

DISSERTATION

Cu-P-Se NANOPARTICLES: UNDERSTANDING THE REACTION PATHWAYS FOR THE
COLLOIDAL SYNTHESIS OF ENERGY CONVERSION AND STORAGE MATERIALS

Submitted by

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ABSTRACT

Cu-P-Se NANOPARTICLES: UNDERSTANDING THE REACTION PATHWAYS FOR THE COLLOIDAL SYNTHESIS OF ENERGY CONVERSION AND STORAGE MATERIALS

Nanotechnology has garnered considerable interest over the last 40 years, owing to the unique, desirable properties that can be targeted through established synthetic methods for tuning the size of materials at the nanoscale. As no one single material has properties suitable for a wide range of applications, property driven synthesis has been at the forefront of the nanoparticle (NP) field. Particularly, colloidal NP syntheses provide a large synthetic landscape to explore as a result of the vast synthetic tunability to target specific parameters such as, particle size, morphology, composition, and defects. Although significant efforts have been made toward deciphering the transformation processes of unary and binary NPs, traditionally the colloidal NP field has been driven by a top-down approach, driven by trial-and-error methods, limiting the design of desired, complex materials. Thus, to further progress nanoparticle technology, understanding the underlying transformation processes occurring throughout the formation of colloidal nanoparticles is essential to develop novel materials as well as control the structure/property relationships. The copious amounts of both organic and inorganic interactions, as well as the complexity of capturing the transformation from molecular to the solid-state regime, complicates the reaction landscape for more complex, ternary phases.

The purpose of the work included and explained in this dissertation is to develop stoichiometric syntheses for both Cu-P-Se ternary phases, Cu_3PSe_4 and Cu_7PSe_6 , and to then understand the reaction pathways for an improved retrosynthetic analysis and enable translation of the synthetic knowledge to other systems. Cu-P-Se ternary chalcogenide NPs are of particular

interest, owing to the synthetic complexity of navigating a rich phase space with thermodynamically stable binary phases close in energy to the desired ternary phases, as well as applicable structural properties for thermoelectrics, photovoltaics, and battery applications. Therefore, to contribute to the progression of the nanoparticle field the general objectives of this study are, (1) analyzing the transformation of commonly employed precursors and solvents (2) capture the influence of precursor reactivity on ternary phase formation, and (3) perform careful characterization of speciation and final nanoparticles, all of which to establish a full scope of Cu-P-Se nanoparticle formation and the impact of individual synthetic parameters on chalcogenide-based precursors.

In Chapter 1, the relevant literature for the following chapters is reported and reviewed to provide the essential background information. This chapter is divided into 6 subsections; (1) Need for renewable energy and how nanoparticles provide solutions, (2) State of nanoparticle synthesis field, current limitations, and progress towards developing a better understanding of nanoparticle reaction pathways, (3) Motivation for exploring the Cu-P-Se phase space, (4) Se reactivity in NP syntheses, (5) Cu_3P – the required precursor for Cu-P-Se formation, (6) Dissertation overview, publications, and presentations.

The first colloidal NP synthesis report on Cu_3PSe_4 was developed by a previous group member, Dr. Jennifer Lee, which demonstrated that the phase purity of Cu_3PSe_4 requires the use of Cu_3P NPs and selenium powder (Se) in ODE as precursors. Alternate reaction precursors, and therefore pathways, were disproven throughout this study, leading to the working hypothesis that the interactions of Se and ODE were a necessary step to form active species that then react with Cu_3P NPs. Although frequently employed in NP research, and heavily characterized, the implications of the Se/ODE solution on Cu_3PSe_4 phase formation are still misunderstood.

Therefore, the studies presented in Chapter 2 are aimed at probing the Cu_3PSe_4 reaction landscape and the findings are separated into (1) ex situ reactions that are characterized with molecular and solid-state characterization techniques to determine the implications of the solution dynamics on Cu-P-Se NP phase formation, and (2) how different Se/ODE speciation can be isolated and subsequently favor the alternate, metastable Cu-P-Se phase, Cu_7PSe_6 .

A persistent limitation to the previous study is that ODE contaminates the final products, making the findings and analysis of Se/ODE rather difficult to interpret, thus requiring a simplified, cleaner reaction to produce phase pure Cu_3PSe_4 . For that reason, Chapter 3 shifts the direction of the Cu_3PSe_4 synthesis towards a more stoichiometric, atom-economical reaction by eliminating ODE as the solvent. Rather, a long-chain, aliphatic solvent, octadecane (ODA) is employed that proves to be an operationally inert solvent under the standard synthetic conditions and produces cleaner, phase pure Cu_3PSe_4 NPs as determined by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). If ODA was reacting with Se^0 powder, the most favorable pathway, commonly cited in literature, is the formation of H_2Se and oxidized ODA (alkene). Hence, molecular characterization techniques, nuclear magnetic resonance (NMR, ^1H and ^{13}C) and fast-Fourier infrared spectroscopy (FT-IR), were utilized to demonstrate the absence of oxidized ODA species, which is consistent with Se^0 preferentially reacting with Cu_3P , promoting a more direct reaction pathway. Eliminating the presence of alternate, competing reaction pathways in the ODE synthesis and establishing a near-stoichiometric reaction, allows us to capture the underlying transformation process of Cu_3P to Cu_3PSe_4 . From these systematic improvements, we hypothesize that Se^0 powder is dispersed in ODA, which promotes a formal eight-electron transfer between Cu_3P and 4 Se^0 .

Extracting the synthetic information from the previous chapters to target the metastable Cu-P-Se phase, Cu_7PSe_6 , provides the framework for Chapter 4. Previous methods to isolate Cu_7PSe_6 are based on traditional, solid-state techniques, where the elemental precursors are ground and subsequently heated to high temperatures ($>1000\text{K}$). Although a colloidal or solution-based synthesis has yet to produce phase-pure Cu_7PSe_6 particles, attempts explained in Chapter 2 provide a basis on the phase space complexity, where the products consisted of Cu_7PSe_6 but with thermodynamic byproducts, Cu-Se phases and Cu_3PSe_4 present. Therefore, an alternate Se precursor, diphenyl diselenide (Ph_2Se_2), is employed to form the metastable phase, which effectively avoids Cu_3PSe_4 formation. Importantly, an alternate route to form Cu_3PSe_4 is with analogous dialkyl diselenide precursor, dibenzyl diselenide, where a key finding is the presence of amorphous phosphorus (P) on Cu_{1-x}Se binaries at low temperatures, which then efficiently reincorporates once the desired 300°C reaction temperature is reached. Thus, in Chapter 4 we investigate why Cu_7PSe_6 is favored with Ph_2Se_2 as a precursor, which is predicated on the formation of byproduct species that effectively “trap” P. A proof of concept is explored to further demonstrate the dynamics of P in solution, where the Cu-P-Se phase space can be controllably toggled across by injecting $\text{P}(5+)$ species.

A drawback for the Cu-P-Se syntheses is the lack of compositional understanding of the pre-synthesized Cu_3P NPs, thus further complicating the reaction stoichiometries. Chapter 5 first investigates the previously published synthesis by Liu et al., by thoroughly characterizing the final Cu_3P nanoparticles under identical reaction conditions and exploring alternate reaction stoichiometries to reduce the presence of residue precursors. From such, it is determined that the particles substantially deviate from the stoichiometric Cu_3P composition, with a Cu:P ratio around 1.5:1.0. Particular focus is also placed on monitoring the degradation of a green phosphorous

source, triphenyl phosphite, $\text{P}(\text{OPh})_3$. Although triphenyl phosphite (TPOP) has been previously used for transition metal phosphide systems, a lack of systematic investigations leads to questions on the reduction of TPOP en route to forming Cu_3P , a formal $\text{P}(3+)$ to $\text{P}(3-)$ event. Additionally, limited characterization of the final organic byproducts in the original synthesis, begs to question what, if any, byproducts could be contaminating the Cu_3P NPs. Therefore, we develop and probe stoichiometric syntheses that isolate phase pure Cu_3P NPs to avoid the original 30-fold excess of P. The transformation of hexadecylamine (reductant and ligand) and TPOP were characterized with ^1H and ^{31}P NMR to evaluate the role of each en route to forming Cu_3P . As this project is still developing, the necessary future directions are given to systematically approach this problem, with an emphasis on first-step experiments and essential characterization methods to completely grasp the decomposition mechanism of TPOP. Ultimately, this has implications when systematically applying TPOP to alternate transitional metal phosphide NP syntheses, as well as developing more precise Cu-P-Se syntheses.

Finally, the work presented herein is summarized in Chapter 6 along with an outlook on the project as a whole. Specifically, future directions and preliminary insight into the underlying reaction pathways and mechanism of Cu_3PSe_4 formation are explored. Additionally, we explore preliminary data on an analogous material Ag-P-Se, which was plagued for years by the lack of a reproducible Ag-P precursor synthesis that limited our ability to extract the synthetic intuition from the Cu-P-Se system. However, recent literature findings on a potential Ag_3P precursor provides promise on synthesizing Ag-P-Se phases in the future, which is critically analyzed to ensure that any bottlenecks in future syntheses are limited.

Ultimately, the work provided in the following chapters is aimed at making strides to developing a more in depth understanding of precursor interactions between transition metals and

main group elements, as well as properly monitoring such reactions to extract synthetic information to analogous systems. With the knowledge gained on the presented studies, we aspire to contribute to the NP field in order to continually improve NP synthesis and therefore nanomaterials. Finally, this work is supported by NSF Macromolecular, Supramolecular, and Nanochemistry (MSN #2109141).

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1.1. Need for Renewable Energy and How Nanoparticles Provide Solutions

High energy demand continues to force the power sector into pulling from the nonrenewable well of resources. For the US to meet the 2050 net zero emission goal, renewable energy will need to grow by ca. 8% every year to offset CO₂ emissions.¹ To achieve zero emission goals, there is a need for the synthesis and development of materials that can efficiently produce energy (**Figure 1.1**) and store energy, using synthetic methods where carbon emissions are reduced.

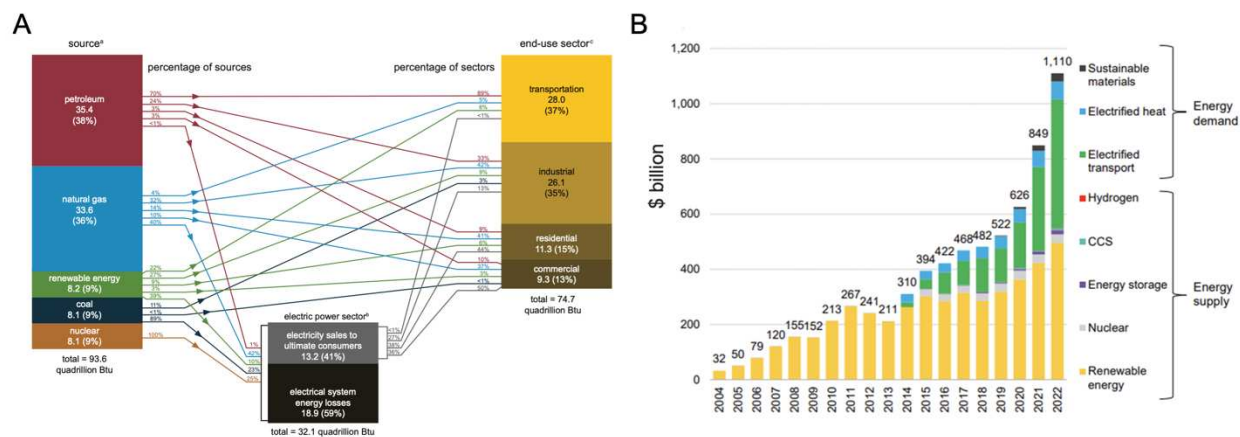


Figure 1.1. (A) US energy consumption by source and sector in 2022. Source: U.S. Energy Information Administration (EIA), Monthly Energy Review (April 2024), Tables 1.3, 1.4c, and 2.1a-2.6.¹ (B) Global investment in energy transition by sector. Source: BloombergNEF, <https://about.bnef.com/blog/global-investment-in-low-carbon-energy-transition-hit-755-billion-in-2021/>. Note: start-years differ by sector, but all are present from 2019 onwards. Nuclear figures start in 2015.

Colloidal nanoparticles (NPs), which are inorganic clusters measured on the nanometer scale (stabilized by organic ligands), have been at the forefront of nanoscience over the last thirty years.² Colloidal NP synthesis was originally established in 1993 by Bawendi et al., which was recently awarded the 2023 *Chemistry Nobel Prize* for the discovery and synthetic method to controllably access cadmium selenide, CdSe NPs with a range of sizes.³ By utilizing a solution-based synthesis,

alternate formation pathways can be isolated which promote the ability to develop novel materials^{4,5} and optimize structural properties^{6–12} (size and morphology) that are distinctly different from the bulk counterparts. For example, a key distinction that separates NP materials is a large surface-to-volume area. From such, physical properties (e.g., quantum confinement of electrons and holes) and chemical properties (e.g., metal-ligand and ligand-ligand interfaces) can be fine-tuned to optimize an array of materials.¹³ Tuning these properties has led to groundbreaking developments in photovoltaic devices,^{14–17} optoelectronics, and ^{18–20} photocatalysis.^{21–23}

However, further application innovations are limited by our current ability to rationally design syntheses for novel materials. As stated above, nanoparticle research has focused on the optimization of particle size and morphology through manipulation of different synthetic and post-synthetic variables that affect nucleation and growth pathways.^{24–28} In order to progress the NP field, the development of an in-depth molecular-level understanding of colloidal NP synthesis is required but remains a *central challenge* due to the synthetic approach being plagued by trial and error methods. Additionally, nanoparticle synthesis is at the cross section of molecular and solid-state chemistry, which further complicates the understanding as the unexplored territory between the two fields encompasses many fundamental challenges.²⁹ Therefore, the field of nanoparticle synthesis is making a concerted effort to exploit the vast tool-kit available in modern day chemistry to precisely fine-tune parameters and attain molecular-level precision. In order to move the nanoparticle field forward, comprehensive formation mechanisms and reaction pathways must be defined to synthesize more materials through “synthesis by design.”^{3,29,30}

1.2. State of Nanoparticle Synthesis Field, Current Limitations, and Progress Towards Developing a Better Understanding of Nanoparticle Reaction Pathways

Traditionally in nanoparticle synthesis, there are only a few initial synthetic components, with three specific categories of reagents, precursors, ligands, and a solvent (can serve as a dual role for ligand).^{31–33} A variety of experimental conditions can then be tuned such as, the nucleation and growth temperature and time, as well as relative precursor concentrations.^{34–36,31,37,32} Yet the transformation of these components to the final NP has proven to be quite complex. A simplified version of precursor conversion to the final products is shown in **Figure 1.2**, where it is generally accepted that the precursors must form active species in solution that then nucleate and grow into the final NP.

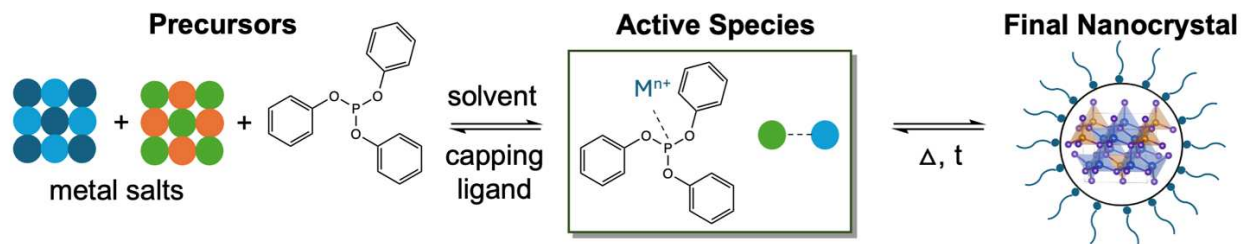


Figure 1.2. General NP synthetic scheme, where the precursor must undergo a transition to active species before forming colloidal NPs.

Although seemingly simple, the transformation processes from the starting precursors to final nanometer sized particles is comprised of thousands of step. Conventionally, the nucleation and growth process is categorized into classical and nonclassical theories. Classical nucleation theory (CNT) is predicated on the thermodynamics of particle formation and is separated into both burst and continuous nucleation.^{38–41} “Burst nucleation”⁴² originates from the LaMer model and is conventionally applied to observed phenomenon in the colloidal NP field but is *not* a valid model to broadly describe the nucleation and growth process of colloidal NP syntheses.^{43,44} Nonclassical nucleation is adapted to include kinetic modelling by accounting for intermediate states before nucleation occurs.^{41,45,46} Thorough investigations into nucleation and growth pathways for

established systems have been performed but will not be discussed in detail herein but point the reader to the following references.^{9,27,28,47,48,48–53}

Although the nucleation and growth processes have been studied in depth, the transformation pathways and underlying mechanisms are rather difficult to capture and understand before nucleation. Throughout the heating profile, the precursors can transition to active species, undergo redox events, decompose to elemental forms, coordinate to ligands, etc., all of which require the use of numerous solid-state and molecular characterization techniques to describe the underlying processes (**Figure 1.3**).^{31,32,54} As these transformation pathways are essential in forming active species that nucleate to the final product, systematically controlling and capturing this process is becoming a significant area of interest in the NP field.^{6,55–58} A contributing factor to alter the transformation reaction pathways is controlling precursor reactivity.^{8,11,31,59–65} Until recently, precursor reactivity has often been vaguely applied to NP syntheses, where generally as the reactivity is tuned, the active speciation can be altered to form different NP phases and change in rate of atom incorporation. However, to capture the underlying transformation processes and contributing factors such as precursor reactivity, a concerted effort needs to be taken to establish reaction stoichiometries, both mass and charge balanced, which allows for pseudoelementary steps to be devised.⁶⁶

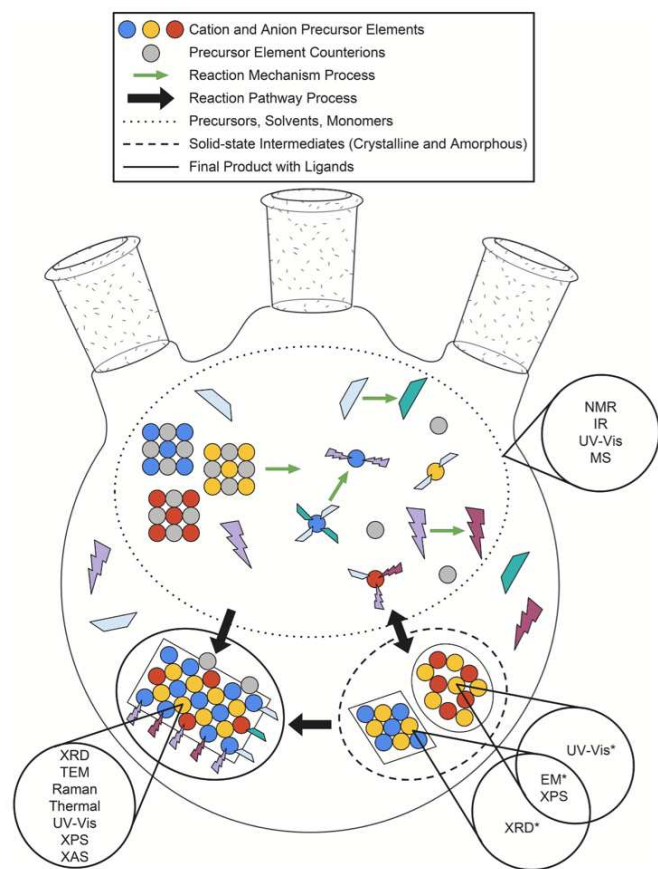


Figure 1.3. A cartoon representation of a dynamic NP synthesis labeled with characterization methods to identify specified reaction species. For example, precursors, solvents, and monomers (encompassed within a dotted circle) can be characterized by NMR, IR, UV–Vis, and MS. Solvent molecules are represented with purple lightning bolts and light blue trapezoids. Subsequent transformations of these species are represented with a color hue change (e.g. purple to magenta and light blue to teal). Rights and Permission from Journal of Solid State Chemistry, 2019, Lee et al.³¹

Thus, this general description to explain many fundamental processes in NP synthesis has led to a bottleneck in extrapolating knowledge from established systems to developing more complex materials. But, the field is making necessary advances in developing tools to understand established reactions more thoroughly, and translate that knowledge in a way that can be used to design new syntheses. One approach to describe precursor reactivity is the application of hard-soft acid-base theory (HSAB), especially when applied to multicomponent systems as the individual ions will have different properties, which is reviewed in many publications.^{31,61,64,67,68}

Alternatively, bond dissociation energies (BDE) can be used to estimate or rank the reactivity of precursors,^{54–57,69–74} due to the preferential formation of active species (reaction pathways can be controlled) and control over relative byproduct energy of atom incorporation, both of which can greatly impact phase formation. Traditionally, the application of such theories has been applied to more established systems, such as CdSe,^{75–84} InP,^{11,85–90} Cu-Se,^{18,20,91–96} CuInSe₂,^{69,69,95,97–100} Cu-Sb-Se,^{64,101–104} etc., which when extrapolated to underdeveloped systems as discussed herein, the underlying reaction pathways and processes need to be fully characterized so that an accurate definition of precursor reactivity can be applied. To develop a better understanding of precursor reactivity we explore how active species can be tuned to isolate reaction pathways for two separate phases (Chapter 2), as well as manipulate the precursor BDE to isolate a metastable phase (Chapter 4). It is important to note that to best capture the underlying processes, stoichiometry is an essential descriptor or parameter that the NP field must focus on, as writing a balanced chemical reaction is the first step in elucidating the underlying mechanistic steps (Chapter 3-5).^{53,105–109}

Ultimately, the field is taking the right and necessary steps forward to further advance more complex materials and improve already established materials. Our aim throughout this dissertation is to (1) contribute to NP field by advancing the knowledge required to develop synthetic methods for complex multinary chalcogenide systems, and (2) more thoroughly understand the role of commonly employed precursors so when applied in the future a more accurate representation of reactivity can inform on the desired synthesis to avoid a trail & error methodology.

1.3. Motivation for Exploring the Cu-P-Se Phase Space

In the presented chapters, we explore the reaction pathways for the Cu-P-Se family of materials. As the nanoparticle field continuously discovers multicomponent and complex materials to target computationally, the synthesis of ternary semiconductor NPs is taking a prominent

position (**Figure 1.4A**).^{17,110} Thus, ternary chalcogenide NPs have gained considerable interest over the years owing to the applicable physical properties that enable application in photovoltaics, thermoelectrics, battery anode or cathode materials, and catalysis, while being composed of non-toxic, earth-abundant elements.^{111–118} However, three areas of concern inspire the work presented herein, (1) although computational methods have drastically improved, a direct recipe is currently not provided (efforts are being made to tackle this problem), (2) previous synthetic methods require harsh reagents to convert precursors into active species,^{119–123} and (3) translation of precursor transformation mechanisms from simpler systems (unary and binary) to complex materials (ternary and quaternary) is challenging.

Traditionally, the synthetic approach to target the Cu-P-Se phases on the ternary phase diagram (**Figure 1.4B**) are high-temperature (HT, 400-1200 °C) elemental, solid-state reactions,^{116,124–131} where one example uses Cu⁰, P₂Se₅, and Se⁰ as precursors in stoichiometric ratios. To develop more tunability over structural properties and processability such as, particle dispersion and morphology, a colloidal, solution-based technique is of interest. Two materials in the Cu-P-Se ternary phase space will be targeted, Cu₃PSe₄ and Cu₇PSe₆, to tackle the previously stated problems and investigate how reaction pathways can be isolated to toggle between the two ternary phases, a process that is underdeveloped for NP syntheses.

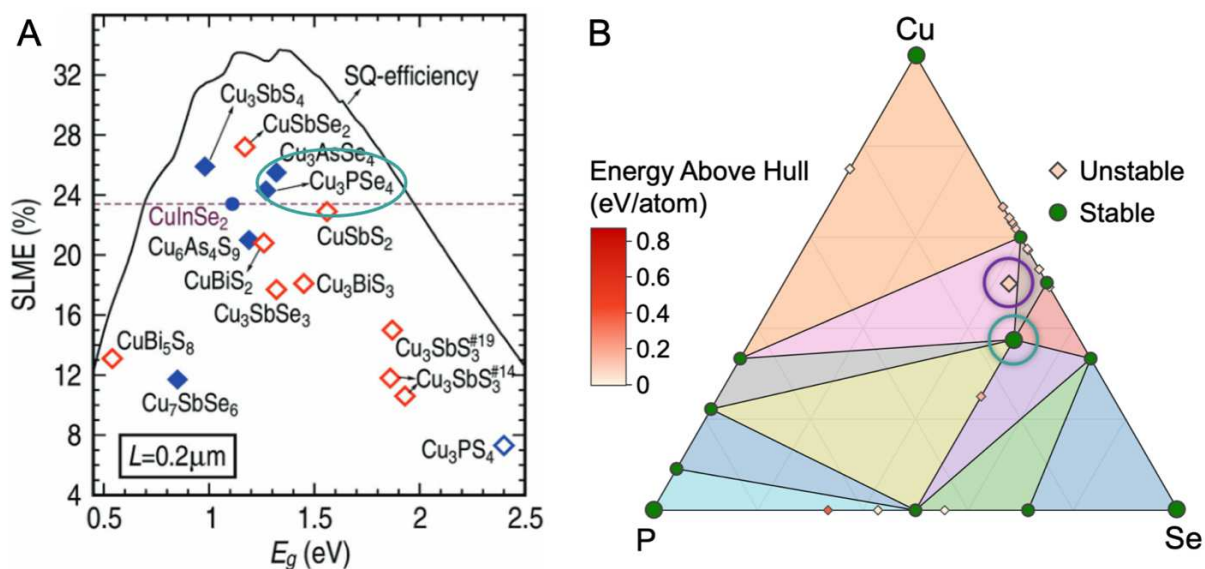


Figure 1.4. (A) Calculated spectroscopic limited maximum efficiency (SLME) for group Cu-V-VI materials. The open (filled) symbols represent indirect (direct) band gap materials. L is the film thickness. Copyright of Advanced energy Materials, 2013, Yu et al.¹⁷ (B) Cu_3PSe_4 ternary phase diagram from materialsproject.org.¹³²

The richness of accessible materials in the Cu-P-Se ternary phase space provides a useful canvas to determine how varying synthetic handles (experimental conditions, precursor reactivity, stoichiometry, etc.) can be used to controllably access Cu_3PSe_4 and Cu_7PSe_6 , predicted to be the thermodynamic and metastable phases (based on calculated formation energies at 0K),¹³² respectively. One approach to systematically control which individual phase is the final product of a reaction is to manipulate the driving forces of particle formation, which relies heavily on the bonding nature of the individual crystal structures. In **Figure 1.4B**, the phase diagram of Cu-P-Se is shown,¹³² which indicates the presence of both binary (indicated by the points on the triangle perimeter) and ternary phases with the respected stability based on the formation energy (eV/atom).¹³² The ternary phases are the points in the middle of the diagram, as indicated in **Figure 1.4B**, the blue outlined circle is indicative of Cu_3PSe_4 , whereas the purple outlined diamond is the Cu_7PSe_6 phase. Thus, the complexity of the Cu-P-Se phase diagram is synthetically appealing, due

to relatively stable binaries that can act as thermodynamic traps when navigating the Cu-P-Se phase space. Many binaries (both stable and metastable relative to ternary phases) exist within the phase space, especially along the Cu-Se coordinate, which is of particular importance as they will be frequently discussed in the following chapters. The persistence of Cu-Se binaries in solution, primarily CuSe and Cu₂Se, was originally noted in the initial Cu₃PSe₄ colloidal NP report by a previous group member, Dr. Jennifer Lee,¹³³ *vide infra*. Although a more thermodynamic outlook to an inherently kinetic process, by simplifying interactions and manipulating precursor reactivity, we aim to target reaction pathways that eliminate the presence of binary byproducts and kinetically trap calculated metastable phases.

Thus, it is clear that we need to develop an in depth understanding of the materials that could be target final products such as, electronic properties, bonding environments, band gap, defects, as well as previous characterization analyses to probe the stated solution dynamics. To fully grasp the research herein, we analyze the relevant literature regarding the structure and composition of Cu₃P, the reactivity of Se⁰ powder, structural information regarding Cu₃PSe₄, and Cu₇PSe₆ in the following subsections. This background is essential to the overarching objectives of the work presented herein, which are:

1. To describe and understand how Se/1-octadecene (ODE) speciation evolves in more complex, ternary systems with an additional aim of targeting particular active Se species to isolate desired reaction pathways.
2. To simplify and improve the Cu₃PSe₄ synthesis, as a common problem in nanoparticle synthesis is isolating and purifying products, making interpretation exceptionally difficult.
3. Why Cu₃P? What makes this precursor a great retrosynthetic synthon when all the bonds in Cu₃P must be cleaved and P must undergo a formal 8-electron oxidation?

4. To extrapolate the previously synthetic intuition to target more metastable phases and how Se precursor reactivity can be tuned to navigate the Cu-P-Se phase space.
5. To exhaust many structural characterization techniques to better define the composition of the presynthesized Cu_3P particles,¹³⁴ and develop a better understanding of how triphenyl phosphite is reduced and decomposes in the presence of copper(I) complexes to make Cu_3P NPs.

1.3.1. Cu_3PSe_4 – A Thermodynamic Ternary Phase

Copper selenophosphate, Cu_3PSe_4 , crystallizes in an enargite structure with an orthorhombic unit cell ($\text{Pmn}2_1$ space group) that is composed of highly symmetric CuSe_4 and PSe_4 tetrahedral units.¹²⁴ The resulting direct bandgap is calculated to be 1.35-1.38 eV^{17,130,135,136} and an experimentally determined value of 1.40 eV.¹³⁰ Cu_3PSe_4 has been measured to be a p-type, semiconductor, with a band character (**Figure 1.5**) that consists of Cu-*d* and Se-*p* orbital contributions at the valence band, while the conduction band consists of Se-*p* and P-*s* antibonding character. This calculation is further confirmed with improved computation compensating for P lone pair that interact strongly with Se *p* orbitals.¹³⁷ Copper vacancies have also been calculated and experimentally analyzed for single crystals, both of which indicating a favorable substoichiometric ratio of 2.9:1 for Cu:P.¹²⁴

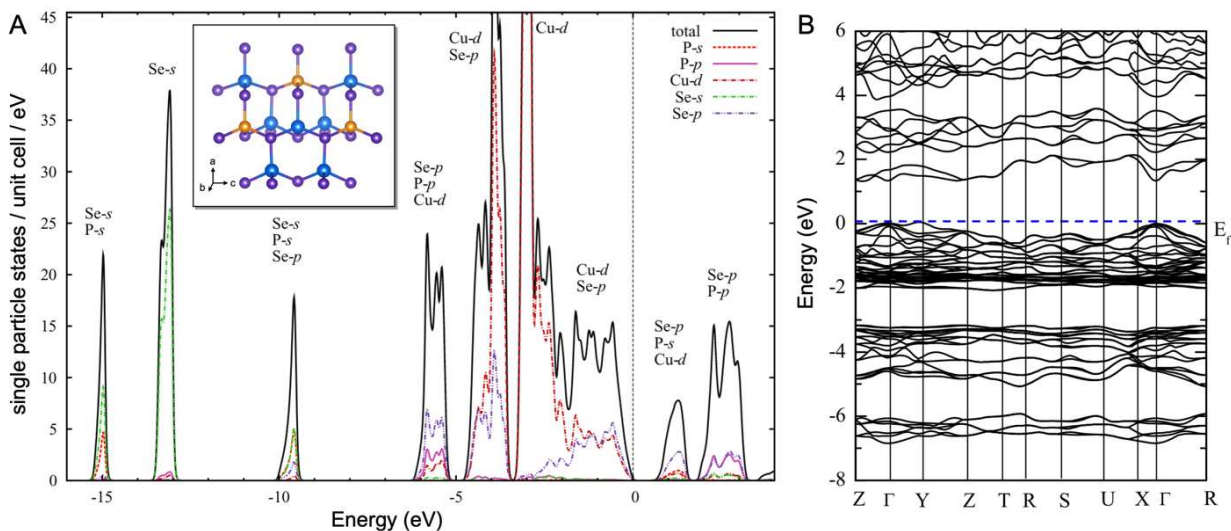


Figure 1.5. (A) Partial density of states for Cu_3PSe_4 unit cell. The individual orbital contributions are indicated by the colors in the top right. The large Cu-d peak rises to a maximum of twice the height of the plot. The vertical dashed line at 0 denotes the valence band maximum. Adapted from *Condensed Matter and Materials Physics*, 2013, Foster et al.¹³⁸ (B) Electronic band structure of Cu_3PSe_4 . Copyright of *Optical and Quantum Electronics*, 2017, Slassi et al.¹¹⁷

The electronic structure Cu_3PSe_4 has made it of interest for applications in photovoltaics,^{17,111,116,118,130,139} thermoelectrics,^{117,138} nonlinear optical materials¹⁴⁰ and recently cathode materials for magnesium batteries.¹³¹ A photovoltaic efficiency of 24% has been predicted by theory, which is attributed to the direct band gap of 1.40 eV.^{130,140} Additionally, Hall and Seebeck measurements demonstrate p-type (hole) character, with concentrations calculated in two separate reports to be 6×10^{17} and $8 \times 10^{18} \text{ cm}^{-1}$, which is attributed to copper vacancies and phosphorus-on-selenium antisite defects.^{116,138} An alternate application of Cu_3PSe_4 is as a cathode material for rechargeable magnesium batteries (RMB).¹³¹ One of the major limitations with RMB is the development of efficient cathode materials that can compensate for the Mg^{2+} ions and two additional, which Cu_3PSe_4 provides a potential target with redox-active polyatomic ions, $[\text{PSe}_4]^{3-}$ (Figure 1.6). A P-Se Mayer bond order of 1.2395 (indicating a strong covalent bond) was shown to delocalize the negative charge across the $[\text{PSe}_4]^{3-}$ unit,¹⁴¹ providing a large storage capacity of

25 mAh g⁻¹ at 50 mA g⁻¹.¹³¹ All of which make Cu₃PSe₄ a desirable material to isolate and tune structural properties to further drive development of renewable energy applications.

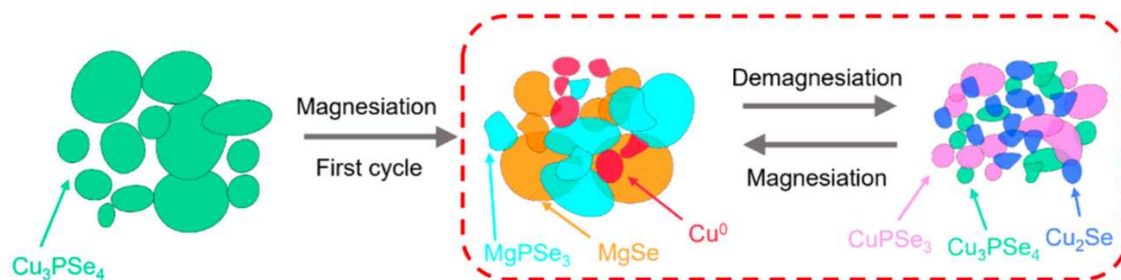


Figure 1.6. Scheme for the reaction mechanism of Cu₃PSe₄ after the first irreversible cycle and the subsequent cycles with the redox-active [PSe₄]³⁻ unit. Adapted from Chemistry of Materials, 2023, Tao et al.¹³¹

1.3.2. Lee et al. Synthesis Provides a Basis for the Research Explored Herein

To date the one colloidal synthetic method for Cu₃PSe₄ is from a previous group member, Dr. Jennifer Lee in 2019.¹³³ A key aspect pertaining to the Cu-P-Se phase space, determined in the first colloidal synthesis of Cu₃PSe₄, is the use of a pre-synthesized Cu₃P precursor,¹³⁴ predicted to be thermodynamically less stable to alternate Cu-P phases, as shown in the phase diagram above as the yellow diamond along the Cu-P coordinate line (**Figure 1.4B**). A variety of pathways were then explored using different precursors (P₄Se₃ or molecular precursors/salts),¹³³ which was essential to examine how thermodynamic factors (e.g., BDE) impact the formation of tetrahedral P-Se and Cu-Se units in the enargite Cu₃PSe₄ structure.¹⁴² However, the formation of Cu-Se binaries were persistent in solution as thermodynamic traps. Of particular attention, noted previously by Lee et al., are the Cu-P and P-Se tetrahedral bonding environments, which indicates that the Cu-P bonds in Cu₃P must be completely cleaved en route to Cu-P-Se phases. A simplified reaction coordinate diagram (**Figure 1.7**) is therefore devised from Lee et al., that demonstrates the energetics of the Cu-P-Se system that will be built upon throughout this dissertation.

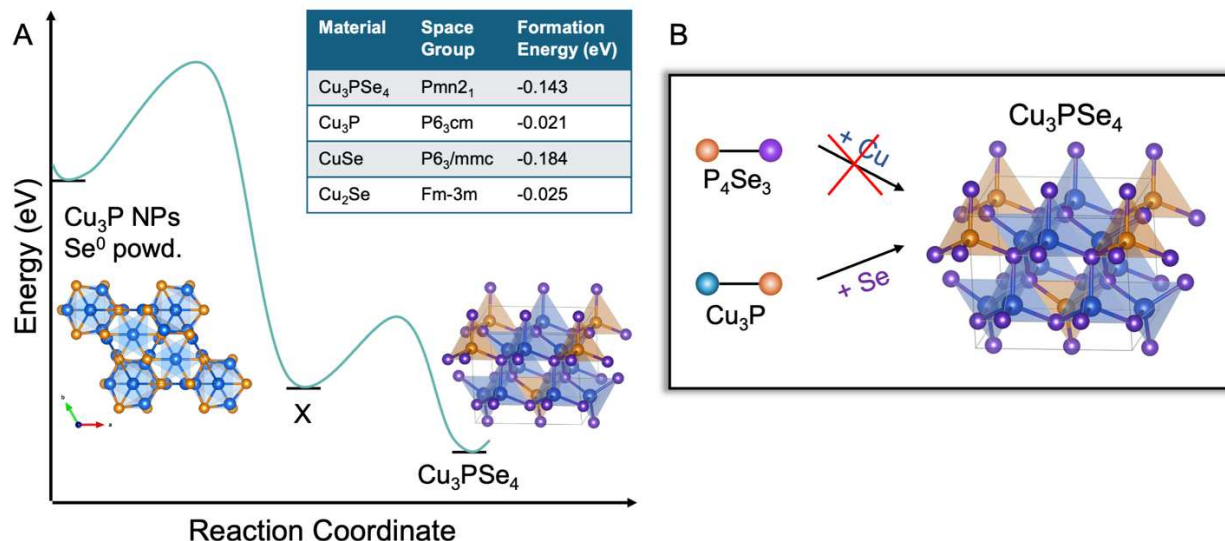


Figure 1.7. (A) Reaction coordinate diagram of Cu₃P reacting with Se⁰ powder to form Cu₃PSe₄, Cu=blue, P=orange, Se=purple. X represents Cu-Se binaries that form en route to Cu₃PSe₄. Formation energies of all the phases are provided in the top right from Materials Project calculated at 0K.¹³² (B) Reaction schemes tested to form Cu₃PSe₄ NPs. Adapted from Angewandte, 2019, Lee et al.¹³³

Another consideration yet to be discussed pertaining to the foundation of Cu₃PSe₄ synthesis, is the incorporation of Se⁰ powder in 1-octadecene (ODE). The inclusion of alternate solvents, such as primary amines and phosphines, alter the reaction pathway to again isolate Cu-Se binaries, which is hypothesized to be a result of varying reactivity of active Se species or the preferential coordination of such solvents to the surface of Cu-Se binaries. It is important to note that ODE has traditionally been referred in literature as a non-coordinating solvent that was claimed to be an innocent reaction medium for diffusion-controlled reactions.^{77,120} However, implementing ODE in syntheses with Se powder proves that this assumption does not hold for every material, as metal-Se binaries are formed from active species produced by Se/ODE interactions^{25,119–123}, such as H₂Se.

To expand our knowledge on the Cu-P-Se phase space, two Cu₃PSe₄ syntheses are evaluated, in which the solvent is changed, ODE and octadecane (ODA). In Chapter 2, we further explore

this synthetic approach to probe *why* the precursors, Cu_3P and Se^0 powder, produce phase pure particles by capturing the transformation of Cu_{3-x}P to Cu-Se binaries, *vide infra*. Additionally, a simplified synthesis with octadecane provides an alternative method to synthesize Cu_3PSe_4 , where a near-stoichiometric, atom-economical reaction is established which produces *cleaner* particles, as described in Chapter 3.

1.3.3. Cu_7PSe_6 – Controlling the Metastability of NP Synthesis

To further understand the Cu-P-Se phase space, controllably isolating the direct pathway for Cu_7PSe_6 NPs, a metastable material, will be explored in Chapter 4. The phosphorous deficient phase, Cu_7PSe_6 , an argyrodite compound, takes the general formula $\text{A}^{x+}_{12-y/x}\text{B}^{y+}\text{C}^{2-}$, which is derived from the first discovered compound with this structure, Ag_8PSe_6 .¹⁴³ Argyrodite compounds are of interest due to the resulting properties from the unique crystal structure and bonding environments.^{144–146} In particular, ordering of the cationic A site leads to high ionic conductivity for the high temperature polymorphs.^{147,148} Polymorphic transitions make these promising semiconductor materials for optoelectronic applications. Two argyrodites, Cu_7PSe_6 and Ag_7PSe_6 , have been previously synthesized by Gaudin et al. through a solid-state synthetic route to analyze the structural composition using atomic displacement parameters.^{149–151} The synthetic conditions require an extensive, 3 week process at high temperatures (973-1093 K). Analogous to the Cu_3PSe_4 ternary compound, the bonding environments for Cu_7PSe_6 (P2_13 space group) consist of Cu-Se and P-Se units but differs in lattice stability due to low-coordinate Cu-Se sites. In particular, Cu_7PSe_6 is composed of $[\text{PSe}_4]^{3-}$ units occupying tetrahedral sites in a cubic-closed framework of Se^{2-} anions (**Figure 1.8**). Depending on the polymorph, the copper ions will occupy different coordination sites with Se, with Cu-Se tetrahedral sites being the most stable in the low-

temperature (α) phase.¹⁵⁰ As the coordination decreases to a linear configuration, the Cu-Se bonds decrease in stability (β and γ), leading to a metastable material.¹⁵¹

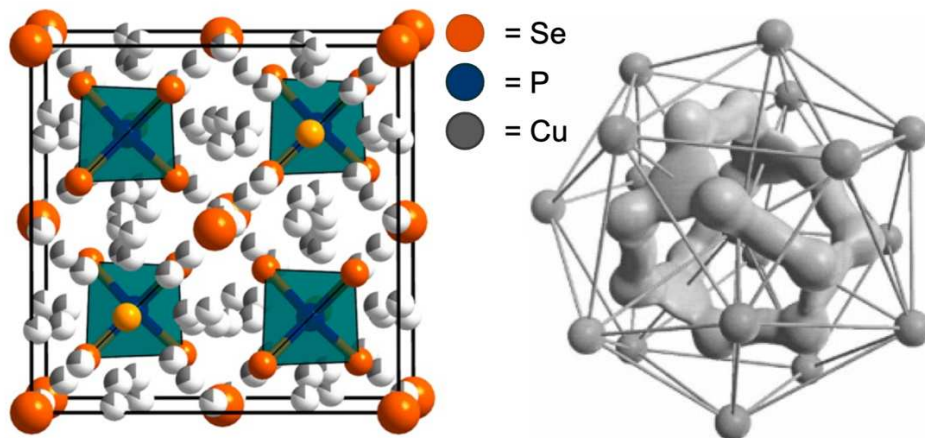


Figure 1.8. Cu_7PSe_6 ($P2_13$ space group) crystal structure. A cubic-closed framework of Se^{2-} anions (orange) with $[\text{PSe}_4]^{3-}$ units at tetrahedral sites and partially filled spheres representing Cu(I) cation site occupancy (left). Reprinted with permission from *J. Am. Chem. Soc.* 2014, 136, 34, 12035–12040. Copyright 2014 American Chemical Society.¹⁴⁷ Cu(I) diffusion pathways via joint probability surface calculations (right). Copyrights and Permission from Acta Crystallographica Section B: Structural Science, 2000, Gaudin et al.¹⁵¹

This alteration in the bonding environment leads to coveted properties applicable to thermoelectric and photovoltaic materials.^{147,152–154} Weldert et al. stated that the presence of high structural disorder and liquid-like behavior of Cu_7PSe_6 leads to very high Cu ionic mobility even at low temperatures,¹⁴⁷ making this material a great model system to study phonon-liquid electron-crystal thermoelectrics.¹⁵⁵ A common metric to evaluate thermoelectric efficiency is the figure of merit,^{156,157} which is optimized when there is high electrical and low thermal conductivity. With a figure of merit of 0.35 at 575K, Cu_7PSe_6 is comparable to the binary superionic conductor Cu_2Se .¹⁵⁸ However, the authors mention that substitution, or high levels of doping of constituent elements could increase the performance. This has recently been shown by substitution of Ag for Cu to get $(\text{Ag}_x\text{Cu}_{1-x})_7\text{PSe}_6$ and chalcogenide substitution making $\text{Cu}_7\text{P}(\text{Se}_{1-x}\text{S}_x)_6$ and $\text{Cu}_7\text{P}(\text{Se}_{1-x}\text{Te}_x)_6$ to tune entropic effects (**Figure 1.9**).^{144,159–161} However, a major practical limitation for pure

Cu_7PSe_6 is that when cycled, phase segregation occurs at the surface, producing Cu-Se binaries and elements,¹⁶² making this material not suitable as a thermoelectric material due to stability demand for high performance. Colloidal synthetic routes can provide solutions to this problem, as the particles can be stabilized with ligands (modified to be conductive once synthesized), thus prohibiting material degradation.

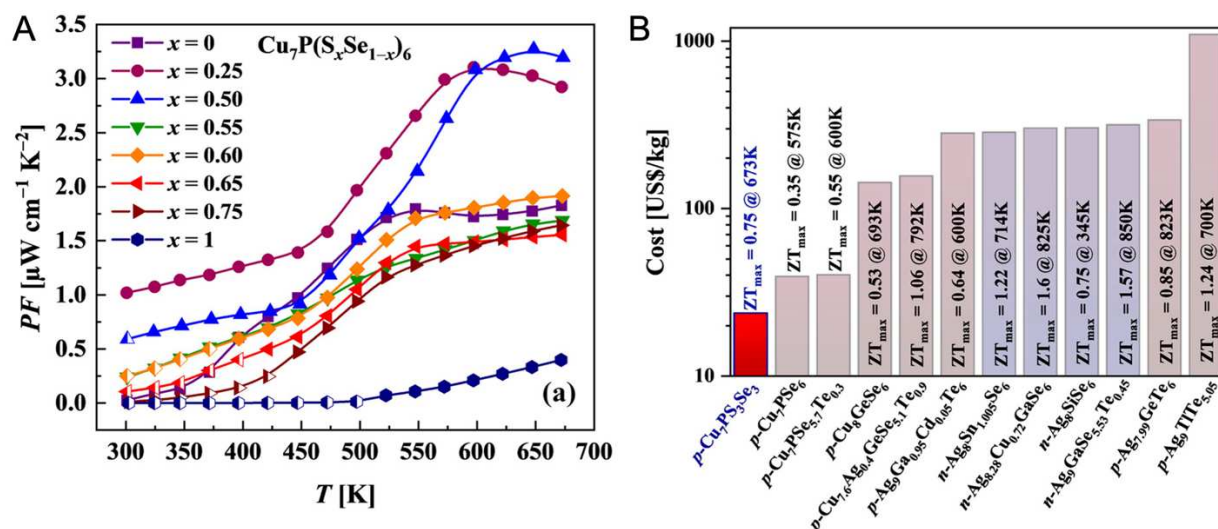


Figure 1.9. (A) Thermoelectric power factor PF for $\text{Cu}_7\text{P}(\text{S}_x\text{Se}_{1-x})_6$ samples (half-filled and filled characters correspond to properties of β - and γ -polymorphic modifications, respectively). (B) Summary of cost (in US\$/kg) of the best argyrodite-type thermoelectric materials (price source: Shanghai Metals Market, SMM). Adapted with permission from *ACS Appl. Mater. Interfaces* 2021, 13, 33, 39606–39620. Copyright 2021 ACS Applied Materials and Interfaces.¹⁴⁴

Although the solid-state route isolates the Cu_7PSe_6 phase, the synthesis is energy intensive and requires an extensive heating profile (973-1093K for 3 weeks) with intermittent grinding.¹⁵⁰ Employing colloidal nanoparticle synthetic strategies developed in this study could instead enable a more facile synthesis and reveal the richness of the reaction landscape that could be home to other useful ternary phases. In Chapter 4, we aim to target the metastable phase by adapting the Cu_3PSe_4 synthesis with dialkyl diselenides, as they have been shown to provide more control over Se precursor reactivity. In particular, we investigate diphenyl diselenide, Ph_2Se_2 , which promotes

the synthesis of Cu_7PSe_6 , but contrary to previously believed concept of reactivity for R_2Se_2 precursors. As previously stated, dialkyl diselenides reactivity can be tuned by changing the C-Se and Se-Se BDE, however, an important aspect that is determined in our work is that the byproduct of dialkyl diselenides can greatly influence the formation of multicomponent, complex materials. For dibenzyl diselenide, the C-Se bond is cleaved first, as it is weaker than Se-Se, and the byproduct, $\text{PhCH}_2\bullet$, rapidly scavenges hydrogen sources ($\text{H}\bullet$) in solution to produce toluene. Whereas, for diphenyl diselenide, the byproduct $\text{Ph}\bullet$ is hypothesized to readily react with P, therefore acting as an in situ phosphorus trap, producing phenyl-based phosphorus species.

1.4. Se Reactivity in Nanoparticle Syntheses

Chalcogenide systems have been widely studied for over 25 years, with the most common materials being binary phases, specifically I-VI and II-VI group systems, for example, Cu-Se and CdSe. In more recent years, though, the knowledge gained from the binary phases has been extrapolated to multicomponent systems (ternary and quaternary), leading to a wide range of materials. In turn, selenium reactivity used in NP syntheses, solvents have been acutely investigated to improve structure properties as well as target different chalcogenide materials. Therefore, a variety of selenium precursors have been employed in common NP solvents, from which, established active Se species are known. It is important to note that controlling Se speciation is limited, due to the presence of numerous Se species that can result when extrapolated to more complex systems. Throughout the work presented herein, two categories of Se precursors will be explored, Se^0 powder and dialkyl diselenides^{69,70} (primarily Ph_2Se_2 and Bn_2Se_2). For the interested reader, literature for alternate Se precursors is provided,^{113,115} particularly SeO_2 ,^{119,163} Se/amines,^{94,101,164–171} Se/phosphine,^{172–174} Se/thiol,^{94,167,169–171} and Se/ NaBH_4 .^{175,176} In the following subsections we explore the most commonly employed precursor combination, Se^0

powder and ODE (Chapter 2), to then understand how Se can be utilized in alkane solvents (Chapter 3). Reactivity of dialkyl selenides is summarized in Chapter 4 introduction.

1.4.1. Role of 1-octadecene in Se Powder Reactivity

As previously mentioned, 1-octadecene (ODE) is a commonly employed solvent for nanoparticle synthesis, resulting in many groups exploring the dynamics of ODE with Se^0 powder. The main advantage of ODE, cited frequently in literature, is the efficiency of Se dissolution, eliminating the use of Se-organophosphines (*n*-trioctylphosphine selenide)^{172–174} that were the primary route to form selenium-based NPs. Toxic, reactive phosphines were therefore no longer required, promoting a new area of research of “phosphine-free” syntheses^{77,80,94,97,121,122,177–180} that provides substantial data as a background for the research explored herein.

The long chain, high boiling point (310 °C) solvent has traditionally been valued for II-VI metal-selenide NCs due to the non-coordinating moieties that produce *fewer* impurities for such systems.¹⁸¹ In addition, the dissolution is achieved by the terminal, vinyl, alkene readily activating Se^0 powder by reducing it to the (2^-) oxidation state.¹²² Numerous preparation methods have been exploited to alternate the resulting Se speciation, including a standard heat-up dissolution of Se in ODE, utilizing fatty carboxylic acids to assist in Se reduction, dissolving Se^0 with sacrificial reducing agents (NaBH_4 or thiols),¹⁷⁵ and forming Se-suspensions under ambient conditions.¹²³ However, an upfront discussion that must take place, is whether the term *dissolution* is being applied correctly. Based on our current knowledge, this term is loosely applied to many systems which oversimplifies the reactions occurring to reduce Se to 2^- species, therefore, this term will not be used unless an accurate dissolution process is occurring. Two primary areas will be investigated throughout this subsection to better grasp what the resulting reduced Se species are in various conditions and the *problem* with ODE.

To that extent, we explore a carefully characterized study by Bullen et al. that evaluates Se reactivity with ODE as a function of experimental parameters, mainly temperature and time.¹²² It was determined the Se-ODE efficiency, measured by CdSe yield, was best achieved when Se/ODE solutions were heated at 180 °C for 5 hours. To further probe the reaction of Se with ODE, a “dissolution” time point was recorded when no Se⁰ powder remained in solution, which was then used to calculate the activation barrier assuming a first-order process, resulting in a value of 126 ± 13 kJ/mol. Additionally, of note by authors, “clearly, changes to the selenium species in solution continue to occur after complete dissolution of the solid selenium,” which is confirmed with XAS, NMR, and EI positive ion impact mass spectrometry. A major finding from these studies is the isomerization of the 1,2-terminal alkene to a mid-chain 2,3 alkene, which is attributed to the formation of R-Se, R₂Se, R₂Se₂ species, and possible H₂Se. Ultimately, the work of Bullen et al. established the efficiency of ODE to produce Se species that are more reactive than organophosphine reagents.

One key problem pertaining to the reaction products discussed by Bullen et al., is that ODE readily polymerizes at common NP conditions. Thus, the formation of polymerized ODE (polyODE) contaminates the final products, further complicating the characterization and capturing the responsible Se speciation. Regardless, the functionality of Se/ODE to isolate Se species with *higher* reactivity, provides promise for isolating the alternate reaction pathways to form Cu₇PSe₆. We, therefore, explore the impact of Se/ODE dynamics in solution to control the Cu-P-Se phase space, information that will help applying Se/ODE solutions in future syntheses.

1.4.2. Se Powder Solubility and Reactivity with Aliphatic Solvents

The dynamics of Se⁰_{powder} in aliphatic hydrocarbon solvents have only been sparsely studied in the context of nanoparticle syntheses, as the alternative solvents discussed above provide *more*

reactive active Se species. However, in the few studies where Se powder is employed in aliphatic solvents, the underlying process leading to incorporation of Se^0 are inconsistent in their conclusions. This is primarily a result of studies with varying systems and additives that complicate the hypotheses. Therefore, although frequently discussed, selenium dissolution, dispersion, and/or reactivity in long chain alkanes or olefins, are terms that have been loosely applied. In some studies, a combination of these definitions or phenomena have been applied, which cause one to find the terminology contradicting and need of clarification. Thus, it is of utmost importance to evaluate the results of a control study from 1933, by Green and Bradt, which is the one system where the process is simplified to just Se^0 powder and aliphatic solvents.¹⁸² If Se^0 powder is to react with an aliphatic solvent, the most favorable product is oxidation to an alkene and H_2Se formation. On this account, Green and Bradt study H_2Se generation after heating Se^0 powder in paraffin oil, motor oil, and ceresin (olefin). Analysis of the paraffin oil (aliphatic, hydrocarbon) includes data points only after 320 °C where the yield is 10.5%, while formation of H_2Se was mentioned to be negligible below 300 °C (**Figure 1.10**).

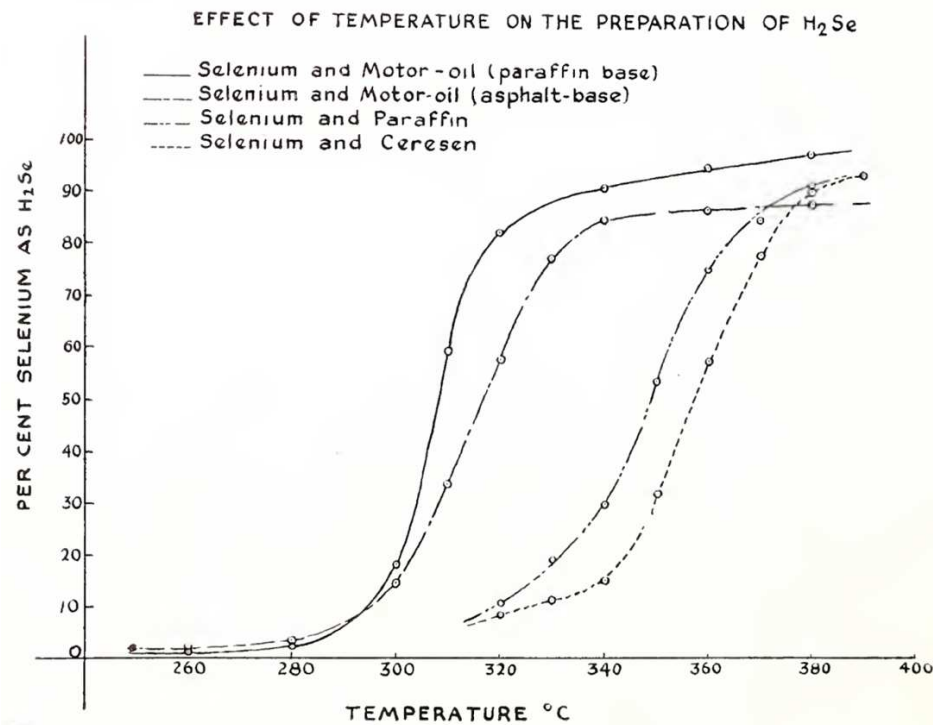


Figure 1.10. Gravimetric analysis to calculate percent of hydrogen selenide, H_2Se produced in paraffin motor-oil, asphalt motor-oil, paraffin, and ceresin solvents (indicated by line type) as a function of temperature. Figure copyright from Proceedings of Indiana Academy of Science, 1933, Green and Bradt.¹⁸²

Therefore, when applied to nanoparticle systems, the aforementioned H_2Se yield must be considered when discussing the role of the solvent. The first system is a cadmium selenide ($CdSe$) nanoparticle synthesis is designed to eliminate the use of toxic phosphorous based reagents (Deng et al., 2005; Yordanov et al., 2008).^{180,183} The formation of H_2Se is hypothesized to be the active Se species in this reaction, while CdO , acids, and paraffin oil (analytical grade) are the other precursors present. The Se powder is said to be the oxidant and a long alkene chain is the oxidation product, whereas the acid is the coordinating ligand for Cd to form a more active complex to react with H_2Se at 300 °C. It is however noted by the authors that this “is a process involving Se powder *dissolved* in paraffin liquid.” Three important roles were proposed for why a stable homogeneous solution is formed: liquid-state Se can be formed in paraffin oil, liquid-state Se can be well

dispersed in long alkane chain solvents, and H_2Se can be decomposed to $\text{Se}^0 + \text{H}_2$ *reversibly* at the reaction temperatures. Fourier transform infrared spectroscopy (FT-IR) was the sole technique used to identify the formation of alkenes for a control of Se and n-hexadecane heated to the reaction temperature (**Figure 1.11**).¹⁸³ It is of note that the peak the authors are referring to is low intensity and broad, thus suggesting other characterization techniques should have been used, that is, ^1H NMR. Thus, we can hypothesize that Se^0 reactivity in aliphatic solvents remains a viable process, however, it is difficult to extrapolate from this paper whether dissolution of $(\text{Se}^0)_n$ or dispersion is the underlying process of Se^0 powder heated in aliphatic solvents.

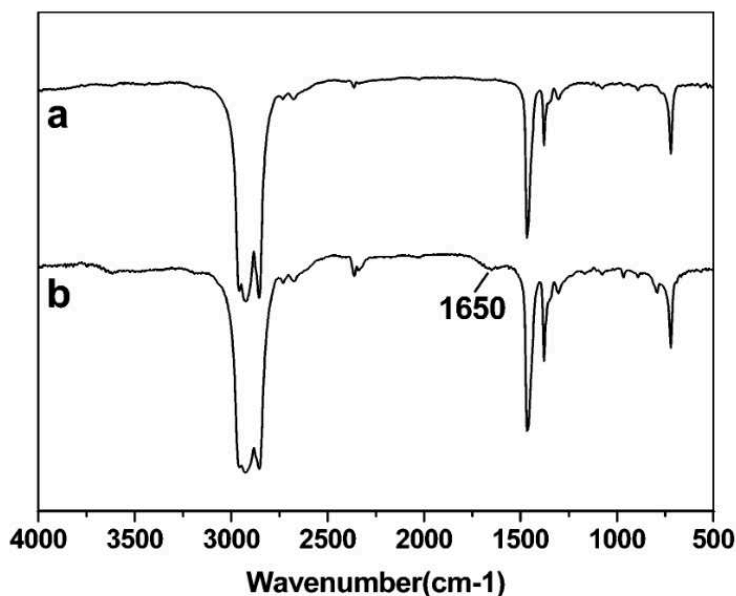


Figure 1.11. FTIR spectra of n-hexadecane mixed with Se powder before heating (a) and after heating (b). The absorption band at 1650 cm^{-1} is characteristic of C=C stretching. Reprinted with permission from *J. Phys. Chem. B* 2005, 109, 35, 16671–16675. Copyright 2005 American Chemical Society, Journal of Physical Chemistry.¹⁸³

Alternatively, a nanoparticle synthesis of CdSe was reported by Shen et al. that involves one-pot synthesis of CdO, Se^0 powder, paraffin oil (analytical grade), and decanoic acid.¹⁸⁴ The one-pot synthesis is of importance here due to the presence of an acid with Se powder during the heating

profile of the reaction, thus H_2Se can be produced. Of note, decanoic acid is also in excess of CdO and Se powder and the reaction is heated to only $200\text{ }^\circ\text{C}$. There are two hypotheses proposed in the paper on the role of $\text{Se}^0_{\text{powder}}$ and paraffin oil, but they are conflicting and lack the supporting characterization data. Firstly, the authors claim that the reason for direct addition of Se powder to the reaction flask, that is, one-pot synthesis, is for it to *react* with the paraffin oil then *react* with Cd complexes in solution. Alternatively, it is hypothesized that “When Se powder is directly *dissolved* in paraffin oil, the reactivity of our Se precursor is doubled than the TOP/TBP- Se .”⁹⁴ However, dissolution and Se powder reaction with paraffin oil are fundamentally different, as dissolution would lead to the interaction of Cd complex with Se allotropes whereas a reaction between Se powder and paraffin oil would likely produce H_2Se based on previous literature.

From the studies analyzed above, where specifically long alkane chain solvents are applied, the terminology that should be applied is that liquid-state of Se is dispersed once the melting point of $221\text{ }^\circ\text{C}$ is reached and produces H_2Se when high temperatures are reached. However, when alternate or additional precursors are present (acids), the favorable reaction is the reduction of Se^0 to H_2Se , which can occur at much lower temperatures. If dissolution was established in long-chain alkanes, then the crystalline form of Se could be recovered from the solvent¹⁶⁷ which is not noted by the aforementioned studies.

This dynamic of Se^0 powder in alkane solvents is utilized in the Cu_3PSe_4 system to promote a stoichiometric and direct, 8-electron redox reaction between Cu_3P and 4 Se^0 (Chapter 3). The rate of Cu_3PSe_4 formation counters the formation of H_2Se at the experimental conditions. Ultimately, the advantage of aliphatic solvent in chalcogenide systems is that when an external reducing agent is present to facilitate any redox events, a systematic and possibly stoichiometric synthesis can be established.

1.5. Cu₃P – The Required Precursor for Cu-P-Se Formation

Copper phosphide, Cu₃P, nanoparticles are further investigated, as they have previously been determined to be crucial in establishing a phase-pure synthesis of Cu₃PSe₄. Although Cu₃P nanoparticles are theoretically not ideal synthons due to the Cu-P bonds that must be cleaved to accommodate the Cu₃PSe₄ binding environments (Cu-Se and P-Se), the initial success as a precursor for a sulfur-based analog, Cu₃PS₄ material,¹⁸⁵ provides a foundation as an omnipresent precursor throughout this work. Two main considerations discussed in this subsection are:

Structural properties: These include factors such as composition, surface dynamics, and bonding environments, which can affect the ternary synthesis.

Synthetic methods: This focuses on the preparation of Cu₃P nanoparticles, with particular attention to the source of phosphorus and the choice of ligands.

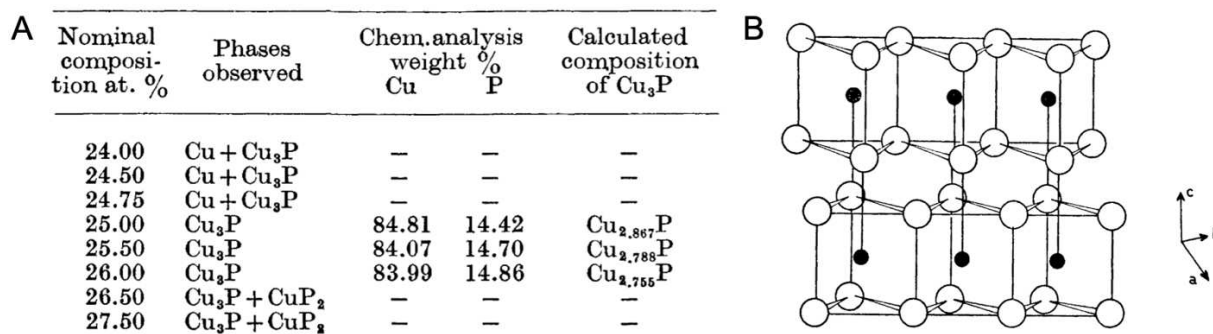


Figure 1.12. (A) Elemental compositions for Cu₃P in two phase alloys quenched from different temperatures. (B) The stacking of trigonal prisms in the c direction. Large circles represent copper atoms. Copper atoms outside the rectangular faces of the prisms are omitted. Copyright from Acta Chemica Scandinavica, 1972, Olofsson et al.¹⁸⁶

In one of the initial reports on Cu₃P, published by Olofsson in 1972, the structural determination and refinement of the Cu₃P structure is provided (P6₃cm space group).¹⁸⁶ From which, and of utmost importance, Olofsson analyzed the homogeneity range of Cu:P at 700 °C (Figure 1.12A). With phase analysis by X-ray diffraction methods and chemical analysis a range

of $\text{Cu}_{2.82}\text{P}$ to $\text{Cu}_{2.73}\text{P}$ was calculated (refinement of occupancy parameters were performed with Si internal standard). Additionally, a synthetic adaption to isolate single crystals allowed for precise structural information, where the ideal structure contains 6 Cu_3P units that can alternatively be explained as an array of Cu_6P triangular prisms with one Cu atom located at trigonal and rectangular faces (**Figure 1.12B**). The substoichiometric composition has been further demonstrated with alternative syntheses (typically characterized with elemental analysis, ICP-MS), *vide infra*, with the Cu:P ratio having great variability (Cu_{3-x}P , $0.13 < x < 1.08$).^{187–193} De Trizio et al., further confirmed the presence of Cu vacancies with DFT calculations (**Figure 1.13**), which correspond to the identical 6(c) positions proposed by Olofsson.¹⁹⁴ Both confirm that Cu_3P is substoichiometric, hence Cu_3P will be denoted as Cu_{3-x}P throughout the presented chapters.

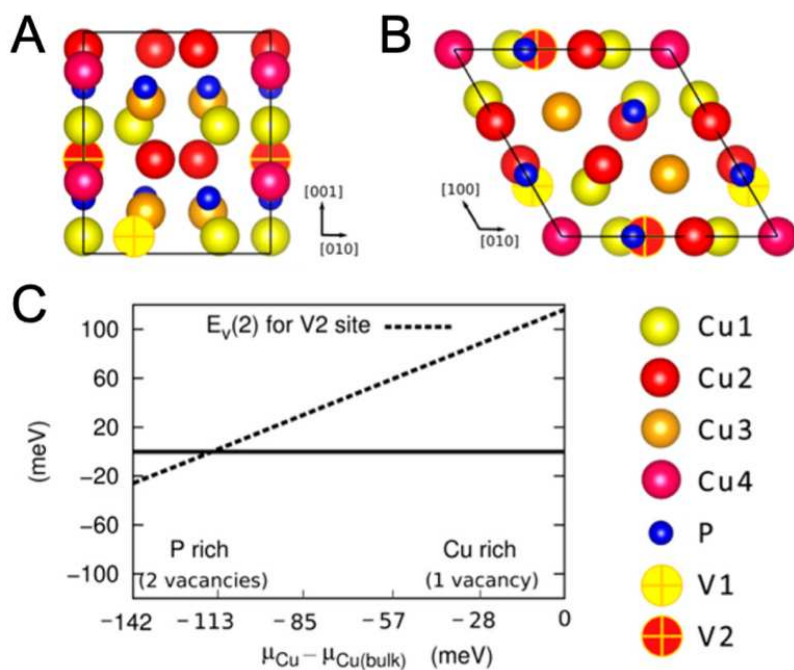
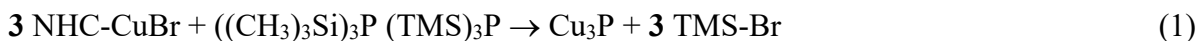


Figure 1.13. (A) [100] and (B) [001] views of the Cu_3P lattice. The projection of the primitive unit cell is given by the solid black line. (C) Free energy profile for $E_v(2)$ at the V2 site, as a function of μ_{Cu} (Cu chemical potential). The value of $E_v(2)$ is given relative to $E_v(1)$. The line $y = 0$ is also shown to help distinguish regions in the free energy profile where 1 or 2 vacancies are energetically favored. Adapted with permission from *Chem. Mater.* 2015, 27, 3, 1120–1128. Copyright 2015 American Chemical Society, Chemistry of Materials.¹⁹⁴

Traditional synthetic conditions targeting bulk Cu_{3-x}P used Cu metal powder or pieces of sheet metal with red phosphorus, which are then heated to 500-1000 °C for an extended period.^{187,195–197} The standard enthalpy of formation of Cu_{3-x}P was calculated from these conditions, yielding a value of $-34.8 \pm 3.4 \text{ kJmol}^{-1}$. An adaption to the traditional synthesis as the first step toward a colloidal NP method was adapting to a solvothermal experiment, where $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, yellow or red phosphorus, and amines (liquid ammonia or ethylenediamine) are heated to roughly ~ 100 °C for 12 h.^{195,198,199} In 2008, Henkes and Schaak reported the first colloidal nanoparticle synthesis, which utilized a reactive, toxic phosphorus precursor, trioctylphosphine (TOP).^{172,200} Copper(I) chloride is initially reduced to form copper(0) particles that then transition to Cu_3P when TOP is injected at high temperature, which is proposed to be due to the strong C-P bond that must be cleaved.¹⁷² The active species that results from TOP degradation are hypothesized to be PH_3 , a precursor that has also been used and injected directly to form Cu_{3-x}P NPs.^{188,201} Alternatively, aminophosphines have been employed²⁰² that preferentially coordinate to Cu(I) and release P when the amine derivative, imines (NHR) dissociates to form aminophosphonium cation byproducts,¹⁹² a process similar to a disproportionation reaction for indium phosphide, InP, NCs.^{32,203} Finally, before proceeding to the Cu_{3-x}P explored herein, the use of tris(trimethylsilyl)phosphine, $(\text{TMS})_3\text{P}$, with n-heterocyclic carbene-CuBr (NHC-CuBr) yields Cu_{3-x}P while stoichiometrically producing 3 TMS-Br (eq. 1).



The reactive $(\text{TMS})_3\text{P}$ precursor can be employed at low temperatures to produce sub 5 nm particles, high ligand density, and without Cu(0) contamination. However, a significant deviation from Cu_3P exists, producing $\text{Cu}_{2.30}\text{P}$ or $\text{Cu}_{1.96}\text{P}$ particles with possible amorphous NPs in the final product, which encourages the development of an alternate synthesis.

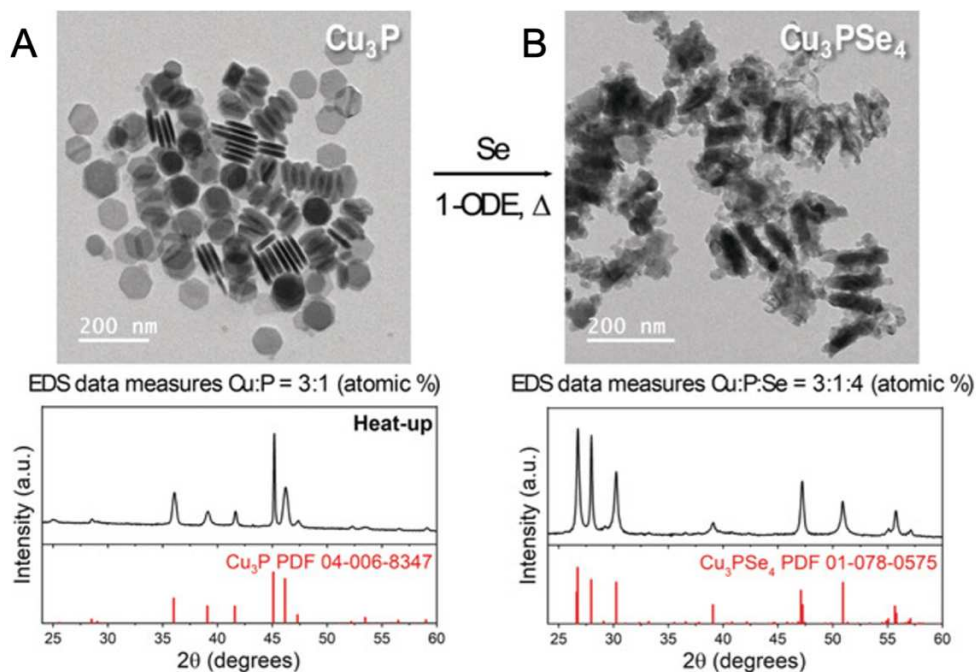


Figure 1.14. TEM images and corresponding XRD patterns of a) Cu_3P synthesized by heat-up and transformation to b) phase-pure Cu_3PSe_4 . Adapted from *Angewandte Chemie*, 2019, Lee et al.¹³³

The previously stated synthetic methods are of importance, as some syntheses were considered by Lee et al., but didn't reproducibly result in phase pure Cu_3PSe_4 particles. Therefore, a synthesis using triphenylphosphite, $\text{P}(\text{OPh})_3$, by Liu et al.¹³⁴ was determined to be best route to synthesize Cu_3PSe_4 , identified with PXRD by the absence of Cu-Se binaries (**Figure 1.14**). Two aspects of the Cu_3P particles were hypothesized to be the cause of Cu_3PSe_4 success, (1) hexadecylamine (HDA) ligand dynamics at the surface that promotes the interaction with in situ formed Se/ODE species, and (2) consistent particle properties such as, low size polydispersity, composition (no Janus particles), and absence of organic byproducts that can contaminate reaction with Se.¹⁴² Further investigations of the stated Cu_{3-x}P NPs reactivity with Se^0 powder in ODE is explored in Chapter 2 to better capture the role of the precursor in the reaction pathway. Chapter 3 investigates a simplified, near-stoichiometric system by incorporating octadecane, which indicates that although Cu_{3-x}P is a required retrosynthetic synthon, more structural information is

required to fully develop a stoichiometric synthesis of Cu_3PSe_4 . In order to tackle such a feat, we return to the Liu et al. synthesis while employing multiple characterization techniques and determine the role of individual precursors (particularly TPP) in Chapter 5, both of which contribute to overall better understanding of the Cu-P-Se phase space.

1.6. Dissertation Overview, Publications, and Presentations

The following chapters strive to develop a better understanding of the Cu-P-Se reaction landscape by first deciphering the transformation pathways of Cu_3PSe_4 in the presence of ODE (Chapter 2). Second, establishing a stoichiometric synthesis of Cu_3PSe_4 by employing an innocent solvent, ODA (Chapter 3). Next, manipulating selenium reactivity with a Ph_2Se_2 precursor to synthesize a metastable phase, Cu_7PSe_6 (Chapter 4). Finally, simplifying and capturing the decomposition of a green-phosphorus reagent, triphenyl phosphite, for the retrosynthetic synthon, Cu_3P (Chapter 5). Work presented herein is either published in a peer-reviewed journal (Chapter 3) or in the process of being submitted (Chapter 4). Chapter 3 and Appendix B, “Copper Selenophosphate, Cu_3PSe_4 , Nanoparticle Synthesis: Octadecane Is the Key To A Simplified, Atom-Economical Reaction” is published in *ACS NanoLetters* (Neisius et al., 2023). Chapter 4, is in progress of being submitted to *Chemistry of Materials* (Neisius et al., 2024).

Research efforts additionally extend to collaborations on many projects. First, a coauthored publication is in the process of being submitted to *Chemistry of Materials* as a methodology paper, “Performing Rietveld Refinements on Complex Nanoscale Systems: A Guide to Extract Physically Meaningful Parameters” (Neisius, Kale et al., June 2024). Next, a second author publication close to the work presented herein and as a follow-up to Chapter 3, is currently near submission, “Dialkyl Diselenides in the Synthesis of Copper Selenophosphate, Cu_3PSe_4 , Nanoparticles: Stoichiometry and Initial Insights into the Reaction Pathway” in *Chemistry of Materials* (MacHale et al., June

2024). Another second author publication is a follow-up to the previous Bn_2Se_2 report, which is also in the process of being submitted to *ACS Nano* (MacHale et al., July 2024). I am also a co-author on a paper led by Daniel Windsor by characterizing films with powder X-ray diffraction and fitting with Rietveld refinements, titled “Multi-functional cyclized-polyacrylonitrile (cPAN) as a Coating for Sb-based Anodes in Sodium-ion Batteries” in preparation of being submitted to *Applied Materials and Interfaces* (Windsor et al., June 2024). According to CRediT (a guide to contributor roles, Contributors, Roles, Taxonomy) my roles in the previously stated co-author publications, include Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, and Writing – review and editing.

Aspects of this research, particularly Chapter 3 and 4, has been presented at several conferences, including the Inorganic Chemistry Gordon Research Conference (2022) and North American Solid State Chemistry Conference (Neisius et al., 2023) as well as the CSU Graduate Student Conference (Neisius et al., 2024, Chapter 5) which received the outstanding scholar award.

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CHAPTER 2: ANALYZING THE FORMATION OF Cu-Se AND Cu-P-Se PHASES TO UNDERSTAND THE NECESSARY INTERACTIONS OF PRECURSORS TO FORM Cu_3PSe_4 AND Cu_7PSe_6

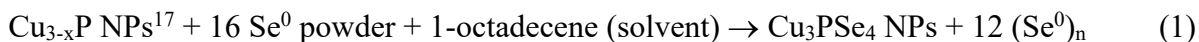
2.1. Overview

Reaction pathways in the nanoparticle synthesis field are often poorly characterized, which has limited the discovery of novel materials and the ability to fine tune synthetic parameters to optimize materials. Developing an understanding of how precursors transform into active species or monomers is essential to establish more targeted synthetic designs. Data reported herein is to support hypotheses describing the reaction pathway for Cu-P-Se based ternary phases. Through investigation of two probing methods, ex situ aliquots and cannula transfer studies, the conversion of precursors to active species essential to target the individual pathways were isolated. Throughout the progression of the reactions, characteristic copper selenium binaries, $\text{Cu}_{0.87}\text{Se}$ and Cu_{2-x}Se , were identified as quenched intermediates in Cu_3PSe_4 and Cu_7PSe_6 , respectively. The analysis of samples collected via these probing methods indicates that the rate of conversion of the precursors to ternary phases is dependent on the dissolution efficiency of selenium powder in 1-octadecene.

2.2. Introduction

Colloidal nanoparticle (NP) synthesis has gained considerable interest since the discovery and synthesis of quantum dots in 1993.¹ Ternary chalcogenide materials are of particular interest due to applicable properties for photovoltaic devices,²⁻⁵ catalysis,⁶⁻⁸ battery materials,^{9,10} optoelectronics,¹¹⁻¹³ and nonlinear optics.^{14,15} From the catalog of desired chalcogenide materials are Cu-P-Se phases, that consist of a thermodynamic and metastable phases, Cu_3PSe_4 and Cu_7PSe_6 , respectively. Previously, these materials were synthesized by traditional high temperature, solid-

state techniques. Recently, Lee et al. developed a colloidal nanoparticle synthesis for, and isolated, phase pure Cu₃PSe₄ NPs in 2019, as shown in eq. 1.¹⁶



The reaction of Cu₃P nanoparticles¹⁷ and selenium (Se) powder in 1-octadecene (ODE) was utilized as precursors under the optimized experimental parameters (300°C). Although the desired product was formed, the reaction is quite complex. In the literature, ODE has conventionally been referred to as a non-coordinating solvent, but Se⁰ powder and ODE interactions produce active species that readily react to incorporate Se into binary and ternary particles.^{18–23}

Based on the work done by Lee et al., we established an alternate synthesis to Cu₃PSe₄, where the incorporation of octadecane (ODA) promoted a stoichiometric 8-electron redox reaction of Cu₃P and 4 Se⁰ powder.²⁴ Even though a *cleaner* reaction was established, the commonality of ODE in NP synthesis has driven the requirement of understanding the necessary interactions for Cu-P-Se phase formation.

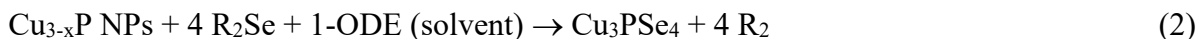
To develop such understanding a more molecular-level, atomically precise approach is required. Coupling molecular (e.g., spectroscopy) and solid-state (e.g., diffraction) techniques allows for an analysis of the ligand dynamics on the surface and structural properties of the inorganic core. These techniques have also been used to study reaction pathways. Although aliquots that are taken from the reaction are quenched species, insight into how the reaction proceeds can still be gained. For example, powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) characterization techniques were utilized to determine that copper (Cu) sulfide binary NCs were intermediates to Cu-M-S (M = V, Cr, Mn) ternary phases.²⁵ Similarly, analysis of CdSe reaction aliquots by ³¹P NMR determined the reactivity of phosphine chalcogenide precursors.²⁶

However, investigating reaction pathways via indirect techniques alone cannot provide a comprehensive picture on how synthetic parameters can be manipulated to isolate specific phases. Thus, molecular-level understanding has also been examined via synthetic methodologies by controlling the reactivity of precursors^{25,27–35} and ligand dynamics.^{36–46} Hard-soft acid-base (HSAB) theory is one underlying principle applied to understand the influence of precursor over phase transformation by describing components, such as metal precursor stability and solubility.^{29,30,33,47,48} Although the transition of species in colloidal NP synthesis is a kinetically driven process,^{49–53} the thermodynamic driving forces (bond dissociation energies, BDE) of metal-ligand complexes should be considered. The ligand dynamics, therefore, are important to balance the stability of the intermediate and final particles formed to control the rate of species transformation.^{25,37,54,55} Ultimately, balancing the reactivity of precursors is exceptionally important for colloidal nanoparticle synthesis of ternary materials to prevent the formation of undesired byproducts, such as binary phases.^{25,48,56}

Although many experimental methods have been optimized,^{57–59} interpretation of results has limited progress of the field as simplified theories have been applied to complicated systems. For example, the widespread acceptance of classical nucleation and growth as the primary NP growth mechanism has limited the exploration of other reaction pathways.⁶⁰ Therefore, combining an experimental tool-kit with theoretical models is required to provide a more concrete analysis of the experimental results.

Current investigations on the dependence of Se-based species with varying reactivity on the Cu_3PSe_4 pathway are underway by our group (Chapter 5 in Dr. Jennifer Lee Dissertation).⁶¹ To understand the impact precursor Lewis acidity versus basicity (LA/LB) has on the interaction with Cu_3P , bridged R_2Se (R=alkyl chains) species and H_2Se were investigated. Chalcogen bonding is

consistent with Lewis acidity due to the polarizable chalcogen groups producing an electrophilic anti-bonding sigma bond (σ^*),^{62,63} while H₂Se is predicted to be Lewis basic along the H-Se bond axis. Direct injection of H₂Se to a Cu₃P/ODE solution isolated an alternative pathway resulting in primarily Cu_{2-x}Se with minimal Cu₇PSe₆ conversion. Whereas when the headspace from a Se/ODE solution at 300°C was cannula transferred to Cu₃P/ODE only minor conversion to Cu_{2-x}Se was identified after 4 hours (manuscript in preparation). It is therefore hypothesized that the interaction of R₂Se and Cu₃P is required to isolate Cu₃PSe₄ through a reductive elimination mechanism (eq. 2).⁶⁴



This hypothesis is further probed herein via ex situ studies to determine the viability of alternative pathways, establishing a refined disproof model.^{65,66} PXRD and ¹H NMR are utilized as the main indirect characterization for each aliquot, with the primary goal of tracking the transformation of species and interpreting the role of each precursor. Ultimately, developing an alternative analysis on the progression of species for the Cu₃PSe₄ pathway will allow for better understanding of how Cu₃P and Se/ODE can control the Cu-P-Se phase space.

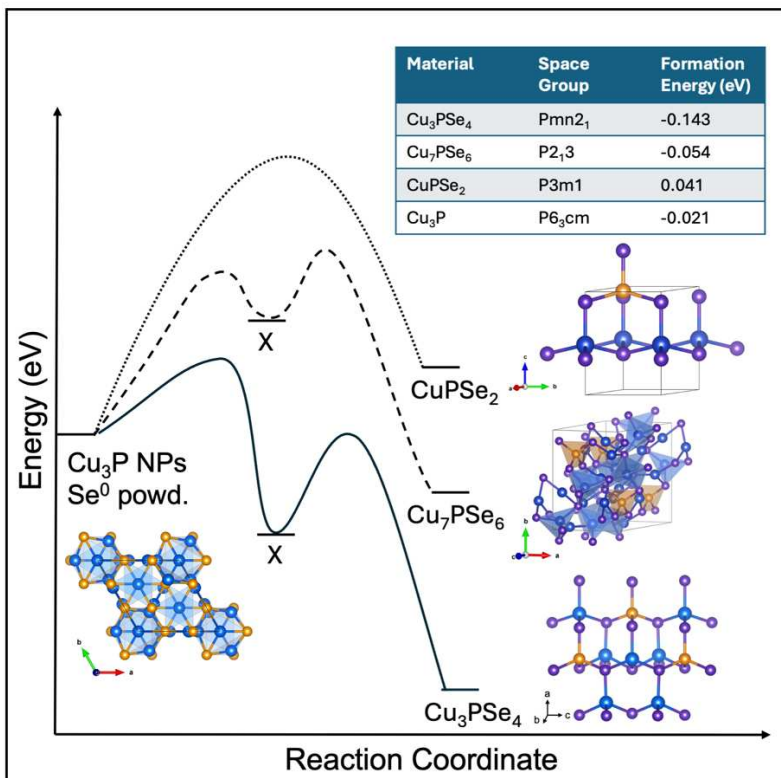


Figure 2.1. Reaction coordinate diagram for Cu-P-Se phases when starting with Cu₃P NPs and Se⁰ powder (Cu=blue, P=orange, Se=purple). The formation energies are shown in the top right table which values come from Materials Project calculated at 0K.⁶⁷

In order to contribute to the molecular-level aspect of the field, investigation of the Cu-P-Se phase space is explored herein (**Figure 2.1**). The toolkit exploited is broken down into three primary approaches:

- I. A combination of indirect characterization or ex situ techniques to identify the quenched phases and provide insight into the transformation of species.
- II. Synthetic manipulation of precursor reactivity and active species to isolate transformation pathways that favor metastable materials.
- III. Applying previously established theoretical models to offer a more comprehensive picture that characterization alone cannot provide.

To systematically control the individual phases, we will manipulate the driving forces of particle formation, which rely heavily on the bonding nature of the individual crystal structures, as well as the precursors will be manipulated. To further understand the Cu-P-Se phase space, we will explore controllably isolating the direct pathway for Cu_7PSe_6 ^{68–73} NPs, while utilizing Cu_3P and Se/ODE as precursors. Similar to the strategies described for the Cu_3PSe_4 phase, it is hypothesized that a robust understanding of the precursor speciation and overlooked components of the reaction flask (i.e., gaseous species) will enable a controlled manipulation to form the metastable, ternary Cu_7PSe_6 phase under lower temperatures and decreased time. Implementing the proposed strategies for the targeted nanoparticle synthesis of a metastable phase, and elucidation of its reaction scheme, can provide insight into how analogous metastable phases can be formed. The development of more elegantly tailored strategies which bypass trial-and-error syntheses to successfully achieve targeted synthetic design is a major challenge in our field.

2.3. Experimental

In the following sections, the conversion of precursors to active species to form Cu_3PSe_4 and Cu_7PSe_6 will be monitored using ex situ aliquots and cannula transfer studies that will be analyzed with PXRD, TEM, ^1H and ^{31}P NMR.

Materials

Anhydrous copper (II) chloride (CuCl_2 , 97%, Ridel-deHaën), hexadecylamine (HDA, Sigma Aldrich, 90%), triphenyl phosphite (TPOP, 97%, Oakwood Chemical), selenium powder (Se, 99.99%, STREM), chloroform (CHCl_3 , 99.8%, Sigma Aldrich), isopropanol (IPA, 99.5%, Fischer Scientific), hexanes (98.5%, Sigma Aldrich), toluene (99.5%, Sigma Aldrich), and ethanol (99%, Fischer Scientific) were used as packaged and received. 1-Octadecene (ODE, 90% Technical grade, Aldrich), Oleylamine (OLA, 70% Technical grade, Aldrich), and squalane (98%, Alfa

Aesar) were sparged with N₂ for 2 hours (hr) before being used. All reactions were performed under inert N₂ atmosphere unless specified otherwise. Post-synthesis solvent washing was performed in ambient conditions on the benchtop unless stated otherwise.

Materials characterization

The crystalline products were characterized with Powder X-Ray Diffraction (PXRD) using a Cu source ($\lambda=1.54$ Å) on a Bruker D8 Discover Series powder X-ray diffractometer. Rietveld refinements were performed using Topas software. Samples were prepared by dispersing the particles in hexanes, followed by drop-casting on a p-type boron-doped Si Zero Diffraction Wafer. Morphology of nanoparticles were characterized using a JEOL JEM 2100F Transmission Electron Microscopy (TEM) at 200 keV. Solvent extracted from ex situ measurements, cannula transfer studies, and overall syntheses were characterized via ¹H NMR and EI-GC MS. ¹H NMR experiments were performed in deuterated chloroform (CDCl₃) on a Bruker NEO400 spectrometer. Spectrum were predicted for Se based species as a complimentary technique on ChemDraw and nmrd.org.

Cu₃P Heat-Up Synthesis

The following reaction procedures were adapted from Lee et al.⁷⁴ CuCl₂, TPOP, HDA, and ODE were massed into a three-neck round bottom flask in a N₂ glovebox. Once extracted from the glovebox, the reaction flask was attached to the Schlenk line while under N₂, cycled between vacuum and N₂ three times. Of note, light blue color was produced upon medium stirring. The flask was heated to 150°C, at a 500°C/hr ramp rate, and kept at this temperature for 1 hr. Upon reaching 150°C, the solution turned clear indicating the reduction of copper. The reaction temperature was then increased to 300°C for 30 min to achieve optimal nanoparticle growth. The

reaction flask was cooled to 200°C while still in the heating mantle, then removed from the mantle for rapid cooling to 80-60°C where the solution is extracted.

Cu₃PSe₄ Heat-Up Synthesis

Washed Cu₃P particles (20 mg) were suspended in hexanes and transferred to a three-neck round bottom flask. The pre-weighed reaction flask and nanoparticles were dried over nitrogen, then pumped into the glovebox overnight. Se powder (84 mg) and ODE (10.7 ml) were measured out into the reaction flask in the glovebox. Once extracted from the glovebox, the reaction flask was attached to the Schlenk line and kept under vacuum. A medium stir rate was set which produced a black solution. The reaction flask was heated up to 150°C, at a 500°C/hr ramp rate. At 150°C, the reaction flask was back filled with N₂ gas (white gas evolved from solution), and the temperature was increased to 300°C. The reaction was held at 300°C for 20 minutes to achieve optimal nanoparticle growth. The reaction flask was raised from the heating mantle to be cooled to 80-60°C for extraction to two centrifuge tubes.

Cu₃PSe₄ Ex Situ Aliquots

The Cu₃PSe₄ procedure was replicated with modifications at the desired temperatures. Ex situ studies consist of temperature aliquots at 150, 200, 225, 250, 300, and 300°C at an allotted time. Instead of continuous ramping from 150°C to 300°C, the digitrol was set to the aliquot temperatures. Once the temperature was reached, the reaction was held for a designated time (described below in results). Next, the syringe was purged three times with N₂, and then inserted into the reaction flask to extract roughly 2-3 mL of the reaction solution. The vial was centrifuged to separate the solution from nanoparticles for future characterization.

Cu₇PSe₆ Cannula Transfer Control

Washed Cu₃P particles (20 mg) were suspended in hexanes and transferred to a three-neck round bottom flask. The pre-weighed reaction flask and nanoparticles were dried over nitrogen, then pumped into the glovebox overnight. ODE (10.70 ml) was added to the pre-weighed Cu₃P. In a separate 50 mL three-neck flask, Se powder and ODE (0.10 M solution) were measured out. Both reaction flasks were extracted from the glovebox, attached to a Schlenk line, then placed under vacuum. The reaction was heated to 150°C, at a 500°C/hr ramp rate, and a medium stir rate was set for both flasks which produced black suspensions. Once 150°C was reached, both reaction flasks were back filled with N₂ gas, and the temperature is increased to 300°C. At 300°C, the Se/ODE solution was quickly cannula transferred to the Cu₃P solution (N₂ flow = 42 psi). After the solution was transferred, the reaction was held at 300°C for 20 minutes. The reaction flask was raised from the heating mantle to be cooled to 80-60°C for extraction to two centrifuge tubes.

Washing Procedure

Organic surfactants were washed to purify the products by the following procedure. After the reactions were cooled to the desired temperature, the solution and suspended nanoparticles were extracted to four centrifuge tubes for Cu₃P and two for the Cu-P-Se ternary syntheses. CHCl₃ (1-2 mL) and IPA (13 mL) were used as the solvent and anti-solvent for Cu₃P, respectively. Toluene (2-3 mL) and ethanol (12 mL) were used as the solvent and anti-solvent for the ternary syntheses, respectively. The particles were centrifuged at 5800 rpm for 15 minutes and the supernatant was discarded. This washing procedure was repeated 2-3 times depending on the color of the supernatant after centrifuging. If the solution consisted of a brown tint, the particles were washed an additional time.

2.4. Results and Discussion

2.4.1. GENERAL CONSIDERATIONS OF $\text{Cu}_3\text{P} + \text{Se/ODE} \rightarrow \text{Cu-P-Se}$ SYSTEM

The transformation of Cu_3P to Cu-P-Se phases is intriguing from a chemical intuition standpoint due to presence of Cu-Se binaries⁷⁴ in the quenched reactions explored herein. In addition, both ternary phases, Cu_3PSe_4 and Cu_7PSe_6 are composed of Cu-Se and P-Se bonding units. Thus, it is of importance to understand the fundamental properties of Cu_3P , as explained in *Chapter 1.5*, when probing Cu-P-Se based phases, as this will allow for more precise control over the interactions with Se-based species and provide rational on why particular phases are favored. Generally, the Cu_3P ($\text{P6}_3\text{cm}$) crystal structure,⁷⁵ is comprised of high coordinate subunits consisting of eleven copper neighbors around phosphorous with an average 2.513 Å crystallographic distance, in which three of the Cu atoms are more localized, with a stoichiometric range that lies between $\text{Cu}_{2.867}\text{P}$ and $\text{Cu}_{2.755}\text{P}$.^{75,76} How these structural parameters impact the reactivity will be analyzed herein by (i) altering the concentration of Cu_{3-x}P to control the rate of species transformation, and (ii) manipulating the temperature of $\text{Cu}_{3-x}\text{P}/\text{ODE}$ solutions to determine the impact of vacant sites.

2.4.2. Cu_3PSe_4 TIME, TEMPERATURE, AND CONCENTRATION STUDIES

With a deeper understanding of how Cu_{3-x}P and Se-based species contribute to isolating the Cu_3PSe_4 pathway,⁷⁴ further analysis into the transformation of active species in solution is explored via ex situ studies. Three parameters investigated herein are time, temperature, and reagent concentration to observe the effect on the speciation change. Certain limitations and influencing factors to consider for these studies include the concentration of species remaining in solution after each aliquot is removed and homogeneity of the aliquots extracted.

As a control experiment, a 0.10 M Se/ODE solution was initially characterized via ^1H NMR to analyze the speciation change in the absence of Cu_{3-x}P . Aliquots were taken from the control solution at the same temperatures that are used for the Cu_3PSe_4 ex situ studies (150, 200, 225, 250,

300°C) and referenced to heated Se/ODE solutions. ^1H NMR spectra (**Figure 2.2**) of the ex-situ control study shows that there is isomerization of ODE to 2-ODE at 300°C (top of **Figure 2.2**). When analyzing the final aliquot of the control study, the ^1H NMR spectra shows that the isomerization is more apparent as the reaction proceeds. The asterisk in **Figure 2.2** represents the proton signals around 1 ppm. It is proposed that these signals represent Se and ODE interactions, due to the shielding effect of Se producing a large up field shift. The triangle and square symbols on the NMR spectra for the 250°C aliquot demonstrates a change in speciation with a doublet forming at 0.9 ppm and the multiplets forming at 1.2 and 1.5 ppm.

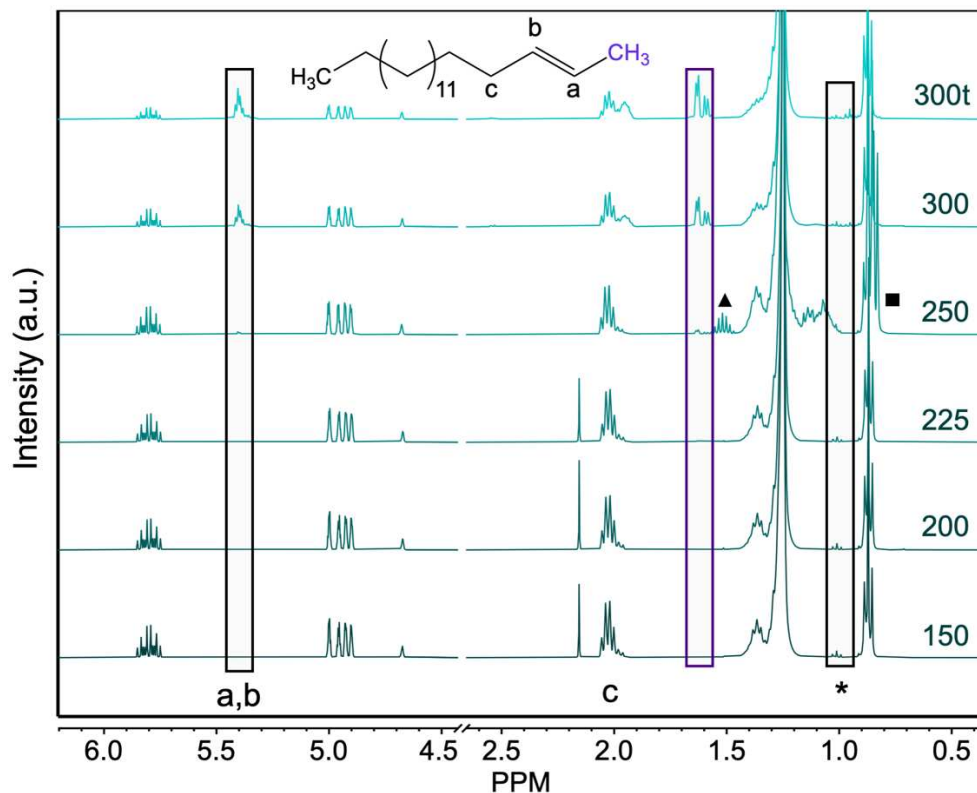


Figure 2.2. ^1H NMR spectra of ex situ aliquots from a Se/ODE (0.10 M) solution using the same heat-up procedure as Cu_3PSe_4 . 150°C is the bottom spectra, and stacked spectra represent the increase in temperature with the top spectra being the cooled down solution.

Notably, these signals have yet to be reported in a Se/ODE reaction, demonstrating that the heat up procedure used herein produces different active species at the desired aliquots.

Unfortunately, these species are difficult to identify due to the complication of integration when multiple species are present with long aliphatic chains, especially with the likelihood of ODE polymerization. Previous reports have shown the reactivity of Se and ODE is highly dependent on solubility. The products of heated Se/ODE solutions have been thoroughly characterized, where it was determined that H_2Se and R-Se (alkyl selenium) species are the main products.^{18–23} However, the heat up procedure that is used in this study could be the reason a difference in speciation is present due to higher temperatures and the presence of negative pressure (vacuum) from 25–150°C. It is therefore of interest to investigate why Cu_3PSe_4 is isolated utilizing this specific heat up procedure.

Initially, the same temperature points used in the control Se/ODE reaction were investigated with the inclusion of Cu_{3-x}P into the system without any additional parameters. PXRD patterns showed that the formation of $\text{Cu}_{0.87}\text{Se}$ was favored at lower temperatures (**Figure A.1**). This is likely due to the melting point of Se powder at 221°C, which significantly increases solubility and accelerates the production of Se-based species. We suspect that the reaction rate between Se species and Cu increases at 225°C. This led to an initial working hypothesis that extended time intervals at the desired temperature aliquots would allow the transformation of species to be better captured.

Extended time periods (2 and 5 minutes) were explored at each temperature aliquot to examine (i) if the increase in temperature is required to isolate the thermodynamic Cu_3PSe_4 phase, or (ii) whether the rate of transformation will govern at lower temperatures to form the ternary. Initially 5-minute periods were taken (**Figure A.2A**), which showed that increased time at each aliquot result in the formation of Cu_3PSe_4 at lower temperatures. The increased time at 150 and 200°C presents a minor conversion of Se to Cu-Se binaries (**Figure A.2A**). After 225°C for 5 minutes,

the active species and limited Cu-Se binaries in solution reacted quickly to form Cu_3PSe_4 . This further emphasizes the importance of the dissolution of Se at 225°C (**Figure A.2B**), suggesting that Se-based species produced when high solubility is achieved, are quickly consumed, which results in a fast rate of transformation to Cu_3PSe_4 .

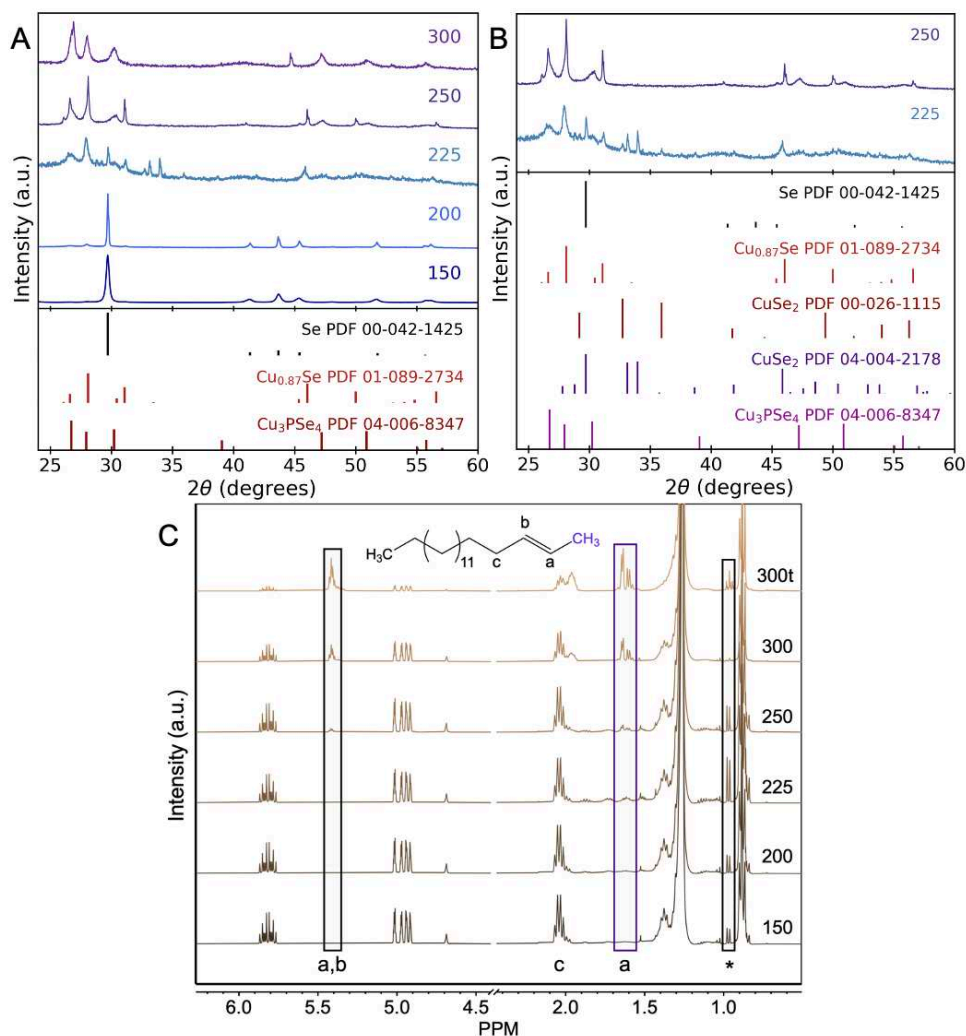


Figure 2.3. Ex situ characterization of reduction Cu_{3-x}P concentration. (A) subplot of diffraction patterns for each temp aliquot. (B) subplot of the 225-250°C with Cu-Se binaries. (C) ^1H NMR spectrum of temp aliquots. 150°C is the bottom spectra, and stacked spectrum represent the increase in temperature with the top spectra being the cooled down solution.

Figure A.3 demonstrates the captured phases and solution species for 2 min aliquots, where a more complete conversion of the precursors to Cu-Se binaries and Cu_3PSe_4 is noticed. PXRD

patterns at 150°C and 200°C both displayed phase pure Se patterns with minimal Cu-Se binaries present (**Figure A.3A**), suggesting that the longer time periods were responsible for captured Cu-Se binaries in the previous studies due to limited solubility and reactivity. However, at 225°C, the conversion of Se to Cu-Se binaries is evident with the diffraction pattern consisting of a minimal amount of Se dispersed in solution, $\text{Cu}_{0.87}\text{Se}$, and other Cu-Se binaries. Notably, the asterisk highlighted region of the NMR spectra (**Figure A.3B**) suggests that when Se converts to the Cu-Se binaries there is reactivity between the ODE and Se. Using previously stated prediction programs, the doublet that occurs at 1.0 ppm is due to either a long aliphatic chain with a terminal or bridged selenium. The consumption of these species after the increase in temperature and time results in phase pure Cu_3PSe_4 , although not in high concentration. Even though the captured species in the extracted aliquot are quenched intermediates, ^1H NMR still gave insight into the reactivity of ODE/Se and the remaining active species in solution.

It is hypothesized that the rate of transformation of species is still significantly high under the reaction conditions described below, which could limit the ability to fully capture interactions in solution. By reducing the concentration of participating reactants, the reaction rate could potentially be reduced, allowing for better insight into the overall reaction. With the reaction dependent on Cu_{3-x}P bonds breaking for both Cu and P to be tetrahedrally coordinated with Se, Cu_{3-x}P was thought to be a participating reactant, thus reduction to half molar equivalents (ca. 2.0 mM) was examined. Substantially better control over speciation was noticed, which was proposed to be due to a reduction in reaction rate. Relating the other reactions to the reduced Cu_{3-x}P aliquots at 225°C shows that the conversion of Se and Cu-Se to $\text{Cu}_{0.87}\text{Se}$ is greater based on a slower rate of conversion (**Figure 2.3A**).

Figure 2.3B presents more intense diffraction peaks of Cu-Se binaries for both 225 and 250°C. With a time period of 2 mins for each temperature aliquot, it is proposed that Cu_{3-x}P is a participating reactant that contributes to the rate of transformation of phases. It is observed that the reduced molar equivalents of Cu_{3-x}P produces a more controlled conversion. In particular, the higher presence of Se and Cu-Se binaries at 225°C transforms into phase pure $\text{Cu}_{0.87}\text{Se}$ with intensified, narrow diffraction peaks at 250°C (**Figure 2.3B**). Furthermore, it is important to note that the transformation of species is consistent with the 2 min aliquots. The intensity of the peaks for the individual phases supports that reduction in rate can provide better control by limiting the Cu_{3-x}P concentration.

^1H NMR further supports this hypothesis with the highlighted regions in **Figure 2.3C**. The doublet appearing in the asterisk region appears when the dissolution of Se in ODE is initiated. As the dissolution continues and the formation of Cu-Se binaries increases throughout the reaction, the doublet rises in intensity. When 300°C is reached and the duration of the reaction is extended, the doublet disappears, and the isomerization of ODE is the resulting species. Therefore, the main working hypothesis for the Cu_3PSe_4 pathway is as follows: if Se/ODE solution is heated in the presence of Cu_{3-x}P , Se-based active species will interact with the individual tetrahedral Cu-P units, initially producing Cu-Se binaries that convert quickly to form $\text{Cu}_{0.87}\text{Se}$, then Cu_3PSe_4 . Further studies will focus on isolating Cu_3PSe_4 by incorporating the computationally and experimentally predicted Se species (H_2Se and R_2Se) or determining if alternative pathways are viable. Data retrieved from these studies will be compared to the Se/ODE solution studies to refine the previously stated hypothesis, for example, by exploring if the quenched intermediates are consistent. In-situ studies will also be employed here, such as solid-state NMR (ssNMR), X-ray diffraction and spectroscopy techniques.

2.4.3. Cu_3PSe_4 CONTROL STUDIES

Previous studies explored the implementation of strongly-coordinating solvents, HDA and TOPO, both of which showed that there was primarily conversion to Cu-Se binaries with minimal Cu_3PSe_4 present.⁷⁴ It was hypothesized that strong coordination of the solvents to Cu(I) reduces reactivity, as the limited dissociation of ligands on the surface prohibits the essential interactions needed to form Cu_3PSe_4 . To further probe the importance of ODE to this synthesis, long-chain aliphatic solvents were examined to determine if alkene addition is essential and whether alternative pathways can be isolated to form Cu_3PSe_4 . Squalane was tested using the Cu_3PSe_4 heat-up procedure, which produced a phase pure XRD pattern of Cu_3PSe_4 consisting of intense, narrow diffraction peaks, indicating more crystalline particles (**Figure 2.4A**). ^1H NMR demonstrates minimal conversion of squalane (**Figure 2.4C**). Thus, it's proposed that instead of reacting with Se particles, squalane acts as a reaction medium to promote a diffusion controlled reaction between Cu_3P particles and Se^0 powder. This hypothesis is further supported by TEM, where the imaged particles are significantly larger with different morphologies than the ODE heat-up reaction (**Figure A.4**). In addition, the color transformation of the solution from clear to red at 270°C , then back to clear after cooling, differs from the ODE heat-up as the solution remains a dark yellow upon cooling. Investigation into the difference in reaction pathways will need to be explored in the future via ex situ studies.

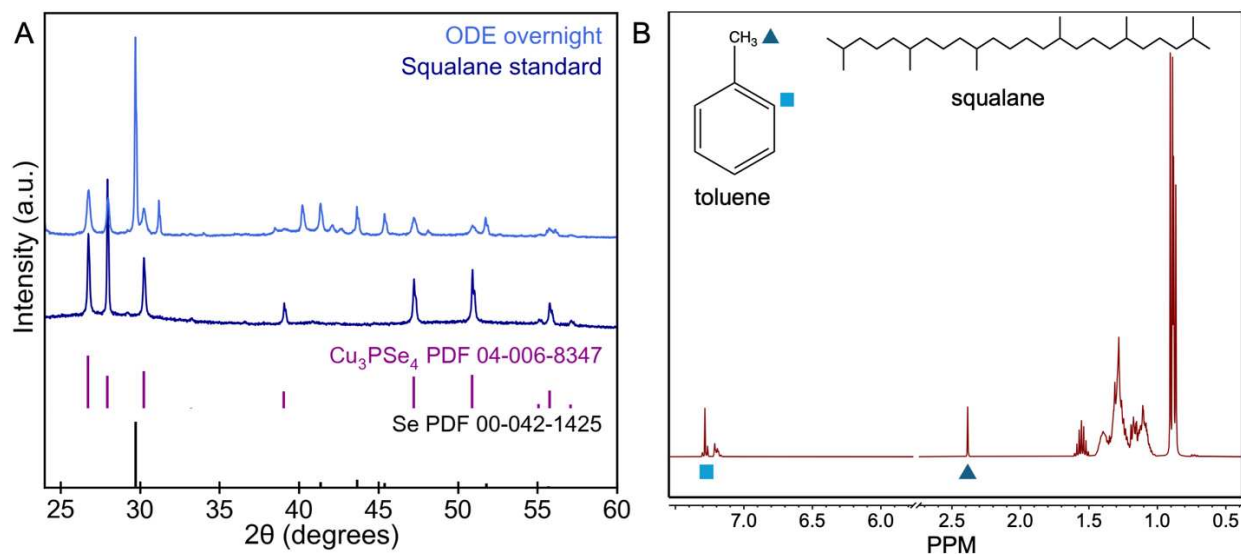


Figure 2.4. Characterization data for squalane and overnight reaction. (A) subplot of XRD patterns for squalane reaction and overnight ODE reaction. (C) NMR of solution for Squalane reaction.

Thermodynamically favored products, in particular colloidal nanoparticles, have been isolated by allowing sufficient time at an increased temperature for the reaction to establish equilibrium, thus relying on thermodynamic factors and Gibb's free energy.⁷⁷ To analyze the stability of Cu_3PSe_4 , the reaction was held at 300°C for 20 hours. The XRD pattern in **Figure 2.4B**, displays the degradation of Cu_3PSe_4 . Extended time shows that Cu_3PSe_4 , which is initially formed when 300°C is reached, degrades primarily into Se particles with minimal amount of Cu_3PSe_4 and Cu-Se binaries. Although Cu_3PSe_4 is the thermodynamically favored phase based on formation energies calculated at 0K, it is proposed that at elevated temperatures the particles degrade due to the thermodynamic values outlined in Appendix A (Thermodynamic Equations), controlling the binding/displacement and precipitation/dissolution equilibria. This information is essential in mapping the Cu-P-Se phase space and guiding future synthetic approaches pertaining to morphology and size control. For example, if displacement of ligands is promoted by exploiting the knowledge from the previous reaction, smaller particles can dissolve into solution to produce

a more monodisperse material and promote growth along a particular facet to produce varying morphologies.

2.4.4. PROPOSED PATHWAY FOR Cu_7PSe_6

We propose that Cu_7PSe_6 , a metastable material, can be synthesized by isolating a pathway to trap this phase over Cu_3PSe_4 . To better define the individual pathways, the works of Ivan Infante and Xiaogang Peng will be incorporated. These authors developed reliable thermodynamic equations to analyze the binding/displacement and precipitation/dissolution equilibria of NC-ligand complexes.^{37,39,42-44} The thermodynamic equations are governed by controlling the free energy factors provided in equations 3-5 obtained from Infante et al.³⁷

$$\Delta G_{\text{solv}}^{\text{total}} = \Delta G_{\text{solv}}^{\text{binding}} + \Delta G_{\text{solv}}^{\text{agg}} \quad (3)$$

$$\Delta G_{\text{solv}}^{\text{binding}} = \Delta G_{\text{gas}}^{\text{binding}} + (\Delta G_{\text{solv}}^{\text{[NC-Ln]}} - \Delta G_{\text{solv}}^{\text{NC}} - n\Delta G_{\text{solv}}^{\text{L}}) \quad (4)$$

$$\Delta G_{\text{solv}}^{\text{agg}} = \Delta G_{\text{gas}}^{\text{agg}} + \Delta G_{\text{solv}}^{\text{[NC-Ln]}^{\text{agg}}} - \Delta G_{\text{solv}}^{\text{[NC-Ln]}} \quad (5)$$

An in-depth explanation of the entropic and enthalpic terms is provided in Appendix, thermodynamic equations (A1-11).³⁷

Figure 2.5 provides a simplified reaction pathway of Cu_{3-x}P and Se/ODE in an attempt to trap Cu_7PSe_6 (more complex pathway including precipitation/ dissolution is provided in **Figure A.5**) that will be referenced and built upon throughout the synthetic manipulations. It is crucial to understand and balance these equilibria, so the Cu_7PSe_6 particles can be stabilized in solution and prevent degradation to the thermodynamically stable Cu_3PSe_4 phase. Of utmost importance to the proposed reaction pathway is the binding/displacement equilibrium, due to the large surface-to-volume ratio of NC-ligand complexes.

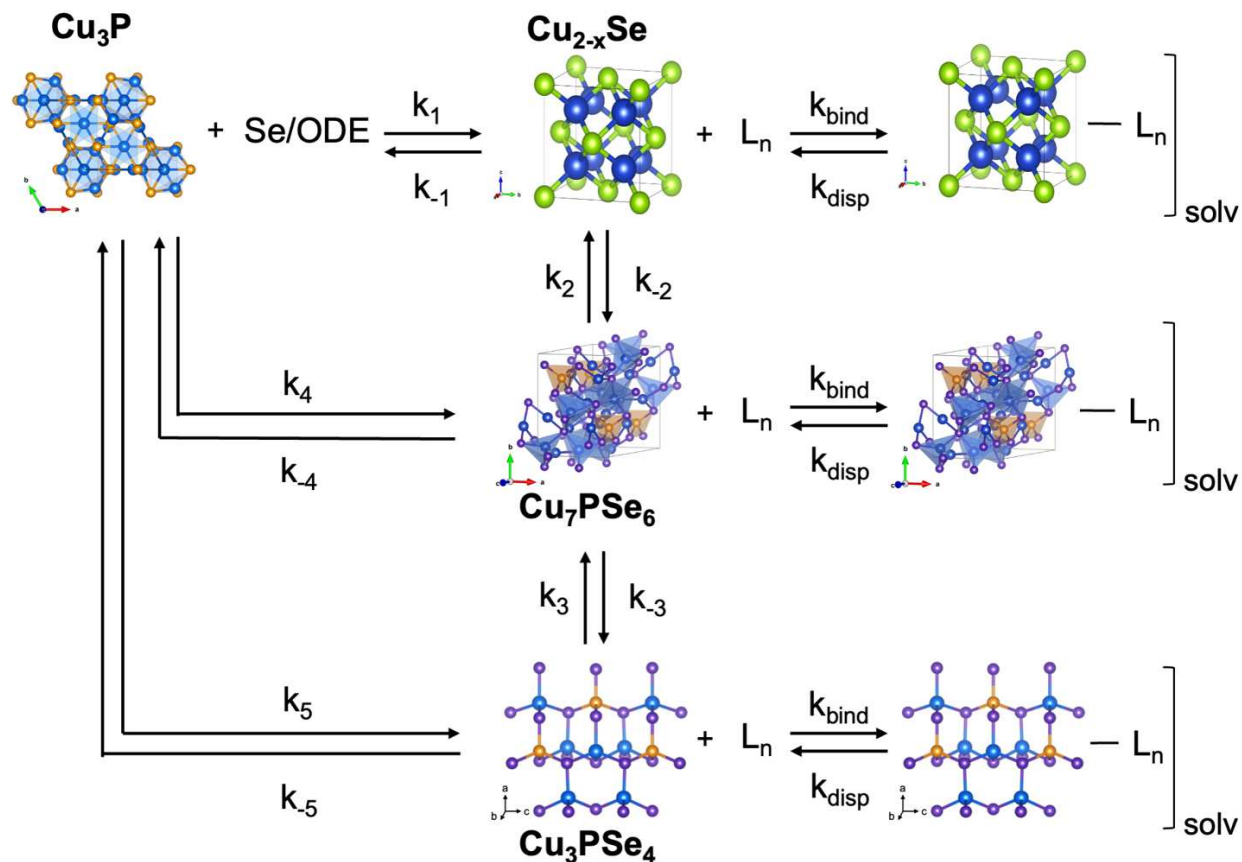


Figure 2.5. Proposed reaction pathway. Rate constants aren't defined herein, but rather used as descriptors of transformation. k_{bind} is the binding efficiency and k_{disp} is displacement favorability.

Importantly, the rate constants (k_x) proposed in **Figure 2.5** are not tested nor defined kinetically; however, these constants are used to describe how the equilibrium can be altered by the applied synthetic parameters. The primary transformation pathway that will be described herein consists of three equilibria (k_1/k_{-1} , k_2/k_{-2} , and k_3/k_{-3}), with Cu_{2-x}Se being a proposed quenched intermediate for Cu_7PSe_6 which degrades to Cu_3PSe_4 . Alternative pathways are also provided for this system, in order to promote a disproof model and a series of working hypotheses.

2.4.5. Cu_7PSe_6 PHASE EXPLORATION – PARAMETERS

Accessing different phases with an emphasis on the control of precursor reactivity to isolate reaction pathways was explored next. To exploit isolated reaction pathways, cannula transfer

studies were developed where active species with specific reactivity from one flask could be isolated, then controllably transferred to a separate reaction flask to yield a more targeted synthesis, thus forming meta-stable phases (**Figure A.6**). Exploring the Cu_7PSe_6 phase is essential to gain chemical intuition on the Cu-P-Se and the individual roles of the precursors. To develop more intuition on the speciation and phase space, synthetic parameters such as, headspace of the flask post transfer, concentration of the Se/ODE solution, temperature of the overall reaction flask, and reaction time were analyzed. Ultimately, the following results will be examined to provide rational for the pathways proposed in **Figure 2.5**.

2.4.5.1. BALANCING EQUILIBRIUM OF HEADSPACE AND SOLUTION

The gaseous species H_2Se formed in-situ by Se powder in alkane or alkene solution has previously been proposed as an active monomer to form metal-chalcogenide binaries,^{21,78,79} which led to previous studies exploring the characterization and role of H_2Se in the Cu_3PSe_4 synthesis. Studies by our group have shown that direct injection of H_2Se led to the isolation of a different reaction pathway that favored the formation of Cu_{2-x}Se and Cu_7PSe_6 (manuscript in preparation), implying that H_2Se formation is key or rather H_2Se reacts to form alternate R-Se species. It was further probed what active Se-based species result from a 0.10 M Se/ODE solution; the gaseous species were transferred to a $\text{Cu}_{3-x}\text{P/ODE}$ solution. Although the reaction was held for four hours, the concentration of species was lower than pure H_2Se , so only minimal conversion to Cu_{2-x}Se was apparent. Analysis of both studies further demonstrates the diversity of the reactivity of the Se-based active species. Therefore, if gaseous species are the participating reactant that favor the formation of Cu_7PSe_6 , then the presence of the gaseous species in the headspace could isolate the alternate pathways.

Analysis of how both the headspace and solution of the Se/ODE reaction contributes to phase formation will be examined to determine why different Cu-Se binaries are isolated and transform to the two Cu-P-Se ternaries of interest. After the Se/ODE 0.05 M solution and gaseous species were transferred to the $\text{Cu}_{3-x}\text{P}/\text{ODE}$ flask, the headspace of the overall reaction can be manipulated by either (i) purging the gaseous species produced from the Se/ODE heat up procedure through the $\text{Cu}_{3-x}\text{P}/\text{ODE}$ solution or (ii) trapping the gaseous species in $\text{Cu}_{3-x}\text{P}/\text{ODE}$ reaction flask with positive pressure of an inert gas, N_2 (**Figure A.6**). Ultimately, this will indicate the dependence of the Cu_7PSe_6 pathway on the gaseous and solution-based Se active species, respectively. Furthermore, balancing the equilibrium between the headspace and solution will show to be crucial in designing hypotheses.

Figure 2.6 summarizes three separate studies of altering the flow of gas produced once the ODE/Se was transferred (A-C), and injection of just the solution (D). Gaseous species generated by the continuous flow of N_2 through the reaction flask, produces both $\text{Cu}_{2-x}\text{Se}_x$ and Cu_7PSe_6 without Cu_3PSe_4 formation (A). Conversely, trapping the gaseous species and altering the flow of gas results in the formation of all three species (B and C). Thus, the three cannula syntheses show that there can be ternary phase control by altering the concentration of the headspace.

Ultimately, this leads to a series of working hypotheses that will be continually exploited throughout this Chapter. The first working hypothesis posits that having gaseous species present or trapped in the headspace with the active species remaining in solution is essential for the formation of Cu_3PSe_4 . This is rationalized as follows: if Cu_3PSe_4 was solely dependent on the species in solution, then injection of just the solution with limited gaseous species should produce primarily Cu_3PSe_4 . Rather, this produces primarily $\text{Cu}_{2-x}\text{Se}_x$ and minimal amount of Cu_7PSe_6

Figure 2.6D.

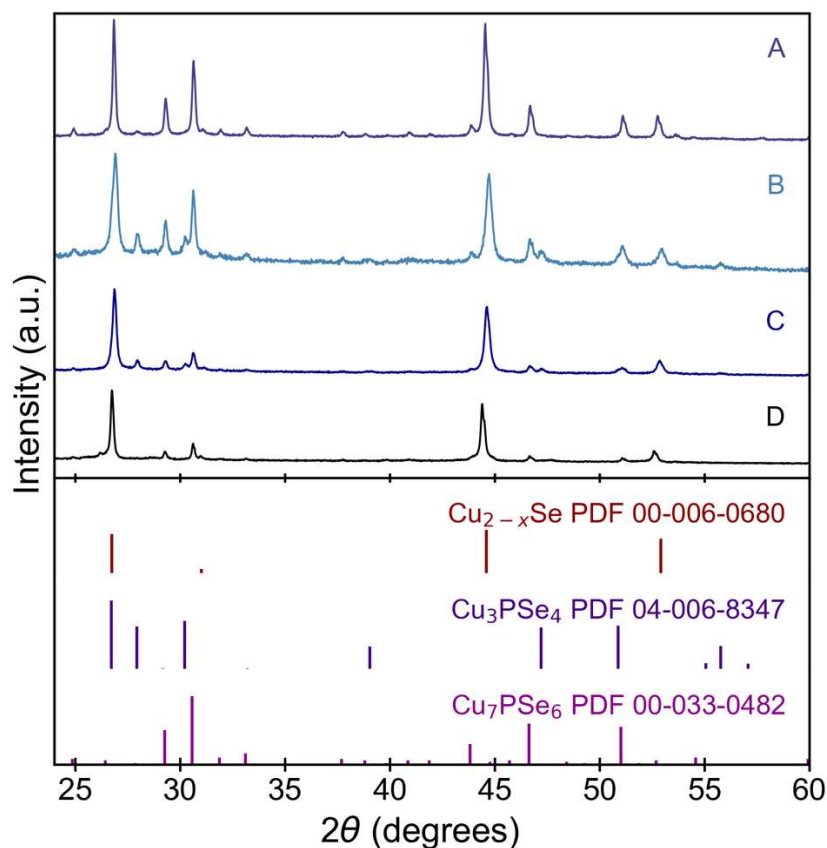


Figure 2.6. Subplot of the cannula transfer studies at 300°C for 20 min. (A) Flowing solution, headspace, and N₂ continuously through main reaction flask to bubbler. (B) Evacuating headspace and trapping gas species each for half the reaction. (C) Trapping gaseous species in solution for the whole reaction. (D) Injection of the solution via syringe.

Another working hypothesis is, if the presence of gaseous species in the headspace is slowing down the transformation of phases, then the Cu₇PSe₆ will degrade to Cu₃PSe₄ at a similar rate, thus k_2 and k_3 are balanced (**Figure 2.5**). This is demonstrated in **Figure 2.6A-C**, as the formation of Cu₇PSe₆ increases as a function of headspace concentration decreasing. To further probe these working hypotheses, the previous parameters are investigated with increased Se/ODE concentrations.

2.4.5.2. ALTERING SE-BASED SPECIES CONCENTRATION

With manipulation of headspace having a significant impact on the isolation of pathways, the concentration of the Se/ODE solution will be further investigated to probe the previous hypotheses

on headspace. Varying the Se/ODE concentration is of utmost interest in this case, since the kinetic control demonstrated herein is proposed to be most effectively achieved when reaction pathways are isolated rather than stabilizing metastable products in an established synthesis.^{77,80} Thus, establishing more concrete hypotheses on the role of Se before progressing to Cu_{3-x}P control is required.

An increase of the Se/ODE solution is displayed in **Figure 2.7A** for trapping the gaseous species. The previous working hypotheses for this approach was that the presence of the headspace reduces the rate of transformation and gaseous species isolate the Cu_3PSe_4 pathway. When doubling the concentration of the Se/ODE solution to be 0.10 M once transferred, the diffraction pattern displays both Cu_{2-x}Se and Cu_7PSe_6 . The concentration was further increased to 0.15 M post transfer, which demonstrated conversion to all three phases (**Figure 2.7A**). This promotes a more in-depth disproof model because if the Cu_3PSe_4 pathway was isolated by the presence of headspace, then the weight percentage calculated by Rietveld refinements^{81–83} should increase as a function of Se/ODE concentration. This provides better insight into the working hypotheses, in particular, it can be confidently disproven that gaseous species isolate the Cu_3PSe_4 pathway.

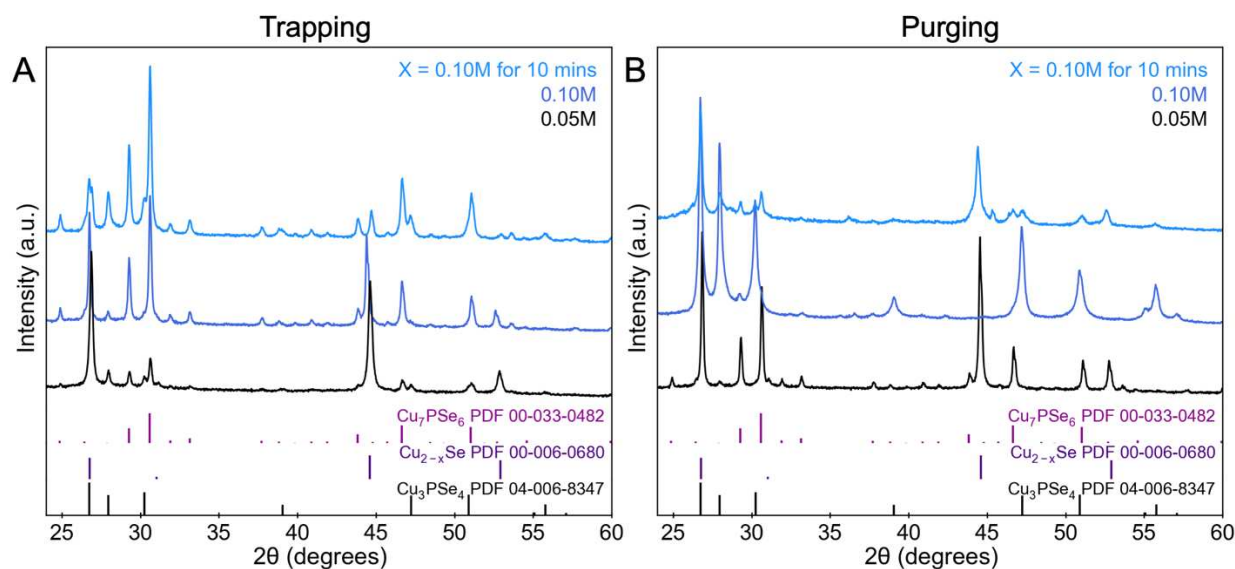


Figure 2.7. Effect of Se/ODE concentration on phase formation. Reactions conditions were held constant at 300°C for 20 min. Values in the top right of each subplot represents the concentration of the Se/ODE solution post transfer.

With this information, the hypothesis that the presence of gaseous species reduces the rate of transformation can be better defined. At lower Se/ODE concentrations the rate of formation of Cu_7PSe_6 isn't sufficient enough for the ternary to build up in concentration, thus the k_2 and k_3 equilibria are altered, resulting in degradation to Cu_3PSe_4 . It is proposed that when the concentration of Se is increased, the k_2/k_{-2} equilibrium is pushed forward (k_2 increases), therefore forming more Cu_7PSe_6 monomers in solution. This could ultimately reduce the favorability of displacement for Cu_7PSe_6 colloidal NPs, leading to more intense peaks for Cu_7PSe_6 in **Figure 2.7A**. When the concentration is increased to 0.15 M, the formation of all three phases, suggests that k_2 and k_3 are favored and the degradation progress can't be systematically controlled. It is also viable that the increased concentration could favor parallel alternate pathways (k_4 and k_5) to form both ternary phases. This is further probed, when the reaction is extended for a longer period of time, it is proposed that the k_3/k_{-3} equilibrium and the binding of ligands to the surface is favored, as greater degradation into Cu_3PSe_4 is observed (**Figure A.7**).

The working hypothesis on the presence of gaseous species reducing the rate of transformation is continually refined herein, as similar synthetic strategies were employed but for purging of the headspace. An increase to 0.10 M post transfer resulted in phase pure Cu_3PSe_4 . As a result of full degradation to Cu_3PSe_4 , a quenched reaction after 10 minutes with the same Se/ODE concentration was examined, resulting in a conversion to all three phases. This further disproves that the presence of gaseous species is required to isolate the Cu_3PSe_4 pathway. Therefore, three refined working hypotheses can be derived from these findings: (I) if gaseous species are trapped in the headspace, then the rate of conversion of species can be reduced leading to better control, (II) if a higher concentration of Se/ODE is employed, then the rate of conversion is larger and degradation to Cu_3PSe_4 is less controlled, (III) if the gaseous species are purged, the reaction will proceed at a faster rate. These hypotheses are further refined in the following sections.

2.4.5.3. MANIPULATING THE TEMPERATURE OF THE Cu_{3-x}P FLASK

Temperature is investigated for primarily two reasons. The heat to overcome the required energy for the interactions of isolated Se-based species and Cu_{3-x}P can be systematically controlled. It is also known that the formation of vacant sites in Cu_{3-x}P is favored as a function of temperature due to configuration entropy,⁷⁶ thus the Cu_{3-x}P particles can be manipulated before interacting with Se-based species. To probe these research directions, controlled experiments are designed based on three hypotheses: (i) degradation to Cu_3PSe_4 can be prevented by reducing displacement of ligands on Cu_7PSe_6 , (ii) lower temperature can favor the formation of the less stable low-coordinate Cu-Se units that are present in both Cu_{2-x}Se and Cu_7PSe_6 , and (iii) higher temperature can push the equilibria forward, increasing rate of transformation, so Cu_7PSe_6 can be extracted with higher purity.

The reference reaction to examine the previous hypotheses is $\text{Cu}_{3-x}\text{P} + 0.15\text{M Se/ODE}$, trapping for 20 minutes at 300°C , which produced 56.14, 9.66, and 34.20% for Cu_7PSe_6 , Cu_{2-x}Se , and Cu_3PSe_4 , respectively. Temperature of the $\text{Cu}_{3-x}\text{P/ODE}$ flask will be altered, while the Se/ODE flask will remain at 300°C . The primary reason for this is to keep the isolated Se-based species constant to grasp the difference in interactions with Cu_{3-x}P as a function of temperature.

Figure 2.8 displays the transformation of phases as a function of temperature. The upper limit of the scale could only extend to 310°C , due to the boiling point of ODE. First to note is the substantial difference in transformation for 250°C , with $\text{Cu}_{0.87}\text{Se}$ being the primary product. This is of interest since the previous reactions produced Cu_{2-x}Se as a trapped intermediate phase in the Cu_7PSe_6 pathway. Furthermore, the $\text{Cu}_{0.87}\text{Se}$ binary is proposed to be an important quenched intermediate for the heat up synthesis of Cu_3PSe_4 . It is therefore hypothesized that the Cu_7PSe_6 pathway is less favored due to the decreased dissociation of ligands on the surface of Cu_{3-x}P (difference in exposed surface facets), or the activation barrier to isolate the Cu_7PSe_6 pathway is too high to overcome at the lower temperature. As the temperature is elevated to 275°C , the Cu_7PSe_6 pathway is better isolated resulting in Cu_{2-x}Se and the two Cu-P-Se ternary phases. The second hypothesis can be workshopped because the rate of formation, k_2 , for Cu_7PSe_6 is reduced, so the particles degrade to Cu_3PSe_4 at a similar rate, thus k_3 still isn't controlled.

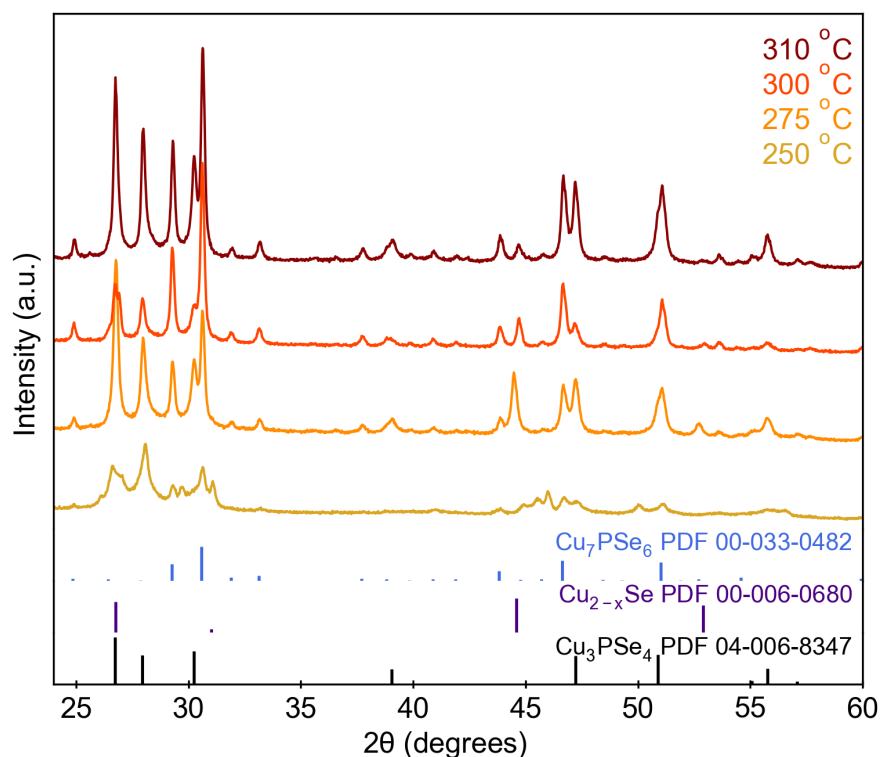


Figure 2.8. Effect of temperature for a $\text{Cu}_{3-x}\text{P} + 0.15\text{M Se/ODE}$ for 20 mins. Colored temperature ($^{\circ}\text{C}$) labels in top right correspond to the individual XRD patterns.

Additionally, when the temperature is increased to 310°C , the diffraction pattern is dominated by the two ternary phases with minimal conversion to Cu_{2-x}Se (**Figure 2.8**). This suggests that the equilibrium between Cu_{2-x}Se and Cu_7PSe_6 is disturbed, as it is apparent that k_2 is increased. A complication with elevated temperatures is that k_3 is not reduced, meaning the degradation to Cu_3PSe_4 is substantial. Although the results shown here align with the third hypothesis, it is still unclear how the temperature alters this rate of conversion. Considering the thermodynamic variables discussed in Appendix A, thermodynamic equations (**eq. A1-11**), the elevated temperature could alter the binding/displacement equilibrium due to the impact of intramolecular entropy of C-C σ bond rotation/bending freedoms. Alternatively, enthalpic terms representing the agglomeration of particles could have a weaker impact on maintaining the stability of Cu_7PSe_6 . For example, n-octadecane has a melting enthalpy of 62 kJ/mol and entropy change of 205

J/mol·K,^{44,84,85} which can have a substantial impact at the elevated temperatures. These concepts will be taken into consideration to better incorporate temperature into future reactions.

2.4.6. PHASE TRANSFORMATION OF Cu_7PSe_6 – ADDITIVES

Further exploration on the surface chemistry and ligand dynamics to trap the metastable Cu_7PSe_6 phase is also needed to gain more knowledge on the Cu-P-Se phase space. Previous studies on Cu_3PSe_4 determined that substituting common ligands, OLA and trioctylphosphine oxide (TOPO), for ODE in the heat up synthesis led to the formation of Cu-Se binaries. However, balancing the equilibrium of binding/displacement of ligands can lead to phase pure Cu_7PSe_6 and more synthetic control. Primary amines are investigated herein due to the formation of Cu_{2-x}Se during the heat up reaction when ODE is replaced by HDA, which has been shown to be a possible intermediate for Cu_7PSe_6 .

Initially, the system was probed by exchanging the solvent of the $\text{Cu}_{3-x}\text{P}/\text{ODE}$ solution with primary amines, HDA and OLA. Incorporating HDA and OLA is of interest due to primary amines strongly favoring the formation of Cu_{2-x}Se , thus the Cu_7PSe_6 pathway can be better isolated. The difference in HDA and OLA is intriguing, since a cis double bond at C8-C9 is present for OLA but not for HDA, and higher surface coverage (less steric hindrance) is expected for HDA. Originally, the primary amines were explored under the same conditions for the cannula transfer syntheses above, both of which produced phase pure Cu_{2-x}Se (**Figure A.8**). Manipulating time and temperature (**A.9 and 10**, respectively) both led to phase pure Cu_{2-x}Se , meaning the incorporation of P-Se units to form Cu_7PSe_6 was not accomplished. This suggests that the binding energy is large for the surface facets on Cu_{2-x}Se and primary amines, so k_2 is prohibited by the excess primary amine in solution, restricting the dissociation of the ligands on the surface. Notably, there wasn't a significant difference between the two primary amine solvents. Preliminary ^{31}P NMR data

(**Figure A.11**) suggests that the primary amine coordinates strongly to phosphorous species, as no signals were present for the ODE solutions. It is hypothesized that the characterized species could be an aminophosphine tautomer, although, more characterization techniques are required to design alternative hypotheses. However, the stability of the aminophosphine-ligated species suggests that the rate of conversion is reduced by restricting the incorporation of phosphorous.

Stoichiometric ratios of HDA/OLA to Cu_{3-x}P are also investigated herein to determine if $[\text{PSe}_4]^{3-}$ units will be favored to form Cu_7PSe_6 when the excess primary amine in solution is decreased. Ultimately, if Cu_7PSe_6 is formed in solution, the surface chemistry of the primary amines will be analyzed in order to understand if binding can be optimized to prevent degradation. Originally, a 1:1 ratio of Cu_{3-x}P :HDA was explored, which resulted in minimal conversion of Cu_7PSe_6 at 20 mins (**Figure A.12A**). Decreasing the HDA to a 2:1 ratio of Cu_{3-x}P :HDA produced a slightly greater conversion to Cu_7PSe_6 . Interestingly, contrary to the ODE reactions above, the degradation of Cu_7PSe_6 to Cu_3PSe_4 is significantly reduced. This is promising, as now we can propose that, we can continue to tune the synthetic parameters that appeared to influence the rate of transformation to kinetically trap more Cu_7PSe_6 before it degrades.

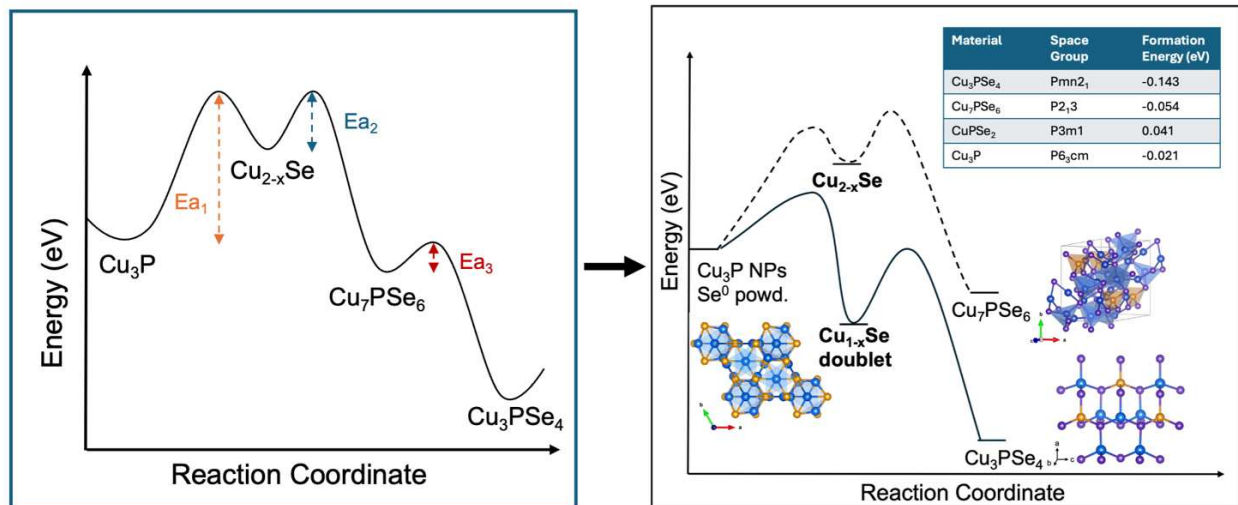


Figure 2.9. Proposed reaction coordinate diagram for Cu₇PSe₆ (left) and both ternary phases (right) based on experimental data. Relative energy values are retrieved from materialsproject.org are based on formation energies at 0K.⁶⁷

Reactions with double the concentration of Cu_{3-x}P, while trapping the gaseous species, were performed with varying growth times (**Figure A.12B**). Intriguingly, the conversion of phases throughout the reaction is non-linear. Cu_{2-x}Se and Cu₇PSe₆ that are present at 20 min, degrade to just Cu_{2-x}Se at 40 min. As the time is extended to 50 min, Cu_{2-x}Se and both the ternaries are characterized. Finally, at 60 min both Cu₃PSe₄ and Cu₇PSe₆ grow in intensity, suggesting that the degradation process is occurring simultaneously as Cu₇PSe₆ is formed. Therefore, the control over the binding/displacement equilibrium that was originally hypothesized has been disproved by a pathway that stabilizes Cu_{2-x}Se particles, but quickly transforms at extended periods of time when the ligands dissociate from the surface. This is promising from a chemical intuition standpoint, as these results demonstrate that the binding/displacement equilibrium can be greatly impacted by slight manipulation of solvent ratios.

2.5. Conclusion

The Cu-P-Se phase space is investigated herein to decipher how a metastable material, Cu₇PSe₆, can be isolated by the knowledge gained from an established, thermodynamic Cu₃PSe₄

phase. Proposed pathways for the transformation of species have been included to better interpret how individual factors impact the formation of each phase (**Figure 2.5 and A.5**). This has resulted in four main working hypotheses: (I) if the concentration of gaseous species present in the headspace are altered, then the equilibria governing the rate of phase transformation can be controlled, (II) if a higher concentration of Se/ODE is employed, then the rate of conversion is larger and degradation to Cu_3PSe_4 is less controlled, (III) temperature can affect the rate of formation, k_2 , for Cu_7PSe_6 by controlling the properties of Cu_{3-x}P particles prior to interaction with Se-based species, and (IV) if ligands are systematically tuned to coordinate to the surface facets of desired products, then metastable phases can be trapped in solution. These hypotheses can be used to design proposed reaction coordinate diagrams that better define the Cu-P-Se phase space (**Figure 2.10**).

A phase-pure synthesis of Cu_7PSe_6 is still being pursued. This is of interest, so better designed, alternative hypotheses from the working hypotheses proposed herein need to be developed. However, preliminary results presented in this Chapter will provide a great starting platform to gain a more refined understanding of how synthetic parameters alter the driving forces of colloidal nanoparticle synthesis. Ultimately, design of the experimental and conceptual aspects of this project is a step that many systems need to take, in order for synthetic approaches of established and novel materials to be targeted more accurately.

2.6. Author Contributions

According to CRediT criteria, my contributions to this work included conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft, and writing – reviewing and editing. Contributions by Jennifer Lee included data acquisition (Squalane

TEM). Contributions by Amy L. Prieto included conceptualization, investigation, and writing – reviewing and editing.

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IS THE KEY TO A SIMPLIFIED, ATOM-ECONOMICAL REACTION¹

3.1. Overview

Nanoparticle syntheses are designed to produce the desired product in high yield, but traditionally neglect atom-economy. Here we report that the simple, but significant, change of the solvent from 1-octadecene (1-ODE) to the operationally inert octadecane (ODA) permits an atom-economical synthesis of copper selenophosphate (Cu_3PSe_4) nanoparticles (**Figure 3.1**).

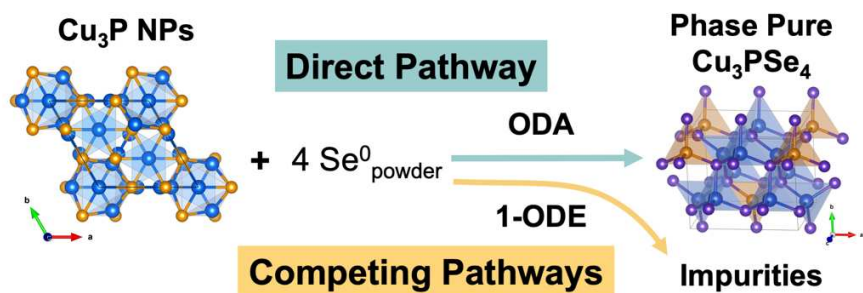


Figure 3.1. Schematic of the reaction pathways for the synthesis of Cu_3PSe_4 NPs with octadecane (top, dark cyan) and 1-octadecene (bottom, yellow). Blue represent copper, orange is phosphorus, and purple is selenium.

This change eliminates the competing selenium (Se) delivery pathways from our first report that required an excess of Se. Instead $\text{Se}^0_{\text{powder}}$ is dispersed in ODA, which promotes a formal eight-electron transfer between Cu_{3-x}P and Se^0 . Powder X-ray diffraction and transmission electron microscopy confirm purity of the Cu_3PSe_4 , while ^1H and ^{13}C NMR indicate the absence of oxidized ODA or Se species. We utilize the direct pathway to gain insights into stoichiometry and ligand identity using thermogravimetric analysis and X-ray photoelectron spectroscopy. Given the

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prevalence of 1-ODE in nanoparticle synthesis, this approach could be applied to other chalcogenide reaction pathways to improve stoichiometry and atom-economy.

3.2. Introduction

Ternary chalcogenide nanoparticles (NPs) have recently gained considerable interest owing to their promising properties for technological relevant applications, such as photovoltaics,^{1–3} thermoelectrics,^{4–6} and cathode materials.^{7–9} Of particular interest is copper selenophosphate, Cu_3PSe_4 , with its theoretical photovoltaic efficiency of 24% and non-toxic, earth abundant elements composition.^{2,10} Historical strategies targeting Cu_3PSe_4 classically involve high temperature solid-state synthetic schemes from traditional elemental precursors (**Table B.1**).^{1,7,10–16} A more recent solution-based synthesis of Cu_3PSe_4 NPs from Lee et al. achieved selenization of pre-synthesized Cu_3P NPs¹⁷ in a one-pot heating method, using a 0.1M Se^0 powder ($\text{Se}^0_{\text{powder}}$) and 1-octadecene (1-ODE) solution.¹⁸ Their approach provides promising tunable syntheses and potentially low temperature device processing. However, as noted in our initial report,¹⁸ the 0.1M Se^0 and 1-octadecene (Se/1-ODE) solution needed to produce Cu_3PSe_4 involves a large excess of Se^0 , leading to poor atom-economy and hindering characterization of the several Se species participating in the reaction, *vide infra*.

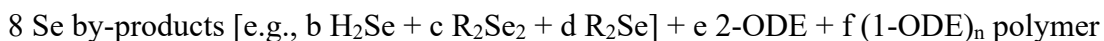
The use of Se/1-ODE has achieved considerable interest in the colloidal nanoparticle field as a “non-coordinating solvent,”^{19,20} that eliminates harsh phosphorous reagents to incorporate Se^{2-} in select binary and ternary systems.^{21–25} In other systems, existing investigations demonstrate that reactions with $\text{Se}^0_{\text{powder}}$ and 1-ODE produces Se species of varying reactivity, notably, H_2Se ,²⁶ R_2Se_2 ,^{27–29} and R_2Se .³⁰ These species introduce multiple reactions, ultimately leading to side reaction and loss synthetic control of Se-reagent formation.²⁴ Additionally, the terminal double

bond, alpha olefin, of 1-ODE readily polymerizes above 120 °C, which can also affect synthetic control and characterization of intermediates and products.^{19,31–35}

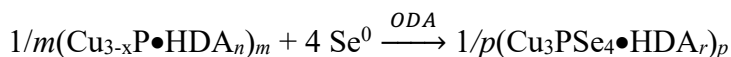
Alternatively, primary amines have been employed as a replacement for 1-ODE in NP syntheses,^{36–41} where depending on the synthesis, the amines can be the solvent,^{42–48} a reagent (reducing agent),^{24,48–50} and/or a coordinating ligand.^{49,51–54} However, for Cu₃PSe₄ NP syntheses, the substitution of 1-ODE with oleylamine¹⁸ or hexadecylamine (**Figure B.1**) produces Cu-Se binary particles, indicating the importance of Se speciation generated in a Se/ODE solution for Cu₃PSe₄ NP formation. Thus, the synthesis of Cu₃PSe₄ NPs with Se/ODE can yield undesired byproducts—in the existing synthesis¹⁸ ~2/3 of the Se⁰ going to the products other than the desired Cu₃PSe₄, as a result multiple, uncontrolled Se species reacting with the metastable,⁵⁵ pre-synthesized Cu₃P NPs (reference supplemental information for synthetic conditions and reproducibility notes, **Figure B.2**). This reaction, therefore, requires a threefold excess of Se⁰ and produces undesired byproducts, **Scheme 3.1**.

Scheme 3.1: Balanced reaction pathways of Cu₃PSe₄ NPs with 1-ODE (A) and ODA (B). Hexadecylamine, HDA, is shown as the capping ligand. Variables *n* and *r* correspond to the ligand coverage of HDA, while *m* and *p* represent the number of monomer units.

A. Non-Stoichiometric, competing Se delivery pathway with 1-ODE.¹⁸



B. Stoichiometric, atom-economical direct pathway with ODA.



Despite the non-stoichiometric excess of Se⁰ powder in our initial reaction,¹⁸ the powder X-ray diffraction (PXRD) pattern of Cu₃PSe₄ under the conditions of Scheme 1A reveals phase purity

and the absence of crystalline Se (**Figure B.3A**).¹⁸ However, ¹H NMR confirms the expected presence of excess Se species (Se/1-ODE) and isomerized 1-ODE (**Figure B.3B**).^{19,23} It follows that a stoichiometric, atom-economical synthesis of Cu₃PSe₄ is not yet in hand, and competing pathways leading to solution by-products plague the existing synthesis. Additionally, the lack of a balanced stoichiometry for the current synthesis inhibits one from obtaining important information to inform on the reaction pathway such as determining the variables laid out in Scheme 1A. Hence, developing a more rational, balanced-reaction is vital to minimize competing pathways⁵⁶ and design minimalistic, disproof-based^{57–59} mechanistic hypotheses^{41,60} that, in turn, can inform other, analogous ternary phase syntheses.

3.3. Results and Discussion

Herein, we report that replacing the solvent, 1-ODE with octadecane (ODA) is a simple, but highly effective method to prepare Cu₃PSe₄ in the form of (Cu₃PSe₄•HDA_r)_p NPs *via* a close-to-stoichiometric, atom-economical synthesis (**Scheme 3.1B**). We find that employing ODA promotes a more direct pathway with a net eight-electron transfer at phosphorus, from formally P³⁻ in Cu₃P to formally P⁵⁺ in Cu₃PSe₄, neatly coupled to the reduction of 4 Se⁰ (powder) to 4 Se²⁻ within Cu₃PSe₄. Additionally, to better establish a stoichiometric synthesis, “Cu₃P” is defined and used herein as the Cu deficient, Cu_{3-x}P (0.133 < x < 1.08),^{61–64} as it has been reported in the literature. We also report preliminary data indicating what amount of HDA is associated with both the starting precursor (Cu_{3-x}P•HDA_n)_m and the resultant Se-containing (Cu₃PSe₄•HDA_r)_p. Finally, the average particle size is determined for both Cu_{3-x}P and Cu₃PSe₄ size via TEM to be 102 (± 21.7) and 32 (± 7.8) nm along the long axis, respectively.

As an initial control, the literature-based expectation that Se⁰ would *not* be incorporated if 1-ODE was replaced with ODA was tested, given the importance of allylic C-H oxidation of the

terminal alkene in 1-ODE. However, the use of ODA and excess $\text{Se}^0_{\text{powder}}$ *did* result in the formation of Cu_3PSe_4 (Pmn2₁, orthorhombic). Importantly, crystalline Se (Se_{cryst} , trigonal) was observed as a side product indicating minimal reaction with ODA (**Figure B.4**). Given that Se is still incorporated even when ODA is an operationally inert solvent, we hypothesized that the use of ODA in the place of 1-ODE would allow the stoichiometric delivery of Se to form pure Cu_3PSe_4 without Se/ODE byproducts, resulting in better overall atom economy.

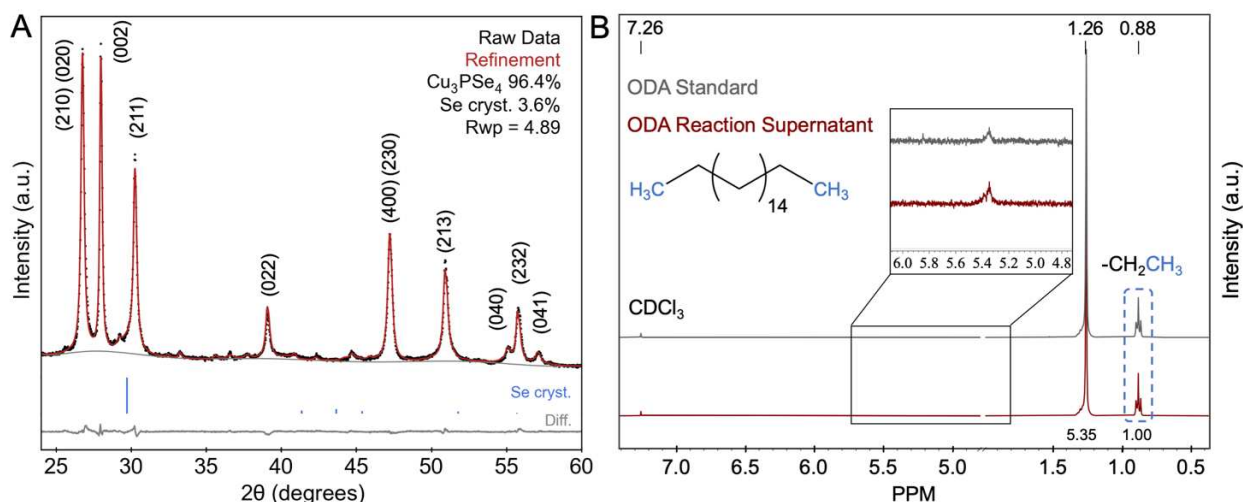


Figure 3.2. Characterization of the stoichiometric reaction with octadecane as the solvent. (A) Powder X-ray Diffraction pattern and Rietveld refinement method of $(\text{Cu}_3\text{PSe}_4 \bullet \text{HDA}_r)_p$ nanoparticles. Se PDF #00-042-2425 (details in Appendix X) is included to identify the pattern that helps fit the asymmetric peak at 30 2θ . (B) ^1H NMR of the reaction supernatant and pure octadecane, with an inset at 5000x intensity from 4.8 to 6.0 ppm.

Indeed, Cu_3PSe_4 NPs were synthesized using the stoichiometrically required 4 molar equivalents of Se^0 powder in ODA for 20 mins (**Scheme 3.1B**). **Figure 3.2A** shows the Rietveld refinements (details in **Table B.2**)⁶⁵ indicating that 97 wt% of the product indexes to Cu_3PSe_4 with a slight excess of Se_{cryst} (3 wt%) which is attributed to the exemption of ligand content of Cu_{3-x}P , *vide infra*. The supernatant was characterized by ^1H , ^{13}C NMR, gas chromatography-mass spectroscopy (GC-MS), and Fourier-transform infrared spectroscopy (FT-IR, **Figure 3.2B**, **B.5-7**,

respectively), which displays no deviation from pure ODA and the absence of oxidized byproducts. The downfield shift of 0.88 and 1.26 ppm represents the terminal methyl group (6H, 1.00) and methylene hydrogen environments (32H, 5.35) respectively. Additionally, the supernatant was spiked with 1 mol% of 1-ODE, an expected byproduct if ODA does react with Se^0 powder, and that 1% 1-ODE proved detectable by ^1H NMR (**Figure B.8**); however, no detectable (i.e., <1 mol%) 1-ODE is present in the supernatant. Interestingly, the formation of very low concentrations of mid-chain alkenes is observed in reactions containing excess selenium, presumably as a result of H_2Se generation after Cu_3PSe_4 formation, *vide infra*. When the excess selenium is reduced to stoichiometric equivalents, the presence of mid-chain alkenes is reduced to a negligible amount (**Figure B.9**). Of note, upon quenching the reaction, the extracted supernatant developed a light red tint over an extended time that is hypothesized to be a slight excess of Se,^{66–74} where temperature studies confirm the presence of amorphous selenium (a-Se, **Figure B.10**).^{67,75} Further details are provided in the SI for the interested reader. In short, the use of ODA as a solvent enables a direct reaction pathway with stoichiometric delivery of Se as defined in the balanced reaction in **Scheme 3.1B**.

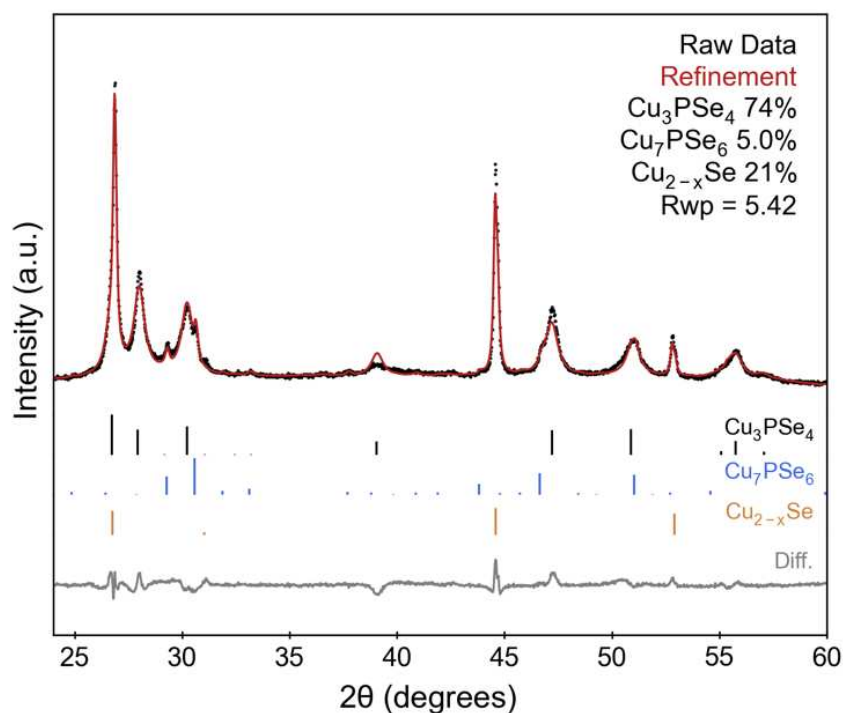


Figure 3.3. Powder X-ray diffraction pattern for the stoichiometric ratio of Cu₃P + 4 Se⁰ powder + 1-ODE with standard synthetic conditions.

As a control, we returned to 1-ODE, but now using just the four equivalents of Se⁰_{powder}, to determine if the stoichiometric Se⁰ will work as well as it did in ODA. However, and consistent with the hypothesis of 1-ODE leading to a variety of side products (**Scheme 3.1A**), a mixture of phases was detected by PXRD (**Figure 3.3**), including Cu_{2-x}Se and Cu₇PSe₆ (refinement details in **Table B.3**). Furthermore, after extending the reaction time to 2 hrs and overnight, the thermodynamically favored⁵⁵ Cu₃PSe₄ is still not the sole phase present, whereas with the same time in ODA yields Cu₃PSe₄ as the major product (**Figure B.11**). Given the above results and literature evidence that Se/1-ODE produces species that include, H₂Se, R₂Se, and R₂Se₂ (**Scheme 3.1A**), the use of ODA is hereby shown to be a simple, effective change to synthesize Cu₃PSe₄. The use of ODA avoids unnecessary, off-path Se traps that, then, requires excess Se⁰ powder to drive formation of Cu₃PSe₄, resulting in an overall poor atom-economical synthesis when using the classic solvent, 1-ODE.

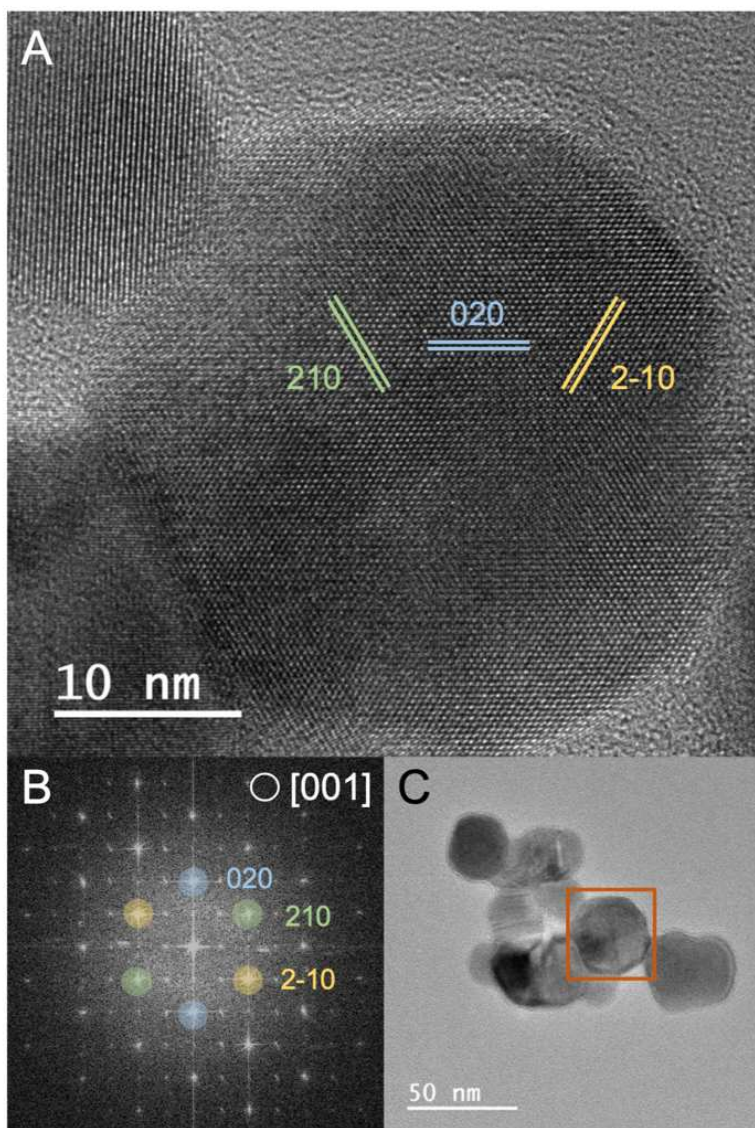


Figure 3.4. (A and C) Transmission Electron Microscopy (TEM) and (B) fast Fourier transform (FFT) of $(\text{Cu}_3\text{PSe}_4 \bullet \text{HDA}_r)_p$ particles under stoichiometric conditions (Scheme 1B).

Further indication of a cleaner, direct reaction pathway is illustrated in the transmission electron microscopy (TEM) images and scanning TEM/energy-dispersive X-ray spectroscopy (STEM/EDS) of $(\text{Cu}_3\text{PSe}_4 \bullet \text{HDA}_r)_p$ (**Figure 3.4, B.12-14**). In our previous publication¹⁸ with Scheme 1A conditions, the resulting Cu_3PSe_4 NPs are noted to have high polydispersity and ill-defined morphology (Figure B.15) as a result of indirect, competing reaction pathways. The stoichiometric conditions in **Scheme 3.1B** demonstrate that polydispersity is significantly

decreased, with size distribution of 24 ± 5.4 nm and 32 ± 7.8 nm along the short and long axis (**Figure 3.4C and B.16**), respectively, now being produced. Additionally, as a result of targeting a more direct reaction pathway, a more crystalline Cu_3PSe_4 product is observed in **Figure 3.4A**, with defined lattice planes as compared to the previous synthesis with 1-ODE.¹⁸ The fast Fourier transform (FFT) of **Figure 3.4A** produces spots corresponding to the lattice planes with respect to a [001] zone axis (**Figure 3B**), with d-spacings consistent with the orthorhombic crystal structure of Cu_3PSe_4 ($\text{Pmn}2_1$). This is further illustrated in **Figure B.12**, where inverse-fast-Fourier transform (iFFT) of masked FFT spots is overlaid on the corresponding TEM images. Ultimately, the combination of lattice parameters extracted from Rietveld refinement with the structural information from TEM allows us to define Cu_3PSe_4 NPs as $(\text{Cu}_3\text{PSe}_4 \bullet \text{HDA}_r)_p$, where $p \approx 2.9 (\pm 0.036) \times 10^5$ (reference **B.17** for calculation).

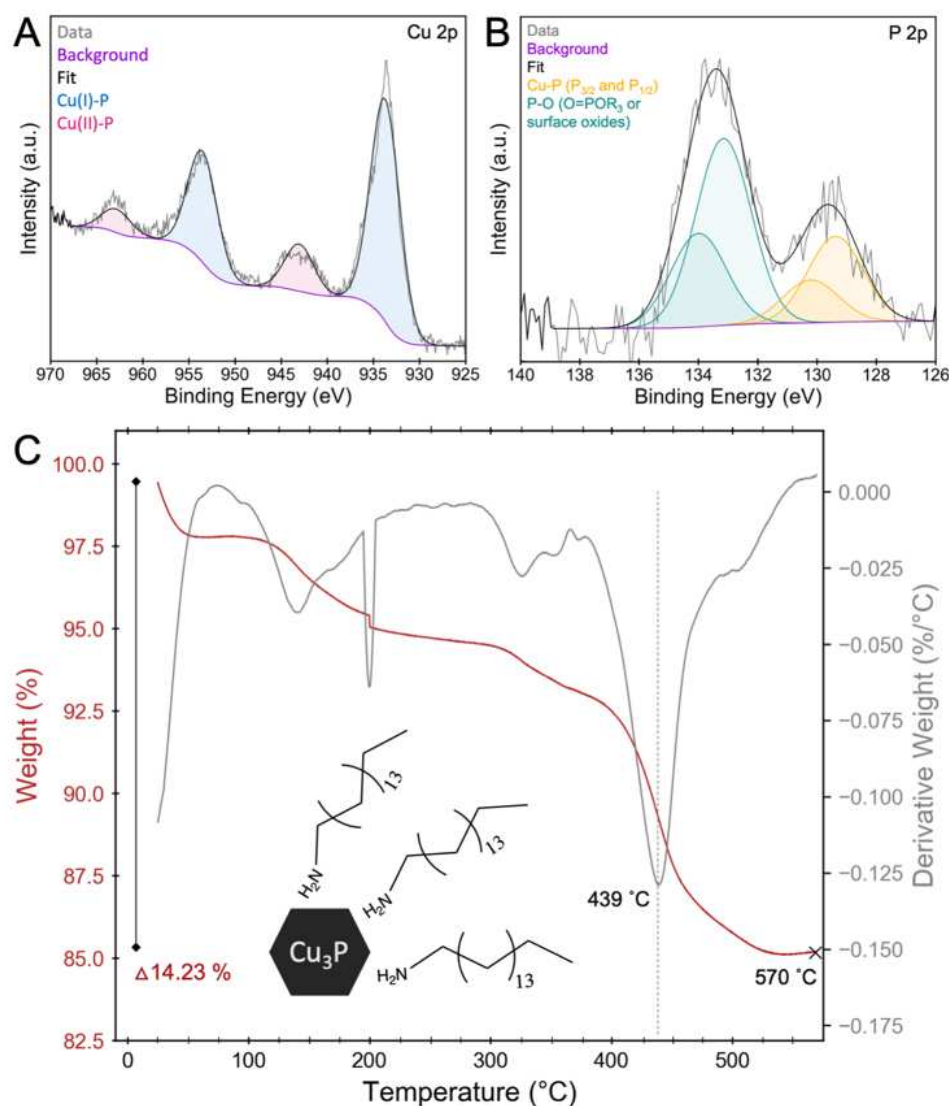


Figure 3.5. Surface characterization of Cu₃P particles. (A) XPS of Cu 2p region and (B) P 2p region. (C) TGA with a 2 °C/min heating profile to 570 °C.

To attain a better understanding of the improved stoichiometry in **Scheme 3.1B**, the surface ligand identity and quantity were investigated for both Cu_{3-x}P and Cu₃PSe₄. The surface composition was initially analyzed with ¹H NMR on Cu_{3-x}P particles, washed to remove excess precursors, which was indicative of long alkyl chains consistent with HDA as the primary, surface-bound ligand (**Figure B.18**). Additionally, X-ray photoelectron spectroscopy (XPS) of the carbon (C) and nitrogen (N) 1s regions (**Figure B.19**) is representative of HDA binding environments

according to previous literature reports.^{54,76,77} Of note, the Cu and P 2p binding region (**Figure 3.5A and B**) demonstrates the characteristic Cu_{3-x}P environments,^{18,78–83} while the satellite Cu(II) peak (**Figure 3.5B**) and P-O peak at 134 eV likely corresponds to surface oxides.^{78–80,83} Finally, Cu₃PSe₄ was characterized with XPS for Cu, P, Se, and C bonding environments (**Figure B.20**). The core bonding environments (Cu, P and Se) were consistent with previous reports of Cu₃PSe₄ and Cu₃PS₄,^{7–9,84} whereas the C region had similar peaks to Cu_{3-x}P NPs but a decrease in C-NH₂ environment (**Figure B.20D**). In summary, the above spectroscopic evidence confirms the sample purity and provides evidence for the nanoparticle surface composition, an important component of the net reaction stoichiometry.

With HDA identified as the surface ligand, the quantity of organic content for Cu_{3-x}P was determined in order to calculate the required Se⁰_{powder} molar equivalence in **Scheme 3.1B**. First, thermogravimetric analysis (TGA) was performed on dried pre-synthesized Cu_{3-x}P nanoparticles over a temperature range of 25-570 °C with a 2 °C/min heating profile, resulting in a 14.23% weight loss (**Figure 4C**) and no degradation of the core particles (**Figure B.21**). Of note, when a 25-800 °C at 10 °C/min heating profile is used (**Figure B.22A and B.23**), 2 wt% degradation of Cu_{3-x}P to Cu⁰ was quantified with Rietveld refinements (**Figure B.22B and B.24**). Of importance to refining the precise stoichiometry, when ~15 wt% organic content is accounted for in the Cu_{3-x}P mol calculation, the Se content measured via PXRD is reduced from 3.6 wt% to 1.3 wt% (**Figure B.25 and B.26**). The HDA content of the refined product, (Cu₃PSe₄•HDA)_r, assuming 85 wt% crystalline Cu_{3-x}P, decreased to 5 wt% (**Figure B.27**); however, the Cu_{3-x}P heating profile required to thermally remove the organic content could not be applied to Cu₃PSe₄ due to degradation to Cu₇PSe₆ and P₂Se₅ above 500°C.¹³ The significant decrease in Se content further supports the improved, near-stoichiometric synthesis in Scheme 1B. That said, two aspects of Cu_{3-x}P

contributing to the variation in stoichiometry are under a separate investigation and will be described in a future report: (i) the elemental composition and Cu vacancy, x , in Cu_{3-x}P ; and (ii) the effect of the Cu_{3-x}P particle-size dispersion (**Figure B.28**) on the reactivity with $\text{Se}^0_{\text{powder}}$.

The results provided herein are consistent with the synthesis of Cu_3PSe_4 as described in **Scheme 3.1B**. Overall, this is an 8 electron (e^-) redox reaction of $(\text{Cu}_{3-x}\text{P}\bullet\text{HDA}_n)_m$ with the surface of suspended $(\text{Se}^0)_n$ is occurring, especially once the solid selenium becomes molten ca. 221 °C.^{66,69,70,85} This raises the question of if there is any other dissolution or speciation $(\text{Se}^0)_n$ under the 221 °C reaction conditions. Literature studies support the claim of dispersed selenium particles, but moderate solubility has only been observed for select solvents,^{45,69,86–88} most notably carbon disulfide,^{66,89} hydrazine,⁹⁰ and ethylenediamine.⁸⁶ However, a binary thiol-amine mixture recorded significantly higher solubility (38 wt% grey selenium) under ambient conditions.⁸⁸ Further evidence of a dispersion of Se^0 species is observed in an ODA/Se temperature control (**Figure B.29**), where a color transition was only noted after the melting point, a color distinctly different from the clear solution when Cu_{3-x}P is present. Additionally, the reactivity of suspended Se^0_n with Cu_{3-x}P NPs was monitored by ex-situ studies (**Figure B.30**), which resulted in high conversion to Cu_3PSe_4 at 250 °C and near phase purity at 300 °C.

An alternative hypothesis to be considered is that Cu_{3-x}P could be reacting with in-situ generated H_2Se to drive ternary formation based on previous investigations of H_2Se production in aliphatic hydrocarbon solvents.^{21,26,91–93} Particularly relevant to the Cu_3PSe_4 system, H_2Se has been proven to be a reactive and efficient selenium precursor for binary nanoparticle syntheses, most commonly cadmium selenide (CdSe). Thermodynamic data for *gas-phase* Se_n species formation from crystalline, trigonal $\text{Se}^0_{\text{cryst;trig}}$ (**Table B.4**) further support these observations, with H_2Se (g) formation being the most favorable, $\Delta G^0_{300} = 7.29 \text{ kcal mol}^{-1}$.⁹⁴ However, of note to our synthetic

conditions, quantitative studies have shown the production of H₂Se from Se⁰_{powder} in aliphatic solvents results in low yields, with gravimetric measurements indicating 10.5% at 320 °C for 1 hour in paraffin oil.⁹² Nonetheless, H₂Se was considered as an alternate precursor through direct addition of the headspace of an ODA/Se solution, which resulted in minor conversion to Cu₂Se_x (P, orthorhombic) under similar synthetic conditions (300 °C, 30 mins, **Figure B.31**). In short, the key to the improved stoichiometry is (i) the lack of participation by ODA to form Se-consuming species prior to Cu₃PSe₄ formation, and (ii) a quantitative redox match between the Cu_{3-x}P reductant and the 4 Se⁰ oxidant resulting in 4 Se²⁻ in the Cu₃PSe₄ product—that is, the complimentary 8 electron redox half reactions of the formally P³⁻ (Cu₃P) " P⁵⁺ (Cu₃PSe₄) + 8 e⁻ and 4 Se⁰ + 8 e⁻ " 4 Se²⁻.

3.4. Conclusion

In conclusion, an improved synthesis of Cu₃PSe₄ has been developed that eliminates Se-containing byproducts that otherwise consume 2/3 of the Se⁰ needed to make phase-pure Cu₃PSe₄ in 1-ODE. Simply by replacing 1-ODE with ODA, a much cleaner, close to stoichiometric, near-atom-economical synthesis was obtained, in which 4 Se⁰ are reduced by the formally 8 e⁻ oxidation of P³⁻ in Cu₃P en route to P⁵⁺ formally present in Cu₃PSe₄, a reaction in which ODA serves predominantly as an inert solvent. Moreover, the results obtained herein form a basis from which more detailed questions regarding the mechanism of formation of Cu₃PSe₄ to be addressed as well as the synthesis of other ternary phases, most notably Cu₇PSe₆, can more rationally and directly be addressed. Finally, the results presented can also be applied to myriad other systems and studies involving 1-ODE, Se⁰, and other chalcogenides.

3.5. Author Contributions

According to CRediT criteria, my contributions to this work included conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft, and writing – reviewing and editing. Contributions by Luke T. MacHale included data reproduction, conceptualization, and editing. Contributions by Erin R. Snyder included data acquisition and analysis of TGA and XPS experiments and editing. Contributions by Richard G. Finke included conceptualization, investigation, and writing – reviewing and editing. Contributions by Amy L. Prieto included conceptualization, investigation, and writing – reviewing and editing.

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CHAPTER 4: TOGGING ACROSS THE CU-P-SE TERNARY PHASE DIAGRAM USING DIPHENYL DISELENIDE, PH_2Se_2 , TO ACCESS Cu_7PSe_6 NANOPARTICLES²

4.1. Introduction

Ternary chalcogenide nanoparticles (NPs) have emerged as promising energy conversion (thermoelectric and photovoltaic)^{1–5} and storage materials (magnesium cathode),⁶ both of which provide avenues to develop sustainable energy with earth-abundant compositions. Copper argyrodites, in particular Cu_7PSe_6 , have been widely studied as a “phonon-liquid electron-crystal” thermoelectrics.^{7–10} The measured high ionic conductivity is attributed to the (de)localization of copper (Cu) ions throughout the $[\text{PSe}_4]^{3-}$ tetrahedral units, resulting in three Cu_7PSe_6 polymorphs that exist as a function of temperature ($\alpha \rightarrow \beta \rightarrow \gamma$).^{11–13} From the crystallographic information, it has been predicted that Cu_7PSe_6 is a more metastable phase (P2_13 space group) in comparison to the ternary analog, Cu_3PSe_4 ($\text{Pmn}2_1$ space group) due to the presence of low coordinate Cu-Se environments. Although both have been synthesized with high-temperature, elemental solid-state reactions (conditions),^{6,14–21} current solution-based techniques, developed by our group, have primarily focused on targeting Cu_3PSe_4 NPs.^{22,23} It is, therefore, of interest to extrapolate the synthetic intuition developed from the Cu_3PSe_4 reactions to target Cu_7PSe_6 , which in return will aid in understanding how reaction pathways can be isolated and manipulated in complex, ternary systems.

² This Chapter is a manuscript prepared for Submission to ACS Nano with Neisius, N., MacHale, L., Tjalkens, J., Finke, R., and Prieto, A. Majority of the data and writing was analyzed and completed by Nathan Neisius with guidance from Amy Prieto. The other author contributions are explained in section 4.5.

To isolate the metastable phase, one must first understand the colloidal synthesis of copper selenophosphate, Cu_3PSe_4 NPs, which was originally synthesized by Lee et al. with the use of pre-synthesized Cu_{3-x}P nanoparticles (x are Cu vacancies, shown to be $0.13 < x < 1.08$)^{24–30} and a Se/1-octadecene (Se/ODE) solution.²² The ODE precursor is a ubiquitous solvent in the chalcogenide NP field, and plays a dual role here, first as a solvent, but also to react with Se^0 to form active Se species (such as H_2Se , R_2Se , and R_2Se_2)^{31–36} that can subsequently react with Cu_{3-x}P . Recently, we improved the synthesis by substituting ODE with an aliphatic, saturated hydrocarbon solvent, n-octadecane (ODA),³⁷ that promoted a near-stoichiometric, atom-economical reaction.²³ Importantly, ODA was shown to be an innocent solvent as it didn't readily react with Se^0 , allowing a complementary formal 8-electron redox reaction, with half reactions of $\text{P}^{3-} (\text{Cu}_{3-x}\text{P}) \rightarrow \text{P}^{5+} (\text{Cu}_3\text{PSe}_4) + 8 e^-$ and $4 \text{Se}^0 + 8 e^- \rightarrow 4 \text{Se}^{2-}$. Thus, it was hypothesized that Cu_{3-x}P particles react with molten Se^0 , to produce Cu-Se binaries at lower temperatures and an intermediate P species reincorporates at the elevated 300 °C reaction temperature. Although a foundation was set for stoichiometric delivery of Se, progressing the reaction pathway understanding and tracking the transformation of Se species in solution was not readily testable with accessible characterization techniques. .To allow easier, more complete monitoring of the reaction

To allow easier, more complete monitoring of the reaction, dibenzyl diselenide ($\text{PhCH}_2\text{SeSeCH}_2\text{Ph}$, Bn_2Se_2) was employed in lieu of Se^0 powder as an efficient Se^0 source to prepare Cu_3PSe_4 . The precursor, Bn_2Se_2 has a C-Se bond with a low bond dissociation energy (BDE) compared to Se-Se BDE,^{38,39} releases Se_2^0 species that favorably reacts with Cu_{3-x}P NPs to isolate the Cu_3PSe_4 reaction pathway. Importantly, full decomposition of Se was quantified and tracked due to a detectable byproduct, toluene (PhCH_3). In the same report, diphenyl diselenide (Ph_2Se_2),

was screened in excess equivalents as a more *reactive* Se precursor that targets Cu_{2-x}Se and Cu_7PSe_6 , which will be applied and explored in detail herein.

Dialkyl diselenide precursors, R_2Se_2 , have gained considerable interest due to the ability to selectively synthesize binary and ternary Se-based nanoparticles, leading to formation of less stable phases and unique morphologies.^{40–46,38,47–52} The systematic incorporation of Se is attributed to the bond dissociation energy (BDE) of C-Se and Se-Se.^{38,39} From such, it has been shown that the difference between the two will alter whether the Se precursor will decompose to $2 \text{RSe}\bullet$ or to $\text{R}\bullet$ and $\bullet\text{SeSeR}$, which have been both experimentally determined and computationally calculated for wide range of R identities.^{38,39,53–57} However, two studies are of particular interest for the work provided herein. First, the CuInSe_2 phase was tuned by Brutchey et al. from a thermodynamic chalcopyrite phase to a metastable wurtzite phase by altering the R_2Se_2 precursor.^{38,40} The R_2Se_2 with a weaker C-Se BDE produced a Cu-Se binary that favored the thermodynamic phase, whereas a stronger C-Se BDE (weaker Se-Se BDE) produced the metastable phase. Additionally, MacDonald et al. analyzed the Cu-Se phases formed from R_2Se_2 degradation and the subsequent byproducts in various experimental conditions (ligands and solvents), confirming that the decomposition products are dependent on the C-Se BDEs.³⁹ Pertinent to the work explored herein, the strong C-Se BDE of Ph_2Se_2 led to (i) Chan-Lam-type decomposition⁵⁸ opposed to peroxide-like, and (ii) Ph_2Se_1 and Ph_2Se_3 are products from a thermolysis control.³⁹

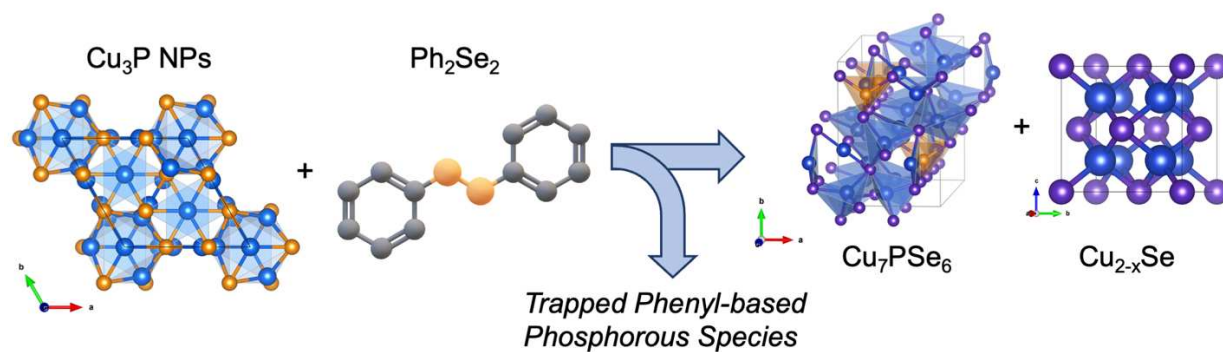


Figure 4.1. Scheme of Cu_3P NPs reacting with Ph_2Se_2 that produces Cu_7PSe_6 and Cu_{2-x}Se phases, but phosphorus species are also trapped in solution.

As previously stated, Ph_2Se_2 demonstrated minimal conversion to Cu_7PSe_6 , which is attributed to the C-Se BDE is higher in energy ($66.4 \text{ kcal mol}^{-1}$, more stable bond) than Se-Se ($44.6 \text{ kcal mol}^{-1}$), meaning the predicted selenium thermolysis product is $2 \text{ RSe}\bullet$. Therefore, herein, we explore the influence of Ph_2Se_2 resulting speciation on the Cu-P-Se phase space (**Figure 4.1**). The transformation pathways are analyzed *via* ex situ techniques to capture the Ph_2Se_2 degradation pathways in the presence of Cu_3P particles en route to forming Cu_7PSe_6 . Two upfront questions are to be addressed: (1) does Ph_2Se_2 fully decompose in the presence of Cu_{3-x}P to efficiently deliver Se^0_n , similar to Bn_2Se_2 , or are there Ph_2Se_x ($x = 1, 2$ or 3) byproduct, and (2) what is the stoichiometric reaction that can inform on why Cu_7PSe_6 forms, and most importantly, when we have a non-phase-pure synthesis, what are the byproducts and what do can they tell us about how to improve the reaction? One observation that provides an alternative perspective on employing R_2Se_2 precursors, is the formation of $\text{Ph}\bullet$ as Se is consumed. Importantly, this byproduct has a significant impact on the isolation of Cu_7PSe_6 , as P can be effectively trapped in solution by $\text{Ph}\bullet$, preventing the formation of the thermodynamic Cu_3PSe_4 phase.

4.2. Experimental

4.2.1. MATERIALS AND PREPARATION

Anhydrous copper (II) chloride (CuCl_2 , 99%, Sigma Aldrich), hexadecylamine (HDA, Sigma Aldrich, 90%), triphenyl phosphite (TPOP, 97%, Oakwood Chemical), selenium powder (Se 200 mesh, 99.99%, STREM), sodium oleate (Na(OA)_2 , >97%, TCI America), Copper(II) dichloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, reagent grade, SigmaAldrich) chloroform (CHCl_3 , 99.8%, Sigma Aldrich), isopropanol (IPA, 99.5%, Fischer Scientific), hexanes (98.5%, Sigma Aldrich), toluene (99.5%, Sigma Aldrich), and ethanol (99%, Fischer Scientific) were used as packaged and received. 1-Octadecene (ODE, 90% Technical grade, Sigma Aldrich where the impurities are 2-octyl-1-decene, 2-butyl-1-tetradecene, 2-hexyl-1-dodecene, n-octadecane) and octadecane (ODA, 99%, Fischer Scientific) were sparged with N_2 for 2 hours (hr) before being used. A lecture bottle of hydrogen selenide (H_2Se , Solkatronic Chemicals Inc., UHP Grade) was used as received. All reactions were performed in a N_2 glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm) unless specified otherwise. Post-synthesis solvent washing was performed in ambient conditions on the benchtop. All glassware was cleaned using a base and acid bath wash, followed by rinsing with Millipore water and dried in a 160 °C oven overnight.

4.2.2. STANDARD SYNTHETIC CONDITIONS

$\text{Cu}_3\text{-xP}$ Synthesis. Adapted from Liu et al. To a 50 mL, 3-neck-round-bottom flask, 0.5 mmol (67 mg) of CuCl_2 , 5.0 mmol (1.207 g) HDA, 5.0 mmol (1.3 mL) TPOP, and 12.70 mL of solvent (ODA or 1-ODE) were added. The 3-neck-round-bottom flask was equipped with a magnetic stir bar, thermal couple, condensor tube, and septa to seal all openings. After preparation in the glove box, the reaction flask was placed on a heating mantle set to 30 °C and constant stirring to dissolve all reagents. Once all reagents had dissolved, the reaction was heated to 150 °C and maintained at that temperature for 1 hour. After 1 hour at 150 °C, the reaction was then heated to 300 °C and maintained at that temperature for 30 minutes. The reaction was left to cool naturally and quenched

at 80 °C in air into 3 tubes and centrifuged to separate the particles from the supernatant. Three mL of chloroform were injected into the flask to disperse the remaining particles adhered to the walls in the round bottom flask. The collected particles were then dispersed in three mL of chloroform and 12 mL of isopropanol. The dispersed particles were centrifuged for 10 mins at 5800 rpm, and then the supernatant was discarded. The washing procedure was repeated two additional times with a 30 second per tube sonication step after the solvent (CHCl_3) and anti-solvent (IPA) were added to aid dispersion.

Cu₇PSe₆ Synthesis – Heat up with diphenyl diselenide. Reaction conditions are similar to published report on Cu₃PSe₄.²³ The pre-synthesized Cu_{3-x}P NPs, synthesized above, from two centrifuge tubes are suspended in hexanes and transferred to a pre-weighed round-bottom flask. After the particles are transferred and dried over N₂, the weight of Cu_{3-x}P particles was determined (typically ca. 15 mg). The flask was then pumped into the N₂ glovebox with a Liebig reflux condensor, Teflon®-coated stir bar, and a thermocouple. Diphenyl diselenide (3 equiv. to 85 wt % pre-weighed Cu₃P NPs)²³ and solvent (ODA, HDA, or ODE, so that the Cu_{3-x}P NP concentration is retained at 8mM) were added into the reaction flask. When using ODA, it was deemed essential to slightly heat the storage vessel (ca. 30 °C) to make sure it doesn't crystallize in the syringe when transferring to the reaction flask. The reaction flask was removed from the glovebox and sonicated at 35 °C for 1 minute (min) to fully suspend the Cu_{3-x}P NPs. It was then attached to the Schlenk line, cycled three times between N₂ and vacuum, and kept under nitrogen. The reaction flask was then heated up to 300 °C at a 500 °C/hr ramp rate and held for the reported times in the results and discussion section. Once the reaction reaches completion, the flask is raised from the heating mantle to cool to 80 °C for extraction to two 15 mL plastic centrifuge tubes, where the total reaction solution is centrifuged for 5 minutes at 5800 rpm. The supernatant was isolated and saved and the

NP precipitate were dispersed in a 1:5 toluene:ethanol mixture (2 mL and 13 mL of ethanol) by sonicating for 30 seconds. The dispersed particles were centrifuged for 15 minutes at 5800 rpm, then the washing solution was discarded. The washing procedure was repeated 2 times with a sonication step after each washing mixture was added to increase dispersion.

Cu₇PSe₆ Synthesis – Phosphorus precursor Injection. A similar synthetic procedure to the heat-up Ph₂Se₂ synthesis is employed for the triphenyl phosphite (TPOP) and phosphorus pentachloride (PCl₅) injection synthesis with the following adaptations. 1) a TPOP/hexadecane and PCl₅/oleylamine (OLA) solution is prepared by taking in a DI water rinsed, pre-dried 20 mL sonication vial to the glovebox. TPOP and PCl₅ is measured out (1 equiv. in relation to Cu₃P, so in excess) into the sonication vial along with 1 mL of hexadecane or OLA, respectively. When the flask reaches 300 °C for 20 minutes, the TPOP/hexadecane or PCl₅/OLA vial is taken out of the N₂ glovebox and sonicated for 30 seconds to achieve a homogenous solution. 2) injection of the solutions were done at the desired temperature point; variations are explained in the results and discussion. The solution dropped ca. 15 °C for each injection. The reaction was held at 300 °C for 15 min, then quenched, washed, and worked up with the same conditions as the heat-up synthesis.

Cu₇PSe₆ Individual, Ex-situ NMR-scale synthesis. The following synthesis is adapted from Macdonald et al.³⁹ The pre-synthesized Cu_{3-x}P NPs were suspended in minimal amount of hexanes and transferred via glass pipette to a pre-weighed, clean, and dry 5 mm x 170 mm NMR tube. The NMR tube was brought into the glovebox and then 9/7 mol equivalents of Ph₂Se₂ were added along with 100 µL of warmed, ca. 30 °C ODA. The NMR tube was sealed with a septa cap and removed from the glovebox, where a needle capped syringe with a N₂ gas balloon attached to top of syringe was injected into the septa cap. Once under that positive N₂ pressure, the tube was wrapped with a small amount of Parafilm[®] film, and if needed a heat gun was applied to the sides to ensure all

ODA (melting point, mp = 28-30 °C) flowed to the bottom of the tube. The sample was then put into a Si oil bath that is already heated to the desired temperature specified the following sections. The reactions were allowed to proceed for 1 min at the set temperature. The NMR tube was removed from the heating bath, allowed to cool in air for five minutes, and then 0.6 mL CDCl₃ was injected through the septa top. The N₂ balloon/syringe was removed, but kept air-free via the septa cap, and the NMR sample was covered in a light-resistant plastic bag before analysis.

Cu₇PSe₆ NP Pseudo In-situ NMR-scale synthesis. The following synthesis is adapted from Macdonald et al.³⁹ and from the ex-situ syntheses. The adaption to the previous, ex-situ NMR-scale synthesis, is that once the solution was analyzed after the desired temperature was reached, the CDCl₃ was vacuumed off on a Schlenk line. While the NMR experiments were running, the temperature of the Si oil bath was set to the next desired temperature. After all the CDCl₃ was removed via vacuum, the NMR tube was back filled with N₂ then placed in the Si oil bath and the N₂ balloon/syringe was added. The reaction was allowed to proceed for 5 min. After the 5 min passed, the NMR tube was again removed from the heating bath, allowed to cool in air for 5 min, and then 0.6 mL CDCl₃ was injected through the septa cap. This process occurred for room temperature (RT), 225, 250, 275, and 300 °C.

Copper oleate, Cu(OA)₂, synthesis. The following synthesis is adapted from Wang et al.⁵⁹ Sodium oleate (Na(OA)₂, 9.85 mmol) and Copper dichloride dihydrate (CuCl₂·2H₂O, 4.95 mmol) were added in a ca. 2:1 mol ratio to a 100 mL round-bottom-flask. Ethanol (10 mL), water (8 mL), and hexanes (17 mL) were added to the flask and heated to 70 °C. After 30 minutes, 10 mL of hexanes was added, and the flask was heated for 4 hours. The Cu(OA)₂ product was collected in the hexanes layer and was purified by washing the product 3 times with 30 mL of water in a separatory funnel. After purification, the product was collected and dried by vacuuming off the

hexanes. A septa was put on the vial, filled with N₂ transferred via the antechamber into the N₂ glovebox.

Cu₇PSe₆ Synthesis with Cu(OA)₂. The following synthesis is adapted from Wang⁵⁹ and Tappan et al.³⁸ Copper oleate (0.58 mmol), Cu(OA)₂, R₂Se₂ (0.25 mmol), and 8 mL of OLA were added into a 25 mL three-neck round-bottom-flask. Phosphorus pentachloride (0.083 mmol), PCl₅, and 4 mL were added into a 10 mL two-neck round-bottom-flask. Both flasks were heated to 70 °C and degassed for 30 m under vacuum. The 2-neck flask was further heated to 120 °C and the three-neck to 140 °C. Both were again degassed for 30 m and refilled with N₂. The three-neck flask, containing Cu(OA)₂ and R₂Se₂ was heated to 255 °C, then the PCl₅/OLA solution was injected, and allowed to react for 1.5 hour. Reaction was quenched by placing the flask in a RT water bath. The collected particles were washed via the same procedure as the standard Cu₇PSe₆ synthesis.

4.2.3. CHARACTERIZATION

Powder X-ray Diffraction (PXRD) and Rietveld Analysis. Powder X-ray Diffraction Spectroscopy (PXRD) was performed on a Bruker D8 Discover Series Powder X-ray Diffractometer (PXRD) using a Cu K α source ($\lambda = 1.54 \text{ \AA}$) and a Lynxeye XE-T positron-sensitive detector. Samples were prepared by dispersing the particles in hexanes, followed by drop-casting on a p-type boron-doped Si Zero Diffraction Wafer (MTI Corporation). Ground samples were first dispersed in hexanes, deposited on a glass plate, and scraped into a mortar and pestle. The samples were then transferred to the diffraction wafer that contained zero-diffraction grease to reduce preferred orientation. Diffraction patterns were indexed using the DIFFRAC.EVA software v5.2 to known powder diffraction files (PDF) patterns in the PDF-4+ database. The PDF patterns used for the following phases are: Cu₃P #01-071-2261, Cu₇PSe₆ #00-033-0482, Cu_{2-x}Se #00-006-0680,

Cu_{1-x}Se #01-089-2734, and Cu₃PSe₄ #04-006-8347. Refinements were performed using TOPAS v6 (Bruker AXS). Specific parameters are included for the selected patterns below.

Nuclear Magnetic Resonance. ¹H and ³¹P NMR experiments were performed on the reaction supernatants in deuterated chloroform (CDCl₃, Thermo Scientific, 99.8%, dried over activated 3 Å molecular sieves) on a Bruker NEO400 spectrometer with automated tuning. ¹H, ³¹P, ⁷⁷Se NMR experiments were collected on an Agilent (Varian) 400MR MHz spectrometer equipped with automated tuning and a 7600-sample changer. Data was processed in the MestReNova, v. 15.0.1.

Gas Chromatography – Mass Spectroscopy (GC-MS) Identification of Organic Species. For GC-MS analysis, a 1.5 mL GC vial with septa top was filled with 1.0 mL hexanes and degassed using a Schlenk line prior to use. A 0.1 mL aliquot was extracted from the supernatant solution of a NP synthesis in section 2.2 and injected into the GC vial (1:10 dilution). The sample was immediately analyzed in the Analytical Resource Core – Materials and Molecular Analysis (ARC – MMA) facility using an Thermo Scientific ISQ Thermal Desorption single quadrupole mass spectrometer interfaced to a Trace 1310 Gas Chromatograph equipped with a 1310 autosampler, Electron Ionization (EI) source and high-energy dynode (HED) electron multiplier detector. The column was flowed from 1 mL/min to 52.8 mL/min with a starting temperature of 60 °C ramping to 325 at 15 °C/min where it was held for 2 minutes before cooling. Gas chromatograms and mass spectra were analyzed using Chromeleon with NIST MS enhanced data analysis to compare mass spectra and identify analyte species. Peaks were visualized using OpenChrome V1.4.0 for figure reports.

Fourier Transform – Infrared Spectroscopy (FT-IR). The copper oleate, Cu(oleate)₂ product was characterized using a Nicolet iS-50 FT-IR spectrometer. An attenuated total reflectance (ATR) method was used with a zinc selenide (ZnSe) crystal. The Cu(oleate)₂ product was transferred to

the ATR crystal with a spatula and was pressed down with ca. 40 pounds of pressure using a concave tip . The scan method used 16 scans for the background and 64 scans for the sample.

Transmission Electron Microscopy (TEM) Imaging and Energy Dispersive Spectroscopy (EDS) Analysis. Morphology of nanoparticles were characterized using a JEOL JEM 2100F Transmission Electron Microscopy (TEM) with acceleration voltage of 200 keV. Scanning transmission electron microscopy (STEM) energy dispersive X-ray spectroscopy (EDS) was carried out with an Oxford X-Max 80 mm² detector and analyzed using AZtecTEM software. Samples were prepared by sonicating one centrifuge tube of particles (ca. 10 mg) with one mL of toluene and hexanes for one minute. 0.1 mL of the particle dispersion was further diluted with 1 mL of toluene, making a 1:10 ratio, which was sonicated for another 5 minutes at 35 °C. Finally, 14 mL of hexanes was added to the solution and sonicated for another minute. Carbon-coated nickel TEM grids (200 mesh, Ted Pella) were dipped into the diluted mixture and dried once removed by touching the grid with a Kimtech Kimwipe. The grid is then dried in the fume hood overnight and pumped down under vacuum for 30 minutes before imaging. Images were analyzed in Digital Micrograph of the Gatan Microscopy Suite software (v3.51).

4.3. Results and Discussion

4.3.1. PRELIMINARY INVESTIGATION OF SELENIUM INTERACTIONS THAT FAVORS Cu_7PSe_6 .

As an upfront control, Ph_2Se_2 and benzeneselenol (PhSeH) were initially tested based on the precedent to produce $\text{PhSe}\bullet$ to evaluate the impact on Cu-P-Se phase formation. Both Se precursors yield Cu_7PSe_6 along with Cu_{2-x}Se binaries via powder X-ray diffraction, PXRD (**Figure C.1**). However, Ph_2Se_2 was determined to be the most promising direction forward as BnSeH has too low of a boiling point (bp) for the standard conditions (300 °C vs bp 71 °C). Next, solvents were investigated for Ph_2Se_2 at excess equivalents (16 equiv. in relation to Cu_3P), as previous Ph_2Se_2

reports demonstrate metastable NP phase formation with primary amines as the solvent.³⁸ PXRD confirmed that oleylamine (OLA) results in Cu_{2-x}Se binaries (**Figure C.2**), which is consistent with previous Cu-P-Se reports,^{22,23} due to primary amines strongly coordinating to Cu(I) at the surface of Cu-Se binaries which prohibits P reincorporation. For octadecane (ODA) and 1-octadecene (ODE) at excess 16 equiv., the impact on Cu_7PSe_6 phase formation was determined to be negligible, as both produced Cu_{2-x}Se and Cu_7PSe_6 phases (**Figure C.2**). Of note, Cu_3PSe_4 was also present in the ODA sample, which is hypothesized to be a result of more efficient Se delivery and lack of interactions between ODA and Ph_2Se_2 . To further probe the influence of solvents on Se delivery, a near-stoichiometric reaction (4 equiv. of Ph_2Se_2) was explored. In ODE, poor selenium delivery was identified with the PXRD pattern consisting of majority Cu_{3-x}P and Cu_{2-x}Se (**Figure C.3**), whereas ODA promoted efficient delivery of Se and produced a cleaner conversion to Cu_7PSe_6 (**Figure C.4**), thus ODA will be used in the following experiments unless otherwise stated.

As a crucial next step in evaluating the Cu-P-Se phase space, Ph_2Se_2 equiv. was further reduced to resemble a more balanced, stoichiometric reaction (3 equiv.), which produced Cu_7PSe_6 and Cu_{2-x}Se particles at 50.5 and 49.5 wt. %, respectively (**Figure 4.2A**, Rietveld^{60–63} refinement details in **Table C.1**). Ultimately, this eliminated the presence of Cu_3PSe_4 , a thermodynamic phase (predicted at 0K by materialsproject.org⁶⁴) that contaminates the products and is hypothesized to be a degradation product of Cu_7PSe_6 (summarized in Chapter 2). The formation of Cu_7PSe_6 nanoparticles were additionally characterized by transmission electron microscopy (TEM, **Figure C.5**) to ensure nanosized particles are isolated.

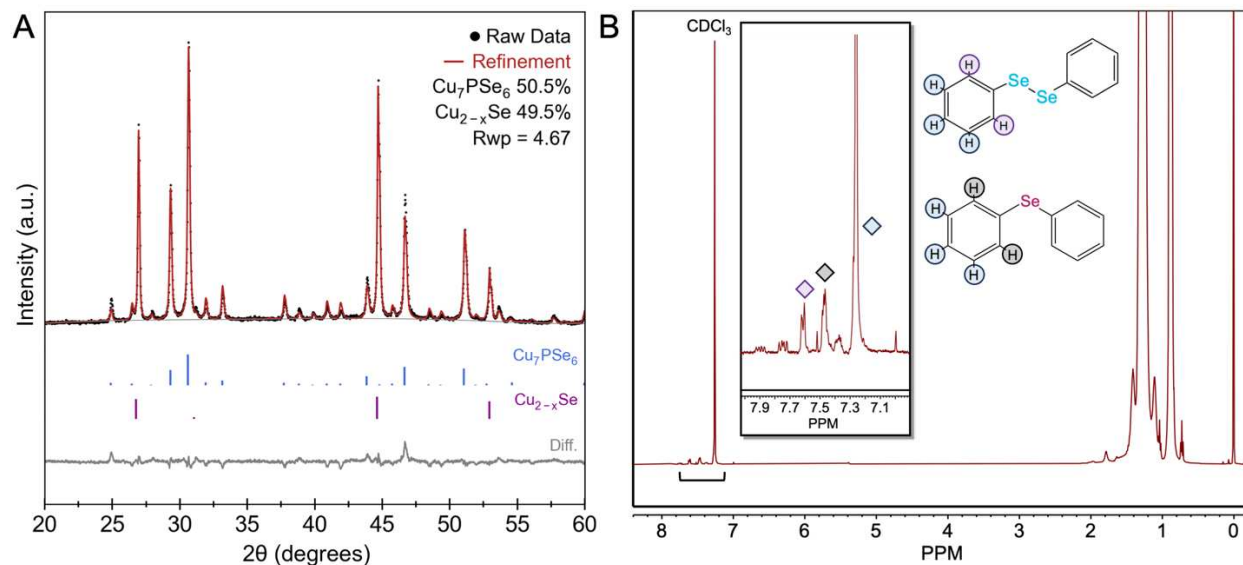


Figure 4.2. Characterization of 3 equiv. Ph₂Se₂ + Cu_{3-x}P reaction at standard synthetic conditions. (A) Rietveld refinement of the powder X-ray diffraction (PXRD) pattern of the final nanoparticle product. (B) ¹H nuclear magnetic resonance (NMR) of the reaction supernatant, the peak environments are labeled with the two colors on the Ph₂Se₂ structure provided.

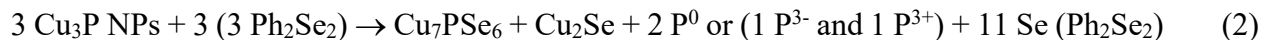
Further exploration of the closer to stoichiometric reaction (3 equiv.) was required in order to decipher why Ph₂Se₂ preferentially forms Cu_{2-x}Se and Cu₇PSe₆ in comparison to Bn₂Se₂ which permits the production of near phase pure Cu₃PSe₄ particles. To that extent, the post-reaction supernatant with 3 equiv. was characterized by ¹H NMR (**Figure 4.2B**), which demonstrated the presence of Ph₂Se₂ ($\delta = 7.61$ ppm) as well as the monoselenide analog, Ph₂Se ($\delta = 7.45$ ppm), a common degradation product of Ph₂Se₂.^{65,66} Thus, three hypotheses can be formulated, either Ph₂Se₂ is limiting the phase formation due to limited decomposition (i.e., limited release of Se), or the Ph₂Se₂ degradation byproducts are prohibiting the transformation of Cu-Se binaries to Cu-P-Se phases, or potentially the combination of the two.

Although both hypotheses are viable options and the formation of Cu_{2-x}Se and Cu₇PSe₆ phases are inherently Se poor (2:1 and 7:6, Cu to Se) compared to Cu₃PSe₄ phase, the excess equiv. reactions provide precedence that Se *availability* is not the underlying cause. Additionally, an

extended reaction time of 1 hour further suggests that the Ph₂Se₂ degradation byproduct hypothesis is the most viable option, as phosphorus incorporation is still limited with only a minor improvement in the transformation to Cu₇PSe₆ noted (**Figure C.6**). Thus, a consideration of the alternate byproducts that form when targeting Cu₇PSe₆ is essential to develop an understanding of why the incorporation of P (and Se) is limited in comparison to systems such as, Se powder and Bn₂Se₂. Therefore, a first approach at a balanced reaction with 3-equiv. Ph₂Se₂ is shown below, eq. 1. The structural characterization of Cu_{3-x}P NPs and quantity of HDA present at the surface is provided in a previous report by our group,²³ and is considered in the calculation of Se equiv. throughout the rest of this chapter.



The crux of isolating Cu₇PSe₆ compared to Cu₃PSe₄ is the 7/3 equiv. that must be applied to Cu_{3-x}P, producing a 4/3 P⁰ byproduct to account for electron balance of 6 Se⁰ reduced to Se²⁻. Additionally, to build upon eq. 1, the stoichiometry for the observed products in **Figure 4.2A**, eq. 2, suggests P can be trapped in either the P³⁻ and P³⁺ state for example, P(Ph)₃ and P(NHR)₃, respectively.



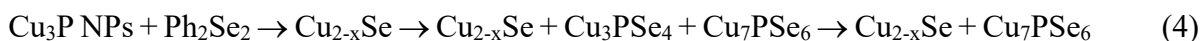
To account for the excess Se in both eq. 1 and 2, we tested a stoichiometric reaction (9/7 Ph₂Se₂, eq. 3) to determine if the binary impurities could be eliminated as any remaining Ph₂Se_x analogs will be reduced. Additionally, reducing Ph₂Se₂ to 9/7 equiv. allows for more systematic characterization of the responsible speciation for Cu₇PSe₆ formation. Indeed, the crystalline phases formed are consistent with 3 equiv. (**Figure C.7**). Of note, for a stoichiometric equiv. (9/7) but at 4-fold higher Se concentration, ¹H NMR demonstrates the presence of Ph₂Se (**Figure C.8A**) is

persistent in solution, while a ^{31}P NMR signal (**Figure C.8B**) indicates that the previously stated *phosphorus trapping mechanism hypothesis* is viable and must be tested in more detail.



4.3.2. VERIFICATION OF TRAPPED PHOSPHORUS IN SOLUTION DUE TO Ph_2Se_2 DECOMPOSITION BYPRODUCTS.

To further probe the dynamics of Cu_3PSe_4 and therefore the *phosphorus trapping pathway*, we performed an ex-situ study with 3 equiv. of Ph_2Se_2 , where according to PXRD of individual aliquots, 300 and 300 °C for 5 min both contained Cu_3PSe_4 in the product (**Figure 4.3**). A route to determine if Cu_3PSe_4 formation from the one-pot heat-up method can be avoided was tested by injecting Ph_2Se_2 /hexadecane into a $\text{Cu}_3\text{P}/\text{ODA}$ dispersion at 300 °C (**Figure C.9**). However, the presence of Cu_3PSe_4 at 10 min that then degrades to Cu_7PSe_6 at 30 min further confirms that the transformation from a phosphorus rich to deficient phases is a side reaction of employing Ph_2Se_2 . Thus, two viable decomposition routes result, one of which is that Cu_3PSe_4 forms en route to Cu_7PSe_6 (i.e., a serial pathway), or alternatively, Cu_3PSe_4 is an off-path product that decomposes in solution to products that can contribute to the formation of Cu_7PSe_6 . Regardless, a phosphorus rich phase (Cu_3PSe_4) is forming that is subsequently being extracted by a hypothesized *phosphorus trapping pathway*, where the crystalline phase transformation is summarized in eq 4.



Additionally, the initial formation of Cu_{2-x}Se then subsequent degradation to Cu_7PSe_6 is a possible indication that the Cu_{2-x}Se formation is a necessary intermediate step to isolate the ternary. Important to note, the Ph_2Se_2 precursor conversion was monitored with ^1H NMR, which demonstrated conversion to Ph_2Se ($\delta = 7.45$) as low as 225 °C (**Figure C.10**), consistent with

previous literature reports.^{65,39} In summary, the formation and subsequent decomposition of Cu_3PSe_4 en route to Cu_7PSe_6 was observed, but it is still unclear whether phosphorus is being trapped in solution as a result of Ph_2Se_2 degradation byproducts, on the surface (amorphous P), or in an alternate species (hexadecylamine from Cu_{3-x}P surface) in solution.

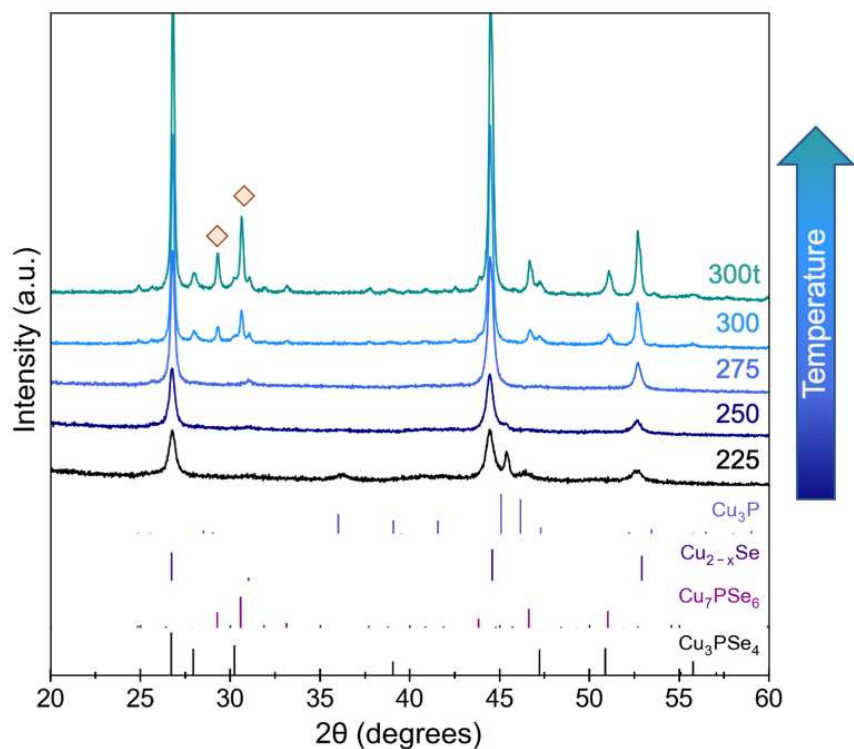
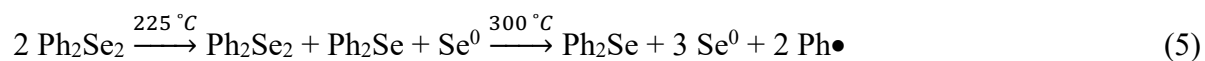


Figure 4.3. Subplot of PXRD patterns for ex-situ aliquots for the synthesis of Cu_{3-x}P NPs + 3 equiv. Ph_2Se_2 . Note that 300t represents a 5 min aliquot. Only partial degradation of the Cu_{3-x}P to Cu_{2-x}Se was identified at 225 °C. The diamonds indicate the representative double ‘fang’ peaks of Cu_7PSe_6 .

While temporal ex-situ studies provide preliminary insight into the Cu-P-Se transformation pathways toward Cu_7PSe_6 , stoichiometric (9/7 Ph_2Se_2 , eq. 3) NMR-tube experiments were performed which are derived from MacDonald et al.³⁹ Two experimental methods were explored, individual (ex-situ) NMR experiments and a single NMR reaction to avoid variations in precursor equivalents (denoted *pseudo* in situ, experimental schematic provided in **Figure C.11**, see experimental section 4.2.2). The adaptations to conduct a single NMR reaction includes heating to

the specified temperature under N₂ for 2 min, then extracting the NMR tube from the Si oil bath to analyze with ¹H, ⁷⁷Se, ³¹P NMR and GC-MS and will be referred to as *pseudo* in situ. For the individual ex-situ reactions, the crystalline product was characterized with PXRD resulting in similar phase transformation in **Figure 4.3** with Cu₃PSe₄ present at 300 °C, but only Cu_{2-x}Se at 300 °C for 30 min (**Figure C.12**).

At high precursor concentrations (ca. 0.3M), the transformation of species was successfully monitored. As expected, and identical to the previous ex situ data, ¹H NMR of both reactions demonstrate decomposition of Ph₂Se₂ to Ph₂Se at 225 °C based on the appearance of a multiplet at δ = 7.45 ppm,^{65,66} with full conversion to the monoselenide at 275 °C (**Figure 4.4A, B and C.13**). Carbon, ¹³C, NMR of the individual reactions further suggests conversion to Ph₂Se as early as 250 °C (**Figure C.14**). Finally, transformation to Ph₂Se is confirmed with ⁷⁷Se NMR, where the Ph₂Se₂ signal at δ = 462 ppm detected at 225-250 °C, disappears and transitions to Ph₂Se₁ (δ = 416 ppm) at 275 °C (**Figure 4.4C**). Similarly, ⁷⁷Se NMR of the individual NMR reactions confirmed Ph₂Se₂ conversion to Ph₂Se but at a slightly elevated temperature, 300 °C, which could be a result of different experimental parameters (**Figure C.15**), where the molecular species transformation is simplified to only 2 equiv. of Ph₂Se₂ and shown in eq 5.



Of note, two signals at δ = 145 and -38.8 ppm are identified in the ex-situ aliquots via ⁷⁷Se NMR, which are believed to have implications on the proposed P speciation, *vide infra*. It is clear to this point that Se transformation in solution is consistent with previous reports, where in summary, Ph₂Se₂ initially thermalizes to Ph₂Se₁ in the presence of Cu_{3-x}P NPs, producing Cu_{2-x}Se particles, which then reacts with the resulting solution speciation (monoselenide and P species) to form Cu-P-Se phases at 300 °C.

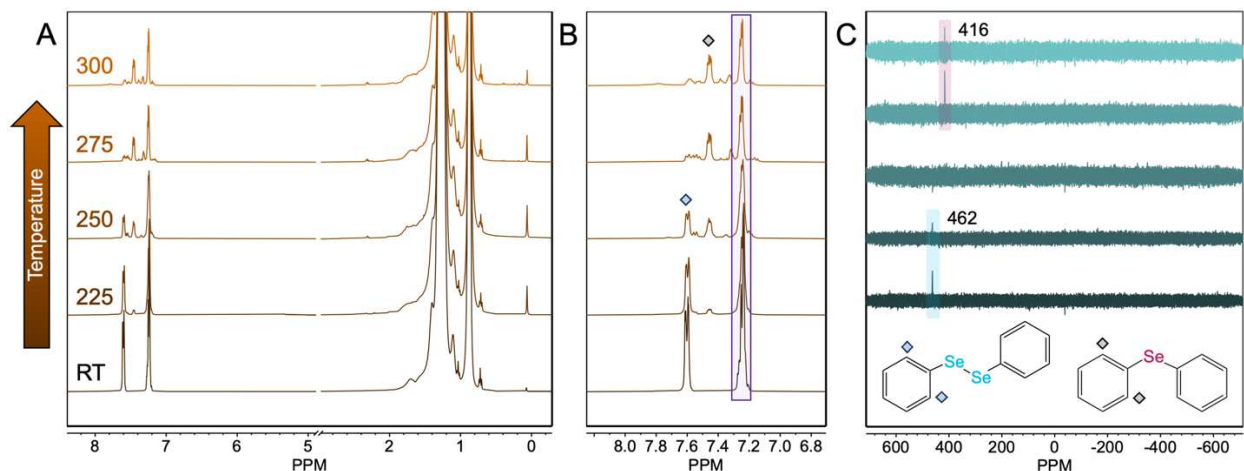


Figure 4.1. ^1H and ^{77}Se NMR subplots for the temperature points of the single NMR tube reaction with Cu_{3-x}P NPs + 9/7 Ph_2Se_2 . (A) Total ^1H spectrum with the 3-5 ppm region omitted due to the absence of peaks. (B) Zoomed in region of 8.0-7.0 ppm, the diamond colors are indicative of Ph_2Se_2 and Ph_2Se ortho hydrogens and the purple highlighted region are the meta and para hydrogens for both Ph_2Se_2 and Ph_2Se . (C) ^{77}Se NMR with diphenyl diselenide and monoselenide identify by the color of Se atom.

To further probe the *phosphorus trapping* mechanism based on the $\text{Ph}\bullet$ present in eq. 5, an upfront question is how P reincorporates into the Cu_{2-x}Se binary and what P speciation is present in solution. Additionally, if phosphorus is trapped in solution when the phase transformation of Cu_3PSe_4 occurs at 300 °C, can the species be identified to inform on the oxidation states of P for previous balanced reactions, eq. 1 and 2? Importantly, no P species were identified in solution for the Bn_2Se_2 reaction when heated to identical temperatures and under similar Cu_{3-x}P and Se concentrations. **Figure 4.5A** shows the ^{31}P NMR spectra of each temperature point for the ex-situ stoichiometric reactions (Cu_{3-x}P NPs + 9/7 Ph_2Se_2), while **Figure C.16A** presents the ^{31}P NMR spectra for the individual, in-situ NMR reactions.

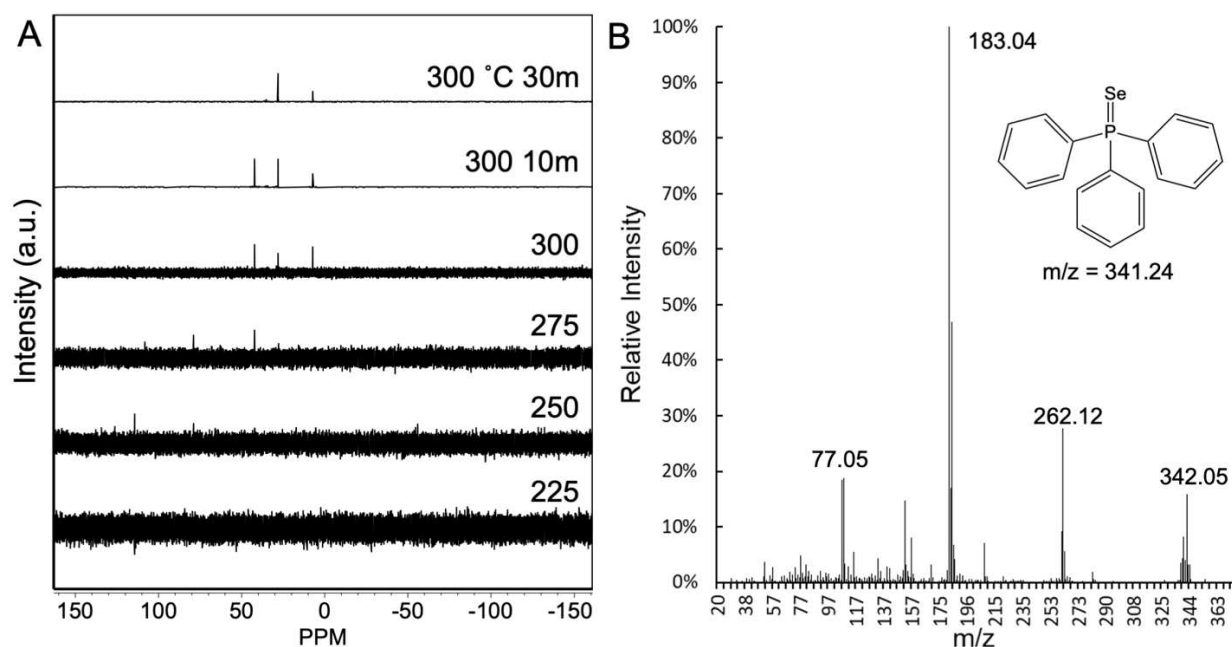


Figure 4.5. Characterization of ex-situ stoichiometric NMR-tube reactions. (A) ^{31}P NMR of the individual temperature reactions, listed on the right side. (B) EI mass spectrum that represents triphenylphosphine selenide, where 342.05 m/z is molecular ion peak, and 183.04 m/z is the base ion peak which is $\text{Ph}_2\text{P}(+)$.

At room temperature (**Figure C.16A**) and 225 °C, either no solution P species were identified for both reactions, or if present they are in too low a concentration to be detected. (**Figure 4.5A**). At 250 °C, a low intensity peak at $\delta = 114$ ppm indicates the first presence of an intermediate P species which corresponds to the thermolysis point of Ph_2Se_2 to Ph_2Se_1 , predicted to be a P(III) species, $\text{P}(\text{SeR})_3$. This species then disappears at 275 °C and transitions to two signals at $\delta \sim 79$ and 42 ppm. The peak at 42 ppm, predicted to be $\text{Ph}_3\text{P}=\text{Se}$,⁶⁷ persists in solution for the 300 °C and 300 10 m aliquots, with two additional peaks at $\delta \sim 28$ and 7 ppm which are present at the final aliquot for both reactions (**Figure C.16A**). Although it is still unclear of the identity for the 7 ppm signal, based on previous reports, the $\delta \sim 27$ ppm is attributed to $\text{O}=\text{PPh}_2\text{R}$ species, which was characterized in the final products with electron ionization gas chromatography mass spectrometry (EI GC-MS, **Figure C16B**). As expected, $\text{Ph}\bullet$ produced in solution when Ph_2Se_x

species decompose to release Se^0 , can strongly coordinate to P, thus favoring a *phosphorus trapping* mechanism, shown below simplified scheme below.

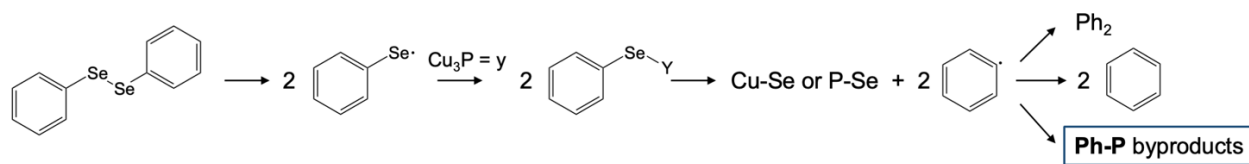
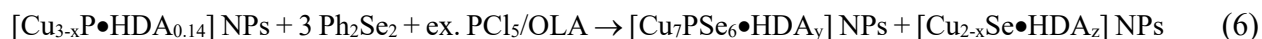


Figure 4.6. Schematic of Ph_2Se_2 transformation and reaction with Cu_3P once the PhSe-SePh bond is cleaved, where the phenyl radical byproduct can readily react with P and is competing with Ph_2 and benzene formation.

This is further confirmed with EI GC-MS for the ex-situ stoichiometric NMR reactions (**Figure C.17**), where the formation of phenyl-based P species are identified for the aliquots with ^{31}P NMR signals (**Figure C.18**). Importantly, from mass spectra, triphenyl selenide, $\text{Ph}_3\text{P=Se}$ was identified (**Figure 4.5B**), which is consistent with the ^{31}P NMR signal at 42 ppm.⁶⁷ Ultimately, the presence of P speciation highlights an attribute of R_2Se_2 precursors that has yet to be discussed in complex systems, which is that the radical byproducts of Se^0 incorporation can influence NP phase formation. Thus, to improve the understanding of R_2Se_2 precursors on NP phase formation one must consider the R byproduct, where herein, $\text{Ph}^\bullet$ has been shown to readily scavenge P.

4.3.3. PHOSPHORUS (P^{5+}) INCORPORATION TO INCREASE Cu_7PSe_6 FORMATION.

As a proof of concept to evaluate how Cu-P-Se phase formation can be influenced by the presence of P species in solution, additives such as triphenylphosphite (TPOP) and phosphorus pentachloride (PCl_5) were injected in a solution of Cu_{3-x}P NPs + 3 Ph_2Se_2 after the standard conditions were complete (300 °C for 30 min) and held for 15 min. This set of conditions (eq. 6) was chosen as it previously provided the best yield of Cu_7PSe_6 (**Figure 4.2A**).



The first experiment investigated the influence of TPOP, a formal P(3+), which must undergo a 2-electron oxidation to P(5+) for Cu₇PSe₆ formation. To that extent, a TPOP/hexadecane injection led to the formation of Cu_{0.87}Se and Cu_{2-x}Se binaries with slight differences in 2 θ , likely a result of a variation of x (i.e., oxidation to Cu 2+) or unit cell parameters,^{68,69} both of which indicate that multiple Cu-Se binary phases form with little Cu₇PSe₆ (**Figure C.19**). Two hypotheses explain the dynamics in solution, either the oxidation of P(3+) to P(5+) reduces the incorporation to form Cu₇PSe₆, or the release of P from P(OPh)₃ is limited as the O-Ph groups don't readily form favorable products that promote P reactivity with Cu_{2-x}Se.

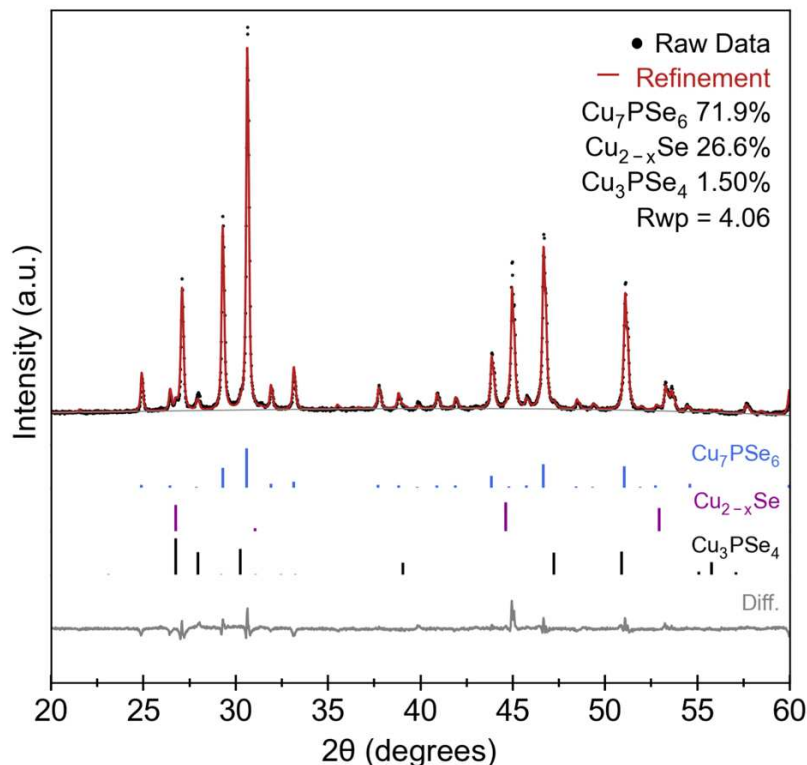


Figure 4.7. Rietveld refinement of the PXRD pattern for the PCl₅/oleylamine solution injection reaction into Cu_{3-x}P NPs + 3 equiv. Ph₂Se₂.

Alternatively, a PCl₅/oleylamine solution was injected into the 3 equiv. reaction (amine was used herein as it dissolves PCl₅), resulting in more Cu₇PSe₆ (71.9 wt. %) and minor Cu₃PSe₄ (**Figure 4.7**, refinement details in **Table C.2**), both of which indicate that additional P

incorporation was accomplished. The PCl_5/OLA precursor provides advantages to both previously stated TPOP hypotheses, due to a formal $\text{P}(5+)$ that doesn't require oxidation for Cu_7PSe_6 and the Cl^- ions can readily dissociate to form an ammonium complex with OLA, both promoting the formation of phosphorus phases over Cu-Se binaries. Time studies further demonstrate P delivery, where the injection of PCl_5 after 15 and 45 min (total 30 min and 1 hour reaction times, respectively) demonstrates further conversion to the Cu-P-Se phases, with only minor Cu-Se binaries (**Figure C.20**). In summary, phosphorus species are *trapped* in solution as Ph_2Se_2 thermalizes; however, when the equivalence with $\text{P}(5+)$ is balanced, one can controllably toggle across the Cu-P-Se phase space.

4.3.4. ADDITIONAL ATTEMPTS TO OPTIMIZE THE ABOVE PHOSPHORUS TRAPPING MECHANISM.

The complicated stoichiometries in eq. 1-3, caused by the Cu_{3-x}P NP precursor (requiring 7/3 equiv. with excess P and Se products), could potentially be avoided with the addition of molecular precursors. Brutchey et al. explored the synthesis of metastable CuInSe_2 phases with the use of $\text{Cu}(\text{oleate})_2$ and dialkyl diselenide precursors to form Cu-Se binary phases that alter CuInSe_2 phase formation post injection of InCl_3 at a specified temperature.³⁸ A similar strategy is employed here, where pre-synthesized $\text{Cu}(\text{oleate})_2$ (characterized with Fourier transform infrared spectroscopy, FT-IR, **Figure C.21A**) and R_2Se_2 (Bn_2Se_2 and Ph_2Se_2) were dissolved in OLA, and PCl_5 was injected at different temperatures, times, and other experimental parameters, all of which result in the formation of Cu_{1-x}Se and Cu_{2-x}Se binaries with no conversion to Cu_7PSe_6 (**Figure C.21B**). The limiting factor here in comparison to the CuInSe_2 synthesis, is poor diffusion of $\text{P}(5+)$ that can be attributed to more favorable interactions of $\text{P}(5+)$ with species in solution, thus trapping it before intercalation, or the large barrier of expelling $5-x$ Cu (compared to only $1-x$ Cu for CuInSe_2). As an alternative, CuCl was added to the one-pot syntheses, to balance the reaction for Cu_3P NPs + 4

$\text{CuCl} + 3 \text{R}_2\text{Se}_2$, but the presence of $\text{Cu}(1+)$ cations with Bn_2Se_2 or Ph_2Se_2 while heating to $300\text{ }^\circ\text{C}$ leads to only Cu_{2-x}Se for Ph_2Se_2 and only minor Cu-P-Se ternary phases for Bn_2Se_2 (**Figure C.22**). With the current set up (one-pot), when Ph_2Se_2 is used, incorporation of selenium doesn't occur until high temperatures suggesting that once this occurs it reacts very readily with CuCl before Cu_3P . With Bn_2Se_2 , the selenium is released at a lower temperature encouraging the interaction with both Cu_3P and CuCl . Both produce Cu-Se binaries that act as thermodynamic sinks, forming stable NPs, preventing the reincorporation of P. However, one key distinction that shall be considered in future reactions is balancing the reaction to capture the counterions of $\text{Cu}(1+)$ precursors, as well as exploring alternate experimental procedures such as, injection that could avoid the formation of Cu-Se binaries at lower temperatures. Ultimately, this indicates that the most promising route to isolate Cu_7PSe_6 is employing Cu_3P NPs and Ph_2Se_2 as precursors and controlling the proposed *phosphorus trapping* pathway.

4.4 CONCLUSION.

In conclusion, the influence of Ph_2Se_2 on Cu-P-Se phase transformation has been studied, where the reactivity of R_2Se_2 precursors promotes synthetic control over thermodynamic and metastable ternary phases. It was determined that diphenyl diselenide, Ph_2Se_2 , favors the formation of Cu_7PSe_6 over Cu_3PSe_4 , due to the result of $\text{PhSe}\bullet$ species in solution. To probe such a hypothesis, both temporal ex situ and *pseudo* in situ studies were utilized to monitor the degradation of Ph_2Se_2 in tandem with crystalline phase formation. What we observe is (i) Ph_2Se_2 thermalizes to Ph_2Se_1 , and (ii) the formation of a more phosphorus rich phase, Cu_3PSe_4 transforms to the less stable Cu_7PSe_6 phase, suggesting that a *phosphorus trapping mechanism* is driving the formation of the metastable phase. Ultimately, the results discussed herein provide an alternate perspective on the reactivity of R_2Se_2 precursors. The traditional outlook on R_2Se_2 reactivity

focuses on the C-Se vs Se-Se BDE, as this influences the efficiency of Se delivery and formation of Se radical species; however, the results herein demonstrate that the resulting byproduct radical species can readily react with other species in solution and significantly alter reaction pathways. Thus, the Cu_3P to Cu_7PSe_6 transformation pathway captured herein provide considerations when applying R_2Se_2 precursors to future chalcogenide systems.

4.5. Author Contributions

According to CRediT criteria, my contributions to this work included conceptualization, data curation, data acquisition, formal analysis, investigation, methodology, visualization, writing – original draft, and writing – reviewing and editing. Contributions by Luke T. MacHale included data acquisition (EI GC-MS and NMR), conceptualization, and editing. Contributions by Jake Tjalkens include data curation (performed reactions) and investigation. Contributions by Richard G. Finke included conceptualization and investigation. Contributions by Amy L. Prieto included conceptualization, visualization, investigation, and writing – reviewing and editing.

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CHAPTER 5: STRUCTURAL CHARACTERIZATION OF Cu_{3-x}P NANOPARTICLES AND INSIGHT INTO THE STOICHIOMETRIC REDUCTION OF TRIPHENYL PHOSPHITE EN ROUTE TO Cu_{3-x}P

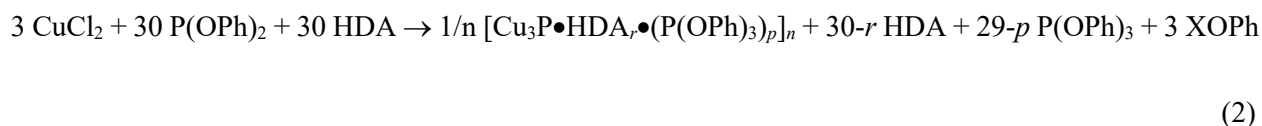
5.1. Introduction

Transition metal phosphide (TMP) are widely studied materials for applicable properties including tunable band gap energy,^{1–3} high theoretical capacity,⁴ and high catalytic activity^{5–10} make them attractive alternatives to scarce and expensive semiconductors. Particularly, copper phosphide, Cu_3P , has emerged as a material of interest for use in batteries,^{11–16} catalysis,¹⁷ oxygen and hydrogen evolution reactions,^{18–21} and supercapacitors.²² Originally analyzed in 1972, Olofsson et al. identified the Cu_3P structure ($\text{P6}_3\text{cm}$ space group) as substoichiometric, denoted as Cu_{3-x}P .²³ This inherent alteration from the 3 to 1 stoichiometric ratio of Cu:P has implications for the synthesis and properties with Cu_{3-x}P as precursors.²⁴ As material synthesis has adapted to isolate nanoparticles (NPs), structural complexity and compositional differences become even more important, due to larger variations in Cu_{3-x}P ($0.13 < x < 1.08$).^{23,25–30} Therefore, in order to further improve the application of Cu_{3-x}P , synthetic control of the x value needs to be more systematically controlled.

Traditional synthetic methods for Cu_{3-x}P nanoparticles (NPs) involve the use of solvothermal routes, where the use of Cu salts and elemental phosphorus are effective.^{31–37} However, elemental phosphorus is highly toxic and corrosive; thus, solution-based syntheses are desired and have been designed to yield colloidal Cu_{3-x}P NPs. Conventional routes to synthesize Cu_{3-x}P NPs employed the use of trioctylphosphine and trioctylphosphine oxide (TOP/TOPO) precursors.^{38–42} This has been extended to other organophosphines such as tris(trimethylsilyl)phosphine ($\text{P}(\text{SiMe}_3)_3$, TMS_3P),²⁸ tris(diethylamino)phosphine,²⁷ and aminophosphines,^{29,43} to develop materials with

more precise control over size, stoichiometry, and morphology. Although organophosphines are capable of producing a myriad of TMPs,^{3,44–47,30} the phosphorus precursor used herein, triphenyl phosphite (P(OPh)₃, TPOP), has recently been shown by Liu et al. to effectively produce Cu_{3-x}P as an inexpensive and non-toxic phosphorous source.⁴⁸

Triphenyl phosphite belongs to a class of organophosphites with the molecular formula P(OR)₃, where R is an aliphatic or aromatic group, (Ph = phenyl). From the Liu et al. study several TMPs of Ni, Co, Cu, Fe, and Mo, were synthesized with P(OPh)₃ using a solution-phase reaction method.⁴⁸ Despite the functionality and potential to isolate TMP materials,^{49–54} little research has been aimed at elucidating a disproof-based, mechanism for the conversion of P(OPh)₃ during NP formation, a reliable mechanism being an essential step to further develop systematic TMP NP syntheses.^{55,56} The Liu et al. study proposed a mechanism in which the presence of water was required to drive the reduction of phosphorous (eq. 1). However, the proposed synthetic conditions involve the preparation of the reaction in an inert atmosphere using an anhydrous metal precursor. Additionally, the stoichiometric equivalents used are inconsistent with the proposed reaction mechanism, where a 29-equivalent excess in phosphorous is noted after Cu₃P is formed, given in eq. 2 (XOPh group is proposed as a byproduct of P incorporation for simplification even though this was not characterized by Liu et al.).



However, alternative studies have investigated the possible formation pathways of nickel phosphide (Ni₂P) and indium phosphide (InP) to decipher the transformation of P(OPh)₃ in solution.^{55,56} The data on the Ni₂P system provided data on the effect of organophosphite precursor

reactivity on nanofabrication.⁵⁵ A series of R groups on P(OR)₃ increasing in steric hindrance were used to devise 5 possible mechanisms, involving coordination of the phosphite to the metal to cleave the P-O bond, homolytic and heterolytic cleavage of the P-O bond prior to M-P coordination, and beta-hydride elimination to produce PH₃. All of these proposed mechanisms were disproven except for the mechanism requiring organophosphite coordination to the metal center that then undergoes intramolecular rearrangement to form a XOR byproduct (X is a halide, amine, or acetate). Additionally, a study by Lee et al. characterized P(OPh)₃ byproducts en route to InP formation, demonstrating that OLA initially reacts with P(OPh)₃, making amine-phosphite complexes that promote effective P incorporation. Finally, relevant to the Liu et al. synthesis is the work by Stone et al.,⁵⁷ who recently demonstrated the effect of Cu(X)₂ precursors on the Cu_{3-x}P pathway, which attributed CuCl₂ to a *direct* Cu_{3-x}P formation pathway compared to initial Cu(0) particle formation.

However, two main considerations for the previous studies and the initial study by Liu et al., is the use of a stoichiometric reaction and simplified synthesis that omits other reagents that can react with P(OPh)₃, both of which can impede one's ability to understand how P(OPh)₃ reacts to incorporate P in the final NPs. Although the Liu et al. synthesis is robust and reproducible, there remains several issues with the proposed synthesis.

1. The current reaction conditions require an excess amount of P(OPh)₃ and HDA (eq. 2).
2. The transformation of P(OPh)₃ from a formal P³⁺ to P³⁻ charge is unknown.
3. There is little evidence to show if so, then how P(OPh)₃ is interacting with the metal precursors before the P bonds are installed.

Therefore, the work presented herein provides the crucial first steps and data to examine the previously stated problems with the Liu et al. synthesis. In order to strategically approach this

problem, the original synthesis will be characterized with a robust suite of structural techniques to better define the Cu_{3-x}P NP composition. Three reactions will then be proposed based on literature precedence of similar phosphorus precursor transformation pathways^{29,43,55,58,59} and the corresponding Cu:P ratios will be tested to determine the impact on Cu_{3-x}P phase purity. Finally, the crucial next steps, considerations, and experiments will be discussed to establish an atom-economical, stoichiometric synthesis of Cu_{3-x}P NPs with a more defined understanding of the structural parameters.

5.2. Experimental

5.2.1. MATERIALS AND PREPARATION.

Anhydrous copper (II) chloride (CuCl₂, 99%, Sigma Aldrich), hexadecylamine (HDA, Sigma Aldrich, 90%), triphenyl phosphite (TPOP, 97%, Oakwood Chemical), chloroform (CHCl₃, 99.8%, Sigma Aldrich), isopropanol (IPA, 99.5%, Fischer Scientific), hexanes (98.5%, Sigma Aldrich), toluene (99.5%, Sigma Aldrich), and ethanol (99%, Fischer Scientific) were used as packaged and received. 1-Octadecene (ODE, 90% Technical grade, Sigma Aldrich where the impurities are 2-octyl-1-decene, 2-butyl-1-tetradecene, 2-hexyl-1-dodecene, n-octadecane) and octadecane (ODA, 99%, Fischer Scientific) were sparged with N₂ for 2 hours (hr) before being used. All reactions were performed in a N₂ glovebox (O₂ < 0.1 ppm, H₂O < 0.1 ppm) unless specified otherwise. Post-synthesis solvent washing was performed in ambient conditions on the benchtop. All glassware was cleaned using a base and acid bath wash, followed by rinsing with Millipore water and dried in a 160 °C oven overnight.

5.2.2 STANDARD SYNTHETIC CONDITIONS.

All reactions were prepared in a N₂ glovebox and performed on a Schlenk line under N₂. To a 50 mL, 3-neck-round-bottom flask, CuCl₂, HDA, TPOP, and the solvent (ODA or 1-ODE) were

added. The ratios of the reagents and volume of the solvent were altered depending on the reaction being performed. The 3-neck-round-bottom flask was equipped with a magnetic stir bar, thermal couple, condensor tube, and septa to seal all openings. After preparation in the glove box, the reaction flask was placed on a heating mantle set to 30 °C and constant stirring to dissolve all reagents. Once all reagents had dissolved, the reaction was heated to 150 °C and maintained at that temperature for 1 hour. After 1 hour at 150 °C, the reaction was then heated to 300 °C and maintained at that temperature for 30 minutes. The reaction was left to cool naturally and quenched at 80 °C in air, into four centrifuge tubes. The resulting mixture was centrifuged to separate the particles from the supernatant. The supernatant was collected in a vial for characterization. The particles were washed in a 1:4 mixture of chloroform and isopropanol. The particles were sonicated in the washing mixture and then separated using a centrifuge. The washing process was repeated 3 times and the resulting particles were left to dry in a capped centrifuge tube.

5.2.3 CHARACTERIZATION.

Powder X-ray Diffraction (PXRD) and Rietveld Analysis.

Powder X-ray Diffraction Spectroscopy (PXRD) was performed on a Bruker D8 Discover Series using a Cu K α source ($\lambda = 1.54 \text{ \AA}$) and a Lynxeye XE-T positron-sensitive detector. Samples were prepared by dispersing the particles in hexanes, followed by drop-casting on a p-type boron-doped Si Zero Diffraction Wafer (MTI Corporation). Ground samples were first dispersed in hexanes, deposited on the Si Wafer, and scraped with a razor blade into mortar and pestle which was ground for ca. 5 min. The samples were then transferred to the diffraction wafer that contained zero-diffraction grease to reduce preferred orientation. For amorphous content quantification, after the sample was ground, Al₂O₃ was added and weighed to determine the exact mass of Al₂O₃. Then when refining the PXRD patterns, Al₂O₃ and the phases present in the sample were fit. The weight

of Al_2O_3 that was previously massed out was added to the refinement program, which then provides the wt. % of amorphous content. This is ultimately the percent of material that is not crystalline. Diffraction patterns were indexed using the DIFFRAC.EVA software v5.2 to known powder diffraction files (PDF) patterns in the PDF-4+ database. The PDF patterns used for the following phases are: Cu_3P #01-071-2261, Cu #00-004-0836, Al_2O_3 #00-046-1212. Refinements were performed using TOPAS v6 (Bruker AXS). Specific parameters are included for the selected patterns below.

Nuclear Magnetic Resonance.

^1H , ^{13}C , and ^{31}P NMR experiments were performed on the reaction supernatants in deuterated chloroform (CDCl_3 , Thermo Scientific, 99.8%, dried over activated 3 Å molecular sieves) on a Bruker NEO400 spectrometer with automated tuning. Data was processed in the MestReNova, v. 15.0.1.

UV-Vis Spectroscopy.

UV-Vis was performed on the complexes using a Cary UV-Vis 4000 Spectrometer. All UV-Vis experiments were prepared in a glove box under N_2 and transferred to an air-free cuvette before UV-Vis analysis outside the glove box.

Transmission Electron Microscopy (TEM) Imaging and Energy Dispersive Spectroscopy (EDS) Analysis.

The morphology of the nanoparticles were characterized using a JEOL JEM 2100F Transmission Electron Microscopy (TEM) with acceleration voltage of 200 keV. Scanning (STEM) energy dispersive X-ray spectroscopy (EDS) was carried out with an Oxford X-Max 80 mm^2 detector and analyzed using AZtecTEM software. Samples were prepared by sonicating one centrifuge tube of particles (ca. 10 mg) with one mL of toluene and hexanes for one minute. 0.1 mL of the particle dispersion was further diluted with 1 mL of toluene, making a 1:10 ratio, which was sonicated for

another 5 minutes at 35 °C. Finally, 14 mL of hexanes was added to the solution and sonicated for another minute. Carbon-coated nickel TEM grids (200 mesh, Ted Pella) were dipped into the diluted mixture and dried once removed by touching the grid with a Kimtech Kimwipe. The grid is then dried in the fume hood overnight and pumped down under vacuum for 30 minutes before imaging. Images were analyzed in Digital Micrograph of the Gatan Microscopy Suite software (v3.51).

Elemental Analysis.

The elemental composition of Cu_3P was performed by an external company, Galbraith Laboratories Inc. Nitrogen was first analyzed with combustion techniques, then the particles were digested with concentrated nitric acid. Copper and phosphorus were analyzed with inductively coupled plasma – optical emission spectroscopy (ICP-OES) and flame atomic absorption (FLAA). All samples were handled under nitrogen.

X-ray Photoelectron Spectroscopy.

X-ray photoelectron spectroscopy was performed on a Physical Electronics ESCA 5800 system using a monochromatic Al $K\alpha$ ($E = 1486.6$ eV) X-ray source for all scans. High resolution scans were used to analyze all possible elements: carbon 1s, oxygen 1s, nitrogen 1s, phosphorus 2p, and copper 2p. CasaXPS was used to process the data. All spectra were calibrated using the aliphatic carbon peak at 285 eV. Fitting utilized a Shirley background and gaussian line shapes for all peaks. Photoelectrons for the copper 2p and the phosphorus 2p showed split peaks were fit using position and area constraints of known values.

5.3. Results and Discussion

5.3.1. STANDARD 1:10:10 REACTION.

Copper phosphide, Cu_{3-x}P , nanoparticles were first synthesized using the reaction conditions described by Liu et al.⁴⁸ Of note, all reactions discussed from here on out will be referenced by the ratio of reagents ($\text{CuCl}_2\text{:HDA:P(OPh)}_3$) unless otherwise specified. Generally, the one-pot reaction produces a blue mixture at room temperature that then transitions to light yellow color once 150 °C is reached, which is attributed to reduction of Cu(II) to Cu(I) and coordination of TPOP and HDA.^{48,57,60–62} Nucleation of Cu_{3-x}P particles was observed at temperatures above 280 °C, as indicated by a darkening of the reaction mixture. Although exact reaction conditions aren't outlined by Liu et al., 300 °C for 30 minutes are used herein, which reproducibly produces phase pure Cu_{3-x}P NPs by powder X-ray diffraction (PXRD, **Figure 5.1**).

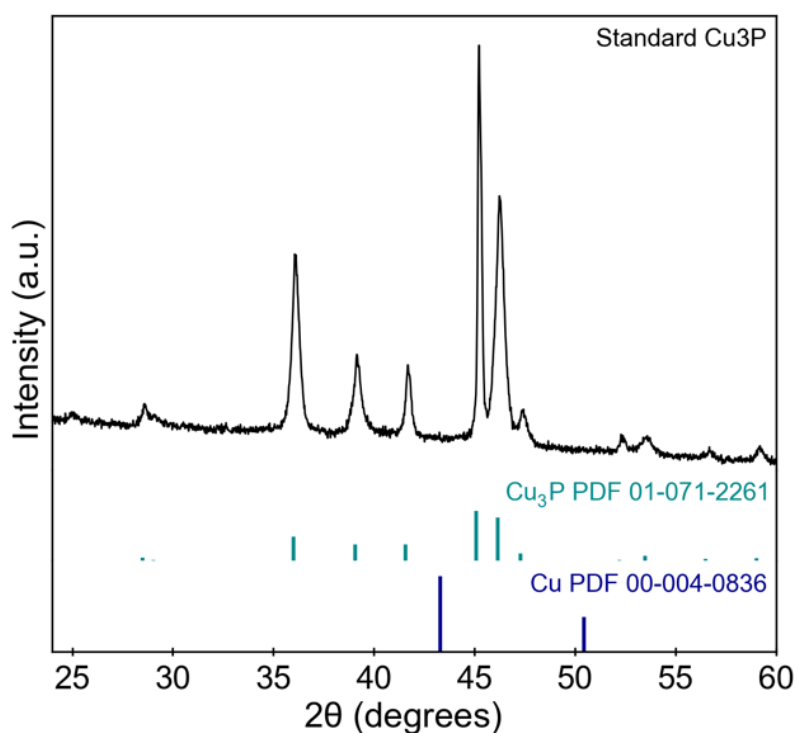


Figure 5.1. Powder X-ray diffraction (PXRD) pattern of standard synthetic conditions from Liu et al. with a precursor ratio of 1:10:10.

Ligand identity and coverage was determined in a previous publication by our group, identifying hexadecylamine as the L-type ligand with ca. 15 wt % of the Cu_3P NPs being contributed to organic content,²⁴ which is consistent with Liu et al. preliminary Fourier-transform

infrared-spectroscopy (FT-IR) data on conjugated phosphide materials.⁴⁸ Along with surface characterization, Cu_{3-x}P particles were identified to be hexagonal sheets with an average size and dispersion calculated to be 102 ± 21.7 nm along the diagonal axis, **Figure B.28**. However, upon closer examination of the Cu_{3-x}P NP composition via scanning TEM/energy-dispersive X-ray spectroscopy (STEM/EDS) indicates an atomic ratio of Cu to P as low as 1.53 along the top-down view and 1.38 for the lateral side – a significant alteration of what has been reported on previously for the exact value of x in Cu_{3-x}P (**Figure 5.2**).

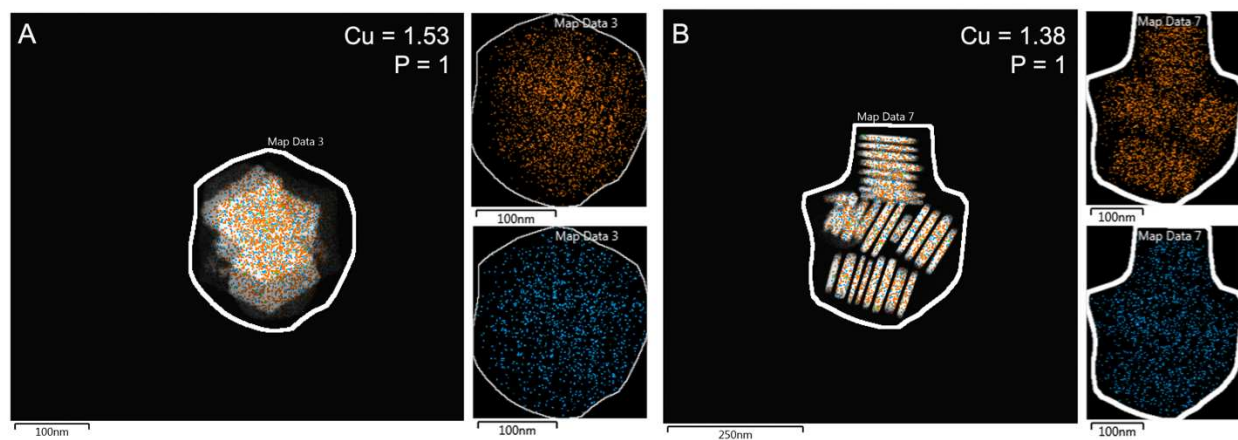


Figure 5.2. Scanning transmission electron microscopy (STEM) – energy dispersive X-ray spectroscopy (EDS) of the standard synthetic conditions from Liu et al. (A) is a top down view giving a Cu:P ratio of 1.53:1.00 and (B) is the side view with a Cu:P ratio of 1.38:1.00.

To further decipher the artifact of substantially high Cu vacancies, elemental analysis performed with ICP-OES further confirms the Cu:P ratio (**Figure 5.3A**), with two separate trials producing 1.59:1.00 and 1.20:1.00 ratios. The significant deviation from stoichiometric Cu_3P was further probed with X-ray photoelectron spectroscopy (XPS) of the 3d and 2p binding regions for Cu and P, provided in Chapter 3 (**Figure 3.5**). From the two regions, the raw area for the Cu and P representative peaks were converted to an atomic %, giving a 1.28:1.00 ratio (**Figure 5.3B**), which is consistent with the previous data. Of note, surface chemistry plays a pivotal role in XPS, which provides insight into the possible contribution of organic species at the surface that can be

affecting the Cu:P ratio. Finally for the structural characterization, the amorphous content was analyzed via PXRD and Rietveld^{63–66} refinements to probe the quantity of non-crystalline material (**Figure 5.3C**). To perform such calculations, the Cu_{3-x}P material was spiked with dried aluminum oxide, Al₂O₃, to quantify the percent of crystalline material compared to the standard. From such, 37.5 wt. % of the sample was determined to be crystalline Cu_{3-x}P, while 62.5 wt. % is amorphous amount. Given that the thermogravimetric results in Chapter 3 (Figure 3.5) attributed 15 wt % of the Cu₃P particles to organic content (HDA ligands), it is likely that the amorphous content is due to both organic content on the surface *and* amorphous species, either Cu-P analogs or surface oxides.

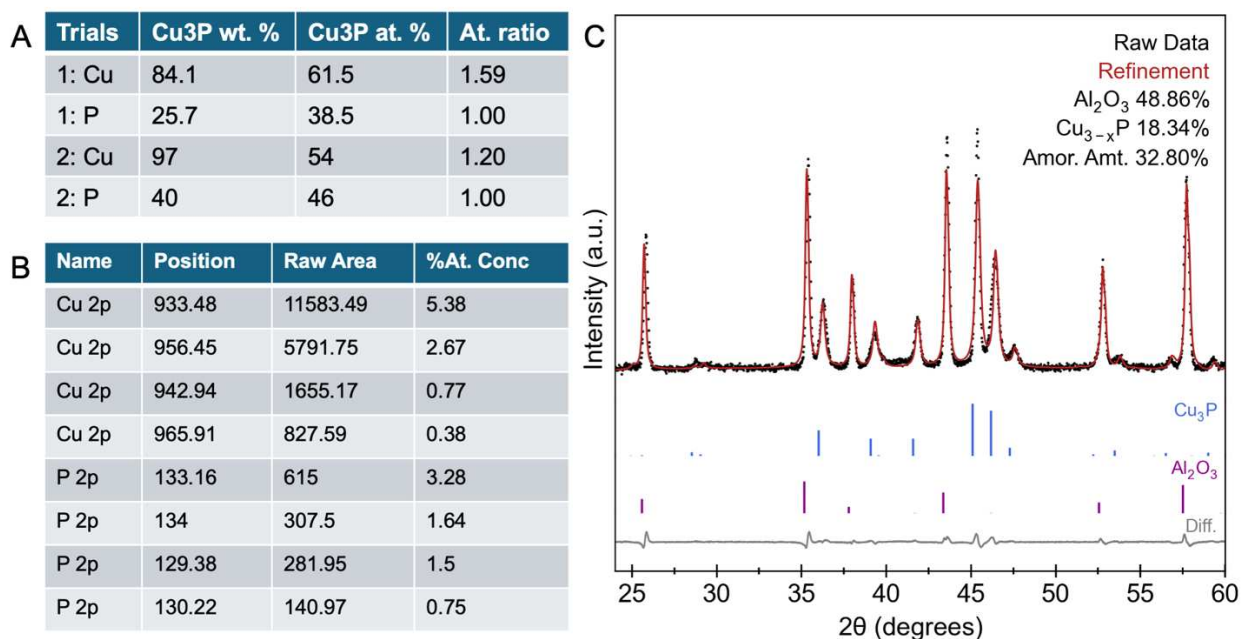


Figure 5.3. Elemental composition analysis of standard 1:10:10 reaction. (A) Elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES). (B) Peak integration of XPS spectra in Figure 3.5 to quantify the percent of Cu and P, resulting in a 1.28:1.00 ratio. (C) Amorphous content quantification with PXRD and Rietveld refinements fitting to a standard Al₂O₃ crystalline material.

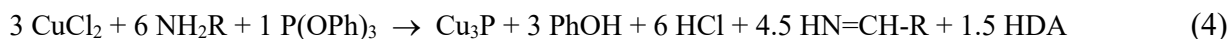
We, therefore, hypothesize that the low atomic percentage of Cu is due to the non-stoichiometric equivalents (29 excess P(OPh)₃, eq. 2) of starting precursors that simultaneously

contaminates the final Cu_{3-x}P NPs and complicates characterizing the formation pathway of Cu_{3-x}P (degradation of $\text{P}(\text{OPh})_3$). Although the drawbacks of the 1:10:10 synthesis have already been addressed, the consistency of phase pure Cu_{3-x}P NPs produced by the standard reaction provides a general framework that will be reference point for the following observations that will guide this investigation into the role of $\text{P}(\text{OPh})_3$.

5.3.2. STOICHIOMETRIC REACTION ANALYSIS.

To address the issue of Cu_{3-x}P composition, the stoichiometric equivalents of $\text{P}(\text{OPh})_3$ and hexadecylamine (HDA) will be reduced and simplify, which will also provide preliminary data into the reduction pathway of $\text{P}(\text{OPh})_3$ en route to forming Cu_{3-x}P NPs. The investigation into the role of TPOP begins with previous research conducted on similar TMP syntheses and the reaction pathways that could be applied to Cu_{3-x}P stoichiometric syntheses explored herein. The first synthetic approach explores the mechanism of InP nanocrystal formation using tris(dimethylamino)phosphine ($\text{P}(\text{NMe}_2)_3$) as the phosphorus source.^{58,59} Buffard et al. used techniques such as ^{31}P -NMR and mass-spectrometry (MS) to gain insight into In–P bond formation, which revealed that a 1:4 ratio of indium to phosphorus (In:P) precursors resulted in the greatest yield of InP particles (70%). An initial transamination step occurs to produce a fully substituted $\text{P}(\text{NHR})_3$ group that then coordinates to the InCl_3 -OLA complex followed by an acid/base reaction releasing 1 equivalent of $[\text{RNH}_3^+]\text{Cl}^-$. What follows is an essential redox reaction in which 1 equivalent of phosphorus is reduced to P^{3-} via oxidation of 3 equivalents to P^{5+} . A similar disproportionation mechanism was also reported for the synthesis of Cu_{3-x}P using $\text{P}(\text{NEt}_2)_3$ as the phosphorous source and $\text{Cu}(\text{I})\text{Cl}$ as the metal precursor. Overall, the provided studies set ample precedent for a proposed disproportionation mechanism (eq. 2). Alternatively, two pathways are proposed based on the previously discussed work from Andaraarachchi et al. An

intramolecular rearrangement mechanism which involves P(OPh)_3 coordination to the metal center, followed by concerted rearrangement of the P–O and M–X bonds ($\text{X} = \text{Cl}$, acetate, or oleylamine) to form M_xP_y and PhOX (eq. 3). Finally, the last pathway involves homolytic bond cleavage of the P–O bond followed by reaction with the metal precursor, forming M_xP_y and a $\bullet\text{OPh}$ species, that can readily scavenge $\text{H}\bullet$ species in solution to produce phenol (eq. 4). The described reactions are provided below.



As an upfront control to ensure that the reaction stoichiometries aren't plagued with impurities from the solvent, octadecene (ODE) was replaced with octadecane based on the findings in the previous chapters.²⁴ Additionally, considering the unfavorable formation of PhOCl compared to PhOH , we hypothesized that the 3:3:4 and 3:6:1 ratios would be the most probable stoichiometries to produce Cu_{3-x}P . This was ultimately confirmed with PXRD, which demonstrated phase pure Cu_{3-x}P particles for 3:3:4 and only minor conversion for 3:6:1 (Figure 5.4). To further probe the 3:6:1 stoichiometric reaction, dihydroanthracene (DHA) was employed as a more efficient source of $\text{H}\bullet$ compared to the linear, aliphatic backbone of HDA or ODA, which drastically improved the purity of Cu_{3-x}P with only negligible $\text{Cu}(0)$ remaining. Thus, the 3:3:4 and 3:6:1:1.5 (1.5 of DHA for 3 $\text{H}\bullet$) data will provide the basis to developing a more stoichiometric synthesis of Cu_{3-x}P NPs.

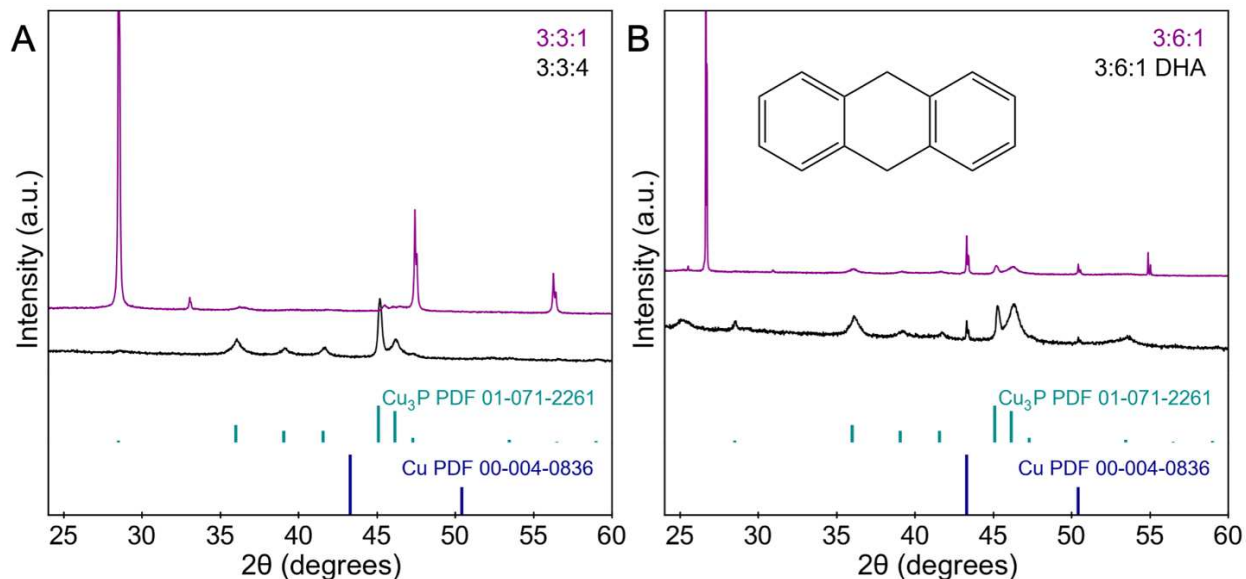


Figure 5.4. PXRD subplots for the proposed stoichiometric reactions in eq. 2-4. (A) Represents the 3:3:4 and 3:3:1 that contains organics that aren't indexed. (B) Represents the 3:6:1 and 3:6: with 1.5 equiv. of DHA.

To understand the reaction pathways, the solution dynamics need to be probed to decipher the role of the individual precursors and determine if the products are consistent with the previously proposed reactions (eq. 2-4). To do so, the 1:10:10 reaction supernatant was first evaluated with ¹H and ³¹P NMR, both of which demonstrate the presence of excess TPOP and HDA, further confirming the non-stoichiometric synthesis that could be contaminating the final NPs. Additionally, the transformation of species in solution is difficult to capture, as many reactions can result at such a high excess of precursors.

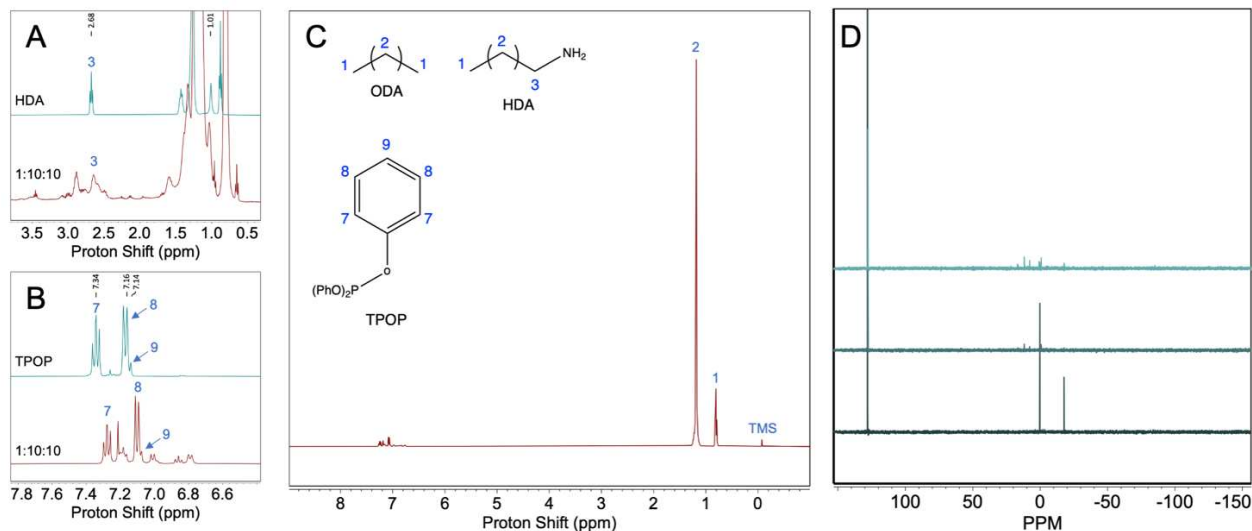


Figure 5.5. NMR characterization of the 1:10:10 reaction conditions. (A) ^1H NMR of the 3.6 to 0.5 ppm region to identify the HDA peaks. (B) ^1H NMR of the aromatic region to identify TPOP peaks. (C) overall ^1H NMR spectrum. (D) ^{31}P NMR of $\text{P}(\text{OPh})_3$ as a standard (bottom), 1:10:10 standard reaction (middle), and a 1:10:10 concentrated reaction (top), all demonstrating remaining $\text{P}(\text{OPh})_3$ by the peak at 128 ppm.

A similar approach is taken for the 3:3:4 and 3:6:1 reactions, for a simplified outlook on the products formed. Initially, the transformation of hexadecylamine was captured in solution to determine the influence of dissociated Cl^- ions on the amine products. In Figure 5.6A and B, the signal corresponding to the $\alpha\text{-CH}_2$ group of HDA (peak 3, blue) was not observed in the ^1H -NMR spectra of the 3:3:4 or 3:6:1 reaction supernatants. The decrease of the ^1H shift corresponding to the $\alpha\text{-CH}_2$ group of HDA suggest a change in hybridization of the $\alpha\text{-sp}^3$ carbon of HDA, resulting in a 1° or 2° imine. Thus, a hypothesized 2° imine, aldimine, is predicted to be the resulting speciation shown in Figure 5.6C, with the corresponding $\dagger$ signal predicted to be obscured by the many other peaks at ca. 7.5 ppm. Regardless, it is clear that the primary amine is being oxidized in the stoichiometric reactions. The donation of hydrogen atoms in solution can be attributed to either to the reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ or the formation of PhOH in eq 4. However, considering

the 3:3:4 spectrum demonstrates the absence of α - sp^3 carbon in HDA (Figure 5.6A), this process is likely due to the Cu(II) reduction step.

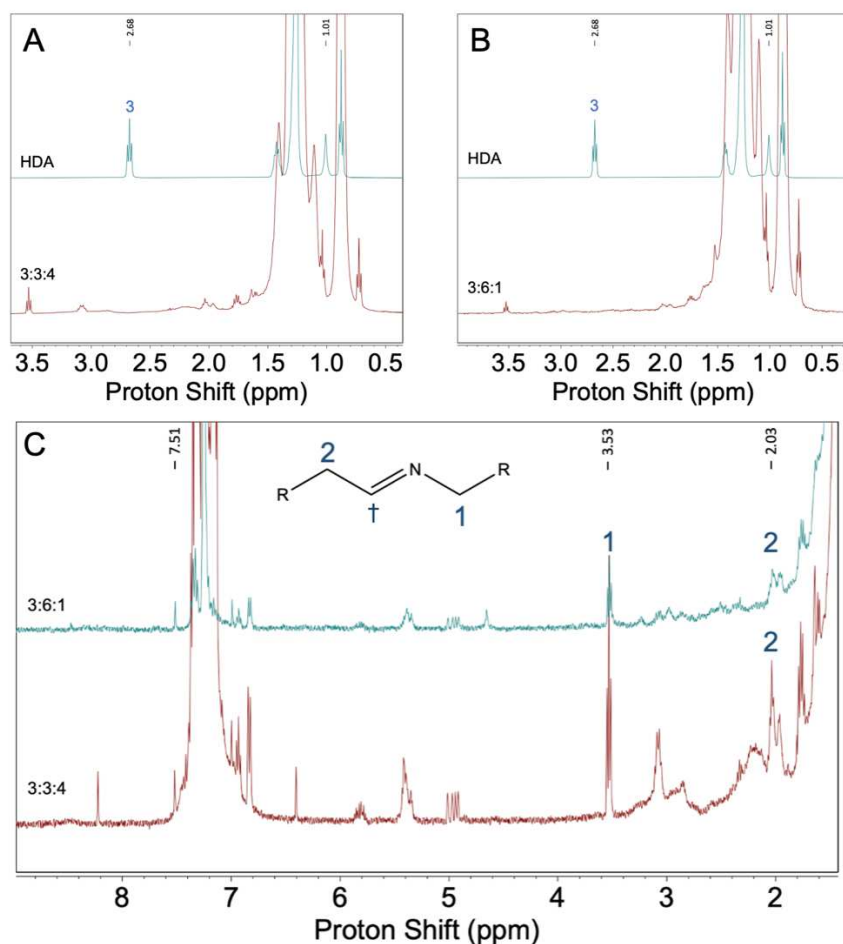


Figure 5.6. ^1H NMR spectra of the (A) 3:3:4 and (B) 3:6:1 reactions to identify the HDA transformation in solution. (C) ^1H NMR spectra of 8.5-1.5 ppm to demonstrate the absence of a primary amine to a proposed imine.

The solution is further explored with ^{31}P to determine the crucial question of whether $\text{P}(\text{OPh})_3$ remains in solution or has fully reacted to the proposed species in eq. 2-4. **Figure 5.7A and B** provides the ^1H NMR spectra for the 8.0-6.5 ppm region of the 3:3:4 and 3:6:1 reactions. For 3:3:4, the peaks corresponding to $\text{P}(\text{OPh})_3$ (7, 8, 9 in **Figure 5.5C**) persist in solution, suggesting that either the $\text{P}(\text{OPh})_3$ doesn't fully convert, or a phosphorus analog is formed as a byproduct of P incorporation (i.e., a phosphonium complex similar to what's provided in eq. 2). The presence of

P byproducts is supported in Figure 5.7C, where two phosphorus signals are identified at 0 and -17 ppm. Based on literature precedence, these two environments are either oxide byproducts of the species formed in situ, considering the reaction supernatant was worked up in air, or remaining oxide impurities from $\text{P}(\text{OPh})_3$.^{67,68} Importantly, for the 3:6:1 reaction, the aromatic region substantially deviates from the $\text{P}(\text{OPh})_3$ standard (Figure 5.5B), and the absence of P species is captured in both 3:6:1 and 3:6:1:1.5. Ultimately, the findings of the P byproducts supports that a more stoichiometric reaction is being established, where P is being efficiently delivered without being littered with excess $\text{P}(\text{OPh})_3$.

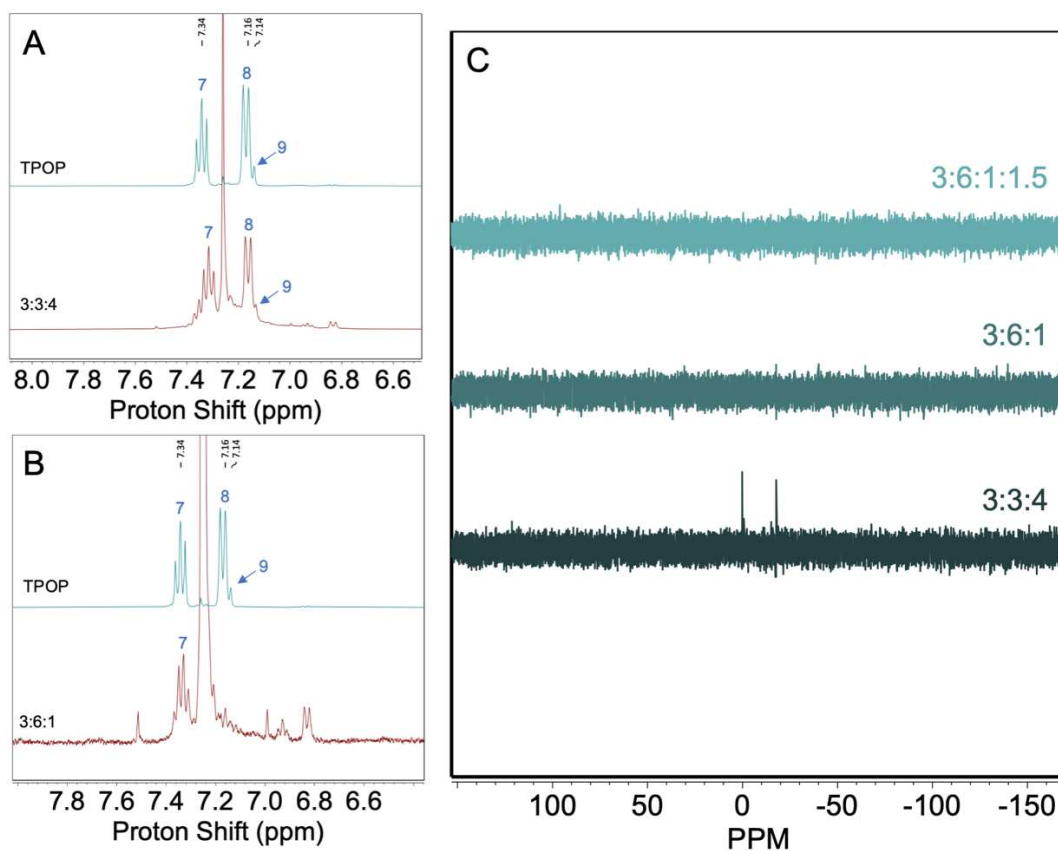


Figure 5.7. ^1H NMR spectra of the (A) 3:3:4 and (B) 3:6:1 reactions to identify the $\text{P}(\text{OPh})_3$ transformation in solution. (C) ^{31}P NMR of the 3:3:4 (bottom), 3:6:1 (middle), and 3:6:1:1.5 (top) all at four-fold concentrated to the standard synthetic conditions.

However, the data provided herein, is only the first step in deciphering the reaction pathway and approaching a sound stoichiometric reaction that can be probed with mechanistically to devise the role of P(OPh)_3 and HDA en route to forming Cu_{3-x}P NPs. The structural characterization proving the deviation from the experimentally and theoretically predicted Cu_{3-x}P composition has significant implications on the use of this material from an application standpoint or as a precursor for NP syntheses. Therefore, to improve the Cu_{3-x}P material and understand the reduction of P(OPh)_3 , the following considerations, experiments, and necessary future directions are discussed below.

5.4. Necessary Future Directions to Establish a Complete Mechanistic Understanding.

The first step to approach this seemingly simple, but mechanistically complex, transition metal nanoparticle synthesis is to thoroughly characterize the first reduction event at 150 °C. Identifying the Cu(I) complexation is essential to determine the reduction events that must occur for the required Cu-P bonds to be installed. As previously stated, a color transition from blue to a pale yellow is seen and identified as the reduction of Cu(II) to Cu(I), **Figure 5.8A**. Preliminary data to characterize the reduction event has been conducted with air-free UV-Vis spectroscopy experiments on the 1:10:10, 3:3:4, and 3:6:1 reaction mixtures to characterize the complexes present before and after copper reduction (**Figure 5.8B and C**).

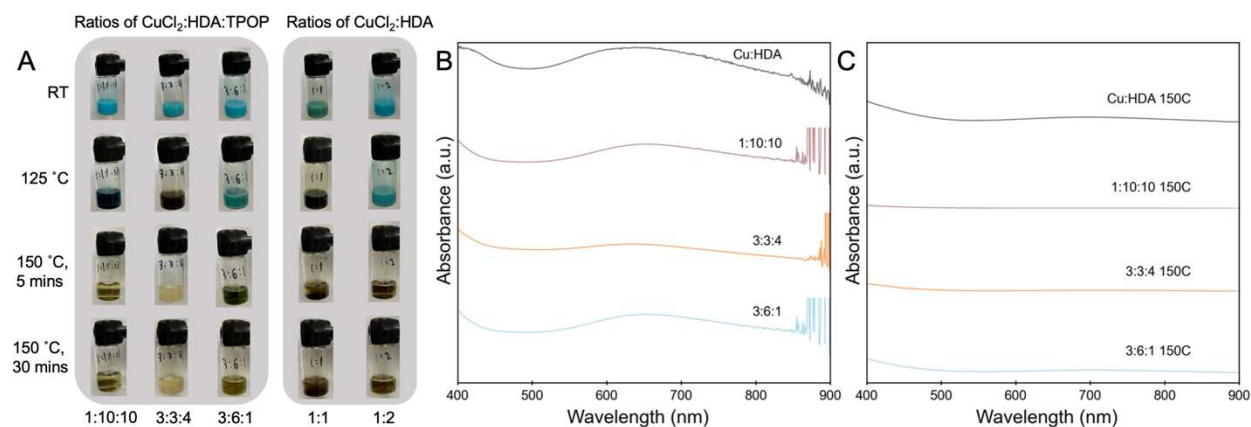


Figure 5.8. Characterization of the Cu(II) reduction event to Cu(I). (A) Images to identify the color transitions at different precursor ratios as a function of temperature. (B) UV-Vis spectra of the stoichiometric ratios (identified by the color of the subplot) and (C) the UV-Vis spectra at 150 °C.

A mixture containing a 1:2 ratio of CuCl₂:HDA was also analyzed as a control. Of note, a mixture containing CuCl₂ and P(OPh)₃ was also prepared but was not analyzed as CuCl₂ failed to dissolve in the absence of HDA. At room temperature, all mixtures analyzed exhibited a broad peak at roughly 650 nm (**Figure 5.8B**). This peak is less apparent in the 3:3:4 mixture, suggesting that more than one equivalent of HDA coordinates to Cu(II) at room temperature. The mixtures were then heated to 150 °C and maintained at that temperature until each mixture exhibited their respective color transition. After the color transition at 150 °C, the broad peak at 650 nm disappears for all mixtures analyzed, which is hypothesized to be the reduction of Cu(II) to Cu(I) (**Figure 5.8C**) based on previous literature.^{60,62} Although the UV-Vis spectroscopy is a great first attempt, in situ molecular characterization techniques are required to fully capture the Cu complexation at 150 °C, due to the reversible oxidation that can occur when cooled to RT. Particularly, an in situ ¹H NMR probe could be used, as the paramagnetic Cu(II) complex will transition to a diamagnetic Cu(I) that will allow for identification of the responsible redox species. Although the data provided above investigates the reduction event at 150 °C, it is important to note that the coordination of

P(OPh)₃ and Cu(I) has been thoroughly studied, which has been shown to form complexes such as, [CuCl(P(OPh)₃)]₄⁶⁹ and [Cu₂Cl₂(P(OPh)₃)₄].^{70,71} From such findings, the Cu(I) complexes that form at 150 °C and throughout the entire heat up procedure (before Cu_{3-x}P formation), must be extensively followed to provide insight into both the stoichiometry and future mechanisms.

Once the Cu(I) complexation and speciation is analyzed throughout the temperature gradient, the proposed reactions (eq. 2-4) will need to be revisited to account for a two-step mechanism. Additionally, the byproducts of Cu_{3-x}P NP formation need to be analyzed with the already employed techniques while keeping the reaction supernatant air-free, as the proposed species can decompose to oxide analogs. As a proof of concept, NMR-tube reactions can be conducted, similar to the studies in Chapter 4, where even though ex-situ the reaction and therefore P decomposition can be tracked as a function of time. Analysis of the byproducts will also need to be expanded to techniques such as, mass spectrometry, due to the ability to separate the complex solution chemistry and the depth of structural information one can receive. Finally, and already underway, in situ ³¹P NMR where the solution can be heated to experimental conditions (300 °C), will allow for the TPOP transformation to be tracked as well as the subsequent Cu_{3-x}P NP formation.

Once the optimal, stoichiometric conditions have been established, the structural characterization that was highlighted in this Chapter will need to be conducted. This will, (1) test whether the significant deviation from stoichiometric Cu₃P is attributed to the surface contamination from the non-stoichiometric excess, and (2) if the surface chemistry is simplified and precisely quantified, the elemental composition can be calculated that will improve the stoichiometry of Cu-P-Se syntheses.

5.5. Conclusion.

The work presented herein provides more thorough structural characterization for the Liu et al. synthesis and preliminary insight into the stoichiometric reduction of TPOP en route to forming Cu_{3-x}P NPs. Importantly, we provide a perspective on the necessary directions and experiments that are required to develop a more complete mechanistic understanding. Ultimately, the copper phosphide literature is comprised of various synthetic approaches and thorough pathway studies that have led to better understanding of Cu_{3-x}P . However, it is necessary to understand and improve the Liu et al. synthesis as it is a crucial, retrosynthetic synthon for the Cu-P-Se phases and precursor for InP cation exchange syntheses. Additionally, as triphenyl phosphite is a cheap, green phosphorus precursor, it is of interest to determine the P reduction mechanism so that future systems can systematically develop a synthesis.

5.6 Author Contributions

According to CRediT criteria, my contributions to this work included conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft, and writing – reviewing and editing. Contributions by Alden Spigel included data curation (experiments), formal analysis (UV-Vis and ^1H NMR), and writing – original draft. Contributions by Amy L. Prieto include writing – reviewing and editing.

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CHAPTER 6: SUMMARY AND OUTLOOK FOR THE Cu_3PSe_4 AND Cu_7PSe_6 REACTION LANDSCAPE AND ALTERNATE BINARY SYSTEMS

6.1. Summary

The work presented herein is aimed at making strides in understanding reaction pathways in colloidal chalcogenide nanoparticle (NP) syntheses (**Figure 6.1**). Significant progress was made capturing the transformation pathways of the Cu_3PSe_4 synthesis with Se/ODE (Chapter 2) and establishing a near-stoichiometric, atom-economical synthesis of Cu_3PSe_4 (Chapter 3).¹ A metastable phase, Cu_7PSe_6 , was also targeted in high weight percent, where the byproduct of the diphenyl diselenide precursor traps phosphorus in solution (Chapter 4). Finally, preliminary structural characterization and mechanistic data is provided on the current best precursor, copper phosphide, Cu_3P , (Chapter 5). However, there is still much to be desired in the presented Cu-P-Se phase space. Thus, the following Chapter outlines the questions and synthetic ideas that we have determined to be most essential going forward, as well as preliminary research on AgP_2 and Ag-P-Se materials that to date have yet to result in the ability to isolate phase pure nanoparticles that provides the foundations for future research.

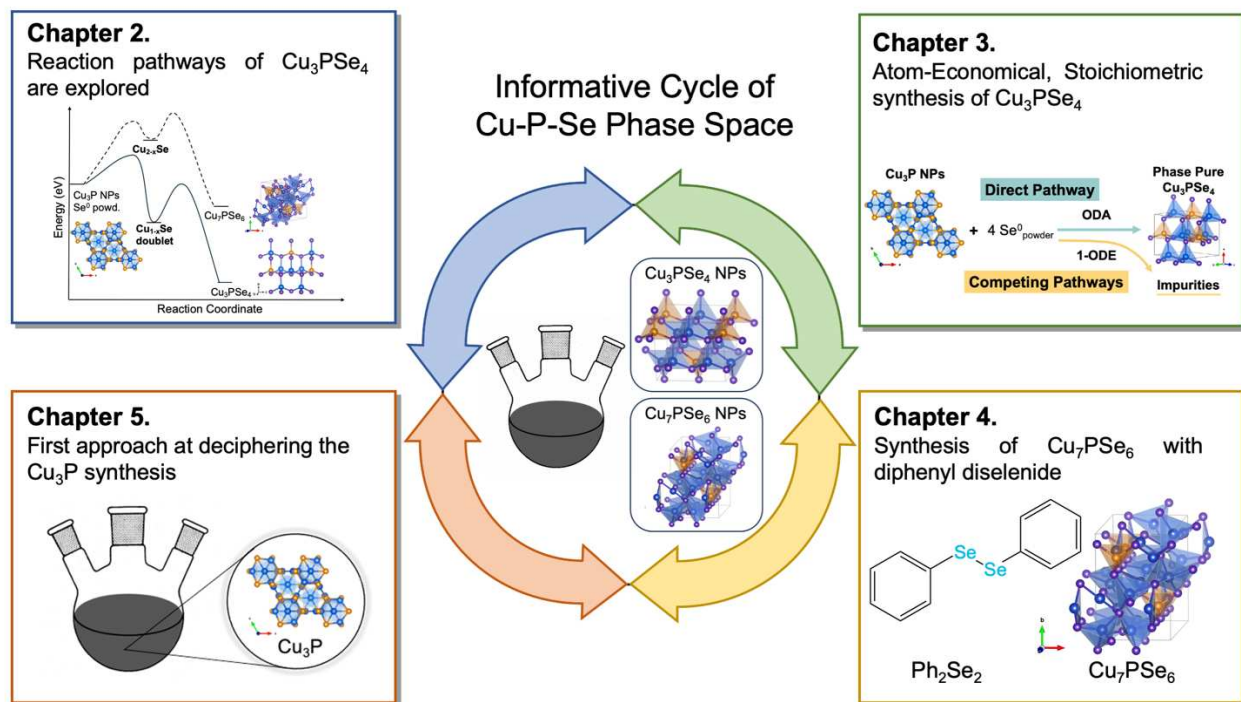


Figure 6.1. Schematic to outline the four areas of research outlined in this report.

6.2. Why further explore the Cu-P-Se phase space?

Although the work presented herein has taken strides to further advancing the chalcogenide NP field, there are specific avenues that still need to be explored to fully capture the underlying mechanisms of the two ternary phases. Transformation pathways and mechanisms of particle formation are essential to provide the field with a full picture on the individual precursor interactions - an aspect that will further drive nanoparticle research to avoid trial & error methodology. What follows synthesis is often property measurements, which could provide, or rather complete, a feedback loop of materials development. Thus, the following are *four* areas of focus that could be future work for the Cu-P-Se phase space.

Mechanistic study of the Cu_3PSe_4 ODA synthesis, further discussed in 6.3.

1. A more in-depth investigation of H_2Se rate of generation versus Cu_3PSe_4 formation ($-\text{d}[\text{H}_2\text{Se}]/\text{dt}$ vs $+\text{d}[\text{Cu}_3\text{PSe}_4]/\text{dt}$) to provide a perspective on alkane solvents that our current

investigations have not yet elucidated. The interactions of Se^0 powder in aliphatic solvents and dynamics at solid interfaces are very underdeveloped but could be used to target select, novel materials or even balance reactions. Further application to other systems is needed.

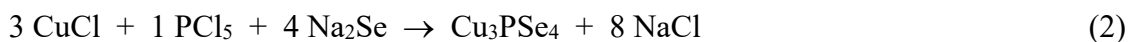
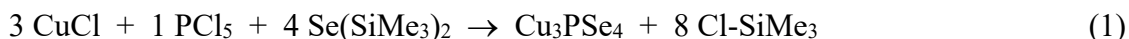
2. Monitoring the formation of Cu_3PSe_4 with in situ techniques such as, magic angle spinning (MAS) nuclear magnetic resonance (NMR) and powder X-ray diffraction (PXRD). Currently, we are in the process of submitting a manuscript where dibenzyl diselenide is used as a substitute for Se^0 powder, which allows us to track the decomposition of Bn_2Se_2 as a function of temperature and the formation of Cu-Se and Cu-P-Se phases. However, a consistent recurring question for this overarching project is, how does P incorporate into the Cu-Se binaries that form en route at lower temperatures? However, potentially reactive byproducts from Bn_2Se_2 decomposition (such as benzyl radicals) that could possibly interact with P, emphasizes the importance of initially analyzing the Se^0 powder system in Chapter 3 and must be done first.

Possible alternative routes to synthesize Cu_3PSe_4 .

1. In relation to the research on dialkyl diselenide precursors, didodecyl diselenide^{2,3} could be incorporated as a Se precursor to resemble the proposed active Se species produced from Se/ODE (long-chain dialkyl selenides). A hypothesis, proposed by Jennifer Lee (Chapter 5 in her dissertation),⁴ is that the Cu_3PSe_4 phase is formed is through a nucleophilic addition of Cu_3P to a chalcogenide-bonding Se species (Lewis-acidic), which has since been shown to have precedent based on the success of Se^0 and Bn_2Se_2 . Didodecyl diselenide could be used to further test this hypothesis, along with a precursor that is Lewis-basic along the R-Se bond (that won't trap P like Ph_2Se_2) to evaluate the influence of R-Se bonding character on Cu_3PSe_4 formation. Currently, our work is aimed at how the degradation products of Se

species alter phase formation, which plays a substantial part in navigating the ternary phase space. However, Ph_2Se_2 is not an ideal precursor to evaluate the influence of R-Se Lewis basicity on phase formation, thus, Se precursors need to be employed that differentiate the influence of $\text{Cu}_2\text{-Cu-P}^{3-}$ reacting at σ^* orbitals (chalcogen bonding⁵⁻⁸) or Cu^{1+} reacting at Lewis basic bonds.

2. Another avenue to research is employing molecular precursors to avoid the bottleneck of NP precursors. As explained in Chapter 5, starting with NP precursors introduces complexity by starting with a material that substantially deviate from the expected composition and requires thorough structural characterization to identify any variations that can affect the reaction stoichiometry. The experimental conditions, however, will have to be altered for the following proposed routes if no Cu_3PSe_4 is formed to confidently disprove whether this is a viable option going forward. An upfront, first attempt to developing a molecular synthesis is provided below, eq. 1 and 2.



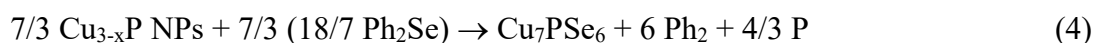
Cu₇PSe₆ synthesis. Chapter 4 thoroughly investigated the synthesis of Cu_7PSe_6 , but one problem still exists – the particles have yet to be synthesized with near 100% purity. The following are reactions that I hypothesize are the best routes forward that have yet to be attempted in detail.

1. Li_7PSe_6 can be used as a material for topotactic cation exchange with a Cu salt (as they both have the same crystal structure for both, $\text{Pna}2_1$ space group, orthorhombic). First, this should be attempted with Li_7PS_6 ,⁹ as there is a solution-based synthesis, and can be done with an established Cu flux method (solid-state).¹⁰ This should be used as a control system to evaluate the parameters needed to accomplish cation exchange, which can then

be adapted to a concentration-dependent *solution* cation exchange, where the solvent should be optimized to drive LiCl formation and that is insoluble in so that post-synthetic filtration can be performed.



2. As diphenyl diselenide decomposes to incorporate Se, monoselenide species form as a function of temperature (Chapter 4).^{11,12} *Starting* with monoselenide Se precursors, for example, diphenyl monoselenide (although not commercially available) can reduce the possible reaction pathways that exist when diselenide precursors decompose (eq. 4). Additionally, based on the results from Cu₇PSe₆, the alkyl group can be further tuned to reduce the effectiveness to trap P.



Application of Cu₃PSe₄. This is already underway by a current Prieto graduate student, Erin Snyder. Photoelectrochemical and transport property measurements will tackle another aspect of the project, by determining how the synthetic approach needs to be adapted in order achieve optimal performance. A particular emphasis is being applied to Cu₃PSe₄ that was not accomplished in the presented work, which is optimizing the surface dynamics and overall particle properties. Through two synthetic approaches, concentration dependent ligand exchange and digestive ripening (more of an impact on particle size and morphology), the poor ligand coverage of Cu₃PSe₄ is being altered to (1) increase ligand coverage for better particle suspension and (2) ligand identity to manipulate defect concentrations (if they are surface bound), interparticle conductivity, and carrier transport.

Another application to consider going forward is implementing Cu₃PSe₄ *nanoparticles* as a cathode material for Na batteries. As previously stated in Chapter 1, the lone literature report of

Cu₃PSe₄ as a cathode material was for rechargeable magnesium batteries (RMBs),¹³ which was synthesized with traditional solid-state techniques (HT, elemental). As this is the first demonstration of Cu₃PSe₄ as a cathode material in RMBs, it was stated by the authors that *further morphological optimizations* could produce higher capacities and better rate capabilities. Thus, the stage is set, as the previously stated work by Erin Snyder to optimize Cu₃PSe₄ photoelectric properties can be applied in a similar manner. The current bottleneck of RMBs are the poor rate capabilities of incorporating Mg²⁺ ions as a result of large electrostatic interactions and compensating for the divalent charge.^{14–18} However, functionalizing Cu₃PSe₄ NPs for improved ionic conductivity at the surface and short diffusion pathways¹⁹ (more exposed surface area) can improve the poor performance of RMBs.^{20–24} Regardless of improvements in engineering materials, a significant amount can be learned about the material itself when the measured properties inform on the overall particle structure, creating a structural/property relationship loop.

6.3 Preliminary Insight into the ODA Cu₃PSe₄ synthesis reaction pathway – Why ODA?

Attempts to understand the reaction pathway of the ODA Cu₃PSe₄ synthesis are ongoing. One hypothesis we previously explored was that in situ H₂Se generation is an active Se species en route to forming Cu₃PSe₄. In Chapter 3, our main objective was to efficiently deliver Se to permit a more direct, near-stoichiometric synthesis of Cu₃PSe₄. In doing so we tested and disproved that H₂Se is responsible for forming Cu₃PSe₄.

The most pertinent control to understand and quantify the interactions of H₂Se with Cu_{3-x}P is to cannula transfer the headspace of an octadecane/selenium solution, due to precedence in isolating H₂Se with similar solvents to form CdSe NPs.^{25,26} If H₂Se is a major product, degradation of Cu_{3-x}P will be apparent via PXRD, and the resulting product will inform whether H₂Se is a contributing active species to the Cu₃PSe₄ formation pathway. However, current results indicated

very little conversion of Cu_{3-x}P occurs (**Figure B.30**). An ex-situ control study on the standard ODA synthesis confirms the formation of Cu_3PSe_4 as early as 250 °C (**Figure B.29**), where formation of H_2Se is highly unfavorable,²⁷ which further confirms H_2Se is not a major of the Se/ODA solution. Therefore, our simplest operating hypothesis is the direct 8-electron (e^-) redox reaction of Cu_{3-x}P with the surface of suspended $(\text{Se}^0)_n$, especially once the selenium becomes molten ca. 221 °C.

Even though the included data helps clarify our claims made throughout Chapter 3, further investigation of how branched alkanes or other aliphatic solvents that can disrupt Cu_3PSe_4 formation should be considered. With an excess of Se^0 powder, oxidation of ODA to an internal alkene was observed, suggesting that H_2Se is present but minimal at the stated experimental conditions (**Figure B.9**). Thus, the rate of H_2Se generation must be lower than Cu_3PSe_4 formation, or rather the selenium is consumed (producing Cu-Se binaries) before H_2Se is favorable. Both of which are viable options and should be explored to develop a better understanding of Se^0 in saturated, aliphatic solvents.

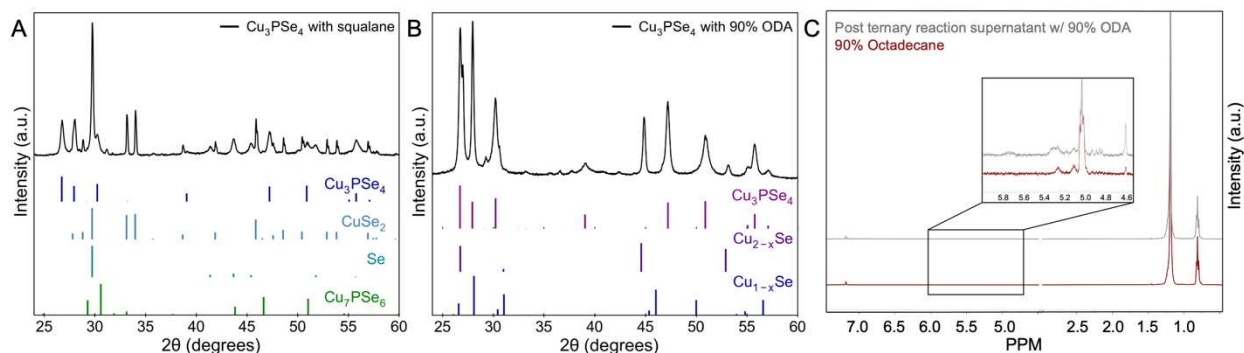


Figure 6.2. Characterization data for branched alkane solvents with 4 eq of Se^0 powder. (A) PXRD of squalane, (B) PXRD of 90% ODA, and (C) ^1H NMR of reaction supernatant and 90% ODA standard.

Branched alkanes have a lower C-H BDE (91 kcal mol⁻¹ vs 95 kcal mol⁻¹) at tertiary or quaternary carbons that can then reduce the temperature at which H_2Se is generated. This can

ultimately interfere with the reaction of Se^0 and Cu_3P once Se begins to melt, leading to more off-path reaction products and H_2Se as a responsible active species. Preliminary data to support this hypothesis was obtained from a stoichiometric reaction of Se^0 powder in squalane (a branched alkane) at the standard experimental conditions outlined in Chapter 3, which produces byproduct Cu-Se phases (**Figure 6.2A**). Moreover, we explored the reaction with less pure (90%) octadecane, which, based on the data provided by the vendor, contains impurities that mainly consist of branched alkanes (> 6%). PXRD of the final nanoparticles using 90% ODA, which demonstrates the presence of Cu_3PSe_4 and binary impurities, Cu_{2-x}Se and Cu_{1-x}Se (**Figure 6.2B**). Moreover, multiplet peaks ca. 5.0 – 6.0 ppm in the ^1H spectra in **Figure 6.2** are indicative of internal alkenes, which is hypothesized to be a result of in situ H_2Se formation creating off path products. Therefore, with the preliminary data, further exploration of the Cu_3PSe_4 reaction pathway can make aliphatic solvents more applicable in chalcogenide NP synthesis.

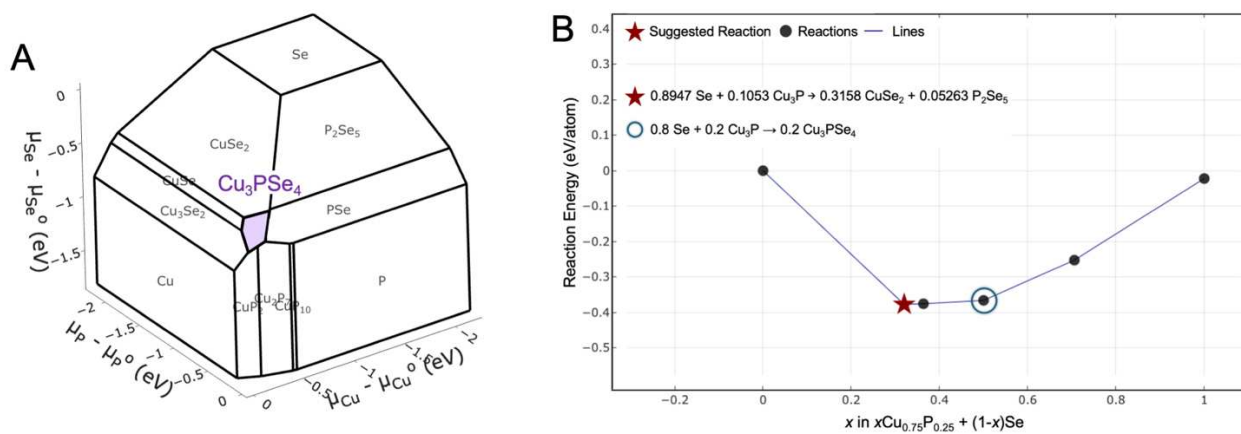


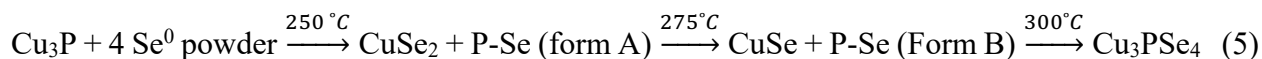
Figure 6.3. (A) chemical potential diagram of Cu-P-Se phase space. (B) Calculated interface reaction of Cu_3P and Se, with the suggested reaction based on lowest ΔE_{rxn} (red star) and Cu_3PSe_4 reaction (blue circle). Data and figures retrieved from materialsproject.org.²⁸

Results presented in this dissertation provide insight into the thermodynamic landscape of Cu-P-Se nanoparticle syntheses, aligning well with theoretical data from materialsproject.org,²⁸ which

suggests an energetically favored reaction due to the metastability of Cu_3P (when calculated at 0K). Although Cu_3PSe_4 is predicted to be less stable compared to Cu-Se binaries on the Cu-P-Se phase diagram, the ΔH calculated from 1 Cu_3P and 4 Se^0 to form Cu_3PSe_4 is largely downhill at ca. -280 kJ mol^{-1} .²⁸ Upon investigation of the three-dimensional Cu-P-Se chemical potential diagram (**Figure 6.3A**), Cu_3P is not on the diagram due to the calculated high formation of energy (metastability) at 0K. Whereas Cu_3PSe_4 shares a small surface meaning it is a readily accessible, more thermodynamic phase. However, retrosynthetic analysis suggests that Cu_{3-x}P would not lead to phase pure Cu_3PSe_4 considering both (1) the uncommon $8 e^-$ transfer the phosphorus must undergo, and (2) that every bond in Cu_3P must be cleaved. *But it works.*

This unlikely result, that inspired the work provided herein, was further analyzed with calculations of interface reactions, as the data based on phase and potential diagrams don't best resemble the physical process of the melted Se and Cu_3P interacting. As previously stated in Chapter 3, it was hypothesized that suspended $(\text{Se}^0)_n$ particles react at the surface of Cu_3P particles, due to the innocence and lack of solubility in ODA. We would therefore expect an interfacial reaction of Cu_3P and Se^0 to result in the formation of Cu_3PSe_4 , which is confirmed with a ΔE_{rxn} of -0.336 eV/atom (**Figure 6.3B**, blue circle) for a 4:1 ratio (stoichiometric). From such calculations, reactions with slight variations in the ratio of Cu_3P and Se are more thermodynamically favorable (larger ΔE_{rxn}), specifically the starred reaction that produces CuSe_2 and P_2Se_5 (**Figure 6.3B**, red star). Thus, it is evident why Cu-Se binaries can contaminate the final products, but despite this, with the most simplified reaction conditions (ODA reaction), phase pure Cu_3PSe_4 particles are produced. Of note, an experiment that shall be considered is the ex-situ aliquot at 250°C (**Figure B.29**) that shows that Cu-Se binaries form en route to Cu_3PSe_4 , of which one is CuSe_2 (the product from the suggested reaction). Based on the preliminary PXRD data (**Figure B.29**) the proposed

reaction pathway is provided below (eq. 5), without accurate stoichiometry as the P speciation is unknown.



An aspect yet to be considered in this analysis is that this isn't a one-step, concerted reaction, thus, to capture the entire energetics of this system we must understand the other components present at once Cu-Se binaries form. Specifically, the composition of P needs to be analyzed and as the product isn't crystalline, amorphous techniques shall be explored such as, ^{31}P MAS NMR (currently underway) and pair distribution function (PDF).

6.4 AgP₂ – Failure to Reproduce Literature of a Now Retracted Paper Taught Many Lessons

Extrapolating the knowledge gained from the Cu-P-Se phase space to the silver analog is of interest to build upon the synthetic toolkit established herein. We, therefore, explore how reaction pathways can be isolated for analogous systems, with particular attention toward the reactivity of a P-based binary nanoparticle precursor and similar Se species with an alternative transition metal cation. This ultimately allows us to evaluate how reactivity can manifest and be altered when a simple, but significant change is made to the relative energy of intermediates and final products. Additionally, Ag and Cu prefer different coordination environments, due to the relativistic effects of silver that cause orbital mixing from 5s orbital contraction and 4d expansion.^{29–31} Thus, the coordination environments that are favorable for Ag are low coordinate,^{29,30} which results in the three ternary phases having similar stability (**Figure 6.4, left**).

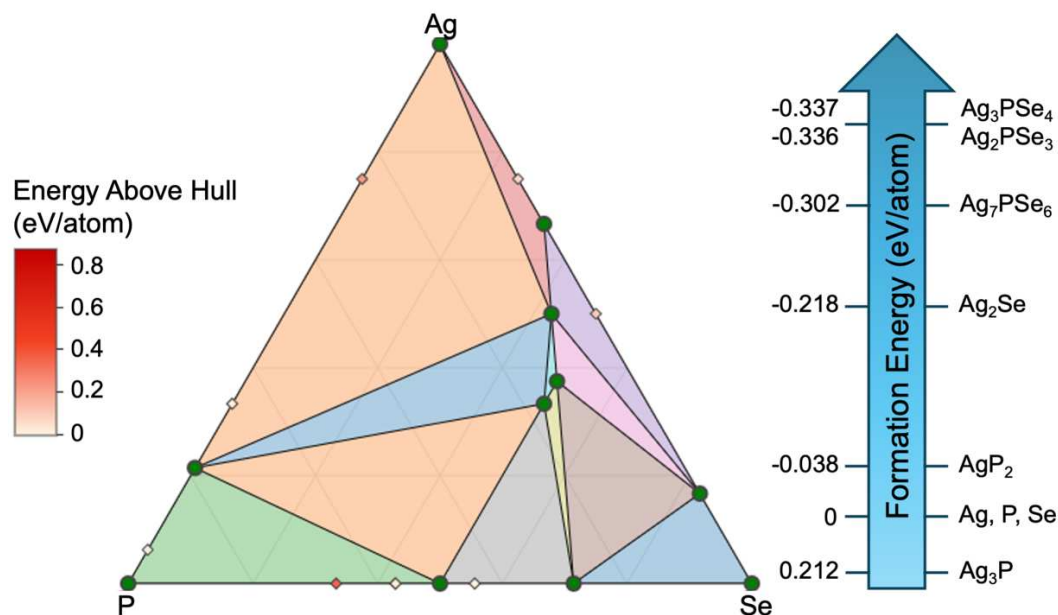


Figure 6.4. Ternary phase diagram of Ag-P-Se, where the color of the shapes indicates stability (energy above hull), green indicates stable phases. The formation energies of the phases are included on the right where the numbers have units of eV/atom. Data is retrieved from materialsproject.org.²⁸

As stated before, a large library of Se reagents and the depth of knowledge on precursor reactivity suggests that the crux of this study will be dependent on employing a similar Ag-P nanoparticle precursor. Copper phosphide, Cu_3P , has been demonstrated to be a phenomenal retrosynthetic precursor for Cu_3PSe_4 NP syntheses, as it promotes a stoichiometric 8 e^- transfer with 4 equivalents of Se^0 (Chapter 3), and even though not fully mass and charge balanced to date it provides a basis for the Cu_7PSe_6 phase (Chapter 4). However, for the Ag-P-Se phase space, until recently³² only a theoretically predicted compound existed with the same stoichiometry as our copper analog, Ag_3P , which is calculated to have an exceptionally high formation energy of +0.212 eV (**Figure 6.4, right**),²⁸ but could now be tested, *vide infra*. In contrary, a more stable phosphorus rich phase, AgP_2 , exists and has been synthesized through multiple routes, mainly with solid state techniques,^{33–35} but poses issues when extrapolating Cu-P-Se synthetic knowledge due to (i) different P oxidation states and (ii) intermetallic bonding character (Ag-Ag and P-P bonding units).

However, with respect to the subsection title, the one *phase-pure* colloidal synthetic route of AgP₂ that we believed to be reproducible, was thoroughly tested and proven to be the contrary, resulting in a retracted article.³⁶ Although, this synthesis consumed the work of an entire undergraduate thesis as well as a year of supplementary mentoring and reactions from myself, many lessons were learned.

Interest in AgP₂ alone is also promising. AgP₂ has been shown to have great performance as a conversion anode material in lithium-ion batteries (LIBs).³⁴ Some key parameters that inspire future optimization is a high theoretical capacity of 1473 mAh g⁻¹, and a high reversible capacity of 785 mAh g⁻¹ at 0.5 A g⁻¹ after 100 cycles,³⁴ which implies good reversibility. Synthetic routes for the metastable AgP₂ phase are predicated on using a reactive red phosphorus precursor and elemental Ag⁰ to drive particle formation.^{33–35} The bonding environments of monoclinic AgP₂ is composed of both Ag-Ag and P-P units in addition to an octahedrally coordinated Ag with P.³³ To isolate such a structure, one synthetic route by Henkes and Schaak synthesized AgP₂ particles with majority Ag(0) impurities,^{37,38} where trioctylphosphine (TOP) was injected at 370 °C (well above its boiling point), cleaving the C-P bond that is proposed to form PH₃ in situ. The AgP₂ nanoparticle products from Schaak et al. was initially screened with Se/ODE by Jennifer Lee (Chapter 7 of her dissertation), which successfully produced Ag₂PSe₃ and Ag₇PSe₆ – a result that holds promise for the future of phase pure AgP₂ particles.

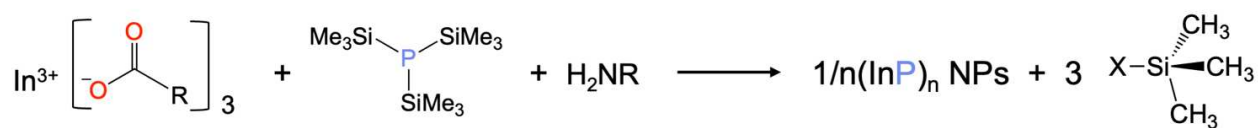


Figure 6.5. Schematic of InP nanoparticle synthesis with tris(trimethylsilyl) phosphine (TMS₃P). The R group represents alkyl groups, C_xH_y (i.e., myristate, C₁₃H₂₇) and X is likely the acetate group.³⁹

However, this method was abandoned, due to a large percentage of Ag(0) impurities and poor applicability of injecting TOP that immediately bumps into the Schlenk line. Alternatively, we attempted the since *retracted* colloidal synthesis of AgP₂ by Li et al.,³⁶ which is predicated by InP literature.^{32,40–52} A strategy to target ultra-small (sub 10 nm) InP nanoparticles is starting with tris(trimethylsilyl) phosphine (P(SiMe₃)₃, denoted TMS₃P) as it reacts at low temperatures at a high rate of P incorporation,^{46,49,53–55} which has led to thorough mechanistic investigations.^{39,42,53,54,56} A general scheme of InP synthesis with similar conditions to the proposed AgP₂ reaction is provided in **Figure 6.5**. Two key aspects are determined for InP that pertain to AgP₂, (1) an InX₃ precursor (X = halogen or carboxylic acids) is commonly used that does not have to undergo formal redox events, and (2) the counteranion stabilizes the trimethylsilyl leaving group.

Despite the success of TMS₃P in InP synthesis, direct translation to AgP₂ has not been successful to date and considerations must be taken into place when approaching this problem in the future. First, the final AgP₂ nanoparticles are intermetallic with mixed Ag and P oxidation states compared to the formal P(3-) and In(3+) in InP, meaning when TMS₃P is reduced to 3- as the trimethylsilyl groups leave, another redox event must occur to produce AgP₂. Additionally, and most importantly, the stability of Ag(1+) must be stabilized in solution to prevent the favorable Ag(0) NP formation,^{57–59} whereas In(3+) does not readily reduce to In(0). Finally, the charge and electron stoichiometry must be balanced with counterions to drive dissociation of TMS leaving groups that can alter reaction thermodynamics, experimental conditions shown below in the unbalanced eq. 5 (where, OLA is oleylamine and OAc is acetate).



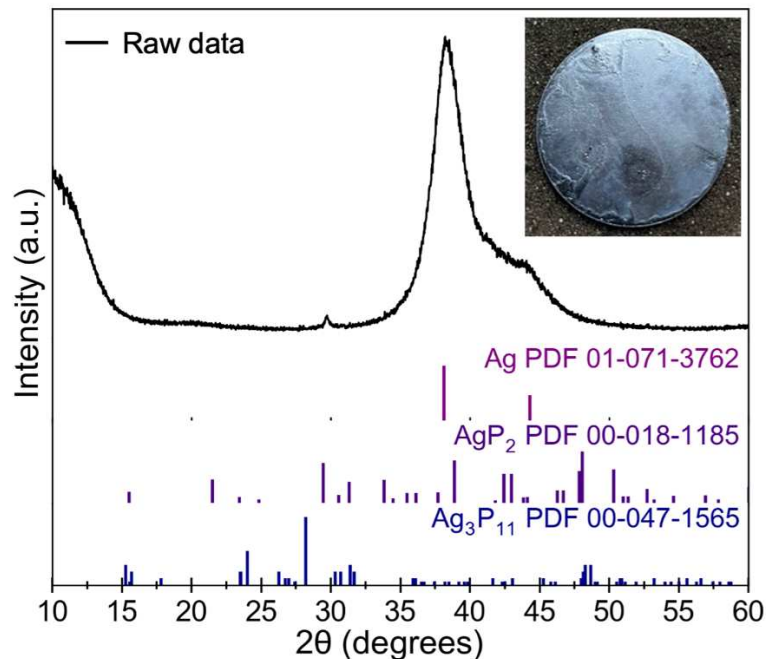


Figure 6.6. PXRD of the standard synthetic conditions from Li et al.,³⁶ explained in eq. 6. The broad peaks present are representative of Ag(0) NPs. An image of drop cast Ag particles is included in the top right of the diffraction pattern.

As mentioned above, all synthetic attempts to reproduce these results were unsuccessful. The specific reaction details that failed are outlined in Devon Leimkuhl's honors thesis, Spring 2022.⁶⁰ The conditions explored all resulted in the formation of Ag(0) NPs, characterized by PXRD (**Figure 6.6**). An image of the resulting Ag particles is also included within the PXRD pattern, where the blue tint is also indicative of small Ag particles that further supports the broad peaks at 37 and 44 2θ .^{61–63,57} Overall, the general finding is that the Ag(1+) precursor is reduced to Ag NPs *prior* to TMS₃P injection. One control experiment that was conducted to further probe this claim, was the injection of TMS₃P at RT in an inert atmosphere, which immediately turned the solution black, suggesting that TMS₃P can also induce Ag(I) reduction. Nonetheless, the conditions stated by Li et al.³⁶ have allowed for us to understand the impact of particular experimental conditions on Ag(1+) reduction, but in order to isolate AgP₂ a more logical, stoichiometric approach needs to

be taken. The following are synthetic considerations, with the caveat that the necessary oxidation of P(3-) in TMS₃P to form AgP₂ still needs to be the highest priority.

1. Stabilize Ag(I) in solution with strongly coordinating ligands to avoid reduction to Ag(0) before TMS₃P is injected or generally P incorporation.
2. Incorporate a silver precursor that doesn't require ligand exchange to form, for example, Ag-amine complexes that can also stabilize the TMS leaving groups. AgCl can also be an option, but again the SiMe₃ groups would need to be balanced with an additive such as a halogen donor, as AgCl doesn't provide enough Cl⁻ counterions.
3. An attractive direction is the use of n-heterocyclic carbene (NHC) based precursors (NHC-AgBr),⁶⁴⁻⁶⁹ where the stability of NHC ligands could promote AgP₂ formation before reduction to Ag(0). One aspect to keep in mind is that the Br⁻ leaving group will not balance the reaction alone (NHC-AgBr + 2 TMS₃P → 1 Br-TMS + 5 X-TMS), so additional precursors are required to balance SiMe₃ leaving groups.

6.4.1. Ag₂Se – AN ALTERNATE ROUTE TO AG-P-SE BUT LIMITED BY PHOSPHORUS INCORPORATION

A hypothesized, alternative route to isolate Ag-P-Se phases is to abandon the P-based NP precursor and start with a more replicable, established Ag₂Se NP precursor.⁷⁰ In a similar manner to AgP₂, the reaction stoichiometry doesn't balance due to a silver rich phase, that will always produce Ag byproducts if no Se is added. Regardless, we decided to explore this approach with the idea that Ag complexes or Ag particles could be separated with a washing procedure. The Ag₂Se NPs were synthesized via the procedure from Wang et al.,⁷¹ where octadecylamine is heated to 180 °C, then AgNO₃ and Se powder is added, reacted for 10 m, washed, and purified (**Figure 6.7A**). Three separate P precursors, phosphorus pentachloride (PCl₅), triphenyl phosphite (P(OPh)₃, TPP), and TMS₃P were then evaluated (**Figure 6.7B**). Both TPP and TMS₃P were

dissolved in ODE and injected at 300 and 180 °C, respectively. Whereas, PCl_5 was added with ODE prior to the heating to 300 °C.

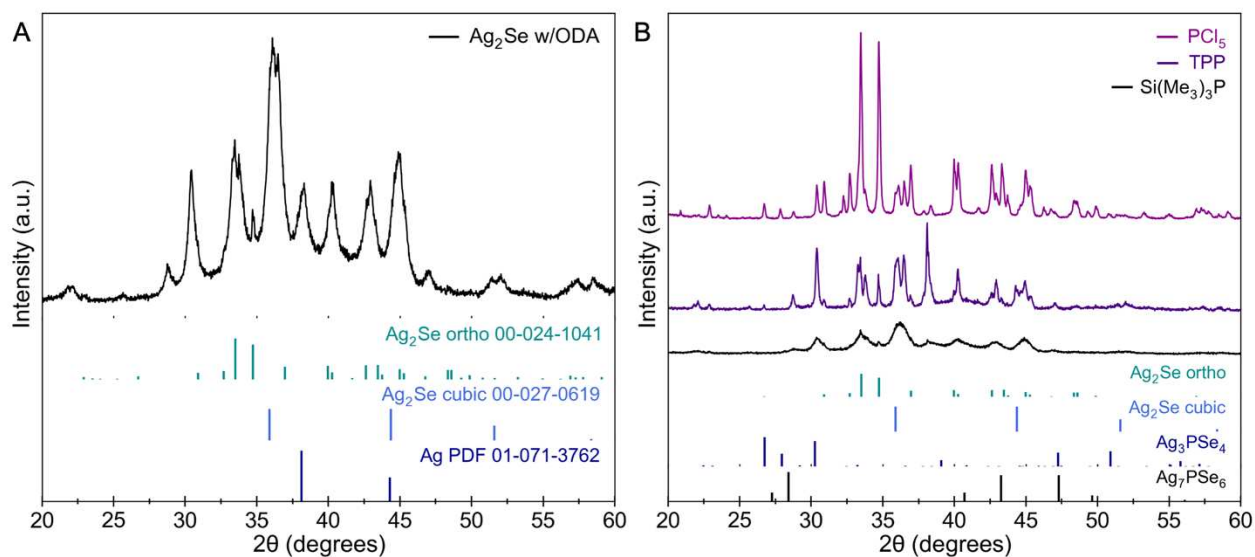


Figure 6.7. PXRD data for the (A) Ag_2Se synthesis by Wang et al.⁷¹ and (B) reactions of the Ag_2Se precursor with the P precursors identified by the label in the top right.

The precursor TMS_3P was first tested and disproved as a possible reagent, as the 8-electron oxidation that must occur to form $\text{P}(5+)$ in Ag-P-Se phases cannot be facilitated by available Se^0 . This hypothesis was confirmed as the Ag_2Se particles don't react and remain as the major product by PXRD (TMS_3P pattern, **Figure 6.7B**, black color). PCl_5 was then tested for a completely different synthetic standpoint, as no redox events are required to isolate $\text{P}(5+)$ and the presence of amines can assist in capturing the Cl^- ions, but only minor conversion of Ag_2Se to Ag_3PSe_4 or Ag_7PSe_6 was captured (PCl_5 pattern, **Figure 6.7B**, dark magenta color). Finally, TPP was analyzed as an intermediate between the two other P precursors, in terms of oxidation state ($\text{TPP} = 3+$) and reactivity, but upon injection no transformation to Ag-P-Se phases was identified (**Figure 6.7B**, indigo color). Despite the unsuccessful attempt to isolate Ag-P-Se phases, PCl_5 is the most promising going forward as a redox event is not required to form the necessary $\text{P}(5+)$ oxidation state but will need to be optimized to remove the Cl^- ions.

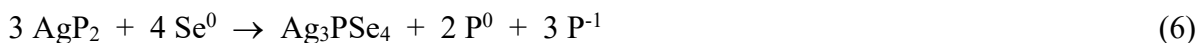
An alternate approach taken was a one-pot heat up synthesis with TPOP present, and interestingly, the black dispersion of Ag₂Se particles completely decomposed to a yellow tint solution at 160 °C. This solution was further heated to 300 °C to determine if particles would nucleate at elevated temperature, but transformation was only observed after multiple hours (10) which was characterized to be Ag particles. However, this holds promise going forward as clearly the Ag₂Se particles decompose, and Ag-Se bonds are cleaved that can be manipulated to form the required Ag-Se and P-Se bonding units in Ag-P-Se phases. One clear distinction that was never revisited after our publication in Chapter 3,¹ is that all the syntheses are performed in ODE, which is known to react with common NP precursors (namely P and Se) that could prevent phase purity in future syntheses. Therefore, the following are avenues to explore.

1. In order for TPP to release P(3+) in solution, the P–OPh bond must be cleaved, thus OPh needs to be captured. To do so, many X–OPh products can be isolated with X being **H**, **R–C=O**, **Cl–C=S**, **R–S(=O)₂**, **Cl₂P=O**, etc., where the coordinated atom is bolded. Based on the available NP precursors and relative stability of the X–OPh byproducts, P could be efficiently incorporated.
2. Similar to TPP, PCl₅ could also be inhibited by not efficiently capturing the chloride ions, and considering this precursor is the only to produce Ag-P-Se phases this should first be explored.
3. Finally, the last method could be using molecular precursors to avoid the Ag and P byproducts. This should be first aimed at performing a heat up system where each precursor is mass and charge balanced. This can then be adapted to an injection method if Ag(1+) reduction needs to be avoided, for example, if the P precursor promotes this the way TMS₃P system demonstrated.

Ultimately, both AgP₂ and Ag₂Se precursors did not result in the formation of Ag-P-Se phases under the previously described conditions, but with the proposed manipulations and control studies, significant progress can be made toward isolating these material colloiddally.

6.4.2 FUTURE DIRECTION OF AG-P-SE PROJECT WITH AG₃P SYNTHESIS

As the previous two synthetic routes provide a basis on how to approach AgP₂ and phosphorus incorporation into Ag₂Se, an avenue that previously wasn't available, but recently has been reported, is Ag₃P nanoparticles as a precursor.³² Importantly, the stoichiometry can now be elegantly balanced, avoiding the impurities from AgP₂ that will produce excess P (eq. 6), an unfavorable byproduct that can prohibit ternary formation.



Our upfront hypothesis is that Ag₃P particles can be employed to directly synthesize Ag-P-Se ternary phases, due to a significant energetic downhill reaction, absence of byproducts that can contaminate the final products, and efficiency to form Ag-P-Se phases with more impure P-based precursors (work by Lee et al., Chapter 7).⁴ Although a promising direction, two areas will be discussed with respect to Ag₃P NPs, (1) considerations of the Ag₃P NPs synthesis as it is a multistep, complex cation exchange synthesis and (2) alternative hypotheses to evaluate when incorporating Se-based precursors.

Eagle et al. has recently published (March 2024)³² on the colloidal synthesis of Ag₃P via cation exchange of pre-synthesized InP magic size clusters (MSCs). InP MSCs were synthesized based on a procedure from Gary et al.,⁴² but generally a similar strategy in **Figure 6.5** was employed with the use of TMS₃P, myristic acid, and In acetate as precursors. The transitional metal phosphide MSC of interest (silver, gold, or copper) was then isolated when large excess of M_xCl (AgCl) is

suspended in a 3:2 toluene to oleylamine ratio at room temperature. This method was extended further to form larger nanoparticles by injecting the converted metal MSCs in an ODE solution at 300 °C for 20 minutes. Both synthetic routes are promising to then extrapolate this material as a precursor to form Ag-P-Se phases, but some considerations before proceeding with this phase are listed below.

1. The first question that surfaces when isolating a metastable material yet to be synthesized, is what characterization techniques were used and to what extent were they applied? Powder X-ray diffraction was used for both synthetic methods and matched to a predicted pattern, but in both syntheses some peaks are not indexed to Ag₃P. Additionally, the peaks that are indexed to the predicted pattern of Ag₃P are also very similar to Ag(0) and should be analyzed against the powder diffraction file (PDF) of these phases. In addition to PXRD, pair-distribution function analysis was used to monitor the change of In-In networks to Ag-P bonds, which was supported by theoretical calculations. Finally, XPS was used to investigate the increase in relative Ag concentration for the various cation exchange experiments, but further analysis (fitting) is required to decipher whether the Ag 3d binding region is composed of Ag(0) or Ag(I). All of the provided characterization techniques provide a great basis for applying this material to subsequent selenization step, but further investigation with STEM/EDS will determine whether Ag(0) particles could be present – an artifact that could plague the Ag-P-Se synthesis with Ag-Se impurities based on work by Lee et al.⁷² with Cu-P-Se and Cu-rich pockets resulting in Cu-Se impurities.
2. Surface dynamics of the particles need to be investigated. As emphasized numerous times throughout the presented herein, the Cu-P-Se synthesis is very sensitive to the pre-

synthesized Cu_3P NPs. Two related, possible major limitations of the Ag_3P are the presence of In even after purification (characterized by elemental analysis), and a different structural backbone to the coordinated amine ligand. Ultimately, the surface composition is underdeveloped and will need to be improved to systematically apply Ag_3P particles.

3. Mid bandgap states were analyzed with transient absorption, which identified a high quantity of states for each metal phosphide material. The presence of such states as well as localized orbitals at the surface could lead to a lack of control over the reaction landscape. So, the synthesis, particularly the step for forming larger nanoparticles, should be focused on eliminating ODE (contaminates final products) and isolating particles with more defined morphology and composition, meaning eliminate the byproducts present at 20 20 (see Figure 5 within their report).

Alternative hypotheses to evaluate when employing Ag_3P NPs with Se-based precursors are outlined below.

- Multiple Ag-P-Se phases will exist at a set condition (replicated from Cu_3PSe_4) meaning control over Ag-P-Se phases is going to be limited.
- Binary formation will be stabilized by the oleylamine ligands.⁷³ Will need to be avoided and possibly can be done by performing ligand exchange with a gel-permeation column.⁷⁴

Although the proposed pathways to form Ag-P-Se are dense and would likely consume the time of an entire Ph.D. dissertation, the preliminary work and considerations will hopefully assist in reducing the required effort to making Ag-P-Se phases.

6.5 Perspective

Ultimately, there is still a great deal of low hanging fruit for the Cu-P-Se phase space that need to be sliced up and served to the field. Two avenues could be explored to build upon the work presented herein, application driven design of Cu_3PSe_4 and Cu_7PSe_6 phases, or further pursuit of the underlying mechanisms of formation. Both come with a plethora of questions that will be beneficial for the NP field, and therefore should be pursued. Although binary colloidal nanoparticle synthetic methodology has drastically improved due to significant progress on mechanistic investigations, translating the synthetic knowledge to complex, ternary phases is exceptionally difficult as the possible precursor interactions exponentially increases. Combine that with a synthesis that uses a nanoparticle precursor, then one can see that there is much to be learned. I, therefore, look forward to analogous Cu-P-Se work led by other lab mates, that I have had the joy to be a part of, finalized and published, as well as any future discoveries on this project.

As the primary objective of the work herein is to develop better understanding of the Cu-P-Se reaction landscape, many areas and questions have been proposed throughout that will provide a basis for mechanistic investigations. To that extent, a direct extension of the work herein is currently being led by Luke MacHale, where a dibenzyl diselenide system is being explored to monitor the transformation and delivery of Se en route to Cu_3PSe_4 formation. Whereas an application feedback loop will provide perspective on the particle properties that can be manipulated synthetically. Currently, Erin Snyder is adapting the current synthetic technology and performing post-synthetic modifications (digestive ripening) to improve the surface dynamics for better suspensions. However, the syntheses, questions, and methodology outlined in this chapter should be explored by another lab mate, as it provides the basis for a project to target novel, metastable materials, and a possible joint project to use NPs for Na-ion batteries. The goal of this project is to further drive disprove-based NP research and inform on the colloidal NP field, built

off the foundations set by Dr. Jennifer Lee and great work from the pioneers in the chalcogenide field, which we hope can provide pieces to an ever-growing puzzle.

6.6 Author Contributions

According to CRediT criteria, my contributions to this work included conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft, and writing – reviewing and editing. Contributions by Devon Leimkuhl included data curation, conceptualization, formal analysis, investigation, methodology (All of which are in Leimkuhl Thesis, Spring 2022), writing – original draft. Contributions by Amy L. Prieto include conceptualization and writing – reviewing and editing.

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APPENDIX A: SUPPLEMENTARY INFORMATION FOR CHAPTER 2

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Thermodynamic Equations¹⁻⁵ (A1-A11)

Figure A.1. Powder X-ray diffraction (PXRD) patterns of the initial ex-situ studies that show major conversion was noticed at 225 °C.

Figure A.2. PXRD of the ex-situ characterization of 5 min aliquots.

Figure A.3. PXRD of the ex-situ characterization of 2 min aliquots.

Figure A.4. Transmission electron microscopy (TEM) images for heat-up reaction with squalane.

Figure A.5. More In-depth pathway including the precipitation and dissolution equilibrium that relies on the aggregation thermodynamic factors.

Figure A.6. Synthetic scheme of Cu₇PSe₆ pathway. Experimental manipulations are explained in Chapter 2.

Figure A.7. PXRD patterns for the investigation of extended time periods on both purging (left) and trapping (right) of the headspace.

Figure A.8. PXRD for the 20 minute reactions for substitution of ODE with HDA (left) and OLA (right).

Figure A.9. PXRD for the one hour reactions for substitution of ODE with HDA (left) and OLA (right).

Figure A.10. PXRD for the increased temperature to 330°C for the substitution of ODE with OLA.

Figure A.11. Decoupled ³¹P NMR for OLA reactions at 330°C (top) and 300°C (bottom).

Thermodynamic Equations¹⁻⁵ (A1-11)

Total free energy of the binding/displacement and precipitation/dissolution for a NC-ligand complex.

$$\Delta G_{solv}^{total} = \Delta G_{solv}^{binding} + \Delta G_{solv}^{agg} \quad (1)$$

$$\Delta G_{solv}^{binding} = \Delta G_{gas}^{binding} + (\Delta G_{solv}^{[NC-Ln]} - \Delta G_{solv}^{NC} - n\Delta G_{solv}^L) \quad (2)$$

$$\Delta G_{gas}^{binding} = \Delta G_{gas}^{prep} + \Delta G_{gas}^{int} \quad (3)$$

$$\Delta G_{gas}^{prep} = \Delta H_{gas}^{prep}(L_n) - T\Delta S_{gas}^{prep}(L_n) \quad (4)$$

$$\Delta\Delta G_{solv} = \Delta G_{solv}^{[NC-Ln]} - \Delta G_{solv}^{NC} - n\Delta G_{solv}^L \quad (5)$$

$$\Delta G_{solv}^{binding}(\theta_c) = \Delta H_{gas}^{prep}(L_n)(\theta_c) - T\Delta S_{gas}^{prep}(L_n)(\theta_c) + \Delta G_{gas}^{int}(\theta_c) + \Delta\Delta G_{solv}(\theta_c) \quad (6)$$

Where,

ΔG_{gas}^{prep} = Rearrangement energy required for proper configuration of ligands and NC monomers.

ΔG_{gas}^{int} = Interaction between NC and surface ligands or relaxation energy (always negative).

$\Delta\Delta G_{solv}$ = Free energy for solvation of NC-ligand complexes.

$(\theta_c) = n/n_{tot}$; n = occupied surface sites, n_{tot} = total surface sites (bulky ligands = low surface coverage).

$$\Delta G_{solv}^{agg} = \Delta G_{gas}^{agg} + \Delta G_{solv}^{[NC-Ln]^{agg}} - \Delta G_{solv}^{[NC-Ln]} \quad (7)$$

$$\Delta G_{solv}^{[NC-Ln]^{agg}} \cong 0 \quad (8)$$

$$\Delta G_{gas}^{agg} \cong n_{facet} \Delta G_{gas}^{facet-facet} \quad (9)$$

$$\Delta G_{gas}^{facet-facet} = \Delta G_{gas}^{L(m)-L(m)} + \Delta G_{gas}^{NC-NC} \quad (10)$$

$$\Delta G_{solv}^{agg}(\theta_c) = n_{facet} \left[\Delta H_{gas}^{L(m)-L(m)}(\theta_c) - T\Delta S_{gas}^{L(m)-L(m)}(\theta_c) + \Delta H_{gas}^{NC-NC}(\theta_c) - T\Delta S_{gas}^{NC-NC}(\theta_c) \right] - \Delta G_{solv}^{[NC-Ln]} \quad (11)$$

Where,

$\Delta G_{gas}^{facet-facet}$ = free energy interaction of a pair facets on two ligand-NC complexes.

$\Delta G_{gas}^{L(m)-L(m)}$ = ligand-ligand interaction of two ligand-NC complexes.

ΔG_{gas}^{NC-NC} = local interaction of adjacent nanocrystals.

Full description of the system, assumptions, and interpretations being made are provided in the cited references. Computational applications have also been explored to better predict a set of structural parameters. Extrapolation of these methods experimentally to design ligands are also included.

Supporting Figures

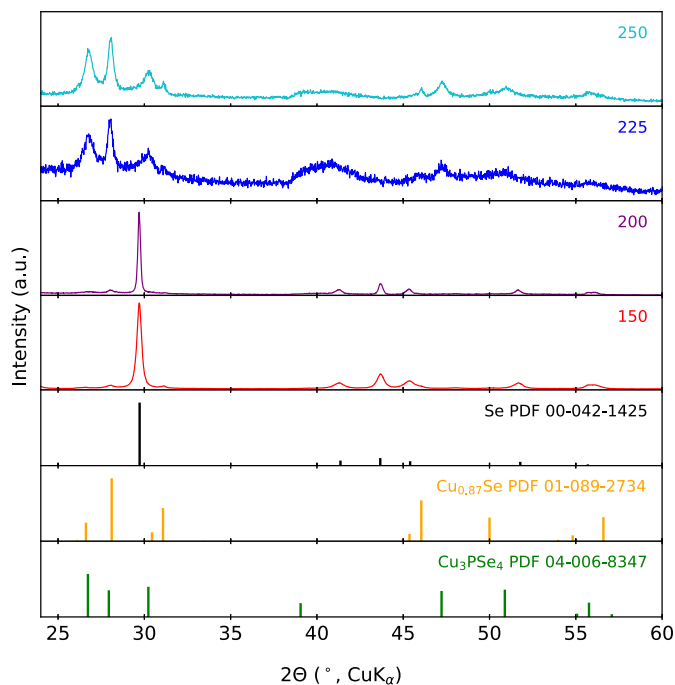


Figure A.2. Powder X-ray diffraction (PXRD) patterns of the initial ex-situ studies that show major conversion was noticed at 225 °C. Further studies will be investigated using the same temperature points.

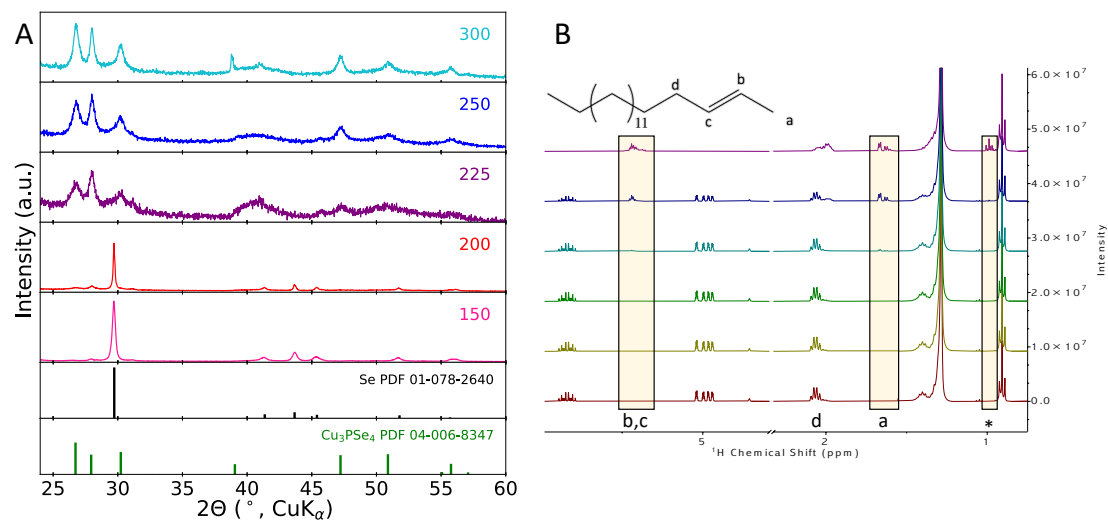


Figure A.3. PXRD of the Ex-situ characterization of 5 min aliquots. (A) subplot of diffraction patterns for each temp. aliquot. (B) ^1H NMR spectrum of temp aliquots. 150 °C is the bottom spectra, and stacked spectrum represent the increase in temperature with the top spectra being the cooled down solution.

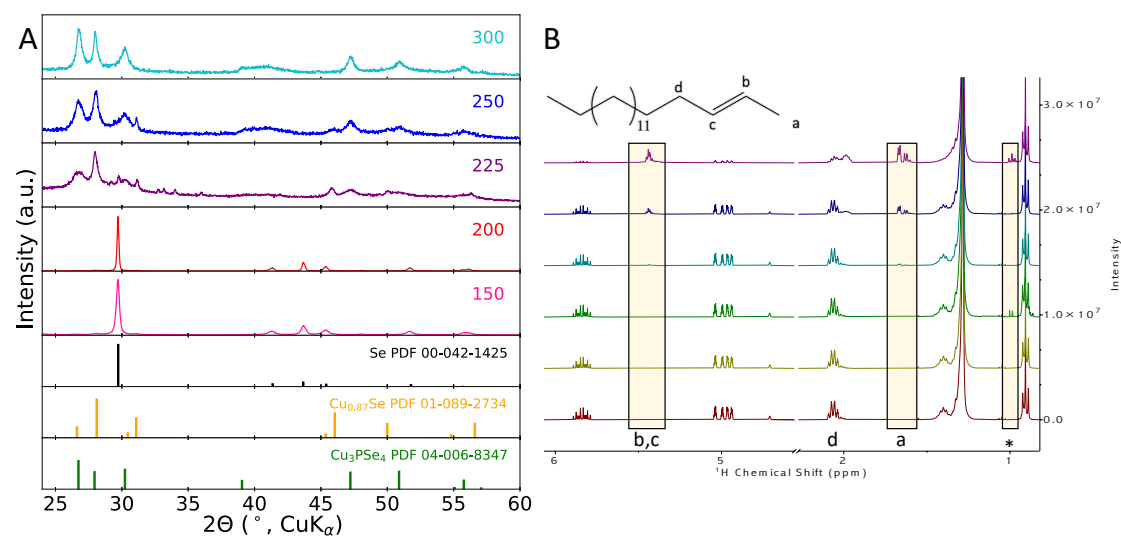


Figure A.4. Ex-situ characterization of 2 min aliquots. (A) subplot of diffraction patterns for each temp. aliquot. (B) ^1H NMR spectrum of temp aliquots. 150 °C is the bottom spectra, and stacked spectrum represent the increase in temperature with the top spectra being the cooled down solution.

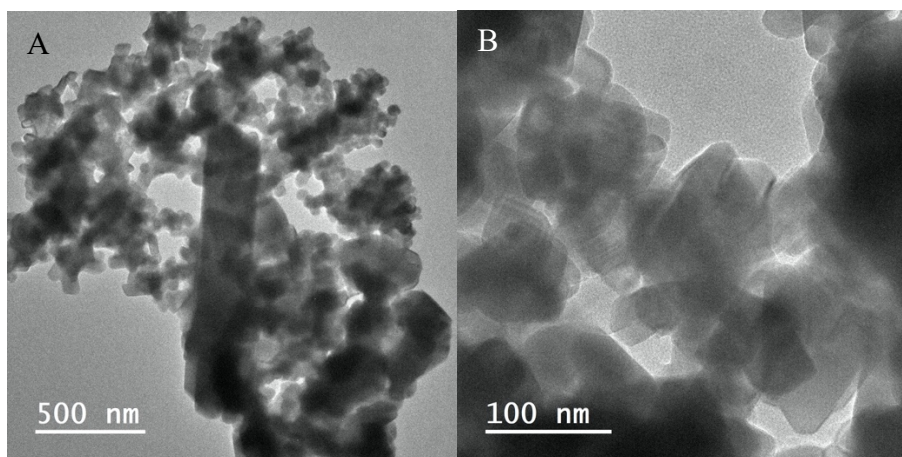


Figure A.5. Transmission electron microscopy (TEM) images for heat-up reaction with squalane.

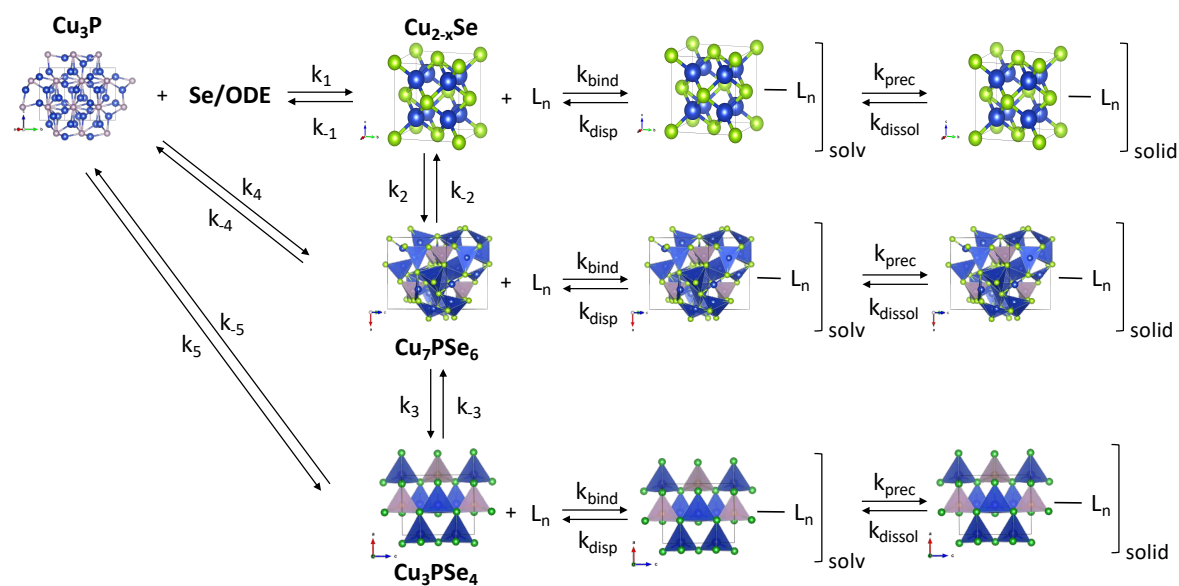


Figure A.6. More In-depth pathway including the precipitation and dissolution equilibrium that relies on the aggregation thermodynamic factors. The binding/displacement equilibrium is mainly focused in the Chapter as this equilibrium is essential for the transformation or degradation of particles.

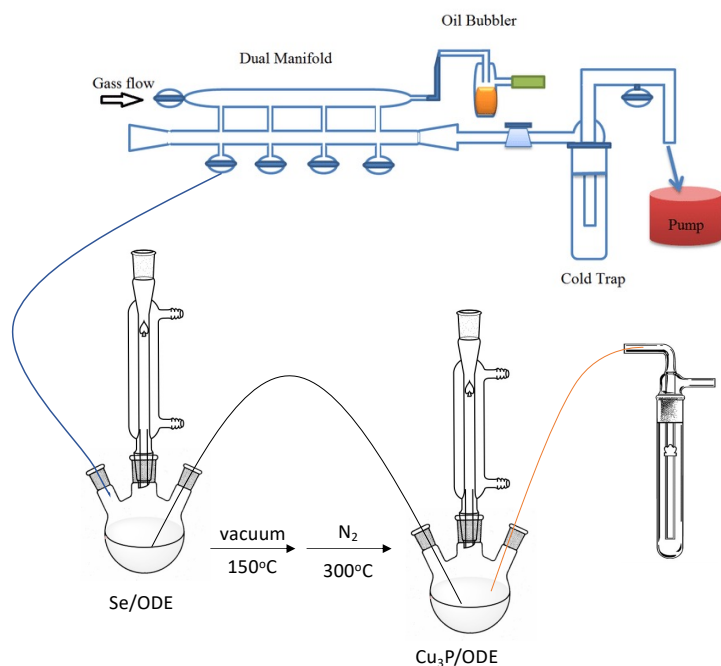


Figure A.7. Synthetic scheme of Cu_7PSe_6 pathway. Experimental manipulations are explained in Chapter 2.

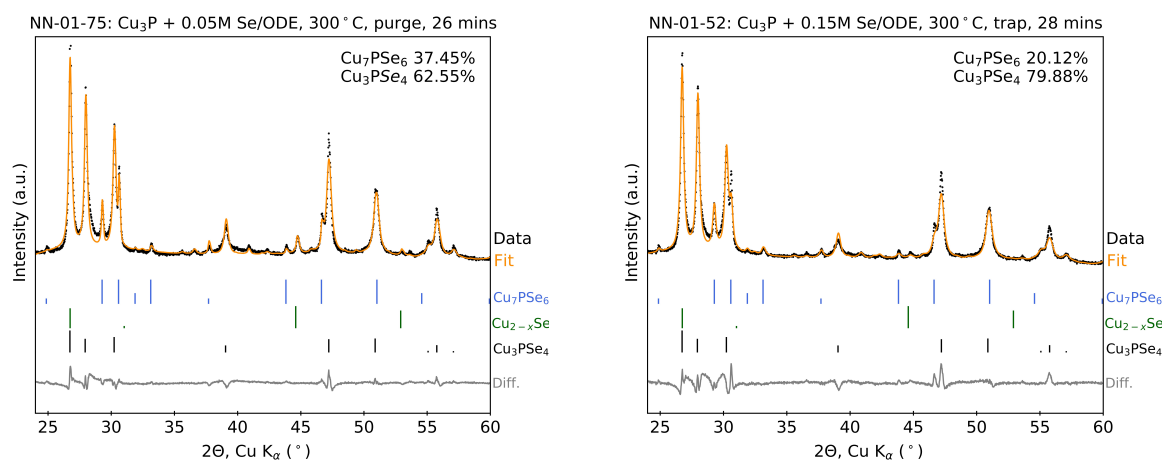


Figure A.8. PXRD patterns for the investigation of extended time periods on both purging (left) and trapping (right) of the headspace. Specific conditions for the individual reactions are on top of each plot.

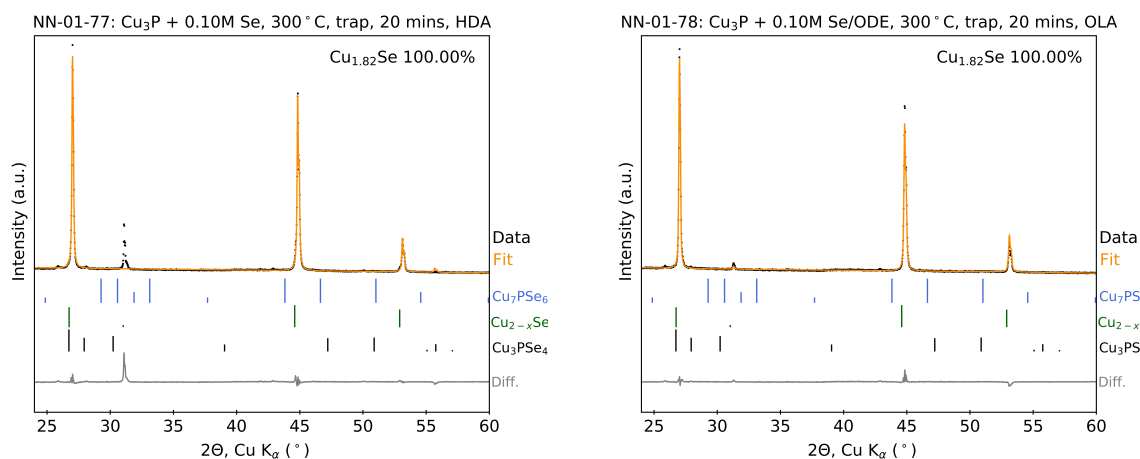


Figure A.9. PXRD for the 20 minute reactions for substitution of ODE with HDA (left) and OLA (right). Specific conditions for the individual reactions are on top of each plot.

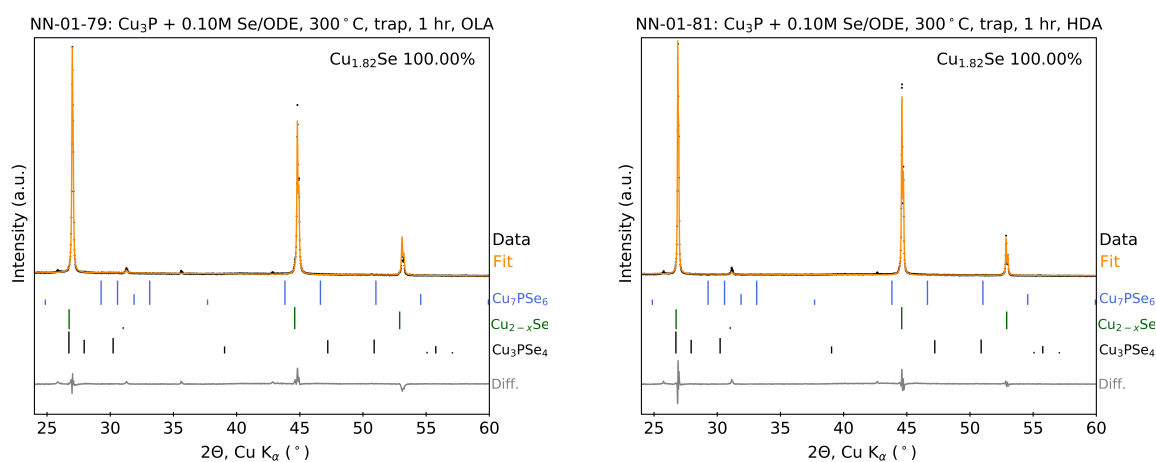


Figure A.10. PXRD for the one hour reactions for substitution of ODE with HDA (left) and OLA (right). Specific conditions for the individual reactions are on top of each plot.

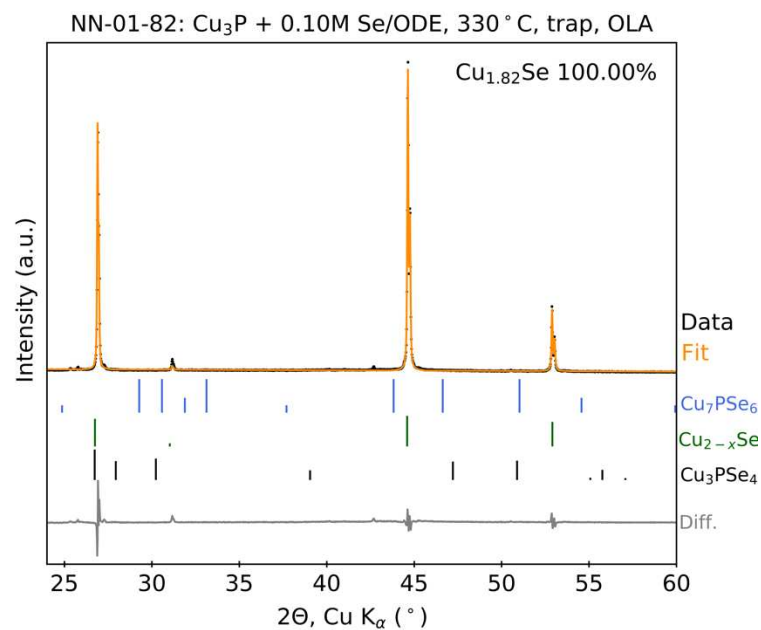


Figure A.11. PXRD for the increased temperature to 330°C for the substitution of ODE with OLA. Specific conditions are on top of the plot.

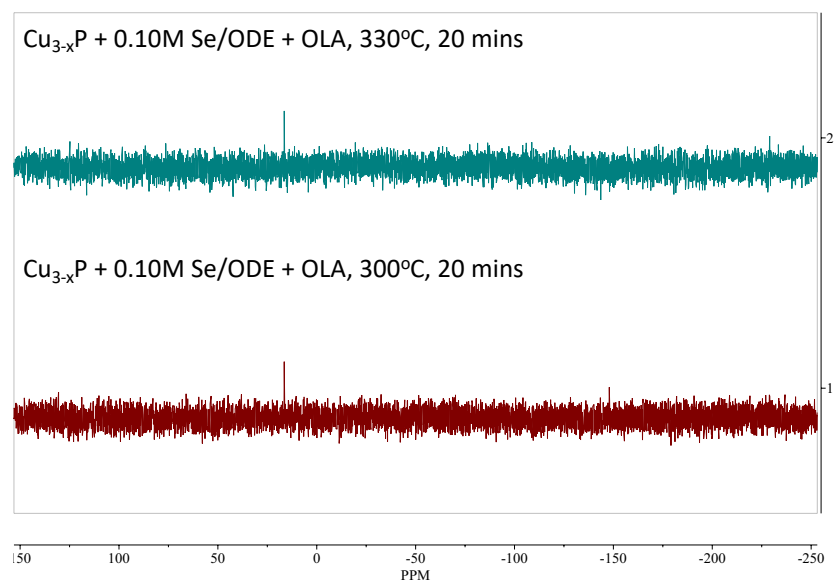


Figure A.12. Decoupled ^{31}P NMR for OLA reactions at 330°C (top) and 300°C (bottom). Singlet at 16.43 ppm is identified for both spectra.

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Figure B.1. Powder X-ray diffraction (PXRD) and ^1H nuclear magnetic resonance (NMR) of a Cu_3PSe_4 reaction where 1-ODE is replaced with HDA using 4 equivalence (eq) of selenium.

Figure B.2. PXRD of the final product with Cu_{2-x}Se binary present due to the reproducibility issues that are listed above and possible oxidation issues.

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Figure B.3. PXRD pattern and ^1H NMR of Cu_3PSe_4 using ODE synthetic conditions.¹

Figure B.4. PXRD pattern and ^1H NMR of Cu_3PSe_4 with ODA as the solvent and excess Se.

Figure B.5. ^{13}C NMR of the stoichiometric 4 eq assuming 100% Cu_3P with octadecane reaction.

Table B.2. Rietveld Refinement parameters for Figure 3.2A in main text (ODA synthesis of Cu_3PSe_4).

Figure B.6. Gas chromatography-mass spectroscopy (GC-MS) data of Cu_3PSe_4 with octadecane at 4 eq assuming 100 and 85% Cu_{3-x}P .

Figure B.7. Fourier-transform infrared spectroscopy (FT-IR) of the Cu_3PSe_4 reaction supernatant with ODA.

Figure B.8. ^1H NMR studies of the ODA Cu_3PSe_4 synthesis supernatant and the supernatant with 1% ODE.

Figure B.9. ^1H NMR of different selenium equivalence to observe the disappearance of mid-chain alkene.

Figure B.10. Images of the stoichiometric reaction supernatant heated at a prolonged time to determine the presence of amorphous selenium.

Table B.3. Rietveld Refinement parameters for Figure 2 in main text (4 eq of Se in ODE).

Figure B.11. PXRD of extended time studies of ODA Cu_3PSe_4 synthesis.

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Figure B.13. Low magnification TEM images of standard Cu_3PSe_4 reaction.

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Figure B.18. ^1H NMR of Cu_{3-x}P pre-synthesized NPs.

Figure B.19. X-ray photoelectron spectroscopy (XPS) of Cu_{3-x}P particles for both carbon and nitrogen 1s binding regions.

Figure B.20. XPS of Cu_3PSe_4 of the Cu, P, Se, and C bonding regions.

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Figure B.22. TGA to 800 °C at a 10 °C/min heating rate and PXRD of the Cu_{3-x}P batches.

Figure B.23. Derivative of the weight loss events for batch 1 in Figure B.21.

Figure B.24. PXRD and Rietveld refinement of Cu_{3-x}P NPs post TGA of batch 1 in Figure B.21.

Figure B.25. PXRD and ^1H NMR of Cu_3PSe_4 reaction with ODA while accounting for the percentage of ligands to have a closer to stoichiometric reaction and reduce the excess amount of Se.

Figure B.26. Rietveld refinement method for the $\text{Cu}_3\text{PSe}_4\text{ODA}$ synthesis assuming 85% ligand content.

Figure B.27. TGA of Cu_3PSe_4 NPs produced from Scheme 1B assuming 85 wt% crystalline Cu_{3-x}P in the precursor.

Figure B.28. TEM images and particle dispersion analysis plot Cu_{3-x}P NPs.²

Figure B.29. Temperature control study of an octadecane/selenium solution at the same concentration for the stoichiometric Cu_3PSe_4 synthesis.

Figure B.30. PXRD of ex-situ aliquots for the standard octadecane, stoichiometric reaction of Cu_3PSe_4 .

Table B.4. Thermochemistry for decomposition of Se_8 rings.³

Figure B.31. PXRD and ^1H NMR of a cannula transfer reaction with the headspace of a selenium/octadecane solution at the same concentration as the standard reaction.

Experimental

Materials

Anhydrous copper (II) chloride (CuCl_2 , 99%, Sigma Aldrich), hexadecylamine (HDA, Sigma Aldrich, 90%), triphenyl phosphite (TPOP, 97%, Oakwood Chemical), selenium powder (Se 200 mesh, 99.99%, STREM), chloroform (CHCl_3 , 99.8%, Sigma Aldrich), isopropanol (IPA, 99.5%, Fischer Scientific), hexanes (98.5%, Sigma Aldrich), toluene (99.5%, Sigma Aldrich), and ethanol (99%, Fischer Scientific) were used as packaged and received. 1-Octadecene (ODE, 90% Technical grade, Sigma Aldrich where the impurities are 2-octyl-1-decene, 2-butyl-1-tetradecene, 2-hexyl-1-dodecene, n-octadecane) and octadecane (ODA, 99%, Fischer Scientific) were sparged with N_2 for 2 hours (hr) before being used. All reactions were performed in a N_2 glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm) unless specified otherwise. Post-synthesis solvent washing was performed in ambient conditions on the benchtop. All glassware was cleaned using a base and acid bath wash, followed by rinsing with Millipore water and dried in a 160°C oven overnight.

Reproducibility Note

The synthetic conditions for Cu_3PSe_4 NPs have been reproduced by the authors 15 times to determine any influential variable that can alter successful results;^{2,3} identified variables are listed below with an outline of how each variable can lead to inconsistencies. (1) Cu-Se binaries (Figure B.1A), mainly Cu_{2-x}Se , are present when the reaction is not prepared in a low oxygen environment, particularly when our box exceeded 6.0 ppm or when adaptors (Teflon O-rings) went bad. (2) Additionally, a $\text{Cu}_{0.87}\text{Se}$ binary was also present in some reactions in which we attribute to changes in the stir rate or the accuracy of the heating mantle to reach 300°C at a 500°C/hr heating ramp rate. To completely remove any Cu-Se binaries, a reaction time of 30 minutes seemed to remove any inconsistencies. (3) Another key factor is the influence of slight deviation of stoichiometric

ratios, which again produced Cu-Se binaries. This is mostly influenced by making sure that the pre-weighed Cu_3P is completely dried to remove all leftover organics from the washing step. When less than four equivalent is used Cu_{2-x}Se persists in solution. (4) The washing procedure of Cu_{3-x}P NPs needs to be rigorously followed, due to possibility of stripping ligands that can lead to oxidation at the surface, resulting in Cu_{2-x}Se binary impurities. (5) Finally, the Schlenk lines were tested for air exposure with a blue solution from the reaction of sodium and benzophenone, the loss of the blue color being a common, ready indicator of water or oxygen contamination.⁴ Ultimately, the above-described list of factors are easily avoidable, but if one isn't taken into consideration, then the presence of impurities will persist.

Standard Synthetic Conditions

Cu_{3-x}P . Synthetic conditions were adapted from Liu et al.² and Lee et al.¹ CuCl_2 (0.5 mmol), TPOP (5 mmol), HDA (5 mmol), and 1-ODE (12.7 mL) were massed into a 50 mL three-neck round-bottomed flask equipped with a Teflon[®]-coated stir bar, Liebig reflux condenser, and thermocouple in a N_2 glovebox using their 1.10.10 ratio. Once extracted from the glovebox, the reaction flask was attached to the Schlenk line, and a light blue color was produced upon medium stirring (400 rpm) and held until all precursors were dissolved (typically 30 mins). The flask was heated to 150 °C, at a 500 °C/hr ramp rate, and kept at this temperature for 1 hr. Upon reaching 150 °C, the solution turned from light blue to light yellow, indicating the reduction of copper (II). The reaction temperature was then increased to 300 °C for 30 min, and glass wool was placed around the flask to cover only the height of the solution. It was noted that when the glass wool was placed higher, a white crystalline solid was present near the top of the flask and in the condenser. After 30 minutes, the reaction flask was cooled to 200 °C while remaining in the heating mantle, then removed from the mantle for rapid cooling to 80 °C where the solution was extracted into

four 15 mL plastic centrifuge tubes. Three mL of chloroform were injected into the flask to remove the remaining particles. The collected particles were then dispersed in three mL of chloroform and 12 mL of isopropanol. The dispersed particles were centrifuged for 10 mins at 5800 rpm, and then the supernatant was discarded. The washing procedure was repeated two additional times with a 30 second per tube sonication step after the solvent (CHCl_3) and anti-solvent (IPA) were added to aid dispersion. While it is important to wash the Cu_{3-x}P thoroughly, any more than three washing steps can result in ligand stripping. When the Cu_{3-x}P NPs were washed five times, we noted poor stability and lack of dissolution, and PXRD analysis of the Cu_3PSe_4 synthesis below (Figure B.2) indicated a Cu_{2-x}Se binary in the products.

Cu_3PSe_4 . Cu_{3-x}P NPs, synthesized above, from three centrifuge tubes are suspended in hexanes and transferred to a pre-weighed 25 mL three-neck round-bottomed flask. Once the particles were dried over nitrogen, the flask was weighed to determine the overall weight of Cu_{3-x}P NP precursor (typically ca. 15 mg). The flask was then pumped into the glovebox equipped with a Teflon[®]-coated stir bar, Liebig reflux condenser, and thermocouple. Se powder (4 equivalents to Cu_{3-x}P minus 15% ligand contribution) and the solvent (ODA or ODE, so that the Cu_{3-x}P NP concentration was retained at 6 mM) were measured out into the reaction flask in the glovebox. When using ODA, make sure to slightly heat the storage vessel (typically an Erlenmeyer flask from sparging the solvent) to make sure it doesn't crystallize in the syringe. Once removed from the glovebox, the reaction flask was sonicated at 35 °C for 1 minute or until the Cu_{3-x}P were fully suspended and attached to the Schlenk line and kept under nitrogen. A medium stir rate (400 rpm) was set which produced a black solution. The reaction flask was heated up to 300 °C at a 500 °C/hr ramp rate and held for 20 minutes. After the reaction reached completion, the flask was raised from the heating mantle to be cooled to 80-60 °C for extraction to two 15 mL plastic

centrifuge tubes. The total reaction solution was centrifuged at 5800 rpm for 5 mins to separate the supernatant. The supernatant was saved and precipitated Cu_3PSe_4 NPs were dispersed with a 1:5 toluene:ethanol mixture (2 mL toluene and 13 mL of ethanol). The dispersed particles were centrifuged for 10 mins at 5800 rpm, then the washing solution was discarded. The washing procedure was repeated 2 times with a sonication step after each washing mixture was added to aid dispersion.

Ex situ Method. The Cu_3PSe_4 synthesis provided above was replicated to extract aliquots at 250 °C, 300 °C, and 300 °C for select times. During the heating profile, 1.5 mL aliquots were extracted from the entire reaction solution. To ensure an air-free environment, the 5 mL glass, Luer lock, syringe and needle were purged with N_2 three times before extracting the aliquot. The extracted solution was then transferred to 20 mL vial to separate the reaction supernatant from the particles and washed using the same procedure as above.

Cannula transfer Method. The Cu_{3-x}P NPs were prepared using the same procedure for the standard Cu_3PSe_4 reaction. Identical glassware (25 mL three-neck round-bottomed flask, stir bar, Liebig reflux condenser, and a thermocouple) was pumped in the glovebox to prepare a separate octadecane/selenium solution. Selenium powder was weighed out in the 25 mL flask and ODA was added before pumping the whole setup out of the glove box. Both flasks were sonicated at 35 °C for 1 minute. Once attached to the line, both flasks were cycled three times then heated to the desired temperature. After the temperature was reached, a heated cannula needle was added to the Se/ODA solution then connected to the Cu_{3-x}P NP/octadecane solution. A vent needle was then added to the Cu_{3-x}P flask, which allowed for the headspace (gaseous species) to bubble through the Cu_{3-x}P solution. After 20 mins, the reaction was cooled and worked up using the procedure for the standard Cu_3PSe_4 synthesis.

Characterization

X-ray Diffraction. Powder X-ray Diffraction Spectroscopy (PXRD) was performed on a Bruker D8 Discover Series Powder X-ray Diffractometer (PXRD) using a Cu K α source ($\lambda = 1.54$ Å) and a Lynxeye XE-T positron-sensitive detector. Samples were prepared by dispersing the particles in hexanes, followed by drop-casting on a p-type boron-doped Si Zero Diffraction Wafer (MTI Corporation). Ground samples were first dispersed in hexanes, deposited on a glass plate and scraped into mortar and pestle. The samples were then transferred to the diffraction wafer that contained zero-diffraction grease to reduce preferred orientation. Diffraction patterns were indexed using the DIFFRAC.EVA software v5.2 to known powder diffraction files (PDF) patterns in the PDF-4+ database. The PDF patterns used for the following phases are: Cu₃P #01-071-2261, Cu₃PSe₄ #04-006-8347, Se #00-042-1425, Cu_{1-x}Se #01-089-2734, Cu_{2-x}Se #00-006-0680, Cu₇PSe₆ #00-033-0482, and Cu₂Se_x #00-047-1448.

Rietveld Refinements. Refinements were performed using TOPAS v6 (Bruker AXS). Specific parameters are included for the selected patterns below.

Nuclear Magnetic Resonance (NMR). ¹H, ¹³C, and ³¹P NMR experiments were performed on the reaction supernatants in deuterated chloroform (CDCl₃, Thermo Scientific, 99.8%, dried over activated 3 Å molecular sieves) on a Bruker NEO400 spectrometer with automated tuning.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed on Cu_{3-x}P and Cu₃PSe₄ samples in ceramic pans using a TA instruments Q500 Thermogravimetric analyzer. After following synthetic and washing procedures described, dried powders were isolated and analyzed at 2 and 10 °C per minute to the desired end temperature defined for Cu_{3-x}P and Cu₃PSe₄. After completion, X-ray diffraction of the material was used to discern weight changes due to degradation.

Imaging. Morphology of nanoparticles were characterized using a JEOL JEM 2100F Transmission Electron Microscopy (TEM) with acceleration voltage of 200 keV. Scanning transmission electron microscopy (STEM) energy dispersive X-ray spectroscopy (EDS) was carried out with an Oxford X-Max 80 mm² detector and analyzed using AZtecTEM software. Samples were prepared by sonicating one centrifuge tube of particles (ca. 10 mg) with one mL of toluene and hexanes for one minute. 0.1 mL of the particle dispersion was further diluted with 1 mL of toluene, making a 1:10 ratio, which was sonicated for another 5 minutes at 35 °C. Finally, 14 mL of hexanes was to the solution and sonicated for another minute. Carbon-coated nickel TEM grids (200 mesh, Ted Pella) were dipped into the diluted mixture and dried once removed by touching the grid with a Kimtech Kimwipe. The grid is then dried in the fume hood overnight and pumped down under vacuum for 30 minutes before imaging. Images were analyzed in Digital Micrograph of the Gatan Microscopy Suite software (v3.51).

Gas Chromatography – Mass Spectroscopy (GC-MS). For GC-MS analysis, a 1.5 mL GC vial with septa top was filled with 1.0 mL hexanes and degassed using a Schlenk line prior to use. A 0.1 mL aliquot was extracted from the supernatant solution and injected into the GC vial. The sample was immediately analyzed using an Agilent 5973N Mass Selective Detector interfaced to a 6890 Gas Chromatograph which is equipped with a 7683 Automatic Liquid Sampler (ALS), Electron Ionization (EI) source and high-energy dynode (HED) electron multiplier detector. The Agilent 122-5532 column was flowed from 1 mL/min to 52.8 mL/min with a starting temperature of 60 °C ramping to 325 at 15 °C/min where it was held for 2 minutes before cooling. Gas chromatograms and mass spectra were analyzed using Enhanced Data Analysis to compare mass spectra to a NIST mass spectral library to identify analyte species.

X-ray Photoelectric Spectroscopy (XPS). X-ray photoelectron spectroscopy was performed on a Physical Electronics ESCA 5800 system using a monochromatic Al K α ($E = 1486.6$ eV) X-ray source for all scans. High resolution scans were used to analyze all possible elements: carbon 1s, oxygen 1s, nitrogen 1s, phosphorus 2p and copper 2p. CasaXPS was used to process the data. All spectra were calibrated using the aliphatic carbon peak at 285 eV. Fitting utilized a Shirley background and gaussian line shapes for all peaks. Photoelectrons for the copper 2p and the phosphorus 2p showed split peaks were fit using position and area constraints of known values.

Supplemental Data

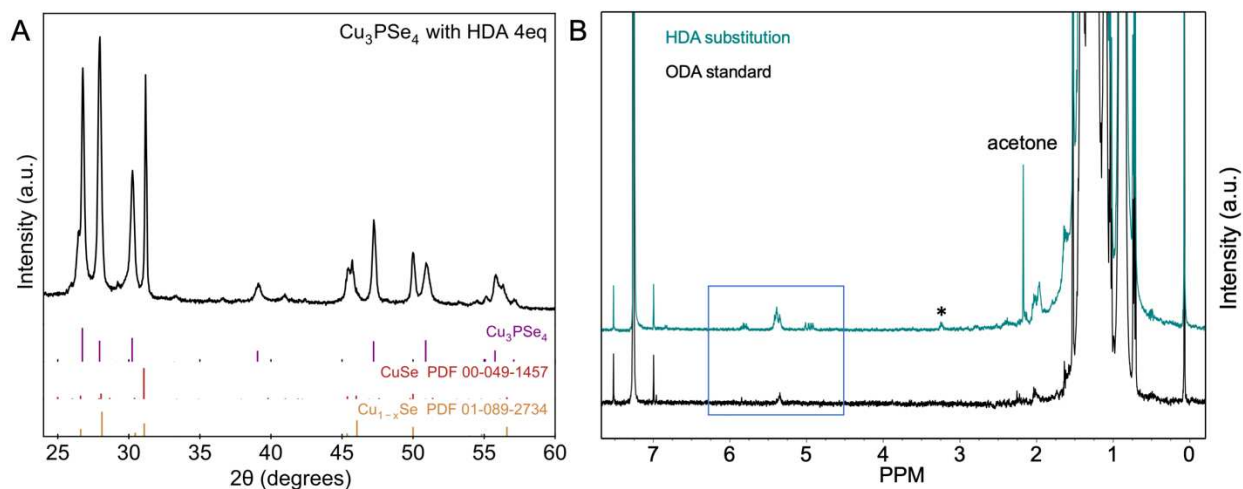


Figure B.1. Powder X-ray diffraction (PXRD) and ^1H nuclear magnetic resonance (NMR) of a Cu_3PSe_4 reaction where 1-ODE is replaced with HDA for the equivalence of selenium. (A) PXRD displays the formation of two different binaries, CuSe and Cu_{1-x}Se . (B) ^1H NMR of ODA and HDA substitution for 1-ODE, which results in the formation alkenes (presence is highlighted in the blue box) and hypothesized aldimine (*).

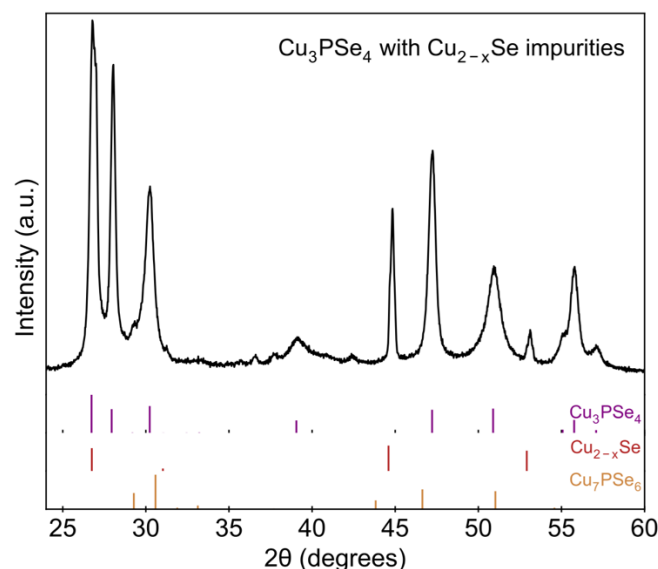


Figure B.2. PXRD of the final product with Cu_{2-x}Se binary present due to the reproducibility issues that are listed above and possible oxidation issues.

Table B.1. Experimental conditions for existing, historical/classical high temperature solid-state syntheses of Cu_3PSe_4 and Sn(IV) tetraselenophosphate.

Balanced Reaction	Conditions
$3 \text{ Cu}_s^0 + \text{P}_s^0 + 4 \text{ Se}_s^0$ (99.99% elemental for all reactants) = Cu_3PSe_4 ⁵⁻⁷	1073K for 10 days then slowly cooled
$3 \text{ Cu}_s^0 + \text{P}_s^0 + 4 \text{ Se}_s^0$ (99.99% elemental for all reactants) = Cu_3PSe_4 ^{8,9}	873K for 24 hrs under argon atmosphere; additional grinding and heating at same T and time
$6 \text{ Cu}_s^0 + \text{P}_2\text{Se}_5 + 3 \text{ Se}_s^0$ (elemental) = Cu_3PSe_4 ¹⁰	Heated in evacuated quartz tube at 600 °C for 24 h then cooled to 50 °C over 12 h.
$3 \text{ Cu}_s^0 + \text{P}_s^0 + 4 \text{ Se}_s^0$ (>99% elemental for all reactants) = Cu_3PSe_4 ^{11,12}	Ground and sealed in evacuated fused silica tubes at 480 °C for 24 h.
$3 \text{ Cu}_{\text{powder}}^0 + \text{P}_s^0 + 4 \text{ Se}_{\text{powder}}^0$ (>99% elemental for all reactants) = Cu_3PSe_4 ¹³	Vacuum sealed in quartz ampoule and heated to 450 °C for 36 h.
Alternate Tetraselenophosphates Reactions	Conditions
$\text{SnCl}_4(\text{H}_2\text{O})_5 + \text{Na}_2\text{SeO}_3 + 2 \text{ Na}_2\text{H}_2\text{PO}_4$ at pH = 0 ¹⁴	Two separate methods, where one is not refluxed and the other is refluxed in 2 mol dm ⁻³ H_3PO_4 + 2 mol dm ⁻³ selenious acid (1:1).

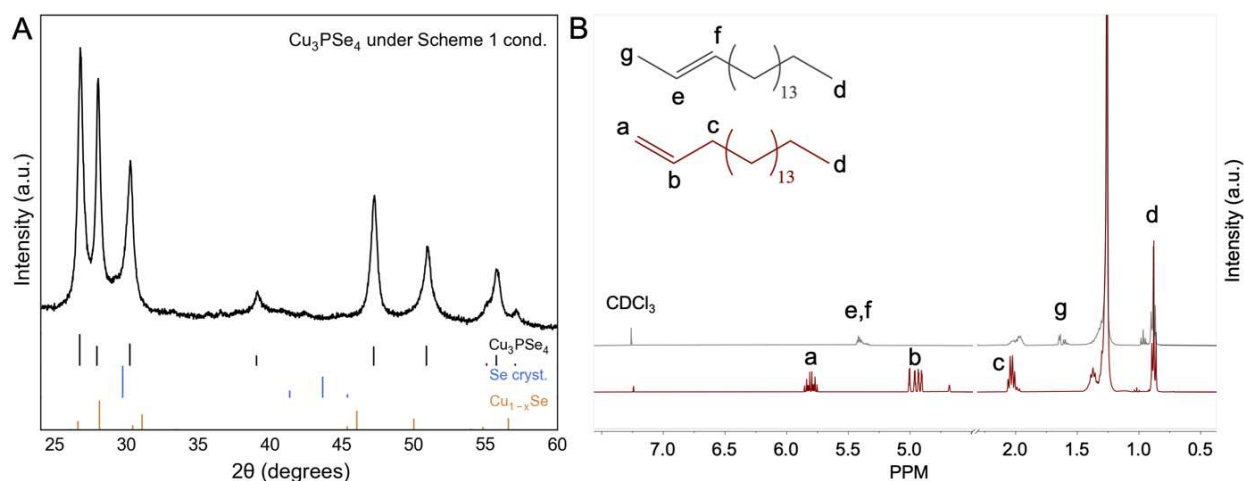


Figure B.3. PXRD pattern and ^1H NMR of Cu_3PSe_4 using ODE synthetic conditions.¹ (A) PXRD and Rietveld refinements of final nanoparticles and (B) ^1H NMR of the supernatant (grey) and 1-ODE standard (red).

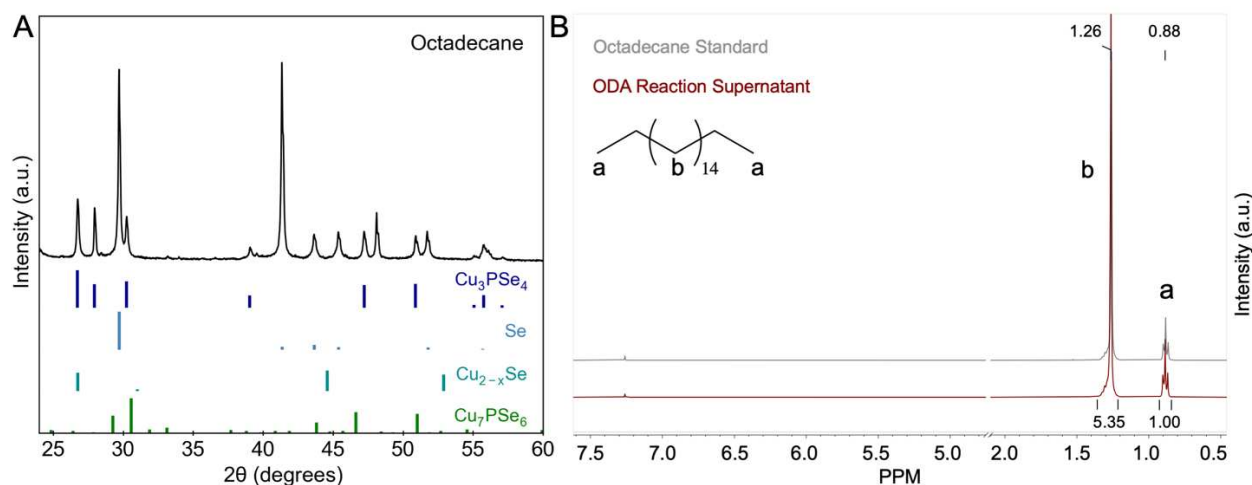


Figure B.4. Standard reaction conditions of Cu_3PSe_4 with ODA as the solvent. (A) PXRD of the final nanoparticles and (B) ^1H NMR of the supernatant (red) shows no deviation from pure octadecane (grey).

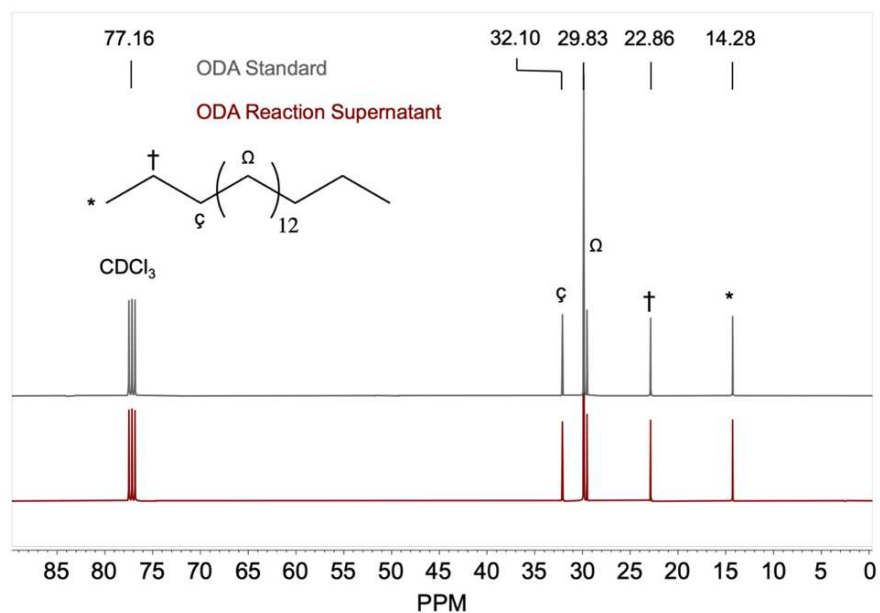


Figure B.5. ^{13}C NMR of the stoichiometric 4 eq assuming 100% Cu_3P with octadecane reaction. The downfield shift and peak intensity further demonstrate that octadecane didn't react with Se^0 .

Table B.2. Rietveld Refinement parameters for Figure 1A in main text (ODA synthesis of Cu_3PSe_4).

Phase	Cu_3PSe_4
Crystal System (space group)	Orthorhombic, $\text{Pmn}2_1$
a, Å	7.700 (2)
b, Å	6.6768 (18)
c, Å	6.3846 (18)
Cell Volume, Å ³	328.26 (16)
Preferred Orientation (two directions)	(002) (400)
Phase	Se
Crystal System (space group)	Trigonal, $\text{P}1\bar{3}12$
a, Å	4.481 (15)
c, Å	4.75 (2)
Cell Volume, Å ³	82.6 (7)
Instrument	
Surface roughness (Pitschke et al.)	0.00 (3)
Z height specimen displacement	-0.154 (9)

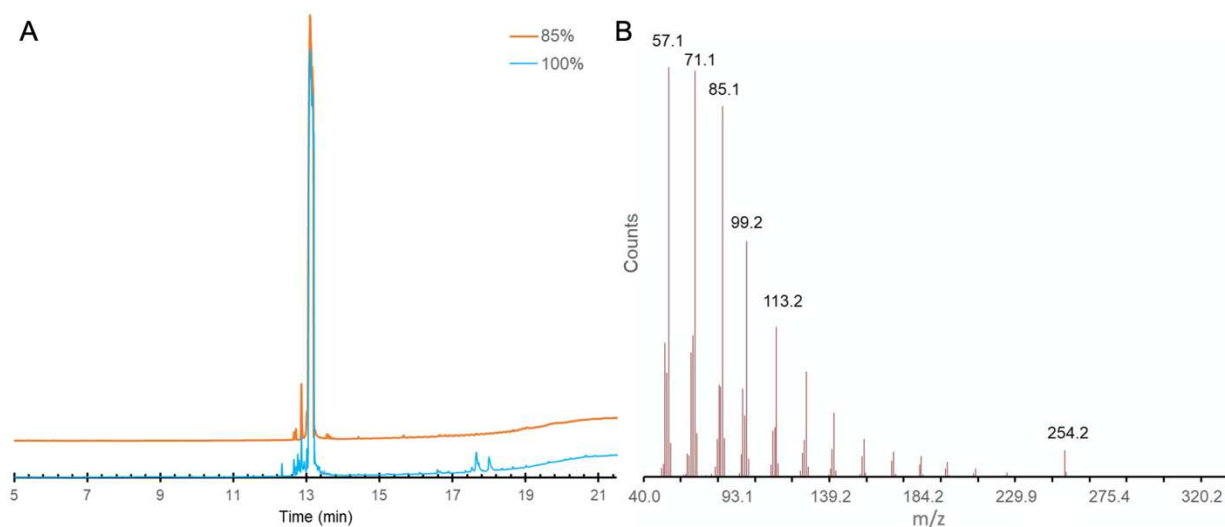


Figure B.6. Gas chromatography-mass spectroscopy (GC-MS) data of Cu₃PSe₄ with octadecane at 4 eq assuming 100 and 85% Cu_{3-x}P. GC data (A) demonstrates that the major peak present is octadecane, attributed by the MS data (B), in both 100 and 85%. However, of note the smaller peaks to the left of the octadecane peak at 13 mins decreases when the ligand percentage was accounted for. Overall, no Se⁰_n was directly observed in GC-MS, as we believe that Se crashes out of solution and is filtered out by glass wool in the injection port.

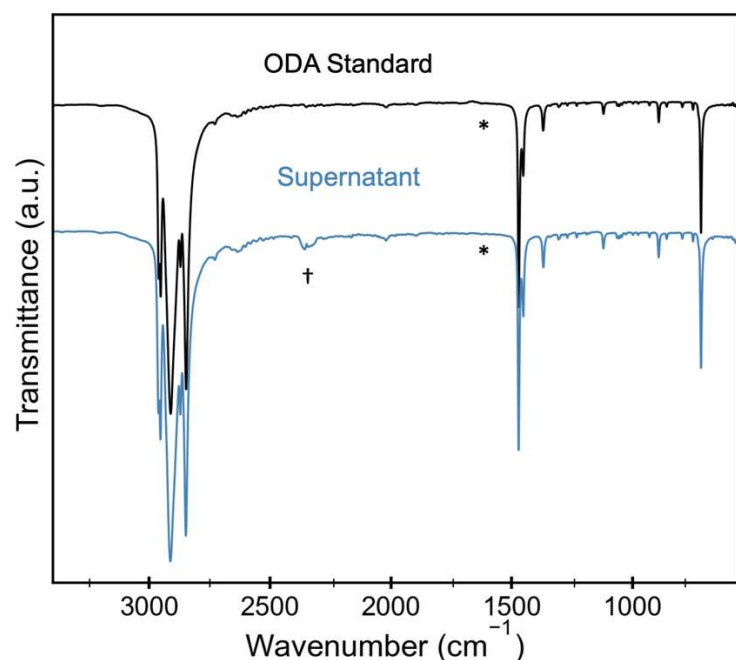


Figure B.7. Fourier-transform infrared spectroscopy (FT-IR) of the Cu₃PSe₄ reaction supernatant. The black spectrum is the ODA standard and royal blue is the supernatant of a stoichiometric Cu₃PSe₄ reaction, while the asterisk symbol (*) is provided to indicate where an alkene C=C stretch would occur if present.¹⁵ The symbol (†) is the presence of CO₂.

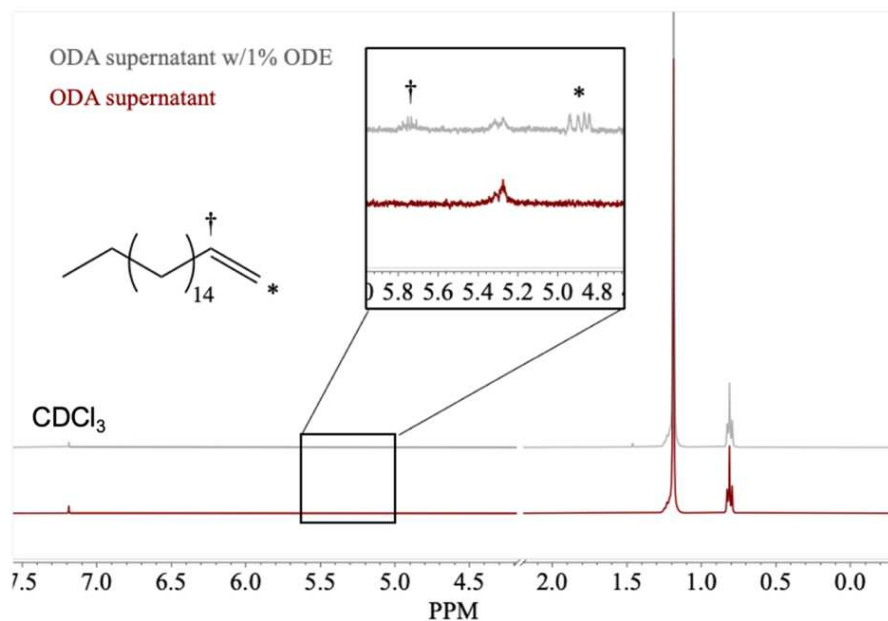


Figure B.8. ^1H NMR studies of the ODA Cu_3PSe_4 synthesis supernatant and the supernatant with 1% ODE. The dark maroon, bottom spectra, is the reaction supernatant. The top spectra, grey, is the reaction supernatant with 1 mol % of 1-ODE added.

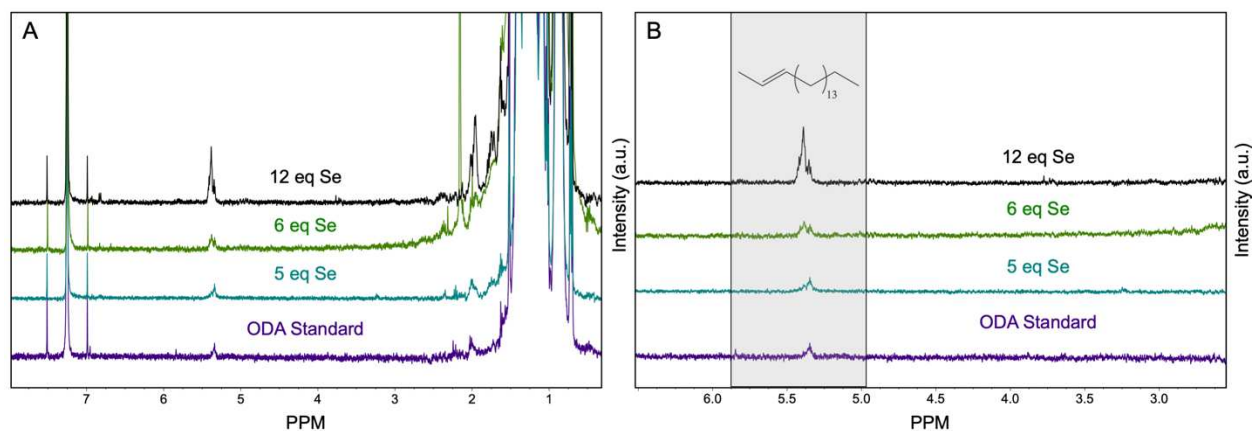


Figure B.9. ^1H NMR of different selenium equivalents to observe the disappearance of mid-chain alkene. (A) Full ^1H NMR spectra from 0.8 to 7.8 ppm and (B) zoomed in spectra from 2.7 to 6.5 ppm. Five equivalence is used as the lowest amount of selenium in this case, as the assumption of 100 wt% Cu_{3-x}P for the pre-synthesized particles (i.e., excluding ligand wt%) results in slight excess of selenium, *vide infra* (Figure B.24 and S25).

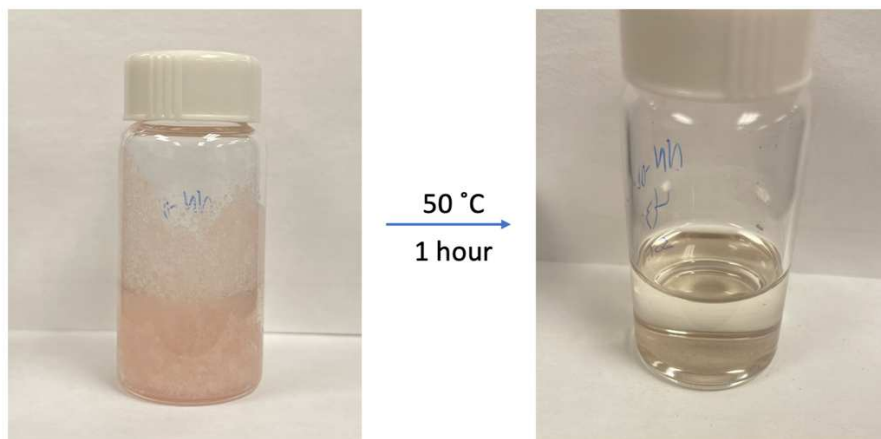


Figure B.10. Images of the stoichiometric reaction supernatant heated at a prolonged time to determine the presence of amorphous selenium. One specific control to determine if amorphous selenium is present is to heat the material to 40 °C for 30 mins, where in which a color transition is induced to produce black selenium.^{16,17} We have performed a similar heating profile for our supernatant containing the red tint, and indeed a color transition is noticed ca. 1 hour at 50 °C. Although not direct characterization, from our current understanding if the source of the red tint was phosphorous, the alternate hypothesis for a byproduct that has a red allotrope, then this transition would only be witnessed at temperatures higher than 200 °C.¹⁸

Table B.3. Rietveld Refinement parameters for Figure 2 in main text (4 eq of Se in ODE).

Phase	Cu ₃ PSe ₄
Crystal System (space group)	Orthorhombic, Pmn2 ₁
a, Å	7.719 (5)
b, Å	6.665 (3)
c, Å	6.3705 (8)
Cell Volume, Å ³	327.7 (2)
Preferred Orientation (two directions)	(002) (212)
Phase	Cu _{2-x} Se
Crystal System (space group)	Cubic, P1312
a, Å	5.7460
Cell Volume, Å ³	189.71
Phase	Cu ₇ PSe ₆
Crystal System (space group)	Cubic, P2 ₁ 3
a, Å	10.1031
Cell Volume, Å ³	1031.25
Instrument	
Surface roughness (Pitschke)	0.03 (3)

Z height specimen displacement	-0.016 (9)
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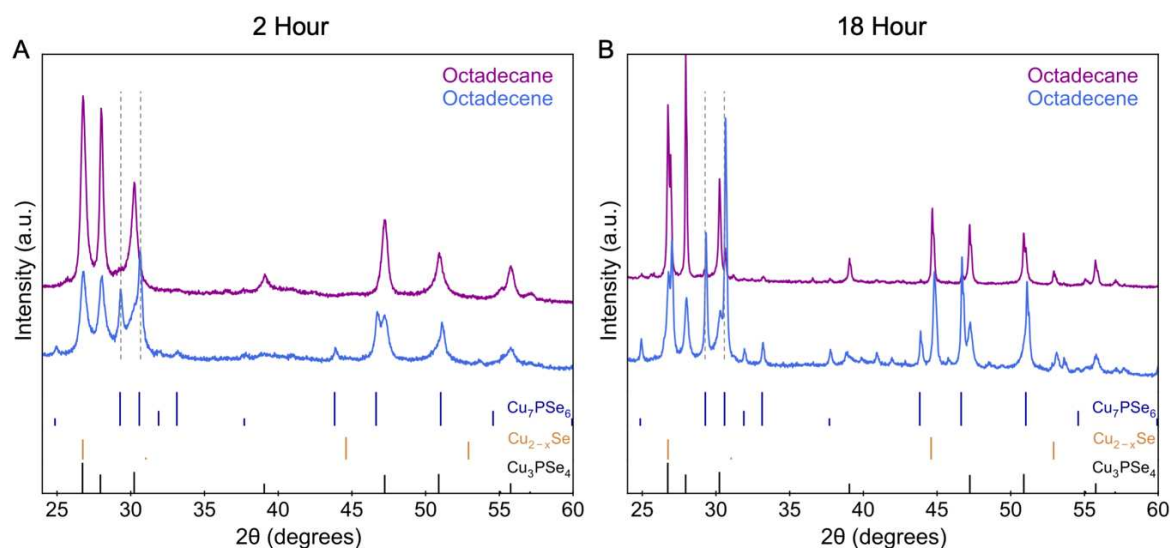


Figure B.11. PXRD of extended time studies of ODA Cu₃PSe₄ synthesis. (A) Two-hour and (B) 18 hour or overnight reaction with 4 eq Se⁰_{powder} in ODA and 1-ODE. The dashed lines indicate the two distinct peaks that represent Cu₇PSe₆.

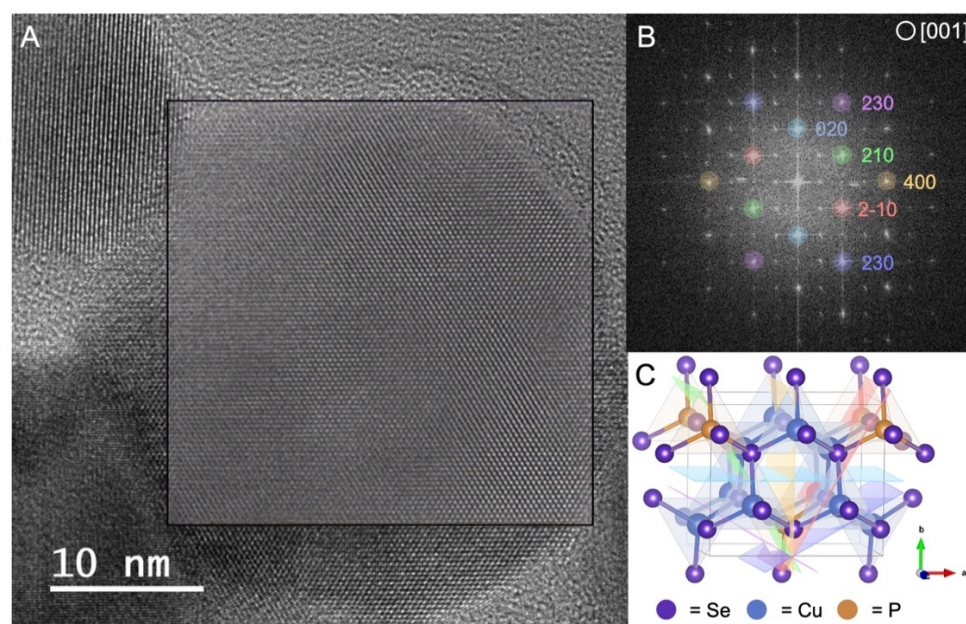


Figure B.12. Transmission Electron Microscopy (TEM) and fast Fourier transform (FFT) of Cu₃PSe₄ ODA synthesis. (A) TEM image overlaid with colored inverse FFT images from the masked planes (020), (210), and (2-10) in (B) with additional planes marked to demonstrate the viewing direction of (001) is consistent. The d-spacing for the planes identified in (B) were compared to the d-spacings for Cu₃PSe₄ (cif: 04-006-8347) using a ratio method where a <1 %

difference between the measured and predicted distance was calculated. (C) Cu_3PSe_4 crystal structure with the corresponding planes masked in B, where the colors are kept consistent.

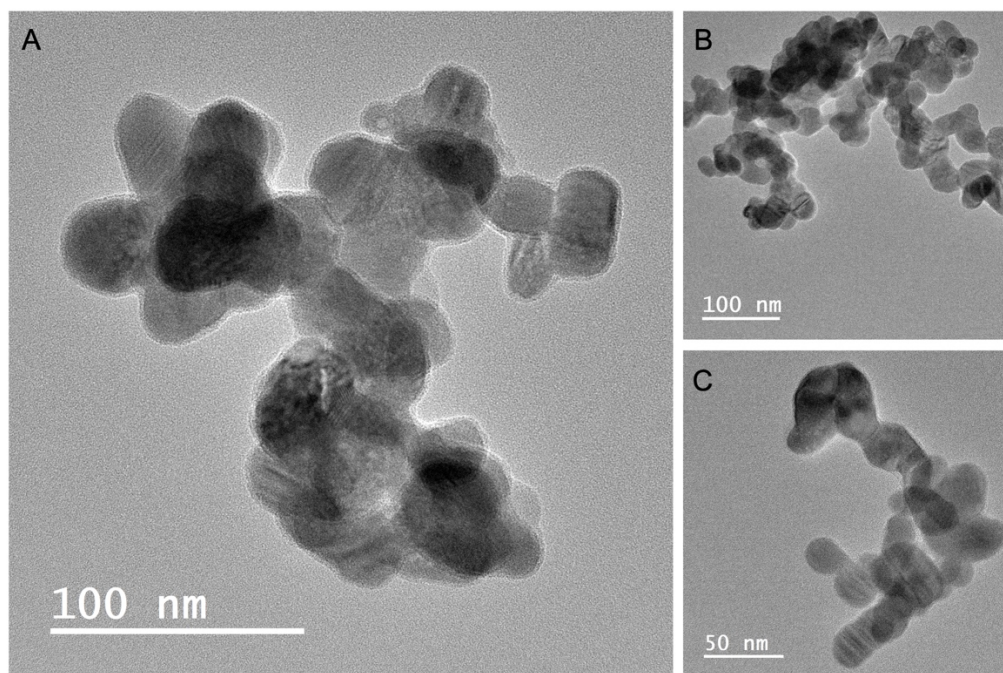
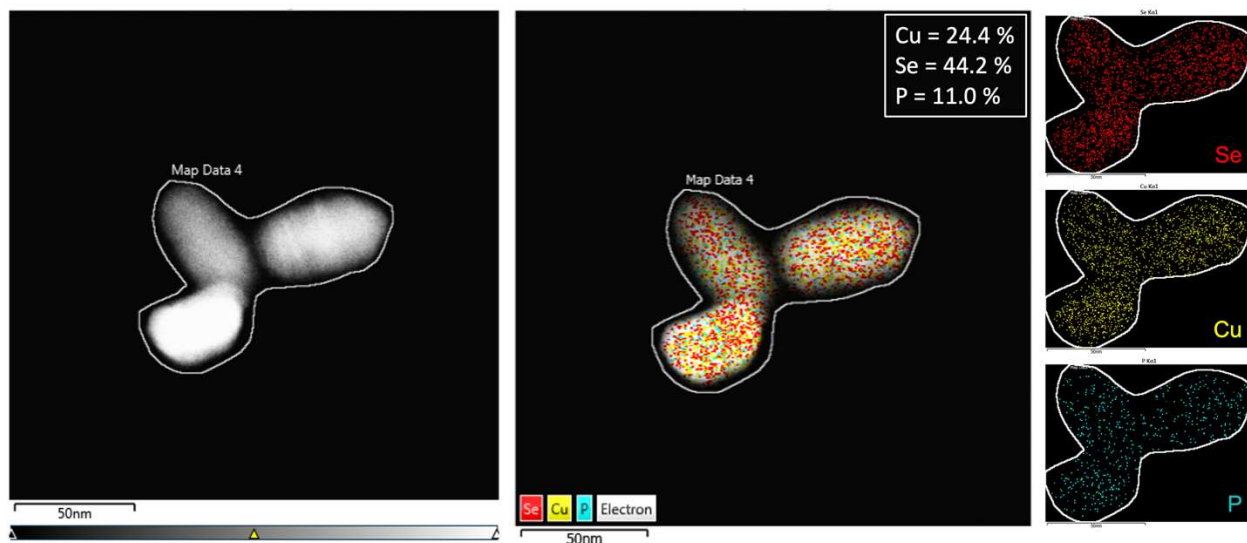


Figure B.13. Low magnification images of standard Cu_3PSe_4 reaction. Images demonstrate that the particles resemble a prolate ellipsoid form, which we plan to use for our calculation of Cu_3PSe_4 monomers.



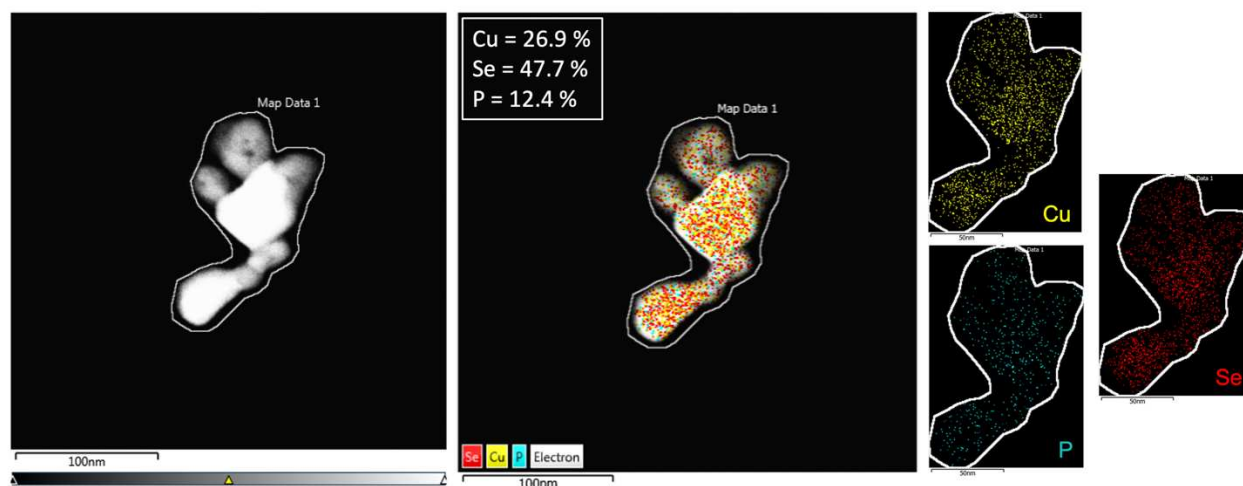


Figure B.14. STEM/EDS data of Cu_3PSe_4 ODA synthesis. The two figures are from different areas with more agglomerated particles in the bottom figure. The percentages included in the mapped data are the atomic percentages of the individual elements, which produces a ratio of 2.22:1.00:4.02 (top) and 2.17:1.00:3.85 (bottom) for Cu:P:Se.

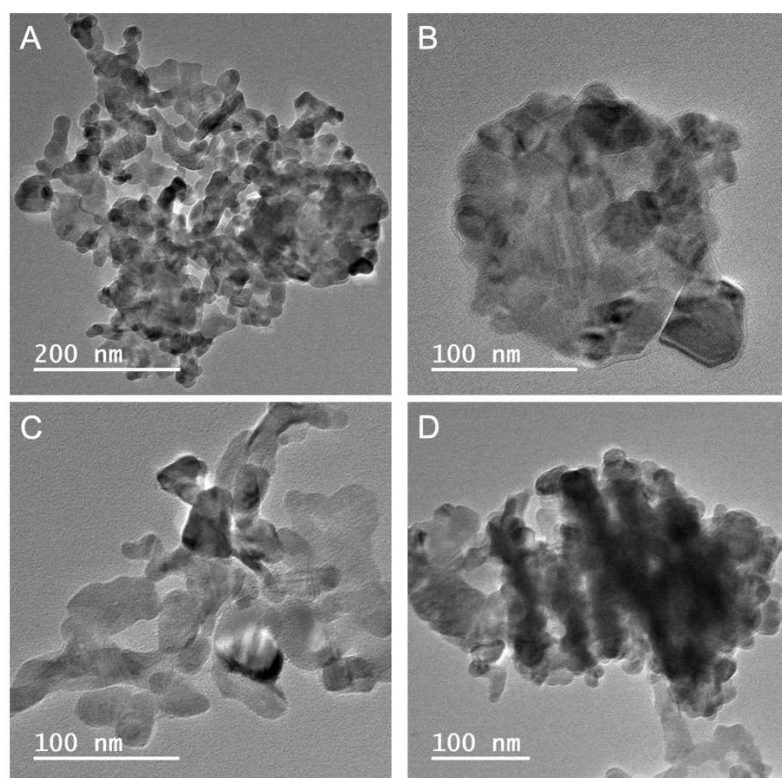


Figure B.15. TEM images at different magnifications of the Cu_3PSe_4 synthesis with Scheme 1A conditions using 1-ODE as the solvent, previously published by our group.¹

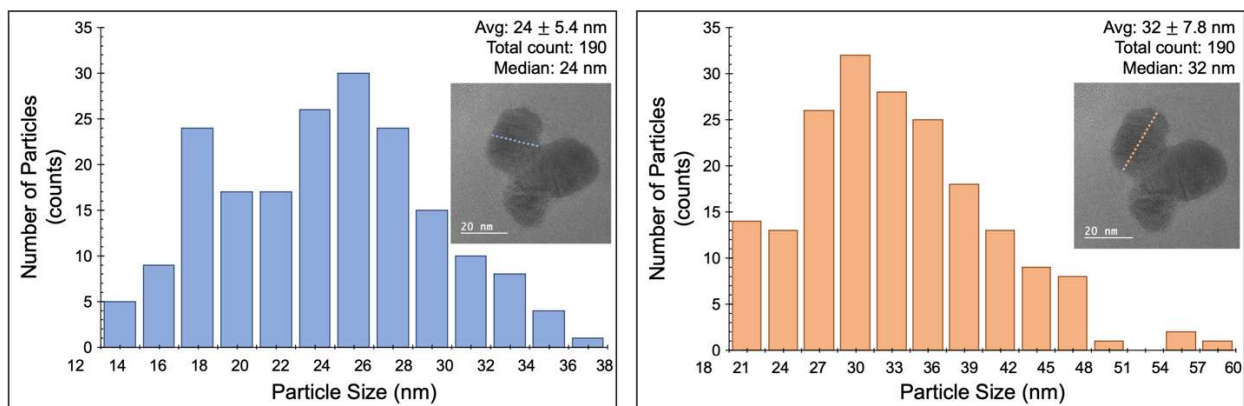


Figure B.16. Particle size distribution plot of Cu_3PSe_4 NPs with average, standard deviation, number of particles measured (total count), and median particle size.

B.17. Calculation of p in $1/p(\text{Cu}_3\text{PSe}_4 \bullet \text{HDA})_p$ with the average particle size calculated in S15.

The unit cell parameters and volume of the unit cell ($328.9 \text{ \AA}^3$) provided from the Rietveld refinements in Table B.2 are used in this calculation. The total volume of the particles is calculated with the assumption that the particles are prolate ellipsoid in shape (eq 1), where $a = 16 \text{ nm}$ and $b = 12 \text{ nm}$. The standard deviation is calculated to be 3.6×10^2 monomer units, while the minimum and maximum monomer units are calculated to be 1.2×10^5 and 5.6×10^3 , respectively.

$$V_{\text{prolate ellipsoid}} = \frac{4}{3} \pi a b^2 = 9.7 \times 10^{-23} \text{ m}^3 \quad (1)$$

$$V_{\text{unit cell}} = 328.9 \text{ \AA}^3 = 3.29 \times 10^{-28} \text{ m}^3 \quad (2)$$

$$p = \frac{V_{\text{prolate ellipsoid}}}{V_{\text{unit cell}}} = 2.9 (\pm 0.036) \times 10^4 \text{ monomers} \quad (3)$$

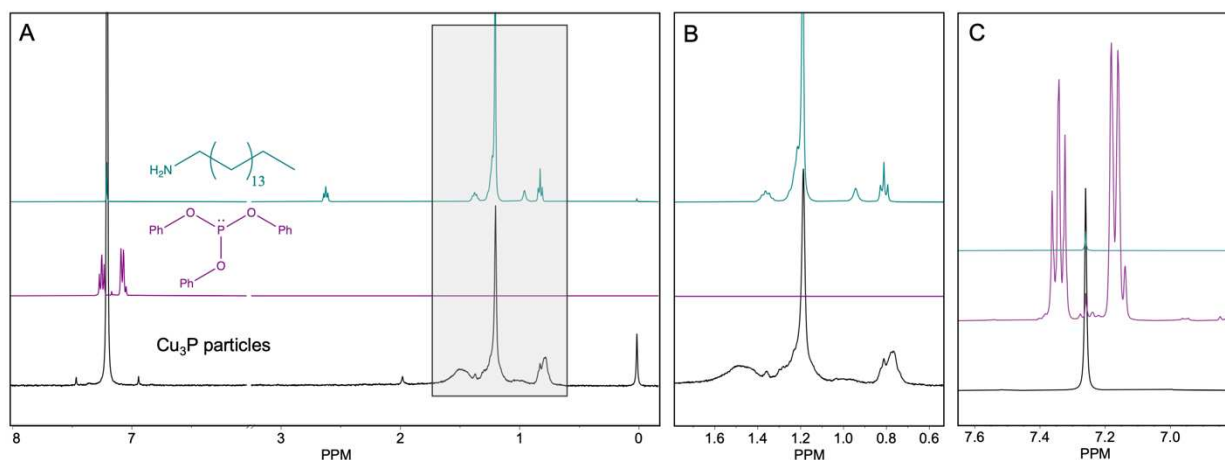


Figure B.18. ^1H NMR of Cu_{3-x}P pre-synthesized NPs. (A) Spectrum of 0-8 ppm for Cu_{3-x}P particles after washings (black), triphenyl phosphite standard (magenta),¹⁹⁻²¹ hexadecylamine (cyan) with a deleted region from 3.2 to 6 ppm as there were no detectable peaks within that region. (B) and (C) zoomed in spectrum (0.5-1.8 ppm and 6.8-7.0 ppm, respectively), to emphasize the major peaks in Cu_{3-x}P particles.

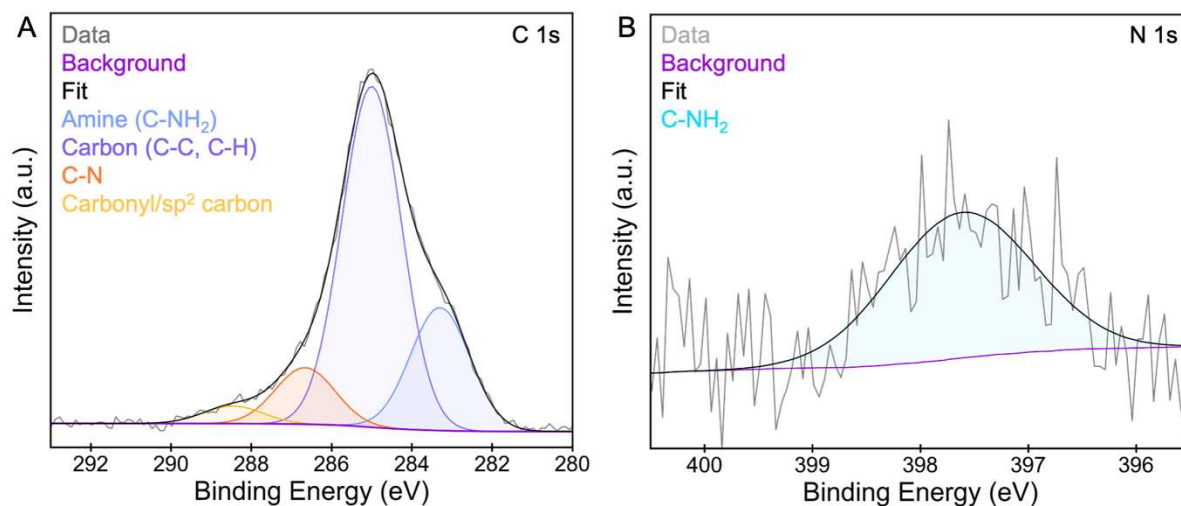


Figure B.19. X-ray photoelectron spectroscopy (XPS) of Cu_{3-x}P particles for both carbon and nitrogen 1s binding regions. Fits for both carbon (A) and nitrogen (B) peaks and the representative environments labeled with the corresponding-colored peaks.

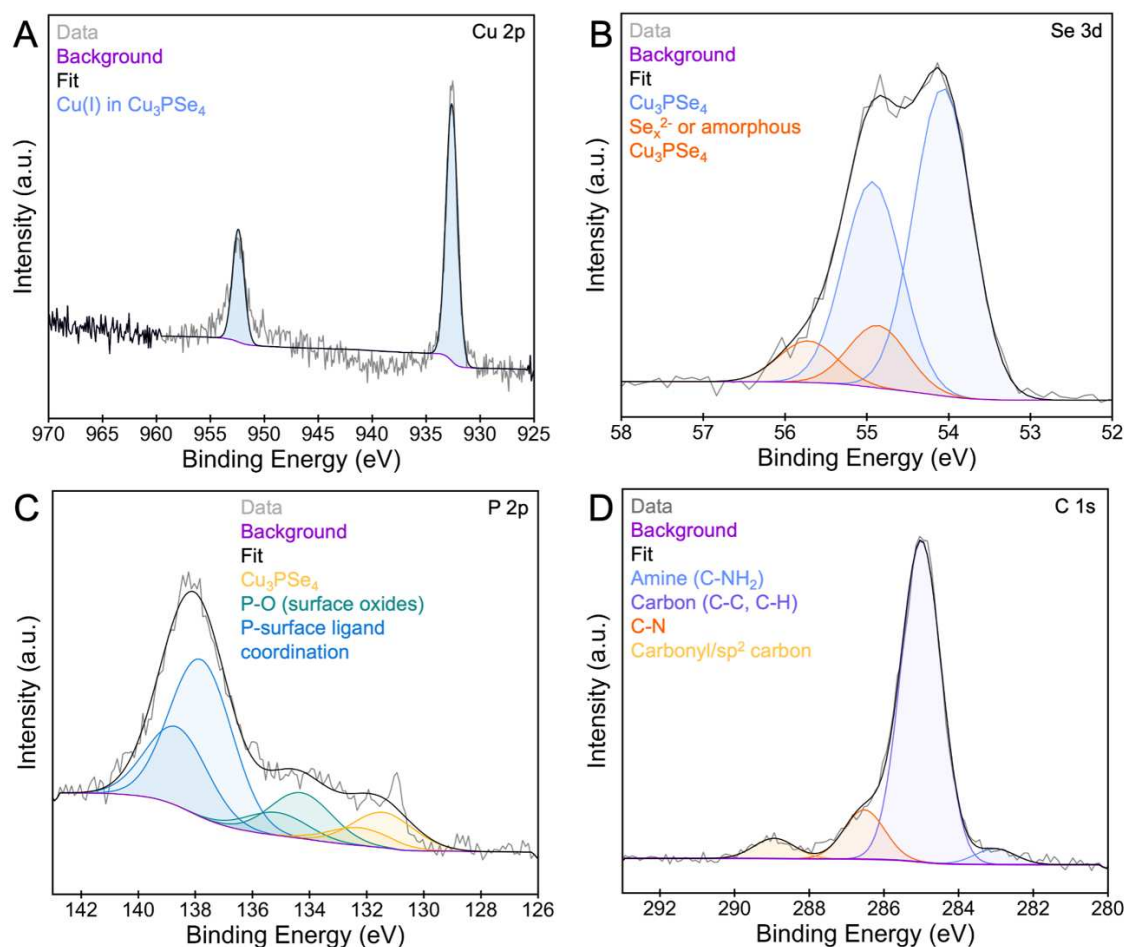


Figure B.20. XPS of Cu_3PSe_4 of the Cu, P, Se, and C bonding regions. Fits for the following (A) copper 2p, (B) phosphorous 2p, (C) selenium 3d, and (D) carbon 1s peaks are the representative environments are labeled with the corresponding-colored peaks. The Cu and Se environments are both representative of previous literature reports.^{13,22} The P environment has two peaks reported previously at ~131 and 134 eV,^{13,22–24} however, an additional peak at ~140 eV is attributed to surface ligand coordination, which isn't present in the previous literature reports due to the solid-state synthesis of Cu_3PSe_4 .

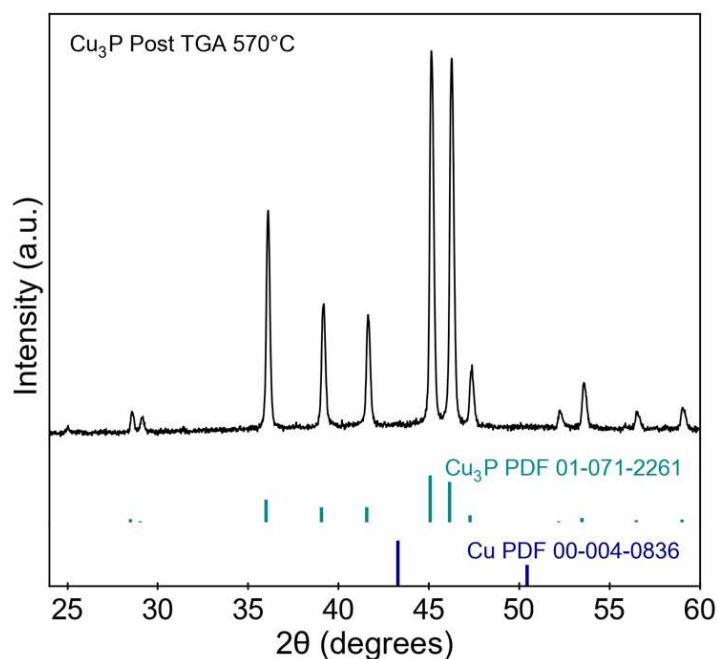


Figure B.21. Post-TGA PXRD of Cu_{3-x}P NPs. The PXRD pattern of the post-TGA particles (black) indexes to the Cu_3P PDF (cyan) without any Cu present (dark blue).

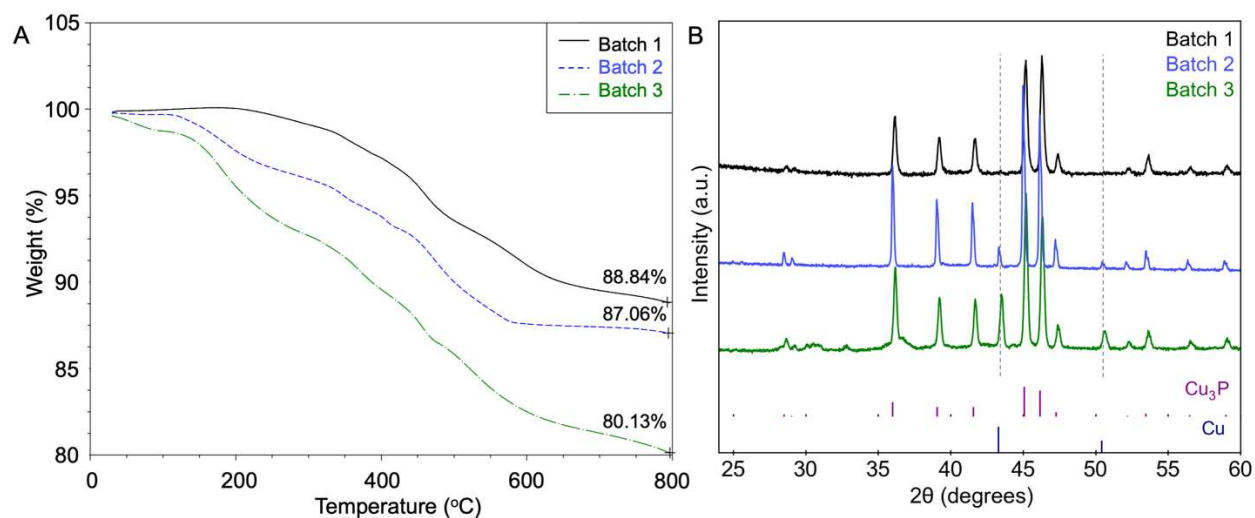


Figure B.22. TGA to 800 °C at a 10 °C/min heating rate and PXRD of the Cu_{3-x}P batches. (A) Thermogravimetric Analysis of the Cu_{3-x}P NP starting material. Batch 1, 2, and 3 represent three separate Cu_{3-x}P samples. (B) PXRD of the corresponding batches after TGA to evaluate degradation of Cu_3P to Cu (gray dashed lines indicate the representative Cu peaks).

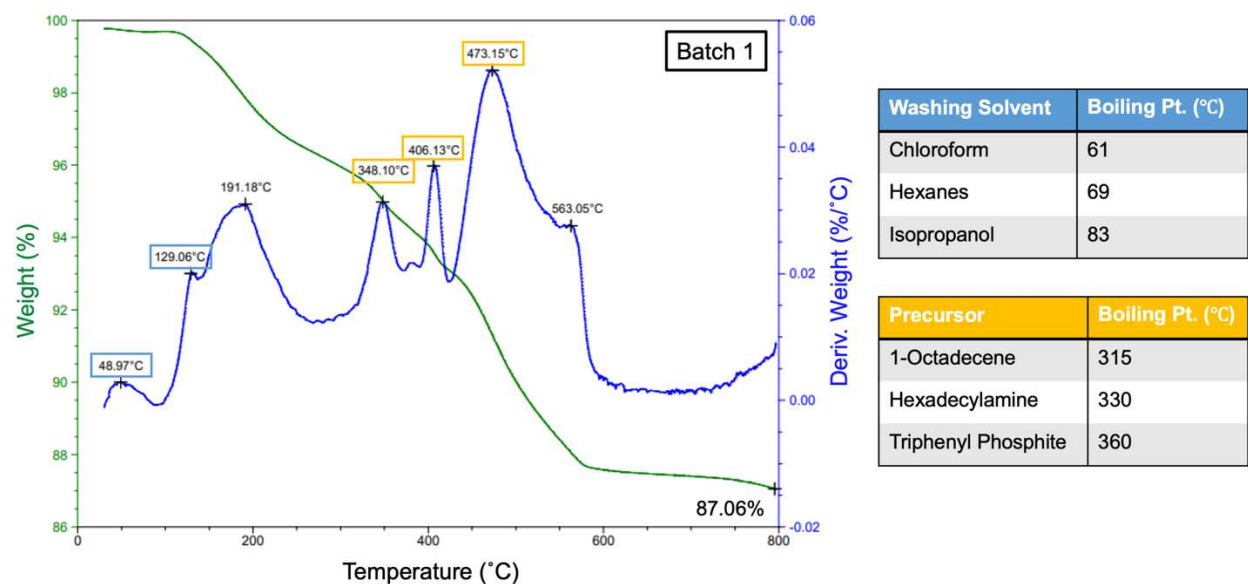


Figure B.3.23. Derivative of the TGA of batch 1 in Figure B.22. The weight loss events are matched to the washing solvents and precursors or coordinating ligands that could be present on the Cu_{3-x}P NPs surface.

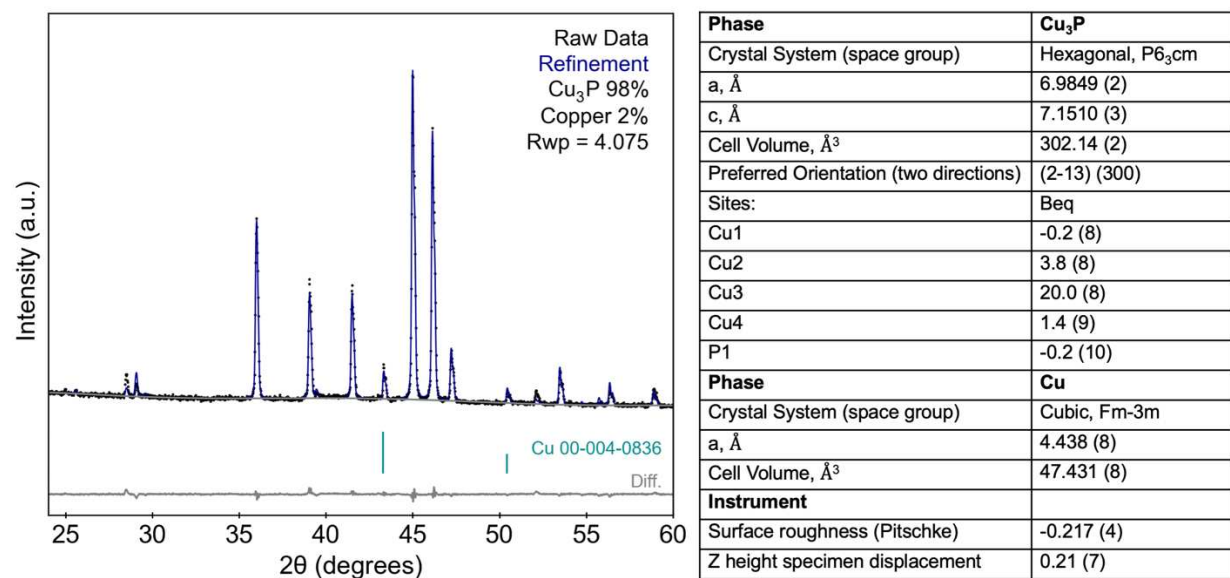


Figure B.24. PXRD and Rietveld refinement of Cu_{3-x}P NPs post TGA of batch 1 in Figure B.22. The refinement displays that the primary phase is Cu_3P with 98 wt% and only 2 wt% of copper (Cu, PDF #00-004-0836), which indicates that the primary weight loss events described above is contributed to the ligand content.

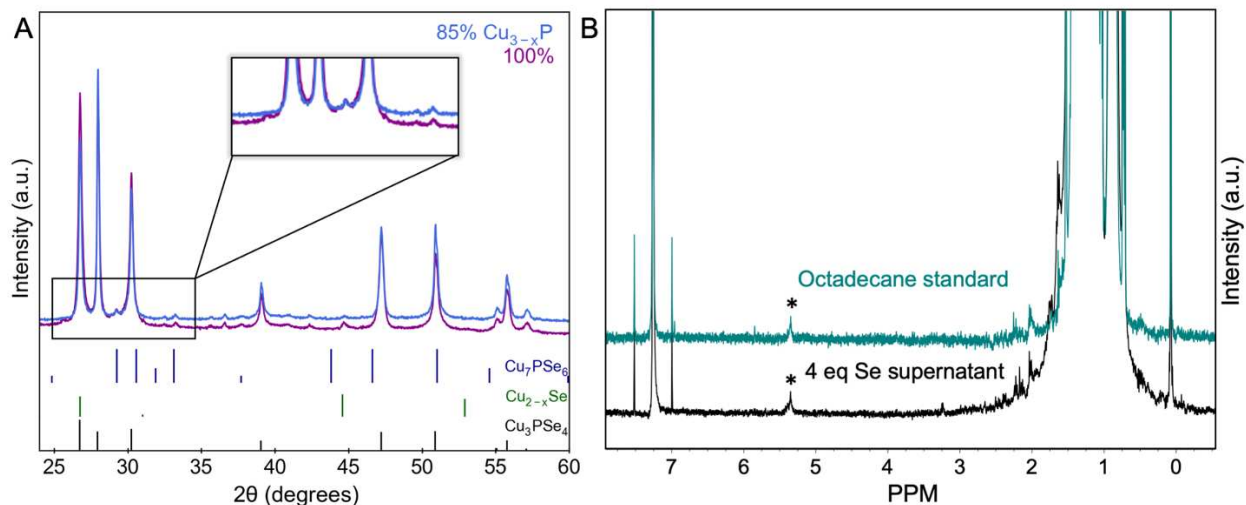


Figure B.25. PXRD and ^1H NMR of Cu_3PSe_4 reaction with ODA while accounting for the percentage of ligands to have a closer to stoichiometric reaction and reduce the excess amount of Se. (A) indicates the reduction of the broad peak around 28 2theta. (B) A zoomed proton NMR spectra to highlight the minimal presence of mid-chain alkene in comparison to an octadecane standard, due to a more accurate stoichiometric reaction of Cu_3PSe_4 when considering the wt% of HDA.

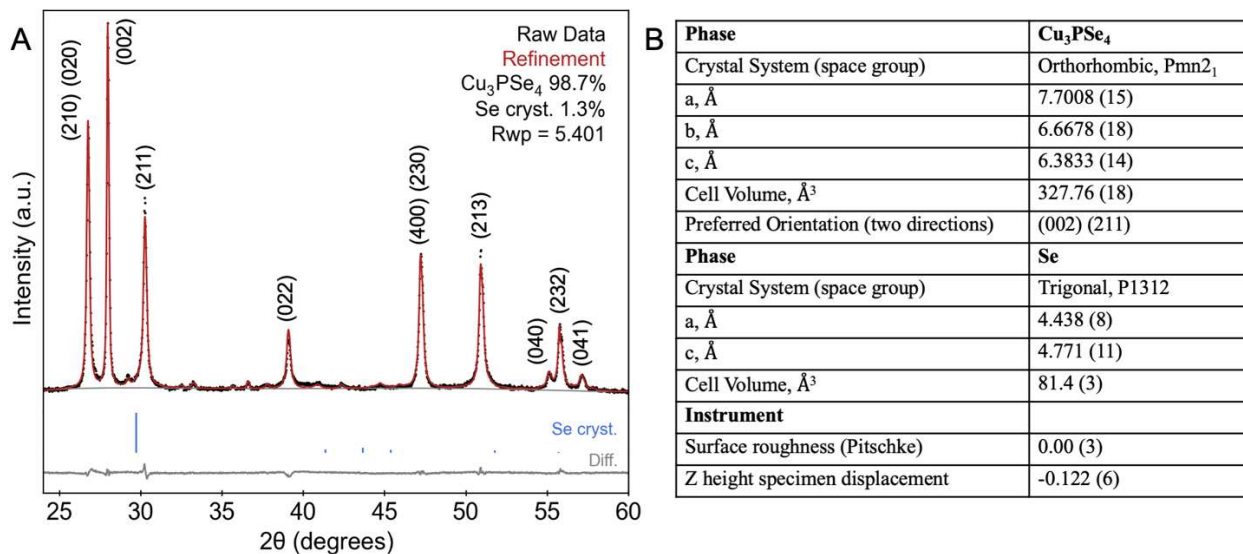


Figure B.26. Rietveld refinement method for the Cu_3PSe_4 ODA synthesis assuming 85% ligand content. (A) Rietveld fit of the PXRD pattern and (B) Refinement details of the fit and the corresponding errors.

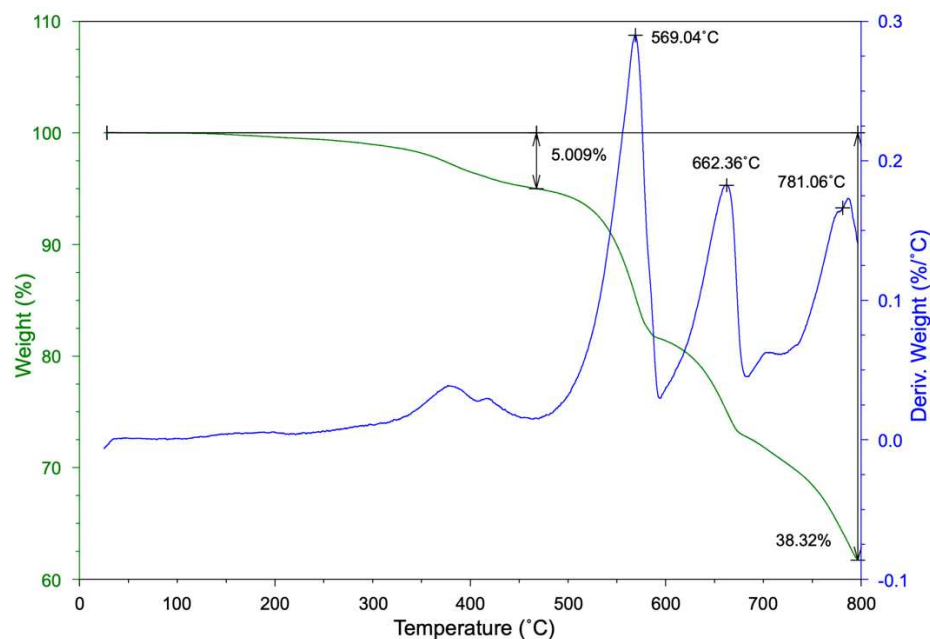


Figure B.27. TGA of Cu_3PSe_4 NPs produced from Scheme 1B assuming 85 wt% crystalline Cu_{3-x}P in the precursor. Degradation of the particles started to occur around 500°C, which is analogous to a previous report of bulk Cu_3PSe_4 .⁷

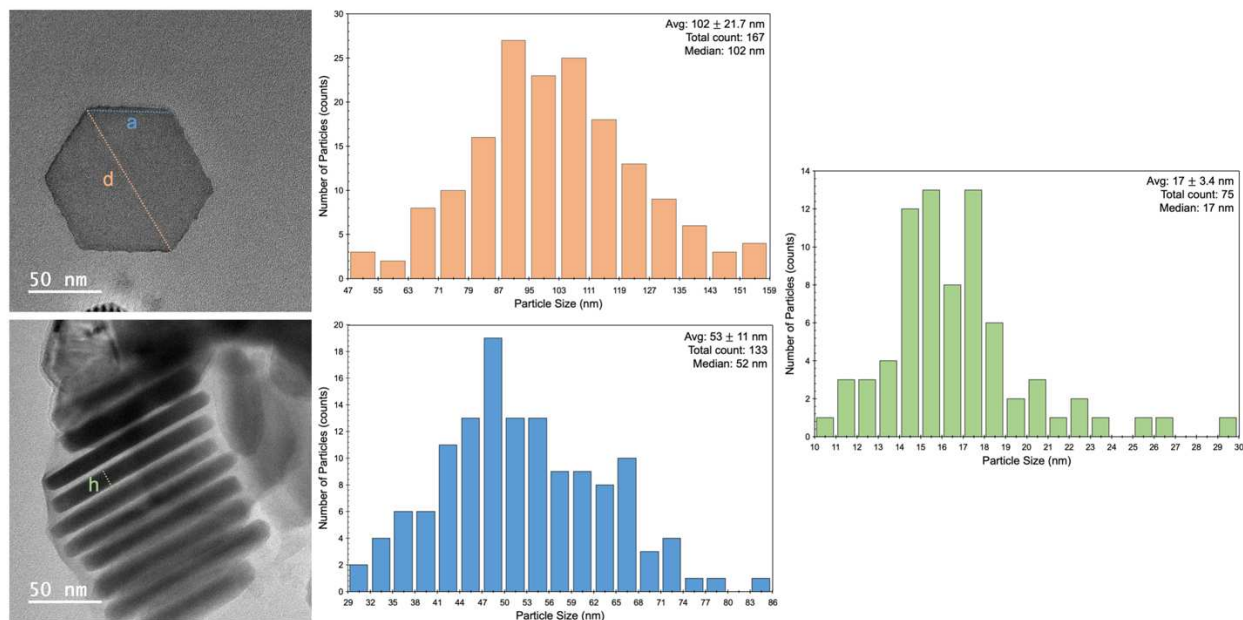


Figure B.28. Transmission Electron Microscopy (TEM) images and particle dispersion analysis plot Cu_{3-x}P NPs where the labels and colors correspond to the individual measurements.

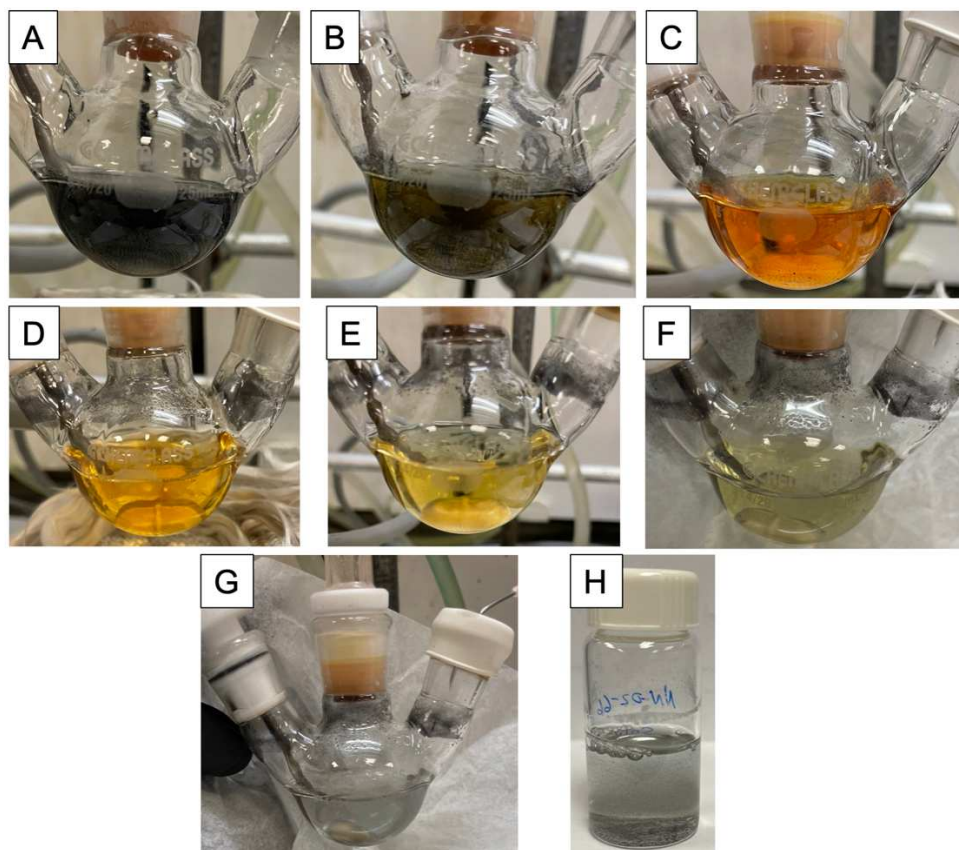


Figure B.29. Temperature control study of an octadecane/selenium solution at the same concentration for the stoichiometric Cu_3PSe_4 synthesis. The temperatures of the individual flasks are (A) 200 °C, (B) 225 °C, (C) 275 °C, (D) 300 °C, (E) 300 °C for 20 mins, (F) 225 °C, (G) 100 °C, and (H) the fully quenched solution. A distinct color transition is noted at 225 °C as this is the melting point of selenium, which is also noted as a reversible process as it can be seen in (F) and (G) that particles crash out at this same temperature point.

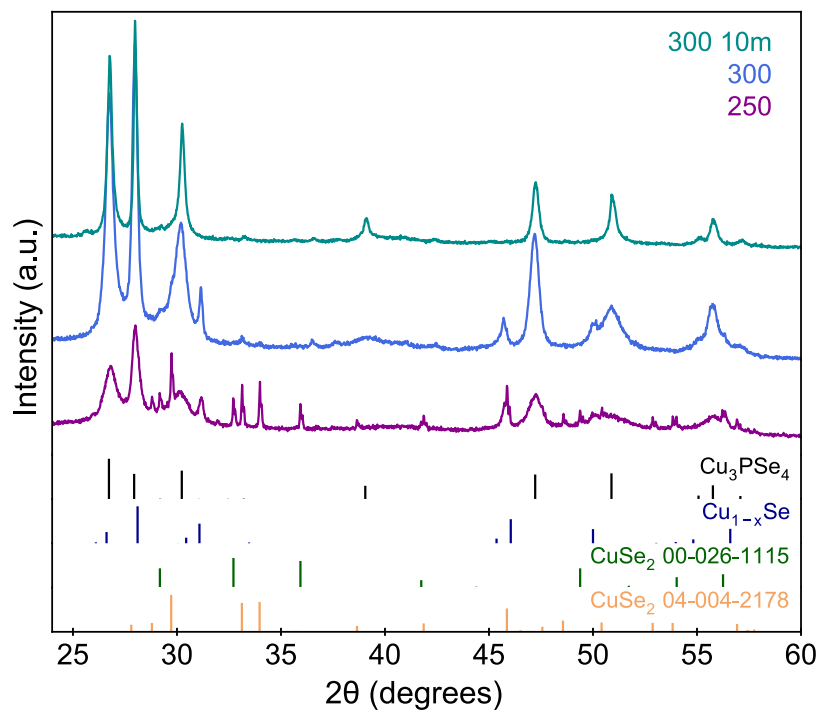


Figure B.30. PXRD of ex-situ aliquots for the standard octadecane, stoichiometric reaction of Cu_3PSe_4 . Aliquots were taken when the desired temperature (denoted in the plot) was reached, and the particles were washed using standard procedure for the complete reaction.

Table B.4. Thermochemistry for decomposition of Se_8 rings.³

x 1/x(Se) _x	for 1/x(Se) _x	ΔS (JK ⁻¹ mol ⁻¹)	ΔH (kcal/mol)	ΔG 25 °C (kcal/mol)	ΔG 300 °C (kcal/mol)	K_{eq} @ 573.15
1		177	56.4	46.8	93.9	1.39E-18
2		247	33.7	22.1	44.3	3.76E-09
3		309	42.5	29.5	59.2	5.50E-12
4		341	38.9	26.7	53.5	6.69E-11
5		398	34.5	21.1	42.4	8.80E-09
6		429	32.5	19.9	40.1	2.39E-08
7		487	35.9	22.2	44.5	3.46E-09
8		526	37.5	23.9	48.1	7.22E-10
H_2Se				3.63	7.29	2.17E-2

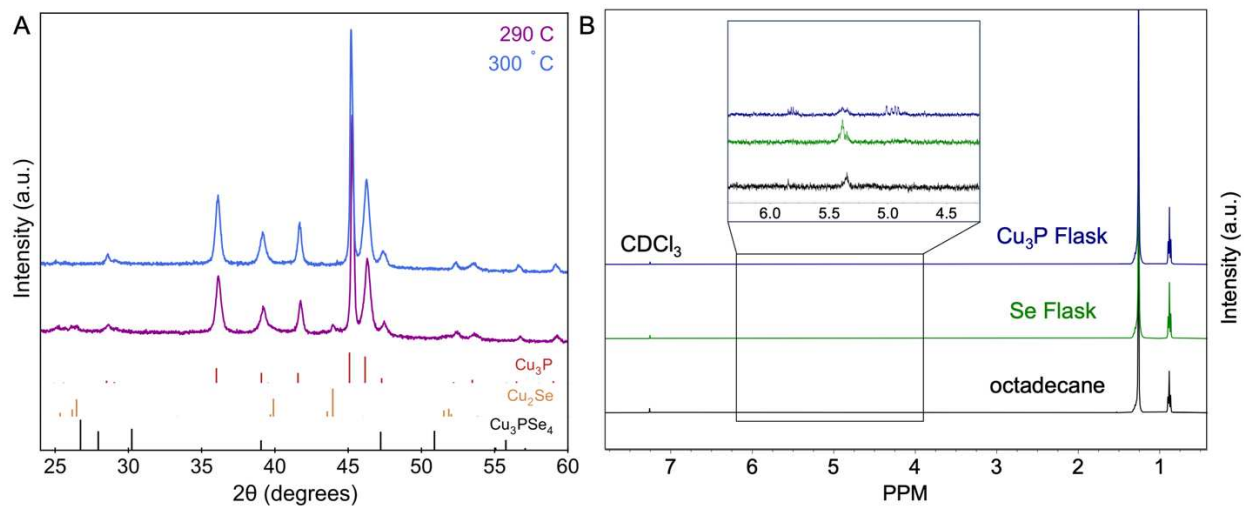


Figure B.31. PXRD and ¹H NMR of a cannula transfer reaction with the headspace of a selenium/octadecane solution at the same concentration as the standard reaction. The zoomed region from 6.0 to 4.5 ppm indicates the formation of mid-chain alkene and 1-ODE formation, which is proposed to be a result of H₂Se formation.

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Supporting Figures

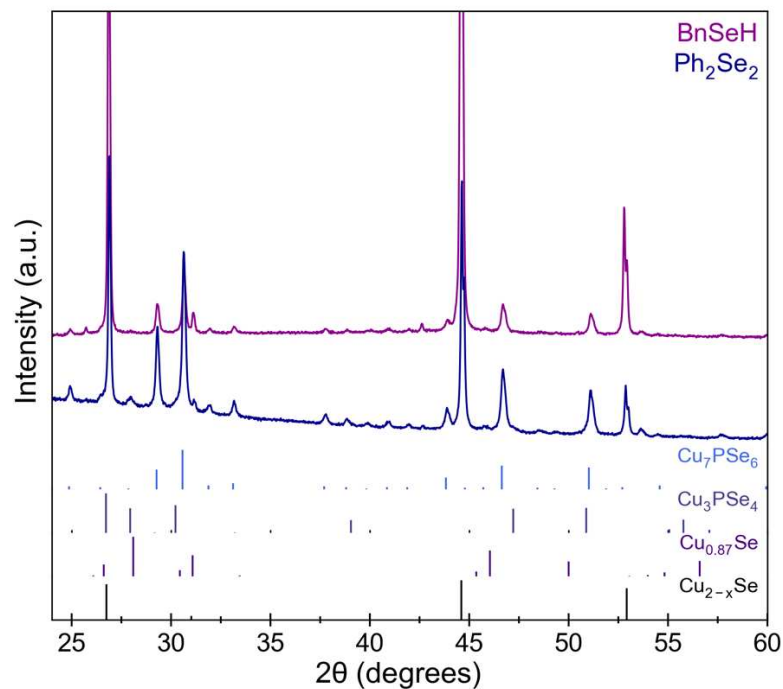


Figure C.1. PXRD patterns of benzene selenol (BnSeH) and diphenyl diselenide (Ph₂Se₂) at 16 equivalents of Se for standard synthetic conditions (300 °C, 30 mins) in 1-octadecene (ODE).

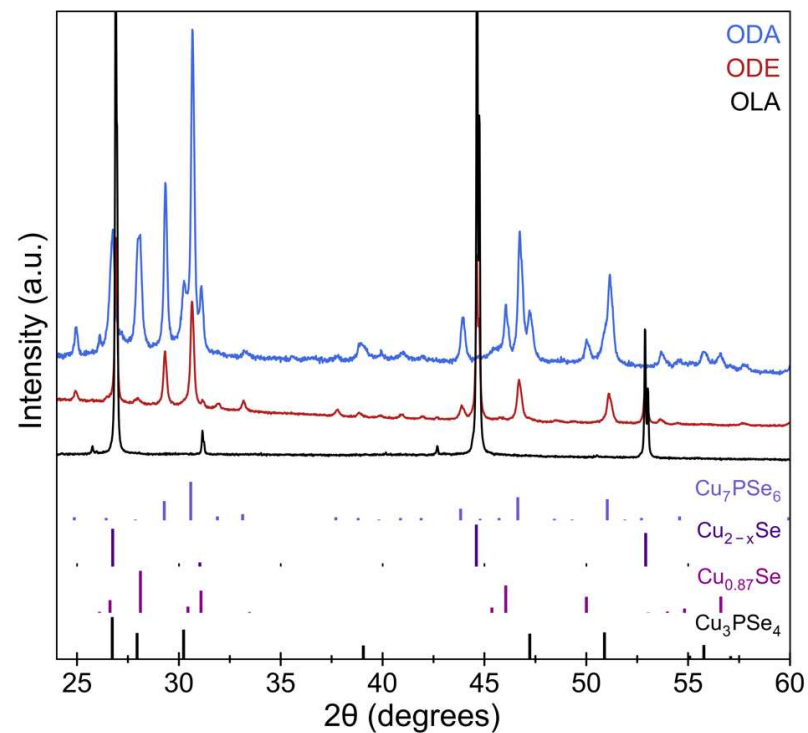


Figure C.2. PXRD patterns for oleylamine (OLA), octadecene (ODE), and octadecane (ODA) at excess equivalents (16 equiv.) at standard synthetic conditions.

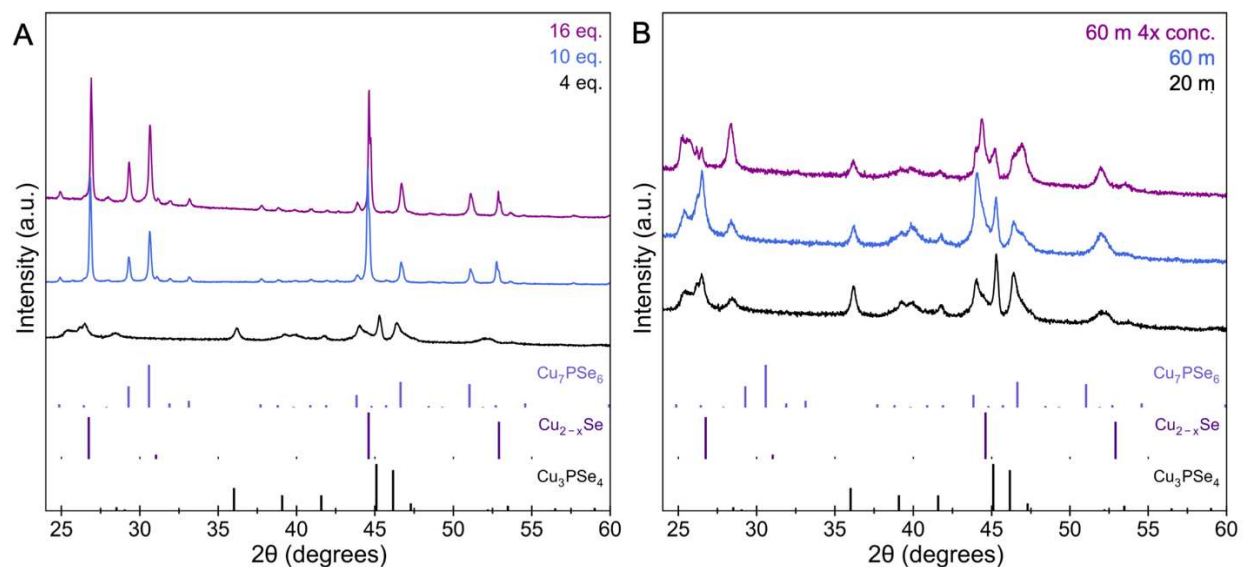


Figure C.3. PXRD patterns of Ph₂Se₂ with 1-octadecene as the solvent at standard synthetic conditions. (A) Reaction with the stated equivalents of Ph₂Se₂ in the top right corner. At higher equivalents (16 and 10 eq.), Cu₇PSe₆ competes with Cu_{2-x}Se, but when Se is reduced to 4 eq. the Cu_{3-x}P is still the primary phase in solution. (B) Time and concentration variations for 4 equiv. of Ph₂Se₂. The black pattern in A is the same in B. *All three conditions Cu₃P is the main product and only minor conversion to Cu_{2-x}Se.*

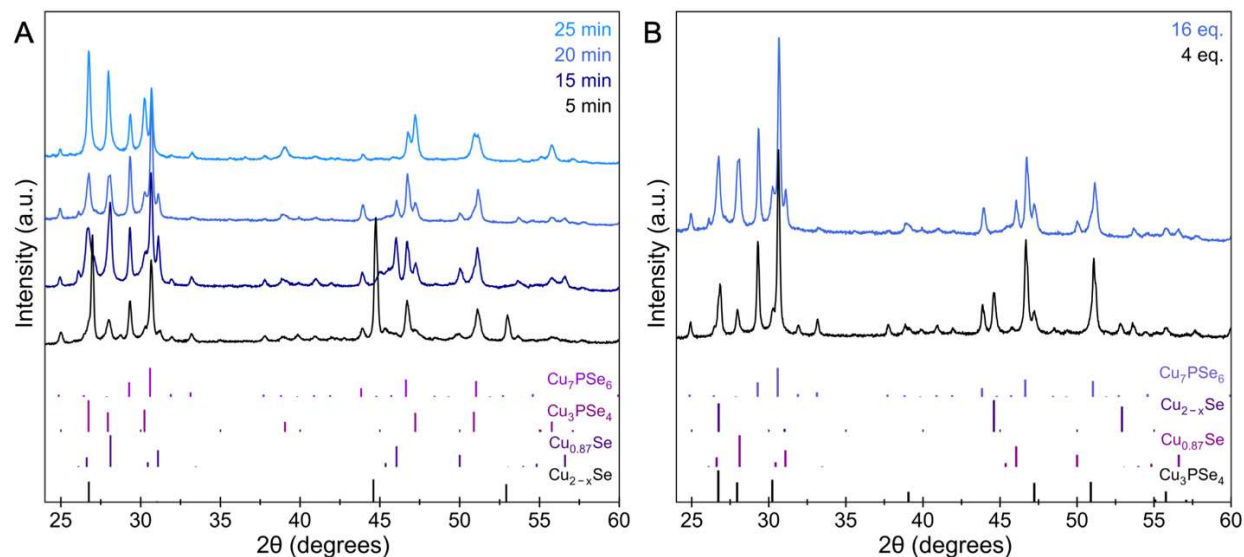


Figure C.4. PXRD subplots of Ph₂Se₂ reacting with octadecane as the solvent at standard synthetic conditions. (A) Represents 16 eq of Ph₂Se₂ as a function of time, which results in two Cu-Se and two Cu-P-Se phases just with different intensity depending on the time of the reaction. (B) Selenium equiv. is decreased to 4 eq., a near-stoichiometric equiv., where Cu₇PSe₆ is primarily isolated with Cu₃PSe₄ and Cu_{2-x}Se in slight abundance.

Phase	Cu₇PSe₆
Space Group	P2 ₁ 3
a, Å	10.1060 (19)
Crystallite size, L	129 (16)
Strain, L	0.13 (3)
Strain, G	0.0 (30)
Cell Volume, Å ³	1032.15 (6)
Preferred Orientation (two directions)	(222) (311)
Phase	Cu_{2-x}Se
Space Group	Fm-3m
a, Å	5.7323 (8)
Crystallite size, L	260 (80)
Strain, L	0.11 (3)
Strain, G	0.0 (16)
Cell Volume, Å ³	188.36 (8)
Preferred Orientation (two directions)	(111) (311)
Instrument	
Surface roughness (Pitschke)	0.133 (3)
Z height specimen displacement	-0.069 (5)

Table C.1. Rietveld refinement details for the Cu_{3-x}P NPs + 3 equiv. Ph₂Se₂ PXRD pattern in Figure 4.2A.

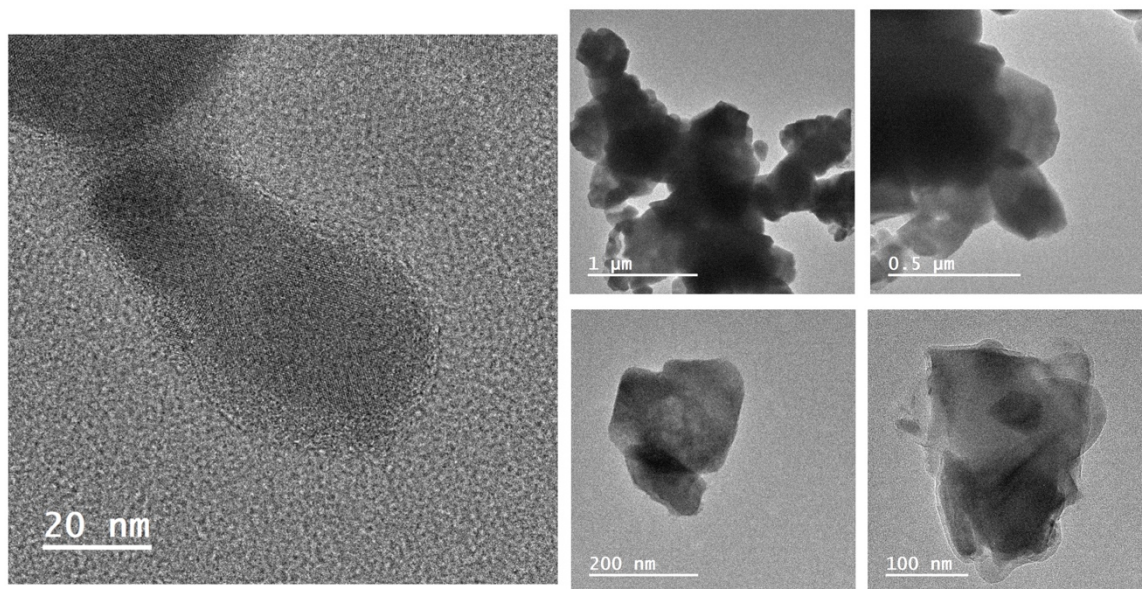


Figure C.5. Transmission Electron Microscopy (TEM) of Cu₇PSe₆ particles with 3 equiv. of Ph₂Se₂ at the standard synthetic conditions.

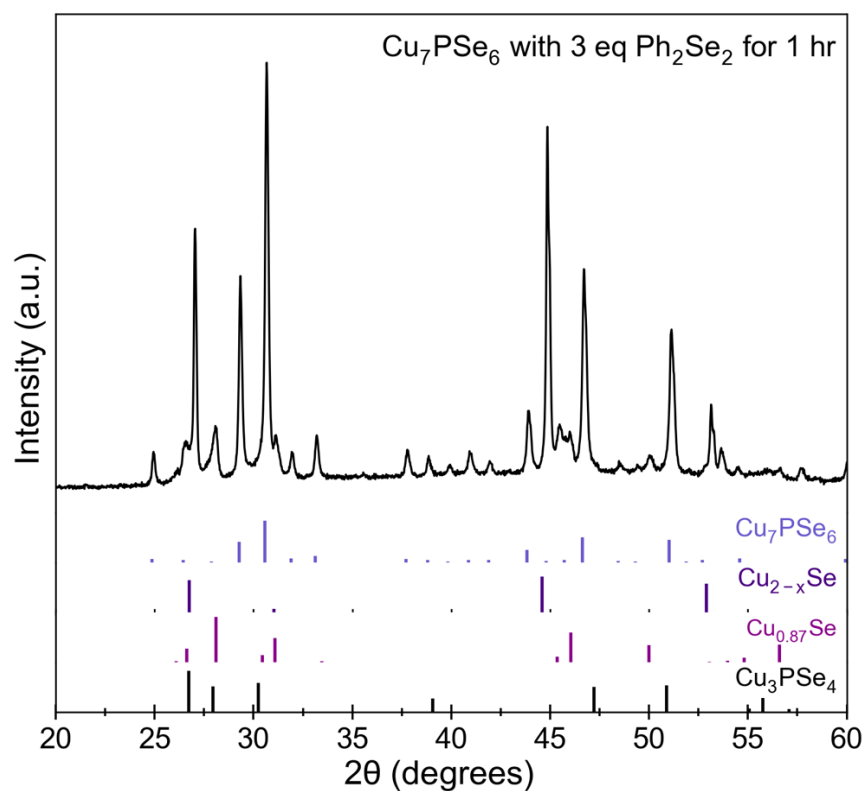


Figure C.6. PXRD pattern of a reaction with Cu_{3-x}P NPs + 3 eq Ph_2Se_2 at standard conditions but with an extended time of 1 hour.

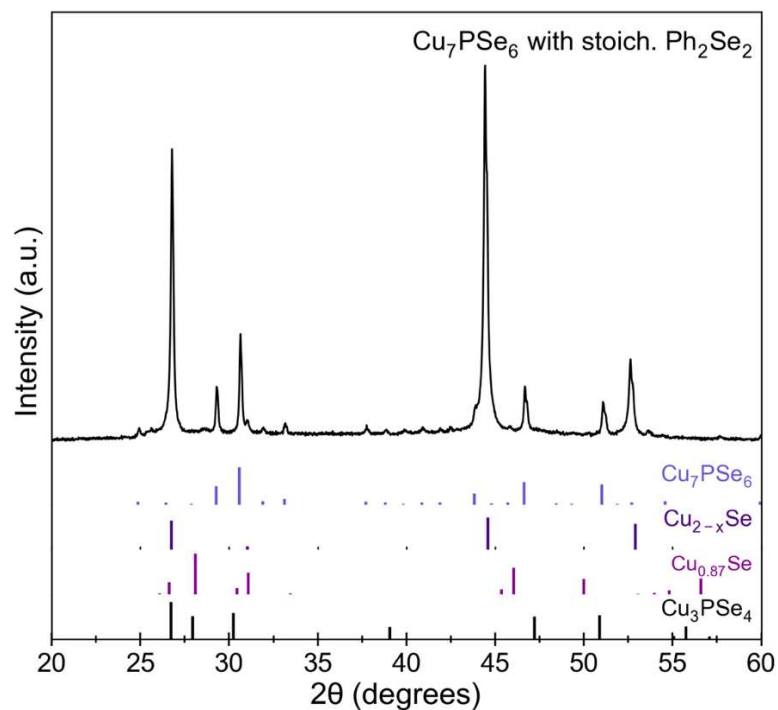


Figure C.7. PXRD pattern of Cu_{3-x}P NPs + 9/7 Ph_2Se_2 at standard synthetic conditions.

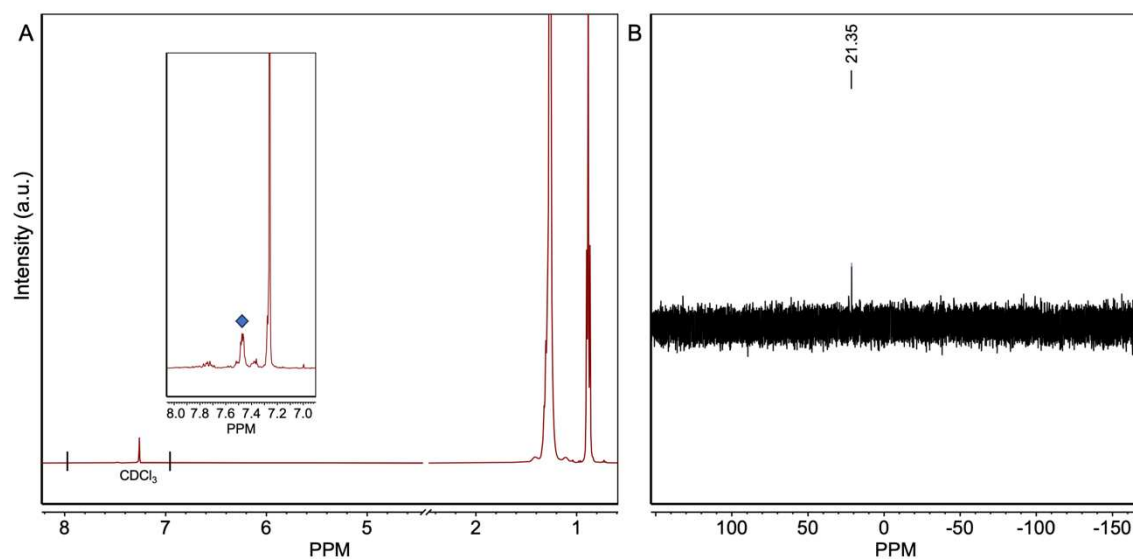


Figure C.8. NMR spectra of Cu_{3-x}P NPs + 9/7 Ph_2Se_2 at 4-fold concentration at standard experimental conditions. (A) ^1H NMR spectrum with a zoomed 8.0-7.0 ppm region indicated by the black lines. The blue diamond represents remaining Ph_2Se_2 . (B) ^{31}P NMR where the peak at 21.35 is indicative of P being trapped in solution.

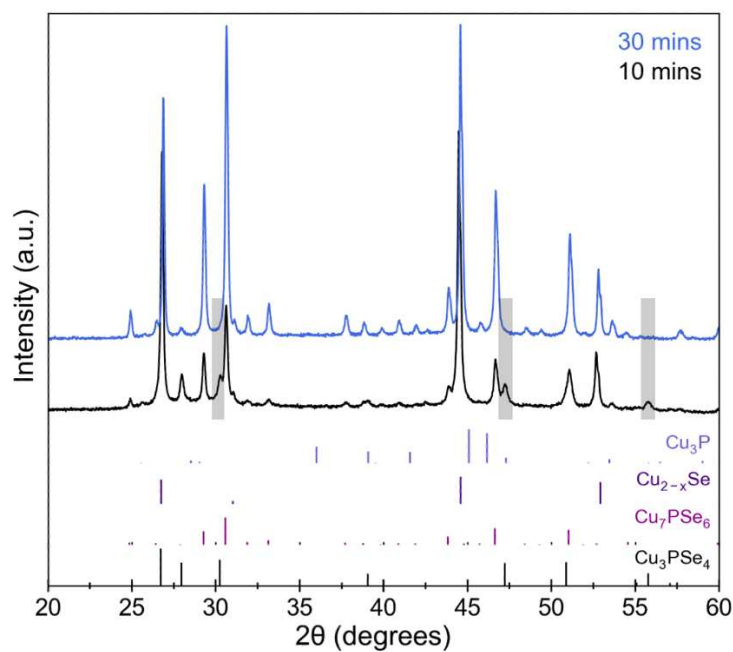


Figure C.9. PXRD subplots of an injection reaction of Ph_2Se_2 /hexadecane at 300 °C for 10 m (black) and 30 m (royal blue). The gray shaded region is added to assist in identifying Cu_3PSe_4 peaks.

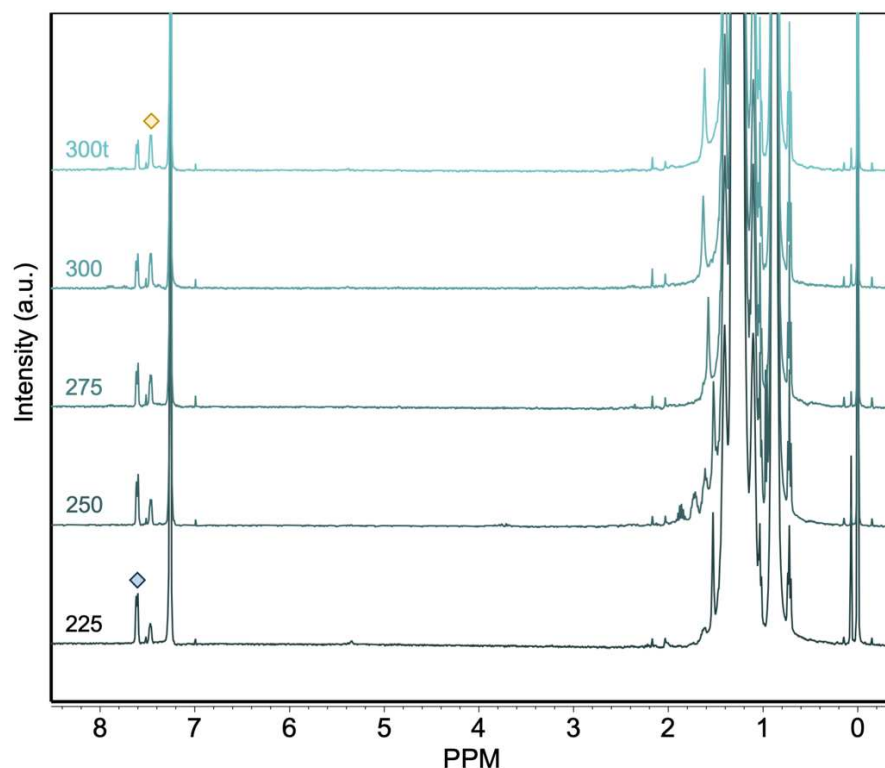


Figure C.10. ^1H NMR spectra of the reaction supernatant of the ex-situ aliquots in Figure 4.3. The temperature is given on the left at $^{\circ}\text{C}$. The blue diamond represents the alpha hydrogen environments on Ph_2Se_2 , whereas the yellow diamond represents the alpha hydrogen on Ph_2Se .

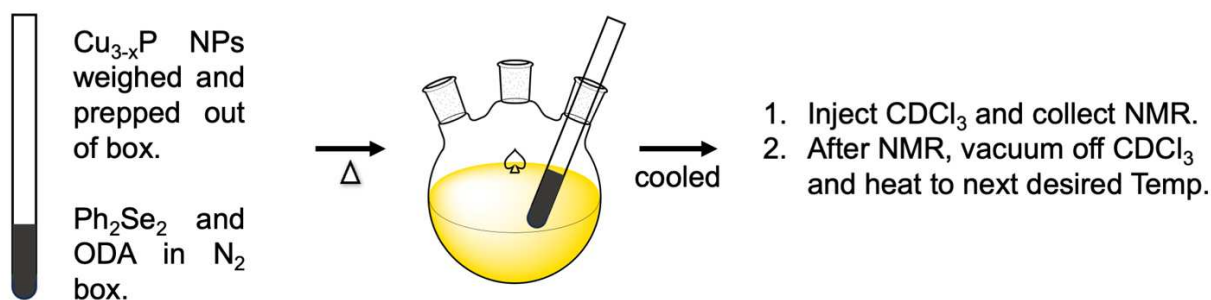


Figure C.11. Schematic of the single NMR reaction where Ph_2Se_2 and Cu_{3-x}P NPs were added and repeatedly heated to keep the precursor ratio consistent throughout the reaction. The purpose of such is to avoid any variations of Cu_{3-x}P to Ph_2Se_2 .

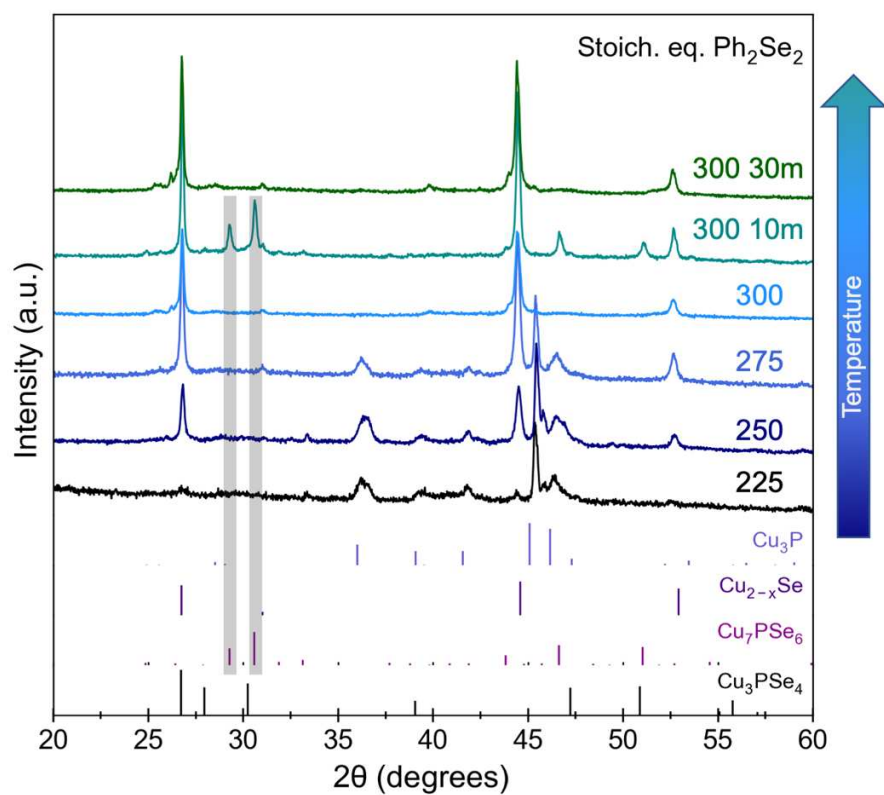


Figure C.12. Subplot of PXRD patterns from individual, ex-situ NMR experiments as a function of temperature. The two shaded gray regions are to assist in identifying the Cu_7PSe_6 phase.

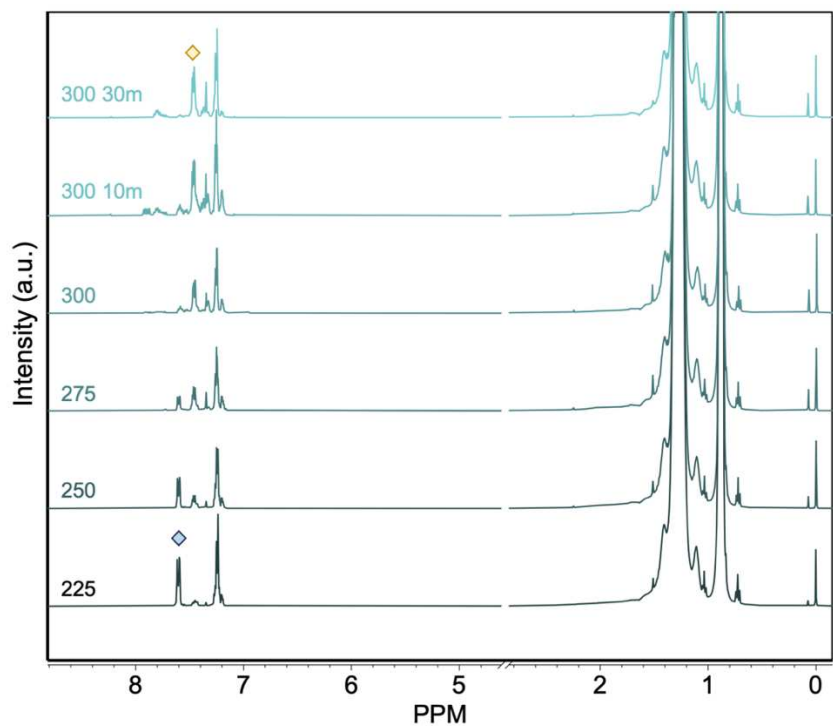


Figure C.13. ^1H NMR subplots of the individual temperature reactions at stoichiometric equiv. Cu_{3-x}P NPs + $9/7 \text{ Ph}_2\text{Se}_2$.

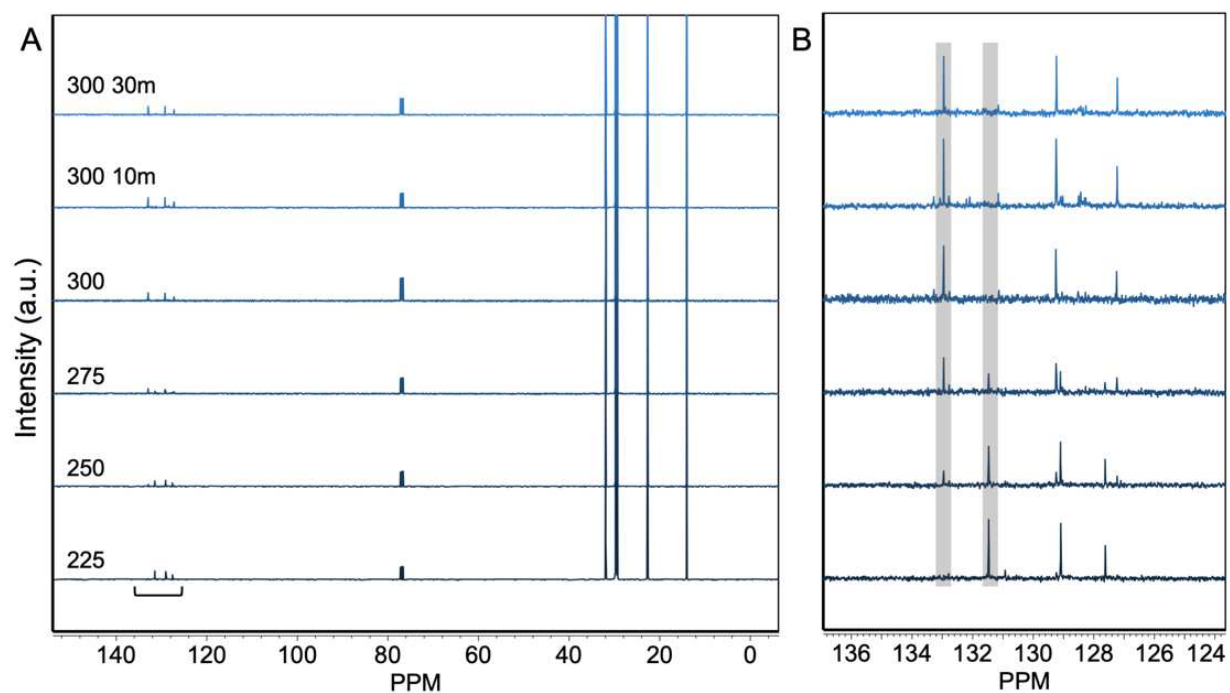


Figure C.14. Carbon, ^{13}C NMR of the individual, ex-situ reactions at stoichiometric equiv. Cu_{3-x}P NPs + 9/7 Ph_2Se_2 . (A) overall spectra with the temperature labeled on the left side. (B) zoomed in region, 136-124 ppm, with two highlighted regions representing Ph_2Se_2 (131.5 ppm) and Ph_2Se (132.9 ppm).

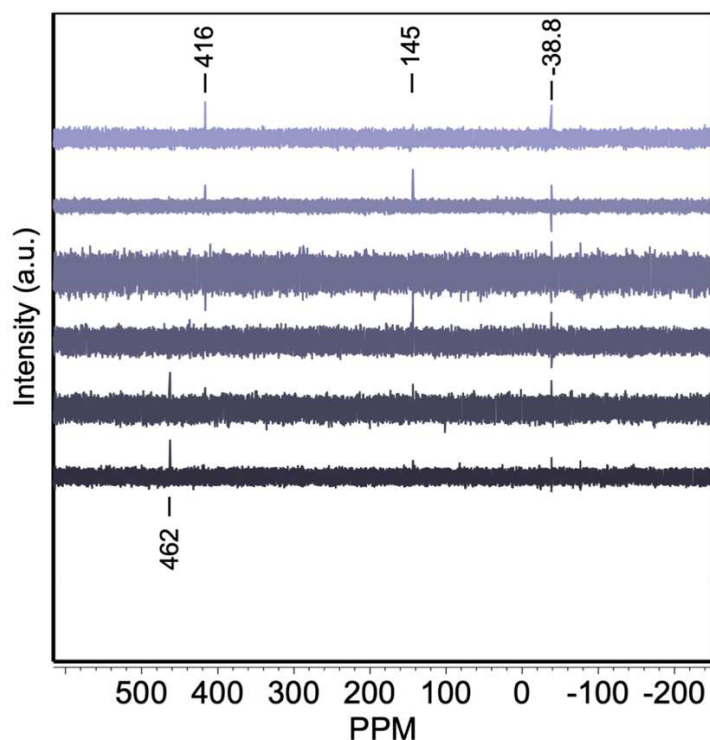


Figure C.15. ^{77}Se NMR ex-situ NMR-tube reactions at stoichiometric conditions, Cu_{3-x}P NPs + 9/7 Ph_2Se_2 . Where the bottom spectrum represents 225 °C, the following increase by 25 °C, and top two are 300 for 10m and 30m.

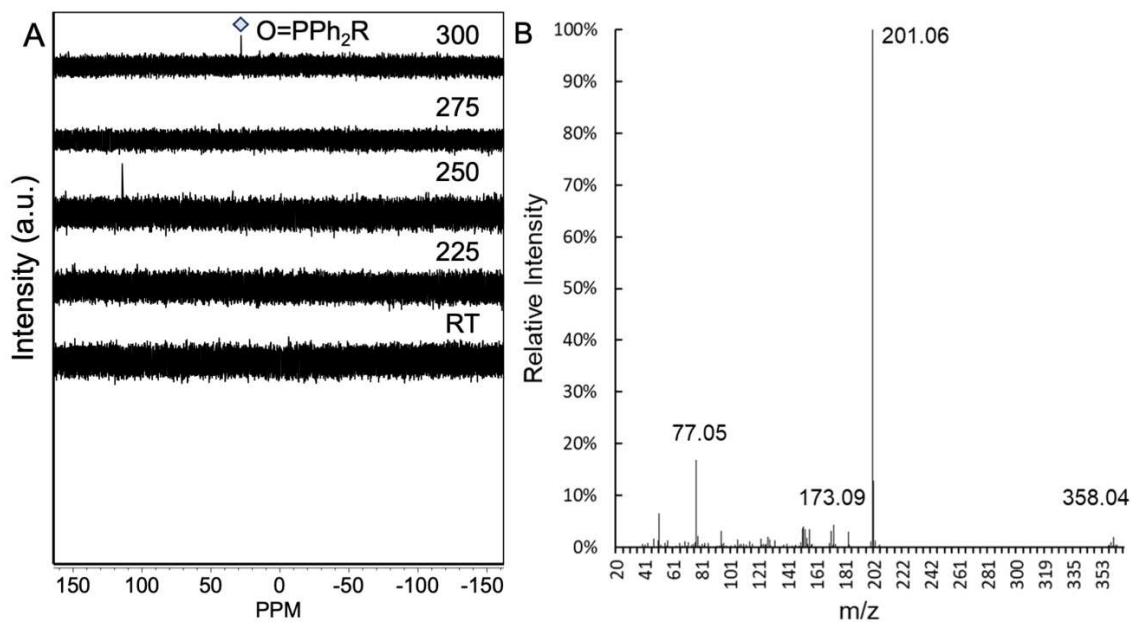


Figure C.16. Characterization of the individual, pseudo in-situ NMR-tube reactions ($\text{Cu}_{3-x}\text{NPs}$ + 9/7 Ph_2Se_2). (A) ^{31}P NMR with a signal at 114 ppm for 250 °C and 28 ppm for 300 °C, the diamond represents a $\text{O}=\text{PPh}_2\text{R}$ species. (B) EI MS spectrum of the 300 °C solution, where the 201.06 m/z

peak represents the base ion of $\text{Ph}_2(\text{P}^+)=\text{O}$ and 358.04 m/z represents the molecular ion peak which is predicted to be a diselenide analog, $\text{Ph}_2(\text{Se}_2)\text{P}=\text{O}$, possibly $(\text{PhSe})_2\text{P}^+=\text{O}$.

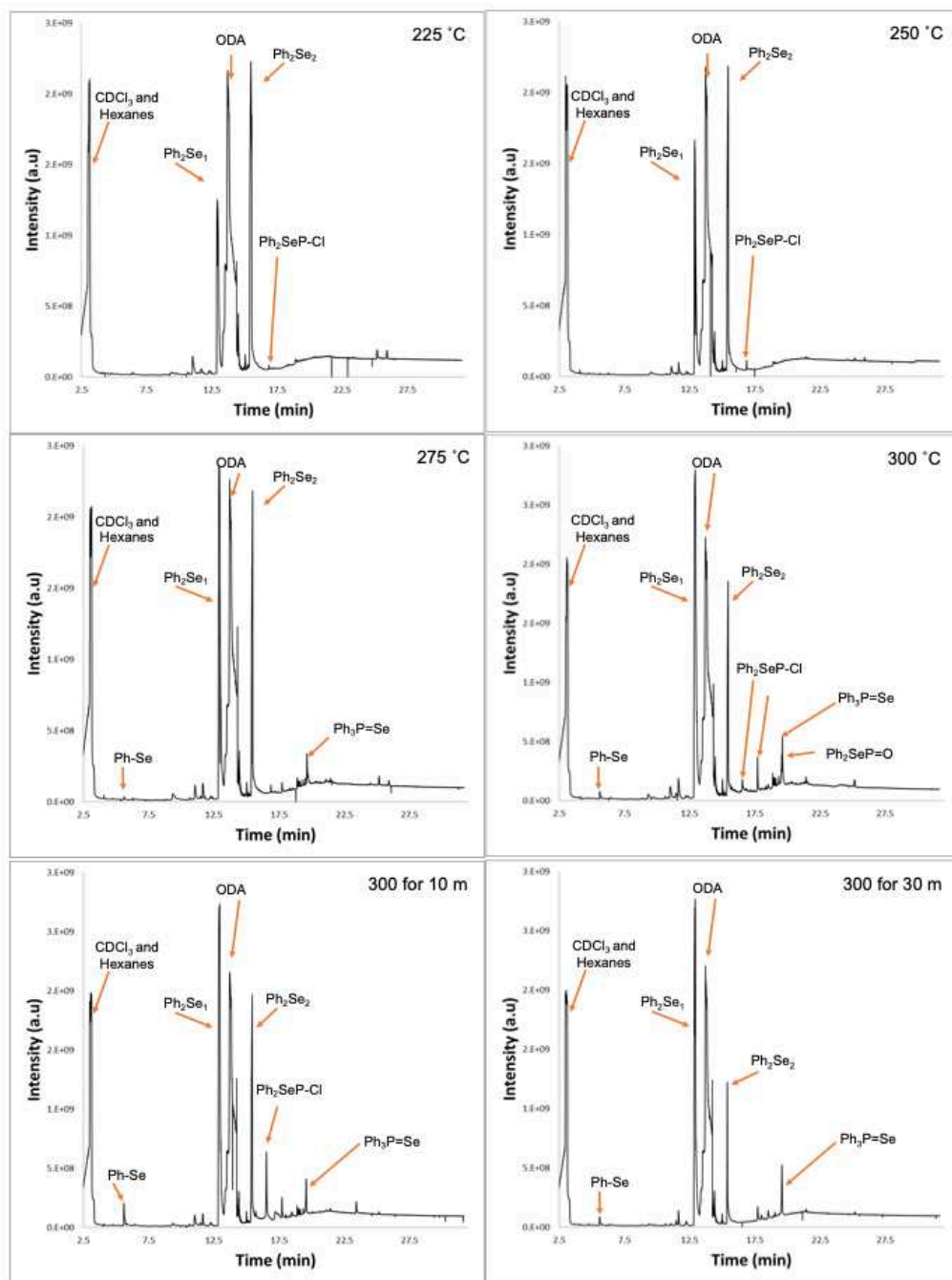


Figure C.17. Chromatograms for the ex-situ, stoichiometric reaction aliquots of Cu_{3-x}P NPs + 9/7 Ph_2Se_2 . The temperature of the aliquot is given in the top right of the plots.

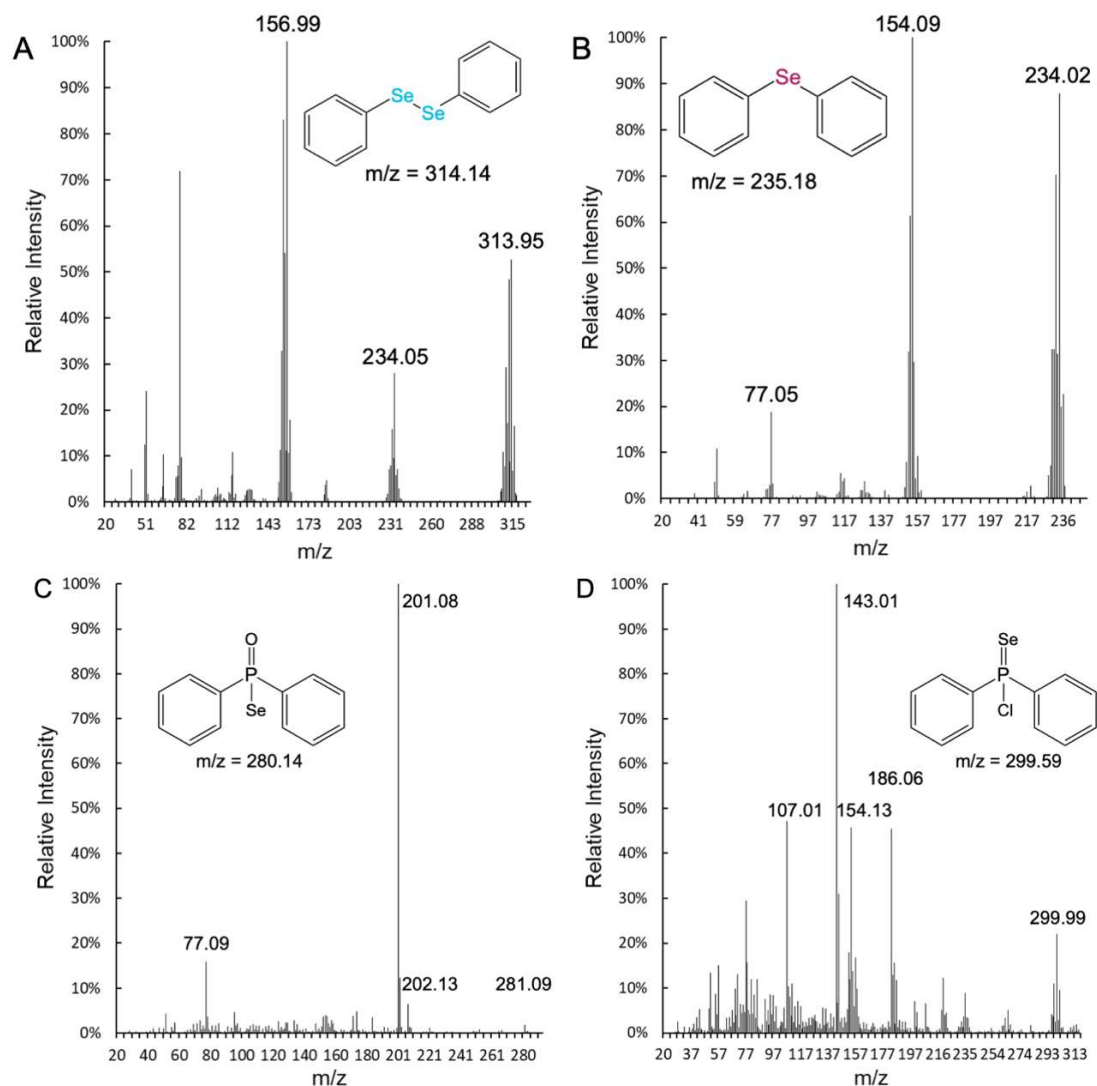


Figure C.18. Mass spectra for the identified peaks in Figure C.18. (A) diphenyl diselenide with 313.95 m/z as the molecular ion (M^+) peak and 156.99 m/z as the base ion ($PhSe^+$). (B) diphenyl monoselenide, 234.02 m/z is M^+ peak and 154.09 m/z is base ion ($PhSe^+$). (C) $Ph_2SeP=O$ (280.14 m/z) is predicted, where 281.09 m/z is M^+ and 201.08 m/z is the base ion ($Ph_2(P^+)=O$). (D) $Ph_2ClP=Se$ (299.59) is predicted, where 299.99 m/z is the M^+ peak and 143.01 m/z as the base ion ($PhP^+(+)Cl$).

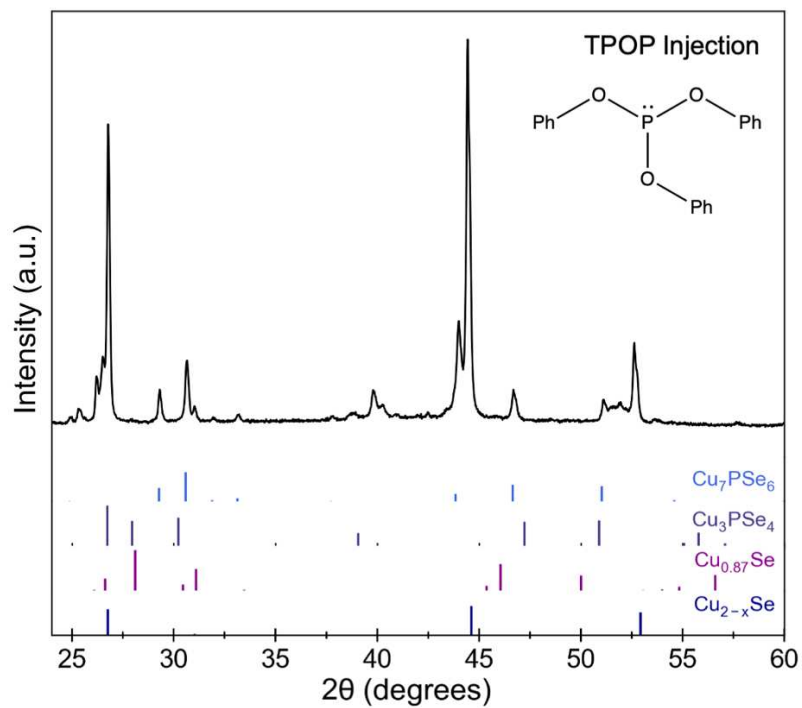


Figure C.19. PXRD pattern for the injection of triphenyl phosphite (TPP)/hexadecane into Cu_{3-x}P NPs + 3 Ph_2Se_2 . Structure of TPOP is given in the plot.

Phase	Cu₇PSe₆
Space Group	P2 ₁ 3
a, Å	10.1059 (2)
Crystallite size, L	184 (14)
Strain, L	0.138 (14)
Strain, G	0.0 (9)
Cell Volume, Å ³	1032.11 (6)
Preferred Orientation (two directions)	(222) (311)
Phase	Cu_{2-x}Se
Space Group	Fm-3m
a, Å	5.69841 (10)
Crystallite size, L	114 (8)
Strain, L	0.00 (2)
Strain, G	0 (4)
Cell Volume, Å ³	158.038 (10)
Preferred Orientation (two directions)	(111) (311)
Phase	Cu₃PSe₄
Space Group	Pmn2 ₁
a, Å	7.708 (3)
b, Å	6.655 (2)
c, Å	6.3738 (16)
Cell Volume, Å ³	326.93 (17)
Crystallite size, L	190 (60)
Instrument	
Surface roughness (Pitschke)	0.0082 (11)
Z height specimen displacement	-0.021 (3)

Table C.2. Rietveld refinement details of the PXRD pattern for the PCl₅/oleylamine solution injection reaction into Cu_{3-x}P NPs + 3 equiv. Ph₂Se₂.

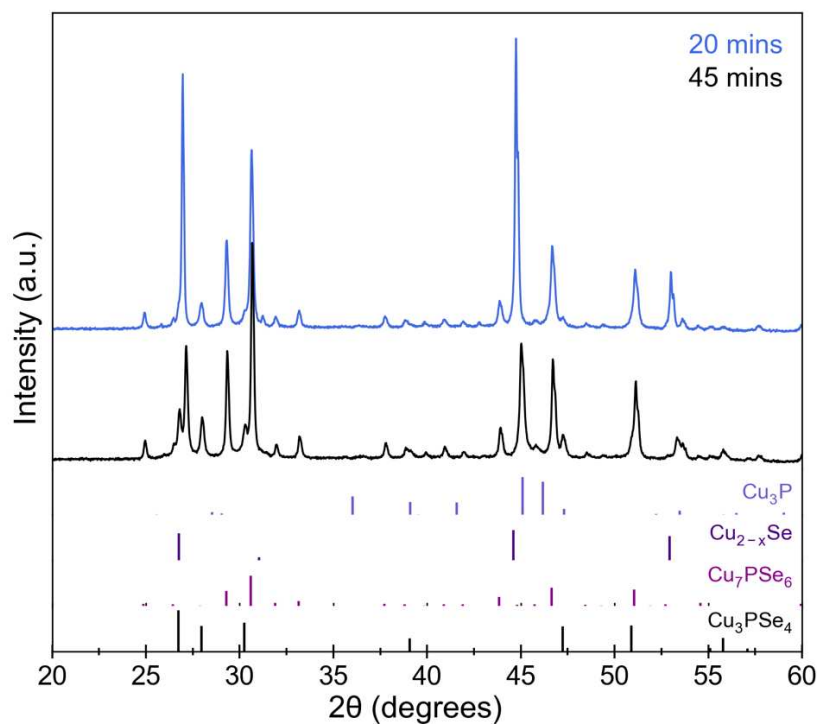


Figure C.20. PXRD pattern subplot of PCl_5 /oleylamine solution into a Cu_{3-x}P NPs + 3 Ph_2Se_2 reaction as a function of temperature which is represented by the color of the subplot (45m is black and 20m is royal blue).

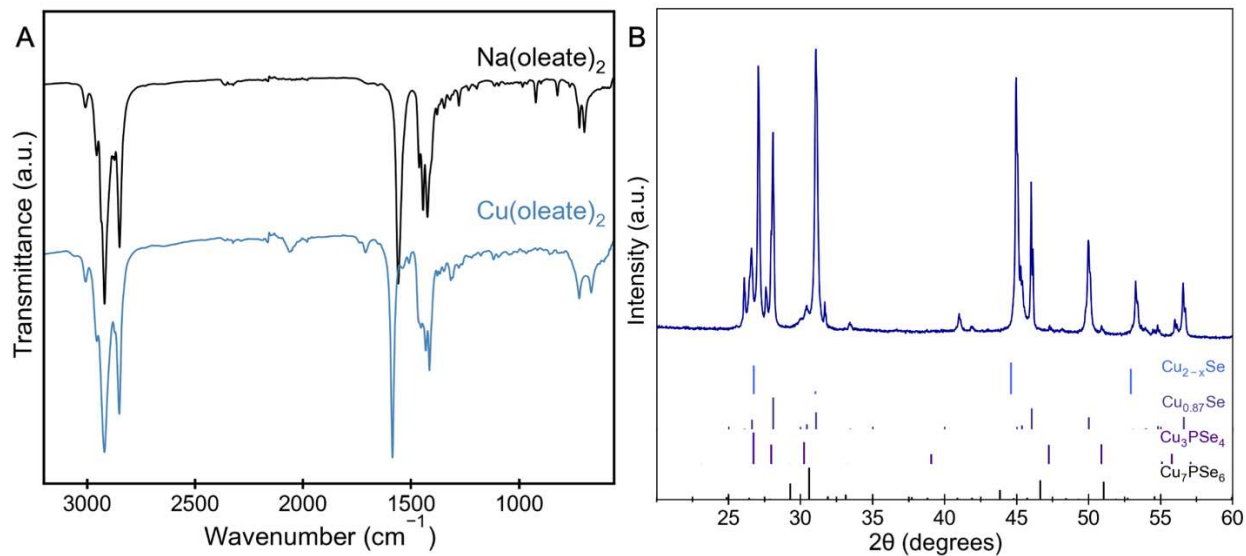


Figure C.21. Characterization of the $\text{Cu(OA)}_2 + 3 \text{Bn}_2\text{Se}_2 + \text{PCl}_5$ (injected at 255°C for 90 m) reaction. (A) Fourier transform infrared spectroscopy (FT-IR) of the presynthesized Cu(OA)_2 precursor. (B) PXRD pattern of the reaction where Cu_{1-x}Se and Cu_{2-x}Se are the crystalline products.

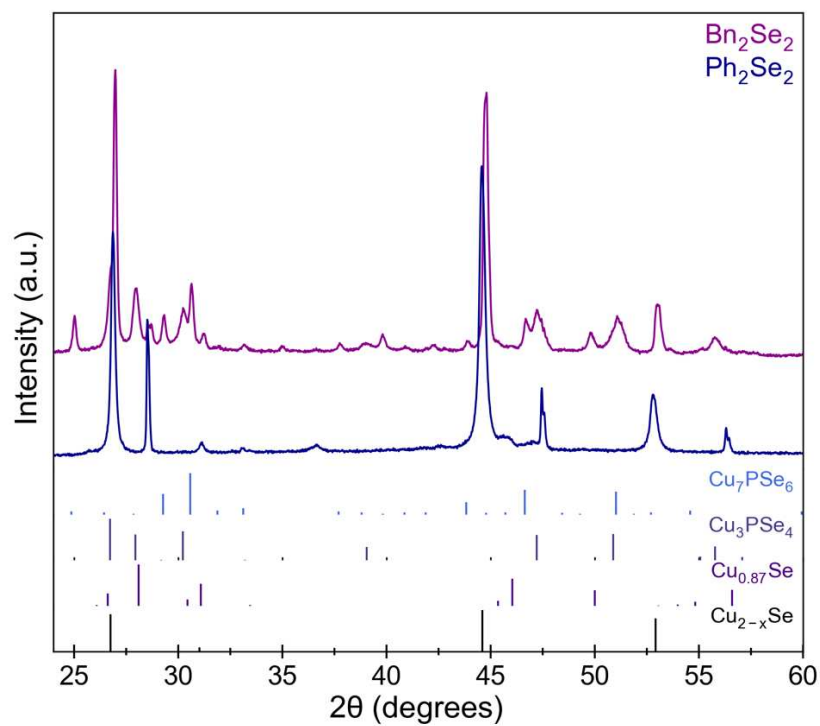


Figure C.22. PXRD patterns of Bn_2Se_2 and Ph_2Se_2 reaction with Cu_3P and CuCl in a one-pot synthesis to balance the reaction stoichiometry, $\text{Cu}_3\text{P NPs} + 4 \text{ CuCl} + 3 \text{ R}_2\text{Se}_2$, at standard synthetic conditions.