyl ligation.

Figure 3.2.1 shows a single crystal X-ray diffraction (SCXRD) structure of \([\text{PPN}]_2[\text{Ru}_6\text{C(CO)}_{16}]\) (\([\text{Ru}_6\text{C}]\)) that closely resembles the previously reported structures.\(^{3,34,35}\) The central carbon atom in this cluster is encapsulated in an octahedral cage of six ruthenium atoms capped by 16 carbonyl ligands - 4 bridging and 12 terminal. The Hg-linked dimeric assembly \([\text{PPN}]_2[\text{Hg(Ru}_6\text{C(CO)}_{16}])_2\) (Hg[\text{Ru}_6\text{C}]_2), and a previously unreported trimeric assembly
[PPN]_2[Hg_2(Ru_6C(CO)_{16})_3] (Hg_2[Ru_6C])_3 are prepared by the reaction of [Ru_6C] and Hg(O_2CCF_3)_2. Following previous work, a pure sample of Hg[Ru_6C]_2 is obtained by adding one equivalent of Hg(O_2CCF_3)_2 to two equivalents of [Ru_6C] cluster in tetrahydrofuran, which immediately induces a color change from an orange-red to a wine-red color. Hg_2[Ru_6C]_3 can also be obtained from a less coordinating solvent, dichloromethane, by adding two equivalents of Hg(O_2CCF_3)_2 to three equivalents of [Ru_6C].

Figure 3.2.2 {^1H}_13C NMR spectra of [Ru_6C], Hg[Ru_6C]_2, Hg_2[Ru_6C]_3 show systematic upfield shift of the principal fast exchange averaged carbonyl resonance upon oligomerization.

The assembly reaction is conveniently monitored using ^13C nuclear magnetic resonance (NMR) spectroscopy where an exchange averaged carbonyl resonance can be observed at a chemical shift that is distinct for each oligomer (Figure 3.2.2). The carbonyl ligands of the monomeric and dimeric assemblies display a single resonance that is the result of fast carbonyl exchange on the ^13C NMR timescale. The spectrum of Hg_2[Ru_6C]_3 is more complex (see below). Initial attempts to prepare the trimeric Hg_2[Ru_6C]_3 assembly by this method resulted in relatively unselective oligomerization following workup. Upon concentrating the reaction mixture, a darkly
colored insoluble precipitate and a deep purple solution of oligomers including Hg[Ru₆C]₂ and Hg₂[Ru₆C]₃ is obtained. However, ¹³C NMR spectra of the product distribution prior to concentration shows the desired trimeric product Hg₂[Ru₆C]₃ in high yield. Over a period of several weeks in solution, the ¹³C NMR signals associated with Hg₂[Ru₆C]₃ are replaced by signals from Hg[Ru₆C]₂ and a dark precipitate forms, suggesting the slow disproportionation of Hg₂[Ru₆C]₃ to large insoluble Hgₙ[Ru₆C]ₙ oligomers and Hg[Ru₆C]₂ as is shown in Figure 3.2.3

![Figure 3.2.3](image)

**Figure 3.2.3** J. Young Tube ¹³C{¹H} spectra of mixtures of [PPN]₂[Ru₆C(CO)₁₆] with Hg(O₂CCF₃)₂ in CD₂Cl₂ taken at various points following mixing of the two reagents (Right 1.61:1 Ru:Hg). An initial distribution of Hg₂[Ru₆C]₃ and Hg[Ru₆C]₂ which is consistent with the stoichiometry was observed. Over time Hg₂[Ru₆C]₃ was seen to disappear eventually leaving Hg[Ru₆C]₂ as the remaining soluble product alongside a dark precipitate.

Removal of the [PPN][O₂CCF₃] metathesis coproduct, which can be demonstrated by ¹⁹F NMR spectroscopy, by filtration through silica gel prior to solvent evaporation prevents the disproportionation reaction and allows Hg₂[Ru₆C]₃ to be isolated. These observations are
consistent with an oligomerization mechanism that is catalyzed by the presence of trifluoroacetate by way of a $[\text{Ru}_6\text{C(CO)}_{16}\text{HgO}_2\text{CCF}_3]^{-1}$ intermediate which has been invoked previously in the formation of $\text{Hg}[\text{Ru}_6\text{C}]_2$.\textsuperscript{27} Thus, $\text{Hg}_2[\text{Ru}_6\text{C}]_3$ is a kinetic product that precedes the formation of thermodynamically preferred precipitates. To the best of our knowledge, $\text{Hg}_2[\text{Ru}_6\text{C}]_3$ is the largest known crystallographically characterized oligomer of $[\text{Ru}_6\text{C}]$ linked by a cationic metal bridge and the first known trimeric $[\text{Ru}_6\text{C}]$ assembly.

The $^{13}\text{C}$ NMR signals of the carbon monoxide ligands in the monomeric and dimeric assemblies appear as a single resonance at room temperature resulting from their rapid exchange on the $^{13}\text{C}$ NMR timescale. Fast chemical exchange of the carbonyl ligands in $[\text{Ru}_6\text{C}]$ and other transition metal carbonyl clusters is commonly observed.\textsuperscript{36,37} However, the trimeric assembly shows a more complex spectrum with signals for the central subunit and a single resonance for the two terminal subunits. This assignment is consistent with the single crystal X-ray diffraction structure where two terminal carbonyl ligand environments and a $\mu_2$-bridging CO ligand type are found on the central $[\text{Ru}_6\text{C(CO)}_{16}]^{2-}$ subunit: (i) 8 carbonyls bound to the equatorial ruthenium atoms, (ii) 6 carbonyls bound to the apical ruthenium atoms, and (iii) two $\mu_2$-carbonyls bridging equatorial Ru atoms. Moreover, the proposed $\mu_2$-carbonyl resonance ($\delta = 246.5$ ppm) is distinct from the other resonances and in the range of reported values for bridging carbonyl resonances for transition metal carbonyl clusters (Figure 3.2.4).\textsuperscript{38-39} As noted earlier, the single $^{13}\text{C}$ NMR resonance of the monomeric and dimeric assemblies and the single resonance of the terminal subunits in the trimeric assembly shift upfield on converting $[\text{Ru}_6\text{C}]$ ($\delta = 214.5$ ppm) to $\text{Hg}[\text{Ru}_6\text{C}]_2$ ($\delta = 210.4$ ppm) and finally $\text{Hg}_2[\text{Ru}_6\text{C}]_3$ ($\delta = 208.8$ ppm) (Figure 3.2.2). A single resonance for $\text{Cd}[\text{Ru}_6\text{C}]_2$ appears at 209.6 ppm. The $^{13}\text{C}$ NMR resonances of the carbide carbons are highly diagnostic of the trimeric assembly. As would be expected for a trimer, two signals in an
approximately 2:1 ratio are observed for the terminal and central carbide $^{13}$C resonances respectively.

Carbonyl vibrations of the oligomeric assemblies were also analyzed using FT-IR spectroscopy. An intense band at 1977 cm$^{-1}$ in the monomer derives from the stretching modes of the terminal carbonyl ligands. As the dianionic monomer is linked with the Hg$^{2+}$ or Cd$^{2+}$ ions, prominent ν(CO) stretches shift to higher frequency. A slightly smaller shift in the most intense ν(CO) vibrational band is observed in the Cd-linked dimer as compared to the Hg-linked dimer. These changes are consistent with decreasing negative charge density on each cluster subunit and reduced 4d(Ru)-π*(CO) backbonding after oligomerization. Oligomers bridged by Cd$^{2+}$ are prepared under similar conditions. With a slightly smaller ionic radius and lower electron affinity than Hg$^{2+}$, we reasoned Cd$^{2+}$ would lead to a weaker, less covalent, linker-cluster bonding interaction. Unlike reactions with Hg(O$_2$CCF$_3$)$_2$, an excess of Cd(O$_2$CCF$_3$)$_2$ is needed to drive the formation of the dimeric cluster, as could be observed again using $^{13}$C NMR spectroscopy.

Using (Cd(O$_3$SCF$_3$)$_2$) as the source of Cd$^{2+}$ allows for the synthesis of the Cd-linked dimer using a stoichiometric ratio of reactants. Upon addition of Cd(O$_3$SCF$_3$)$_2$ to a solution of [Ru$_6$C] in acetonitrile, a rapid color change from red-orange to a deep red is observed. The product is isolated by silica gel chromatography, and characterized using $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectroscopies. Additionally, $^{19}$F NMR spectroscopy was again used to demonstrate removal of [PPN][O$_3$SCF$_3$] and Cd(O$_3$SCF$_3$)$_2$. To our knowledge, this is the first report of a cadmium bridged oligomer of [Ru$_6$C].
Figure 3.2.4 (A) atomic positions from SCXRD of Hg$_2$[Ru$_6$C]$_3$ (Hg = orange, Ru = blue, C = black, O = black) illustrating the variety of carbonyl ligands. $^{13}$C{${}^1$H} NMR spectra of the carbonyl (B) and carbide (C) regions of the spectrum in CD$_2$Cl$_2$. *minor Hg[Ru$_6$C]$_2$ and unknown oligomeric impurity.

3.2.2 Single Crystal X-ray Diffraction

Single crystals of Hg[Ru$_6$C]$_2$, Hg$_2$[Ru$_6$C]$_3$ and Cd[Ru$_6$C]$_2$ suitable for X-ray diffraction are grown from saturated solutions of dichloromethane and pentane at -20 °C. Atomic structures of the cluster cores of all oligomeric assemblies are shown in Figure 3.2.5 and Figure 3.2.6 and Table 1. lists relevant interatomic distances. Each bridging atom in Hg[Ru$_6$C]$_2$, Hg$_2$[Ru$_6$C]$_3$, and Cd[Ru$_6$C]$_2$, forms two irregular triangles with an edge of the neighboring [Ru$_6$C] octahedron. The Ru–Ru distance of these edge atoms are ~0.2 Å longer than the average of the remaining Ru-Ru
bond lengths due to the bonding interaction with the linker atom. The distance between the interstitial carbide atoms in each cluster subunit, is similar for both Hg[Ru₆C]₂ (7.32 Å) and Cd[Ru₆C]₂ (7.32 Å). The nearest intercluster Ru–Ru contact in the Hg²⁺ bridged dimer (5.0 Å) and trimer (4.9 Å) are 0.1–0.2 Å shorter than the Cd-linked dimer, but well outside the sum of the Van der Waals radii in both cases.

The shorter contact in Cd²⁺-bridged cluster is due to a smaller dihedral angle between the planes defined by Ru₁-Ru₂-Cd₁ and Ru₁a-Ru₂a-Cd₁ (42.6°) compared to the analogous angles in the Hg[Ru₆C]₂ (72.7°), and Hg₂[Ru₆C]₃ (51.5°) structures. Consequently, following Yang et al., the calculated τ₄ geometries of the linker metal atom lies closer to a distorted square planar geometry for Cd[Ru₆C]₂ (τ₄ = 0.32) and Hg₂[Ru₆C]₃ (τ₄ = 0.39) than Hg[Ru₆C]₂ (τ₄ = 0.54). Given the large intercluster spacing relative to the covalent radii of Ru, we conclude that intercluster bonding is entirely mediated by the linker atom.
**Figure 3.2.5** Perspective view of the cluster core of Hg[Ru₆C]₂ and Cd[Ru₆C]₂ with thermal ellipsoids at the 50% probability level. Hg[Ru₆C]₂ crystallizes in the triclinic P-1 space group and closely resembles the previously reported structure.²⁵ Cd[Ru₆C]₂ crystallizes in the orthorhombic space group Aea₂. While both clusters lie in the asymmetric unit for Hg[Ru₆C]₂, only one cluster lies in the asymmetric unit for Cd[Ru₆C]₂.

**Figure 3.2.6** Perspective view of the cluster core of the cluster core of Hg₂[Ru₆C]₃ with thermal ellipsoids at the 50% probability level. The molecule crystallizes in the triclinic P-1 space group with one terminal cluster and one half of the central cluster lying in the asymmetric unit.
Table 1. Bond distances table. For the dimer and trimer, the \(<\text{Ru-Ru}>\) distances include all Ru-Ru bonds excluding those between the two Ru atoms bound to either Hg or Cd, \(<\text{Ru}_{11}-\text{Ru}_{12}>\) and \(<\text{Ru}_{21}-\text{Ru}_{22}>\). We omit bond distances that are identical by crystallographic symmetry.

<table>
<thead>
<tr>
<th>Distance</th>
<th>([\text{Ru}<em>6\text{C(CO)}</em>{16}]^2)</th>
<th>([\text{Hg}2(\text{Ru}<em>6\text{C(CO)}</em>{16})^3)]^2</th>
<th>([\text{Cd}(\text{Ru}<em>6\text{C(CO)}</em>{16})]^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Edge (&lt;\text{Ru-Ru}&gt;)</td>
<td>2.89 ± 0.07 Å</td>
<td>2.88 ± 0.04 Å</td>
<td>2.88 ± 0.04 Å</td>
</tr>
<tr>
<td>Min. Edge (&lt;\text{Ru-Ru}&gt;)</td>
<td>2.8001(7) Å</td>
<td>2.8224(5) Å</td>
<td>2.8198(7) Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{11}-\text{Ru}</em>{12}&gt;)</td>
<td>-</td>
<td>3.1297(5) Å</td>
<td>3.0505(6) Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{21}-\text{Ru}</em>{22}&gt;)</td>
<td>-</td>
<td>3.1153(6) Å</td>
<td>3.0826(5)Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{1}-\text{Ru}</em>{2}&gt;)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{11}-\text{Hg}</em>{1}&gt;)</td>
<td>-</td>
<td>2.8812(4) Å</td>
<td>2.8223(5) Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{21}-\text{Hg}</em>{1}&gt;)</td>
<td>-</td>
<td>2.7787(6) Å</td>
<td>2.7757(5) Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{12}-\text{Hg}</em>{1}&gt;)</td>
<td>-</td>
<td>2.7642(6) Å</td>
<td>2.8507(5) Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{22}-\text{Hg}</em>{1}&gt;)</td>
<td>-</td>
<td>2.8758(6) Å</td>
<td>2.8782(5) Å</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{1}-\text{Cd}</em>{1}&gt;)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(&lt;\text{Ru}<em>{2}-\text{Cd}</em>{1}&gt;)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Avg. (&lt;\text{C-O}&gt;)</td>
<td>1.15±0.009 Å</td>
<td>1.15±0.01 Å</td>
<td>1.14±0.01 Å</td>
</tr>
</tbody>
</table>

Table 2. Geometry index \(\tau_4\) around linker atom for the reported cluster compounds

<table>
<thead>
<tr>
<th>Molecule</th>
<th>B</th>
<th>A</th>
<th>(\tau_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cd}(\text{Ru}<em>6\text{C(CO)}</em>{16})]^{2})</td>
<td>153.63(^\circ)</td>
<td>160.63(^\circ)</td>
<td>0.32</td>
</tr>
<tr>
<td>([\text{Hg}(\text{Ru}<em>6\text{C(CO)}</em>{16})^2]^{2})</td>
<td>138.46(^\circ)</td>
<td>145.16(^\circ)</td>
<td>0.54</td>
</tr>
<tr>
<td>([\text{Hg}_2(\text{Ru}<em>6\text{C(CO)}</em>{16})^{3}]}^{2})</td>
<td>149.56(^\circ)</td>
<td>155.71(^\circ)</td>
<td>0.39</td>
</tr>
</tbody>
</table>

\[\tau_4 = \frac{360 - \alpha - \beta}{141}\]

where \(\beta\) and \(\alpha\) are the two largest valence bond angles. For an ideal square planar geometry \(\tau_4=0\), and for a tetrahedral geometry \(\tau_4=1\).

3.2.3. Pair Distribution Function Measurements

As discussed, large insoluble oligomers of the general form \(\text{Hg}_n[\text{Ru}_6\text{C}]_n\) are formed when \([\text{Ru}_6\text{C}]\) and \(\text{Hg}2(\text{O}_2\text{CCF}_3)\) are combined in dichloromethane particularly when the ratio of \([\text{Ru}_6\text{C}]\) to \(\text{Hg}2(\text{O}_2\text{CCF}_3)\) is close to 1. Previously, Johnson and coworkers had identified a black precipitate resulting from the 1:1 combination of these reagents as “\(\text{Hg}_n[\text{Ru}_6\text{C}]_n\)” although no structural analysis was performed.

Pair distribution function measurements of this presumably polymeric...
material provide the first structural measurements of this material. We see that the local structure between the polymer and [Ru₆C] are in rather good agreement in the first few correlations suggesting the polyhedral framework of the [Ru₆C] clusters is intact in agreement with Johnson’s report. Higher $r$ correlations are consistent with intercluster distances found in SXCRD of the trimeric structure. Past 1 nm correlations are increasingly broad and appear to represent intermolecular correlations between clusters or a spectrum of different distances from different oligomers. While the unique assignment of chain length seems complicated by a plethora of potential explanations for the poor longer range order including thermal and static disorder of the chains, as well as effects of non-selective oligomerization, the previous assignment of this insoluble precipitate as “Hgₙ[Ru₆C]ₙ” oligomers is corroborated by this measurement.

Figure 3.2.7 “Hgₙ[Ru₆C]ₙ” Pair Distribution Function and Comparison to the Monomer.

3.2.4 UV-vis Absorbance Spectroscopy

UV-Visible absorption spectra of the Hg and Cd linked assemblies are shown in Figure 3.2.8. Following Wooley and co-workers, the frontier orbitals of octahedral transition metal
carbonyl clusters are derived from filled metal–metal bonding (M–M), metal-metal antibonding (M–M)*, and empty CO(π*) states.\textsuperscript{42} The most intense optical transitions are M → CO(π*) metal to ligand charge transfer bands (MLCT) that originate from filled (M–M) and (M–M)* states. Much weaker (M–M) → (M–M)* transitions associated with the HOMO-LUMO gap have been assigned at even lower energies.\textsuperscript{42,43} A previous study on an analogous Hg\textsuperscript{2+} bridged osmium cluster [Hg[Os\textsubscript{10}C(CO)\textsubscript{24}]\textsubscript{2}]\textsuperscript{2−} concluded that formation of the dimeric assembly splits the (M-M) and (M-M)* d-orbital manifolds into a broader band of valence orbitals, causing a red-shift of the (M–M)* to CO(π*) MLCT band.\textsuperscript{42}

![Figure 3.2.8 UV-Vis absorption spectra of [Ru\textsubscript{6}C], Cd[Ru\textsubscript{6}C]\textsubscript{2}, Hg[Ru\textsubscript{6}C]\textsubscript{2}, and Hg\textsubscript{2}[Ru\textsubscript{6}C]\textsubscript{3}.](image)

Similar splitting can explain the red shifted absorption bands of the Hg- and Cd-linked assemblies observed in the present study. These changes can be explained by a lower energy Hg 6s orbital, which is closer in energy to the Ru d-orbital manifold than the Cd 5s orbital. The much larger red-shift of the lowest energy absorbance feature of the trimer is consistent with a greater
valence bandwidth in the trimer, and is influenced by the charge distribution on the terminal and central cluster subunits, which is asymmetric (see below).

3.3. Density Functional Theory Calculations on [Ru₆C(CO)₁₆]²⁻ Oligomers

3.3.1 Density of States of Hg Linked Oligomers

To further explore the effect of the bridging atom and oligomer length on the Ru(4d)-orbital manifold, we turned to DFT calculations. The density of states (DOS) for [Ru₆C], Hg[Ru₆C]₂, and Hg₂[Ru₆C]₃ are plotted in Figure 3.3.1. To carry out this analysis for a discrete system, the discrete eigenspectrum is visualized by approximating Dirac-delta functions as gaussian functions with a standard deviation of 5 meV centered at the energy of the discrete energy states. As the clusters are linked together both the filled and empty DOS broaden. Inspection of both the highest filled states and the lowest empty states shows they are primarily derived from ruthenium 4d-orbitals. Approximately 1 eV higher into the empty states, the CO(π*) orbitals make up a larger fraction of the DOS. This is consistent with prior descriptions of the electronic structure and M → CO(π*) charge transfer transitions discussed above. Both the HOMO–LUMO and HOMO–CO(π*) gaps narrow by 0.3–0.5 eV with increasing oligomer length (Figure 3.3.2), a trend that correlates with the appearance of red-shifted features in UV-Vis absorbance (Figure 3.2.8)
Figure 3.1 DFT calculations on [Ru₆C], Hg[Ru₆C]₂, and Hg₂[Ru₆C]₃. Calculated total and orbitally projected electronic density of states, showing HOMO-LUMO bands of primarily Ru(4d) and carbonyl 2π* character.

Figure 3.2 HOMO-LUMO gap and (M-M)-(M-M)* valence band width for Hg linked oligomers showing broadening of the distribution of electronic states during oligomerization. Energies used to calculate energy gaps in are illustrated by dotted lines in Figure 3.3.1.
3.3.2 Comparison of Hg linked Oligomers

The HOMO and LUMO of [Ru₆C], Hg[Ru₆C]₂, and Hg₂[Ru₆C]₃ are plotted showing substantial electron density delocalized across all six Ru atoms in [Ru₆C], and across multiple [Ru₆C] subunits in the oligomers. While the HOMO and LUMO are symmetrically distributed between cluster subunits within the monomer and dimer, they are unevenly distributed within the trimer, with the filled orbital concentrated at the termini and the empty orbital concentrated on the central [Ru₆C] subunit and mercury bridging atoms (Figure 3.3.4). These differences reflect the charge density distribution across the oligomer; the terminal cluster units in Hg₂[Ru₆C]₃ carry more negative charge as compared to the central cluster unit, which is involved in two bonding interactions with Lewis acidic Hg²⁺. As expected, electronic states associated with the terminal clusters are higher in the occupied band, while the states of the central cluster appear lower (Figure 3.3.5).

Figure 3.3.3 The HOMO (a) and LUMO (b) of [Ru₆C] and contribution from each Ru atom on the cluster.
Figure 3.3.4 The HOMO and LUMO of Hg$_2$[Ru$_6$C]$_3$ and Hg$_2$[Ru$_6$C]. Ruthenium is indicated in blue, mercury in purple, carbon in grey, and oxygen in red.

Figure 3.3.5 Ru:4d Electronic density of states for Hg$_2$[Ru$_6$C]$_3$ illustrating the electronic asymmetry of central vs. terminal clusters.
3.3.3 Comparison of Hg and Cd Linked Oligomers

The Hg(6s) orbital appears ~0.6 eV deeper within the valence band of the dimeric assembly than the Cd(5s) orbital. Both Hg and Cd contribute to the unfilled states at the band edge. The greater splitting between filled and empty Hg(6s) derived orbitals, supports a stronger covalent interaction between Hg(6s) and Ru(4d) than Cd(5s) and Ru(4d).

Figure 3.3.6 Calculated density of states of [Hg(Ru₆C(CO)₁₆)₂]²⁻ and [Cd(Ru₆C(CO)₁₆)₂]²⁻ showing the filled and empty mercury and cadmium states (Hg 6s and Cd 5s states are multiplied by a factor of 10 for clarity).
3.4. Density Functional Theory Calculations on [Ru$_6$C(CO)$_{16}$]$^2^-$ Polymers

3.4.1 Semiconductor Band Structure of 1D Assemblies

Electronic structure calculations were also performed on hypothetical linear polymers (\{M[Ru$_6$C]\}_\infty, M = Hg, Cd, Mg). The structure of \{Hg[Ru$_6$C]\}_\infty was fully relaxed using DFT and a two-cluster unit cell, which was chosen to optimize the dihedral angle between [Ru$_6$C] clusters. Cadmium and magnesium linked polymers were also studied by performing a single point calculation where the new linker atom is substituted into the structure of the Hg linked polymer. Although Mg is not known to link [Ru$_6$C], it was chosen to illustrate the effect of the valence s orbital energy alignment with the Ru 4d orbitals on the electronic structure. Mg$^{2+}$ also reduces the probability that empty p or d orbitals meaningfully influence the bonding. Band structure diagrams for each polymer are shown in Figure 3.4.1. Differences in the dispersion at the band edges can be seen that depend on the metal atom linker. In each case, direct gap semiconductors are obtained, with a minimum band gap of 1.48 eV in the case of the Hg-linked polymer.
Figure 3.4.1 (a) Energy versus momentum diagrams for 1D polymers M\text{∞}[Ru\text{6}C]\text{∞}, M = Mg, Cd, Hg. The top of the valence band of Hg\text{∞}[Ru\text{6}C]\text{∞}, is referenced to 0 eV. (b) Decomposition of electronic states for Hg\text{∞}[Ru\text{6}C]\text{∞} around bandgap showing contributions from Ru(4d) orbitals (blue), CO orbitals (red) and Hg(6s) orbitals (green). Ru: s states are at lower energies that are not shown here.

3.4.2 Effect of the Orbital Alignment on the Electronic Structure

The greatest dispersion can be observed in the first conduction band, which has a band width of 0.53 eV, although the valence band also shows more than 0.25 eV of width. Weaker dispersion is found in the Cd- and Mg-linked polymers, illustrating the importance of covalent interactions with the linker atom in forming the band structure. The orbitally projected DOS of the Hg-linked polymer is shown in Figure 3.4.1.B, where a significant contribution from Hg 6s orbitals to the conduction band edge can be observed. The projected DOS for extended systems with
different linkers were also obtained. Notably, contributions from linker valence $s$ orbitals to the LUMO band decrease from Hg (9.1 %) to Cd (5.6 %) and Mg (1.1 %), which is consistent with the observed changes to the band width. These calculations suggest that electron transport between the cluster subunits can be facilitated through the single atom bridges, provided that the metal atom has appropriate energy level alignment and orbital overlap.

Additionally, this band width was shown to be independent of the dihedral angle between the clusters for $\text{Hg}_x[\text{Ru}_6\text{C}]_x$, consistent with the dispersion being mediated by a spherically symmetric $6s$ orbital. The dependence of electronic coupling on the twist angle ($\theta$) between two neighboring clusters was examined. We focus on the LUMO band, where electronic dispersion is most significant. The LUMO band width is shown below in Figure 3.4.2 as a function of this twist angle ($\theta$).

![Figure 3.4.2 Band width of LUMO band of Hg$_x$[Ru$_6$C]$_x$ as a function of the twist angle, $\theta$ (Middle Panel). Calculations were performed with a fixed lattice constant.](image)

As we can see, the band width of the LUMO band basically remains the same as the twist angle between the two clusters is adjusted. As we vary $\theta$ from 0 to $\frac{\pi}{2}$, the LUMO band width varies
between only 0.525eV and 0.535eV. We explain this fact by noting the connection between the clusters is mediated by a spherically symmetric Hg 6s orbital. On the other hand, the total energy of this system is very sensitive to this twist angle between clusters. When the two octahedrons are parallel to each other, the total energy of the system is much higher (3.2eV) as compared to the dihedral that minimize the total energy. In calculations, the ground state dihedral angle is reached at about $\theta=32.7^\circ$ in the dimer. This total energy dependence on the twist angle probably comes from electrostatic repulsion between carbonyl groups of neighboring clusters. In support of this we show that the energy dependence on twist angle can be captured by the electrostatic energy of a point charge model using Lowdin partial charges from the DFT calculation. So, there should be a dihedral angle in the ground state, as we have seen in the experimental structure of the dimeric and trimeric assemblies. However, overall electronic coupling is hardly affected by this dihedral angle, since it does not significantly affect the linker-cluster bonding mediated through a spherically symmetric s orbital.
3.5. Summary

In this work, we describe the synthesis and characterization of several novel derivatives of \([\text{Ru}_6\text{C(CO)}_{16}]^2\) and explore how the electronic structure depends on the degree of oligomerization as well as the linker atom identity. The bonding between the linker metal atom and the hexaruthenium cluster is mediated by the \(s\) orbitals of the linker metal. This bonding is strongest in the case of the mercury linked oligomer, consistent with the better energetic alignment of the Hg \(6s\) orbital with the Ru \(4d\) orbitals of the cluster. On this basis, the electronic structures of these
cluster assemblies can be designed by appropriately matching the energy of the ruthenium $d$ orbitals and the linker $s$ orbital. These observations suggest that linking atomically precise clusters by appropriately chosen single-atom bridges is a powerful molecular design strategy to build one-dimensional semiconducting materials with meaningfully strong electronic dispersion.

3.6. Experimental Details

3.6.1 Materials and Methods

Acetone (≥99.5%), hexanes (≥98.5%), 2-propanol (≥99.5%), dichloromethane (≥99.5%), tetrahydrofuran (≥99.0%), acetonitrile (≥99.5%), mercury trifluoroacetate (98%), tetrathyrammonium chloride (98%), tetraphenylphosphonium chloride (98%), $\text{bis(triphenylphosphine)}$iminium chloride (97%), trifluoroacetic acid (99%), trifluoroacetic anhydride (≥99%), and trifluoromethanesulfonic acid (98%) were purchased from Sigma Aldrich and used as received. Anhydrous diethylene glycol dimethyl ether (“diglyme,” 99.5%), anhydrous tetrahydrofuran (≥99.9%), and anhydrous acetonitrile (99.5%) were purchased from Sigma Aldrich, shaken with activated alumina, filtered, and stored over 4 Å molecular sieves for at least 24 h prior to use. Diethyl ether (technical) was purchased from Acros Organics. Ruthenium carbonyl (99%) and cadmium oxide (99.99+%) are purchased from Strem Chemical and used as received. Diethyl ether, dichloromethane, and pentane were dried over alumina columns and stored over 4 Å molecular sieves for at least 24 h prior to use. Dichloromethane-$d_2$ was purchased from Cambridge Isotope Laboratories and used as received. Sodium dispersion (40% in oil, 99+%) is purchased from Alfa Aesar and stored in a nitrogen-filled glovebox. Sodium powder is prepared in the glovebox by adding 20 mL pentane into 2 mL of sodium dispersion, allowing it to settle,
and then the solvent is decanted. This process is repeated five more times and finally residual solvent remaining is pumped off under high vacuum. NMR spectra were recorded on Bruker Avance III 400 and 500 MHz instruments and internally referenced to the resonances of protio-impurities in the deuterated solvent. $^{19}$F NMR spectra were referenced to added hexafluorobenzene as an internal standard. Coupling constants are reported in hertz. UV–visible absorption data were obtained using a Perkin-Elmer Lambda 650 spectrophotometer equipped with deuterium and tungsten halogen lamps. Fourier Transform Infrared Spectroscopy (FT-IR) was performed on a Nicolet 6700 FT-IR from Thermo Fisher using a liquid cell with calcium fluoride windows in dichloromethane.

3.6.2 Synthesis

**Synthesis and isolation of [PPN]$_2$[Cd(Ru$_6$C(CO)$_{16}$)$_2$].** In a nitrogen-filled glovebox, a solution of 8.8 mg of cadmium trifluoromethanesulfonate (0.021 mmol) in 5 mL of acetonitrile is added to a red-orange solution of 150 mg of [PPN]$_2$[Ru$_6$C(CO)$_{16}$] (0.043 mmol) in 10 mL of acetonitrile, which becomes noticeably darker moments after the addition. After stirring for three hours, silica gel (~1 g) is added, the mixture is filtered, and the filtrate is concentrated under reduced pressure. The crude product is further purified by silica gel column chromatography to produce a waxy solid using DCM as the eluent. Washing and tritutating this solid with 3x2mL of cold 2-propanol, diethyl ether and hexanes produces a deep red powder (45 mg, 63% yield). Diffraction quality crystals of this product are prepared from a saturated solution of dichloromethane and hexanes. Over the course of a few days at -20 °C, red diffraction-quality, needle-like crystals of the desired product are obtained. $^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$) $d =$ 127.9 ($d, J = 110$ Hz, PPN), 130.3 (m, PPN), 133.0 (m, PPN), 134.6 (s, PPN), 209.6 (s, terminal CO). IR (CH$_2$Cl$_2$): ν$_{CO}$ 2019 (s). IR (CH$_2$Cl$_2$):
$\nu_{\text{CO}}$ 2065 (w), 2052 (m), 2019 (s), 1984 (br, sh, m) cm$^{-1}$. Anal. Calcd for C$_{106}$H$_{60}$N$_2$O$_3$P$_4$Ru$_{12}$Cd: C, 38.32; H, 1.82; N, 0.84. Found 37.65; H 1.84; N, 0.76.

**Synthesis and isolation of [PPN]$_2$[Hg$_2$(Ru$_6$C(CO)$_{16}$)$_3$].** In a nitrogen-filled glovebox, a solution of .035 mg of mercury trifluoroacetate (0.0820 mmol) in 20 mL of dichloromethane is added dropwise to a 250 mL round bottomed flask containing a red-orange solution of 260 mg of [PPN]$_2$[Ru$_6$C(CO)$_{16}$] (0.121 mmol) in 30 mL of dichloromethane with vigorous stirring over a period of three minutes during which the solution becomes cloudy and turns a deep reddish purple. The reaction solution is then removed from the glovebox and poured over a silica gel column and the fractions are analyzed by UV-Vis. The desired product is found in the earliest band running off of the column. The collected crude first fractions are dried by rotary evaporation and redissolved in minimal DCM (3 mL) and purified by an additional silica gel column using more DCM as eluent. A waxy solid is recovered following further rotary evaporation of DCM, which is then washed and triturated by 3x2mL of Toluene and then pentane producing a fine purple powder (30 mg, 16% yield). X-ray diffraction quality crystals were grown by vapor diffusion of pentane into a dichloromethane solution at -20 °C over the course of a week. $^{13}$C{$_1^1$H} NMR (125 MHz, CD$_2$Cl$_2$) $d = 127.9$ ($d, J = 110$ Hz, PPN), 130.3 (m, PPN), 133.0 (m, PPN), 134.6 (s, PPN), 193.7 (s, 6 $\mu_\text{1-CO}$), 198.8 (s, 8 $\mu_\text{1-CO}$), 208.8 (s, 32 terminal subunits CO), 246.48 (s, 2 $\mu_\text{2-CO}$), 449.76(s, $\mu_\text{6-C}$), 455.97(s, 2 $\mu_\text{6-C}$). IR (CH$_2$Cl$_2$): $\nu_{\text{CO}}$ 2063 (s), 2042 (s), 2017 (s), 2011 (sh, s) cm$^{-1}$.

**J. Young Tube** $^{13}$C{$_1^1$H} Experiments of Hg(O$_2$CCF$_3$)$_2$ reaction with [Ru$_6$C(CO)$_{16}$]$^2$- In a nitrogen-filled glovebox, stock solutions of mercury trifluoroacetate (6.09 mM) and [PPN]$_2$[Ru$_6$C(CO)$_{16}$] (3.39 mM) are prepared in CD$_2$Cl$_2$. Using a volumetric syringe .250 mL of 167
the Hg stock solution is injected into separate stirring .800 mL Ru stock solution. .600 mL of the new reaction solution is transferred to a J-Young valve NMR Tube in the glovebox and sealed under inert atmosphere. The reaction is then monitored in inert conditions by $^{13}\text{C}\{^1\text{H}\}$ spectroscopy periodically over a period of weeks to observe the distribution of soluble oligomers as a function of time.

3.6.3 Single Crystal X-ray Diffraction

Single crystal X-ray diffraction methods. X-ray Diffraction Data was Collected on an Agilent SuperNova diffractometer using Cu K-alpha or Mo K-alpha radiation. Data collection, integration, scaling, and face-indexed Gaussian integration\textsuperscript{44} or numeric analytical methods\textsuperscript{45} absorption corrections were carried out in in CrysAlisPro.\textsuperscript{46} Correction for crystal decay during data collection for [PPN]$\text{[Hg}_2\text{(Ru}_6\!\text{C(CO)}_{16})_3\text{]}$ and [PPN]$\text{[Cd(Ru}_6\text{C(CO)}_{16})_2\text{]}$ was performed by scaling of the A and B parameters. ShelXS or ShelXT were used for structure solution.\textsuperscript{47} Further refinement was achieved by full-matrix least-squares on F$^2$ in ShelXL. Olex2\textsuperscript{48} was used for visualization and preparation of CIFs. TwinRotMat was performed with PLATON\textsuperscript{49}. Thermal ellipsoids are rendered at the 50% probability level. Anisotropic ADPs for all non-H atoms and H atoms are placed in calculated positions and refined with riding coordinates and isotropic ADPs. The structure of [PPN]$\text{[Hg}_2\text{(Ru}_6\text{C(CO)}_{16})_3\text{]}$ possesses a solvent accessible void of 162 Å$^3$, however, the Fourier difference features could not be used to determine an explicit solvent model using either dichloromethane or pentane. The structure of [PPN]$\text{[Cd(Ru}_6\text{C(CO)}_{16})_2\text{]}$ contains two disordered methylene chloride molecules which were modeled using molecular geometries from the Idealized Molecular Geometry Library utilizing SIMU, RIGU, and SAME restraints.\textsuperscript{50}
3.6.4 DFT Modeling and Computational Methods

Discrete molecules $[\text{Ru}_6\text{C(CO)}_{16}]^{2-}$, $[\text{Hg} (\text{Ru}_6\text{C(CO)}_{16})_2]^{2-}$ and $[\text{Hg}_2(\text{Ru}_6\text{C(CO)}_{16})_3]^{2-}$ were modeled as dianionic metal carbonyl clusters without charge-balancing species using structures determined by SCXRD. Computationally-simulated one-dimensional polymers are charge neutral. DFT calculations were carried out using the PBE exchange-correlation functional at the general-gradient approximation level. The projector augmented wave method was utilized on a real space grid as implemented in the GPAW package. Periodic Boundary Conditions are applied for the polymers using a two cluster unit cell. Maximally-localized Wannier functions (MLWFs) were used for decomposition of the density of states using energy windows within 6 eV of the Fermi level.

3.6.5 X-ray Total Scattering Measurements

The experiments were carried out using XPD beamline 28-ID-2 of the National Synchrotron Light Source (NSLS-II) at Brookhaven National Laboratory. Samples were sealed in 1 mm ID Kapton capillaries, and measured using the rapid acquisition PDF method (RAPDF) with an incident X-ray wavelength of 0.1835 angstroms. Diffracted intensities were collected on a 2D PerkinElmer detector (2048 × 2048 pixels and 200 × 200 µm pixel size) mounted orthogonal to the incident beam path. Ni standard was measured at room temperature in order to calibrate the detector geometry, and an empty kapton capillary was measured for background subtraction. The detector calibration and image integration was performed using the software Fit2D. Raw data images were summed and corrected for polarization effects then azimuthally integrated to produce 1D powder diffraction patterns. Further corrections and data normalization were carried out to obtain
the total scattering structure function, \( F(Q) \), which was Fourier transformed to obtain the PDF using PDFgetX3\textsuperscript{58} within xPDFsuite\textsuperscript{59} using a \( Q_{\text{max}} \) of 18 inverse angstroms.
3.8. References


(26) Ansell, G. B.; Modrick, M. A.; Bradley, J. S. Structure of Tetraphenylarsonium Bis(μ₆-Carbido-2,3;4,5-di-μ-Carbonyl-1,1,1,2,2,3,3,-4,4,5,5,6,6,6-Tetradecacarbonyl-Octahedro-Hexaruthenio-Ru₃,Ru₄)Thallate(1-)(4TI-Ru)[As(C₆H₅)₄][{Ru₆C(CO)₁₆}₂TI]. Acta. Cryst. C. 1984, 40, 1315-1318.


(33) Hayward, C. M. T.; Shapley, J. R. Systematic and Efficient Syntheses of Ru$_6$(CO)$_{18}^{2-}$, Ru$_6$(CO)$_{16}^{2-}$, Os$_6$(CO)$_{18}^{2-}$, and Os$_{10}$(CO)$_{34}^{2-}$ - Isolation and Characterization of Os$_6$(CO)$_{17}$. *Inorg. Chem.* **1982**, *21*, 3816-3820.


(56) See Chapter 2 Ref. 55

(57) See Chapter 2 Ref. 56

(58) See Chapter 2 Ref. 58

(59) See Chapter 2. Ref. 57
3.8. Supplementary Data and Figures

### 3.8.1 SCXRD

Crystallographic data

<table>
<thead>
<tr>
<th>Compound</th>
<th>[PPN]$_2$[Ru$<em>6$C(CO)$</em>{16}$]$_2$Hg</th>
<th>[PPN]$_3$[Ru$<em>6$C(CO)$</em>{16}$]$_3$Hg$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{107}$H$</em>{62}$Cl$_2$HgN$<em>2$O$</em>{32}$P$<em>4$Ru$</em>{12}$</td>
<td>C$<em>{123.2}$H$</em>{60.4}$Cl$_{0.4}$Hg$_2$N$<em>2$O$</em>{49}$P$<em>4$Ru$</em>{18}$</td>
</tr>
<tr>
<td><strong>MW</strong></td>
<td>3495.79</td>
<td>4696.48</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>16.4231(2)</td>
<td>9.87243(10)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>19.5304(3)</td>
<td>17.2019(4)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>20.3932(4)</td>
<td>20.5048(2)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>99.9253(14)</td>
<td>91.4981(15)</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>103.9640(14)</td>
<td>94.4076(9)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>112.7071(14)</td>
<td>96.7219(14)</td>
</tr>
<tr>
<td><strong>V (Å$^3$)</strong></td>
<td>5592.28(17)</td>
<td>3445.87(9)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>ρ$_{\text{calc}}$ (g cm$^{-3}$)</strong></td>
<td>2.076</td>
<td>2.263</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>λ (Å)</strong></td>
<td>1.54184</td>
<td>1.54184</td>
</tr>
<tr>
<td><strong>2θ$<em>{\text{min}}, 2θ</em>{\text{max}}$</strong></td>
<td>9, 143</td>
<td>9, 144</td>
</tr>
<tr>
<td><strong>Nref</strong></td>
<td>88844</td>
<td>108281</td>
</tr>
<tr>
<td><strong>R(int), R(σ)</strong></td>
<td>.0517, .0494</td>
<td>.0818, 0.0451</td>
</tr>
<tr>
<td><strong>μ(mm$^{-1}$)</strong></td>
<td>16.756</td>
<td>20.572</td>
</tr>
<tr>
<td><strong>Size (mm)</strong></td>
<td>.06 x .05 x .02</td>
<td>0.08 x 0.03 x 0.02</td>
</tr>
<tr>
<td><strong>T$<em>{\text{max}}, T</em>{\text{min}}$</strong></td>
<td>.772, .473</td>
<td>0.753, 0.387</td>
</tr>
<tr>
<td><strong>Data</strong></td>
<td>21736</td>
<td>13403</td>
</tr>
<tr>
<td><strong>Restraints</strong></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
### Parameters

<table>
<thead>
<tr>
<th></th>
<th>$1441$</th>
<th>$897$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1(&gt;2\sigma)$</td>
<td>0.0299</td>
<td>0.0366</td>
</tr>
<tr>
<td>$wR_2$(all)</td>
<td>0.0633</td>
<td>0.0874</td>
</tr>
<tr>
<td>$S$</td>
<td>1.034</td>
<td>1.059</td>
</tr>
<tr>
<td>Peak, hole (e$^{-}$ Å$^{-3}$)</td>
<td>$0.90$, $-0.86$</td>
<td>$1.82$, $-1.85$</td>
</tr>
</tbody>
</table>

### Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>$[\text{PPN}]_2[\text{Ru}<em>6\text{C(CO)}</em>{16}]_2\text{Cd}$</th>
<th>$[\text{PPN}]_2[\text{Ru}<em>6\text{C(CO)}</em>{16}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$\text{C}<em>{110}\text{H}</em>{68}\text{Cl}<em>{88}\text{CdN}</em>{2}\text{O}<em>{32}\text{P}</em>{4}\text{Ru}_{12}$</td>
<td>$\text{C}<em>{91}\text{H}</em>{64}\text{Cl}<em>{4}\text{N}</em>{2}\text{O}<em>{16}\text{P}</em>{4}\text{Ru}_{16}$</td>
</tr>
<tr>
<td><strong>MW</strong></td>
<td>3662.38</td>
<td>2313.54</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>Aea2</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>$a$ (Å)</strong></td>
<td>30.6061(7)</td>
<td>12.5492(3)</td>
</tr>
<tr>
<td><strong>$b$ (Å)</strong></td>
<td>23.7883(5)</td>
<td>24.8328(5)</td>
</tr>
<tr>
<td><strong>$c$ (Å)</strong></td>
<td>16.7852(5)</td>
<td>28.6864(5)</td>
</tr>
<tr>
<td><strong>$\alpha$ (°)</strong></td>
<td>90</td>
<td>89.1793(15)</td>
</tr>
<tr>
<td><strong>$\beta$ (°)</strong></td>
<td>90</td>
<td>88.0689(16)</td>
</tr>
<tr>
<td><strong>$\gamma$ (°)</strong></td>
<td>90</td>
<td>87.4335(16)</td>
</tr>
<tr>
<td><strong>$V$ (Å$^3$)</strong></td>
<td>12220.7(5)</td>
<td>8924.8(3)</td>
</tr>
<tr>
<td><strong>$Z$</strong></td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>$\rho_{\text{calc}}$ (g cm$^{-3}$)</strong></td>
<td>1.991</td>
<td>1.722</td>
</tr>
<tr>
<td><strong>$T$ (K)</strong></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>$\lambda$ (Å)</strong></td>
<td>1.54184</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>$2\theta_{\text{min}}$, $2\theta_{\text{max}}$</strong></td>
<td>7.062, 146.45</td>
<td>5, 53</td>
</tr>
<tr>
<td><strong>$N_{\text{ref}}$</strong></td>
<td>57741</td>
<td>183899</td>
</tr>
<tr>
<td><strong>$R$(int), $R(\sigma)$</strong></td>
<td>0.1239, 0.0973</td>
<td>0.0643, 0.0565</td>
</tr>
<tr>
<td><strong>$\mu$(mm$^{-1}$)</strong></td>
<td>15.742</td>
<td>1.248</td>
</tr>
<tr>
<td><strong>Size (mm)</strong></td>
<td>0.05 x 0.03 x 0.03</td>
<td>.09 x .06 x .06</td>
</tr>
<tr>
<td><strong>$T_{\text{max}}$, $T_{\text{min}}$</strong></td>
<td>1.000, 0.614</td>
<td>.978, .962</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td><strong>Data</strong></td>
<td>11587</td>
<td>36486</td>
</tr>
<tr>
<td><strong>Restraints</strong></td>
<td>713</td>
<td>43</td>
</tr>
<tr>
<td><strong>Parameters</strong></td>
<td>819</td>
<td>2243</td>
</tr>
<tr>
<td>$R_1(&gt;2\sigma)$</td>
<td>0.0596</td>
<td>0.0417</td>
</tr>
<tr>
<td>$wR_2$(all)</td>
<td>0.1437</td>
<td>0.0816</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>1.008</td>
<td>1.087</td>
</tr>
<tr>
<td><strong>Peak, hole (e^- Å^-3)</strong></td>
<td>1.42, -1.52</td>
<td>0.92, -0.84</td>
</tr>
<tr>
<td><strong>Flack</strong></td>
<td>-0.039(13)</td>
<td></td>
</tr>
</tbody>
</table>
3.8.1 NMR Characterization

$^{13}$C($^1$H) NMR spectrum of Hg$_2$[Ru$_6$C]$_3$ in CD$_2$Cl$_2$ at 25 °C

$^1$H NMR spectrum of Hg$_2$[Ru$_6$C]$_3$ in CD$_2$Cl$_2$ at 25 °C
$^{31}\text{P}^{(1}\text{H})$ NMR spectrum of Hg$_2$[Ru$_6$C]$_3$ in CD$_2$Cl$_2$ at 25 °C

$^{19}\text{F}$ NMR spectrum of Hg$_2$[Ru$_6$C]$_3$ in CD$_2$Cl$_2$ at 25 °C. 10 µl C$_6$F$_6$ is used as an internal standard.
$^{13}\text{C}(^{1}\text{H})$ NMR spectrum of Cd[Ru$_6$C]$_2$ in CD$_2$Cl$_2$ at 25 °C

$^{1}$H NMR spectrum of Cd[Ru$_6$C]$_2$ in CD$_2$Cl$_2$ at 25 °C.
$^{31}$P\(^{1}H\) NMR spectrum of Cd[Ru\(_{6}\)C\(_{2}\)] in CD\(_{2}\)Cl\(_{2}\) at 25 °C

$^{19}$F NMR spectrum of Cd[Ru\(_{6}\)C\(_{2}\)] in CD\(_{2}\)Cl\(_{2}\) at 25 °C. 10 µl C\(_{6}\)F\(_{6}\) is used as an internal standard.
Transmittance FT-IR spectra taken in CH$_2$Cl$_2$ of [(Ru$_6$C(CO)$_{16}$)$_2$$]^2-$ [Cd(Ru$_6$C(CO)$_{16}$)$_2$$]^2-$ and [Hg(Ru$_6$C(CO)$_{16}$)$_2$$]^2-$ [Hg$_2$(Ru$_6$C(CO)$_{16}$)$_3$$]^2-$ and [Ru$_6$C(CO)$_{16}$$_2$] illustrating the most prominent carbonyl stretch which systematically shifts upfield following oligomerization. Sharp lines below the main stretches are an instrumental artifact.
3.8.4 Carbide $^{13}$C NMR Comparison Monomer/Dimer

$^{13}$C Carbide Resonances for Monomer (Left) and Hg Linked Dimer (Right)